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Nitride Materials for Use in Downscaled Interconnect Technology

Thesis presented by

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Declaration

This is to certify that the work I am submitting is my own and has not been submitted for another degree, at either University College Cork or elsewhere. All external references and sources are clearly acknowledged and identified within the contents. I have read and understood the regulations of University College Cork concerning plagiarism.

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Abstract

Copper interconnects will struggle to keep up with the advances in transistor miniaturisation. This creates a significant limiting factor in trying to keep Moore's Law on track into the 2020's. At smaller dimensions, Cu prefers to form non-conducting Cu islands. To prevent this, a liner material that promotes 2D conducting Cu needs to be deposited in the interconnect via in addition to the diffusion barrier that prevents the migration of Cu into the surrounding dielectric. However, the lowest, and smallest, levels of interconnects have extremely high aspect ratios and the bilayer of diffusion barrier and liner material takes up too much volume to allow for the deposition of a sufficient amount of Cu. A change to an alternative metal could solve some of these issues, but this brings its own challenges. Additionally, Cu is expected to remain in use at global interconnect level. For these reasons it is essential to optimise the performance of Cu interconnects and extend the use of Cu as the interconnect metal for as long as possible. One approach to this is to replace the separate diffusion barrier and liner bilayer for a single material that exhibits both properties and can be deposited in an ultra-thin layer, e.g. using atomic layer deposition. In this thesis I explore, using first principles simulations, two different approaches to developing such a combined barrier+liner material. One is to study how known liner and barrier materials could be combined through doping and passivation to create a new material that delivers both properties. Our model system is TaN (diffusion barrier) modified with Ru, Co and W. Secondly, an intrinsically ultra-thin 2D material that has both barrier and liner properties could be used to replace the barrier/liner bilayer. MoS₂ has diffusion barrier properties but its liner properties have not been studied and is thus used as a model system for this approach. The literature on studying barrier and liner materials using theoretical methods is quite limited. Therefore, this thesis also presents an approach for predicting thin film morphology using density functional theory (DFT). Applying this method to Cu adsorption on TaN modified with Ru, Co and W as well as monolayers of MoS₂ showed that the most important factor in controlling thin film morphology is the competition between metal-metal and metal-substrate interaction. Results show that 50% doping of TaN with Ru and 25% doping with Co or W in the surface layer can promote liner properties in TaN and thus promote the growth of 2D, conducting Cu while also preventing Cu diffusion through the material. The study of Cu as well as Ru and Co, which are of interest as alternative interconnect metals, on MoS₂ showed that the metal-substrate interaction of Cu and Ru on MoS₂ must be improved in order to promote a 2D film, while Co shows very strong metal-substrate interactions and should thus form a 2D film on MoS₂.

Chapter 1: Introduction

1.1 The Interconnect Bottleneck

The transistor is unquestionably one of the most important inventions of the twentieth century. Figure 1 illustrates some examples of technologies that have been made possible by the transistor. It changed the nature of communications and paved the way for the modern electronic devices that pervade all aspects of society. The first transistor was developed at Bell Labs by William B. Shockley, John Bardeen and Walter H. Brattain in 1948. [1, 2] From this transistor concept, it was only a small step to the integrated circuit, first developed by two separate teams, one led by Kilby at Texas Instruments, Inc and one led by Moore at Fairchild Semiconductors Corporation. [2–4] The idea of the integrated circuit (IC) is to facilitate communication between multiple transistors in order to increase computing power. This is done by placing at least two transistors on a semi-conducting substrate such as silicon at the front-end-of-line (FEOL) and connecting them via some form of electronic connection at the back-end-of-line (BEOL). [5] This electrical connection is called the interconnect. Images of the interconnect architecture are shown in Figure 2. Based on the pace of technology progress enabled by the introduction of the IC, Gordon Moore predicted that the number of transistors per circuit would double approximately every two years, while at the same time the relative price of devices would decrease. This means that as the computing power of devices increases they also become more economically accessible both in commercial and private settings. [6] This trend is referred to as Moore’s Law, and has held true until today, as shown in Figure 1.

However, in order to keep fitting more and more transistors onto a single chip and ensure that Moore’s Law continues, their size needs to constantly decrease. To keep these miniaturised devices connected, the size of the interconnect must also decrease. However, interconnect scaling is now reaching its limits with current materials. This has caused the rate of increase in the number of transistors on a chip to slow compared to Moore’s Law and makes interconnect scaling a serious bottleneck and highly limiting factor in future device miniaturisation.

In order to allow all the transistors in an IC to be connected, several layers of interconnect lines of different sizes are required, as illustrated in Figure 2a), b) and c). Interconnect line width decreases the closer the interconnect

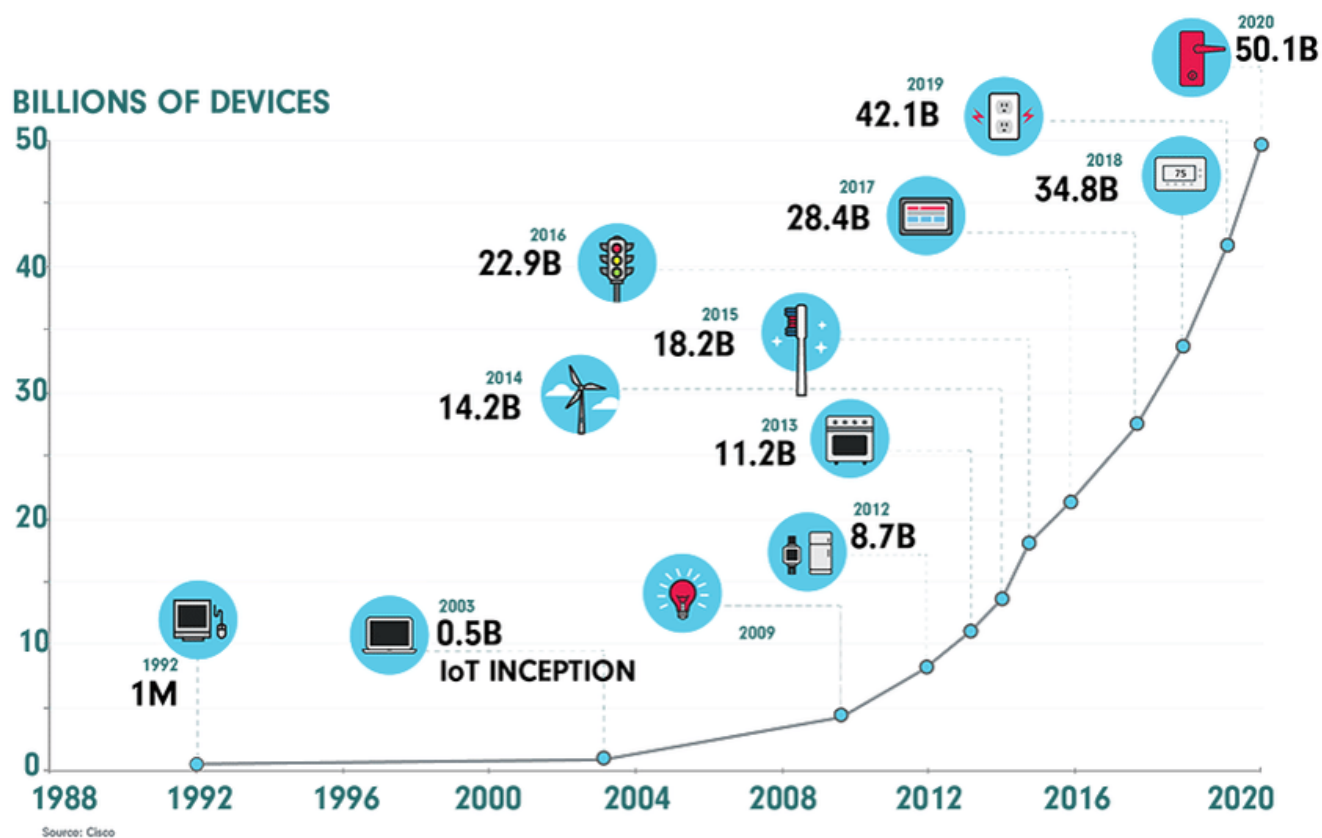


Figure 1: The number of devices per IC over time, highlighting important new technologies and the possibilities of the Internet of Things (IoT). M = million, B = billion. Adapted from ref. [7] License: <https://creativecommons.org/licenses/by-nc-nd/4.0/>

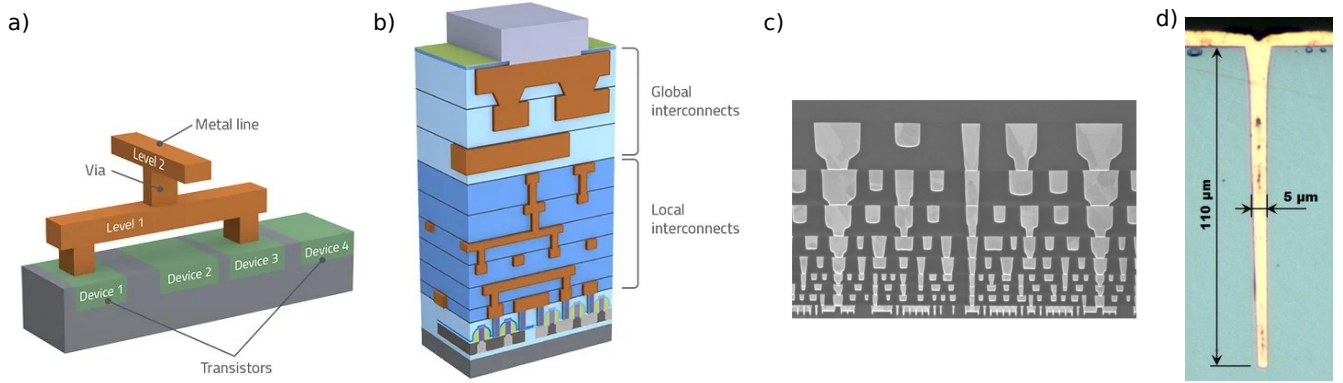


Figure 2: a) Connection of several transistors using Cu lines. b) Overall architecture of transistors and local and global interconnects. c) Cross section of the interconnect stack used for Intel's M1-8 chip at the 45 nm technology node. d) High aspect ratio Cu via with ALD barrier/liner stack. Images a) and b) adapted from ref. [8], image c) adapted from ref. [16], image d) adapted from ref. [17]

layer is to the transistor (see Figure 2b) and c)). This leads to extremely high-aspect ratio interconnect structures, an example of which is shown in Figure 2d). The original interconnects were made from Al metal, however in 1997 Intel announced their first ever IC with Cu based interconnects, which were shown to have superior performance to Al interconnects in terms of resistivity, resistance-capacitance (RC) delay, scalability and durability. [8–11] However, Cu resistivity increases abruptly as interconnect sizes reach the electron mean free path of Cu. [12–15] Additionally, the fabrication process for Cu interconnects is much more complex than that for Al interconnects and as the line width decreases this causes severe issues, necessitating the development of alternative interconnect architectures. [8, 11]

To create a functioning interconnect, a diffusion barrier and a seed liner (also referred to as adhesion promoter) need to be deposited in the interconnect via, see Figure 3. As the name suggests, the role of the diffusion barrier is to prevent the diffusion of Cu atoms into the surrounding dielectric, while the liner material promotes deposition of smooth, conductive Cu. Current diffusion barriers are unable to promote the deposition of conductive Cu without the addition of the liner material. The typical materials used for this are bilayers of Ru/TaN or Ta/TaN, where Ru and Ta are liner materials and TaN is the barrier material. [18, 19] The barrier and liner materials take up precious volume in the interconnect via, to the point that even with modern deposition methods such as Atomic Layer Deposition (ALD) they cannot be thinned further without compromising their efficiency and this means that insufficient volume remains in the via to deposit the amount of Cu needed for a functioning interconnect, as shown in Figure 3. [20, 21] The consequence of this is that new approaches are necessary to reduce the volume taken up by the barrier/liner materials while promoting Cu deposition.

One solution is to change the interconnect metal from Cu to a metal that can be deposited without the need for a barrier or liner material, as this would free up volume in the interconnect via and reduce the interconnect resistivity which leads to an increase in overall device performance. [22–24] More realistically, this change to an alternative interconnect metal will only occur at the very lowest, and thus smallest levels of the device, while Cu will remain in use for the upper interconnect levels. Additionally, Ru and Co, the more promising candidates to replace Cu as the interconnect metal, have both been shown to require at least a liner material for successful deposition. [25, 26] There are also some other reliability issues that have prevented the change from Cu to an alternative. For example, Ru shows some issues with self-heating and crystal structure dependant resistivity. [25, 26] Additionally, the resistivity of Co and Ru is only improved compared to Cu at interconnect sizes below 14 nm, which means that they cannot outperform Cu at the higher level interconnects. [25, 27, 28] For these reasons, extending the use of Cu for further technology nodes and optimising its performance by developing a reasonable alternative to the barrier/liner stack is an important step that keeps material and process costs low and will aid in continuing Moore’s Law. Any insights gained from improving the barrier/liner stack for Cu can of course be applied to alternative interconnect metals.

There are two main approaches that can be taken to thin the barrier/liner stack, which I will explore in this thesis.

1. Developing a single-phase material with both barrier and liner properties
2. Using an intrinsically ultra-thin material, such as a 2D material e.g. MoS₂

The idea is that using either approach, the barrier/liner stack could then consist of a single material, that does not require as many process steps. It is not yet known how a combined barrier/liner with the potential to be thinned to a single monolayer would affect the device performance, especially in terms of preventing Cu migration or promoting deposition of conducting Cu. A range of different materials have been tested for both barrier and liner properties and will be discussed in more detail in Chapter 2. Some examples of frequently studied diffusion barriers are TaN, [20, 21, 31–60] TiN, [34, 39, 46, 47, 61–79], W_xN_y [36, 39, 79–90] and SiC_xN_y. [91–96] As part of this thesis we will consider both combined barrier/liner materials and 2D materials. For the first approach, instead of attempting to find a barrier material that could also show liner properties, we study how known liner and barrier materials could be combined through doping and passivation to create a new material that delivers both properties. Our model system is TaN (diffusion barrier) with surface doping using Ru, Co and W. As MoS₂ has shown promise to act as a Cu diffusion barrier [97–100], this material was selected as a suitable candidate for the second approach with a focus on its potential liner properties. The literature on studying barrier and liner materials using theoretical methods is quite limited. For this reason, the focus of this thesis goes beyond discovering novel

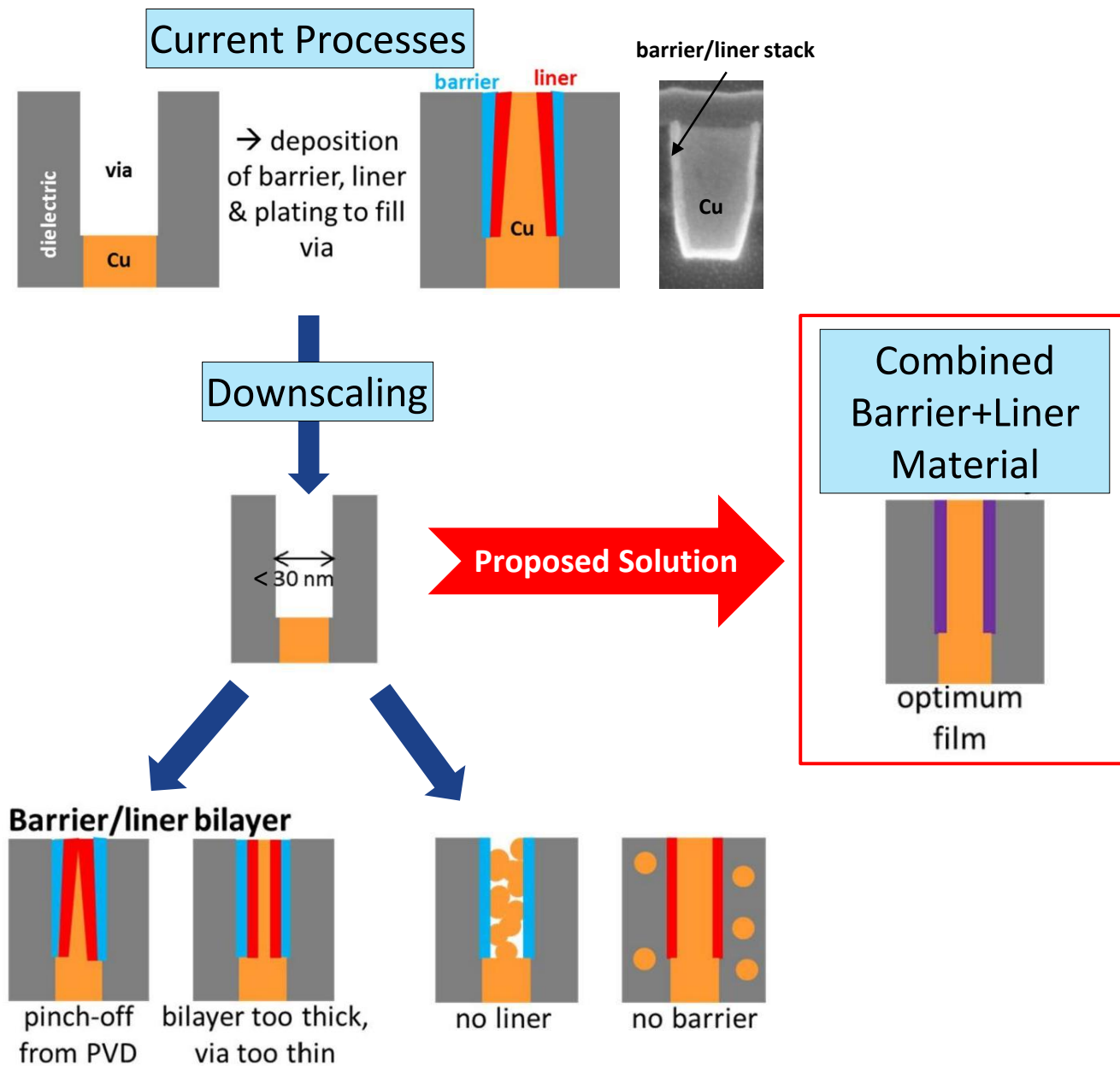


Figure 3: Issues associated with interconnect manufacturing. This Figure was adapted from ref. [29] The SEM cross-section of a Cu line with a barrier/liner stack is taken from ref. [30]

barrier/liner materials and also presents an approach for predicting thin film morphology using density functional theory (DFT). Based on our analysis of different types of Cu models and an understanding of the relevant growth mechanisms from the literature, we were able to develop a computational method that allows for the prediction of film morphology on different substrates. This is focused around selecting

models that yield the maximum amount of information about the system in terms of factors that drive the stability of the metal cluster, the competition between metal-substrate and metal-metal interaction and the influence of temperature. Figure 4 describes the different steps and models in this method, which will be applied throughout this thesis.

Applying this method to Cu adsorption on TaN modified with Ru, Co and W as well as monolayers of MoS₂ showed that the most important factor in controlling thin film morphology is the competition between metal-metal and metal-substrate interaction. Dopants with liner properties in the TaN surface create nucleation sites for a Cu film if their interaction with Cu is strong enough. An ionic radius smaller than Cu is useful in creating gaps into which Cu can migrate thus increasing the strength of the interaction with the substrate. However, gaps that become too large can cause severe distortion of the surface layer and lead to thermal instability. This can also occur if the dopant concentration is too high. We find that 50% doping with Ru and 25% doping with Co or W can promote liner properties in TaN, our model diffusion barrier material, and thus promote the growth of 2D, conducting Cu while also preventing Cu diffusion through the material. On MoS₂, also a known barrier material, the adhesion must be improved in order to promote 2D Cu growth. Based on our initial results this can be achieved by creating a MoS₂ monolayer with some amount of sulfur vacancies, which occurs naturally in MoS₂. Adsorption of Ru and Co showed that similarly to Cu, adhesion of Ru is improved in the presence of a sulfur vacancy. Combined with a stronger adhesion compared to Cu on pristine MoS₂, Ru is likely to grow in a smooth, 2D film on defective MoS₂. Co on the other hand shows very strong adhesion to MoS₂, which should cause a 2D Co film on pristine MoS₂. However, in the presence of a sulfur vacancy, Co can form sulfides and induce an additional vacancy which could cause issues during the manufacturing process. Similarly, Ru can also induce additional vacancies through sulfide formation, specifically when it is adsorbed at the hollow site.

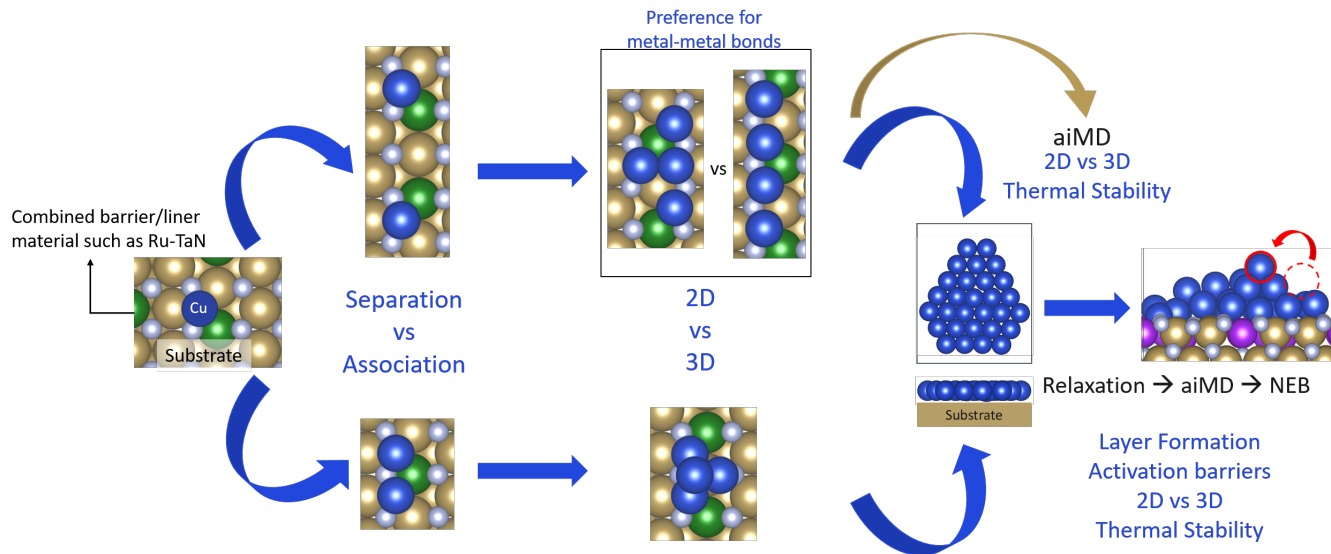


Figure 4: Metal structures of increasing size to predict thin film morphology. Information gained from the different calculations is labelled in blue. aiMD = ab initio molecular dynamics, NEB = nudged elastic band calculation.

1.2 Thesis Outline

Chapter 2 provides a review of the literature on materials for interconnects, with a specific focus on diffusion barrier and seed liner materials. Typical experimental methods for deposition and performance evaluation of barrier/liners are discussed, along with the properties necessary for good barrier and liner materials. We also provide a review of the relevant growth mechanisms for metal thin films and detail how these insights can be applied to our computational models.

Chapter 3 is split into two sections. In Section 3.1, the theoretical background of several approaches to solve the many-body Schrödinger equation is discussed, with an emphasis on DFT and its implementations as this is the method used for the work detailed in this thesis. Section 3.2 gives the computational methods used for the different systems studied as part of this thesis.

Chapter 4 presents the first part of the results of our study of Ru-modified TaN as a combined barrier/liner material. We study the interactions between Cu adatoms and Ru and TaN surfaces. This is followed by studying different modified TaN surfaces, namely 1 and 2 monolayers of Ru passivation and 8%, 25%, 50%, 75% and 100% Ru-doping in the surface layer of the TaN slab. Using 50% Ru-doping as an example we study the effects of changing the dopant distribution. Finally, we analyse the interactions of a variety of Cu_n structures (where $n = 1, 2, 3$ or 4) focusing on geometry, adsorption energy, activation energy to migration from one adsorption site to another, Bader charges and bond distances. Based on results from this study we can understand how Ru dopants interact with TaN and Cu adatoms and which interactions drive the stability of 2D or 3D structures. The results in this chapter have been published in two papers, "Ru Passivated and Ru Doped ϵ -TaN surfaces as Combined Barrier and Liner Material for Copper Interconnects: A First Principles Study" [101] and "The role of Ru passivation and doping on the barrier and seed layer properties of Ru-modified TaN for copper interconnects" [29] published in the Journal of Materials Chemistry C and the Journal of Chemical Physics, respectively.

Chapter 5 presents the second part of the results of our study of Ru-modified TaN. Here, we use a model made up of 29 Cu atoms, which is a reasonable size to gain further insight into the forces that drive 2D vs 3D growth without consuming a prohibitive amount of resources. Applying our understanding of potential growth mechanisms, we use geometry relaxations, *ab initio* molecular dynamics (aiMD) calculations and nudged-elastic band (NEB) calculations of select atom migrations to predict the final Cu film morphology on TaN and the Ru-modified TaN surfaces detailed in Chapter 4. This yields an understanding of the driving forces behind 2D vs 3D growth and how these can be controlled through doping of TaN with Ru. This chapter has been published in Chemical Science under the title "Control of the Cu morphology on Ru-passivated and Ru-doped TaN surfaces –

promoting growth of 2D conducting copper for CMOS interconnects”. [102]

Chapter 6 details a study of using W and Co as dopants in TaN instead of Ru. We use the same dopant concentrations and distributions as in Chapters 4 and 5, limiting the selection of 50% doped surfaces to the most and least favourable dopant distributions. We explore different Cu_n (where $n = 1, 2, 4$ or 29) structures based on the information they can provide about the Cu-surface interactions and the final film morphology. Studying the interaction of different Cu structures with W and Co doped TaN allows us to assess the effect of different dopants compared with Ru doping of TaN, while also gaining insight into the limitations of the different Cu models used to study the various interactions that control film morphology.

Chapter 7 presents a study of Cu_n , Ru_n and Co_n clusters on monolayers of stoichiometric and defective MoS_2 . MoS_2 has been shown to function as a Cu diffusion barrier. The work in this chapter focuses on understanding the factors that drive the stability of small metal clusters on MoS_2 , while gaining insight on the potential diffusion barrier and liner properties of MoS_2 for Cu, Ru and Co interconnects. The work presented in this chapter has been published in two papers in the Beilstein Journal of Nanotechnology: ”DFT calculations of the structure and stability of copper clusters on MoS_2 ” [103] and ”Prediction of Co and Ru nanocluster morphology on 2D red MoS_2 from interaction energies”. [104]

In **Chapter 8** we review the conclusions drawn based on the research presented in this thesis and give an overview of potential future work.

1.3 List of Publications and Author Contributions

1. Suresh Kondati Natarajan, Cara-Lena Nies, and Michael Nolan. "Ru passivated and Ru doped ϵ -TaN surfaces as a combined barrier and liner material for copper interconnects: a first principles study." *Journal of Materials Chemistry C* 7.26 (2019): 7959-7973. doi:10.1039/C8TC06118A
2. Suresh Kondati Natarajan, Cara-Lena Nies, and Michael Nolan. "The role of Ru passivation and doping on the barrier and seed layer properties of Ru-modified TaN for copper interconnects." *The Journal of Chemical Physics* 152.14 (2020): 144701. doi:10.1063/5.0003852
3. Cara-Lena Nies, Suresh Kondati Natarajan and Michael Nolan. "Control of the Cu morphology on Ru-passivated and Ru-doped TaN surfaces—promoting growth of 2D conducting copper for CMOS interconnects." *Chemical Science* (2022). doi:10.1039/D1SC04708F
4. Cara-Lena Nies, and Michael Nolan. "DFT calculations of the structure and stability of copper clusters on MoS₂." *Beilstein Journal of Nanotechnology* 11.1 (2020): 391-406. doi:10.3762/bjnano.11.30
5. Cara-Lena Nies, and Michael Nolan. "Prediction of Co and Ru nanocluster morphology on 2D MoS₂ from interaction energies." *Beilstein Journal of Nanotechnology* 12.1 (2021): 704-724. doi:10.3762/bjnano.12.56

For the work presented in this thesis it was my role to conceptualise the studies with my co-authors, prepare the models, optimise calculation parameters, run the different types of DFT calculations (geometry relaxation, ab initio molecular dynamics and nudged elastic band calculations), analyse the results, carry out additional analysis including bond length measurements, computing Bader charges, plotting the density of state and visualising charge density differences, present the results, prepare manuscripts for publication and respond to reviewer comments.

Chapter 4 includes publications 1 and 2 from the list above. Authors Cara-Lena Nies and Dr. Suresh Kondati Natarajan contributed equally to both publications. The workload in terms of modelling, analysis and preparation of the manuscripts were shared equally. I was in charge of all work related to Ru-doped TaN, while Dr. Natarajan was responsible for all work relating to Ru passivated TaN.

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Chapter 2: Literature Review

2.1 Interconnect Bottleneck

The continuous drive in miniaturisation of electronic devices motivated by keeping Moore's Law¹ on track is becoming severely limited by the scaling of the interconnect. The interconnects are metal lines that connect two or more transistors in an integrated circuit, as shown in Figure 1a). Typically, there are several layers of these metal lines to allow the connection of all transistors in the device, creating a stack of local and global interconnects as illustrated in Figure 1b) and c). [2] These figures also show that the size of the interconnect via depends on how close it is to the transistor, with the smallest interconnects directly above the transistors. It follows that decreased size of transistors necessitates even smaller interconnects at the lowest levels of the stack. However fabricating these is not a straightforward task and the properties of metals can change at nanoscale dimensions, further complicating the process. Currently, Cu is used as the interconnect metal. It replaced Al in 1997 due to superior performance at smaller sizes. [3–5] Now, Cu faces similar issues, creating a second interconnect bottleneck for complementary metal oxide semiconductor (CMOS) devices. [3] Copper's scalability issues arise mainly from the need for a diffusion barrier and seed liner to prevent diffusion of Cu into the surrounding dielectric and ensure a uniform, conductive film, respectively. This bilayer, typically TaN/Ta or TaN/Ru [6, 7], takes up precious volume in the interconnect via. A large part of down-scaling of devices is decreasing the overall size of the interconnect, which means the volume of barrier and liner material needs to be significantly reduced in order to achieve a sufficient volume of Cu in the via for a functioning device. Additionally, deposition of barrier/liner materials becomes a critical issue in the high aspect ratio vias of advanced CMOS devices, as traditional deposition methods such as physical vapour deposition (PVD) and chemical vapour deposition (CVD) do not have the required accuracy and conformity to coat the structure without causing pinch-off which in turn prevents the deposition of Cu. [8] An example of such a high aspect ratio structure is shown in Figure 1d). Even though studies show that in order to minimise resistivity, a barrierless interconnect conductor would be preferable [9–11], to extend the use of Cu beyond current technology

¹Moore's Law refers to Gordon Moore's 1965 paper "Cramming more components onto integrated circuits", [1] where he predicts that the number of transistors on an integrated circuit will double approximately every two years.

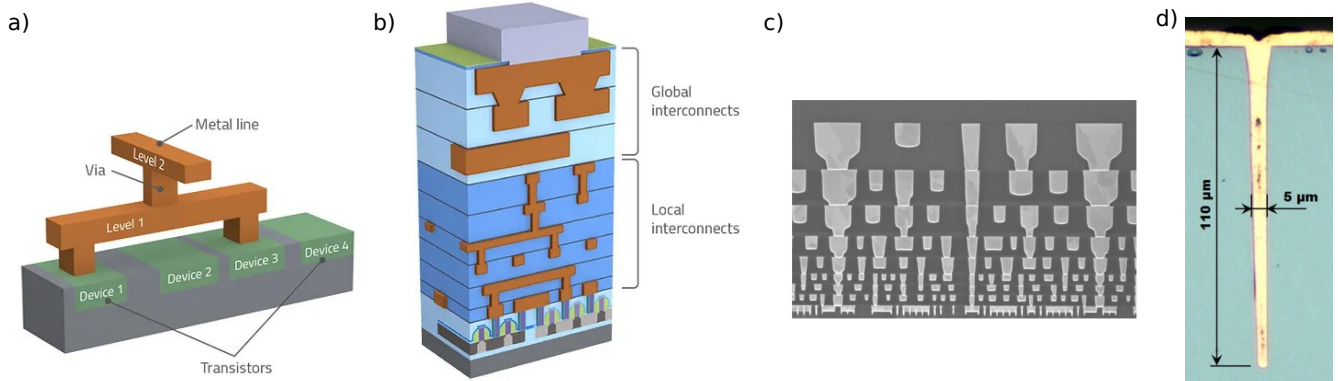


Figure 1: a) Connection of several transistors using Cu lines. b) Overall architecture of transistors and local and global interconnects. c) Cross section of the interconnect stack used for Intel's M1-8 chip at the 45 nm technology node. d) High aspect ratio Cu via with atomic layer deposition (ALD) barrier/liner stack. Images a) and b) adapted from ref. [2], image c) adapted from ref. [12], image d) adapted from ref. [13]

nodes and keep material and process costs low, an alternative to the current barrier/liner stack is essential and more likely to be relevant. Further, Cu is expected to be replaced only at the lowest interconnect levels, therefore any improvements that can be made to the performance and reliability of Cu interconnects will remain useful throughout future technology nodes. [5] Figure 2 illustrates the issues discussed above, which form the core research question in this thesis, and the solution of a combined barrier/liner material that I have proposed in this thesis.

Key requirements to maximise the efficiency and stability of Cu interconnects while overcoming potential challenges were identified early on in the use of Cu interconnects. Havemann et al. [16] give an overview of how dual damascene² is used to decrease the number of process steps, decrease the resistance of the via and improve overall device reliability by reducing the number of interfaces in the interconnect via.

Cu was chosen to replace Al as the interconnect conductor due to its superior resistivity and reliability. [4] However, due to finite size effects, as interconnect dimensions approach the electron mean-free path of Cu, the resistivity increases abruptly, as shown in Figure 3. [16, 19–21] Cu becomes polycrystalline at smaller sizes, which changes the main failure mechanism from electromigration (EM) to grain boundary diffusion. For this reason, the grain size of Cu directly impacts the device lifetime. [16, 19, 22, 23] Other factors that contribute to resistivity are interfaces between Cu and other parts of the interconnect and possible impurities. [24]

In trying to find novel materials to extend the use of Cu in interconnects, it is important to understand the challenges of manufacturing a Cu interconnect and the main failure mechanisms. First and foremost, the resistivity of the interconnect must be kept to a minimum, while also maximising the volume of Cu in the various

²Dual damascene is the name of the common process by which Cu interconnects are manufactured. This involves the simultaneous formation of trenches and vias into which Cu is then deposited. The single step formation of both trench and via reduced the number of processing steps compared to the previous single damascene process where trench and via were formed one at a time. [17, 18]

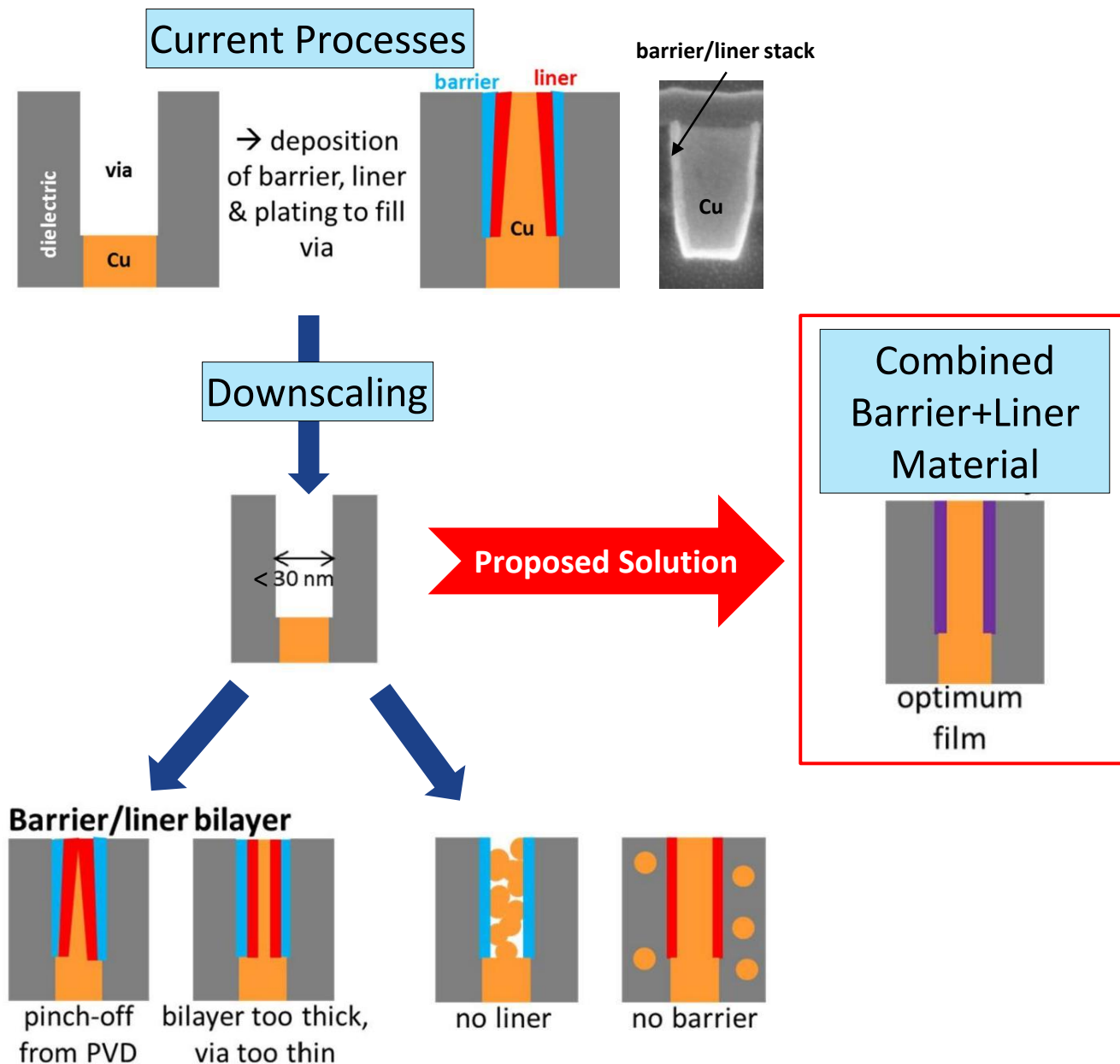


Figure 2: Issues associated with interconnect manufacturing. This figure was adapted from ref. [14] The scanning electron microscope (SEM) cross-section of a Cu line with a barrier/liner stack is taken from ref. [15]

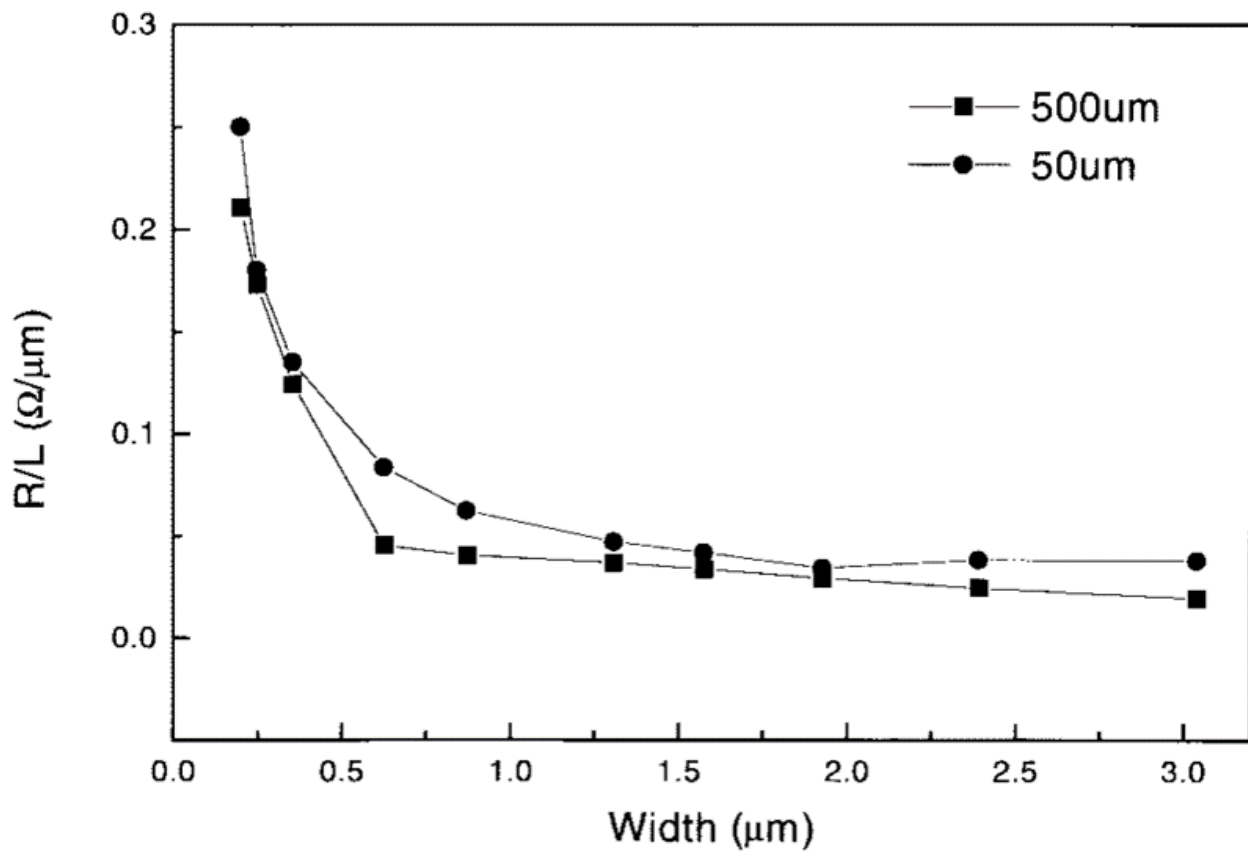


Figure 3: Cu resistivity compared to changing interconnect line width. Image from ref. [\[21\]](#)

structures. [19, 22, 25, 26] Secondly, electromigration has been identified as the main failure mechanism for Cu interconnects. [22] Therefore, to increase their reliability, steps should be taken to decrease electromigration and slow down Cu transport. [19] One way to do this is through slowing down surface and grain boundary diffusion of Cu. [22, 27] Surface diffusion tends to be the main EM mechanism, especially for narrow Cu lines. [16] Additional issues include resistance-capacitance (RC) delay and dielectric breakdown, although RC delay can be improved through the increased aspect ratio of vias and the time to dielectric breakdown is directly affected by the quality of the diffusion barrier. [8, 20, 28, 29]

Li et al. [19] identify several different types of scaling relevant to interconnects.

1. **Physical scaling**, implemented through dimensional shrink and increasing the number of devices per area
2. **Material scaling** which involves the change to alternative materials to improve performance
3. **Electrical scaling** which focuses on reduction of the power and operating voltage
4. **Integration scaling** which involves implementation of totally new integration schemes to enhance performance

Electrical scaling in particular is the best way to improve time-dependent dielectric breakdown (TDDB) and EM reliability. It is however essential to consider the impact of improvements on the whole device, particularly in terms of compatibility with the metallisation scheme, the manufacturing costs and interaction with the existing mechanisms to improve time to device failure. [19]

2.1.1 Barrier Materials

A variety of barrier materials have been tested for Cu interconnects. This section will review the different types of materials used and how their performance was evaluated. Both experimental and theoretical approaches are considered. The first diffusion barriers used for Cu interconnects were Si_3N_4 and Ta. [5, 30–35] Ta and TaN are still in use as barrier materials. [6] Kaloyeros and Eisenbraun [36] identified seven different material categories that have been for diffusion barriers for Cu interconnects. All of these are based on refractory metals which have high melting points. As grain boundary diffusion is one of the main failure mechanisms for Cu interconnects, using a barrier material with a particularly high melting point is useful, because in such materials fast diffusion processes are limited at device operating temperatures. This tends to improve the lifetime of the barrier material and by extension the lifetime of the device. Additionally, amorphous materials are of particular interest as they eliminate the possibility of grain boundary diffusion entirely and often perform better than the polycrystalline phases. [37]

In the following we present a list of the large variety of materials that have been studied as diffusion barriers in almost 30 years of Cu interconnect research.

Groups 1 and 2: Refractory Metals and Refractory Metal alloys

The first category comprises the simplest materials that have been studied as diffusion barriers. The materials studied include Ta [31, 32, 34, 37–52], Ti [43, 47, 53–56] W [43, 57–59], Mo [43, 60, 61], Cr [43, 62], Co [63, 64], Os [65], Ir [66, 67] Ru [68–71], Ni [72], Mn [73] Hf [74, 75], Nb [41, 43], RuCr [76], TaRh_x [77], Ta-Ni alloy [78, 79], Ta-Ti [79], Ta-Cr [79], Ta_{1-x}W_x [80], Ta-Fe [81], Ta-Co alloy [81, 82], V-Ta [83], Nb-Ni [84], CuAl [85, 86], Cu-Mg alloy and Cu-Ru alloy [87], Cu-Mn alloy [88–93], CuTi [90], CuZn [94], CuZr [90, 95], Cu(Ni) alloy [96], CuHf₂ [74], Cu(Re) alloy [97], TiW alloy [98, 99], CoW alloy [100–102], Ru-Mo alloy [103], RuZn alloy [104], RuMn [105], Ru-Zr [106] and Ru-Ta alloy [107]. Many of the materials in this group were studied very early on in the development of Cu interconnects. Ta has been studied for the longest time, with studies on Ta based barriers published in the early 90s [31, 32] before the "official" industry switch to Cu interconnects with recent work on Ta used as a benchmark for other barrier materials [107], and when studying the effects of processing techniques [42, 50] or changing process conditions. [47] Metal alloys have generated significant interest in more recent years. This is in part due to the discovery of self-forming or self-assembled barriers.³ The majority of the Cu alloys listed are all precursors of self-forming barriers, where the alloyed metal reacts with the dielectric to form an oxide or silicide that prevents further Cu diffusion. This is also true for the Ru alloys. [104, 105]. Similarly, a type of barrier referred to as "Mn-based" barrier has emerged. This is typically also a self-forming barrier, although the exact composition of Mn barriers is usually not described in the research. [73, 108, 109] Some of the materials that were studied as diffusion barriers in this group have turned out to be inferior to other barrier materials, however they are now used as liner materials instead. The main examples are Ta, Ru and Co. [31, 32, 34, 37–52, 63, 64, 68–71]. For example, Arunagiri et al. [69] and Chyan et al. [68] demonstrated Ru as a potential diffusion barrier, however it was later shown that due to the microstructure of polycrystalline Ru, it does not have good reliability as a barrier despite its excellent liner properties. [71, 110, 111]

³Self-forming barriers are typically Cu-based alloys which are deposited directly onto the dielectric. Heat treatment promotes the migration of the alloyed element towards the interface with the dielectric. Reaction between the alloyed element and the dielectric subsequently leads to the formation of a thin barrier material. [93]

Groups 3 and 4: Refractory Metal Nitrides, Oxides, Carbides, Borides and Silicates

These materials occur in both polycrystalline and amorphous phases, although amorphous material is preferred as it prevents grain boundary diffusion. The particular materials studied in this group include Ta_xN_y [33, 38, 49, 50, 53, 67, 73, 112–136], TaB_x [137], TaO [138], Ta_2O_5 [139], $Ta(O)$ and $Ta(N,O)$ [39], TaC_x [140–142], amorphous Ta_xSi_y [48, 143, 144], TiN_x [53, 55, 113, 117, 124, 145–162], TiC_x [163], TiO_x [139, 164], amorphous TiB_2 [165–167], W_xN_y [114, 117, 162, 168–178], WC_x [140, 179–182], WSi_x [144, 183], VN [184], $MoSi$ [144], Mo_2N [185], CoB [186], Co_xP_y [187], CrN_x [62], CuO_2 [188], $Cu(C)$ [189], RuC [190], Ru_xN_y [191, 192], Mn_xO_y [193–195], $Mn_2O_{3-x}N$ [196], NiB [197–199], NiP [200], Mo_2N [201], $Zr-Si$ [202–204], ZrN_x [205–207], ZrB [208], HfO_2 [209], HfN_x [74, 75, 210], NbN_x [211], Al_2O_3 [209], $Ru(B)$ [212, 213] and $Ru(P)$ [212–214]. Of all the barrier materials studied, TaN has been the most thoroughly investigated material. In some of the earliest published studies of Cu diffusion barriers, Holloway et al. [32] and Kyung et al. [215] studied the failure mechanism of Ta , Ta_2N , TaN and nitrogen-alloyed Ta with an additional focus on the effect of nitrogen addition. There are two competing failure mechanisms for the barrier; interfacial reaction between the barrier and Si and diffusion of Cu into Si . The nitrogen content during film deposition affects the phase of the material and increased nitrogen content in the barrier was shown to enhance its barrier properties. Ta_2N and TaN were shown to exhibit superior barrier performance compared to the other materials using in-situ resistance measurements and characterisation with cross-sectional transmission electron microscopy (TEM) and X-ray diffraction (XRD). These showed that Ta_2N and TaN were able to prevent reaction between Cu and Si for 30 mins at temperatures between 650 °C and 700 °C, while reaction occurred for Ta and nitrogen-alloyed Ta after 30 mins at 500 °C. Additionally it was found that the two materials have different failure mechanisms. Ta_2N fails due to an interfacial reaction with Si , while TaN fails because of Cu migration. [32, 215]

As the current industry standard there is a lot of interest in adapting TaN for continued use as a barrier material. For example, Xu et al. [50] and Witt et al. [132] showed that TaN continues to function as a barrier material when thinned to 0.5 nm. In addition, this has led to interest in other Ta based materials. Like Ta , TaN is also used frequently as the benchmark for new barrier materials. [107, 216, 217] Refractory metal nitrides are the largest subgroup of materials used as Cu diffusion barriers. Beyond TaN , TiN_x and W_xN_y are some of the most frequently studied materials, both showing good reliability and thermal stability, although the performance of TiN can be significantly improved with the addition of a layer of Ti . [55] The stability of W_xN_y varies with metal content. Too much W means that pure W begins to crystallise which facilitates device failure through grain boundary diffusion. [111] W_2N has been shown to be the most reliable W_xN_y diffusion barrier. [168]

Groups 5, 6 and 7: Silicon Nitrides and Carbides, Ternary Materials and Carbon Based Compounds

These materials are either non-metals such as silicon and carbon based materials or more complex ternary (and more) nitrides and alloys. Materials studied included Si_4N_3 [30, 35, 218, 219], Si_xN_y [220–223], SiC_x [221, 224–228], SiC:H [229, 230], SiCO [225, 228], SiOC:H [231], SiC_xN_y [225, 226, 230, 232–234], SiCNH [235, 236], SiOCNH [237], SiCOF [238], SiO_xN_y [239], NiSi_x [240, 241], silane based polymers [242], TaSi_xN_y [144, 243–249], TaSi_xC_y [250, 251], TaC_xN_y [252, 253], TaCoN [254], Ta(Al)N [255], VTaN [83], TiZrN [113], $\text{Ti}_{1-x}\text{Al}_x\text{N}$ [256], TiSiN [257–261], TiCN [262], TiW(N) [99], MnSiO_3 [263], amorphous carbon [264], FCN [265], $\text{Ta}_x\text{Mn}_y\text{O}_z$ [266], Ta-Ge-(O)N [267], $\text{Co}_x\text{W}_y\text{P}_z$ [187, 197–199, 268], CoWB [186, 269], CuSiN [270–272], WN_xC_y [273–276], WBN [277], WSiN [144, 183, 278], CrWN [279], IWO [134], MoSiN [144], NiWP [200], NiCoP [280], WGeN [281], ZrGeN [205] manganese oxynitride [282], RuTiN and RuTiO [283], RuTaN [191], RuMoC [284], RuBC [285], $\text{In}_x\text{Sn}_y\text{O}_z$ [286–288], ZrSiN [289], ZrTiNi [290] and ZrBN [291]. This group contains the largest variety of materials, although the majority of potential barriers continue to be based on Ta, Ti and W, likely because these materials already demonstrate barrier properties and are compatible with CMOS processing. The addition of a third element to a known barrier material can improve the barrier characteristics. For example, Lee et al. [113] found that TiZrN outperforms both TiN and TaN . All nitride films in this study were near-stoichiometric to avoid formation of defects typical for non-stoichiometric nitride films. Similarly, studies by Zhou et al. [245] and Kumar et al. [292] show that TaSi_xN_y and multi-phase Ru-TaN have better reliability compared to TaN . Additionally, the inclusion of a third element in a known barrier can also improve adhesion of Cu. [111] This will be discussed in more detail in terms of combined barrier/liner materials in Section 2.1.3.

Novel Materials: 2D Materials, Carbon Nanotubes, Polymers, Thin-film Metallic Glasses (TFMG's), Complex Alloys

This category includes novel materials that have become of interest as potential diffusion barriers, since the publication of the review by Kaloyeros and Eisenbraun in 2000. 2D materials make up the largest subgroup of these novel materials. The potential to use atomically thin layers of material as novel diffusion barriers holds a lot of attraction, as this is the ideal way to overcome the challenges associated with the thickness of the barrier layer. As the exfoliation of graphene was only demonstrated four years after Kaloyeros and Eisenbraun published their review, including a category for these materials would have been impossible. [293] Graphene, h-BN and MoS₂ are the most commonly studied 2D materials. Hence, they are also most frequently considered as potential diffusion barriers. Most studies involving other 2D materials are benchmarked against performance of graphene, MoS₂ or TaN. Transition metal dichalcogenides are the largest group of 2D materials. To the best of our knowledge, other 2D materials such as black phosphorous have not been studied as potential diffusion barriers for Cu metallisation. Graphene derivatives such as graphene oxide and reduced graphene oxide have been included here to avoid confusion, although they are not strictly two dimensional.

Examples of specific materials studied are: (multilayer) graphene [294–303], graphene oxide [294], reduced graphene oxide [294], h-BN [28, 29, 298, 304], MoS₂ [28, 29, 304–310], Nb doped MoS₂ [311], MoSe₂ [308, 310], MoTe₂ [310], WS₂ [308, 310], WSe₂ [305, 308, 310], WTe₂ [310], VS₂ [310], VSe₂ [310], VTe₂ [310], NbS₂ [310], NbSe₂ [310], NbTe₂ [310], TiS₂ [310], TiSe₂ [310], TiTe₂ [310] and TaS_x [216, 312]. Experimental studies carried out by Lo et al. supported by density functional theory (DFT) calculations from Helfrecht et al. [310, 313] show that transition metal dichalcogenide (TMD) sulfides have the highest energy barriers towards Cu diffusion through the monolayer (ML) compared to TMD selenides and tellurides. The two highest energy barriers were found for MoS₂ (4.5 eV) and WS₂ (5 eV). These results were compared to energy barriers for TaN, h-BN and graphene from the literature and indicate that WS₂, MoS₂ and TaS₂ have a higher barrier to diffusion than TaN, while single crystal h-BN and graphene have much higher energy barriers of 6 eV and 30 eV, respectively. However, activation energies for grain boundary diffusion were available for graphene, TaN and TaS₂. Here, the energy barrier for Cu migration along graphene grain boundaries was reduced drastically to 0.5 eV, while TaS₂ performed best of the three materials with an energy barrier of 1.5 eV. Of these materials TaS_x shows great promise as a barrier material, with improved Cu blocking compared to TaN, based on the above DFT calculations and TDDB measurements, which show that 1.5 nm of TaS₂ has a time to breakdown equivalent to 2 nm of TaN. Most importantly, strong adhesion to Cu is also demonstrated, along with a smooth, conductive Cu film, indicating that it can also act as a liner, which gives it an advantage compared to the other TMD's studied by Lo et al. [216, 313] 2D TaS_x is not

the only TMD which has been shown to have both barrier and liner properties. h-BN and WSe₂ have recently also been shown to act as both barrier and liner material. [305, 314]

Complex high entropy alloys and thin film metallic glasses are another category that has garnered interest in recent years. These materials excel through their excellent thermal stability and are often amorphous, thus eliminating failure via grain boundary diffusion. The specific materials studied as diffusion barriers include: Zr-Cu-Ni-Al [315], Zr-Cu-Ni-Al-N [316, 317], AlCrTaTiZr [318], AlCrTaTiZrN [319], high entropy single-layer alloy NbMoTaW [320] and high entropy alloy TiVCrZrHf [321]. Miscellaneous materials that were studied by individual groups but do not fit into any particular category but which can be mentioned for completeness are: poly(allylamine) hydrochloride (PAH)/polystyrene sulfonate (PSS) bilayers as diffusion barrier for 3D through-silicon-via integration [322] and organosiloxane nanolayers [323].

Bilayer Barriers

There has been a whole series of studies where bilayers of materials have been employed as diffusion barriers. These tend to be made up of two materials of equal thickness. [67, 70, 199, 324] Typically the focus is on how the addition of a second diffusion barrier can improve the reliability of the first barrier material and thus the whole device, in terms of thermal stability, resistivity or by adding additional properties such as acting as a liner layer. For example, Qu et al. [70] and Leu et al. [67] added a layer of Ru or Ir onto TaN to improve the overall barrier properties. The presence of TaN improved the thermal stability of the bilayer, by preventing reaction between Ru or Ir and Si. Meanwhile, the addition of Ru or Ir improved the adhesion and gapfill of Cu compared to only TaN. However, Ru and Ir were not studied explicitly as liner materials, rather they were chosen for their liner properties and the bilayer was evaluated for its diffusion barrier properties compared to the individual materials. Osaka et al. [199] and Mitsumori et al. [197] used a NiB/CoWP bilayer. Here, NiB was used as a catalytic layer to improve nucleation of CoWP which is known to be a good diffusion barrier but does not grow well on SiO₂. Kim et al. [325] studied the effect of adding a Cr, Zr or Ru interlayer between layers of TiN barrier (TiN/interlayer/TiN/Si), while a different group studied how the addition of a MgO layer on TiN affects the barrier properties of TiN. [276] For TiN barrier with different metal interlayers, failure of the barrier is determined by abrupt changes in the sheet resistance that occur when Cu reacts with the dielectric to form Cu₃Si. Addition of the metal interlayer increased the temperature at which this reaction occurs from 600 °C for Cu/TiN/Si to 650 °C for test structures with interlayers of Ru and Cr and 800 °C for a Zr interlayer. This indicates that the presence of the interlayer significantly improves the thermal stability of the TiN diffusion barrier. [325] Meanwhile, the main advantage of the addition of the MgO

layer to TiN is that it acts as an oxygen diffusion barrier and has a small lattice mismatch with TiN which means the bilayer can be grown with minimal grain boundaries thus inhibiting Cu diffusion. [276] Chen et al. [51] studied how SiCO, SiCN and SiC layers between Ta and the dielectric can improve the barrier performance for devices with ultra low-k dielectrics. Rawal et al. showed that a bilayer of Ge/HfN_x has superior barrier properties compared to HfN_x. Xu et al. [50] compared the effect of thickness scaling on thermal and permeability stability of Ta and TaN to Ta/TaN bilayer. This study along with work done by Witt et al. [132] confirmed that TaN does not lose its barrier properties even at extremely reduced thicknesses. Yang et al. [324] compared the barrier reliability of Ru/WHfN and Ru/WN. They found that by enhancing the crystallisation temperature of the barrier through incorporation of Hf, WHfN stays amorphous at higher temperatures than WN and can thus prevent failure by grain boundary diffusion. Kudo et al. [326] encapsulated CuSiN with MnO and Ta to create a MnO/MnSi/MnSiN trilayer between Cu and the substrate. This trilayer decreased the overall wire resistance by 10% compared to control samples without the CuSiN barrier and enhanced the device reliability under electric and thermal stress by suppressing surface Cu diffusion, vacancy diffusion and Cu ion drift.

Some material combinations studied have never been separately investigated as barrier materials. An example are the studies by Li and Ma et al. [320] and Li and Chen et al. [327] which investigated NbMoTaW/TiVCr high entropy multilayers and a bilayer of amorphous AlCrTaTiZrRu/(AlCrTaTiZrRu)N as barrier materials, respectively. Other bilayers studied include Ta/TaN [120, 328], Ti/TaN [329], Ti/TiN [55], Hf/HfN [74], WSiN/WSi_x [183], VTa/VTaN [83], WN_x/W [59] and SiCN:H/SiCo:H [236]. However, as material thickness of barrier and liner materials is a large concern in device miniaturisation, unless the layers of material are ultrathin, using a bilayer as the diffusion barrier is not a reasonable way forward, especially considering that TaN has been shown to continue functioning as a diffusion barrier when thinned to only 0.5 nm. [50, 132] An exception to this is the study carried out by Torazawa et al. [107] who studied a bilayer of RuTa/RuTa(N) and additionally investigated the resistivity and gap-fill performance. They showed that due to the surface orientation of RuTa, the lattice mismatch is reduced compared to Ta. While the barrier properties of RuTa/RuTa(N) were found to be equivalent to Ta/TaN, reduced resistivity and improved wettability of Cu make this a reasonable alternative to the Ta/TaN bilayer.

2.1.2 Liner Materials

The main focus of research in interconnect manufacturing has been on diffusion barrier materials. Thus a limited range of materials have been studied as liner materials. The purpose of the liner is to increase the adhesion of Cu, which can aid in preventing damage during chemical mechanical polishing (CMP) processing, and to ensure that the interconnect metal forms smooth, conductive films, rather than non-conducting islands. An additional challenge lies in finding materials that do not diffuse into the interconnect material and that wet on the barrier surface. Liner materials are almost always studied in combination with a barrier material or are tested for both barrier and liner properties. Han et al. [330] studied a series of potential liner materials for Cu with a TaN barrier using DFT. By determining the adhesion energies of a ML of Cu on TaN (1 1 1) and on a liner/TaN (1 1 1) bilayer they were able to determine that Ru, Nb, Zr and Ti could act as suitable liners for the Cu/TaN system. Additionally, they were able to establish a series of guidelines that allow the selection of a liner for any barrier and metal system based on relative adhesion energies. These guidelines are as follows:

1. Agglomeration of the interconnect is prevented, if the adhesion of the interconnect metal on the liner is stronger than adhesion on the barrier.
2. Agglomeration and diffusion of the liner is prevented, if the adhesion between liner and barrier is stronger than the diffusion between both the interconnect and the liner and the interconnect and the barrier.

While adhesion is an important factor, and using these guidelines is certainly helpful in narrowing down potential material combinations, no insight is gained into other energies that compete to control film morphology and the potential growth mechanisms. Understanding how to control the morphology through controlling the growth mechanism allows for the design of good liner materials in a more targeted way. Section 2.2 discusses potential growth mechanisms in detail. Additionally, focusing only on adhesion does not allow an insight into the barrier properties of the material and is therefore not suitable for our purposes of creating a combined barrier/liner material. From an experimental perspective, Cu gap-fill and resistivity are liner properties that are often considered in addition to adhesion.

Unlike barrier materials, the most frequently used liners are elemental metals. Materials that have been studied as liner materials include Ta, [52, 330–338], Co [73, 108, 109, 131, 178, 330, 335, 339–349] and Ru [15, 71, 73, 94, 108, 109, 133, 255, 330, 331, 333, 335, 336, 338, 342, 344, 350–364], as well as some less common materials such as Rh, Ir and Pd [335], Mo and Os [335, 336], Ti [173, 330, 365], Zr [330, 365], Hf, [365] Ni [149, 330, 366], Al and Nb [330], RuTa alloy [217, 338], Cu(Mn) [102] and polyimide [161].

The liner properties of some 2D materials were examined as part of testing their barrier properties. Lo et al. showed that 2D TaS₂ acts as a Cu liner. [216] Tape tests showed poor wettability of Cu to h-BN, which means it is unsuitable as a liner. [28, 313] Similarly, graphene showed poor adhesion and is also deemed an unsuitable liner. [216, 313] MoS₂ showed reasonable wettability with Cu that makes it relevant for further study. [28, 306, 307, 313]

Studies of liner materials take many different approaches and focus on a variety of aspects of the manufacturing process. Frequently the focus in studying a liner material is in determining how traditional liners such as Ru interact with different barrier materials. [94, 108, 109, 255, 364] For example, Kikuchi et al. [255] studied the effectiveness of a novel Ta(Al)N barrier in combination with a Ru liner. Similarly, van der Veen et al. [108] and Jourdan et al. [109] studied the effectiveness of Mn-based barriers in a test structure with Co and Ru liners and Joi et al. [94] studied self-forming Cu-Zn barriers in conjunction with a Ru liner. Kitamura et al. [364] investigated the effect of adding a Ru liner to a TiN/Ti diffusion barrier. In contrast, Chae et al. [149] tested Ni as a novel liner material for use with TiN, an established diffusion barrier.

Other work, for example by Kim et al., [336] has focused directly on the effects of using a liner material in the interconnect architecture by investigating how to improve adhesion between Cu and the diffusion barrier by inserting Ru, Ta, Os or Mo as an adhesion promoter. Similarly, Meyer et al., investigated the liner properties of CoWP [367] which has also been studied as a diffusion barrier [187, 197–199, 268], while Besling et al. [368] and van der Straten et al. [337] tested the interactions between Cu and TaN in terms of wettability and adhesion. [337, 368] Li et al. [178] also focused solely on the liner properties in their study of the nucleation and adhesion of a Cu seed layer on a WN barrier with Co liner. They found that Cu forms a conformal, continuous seed layer on the Co/WN stack and that the adhesion between Cu/Co/WN was strong enough that the whole stack was removed from the SiO₂ substrate during the tape test. The addition of the Co liner also reduced the sheet resistance compared to using only WN.

Studies of liner materials focus on comparing the performance of liners to a benchmark material that is already in use, such as Ta. For example, He et al. [347] showed that using Co instead of Ta as a liner material yields improved Cu gap-fill. Similarly, Jang et al. [344] compared the performance of Ru and Co as liner alternatives to Ta on TaN to determine whether Ru and Co affect the device reliability as well as improving Cu gapfill. The Cu/Ru/TaN system performed best during the electromigration (EM) reliability test. The EM test was carried out using an EM tester which creates accelerated operating conditions for test devices in a specific temperature and current range, in this case 225 - 350 °C and a current density of DC 1 - 3 MA/cm². There was no open circuit failure even after 160 hours and the resistance increased only gradually over time instead of increasing rapidly and causing

device failure, as for Co and Ta liners. This means that the strong adhesion between Cu and Ru allows Cu to act as a shunt layer for the conduction path and thus prevent a rapid resistance increase. Zhang et al. [346] examined the electrical characteristics of Ta and Co liners to determine how the liner can be used to decrease the Cu line resistance. They found that systems with Co liners have a higher line resistance due to the influence of Co on the Cu microstructure. However, as the resistance is largely controlled by the grain size and orientation, if the Co liner process can be improved to increase the coherence of grain boundaries it is expected that the Cu line resistance can be reduced compared to using Ta liner. The work carried out by Yang et al. [217] is a good example of a study that examines both barrier and liner properties. They compared the use of Ru/TaN and RuTa/TaN to Ta/TaN and found that the Ru stacks have comparable diffusion barrier properties to Ta/TaN, but improve the gapfill and show enhanced EM reliability. Consequently the resistivity of the deposited Cu should be improved and the devices will have a longer lifetime as electromigration is inhibited. Some work focuses specifically on the effects of different deposition methods on the performance of the liner. For example, Van der Straten et al. [337] in particular focused on wettability of Cu on sputtered Ta and sputtered and atomic layer deposition (ALD) TaN in order to determine the effect of different film deposition methods on morphology. They found that the addition of a surfactant to the ALD deposition process affects the wettability of Cu on the deposited film. Ta cannot be deposited via CVD or ALD with halogen free methods which are needed for back-end-of-line (BEOL) manufacturing conditions. This necessitated the consideration of alternatives for smaller scales where the accuracy of ALD is required. [15] Lanzillo et al. [349] focused on failure mechanisms of Ru/Ta barrier/liner bilayers. In particular, they studied how oxygen contamination during manufacturing causes oxidation of the barrier/liner bilayer and increases the resistivity of the device.

Typically, devices are manufactured with the same thickness for both the barrier and the liner [217, 344, 346], while some vary the thickness of the liner [15, 339] or both barrier and liner [131]. The latter studies where the barrier and liner have different thicknesses tend to focus specifically on the effects of decreasing the thickness of the liner and/or barrier. As an example, in two further studies by Lanzillo et al., they demonstrated how thinning a Co/TaN barrier/liner stack effects the reliability and resistivity of the interconnect. [131, 339] They found that thinning TaN to below 1 nm significantly reduces the resistivity, while the resistivity is mostly unaffected by the thickness of the Co liner, which was varied from 3 to 0.5 nm. Thinning the Co liner was found to decrease the RC delay of the devices, but it was also found to have a negative impact on the electromigration reliability of the system despite the presence of a PVD TaN barrier. The results suggest that these negative effects can be avoided by adding a thin layer of ALD TaN onto PVD TaN. Test devices with such a ALD/PVD TaN layer and a Co liner thinned to 1 nm showed a 14% reduction in RC delay without any negative effect on electromigration reliability

and TDDB. [339]

As Han et al. demonstrated, DFT is a useful tool in determining the adhesion between metal and liner layer. Ding et al. [335, 338] also used DFT to examine the effectiveness of a series of different metals as liners and adhesion promoters. They initially tested various Ru and Ta based materials: Ta (1 1 0), Ru (0 0 0 1), O and N doped Ru and Ta and RuTa alloy. By examining adsorption energy, electron density difference, geometrical structure and agglomeration of Cu on these surfaces they are able to determine that Ru doping improves adhesion of Cu to Ta and that N and O contamination, as well as the large lattice mismatch between Cu and Ta, encourage agglomeration. This means that of the materials studied RuTa alloy is the most promising candidate for a good liner material. In their following study [335] the work expands to include a whole series of different metals. Using DFT, the stability of different coverages of Cu, from $\frac{1}{4}$ coverage (single atom) to 5 ML coverage, on the most favourable surface of Rh, Ir, Pd, Ta, Mo, Ru, Co, and Os was investigated. Findings showed that Cu adhesion is affected by chemical interaction, lattice mismatch and lattice type. Up to $\frac{3}{4}$ coverage, Cu adhesion on Ta is most favourable. However, as coverage increases to 5 ML of Cu, adhesion is strongest on Co, followed by Rh, Ru, Os and Ir. Co, Ru, Os and Ir have the strongest adhesion energies across the different coverages making them the most suitable candidates for liner materials. However, these studies focus almost solely on the change in the adhesion for different coverages of Cu on a variety of liners. This can be useful when trying to choose the liner with the strongest adhesion to Cu, however it gives little to no insight into potential film morphologies or the interactions which drive favourable adhesion. The work presented in this thesis aims to address this knowledge gap. When agglomeration was studied, insights were based on the formation energy of a 3D, tetrahedral Cu_4 structure on the liner, with no consideration to other possible geometries. Further, the supercells used are 2x2, 2x1 and 1x1. They are based on the computed lattice parameters for Ta and Ru (Ta(bcc) $a=b=c=3.368 \text{ \AA}$, Ru(hcp) $a=b=2.717 \text{ \AA}$, $c=4.282 \text{ \AA}$). This is quite small as the various surfaces have only ca. 5 atoms per layer, which leaves the tetrahedrons close enough to interact with periodic images or even within the cell. No comment was made on the potential effect of these interactions on the formation energy and stability of the Cu clusters. Lastly, the liners are studied without a barrier material although it is important to understand not only the interaction between Cu and the liner material but also between the liner and the potential diffusion barrier.

2.1.3 Combined Barrier/Liner Materials

When selecting potential alternatives for diffusion barriers, it is vital to keep the essential characteristics of a good barrier material in mind. Some studies use bilayers of material and study the barrier and liner together. [107, 369] However, as discussed previously, this is not practical for reducing the material thickness. One way to build on

existing knowledge and reduce material thickness is through combination of materials. Combining known barrier and liner materials to achieve a material with properties of both has some precedence but still needs further work. Chakraborty et al. studied mixed-phase RuTaN. [110, 370] Eisenbraun [133] uses plasma enhanced ALD (PEALD) to create mixed phase barrier/liner materials by layering known barrier (TaN, WCN) and liner materials (Ru, Co), starting with the barrier and ending with a liner layer. The possible combinations show comparable barrier properties to TaN. Additionally, the concentration ratio of metals can be used to tune the material to have low resistivity and good wettability while maintaining strong barrier properties. However, compared to the extremely thorough research on diffusion barriers, the work on combined barrier/liner materials is more limited. Some of the materials studied as combined barrier/liner materials include NiP alloy [371], Cr [76], RuMo alloy [103], CoWB [269], Ru [71], MoC doped Ru [372], Ru(P) [373], RuCo [6], Co [348, 374], Co(W) [101, 375–377], MnN [378] and Ti [379]. Some work already focuses beyond Cu interconnects. For example, Zhang et al. study amorphous Co-Ti as combined barrier/liner for both Cu and Co interconnects. [380–383]

Based on the review of the literature we find that the desired properties for good barrier and liner materials are as follows:

- Thermal stability
- Low grain boundary diffusion
- Low overall resistivity
- Wettability and adhesion of Cu
- Low electromigration
- Reduced material thickness

There is a large variety of experimental methods for studying these properties to determine barrier and liner performance. As the name suggests, the commonly used TDDDB measurements can determine the time it takes for the dielectric to break down given thermal or electrical stress. The breakdown refers to the phase transition of the dielectric from insulating to conductive phase. By carrying out these stress tests for dielectric-metal interfaces it can be used as a measure of device lifetime which is typically expressed in terms of time and cumulative probability of breakdown. [29, 384] It also allows insight into thermal and electrical stability. [7, 8, 23, 28, 29, 216, 306, 307, 311, 385, 386]. Microscopy methods such as scanning electron microscopy (SEM) and cross-sectional TEM are essential in determining gap fill and wettability but also in analysing the grain structure and any potential reactions

at the interface such as silicide and void formation. Using microscopy after a reliability test also allows insight into the failure mechanism. [6, 29, 34, 37, 39, 68, 107, 178, 217, 308, 311, 346, 347, 382, 385, 387–390] Atomic force microscopy (AFM) measures surface roughness and can thus aid in studying nucleation and wettability. [178, 385] X-ray photoelectron spectroscopy (XPS) is used to study film composition and characterise potential impurities. [107, 385, 388] XRD can be used to determine crystal structures and surface orientation [37, 67, 68, 107, 145, 168, 215, 217, 385, 388, 389] and x-ray reflectometry (XRR) is used to determine the thickness of the deposited film. [388, 389] Using scotch tape to attempt to exfoliate various layers is a useful approach to determine the adhesion experimentally. [68, 178, 391] Resistance measurements are most important in determining both the overall line resistance and as an indicator of device failure. Typically there is an abrupt increase in the resistance when the diffusion barrier fails and reaction between the substrate and Cu and/or the barrier materials occurs. Resistance is typically measured using sheet resistance measurements, [107, 145, 178, 215, 387, 389] or triangular voltage sweep (TVS) [6, 217].

Just as a wide variety of experimental methods is needed to study all aspects of a potential barrier and liner material, theory also requires a wide range of methods to attempt to study all of the above properties. This is usually not possible as it would require a large amount of time and resources which are not within the scope of a typical research project. Thus it is reasonable to select the properties of interest and focus on modelling these. Adhesion is the property that is most easily studied using theoretical methods. [310, 330, 335] Activation energy for atom diffusion can be determined using nudged elastic band calculations and can give insight into surface mobility of atoms as well as the diffusion barrier properties. [38, 298, 313] Ab initio molecular dynamics calculations can be used to gain some insight into thermal stability as well as wettability and growth processes. [330, 392] Additionally, electronic properties such as density of states (DOS), atomic charges and electron density can be studied, which give useful insight into conductivity and band gap of the material and can also reveal trends that drive the formation of favourable structures. [310] These are useful in determining the basic material properties such as conductivity and band gap. Models have also been developed to screen for materials based on their electronic properties. These are particularly useful when combined with experimental methods. [10] Additionally, machine learning can now be applied to modelling the overall performance of interconnects which can save valuable time and resources during the development process. [393] Overall, theoretical studies make up only a small fraction of the research on advancing interconnect manufacturing leaving plenty of room to gain further insight into growth mechanisms and material interactions relevant for application in interconnect technology.

2.1.4 Deposition Methods

With changing device specifications, the deposition methods for materials have also changed over time. While PVD, [107, 217, 347, 389] CVD [7, 35, 217, 344, 347, 385] and sputtering [67, 70, 215, 382, 392, 394] are still in use, often a more precise method such as ALD is needed to create conformal films on very small and complex features. [6, 13, 26, 178, 344, 375, 385, 386, 388, 395] The wide variety of options allows tailoring of the deposition process to the particular material and device. While deposition methods are still being optimised for novel materials such as MoS₂, [28, 216, 306, 307, 311, 396–399] there is also some work on adjusting reactants, addition of surfactants and process optimisation in an effort to control physical properties of traditional diffusion barriers through the deposition process. [8, 15, 36, 337, 400, 401]

2.1.5 Alternative Interconnects

Alternative interconnects, that would not have the same challenges as Cu, were already under investigation four years after the first devices with Cu interconnects were introduced to the market. These include alternative interconnect metals, 3D integration, radio-frequency (RF) interconnects and optical interconnects and continue to be of interest today. [16] Since then various metals and other materials have been considered as alternatives to Cu for the lowest levels of interconnects. Other refractory metals have been studied thoroughly to determine whether they can perform better than Cu at small sizes. As Cu resistivity increases at smaller interconnect sizes, finding materials with low resistivity at small sizes is a particular challenge. Adelmann et al. [400] suggested that the melting point and bulk resistivity are good initial indicators for elemental metals that could be used as alternatives to Cu. Oftentimes these do not perform well at present device sizes and only begin to perform better than Cu at smaller sizes. For example Bekiaris et al. [385] showed the resistivity of Co drops below that of Cu at 14 nm film thickness. Co fill down to 10 nm was demonstrated, with improved reliability compared to Cu. As adhesion of Co on SiO₂ is poor, a TiN liner was used which also acts as a diffusion barrier and further improves reliability.

Another alternative to Cu is Ru. Barmak et al. [387] showed that 10 nm Ru films are defect-free, while Ru films of 20 nm thickness had many defects when grown using epitaxial electrochemical deposition. Ru also showed decreased resistivity compared to Co below 20 nm. The authors suggested a damascene-like system of layers of Co and Ru as an alternative to traditional interconnects. In fact, Pedreira et al. [386, 402] suggested that Ru might be an even better alternative to Co as EM reliability tests at 330 °C show no diffusion into the dielectric for 550 h. Adhesion to the substrate is also improved compared to Co, although a thin TiN liner of 0.3 nm was used in their second study to improve adhesion further. In contrast, Philip et al. [403] found that the adhesion of Ru to SiO₂ is

stronger than to TiN or TaN, although the liner may be needed regardless to aid deposition. They were also able to show that the crystal structure of Ru affects its resistivity, indicating that Ru growth must be controlled to be fcc rather than hcp in order to ensure optimised resistivity.

Some work on interconnects also involves completely novel materials, such as ZrTe_3 , a van der Waal's material that forms quasi-1D nanoribbons and was demonstrated by Wen et al. [404] to have promising characteristics for advanced interconnect structures. In particular, ZrTe_3 is found to be metallic, can be synthesised as high quality single-crystals via CVD, shows size-independent resistivity and displays a non-linear increase in the maximum current density with decreasing line width. Another example is the use of graphene based materials. [405–407] Various possible structures of graphene nanoribbons were tested by Kumari et al. [405] This work focused on how multilayer vertical graphene nanoribbon interconnects compare to horizontal graphene nanoribbon structures and traditional Cu interconnects and finds that they perform well in terms of cross-talk and power consumption and show good potential for further scaling. Meanwhile, Mudavath et al. [406] studied the signal integrity of multi-walled carbon nanotubes (CNTs) in comparison to Cu interconnects and found that a passive shielding can reduce cross-talk significantly in both types of interconnects. Despite the reduction the overall cross-talk for Cu interconnects is still higher than for bundled multiwalled CNTs.

A common approach is to use doped or alloyed Cu instead of pure Cu. Zhang et al. [408] used 4 at.% C-doped Cu for a barrierless metallisation process. The carbon content prevents the reaction of Cu with Si, eliminating the need for a diffusion barrier. Similarly, Cu(RuHfN) [409], CuNiNb, [410] CuAl_x [411, 412], Cu(Ru) [413], Cu(Ti) and Cu(Zr) [414] have all been suggested as alternatives to pure Cu for a barrierless metallisation process. NiAl alloy has also been suggested as a low resistivity, non-Cu alternative. [415] Similarly, there has been increased interest in using carbon nanotubes (CNTs) as part of an alternative metallisation scheme. For example, Kumari et al. [416] showed hybrid interconnects using Cu-CNTs which were encapsulated in a layer of graphene which acts as a diffusion barrier. This Cu-carbon structure showed enhanced reliability and conductivity compared to Cu-CNTs. Similarly, Sun et al. [417] also studied Cu-graphene hybrid interconnects using multiphysics modelling to predict various properties of the proposed alternative interconnects. In another study Kumari et al. [418] also demonstrated the use of multi-walled CNTs to reduce breakdown of interconnects caused by self-heating.

Another approach is to consider the interaction between TaN and various metals that could be used as an alternative to Cu, as shown by Grumski. [112] However, at the current state of the art, this approach is quite limited since apart from improving the function of Cu at small dimensions, the main goal should be to find barrier and liner free alternatives to Cu for new metallisation schemes. One way to achieve this would be through the use of doped graphene nanoribbons as the interconnect, which was demonstrated by Jiang et al. [419]

2.2 Growth Mechanisms

As one of the main characteristics of a combined barrier/liner material must be to promote smooth, conducting films, it is essential to understand the underlying mechanisms of film growth that control the final film structure. While adhesion plays an important role in this, gaining insight into how exactly the surface composition and morphology affects the growth mechanism is an essential step in learning how to tailor materials to promote the desired film morphology for any application. This can be split into two stages of growth, the initial particle growth and agglomeration. For the initial growth there are two possible growth mechanisms, characterised by the strength of the interaction between the deposited material and the substrate.

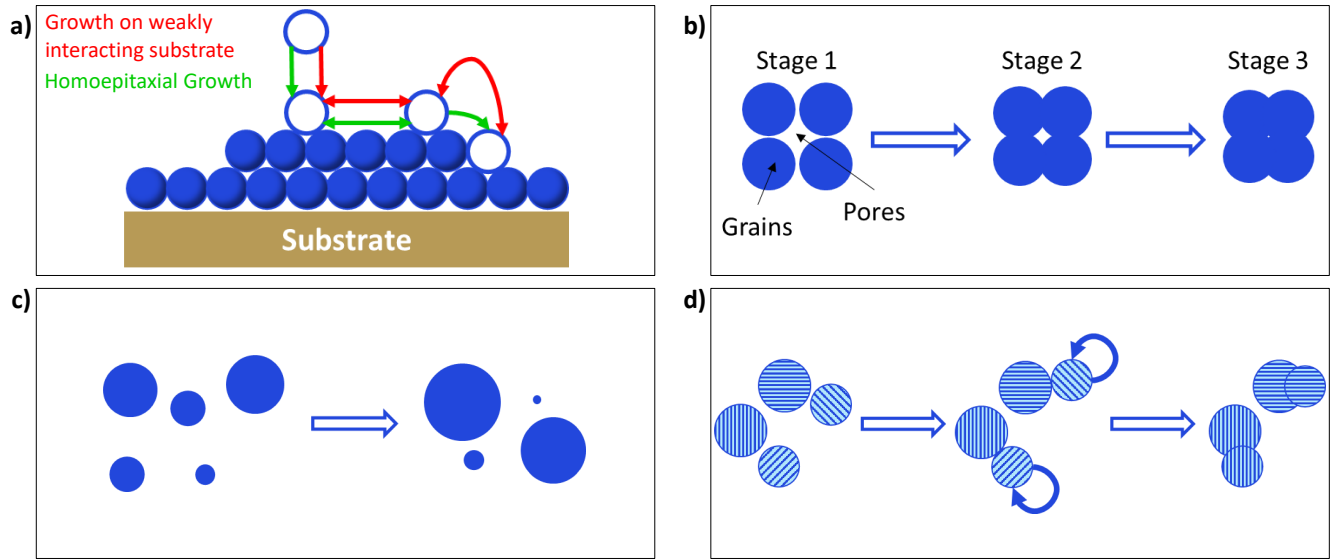


Figure 4: a) Mechanism for homoepitaxial growth and growth on weakly interacting substrates. Adapted from ref. [420] b) The three stages of sintering. Adapted from ref. [421] c) Ostwald ripening. Adapted from ref. [422] d) Grain rotation induced grain coalescence (GRIGC). Adapted from ref. [422]

Materials tend to follow a classical homoepitaxial growth mechanism [423–425] when there is a strong interaction between the deposited material and the substrate. [420] An example of this would be aluminium grown on aluminium substrate. [426] For strongly interacting substrates, the interaction with the substrate is stronger than the interaction between atoms of the deposited material. A higher temperature is associated with 2D growth, making annealing a reasonable approach to create a conformal film. In contrast, the opposite becomes true for growth on a weakly interacting substrate. Here, the interactions between the atoms in the deposited material are stronger than the interaction with the substrate. Consequently, increased temperature tends to promote 3D growth. This leads to faceted structures and rough surfaces which are not desirable for interconnects. [392, 420, 427–430] Additionally,

while migration of atoms across the surface can occur, Gervilla et al. [420] described that upward migration of atoms to form new layers is not possible on strongly interacting substrates. This is a crucial difference between the two mechanisms. By enhancing the adhesion between the adatoms and the substrate a homoepitaxial growth mechanism can be promoted, which in turn promotes 2D growth of the thin film. Computing the activation energies for atoms to migrate between layers lets us determine which mechanism is dominant based on the magnitude of the activation energy. The different migration pathways for homoepitaxial growth and weakly interacting substrates are shown in Figure 4a).

It is difficult to unambiguously define what counts as a strong or a weak interaction, outside of the competition between material and substrate interactions. Gervilla [431] defined a weak interaction as one in which the bond strength between the metal and the substrate is no more than half the bond strength of the metal, based on a review of thin film growth on oxides by Campbell. [432] For our purposes we will consider the adsorption energy relative to the cohesive energy of the interconnect metal as a guide to the strength of the interaction. If the binding energy is close to or greater than the cohesive energy of the metal, the interaction will be considered strong.

To the best of our knowledge, studies of growth mechanisms for systems like this tend to be carried out using kinetic Monte Carlo (kMC) or mean field approximation methods, [420, 427, 428, 430] with some studies choosing to use classical molecular dynamics. [392, 429] Using these methods, significant insight has been gained, in particular into the growth mechanisms on weakly interacting substrates. Gervilla et al. [420] were able to show that the formation of the top layer at higher temperatures can promote island formation, i.e. once the top layer has reached a critical size it becomes easier for more atoms to move upward. However, the type of side wall facet has some control over the ease of this process. Grillo et al. [427] focused their study on growth mechanisms during ALD processes. Using the example of Ru, they showed that during the growth of a nanoparticle using ALD, the morphology of the particle cannot be controlled via the number of deposition cycles. Instead, the process must be carried out below 100 °C. Here, the particle growth is driven by atom attachment processes instead of nanoparticle coalescence and diffusion. Jamnig et al. [401, 429] also published two studies on nanoparticle growth. They found that the overall mobility of the nanoparticle is dependent on the metal and that the addition of gaseous surfactants at various stages of the deposition process can be used as a means to promote either 2D or 3D growth.

Agglomeration and film morphology after the initial growth are controlled through processes referred to as sintering, Ostwald ripening and grain rotation induced grain coalescence (GRIGC). Sintering is a process by which heat causes a densification of a material without transition to the liquid phase. This decreases the porosity of the material and can thus improve the material quality. [433] There are three stages associated with the sintering process, as shown in Figure 4b). At the initial stage, the grains are small and separated by large pores. During the sintering

process, the material reaches the second stage, where pore size decreases and grain size increases. Finally, after sintering is complete the material reaches the third stage with large grain size and small pores. [434] The sintering mechanism can be controlled through temperature and sintering additives. [435–437] Sintering mechanisms are particularly relevant to control the morphology of ceramics and steel. Additionally, some covalent materials such as carbon and BN are known not to sinter due to inhibition of vacancy diffusion by directional bonding and require additives to promote densification. [436] For Cu nanoparticles, sintering can also be used as a method to remove surface oxide from the nanoparticle. Control of the sintering process in Cu becomes particularly relevant at the packaging stage of device fabrication to ensure a high quality Cu bond pad is formed. [438, 439]

Ostwald ripening and GRIGC are crystal growth mechanisms by which particles combine to form a larger particle. By controlling these growth mechanisms, the particle size in nanocrystalline materials can be controlled. [422] Ostwald ripening is driven by surface diffusion processes. Here smaller particles coalesce with larger ones as the latter are more energetically favourable. Ostwald ripening in solution occurs because the solubility of a particle increases as the radius of the particle decreases. The smaller particles dissolve and are redeposited on the surface of a larger particle leading to coalescence. [440, 441] A similar process also occurs for solids. [442] This means that in both liquids and solids, the larger particles ripen at the expense of the smaller particles, i.e. material from the smaller particle is transported to the larger particle until the small particle disappears. In GRIGC, rotation of grains in the system can cause alignment of grains along grain boundaries with the same crystallographic orientation, as shown in Figure 4d). This leads to the coalescence of the two grains to form one larger, continuous grain. GRIGC has been observed to occur in colloidal systems at room temperature. The favoured directionality of growth in this mechanism depends on the relative stability of the different surface facets. [422] While sintering and GRIGC require proximity of particles for coalescence to occur, Ostwald ripening can occur regardless of the particle distribution. [443]

Unlike the two mechanisms discussed for initial particle growth, sintering, Ostwald ripening and GRIGC are not necessarily mutually exclusive and can occur simultaneously. As sintering and Ostwald ripening are driven by diffusion processes, the rate of coalescence tends to increase at higher temperatures where diffusion processes become more frequent. [443]

Coalescence processes can be studied by using DFT to model the stability of different surface facets and mobile atomic species on these surfaces. Applying the results to the kinetic equations that describe these processes or computing activation energies for different migration processes allows insight into the mechanisms of coalescence processes for different materials. [422, 444–448] Molecular dynamics, mean-field approaches and mesoscale simulations have also been used, in particular to study the mechanism of GRIGC in various materials. These are used, as larger models than achievable with DFT are required to study the interaction of several grains. [449–451] Of the

three processes, sintering is most studied using a combination of experiment and DFT, where the DFT calculations are used to support experimental insights, rather than modelling the sintering mechanism. [452–454]

2.3 Conclusion

Reviewing 30 years of research on Cu interconnects has revealed the large spectrum of work that has been carried out in an effort to optimise the interconnect across several technology nodes to meet increasingly demanding device specifications. This has allowed Moore’s Law to stay on track into the 2020’s, however while much progress has been made, Cu is reaching its limits as a conductor. Despite this there is merit to optimising the Cu interconnect as much as possible before moving to replace it with an alternative conductor, especially as Cu will continue to be the best performing conductor for the higher interconnect levels. To achieve this, there is a need to understand how to control the morphology of Cu films and to develop ultrathin barrier/liner materials to facilitate manufacturing of interconnects with high reliability and low resistivity at the nanoscale.

More specifically, this review showed several outstanding research questions that have not been addressed in the literature some of which can be addressed using DFT:

1. **What are the detailed, atomic interactions between Cu and known barrier materials?**

The focus of most research on barrier materials is on their failure mechanism. But what are the specific interactions between Cu and a barrier material that allow it to function as such? What interactions prevent wetting of Cu? This question can be addressed by studying the adsorption and migration behaviour of a variety of Cu structures on a known barrier material.

2. **What is the minimum effective amount of liner material?**

As discussed above, barrier and liner materials are typically fabricated with equal thickness. However, it is possible that there is a way to thin the barrier/liner stack simply by reducing the thickness of the liner material. The effectiveness of such an ultra-thin liner can be determined by studying the interactions of Cu with a barrier surface that has been passivated with a single layer of liner material.

3. **Can we develop a combined barrier/liner material from TaN and known liner materials?**

Binary, ternary or mixed-phase materials of known barrier and liner materials have been demonstrated to act as combined barrier/liner materials. However, ternary materials of the two most common barrier and liner materials, TaN and Ru, have only been predicted to be stable [455] and tests in my thesis work showed that surfaces cut from the predicted structures undergo significant rearrangement upon relaxation. Some example structures are shown in Figure A1 of the Appendix. Doping of liner atoms into only the surface layer of the

barrier material is one way to avoid such rearrangements, while creating a surface that retains both barrier and liner properties.

4. What can we learn about the interactions between metal and substrate from different shapes and sizes of metal structures?

Many studies of metal adsorption on barrier or liner materials focus either on single atom adsorption, entire monolayers or one single geometry of Cu. However, studying different cluster geometries and different sizes of metal clusters can give a variety of insights on the factors that govern adsorption and drive favourable interactions.

5. What is the smallest model of Cu that is representative of the final film morphology?

A tetrahedron of Cu has been used to represent agglomeration of the Cu film. But is this a representative model on its own? By comparing the interaction of tetrahedral Cu with other four atom structures we can gain more detailed insight into 2D vs 3D geometries. Putting these results into the context of results from a larger Cu model on the same substrate allows us to evaluate how conclusions drawn from different model sizes compare.

6. Can we target specific metal-substrate interactions in our calculations to predict the growth mechanism?

Knowing that the competition between metal-substrate and metal-metal interactions controls the initial growth mechanism of a thin film allows us to specifically target these interactions in our studies and predict the film morphology. Conclusions based on metal-substrate and metal-metal interactions can be supported by computing the activation energies for different migration paths.

7. How do the interactions between Cu and a potential barrier/liner material compare to the interactions of alternative interconnect metals on the same material?

Given that alternative interconnect metals such as Co and Ru most likely cannot be plated directly onto the dielectric, it is useful to understand how their interactions with potential barrier or liner materials compare to the interactions of the same material with Cu.

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Chapter 3: Theoretical Background and Methods

3.1 Survey of Quantum Chemistry

This section describes the underlying quantum mechanical theory used to determine the electronic and atomic structure of a given system composed of electrons and nuclei, be it molecule, bulk material or surface.

3.1.1 The Many-Body Problem

The ultimate goal of quantum chemistry is the solution of the many-body Schrödinger Equation, which describes the electronic structure of a given, time-independent quantum system. In a given system with n electrons at coordinates $[r_1...r_n]$ and N nuclei at coordinates $[R_1...R_N]$ the time-independent, many-body Schrödinger Equation is: [1]

$$\hat{H}\Psi(\mathbf{r};\mathbf{R}) = E\Psi(\mathbf{r};\mathbf{R}) \quad (1)$$

where $\hat{H}$ is the Hamiltonian operator which acts upon the many-body wavefunction $\Psi(\mathbf{r};\mathbf{R})$ and returns the total energy of the system, E . The Hamiltonian operator contains functions for all the kinetic and potential energies of this system, while the wavefunction contains the characteristics of all particles in the system.

Assuming there are no magnetic or electric fields, the Hamiltonian takes the form: [2]

$$\hat{H} = \kappa_n + \kappa_e + \nu_{nn} + \nu_{ne} + \nu_{ee} \quad (2)$$

where κ_n and κ_e describe the kinetic energy of the nuclei and the electrons, respectively, and ν_{nn} , ν_{ne} and ν_{ee} describe the potential energies of nucleus-nucleus, nucleus-electron and electron-electron interactions. By using atomic units and setting the mass and charge of the electron, the reduced Planck's constant, $\hbar$, and $4\pi\epsilon_0$ (where ϵ_0 is the vacuum permittivity) to 1, the Hamiltonian can be expressed more compactly as: [2]

$$\hat{H} = - \sum_A \frac{1}{2m_A} \nabla_A^2 - \sum_i \frac{1}{2} \nabla_i^2 + \sum_{A>B, A \neq B} \frac{Z_A Z_B}{R_{AB}} - \sum_{A_i} \left(\frac{Z_A}{r_{A_i}} \right) + \sum_{i>j} \frac{1}{r_{ij}} \quad (3)$$

Here, the terms are in the same order as they have been stated in Equation 2. m_A and Z_A are the mass and atomic number of nucleus A.

The Coulomb interaction of two electrons is the cause of the so-called "many-body problem" and the reason why the Schrödinger Equation cannot be solved exactly for a system with more than one electron. It is impossible to account for such simultaneous, instant electron-electron interactions especially because the interactions of all electrons in the system are correlated. Approximations to the many-body problem must be made in order to find a solution to the Schrödinger Equation for any system beyond hydrogen.

There are several simple approximations and some more complex ones, which will be discussed in more detail. One way to resolve the issue of ν_{ee} is to treat ions as having a single electron. This removes ν_{ee} entirely and allows us to compute the atomic orbitals. Another method is using the Born-Oppenheimer Approximation. [3] Here, it is assumed that due to the vast difference in the mass of an electron and a nucleus, the nuclei move so slowly compared to the electrons that they remain static while the electrons are dynamic. This means that the nuclei have no kinetic energy which allows κ_n and ν_{nn} to be set to zero, creating a Hamiltonian that describes only the electrons, denoted $\hat{H}_e$:

$$\hat{H}_e = - \sum_i \frac{1}{2} \nabla_i^2 - \sum_{A_i} \frac{Z_A}{r_{A_i}} + \sum_{i>j} \frac{1}{r_{ij}} \quad (4)$$

In a practical setting, use of this approximation allows us to compute an energy surface by solving the electronic Schrödinger Equation (Equation 5) for a series of different, fixed nuclei positions in a system, thus determining the lowest energy geometry of the system.

$$\hat{H}_e \Psi_e = E_e \Psi_e \quad (5)$$

However, we still have to account for ν_{ee} and therefore the wavefunction remains prohibitively complex. A further approximation includes the Linear Combination of Atomic Orbitals (LCAO). LCAO, which takes the general form given in Equation 6, makes use of the fact that an unknown wavefunction Ξ can be described as a linear, infinite expansion of a set of known functions, χ_i , each of which has a weight of c_i in the expansion. As it is known that molecular orbitals are created from the combination of atomic orbitals, molecular orbitals can be computed from the known, atomic orbitals.

$$\Xi = \sum_i^{\infty} c_i \chi_i \quad (6)$$

The Variational Principle is based on using multiple iterations of guess functions to approach the minimum total

energy of a system based on a guess wavefunction with a number of parameters describing the system. This is under the condition that the derivative of the energies with respect to the parameters in the guess function becomes zero:

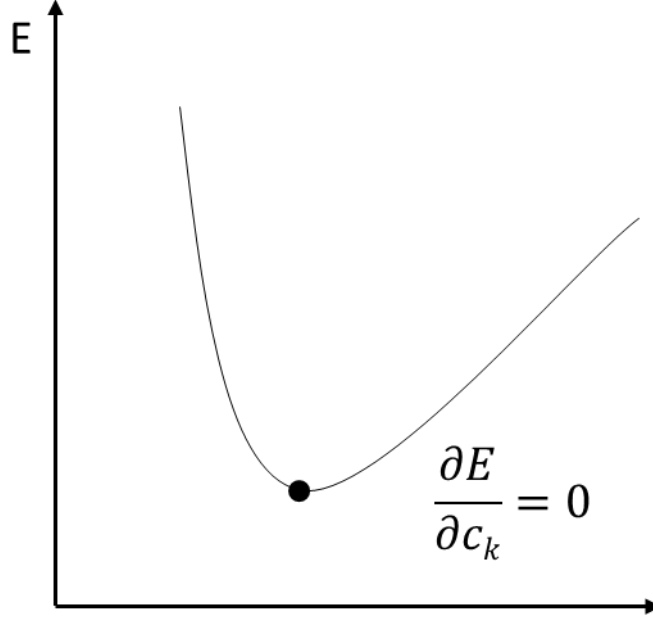


Figure 1: Minimum energy computed with Variational Principle.

3.1.2 Hartree and Hartree-Fock Approximations

Hartree's Approximation for solving the Schrödinger Equation is based on the assumption that the electrons are not interacting and move independently. [4, 5] This means that an effective Hamiltonian $\hat{h}$ can be written for single electrons such that:

$$\hat{H} = \sum_i \hat{h}(i) \quad (7)$$

This means that the electron-electron interaction is not described explicitly, but as one electron interacting with an average potential of the remaining (N-1) atoms. From Equation 7 we arrive at a modified Schrödinger equation to describe the i th electron:

$$\hat{h}_i \psi_i(\mathbf{r}_i) = \varepsilon_i \psi_i(\mathbf{r}_i) \quad (8)$$

By applying this approximation we then know that for a system with n electrons, the wavefunction is a product of one electron wavefunctions:

$$\Psi_H(\mathbf{r}_n) = \prod_n \psi_n(\mathbf{r}_n) \quad (9)$$

and the total energy is the sum of the one-electron energies, i.e.

$$E_H = \varepsilon_1 + \varepsilon_2 \dots + \varepsilon_n \quad (10)$$

However, there are several issues with this approximation. Firstly, the wavefunction determined with Equation 9 is an independent particle wavefunction as it does not account for the correlated motion of electrons. Additionally, Hartree gives a unique label to each electron. As it is impossible to distinguish one electron from another and the n electron wavefunction cannot change based on how the electrons are labelled, the wavefunction must be anti-symmetric when particles are exchanged. This is demonstrated by applying a permutation operator P as follows:

$$P_{kl}\Psi(1, 2\dots\mathbf{k}, \mathbf{l}\dots n) = \lambda\Psi(1, 2\dots\mathbf{l}, \mathbf{k}\dots n) \quad (11)$$

where λ reflects the number of permutations. This mathematical operation does not affect the physical properties of the system. By applying P_{kl} a second time to the permuted wavefunction, the original function is returned.

$$P_{kl}\Psi(1, 2\dots\mathbf{k}, \mathbf{l}\dots n) = \lambda^2\Psi(1, 2\dots\mathbf{l}, \mathbf{k}\dots n) \quad (12)$$

As the second permutation returns the original function, $\lambda = \pm 1$. $\lambda = -1$ describes an anti-symmetric function, which is the correct form for electrons. As only two electrons can be exchanged at any time, every other permutation is anti-symmetric but describes the same system. These permutations lead to the following determinant form which shows all of the ways in which n electrons can be distributed in n orbitals.

$$\Psi_{HF} = \frac{1}{\sqrt{n!}} \begin{bmatrix} \psi_1(1) & \psi_1(2) & \psi_1(3) & \cdots & \psi_1(n) \\ \psi_2(1) & \psi_2(2) & \psi_2(3) & \cdots & \psi_2(n) \\ \psi_3(1) & \psi_3(2) & \psi_3(3) & \cdots & \psi_3(n) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \psi_n(1) & \psi_n(2) & \psi_n(3) & \cdots & \psi_n(n) \end{bmatrix} \quad (13)$$

This form of the wavefunction is also referred to as the Slater Determinant or the Hartree-Fock wavefunction. The main benefit of the Hartree-Fock approximation is that it accounts for the so-called exchange-correlation, which

means that the motion of electrons with the same spin is correlated and that the wavefunction remains constant under exchange of electrons.

Using the Hartree-Fock wavefunction, the energy of the system can be expressed as:

$$\begin{aligned} E_{\text{HF}} &= \sum_{\mathbf{k}} \langle \psi_{\mathbf{k}}(\mathbf{i}) | \hat{h}(\mathbf{i}) | \psi_{\mathbf{k}}(\mathbf{i}) \rangle + \sum_{\mathbf{k}} \sum_{\mathbf{l} \neq \mathbf{k}} [\langle \psi_{\mathbf{k}}(\mathbf{i}) \psi_{\mathbf{l}}(\mathbf{j}) | h_{ij} | \psi_{\mathbf{k}}(\mathbf{i}) \psi_{\mathbf{l}}(\mathbf{j}) \rangle] - \langle \psi_{\mathbf{k}}(\mathbf{i}) \psi_{\mathbf{l}}(\mathbf{j}) | h_{ij} | \psi_{\mathbf{l}}(\mathbf{i}) \psi_{\mathbf{k}}(\mathbf{j}) \rangle] \\ &= \hat{h}_{\mathbf{k}} + \sum_{\mathbf{k}} 2J_{\mathbf{k}\mathbf{l}} - K_{\mathbf{k}\mathbf{l}} \end{aligned} \quad (14)$$

where $\hat{h}_{\mathbf{k}}$ is the single-electron kinetic energy operator and $J_{\mathbf{k}\mathbf{l}}$ describes the Coulomb interaction, as in the Hartree Approximation, while $K_{\mathbf{k}\mathbf{l}}$ is the Fock exchange interaction which is purely quantum mechanical in nature and arises as a consequence of the antisymmetry under electron exchange. This antisymmetry means that due to their negative charge, electrons repel each other. Consequently, the motion of electrons in a system is correlated, however as the Hartree-Fock system is static, correlation is not accounted for. The energy associated with electron correlation can be expressed as:

$$E_{\text{correlation}} = E_{\text{exact}} - E_{\text{HF}} \quad (15)$$

where E_{exact} is the exact energy of the system and E_{HF} is the energy as computed using the Hartree-Fock approximation.

So called post-HF methods allow for an evaluation of the correlation energy. One such method is the configuration interaction (CI) method. [6] CI expresses the exact wavefunction as a linear combination of N-electron single particle functions. This yields the full CI-matrix which includes the ground state and all possible excited states for the system. Based on this, the exact wavefunction, Ψ , can be written as:

$$|\Psi\rangle = c_0|\Psi_{\text{HF}}\rangle + c_S|S\rangle + c_D|D\rangle + \dots + c_n|n\rangle \quad (16)$$

where Ψ_{HF} is the HF wavefunction, c is the weight, and $|S\rangle$ represents the terms for single excitations, $|D\rangle$ the terms for double excitation and so on all the way to n excitations ($|n\rangle$).

Examples of single and double excitations from a HF determinant are shown in Figure 2

The eigenvalues of the CI matrix enable the ground state and excited state energies to be evaluated. The lowest eigenvalue is an upper limit to the ground state energy, while the higher eigenvalues are upper limits for the various excited states. This method is referred to as full-CI. For CI, Equation 15 can be expressed as

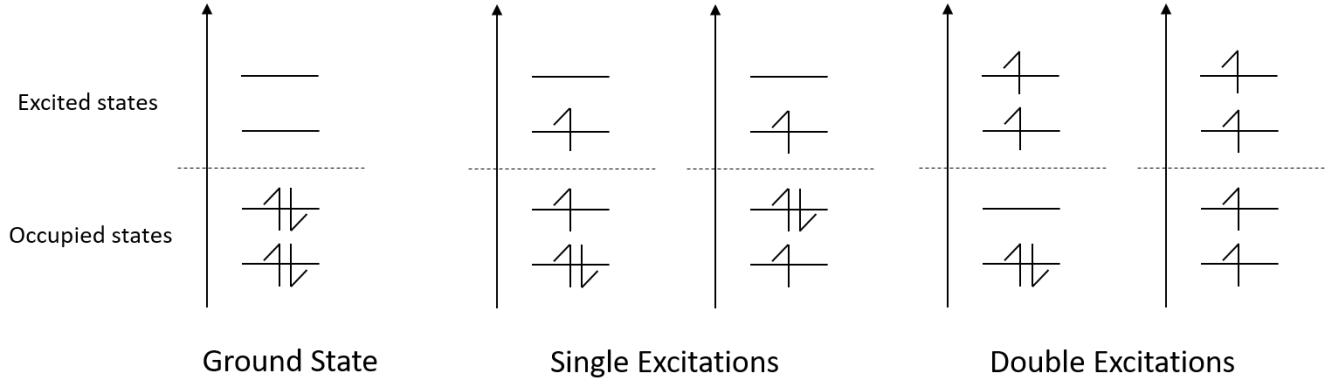


Figure 2: Showing example ground state, single excitation and double excitation states for a system.

$$E_{CI} = E_{HF} + E'_{correlation} \quad (17)$$

where E_{HF} is the energy computed using the Hartree-Fock approximation and $E'_{correlation}$ is correlation energy within the basis set used. Full-CI is exact within a given basis set and the closer the basis set is to completeness the closer the basis set correlation energy obtained will be to the exact correlation energy. This means that for a given one electron basis set, a full-CI is the most accurate method available to obtain the energy of the system. However, it is not computationally tractable to use full-CI for systems with more than 10 to 15 electrons as this involves solving for an extremely large set of N-electron functions. In fact, the number of functions increases so quickly even for moderately sized one-electron basis sets that the number of functions must be restricted, so that only a fraction of the possible functions is used. There are methods available to limit the length of the CI expansion and thus use it for multi-electron systems. These include singly and doubly excited CI (SDCI), which is restricted to singly and doubly excited states, and the multiconfiguration self-consistent field method (MCSCF), which uses the variational principle to choose the orbitals used for the CI expansion. [6]

3.1.3 Density Functional Theory

Another approach to the many-body problem is to ignore the complex many-body wavefunction and instead consider the electron density which can be measured by targeting a sample with X-rays of a certain wavelength, to collect probabilistic measurements of the location of the electrons over time in a given volume. Electron density is expressed as: [7, 8]

$$n(\mathbf{r}) = N \int d\mathbf{r}_2 \cdots \int d\mathbf{r}_N \Psi^*(\mathbf{r}, \mathbf{r}_2 \dots \mathbf{r}_N) \Psi(\mathbf{r}, \mathbf{r}_2 \dots \mathbf{r}_N) \quad (18)$$

The electron density is the probability of finding an electron in a given volume dr , given there are $N-1$ electrons in arbitrary positions in the system, defined by the wavefunction Ψ . Hohenberg and Kohn [9] established the use of the electron density as a means of dealing with the many-body problem without losing any information about the system. Their theorems are the framework upon which Density Functional Theory (DFT) is built. A functional as used in DFT is like a function, however instead of acting upon a number and returning another number, it acts upon a function to return a number.

Hohenberg-Kohn Theorems

There are two theorems developed by Hohenberg and Kohn, known as the Hohenberg-Kohn Theorems, that are the basis of modern implementations of DFT. [9] The first theorem states that if N interacting particles are moving within an external field ν_{ext} , the external field is determined up to a constant by the ground state electron density, $n_0(r)$. This means that two different ν_{ext} will never yield the same electron density unless they differ by less than a constant. Therefore ν_{ext} is a functional of the electron density. Considering the Born-Oppenheimer Hamiltonian as stated in Equation 4 and restating it so that ν_{ne} is represented by the external field means that:

$$\hat{H}_e = \kappa_e + \nu_{ee} + \nu_{ext} \quad (19)$$

From this it becomes clear that all terms can now be solved. κ_e and ν_{ee} are constant and can be computed explicitly independent of the system. Applying the first Hohenberg-Kohn theorem means that the many-body ground state of the system is dependent only on the functional of the electron density, n , which is unique to the system. The second theorem then states that the ground state energy is the minimum of the functional $E_{HK}[n]$ which describes the total energy for any applied external potential. As it is defined based only on electron densities, the ground state energy is a functional of the ground state electron density, and is exact for the exact ground state electron density:

$$E_{GS} = \min(E_{HK}[n]) = E_{HK}(n_0) \quad (20)$$

The total energy can then be expressed as a functional of the wavefunction:

$$E[\Psi] = \langle \Psi | \hat{H} | \Psi \rangle = \langle \Psi | \kappa_e + \nu_{ee} | \Psi \rangle + \langle \Psi | \nu_{ext} | \Psi \rangle \quad (21)$$

or as shown below we can redefine the same equation in terms of the electron density:

$$E_{HK}[n(r)] = \kappa_e[n(r)] + \nu_{ee}[n(r)] + \nu_{ext}[n(r)] = F_{HK}[n(r)] + \int n(r)\nu_{ext}(r)dr \quad (22)$$

Here, $F_{HK}[n(r)]$ is a universally valid functional which describes the kinetic and potential energies $\kappa_e[n(r)]$ and $\nu_{ee}[n(r)]$, while $\int n(r)\nu_{ext}(r)dr$ accounts for the electron-nucleus interaction and is system dependant. If $F_{HK}[n(r)]$ was known, it would be possible to minimise Equation 22 and determine the exact ground state energy and electron density of any system. [10] While no exact expression for $F_{HK}[n(r)]$ is known today, understanding that it exists makes DFT-based computational chemistry possible. By approaching the many-body problem in terms of the electron density, no approximations are necessary. Unlike HF, which aims to find an exact solution to an approximation, DFT uses approximations to the functional to solve an exact theorem.

Kohn-Sham Ansatz

The main outcome of the Hohenberg-Kohn Theorems is to prove that the electron density is a variable from which all system properties can be determined. The Kohn-Sham Ansatz [11] builds on this and provides a practical approach in which DFT can be implemented without knowing the exact form of the functional $F_{HK}[n(r)]$. Kohn-Sham assumes that there exists a reference, non-interacting system with a ground-state density that is the same as the ground state density of the real, interacting system. In a practical sense this means the electrons are replaced with fictitious, non-interacting particles while keeping the density $n(r)$ the same such that:

$$n(r) = \sum_i |\phi_i(r)|^2 \quad (23)$$

The particles occupy the Kohn-Sham (KS) orbitals ϕ_i , which allows the kinetic energy to be computed. Based on this same system of non-interacting particles, Equation 22 can be rewritten as the Kohn-Sham functional:

$$E_{KS}[n(r)] = \sum_i \langle \phi_i | -\frac{1}{2}\nabla_r^2 | \phi \rangle + \frac{1}{2} \iint \frac{n(r)n(r')}{|r-r'|} dr dr' + E_{xc}[n(r)] + \int \nu_{ext}(r)n(r)dr \quad (24)$$

The bulk of the kinetic energy is computed using $\sum_i \langle \phi_i | -\frac{1}{2}\nabla_r^2 | \phi \rangle$. However, some non-classical kinetic energy arises from the difference between the interacting system and the reference, non-interacting system and this is contained in the exchange-correlation functional $E_{xc}[n(r)]$. The final, Schrödinger-like Kohn-Sham equation to describe the ground state energy, E_0 , can be derived from Equation 24 by applying the variational principle:

$$E_0 = \left(-\frac{1}{2}\nabla_{\mathbf{r}}^2 + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\partial E_{xc}[n(\mathbf{r})]}{\partial n(\mathbf{r})} + \nu_{\text{ext}}(\mathbf{r})\right)\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r}) \quad (25)$$

All unknowns are contained in E_{xc} and its derivatives:

$$\nu_{xc} = \frac{\partial E_{xc}}{\partial n} \quad (26)$$

where E_{xc} describes all exchange and correlation effects. As for $F_{HK}[n(r)]$, if ν_{xc} and E_{xc} were known exactly, then the Kohn-Sham equations could be solved to give the exact ground state energies and ground state electron densities. The next section presents practical implementations of ways to approximate to these terms in order to solve the Kohn-Sham equations.

3.1.4 Implementation of DFT using Plane Waves

A theoretical model implements the Kohn-Sham equations in a practical way. These include

1. Basis sets
2. Pseudopotentials
3. Approximations to the exchange-correlation functional

The Vienna ab initio Simulation Package (VASP) [12] is the DFT code used for this thesis. As it is based on plane waves, this discussion is carried out with plane wave implementations in mind, although many aspects are also relevant to other DFT implementations, for example using localised atomic orbital basis sets.

Basis Sets

Basis sets contain a series of functions, $\alpha_j(r)$, which can be used in a linear combination of the LCAO expansion to express the Kohn-Sham orbitals, ϕ_n . [13]

$$\phi_n(\mathbf{r}) = \sum_j^{\infty} c_j^n \alpha_j(\mathbf{r}) \quad (27)$$

These functions approximate the atomic orbitals of atoms in the modelled material. As a solid is essentially an infinite system of a periodically repeating crystal structure, this repeating unit can be used as a model for the whole material. Electrons within such a periodic crystal structure move in a periodic potential. This means that

the wavefunctions of the electrons and the effective potential in the Kohn-Sham equations will have a periodicity that is equal to the crystal lattice parameter. According to Bloch's Theorem, wavefunctions of electrons in a periodic crystal can be expressed as the product of a function with the same periodicity as the crystal lattice and a plane wave. [14] The non-interacting Kohn-Sham particles behave like electrons by definition and therefore Bloch's theorem can be used to express the Kohn-Sham orbitals as follows:

$$\phi_n(\mathbf{r}) = e^{i\mathbf{q}\cdot\mathbf{r}}u(\mathbf{r}) \quad (28)$$

where $e^{i\mathbf{q}\cdot\mathbf{r}}$ is a plane wave and $u(\mathbf{r})$ is a function with the same periodicity as the crystal lattice. As the periodicity matches the crystal lattice, $u(\mathbf{r})$ can also be expressed as a linear combination of plane waves with wave vectors in the reciprocal lattice ($\mathbf{K}$):

$$u(\mathbf{r}) = \sum_{\mathbf{k} \in \mathbf{K}} c_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} \quad (29)$$

where the set of expansion coefficients is denoted by $c_{\mathbf{k}}$. The single particle wave function can then be expressed in terms of plane waves by combining Equations 28 and 29:

$$\phi_n(\mathbf{r}) = \sum_{\mathbf{k} \in \mathbf{K}} c_{\mathbf{k}}^n e^{i(\mathbf{q}+\mathbf{k})\cdot\mathbf{r}} \quad (30)$$

where $\mathbf{q}$ is a wave vector in the first Brillouin zone of the reciprocal lattice. In this equation, $\sum_{\mathbf{k} \in \mathbf{K}}$ is an infinite set of reciprocal lattice vectors. In practice an infinite set of vectors cannot be used and is instead limited to $k > k_{max}$ with a cutoff chosen to ensure the wavefunction is described with reasonable accuracy by the basis set. Applying such a finite basis set reduces the solution to the Kohn-Sham equations to a matrix equation:

$$\mathbf{H}\mathbf{C} = \mathbf{S}\mathbf{C}\mathbf{E} \quad (31)$$

where $\mathbf{H}$ is the Hamiltonian matrix, made up of the single-particle Hamiltonian operators, $\mathbf{C}$ is a square matrix based on the expansion coefficients, $\mathbf{S}$ is the overlap matrix of basis functions and $\mathbf{E}$ is a diagonal matrix which contains the energy eigenvalues.

Pseudopotentials

Plane wave implementations of DFT replace the nuclei with ions that encompass both the nuclei and the core

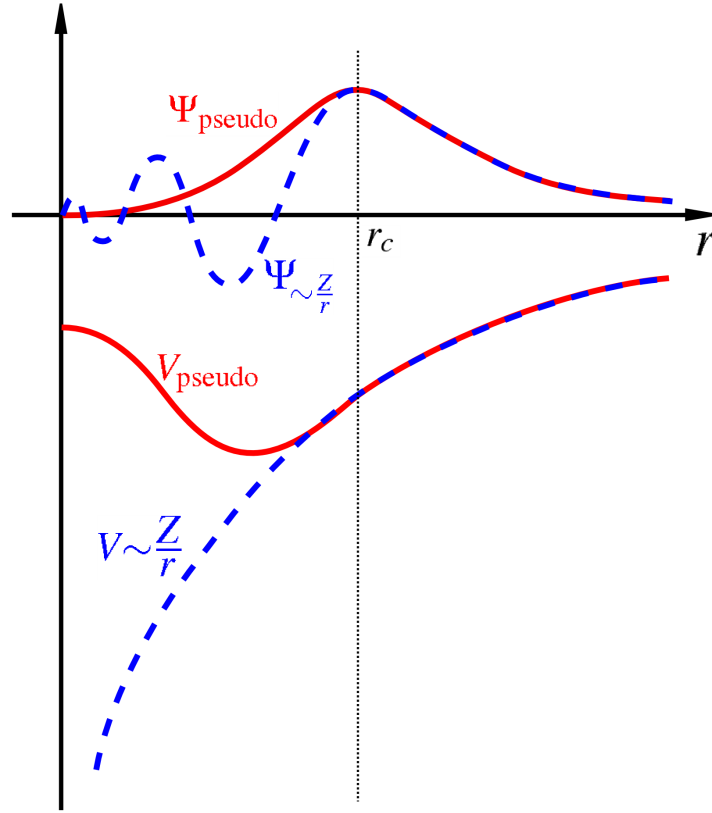


Figure 3: Graph showing how the pseudopotential replaces the real potential for $r < r_c$ to prevent oscillation of the wavefunction near the nucleus.

electrons, also referred to as the "frozen core approximation". As the core electrons are strongly bound to the nucleus of the atom they cannot interact with other atoms in the same way that valence electrons do and may be ignored for this reason. Using the frozen core approximation reduces the degrees of freedom of the system considerably as the relevant equations must be solved only for the valence electrons. However, in order to maintain orthonormality to the core wavefunctions, the wavefunctions of the valence electrons vary greatly in proximity to the ion. A very large basis set would be required to account for this. To avoid this, the potential of the ion is replaced by a pseudopotential at a "core distance" r_c . This means that the potential and the wavefunction are described exactly when $r > r_c$. When $r < r_c$, a pseudopotential is used instead. This causes less oscillating of the wavefunction near the nucleus, which in turn decreases the amount of basis functions necessary. A graphical depiction of the pseudopotential compared to the real potential is shown in Figure 3.

There are three implementations of pseudopotentials that are used in materials modelling: norm-conserving, ultrasoft and projector augmented waves. Projector augmented waves is the type of pseudopotential used for the work in this thesis and is discussed in detail below.

Projector Augmented Waves (PAW)

The projector augmented wave approach (PAW) is used in combination with pseudopotentials to derive the wavefunctions $\phi_n(r)$. [15] PAW partitions space into core and interstitial regions where $r < r_c$ and $r > r_c$, respectively. The Kohn-Sham orbital is then expressed as a sum of three contributions:

$$\phi_n(r) = \tilde{\phi}_n(r) + \sum_a \phi_n^a(r) - \sum_a \tilde{\phi}_n^a(r) \quad (32)$$

where $\tilde{\phi}_n(r)$ is the pseudo wavefunction, which can be expressed with a plane wave basis set, and $\sum_a \phi_n^a(r)$ and $\sum_a \tilde{\phi}_n^a(r)$ are summations of the all-electron ($\phi_n^a(r)$) and pseudo-one-center functions ($\tilde{\phi}_n^a(r)$) for all ions in the core region of the system, respectively. In the interstitial region, where $r > r_c$ and the wavefunctions and potentials are expressed exactly, $\tilde{\phi}_n(r)$ is equal to $\phi_n(r)$. If $\phi_n^a(r)$ and $\tilde{\phi}_n^a(r)$ are expressed in terms of partial and pseudo partial wave basis sets, $[\alpha_i]$ and $[\tilde{\alpha}_i]$, they can be rewritten to allow $\phi_n(r)$ to be derived. This is done by solving the modified Kohn-Sham equation for $\tilde{\phi}_n(r)$ and using the following transformation:

$$|\phi_n\rangle = |\tilde{\phi}_n\rangle + \sum_a \sum_i (|\alpha_i^a\rangle - |\tilde{\alpha}_i^a\rangle) \langle p_i^a | \tilde{\phi}_n \rangle \quad (33)$$

where $[p_i^a]$ describes the species-specific projector functions.

Approximations to the exchange-correlation functional

There are various different methods of approximating the exchange-correlation functional. Here, we will focus on the local density approximation (LDA) and the generalised gradient approximation (GGA). LDA uses the energy of a homogeneous electron gas to approximate exchange and correlation contributions to the total energy. [4]

$$E_{xc}^{LDA}[n(r)] = \int n(r) \epsilon_{xc}(n(r)) dr \quad (34)$$

where $\epsilon_{xc}(n(r))$ is the exchange-correlation energy of a particle in a homogeneous electron gas with a density $n(r)$. In Equation 34 the ground state energy depends on the local value of the electron density at position r . ϵ_{xc} can also be expressed as the sum of the exchange and correlation energy contributions, ϵ_x and ϵ_c :

$$\epsilon_{xc} = \epsilon_x + \epsilon_c \quad (35)$$

ϵ_x is known analytically, while ϵ_c is known analytically only for very high and very low densities. These

restrictions mean that LDA performs best for models of extended systems with little variation in the electron density. Therefore, LDA is best used for solid-state physics and so long as LDA remained the best approximation to the exchange-correlation functional, implementation of DFT had significant limitations for chemical problems.

However, the development of GGA removed this limit. GGA expands LDA by including a density gradient to account for the non-homogeneous nature of the true electron density. [16] By expressing E_{xc} as a functional of both the density, n , and its gradient, ∇n , the general form of GGA can be written as:

$$E_{xc}^{GGA} = \int f(n, \nabla n) dr \quad (36)$$

GGA-type exchange-correlation functionals are frequently used as so-called "standard" DFT. Examples of these include the exchange-correlation functionals of Perdew-Burke-Ernzerhof (PBE) functional, [17] and Perdew and Wang functional (PW91), [18] as well as the Lee-Yang-Parr functional (LYP) [19]. The latter is a correlation-energy functional that needs to be combined with an exchange functional. The appropriate functional for a calculation typically depends on the exact property being studied, although in general the performance of GGA potentials is very similar. [20–22] As all approximations, GGA functionals have their limitations. Due to the self-interaction error, [23, 24] band gaps are underestimated [25–27] and delocalisation of charges is favoured, e.g. for p-orbitals of O, d-orbitals of transition metals and f-orbitals of rare earth metals. [28, 29] There are other approximations that can be used to avoid these issues, such as hybrid DFT, where a hybrid functional is used that includes both Hartree-Fock exchange and DFT exchange, and DFT+U where an empirical parameter U is used to correct the localisation of states. [30] However, for the purposes of this thesis accurate descriptions of these properties are not essential and therefore GGA and in particular the PBE functional are used throughout.

3.2 General Computational Approach

In this thesis we study the interactions of the interconnect metals Cu, Co and Ru with different substrates chosen as potential combined barrier+liner materials. All calculations presented are performed within DFT using the Vienna Ab initio Simulation Package (VASP) version 5.3 (for calculations in Chapter 4.1) and 5.4 (for all other calculations). [12] The valence electrons are described explicitly by expanding their wave function in a plane wave basis set with an energy cutoff of 400 eV (TaN systems) or 450 eV (MoS₂ systems) whereas the core electrons are treated by PAW potentials. [15, 31] The valence electronic configuration for each atomic species is shown in Table 1. The DFT calculations are based on spin polarised GGA using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional. [17] The energy in the geometry relaxation calculations as well as the NEB forces in the activation energy computation is converged to 0.0001 eV and the forces acting on the unconstrained atoms are converged to 0.02 eV/Å. All calculations include spin polarisation. Van der Waal’s (vdW) corrections were not used for any of the systems studied as part of this thesis as they would either be negligible compared to the adsorption energies or are known not to dominate the interactions. This is particularly relevant for the MoS₂ systems and is thus discussed in Section 3.4. Electronic charges were computed using the Bader charge partitioning scheme. [32, 33] All charges discussed throughout this thesis are relative to the number of valence electrons for the particular element, which are given in Table 1. Any discussion on the oxidation state that is equivalent to a particular Bader charge for a certain species is based on results in references [34–36]. All TaN and MoS₂ models were built based on crystal structures from Materials Project [37, 38] and edited using the Atomic Simulation Environment (ASE). [39] All geometry images were created using the “Visualization for Electronic and Structural Analysis” (VESTA) package. [40] The colour coding for the different atomic species is shown in Figure 4.

Table 1: Valence Electron Configurations for each atomic species used.

Atomic species	Valence Electron Configuration
Ta	6s ² 5d ³
N	2s ² 2p ³
Mo	5s ¹ 4d ⁵
S	3s ² 3p ⁴
P	3s ² 3p ³
W	6s ² 5d ⁴
Cu	3d ¹⁰ 4s ¹
Co	4s ² 3d ⁷
Ru	4d ⁷ 5s ¹

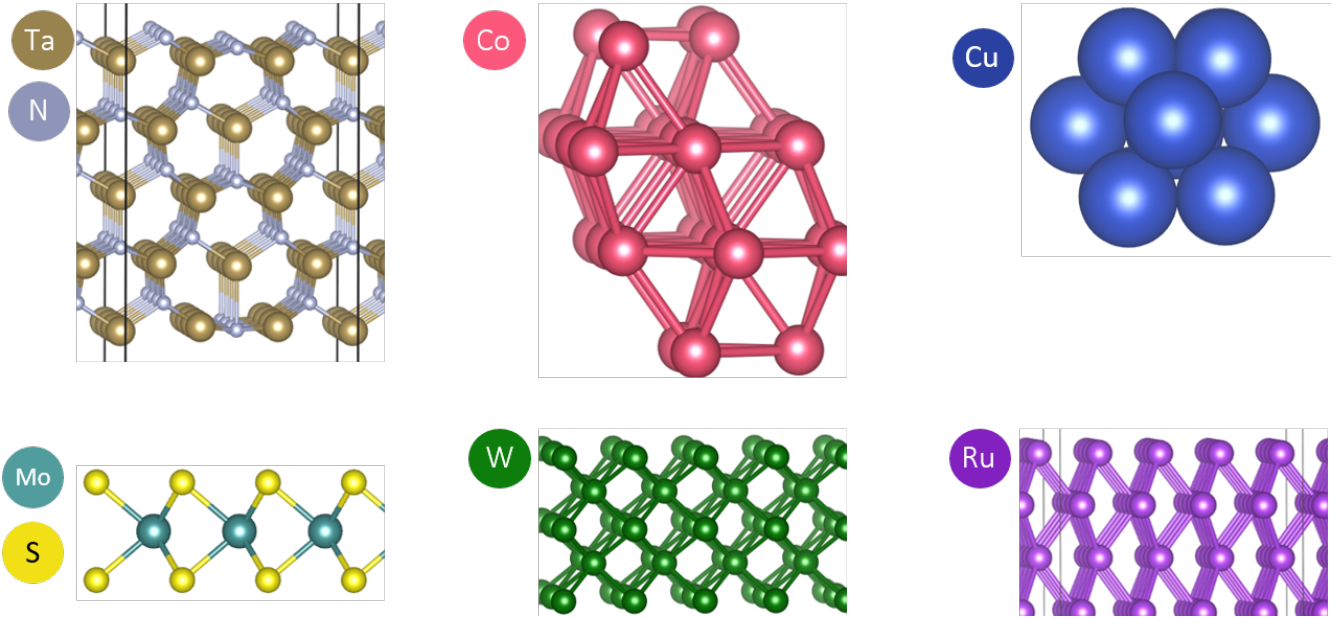


Figure 4: Colour coding for the different atomic species used in this thesis. Ta = gold, N = silver, Co = pink, Cu = blue, Mo = teal, S = yellow, W = green, Ru = purple.

3.3 TaN Systems

The following methodology details were published as part of refs. [41–43] The bulk structure of ε -TaN with Fe_2P crystal structure is chosen from the Materials Project database [37] and the geometry is optimised by simultaneously relaxing the ionic positions, cell volume and cell shape at a higher plane wave energy cutoff of 550 eV and a Monkhorst-Pack K-point mesh of $6 \times 6 \times 12$. From this calculation, we arrive at the following equilibrium lattice parameters: $a=b=5.23 \text{ \AA}$, $c=2.92 \text{ \AA}$, $\alpha=\beta=90^\circ$ and $\gamma=120^\circ$. This agrees closely with the experimental results of $a=b=5.20 \text{ \AA}$ and $c=2.91 \text{ \AA}$. [44] The equilibrium geometry of bulk ε -TaN is shown in Figure 5a.

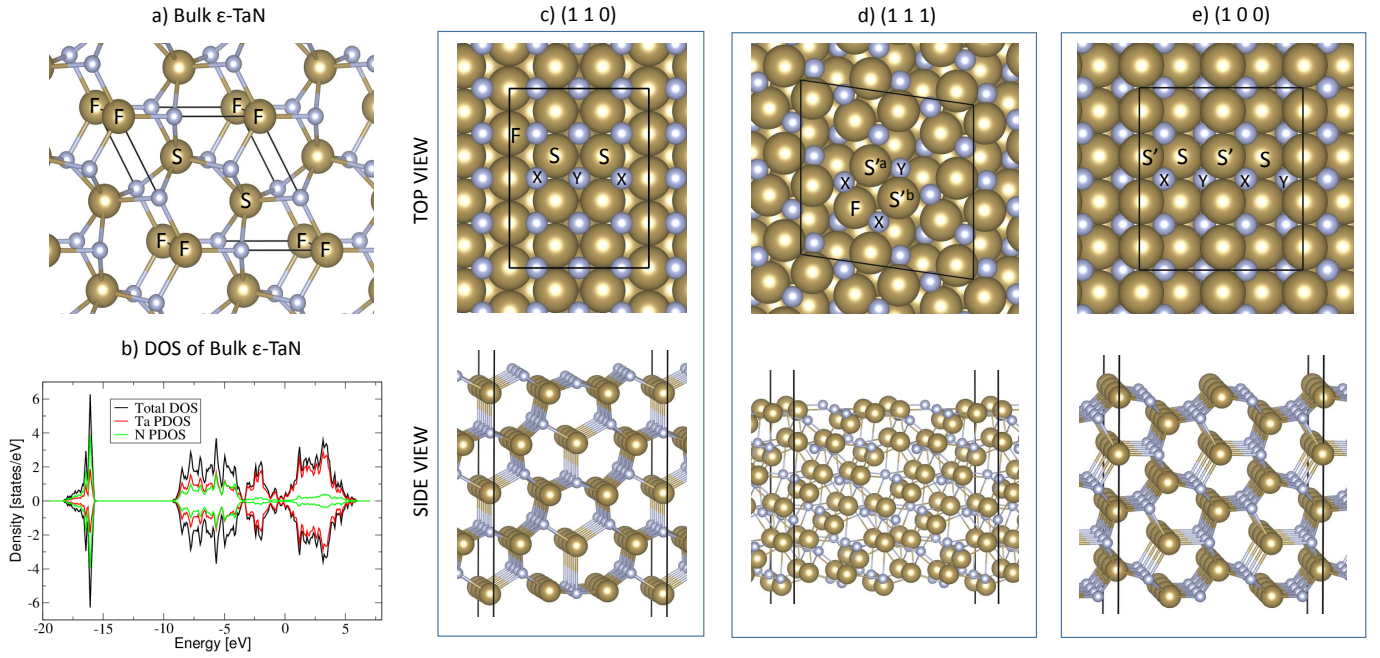


Figure 5: Panel a) shows the bulk geometry of ϵ -Ta₂N₃ and panel b) shows the total (black line) and partial density of states (Ta in red and N in green) of ϵ -Ta₂N₃ where 0 eV in x-axis marks the Fermi level. The top and side views of (1 1 0), (1 1 1) and (1 0 0) surfaces of ϵ -Ta₂N₃ are given in panels c), d) and e), respectively. The Ta and N atoms are shown in ochre and light blue, respectively. The (1 1 0) surface consists of F and S type Ta atoms with valence charges (Q) of 3.6 and 3.0, respectively and N atoms with $Q=6.3$ (X) and $Q=6.4$ (Y). Valence charges are computed with respect to total charge density using the Bader code from Henkelman's group. [32, 33] On the (1 1 1) surface, we have the S type Ta atoms coordinated by 4 N atoms only (indicated as S') with $Q=3.5$ (S'^a) and $Q=3.6$ (S'^b), F type Ta atoms with $Q=3.7$ and N atoms with $Q=6.5$ (X) or $Q=6.4$ (Y). On the (1 0 0) surface, we have both S and S' type Ta atoms with $Q=3.2$ and $Q=3.7$, respectively and N atoms with $Q=6.5$ (X) or $Q=6.4$ (Y).

Table 2: Details of the computation models of the low index surfaces of ϵ -Ta₂N₃.

Surface	Supercell	K-points	Surf. Area [nm ²]	Layers	TaN/layer	Slab Thickness [Å]	No. Atoms	E _{Surf} [J/m ²]
(1 1 0)	(1×4)	3×2×1	1.06	5	12	11.8	120	2.6
(1 1 1)	(2×2)	3×3×1	1.42	6	12	10.5	144	2.7
(1 0 0)	(1×4)	2×2×1	1.22	8	8	10.2	128	2.7

Here, the Ta atoms marked with label ‘F’ are 3 fold coordinated by N atoms and the resulting coordination polyhedron of this TaN_3 fragment is a planar triangle. Ta atoms marked with label ‘S’ are 6 fold coordinated by N atoms forming two trigonal pyramids connected by their vertices. All N atoms in this geometry are coordinated by 3 Ta atoms out of which two are ‘S’ type and one is ‘F’ type. From Bader charge partitioning scheme [32, 33] we find that the ‘F’ Ta atoms have a valence charge of 3.8 electrons, the ‘S’ Ta atoms have a charge of 3.3 electrons and the N atoms have a charge of 6.5 electrons. We have used the total charge density of the system including the core charges as the reference to compute these charges. The results show that the bonding between Ta and N atoms is of a combined ionic and covalent character. The electron affinity (EA) values of Ta and N atoms are 0.32 eV and -0.07 eV, respectively. Therefore it is not surprising to see that the Ta atoms were oxidised and N atoms were reduced. The total density of states (TDOS) of ϵ -TaN and the contributions from Ta and N atoms are shown in Figure 5b. It is clear that there is no band gap present and the valence and conduction bands are dominated by the electronic states of Ta. However, it is also observed that the DOS is significantly reduced in the region between the valence and conduction bands suggesting some resistance to electron flow which makes this material a semi-metal. The cohesive energy of ϵ -TaN is -1.20 eV/atom with reference to bulk Ta [45] and N_2 molecule.

The three low index surfaces ((1 1 1), (1 0 0), (1 1 0)) of ϵ -TaN are considered for this study as they have the lowest surface energies among the 7 possible low index surfaces (see section A1.2 of the Appendix). The surface models are generated with the help of the ASE package [39] and the properties of these surfaces are listed in Table 2. 12 Å of vacuum separating the slabs along the surface normal direction is included to avoid interactions between the two surfaces of the slab. Out of the three surfaces, the (1 1 0) surface was found to have the lowest surface energy followed by the (1 1 1) and (1 0 0) surfaces as shown in Table 2. The top and side views of the equilibrium geometries of the low-index surfaces along with the valence charges of the top layer atoms are given in Figure 5c-e. From the valence charges obtained from the Bader charge partitioning scheme, we find that (1 1 0) and (1 0 0) surfaces have surface Ta atoms that show different charges (Figure 5). The role of this in the adsorption of Cu and Ru is discussed in Chapter 4. The electron affinity values of Cu and Ru are 1.24 eV and 1.05 eV, respectively, which are much larger than that of Ta and N. Therefore we may expect the Cu and Ru adatoms to be oxidised, Cu more so than Ru, when adsorbed on the TaN surfaces. For the adsorption calculations on the low index surfaces, the bottom two layers of the TaN slab are constrained to their bulk positions.

Bulk Ru in the hexagonal close packed (HCP) lattice is chosen to study the interaction between Cu and a liner material and as a reference to study Ru-passivation of TaN. The initial geometry was taken from the Materials Project database. [46] The geometry was relaxed in a similar way to the TaN case with an increased energy cutoff of 550 eV and a dense K-point mesh of $12 \times 12 \times 6$. From this set up the equilibrium lattice constants are $a=b=2.71$ Å,

$c=4.28 \text{ \AA}$, $\alpha=\beta=90^\circ$ and $\gamma=120^\circ$, which compares well with the experimental results. [47] The computed cohesive energy per atom with reference to atomic Ru is -6.81 eV, which also agrees with the experimental value of -6.74 eV. [48, 49] The geometry of bulk Ru showing the HCP arrangement is shown in Figure A3 of the Appendix.

The total DOS of Ru is plotted in Figure A3b of the Appendix which shows its metallic nature. For the Cu adsorption calculations, a $10.5 \text{ \AA}$ thick, 6 layered Ru(0 0 1) slab with a surface energy of 2.53 J/m^2 , as shown in Figures A4c and A4d, Section A2.3 of the Appendix, is chosen and a Monkhorst-Pack K-point mesh of $3 \times 3 \times 1$ is used.

In Chapter 4.1 we use a (1×4) and (2×4) supercell of TaN(1 1 0). We chose a Monkhorst-Pack K-point mesh of $1 \times 2 \times 1$ to account for the increased size of the (2×4) TaN(1 1 0) surface supercell. This is sufficient for a study with a single dopant and up to 2 Cu adatoms. However a larger surface is necessary for the work detailed in Chapters 4.2, 5 and 6. For this reason we use a (2×8) reproduction of the TaN(1 1 0) surface. This clean TaN (1 1 0) surface is a 5 layered (2×8) supercell with 240 Ta and 240 N atoms, Fig. 6a. In each layer there are 48 Ta and 48 N atoms, and 64 Ru atoms fit in 1 monolayer (ML) of Ru to passivate TaN. A vacuum of $18.7 \text{ \AA}$ along the surface normal direction is included in the supercells of the clean and doped surfaces. In the supercells of the 1 ML Ru and 2 ML Ru passivated surfaces, vacuum thicknesses of $16.4 \text{ \AA}$ and $14.4 \text{ \AA}$ are present. These vacuum thicknesses are sufficient to isolate the two slab surfaces. The large size of the (2×8) supercell means that the Monkhorst-Pack K-point mesh is restricted to $1 \times 1 \times 1$ (Γ -Point Sampling).

Metal binding energies reported are computed per atom from:

$$E_{\text{bind}} = (E_{\text{int.sys.}} - (E_{\text{bare}} + nE_{\text{M-atom}}))/nM. \quad (37)$$

Here, $E_{\text{int.sys.}}$ is the total energy of the relaxed interacting system where n metal (M) atoms are adsorbed on the respective TaN surface, E_{bare} refers to the relaxed energy of the corresponding bare surface and $E_{\text{M-atom}}$ is the total energy of an isolated metal atom. Therefore, E_{bind} also includes metal-metal interactions. nM is the total number of metal atoms in the adsorbed nanocluster. For certain doped surfaces, the adsorption of the Cu atoms distorted the surface atomic arrangements. Therefore we compute E_{surf} which refers to the single point energy of the relaxed, distorted lower symmetry surface with the copper atoms removed. E_{surf} will be close to E_{bare} if the surface distortion is minimal. For some surfaces we found the difference between these two terms, termed as surface rearrangement energy (E_{SR}), is significant, e.g. Chapter 4. Therefore, to make a fair comparison of the Cu binding energies computed at different surfaces, we removed this E_{SR} contribution from E_{bind} . Thus the above equation

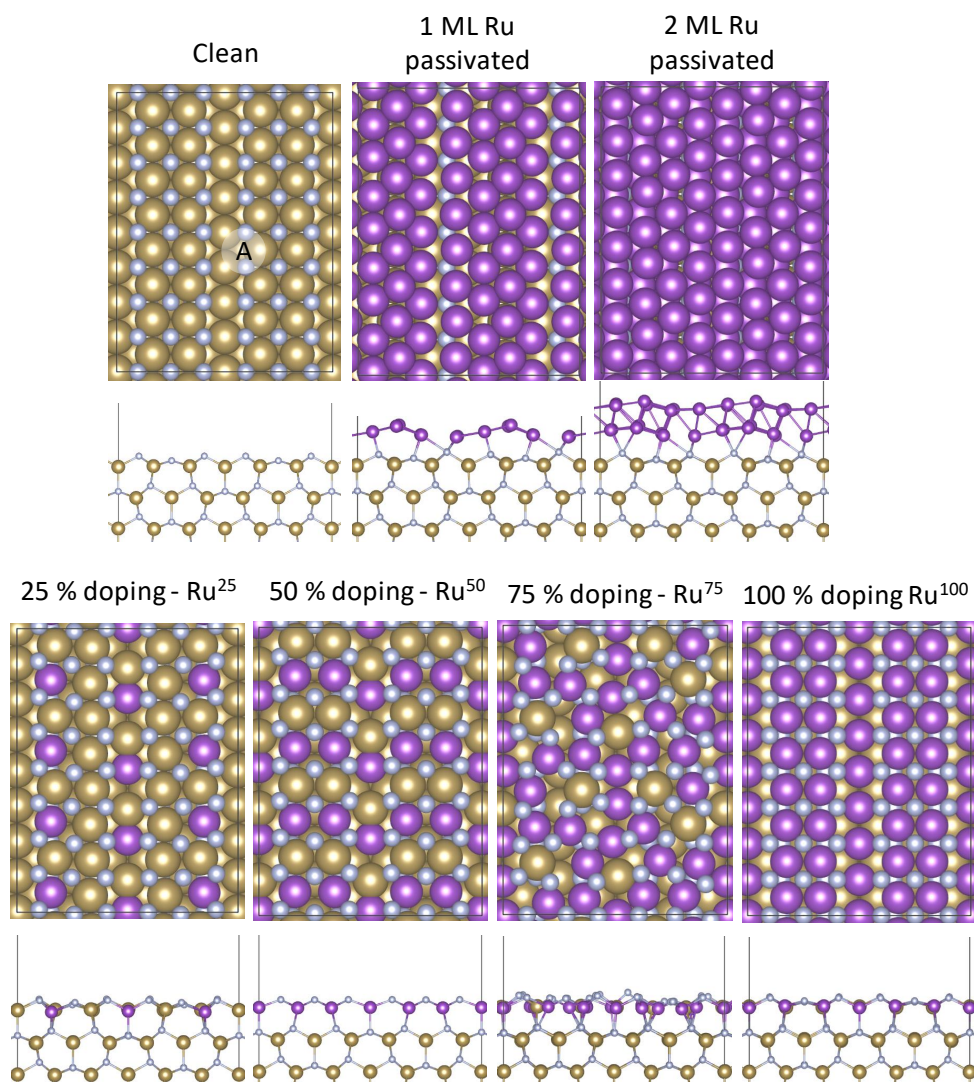


Figure 6: Panels a) - g) show the top and side views of the relaxed atomic structures before Cu adsorption on the clean, 1 ML Ru passivated, 2 ML Ru passivated, 25%, 50%, 75% and 100% Ru doped TaN surfaces, respectively. Ta, N, Ru atoms are shown in gold, light blue and purple, respectively. On the clean surface, the 5 fold adsorption site coordinated by 3 Ta and 2 N is marked with 'A'.

becomes

$$E_{\text{bind}} = (E_{\text{int.sys.}} - (E_{\text{surf}} + nE_{\text{M-atom}}))/nM \quad (38)$$

We compute $E_{\text{metal-substrate}}$, which is the binding energy of the Metal_n cluster relative to a gas-phase Metal_n cluster.

$$E_{\text{metal-substrate}} = (E_{\text{int.sys.}} - (E_{\text{surf}} + E_{\text{M-cluster}}))/n \quad (39)$$

Here, $E_{\text{int.sys.}}$ and E_{surf} are the same as in Eq. 36, while $E_{\text{M-cluster}}$ refers to the single point energy of the metal-cluster isolated from the TaN surface after relaxation. Now, an estimate of the metal-metal interaction energy can be computed from

$$E_{\text{interact}} = E_{\text{bind}} - E_{\text{metal-substrate}} \quad (40)$$

As discussed in Chapter 2, the competition between the metal-substrate interaction and the metal-metal interaction is a key feature in the thin film growth mechanism. [50] A strong metal-substrate interaction (with $E_{\text{bind}} \geq E_{\text{cohesive}}$), and a metal-substrate interaction that exceeds the metal-metal interaction are factors that contribute to promoting thin film wetting. The opposite holds for 3D island formation.

The doping energy per dopant is computed as

$$E_{\text{dope}} = \frac{E_{\text{total}} - (E_{\text{clean}} + n \times (E_{\text{dopant}} - E_{\text{Ta-atom}}))}{n} \quad (41)$$

in which n is the number of Ru dopants in the surface layer. $E_{\text{Ta-atom}}$ and E_{dopant} are the energy of a single Ta and dopant atom (Ru, Co or W) in vacuum, respectively. E_{total} is the total energy of the relaxed doped surface and E_{clean} is the total energy of the clean TaN(1 1 0) surface. Using this equation we can obtain an estimate of the relative energy required to create the doped system from pure TaN and compare how this is influenced by the concentration and distribution of metal dopants.

For our work detailed in Chapter 5 and Chapter 6 *ab initio* molecular dynamics (aiMD) calculations were used. These were carried out within the NVT ensemble (constant number of particles, N , constant volume, V , and constant temperature, T). The kinetic energy cutoff is 250 eV. The temperatures used are 300, 500 and 800 K for Chapter 5. We run at 800 K as this is above the typical temperature for processing in back end of line (BEOL), so that stability at this temperature indicates that the structure will be stable at typical BEOL temperatures. However, calculations in Chapter 6 are carried out only at 500 K to limit the resources used and as this temperature was found to be sufficient to indicate thermal instabilities. A time step of 5 fs over a total of 1000 steps was applied to each run, yielding a simulation of 5 ps in length. These aiMD simulations are used to explore how Cu atoms may

migrate to form Cu islands on our set of modified TaN materials.

To characterise the impact of the TaN modification on the structure of adsorbed copper, we examined the position of the Cu atoms during the 0 K relaxation and during the finite temperature aiMD simulations as a function of MD time. We collected the z-coordinate (coordinate normal to the surface) of each Cu atom at each relaxation or time step, from the VASP XDATCAR file. The z-coordinates are adjusted such that the original position of the copper atom is taken as the zero and we can plot the resulting change in z-coordinate with respect to relaxation or time step.

$$\Delta Z = Z_n - Z_0 \quad (42)$$

Here, Z_n is the z-coordinate at the n th relaxation/time step and Z_0 is the z-coordinate at the first step. This yields information about which atoms are displaced from their original positions in the adsorbed 2D copper structure and migrate to form a second or third layer in the Cu_n structure or if copper atoms migrate into the surface layer. Our convention is that copper atoms have migrated into the next layer if they are displaced along the Z-direction by more than 1 Å from their original position. For migration into the TaN surface, an atom is buried, when it is displaced by more than -1 Å (downwards) from its original position.

Activation energies for specific atom migrations from state A to B are computed in both Chapters 4 and 5 using the climbing image nudged elastic band (CI-NEB) approach [51, 52] with five images and with the following equation:

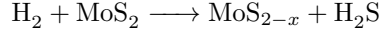
$$E_{A-B} = |(E_A - (E_{\text{TS}_{AB}}))|. \quad (43)$$

Here, E_{A-B} is the activation energy for migration of an atom from state A to state B, E_A is the total energy of state A and $E_{\text{TS}_{AB}}$ is the total energy of the transition state between state A and state B. Total energies were converged to 10^{-4} eV and forces to 0.02 eV / Å

3.4 MoS₂ Systems

The following methodology details were published in. [53, 54] The unit cell of bulk MoS₂ is made up of two layers. To create the pristine ML one of these was removed, which also creates the vacuum necessary to avoid interaction along the z-axis; the vacuum region is 8 Å. The model used for calculations presented on MoS₂ is a (5×5) supercell, based on the crystal structure of bulk MoS₂ from the Materials Project database. [38] No vdW corrections were applied, as both the literature and our own tests (Appendix Section A5.10) show that vdW forces do not dominate

in these monolayer structures. The bond lengths in bulk structures that are used for comparison are based on the crystal structures in references [55–60]. Only a theoretical crystal structure was available for RuMo, all other structures used are experimental. The defective ML has the same structure as the pristine ML, except that a single S atom has been removed to create a vacancy and the ions are relaxed with no symmetry constraints. The vacancy formation energy was calculated based on the following reaction:



where x indicates S vacancies are present.

The sulfur vacancy formation energy is then calculated as:

$$E_{\text{form}} = (E_{\text{MoS}_{2-x}} + E_{\text{H}_2\text{S}}) - (E_{\text{MoS}_2} + E_{\text{H}_2}) \quad (44)$$

In this case, the computed sulfur vacancy formation energy is -6.16 eV. This favourable energy is consistent with the fact that sulfur vacancies occur naturally in MoS₂ [61] and have been shown to form with relative ease. [62] Vacancy formation energies have also been calculated previously in the literature, however, approaches and the conditions under which the vacancy might be formed vary widely and are therefore not comparable. [62, 63]

To understand the binding of metal atoms to the MoS₂ monolayer, four different energies are computed.

1. E_{bind} : Binding Energy per metal atom as per Equation 38
2. $E_{\text{metal-substrate}}$: Binding Energy with reference to a free Metal_(n) cluster in vacuum as per Equation 39
3. E_{interact} : Metal-Metal Interaction Energy as per Equation 40
4. Addition Energy, E_{add} :

$$E_{\text{add}} = E_{\text{total}} - E_{\text{monolayer}+(n-1)\text{metal}} - E_{\text{metal_atom}} \quad (45)$$

where n is the number of metal atoms. This models the addition of a metal atom to an existing adsorbed cluster with (n-1) metal atoms.

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Chapter 4: Small Cu structures (1 to 4 atoms) on Ru doped and Ru passivated ϵ -TaN

In Chapter 2 we reviewed the different types of materials used as barrier and liner materials, including the use of TaN barriers and Ru liners in interconnects. We also discussed the various properties desirable in barrier and liner materials. In this chapter we present the first part of our work on using Ru doping and passivation of TaN as a method of reducing the thickness of the barrier/liner layer and thus creating a combined barrier+liner material. TaN has been shown to act as an effective diffusion barrier for layers as thin as 0.5 nm. [1, 2] To the best of our knowledge no studies testing the limits of liner thickness have been carried out. Typical liner thicknesses range between 1 and 3 nm. [3-5] We study the interaction of small Cu clusters with up to 4 atoms on 1 and 2 monolayer (ML) Ru passivated TaN as well as 8% (one dopant per supercell), 25%, 50%, 75% and 100% Ru doped TaN. In order to understand the behaviour of Cu on these surfaces, we first study atom association vs separation followed by various 2D and 3D structures with three and four Cu atoms. This allows us to gain insight into the initial nucleation of a Cu thin film on the different Ru-TaN surfaces. Additionally, in Section 4.8, we compute a metal-metal interaction energy, which competes with the metal-surface interaction (binding energy) and contributes to determining whether a thin-film may wet or agglomerate on a particular surface. The analysis of 2D vs 3D growth will be described in Chapter 5.

Sections 4.1 to 4.5 are published under the title "Ru Passivated and Ru Doped ϵ -TaN surfaces as Combined Barrier and Liner Material for Copper Interconnects: A First Principles Study" in the Journal of Materials Chemistry C, <https://doi.org/10.1039/C8TC06118A>. [6]

The results in Sections 4.6 to 4.10 are published under the title "The role of Ru passivation and doping on the barrier and seed layer properties of Ru-modified TaN for copper interconnects" in the Journal of Chemical Physics, <https://doi.org/10.1063/5.0003852>. [7]

In the first half of this Chapter (Sections 4.1 to 4.5), we will first investigate the adsorption and diffusion of Ru and Cu adatoms at the most favourable low index surfaces of TaN. We chose the stoichiometric ϵ -TaN phase, as it

has the lowest formation energy [8], see phase diagram in Figure A2 in Section A2.1 of the Appendix. Following this, similar calculations for Cu adatoms at a hexagonal Ru(0 0 1) slab will be reported. In the next subsection, Ru passivation on TaN and subsequent adsorption and diffusion of Cu atoms will be investigated. Finally, we discuss Ru incorporation into TaN and the interaction with Cu adatoms. As described in Chapter 2, any Cu interconnect requires both a diffusion barrier and a liner material. A Cu seed layer is deposited on top of this bilayer before the remaining amount of Cu is electroplated into the interconnect via. For the purposes of our study, we use a known diffusion barrier (TaN) and a known liner material (Ru) and test how they can be combined to create a material with reduced thickness compared to a TaN/Ru bilayer, while ensuring that diffusion barrier and liner properties are retained. Adsorption of Cu and Ru atoms on TaN is used as a benchmark to show that TaN prevents spontaneous Cu diffusion through the barrier and to check how Ru liner interacts with the diffusion barrier. Similarly, Cu adsorption on Ru is used to confirm the liner properties and to show that Ru does not act as a diffusion barrier. Carrying out these initial calculations allows us to then compare the behaviour of Cu on a diffusion barrier and a liner material to the behaviour on Ru-modified TaN. Detailed descriptions of the TaN and Ru surfaces are given in Chapter 3.3.

The second half of this chapter (Sections 4.6 to 4.10) builds on our initial findings. We study the effects of increased doping concentrations and dopant distributions on both surface stability and interaction with small Cu clusters with up to four atoms. The different Cu clusters are designed so that they can allow us an insight into 2D vs 3D stability on the various surfaces.

4.1 Ru and Cu Adatoms on Bare ϵ -TaN Surfaces

Ru and Cu atoms are adsorbed at various unique sites on the most favourable low index ((1 1 0), (1 1 1) and (1 0 0)) ϵ -TaN surfaces. Details of all low index ϵ -TaN are included in Section A2.2 of the Appendix. The stable sites found after relaxation along with schematic pathways connecting them are shown in Figure 1. This figure also includes the top and side views of the most favourable minimum-energy geometries of the respective surfaces. For these geometries, the adatom binding energies, selected interatomic distances (Cu-Ta, Ru-Ta, Cu-N and Ru-N) and Bader charge on the adatom are listed in Table 1. The corresponding values for all the computed minima and their geometries are given in Section A2.4.1 of the Appendix.

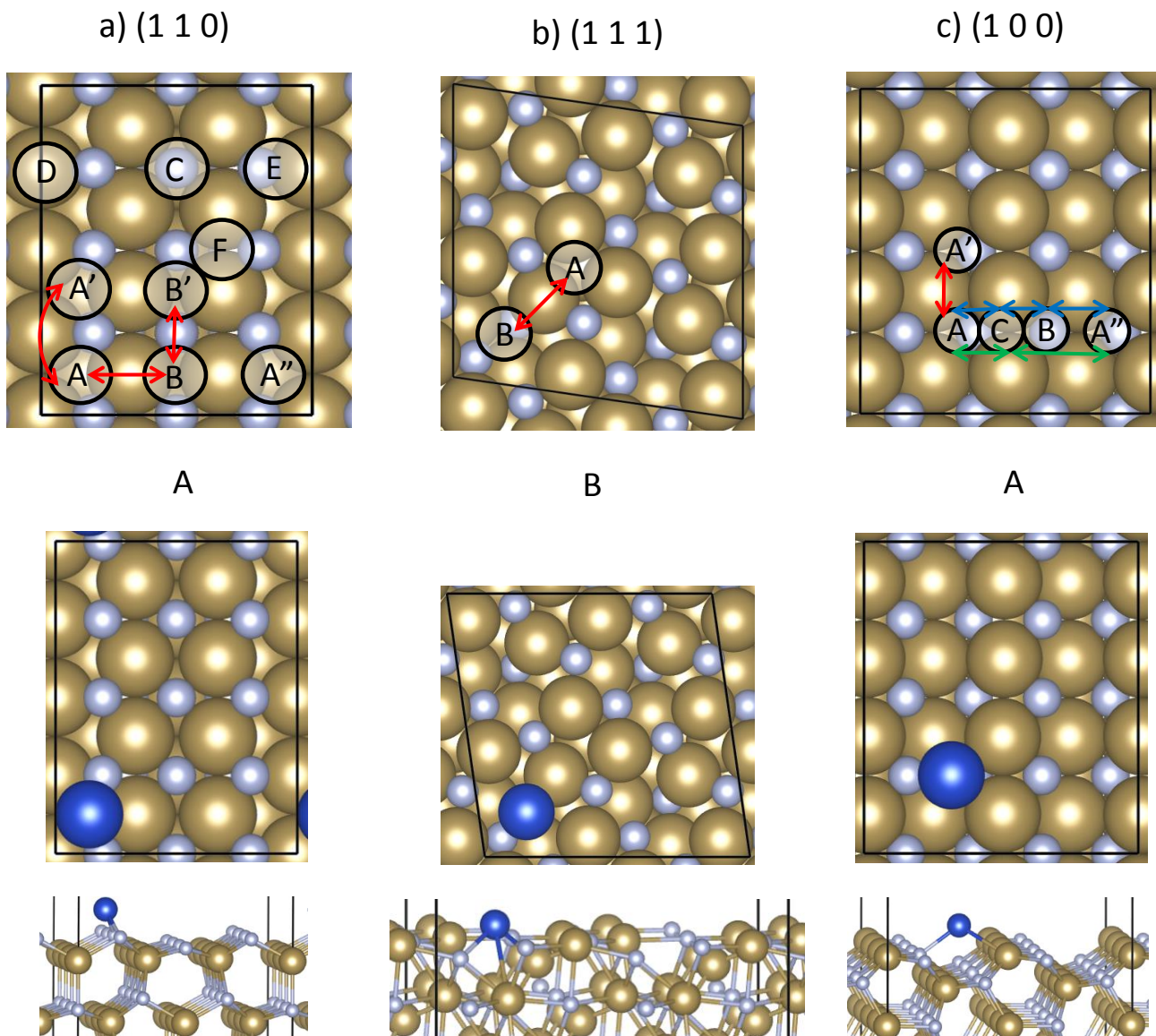


Figure 1: The low index surfaces of TaN showing the unique binding sites, which are also the end points used for the climbing image nudged elastic band (CI-NEB) calculations to compute the activation energies for lateral diffusion of a single adatom. The red arrows indicate pathways for both Ru and Cu adatoms, green arrows are for Cu adatoms and blue arrows are for Ru adatoms. All figures follow the colour code in Chapter 3 unless otherwise indicated. Adsorbed metal atoms in this figure are indicated as blue spheres. The top and side views of the most favourable minimum-energy geometry are also provided for each surface.

Table 1: Binding energies, average distances and valence electronic charge of Cu and Ru adatoms on the low index surfaces of ϵ -TaN. $d(X-Y)$ gives the average bond length between the neighbouring X and Y species in the corresponding minimum-energy geometries. $Q(X)$ gives the computed charge of atom X according to the Bader charge partitioning scheme. Cu has 11 valence electrons and Ru has 8.

Surface	Sites	E_{bind} [eV/ads.]		Interatomic distance [Å]							$Q(\text{Cu})$	$Q(\text{Ru})$
		Cu	Ru	Cu-Cu	Ru-Ru	Cu-N	Ru-N	Cu-Ta	Ru-Ta			
1 Cu/Ru adatom												
(1 1 0)	A	-2.82	-4.95			1.9	1.9	2.8	2.6	10.5	7.8	
(1 1 1)	B	-3.21	-5.64			2.0	2.0	2.5	2.4	11.2	8.4	
(1 0 0)	A	-3.26	-5.67			2.1	2.1	2.7	2.6	11.1	8.3	
2 Cu/Ru adatom												
(1 1 0)	AA''	-2.98	-5.04	2.4	2.4	2.0	2.0	2.8	2.8	10.6/10.6	7.7/7.5	
(1 1 1)	AB	-3.04	-5.37	3.8	4.0	2.5	2.6	2.6	2.4	11.2/11.3	8.4/8.7	
	A2B	-2.96	-5.53	2.4	2.4	2.0	2.0	2.7	2.6	11.0/11.1	8.3/8.2	
(1 0 0)	AA'c	-3.37	-5.64	2.7	3.0	2.1	2.0	2.7	2.7	11.0/11.1	8.3/8.2	
	AA'a	-3.25	-5.74	5.9	5.8	2.1	2.1	2.7	2.7	11.1/11.1	8.3/8.3	

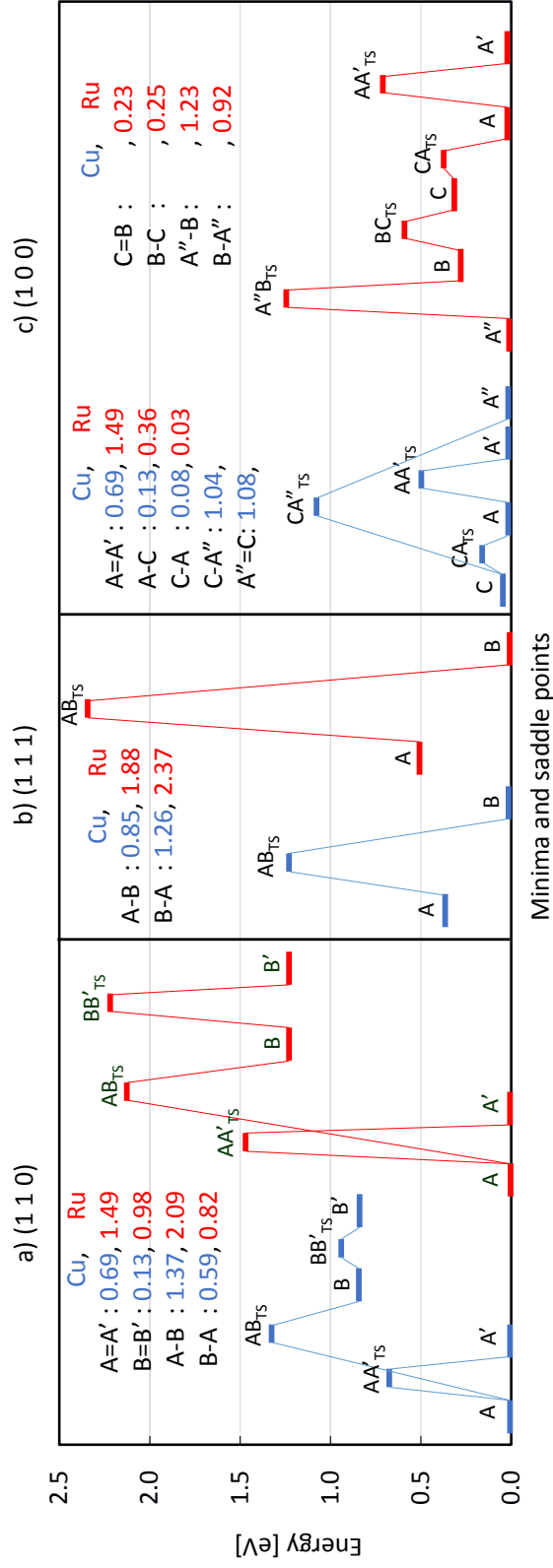


Figure 2: Panels a), b) and c) show the saddle points and activation energies for the on-surface hopping of the Cu/Ru adatoms on the (1 1 0), (1 1 1) and (1 0 0) surfaces of ϵ -TaN, respectively. The numbers and edges in blue correspond to Cu and those in red correspond to Ru. Blanks indicate interaction energies that were not computed. Transition states are indicated by the subscript "TS".

On the (1 1 0) surface, shown in Figure 1a, site A, a 5 fold hollow site coordinated by 3 Ta and 2 N atoms, is the most favourable adsorption site for both Ru and Cu adatoms. At this site, the Ru adatom binds with an energy of -4.95 eV, which is 2.13 eV stronger than that of the Cu adatom. The Cu-N and Ru-N distances are very similar (1.9 Å), but the Ru-Ta distance is about 0.2 Å shorter than the Cu-Ta distance. From the Bader charge analysis we find that both Cu and Ru adatoms are oxidised with net computed Bader charges of 0.5 and 0.2 e⁻, respectively (see Table 1). The different oxidation for Ru and Cu is due to the electron affinity differences between Cu/Ru and Ta/N.

On the (1 1 1) surface, site B, a wide hollow site between a pair of N and Ta atoms, is favoured by both Ru and Cu adatoms. Similar to the (1 1 0) surface, we find that the Ru adatom binds 2.43 eV stronger than the Cu adatom. However, in contrast to the (1 1 0) surface we find that both Cu and Ru adatoms are reduced on this surface, Table 1. The adatoms gain electrons from the neighbouring Ta atoms, which are less oxidised than those in the (1 1 0) surface (see Section A2.5 of Appendix for detailed analysis). On the (1 0 0) surface, site A, a three fold site coordinated by 2 Ta and 1 N atoms, is the most favourable site for both Ru and Cu adsorption. Similar to the (1 1 1) surface, the Cu and Ru adatoms are partially reduced at this surface as evident from the computed Bader charges reported in Table 1.

The density of states (DOS) confirms the results from the Bader charge analysis, and shows that Cu and Ru atoms on the (1 1 0) surface are oxidised while Cu and Ru atoms on the (1 1 1) and (1 0 0) surfaces are metallic or partially reduced. Additionally, we find that the conduction and valence bands of Cu on the (1 1 0) surface are separated, with zero DOS contribution at the Fermi level, while Ru atoms on the same surface have a non-zero contribution to the DOS at the Fermi level. This suggests that Ru is metallic on all three surfaces, while Cu is only metallic on the (1 1 1) and (1 0 0) surfaces. Section A2.6 of the Appendix provides additional analysis on the density of states (DOS) for Cu and Ru adsorption on ε -TaN surfaces to further understand how the electronic properties differ between the different surface facets.

As the next step, the activation energies for adatom hops on these surfaces are shown in Figure 2. From the most stable site A on the (1 1 0) surface, the Cu and Ru adatoms can hop to an adjacent identical site along the trench (site A') by overcoming activation energies of 0.69 eV and 1.49 eV, respectively. Similarly, the adatoms can also hop back and forth between sites B and B' by overcoming a small barrier of 0.13 eV in the case of Cu and 0.98 eV in the case of Ru. There is a larger activation energy for the adatoms to diffuse from site A to site B (1.37 eV for Cu and 2.09 eV for Ru) when compared to the reverse hop (0.59 eV for Cu and 0.82 eV for Ru) because site A is the most favourable binding site on this surface. The activation energies for hopping are larger for Ru than Cu, which is expected due to the relatively stronger binding of Ru on the (1 1 0) surface as mentioned above. This

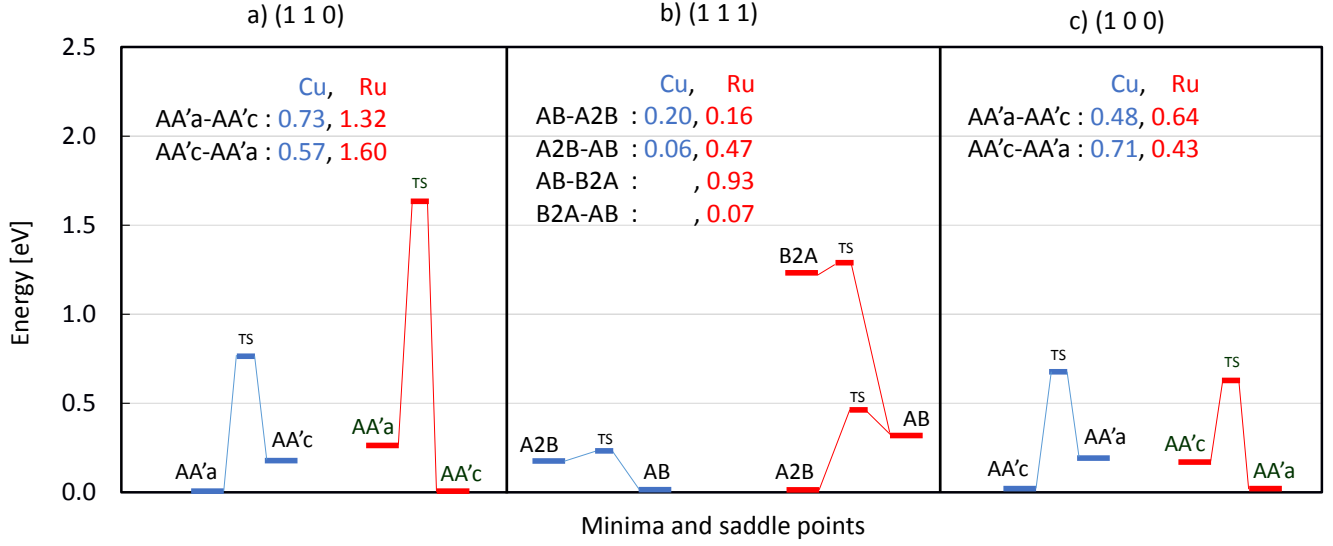


Figure 3: Panels a), b) and c) shows the saddle points and activation energies for the on-surface association of two Cu/Ru adatoms on the (1 1 0), (1 1 1) and (1 0 0) surfaces of ϵ -TaN, respectively. The numbers and edges in blue correspond to Cu and those in red correspond to Ru. Blank entries indicated activation energies that were not computed. Transition states are indicated as "TS".

suggests that Cu atoms are mobile on the surface, while Ru is more likely to stay where it first interacts. On the (1 1 1) surface, we find that the activation energies for Ru migration from the most favourable site B to site A is about 2.37 eV which is 1.11 eV larger than that of Cu. On the (1 0 0) surface, the activation energy to hop from site A to A' along the trench (red arrow in Figure 1c) is significantly smaller than the combined activation energy for a hop across the trench (green arrows for Cu and blue arrows for Ru in Figure 1c). Unlike the (1 1 0) and (1 1 1) surfaces, the activation energies for hops are almost comparable for both Cu and Ru adatoms on the (1 0 0) surface. Figure 2 illustrates the activation energies discussed above.

To summarise, stronger adatom binding is observed on the (1 1 1) and (1 0 0) surfaces of TaN as compared to the (1 1 0) surface. Ru binds significantly stronger than Cu on the TaN surfaces. Cu generally shows lower activation energies than Ru. The lowest activation energies for on-surface diffusion are observed on the (1 0 0) surface followed by the (1 1 0) and (1 1 1) surfaces. We also find that the Ru and Cu adatoms are oxidised on the (1 1 0) surface, while they are reduced on the (1 1 1) and (1 0 0) surfaces. Clearly, the (1 1 0) surface behaves differently than the other two surfaces.

4.2 Ru and Cu dimers on Bare ϵ -TaN Surfaces

As the next step adsorption of 2 Cu or 2 Ru atoms is studied on the most favourable low index surfaces. This is carried out in such a way that the first adatom is placed at the most favourable site on the respective surface and the second adatom is placed at the remaining sites adjacent to the first adatom. The binding energies, selected interatomic distances and adatom charges in the most favourable minimum-energy geometries are listed in Table 1 and the corresponding geometries are shown in Figure 4. This figure also includes the geometries (AA'a and AA'c) that are used to compute activation energies for atom association. AA'c and AA'a refer to geometries where A' is adjacent to A and A' is away from A, respectively. The energies and geometries of the other minima are discussed in Section A2.4.2 of the Appendix.

On the (1 1 0) surface, the most favourable binding is observed when the Cu or Ru atoms are adsorbed at sites A and A'' (AA'') which are located adjacent to each other on the (1 $\times$ 4) supercell of the TaN (1 1 0) surface (see Figure 4a). Comparing the results of the 2 adatom case with the 1 adatom case, we do not find a significant increase in the binding energies per Cu/Ru atom even though the two adatoms are close to each other. Therefore the adatom-adatom interaction must be small. Similar to the 1 adatom case, the Ru and Cu adatoms are oxidised at all sites on this surface. On the (1 1 1) surface the two adatoms are first adsorbed at sites A and B (AB) to represent the separated state. To examine the association of the adatoms to form Cu-Cu/Ru-Ru bonds, two geometries are constructed by keeping one of the adatoms at either site A or B and the other immediately next to it (A2B and B2A in Figure 4). It appears that Cu adatoms prefer to stay separated (AB is more stable than A2B) while the Ru adatoms prefer to associate close to site B (A2B more stable than AB). On the (1 0 0) surface, the associated state AA'c is the most favourable 2 atom mode for Cu adatoms whereas the separated state AA'a is the most favourable for Ru adatoms. Similar to the 1 adatom case, the adatoms at (1 1 1) and (1 0 0) surfaces are moderately reduced or remain neutral, while atoms are oxidised on the (1 1 0) surface.

We have computed the activation energies for adatom association at these surfaces, see Figure 3. For (1 1 0) and (1 0 0) surfaces, the migration of the adatom at site A' from AA'a to AA'c could be regarded as adatom association. For the (1 1 1) surface this will be the migration of adatom at site A towards the adatom at site B (AB to A2B) or vice-versa (AB to B2A). On the (1 1 0) surface, Cu prefers the separated state (AA'a) while the Ru prefers the associated state (AA'c). When initialized from the separated state (AA'a), activation energies of 0.73 eV (Cu) and 1.32 eV (Ru) are needed to reach the associated state. For Cu and Ru, the reverse process requires energies of about 0.57 eV and 1.60 eV. On the (1 1 1) surface, while Cu adatoms prefer the separated state, the activation energy needed for them to associate is just 0.16 eV. While Ru adatoms prefer the associated state, the activation energy to separate is 0.47 eV. In contrast to the (1 1 0) surface, the Cu and Ru adatoms on the (1 0 0) surface

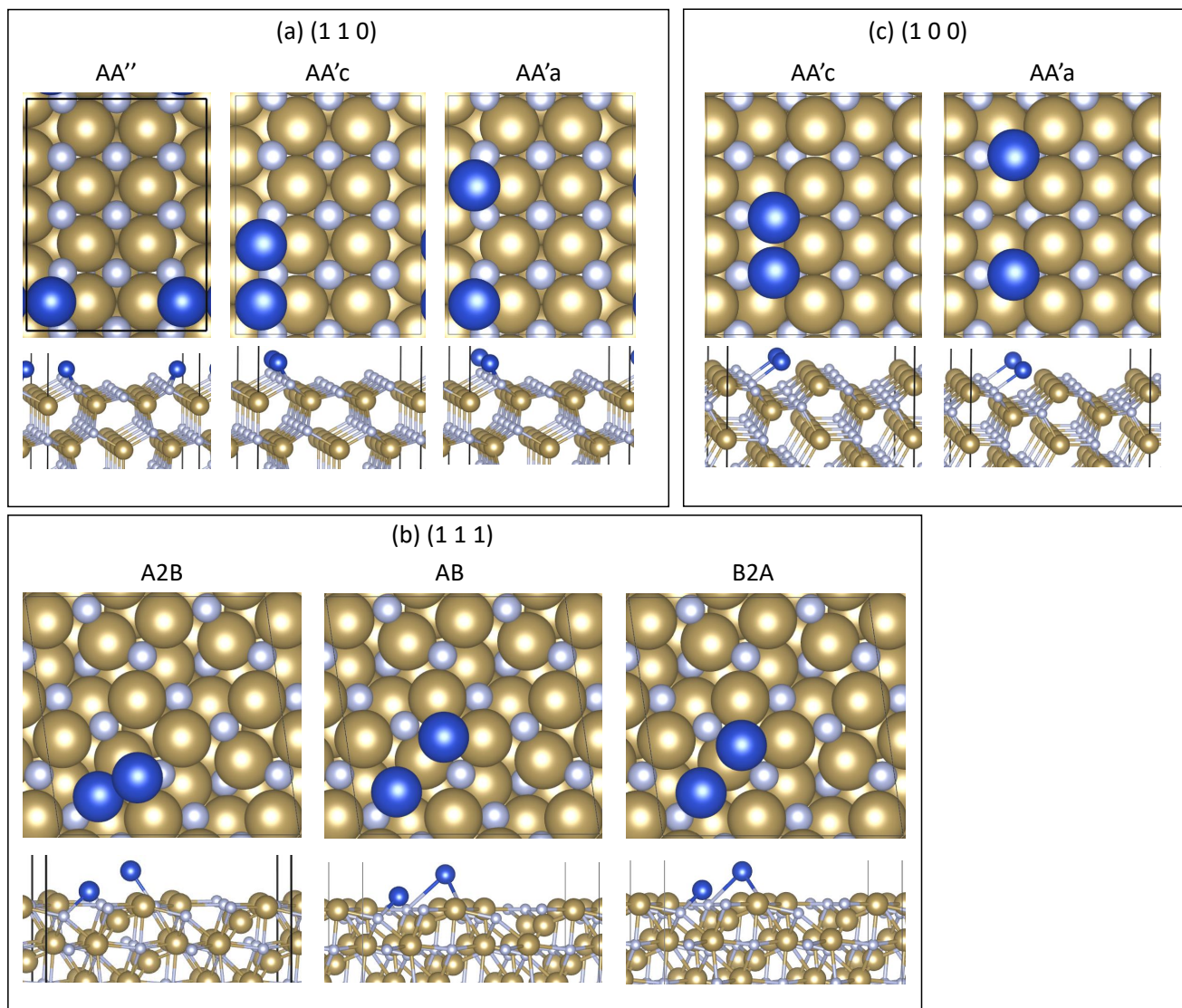


Figure 4: Most favourable minimum energy geometries of 2 adatoms (Cu/Ru) at the selected low index surfaces of ϵ -Ta_N. Here A2B represents the geometry where the adatom at site A moved towards the adatom at site B and vice-versa. AA'c and AA'a represents 2 atom sites where the adatoms are close to each other and distant from each other, respectively. The adatom (Cu or Ru) is shown in blue, all other atoms follow the colour code in Chapter 3.

prefer the associated and separated states, respectively. Activation energies of 0.48 and 0.64 eV are required for the Cu and Ru adatoms to associate on this surface.

In summary, similar to the 1 adatom case, the adatoms bind more strongly on the (1 0 0) and (1 1 1) surfaces as compared to the (1 1 0) surface. Further, the adatoms are either metallic or slightly reduced on the (1 1 1) and (1 0 0) surface while they are oxidised on the (1 1 0) surface due to the different numbers of F- and S-type Ta atoms on these surfaces. The Cu adatoms at (1 1 0) surface prefer to stay separated and offer the highest activation

energy towards association when compared with the other surfaces. Therefore, Cu atoms may wet on the (1 1 0) surface as compared to the other low-index surfaces. Thus, we chose to use the (1 1 0) surface for Ru passivation and doping studies.

4.3 Cu on Hexagonal Ruthenium

Before investigating the interaction of Cu at Ru doped and Ru passivated surfaces, we have to understand the interaction between Cu adatoms and the bare Ru surface.

Table 2: Binding energies of Cu adatoms on the (0 0 1) surface of Ru.

Sites	Q(Cu)	E _{bind} [eV/ads.]
1 Cu adsorption		
A (HCP)	10.9	-3.18
B (HOLLOW)	10.9	-3.14
C (ATOP)	-	-
A _{exch}	10.9	-2.07
B _{exch}	11.0	-1.52
2 Cu adsorption		
AAc	10.9/10.9	-3.26
AAa	10.9/10.9	-3.16
BBc	10.9/10.9	-3.22
BBa	10.9/10.9	-3.11

Figure A5a in Section A2.3 of the Appendix shows the bare Ru(0 0 1) surface along with the stable binding sites for Cu adsorption namely A, B and C, where A is a hcp site, B is a hollow site and C is an atop Ru site. We have also included the geometries where the Cu adatom from a hcp and a hollow site is exchanged with a surface Ru atom labelled as A_{exch} and B_{exch}, respectively. The binding energies and valence charge of one Cu adatom at these sites are given in Table 2. Adsorption of Cu adatoms on the Ru(0 0 1) surface has been studied previously by Ding and co-workers [9, 10] using DFT and ultrasoft pseudopotentials. The binding energy of a single Cu atom on Ru(0 0 1) computed in those works are consistent with. However, they did not compute the hopping/association activation energy or sub-surface diffusion activation energy of the adatoms, which we have focused on in this section.

The Cu atom was not stable at the atop Ru site. The Cu adatom binds with similar binding energies at sites A and B, ranging from -3.14 eV to -3.18 eV which is comparable to the TaN surfaces discussed earlier. However, while the binding energy is considerably weaker when the Cu atom is exchanged with a surface Ru atom (-1.52 at B_{exch} and -2.07 eV at A_{exch}), it is nonetheless favourable for Cu to be present at a Ru site. The Cu adatom remains metallic on the Ru surface. The activation energies involved in the on-surface hop and sub-surface exchange of Cu

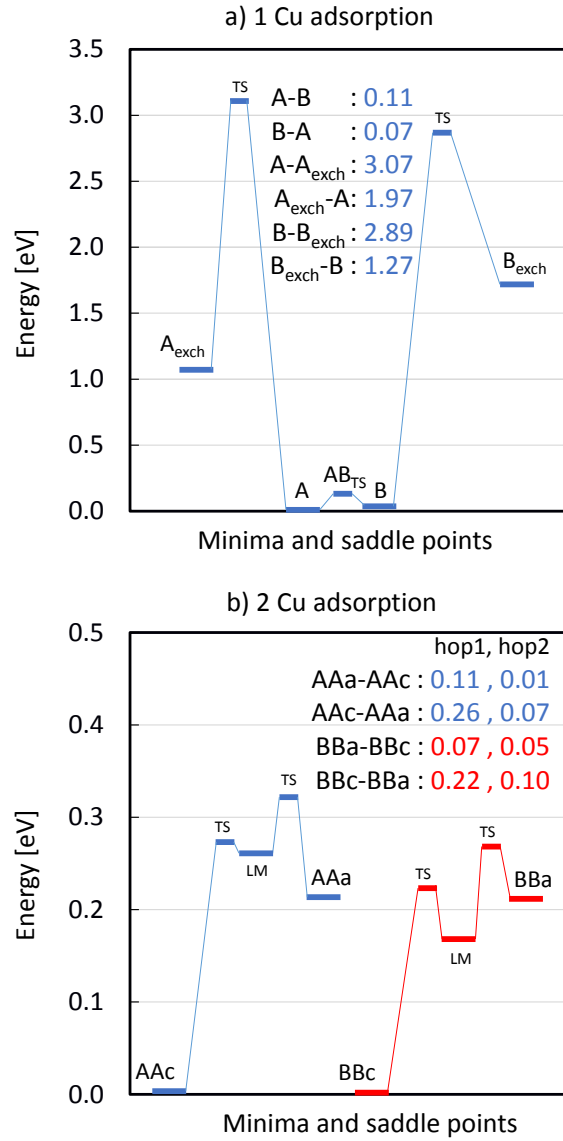


Figure 5: Panels a) and b) show the minima, saddle points and activation energies for the on-surface diffusion and association of Cu adatoms on the Ru(0 0 1) surface, respectively. Here, "LM" refers to local minimum and "TS" refers to transition state.

adatoms are given in Figure 5 and the minimum-energy geometries used in the corresponding CI-NEB calculations can be seen in Figure A5b of the Appendix. We find that the activation energy for facile diffusion of a Cu adatom on Ru(0 0 1) is in general very small. The activation energy to hop from a hcp to a hollow site (A to B) is only 0.11 eV and the reverse hop is just 0.07 eV supporting the fact that the hcp site is slightly more preferred by the Cu adatom. In contrast, the activation energy for the exchange process is very large. The activation energy to exchange from a hcp site is about 3.07 eV and from a hollow site is 2.89 eV. The reverse exchange processes have

relatively smaller activation energies which are about 1.97 eV for the hcp site and 1.27 eV for the hollow site. In any case, these exchange processes are unlikely due to the high activation energies impeding them.

In the next step two copper atoms are adsorbed on the Ru(0 0 1) surface and we consider two cases. In the first case, the two copper atoms are bound only to hcp sites (AAa and AAc) and in the second case they are bound only to hollow sites (BBa and BBc). The corresponding geometries used for this study are shown in Figure A5c of the Appendix and the energies are listed in Table 2. The geometries at sites AAa and BBa represent cases where the adatoms are separated and those at AAc and BBc are cases where the adatoms are adjacent to each other. The binding energies per adsorbed Cu are very similar, in the range of -3.11 eV to -3.26 eV. Therefore, we studied the activation energies separating them as indicated by the arrows in Figure A5c of the Appendix. A copper atom can diffuse along the surface via two types of hops - hcp to hollow and hollow to hcp. So to migrate from one hcp site to another the adatom must first hop to a hollow site and then to the hcp destination site which involves crossing two activation barriers. From Figure 5 we find the greatest activation energies for the first hop from the associated states AAc (0.26 eV) and BBc (0.22 eV) and the lowest activation energies for the second hop toward the same states (0.01 eV and 0.05 eV). The Cu adatoms are therefore very mobile on the Ru(0 0 1) surface and prefer to associate.

Table 3: Binding energies and activation energies for the diffusion of Cu adatoms on 1 and 2 ML of Ru passivated TaN (1 1 0) surfaces. A '-' for the E_{bind} indicates that the respective geometry is found to be unstable and a '-' for $E_{\text{activation}}$ indicates that we could not find a transition state connecting the minima.

Adatoms	Sites	Q(Cu)	E_{bind} [eV/ads.]	d(Cu-Cu) [Å]
1 ML Ru				
1 Cu	A (3 fold atop N)	10.9	-3.24	
	B (3 fold atop Ta)	11.0	-3.44	
	C (2 fold)	10.9	-3.35	
2 Cu	BB'	11.0/11.0	-3.60	2.5
	BA	11.0/11.0	-3.48	2.6
	BC	11.0/10.9	-3.49	2.9
	BB''	11.0/10.9	-3.52	5.2
2 ML Ru				
1 Cu	A (2 fold)	11.0	-3.44	
	B (3 fold wide)	11.0	-3.42	
	C (3 fold hcp)	10.9	-3.18	
	D (3 fold hollow)	10.9	-3.13	
2 Cu	AA'	11.0/10.9	-3.43	2.7
	AB	11.0/11.0	-3.43	2.5
	AC	11.0/10.9	-3.35	2.4
	AB'	10.9/11.0	-3.31	4.8
	AC'	11.0/10.9	-3.30	4.6

4.4 Ru Passivated TaN Surfaces (1×4) supercell

In this section, adsorption and diffusion of Cu adatoms on Ru passivated TaN(1 1 0) surfaces will be studied. A discussion on the adsorption of Ru adatoms that resulted in the formation of a passivated layer is given in Section A2.7 of the Appendix. For our purposes, we will perform the Cu adsorption and diffusion calculations on 1 ML and 2 ML of Ru passivated TaN(1 1 0) surfaces (in Figures A12e and A12f in the Appendix).

4.4.1 Cu Adatoms at 1 ML Ru passivated TaN(1 1 0) surface

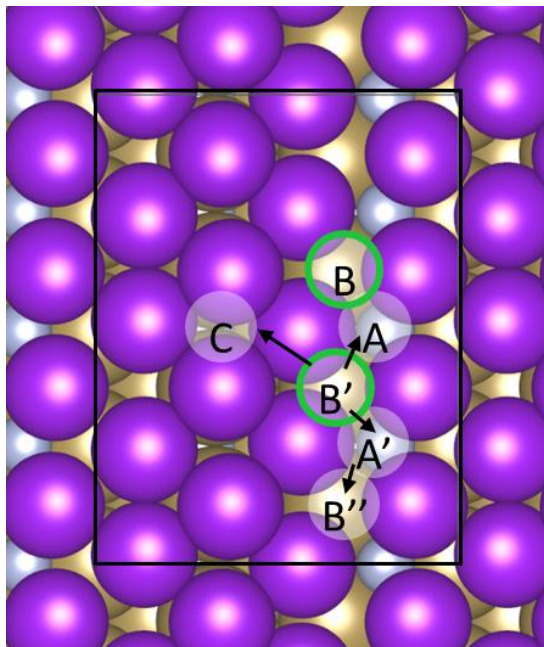
From the three stable binding sites (A, B and C) shown in Figure 6a, the strongest binding is seen at site B, a wide 3 fold site above a sub-surface Ta atom. The binding energies listed in Table 3 are stronger than on the bare (1 1 0) surface suggesting that Ru passivation also promotes Cu binding. We did not find significant changes in the valence charge of the adsorbed Cu atom which indicates that there is no significant electron transfer between the Cu adatom and the Ru layer.

The on-surface hopping activation energies of a Cu adatom between sites A-B and B-C (shown in Figure 7a) are in the range of 0.01 eV - 0.45 eV. The greatest activation energy of 0.45 eV is found for the Cu atom to migrate from site B to site C and the lowest activation energy of 0.01 eV is found for its diffusion from site A to B. These activation energies are comparatively larger than on the bare Ru(0 0 1) surface but smaller than on the bare TaN (1 1 0) surface. We also studied the energies of sub-surface adsorption of the Cu adatom from the above mentioned stable sites, as shown in Figure 6b. All the sub-surface adsorption geometries had weak binding energies and large diffusion barriers (see Figure 7a) as compared to the corresponding on-surface adsorption geometries. More discussion can be found in Section A2.7 of the Appendix.

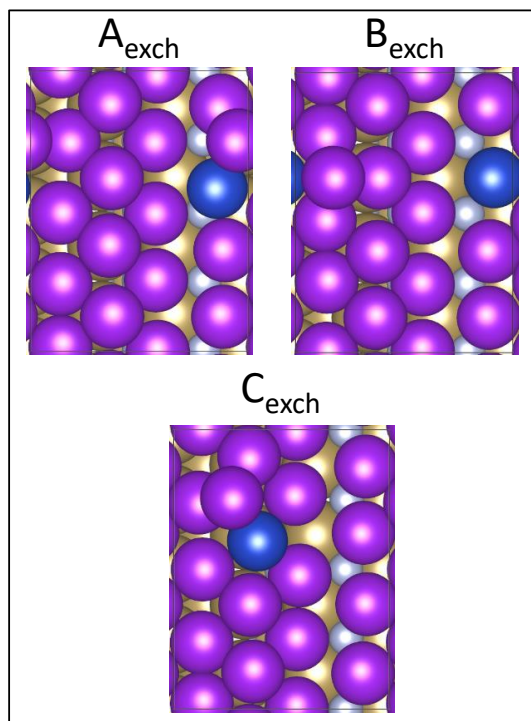
As the next step, adsorption of 2 Cu is investigated where the geometry at site BB' (combined site notation: one adatom at B and the other at B') is found to be the most favourable where the Cu atoms are at a distance of 2.5 Å. Details of the other geometries are discussed in Section A2.7 of the Appendix. Compared to the 1 Cu adsorption case, we find that the binding energies have decreased slightly, probably due to the additional Cu-Cu interaction and associated surface rearrangements.

We have chosen the geometry at site BB' as the associated state (shown by green circles in Figure 6a) and computed the activation energies associated with the diffusion of the second Cu atom from site B' to sites A, C and B". The forward activation energies from BB' to the other sites are in the range of 0.35 - 0.48 eV and the reverse activation energies are significantly lower as shown in Figure 7b. This suggests that the Cu adatoms, in addition to diffusing on the surface, prefer to associate more so than on the bare TaN (1 1 0) surface.

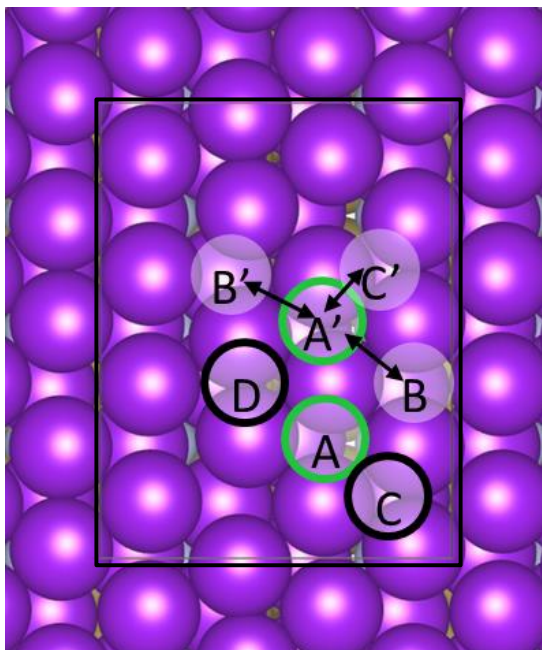
a) Sites and Paths on 1ML Ru



b)



c) Sites and Paths on 2ML Ru



d)

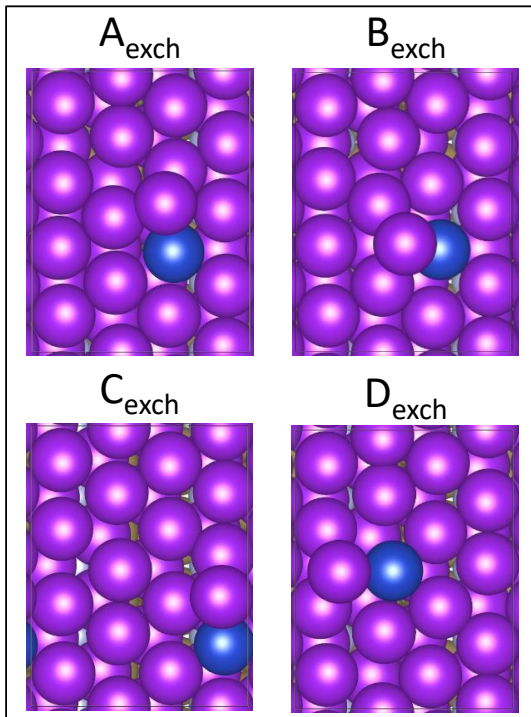


Figure 6: Unique adsorption sites for Cu adsorption on 1 and 2 ML of Ru passivated TaN (1 1 0) surface are shown in panels a and c, respectively. It also includes pathways to compute activation energies for association in two Cu adsorption, where the Cu sites in associated states are highlighted in green and the arrows indicate the pathway. Panels b and d show the geometries where a Cu adatom is adsorbed at sub-surface sites.

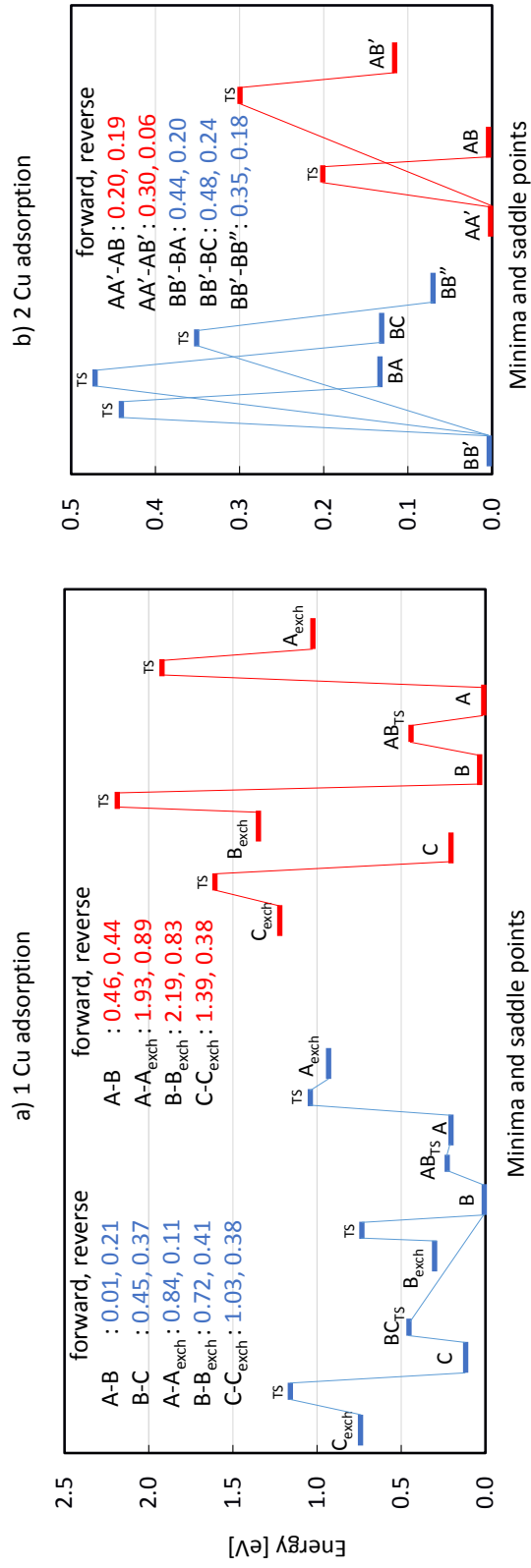


Figure 7: Panels a) and b) show the minima, saddle points and activation energies for the on-surface/ subsurface diffusion of 1 Cu adatom and association of 2 Cu adatoms on the Ru passivated TaN surfaces, respectively. Here, blue and red colours represent 1 ML and 2 ML of Ru passivated surfaces, respectively. Transition states are indicated as "TS".

4.4.2 Cu Adatoms at 2 ML Ru passivated TaN(1 1 0) surface

On the 2 ML Ru passivated TaN(1 1 0) surface shown in Figure 6c, the two fold Ru coordinated site A is found to be the most favourable. Similar to the 1 ML case, there is no significant charge transfer between the Cu and Ru atoms.

The computed activation energy for the Cu adatom to hop from the most favourable site A to site B is 0.46 eV and the activation energy for the reverse process is almost the same as shown in Figure 7a. Pathways connecting site A to sites C and D could not be found in our investigation. The sub-surface exchange geometries given in Figure 6d are found to be approximately 1 eV lower in binding energy than the corresponding on-surface adsorption cases. More details can be found in Section A2.7 of the Appendix.

For 2 Cu adsorption, the first Cu is placed at site A and the second Cu is placed at sites B, C, A', B' and C' (see Figure 6c). The binding energies per Cu are in the range of -3.30 eV to -3.43 eV which is comparable to the 1 Cu adsorption energies on this surface.

The activation energies for Cu association are computed by keeping the geometry at AA' as the starting point and moving the Cu at A' to sites B, B' and C' as indicated by arrows in Figure 6c. We find that the two atom sites AA' and AB are equally favourable. For the minimum energy pathways connecting AA' with AB', the forward activation energy is greater than the reverse activation energy indicating a preference for Cu atoms to coordinate with each other.

Overall, the Cu adatoms bind more strongly at the Ru passivated surfaces as compared to the bare Ru and the bare TaN (1 1 0) surfaces. We also did not observe any significant charge transfer between the Cu and Ru atoms. The on-surface Cu diffusion activation energies are moderately larger than those on bare Ru, but significantly smaller than those on the bare TaN (1 1 0) surface. Therefore, the Cu adatoms are mobile on this surface and might show a preference toward association like they do on the bare Ru surface.

4.5 Ru doped TaN (2×4) supercell

As an alternative to the Ru passivated surfaces we will now study the Ru doped TaN (1 1 0) surfaces as a single barrier+liner material. All calculations for Cu adsorption on Ru-doped TaN (1 1 0) were carried out using a (2×4) supercell in order to eliminate any finite size effects caused by Ru doping of the (1×4) supercell.

However, as will be shown in this section, the effects of Ru in the surface are very localised and thus it is possible to use the smaller (1×4) supercell for the NEB calculations. Although Ru is suitable for copper electroplating, it does not function well, by itself, as a diffusion barrier material. The Ru passivated TaN surfaces studied in the previous section were found to have small activation energies for the on-surface diffusion of copper atoms and may allow Cu association. Additionally, Ru passivated TaN is made up of two layers of material, limiting thickness reduction. Therefore, given the properties of Ru and TaN, the possibility of tuning the TaN surface to allow wetting of Cu through doping with Ru, while retaining the barrier properties of TaN, is the focus of this section. Ta atoms from two surface sites are replaced with Ru as shown in Figure 8a to determine the more favourable doping site.

Ru^S replaces a surface Ta atom (S type) coordinated to 4 surface N atoms while Ru^F replaces a surface Ta atom (F type) that is coordinated to 2 surface N atoms. The TaN surface doped with Ru^F is 2.34 eV more stable than that doped with Ru^S . Charge analysis of the surface shows that the charges on Ru^S and Ru^F are 7.1 and 7.5 respectively. This difference in Ru oxidation and coordination environment is likely the cause of the different surface energies. Details of the surface charges are shown in Section A2.5 of the Appendix. The introduction of Ru into the surface did not affect the TaN surface lattice.

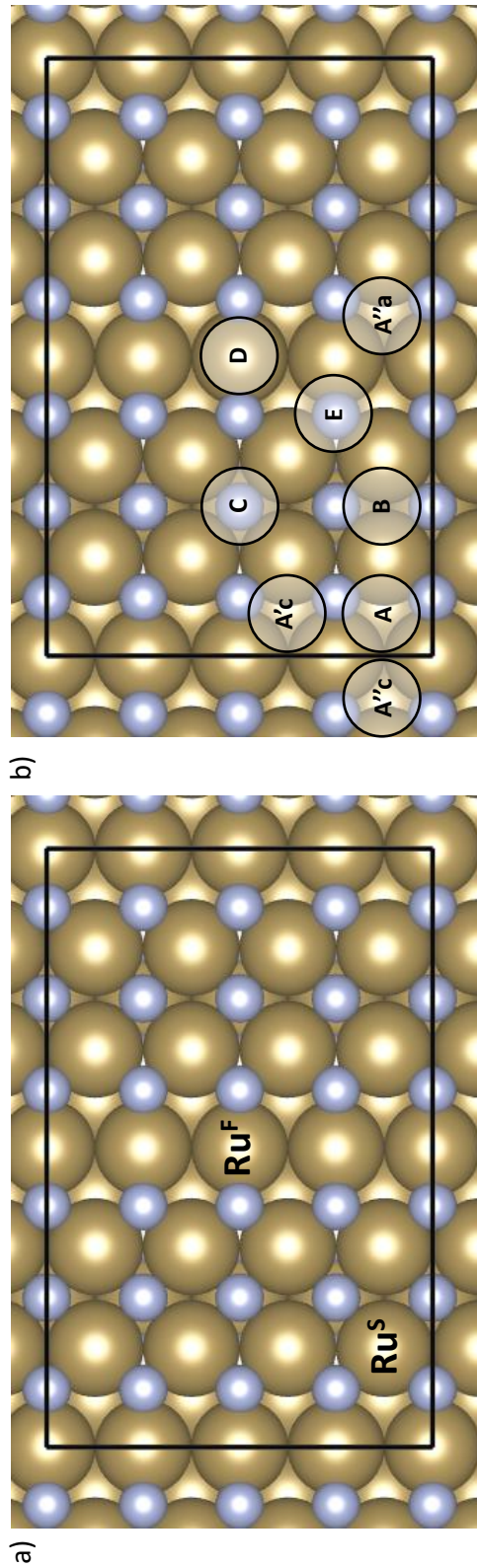


Figure 8: a) Ru-doping sites and b) Cu adsorption sites on the TaN(1 1 0) surface.

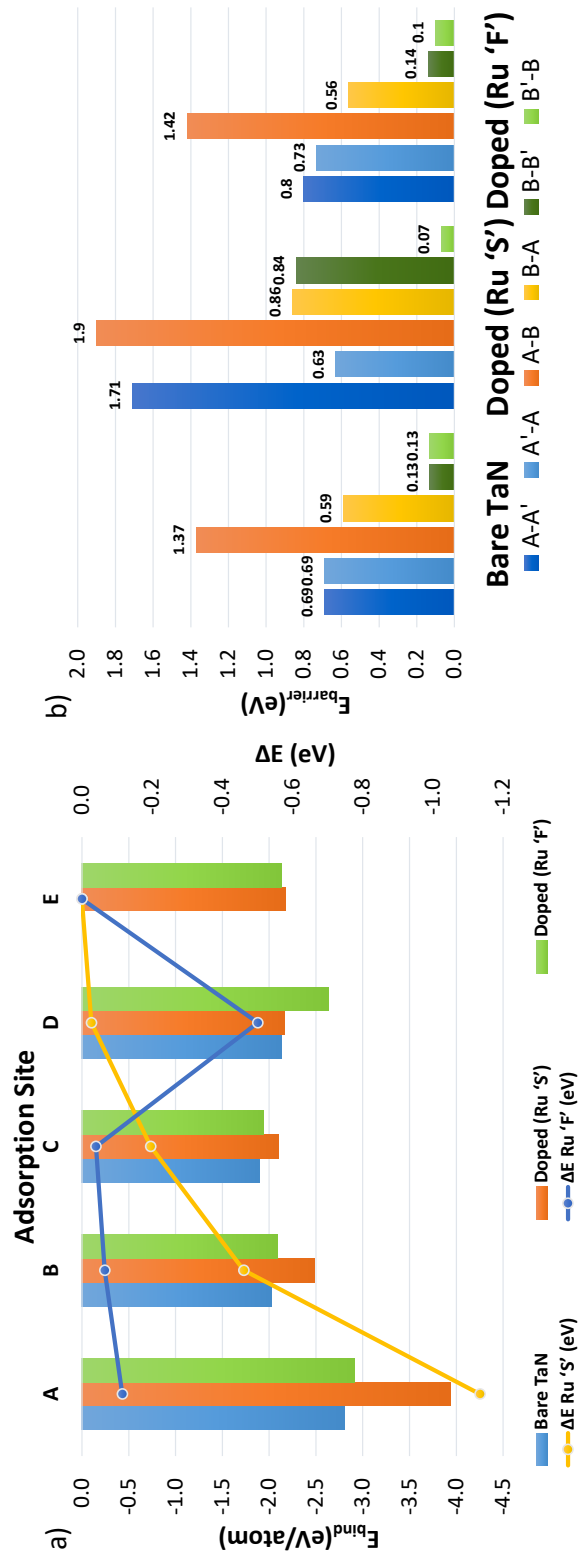


Figure 9: Comparing changes in a) adsorption energies and b) activation energies between bare (2×4) TaN and Ru-doped (2×4) TaN for each adsorption site.

4.5.1 One Adatom Adsorption on Ru-doped TaN(1 1 0)

On the bare (2×4) supercell of the TaN (1 1 0) surface, five unique Cu adsorption sites (A, B, C, D and E) were identified as shown in Figure 8b. The binding energies of a Cu adatom at these five sites on the bare (2×4) surface as well as on the doped surfaces are compared in Figure 9a and the corresponding geometries for the most favourable site on Ru^S and Ru^F doped TaN surfaces are given in Figure 10. All other geometries are shown in Section A2.8 of the Appendix.

Binding energies for Cu at the different sites range from -2.01 eV to -3.93 eV for the Ru^S doped surface, from -1.94 eV to -2.92 eV for the Ru^F doped surface compared to -1.90 eV to -2.80 eV for the bare TaN (1 1 0) surface. Overall, site A is the most stable and site C is the least stable for Cu adsorption on all the three surfaces. It is evident from Figure 9a that the Cu adatom binds slightly more strongly on the Ru doped TaN surfaces as compared to the bare TaN surface. The figure also shows the binding energy difference (ΔE) between the bare and Ru doped surfaces from which the largest change for Ru^S and Ru^F doped surfaces is found to have occurred at the sites A (1.13 eV) and D (0.50 eV), respectively. Ru^S doped surface shows enhanced Cu binding at sites A, B, C and E as compared to Ru^F doped surface, whereas Ru^F doped surface shows enhanced Cu binding at site D as compared to Ru^S doped surface. Therefore, it is clear from the ΔE plot in Figure 9a that those Cu adsorption sites that are closer to the doped Ru atom show enhanced binding as compared to the bare surface. Bader charge analysis showed that the Cu adatom is partially oxidised and that the charge of Cu is mostly independent of adsorption site and number of adatoms, although a correlation between binding energies and charge can be observed. The changes in charge are no larger than 0.2 electrons, however atoms that are more oxidised have a larger binding energy. All Cu charges are shown in Table 4.

Table 4: Binding Energies of Cu on Ru-doped TaN(1 1 0). Q(Cu) is the Bader charge on the Cu atom adsorbed to a doped surface, where there are two adatoms the charges are separated by a "/". Cu has 11 valence electrons.

No. Cu	Ru doping site	Cu adsorption site	E _{bind} [eV/ads.]			Q(Cu)
			doped 1x4	doped 2x4	bare 2x4	
1 Cu	Ru ^F	A	-2.88	-2.92	-2.80	10.5
		B	-2.02	-2.09	-2.02	10.5
		C	-1.88	-1.94	-1.90	10.6
		D	-2.56	-2.63	-2.13	10.4
		E	-	-2.14	-	10.5
2 Cu	Ru ^S	AA''c		-3.12	-3.03	10.5/10.6
		AA''a		-3.34	-2.79	10.5/10.5
		AB		-3.21	-2.42	10.6/10.5
		AD		-3.05	-2.42	10.5/10.4
	Ru ^F	AA''c		-3.03	-3.03	10.5/10.6
		AA''a		-2.88	-2.79	10.5/10.5
		AB		-2.51	-2.42	10.5/10.5

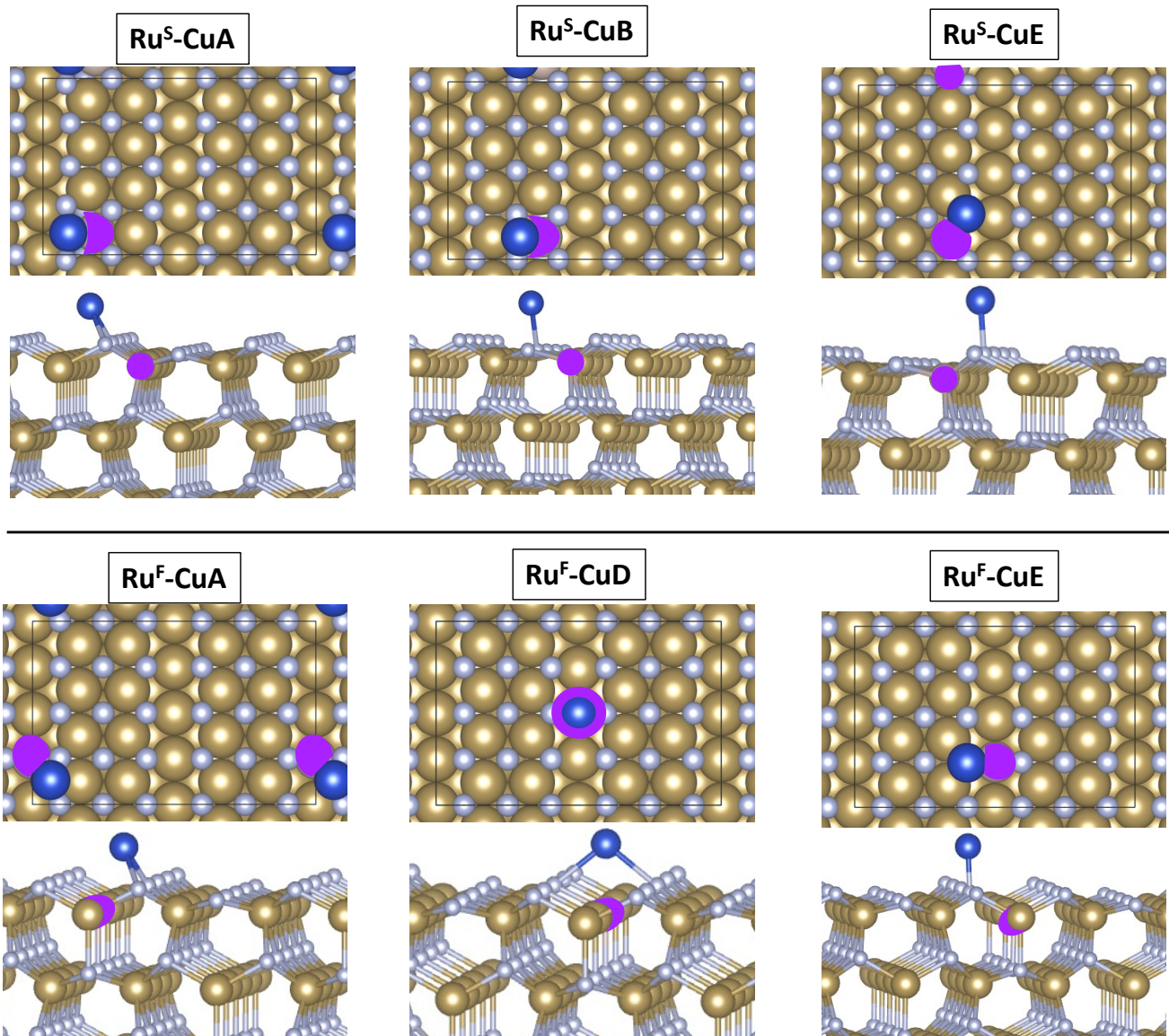


Figure 10: Relaxed adsorption geometries of most favourable 1 Cu atom on Ru^S-doped and Ru^F-doped TaN(1 1 0).

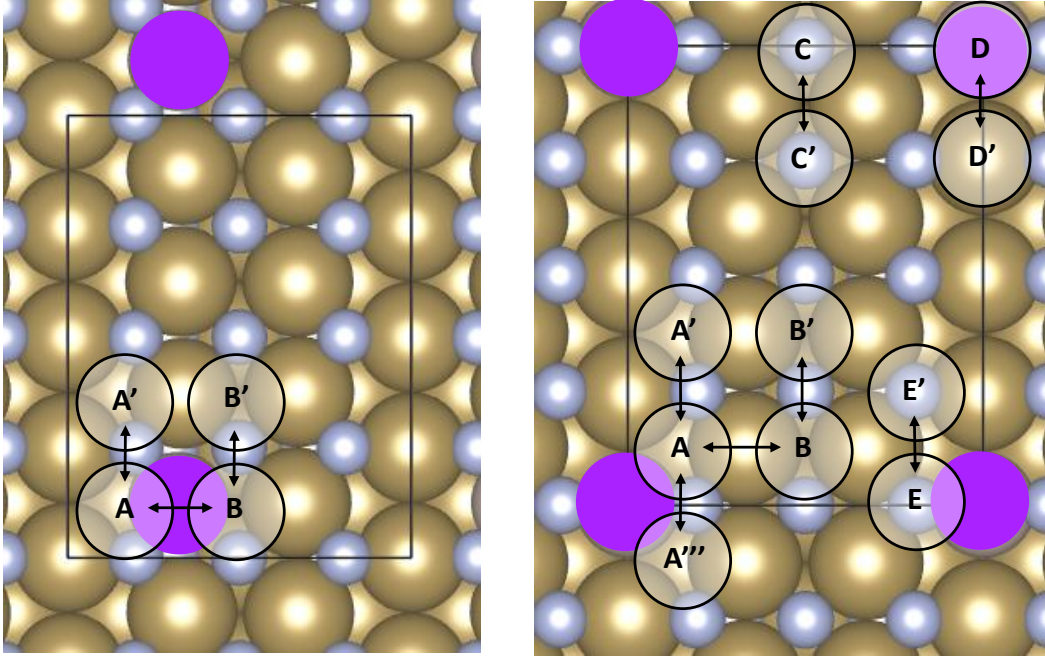


Figure 11: Migration pathways of Cu adatoms on both doped surfaces a) Ru^S and b) Ru^F .

To determine how the adsorption of Cu atoms affects the surface atomic structure of the Ru doped surfaces, the Ta-N bond lengths near the Cu adsorption sites (Ta-N adsorbed) are compared to those near an equivalent distant site on the same surface (Ta-N distant) and to those near an equivalent site in the bare Ru doped surface (Ta-N bare). The range of distances for these three cases are displayed in Figure A13 of the Appendix. The bond lengths of Ta-N distant are similar to those of Ta-N bare, while the Ta-N bonds near the adsorption sites appear somewhat elongated. The changes between any of the Ta-N bonds measured across all surfaces, bare and doped, are no more than 0.1-0.2 Å. Therefore, the effect of Cu adsorption and Ru-doping is localised to the adsorption/doping sites in terms of geometry.

Due to the localised effect of Ru doping, the CI-NEB calculations were carried out using the smaller (1×4) supercell of TaN ($1\ 1\ 0$). To facilitate this, the minimum-energy geometries and binding energies for 1 Cu adsorption were also computed on the smaller (1×4) supercell and compared with the (2×4) supercell in Table 4. The binding energies are very similar for both supercells, supporting the localised effect of Ru doping.

As the next step, the activation energies impeding the migration of a Cu adatom on the Ru doped surfaces were computed. Firstly, we determined the activation energies for migration from the most favourable site (A) to the closest non-equivalent site (B) for both Ru^S and Ru^F doped surfaces as shown in Figure 9b and the corresponding pathways in Figure 11a. On the Ru^F surface there is only a small increase in the on-surface diffusion activation

energies, connecting sites A-A', B-B' and A-B, compared to the bare surface. The large increase in the activation energy for migration for Ru^S can be attributed to Cu moving across a doped Ru instead of the Ta atom. Transitions on the Ru^S surface require a greater activation energy than those on the Ru^F surface. However, this is due to the proximity of the dopant to the adsorption site, which means that the interaction with Cu is much stronger on Ru^S . It follows that such a stronger interaction requires a greater activation energy to break it. This indicates that our small model with 8% doping is insufficient to compare the effects of dopants at different doping sites. For this reason, Section 4.7 studies the effects of dopant concentration and distribution on the behaviour of Cu adatoms.

For our purposes, we studied in detail the migration pathways and the corresponding activation energies on the more favourable Ru^F surface. The particular migration pathways are shown in Figure 11b, while the corresponding activation energies are listed in Section A2.8 of the Appendix and are also shown in Figure 9b. The forward and reverse activation energies in the table indicate the activation energies required for the Cu atom to migrate away from and towards the doped Ru, respectively. We observe that it is more favourable for Cu adatom to move towards the doped Ru on the surface than away from it. This is seen in the case of migration from site B to A (towards Ru) where the activation energy is almost 2.5 times lower than the migration from A to B (away from Ru). No migration pathways connecting the endpoints C-C', D-D' and E-E' were found. For the migration pathway B-B', very small activation energies of around 0.10 eV were found. The noted exception of this is the activation energy of 0.84 eV required to move a Cu atom away from site B on the Ru^S surface, where the adatom is directly adjacent to the Ru atom. The activation energy for the exchange of a Cu atom with the doped Ru in the surface is also determined. For Ru to move out of the surface and Cu to take its place the activation energy needed is as high as 3.78 eV. The reverse process has an activation energy of just 1.88 eV. This indicates that Ru doping is unlikely to allow sub-surface Cu adsorption and diffusion which allows the barrier properties of TaN to be maintained.

4.5.2 Two Adatom Adsorption on Ru-doped TaN

In this section we investigate the adsorption of 2 Cu atoms and the activation energy for Cu association on the Ru doped surfaces. The 2 adatom adsorption calculations are set up so the first Cu atom is placed at site A, which is the most favourable site, and the second Cu atom is placed at all the other sites shown in Figure 8b and the geometry is relaxed. Figure 12 shows the geometries for 2 adatoms on the doped surfaces, while Table 4 presents the computed binding energies of 2 Cu on the bare and doped surfaces.

As with the single adatom case, the binding energy per adatom was enhanced, by an average of 0.30 eV, when adsorbing 2 Cu atoms on the doped surfaces when compared to the bare surface. On the bare surface, the combination of AC and AE is unstable. The combination of adsorption sites A and E is unstable on the Ru^S doped

surface, while AC is stable. On the Ru^F -doped surface, AC, AD and AE are all unstable configurations. As the atoms are too far apart on the surface to coordinate, the Cu atom placed at the E site migrates to another A site (the A''a site) on both Ru^S and Ru^F doped surfaces. Once the two Cu atoms migrate to the A site, two atoms in adjacent A sites (AA''c) is the most favourable configuration on the Ru^F -doped surface, with a binding energy of -3.03 eV.

This same AA''c combination has a binding energy of -3.12 eV on the Ru^S doped surface. Interestingly, this is not the most stable configuration here. Instead with a binding energy of -3.34 eV, it is more favourable for the second Cu atom to adsorb at a distant A''a site. In addition to testing Cu adsorption directly on the surface, 2 Cu atoms were adsorbed on top of each other at an A site. When carrying out this calculation on the bare (1×4) surface and the doped surface, the Cu atoms remain stacked. On the bare (2×4) surface, the top Cu migrates to the surface and coordinates at the nearest available A site. This is possibly due to finite supercell size effects in the smaller surface.

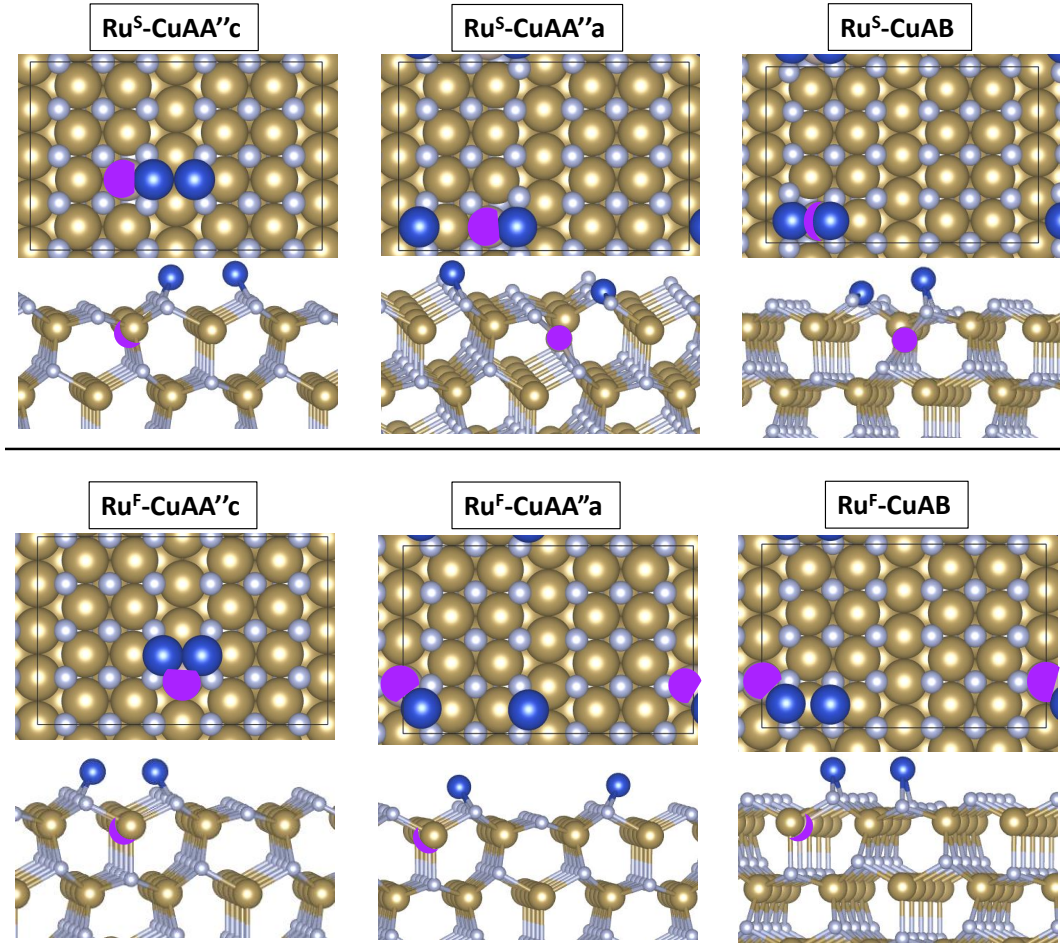


Figure 12: The most favourable adsorption geometries of 2 Cu atoms on Ru^S -doped and Ru^F -doped $\text{TaN}(1\ 1\ 0)$.

As for one adatom calculations, the distances between Cu-Ru, Cu-Ta, Cu-N, Ru-Ta and Ru-N were measured for all adsorption modes and compared to those measured for the bare surface. Results were consistent with the observations made for the one adatom calculations.

To study association using CI-NEB calculations, 2 Cu atoms were placed at adjacent A sites (AA''c) and the activation energy for one of the atoms to move to the next-nearest A site (AA''a) was computed. On the Ru^S surface, the activation energy needed to separate the two Cu atoms was 0.70 eV, while the energy to associate was 0.66 eV. On Ru^F , the activation energy for separation is 0.60 eV and the activation energy for association is 0.72 eV. The activation energies for migration are almost symmetrical for Ru^S , which could be due to competing effects of Cu-Ru interactions and Cu-Cu interactions. On Ru^F , the preference, by only 0.10 eV, is for Cu atoms to migrate away from each other with one atom anchored at the Ru site.

To summarise, the doping of Ru in the TaN surface improves the binding strength of Cu and increases the

activation energies for on-surface Cu migration as compared to bare TaN surfaces. We also find that the activation energy to migrate toward the Ru site is smaller than the activation energy to migrate away from it suggesting that the Ru dopants can act as anchor points during copper nucleation. However, the computed activation energies appear to be sensitive to the location of the doping site, therefore, Section 4.7 details the effects of doping concentration and distribution on a (2x4) supercell of TaN.

4.6 1 ML and 2 ML Ru Passivated and 25%, 50%, 75%, 100% Ru Doped TaN Surfaces

The (Ru)TaN (1 1 0) surfaces used in this section are shown in Figure 13 and Figure 14. The clean TaN surface, TaN with 1 & 2 monolayer (ML) of Ru and Ru doped TaN surfaces with 25%, 50%, 75% and 100% Ru content in the outermost Ta layer are shown in Figure 13a-g, respectively, while Figure 14 shows the various dopant distributions studied with 50% doping, which will be discussed in detail in Section 4.7 and in Section A2.9 of the Appendix. For brevity, we will refer to these doped surfaces as Ru^X with $X=25, 50, 75, 100$. The ten different Ru^{50} surfaces in Figure 14 are labelled in the order they appear in Figure 14, as Ru^{50-n} where $n=1-10$.

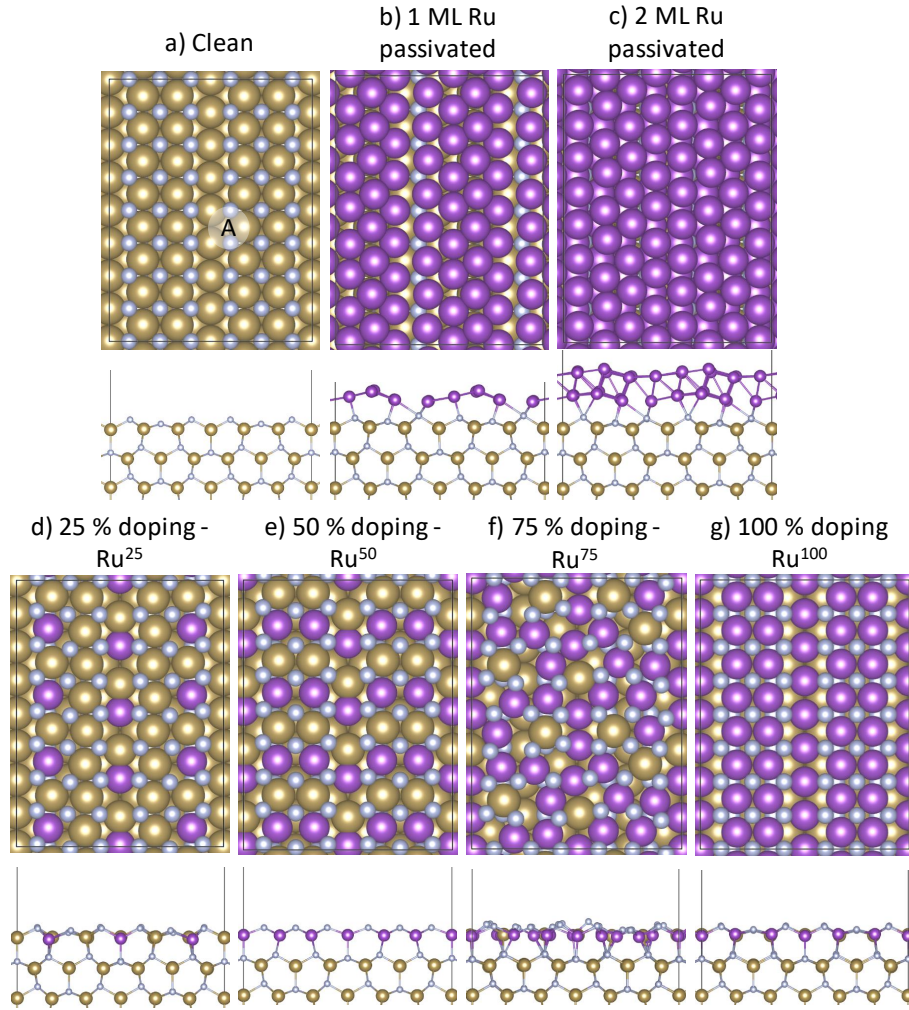


Figure 13: Panels a) - g) shows the top and side views of the relaxed atomic structures of the clean, 1 ML Ru passivated, 2 ML Ru passivated, 25%, 50%, 75% and 100% Ru doped TaN surfaces, respectively. On the clean surface, the 5 fold adsorption site coordinated by 3 Ta and 2 N is marked with 'A'.

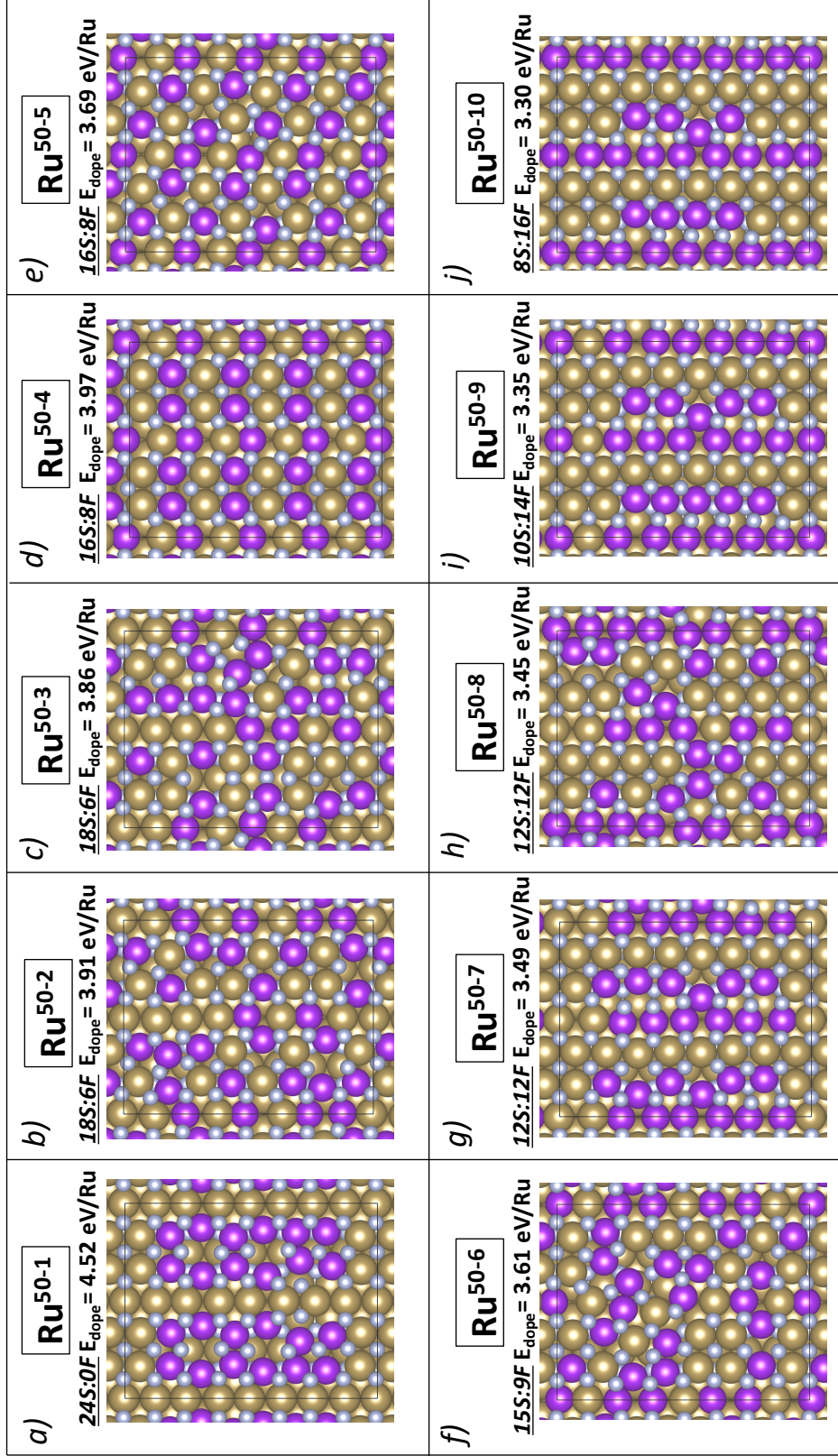


Figure 14: Relaxed atomic structures for 10 different Ru doping distributions in the Ru⁵⁰ TaN(1 1 0) surface are shown in panels a) - j). The ratio of S:F type Ru atoms (see Section 4.7) is shown, as well as the doping energy per Ru atom for each surface.

For the Ru²⁵, Ru⁵⁰ and Ru⁷⁵ surfaces, Figure 13 shows one arrangement for the distribution of Ru dopants after relaxation. On the Ru²⁵ surface shown in Figure 13d, the Ru atoms are preferentially arranged as far as possible from each another. On the Ru⁵⁰ surface in Figure 13e, the doped Ru atoms form horizontal zig-zag chains on the surface. The Ru atoms are randomly arranged on the Ru⁷⁵ surface in Figure 13f after relaxation. The side view of this surface clearly shows a high degree of rearrangement of the surface layer atoms. In terms of the number of structures for Ru-doped TaN, there are approximately 69×10^9 , 32×10^{12} and 69×10^9 possible ways to arrange 12, 24 and 36 Ru atoms, respectively, on a surface lattice containing 48 Ta atoms without considering symmetry. The total number of possible symmetry restricted arrangements would still be prohibitive. The arrangements we have chosen, as shown in Figure 13, are to be understood as representative arrangements. However, to study more possible arrangements of the Ru doping sites we use the example of the Ru⁵⁰ surface, to understand the effect that the arrangement of dopants will have on the stability of the surface. The surface area of all the supercells shown in Figure 13 and 14 is 4.23 nm².

From the surface geometries given in Figure 13, we find that only the Ru⁷⁵ surface is distorted upon relaxation. This is due to the increase in Ru-Ru interactions as a result of having more Ru neighbours per Ru dopant and the shorter Ru-N distances compared to TaN. While the Ru¹⁰⁰ surface has the highest number of Ru neighbours per Ru dopant, it shows a regular high symmetry structure in Figure 13g which is likely a local minimum. A distorted, lower symmetry structure of the Ru¹⁰⁰ surface can be obtained through adsorption of a single Cu atom, which upon relaxation strongly distorts this surface, as shown in Figure 15b. The surface retained the distortions upon relaxation after the removal of the Cu atom and is more stable than the high symmetry surface by -0.57 eV per Ru dopant. The smaller ionic radius of the Ru atom ((1.78 Å)[11] as compared to the Ta atom (2.00 Å)[11]) is the primary origin of this distortion and we can clearly see recesses (in Figure 15c) caused by this distortion that will potentially trap Cu atoms, which in turn could act as nucleation points for the Cu film growth. However, determining whether this phenomenon will promote Cu wetting or Cu agglomeration requires large Cu models, the study of which is discussed in Chapter 5.

We do not discuss the geometries of other doped surfaces with an adsorbed Cu atom, as no significant surface distortions were observed as shown in Section A2.10 of the Appendix. However, a similar distortion is also found on the Ru⁵⁰ surface on adsorbing two or more Cu atoms which will be discussed in Section 4.8. The surface distortion upon Cu adsorption was smaller on the Ru²⁵ and Ru⁷⁵ surfaces as the Ru atoms are well separated in the former and the relaxed bare surface itself is already distorted in the latter. For fair comparison between different arrangements the surface rearrangement energy, which is computed by subtracting the energy of relaxed bare surface from the energy of the resulting distorted system upon Cu adsorption (without Cu atoms), is removed from the Cu binding

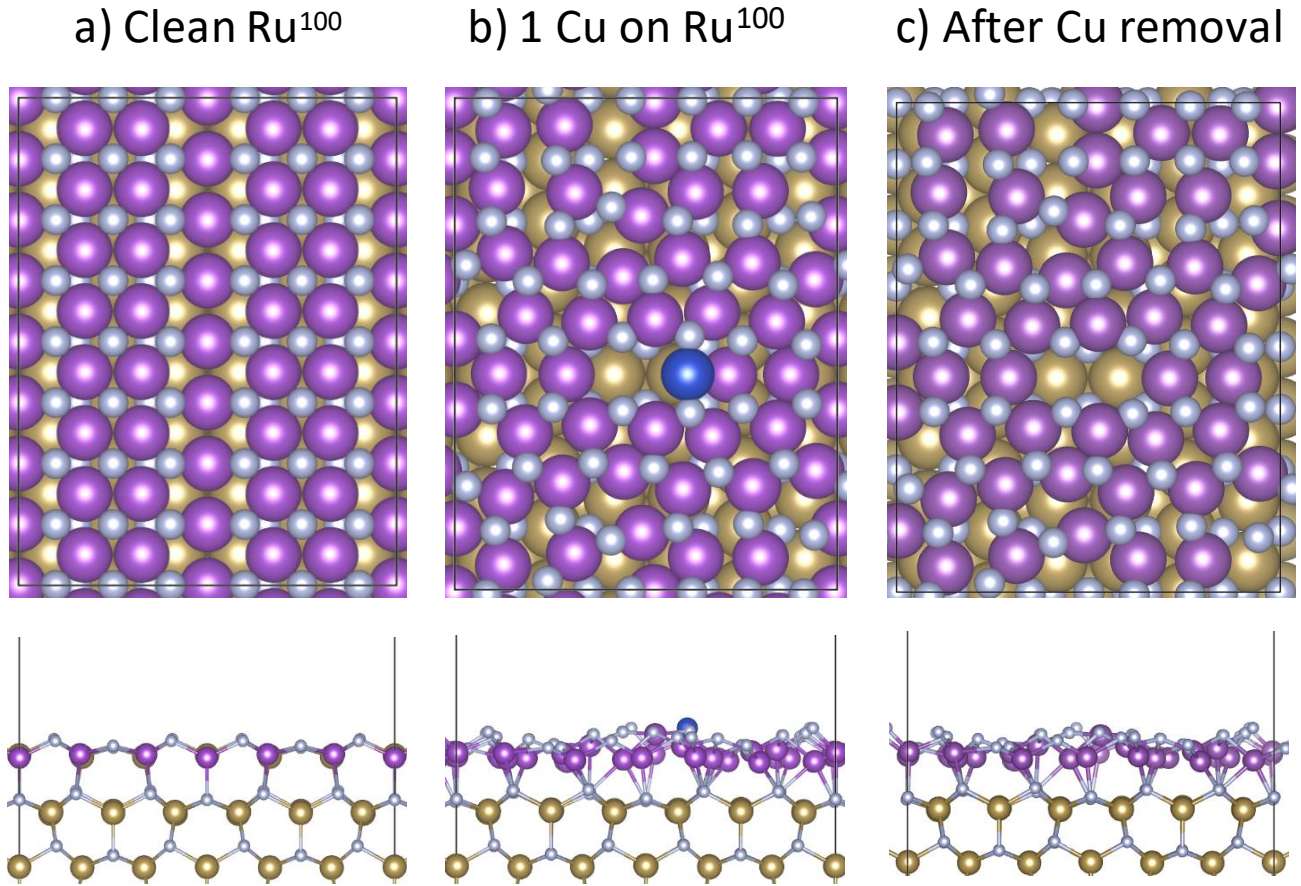


Figure 15: Top and side views of the relaxed Ru¹⁰⁰ surface before Cu adsorption is shown in (a), after the Cu adsorption in (b) and after the removal of the adsorbed Cu atom in (c).

energy calculation as described in Section A2.13 of the Appendix.

4.7 Effect of Dopant Distribution on Surface Stability

We chose the 50% Ru-doped surface to study the effect of dopant distribution in the surface. A total of 10 surfaces were created, including both symmetric distributions, and less ordered, asymmetric structures, as shown in Figure 14. To understand the stability of each distribution, the doping energy (Equation 41 in Chapter 3) was computed for each surface and is compared with doping energies of the other Ru^X surfaces in Table A6 and Figure A17 of the Appendix.

Whether Ru atoms are clustered or more distributed over the surface layer appears to have no significant impact on the doping energy. However, there is a particular effect on the surface structure in the doped layer that can be clearly observed. Some surface rearrangement occurs and recesses tend to be formed where Ru atoms are adjacent

to each other, due to the smaller atomic radius of Ru (1.78 Å) compared to Ta (2.00 Å). [11] Such recesses are found in all surface structures, although different arrangements show some variations in the amount of recesses present. The size of the recess depends on the overall environment and an increase in the number of Ru-Ru interactions leads to larger recesses, with the exception of the bare Ru^{100} surface, where the recesses are very regular due to the high symmetry of the structure. Consequently, it is to be expected that Cu atoms will be more prone to bury into a recess on those surfaces where they are larger or more frequent. Examples of some of the recess structures formed are shown in Figure 16.

In Section 4.1, we found that there were two different doping sites on the surface, due to the two different types of Ta atoms in TaN. F-type sites are 3-fold coordinated with N and S-type sites are 6-fold coordinated with N. Ru doping at the F-site is more favourable than doping at the S-site. [6] The ratio of S:F sites in TaN is 2:1. The ratio of dopants for Ru^{100} , Ru^{75} and Ru^{25} is also 2:1. By changing the ratio of S-type to F-type dopants in the Ru^{50} surface, we can explore how the distribution of Ru influences the stability. The doping energy for each surface is detailed in Section A2.9, Table A6 of the Appendix. We find that a higher level of S-site doping relative to F-site doping correlates with a less favourable surface. The high S-site content in the Ru^{50-1} surface gives it the largest

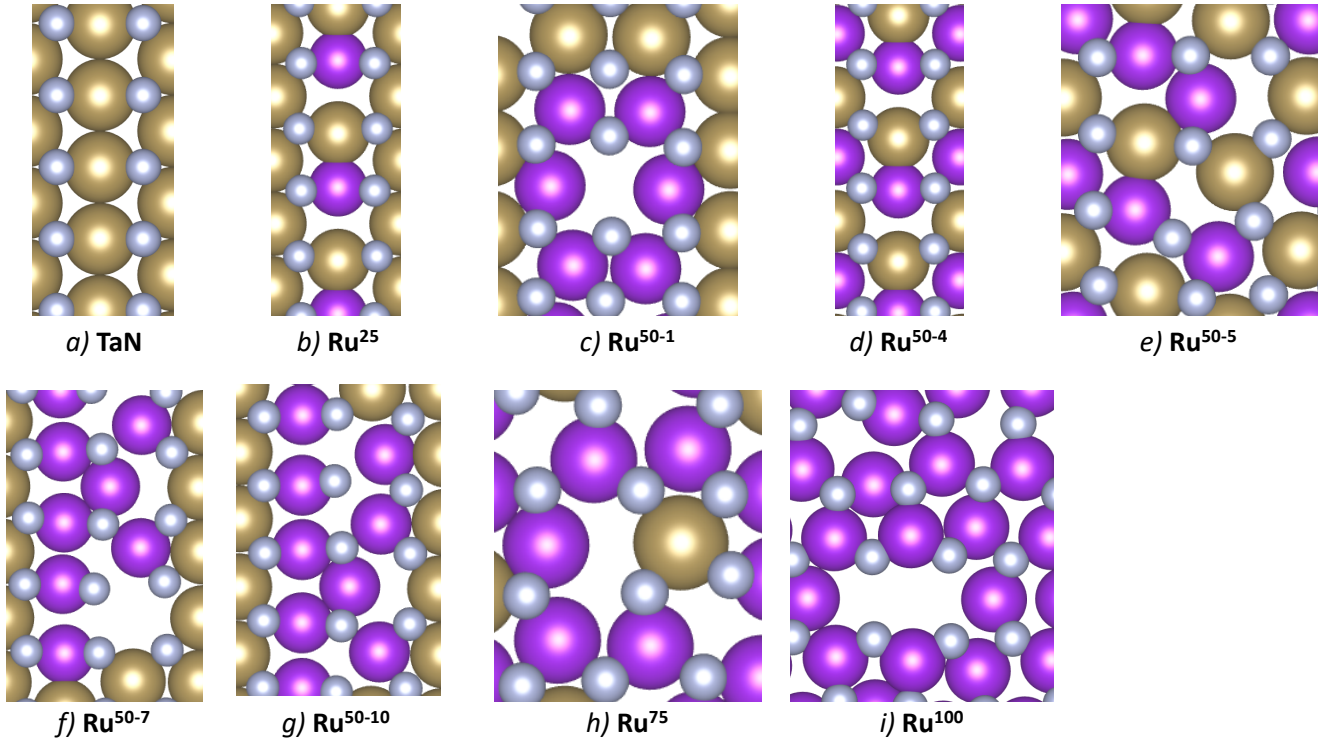


Figure 16: Examples of the recesses formed on various surfaces are shown in panels a) - i). All but the top layer of the surface slab were removed to make the recesses clearly visible.

doping energy of all the surfaces studied, followed by the Ru^{100} surface. Interestingly, the Ru^{100} surface has an even larger number of S-site dopants compared to the Ru^{50-1} surface, with 32 S-site and 16 F-site Ru dopants. The effect of the additional S-site dopants is most likely tempered by the presence of some F-site doping as opposed to no F-site doping in Ru^{50-1} . The Ru^{75} surface originally has 24 S-site and 12 F-site Ru dopants. However, due to the significant rearrangement the surface underwent during relaxation there are no longer unambiguous S and F sites. In fact, coordination environments other than 3- and 6-fold can be observed for Ru atoms in this surface. This could explain why this surface has a lower doping energy than the Ru^{25} surface. The most favourable doping energy is observed for the Ru^{50-10} surface, which has the highest amount of F-site doping, confirming that the doping energy is significantly affected by the dopant distribution.

Ru^{50-4} does not follow this overall trend. Although it has an S:F ratio of 16:8, the doping energy is 0.28 eV/Ru larger than that of Ru^{50-5} , which has the same 16S:8F ratio. For all other structures with the same S:F ratios this difference is <0.10 eV/Ru. Further, Ru^{50-2} and Ru^{50-3} have a larger amount of S-site Ru atoms with a ratio of 18:6, which should make them less stable, but they have a more favourable doping energy than structure Ru^{50-4} instead. The origin of this is probably the high symmetry in the Ru distribution in this structure. Such structures with high symmetry, although stable, tend to be less favourable in energy. Overall, surface stability, and thus reactivity, are found to be most affected by the S:F ratio, rather than the exact distribution of Ru atoms. The effect of this change in stability on the behaviour of Cu adatoms is the subject of Chapter 5.

4.8 Adsorption of single Cu and 2, 3 and 4 atom Cu Nanoclusters

In this section, we study the adsorption of a single Cu adatom and Cu_n nanoclusters with $n = 2, 3$ and 4 atoms on the doped and passivated TaN surfaces given in Figure 13. At least one of the Cu atoms is adsorbed at the 5-fold site (marked with A on the clean surface in Figure 13a) coordinated by 3 Ta (Ru if doped) and 2 N atoms, which is the most stable site for Cu adsorption on the bare surface. [6] We use these small metal clusters to understand the competition between Cu-Cu interactions and Cu-slab interactions on TaN and how Ru doping can influence this, which gives initial insights into the potential for wetting of Cu or association of Cu atoms into 3D-like structures. This analysis serves as a precursor to the more detailed study of the stability of larger 2D and 3D Cu structures on Ru-modified TaN surfaces in Chapter 5.

A Cu atom on the clean (2×8) TaN (1 1 0) surface adsorbs at the 5 fold site with a binding energy of -3.13 eV according to Equation 36. On the 1 and 2 ML Ru passivated TaN (1 1 0), a Cu atom binds relatively stronger, with computed adsorption energies of -4.17 eV and -3.28 eV, respectively. Among the doped surfaces, the Ru^{100} surface offered the strongest single Cu binding energy of -4.47 eV which also resulted in significant distortion of the surface

atoms as discussed earlier. On the Ru^{25} , Ru^{50} and Ru^{75} surfaces, a Cu atom adsorbs with an energy gain of -3.07 eV, -2.80 eV and -2.83 eV, respectively without distorting the arrangement of surface atoms. From the above, the Ru^{100} and the 1 ML Ru passivated surfaces offer significantly enhanced Cu adsorption energies compared to the clean surface. Figure A18 of the Appendix shows the relaxed geometries of the different surfaces with one adsorbed Cu atom at the 5-fold site.

In Figure 17, we show templates for the shape and location of the Cu atoms relative to the TaN surface supercell and present the notation used for the different atomic arrangements of the adsorbed Cu structures. For adsorption of 2 Cu atoms (in Figure 17a), there are two configurations in which the Cu-Cu bond axis is oriented in either a vertical ($\text{Cu}_2^{\text{c-v}}$) or horizontal ($\text{Cu}_2^{\text{c-h}}$) direction relative to the surface. The 'c' in the notation represent geometries where every Cu atom in the arrangement is bonded to at least one other Cu atom. In all structures, notation (Cu_x^{far}) means Cu atoms are separated, with up to 12 Å between them. In the case of Cu_3 and Cu_4 , the templates (in Figure 17b and 17c) include triangles for Cu_3 , a rhombus and tetrahedron for Cu_4 and linear structures for both.

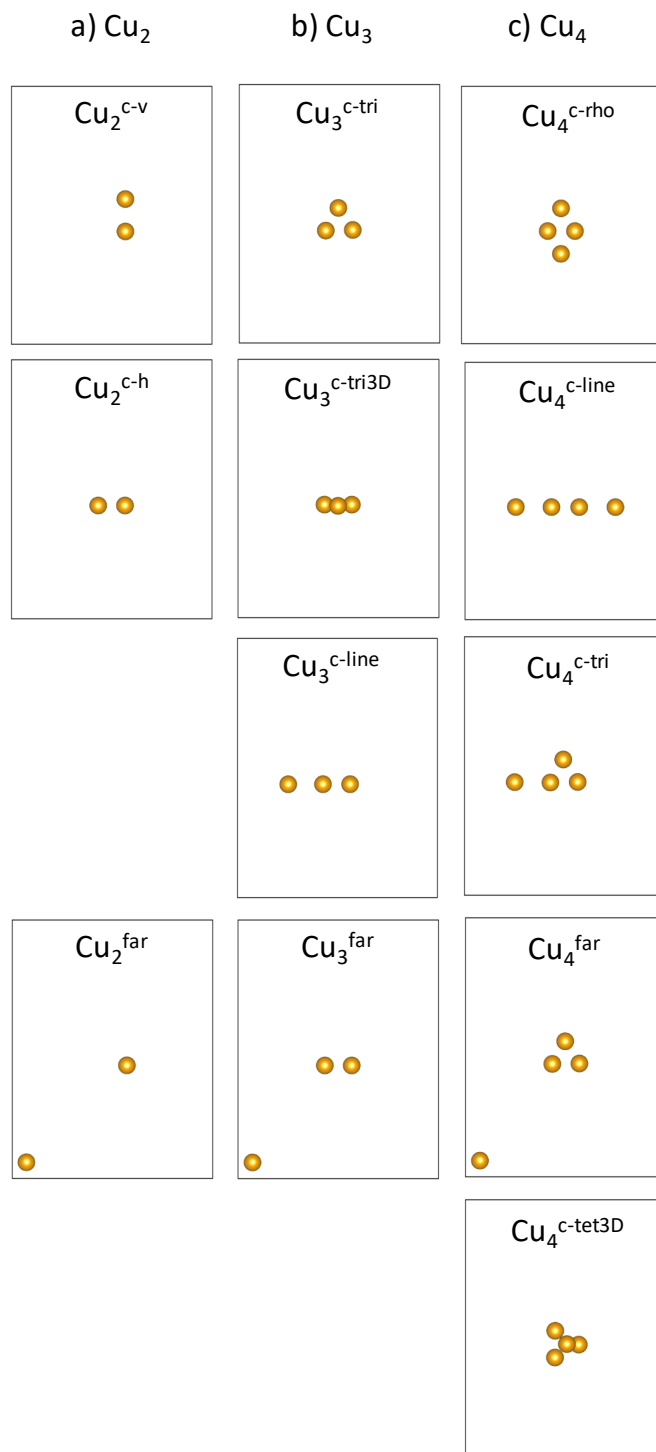


Figure 17: Template arrangements of a) 2, b) 3 and c) 4 atom nanoclusters showing the location of the Cu atoms adsorbed on the surfaces shown in Figure 13. The label "c" (in $\text{Cu}_2^{\text{c-v}}$ and others) stands for "clustered", i.e. each Cu atom binds to at least one other Cu atom.

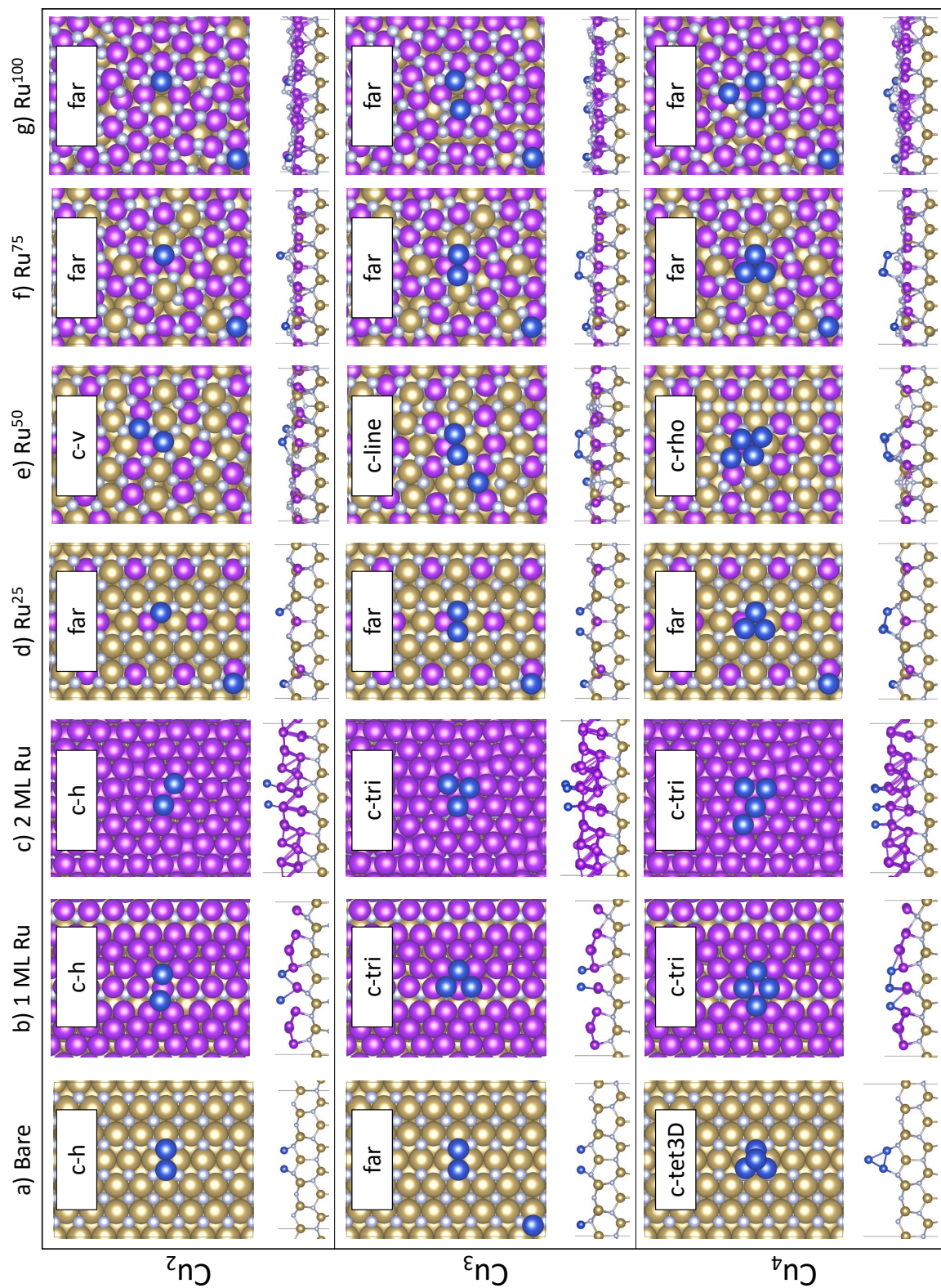


Figure 18: Geometries of bare, 1 and 2 ML Ru passivated, Ru²⁵, Ru⁵⁰, Ru⁷⁵, Ru¹⁰⁰ surfaces that provide the most favourable binding energy for Cu_n nanocluster (n = 2, 3 and 4) adsorption are shown in panel columns a) - g), respectively.

The most stable adsorption geometries of Cu_n nanoclusters ($n = 2, 3$ and 4) on the different surfaces are shown in Figure 18 and the other geometries are given in Section A2.11, Figures A19, A20 and A21 in the Appendix. In general, the closely packed configurations of Cu are predominantly preferred on the Ru passivated surfaces while the sparse 'far' arrangements are mostly preferred on the doped surfaces with the exception of Ru^{50} surface as shown in Figure 18e. The tetragonal close packed 3D arrangement, $\text{Cu}_4^{\text{c-tet3D}}$, was the most favourable only on the clean surface while the flat configurations of Cu_4 are favoured by all the other surfaces. This already suggests a preference to 2D Cu on the Ru passivated and Ru doped surfaces. The other 3D arrangement, $\text{Cu}_3^{\text{c-tri3D}}$, resulted in a 2D structure on the Ru passivated and Ru^{100} surfaces (see Figure A19 in Appendix). In contrast, the $\text{Cu}_4^{\text{c-tet3D}}$ arrangement remained stable, though not the most favourable, on all the studied surfaces due to the local stabilization of the Cu atoms in the tetrahedral arrangement. Another interesting observation was that the 2D $\text{Cu}_4^{\text{c-rho}}$ arrangement on the Ru^{25} surface resulted in the 3D $\text{Cu}_4^{\text{c-tet3D}}$ arrangement on relaxation as shown in Section A2.12, Figure A22 of the Appendix, suggesting this Ru content is not sufficient to promote 2D Cu.

The binding energies (E_{bind}) for all the arrangements on all the surfaces are plotted in Figure 19 and are also listed in Section A2.13, Tables A7 to A10 in the Appendix. The binding energies including the contribution from Cu-Cu interaction (Equation 38 in Chapter 3) are plotted in Figure 19(a) and 19(b), and those without the Cu-Cu interaction (Equation 39 in Chapter 3) are plotted in Figure 19(c) and 19(d). As expected, comparing the above plots shows that the Cu-Cu interactions approximately increase as the size of the cluster increases. Among the Ru passivated surfaces, for all Cu arrangements, the 1 ML Ru passivated surface always shows stronger Cu-slab binding compared to clean TaN (1 1 0) and the 2 ML Ru passivated TaN surfaces (Figure 19(a) and 19 (c)). This arises from the structure of 1 ML of Ru on TaN, which permits Cu atoms to sink into the Ru layer and promote strong binding between Cu and Ru. Within the Ru doped surfaces (see Figure 19(b) and (d)), the Ru^{100} surface (red data points) has the strongest Cu binding energy for all arrangements except in the cases of $\text{Cu}_3^{\text{c-line}}$ and $\text{Cu}_4^{\text{c-tri}}$ for which binding at the Ru^{50} surface is stronger. Flat and sparse arrangements such as Cu_2^{far} and Cu_4^{far} were the most favourable Cu_2 and Cu_4 arrangements respectively (see Figure 19(b) and Figure 19(d)), on the Ru^{100} surface, showing that wetting, even with a small number of atoms, could be promoted on the Ru doped surfaces. This would permit use of thinner, combined barrier+liner films.

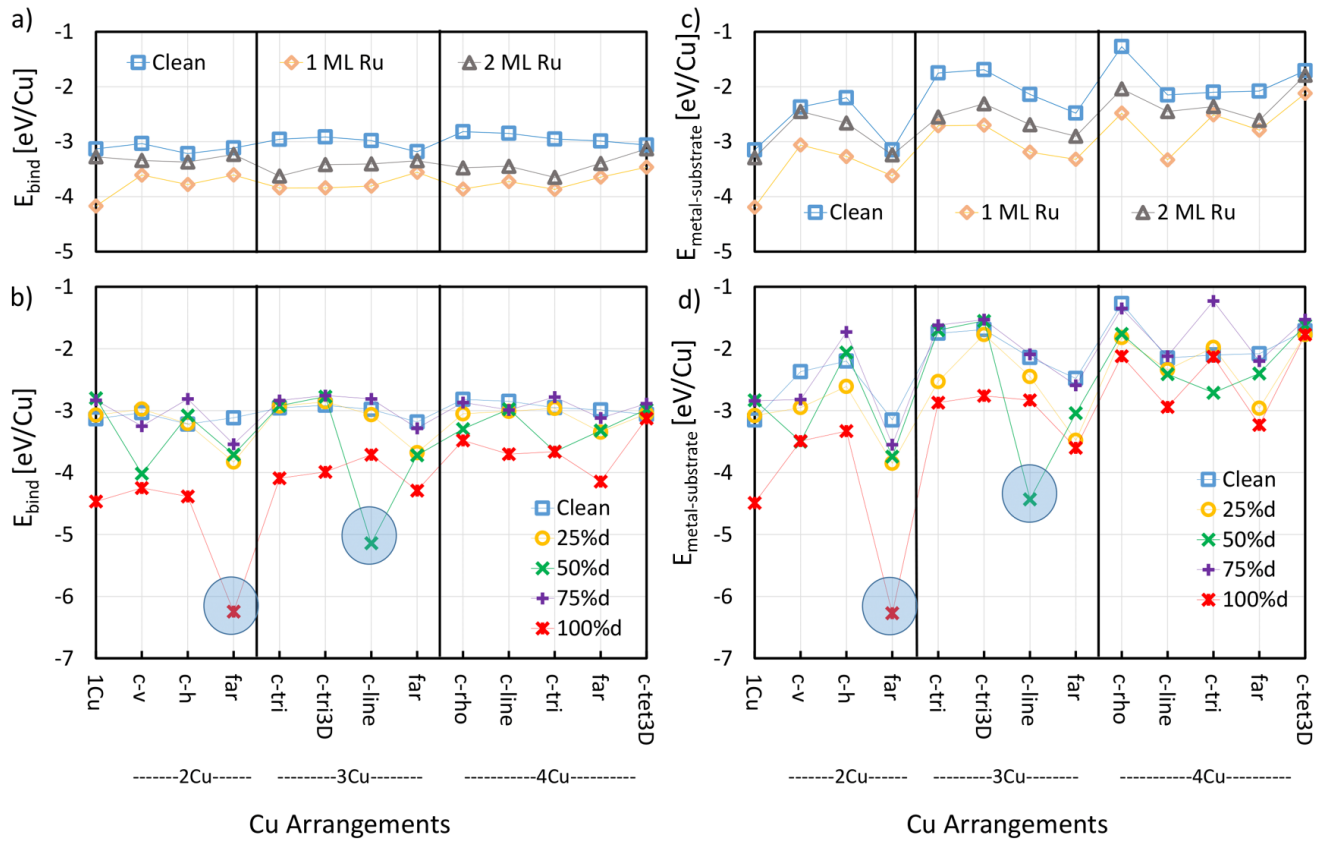


Figure 19: The binding energies per adsorbed Cu adatom for all studied arrangements on the (a) Ru passivated and (b) Ru doped surfaces are compared to the clean surface. Panels (c) and (d) show binding energy excluding the contribution from Cu-Cu interaction. Lines are included to guide the eye.

$\text{Cu}_3^{\text{c-line}}$ on the Ru^{50} surface was the most favourable Cu_3 arrangement. We noted that this arrangement has the second smallest Cu-Cu coordination number apart from the Cu_3^{far} configuration, which is the second most favourable configuration on the Ru^{50} surface. From the side views of these most favourable arrangements in Figure 18d-g, we find that at least one of the Cu atoms is trapped in the recess formed on the doped surface, showing that this structure feature is important in strong Cu adsorption. In general, the most favourable configurations of Cu adsorption appear on the doped surfaces which offer the advantage of being thinner materials when compared to Ru passivated TaN.

The Cu-Cu interaction energies computed according to Equation 38 are plotted in Figure 20. The strongest overall $E_{\text{interact}}^{\text{avg}}$ was observed for the $\text{Cu}_4^{\text{c-rho}}$ arrangement (-1.43 eV) where the Cu atoms form a closely packed structure, a rhombus, with each Cu atom having two closest Cu neighbours. Among the Cu_2 arrangements, $\text{Cu}_2^{\text{c-h}}$ has the shortest Cu-Cu distance and among the Cu_3 arrangements, $\text{Cu}_3^{\text{c-tri3D}}$ is the only 3D arrangement with maximum Cu-Cu coordination. Both structures have the most favourable E_{interact} for Cu_2 and Cu_3 clusters. In general, the weakest Cu-Cu interactions are observed in structures such as Cu_2^{far} , $\text{Cu}_3^{\text{c-line}}$ and Cu_4^{far} , due to reduced Cu coordination.

The average Cu binding energies ($E_{\text{bind}}^{\text{avg}}$ and $E_{\text{metal-substrate}}^{\text{avg}}$, as per Equations 38 and 39 in Chapter 3) and the average Cu-Cu interaction energies ($E_{\text{interact}}^{\text{avg}}$) extracted from all Cu cluster adsorption energies are listed in Table 5. The strongest overall binding of Cu and Cu_n ($E_{\text{bind}}^{\text{avg}}$ and $E_{\text{metal-substrate}}^{\text{avg}}$) is observed on the Ru^{100} surface and the weakest overall binding is found on the Ru^{75} and the clean TaN surfaces. Our work in Sections 4.1 and 4.3 showed that the Ru-Cu interaction is stronger than the Ta-Cu interaction. Therefore, the Ru^{100} surface, with all Ta atoms in the surface layer replaced with Ru, should enhance Cu binding compared to clean TaN. While the

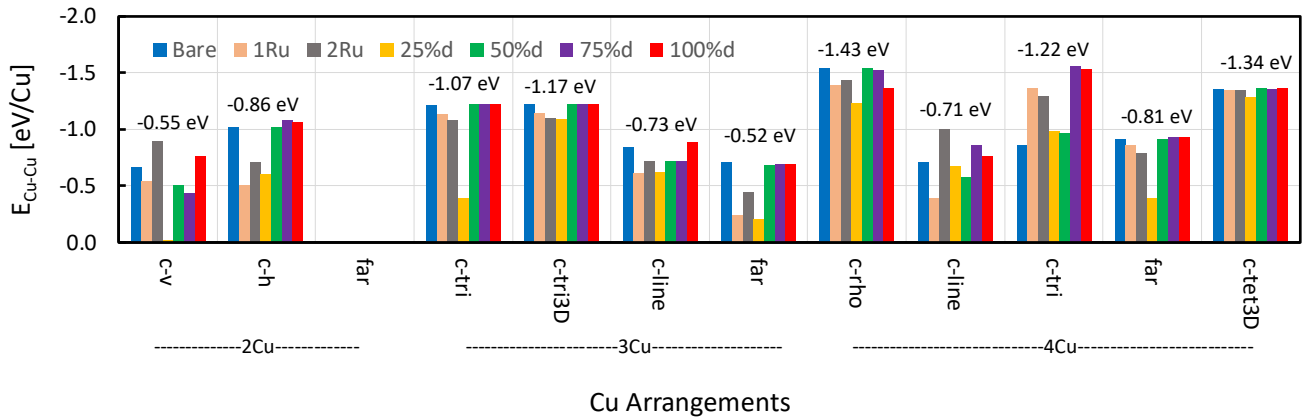


Figure 20: Bar chart showing the Cu-Cu interaction energy contribution computed according to Equation 38. The average Cu-Cu interaction energy per arrangement is also indicated above the bars.

Table 5: Average values of binding energies and interatomic distances of Cu adsorbed on the studied surfaces are listed. $E_{\text{bind}}^{\text{avg}}$ is the average of the binding energies calculated as per Equation 36, $E_{\text{metal-substrate}}^{\text{avg}}$ is the average of the binding energies calculated as per equation 37, $E_{\text{interact}}^{\text{avg}}$ is the average Cu-Cu interaction energy as per Equation 38, $E_{\text{SR}}^{\text{avg}}$ and $E_{\text{SR}}^{\text{max/min}}$ are the average, minimum and maximum surface rearrangement energies and $d_{\text{Cu-slab}}^{\text{avg}}$ and $d_{\text{Cu-slab}}^{\text{max/min}}$ are the average, minimum and maximum Cu-slab distances.

Surface	$E_{\text{bind}}^{\text{avg}}$ [eV/Cu]	$E_{\text{metal-substrate}}^{\text{avg}}$ [eV/Cu]	$E_{\text{interact}}^{\text{avg}}$ [eV/Cu]	$E_{\text{SR}}^{\text{avg}}$ [eV]	$E_{\text{SR}}^{\text{max/min}}$ [eV]	$d_{\text{Cu-slab}}^{\text{avg}}$ [Å]	$d_{\text{Cu-slab}}^{\text{max/min}}$ [Å]
Clean	-3.01	-2.17	-0.84	0.77	1.36/0.40	1.89	3.99/1.67
1 ML Ru	-3.75	-3.02	-0.73	0.58	0.42/0.89	1.67	3.58/1.13
2 ML Ru	-3.39	-2.57	-0.83	-0.98	-1.29/-0.16	2.06	4.18/1.62
Ru ²⁵	-3.16	-2.59	-0.57	0.65	0.28/1.44	1.88	3.93/1.08
Ru ⁵⁰	-3.41	-2.60	-0.82	-3.25	-11.74/0.04	1.81	3.92/0.75
Ru ⁷⁵	-2.98	-2.09	-0.89	0.83	0.19/1.30	1.92	4.03/1.03
Ru ¹⁰⁰	-4.12	-3.22	-0.90	-24.66	-27.46/-21.27	1.13	3.43/0.45

average Cu-Cu binding energies were very similar on all the doped surfaces, the strongest $E_{\text{interact}}^{\text{avg}}$ was found for the Ru¹⁰⁰ surface closely followed by Ru⁷⁵, Ru⁵⁰ and Ru²⁵ surfaces. This lets us conclude that the Cu-Cu interaction increases, albeit by a very small amount, with an increase in surface doping. Therefore, the Ru¹⁰⁰ surface offers the strongest Cu-Cu interaction as well as the strongest Cu-slab interaction. For all surfaces, including the clean surface, the Cu_n-slab interaction ($E_{\text{metal-substrate}}^{\text{avg}}$) is much stronger compared to the Cu-Cu interaction ($E_{\text{interact}}^{\text{avg}}$). Consequently, we might speculate that all surfaces would promote wetting over association. However, we know that the clean TaN surface promotes Cu association, therefore this cannot be the only criterion to predict Cu association.

The surface rearrangement energy, E_{SR} , due to the distortion caused by Cu adsorption is positive and small (absolute value < 1.5 eV per surface supercell) for all geometries of the clean, 1 ML Ru passivated, Ru²⁵ and Ru⁷⁵ surfaces, while it is negative for all geometries of the 2 ML Ru passivated and Ru¹⁰⁰ surfaces (see Section A2.14, Table A11 of the Appendix for individual energies). A positive E_{SR} indicates that the undistorted surface is more favourable than the distorted surface and vice-versa. A small $|E_{\text{SR}}|$ indicates that the adsorption of Cu leads to minimal distortion and vice-versa. For example, the $E_{\text{SR}}^{\text{avg}}$ value for Ru¹⁰⁰ in Table 5 is -24.66 eV. This is the main reason to exclude this contribution in the E_{bind} calculations. Ru⁵⁰ is not included in the above discussion because it showed negative E_{SR} for some arrangements and positive values for the others (Section A2.14, Table A11 of the Appendix). When the values are negative they are very large in magnitude compared to the positive values in Table 5. Large values of E_{SR} are always associated with the formation of recesses on the surface due to association of the doped Ru atoms. On the doped surfaces, the distorted surface geometries are favourable only in Ru⁵⁰ and Ru¹⁰⁰ surfaces. However, for the Ru¹⁰⁰ surface the favourable distortion was observed for all of the Cu_n arrangements but not so for Ru⁵⁰ surface. Specific Cu_n arrangements such as Cu₂^{c-v}, Cu₂^{far}, Cu₃^{c-v} and all of Cu₄ clusters except the Cu₄^{tet3D} arrangement are found to trigger the distortion in this surface. This could be due to the unique 'zig-zag'

arrangement of the Ru dopants in the surface.

Section A2.15, Table A12 in the Appendix summarises the most and least favourable arrangements of the Cu_2 , Cu_3 and Cu_4 nanoclusters on the respective surfaces. From this table, the 'far' arrangement has the most favourable Cu-slab interaction ($E_{\text{metal-surface}}$) and although it has the least favourable Cu-Cu interaction, the adsorption of Cu is driven primarily by the Cu-surface interactions. The closely packed arrangements of copper atoms show the strongest Cu-Cu interaction and weakest (although still stronger than the Cu-Cu interaction) Cu-surface interactions, which might promote formation of 3D-like structures.

From the Cu_4 arrangements, it was surprising to find that the strongest Cu-Cu interaction is for the 3D arrangement ($\text{Cu}_4^{\text{c-tet3D}}$) only on the 25% doped surface, but not on the other Ru-doped surfaces. Since this $\text{Cu}_4^{\text{c-tet3D}}$ arrangement can be considered as a simple model for association of Cu atoms into 3D structures, we would expect it to have the strongest Cu-Cu interactions. But this is clearly not the case, particularly on the highly doped TaN surfaces and the Ru-passivated surfaces. Therefore, using the Cu-Cu interaction energy as the sole indicator of Cu association/wetting is not sufficient. This $\text{Cu}_4^{\text{c-tet3D}}$ arrangement has one of the weakest Cu-slab interactions, which would be as expected. Clearly the details of the surface structure are playing a role in promoting the stability of particular Cu nanocluster adsorption structures.

4.9 Influence of Cu-Cu and Cu-Slab Distances on the Stability of Cu_n adsorption

In Figure 19b and 19d, we highlighted the examples Cu_2^{far} on the Ru^{100} surface and $\text{Cu}_3^{\text{c-line}}$ on the Ru^{50} surface for showing the lowest E_{bind} . To understand the reason for this observation, we computed the minimum distance between the slab and the adsorbed Cu-cluster along the surface normal direction (Z-axis) as shown in Figure 21a, with the results plotted in Figure 21b. The distance is measured between the top most atom in the slab (which can be a Ta, Ru or N atom) and the bottom most Cu atom in the cluster along the surface normal (Z) direction. This will be referred to as $d(\text{Cu-slab})$ throughout the text for clarity. There are only two data points beyond -5 eV ($\text{Cu}_3^{\text{c-line}}$ on Ru^{50} and Cu_2^{far} on Ru^{100}) and these are the same two arrangements marked in Figure 19b and 19d. In these structures at least one of the Cu atoms is buried in the surface (indicated by the negative $d(\text{Cu-slab})$ in Figure 21b) resulting in a higher coordination and increased binding. Even though there exists a data point below -1.0 Å in the case of the Ru^{100} surface ($\text{Cu}_2^{\text{c-v}}$ arrangement), it still has a less favourable binding energy than the marked arrangements.

The reason for lower $d(\text{Cu-slab})$ in the $\text{Cu}_2^{\text{c-v}}$ arrangement when compared to the Cu_2^{far} is that in the former the distance is between the Cu and a surface N, while in the latter it is the distance between the Cu and a surface Ru atom. Since the N atoms are the top-most along the surface normal on the clean and doped surfaces (see

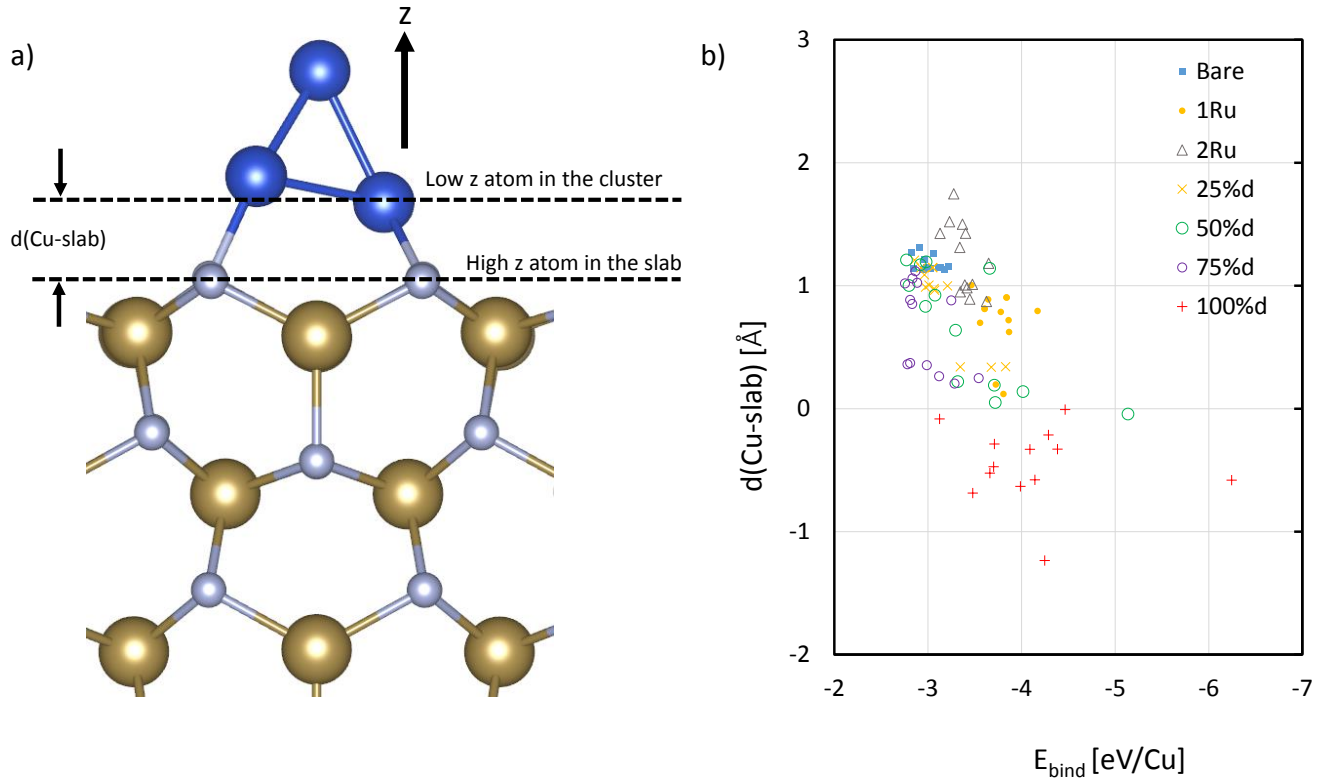


Figure 21: The schematic in panel a) describes the measurement of the distance values plotted in panel b). Zero distance indicates that the lowest Cu and highest surface atom are in the same plane.

Figure 13), the distance between the surface Ru/Ta and Cu is a better indicator of whether the Cu atom is buried in the surface or not. Therefore, we computed the minimum distance along the Z direction between all the element pairs, namely $d(\text{Cu-Ta})$, $d(\text{Cu-Ru})$ and $d(\text{Cu-N})$ as shown in Section A2.16, Figures A23a, A23b and A23c of the Appendix, respectively. From these results we find that N atoms are the top most atoms of the slab and closest to the Cu followed by Ru and Ta atoms. Additionally, this thorough analysis shows that a decrease in the distance between Cu and the surface is directly correlated with more favourable binding energy. Shortest distances between Cu and any of the slab atoms are observed when Cu atoms are buried in the Ru-TaN layer. For additional discussion see Section A2.16 of the Appendix.

Furthermore, the average $d(\text{Cu-slab})$ are also listed in Table 5 in which $d(\text{Cu-slab})$ is computed as the average distance along the Z-direction between each Cu atom in the nanocluster and the first layer of the material surface. The lowest average $d(\text{Cu-slab})$ (1.13 Å) is found for the Ru^{100} suggesting that the Cu atoms undergo larger migration into the recesses on this surface compared to the other surfaces. The next higher average $d(\text{Cu-slab})$ value is for 1 ML Ru passivated surface (1.67 Å, which is about 0.5 Å larger than that of the Ru^{100} surface). The Cu-Cu and

Cu-slab distances in each arrangement on each surface are provided in Tables A7 to A10 in the Appendix and also discussed in detail in the next section. The surfaces with the least $d(\text{Cu-slab})$, i.e. Ru^{100} and 1 ML Ru passivated surfaces, are also the surfaces with the most favourable E_{bind} .

When analysing the Cu-Cu distances, we find that they are in a similar range on different surfaces. It is particularly clear, for example on the Ru^{100} surface, and similarly on the 1 ML Ru passivated surface, that a longer Cu-Cu distance (sparse arrangements) and a shorter Cu-slab distance (Cu sinking into the surface recesses) lead to a more favourable binding energy. In contrast, only on the bare surface, a short Cu-slab distance and a short Cu-Cu distance are associated with favourable adsorption. The former surfaces are expected to promote wetting of the surfaces with the Cu, while the latter is expected to promote the formation of 3D structures.

4.10 Effect of Doping on the Cu Binding Energies

We have seen that increased surface doping with Ru does not always result in enhanced Cu binding. For example, the Ru^{75} surface did not produce more favourable binding energies compared to the Ru^{50} surface (see Figure 19 and Table 5). To understand this observation better, the individual binding energy differences between the doped surfaces and the clean surface

$$\Delta E = E^{\text{Ru}^x} - E^{\text{Clean}} \quad (1)$$

for E_{bind} , $E_{\text{metal-substrate}}$ and E_{interact} are plotted in Figures 22a, 22b and 22c, respectively, in which we observe that for 7 out of 13 Cu arrangements on the Ru^{75} surface, the ΔE_{bind} values are positive. This shows that the Ru^{75} surface is less reactive to Cu adsorption than the clean surface. In contrast, the Ru^{25} and Ru^{50} surfaces have 6 out of 13 and 5 out of 13 arrangements that have positive ΔE_{bind} values and smaller deviations than Ru^{75} . This deviation for Ru^{75} mainly arises from the Cu-slab interaction and not from Cu-Cu interaction. This less favourable binding to the surface could promote formation of 3D structures.

The Ru^{100} is the only doped surface that shows enhanced Cu binding for every Cu_n arrangement when compared to the clean surface. Therefore, not only the fraction of Ru dopants, but also the arrangement of the dopants must come into play when deciding which surface promotes enhanced binding or trapping of the Cu atoms. However, at this juncture it is difficult to assess if the trapped Cu atoms act as a nucleation point for Cu wetting or if agglomeration is promoted, thus this is studied further in Chapter 5.

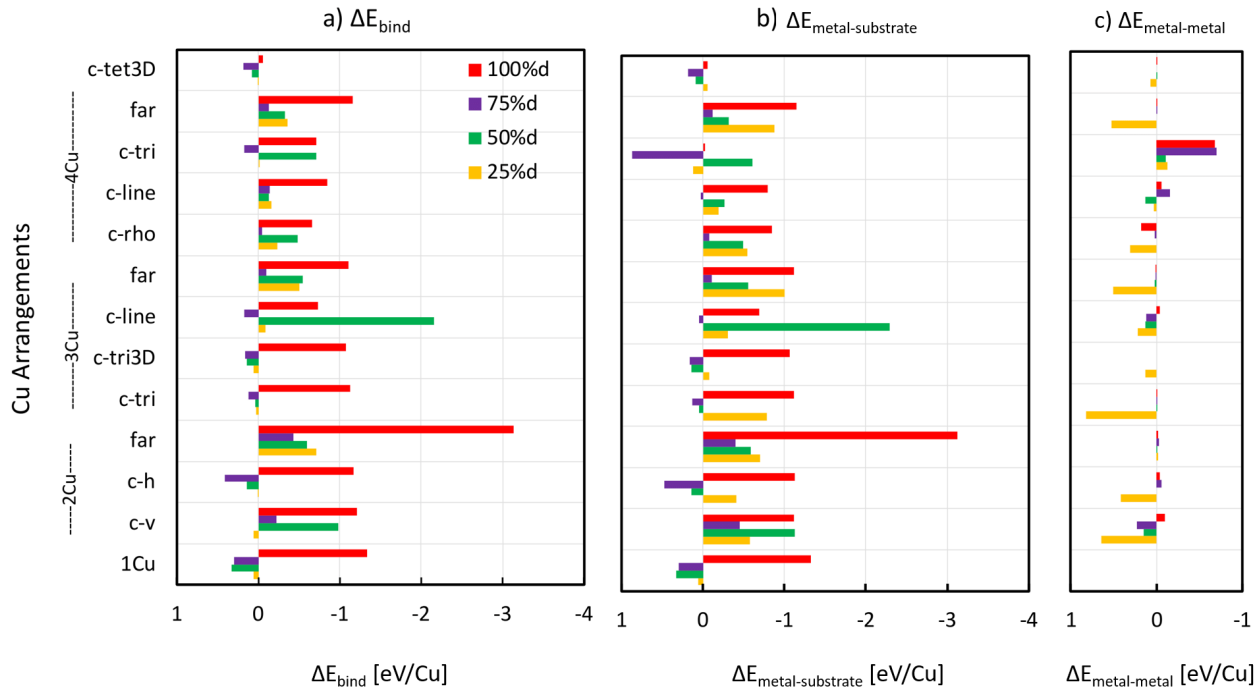


Figure 22: Bar charts a, b and c compare the binding energy differences ΔE_{bind} , $\Delta E_{\text{metal-substrate}}$, $\Delta E_{\text{interact}}$, respectively, calculated with respect to the clean surface per adsorbed Cu adatom on all the studied doped surfaces with respect to the clean surface. ΔE_{bind} is calculated using Equation 36.

4.11 Discussion

The objective of Sections 4.1 to 4.5 was to investigate the structure and stability of Ru-modified TaN, including some initial tests to confirm diffusion barrier and liner properties of the materials. To begin we make use of the three critical conditions for the selection of an ideal liner material for copper electroplating laid down by Cheng and co-workers [12], to confirm whether Ru is a good choice for a liner material with Cu interconnects and TaN diffusion barriers. These are discussed in more detail in Chapter 2. For the Cu/Ru/TaN system these conditions are as follows: i) adhesion of Cu on Ru must be stronger than on TaN, ii) adhesion of Ru on TaN must be stronger than that of Cu on TaN and iii) adhesion of Ru on TaN must be stronger than that of Cu on Ru.

Our investigation that compared the interactions of one Cu/Ru adatom on low-index ε -TaN surfaces shows that all three conditions are met for the Cu/Ru/ ε -TaN system.

- i) The average binding energy of Cu on Ru(0 0 1) is -3.16 eV, which is about 0.6 eV stronger than Cu binding on the TaN surfaces.
- ii) We found that the Ru adatom binds to TaN 1.5 to 2 times stronger than the Cu adatom. Complementing this, the Ru adatom was found to have a higher activation energy for on-surface diffusion (1.02 eV) as compared to the Cu adatom (0.73 eV).
- iii) The average binding energy of Cu on Ru(0 0 1) is about 1.8 eV weaker than Ru binding on TaN.

These findings establish Ru as a suitable liner/glue material for the Cu- ε -TaN interface.

From the two adatom adsorption calculations on the low-index TaN surfaces, we found that the Cu and Ru adatoms bind with an average binding energy of -2.85 eV and -5.02 eV, which are 0.28 eV and 0.07 eV stronger than the one adatom cases, respectively. As discussed previously, this is not a large increase in binding energy. The additional binding energy comes from an enhanced M-M (M = Cu, Ru) interaction and the associated surface relaxations/rearrangements. Studying the activation energies for two adatoms to associate showed that Cu atoms associate with a lower activation energy than the Ru atoms except in the case of the (1 1 1) surface where the activation energies for the two metals were comparable.

The (1 1 0) surface of ε -TaN, with the most favourable surface energy among the low index surfaces, behaved differently from the (1 1 1) and (1 0 0) surfaces in two aspects. Firstly, the Cu and Ru adatoms are bound more strongly at the (1 1 1) and (1 0 0) surfaces compared to the (1 1 0) surface. Secondly, the Cu and Ru adatoms were oxidised on the (1 1 0) surface while they were reduced on the (1 1 1) and (1 0 0) surfaces. This is probably because of the significant difference in the Ta/N charges and coordination geometry in the top layer of these surfaces. The Ta atoms in the first layer of the (1 1 0) surface were more oxidised than those on the other two surfaces which

allowed subsequent oxidation of the Cu/Ru atoms on this surface by reduction of the Ta atoms. Additionally, the largest activation energy for the association of two atoms for both Ru and Cu was found on the (1 1 0) surface. Cu showed a smaller activation energy for the reverse process (to keep them separated), while the opposite is true for Ru. This indicates a clear preference towards Cu atom separation. Although association of Ru atoms may be preferred to separation, the large magnitude of the activation energies for Ru migration suggests a reduced atom mobility.

It is important to note that the on-surface diffusion of Cu adatoms on bare Ru(0 0 1) is more favourable, along with significantly lower activation energies for two atom association, compared to the bare TaN surfaces. If a thick layer of Ru is used to passivate the TaN surface, then the deposited copper atoms might diffuse and associate easily and could result in islands of Cu instead of a film. Therefore we first tested the copper activity on TaN surfaces passivated with 1 ML and 2 ML of Ru, where the hexagonal close packing arrangement of the Ru atoms was already visible. The average adsorption energy of a Cu adatom was very similar (-3.29 eV and -3.34 eV) on these surfaces and was comparable to adsorption on the bare Ru(0 0 1) surface. However, the average computed activation energy for on-surface Cu diffusion was about 0.3 eV on the passivated surfaces which is slightly less favourable than on the bare Ru(0 0 1) surface, but considerably more favourable than on the bare TaN(1 1 0) surface. This activation energy of 0.3 eV would be easily breached under process temperatures, so we can expect very mobile Cu adatoms on Ru passivated TaN surfaces. Cu₂ adsorption calculations showed a preference to atom association on the passivated surfaces. The average energy needed to separate associated copper atoms was found to decrease from 0.42 eV in the 1 ML case to 0.25 eV in the 2 ML case. This means that despite the improved mobility of single Cu atoms on the 1 ML passivated surface, atoms are also more likely to associate than on the 2 ML passivated surface. This difference could be because 2 ML of passivation behave similarly to bulk Ru. However, the activation energy for dissociation is still relatively small on 1 ML passivated TaN, indicating that this thinner structure could nevertheless act as a barrier+liner film.

The average sub-surface adsorption energies of a Cu adatom were -2.78 eV and -2.22 eV for the 1 and 2 ML of Ru passivated surfaces, respectively, which are significantly more favourable than on the bare Ru(0 0 1) surface (-1.79 eV). This is accompanied by the fact that the average activation energy for the exchange of Cu and Ru atoms is about 0.86 eV and 1.83 eV for the 1 and 2 ML of Ru passivated surfaces, which are almost twice as low as that on the bare Ru(0 0 1) surface (2.98 eV). This means the sub-surface diffusion of Cu adatoms through the Ru layer via exchange process is more probable on the Ru passivated surfaces than on bare Ru. The activation energy for this exchange mechanism will likely increase when more layers of Ru are considered. Therefore, passivation of TaN surfaces with Ru may have some reliability issues that could impact its ability to perform as a barrier+liner

material. As an alternative, Ru doped TaN surfaces were studied which would also provide a more significant reduction of the overall layer thickness compared to passivation.

We considered two Ru doped TaN (1 1 0) surfaces where a S or F type surface Ta atom is replaced by a Ru atom (Ru^S or Ru^F). The Ru^F doped surface is energetically more favourable than the Ru^S doped surface and the Ru^S atom is more oxidised than the Ru^F atom. Ru doping does not introduce significant changes in the surface lattice or the surface charge distribution. Differences, if any, are small and localised to the doping site. Overall the Cu binding energy is more favourable when Ru is present in the TaN (1 1 0) surface, particularly when the Cu atom is bound to the doped Ru. The Cu binding energies and the surface geometry did not change with a larger surface supercell, which suggested that the effect of Ru doping is localised. The average single Cu binding energy on the Ru doped surface is -2.46 eV, which is 0.86 eV weaker than that on the Ru passivated surfaces. However, the adsorption energies are on average -2.88 eV when 2 Cu atoms are adsorbed, due to the enhanced Cu-Ru and Cu-Cu binding. On the other hand, the on-surface diffusion of Cu atoms and two atom association are considerably hindered on the Ru doped surfaces as compared to the Ru passivated surfaces. In fact, the two atom association activation energies on the doped surfaces are comparable to those on the bare TaN surface. Results showed that Cu migration towards the doped Ru is more favourable than the migration away from it. This suggested clearly that the Ru binding sites can be anchor points for Cu nucleation during the initial stages of the deposition process. Therefore, a higher percentage of Ru doping could ensure that the Cu atoms wet the modified TaN surface.

Compared to the Ru passivated surfaces where the Cu atoms diffuse and associate easily despite the more favourable binding of Cu, the Ru doped surfaces provide smaller activation energies toward diffusion and association of the adsorbed Cu atoms. Moreover, the Cu binding energies on the Ru doped surfaces are more favourable as compared to bare TaN surfaces and we expect further improvements as the percentage of Ru doping is increased.

The first objective of the second half of this Chapter (Sections 4.6 to 4.10) is to compare and characterise models of the TaN(1 1 0) surface and its modification with Ru passivation and Ru doping in the surface layer and the impact of this modification on the adsorption of small Cu_n clusters, with up to 4 Cu atoms. This allows us to explore the fundamental interactions between copper atoms and the nitride surfaces as well as examine the role played by Cu-surface and Cu-Cu interactions in determining the stability of small Cu nanocluster structures. Twelve different arrangements of Cu_2 , Cu_3 and Cu_4 clusters were studied on seven different (Ru)-TaN (1 1 0) surfaces. These surfaces include the clean TaN (1 1 0) surface, two Ru passivated surfaces with 1 and 2 monolayer (ML) of Ru coated onto clean TaN (1 1 0) and four Ru-doped TaN (1 1 0) surfaces with 25%, 50%, 75% and 100% substitutional surface doping on Ta sites. The 1 ML Ru passivated surface is unique due to the absence of closely packed Ru atoms, whereas the 2 ML Ru passivated surface resembles the hexagonal symmetry of Ru(0 0 1). At

increased Ru doping concentrations the surfaces show strong distortions. This distortion causes the formation of recesses in the surface, with a large distance between atoms, and arises from the increased Ru-Ru attraction in the surface layer and the smaller ionic radius of Ru compared to Ta. Such a recess could act as a trap/anchor point for Cu seed layer formation. We also find similar recesses in the 1 ML Ru passivated surface where the adsorbed Cu atoms could be trapped. However, the trapped Cu atoms will not diffuse through the film due to the excellent barrier properties of the underlying TaN already demonstrated.

Studying the effect of different dopant arrangements using the Ru⁵⁰ surface showed us that the surface stability is largely dependant on the ratio of Ru in S and F sites in each surface. We find that surfaces with a larger content of F-site dopants have more favourable doping energies. It is however possible that in a kinetically driven process such as atomic layer deposition (ALD), surfaces with a high concentration of S-site Ru in the surface can be formed. Further, we found that recesses continue to form in the surface layer regardless of Ru distribution. Recesses are formed in areas on the surface where at least 3 Ru atoms were able to associate and thus cause a distortion of the regular (1 1 0) layer structure. Further study with a larger number of Cu atoms will be necessary to understand how these recesses might act as a trap for Cu adatoms and how this will affect the growth of a Cu film. This is covered in Chapter 5.

A decrease in surface stability with an increase in the concentration of Ru doping is observed. With the exception of the Ru⁷⁵ surface all modified TaN surfaces show enhanced Cu-slab interactions compared to the clean TaN (1 1 0) surface. The outlying behaviour of the 75% doped surface is likely caused by the over-stabilization of this surface upon relaxation, which makes it less reactive to the adsorbed Cu atoms. The most favourable $E_{\text{bind}}^{\text{avg}}$, $E_{\text{metal-substrate}}^{\text{avg}}$ and $E_{\text{interact}}^{\text{avg}}$ values are observed for the Ru¹⁰⁰ doped surface. $E_{\text{interact}}^{\text{avg}}$ is of similar magnitude on all surfaces, with the exception of the 1 ML passivated surface and the Ru²⁵ doped surface, which have less favourable $E_{\text{interact}}^{\text{avg}}$, as compared to the clean surface. In contrast to the above, the Cu-Cu interaction energy became more favourable with an increase in Ru doping. Therefore, the 1 ML Ru passivated surface and Ru¹⁰⁰ surface do not behave similarly. The Ru²⁵ and Ru⁵⁰ surfaces showed weaker average Cu-Cu interactions with respect to the clean surface, while the Ru⁷⁵ and Ru¹⁰⁰ surfaces show enhanced average Cu-Cu interaction with respect to the clean surface. We also observed that, on doped and passivated surfaces, configurations with longer Cu-Cu distances and shorter Cu-slab distances (arising from partially buried Cu atoms) were associated with a more favourable binding energy, indicating that Cu atoms prefer to be separated on these surfaces. The same was not true on the clean surface, where favourable binding was associated with shorter Cu-Cu distances, showing a possible preference towards association of atoms.

We found that the Cu-slab interaction is stronger when the Cu atoms are separated from the cluster, as in the 'far' arrangement, where the Cu-Cu interactions are weaker. The opposite is true for the 'close' arrangements. The

Cu-slab interaction strengthens even more when the Cu atoms are buried into the surface recesses, as is evident from the Cu-slab distances vs binding energy plots. To understand the importance of the trapped atom in the Cu seed layer formation, wetting/association of Cu, a Cu cluster/film larger than used in this chapter is the focus of Chapter 5.

If we consider the competition between Cu-slab interactions and Cu-Cu interactions as an indicator of whether Cu associates or wets on the surface, we could form two possible conditions.

1. Association is preferred over wetting if the Cu-Cu interaction energy is more negative and thus more favourable than the Cu-slab binding energy, ($E_{\text{interact}}^{\text{avg}} < E_{\text{metal-substrate}}^{\text{avg}}$) and if $E_{\text{interact}}^{\text{avg}}$ reaches the cohesive energy of bulk copper (-3.49 eV/atom [13]).
2. For wetting to be preferred over association, the Cu-slab binding energy must be more negative than the Cu-Cu interaction energy ($E_{\text{metal-substrate}}^{\text{avg}} < E_{\text{interact}}^{\text{avg}}$) and the adhesion energy must be more negative than the cohesive energy of Cu ($E_{\text{bind}}^{\text{avg}} < -3.49$ eV/atom).

On all surfaces, including the clean surface where we know that Cu associates, we found $E_{\text{interact}}^{\text{avg}} > E_{\text{metal-substrate}}^{\text{avg}}$ and the value of $E_{\text{interact}}^{\text{avg}}$ was much more positive than the bulk cohesive energy of Cu (for example, on Ru¹⁰⁰ surface $E_{\text{interact}}^{\text{avg}} = -0.90$ eV and $E_{\text{metal-substrate}}^{\text{avg}} = -3.22$ eV). However, if we look at the individual energies, Cu₄^{c-rho} arrangement on the clean surface and Cu₄^{c-rho} and Cu₄^{c-tri} arrangements on the Ru⁷⁵ surface have lower E_{interact} than corresponding $E_{\text{metal-substrate}}$. It was surprising to see the Cu₄^{c-top3D} arrangement, a simple model for associated Cu, to have $E_{\text{metal-substrate}} < E_{\text{interact}}$ on all the surfaces. Therefore, condition 1 is likely not the deciding factor of Cu associating on the surface. While all the surfaces fulfill the first part of the condition 2 (including the clean surface), only 2 surfaces, namely, 1 ML Ru passivated surface and Ru¹⁰⁰ surface fulfill both parts of condition 2. These are the same two surfaces that offer the strongest Cu-slab binding and the lowest Cu-slab distance. The Ru⁵⁰⁻¹⁰ surface might also be viable, as it is close to fulfilling condition 2, in that $E_{\text{bind}}^{\text{avg}}$ is approximately equal to the cohesive energy of Cu. Based on the above observation, these three surfaces are strong possibilities for a combined barrier+liner material for copper interconnects which can be produced by atomic layer deposition. The advantage of using either of these surfaces as the combined barrier and liner material is that it significantly decreases the volume of the interconnect via that is occupied by the barrier+liner material, see Chapter 1 Figure 3, compared to the multi-layer stack that is currently in use. [14]

4.12 Conclusions

We have investigated the viability of Ru passivated and Ru doped ϵ -TaN surfaces as an effective diffusion barrier+liner material for copper interconnect technology. We started in Section 4.1 by studying the activity of Cu and Ru adatoms on bare ϵ -TaN surfaces and found that Ru binds significantly stronger and diffuses more slowly than Cu. Cu was found to bind at the Ru(0 0 1) surface with roughly the same average binding energy as at the TaN surfaces, however, Cu diffused faster on the Ru surface. On-surface association and sub-surface adsorption of Cu atoms were relatively more favourable at the Ru(0 0 1) surface. Therefore, several monolayers of Ru deposited on TaN can not be considered as the most effective barrier+liner material.

The TaN (1 1 0) surface was chosen for the Ru passivation and doping studies since both Ru and Cu adatoms did not prefer to associate on it as compared to (1 1 1) and (1 0 0) surfaces. On the Ru passivated (1 1 0) surfaces, Cu atoms bind more strongly than on the bare TaN and Ru surfaces. However, the adsorbed Cu atoms diffused faster than on the bare TaN surfaces and preferred to associate. Although 1 or 2 ML of Ru passivation on TaN is a better alternative to several layers of Ru on TaN, it still lacks the association behaviour that we are expecting in the combined barrier+liner material. Finally, we looked at a Ru doped TaN surface as a viable alternative. On the Ru doped surfaces, even though the Cu adatoms showed decreased Cu binding as compared to the Ru passivated surfaces, they offered significantly larger activation energies for the on-surface and sub-surface diffusion as well as association of Cu atoms.

In Section 4.6 the stability and reactivity of Ru passivated and Ru-doped surfaces of ϵ -TaN(1 1 0) with respect to adsorption of Cu_2 , Cu_3 and Cu_4 clusters was studied. Of particular interest were the competing forces of Cu-surface and Cu-Cu interactions. A condition to favour wetting of Cu atoms can be achieved when the Cu-slab interaction is stronger than the cohesive energy of bulk Cu. The strongest Cu-surface and Cu-Cu interactions were observed on the 100% doped surface. On the other hand, the 1 ML Ru passivated surface offered weaker Cu-Cu interaction than the clean surface and exhibited the second most favourable Cu-surface interaction. An increased Cu-slab interaction was possible by trapping Cu atoms in the recess formed on the higher % of Ru doped and 1 ML of Ru passivated surfaces. The condition for wetting was satisfied for the 50%-10 and 100% Ru doped surfaces and the 1 ML Ru passivated surface, which makes them top contenders for the combined barrier+liner material. While the 1 ML Ru passivated surface shows great promise, the Ru doped TaN surfaces are ultimately preferable as a potential combined barrier+liner material as they provide thickness reduction along with both the liner properties of Ru and barrier properties of TaN.

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Chapter 5: Growth Mechanism and Morphology

Prediction of Cu on Ru passivated and Ru doped TaN

The research presented in this chapter was published under the Title "Control of Cu morphology on Ru-passivated and Ru-doped TaN Surfaces – promoting growth of 2D conducting copper for CMOS interconnects" in Chemical Science, <https://doi.org/10.1039/D1SC04708F>. [1] In this Chapter, we continue on from the work presented in Chapter 4. Using the same Ru-modified TaN surfaces presented in Chapter 4, we now use a 29 atom copper structure that is interfaced with Ru-TaN as our model system; a similar cluster has been used in DFT studies of copper-MoS₂ chemistry for catalysis [2]. It is large enough to show distinct 2D and 3D structures and permit analysis of Cu atom migration and morphology, while still being computationally tractable. For the purposes of this study we consider the Cu structure to be 2D if it does not exceed two layers of Cu atoms. A thin film is unlikely to grow perfectly layer by layer and thus we consider both a one layer or two layer structure to be representative of a system where a smooth film will be grown over time.

All calculations begin with a single layer of Cu₂₉ adsorbed on the various Ru-modified TaN surfaces, see Figure 1a), and we explore how the structure evolves during 0 K relaxations and ab initio molecular dynamics (aiMD) simulations at finite temperatures, as described in Chapter 3. Following Chapter 4, Ru doped TaN surfaces are referred to by Ru^x, where x is the doping concentration. Ru^{1ML} is used for the 1 ML Ru passivated surface. The surfaces selected for adsorption of Cu₂₉ from our work in Chapter 4 are TaN, Ru²⁵, Ru⁵⁰⁻¹, Ru⁵⁰⁻⁴, Ru⁵⁰⁻¹⁰, Ru⁷⁵, Ru¹⁰⁰ and Ru^{1ML}. We selected for detailed discussion those surfaces that gave the best overview of the effects of the different doping concentrations on the morphology of Cu: TaN, Ru²⁵, Ru⁵⁰⁻¹⁰, Ru¹⁰⁰ and Ru^{1ML}. The Ru⁵⁰⁻¹, Ru⁵⁰⁻⁴ and Ru⁷⁵ surfaces are discussed in Section A3.1 of the Appendix. Geometries for these surfaces are shown in Figures A24 and A25, z-plots based on Equation 42 in Chapter 3 are shown in Figure A26 in Section A3.1 of the Appendix. Density of States and Bader charge analysis for the surfaces discussed in this chapter are presented in Section A3.3 of the Appendix.

Figure 1(a) shows a schematic structure of Cu₂₉ adsorbed on a substrate in a single layer. A 0 K relaxation

calculation was carried out on each TaN and Ru-TaN surface. For each relaxed structure three aiMD calculations were run for 5 ps at 300 K, 500 K and 800 K (each starting from the 0 K relaxed structure). From analysis of these structures, selected Nudged Elastic Band (NEB) calculations were further carried out to determine the activation energy for the transition of copper atoms between layers. Figure 1(b) shows the labels used for each layer.

Potential Cu atom transitions are shown in Figure 1(c) and include Cu atom migration from the layer directly bound to the surface, the *surface layer*, to the first layer away from the surface, *the $S+1$ layer* or from *the $S+1$ layer* to the next layer away from the surface, *the $S+2$ layer*. We also consider Cu migration from the surface layer to the $S + 1$ layer after another Cu atom has migrated to the $S + 1$ layer. This is motivated by the findings that upwards migration of a metal atom from the surface layer can promote the further migration of metal atoms from the surface, thus enhancing island formation. [3]

5.1 Structure of copper on bare TaN and 1 Monolayer Ru passivated TaN

We begin the analysis with the structure of two extreme examples: adsorption of copper on the bare TaN surfaces, Figure 2(a), and on 1ML Ru-passivated TaN, Figure 2(b). In both figures we show top and side views after relaxation and the final snapshots after 5 ps aiMD runs at 500 K. A comparison of Cu₂₉ on all surfaces after relaxation is shown in Figure 4. In the Appendix, Section A3.2 Figure A27 we show snapshots for the other aiMD runs at 300 K and 800 K. Bare TaN promotes Cu island formation, while Ru^{1ML} promotes 2D Cu growth.

The binding energies of the relaxed Cu₂₉ structures are shown in Table 1. The binding energy of Cu₂₉ on bare TaN is -3.49 eV/atom, which is the least favourable binding energy of all the surfaces studied. The structure of Cu on the Ru²⁵ and Ru⁵⁰ surfaces is discussed in the next Section. The Ru^{1ML} surface has the most favourable E_{bind} , at -4.12 eV/Cu. Note that a high Ru content increases the binding energy of Cu on Ru-modified TaN, similar to results in Chapter 4 for smaller Cu clusters.

On bare TaN we observed a spontaneous transition from the initial 2D structure to a two-layer structure during the 0 K relaxation, as seen in Figure 2(a), indicating that the TaN layer is not able to promote 2D wetting of copper; this is consistent with the known properties of TaN. In the finite temperature aiMD simulations, we see that further upwards copper migration takes place. Copper atoms migrate from the $S+1$ layer to form a third layer ($S+2$) and we see an incipient (1 1 1)-like facet on the copper island. This is further illustrated when plotting the change in the z-coordinate of each Cu atom with respect to simulation time as shown in Figure 3(a), b) and c). Bare TaN therefore promotes the formation of 3D copper islands. The TaN surface itself remains unaffected during this relaxation and no Cu atoms migrate into the surface, as expected given the known barrier properties of TaN.

Next, we consider how our copper model interfaces with 1 ML Ru passivation of TaN. From our previous studies

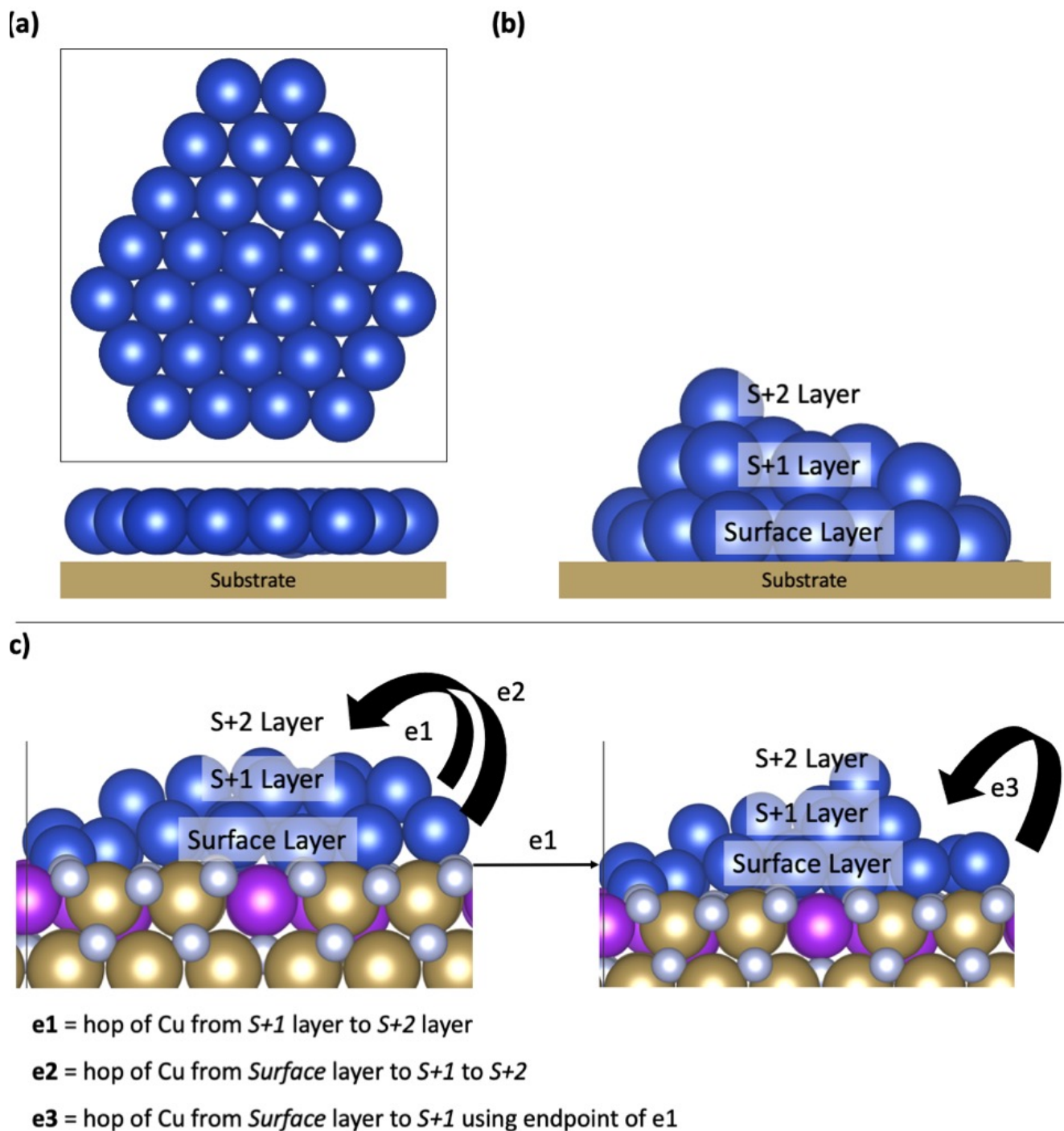


Figure 1: (a) The Cu₂₉ model adsorbed and relaxed on all surfaces and (b) labels used to refer to the different layers of 3D structures. (c) Schematic describing different copper atom transitions between different layers in copper interfaced with a Ru-TaN surface. Cu is shown in blue, Ru in purple, Ta in gold and N in silver for all figures, as per the colour code given in Chapter 3.

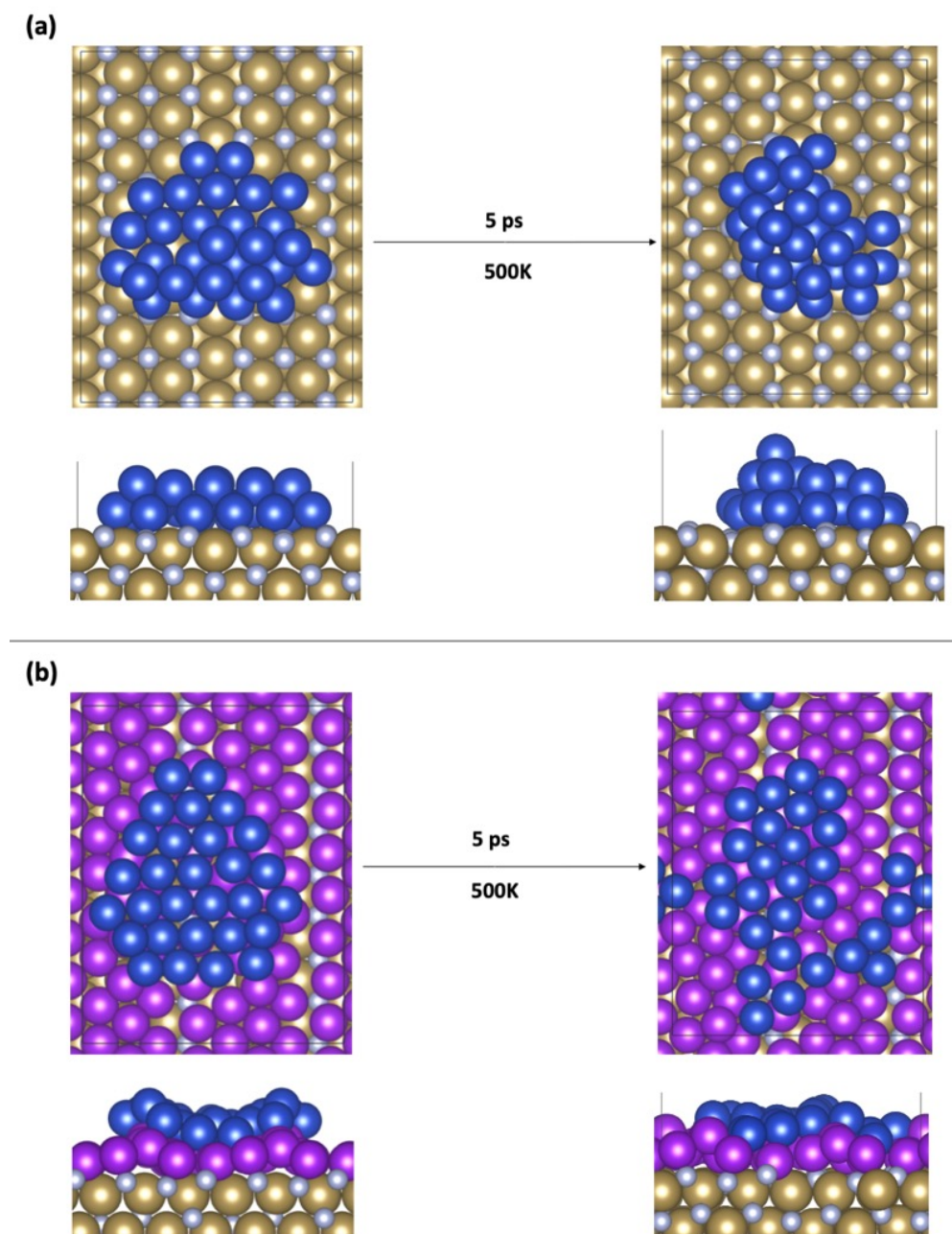


Figure 2: Structures of Cu_{29} obtained after relaxation and 500 K aiMD on (a) bare TaN and (b) 1ML Ru passivated TaN

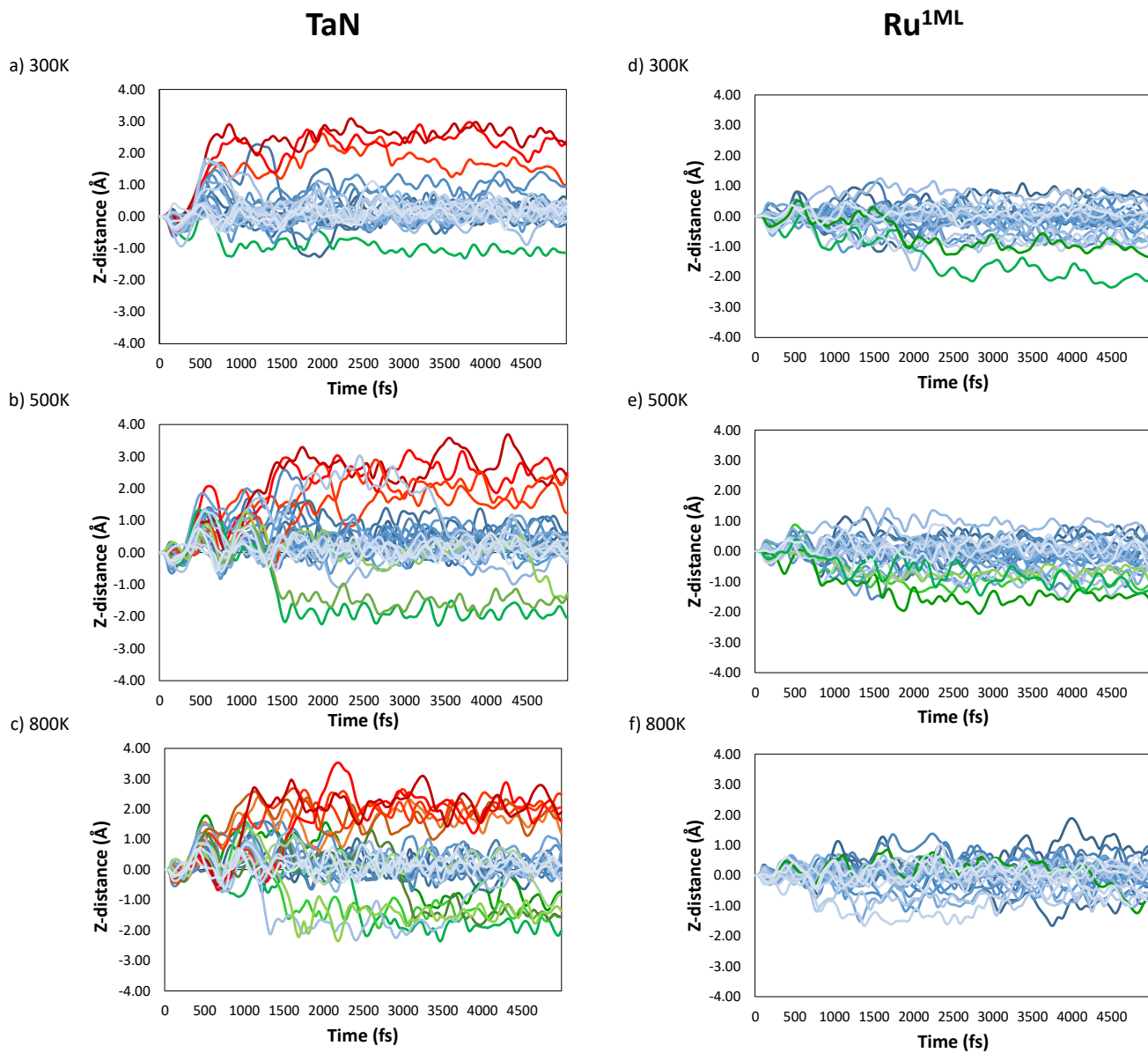


Figure 3: Change in Z-position with respect to aiMD simulation time for Cu_{29} on TaN and Ru^{1ML} during aiMD runs at 300 K, 500 K and 800 K.

Table 1: Binding energies, E_{bind} (Equation 37 in Chapter 3), Cu-substrate interaction energies, $E_{metal-substrate}$ (Equation 39 in Chapter 3) and Cu-Cu interaction energies, $E_{interact}$ (Equation 40 in Chapter 3) of the Cu_{29} cluster on each Ru-modified TaN surface. Ru^x indicates the Ru doping content in the TaN surface layer.

Surface	E_{bind} (eV/atom)	$E_{metal-substrate}$ (eV/atom)	$E_{interact}$ (eV/atom)
TaN	-3.49	-0.74	-2.75
Ru^{25}	-3.58	-0.85	-2.72
Ru^{50}	-3.59	-0.85	-2.74
Ru^{100}	-3.64	-1.04	-2.59
Ru^{1ML}	-4.12	-1.46	-2.66

on adsorbates with 1 - 4 copper atoms (see Chapter 4), we know that Ru-passivation increases the strength of binding of Cu compared to Cu binding on TaN and that Cu atoms prefer to remain separated rather than associating. This is confirmed during the relaxation of a 2D Cu_{29} , in which there is no migration of copper from the surface layer to the $S+1$ layer and copper remains flat while rearranging to conform to the corrugated Ru-passivated surface. This indicates that the 1 ML Ru can indeed promote copper wetting.

During the aiMD calculations the flat structure persists at temperatures up to 800 K (which exceeds process temperatures during back end of line processing), and we observe some of the copper atoms at the edge of the sheet migrating away from the remainder of the cluster. This shows that association of copper, which is required for the 3D structure to form, is not favourable at finite temperature on the 1 ML Ru-passivated surface. This originates in part from the strong Cu-surface interaction (Table 1) facilitated by the incorporation of some Cu atoms into the Ru layer, which inhibits upward migrations and the formation of a 3D structure (see Chapter 4). Section A3.3, Figure 3d), e) and f) shows the change in z-position for Cu_{29} on Ru passivated TaN at 300 K, 500 K and 800 K to illustrate the incorporation of Cu into the Ru layer. This shows that, depending on the temperature, up to 4 Cu atoms migrate downwards by up to 2 Å, which means they have migrated into the Ru layer. Based on our density of states (DOS) plots and the DOS of known Ru-Co alloys, [4] this has no impact on the metallic character of the Ru monolayer or copper (see DOS plots in Section A3.3, Figure A28 of the Appendix). There is also no migration of copper into the TaN layer, confirming that the barrier properties are unaffected.

If we compare the computed Cu-Cu interaction energies (see Table 1), then we see that they are weaker on the 1 ML Ru-TaN surface compared to the bare TaN surface and are weakest for highest Ru contents. This is consistent with our observation that copper atoms prefer to separate on the Ru-passivated TaN surface. This analysis shows that the presence of Ru on the TaN surface enhances the Cu-surface interaction. This is due, in part, to the stronger interaction between Cu and Ru compared to Cu and Ta (see Chapter 4.1 and 4.3). Further, we find that the Cu-Cu interaction energy is strongest on the bare TaN surface. This also partially explains why Cu atoms prefer to associate on this surface.

Overall, these findings indicate that a monolayer of Ru deposited on TaN is effective as a liner for Cu. Manufacturing interconnects using Ru-passivated TaN will significantly thin the barrier/liner stack especially knowing that TaN in a Ru/TaN stack can be thinned to 0.5 nm without losing its effectiveness as a barrier [5]; however as discussed in Chapter 2 a single material is preferable as it can be thinned further, does not introduce an additional interface and can be deposited in a single deposition run.

5.2 Impact of Ru Incorporation in TaN on 2D/3D copper stability

In this section we examine the impact of Ru doping in the surface layer of TaN to develop a single barrier+liner material. To avoid disruption of the barrier function of TaN caused by the difference in atomic radius between Ta and Ru and the lattice mismatch between Ru metal and TaN, we chose to incorporate Ru dopants only into the surface layer of TaN, rather than throughout the material.

This type of film can be grown using atomic layer deposition (ALD) [6–10], which is ideal for high aspect ratio structures such as interconnect vias and controlled incorporation of a second cation into the barrier film. For our system, this would mean growing several layers of ALD-TaN [11, 12] followed by a growth step using a mixture of Ta and Ru precursors to achieve a single layer doped with the desired concentration of Ru as in the models discussed in this thesis. [13–15]

We have considered three examples of Ru incorporation, with 100%, 50% and 25% substitution of Ta with Ru. Top and side views of Cu₂₉ after relaxation are shown in Figure 4 and geometries after a 500 K, 5 ps aiMD run on Ru¹⁰⁰, Ru⁵⁰ and Ru²⁵ are shown in Figure 5(a), (b) and (c), respectively. Figure 7 shows the corresponding plots of the change in Z-coordinate of the Cu atoms during the 300 K, 500 K and 800 K ab aiMD simulation.

The Ru¹⁰⁰ surface has the second most favourable E_{bind} out of the surfaces studied, with $E_{bind} = -3.64$ eV/Cu, Table 1. Examining the plots of z-coordinate *vs.* relaxation step in Figure 6, we see that during the relaxation four copper atoms migrated by up to 1.7 Å into the Ru-TaN surface. While 3 Cu atoms appeared to migrate out of the 2D structure, this upwards migration is <1 Å, and overall, we can say that the copper film is not transitioning to a 3D structure, as can be seen in the top view shown in Figure 5(a).

Migration into the surface is facilitated by surface recesses that are present as a result of Ru doping, due to the smaller atomic radius of Ru compared to Ta. These form on all Ru-doped TaN surfaces studied. The size and density of recesses formed depends on the percentage of Ru as well as the distribution of the Ru atoms in the surface, as discussed in Chapter 4. This distortion of the surface structure facilitates the movement of Cu atoms into the Ru-TaN layer.

Despite the relatively flat structure observed during relaxation, a number of Cu atoms immediately migrate to

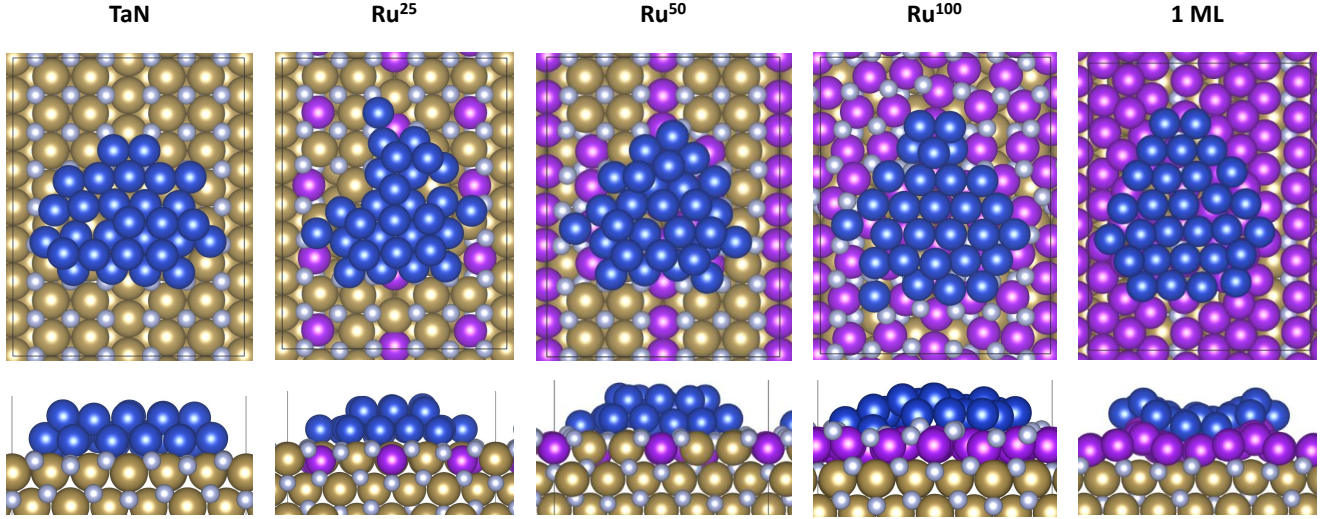


Figure 4: Structures of Cu_{29} obtained after relaxation on TaN, Ru^{25} , Ru^{50} , Ru^{100} , and Ru^{1ML} .

the S+1 layer of Ru^{100} at 300 K, with several more atoms migrating into the surface layer. This can be seen in the plot in Figure 7(a). At 500 K Cu atoms begin to exchange with surface Ru and N atoms, creating a mixture of Cu, Ru and N and individual layers are no longer distinguishable in the structure. Figure 7(b) shows the migration of Cu atoms both upwards and downward into the surface, by as much as 3 Å from their original positions. However, as the deposited copper structure now contains both Ru and N, it is not immediately obvious if such a thin film would be sufficiently conductive or thermally stable for use in interconnects. Certainly a Cu-Ru intermetallic layer would be metallic, however nitrides of copper and ruthenium can be semiconducting, semi-metallic or metallic, depending on the exact composition and phase. [16–18] Further, the atoms begin to associate and while there are no distinct layers as observed on other surfaces, the mixture is no longer a single layer film. The intermixing of elements increases at 800 K, as seen in Figure A27 of the Appendix and Figure 7(c). The migration of Ru and N atoms out of the Ru-TaN structure is not reflected in the z-plot, but can be clearly observed in Figure A27. The potential replacement of Ru and N atoms with Cu atoms could account for the Cu atoms that are displaced to nearly -3 Å at 500 K and 800 K. Despite this, as we have noted in Chapter 4, atoms that migrate into the Ru-TaN surface layer do not migrate any deeper into the TaN film, thus confirming that the presence of Ru in the surface layer does not negatively impact the barrier properties of TaN.

For 50% Ru doping, we focused on what we termed the Ru^{50-10} surface in Chapter 4, which is the most stable of the ten different dopant distributions studied for 50% surface doping. This is referred to as Ru^{50} throughout the main text; examples for the remaining Ru^{50} surfaces are discussed in the Appendix, Section A3.1. The binding

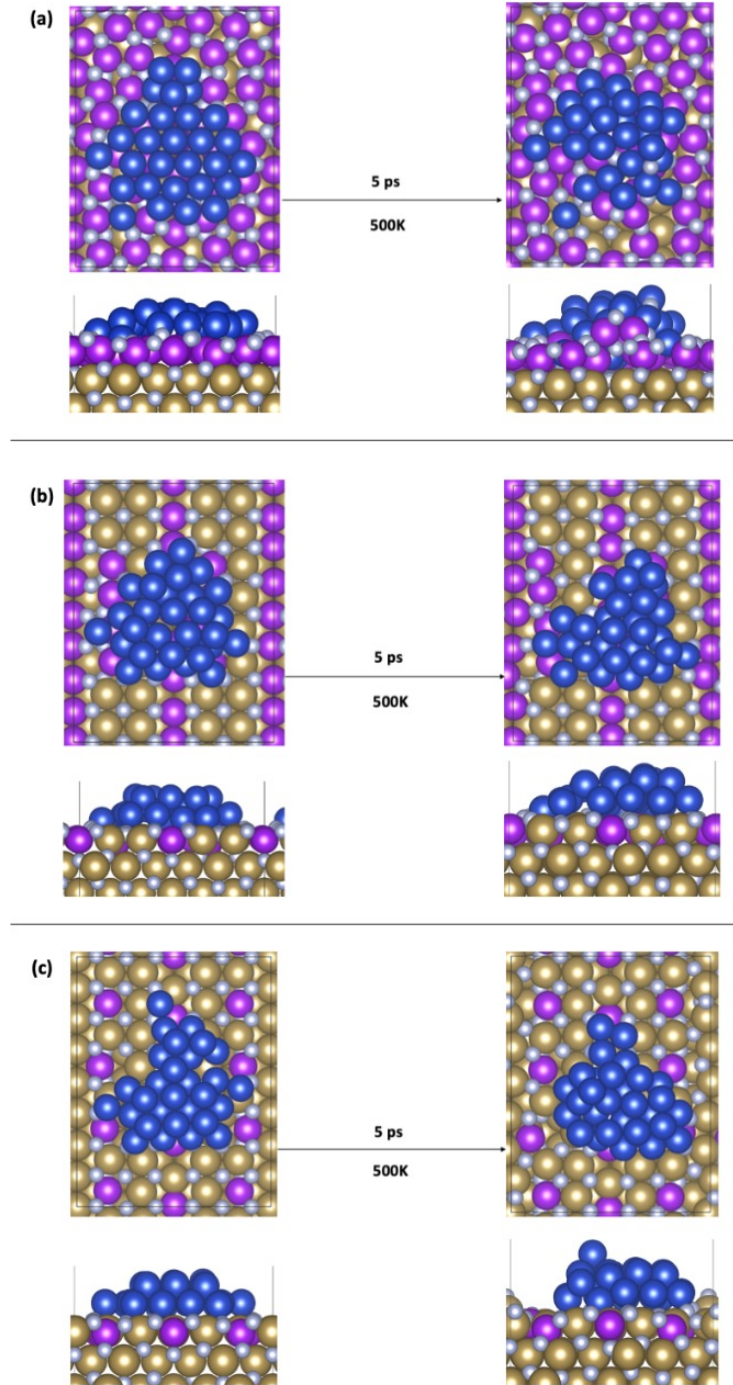


Figure 5: Structures of Cu_{29} obtained after relaxation and 5 ps aiMD at 500 K on (a) Ru^{100} , (b) Ru^{50} and (c) Ru^{25} .

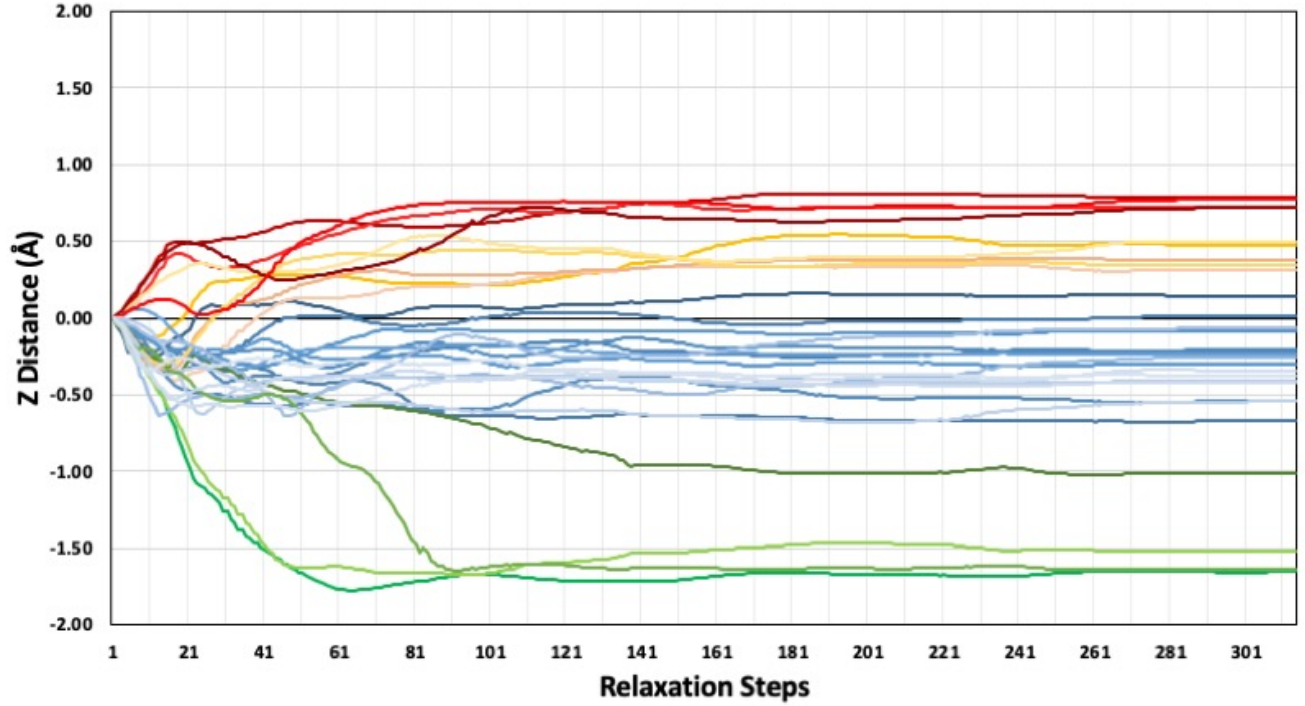


Figure 6: Change of Z position with respect to relaxations steps at 0 K for Cu_{29} on Ru^{100} . Each line represents one Cu atom. Blue lines are atoms that did not move from their original Z position. Atoms in yellow are slightly elevated but are not part of the second layer. Red lines indicate atoms in the second layer, while green lines are for atoms that have migrated into the top surface layer.

energy of Cu_{29} calculated on this Ru^{50} surface is -3.59 eV/Cu . The single layer copper transitions into a two-layer structure during the relaxation. The plots of copper z-coordinates in Figures 7(d) and (e) show that Cu atoms are not incorporated into the surface layer below 500 K. The number of incorporated Cu atoms increases with temperature (see Figure 7(f)), with Cu atoms displaced by ca. $-2.0 \text{ \AA}$. Similarly, only one atom has transitioned slightly upward from its original position during the 300 K aiMD calculation. Three and then four Cu atoms are displaced by around $1.5 \text{ \AA}$ indicating the migration of additional atoms to the S+1 layer at 500 K and 800 K respectively. This is a smaller number of S+1 atoms than for any other structure on doped Ru-TaN at these temperatures. The larger number of atoms in the central area (coloured in blue in Figure 7) shows that the majority of atoms do not move away from their original location. Study of the geometry in Figure 5(b) shows that this upward migration is not sufficient to confirm the formation of the S+2 layer and therefore we conclude that 50% Ru doping prevents formation of 3D copper islands. Similarly to Cu_{29} adsorption on the passivated surface, at 800 K the atoms begin to interact at the periodic boundary, forming the beginning of a pseudo 1D ribbon structure, which could indicate the transition to a conducting, 2D film.

On the Ru²⁵ surface, Cu₂₉ binds with similar strength to the bare TaN and Ru⁵⁰ surface, with $E_{bind} = -3.58$ eV/Cu. During our 0 K relaxation we observe a spontaneous transition from the single layer to a two-layer structure, similar to what is observed for the bare and Ru⁵⁰ surface (see Figure 5(c)). In a 300 K aiMD run, the two-layer structure for copper persists, with a slight upward migration observed for two Cu atoms as seen in Figure 7(g). At 500 K, we observe that over the short simulation timescale a single atom migrates from the second to the third layer. Over longer timescales, beyond those accessible to our simulations, this migration will promote further upwards Cu migration to produce a 3D morphology, as described in the models of film growth mechanism discussed in Chapter 2. The split between layers is very clearly visible in the plot in Figure 7(h), where there is very little fluctuation in the z-position once atoms have moved either into a surface recess or a new layer. This becomes more pronounced at 800 K, as illustrated in Figure 7(i). Here, there are strong distortions to the structure of copper and a tetrahedral Cu₄ appears to split off from the remainder of the structure, which remains as a two-layer structure with two copper atoms having migrated upwards into the $S+2$ layer and 3 atoms burying into one of the recesses created by the surface Ru. It is difficult to distinguish $S+2$ layer atoms from $S+1$ layer atoms. These are best identified visually (see Section A3.2, Figure A27 in the Appendix.)

Some of the behaviour of Cu atoms on surfaces with different Ru contents can be explained through study of the competition between Cu-Cu and Cu-surface interactions. As Ru content increases the contribution from Cu-Cu interactions to the overall binding energy decreases and the Cu-surface ($E_{metal-substrate}$) contribution increases. The increased Cu-surface interaction causes the promotion of 2D growth. However, both energies must be considered together, as the Ru¹⁰⁰ surface has the least favourable Cu-Cu interaction energy of -2.59 eV/Cu, but the Cu₂₉ structure does not remain completely flat, as the competing Cu-surface interaction of -1.04 eV/Cu is not sufficient to prevent all 3D growth.

This does not explain, however, why the Ru²⁵ and Ru⁵⁰ have almost identical binding energies, Cu-Cu interactions and Cu-surface interactions, yet on the Ru⁵⁰ surface the formation of an $S+2$ layer is prevented even at 800 K. To understand what limits Cu migration and island formation, we study the specific activation energies for the migration of an atom between the various layers.

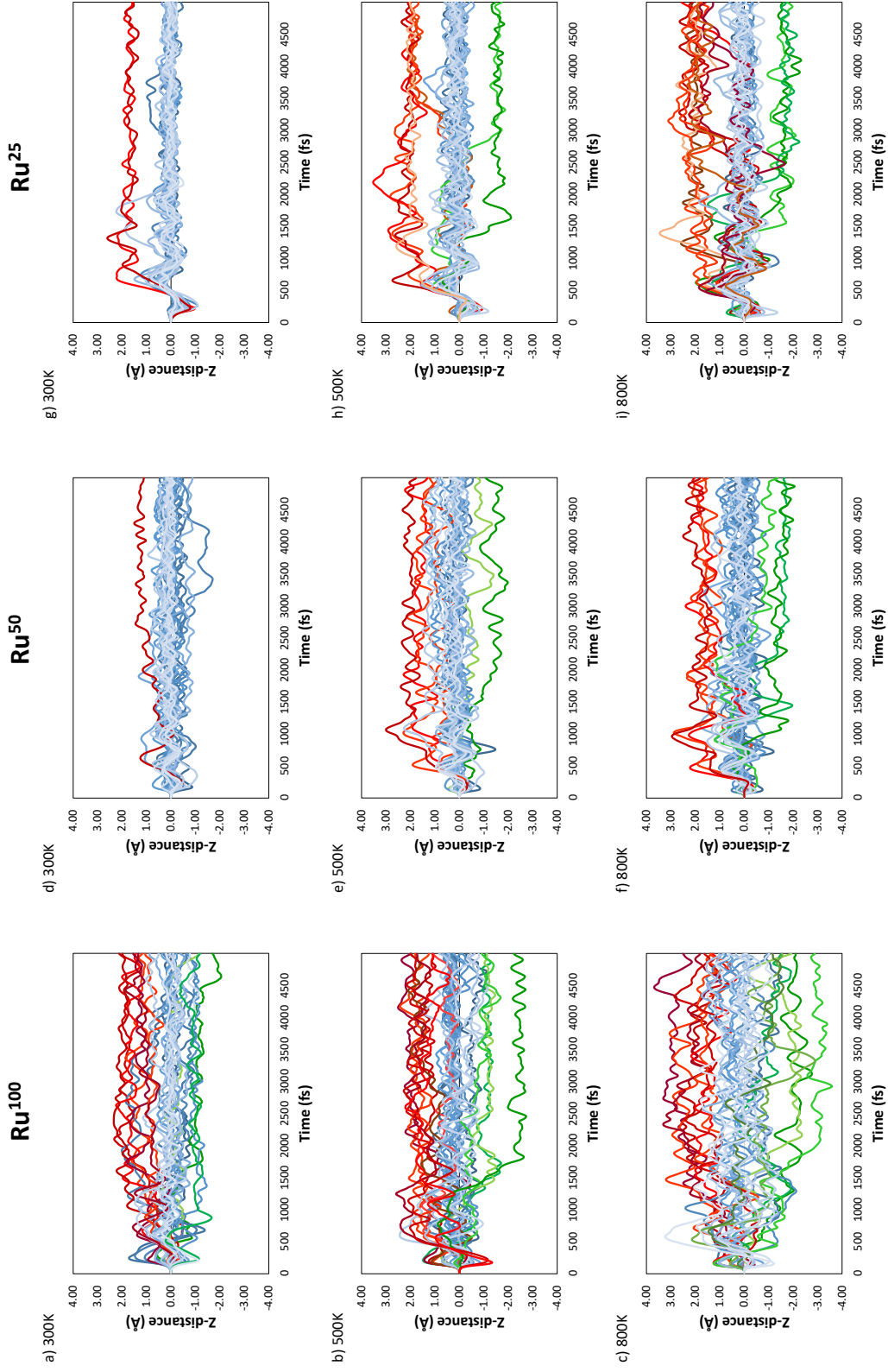


Figure 7: Change in Z-position with respect to MD simulation time for Cu₂₉ on Ru¹⁰⁰, Ru⁵⁰ and Ru²⁵ during aiMD runs at 300 K, 500 K and 800 K. Blue lines are atoms that did not move from their original Z position. Red lines indicate atoms in the second layer, while green lines are for atoms that have migrated into the top surface layer.

5.3 Study of growth mechanism of Cu thin film

Studying the migration pathways of atoms into the $S+1$ and $S+2$ layers allows us to gain insight into the growth mechanism of a Cu structure on Ru-modified TaN and how the morphology of copper can be controlled by the Ru content in the TaN surface. Pathways were studied for the bare surface, the Ru²⁵ and Ru⁵⁰ surfaces. The Ru²⁵ surface allows us to explore the activation energies for a composition that appeared to promote formation of a third layer of copper. The Ru¹⁰⁰ surface was not studied due to concerns relating to the electronic properties, morphology and thermal stability of the Cu structure with incorporated Ru and N.

For these calculations, we take the snapshot at the end of the 500 K aiMD simulation and relax at 0 K using the computational setup described in Chapter 3. This yields no Cu migration. We then allow one Cu atom to migrate from a layer to the next layer up (as defined in Figure 1(c)). Activation barriers for this Cu migration are presented in Table 2.

On bare TaN, the activation barrier to Cu migration is 0.70 – 0.84 eV depending on the transition in question. The largest barrier is for Cu migration from the $S+1$ Layer to the $S+2$ Layer (e1). When we consider Cu migration to the $S+2$ Layer given the previous migration of copper (e3), then the barrier is reduced. This is consistent with the idea that prior migration of a metal atom from the surface to the next layer can promote the migration of surface bound metal atoms.[19] In particular, the e2 migration, where a Cu atom migrates up two layers (from *Surface* to $S+2$ Layer) has a moderate activation barrier, suggesting that this transition will be important in 3D copper formation. The reverse migrations, i.e. where Cu migrates towards the surface, have lower activation barriers, suggesting that the process of 3D island formation will be dynamic.

When we consider the Ru-doped TaN systems, our results show that as little as 25% Ru doping increases the activation barrier to upward migration compared to bare TaN. For example, the e1 migration has an increased activation barrier compared to TaN, while the reverse migration of copper has a decreased activation barrier indicating it is difficult to promote the initial Cu migration to the $S+1$ and $S+2$ layers.

Table 2: Activation Energies for NEB transitions (Equation 43 in Chapter 3) on bare TaN, Ru²⁵ and Ru⁵⁰. *Forwards* and *reverse* signify a Cu atom transitioning up one layer and down one layer, respectively. Migration pathways e1, e2 and e3 are defined in Figure 1(c).

	e1		e2		e3	
	Forward (eV)	Reverse (eV)	Forward (eV)	Reverse (eV)	Forward (eV)	Reverse (eV)
TaN	0.84	0.44	0.76	0.74	0.70	0.33
Ru ²⁵	0.94	0.30	1.21	1.25	0.92	1.58
Ru ⁵⁰	1.18	1.08	1.86	1.82	0.62	0.78

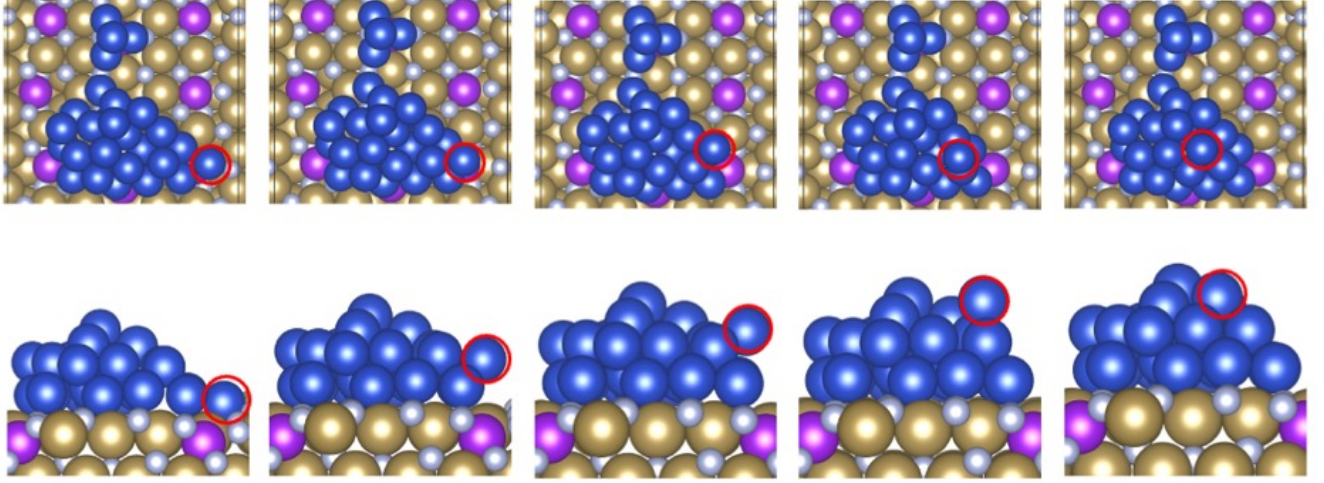


Figure 8: Transition of a copper atom from the surface layer to the $S+2$ layer (e2) on Ru^{25} . The top row shows the top view and the bottom row the side view. The migrating Cu atom is highlighted with a red outline.

This matches our previous understanding of Ru dopants acting as nucleation sites in the surface, as detailed in Chapter 4. The transition from the *surface* to the *S+2 layer* (e2 in Figure 1(c)) shows a strong increase in the activation energy compared to the bare surface. This is caused by the incorporation of the migrating atom into one of the surface gaps at the start of the migration, which is shown in Figure 8 and is an important mechanism for the stabilisation of 2D copper on Ru-modified TaN.

Calculating the activation energy towards migration of a Cu atom from the *S+1* layer to the *S+2* layer (e1 in Figure 1(c)) on Ru^{50} shows that the presence of Ru significantly increases the energy required for this initial upward migration, from 0.84 eV on bare TaN to 1.18 eV. The activation energy for the reverse migration to the *S+1* layer is also increased compared to the bare TaN surface, to 1.08 eV. Similarly, both upward and reverse migrations from the *surface layer* to the *S+2* layer (e2 in Figure 1(c)) have increased activation barriers compared to bare TaN and Ru^{25} . The transition of a second atom following the first *S+1* to *S+2* migration (e3 in Figure 1(c)) has a decreased activation energy compared to bare TaN and Ru^{25} indicating that once the first barrier to migration has been overcome, upward migration is promoted. However, given that the activation energies for an initial upward migration are quite large, it is unlikely that this copper migration will take place at typical processing temperatures. Further, the literature indicates that, so long as the metal-substrate interaction is strong enough, any upwards migration becomes extremely difficult. [20] This fits with our study of Cu_2 to Cu_4 clusters on Ru-modified TaN in Chapter 4. Here, we observed much lower metal-metal interaction energies overall compared to Cu_{29} , but a stronger metal-metal interaction for surfaces with a high Ru content, and weaker metal-metal interactions for Ru^{25}

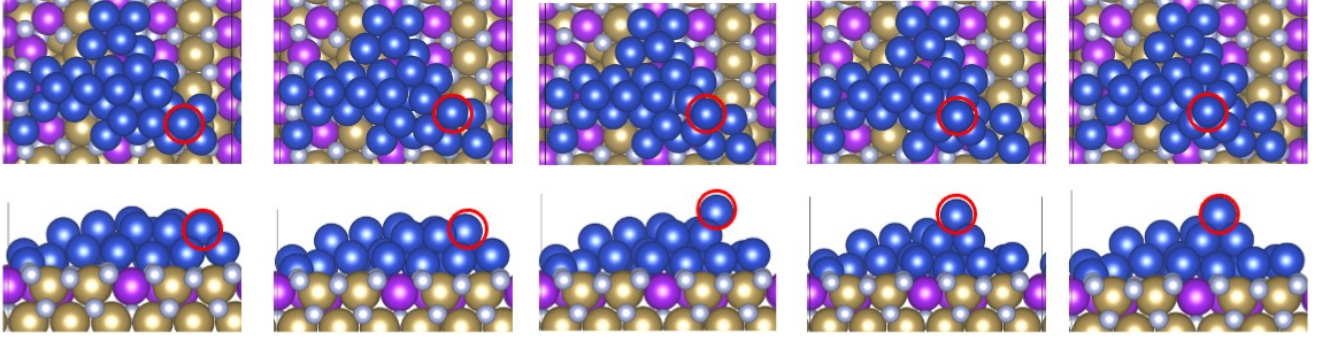


Figure 9: Transition of an atom from the S+1 layer to the S+2 layer (e1) on Ru^{50} . The top row shows the top view and the bottom row the side view. The migrating Cu atom is highlighted with a red outline.

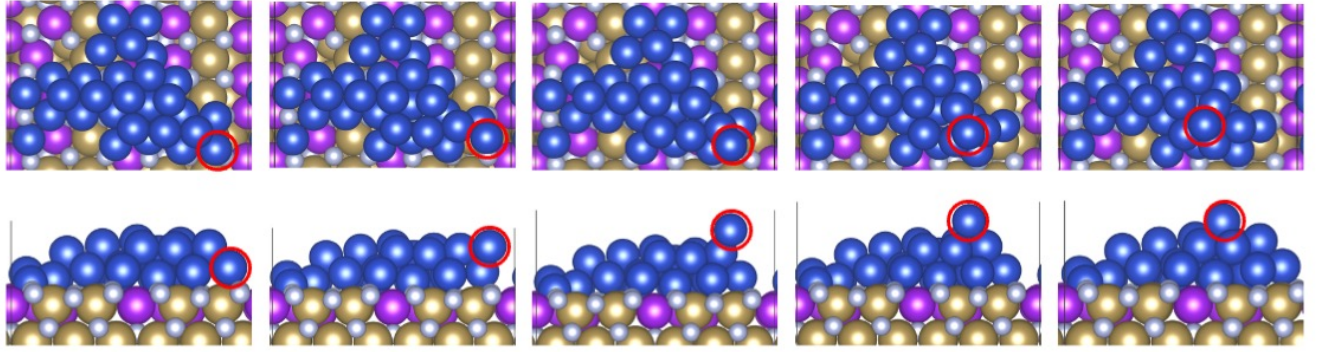


Figure 10: Transition of an atom from the surface layer to the S+2 layer (e2) on Ru^{50} . The top row shows the top view and the bottom row the side view. The migrating Cu atom is highlighted with a red outline.

and Ru^{50} .

However, both of the high Ru content surfaces showed extremely strong metal-substrate interactions with small Cu clusters, allowing us to conclude correctly that 2D growth would be promoted regardless. This trend is partially reversed here, with slightly weaker metal-metal interaction on surfaces with a high Ru content, while the interaction on Ru^{25} and Ru^{50} is very close to what is observed for bare TaN. This is likely due to a large contribution to the metal-metal interaction from atoms in the S+1 and S+2 layers.

Detailed atom migration steps for the e1 and e2 migrations on the Ru^{50} surface are shown in Figure 9 and Figure 10, respectively.

Overall, from the analysis of these Ru-TaN structures, our results indicate that if we want to incorporate Ru into TaN, then some Ta atoms are needed in the surface layer in order to ensure the thermal stability of the Ru-containing surface layer and reduce Cu, Ru and N migration around the interface region.

Based on our analysis, a Ru dopant content of around 50% appears to be suitable to promote 2D deposition of

copper rather than 3D island growth. We can clearly see that as Ru content increases, the Cu-substrate interaction also increases, however due to possible thermal instabilities, dopant concentrations above 50% are inadvisable, while at 50% doping the activation barrier for upwards migration of copper to form the third and subsequent layers of the 3D structure are significantly increased when compared to bare TaN. Further, both Ru²⁵ and Ru⁵⁰ surfaces show Cu binding energies more favourable than the cohesive energy of Cu and no transition beyond a two-layer structure is observed with increased temperature for Ru⁵⁰ surfaces.

While the exact distribution of dopants in the surface cannot be controlled during the growth process, if the growth is driven by thermodynamics, a structure like the one seen in the Ru⁵⁰⁻¹⁰ would be obtained. Other 50% distributions have also shown promising results (see Section 3.1 of the Appendix for $T = 0\text{K}$ and aiMD geometries in Figures A24 and A25, as well as a detailed discussion). Based in particular on our results for the other two 50% doped distributions and the Ru⁷⁵ surface, we find that while S:F ratio controls the stability of the surface and the interactions with Cu, too many Ru dopants localised in one region of the surface cause thermal instability similar to the Ru¹⁰⁰ surface. This means that provided there is a relatively even distribution of Ta and Ru in the surface layer, the exact distribution does not matter. Such a thermally stable distribution does not appear to be achievable for doping concentrations greater than 50%.

5.4 Conclusion

The search for new barrier+liner materials that will allow the continued use of copper in downscaling of CMOS devices is a significant challenge and one of the bottlenecks for further device scaling. We propose that the previously separate barrier and liner materials can be integrated into a single material, based on modifying the existing TaN barrier through surface doping, replacing Ta with Ru. A combination of static geometry relaxations, *ab initio* molecular dynamics at finite temperatures and activation barriers from nudged-elastic band calculations of copper atom migrations, have demonstrated how the Ru content of Ru-modified TaN controls the 2D *versus* 3D morphology of a Cu₂₉ structure, representative of a growing Cu thin-film. This Ru-TaN film can be deposited through atomic layer deposition which provides a high degree of control over thickness and composition.

We show that the incorporation of Ru into the TaN surface strengthens the metal-substrate interaction and thus should inhibit the 3D growth of Cu on the surface. A dopant concentration in the surface layer of 50% is sufficient to promote 2D growth while also showing improved thermal stability compared to higher concentrations of Ru which show mixing of Cu, Ru and N at the interface. The 50% Ru doping increases the activation barrier to copper atom migration to upper layers and will therefore promote 2D growth of copper. This will result in deposition of conducting films rather than non-conducting islands. These findings further confirm our earlier hypotheses on the

effect of Ru dopants in TaN on Cu growth based on our previous work with smaller Cu structures.

This new information gives vital insight into a solution for extending the use of Cu in interconnects, as well as a more detailed understanding of factors controlling 2D *vs.* 3D growth of metals on nitride substrates.

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Chapter 6: Stability of Copper on W- and Co-TaN

The aim of this chapter is to study how the interaction between Cu and modified TaN changes with different metal dopants. We have chosen Co and W as the dopants. Co was chosen as it is known as a useful liner material for Cu. [1–18] Additionally, it allows us to further investigate the effects of the difference in ionic radius between Ta and the dopant, because Co has the smallest ionic radius from Ta, Co, Ru and W. Co is magnetic, therefore we tested the effects of high-spin vs low-spin on geometry and adsorption energy; this is discussed in the Appendix, Section A4.8. To the best of our knowledge, while neither W nor W_xN_y have been studied as a liner material, we discussed in Chapter 2 that W_xN_y is a known barrier material. [18–30] As W has a similar ionic radius to Ta, this allows us to study how a dopant that is similar in size to Ta affects the surface structure. Further, we can study the potential liner properties of W and WN incorporated into TaN. Finally, atomic layer deposition (ALD) process chemistries are known for Co, [31–33] W [34, 35] and their respective nitrides, [22, 36–38] permitting their introduction into TaN through ALD.

Similarly to the approach described in Chapters 4 and 5, we have doped the top layer of a ε -TaN(1 1 0) slab with W and Co. To do this, 25%, 50% or 100% of the Ta atoms in the top layer were replaced with the dopant. The surfaces will be labelled as $W^{\text{dopant-concentration}}$ or $Co^{\text{dopant-concentration}}$. For 50% doping, we chose two different doping distributions, namely the most and least favourable 50% dopant distributions from our previous work. These will be distinguished as W^{50-S}/W^{50-F} and Co^{50-S}/Co^{50-F} , as they contain the maximum number of S-site and F-site dopants, respectively. The resulting surfaces are shown in Figure 1 for W doping and in Figure 7 for Co doping. The selected sites for single Cu adsorption are also highlighted.

Due to the smaller ionic radius of Co (0.55 or 0.61 Å, depending on high or low spin) compared to Ta (0.72 Å), [39] strong surface rearrangements were observed on the Co^{50-S} , Co^{50-F} and Co^{100} surfaces. For this reason, the adsorption energy and the metal-metal interaction energy for these surfaces were computed as described in Chapter 3, by using E_{surf} , the single point energy of the rearranged surface instead of E_{bare} , the total energy of the relaxed surface before metal adsorption, as a reference. This is the same energy used to compute $E_{\text{metal-substrate}}$, which has the consequence that the metal-metal interaction energies are based solely on the difference in the Cu reference

energies. However, they are still a reasonable indicator of the contributions of metal-substrate energy and metal-metal energy to the total adsorption energy and can be used to predict the likely growth mechanism, as in previous chapters.

6.1 W-doped and Co-doped TaN surfaces

To determine the relative stability of the different surfaces we have computed a doping energy for each surface using Equation 41 in Chapter 3. Doping energies for each W and Co surface are shown in Table 1 and are compared to doping energies for Ru doping from Chapters 4 and 5. W doping is more favourable than Ru doping and the doping energies for the two 50% doped surfaces are both negative and quite large in magnitude indicating that doping with this W content is more favourable than the bare TaN surface or doping with Co or other W contents. While all of the Co-doped surfaces have negative doping energies the most stable surfaces are Co^{25} and Co^{50-F} .

Table 1: Doping Energies for each W, Co and Ru doped TaN surface, calculated using Equation 41 in Chapter 3. Doping energies for Ru are taken from reference [40]/Chapter 4.

Doping Concentration	E_{dope} (eV/dopant)		
	W	Co	Ru
25%	1.70	-0.82	3.91
50%-S	-6.60	-0.60	4.52
50%-F	-7.08	-1.59	3.30
100%	1.84	-0.69	3.99

6.2 Structure of one, two and four Cu atoms on W-doped TaN

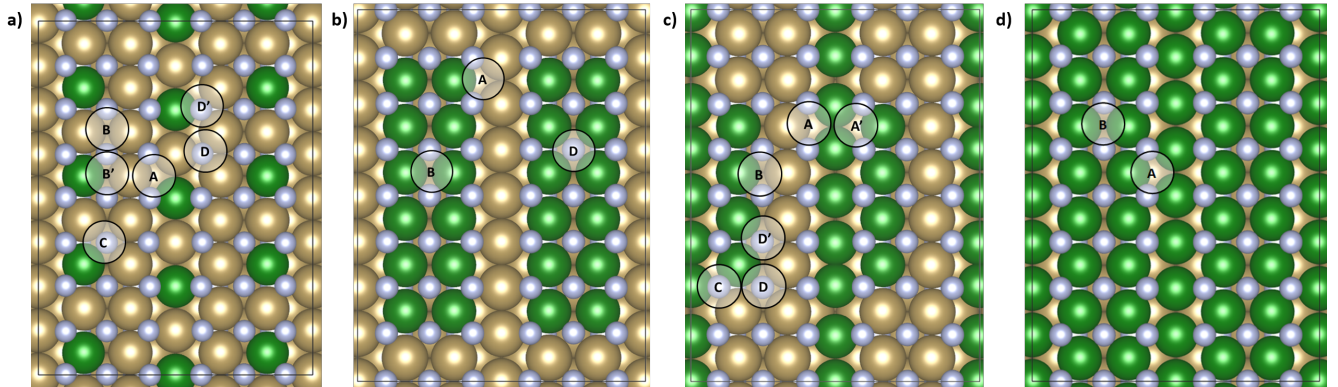


Figure 1: W^{25} , W^{50-S} , W^{50-F} and W^{100} relaxed surfaces. The individual adsorption sites for each surface are highlighted. Atoms are coloured according to the colour code in Chapter 3.

Adsorption of single Cu atoms at the adsorption sites shown in Figure 1 shows that site A is the most favourable

adsorption site for all W contents in TaN, with computed adsorption energies ranging from -2.57 eV to -3.94 eV depending on the W content. Site A is a 5 coordinate site bonding to two N atoms and three metal atoms, at least one of which is W. This site is also most favourable on bare TaN. The largest energy gain is observed for the W^{100} surface, closely followed by the W^{50-F} surface. Binding energies and geometries for single Cu atom adsorption are shown in the Appendix, Section A4.1.1.

Adsorption is less favourable on W^{50-S} than on W^{50-F} . This indicates that as for Ru doping, the distribution of dopant atoms and the dopant S:F ratio affects the surface reactivity.

All Cu_2 and Cu_4 clusters were adsorbed at site A. The full set of relaxed geometries is shown in Section A4.1.2 of the Appendix, while the most favourable Cu_2 and Cu_4 adsorption structures are shown in Figures 2 and 3, respectively. Table 2 shows the adsorption energies for Cu_1 , Cu_2 and Cu_4 adsorption, as well as the metal-substrate and metal-metal interaction energies for Cu_2 and Cu_4 adsorptions.

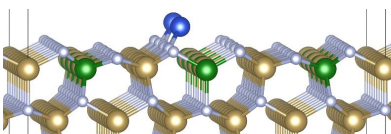
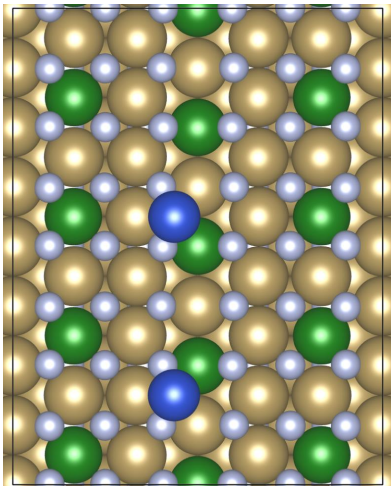
For two atom adsorption, we compare the stability of associated atoms (close) and separated atoms (apart). The close configuration is most favourable for Cu_2 on TaN, indicating that this small model gives a reasonable first insight into preferences towards association or separation, as the results match our expectations for TaN where Cu does not wet. For all surfaces except W^{50-F} , the separated structure is more favourable by about 0.1 eV, indicating a slight initial preference towards structures with fewer Cu-Cu bonds on all W-doped surfaces. However the energy difference is small enough to necessitate a larger number of Cu atoms to gain a more accurate understanding. On W^{50-F} , the close configuration is most favourable and with an adsorption energy of -3.97 eV it is the most favourable of all Cu_2 and Cu_4 adsorption modes on the different W-doped surfaces. This is particularly interesting as the atoms interact only with W and N atoms and not with Ta atoms, as shown in Figure 2C. However on the W^{100} surface, in essentially the same adsorption environment, the same geometry is not as favourable and the two Cu_2 geometries are competitive in energy.

There are three different Cu geometries for Cu_4 : line, rhombus and tetrahedral. The line and rhombus configuration are 2D structures, with all Cu atoms directly interacting at the W-TaN surface, while the tetrahedral configuration is 3D, with three atoms in a triangle at the base, bound to W-TaN and a fourth atom sitting atop the triangular base. The line configuration is the least favourable for all surfaces, indicating that configurations with more Cu-Cu bonds are more favourable. On W^{25} the tetrahedral configuration is most favourable, while on W^{50-S} both rhombus and tetrahedral configuration are equally favourable. On W^{50-F} and W^{100} the rhombus configuration is most favourable. These are also the surfaces with the largest difference in energy of 0.6 eV between the rhombus and tetrahedral configurations. The smaller energy differences on the other surfaces indicate that 2D and 3D structures are competitive at the initial stage of film growth. Additionally, it is of interest that de-

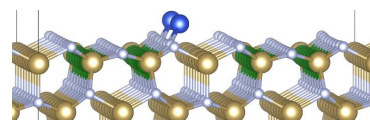
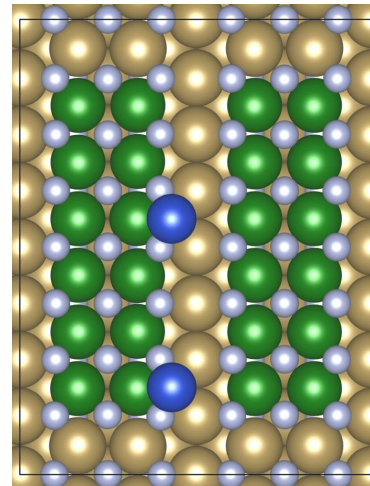
Table 2: Binding energies (Equation 37 in Chapter 3), metal-substrate interaction energies (Equation 39 in Chapter 3) and metal-metal interaction energies (Equation 40 in Chapter 3) for Cu₁, Cu₂ and Cu₄ adsorptions.

Surface	Cu _n	Cluster Geometry	E _{bind} (eV/Cu)	E _{metal-substrate} (eV/Cu)	E _{interact} (eV/Cu)
W ²⁵	Cu ₁	A	-2.85		
		B	-2.06		
		B'	-2.21		
		C	-1.96		
		D	-2.09		
		D'	-1.99		
	Cu ₂	close	-2.73	-2.16	-0.57
		apart	-2.83	-2.92	0.09
	Cu ₄	line	-2.67	-2.13	-0.54
		rhombus	-2.82	-2.01	-0.81
		tetrahedron	-2.91	-1.65	-1.26
	Cu ₂₉		-2.89	-0.67	-2.21
W ^{50-S}	Cu ₁	A	-2.57		
		B	-1.96		
		D	-1.65		
	Cu ₂	close	-2.50	-1.93	-0.58
		apart	-2.61	-2.72	0.10
	Cu ₄	line	-2.50	-1.81	-0.70
		rhombus	-3.35	-1.33	-2.02
		tetrahedron	-3.35	-1.51	-1.84
	Cu ₂₉				
W ^{50-F}	Cu ₁	A	-3.58		
		A'	-3.33		
		B	-2.00		
		C	-2.69		
		D	-2.71		
		D'	-1.78		
	Cu ₂	close	-3.97	-1.99	-1.98
		apart	-2.99	-2.73	-0.26
	Cu ₄	line	-2.66	-1.86	-0.79
		rhombus	-3.50	-1.28	-2.22
		tetrahedron	-2.87	-1.40	-1.47
	Cu ₂₉		-3.00	-0.62	-2.37
W ¹⁰⁰	Cu ₁	A	-3.94		
		B	-3.36		
	Cu ₂	close	-3.06	-1.83	-1.23
		apart	-3.10	-2.49	-0.61
	Cu ₄	line	-2.67	-1.84	-0.83
		rhombus	-3.60	-1.20	-2.40
		tetrahedron	-3.03	-1.35	-1.68
	Cu ₂₉		-3.00	-0.60	-2.40

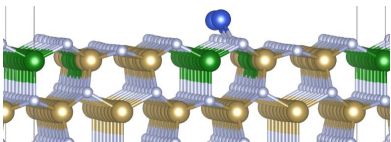
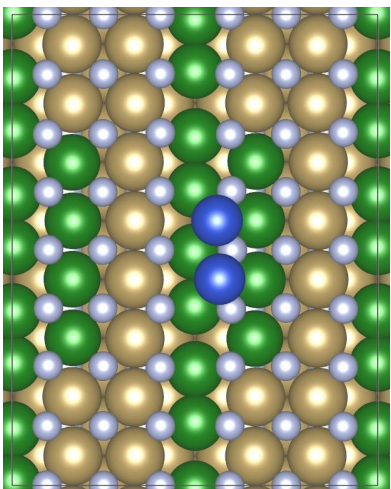
(A) W^{25} apart $E(bind) = -2.83$ eV



(B) W^{50-S} apart $E(bind) = -2.61$ eV



(C) W^{50-F} close $E(bind) = -3.97$ eV



(D) W^{100} apart $E(bind) = -3.10$ eV

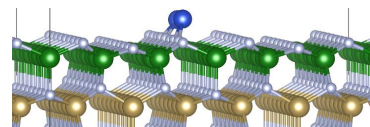
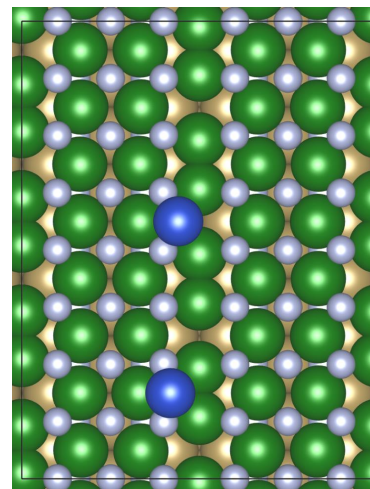


Figure 2: Most favourable adsorption geometries for Cu_2 on W-doped TaN.

spite the different behaviour for Cu_2 adsorption, W^{50-F} and W^{100} show similar behaviour and similarly favourable adsorption for Cu_4 adsorptions.

Unlike Ru-doped TaN, W-doped TaN does not show any rearrangements of the surface atoms and no gaps are formed that could trap a Cu atom and enhance the metal-substrate interaction. This is due to the similar ionic radius of W and Ta atoms, which leaves no gaps or recesses in the lattice when dopants are introduced. It is possible that this smaller mismatch in atom size could contribute to a more stable surface as the structure does not distort from the structure of TaN, in contrast to Ru-TaN.

The metal-metal interaction energies are strongest for the rhombus structures on all but the W^{25} surface. This is most likely due to the difference in the shape of the rhombus on W^{25} which upon relaxation, resembles the line configuration and thus has fewer interactions between the Cu atoms. The tetrahedral configuration tends to be quite favourable on all of the surfaces, but it also has a medium metal-metal interaction energy compared to all other geometries indicating that while the tetrahedron is 3D, as the film grows, further tetrahedrons could join into a 2D film. The metal-substrate interaction is greater than the metal-metal interaction for all geometries except rhombus and tetrahedron on the various surfaces. This indicates that the strength of the metal-metal interaction is driven primarily by the number of Cu-Cu interactions. On the W^{50-F} and W^{100} surfaces where the 2D rhombus is most favourable, a 2D film could form based on this preference, as the metal-substrate interactions remain favourable despite the strong metal-metal interaction energy. Additionally, the W^{25} surface shows some promise, although the tetrahedron is most favourable here, as this is the only surface where all geometries have a metal-substrate interaction that is stronger than the metal-metal interaction. Based entirely on the competition between metal-substrate and metal-metal interaction Cu should wet on this surface. However, the overall binding energy of Cu on this surface is weaker than that computed for Cu on TaN (see Chapter 4). Given that Cu does not wet on TaN, but has a stronger adhesion compared to W^{25} , it is unclear at this point if this surface would promote 2D growth. Study of a larger Cu structure will provide further insight into this, see Section 6.4.

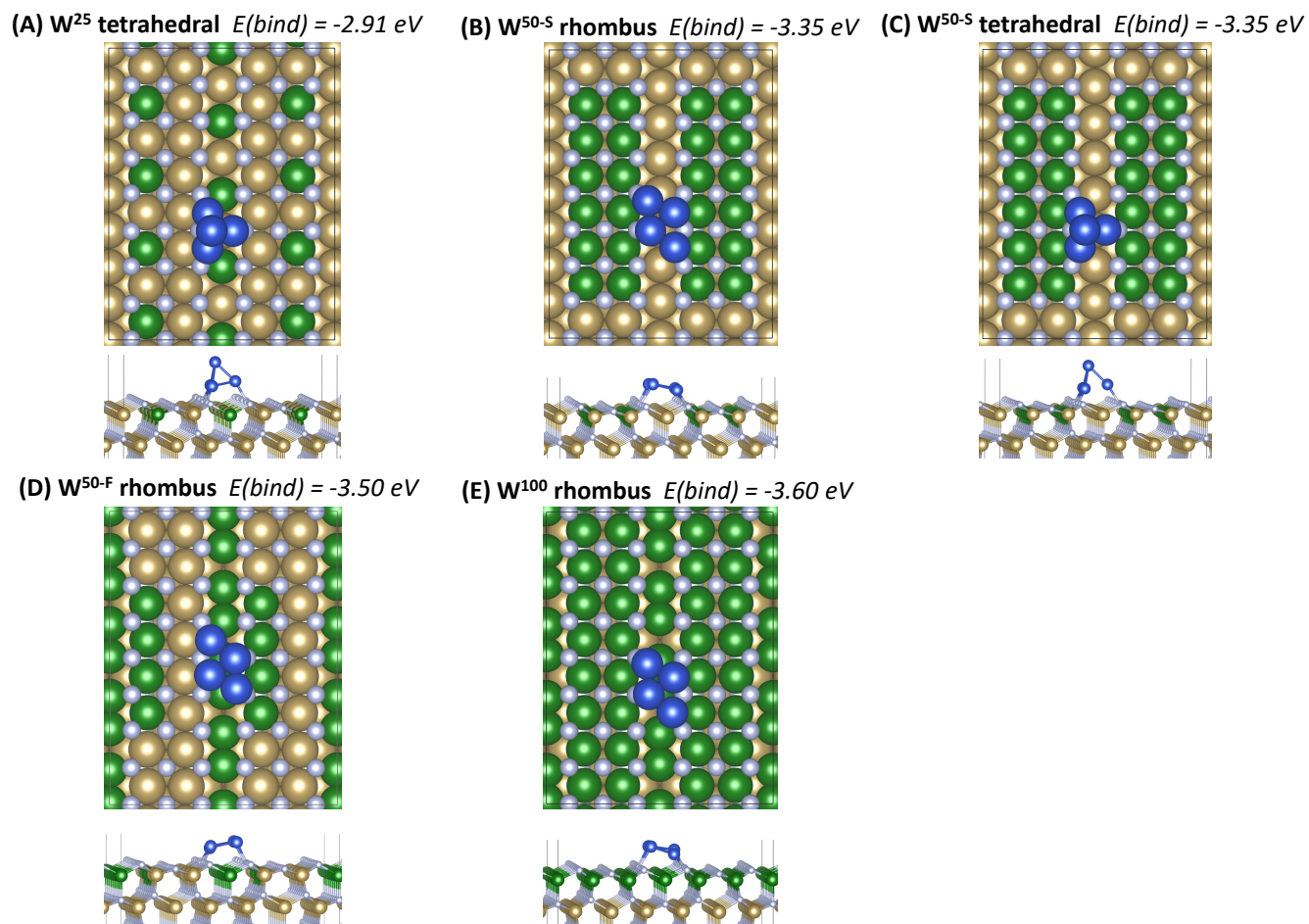


Figure 3: Most favourable adsorption geometries of Cu_4 on W-doped TaN.

6.3 Ab initio Molecular Dynamics (aiMD) of Cu rhombus on 25%, 50% and 100% W-doped TaN

After running an aiMD simulation for 5 ps at 500 K, on W^{25} the less favourable rhombus with three atoms in a line rearranges into a square, with each atom at a site A, thus increasing the number of metal-metal interactions compared to the 0 K geometry (see Figure 4A). The Cu_4 structure on W^{50-S} remains unchanged after 5 ps at 500 K (see Figure 4B). On W^{50-F} , it appears that the atoms migrate across the surface toward the nearest A sites and begin forming into the same square structure observed for W^{25} (see Figure 4C). On W^{100} , the rhombus rearranges into a tetrahedron, even though this geometry was not as favourable during the standard geometry relaxations (see Figure 4D). The tetrahedron was most favourable on W^{25} , however the fact that the rhombus structure did not rearrange into a 3D structure at 500 K indicates that 25% W could be enough to prevent Cu island formation, while 100% W is potentially too high of a doping concentration, being similar to TaN. Experimental results for W_xN_y barriers [19] showed that W_2N has good barrier reliability up to 790 °C while WN breaks down at 500 °C. No study of the liner properties of W-based materials has been carried out to the best of our knowledge; however it is reasonable to propose that a W doped TaN surface might have enhanced barrier reliability compared to W^{100} , which is essentially a layer of WN passivation on TaN. Table 2 also gives the metal-metal interaction energy of the geometries obtained after the aiMD run. Given the improved adhesion and apparent atom mobility on W^{50-F} compared to pure TaN, this surface seems to be the most promising for a combined barrier/liner material.

6.4 Cu_{29} on W-doped TaN

To deepen our understanding of the interaction between Cu and the various doped surfaces, we continue with the Cu_{29} structure used in Chapter 5 with Ru doping and study its structure on W^{25} , W^{50-F} and W^{100} . W^{50-F} and W^{100} were selected as their interactions with the Cu_4 cluster indicated the potential to promote 2D conducting Cu. Cu_2 and Cu_4 showed a weaker adhesion to W^{25} than to the bare TaN surface. However, this is the surface with the strongest metal-substrate interactions compared to the other W-doped surfaces. Based on our prediction methods this means that Cu should wet on this surface despite the weaker adhesion. Using the Cu_{29} structure, we can gain better insight into the behaviour of a Cu model with larger number of atoms at a different stage of the film growth process and assess our predictions based on metal-metal and metal-substrate interactions.

As on Ru-doped TaN, a transition occurs from the completely 2D Cu sheet to a two-layered Cu structure. On both W^{50-F} and W^{100} , the Cu structure is very regular and resembles facets on the $Cu(1\ 1\ 1)$ surface. This is the desired crystal structure for Cu in interconnects as it has the best electromigration reliability. [41] On W^{25} , only 6

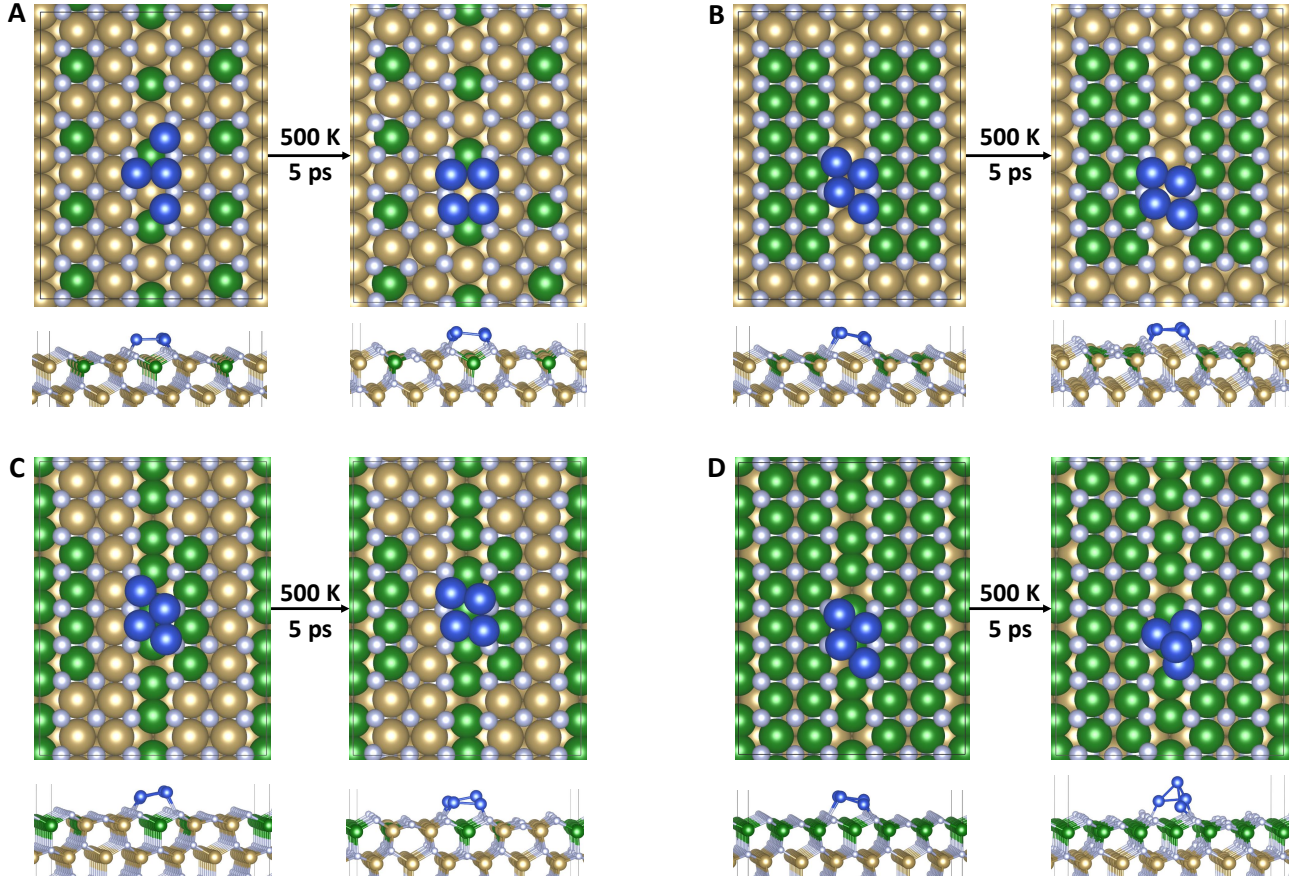


Figure 4: Cu rhombus before and after a 5 ps aiMD run at 500 K on A) W^{25} , B) W^{50-S} , C) W^{50-F} and D) W^{100} .

Cu atoms migrate into the second layer and the overall geometry continues to resemble the original Cu_{29} geometry, as shown in Figure 5.

On W^{50-F} there are 10 atoms in the second Cu layer and on W^{100} there are 9 atoms in the second Cu layer. During the aiMD calculation the atoms rearrange to be more close packed. There are no transitions to a third layer observed over the course of 5 ps on W^{100} , however a Cu atom migrates to the third layer on W^{50-F} after approximately 2 ps. Further upward migration occurs creating a clustered structure as shown in Figure 6. The metal-metal interaction for Cu_{29} on both W^{50-F} and W^{100} was calculated (see Table 2). We find that the metal-metal interaction energy is significantly larger than the metal-substrate interaction and that the magnitude of these interactions are similar on both surfaces. For W^{50-F} this is consistent with migration of Cu atoms into a third layer. However, there are no Cu atoms migrating into a third layer on W^{100} . Given the large number of possible Cu-Cu interactions compared to the Cu-substrate interactions, it appears that the competition between

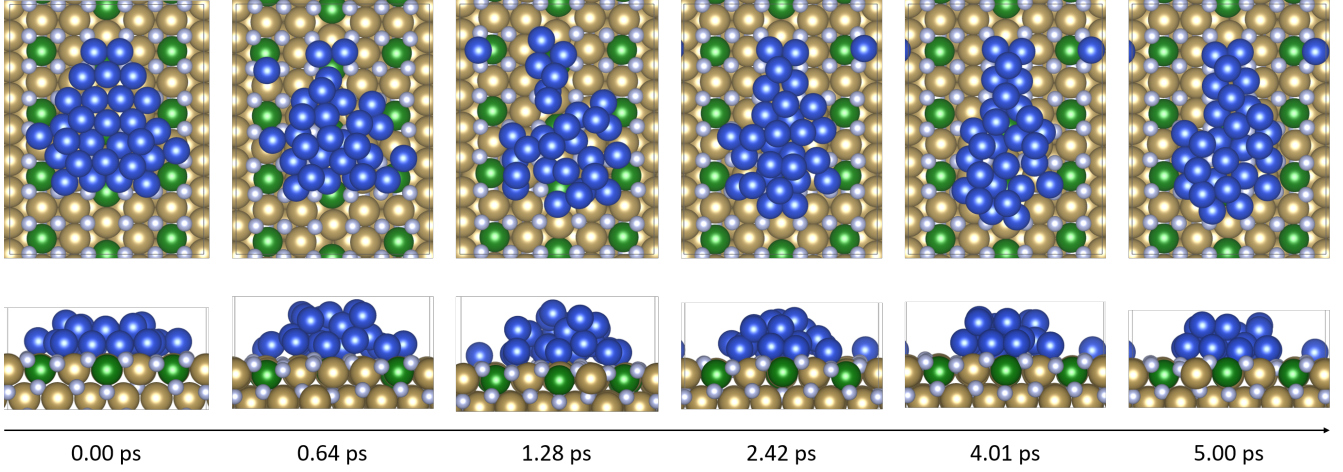


Figure 5: Evolution of the Cu_{29} structure on W^{25} during 5 ps of aiMD at 500 K.

these two interactions may not be indicative of film morphology for large Cu models and is instead most reliable for predicting possible film morphology based on small Cu models.

Overall, the fact that the Cu_4 rhombus structure was preferred during the geometry relaxation together with these results indicates that W^{100} actually inhibits upward migration of Cu atoms and prevents Cu cluster formation. It therefore acts as a liner. As we see no exchange of Cu and surface atoms combining WN and TaN like this should yield a thermally stable materials that can act as a barrier, despite the concerns in terms of W_xN_y 's inferior barrier reliability compared to TaN. [19]

On W^{25} , the Cu atoms rearrange into a wire-like structure. Additionally, a single Cu atom breaks away from the cluster and migrates across the surface, indicating promoted atom mobility. We also observe several transient states throughout the aiMD run-time where the Cu_{29} structure separates into smaller clusters, before rearranging into the wire-like structure. This is shown in Figure 5. As the W dopants are uniformly distributed throughout the surface, meaning that there are no W-rich areas, this rearrangement is clearly not caused by enhanced interaction between Cu and W. Given that the only difference between the interactions of Cu with W^{25} compared to the other W-doped surfaces is an increased metal-substrate energy, it is possible that the distribution of W-dopants in TaN can strengthen the interaction with Cu. Even though there are no clear indications in our analysis why W^{25} behaves differently in this respect, provided that these wire-like structures would join into a smooth thin-film, 25% W-doped TaN may be a candidate for a combined barrier/liner material. While the weaker overall adhesion of Cu atoms is of some concern, due to the lack of rearrangements and surface gaps in W^{25} it is likely to have superior stability compared to Ru- and Co-doped TaN.

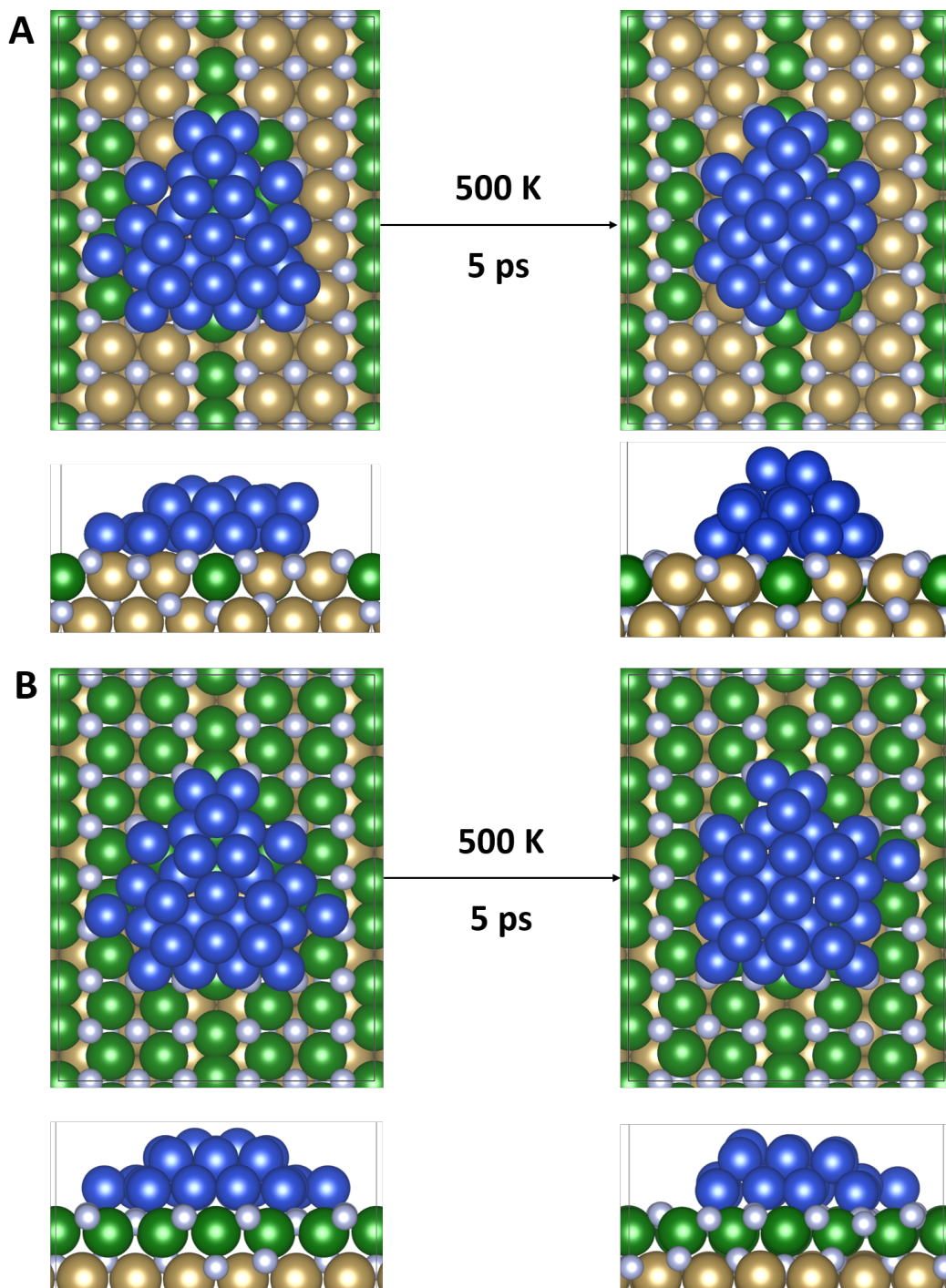


Figure 6: Cu_{29} after geometry relaxation (left panels) and 5 ps aiMD run at 500 K (right panels) on A) W^{50-F} and B) W^{100} .

6.5 Adsorption of one, two and four Cu atoms on Co-doped TaN

The relaxed Co-doped TaN surfaces and their unique adsorption sites are shown in Figure 7. All single atom, Cu_2 and Cu_4 adsorptions are shown in Section A4.4 of the Appendix. Figures 8, 11 and 12 show only the most favourable adsorption geometries. The binding energy of single Cu adatoms on Co-doped TaN tends to be more favourable than the same adsorption modes on Ru- and W-doped TaN.

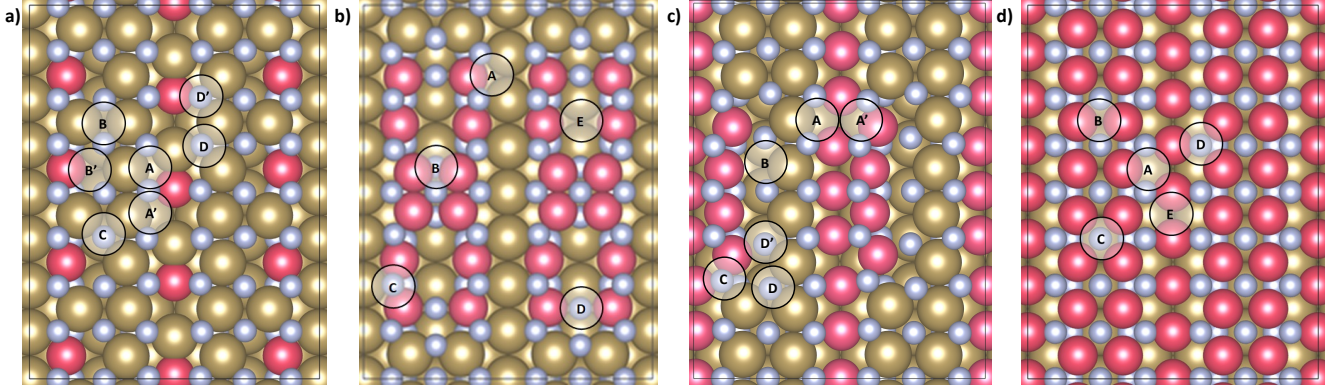


Figure 7: Relaxed Co-doped TaN surfaces and their unique adsorption sites. a) Co^{25} , b) Co^{50-S} , c) Co^{50-F} , d) Co^{100} .

All Co-doped surfaces rearrange to some degree upon Cu adsorption, creating gaps on the surface that trap the Cu atom, depending on the adsorption site. This is due to the difference in ionic radius between Co (0.55 or 0.61 Å, depending on spin) and Ta (0.72 Å). [39] While for TaN and all W- and Ru-doped surfaces the 5 coordinate site A is most favourable, only Co^{50-S} shares this most favourable adsorption site. On Co^{25} and Co^{50-F} site B is the most favourable, as shown in Figure 8A and C. Site B is a four coordinate site with two metal atoms (in this case one Ta atom and one Co atom) and two N atoms. This site is likely more favourable than site A as the difference in ionic radius creates a gap between the Co and Ta atom that Cu can partially occupy. On Co^{50-S} , there are two Co atoms at site B and a surface rearrangement occurs. This rearrangement leaves a gap for Cu to occupy (Figure A46 in Section A4.4.1 of the Appendix). The result is a strong adsorption energy of -3.82 eV/atom. However site A on this surface forms a larger gap that allows Cu to fully incorporate into the surface layer leading to a particularly large adsorption energy of -4.61 eV/atom, as shown in Figure 8B.

The Co^{100} surface rearranges to the point where it becomes difficult to determine the exact adsorption site after relaxation. This is similar to Ru^{100} in Chapter 4. Just like the surface gaps formed for lower Co and Ru contents, this is likely caused by the difference in the size of the ionic radius of Co and Ru compared to Ta. [39] Figure 9 compares the Ru, Co and W 100% doped surfaces before and after Cu adsorption. Here, the effect of the

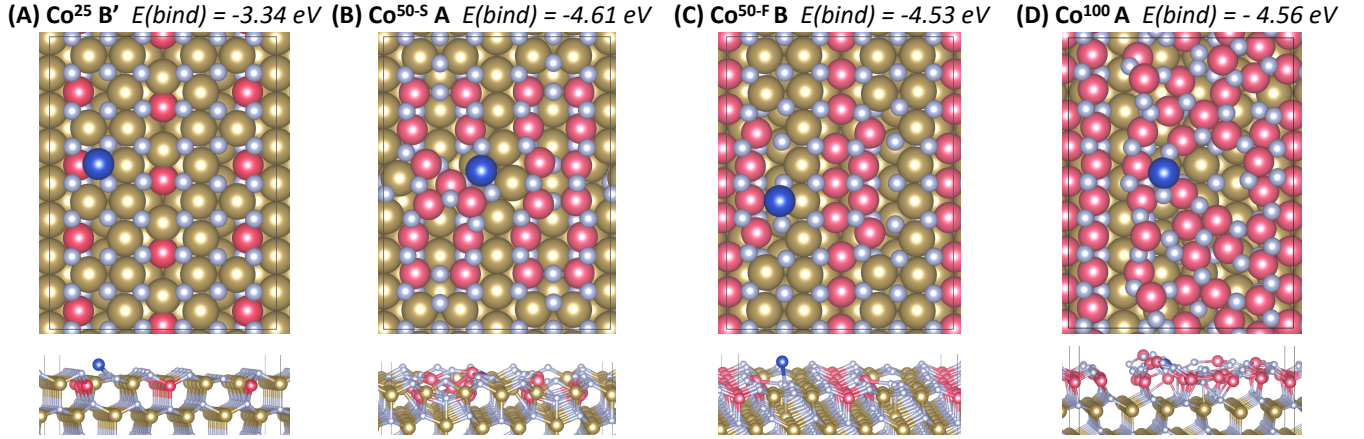


Figure 8: Most favourable single Cu adsorption structures on Co-doped TaN.

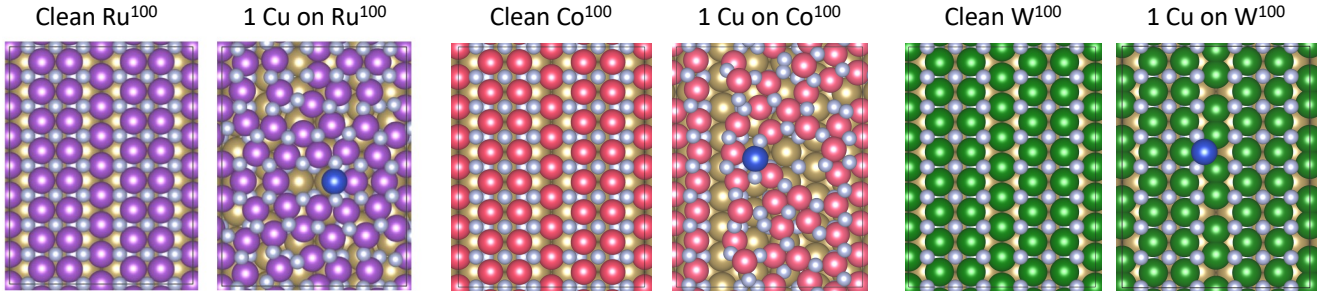


Figure 9: 100% Ru, W and Co doped surfaces before and after Cu adsorption.

difference in ionic radius becomes clear. From largest to smallest the ionic radius of the different atoms compares as follows: $\text{Ta} > \text{W} > \text{Ru} > \text{Co}$. No rearrangements are observed for W^{100} due to the similar size of W and Ta. Some rearrangements are observed for Ru^{100} , while Co^{100} shows the most significant rearrangements due to the large size difference. Additionally, without the presence of Ta atoms this CoN "passivation" layer begins to distort as illustrated in Figure 10. Here, we observe extremely large gaps exposing the TaN slab. Additionally, several Co and N atoms are now completely removed from TaN and instead form a second layer of CoN. These rearrangements are most likely caused by the lattice mismatch and different unit cell shapes for CoN and TaN. More details on this are included in the Section A4.9 of the Appendix.

It is important to note that despite the significant rearrangements in the surfaces, no mixing of the doped TaN layer and the rest of the slab occurs. Some N atoms are moved slightly closer to the surface or slightly closer to the underlying TaN slab for some of the geometries, however there are never more than 48 N atoms per slab layer.

Adsorption of Cu_2 in the "close" and "apart" geometries shows an initial preference towards association on all

Table 3: Binding energies (Chapter 3, Equation 38), metal-substrate interaction energies (Chapter 3, Equation 39) and metal-metal interaction energies (Chapter 3, Equation 40) for Cu₂ and Cu₄ adsorptions on Co-TaN surfaces.

Surface	Cu _n	Cluster Geometry	E _{bind} (eV/Cu)	E _{metal-substrate} (eV/Cu)	E _{metal-interact} (eV/Cu)
$\overline{\text{Co}}^{25}$	$\overline{\text{Cu}}_1$	A	-3.01		
		A1	-3.11		
		B	-2.59		
		B'	-3.34		
		C	-3.28		
		D	-2.23		
		D'	-2.40		
	Cu ₂	close	-2.93	-3.00	0.07
		apart	-3.33	-3.67	0.34
	Cu ₄	line	-2.92	-3.06	0.14
		rhombus	-3.00	-2.71	-0.30
		tetrahedron	-2.90	-1.70	-1.20
$\overline{\text{Co}}^{50-S}$	Cu ₂₉		-3.16	-0.86	-2.30
	$\overline{\text{Cu}}_1$	A	-4.61		
		B	-3.82		
		C	-2.43		
		D	-2.63		
		E	-2.40		
	Cu ₂	close	-4.54	-4.23	-0.31
		apart	-3.56	-3.55	-0.01
	Cu ₄	line	-3.83	-3.06	-0.77
		rhombus	-3.61	-2.10	-1.51
		tetrahedron	-3.29	-1.88	-1.41
$\overline{\text{Co}}^{50-P}$	$\overline{\text{Cu}}_1$	A	-3.73		
		A1	-2.81		
		B	-4.53		
		C	-3.55		
		D	-2.38		
		D'	-4.04		
	Cu ₂	close	-6.18	-4.26	-1.92
		apart	-4.59	-4.58	-0.01
	Cu ₄	line	-4.82	-3.91	-0.91
		rhombus	-3.69	-2.47	-1.22
		tetrahedron	-3.26	-1.89	-1.37
	Cu ₂₉		-3.38	-1.06	-2.32
$\overline{\text{Co}}^{100}$	$\overline{\text{Cu}}_1$	A	-4.56		
		B	-3.93		
		C	-4.76		
		D	-3.68		
		E	-3.51		
	Cu ₂	close	-4.50	-4.02	-0.48
		apart	-4.42	-4.41	-0.02
	Cu ₄	line	-4.34	-4.09	-0.25
		rhombus	-4.07	-3.21	-0.86
		tetrahedron	-4.10	-3.27	-0.83

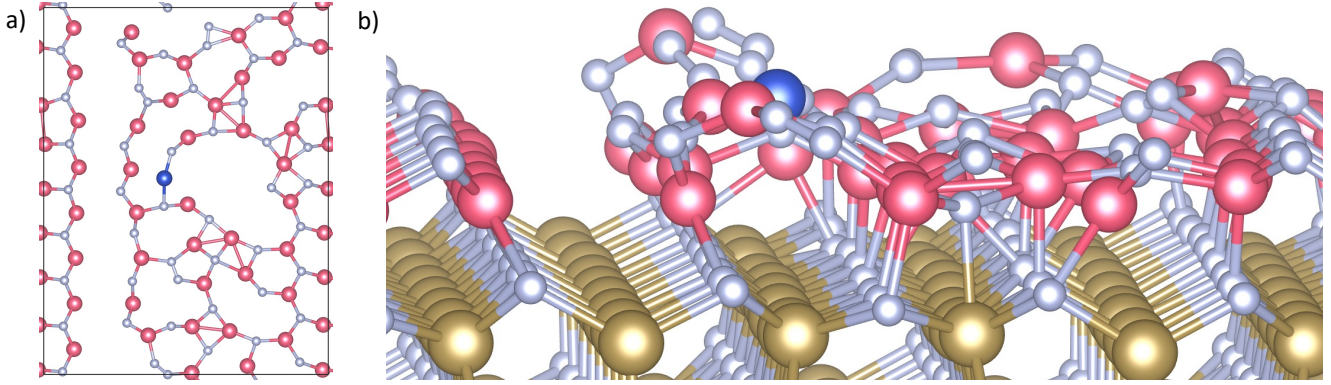


Figure 10: a) Top view of the Co-N toplayer of the Co^{100} slab after single Cu adsorption to show the large gaps in the surface caused by rearrangements and layering of Co. b) Side view of the same Co^{100} surface with single atom adsorption highlighting the agglomeration of CoN.

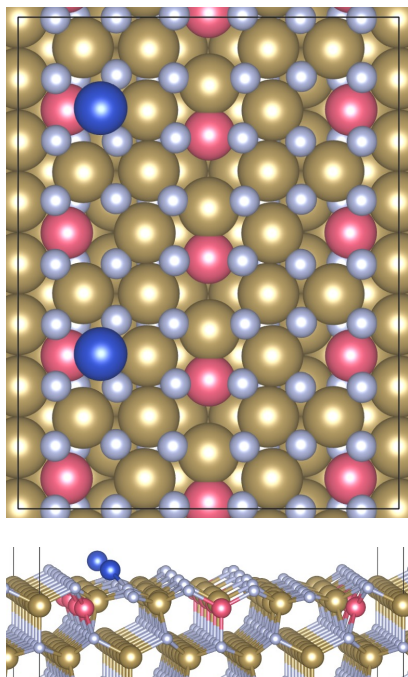
surfaces except Co^{25} , where separated atoms are preferred, as shown in Figure 11. On the two Co^{50} surfaces, the difference in stability between close and apart geometries is largest, being ca. 1 eV for Co^{50-S} and ca. 1.5 eV for Co^{50-F} . For the Co^{50-S} surface, this contrast between the two adsorption modes arises from the geometry differences between the two structures. As seen in Figure 11C, the Cu atoms migrate into the surface which increases the metal-substrate interaction. This does not occur when the atoms are adsorbed apart from each other. On the Co^{50-F} surface, the atoms incorporate into the surface layer for both adsorption modes. Incorporation enhances the stability of adsorbed Cu, since it has more metal-substrate interactions and helps to explain why Cu_2 adsorption on this surface is more favourable than on the other surfaces. Due to this, both structures have very similar metal-substrate interactions (see Table 3). The stability difference between both structures is thus caused solely by the metal-metal interaction of -1.92 eV between the two Cu atoms in the close arrangement.

The Co^{25} surface continues to behave differently compared to the other three Co-doped TaN surfaces for Cu_4 adsorption. Here, the rhombus configuration is most favourable, while Co^{50-S} , Co^{50-F} and Co^{100} prefer the line configuration, which has the fewest Cu-Cu interactions. On Co^{50-F} and Co^{100} , the stability of the line configuration is further enhanced by incorporation into the surface layer by the gaps formed next to the Co dopants. However, as one of the atoms moved slightly away for the rhombus geometry on Co^{25} (see Figure 12A side view), this geometry has fewer Cu-Cu interactions than any of the other Cu_4 geometries. This indicates that on all Co-doped TaN surfaces Cu_4 adsorption is driven by minimising the Cu-Cu interaction, which is supported by the metal-metal interactions shown in Table 3. Here, the apart and line geometries have the weakest metal-metal interaction energies on all surfaces. It is of note that the metal-metal interaction of the rhombus on Co^{25} is the weakest metal-metal interaction for a rhombus on all surfaces. However, the metal-metal interaction for the line configuration on Co^{25}

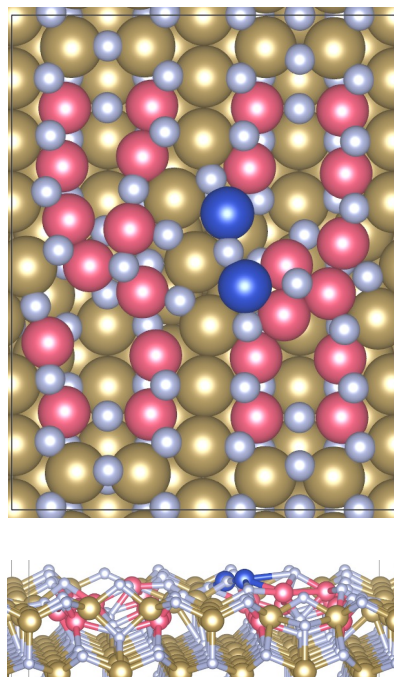
is positive. This means that while the rhombus is most favourable in terms of overall adsorption energy, the line configuration has the most favourable metal-substrate interaction.

Considering the competition between metal-substrate and metal-metal interaction for all four Co-doped TaN surfaces shows that the metal-substrate interaction is stronger than the metal-metal interaction for all geometries. The most significant differences between the two energy contributions occurs for Co^{25} and Co^{100} , while the magnitude of the interactions is somewhat more competitive for Co^{50-S} and Co^{50-F} . Co^{25} has the weakest metal-metal interactions of all four surfaces. In fact, the metal-metal interactions for the close, apart and line geometries are positive, indicating that the incorporation of adatoms into the surface layer is able to prevent interaction between the Cu atoms. Combined with the favoured separated geometries, this makes Co^{25} a candidate for our target combined barrier/liner material. Co^{50-F} is also a candidate, showing some of the strongest Cu binding energies and metal-substrate interactions, although all surfaces should promote wetting based on the favourable metal-substrate interactions compared to metal-metal interactions. While Co^{100} shows both strong metal-substrate interactions and weak metal-metal interactions, the distortion of the surface CoN layer indicates that this surface might not be suitable to promote a smooth Cu film, due to the large gaps in the surface that arise from surface distortion, during Cu adsorption providing opportunities for enhanced metal-substrate interactions. An example of this is observed for the tetrahedron, which flattens due to incorporation of atoms into this large gap (see Figure A52 in Section A4.4.2 of the Appendix).

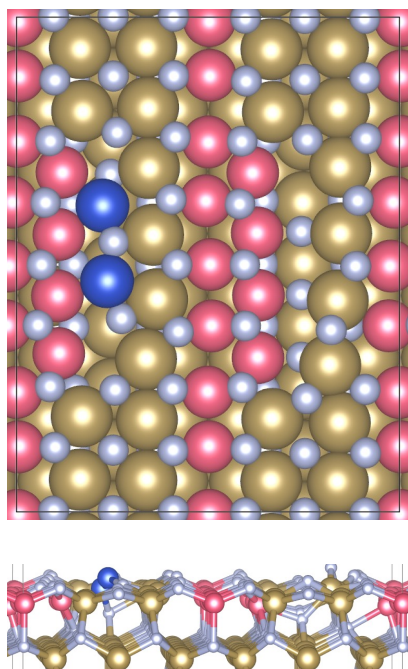
(A) Co²⁵ apart $E(bind) = -3.33 \text{ eV}$



(B) Co^{50-S} close $E(bind) = -4.54 \text{ eV}$



(C) Co^{50-F} close $E(bind) = -6.18 \text{ eV}$



(D) Co¹⁰⁰ close $E(bind) = -4.50 \text{ eV}$

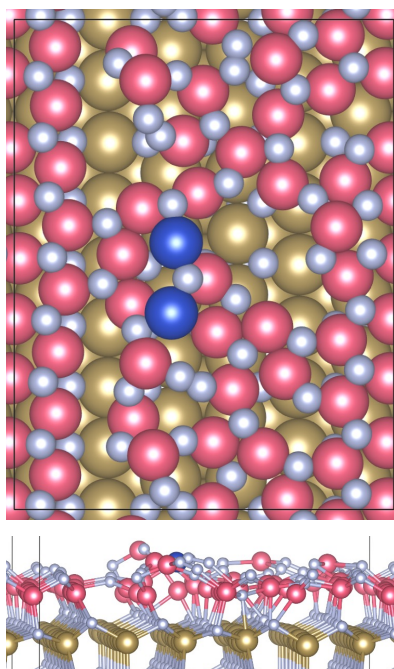
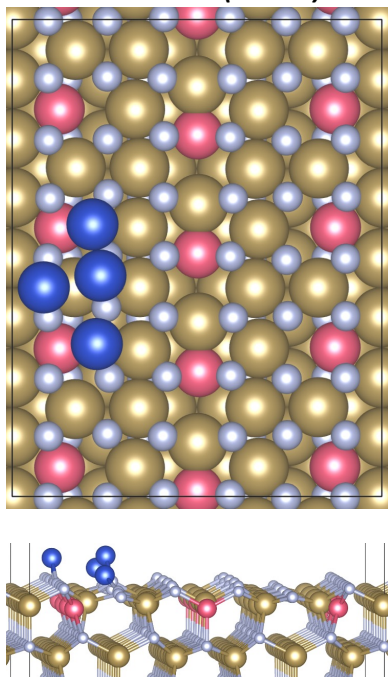
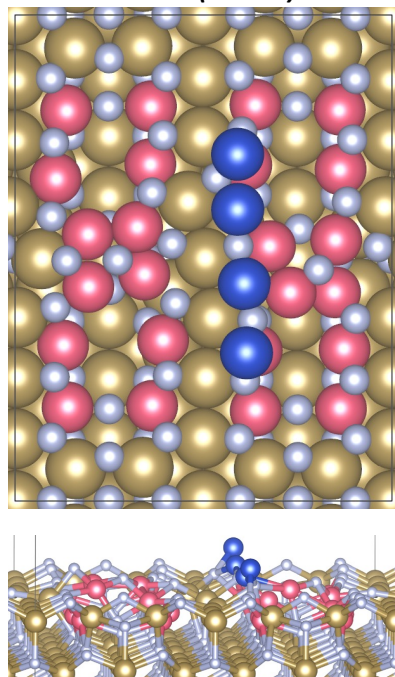


Figure 11: Most favourable adsorption geometries for Cu₂ on Co-doped TaN.

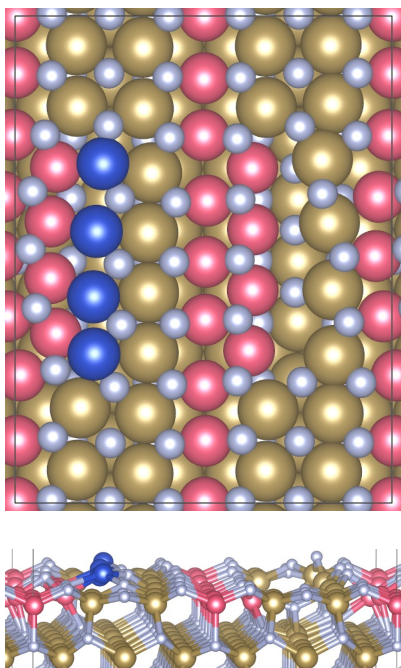
(A) Co²⁵ rhombus $E(\text{bind}) = -3.00 \text{ eV}$



(B) Co^{50-S} line $E(\text{bind}) = -3.83 \text{ eV}$



(C) Co^{50-F} line $E(\text{bind}) = -4.82 \text{ eV}$



(D) Co¹⁰⁰ line $E(\text{bind}) = -4.34 \text{ eV}$

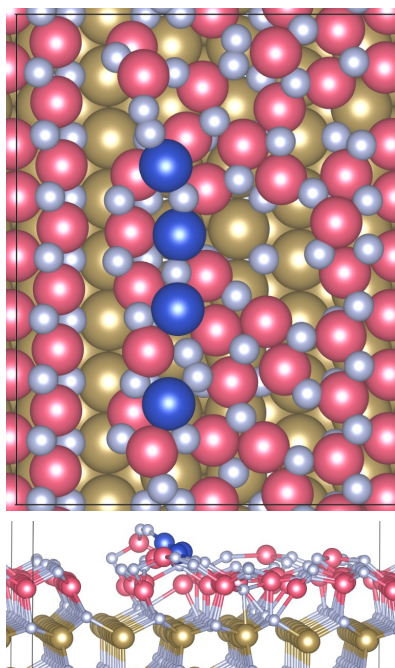


Figure 12: Most favourable adsorption geometries for Cu₄ on Co-doped TaN.

6.6 Ab initio MD of Cu rhombus on 25%, 50% and 100% Co-doped TaN

Both Co^{50-S} and Co^{100} were found to be thermally unstable in this stoichiometry during the aiMD simulation. Co^{50-S} loses N_2 after 0.5 ps at 500 K, while Co^{100} loses five N atoms after 0.5 ps at 500 K. Geometries at the relevant snapshot are shown in the Appendix Section A4.7, Figure A61. Table 4 shows formation energies, types of unit cell and lattice parameters for selected Ta, Co, Ru and W nitrides. CoN is the cobalt nitride stoichiometry with the most favourable formation energy, [42] closely followed by Co_2N . [43] Given that CoN is the most favourable stoichiometry, the distortion of the Co^{100} surface and its thermal instability likely do not arise from the particular stoichiometry. However, bulk CoN has a cubic unit cell and bulk TaN has a hexagonal unit cell. This leads to different coordination environments for Co when doped into TaN and in bulk CoN. Additionally, there is a lattice mismatch between CoN and TaN. Bulk CoN has lattice parameters of $a = b = c = 3.01 \text{ \AA}$, while bulk TaN has lattice parameters of $a = b = 5.23 \text{ \AA}$, $c = 2.93 \text{ \AA}$. The combination of lattice mismatch and different shapes of unit cell are likely the largest contributing factors to the instability of the Co^{100} surface, along with the different ionic radii of Co and Ta. Similarly, Co dopants in the Co^{50-S} surface are all concentrated in two areas. As such, these are essentially areas of 100% Co doping and thus show the same instabilities as Co^{100} . Additional analysis on the stable metal nitrides of Ta, Ru, Co and W and the effect this has on the 100% doped surfaces is detailed in Section A4.9 of the Appendix.

Co^{25} and Co^{50-F} are both thermally stable and the geometry of the rhombus before and after the aiMD run are shown in Figure 13. The results from the aiMD simulations also support our initial hypothesis that these surfaces should promote wetting. On Co^{25} , one of the Cu atoms separates from the cluster and incorporates into the surface layer, as shown in Figure 13A. This is accompanied by some surface distortions, which cause a Ta atom be pushed partially out of the surface layer. The effect such distortions would have on surface roughness and stability require a much larger model and are outside the scope of this study. The other three atoms remain at their original positions from the relaxed starting geometry, however a single atom migrating away from the cluster supports that less metal-metal interactions are preferred. Similarly, on Co^{50-F} , the rhombus rearranges into a line configuration

Table 4: Materials Data on various metal nitrides based on experimental crystal structures. *No experimental crystal structures are currently available for ruthenium nitrides. ^aLow-spin. ^bHigh-spin.

Metal Nitride	Formation Energy (eV/atom)	Unit Cell	Lattice Parameters ($\text{\AA}$)	Metal Ionic Radius ($\text{\AA}$)
TaN [44]	-1.36	hexagonal	$a = b = 5.23, c = 2.93$	0.72
RuN* [45]	0.07	cubic	$a = b = c = 3.23$	0.62
CoN [42]	-0.09	cubic	$a = b = c = 3.01$	$0.55^a, 0.61^b$
Co_2N [43]	-0.06	orthorhombic	$a = 2.84, b = 4.29, c = 4.54$	$0.55^a, 0.61^b$
WN [46]	-0.26	hexagonal	$a = b = 2.88, c = 2.91$	0.66
W_2N_3 [47]	-0.32	hexagonal	$a = b = 2.92, c = 15.84$	0.66

along a row of Co dopants, as shown in Figure 13B. This is likely caused by the strong interactions between Co and Cu, allowing the Co dopant to act as a nucleation site in the surface, similarly to Ru dopants as discussed in Chapter 4.

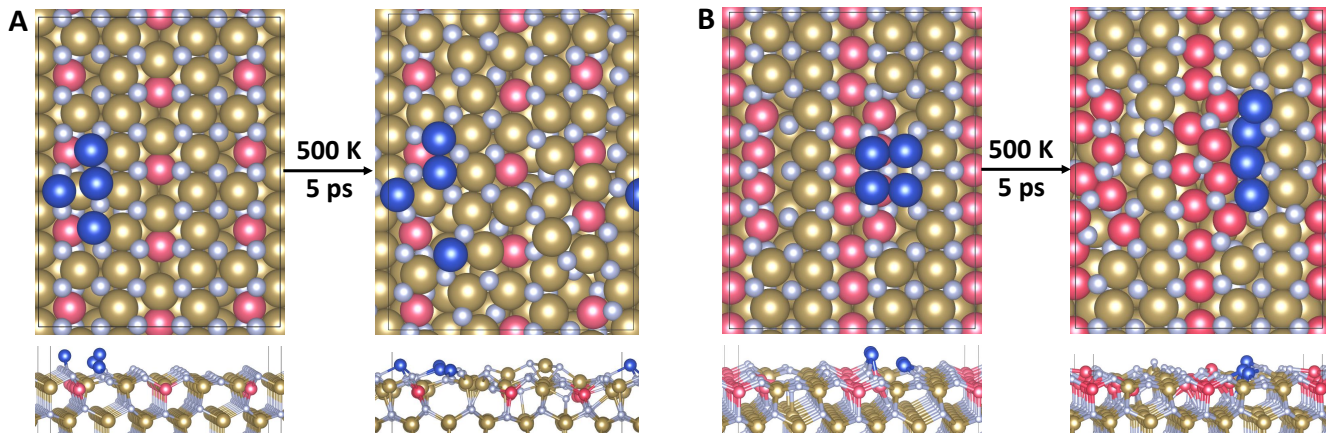


Figure 13: A: Cu_4 rhombus before and after 5 ps of aiMD at 500 K on Co^{25} . B: Cu_4 rhombus before and after 5 ps of aiMD at 500 K on Co^{50-F} .

6.7 Cu_{29} on Co-doped TaN

In order to further confirm our predictions of film morphology, we chose to study Cu_{29} on the two most promising surfaces, Co^{25} and Co^{50-F} , due to their thermal stability and favourable metal-substrate interactions. As on other surfaces, we observe transition from the single layer of Cu_{29} to a two-layered structure on both surfaces. On Co^{25} , 7 Cu atoms move to the second layer, while on Co^{50-F} 6 atoms migrate to form a second layer, as shown in Figure 14. This reduced number of atoms in the second layer compared to Cu_{29} on W-doped TaN shows that Co doping is better at preventing upward migration, as expected given the more favourable adhesion between Cu and Co as compared to Cu and W. As for W, the metal-metal interaction is much more favourable than the metal-substrate interaction for Cu_{29} on Co-doped TaN (Table 3). This confirms once more that these energies are most representative of the final film morphology when computed for small metal clusters of up to 4 atoms.

A 5 ps aiMD run at 500 K shows that more Cu atoms begin to migrate into the second layer on Co^{25} , however no migrations to form a third layer occur. Additionally, we observe a Cu atom detaching from the main Cu cluster and migrating away towards a Co dopant, while another migrates along the edges of the cluster, indicating mobility of Cu atoms over the surface. Such Cu atom detachment from the Cu_{29} structure was only observed on two other surfaces, the 1 ML Ru passivated surface discussed in Chapters 4 and 5 and the W^{25} surface discussed in

Section 6.4 of this chapter. The favourable metal-substrate interactions, along with the lack of formation of further Cu layers and the Cu atoms that migrate away from Cu₂₉ suggest that 25% Co-doped TaN is a strong candidate for a combined barrier/liner material.

The aiMD run for Cu₂₉ on Co^{50-F} shows that this surface can also promote 2D growth of Cu, see Figure 14B. Cu atoms appear quite mobile on the surface and split off from the main structure in smaller clusters. One such structure begins to incorporate into the surface gaps and resembles the geometry of the Cu₄ rhombus on Co^{50-F}, shown in Figure 13B. There is an equivalent surface gap underneath the main Cu structure, however atoms do not incorporate here. This indicates that the regular Cu structure formed here is favoured compared to incorporation into the surface when there is a large number of Cu atoms.

These results additionally show that Cu preferentially migrates towards the areas of Co dopants in the surface, as observed for Cu₂ and Cu₄ adsorption on Co-doped TaN. In Chapter 4 we found that Ru also acted as a nucleation site for Cu films, however we did not observe such preferential migration during the aiMD runs on the equivalent Ru-doped surface in Chapter 5. While a smooth film can likely be achieved with 50% Co doping, for interconnect applications a surface like Co²⁵, where the dopants are more distributed should have an advantage in promoting growth of a spread out, 2D Cu film. However, it is possible that area selective growth of Cu on CoN could be achieved by combining CoN and TaN. Based on our results, atoms should selectively migrate towards the Co-rich areas. The stronger adhesion of Cu on CoN compared to TaN also means that it could be possible to selectively remove any unwanted Cu atoms in the Ta-rich areas of the surface.

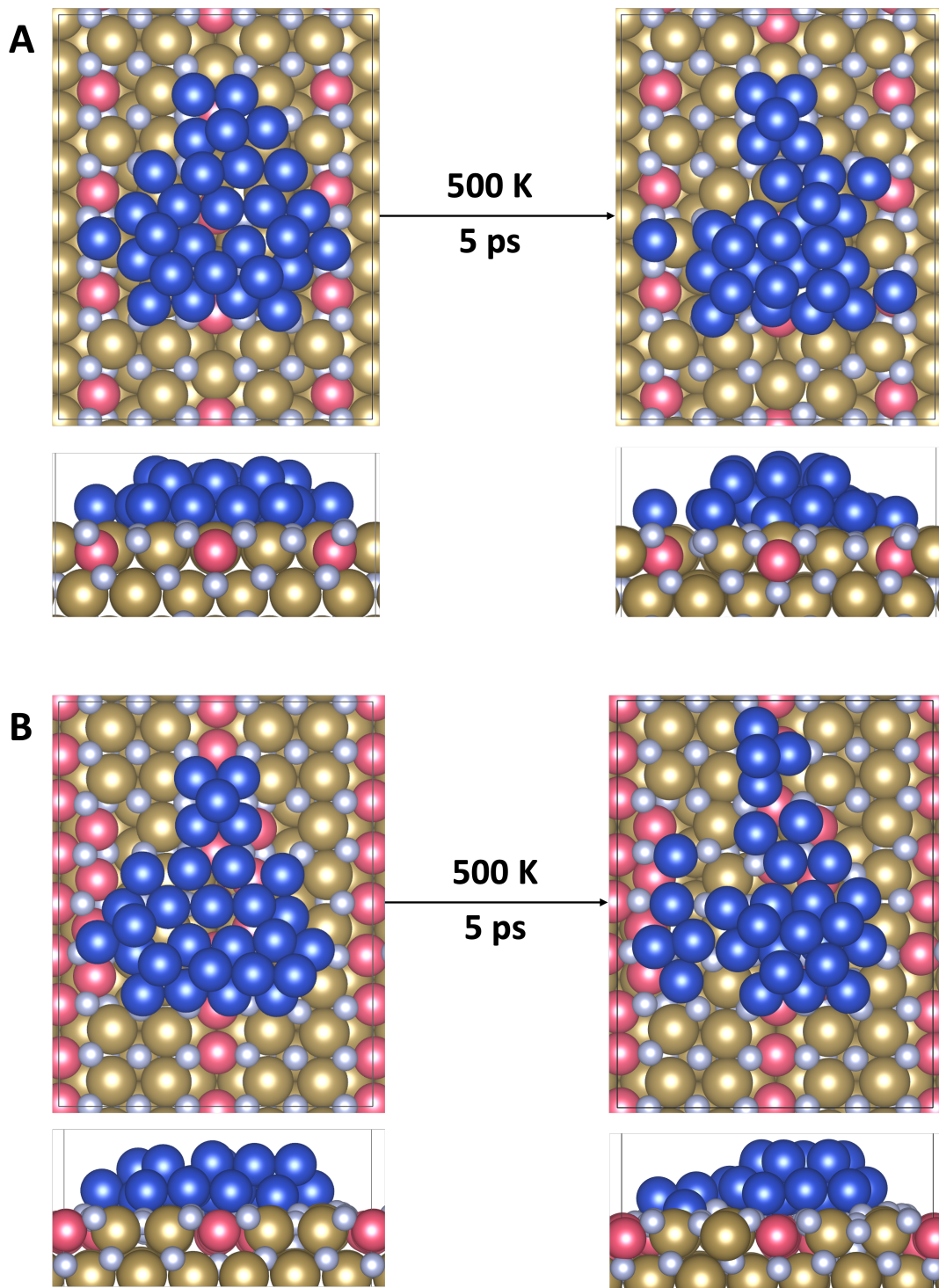


Figure 14: A) Structure of Cu_{29} after 0 K relaxation (left panel) and 5 ps at 500 K (right panel) on Co^{25} . B) Structure of Cu_{29} after 0 K relaxation and 5 ps at 500 K (right panel) on Co^{50-F} .

6.8 Bader Charges and Density of States

The computed Bader charges for each Cu atom are shown in the Appendix, Section A4.3 (Cu on W-doped surfaces) and A4.6 (Cu on Co-doped surfaces).

Ta and N have 5 valence electrons, W has 6 valence electrons, Ru has 8 valence electrons, Co has 9 valence electrons and Cu has 11 valence electrons.

S-type and F-type Ta and dopant atoms are oxidised, but given their different coordination environments the magnitudes of Bader charges are different. On bare TaN, S-type Ta has a Bader charge of 3.0 electrons and F-type Ta has 3.6 electrons. W dopants affect the oxidation of Ta atoms in the surface only slightly. There is no change to S-type Ta. In the presence of F-type W dopants, as occurs on W₂₅, F-type Ta atoms are more oxidised with Bader charges of 3.4 and 3.5 electrons. No changes are observed for W^{50-F} or W^{50-S}, as there are no F-type Ta atoms on the former surface and no F-type W dopants to affect the Ta atoms on the latter. Co, like Ru, modifies the oxidation states more strongly than W. Here, there is a slight change to the oxidation of S-type Ta atoms, which are oxidised with a Bader charge of 2.9 electrons, while F-type Ta atoms are oxidised with a Bader charge of 3.2 electrons. This occurs for Co²⁵, Co^{50-S} and Co^{50-F}, and is also observed for the equivalent Ru surfaces. As there are no surface Ta atoms in Co¹⁰⁰, no changes to the oxidation state of the Ta atoms in the remaining slab are observed. The oxidation state of the dopants also varies depending on whether they are S-type or F-type. Ru atoms have charges of 7.1 or 7.5 electrons for S- and F-type respectively. S-type W has a charge of 4.3 electrons, while F-type W has a charge of 4.9 electrons. This indicates that F-type W is lightly oxidised. The charge difference for Co atoms is smaller, with 8.5 electrons for S-type Co and 8.4 electrons for F-type Co. W and Co atoms near an adsorbed Cu atom are slightly less oxidised.

As for Cu systems discussed in previous chapters, Cu atoms on W-doped surfaces are oxidised when bound to the surface, otherwise they remain metallic. Cu atoms with a Bader charge smaller than 10.8 electrons are considered oxidised to Cu⁺, while metallic Cu atoms have Bader charges of 10.9 to 11.0 electrons. The details of Bader charges depend on the adsorption mode and geometry. Bader charges for Cu atoms on W-TaN are shown in the Appendix, Table A13. The range of Bader charges observed for Cu is similar on TaN, Ru-TaN and W-TaN. Bader charges change depending on the Cu adsorption geometry, but are not affected by the W content of the surface, indicating that the charge is affected by interactions with other Cu atoms instead of interactions with the surface. This also holds true for the Cu₂₉ geometry, where those atoms adsorbed on the surface are partially oxidised with Bader charges of 10.7 electrons and the second layer of Cu atoms remains metallic, with Bader charges around 11.0 electrons.

We find that Cu atoms tend to be more oxidised on the Co-doped surfaces than on Ru- and W-doped TaN. This is particularly obvious for single Cu atom adsorption, where atoms have Bader charges as small as 10.0 electrons, which would be equivalent to a Cu^{2+} oxidation state, while adsorption geometries with Cu-Cu interactions have typical Bader charges of 10.5 to 10.6 electrons, which is equivalent to Cu^+ . [48–50] Most of the oxidised Cu atoms with smaller Bader charges have ca. 10.3 electrons and are observed for single atoms on Co^{25} , Co^{50-F} and Co^{100} , the apart geometries on Co^{25} and Co^{100} and the line configuration on Co^{50-F} . Compared to the other Co-doped surfaces, atoms have a larger Bader charge on Co^{50-S} , where all single atom adsorptions are around 10.5 electrons. The Cu atom adsorbed at site E (see Figure A46 of the Appendix) makes a slight exception. It is incorporated into the surface like atoms adsorbed at sites A and B, however it is less oxidised than any other Cu atom with 10.8 electrons. This is most likely caused by the lack of coordination to any N atoms at this site.

At first it appears that there is a correlation between the degree of oxidation (Bader charge) and the distance to the surface. For example, on the Co^{50-F} surface, a shorter distance to the surface as observed for Cu adsorption at sites A, A' and C causes a stronger oxidation of 10.3 and 10.4 electrons. However, this does not hold for the Co^{25} surface, where a Bader charge of 10.5 electrons is associated with adsorption at sites D and D'. Here the Cu atom is at the longest distance to the surface with a single Cu-N bond. In contrast, a Bader charge of 10.4 electrons is observed at site B which has a similar distance to the surface. Closer analysis shows that it is the interaction with N atoms that controls the magnitude of the Bader charge on these surfaces. The Cu atoms at site D and D' on the Co^{25} surface are interacting with only a single N atom, while the Cu atom at site B is bridged between two N atoms and two Ta atoms. This also explains why there is no relation between the proximity of a Co dopant to the Cu atom and the magnitude of the Bader charge. It could also explain the strong oxidation of the Cu atom at site B' on Co^{25} , which has formed bonds to two N atoms, but is also close to a further two N atoms due to the small surface gap created by the adjacent Co dopant. See Figure A45 in the Appendix for the geometries of single Cu atoms on Co^{25} . Correlation between the coordination with N and the oxidation of the metal atoms also explains the different charges for S-type and F-type surface atoms.

Additionally, we find that Cu atoms that are not interacting with the surface, ie the top atom in the tetrahedral geometry, remain metallic, only on Co^{25} and Co^{50-F} . On Co^{100} , there are no Cu atoms that do not interact with the surface, as Cu_n takes a 2D flat structure with all but one Cu atom incorporated into the surface layer (see Figure A52 of the Appendix). As oxidised Cu is not conducting, it is important to know whether or not Cu will remain metallic to ensure a conducting Cu layer. However, similar to other geometries, any Cu atoms that do not interact with the surface are metallic, this is not a concern for these systems. As Co^{100} has already been discounted as a potential barrier/liner material due to its surface distortion and thermal instability, determining the oxidation

of Cu atoms in a layered or 3D structure is outside of the scope of this study. On Co^{50-S} the atop atom in the tetrahedral geometry has a Bader charge of 10.8 electrons, which is partially oxidised. One of the base atoms does not have a bond to the surface due to the nearby surface gap, see Appendix, Figure A50. This Cu atom also has a Bader charge of 10.8 electrons, indicating that neither atom is fully metallic, however they are not fully oxidised either. Given the unique geometry of this structure, it is likely that in a larger Cu geometry, the atop Cu atoms would be metallic. However, given the thermal instability of this surface, which makes it unsuitable as a combined barrier/liner material, the resistivity of Cu on Co^{50-S} is not a major concern.

Atoms in the Cu_{29} structure are not as oxidised on Co-doped TaN as the smaller Cu_1 , Cu_2 and Cu_4 structures. On Co^{25} , for example, we observe a similar range of Bader charges compared to Cu_{29} on Ru- and W-doped TaN. Bader charges range from 10.72 to 11.01 electrons. Once more, the Cu atoms directly interacting with the surface are partially oxidised, while the Cu atoms that do not interact with the surface remain metallic. This indicates that as for Ru- and W-doping Cu on Co-doped TaN should remain conducting.

Density of States (DOS) plots for the most favourable Cu_4 adsorptions on Co- and W-doped surfaces are shown in Figure 15. The remaining DOS plots for all other 1 to 4 atom structures are shown in Sections A4.2 (W-doped TaN) and A4.5 (Co-doped TaN) of the Appendix. The contributions of Cu and W to the total DOS are quite small given that there are fewer Cu and W atoms compared to Ta and N atoms. However, the DOS shows metallic character dominated by TaN.

The contribution of Co to the total DOS is much larger than that of W, however the contribution of Cu remains small due to the small number of Cu atoms. All DOS plots indicate a metallic system, confirming that the presence of a Co dopant does not change the metallic character of TaN. Like Cu on W-doped TaN, Cu on Co-doped TaN should have reasonable resistivity overall, despite the strong oxidation of atoms at the surface-Cu interface observed for small Cu clusters.

Based on the DOS plots for up to 4 atoms and DOS plotted for Cu_{29} on Ru-doped TaN we do not expect any significant changes with the addition of more Cu atoms. For this reason we did not plot the DOS for Cu_{29} on Co- and W-doped TaN. As additional layers of Cu remain metallic and the DOS shows that the whole surface slab is metallic, the system should have reasonable resistivity for Cu interconnects, although experimental measurements are needed to confirm this.

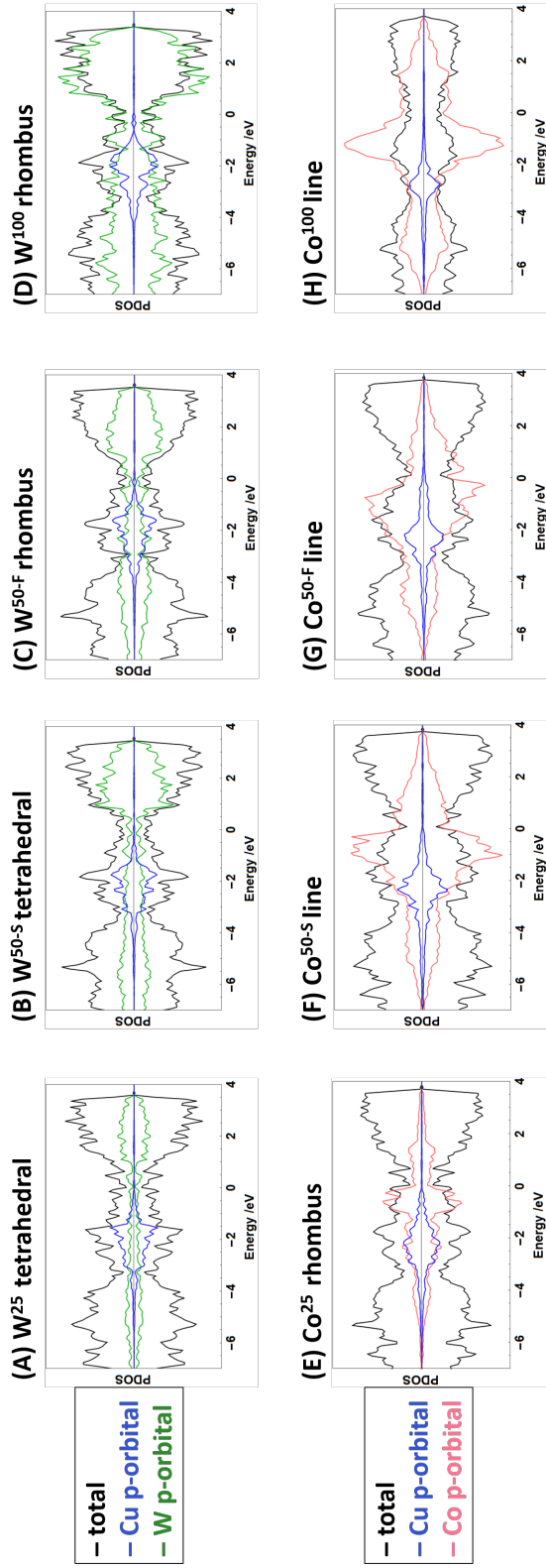


Figure 15: Density of States plots for the most favourable Cu₄ adsorptions on all Co- and W-doped surfaces. Black - total DOS, blue - Cu p-orbital contribution, green - W p-orbital contribution, pink - Co p-orbital contribution.

6.9 Conclusion

In this chapter we studied the effect of different dopants on the TaN surface and its interactions with different Cu structures. By applying knowledge gained from our work in Chapters 4 and 5 we were able to select Cu structures that would yield the maximum amount of information on 2D vs 3D stability and the competition between metal-substrate and metal-metal interaction which drives the growth mechanism. Additionally, comparing the conclusions drawn based on results from different sizes of Cu cluster we are able to evaluate the limits of our models. We find that metal-metal vs metal-substrate interactions can be a useful indicator of film morphology for small Cu clusters, however they are no longer indicative when computed for the Cu₂₉ model. We find that W¹⁰⁰ acts as a liner material, however given the weaker interactions with Cu, the main advantage of this surface compared to Ru- and Co-doped TaN is in the lack of surface rearrangements. On W²⁵, the Cu₂₉ model remains 2D as predicted based on the favourable metal-substrate interactions, however the atoms form a wire-like structure and it is unclear how this might affect the morphology of a larger film. Additionally, we find that 25% Co doping is sufficient to promote a 2D Cu morphology, due to the strong interactions with the surface, while the Co^{50-F} surface shows selective migration of Cu to Co-rich areas.

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Chapter 7: Small Cu, Co and Ru clusters (1 to 4 atoms) on 2D MoS₂

In Chapter 2 we reviewed the potential use of MoS₂ as a novel barrier material in advanced interconnects. However, since the first exfoliation of graphene in 2004 [1], 2D materials and in particular MoS₂ have garnered interest across all different applications of materials science beyond electronics. These applications include batteries [2, 3], sensors [4–7], catalysis [8–10], solar cells [11–13] and photonics [14, 15]. This wide interest is mainly due to the fact that exfoliating a single layer from one of these materials can often change the material properties compared to the bulk. For example, bulk MoS₂ has an indirect band gap, while single layer MoS₂ has a direct bandgap. [16] Additionally, an inherently ultrathin material can be essential in any application that requires the manufacturing of devices with extremely small feature sizes and could help to avoid defects caused by etching or CMP of materials to the desired thickness. MoS₂ quickly became one of the most studied 2D materials, largely because it occurs naturally and has more favourable properties for certain applications compared to graphene [14, 17].

Interest in such a wide range of areas means that there has been a lot of investigation into fundamental interactions between 2D materials and other elements, in particular metals. While experimental studies tend to focus on incorporating the 2D material into a device for a particular application or on optimising growth methods [18–21], theoretical studies tend to focus on interactions between the chosen 2D material and a single atom of a variety of elements. The main interest is in transition metals [9, 22–27], with some interest in main group metals [28–30] and non-metals such as H, B, C, O and N [30]. While there is some work on larger metal structures [22, 23], this focus on single atom adsorption reveals a knowledge gap in terms of understanding the nucleation and growth of metal thin films on 2D materials. For this reason we chose to address this in our research, instead of focusing solely on the application of MoS₂ in Cu interconnects.

In this chapter we present our work on predicting the morphology of small metal clusters with up to 4 atoms on a ML of MoS₂. As S vacancies occur frequently in MoS₂, [31] we also consider the adsorption of 1 and 4 metal atoms on a ML with a single S vacancy. The metals of interest are Cu, Co and Ru, chosen especially for their use

as interconnect metals in advanced CMOS devices. Both Ru and Co have been shown to require a liner or diffusion barrier and as for Cu, MoS₂ presents an excellent ultrathin alternative. [32–35] Other applications of Ru and Co include Pt-free hydrogen evolution catalysts [36–40]. Predicting the likely morphology of the metal thin film allows for selection of the most beneficial material combination for the needs of each application.

The results presented in this chapter were published as two papers, **”DFT calculations of the structure and stability of copper clusters on MoS₂”**, <https://doi.org/10.3762/bjnano.11.30>, and **”Prediction of Co and Ru nanocluster morphology on 2D MoS₂ from interaction energies”**, <https://doi.org/10.3762/bjnano.12.56>, in the Beilstein Journal of Nanotechnology. [41, 42]

Three different adsorption sites for a single atom, denoted as atop_S, atop_Mo and hollow are present on the MoS₂ monolayer, as shown in Figure 1. Site atop_S has a metal atom adsorbed directly atop an S atom. Site atop_Mo has a metal atom binding to 3 S atoms directly above an Mo atom and site hollow has a metal atom binding to 3 S atoms, but with no Mo atom underneath.

To study how Cu, Co and Ru atoms begin to nucleate into a film on the MoS₂ ML, we adsorb Cu_n, Co_n and Ru_n species with 1, 2, 3, and 4 atoms on MoS₂. The competition between 2D and 3D structures is of particular interest when predicting the morphology of the thin film. A structure is considered 2D when all metal atoms are bound directly to the MoS₂ ML. For 3D structures, at least one of the metal atoms is bound to other metal atoms, but not to MoS₂.

In the following sections we elaborate how factors influencing structure stability vary as the cluster size increases. Such factors include presence or absence of metal-metal bonds, symmetrical versus asymmetrical addition, incorporation of atoms into the ML, adsorption site and changes to stability in the presence of an S vacancy. The results presented in this chapter were published in two separate papers, one focusing on Cu and the other on Co and Ru. For this reason, we discuss first Cu and then Co and Ru together, followed by a comparison between all three metals. Section 7.1 covers the adsorption of up to four Cu atoms on pristine monolayers of MoS₂, Section 7.2 shows the results for small Co_n and Ru_n structures, Section 7.3 details the results for metal adsorption on the defective ML and Section 7.4 discusses the similarities and differences in the behaviour of the three metals. Our findings are supported through analysis of geometry variations, bond lengths, adsorption, addition and metal-metal interaction energies and Bader charges.

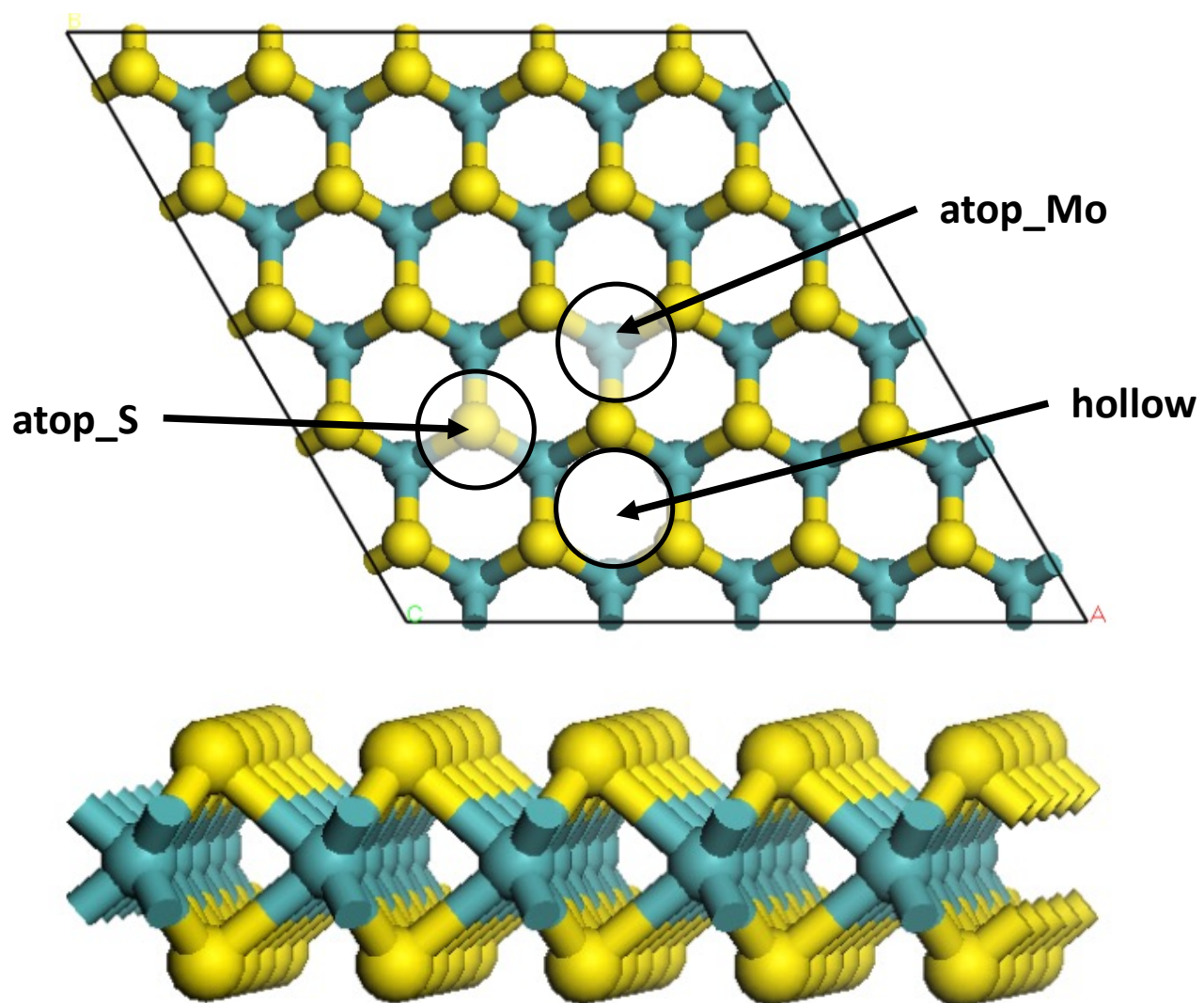


Figure 1: Adsorption sites on MoS₂ monolayer.

7.1 Cu_n on pristine MoS₂

To investigate how Cu begins to nucleate on a monolayer of MoS₂, we start by adsorbing small Cu_n ($n=1,2,3,4$) species on an MoS₂ monolayer. All binding energies for the different structures calculated from Equation 37 in Chapter 3 are shown in Table 1. Metal-metal interaction energies calculated with Equation 40 are shown in Table 3 and addition energies calculated using Equation 45 in Chapter 3 are shown in Table 2.

All relaxed Cu_n geometries with 1,2,3 and 4 Cu atoms are shown in Figure 2, Figure 3, Figure 4 and Figure 5, respectively. The binding energies shown in these images are the binding energies per atom from Equation 37 in Chapter 3.

When a single Cu atom adsorbs at each of the three adsorption sites, Cu binds exothermically with adsorption energies of -0.81, -1.32 and -1.18 eV at sites **atop_S**, **atop_Mo** and **hollow**, respectively. Site atop_Mo is the most favourable site for a single Cu atom. This is most likely due to the particular geometry, as it is a continuation of the MoS₂ structure, with Cu above an Mo site (see Figure 2C). This order of stability for single atom adsorption matches results previously published by Li [28] and Wang [24] for Cu adsorption on MoS₂. The geometries for single Cu adsorption are shown in Figure 2.

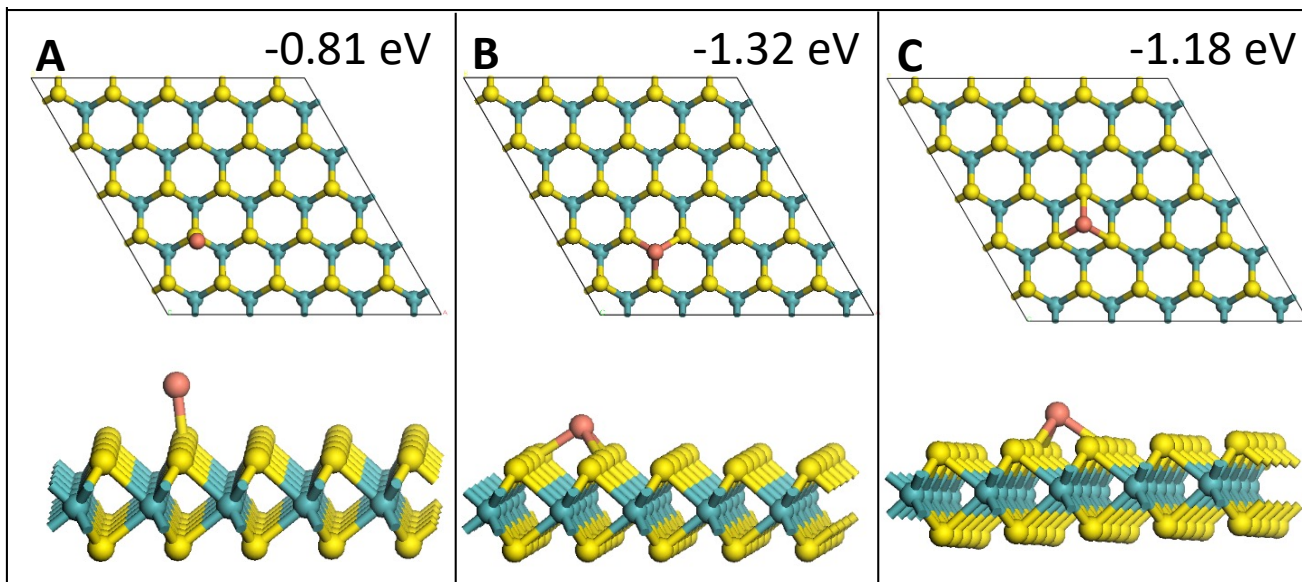


Figure 2: Relaxed structures after adsorption of 1 Cu on monolayer at sites atop_S (A), atop_Mo (B) and hollow (C). Cu atoms are shown in orange throughout the chapter. All other atoms follow the colour code in Chapter 3.

Two Cu adatoms were adsorbed in three different configurations: as a Cu₂ species with Cu atoms at adjacent equivalent sites, at two Cu adatoms at separated equivalent sites and as two Cu adatoms at adjacent but non-

equivalent sites. At site atop_S, whether the Cu atoms adsorb as a Cu₂ or as two separated adatoms makes little difference for the stability; the difference in the binding energy is only 0.05 eV. The addition energy of the second Cu atom is similar to the binding energy in both cases, indicating that adding a second atom yields approximately the same energy gain as the adsorption of the first atom. For adsorption of two Cu atoms at sites atop_Mo and hollow on the MoS₂ ML, it is more favourable by up to 0.3 eV to adsorb as Cu₂ compared to separated adatom adsorption. This is also reflected in the addition energy for Cu₁ to Cu₂, as this is slightly more negative than both the binding energy per atom for this configuration as well as the binding energy of a single atom at each site.

Out of the non-equivalent Cu adatom adsorption modes, Cu₂ as a combination of a Cu adatom at site atop_Mo and hollow was most favourable, because sites atop_Mo and hollow are both more favourable than a Cu adatom at site atop_S. The addition energies were computed for addition of an atom at both sites, with a Cu atom already at the other site. With an atom adsorbed at site atop_S, adding a second atom at sites atop_Mo or hollow gives an energy gain of -1.37 eV and -1.75 eV respectively, while adding an atom at site atop_S gives an addition energy of -0.86 eV if the first atom is at site atop_Mo and -0.82 eV if the adatom is at site hollow. Thus, the more favourable addition energies are observed when adding an atom to the more favourable adsorption sites.

Overall, adsorbing Cu at equivalent sites instead of non-equivalent sites yields a more favourable binding energy per atom, except for the less stable site atop_S, where the combination with a more favourable adsorption site causes a more favourable binding energy per atom.

Four different configurations were relaxed for the adsorption of 3 adatoms, as shown in Figure 4. Of these, three configurations are 2D and one is a 3D configuration in which only 2 Cu atoms bind to MoS₂. For the 2D adsorptions, the atoms are adsorbed either in a line, as a triangle with all atoms at equivalent adsorption site or as a triangle with the third atom away from the other two (off-set configuration). For the 3D geometry, a third atom is adsorbed atop two neighbouring Cu atoms. The computed binding energies show that the 3D configuration is the most stable of the four, see Table 1. It is of note that the atoms remain at the site where they originally adsorbed throughout relaxation. Depending on the exact adsorption site and adsorption configuration, the 3D Cu₃ adsorption structure is more stable by between 0.16 and 1.03 eV, compared to the various 2D structures. While site atop_S continued to be less favourable than sites atop_Mo and hollow for the 2D configurations, for the 3D adsorption mode this difference disappears, with similar binding energies for all sites, suggesting that once 3D clusters begin to form on MoS₂ the binding energy is not influenced by the adsorption site. This is also apparent from the computed addition energies. The addition of an atom to Cu₂ to form the 3D Cu₃ cluster is very favourable, with computed addition energies lying between -2.25 eV and -3.86 eV. The addition energy of -3.86 eV for site atop_S reflects that this configuration is much more stable than any other three atom configuration at site atop_S.

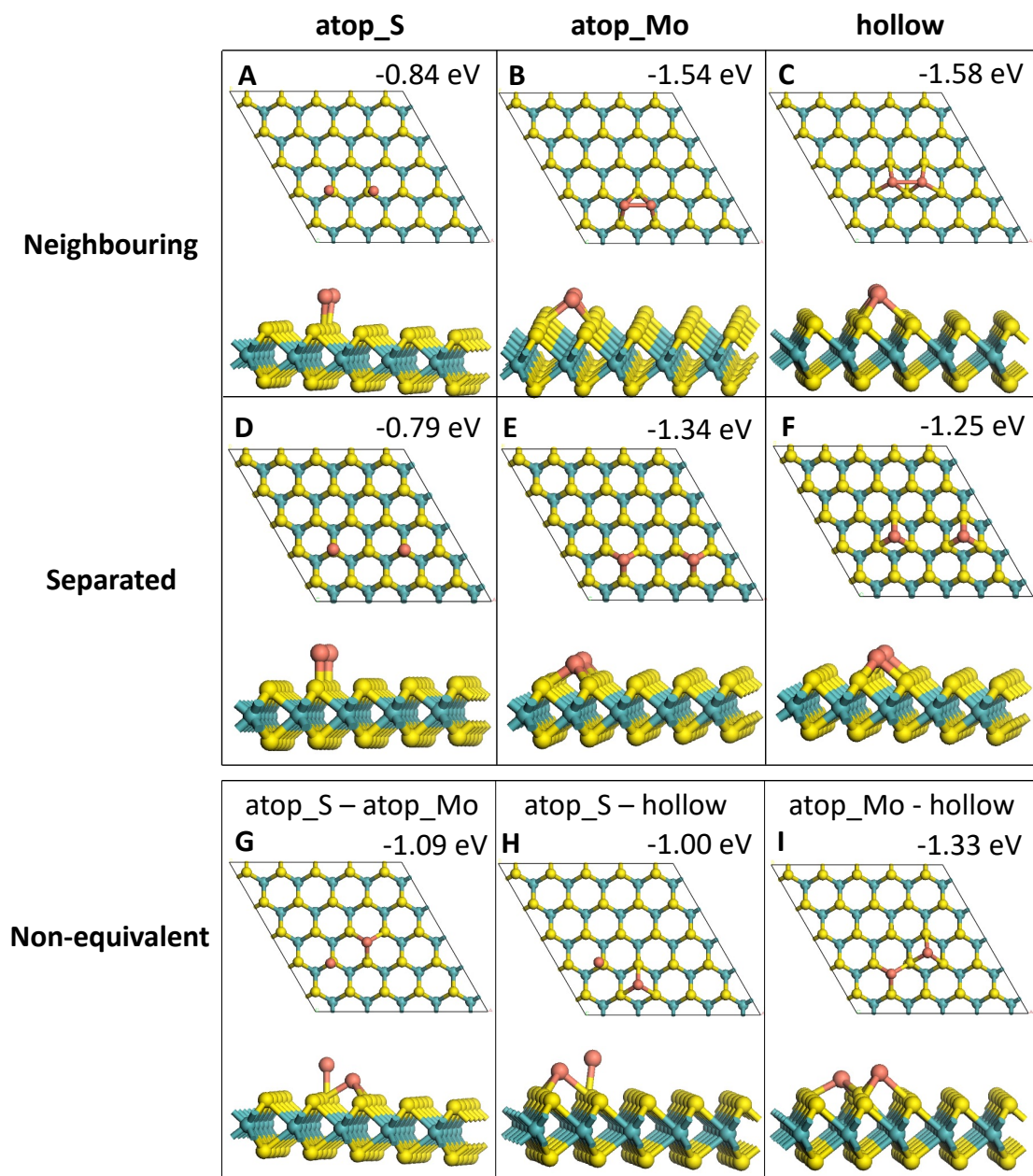


Figure 3: Adsorption configurations with 2 Cu adatoms. A through F show adatoms at equivalent sites, while G, H and I show combinations of two atoms adsorbed at different sites on the MoS₂ ML

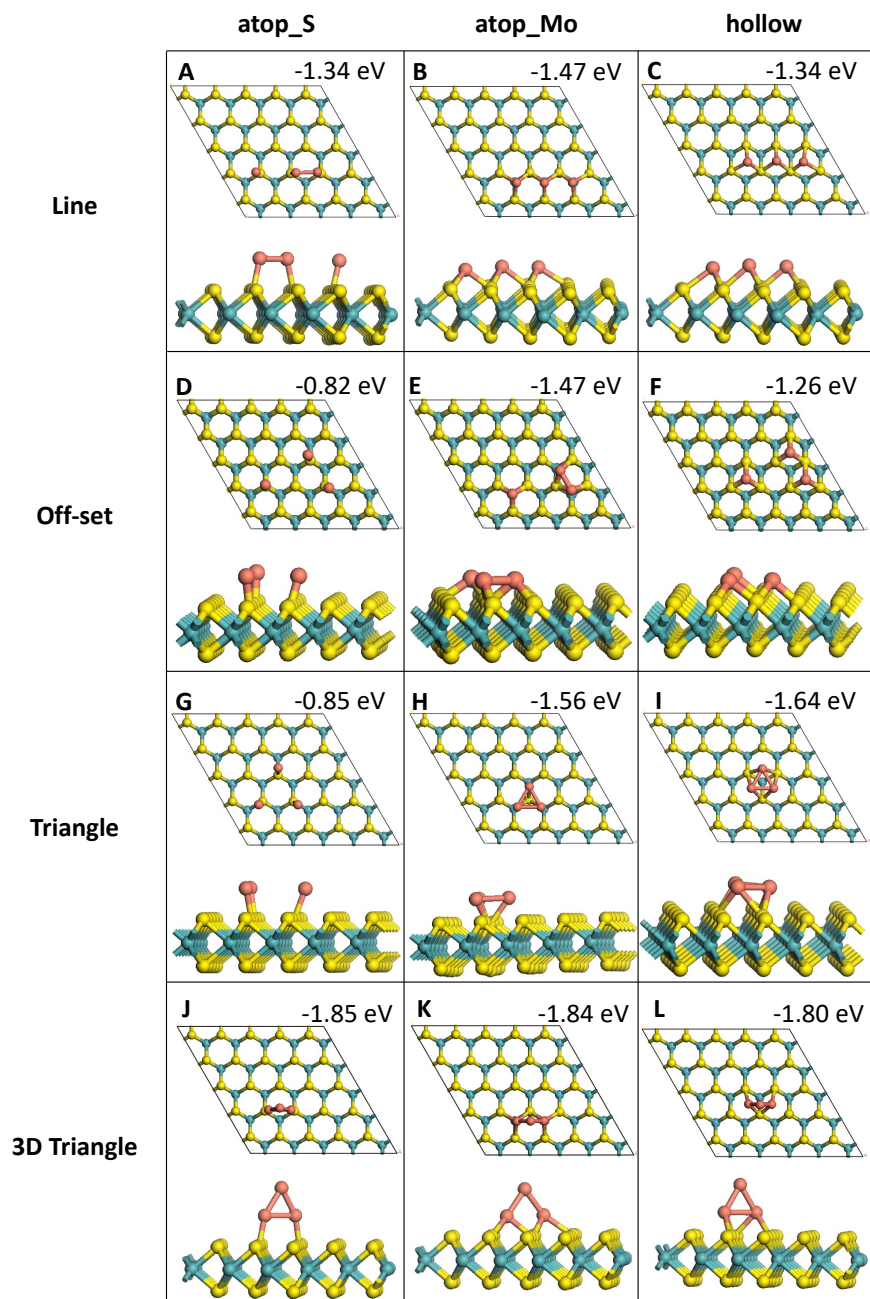


Figure 4: Relaxed structures after adsorption of Cu_3 structures.

Finally, for the adsorption of 4 Cu atoms, four configurations were examined.

Two configurations are flat (2D) and two configurations are 3D nanoclusters. For the flat adsorption structures, the 4 Cu atoms are adsorbed in a linear configuration, with Cu-Cu distances of around 3.2 Å, depending on the adsorption site, or in a 4-membered flat structure (rhombus). For the 3D clusters, one configuration is a rhombus with two Cu atoms bound to MoS₂ and another two atop and the other 3D configuration is a tetrahedron with three atoms bound to MoS₂ and an apex atom bound to the triangular base. Interestingly, for the 2D structures, binding of Cu atoms at site atop_S becomes more favourable than binding of Cu atoms at site hollow and in the case of the rhombus and tetrahedral structures also more favourable than adsorption at site atop_Mo. As for the Cu₃ structures, the atoms remain at their original adsorption sites throughout the relaxation of all Cu₄ structures. For the linear Cu₄ configuration the binding energy at site atop_S is only 0.06 eV per Cu more negative than at site hollow and 0.07 eV less negative than at site atop_Mo, indicating little difference in stability. We see that this is the weakest adsorption configuration of Cu₄ at site atop_S. This is presumably as a result of fewer Cu-Cu bonds, as there is little variation in the Cu-Cu bond lengths, which range from 2.24 Å to 2.41 Å for structures at site atop_S. However for the 2D rhombus adsorption configuration, site atop_S is the most favourable site, with a binding energy that is 0.14 eV more negative than site atop_Mo and 0.70 eV more negative than the binding energy at site hollow. This is likely due to the Cu-Cu interactions, which are in fact absent when adsorbing the rhombus structure at site hollow, the weakest overall Cu₄ adsorption configuration, due to long Cu-Cu distances of 3.0 to 3.5 Å.

The rhombus configuration of Cu₄ at site atop_S has a computed addition energy of -5.48 eV relative to Cu₃, which is the most favourable addition energy calculated, while the addition energy for the tetrahedral configuration at site atop_S is similar at -5.37 eV. This indicates that Cu much prefers this Cu₄ structure with Cu-Cu interactions compared to the corresponding Cu₃ structure at site atop_S, which has no Cu-Cu interactions. Site atop_Mo has favourable addition energies for all four configurations. By contrast, site hollow has a much less favourable addition energy of only -0.33 eV for the rhombus configuration. The 3D rectangle and the tetrahedron each have very similar adsorption sites regardless of the site they are adsorbed at. Energy differences between the same structure at the three different sites are around 0.1 eV, illustrating the lack of influence of the adsorption site on the preferred configuration for Cu₄ structures. The addition energies for the tetrahedral configuration are much larger than those for the upright 3D adsorption configuration, with a difference of about 0.8 eV for sites atop_Mo and hollow and a difference of 4.48 eV for site atop_S. The 3D structures are more favourable than the 2D structures at site hollow. However for sites atop_S and atop_Mo, the rhombus configuration has a binding energy that is approximately the same as that of the tetrahedron. The instability of the rhombus at site hollow compared to the same configuration at sites atop_S and atop_Mo is likely due to the lack of Cu-Cu bonds, which are present in structures at sites atop_S

Table 1: Computed binding energies for Cu₁, Cu₂, Cu₃ and Cu₄ on MoS₂ ML for various atom configurations using Equation 37 in Chapter 3. For the "non-equivalent" configurations of Cu₂, the column "atop_S" has atoms at sites atop_S and atop_Mo, "atop_Mo" has atoms at atop_S and hollow and "hollow" has atoms at sites atop_Mo and hollow.

Number of Cu atoms	Adsorption Configuration	E _{bind} /atom [eV]		
		atop_S	atop_Mo	hollow
1	-	-0.81	-1.32	-1.18
2	neighbouring	-0.84	-1.54	-1.58
	separated	-0.79	-1.34	-1.25
	non-equivalent sites	-1.09	-1.00	-1.33
3	line	-1.34	-1.47	-
	off-set	-0.82	-1.47	-
	triangle	-0.85	-1.56	-1.64
	3D triangle	-1.85	-1.84	-1.80
4	line	-1.41	-1.48	-1.35
	rhombus	-2.01	-1.87	-1.31
	3D rectangle	-1.87	-1.87	-1.77
	tetrahedral	-1.98	-1.86	-1.83

and atop_Mo but not at site hollow; see Figure 5F.

It is of note that, even though for single atom adsorption, site atop_S is the least favourable adsorption site, the most favourable binding energies are found for the rhombus and tetrahedral Cu₄ configuration at site atop_S. These also had the most favourable addition energies, reflecting the large increase in stability of configurations at site atop_S as subsequent Cu atoms are added. Overall, the binding energies per copper atom increases as more atoms are added, which is most likely due to the formation of Cu-Cu bonds and more Cu-surface bonds. The addition of Cu atoms also becomes more favourable, except for the rhombus configuration of Cu₄ at site hollow.

This analysis indicates that the relative stability of an adsorption configuration of a Cu_n species appears to be generally determined by the presence or absence of Cu-Cu bonding. Those configurations with a larger number of Cu-Cu bonds tend to have a more favourable binding energy. This becomes particularly clear for Cu₄, where all structures are less favourable at site hollow than at sites atop_S and atop_Mo. The distance from site hollow to another equivalent site is longest at approximately 3.2 Å, which then results in very long Cu-Cu bonds, or in the case of Cu₄ line and rhombus structures, no Cu-Cu bonds. This is further supported by the metal-metal interactions detailed in Table 3. We find a direct correlation between the relative stability of the adsorption configuration, the number of Cu-Cu bonds and the strength of the Cu-Cu interaction. While the rhombus and tetrahedral configurations are competitive in energy the strong Cu-Cu interaction, especially of the structures at

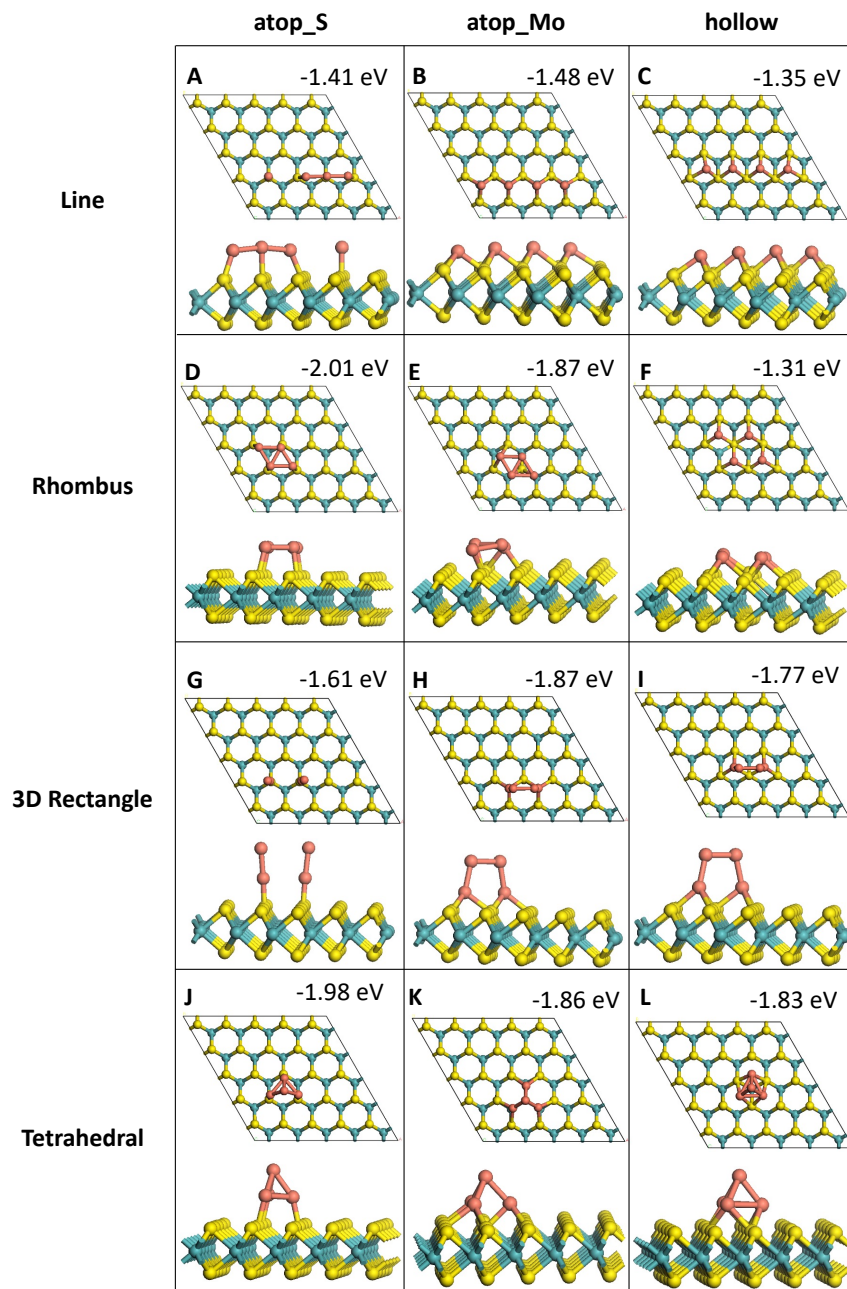


Figure 5: Relaxed structures after adsorption of Cu_4 structures.

Table 2: Computed addition energies for each configuration ($\text{Cu}_{n-1} + \text{Cu} \rightarrow \text{Cu}_n$) calculated using Equation 45 in Chapter 3.

Number of Cu atoms	Configuration	E_{add} [eV]		
		atop_S	site atop_Mo	hollow
2	neighbouring	-0.87	-1.75	-1.98
	separated	-0.77	-1.36	-1.31
	non-equivalent sites	-1.37/-0.86	-1.75/-0.82	-1.34/-1.48
3	line	-2.35	-1.34	-
	off-set	-0.78	-1.32	-
	triangle	-0.88	-1.62	-1.75
	3D triangle	-3.86	-2.46	-2.25
4	line	-1.60	-1.52	-
	rhombus	-5.48	-2.79	-0.33
	3D rectangle	-0.89	-1.95	-1.65
	tetrahedral	-5.37	-2.75	-2.41

site **atop_S** indicates a potential towards association during film growth. However, the rather weak interactions for the rhombus at site **hollow** suggest the possibility to promote dissociation if atoms adsorb at a sufficient distance to prevent bond formation.

Cu-S distances also vary with adsorption site and are found to be shortest for Cu atom adsorption at site atop_S, with Cu-S distances in the range of 2.16 to 2.31 Å. This is due to the Cu atom being adsorbed directly atop the S atom. In comparison, Cu-S bond lengths are somewhat longer at the other sites, ranging from 2.23 Å to 2.54 Å at site atop_Mo and 2.26 Å to 2.58 Å at site hollow. Overall, the bond lengths appear to be determined by the adsorption site and do not have a strong effect on the strength of adsorption.

Bader charge analysis of Cu atoms and adjacent Mo and S atoms shows that Cu atoms that bind directly with multiple sulfur atoms on the MoS₂ layer, for example sites atop_Mo and hollow, are clearly oxidised, with computed Bader charges of 10.6 electrons (the number of valence electrons in Cu is 11). By contrast, those Cu atoms that bind to a single sulfur atom, e.g. site atop_S, with a computed Bader charge of 10.8 electrons, are less oxidised.

Table 3: Computed metal-metal interaction energies for Cu₄ geometries on pristine MoS₂ using Equation 40 in Chapter 3.

No. metal atoms	Configuration	$E_{\text{interact}}/\text{Cu-atom}$ [eV]		
		atop_S	atop_Mo	hollow
4	line	-0.87	-0.68	-0.71
	rhombus	-1.58	-1.52	-0.16
	3D rectangle	-1.16	-1.25	-1.26
	tetrahedral	-1.39	-1.23	-1.31

Cu atoms that do not bind to the surface are metallic, with computed Bader charges of 11.0 to 11.1 electrons. The charges for each Cu atom for the various adsorption geometries are shown in the Appendix, Section A5.2, Tables A16, A17 and A18. There are no significant changes in the computed Bader charges of Mo and S atoms in the monolayer, which are ca. 4.9 and 6.5 electrons respectively. Analysis of the charge density difference after Cu_n adsorption confirms the observations made from the Bader analysis. Charge density is localised mainly to the adsorbed Cu atoms, with less charge density on those Cu atoms that are not bound to the surface. Some charge density is also observed in the surface S atoms interacting with Cu atoms, as well as those Mo atoms that are bound to the interacting S atoms. Figure A75 A to G, in Section A5.5 of the Appendix shows the charge density difference of the most favourable Cu_n adsorptions.

Similarly, the bond lengths between Mo and S atoms in the monolayer do not vary significantly from those in the bare MoS_2 monolayer after adsorption of Cu atoms. Cu-S bonds can vary from lengths in CuS bulk material (2.31 Å [43]) by up to +0.27 Å, as in the case of adsorption at site hollow, in particular the Cu_4 line configuration, or by -0.15 Å, as in the case of most of the adsorptions at site atop_S. Mo-S distances are found to be within +0.09 Å and -0.05 Å of the Mo-S distance in the bare ML (2.41 Å); thus no significant structural distortion occurs in MoS_2 due to Cu adsorption. We conclude that there is no clear correlation between the Cu-S or Mo-S distances and the favourability of a binding site.

Analysis of the densities of states (DOS) (see Figure 6 for most favourable adsorption structures for each Cu_n) shows the emergence of mid-gap states as Cu atoms are added to the monolayer. These states arise from the partial oxidation of Cu atoms to produce Cu^+ cations and include contributions from all three elements. Exceptions to this are the 3D triangle configurations at adsorption sites atop_S and hollow where there are no mid-gap states, with all of the Cu contributions at the Fermi level. Densities of states for all Cu_n structures can be found in the Appendix, Section A5.1, Figures A62, A63 and A64.

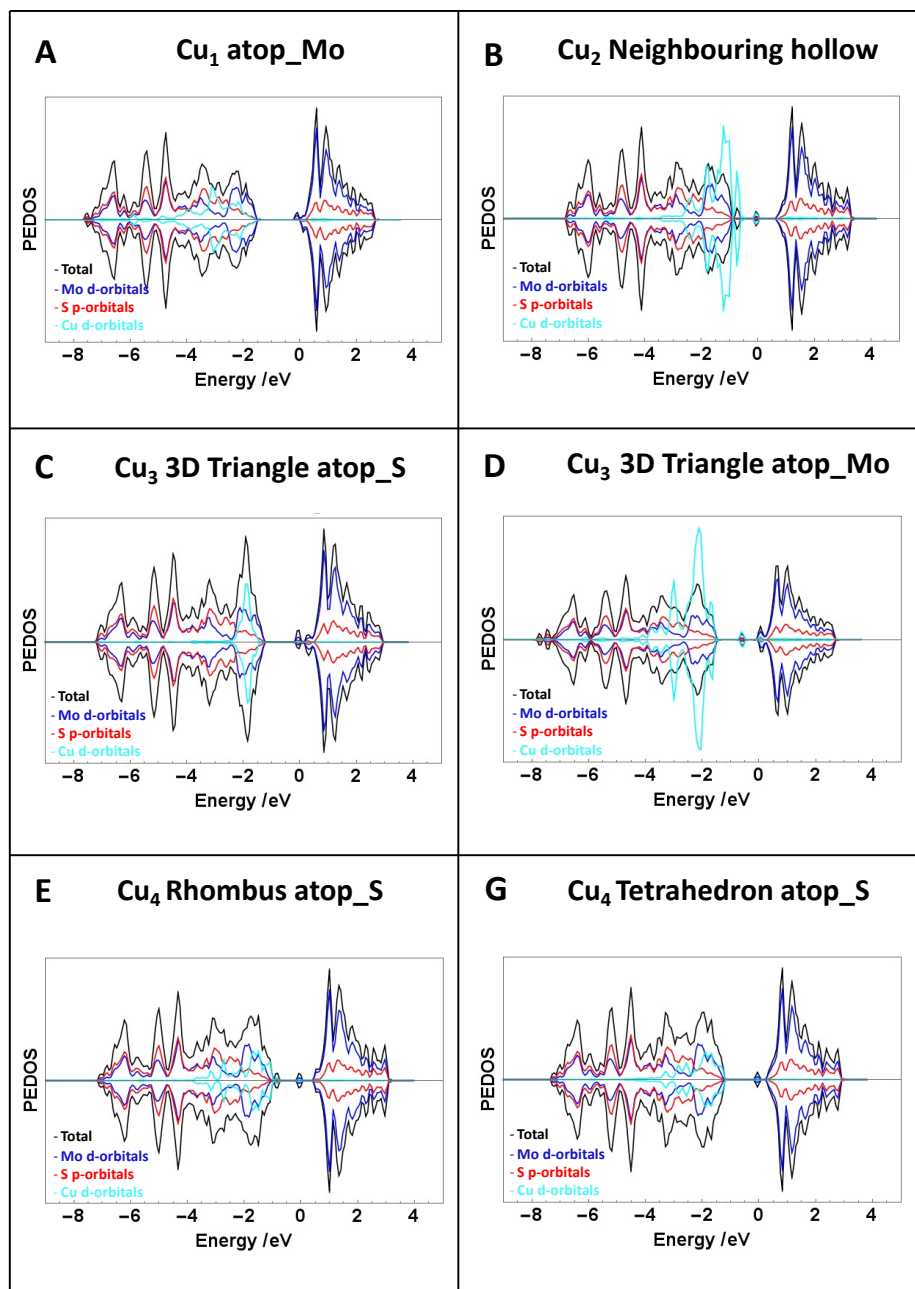


Figure 6: DOS plots of most favourable adsorption for each Cu_n structure on MoS_2 . The contribution of the Cu d-orbitals has been increased by a factor of 5 for ease of comparison and zero on the "Energy" scale is the Fermi level.

7.2 Co_n and Ru_n on pristine MoS₂

The relaxed geometries of the various Co_n species are shown in Figures 7, 8, 10, and 12 while the geometries for Ru_n species are shown in Figures 7, 9, 11, and 13. The energies shown in these figures are the binding energies computed using Equation 37 in Chapter 3. To give a better overview, the same binding energies are also shown in Table 4. Structures are referred to and labelled according to the initial cluster adsorption structure, to avoid confusion due to any geometry rearrangements that occur.

Table 4: Computed binding energies for Co₁, Co₂, Co₃, Co₄, Ru₁, Ru₂, Ru₃ and Ru₄ on MoS₂ ML for various atom configurations using Equation 37 in Chapter 3. For the "non-equivalent" configurations for 2 metal atom adsorption, the column "atop_S site" has atoms at sites atop_S and atop_Mo, "atop_Mo site" has atoms at atop_S and hollow and "hollow site" has atoms at atop_Mo and hollow.

No. metal atoms	Configuration	E _{bind} /Co-atom [eV]			E _{bind} /Ru-atom [eV]		
		atop_S	atop_Mo	hollow	atop_S	atop_Mo	hollow
1	-	-4.21	-5.82	-5.55	-2.47	-3.92	-3.40
2	neighbouring	-6.05	-6.05	-5.73	-4.45	-4.45	-3.75
	separated	-4.20	-5.81	-4.92	-2.45	-3.92	-3.19
	non-equivalent	-5.56	-5.37	-5.85	-3.99	-3.71	-3.87
3	line	-5.61	-6.08	-5.88	-4.07	-4.47	-4.41
	triangle	-5.43	-6.13	-5.89	-2.57	-4.65	-4.46
	3D triangle	-5.53	-6.05	-5.56	-4.22	-4.72	-4.36
4	line	-6.11	-6.10	-5.95	-4.28	-4.55	-4.76
	rhombus	-5.86	-5.93	-5.87	-4.61	-4.28	-4.37
	3D rectangle	-6.28	-6.33	-5.93	-3.29	-4.93	-4.62
	tetrahedral	-5.85	-6.32	-6.05	-4.70	-5.14	-4.74

7.2.1 Single Atom Adsorption

Co and Ru atoms adsorb exothermically at all three adsorption sites. A single Co atom adsorbs most strongly at site **atop_Mo**, with an energy gain of -5.82 eV, followed by site **hollow** and site **atop_S**, with energy gains of -5.55 eV and -4.21 eV. A single Ru atom adsorbs preferentially at site **atop_Mo** with an energy gain of -3.92 eV, followed by site **hollow** and site **atop_S**, with energy gains of -3.40 eV and -2.47 eV.

As for Cu, for both Co and Ru, site **atop_Mo** is the most favourable adsorption site. We find that for a single adatom, Co-S distances are the shortest of all the metals studied, measuring between 1.99 and 2.16 Å depending on the adsorption site. These Co-S distances are shorter than the Co-S distance of 2.31 Å in bulk CoS₂ [44]. Similarly, the Ru-S distances are between 2.13 and 2.24 Å, compared to 2.37 Å in bulk RuS₂ [45]. The shortest metal-S bonds

are measured at site **atop_S**, compared to those measured for sites **atop_Mo** and **hollow**. There are some Co-Mo bonds observed, with Co-Mo distances of 2.85 Å, but there are no Ru-Mo bonds or Cu-Mo bonds [41]; the presence of these could be one origin for the enhanced interaction between Co and the MoS₂ ML. The relaxed geometries for adsorption of Co₁ and Ru₁ are shown in Figure 7.

7.2.2 Two Atom Adsorption

For two adatom adsorption, there are three different M₂ geometries. All of these are 2D. They involve atoms adsorbed at adjacent equivalent surface sites, at equivalent but separated sites and atoms at adjacent but non-equivalent sites. Relaxed geometries for adsorption of Co₂ and Ru₂ are shown in Figures 8 and 9, respectively.

For Co, adsorbing two atoms at equivalent adjacent sites corresponding to adsorption site **atop_Mo** is the most favourable Co₂ configuration, with a computed adsorption energy of -6.05 eV/atom. Adatoms originally adsorbed as equivalent neighbours at site **atop_S** migrate to site **atop_Mo** instead (Fig 8A and B). This adsorption mode is more favourable by 0.32 eV compared to equivalent neighbours at site **hollow** (Fig 8C).

The adsorption of two separated Co atoms is preferred at equivalent, separated sites corresponding to adsorption mode **atop_Mo** (Fig 8E). We propose that this is due to the geometry match with the substrate as there are no Co-Co bonds to contribute to the binding energy and all adsorption sites have metal interaction energies within at most 0.1 eV of each other. Adsorption of separated atoms at site **atop_S** is the least favourable configuration for Co₂ (Fig 8D).

Starting from a configuration of Co₂ adsorbed at site **hollow**, during relaxation one Co atom migrated to site **atop_S**, making this a non-equivalent adsorption at separated sites **atop_S - hollow**, as shown in Figure 8F. This explains the less favourable binding energy of -4.92 eV compared to -5.73 eV at equivalent neighbouring sites **hollow** and -5.37 eV at non-equivalent, neighbouring sites **atop_S - hollow**.

Adsorption of Co atoms at neighbouring, but non-equivalent sites is overall more favourable than adsorption of separated atoms, in particular where the Co atoms bind to sites **atop_Mo - hollow** (Fig 8I). These structures also have the strongest metal-metal interaction energies, Table 6. This is due to Co-Co bonding, which is present exclusively for these Co₂ adsorption modes due to the decreased distance between atoms compared to equivalent sites. We also observe large magnitudes of addition energies (see Appendix, Section A5.8, Table A24) for these structures, showing that addition of a second atom can stabilise any atoms that may be initially adsorbed at a less favourable site.

During the adsorption of Ru₂, several rearrangements were observed. While adsorption of two adjacent equivalent Ru atoms at site **atop_Mo** is most favourable (Fig 9B), with E_{bind} = -4.45 eV, the initial adsorption at adjacent

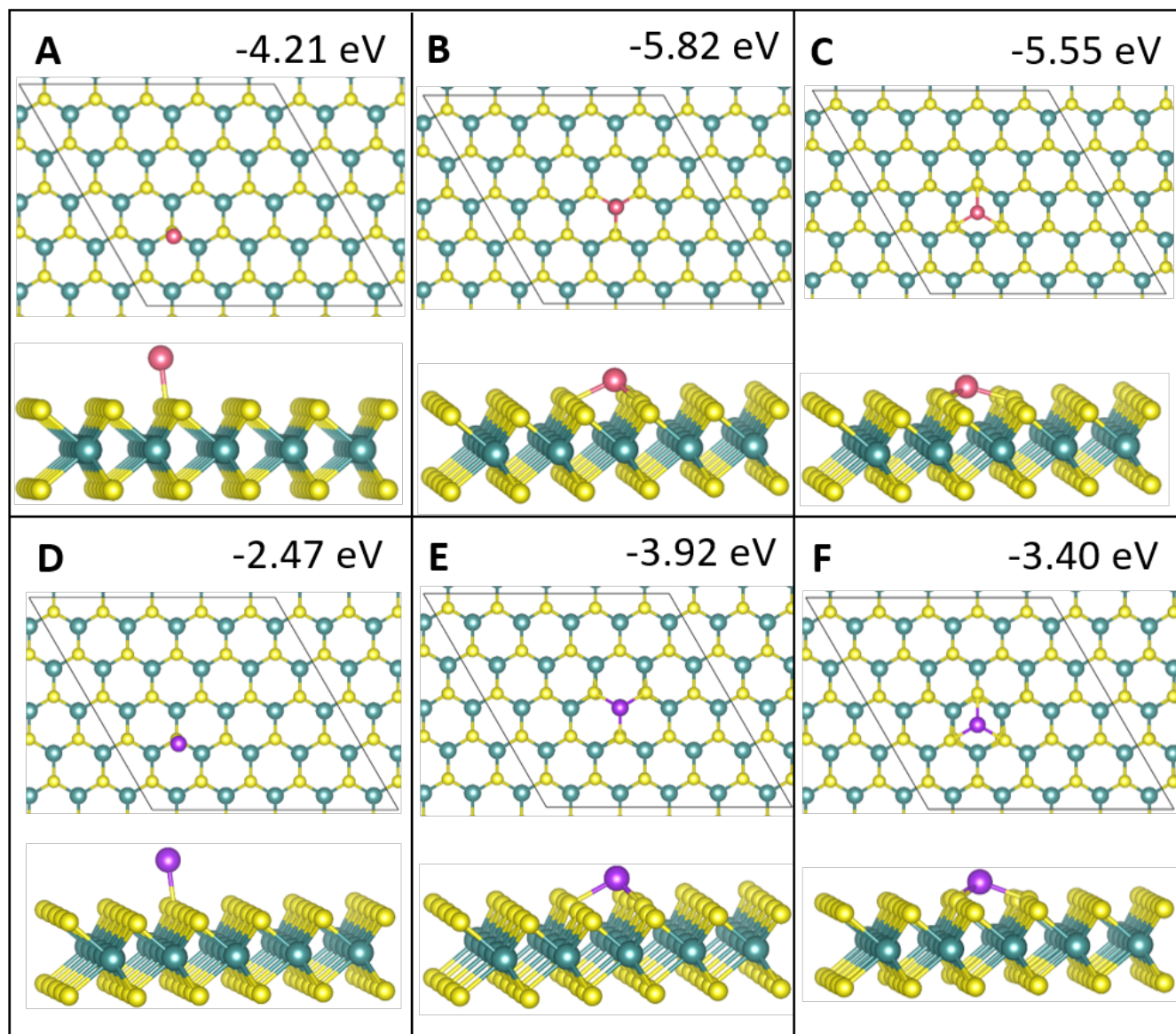


Figure 7: Atomic structures and energies of Co_1 and Ru_1 adsorption modes on perfect MoS_2

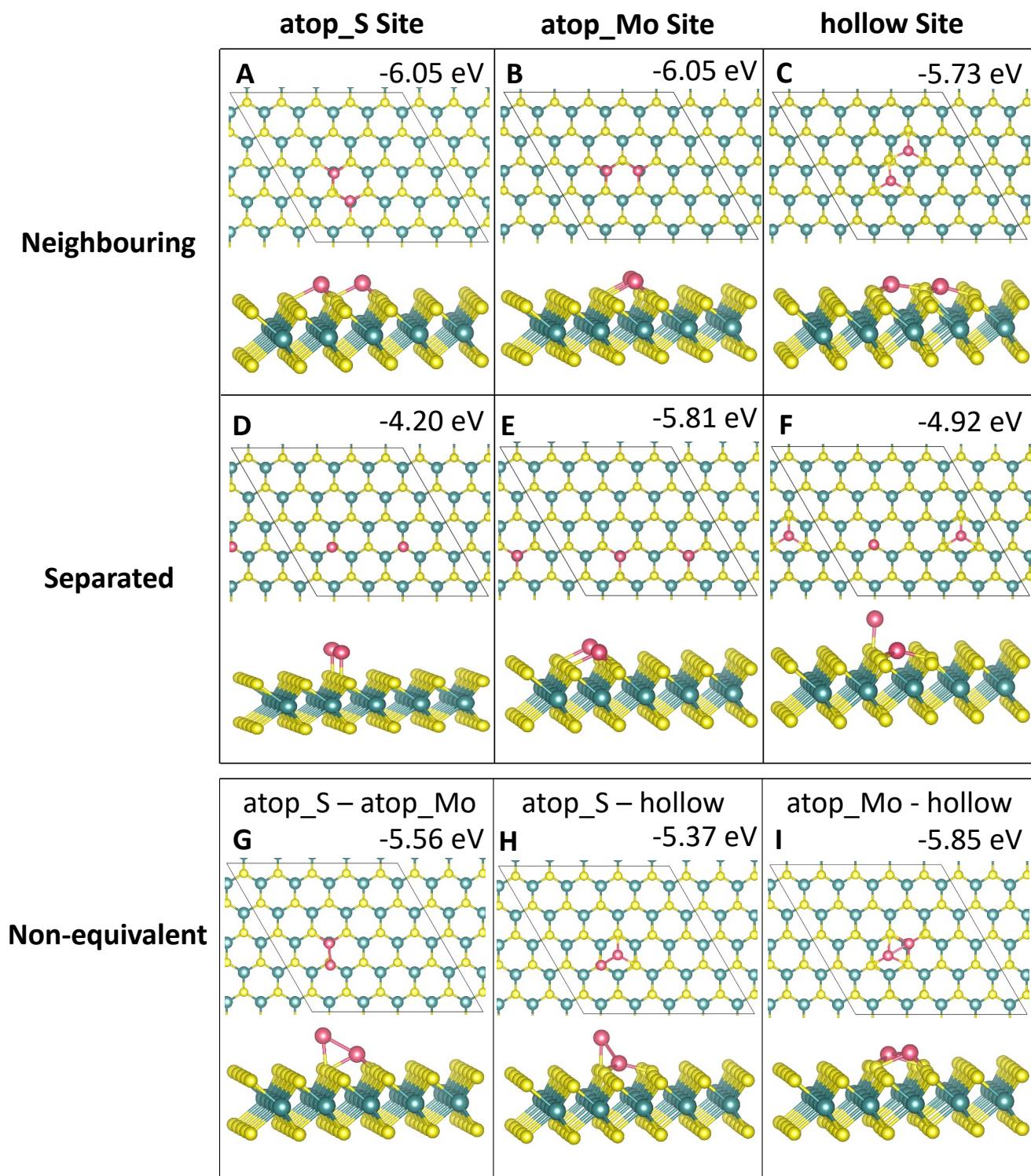


Figure 8: Atomic structures and energies of Co_2 adsorption modes on perfect MoS_2

equivalent sites **atop_S** resulted in both atoms migrating to site **atop_Mo** (Fig 9B), similar to Co_2 , indicating that this particular configuration is unstable for metal atoms adsorbed at site **atop_S**. The adsorption of Ru at separated sites **atop_S** (Fig 9D) is the least favourable configuration for Ru_2 , as well, although no rearrangements or migrations occur here.

Similar to Co_2 , adsorption of Ru at equivalent separated sites **atop_Mo** (Fig 9E) is the second most favourable of the equivalent Ru_2 adsorptions. The large distortions of the MoS_2 ML for an initial configuration of neighbouring Ru at site **hollow** (Figure 9C) are caused by the attempted incorporation of one Ru atom into the S layer during relaxation. This has also caused an S atom adjacent to Ru to move out of the surface and bond to both Ru atoms from above, forming a triangular Ru_2S structure. With a binding energy of -3.99 eV, the combination of sites **atop_S - atop_Mo** (Fig 9G) is as favourable as separated atoms at site **atop_Mo** (Fig 9E). This indicates that at this very early stage of film growth there is no preference yet between structures with separated atoms and those with Ru-Ru bonds.

Those configurations that underwent strong rearrangements during relaxation, i.e. adjacent equivalent atoms at site **hollow** (Fig 9C) and adjacent atoms at non-equivalent site **atop_Mo - hollow** (Fig 9I), have very weak metal-metal interaction energies, from Table 6. The neighbouring site **hollow** has a positive metal-metal interaction energy, while the non-equivalent site **atop_Mo - hollow** has an interaction energy close to zero. The latter should mean that metal atoms do not agglomerate or separate, while a positive metal-metal interaction should be indicative of a separation of atoms. However, a zero or positive metal-metal energy can only be computed when $E_{\text{metal-substrate}}$, calculated from Equation 39 in Chapter 3, is larger than or almost equal to E_{bind} , calculated from Equation 37 in Chapter 3. As $E_{\text{metal-substrate}}$ is calculated using the structure of the MoS_2 ML after metal relaxation and the energy of the metal cluster in vacuum as references, this indicates that for these structures E_{bind} reflects energy changes during rearrangement which in turn affects the magnitude of the metal-metal interaction energy.

7.2.3 Three Atom Adsorption

Three atom adsorption involved the study of three different geometries, two of which are 2D and one of which is 3D. These are shown in Figures 10 and 11. For the first configuration, the three adatoms are adsorbed in a line along neighbouring, equivalent sites. In the other two configurations the adatoms are arranged in a triangle, one 2D on the surface and the other in a 3D triangle; in the latter, the third adatom sits atop the two other adatoms. The off-set geometry studied for Cu_3 adsorption was not repeated for Co and Ru, as it did not add any significant insights into a preference towards 2D or 3D growth.

The most favourable configuration for Co_3 is the 2D triangle at site **atop_Mo** with a computed adsorption

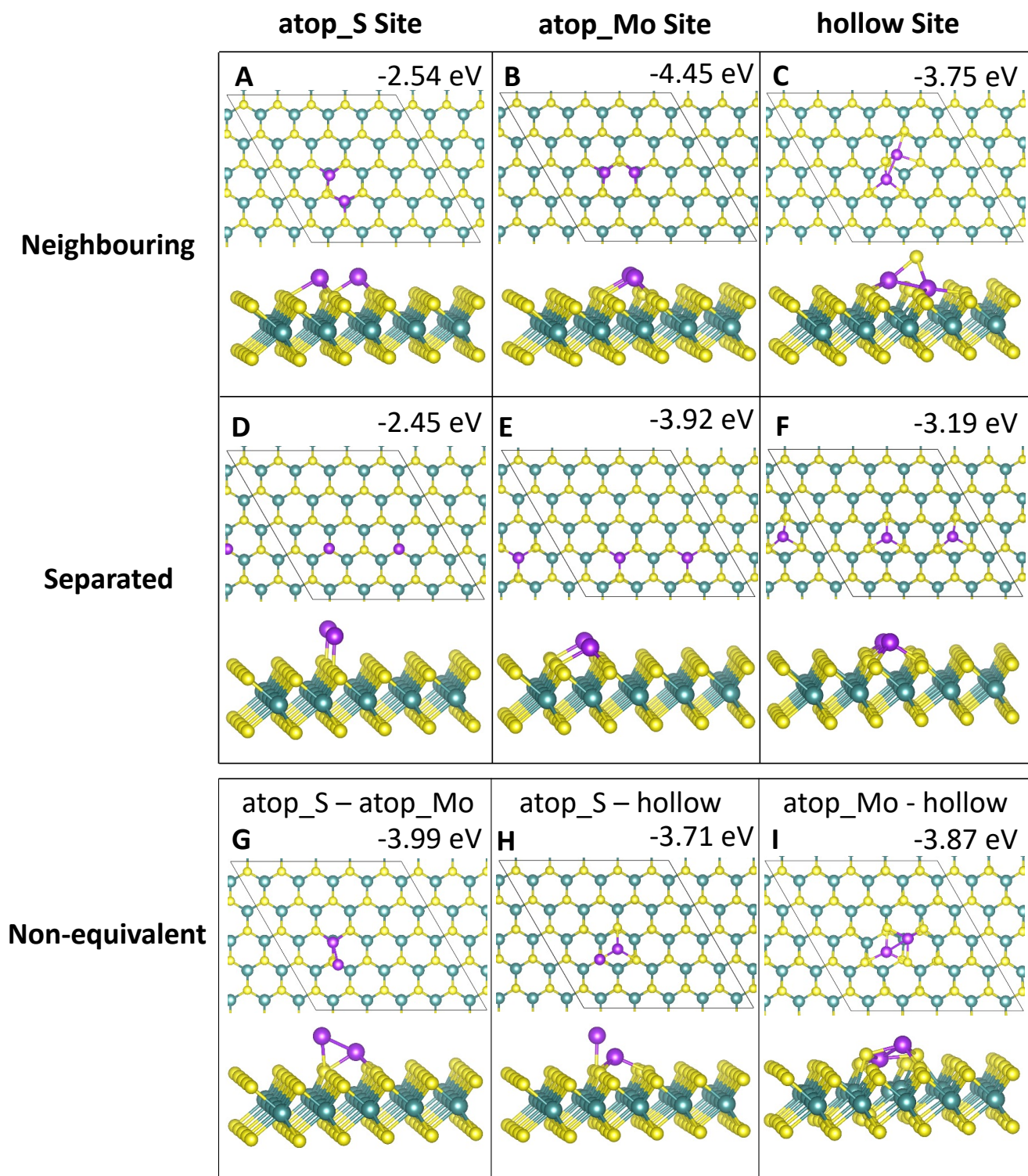


Figure 9: Atomic structures and energies of Ru₂ adsorption modes on perfect MoS₂

energy of -6.13 eV/atom (Fig 10E). The line and 3D triangle configurations are however competitive in energy, with the line configuration the more favourable by between 0.03 and 0.32 eV depending on the initial site at which the Co atoms bind. The 2D triangle with Co atoms at site **atop_S** has the least favourable adsorption energy at -5.43 eV/atom (Fig 10D). This configuration also has the weakest metal-metal interaction energy of -0.98 eV, as the Co atoms move away from each other; the Co-Co distances are 2.08 Å between the adjacent Co atoms and 4.89 Å to 4.98 Å to the separated atom.

The largest metal-metal interaction energies, all of which are greater than 4 eV in magnitude, can be observed for all 3D triangle configurations (Fig 10G, H and I) as well as the line configuration at site **atop_S** (Fig 10A). This is due to the presence of Co-Co bonds in all of these configurations, as there is no metal-metal bonding observed in the other structures. The Co-Co distances are between 2.20 and 2.25 Å, with some few longer bonds of approx. 2.6 Å compared to 2.48 Å in bulk Co [46].

For Ru₃, a different trend is seen. Here, the most favourable adsorption occurs for the 3D triangle configuration with the Ru atoms at site **atop_Mo** (Fig 11H); however, all Ru₃ configurations, with the exception of the 2D triangle configuration at site **atop_S**, with an adsorption energy of -2.57 eV/atom (Fig 11D), differ by no more than 0.7 eV/atom from this. This least favourable adsorption structure displays Ru atoms that migrate significantly from their original adsorption sites. While one atom remains at site **atop_S**, the second atom bridges between two S atoms between site **atop_Mo** and site **hollow**. The third atom has migrated to bind at site **atop_Mo**. Even though there are Ru-Ru bonds, this structure is distorted, compared to the more stable structures, leading to a less favourable adsorption energy.

Compared to Co₃, the metal-metal interactions are not as strong for Ru₃. Similarly to Co₃, the strongest metal-metal interactions are found for those structures where Ru-Ru bonding is present. Similar to Ru₂, adsorption in a linear configuration, at site **hollow** (Fig 11C), yields a positive interaction energy. The reason for this is the significant distortions to the ML, in which S atoms migrate out of the surface. Similar rearrangements can be observed for all Ru₃ structures at site **hollow** (Fig 11C, F and I) as well as for the 2D Co₃ structures at site **hollow** (Fig 10C and F). Compared to copper, where we did not observe this distortion, the smaller size of Co and Ru compared to Cu may promote these distortions when the metal atoms are adsorbed above the hollow site **hollow**. In response the S atoms can migrate and rearrange to accommodate the additional metal atom.

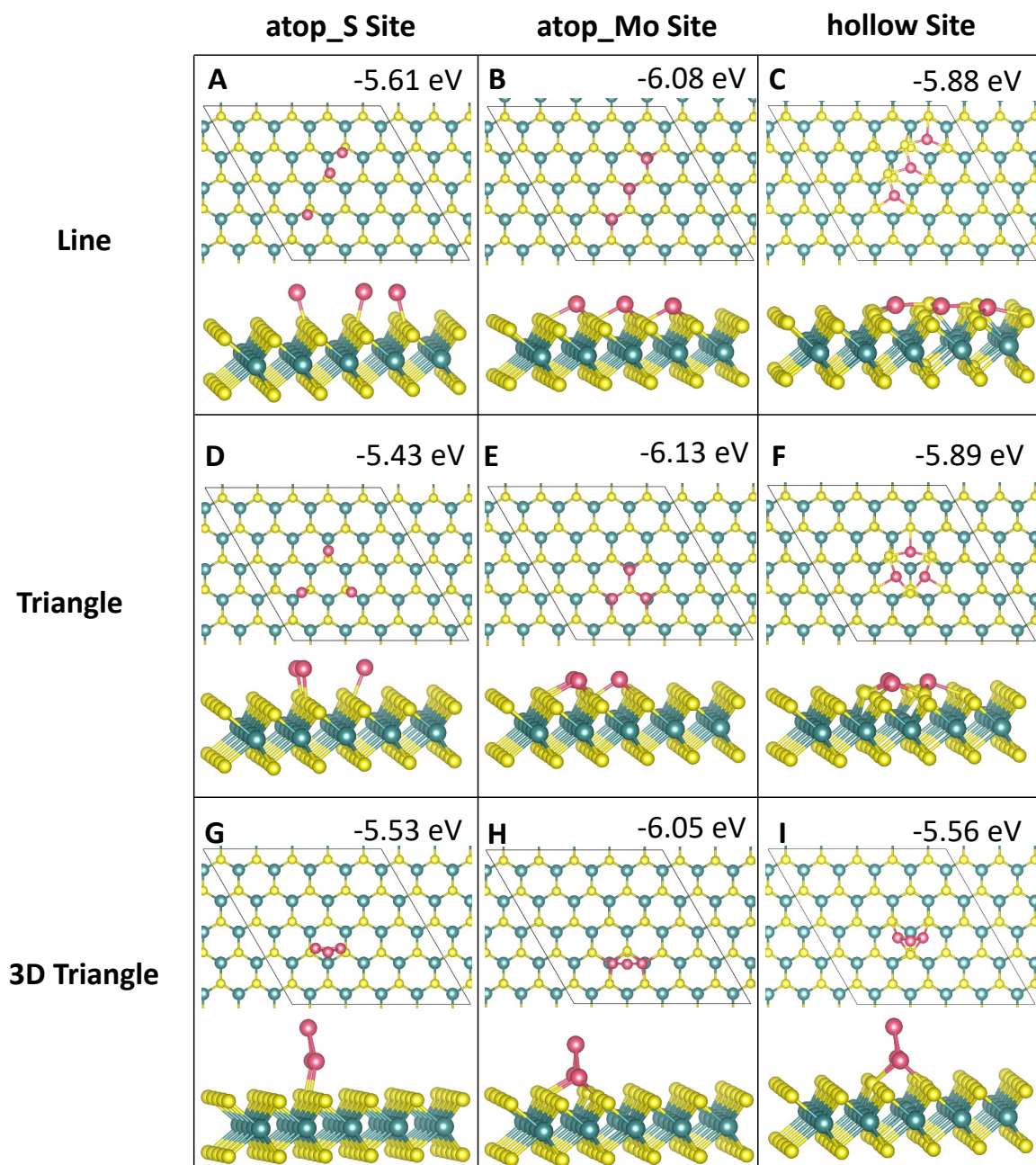


Figure 10: Atomic structures and energies of Co_3 adsorption modes on perfect MoS_2

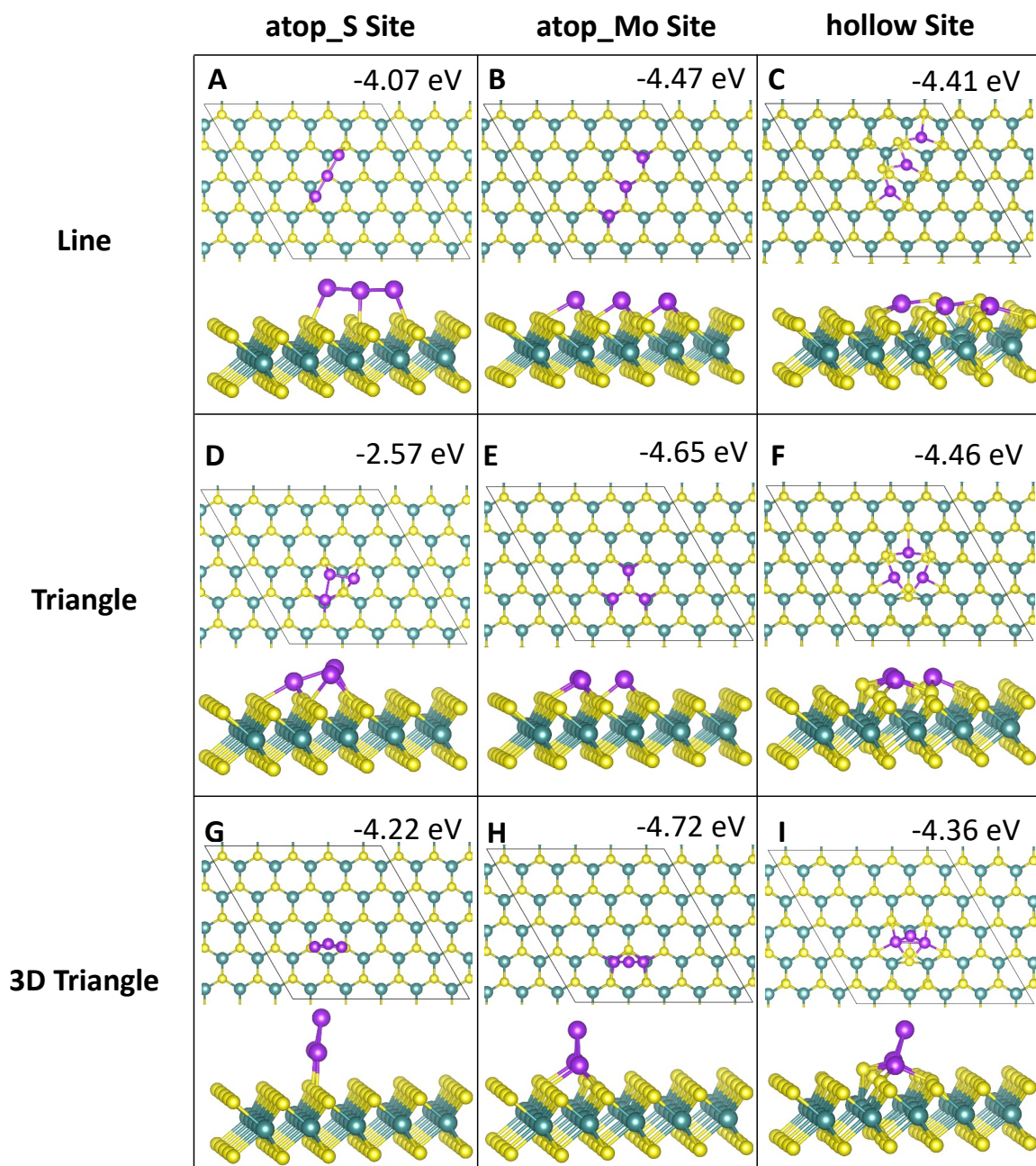


Figure 11: Atomic structures and energies of Ru_3 adsorption modes on perfect MoS_2

7.2.4 Four Atom Adsorption

For four atom adsorption, four different cluster geometries were explored; there are two 2D clusters and two 3D clusters. The relaxed geometries are shown in Figures 12 and 13. For the 2D structures, 4 atoms are adsorbed in a line along equivalent sites and in a rhombus shape with metal atoms binding to adjacent, equivalent sites. For the first 3D structure, two atoms are adsorbed at equivalent sites, with two atoms atop these to create a 3D rectangle. Similarly, for the tetrahedral geometry, three atoms are adsorbed to the ML, with a fourth atom atop these to create a tetrahedron.

Adsorption of Co at site **atop_Mo** in the 3D tetrahedral configuration (Fig 12G, H and K) is the most favourable geometry with a binding energy of -6.33 eV/atom, with a linear adsorption mode at site **atop_Mo** (Fig 12B) and a 3D tetrahedral configuration at site **hollow** (Fig 12L) showing binding energies of -6.10 eV and -6.05 eV, respectively. Generally, the 3D rectangle structure is not as favourable, so that the 3D tetrahedral motifs predominate for 4 atom clusters, with the 2D linear configurations also favourable.

Of the twelve initial binding configurations, upon relaxation five structures show atoms migrating from their original positions. Three of these are the 3D rectangle configuration, which shows that this geometry is not favourable for Co_4 . At sites **atop_S** and **atop_Mo** (Fig 12G and H), this configuration rearranges to the most favourable tetrahedral geometry with the base atoms adsorbed at site **atop_Mo**. At site **hollow**, one of the atop atoms moves to the surface to adsorb at a site **atop_S**, while the second atop atom migrates to rest between the two base atoms, which remain at site **hollow**, forming a 3D rhombus structure shown in Figure 12I. The remaining rearrangements are discussed in Section A5.7.1 of the Appendix.

Rearrangements of the MoS_2 ML can also be observed. In the 2D configurations we can clearly see the Co atoms integrating into the S layer of the ML; see, for example, Figures 12C, F and L. Co atoms from the line configuration at site **hollow** incorporate into the S layer with little movement away from the original lattice, which could be one of the origins for the relative stability of this structure. For Ru_4 adsorption, we find that similar to Co_4 , a 3D tetrahedral configuration at site **atop_Mo** is the most favourable geometry with an adsorption energy of -5.14 eV (Fig 13K). Similarly to Co_4 and Ru_3 , in five of the twelve Ru_4 configurations, atoms migrate to different sites or cause the ML to rearrange, or in some cases both.

However, in contrast to Co_4 , the tetrahedral configuration is not favoured in these rearrangements. Instead, we observe more structural distortions to the Ru_4 geometries and the MoS_2 lattice. In the case of the 3D rectangle at site **atop_S** these distortions cause a transition from a 3D structure to a 2D structure, as shown in Figure 13G. As for adsorptions at site **hollow** discussed previously, the most dramatic distortions to the MoS_2 ML occur at

this site. The line and tetrahedral configurations (Fig 13C and L), in particular, caused strong lattice distortions. While the Ru atoms have remained at their original adsorption sites, several S atoms migrated out of the surface to accommodate their incorporation into the S layer and have formed bonds with the Ru adatoms, creating a Ru_4S_3 cluster. More details on the various geometries are given in Section A5.7.2 in the Appendix.

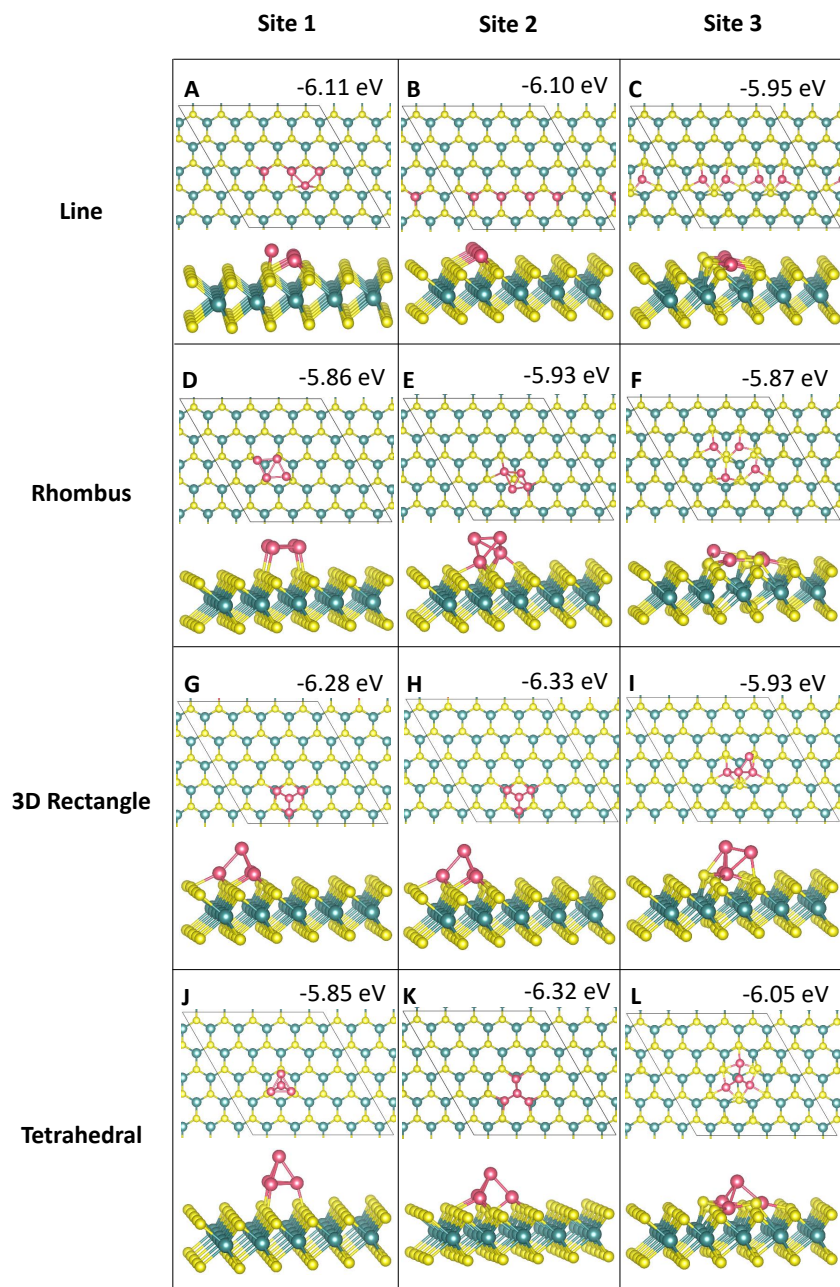


Figure 12: Atomic structures and energies of Co_4 adsorption modes on perfect MoS_2

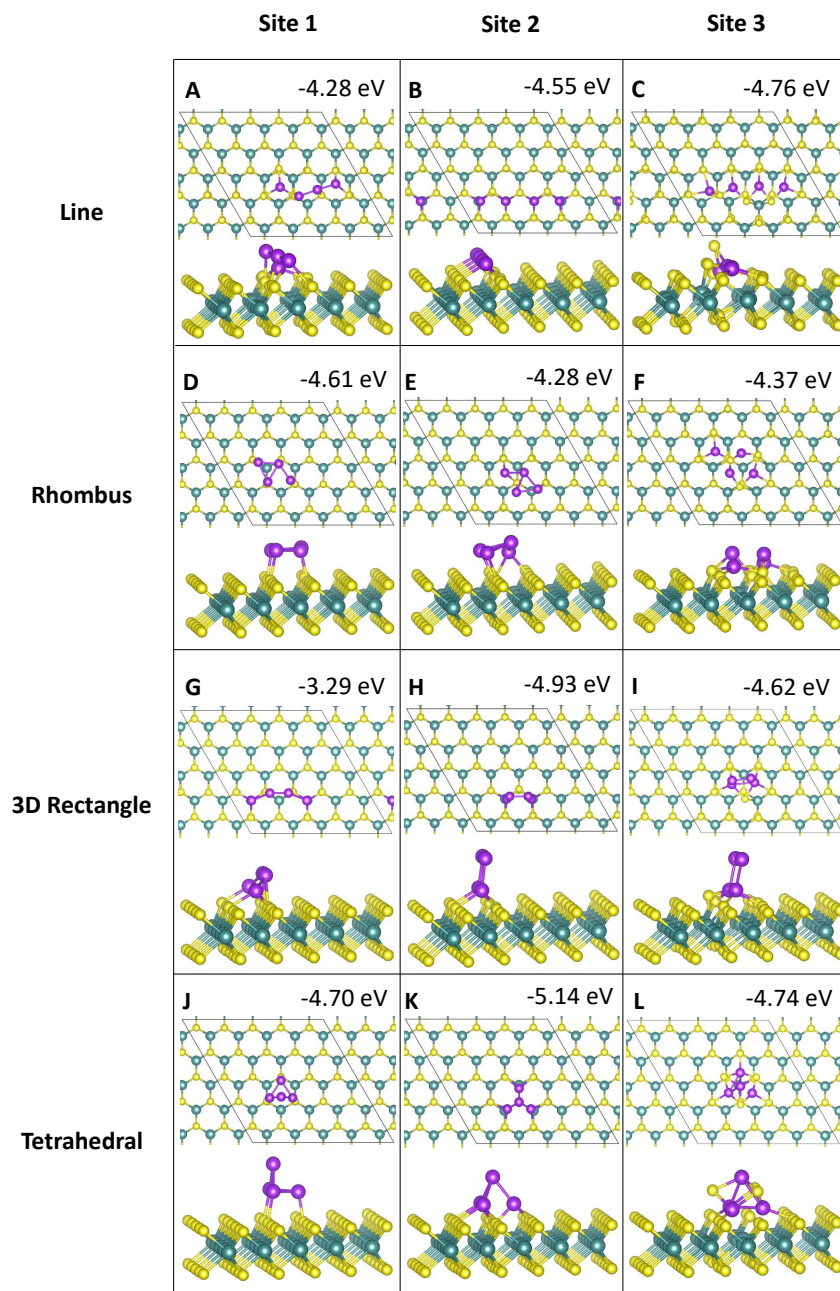


Figure 13: Atomic structures and energies of Ru_4 adsorption modes on perfect MoS_2

7.2.5 Metal-metal interactions, bond lengths and electronic properties

The metal-substrate interaction energies are shown in Table 5 and the metal-metal energies in Table 6. Comparing the contributions of metal-metal and metal-substrate interaction energies to the total binding energy is an important way of determining a preference towards 2D or 3D growth. Here, it is also important to consider that the metal-substrate interaction and the total binding energy reflect any energy changes associated with rearrangements in the MoS₂ ML. With this in mind there are three different factors that can influence the metal-substrate interaction. These are (a) presence or absence metal-metal bonds, (b) ML rearrangements including incorporation of metal atoms into the S layer and (c) formation of metal-S clusters. Incorporation of adatoms into the surface layer is known to increase the metal-substrate interaction, as is the lack of metal-metal bonds. [47] A gain in the metal-substrate interaction energy from formation of a metal-S cluster is due to Equation 39 in Chapter 3 not accounting for this, meaning that energy contributions from the formation of metal-S clusters are included in the metal-substrate interaction energy and thus it cannot be used in a straightforward manner as an indicator of 2D vs 3D growth for these geometries.

Table 5: Computed metal-substrate interaction energies for Co₂, Co₃, Co₄, Ru₂, Ru₃ and Ru₄ on MoS₂ ML for various atom configurations using Equation 39 in Chapter 3. For the "non-equivalent" configurations for 2 metal atom adsorption, the column "atop_S site" has atoms at sites atop_S and atop_Mo, "atop_Mo site" has atoms at atop_S and hollow and "hollow site" has atoms at atop_Mo and hollow.

No. metal atoms	Configuration	E _{metal-substrate} /Co-atom [eV]			E _{metal-substrate} /Ru-atom [eV]		
		atop_S	atop_Mo	hollow	S_atop	atop_Mo	hollow
2	neighbouring	-2.71	-2.64	-2.97	-2.71	-2.67	-4.55
	separated	-1.47	-3.00	-2.05	0.58	-1.21	-0.60
	non-equivalent	-1.44	-1.54	-2.02	-1.61	-1.36	-3.96
3	line	-1.17	-2.78	-4.78	-0.79	-3.17	-5.14
	triangle	-1.66	-2.31	-2.29	0.12	-2.07	-2.61
	3D triangle	-0.77	-1.42	-0.92	-0.66	-1.32	-1.88
4	line	-1.79	-2.46	-3.77	-0.16	-14.10	-4.65
	rhombus	-0.69	-0.98	-3.42	0.62	1.01	-0.86
	3D rectangle	-1.69	-1.55	-1.50	-0.24	-1.24	-1.49
	tetrahedral	-0.85	-1.69	-2.40	-0.79	-1.67	-5.19

We find that there are five Co_n geometries where the metal-substrate interaction is more favourable than the metal-metal interaction. These are the two linear site **hollow** adsorptions for Co₃ and Co₄ clusters, the Co₃ triangle at site atop_S and the Co₄ rhombus at site hollow. For these structures the increase in the metal-substrate interaction is caused by the lack of metal-metal bonds, and for the site **hollow** structures the incorporation of Co into the S layer as well as the limited metal-metal interactions in a linear structure.

Table 6: Computed metal-metal interaction energies using Equation 40 in Chapter 3. For the "non-equivalent" configurations for 2 metal atom adsorption, the column "atop_S site" has atoms at sites atop_S and atop_Mo, "atop_Mo site" has atoms at atop_S and hollow and "hollow site" has atoms at atop_Mo and hollow.

No. metal atoms	Configuration	$E_{\text{interact}}/\text{Co-atom [eV]}$			$E_{\text{interact}}/\text{Ru-atom [eV]}$		
		atop_S	atop_Mo	hollow	atop_S	atop_Mo	hollow
2	neighbouring	-3.34	-3.42	-2.76	-1.74	-1.77	0.79
	separated	-2.73	-2.82	-2.88	-3.04	-2.71	-2.59
	non-equivalent	-4.11	-3.84	-3.84	-2.38	-2.34	-0.09
3	line	-4.43	-3.30	-1.09	-3.28	-1.30	0.73
	triangle	-0.98	-3.82	-3.60	-2.68	-2.58	-1.86
	3D triangle	-4.77	-4.63	-4.64	-3.56	-3.40	-2.48
4	line	-4.32	-3.64	-2.18	-4.12	9.56	-0.11
	rhombus	-5.17	-4.95	-2.45	-5.23	-5.29	-3.50
	3D rectangle	-4.59	-4.79	-4.43	-3.05	-3.69	-3.13
	tetrahedral	-5.00	-4.63	-3.66	-3.92	-3.48	-4.72

There are ten Ru_n structures where the metal-substrate interaction is more favourable than the metal-metal interactions. However, as we observe significant ML distortions for Ru_n adsorption, this should not be used as the only indicator for potential 2D vs 3D growth.

Similar to Co_n , the majority of the structures that have a more favourable metal-substrate interaction are those that do not involve any metal-metal bonds or those where the Ru adatoms were incorporated into the S layer. Several of these structures involved the formation of metal-S structures, which can account in part for the larger number of structures with a more favourable metal-substrate interaction.

Bond length analysis shows that the length of Co-Co and Ru-Ru bonds is directly influenced by the geometry of the adsorbed structure. This means that the majority of metal-metal bonds are shorter than the bulk metal-metal distances of 2.48 Å [46] for Co and 2.67 Å [48] for Ru, with some configurations showing longer distances depending on the arrangement of Co and Ru atoms. Co-S and Ru-S bonds change in length depending on the adsorption site, with the shortest bonds measured for site **atop_S** adsorptions. Bonds can also be longer due to structural distortions. Mo-S bonds are generally unaffected or slightly shorter than their equivalent on the bare ML. However, the local distortions described above can cause Mo-S distances to change by between -0.17 Å and +0.28 Å for Co adsorption and between -0.26 Å and +0.23 Å for Ru adsorption. Section A5.9 of the Appendix presents a more detailed analysis of the bonding.

Calculating addition energies allows us to study the energy gain as more atoms are added to a structure. Due to the many rearrangements of configurations observed, the energy gain computed from Equation 45 in Chapter 3 also contains the energy gained from the local atomic rearrangements previously described.

We observe particularly large magnitudes of addition energies for structures such as the Co₄ line and 3D rectangle configurations, when rearrangements occur to realise a particularly favourable structure. Smaller addition energy magnitudes are observed for rearrangements to a structure that is less favourable. Where no rearrangement occurs, the addition energies are of similar magnitude for different configurations, indicating that the variation arises only from the structure. Further details on addition energy are given in Section A5.8 of the Appendix.

We now discuss the electronic properties of Co and Ru clusters adsorbed on MoS₂. From the computed Bader charges, a metallic Co atom has 9.0 valence electrons, while a Co atom is considered oxidised when it has a Bader charge of less than 9.0 electrons. Similarly, metallic Ru has 8.0 valence electrons, and oxidised Ru will have a Bader charge of less than 8.0 electrons.

Analysis of the Bader charges for Co adsorption shows that in general atoms bound to the MoS₂ ML are oxidised. Adatoms that are only bound to other Co atoms remain metallic. Overall oxidation of Co atoms varies with atom coordination.

For Ru we find that atoms are partially oxidised when adsorbing to the MoS₂ ML, with a computed Bader charge in the range of 7.6 to 7.8 electrons, compared to metallic Ru with 8.0 electrons. As the number of metal adatoms increases, atoms tend to be less oxidised and show more metallic character. Any Ru atom in a 3D configuration that is only adsorbed to other Ru atoms remains metallic with Bader charges of 7.9 to 8.0 electrons. The tetrahedral configuration at site **hollow**, which has formed a Ru₄S₃ cluster, has a Bader charge of 7.6 electrons for the atop Ru atom that forms new Ru-S bonds. Further details of the Bader charge analysis and the exact charge for each Co and Ru atom are given in Section A5.3 of the Appendix.

The changes in charge density are localised around the adatoms and the Mo and S atoms in the immediate surroundings of the adatoms. Atoms that were found to be near metallic during the Bader analysis are also found to have somewhat less charge density compared to atoms that were oxidised. There is no distinct difference in how Co and Ru affect the charge density with adsorption to MoS₂. Examples of the charge density differences are shown in Section A5.5, Figures A76 and A77 of the Appendix, with some additional discussion on same.

Analysis of DOS plots shows that the Mo d-orbital or the S p-orbital contributions are largely unaffected by adatom adsorption. The metal d-orbital contribution increases for both Co and Ru as more adatoms are added, causing the total DOS to become increasingly more metallic compared to bare MoS₂, which is a semi-conductor. Metal d-orbital states appear in the band gap for as little as a single adatom. These increase in magnitude as the overall metal contribution increases with added adatoms. Some mid-gap states for Mo d-orbitals and S p-orbitals also begin to appear as more adatoms are added, contributing to the increasingly metallic nature of the systems. DOS plots for all configurations are shown in Section A5.1 in the Appendix.

A brief analysis of the magnetism of Co structures is given in the Appendix Section A5.12.

7.3 Adsorption of metal clusters on Defective MoS₂

S vacancies can form in MoS₂ monolayers with relative ease. [8] Le and coworkers showed that these vacancies become more stable when a row of vacancies is present in the monolayer. For the purpose of this study we limit ourselves to a single vacancy in the monolayer (a vacancy concentration of 2% per supercell), giving us a first insight of how metal adsorption is affected by the presence of the sulfur vacancy. As detailed in Chapter 3, using formation of H₂S from H₂, we computed a vacancy formation energy of -6.16 eV which confirms that defects are easily formed. There is no consistent approach to compute the vacancy formation energy of sulfur in transition metal dichalcogenides. We use this energy as an indicator to show that it is favourable to form a sulfur vacancy in MoS₂. Our result is consistent with other studies [8, 49] and what is known from experiment [17] in so far that the vacancy formation is favourable.

Single metal atoms and Metal₍₄₎ nanoclusters were adsorbed on the defective MoS₂ surface with a single sulfur vacancy. This allows us to assess adsorption modes and 2D vs 3D preferences as on the stoichiometric surface.

7.3.1 Copper

While all single atom adsorption configurations that we investigated are stable, only five of the twelve Cu₄ nanocluster structures were stable upon relaxation. For those adsorption structures that were not stable we generally find Cu atoms repelled from the surface and an endothermic adsorption energy. An example of the former is shown in the Appendix, Section A5.6 Figure A78, where a Cu atom is repelled from the defective monolayer during the geometry relaxation of a Cu₄ rhombus structure adsorbed at site atop_S and near the sulfur vacancy.

The binding energies of Cu and Cu₄, using Equations 37 and 39 from Chapter 3, are presented in Table 7 and

Table 7: Computed binding energies per Cu atom of 1 and 4 Cu atoms and binding energies of the Cu₄ nanocluster relative to a free Cu₄ nanocluster on MoS₂ with a sulfur vacancy for adsorption of a single Cu atom and the Cu₄ nanocluster. Dashes indicate geometries that were unstable on the defective monolayer.

Number of Cu atoms	Configuration	E _{bind} /atom [eV]			E _{bind} [eV]		
		atop_S	atop_Mo	hollow	atop_S	atop_Mo	hollow
1	-	-2.76	-1.35	-1.24	-2.76	-1.35	-1.24
4	line	-1.75	-1.83	-	-3.01	-3.30	-
	rhombus	-	-2.26	-	-	-5.02	-
	3D rectangle	-	-	-	-	-	-
	tetrahedral	-	-2.05	-1.93	-	-4.20	-3.31

Table 8: Computed metal-metal interaction energies for Cu₄ geometries on defective MoS₂ using Equation 40 in Chapter 3. Dashes indicate geometries that were unstable on the defective monolayer.

No. metal atoms	Configuration	E _{interact} /Cu-atom [eV]		
		atop_S	atop_Mo	hollow
4	line	-0.79	-0.92	-
	rhombus	-	-0.81	-
	3D rectangle	-	-	-
	tetrahedral	-	-1.25	-1.32

the stable adsorption geometries are shown in Figure 14. Comparing with the stoichiometric MoS₂ monolayer, all binding energies of the stable geometries are more favourable for adsorption on the defective monolayer. The largest increase in the computed binding energy is 1.95 eV, and this was observed for the single Cu atom adsorption initially at site atop_S. Upon relaxation, the adsorbed Cu atom migrates into the vacancy site and replaces the missing S atom. This results in Cu-Mo distances of 2.60 to 2.63 Å and there are no bonds to the surrounding S atoms. In contrast, adsorption of the Cu atom at sites atop_Mo and hollow, away from the vacancy site, results in an increase in the binding energy of only 0.03 and 0.06 eV. Cu-S bonds are ca. 2.18 Å for adsorption at sites atop_Mo and hollow, which is only slightly longer than the Cu-S distance of 2.15 Å for adsorption on the pristine surface. This indicates that the influence of a single sulfur vacancy in the monolayer is localised.

For adsorption of the four atom nanocluster, the largest increase in the computed binding energy is found for the initial flat rhombus configuration at site atop_Mo. Upon relaxation, three of the four Cu atoms migrate towards the vacancy and rearrange to a 3D triangle structure; the fourth atom remained at site atop_Mo, which is located away from the vacancy, as shown in Figure 14G. The change in the binding energy is 0.39 eV compared to the Cu₄ rhombus configuration at site atop_Mo and 0.42 eV compared to the 3D triangle at the same site, making this structure the most favourable of the 4 atom configurations. Cu-S distances are between 2.22 Å and 2.33 Å, while Cu-Cu distances are 2.33 Å and 2.35 Å. The Cu-S bonds are shorter compared to the 3D triangle at site atop_Mo on the pristine surface, which has Cu-S distances between 2.31 Å and 2.46 Å, while the Cu-Cu distances are of similar length, ranging between 2.35 Å and 2.36 Å. The shorter Cu-S distances likely contribute to the more favourable binding energy. Similar to the stoichiometric monolayer, the stable tetrahedral configurations (at sites atop_Mo and hollow, Figure 14H, I) are close in energy, with a difference in stability of only 0.12 eV. Cu-S distances are between 2.29 Å and 2.36 Å and Cu-Cu distances are between 2.40 Å and 2.50 Å. These are some of the longest distances observed on the defective ML. However, they are somewhat shorter than on the pristine surface, where the maximum Cu-S and Cu-Cu distances are 2.59 Å and 2.73 Å, respectively. This difference could contribute to the enhanced binding at the defective MoS₂ ML. The Cu-Cu interaction energies shown in Table 8 are stronger for the stable line

configurations (sites atop_S and atop_Mo) than for the equivalent adsorptions on the pristine ML. The rhombus configuration at site atop_Mo has a weaker Cu-Cu interaction, while the two stable tetrahedral configurations (sites atop_Mo and hollow) have very similar Cu-Cu interaction energies to their respective counterparts on the pristine ML. The weakened Cu-Cu interaction for the rhombus geometry is the most significant change observed compared to the pristine ML. This indicates that the Cu-Cu interaction energy is likely affected by changes in the Cu geometry rather than the presence of the vacancy.

The adsorption of 4 Cu atoms in a linear fashion, shown in Figure 14E and F, is stable for both atop_S and atop_Mo adsorption modes on the defective ML, although these adsorption structures are not as favourable as the clustered structures, which is again due to the lack of Cu-Cu bonds. At site atop_S, one of the four Cu atoms moves into the vacancy site, while two of four Cu atoms bind at the vacancy site for the site atop_Mo configuration. These are the only two 4 atom configurations where Cu-Mo interactions were observed, with distances between 2.62 Å and 2.65 Å. Cu-S distances lie between 2.17 Å and 2.27 Å, while Cu-Cu distances are 2.28 Å at site atop_S and 2.29 Å at site atop_Mo. Overall, the range of distances for Cu adsorption on the defective MoS₂ monolayer is narrower compared to the range of distances on the perfect surface. Cu-Cu distances are of similar lengths to those measured for structures on the pristine surface, and are slightly shorter than the distances in bulk copper. As for the pristine surface, there is no clear correlation between the geometry and the strength of binding.

The presence of a defect did not cause any notable geometry distortions in the monolayer. This is supported by Mo-S distances at the copper adsorption sites, which lie between 2.38 Å and 2.49 Å, which is close to the Mo-S distance of 2.42 Å in bare MoS₂. Some distortion was observed for the 3D Cu clusters (see Figure 14F and G in particular), which is caused by the migration of one or more Cu atoms towards the vacancy site.

The computed Bader charge on Cu at site atop_S indicates little oxidation of the Cu atom. This arises due to coordination of Cu to three Mo atoms so that oxidation of the Cu is not favourable. The other binding sites have computed Bader charges consistent with oxidation of Cu⁰ to Cu⁺, and are similar to the computed Bader charges for Cu adsorption at the bare monolayer, as detailed in Table A16 and Table A19 of the Appendix, Section A5.2.

Comparing the different Cu₄ adsorption structures, we find that in the two linear configurations the adsorbed Cu atoms are partially oxidised, with computed Bader charges of 10.8 to 10.9 electrons for adsorption at site atop_S and 10.6 to 10.8 electrons for adsorption at site atop_Mo. In the case of adsorption at site atop_Mo, the two atoms closest to the vacancy (Cu_1 and Cu_2 in Table A19, Appendix Section A5.2) are less oxidised than those away from it. In the tetrahedral/triangular structures, the computed Bader charges for the Cu atoms directly bound to the monolayer are consistent with oxidation to Cu⁺, while the remaining Cu atoms that do not interact with the monolayer are metallic. We further note that atoms are only partially oxidised when they are bound at the vacancy,

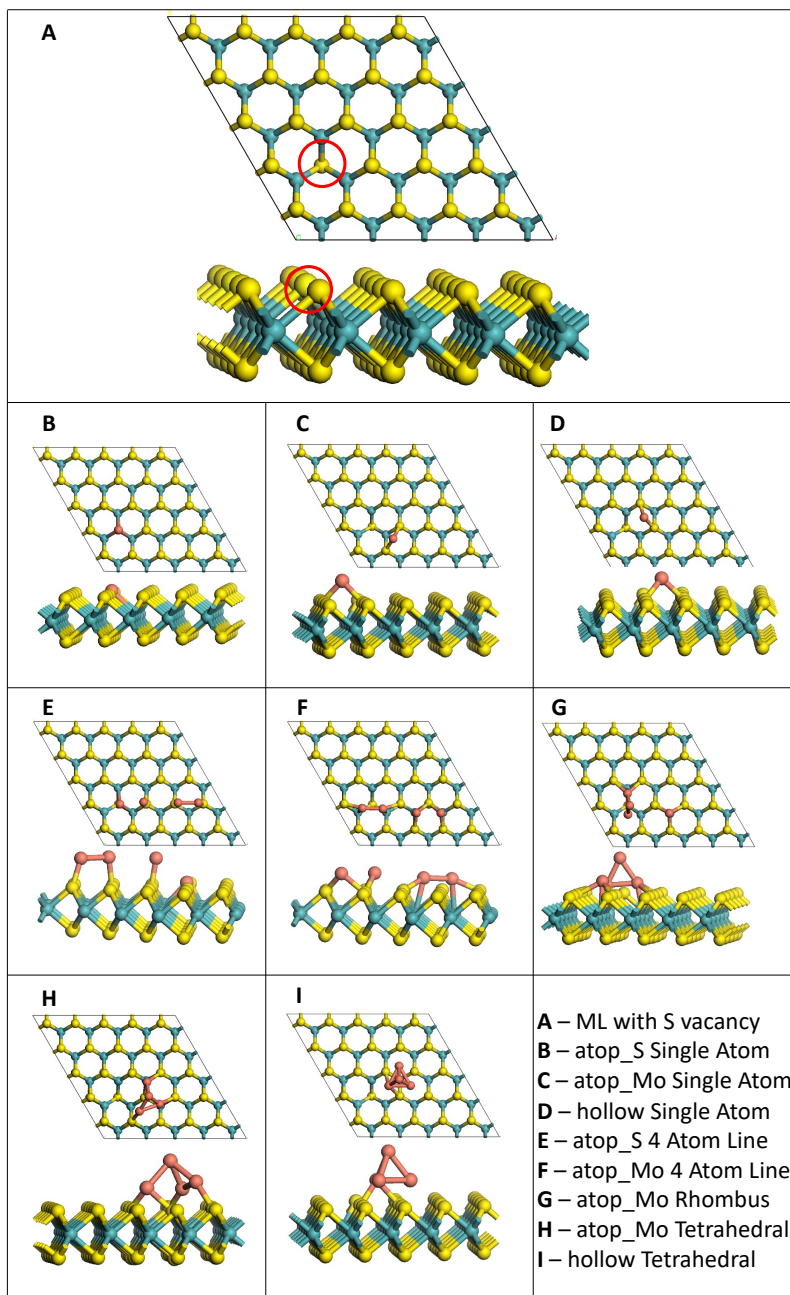


Figure 14: Bare MoS₂ ML with S vacancy (highlighted in red) and adsorption structures for Cu₁ and Cu₄ adsorbed on MoS₂ with one sulfur vacancy

while oxidation to Cu^+ occurs for atoms further away from the vacancy. The same observations were also found for the pristine surface, indicating that the presence of the vacancy does not directly affect the charge transfer unless the Cu atom is adsorbed in or beside the vacancy site. Bader charges for all Cu adsorptions on the defective ML are shown in the Appendix, Section A5.2, Table A19. Analysing the charge density difference for the two most favourable adsorption modes shows that in contrast to the pristine surface the charge density is not limited to just adsorbed Cu atoms and the S and Mo atoms interacting directly with the Cu atoms. Instead, some charge density is delocalised to the S and Mo atoms neighbouring the S vacancy. Figures A75I and A75H in Section 5.5 of the Appendix show the charge density difference of the most favourable Cu_n adsorption modes on defective MoS_2 .

Figure 15 shows the densities of states for the three most favourable Cu adsorption configurations on defective MoS_2 . Densities of states for all other adsorptions can be seen in the Appendix, Section A5.1, Figure A65. The general features of the DOS are similar to the pristine surface, in which mid-gap states originating from the presence of adsorbed copper, can be seen for all configurations.

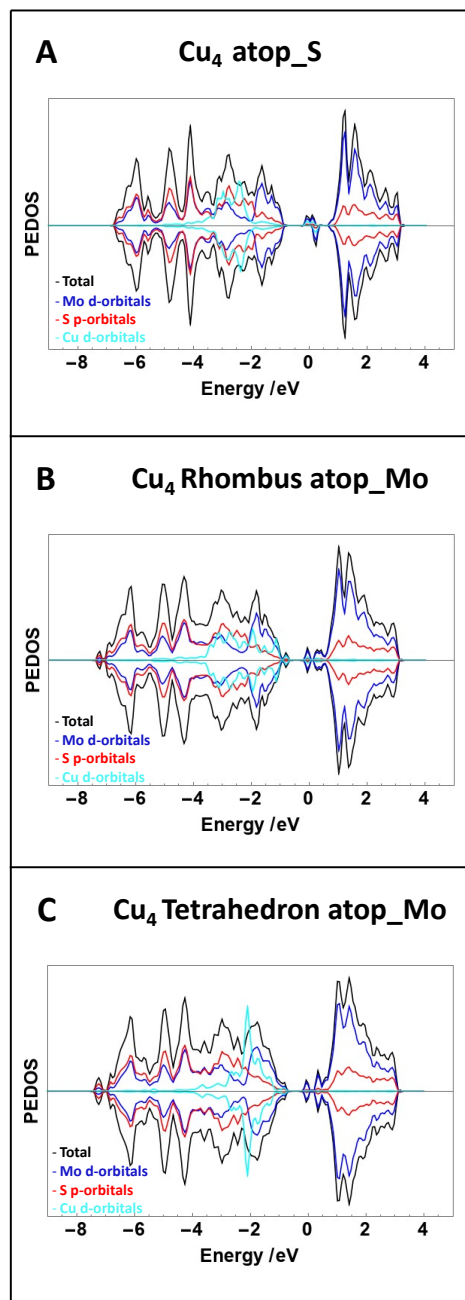


Figure 15: DOS plots of most favourable Cu₁ and Cu₄ adsorption structures on defective MoS₂. The contribution of the Cu d-orbitals has been increased by a factor of 5 for ease of comparison and zero on the "Energy" scale is the Fermi level.

7.3.2 Cobalt and Ruthenium

The binding energies, the metal-substrate interaction energies and the metal-metal interaction energies for all structures on defective MoS₂ are shown in Tables 9, 10 and 11, respectively. Discussion on bond lengths can be found in Section A5.9 of the Appendix.

For single atom adsorption, we find that the metal-ML interaction is stronger at site **atop_S**, where, similarly to Cu [41], Co and Ru fill the vacancy site. This leads to a stronger binding energy by ca. 2 eV for Co and ca. 3 eV for Ru, compared to the same initial adsorption site on the pristine ML. While for Cu we found that the metal-ML interaction was enhanced at all sites, for Co and Ru we find that the initial adsorption at sites **atop_Mo** and **hollow** is not stable. For Co, a single atom at either site **atop_Mo** or **hollow** migrates away from its original adsorption site and the vacancy to bridge between two S atoms between site **atop_Mo** and **hollow** (bridge site). The same occurs for a Ru atom at site **hollow**, while adsorption at site **atop_Mo** led to the atom migrating to the nearest site **hollow**. These adsorption configurations are less favourable by approximately 0.5 eV, than adsorption at the corresponding sites **atop_Mo** and **hollow** on the pristine ML, but more favourable than adsorptions at site **atop_S** on the pristine ML. These geometries are shown in Fig.16.

For Co₄, a decrease in the interaction strength is observed for the line configuration at site **atop_S**, and the 3D rectangle at site **atop_Mo**. For the line configuration at site **atop_S**, this is due to the atoms remaining in a line, compared to the migration to a different site that was observed on the pristine surface. Despite the formation of a bond between two of the Co atoms and one of the Co atoms migrating into the vacancy, the binding energy of -5.43 eV is less favourable compared to -6.11 eV on the pristine surface. The tetrahedral geometries on the defective ML behave similarly to their counterparts on the pristine ML. The binding energies are comparable with differences of ca. 0.1 eV and the geometries do not distort. All geometries for Co₄ are shown in Figure 17.

An increase in the interaction strength is observed for the line and rhombus configurations at site **atop_Mo**

Table 9: Computed binding energies for Co₁, Co₄, Ru₁ and Ru₄ on defective MoS₂ ML for various atom configurations using Equation 37 in Chapter 3. Dashes indicate geometries that were unstable on the defective monolayer.

No. metal atoms	Configuration	E _{bind} /Co-atom [eV]			E _{bind} /Ru-atom [eV]		
		atop_S	atop_Mo	hollow	atop_S	atop_Mo	hollow
1	-	-6.83	-5.22	-5.12	-5.59	-3.32	-2.91
4	line	-5.43	-6.22	-	-4.48	-4.91	-5.16
	rhombus	-	-6.25	-6.64	-	-4.83	-4.33
	3D rectangle	-	-5.78	-6.29	-	-4.89	-4.71
	tetrahedral	-	-6.22	-6.00	-	-4.95	-4.72

Table 10: Computed metal-substrate interaction energies Co₄ and Ru₄ on defective MoS₂ ML for various atom configurations using Equation 39 in Chapter 3. Dashes indicate geometries that were unstable on the defective monolayer.

No. metal atoms	Configuration	E _{metal-substrate} /Co-atom [eV]			E _{metal-substrate} /Ru-atom [eV]		
		atop_S	atop_Mo	hollow	atop_S	atop_Mo	hollow
4	line	-1.79	-2.30	-	-0.16	-2.68	-4.52
	rhombus	-	-1.96	-4.15	-	-2.76	-2.88
	3D rectangle	-	-0.73	-1.58	-	-1.01	-0.70
	tetrahedral	-	-1.37	-1.17	-	-1.60	-1.06

Table 11: Computed metal-metal interaction energies using Equation 40 in Chapter 3 for Co₄ and Ru₄ on defective MoS₂. Dashes indicate geometries that were unstable on the defective monolayer.

No. metal atoms	Configuration	E _{interact} /Co-atom [eV]			E _{interact} /Ru-atom [eV]		
		atop_S	atop_Mo	hollow	atop_S	atop_Mo	hollow
4	line	-4.05	-3.92	-	-2.35	-2.22	-0.64
	rhombus	-	-4.29	-2.49	-	-2.07	-1.45
	3D rectangle	-	-5.05	-4.71	-	-3.88	-4.00
	tetrahedral	-	-4.86	-4.83	-	-3.35	-3.67

and the rhombus and 3D rectangle configurations at site **hollow**. Depending on the configuration this change can be attributed to bond formation, structural rearrangement compared to the same adsorption configuration on the pristine ML, or in the case of the rhombus at site **hollow**, surface distortion and Co_xS_y formation, which also creates an additional S vacancy. The latter is facilitated by the presence of the vacancy and does not occur on the pristine ML.

The presence of the vacancy changes the charge distribution compared to the pristine surface. Atoms near the vacancy are less oxidised (with computed Bader charges of 8.7 to 8.8 electrons) and atoms further away from the vacancy site are more oxidised (Bader charges of 8.5 electrons). The apex atoms in 3D structures are metallic, even for structures where these were slightly oxidised on the pristine surface.

Even though the effects of the vacancy and the adsorption of Co remain localised, the charge density difference shows that the area over which significant changes in charge density take place is larger than on the pristine surface. Visualisations of the charge density differences on the defective ML are included in Figures A76 and A77 in Section A5.5 of the Appendix. Metal-metal interaction energies for Co are found to be generally of the same magnitude as on the pristine surface. There is no clear correlation between the binding energy and the metal-metal interaction energy. There are no Co geometries on the defective surface where the metal-substrate interaction is more favourable than the metal-metal interaction. The interaction energy is also not affected by the incorporation of S into the Co cluster as is observed for the rhombus configuration at site **hollow**. This structure has very

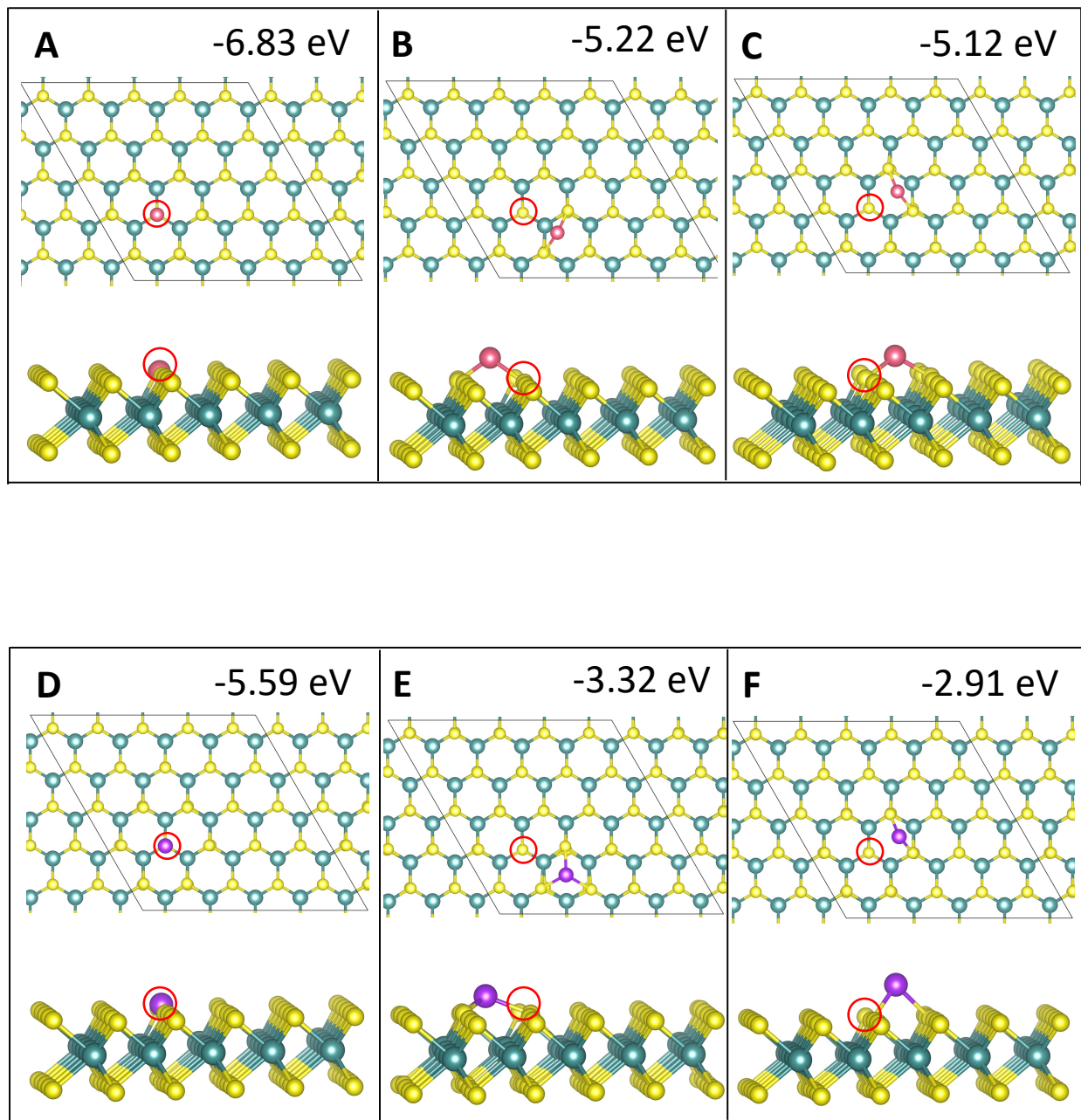


Figure 16: Adsorption modes of single Co (pink) and Ru (purple) atoms on defective MoS₂.

favourable adhesion to the ML, but the metal-metal interaction energy is similar compared to the pristine surface.

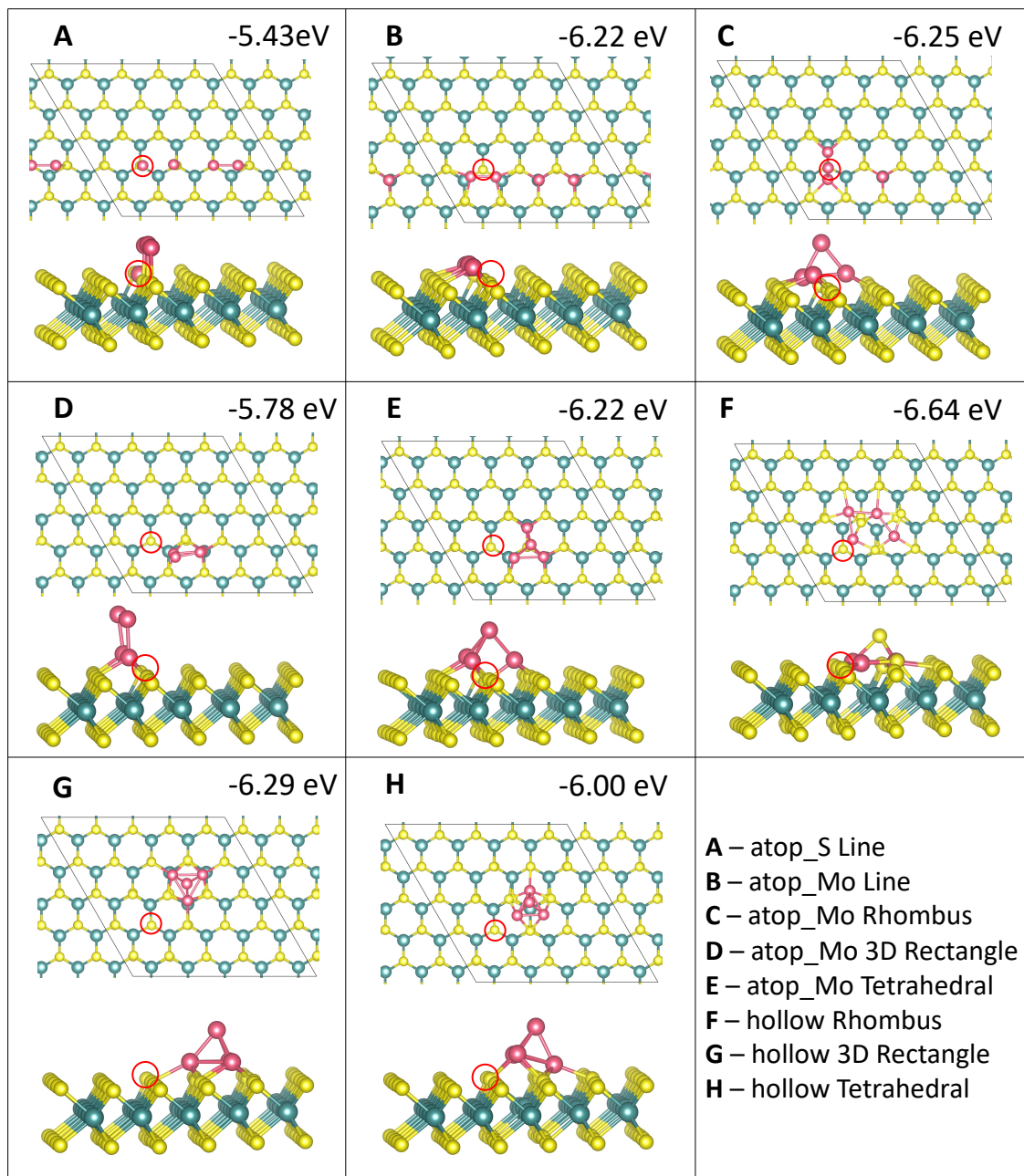


Figure 17: Atomic structures and energies of Co₄ adsorption modes on defective MoS₂.

Ru₄ structures remained largely unchanged compared to the pristine ML; all Ru₄ geometries are shown in Figure 18. The only decrease in stability is observed for the tetrahedron at site **atop_Mo**, which distorts away from the vacancy. An increase in stability of between 0.1 and 0.4 eV is observed for all line configurations, the rhombus configuration at site **atop_Mo** and the 3D rectangle configuration at site **hollow**.

The line configuration initially at site **atop_S** relaxes to produce two separated Ru₂ clusters. Of the two atoms near the vacancy, one has moved into the vacancy to replace S, while the other is adsorbed at a site **hollow**. The energy gain compared to the pristine surface can be attributed to the incorporation of Ru into the vacancy, which is always favourable. The line configuration at site **atop_Mo** has the same geometry for Ru₄ as Co₄ and Cu₄, with two Ru atoms bridging over the vacancy, as shown in Fig.18B. Similarly, the rhombus configuration at site **atop_Mo** has rearranged to the same 3D triangle over the vacancy with the fourth atom at the nearest site **atop_Mo** that was observed for Co₄ and Cu₄ on the defective ML.

Even though the binding energy for the tetrahedron at site **hollow** is similar on the defective ML and the pristine ML, the presence of the vacancy prevents the incorporation of the basal Ru atoms into the S layer. This is the case for all the structures at site **hollow**, which cause less distortion on the defective ML compared to the pristine ML. The exception to this is the line configuration at the **hollow** site (Fig 18F). Here, two Ru₂ dimers are formed, with a S atom bridging between them, creating a Ru₄S structure and an additional vacancy in the ML. This is also the most favourable Ru₄ structure on the defective ML.

Ru atoms are similarly oxidised on both the pristine and the defective ML, although as for Co, atoms near the vacancy tend to be less oxidised with approx. 7.8 electrons. Once again, atop Ru atoms in 3D structures remain metallic, with computed Bader charges of 7.9 to 8.0 electrons. Interestingly, the atop atom in the rearranged rhombus structure at site **atop_Mo** is reduced, with a computed Bader charge of 8.1 electrons, making it the only metal atom in any of the configurations to become reduced. Additional Bader analysis is detailed in Section A5.4 of the Appendix.

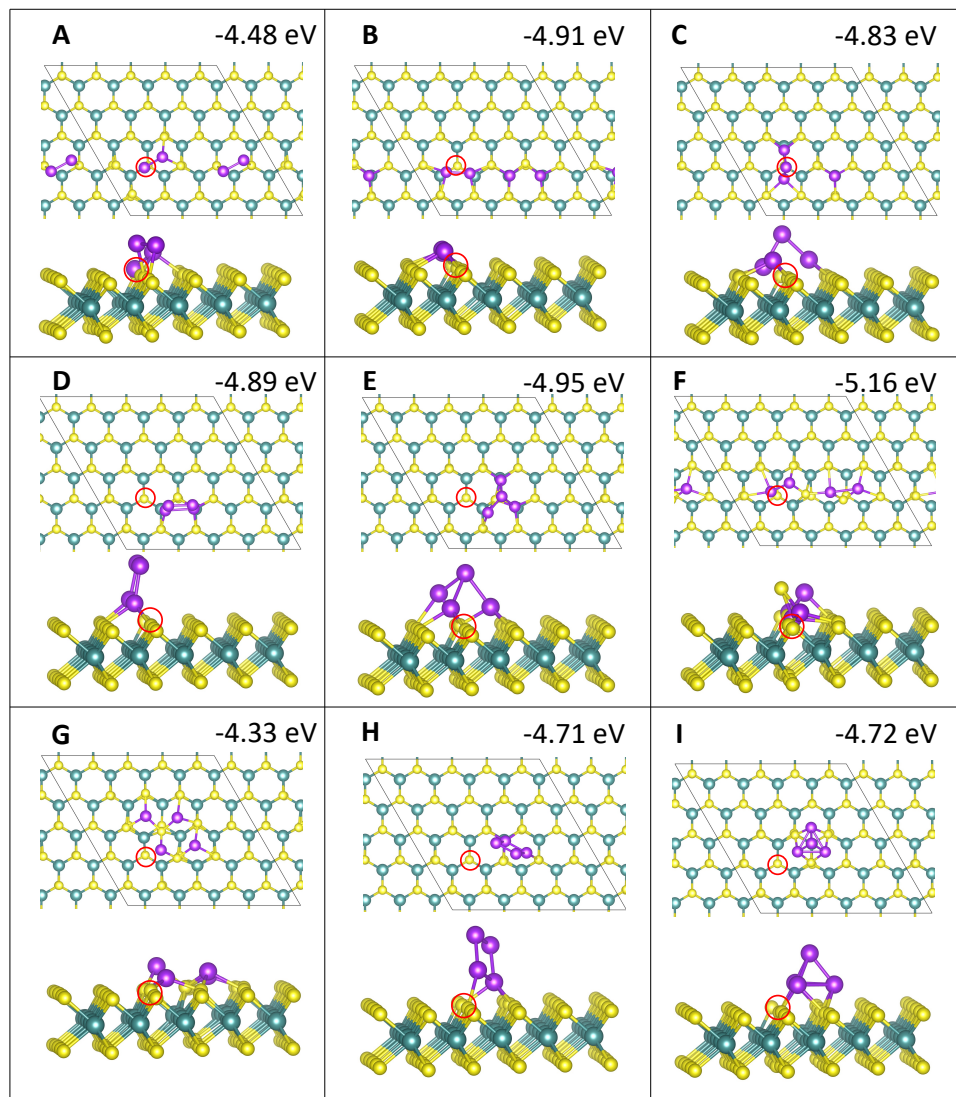
The charge density difference for Ru on the defective ML is similar to the pristine ML, Figure A77G and H in Section A5.5 of the Appendix.

The effect of the vacancy on the metal-metal interaction energy of adsorbed Ru structures is significant. For most structures, the magnitude of the metal-metal interaction energies is approximately half that of the pristine ML. This is best illustrated using the example of the rearranged rhombus configuration at site **atop_Mo** as this same rearrangement also occurs for Co. While for Co the interaction energy weakens by approximately 0.7 eV due to the separated fourth atom, for Ru the interaction is weakened by over 3 eV from -5.29 eV on the pristine surface to -2.07 eV on the defective surface.

This change can be attributed to the effect of the vacancy on adsorbed Ru structures. There are some exceptions, where the metal-metal interaction is strengthened compared to the pristine ML, however this is due to a difference in geometry compared to the pristine surface.

There are three geometries adsorbed on the defective ML that have a metal-substrate interaction more favourable than the metal-metal interaction. These are the linear configurations at site **atop_Mo** and **hollow** and the rhombus at site **hollow**. All three of these structures have none or few metal-metal bonds and both the configurations at site **hollow** involve incorporation into the S layer which increases the strength of the metal-substrate interaction.

The Appendix contains additional discussion for Ru and Co on defective MoS₂, including Bader charges (Section A5.4) and bond lengths (Section A5.10). Section A5.11 gives a brief explanation on the influence of van der Waal's interactions.



A – atop_S Line
B – atop_Mo Line
C – atop_Mo Rhombus
D – atop_Mo 3D Rectangle
E – atop_Mo Tetrahedral
F – hollow Line
G – hollow Rhombus
H – hollow 3D Rectangle
I – hollow Tetrahedral

Figure 18: Atomic structures and energies of Ru₄ adsorption modes on defective MoS₂

7.4 Comparison of behaviour of Cu, Co and Ru on 2D MoS₂

The interaction of the metals Cu, Co and Ru with the pristine and defective MoS₂ ML is clearly dependent on the nature of the metal. This is most obvious from the magnitude of the binding energies of a single atom. This follows the trend $\text{Co} > \text{Ru} > \text{Cu}$. A single Cu atom binds to pristine MoS₂ with energies ranging from -0.8 to -1.3 eV. The adsorption energy of a Co atom ranges between -4.2 and -5.8 eV, while the adsorption energy of a Ru atom ranges between -2.5 and -3.9 eV.

For metal atoms and dimers, the stability of Cu and Ru adsorption is governed by the adsorption site, with site **atop_Mo** the most favourable site for both. Ru atoms at site **hollow** cause distortions in the ML. For Co, the adsorption site can also influence the stability, with site **atop_Mo** the most favourable overall. Site **atop_Mo** is favoured, as it continues the MoS₂ lattice structure. We find that this, as well as the symmetrical addition of atoms at equivalent sites instead of non-equivalent sites is correlated with the strength of adhesion.

For $n=3-4$, the stability of structures is governed by the number of Cu-Cu bonds and Cu adsorption becomes independent of adsorption site for $n=3$. This means that all geometries have very similar binding energies. For $n=4$, 2D and 3D structures are most stable at site **atop_S**. This is due to the decreased distance between neighbouring sites **atop_S** compared to sites **atop_Mo** and **hollow** which facilitates Cu-Cu bond formation. Additionally, there is no clear preference for either 2D or 3D structures.

Co adsorption continues to be controlled by the adsorption site for $n=3$. Different geometries have very similar energies at the same site, with the most favourable adsorption configurations at site **atop_Mo**. Co₄ prefers tetrahedral-type geometries on pristine MoS₂, as is evident from the rearrangement of the atomic structure when Co atoms are close enough that Co-Co bonds can form. However, linear configurations without Co-Co bonds are competitive in energy with these tetrahedral geometries. This likely originates from the incorporation of Co atoms into the S layer in such structures. In turn, this indicates a strong interaction with the MoS₂ ML, while tetrahedral geometries have an energy gain originating from Co-Co interactions instead. If we compare with Cu, the Co-S bond enthalpy [50] is much higher than the Cu-S bond enthalpy, [50] at 331 kJ/mol and 274.5 kJ/mol respectively and the Co cohesive energy is larger at 4.39 eV, compared to 3.49 eV for Cu. A stronger bond enthalpy and cohesive energy compared to Cu explain the origins of the strong interactions observed.

Similarly to Co, Ru₃ adsorption is mainly influenced by the adsorption site, with some influences from the overall geometry which is particularly noticeable at site **atop_S**, where the triangle configuration has a binding energy that is 1.5 eV weaker compared to the other two geometries. This is also clear evidence that Ru atoms prefer to be associated, as the lower binding energy for the triangle at site **atop_S** arises from the separation of the

atoms. In contrast, Ru_4 does not have the same preference for tetrahedral motifs as Co_4 , despite the tetrahedral configuration at site **2** being the most favourable adsorption mode. Nevertheless, clustered geometries are preferred compared to linear adsorption, probably as a result of the larger Ru cohesive energy of 6.74 eV. Structures with minimal distortion are particularly favoured, as well as those where Ru incorporates into the S layer of MoS_2 and Ru_xS_y clusters are formed. Ru-S has an even larger bond enthalpy of 531.8 kJ/mol [51] compared to Cu-S and Co-S, which likely contributes to Ru_xS_y formation.

For Cu, Co and Ru, adsorption of a single atom on the defective ML is most favourable when the metal atom fills the vacancy. Cu adsorption at sites **atop_Mo** and **hollow** is also enhanced, while these adsorption sites become unfavourable for Co and Ru due to adatom migration away from the vacancy during the relaxation. Adsorption at the bridge site for Co and site **hollow** for Ru is less favourable than adsorption on the pristine ML.

The presence of the S vacancy enhances the adsorption of Cu_4 and Ru_4 , however adsorption of Co_4 is only enhanced for some geometries and decreased for others. Only a limited number of Cu geometries were stable, while others were repelled from the ML. The stable configurations showed a preference to be 3D. 2D and 3D Co_4 structures were competitive in energy, with a preference towards structures that incorporated into the S layer. Further, the vacancy facilitated the transfer of an S atom from the ML onto the Co structure to create a Co_4S cluster, which was also overall the most favourable Co_4 structure on the defective ML. This shows that in the presence of Co, further vacancies can be formed through the transfer of S atoms onto the metal cluster. The most favourable Ru_4 structure on the defective ML is the line configuration at site **3** where transfer of an S atom onto the Ru structure has occurred to form a Ru_2S cluster with two adjacent Ru atoms, similar to the same Co_4 adsorption. Despite this, we find that Ru atoms are less likely to incorporate into the S layer on a defective surface and that the metal-metal interaction energy is weakened, indicating that in the presence of more vacancies 2D growth of Ru should be promoted.

It is difficult to predict whether a thin film will grow in a 2D or 3D structure, but a useful descriptor is how the metal-substrate interaction compares to the metal-metal interaction and how the total binding energy compares to the bulk metal cohesive energy. While the metal-substrate interaction exceeds the metal-metal interaction energy for several Co_n and Ru_n structures, only Co has a total binding energy that is more favourable than the cohesive energy. The most favourable adsorptions for both Ru and Cu are 1 eV less favourable than their respective cohesive energies. [52] Despite this, we have shown that Ru incorporation into the S layer on the pristine surface and the presence of a vacancy both enhance Ru-substrate interaction and weaken metal-metal interaction. It is therefore possible that the presence of more vacancies in the MoS_2 ML could promote 2D growth of Ru.

Further work including the calculation of the activation energies for 2D or 3D clusters will give a more detailed

insight into the processes that control aggregation on the surface. However, this is out of the scope of this thesis.

7.5 Conclusions

The adsorption of metal species on semiconducting supports such as 2D monolayers of MoS₂ is a subject of significant interest in a range of applications, particularly in catalysis and more recently in semiconductor nanodevices where 2D materials can function as barrier materials to prevent copper diffusion into the underlying dielectric material. Cu, Ru and Co are all metals that can be used either as (alternative) interconnect metals or catalysts.

As detailed in Chapter 2, while there have been studies of single atom adsorption at MoS₂ [24, 28] and the adsorption of larger nanoclusters of noble metals, [23] there is as yet no comprehensive study of the interactions of small sub-nanometer metal species with an MoS₂ ML, which is useful to probe the fundamental metal-MoS₂ interactions. In this chapter, we have presented an extensive study of the interaction of Cu_n, Co_n and Ru_n species, with $n = 1 - 4$, at the perfect and defective MoS₂ monolayer; we also discuss how interactions between MoS₂ and the three metals compare.

We find that the stability of single atom adsorption follows the trend $\text{Co} > \text{Ru} > \text{Cu}$. Furthermore, this trend holds for the adsorption of all metal structures studied, regardless of the number of adatoms. Co typically adsorbs more strongly than Ru to the MoS₂ ML by up to 2.0 eV, while adsorption is stronger by up to 5.0 eV compared to Cu.

Based on our analysis, we were able to determine that the stability of Cu structures on MoS₂ is driven by achieving the maximum number of Cu-Cu bonds. Ru structures are most stable when they conform with the MoS₂ lattice by adsorbing at site **atop_Mo** and cause minimal distortions in the ML. In comparison, Co structures prefer to be in a tetrahedral arrangement and become more stable by incorporating into the surface S-layer of the MoS₂ lattice.

Our overall findings indicate that for Co 2D and 3D cluster adsorption structures are competitive. However, the binding energy of Co on MoS₂ is significantly more favourable than the cohesive energy of Co. This strong binding energy, as well as favourable metal-substrate interaction should inhibit migration of atoms to form 3D structures during thin film deposition, resulting in a 2D film suitable for interconnect applications, without the need of an additional liner material to promote wetting. There are however some concerns how the transfer of S atoms from the ML to Co_n might affect the purity of the interconnect.

It is difficult to say whether Cu will form 2D or 3D structures, as the rhombus and tetrahedral structures are competitive in energy. The cohesive energy of Cu is more favourable than the adsorption of Cu on MoS₂ indicating a likely tendency towards 3D structures, unless the interaction with the ML can be further enhanced with, for

example, additional S vacancies. A study of larger Cu systems on a MoS₂ ML is necessary to make a more accurate prediction of the film morphology. An application in catalysis, where 3D structures with large surface to volume ratios are desired, is possible, should a 3D morphology be preferred.

Similarly, Ru also has a binding energy that is less favourable than its cohesive energy. This suggests that 3D growth of Ru on MoS₂ will be promoted, making this system more suitable for catalysis applications. However, with several structures where the metal-substrate interaction is more favourable than the metal-metal interaction and the overall weakening of the metal-metal interactions caused by an S vacancy, a 2D Ru thin film could be formed in the presence of S vacancies.

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Chapter 8: Conclusions and Outlook

8.1 Conclusions

In this thesis I have explored the potential of single materials based on modifying TaN to function as combined barrier/liner materials for advanced interconnect applications. The key to fabricating high quality interconnects at the dimensions of nanoelectronic devices is to reduce the thickness of the barrier/liner stack, while still maintaining good barrier properties and promoting the growth of conducting Cu films. Removing either the barrier or liner entirely is not possible without compromising the integrity of the interconnect, even for alternative interconnect metals such as Ru and Co.

From the literature we know that the necessary properties for good barrier and liner materials are as follows:

- Thermal stability
- Low grain boundary diffusion
- Low overall resistivity
- Wettability and adhesion of interconnect metal
- Low electromigration
- Reduced material thickness

Trying to investigate all of these properties computationally is highly resource intensive, not necessarily amenable to first principles simulations and outside the scope of a single thesis. Therefore, we chose to focus on finding new materials that can yield a reduction in the material thickness and enhance the wettability and adhesion of Cu to promote deposition of conducting films and examine Ru and Co on MoS₂ as alternatives for interconnect metals and barrier layers.

We considered two different approaches to reducing the thickness of the barrier/liner material. First, we modified TaN, the most thoroughly studied barrier material, with elements that show liner behaviour, through passivation

and surface doping. These materials can be deposited with precise thicknesses using atomic layer deposition (ALD), which is widely used in semiconductor manufacturing. The second approach is to investigate the potential of 2D materials, as exemplified by MoS_2 , which can also be deposited by ALD. [1, 2]

Through investigating the interactions between different metal structures and our potential barrier/liner materials using density functional theory (DFT) we are able to assess the strength of adhesion of the metal and have extracted the metal-substrate and metal-metal interactions. Based on the theory of the relevant growth mechanisms, these are the main forces in competition to promote either 2D or 3D growth. The approach we use is a resource friendly and efficient way to determine the wettability of Cu and other interconnect metals on the relevant surfaces, without having to use very large models or synthesise the materials in the lab. However, studying wettability and adhesion also allows some insight into other desirable barrier/liner properties. As good wettability coincides with conductive Cu films, wettability in combination with the total density of states (DOS) and Bader charges is a good indicator of the overall resistivity.

We used ab initio molecular dynamics (aiMD) calculations to help confirm our predictions of film morphology on modified TaN. Such finite temperature calculations additionally allowed us an insight into the relative thermal stability of these materials.

In **Chapter 4**, we started by examining the fundamental interactions between one and two Cu adatoms and Ru (0 0 1), TaN (1 0 0), TaN (1 1 0), TaN (1 1 1), TaN (1 1 0) passivated with one and two monolayers of Ru and 8% (single atom) Ru doped into the surface layer of the TaN (1 1 0) slab. This showed that the interaction between Ru and Cu was stronger than between Cu and TaN, which explains why Ru is a liner but TaN is not. We also found that the (1 1 0) surface was the most stable of the TaN low-index surfaces and that association of atoms was least favourable on this surface. We selected TaN (1 1 0) to study the modification of TaN via Ru doping and passivation.

Passivation with one monolayer of Ru improves the adhesion of Cu compared to bare TaN or bare Ru. However, despite low Cu diffusion barriers, adatoms preferred to associate on this surface. In combination with the fact that passivation does not provide maximum thickness reduction, this surface was deemed reasonable as a stepping stone to move fabrication from thicker bilayers of Ru/TaN to a combined barrier/liner material, but is not a longer-term solution.

Cu on Ru-doped TaN showed decreased binding compared to Ru passivated surfaces. However, adsorption near and diffusion towards the Ru dopant proved very favourable, indicating that the dopant acts as a nucleation site.

Consequently, higher doping concentrations of Ru were considered next, as it is reasonable that nucleation sites distributed throughout the surface would aid in wetting of the Cu film across the surface.

Using two, three and four Cu atoms in various arrangements we studied the interaction between Cu and bare TaN, 1 and 2 ML Ru passivated TaN and 25%, 50%, 75% and 100% Ru doped TaN. Based on the example of 50% doping, we find that the distribution of dopants affects the stability of the surface. There are two coordination environments for surface atoms (three or six coordinate with N). The surface is more stable if the dopants are three coordinate rather than six coordinate.

Exploring the interaction of different Cu structures with the various Ru-modified TaN surfaces, we firstly focus on the competition between Cu-substrate and Cu-Cu interactions and how they control wetting. Based on our study of the different interactions, wetting should be promoted where the adsorption energy is stronger than the cohesive energy of the adsorbed metal and for those surfaces with Cu-substrate interactions that are more favourable than the Cu-Cu interactions. The average metal-substrate interaction is more favourable than the Cu-Cu interaction on all Ru-modified TaN surfaces and on bare TaN. However, only the 1ML Ru passivated surface, 100% and 50%-10 Ru-doped TaN surfaces have an adhesion energy that is as favourable or more favourable than the cohesive energy of Cu. This suggests that these surfaces should promote wetting of Cu instead of formation of 3D islands.

We also found that due to the smaller ionic radius of Ru compared to Ta, the surface atoms rearranged creating gaps. Incorporation of Cu into these gaps increased the strength of the Cu-substrate interaction, but did not impact the barrier function of the underlying TaN slab.

In **Chapter 5**, we applied the findings from Chapter 4 to a larger model Cu structure with 29 atoms. This model allows more detailed insights into the factors that control the stability of 2D vs 3D Cu structures. Using a combination of static geometry relaxations, finite temperature aiMD calculations and activation energies obtained from nudged elastic band (NEB) calculations, we showed that 50% Ru surface doping of TaN is sufficient to promote formation of a 2D Cu film and prevent island formation. Ru passivated TaN also promotes formation of 2D Cu. While the 100% Ru doped TaN surface was expected to promote 2D copper formation, it is in fact thermally unstable above 300 K undergoing significant rearrangements and strong Cu and N migration. This highlights that one needs to be careful in making stability predictions from analysis of 0 K energies.

Based on our enhanced understanding of the Cu-Cu and Cu-substrate interactions gained from Chapters 4 and 5, we selected the Cu structures that allowed us the most insight into these interactions to create a streamlined approach for testing potential combined barrier/liner materials.

In **Chapter 6** we use this approach to predict the morphology of Cu on Co and W doped TaN surfaces.

We adsorb Cu structures with one, two, four or twenty-nine atoms on 25%, 50% and 100% Co and W doped TaN. As for Ru, doping at the three-coordinate Ta site is the most favourable option for Co and W dopants. We selected the most and least favourable dopant distributions of the 50% W/Co doped surface. Using static geometry

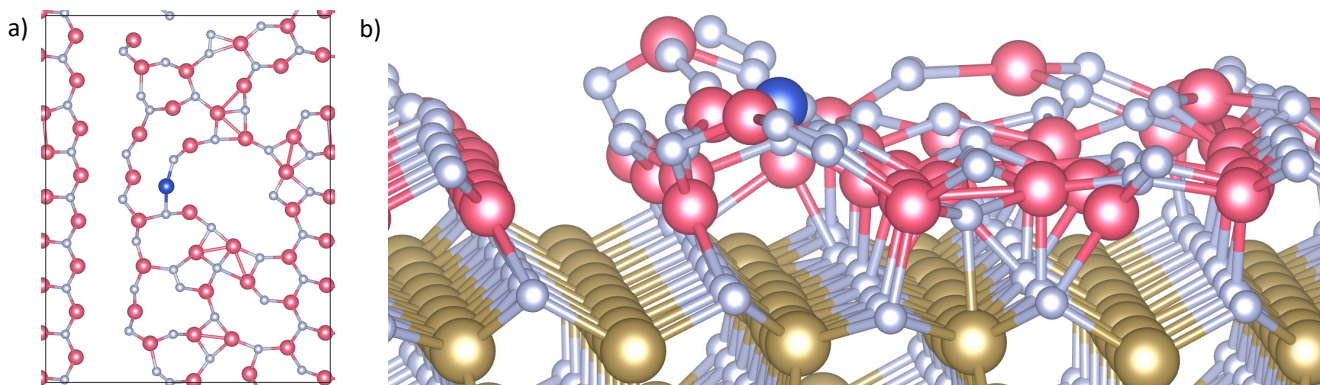


Figure 1: a) Top view of the Co-N toplayer of the Co^{100} slab after single Cu adsorption to show the large gaps in the surface caused by rearrangements and layering of Co. b) Side view of the same Co^{100} surface with single atom adsorption highlighting the agglomeration of CoN.

relaxations and aiMD calculations at finite temperature, we determined that 25% Co-doping and 25% W-doping inhibit the 3D growth of Cu structures, instead promoting wetting of Cu. The more favourable arrangement of 50% Co doping as well as 100% W-doping also inhibit 3D growth. Co has an ionic radius that is smaller than that of both Ta and Ru. This causes significant surface rearrangements. The 100% Co-doped surface was found to rearrange significantly upon Cu adsorption. A large gap is formed in the surface due to the smaller ionic radius, exposing the TaN slab. Additionally, some Co and N atoms migrate to create areas of clustered CoN, with some Co atoms migrating to adsorb atop the CoN layer, as shown in Figure 1. Both the 100% and the less favourable 50% Co-doped surfaces are thermally unstable with Cu adsorption. However, the favourable Cu-slab interactions on the 25% doped surface, along with the lack of surface rearrangements due to the lack of Co-Co interactions, make this a promising candidate for a combined barrier/liner material - in this case we see migration of only a small number of Cu atoms into a second layer during the relaxation and the aiMD at 500 K, indicating that it should inhibit formation of 3D islands.

50% W doping does not prevent 3D growth. This is partially due to the lack of surface gaps formed as a result of the similar ionic radii of Ta and W and which are therefore not available to enhance the Cu-substrate interaction. This property could however be an advantage, as this seems to improve the thermal stability compared to Ru and Co, e.g. Figure 2. Additionally, the interactions between Cu and W-doped TaN with W concentrations above 25% are quite strong, indicating that 100% doping, or essentially passivation with WN can create a combined barrier/liner material. To the best of our knowledge this is also the first time that liner properties of WN have been studied.

25% W doping does not improve the binding energy of Cu compared to TaN, but it improves the metal-substrate

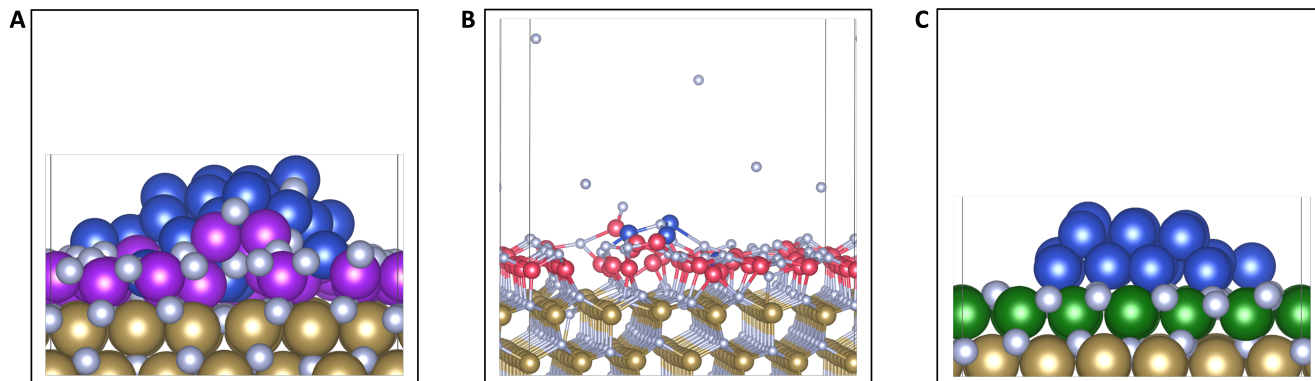


Figure 2: Thermal stability of Ru-, Co- and W-doped TaN. A) Mixing of Ru, N and Cu on 100% Ru-doped TaN after aiMD at 500 K for 5 ps. B) Desorption of N atoms on 100% Co-doped TaN after aiMD at 500 K for 0.5 ps. C) 100% W-doped TaN after aiMD at 500 K for 5 ps. No rearrangement of the surface has occurred, indicating superior thermal stability.

interaction significantly compared to the other W-doped TaN surfaces. This result suggests that this surface can also act as a combined barrier/liner material.

Due to the gaps created in the surface by Ru and Co doping and the subsequent incorporation of Cu into this layer, these combined barrier/liner materials must be at minimum made up of two atomic layers (one layer of TaN and one layer of doped TaN) to retain their integrity as diffusion barriers. While this is not an issue for W doping, tungsten nitrides have been shown to have inferior barrier properties. For this reason, the "100% W-doped" layer of WN cannot be used on its own and will also require an additional layer of TaN. 25% W doping showed that 2D film morphology was promoted, however the inferior adhesion of Cu could cause issues during the manufacturing process. Instead of this course of action, Ru-passivated TaN surface made up of only two layers may show superior performance to W-doped TaN, based on our results.

In **Chapter 7** we moved away from modified TaN and instead investigated the interactions of Cu, Co and Ru with stoichiometric and defective monolayers of MoS₂. As MoS₂ was demonstrated to function as a barrier material, [3–6] Cu, Co and Ru interconnects will require only a liner layer and in this chapter we focus on the liner properties of MoS₂. As in the previous chapters, we study the interaction between MoS₂ and metal clusters with up to four atoms of various geometries. We find that the strength of adhesion follows the trend Co > Ru > Cu, regardless of the number of adatoms. The stability of Cu structures is driven by maximising the number of Cu-Cu bonds, which leads to Cu₄ structures preferentially adsorbing at the atop_S site, as this minimises the distance between atoms. Ru structures are most stable when they adsorb at the atop_{Mo} site, where they conform with the geometry of the MoS₂ lattice and cause minimal distortions to the monolayer. In comparison, Co structures prefer

to be in the tetrahedral configuration, with other geometries rearranging into a tetrahedron during relaxation. Co also incorporates into the top sulfur layer of the monolayer, which increases the interaction with the substrate, as for Cu adsorption on Ru and Co doped TaN.

Based on the metal-substrate and metal-metal interaction energies, Cu and Ru are likely to form 3D structures. However, adhesion to the substrate is stronger in the presence of a sulfur vacancy. This means that it might be possible to promote a 2D film on defective MoS₂. While the 2D and 3D clusters of Co adsorbed in this chapter are competitive in energy, the metal-substrate energies are very favourable and the adsorption energy of Co on MoS₂ exceeds the cohesive energy of Co. Therefore, 2D films should be promoted. This means that single layer MoS₂ could replace TiN as the liner material in Co interconnects.

Based on our results, combining known barrier materials with elements that show liner behaviour to create a single material with both properties proved to be a viable strategy. The increased interaction between Cu and the liner material helps to drive a homoepitaxial growth mechanism, where flat structures can be promoted by increasing the temperature. This in turn allows for the deposition of smooth, conducting Cu. It is important to ensure that the presence of the liner material does not impede the existing barrier properties of the second material. Size differences in the ionic radius in particular can cause gaps for Cu diffusion to occur. In the case of TaN this can be resolved by depositing pure TaN followed by a layer of the modified TaN. With ALD this is possible to do in a well-controlled manner. It will be interesting to investigate how thin the TaN layer can be while still functioning as a diffusion barrier.

Using a 2D material such as MoS₂ is another viable alternative, although the fact that 2D growth of Cu is most likely promoted only in the presence of S vacancies could cause issues in the barrier reliability if these vacancies provide a pathway for Cu to migrate through the monolayer. Although MoS₂ is a semiconductor, all the systems studied showed metallic character in their density of states plots. Bader charges showed that oxidation of Cu only occurs at the immediate interface with the substrate, indicating that the overall resistivity should be low.

Finally, based on the different materials studied, we were able to develop a series of models that allow significant insight into the interactions of metals with various substrates without the need to carry out resource intensive calculations, such as the NEB calculations in Chapter 5. This is highly relevant to any materials science application where the morphology of a metal on a particular substrate must be controlled and could aid significantly in narrowing down material choices for the system in question.

8.2 Future Outlook

The possible future avenues for this project will be discussed from two perspectives: additional computational work and complementary experimental work.

8.2.1 Computational Work

TaN based materials

As grain boundary diffusion is a major concern as a failure mechanism in interconnects, an amorphous barrier/liner material would be of significant advantage in extending the device lifetime. Having narrowed down the material choices based on our models of modifying crystalline TaN, it would now be valuable to study the interactions of Cu with amorphous Ru and Co doped TaN. However, creating an amorphous model requires significant resources. Such a model can be created using ab initio molecular dynamics as outlined by Aykol et al. [7] or using an appropriate force field and classical molecular dynamics as outlined by Mullins et al. and Saiz et al. [8, 9] If a force field is available the latter method is likely to be superior, as it allows for a large model and a statistically more accurate representation of the amorphous state of the material.

As these materials will be deposited via atomic layer deposition (ALD) it would also be valuable to carry out a computational study of the deposition process. This would allow for optimisation of some parameters, such as selection of precursors, in advance of beginning deposition experiments.

The mechanism of ALD processes for Ru and Co deposition have already been studied by other members of this research group [10–13], while work on studying the TaN and modified TaN ALD processes is currently ongoing.

2D Materials

While our study of small metal clusters on MoS₂ shows that the material holds promise as a combined barrier/liner material, some additional work to help confirm some of our predictions would be helpful. This could involve MD calculations of the various four atom structures, as detailed for Cu on Co and W doped TaN in Chapter 6, as well as some tests of the interactions in the presence of more than one sulfur vacancy. The effect of additional vacancies is of particular interest, as S vacancies naturally occur in MoS₂ and it has been shown that the formation energy of the vacancy is decreased when it forms adjacent to an existing vacancy. [14–16] As our results in Chapter 7, as well as a study of metal nanoparticles on MoS₂ by Rawal et al. [17] suggested that the presence of the vacancy can strengthen the adhesion of metal atoms on MoS₂, understanding how vacancy concentration affects the interactions with metal adatoms is an important step to controlling film morphology on MoS₂. Experimental methods to control the amount of sulfur vacancies have been demonstrated, such that findings on the role of vacancies in the

metal-substrate interaction can be applied during device fabrication. [18]

Additionally, confirming the diffusion barrier properties of MoS₂ using simple NEB calculations could also give insight into the effects of defects on the barrier performance. Some work on this has been previously carried out by Lo et al. [19], who computed a barrier of 4.5 eV for diffusion of a single Cu atom through a monolayer of MoS₂, however they considered only pristine 2D materials and did not study the effect of a vacancy on the activation energy for Cu diffusion.

As detailed in Chapter 2, there are other 2D materials, namely h-BN, WSe₂ and TaS₂, that have shown promise as barrier or barrier/liner materials. [19–22] There are also many other 2D materials that could act as potential barrier/liner materials and might have stronger interactions with Cu than MoS₂. In particular, any metallic 2D materials would be of particular interest to ensure that the interconnect via retains high conductivity.

Another 2D material of interest is black phosphorous (BP). BP is a semi-conducting van der Waal’s material with many potential applications. Recently, Nerl et al. [23] demonstrated that Cu spontaneously forms chiral, wire-like structures between layers of BP. Models to complement these experimental results were developed by our collaborators and we carried out further study on some of the thermodynamically favourable Cu heterostructures that did not match the experimental structures. Our analysis found that while adding too many Cu atoms would cause the structure to become unstable, the presence of Cu induces metallic character in BP. Even though not all of the pseudo wires formed were continuous, this suggests that they are likely to be conducting. This makes them of interest for advanced interconnect applications, where such self-assembled Cu structures could be of use in creating nano-scale interconnects. Some examples of Cu heterostructures in BP are shown in Figure 3.

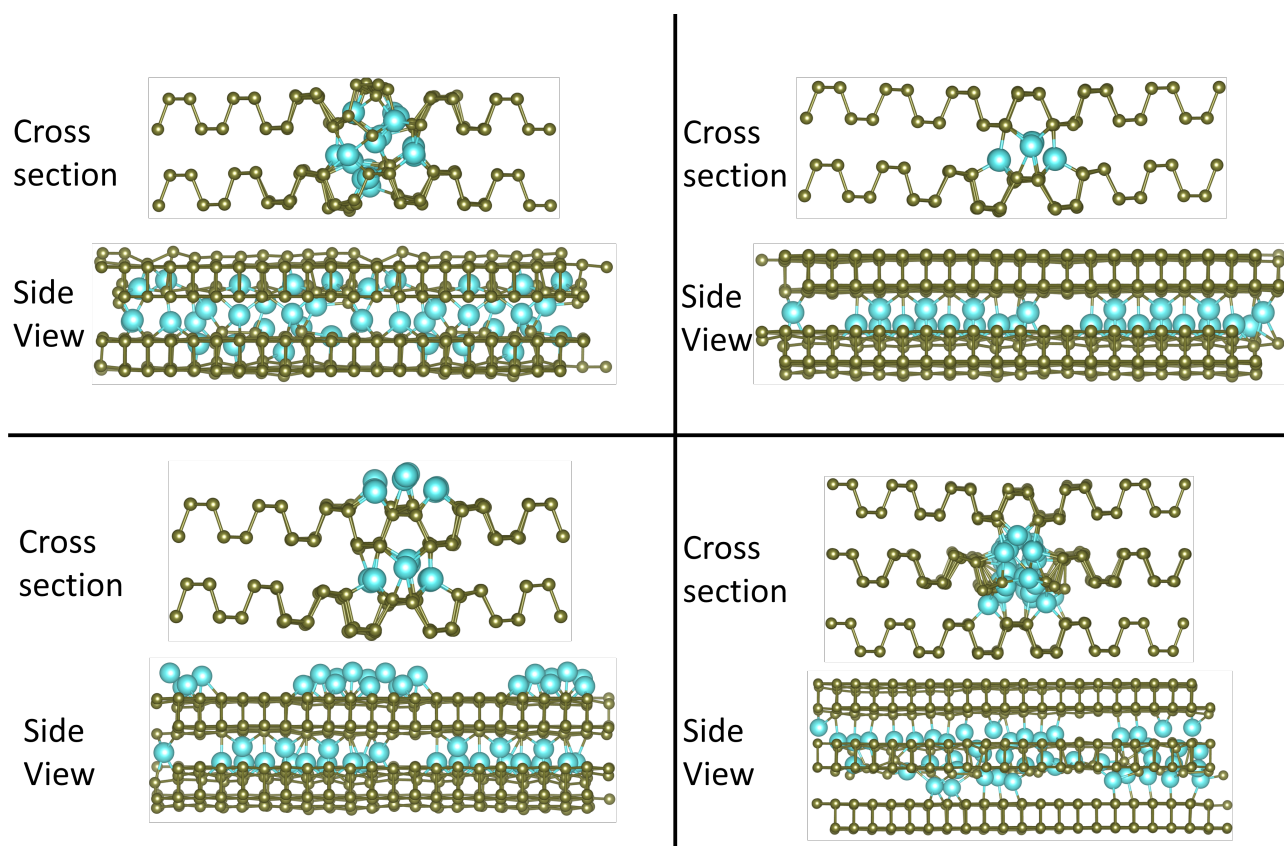


Figure 3: Cross sections and side views of various stable Cu-BP heterostructures. Cu atoms are shown in teal and P atoms in green.

Alternative Interconnects

The use of Cu as the interconnect metal should be extended for as long as possible to keep process and material costs low. However, there must eventually be a change to a different interconnect metal, in order to facilitate continued downscaling of interconnects. For this reason such potential alternatives must be examined. The most promising candidates, Ru and Co, were shown to require a liner material for deposition and it is thus relevant to determine the liner properties of ultrathin materials that could be used with these metals. [24, 25] Alternatively, different types of dielectric that might eliminate the need for a liner material altogether could also be considered. Both potential liner materials and alternative dielectrics could be screened for their interactions with Co and Ru using the computational method detailed in this thesis. Results from this study could then be used to narrow the selection for experimental analysis.

Computational Method

Other approaches can be taken to model a larger system and gain more accurate insights into the 2D vs 3D growth processes. There have been many recent advances in using machine learning to create force fields for classical MD approaches. [26, 27] We are currently using a machine learning algorithm in Quantum ATK [28] to create such a force field for carrying out classical MD calculations of the Ru-TaN system. The many different geometries studied for this thesis are being used as the data set to help create a potential. Classical MD calculations of the Ru-TaN system allow us to study a much larger system and many more materials using an automated workflow. This enables us to investigate growth mechanisms such as Ostwald Ripening of Cu on Ru-TaN. Additionally, this approach can be used to create amorphous models of the material or to study the effect of grain boundaries.

It is also possible to use other computational approaches to target some of the desirable material properties of a combined barrier/liner material that were not studied in this thesis. For example, modelling the electron transport in a Cu/modified-TaN system would allow insight into the resistivity. [29]

8.2.2 Experimental Work

While computational studies are useful in probing mechanisms and interactions not accessible via experiment, DFT studies are at their most useful when combined with results from appropriate experiments.

Both modified TaN materials and MoS₂ can be deposited using atomic layer deposition (ALD). [1, 2, 30–33] The next step to testing the viability of the potential barrier/liner materials presented in this thesis would be to develop an ALD process. Following this, creating test interconnect structures with the potential combined barrier/liners would clearly be the best way to test the fidelity of our predictions and to study any of the properties that were outside the scope of this thesis.

The experimental methods used to determine barrier and liner properties of materials were detailed in Chapter 2. Some examples include resistivity measurements, [34–36] tape exfoliation tests to measure adhesion, [37–39] electromigration reliability tests to determine the effects of current and temperature on the device [40] and electron microscopy to determine the main failure mechanisms. [35–37]

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Appendix

A1: Supplementary Material for Chapter 2

Figure A1 includes examples of the low-index surfaces of various ternary RuTa₃N materials before and after relaxation. These are based on bulk structures published by Schmidt et al. [1].

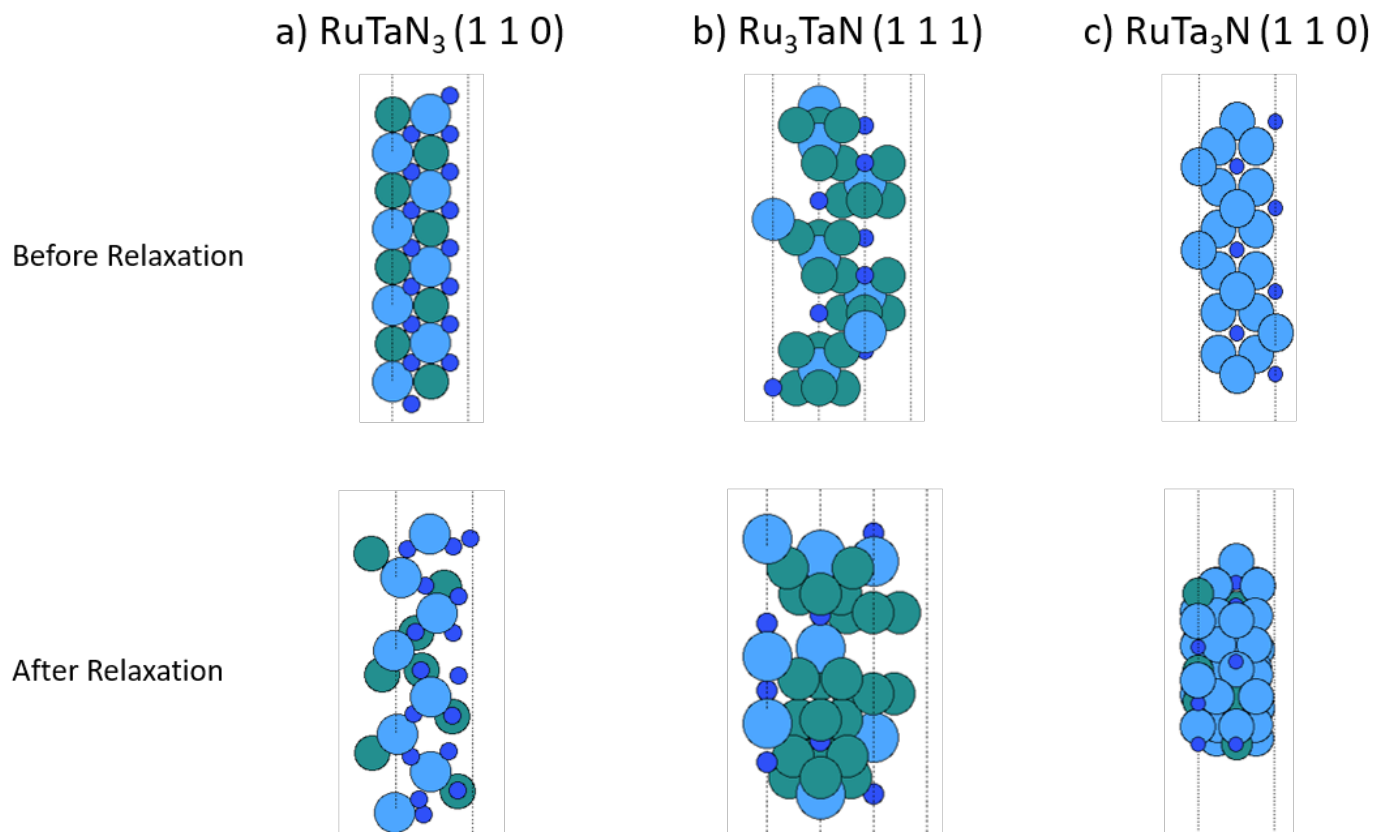


Figure A1: Examples of the low-index surfaces of various RuTa₃N ternary materials before and after relaxation. a) An 8 layer (1x1) model slab of RuTa₃N₃ (1 1 0). b) A 7 layer (1x1) model slab of Ru₃TaN (1 1 1). c) A 7 layer (1x1) model slab of RuTa₃N (1 1 0). Light blue = Ta, dark blue = N, green = Ru.

A2: Supplementary Material for Chapter 4

A2.1: TaN phase diagram

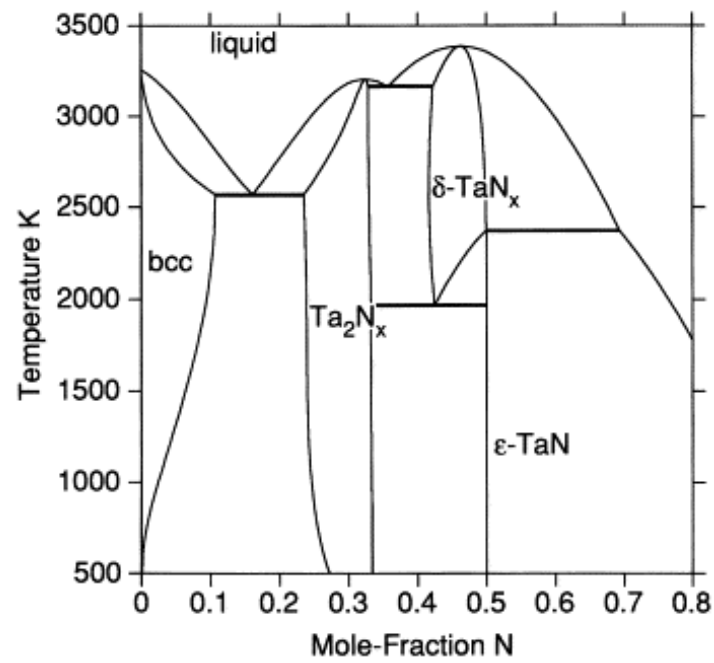


Figure A2: TaN phase diagram [2]. Licence no. to reuse figure: 4481420260380

A2.2: ϵ -TaN low index surfaces

Table A1 lists the essential geometric properties and surface energies of the low index surfaces. Figure A3 shows the geometries of all ($2^3-1 = 7$) low index surfaces of ϵ -TaN. Here, the geometries of (0 1 0) and (1 0 0) surfaces are symmetrically identical, so are the geometries of (1 0 1) and (0 1 1). The surfaces (1 1 0), (1 1 1) and (1 0 0) are the three lowest energy surfaces and thus these surfaces are considered for detailed analysis in Chapter 7.

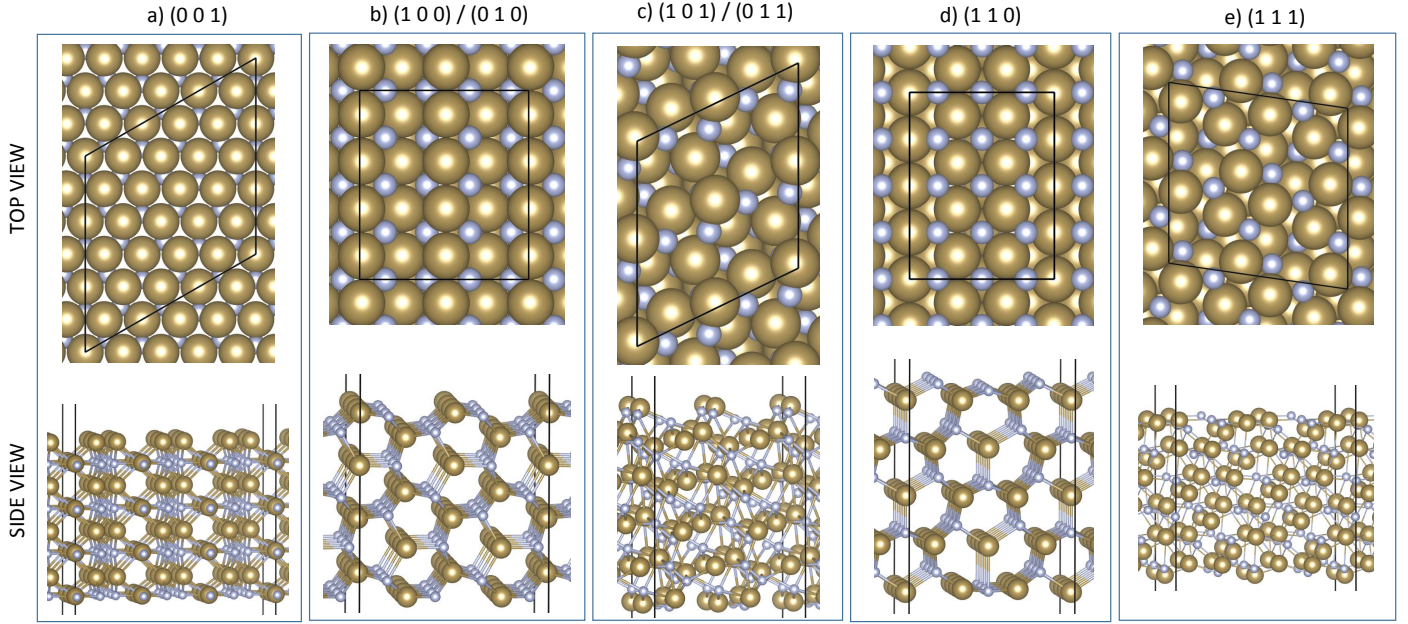


Figure A3: All low index surfaces of ϵ -TaN

Table A1: Details of the computation model of the low index surfaces of ϵ -TaN.

Surface	Supercell	K-points	Surf. Area [nm ²]	Layers	TaN/layer	Slab Thickness [Å]	No. Atoms	E _{Surf} [J/m ²]
(0 0 1)	(3×3)	1×1×1	2.1	4	27	10.0	216	3.3
(1 0 0)/(0 1 0)	(1×4)	2×2×1	1.2	8	8	10.2	128	2.7
(1 0 1)/(0 1 1)	(2×2)	2×2×1	1.1	5	12	11.4	120	3.4
(1 1 0)	(1×4)	3×2×1	1.1	5	12	11.8	120	2.6
(1 1 1)	(2×2)	3×3×1	1.4	6	12	10.5	144	2.7

A2.3: Bulk Ru, Ru (0 0 1) surface and Cu on Ru(0 0 1) surface

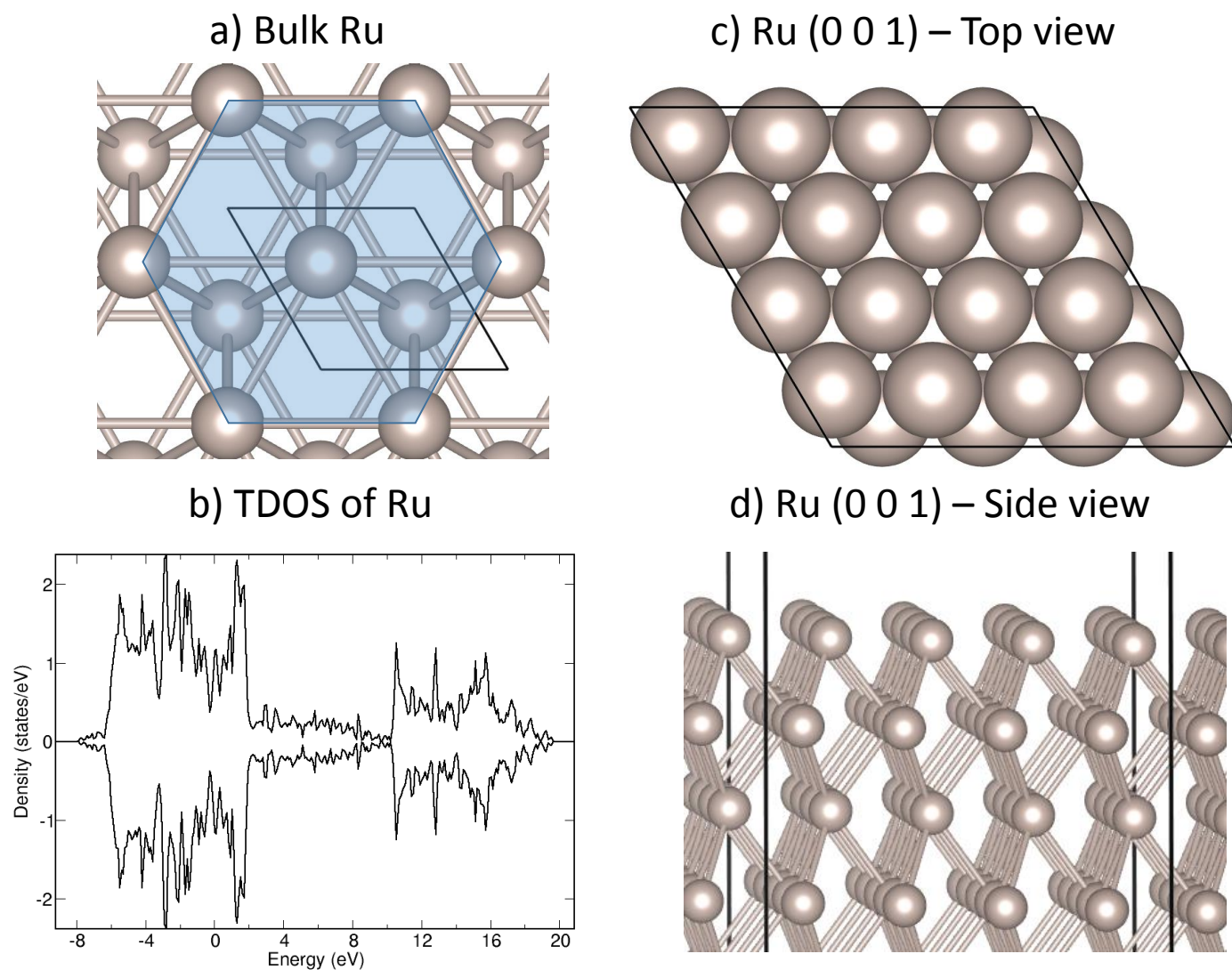


Figure A4: Panel a) shows the bulk geometry of Ru metal (brown spheres) in HCP lattice where the unit cell is marked by solid black lines and the blue shaded region represents the hexagonal symmetry. Total DOS of bulk Ru showing metallic character is given in panel b). Top and side views of Ru(0 0 1) surface are shown in panels c) and d), respectively.

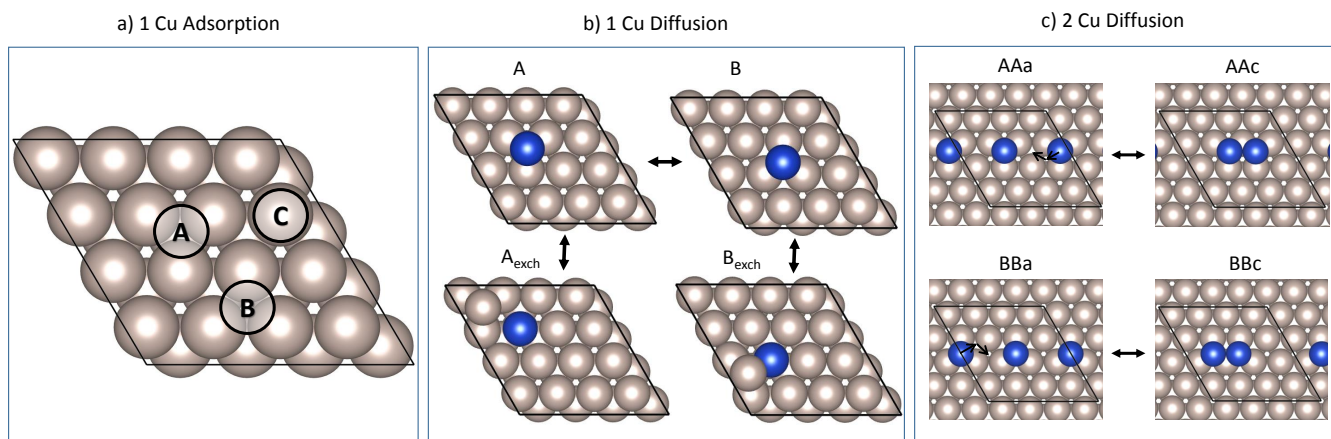


Figure A5: Panel a) shows stable binding sites for Cu adatoms at the (0 0 1) surface of Ru. Endpoints (minima) used to compute the activation energies for the facile as well as sub-surface diffusion of one Cu adatom on the Ru(0 0 1) surface are shown in panel b) and the endpoints for the facile diffusion of two Cu adatoms are shown in panel c). The Ru and Cu atoms are shown in brown and blue, respectively.

A2.4: Cu/Ru on TaN surfaces

A2.4.1: 1 Cu/Ru on TaN

On the (1 1 0) surface, five other stable sites B, C, D, E and F with relatively lower binding energies are also identified. Site B is a 4-fold site coordinated by 2 N and 2 Ta atoms, while C is atop N site coordinated by 4 surface Ta atoms, D is atop Ta site, E is atop N site coordinated by 3 surface Ta atoms and F is another 4-fold site coordinated by 2 Ta and 2 N atoms. The binding energies are in the range of -1.92 eV to -2.81 eV for Cu and -3.68 eV to -4.95 eV for Ru. The least preferable adsorption site for Cu adatom is the site C, and site B is the least favourable for Ru adsorption. Ru adatom was unstable at sites C, D and E. At all the sites the Ru-Ta distances are shorter than the Cu-Ta distances, whereas the Ru-N and Cu-N distances are almost the same. From the Bader charge analysis we find that both Cu and Ru adatoms are oxidized with average Bader charges of 0.53 and 0.21 |e| (see Table A2) at this surface as expected due to the electron affinity differences between Cu/Ru and Ta/N. The electron affinity values of Cu, Ru, Ta and N are 1.235, 1.046, 0.32 and -0.07, respectively. An in-depth analysis of the surface valence charges for Cu/Ru binding at site A is given in section* S5 of the ESI. In addition to that, the PDOS plots of the Cu and Ru adatoms at the most favourable sites on the low-index surfaces of TaN are discussed in section* S6 of the ESI.

On the (1 1 1) surface there are two unique stable sites A and B, where A is a two fold bridge site and B is a wide hollow site between a pair of N and Ta atoms. Site B is more favoured (about 0.4 - 0.5 eV) than site A by both Ru and Cu adatoms. Similar to the (1 1 0) surface, we find that the Ru adatom binds at least 2 eV stronger than the Cu adatom. In contrast to the (1 1 0) surface we find that both Cu and Ru adatoms are reduced, Ru more so than Cu (see Table A2). Reduction is most prominent at site A for both Ru and Cu adatoms where the surface N atoms are farther from them than the surface Ta atoms. At site B, where the N atoms are moderately closer to the adatoms, we find a considerably decreased charge gain by the adatoms. This indicates that the adatoms gain electrons from the neighbouring Ta atoms, which are not as oxidized as those in the (1 1 0) surface. Ta atoms also have a larger electron affinity than N.

On the (1 0 0) surface there are three stable sites A, B and C, where site A is along the surface trench coordinated by 2 Ta and 1 N atoms, B is a three fold site made by 2 Ta and 1 N atoms and C is a two fold bridge site coordinated by 2 Ta atoms. Moreover, site C is present along the pathway connecting sites A and B. The Cu adatom binds with almost the same binding energy at sites A and C, with A being the most favourable for both Ru and Cu, but does not bind at site B as it relaxes to site C, however, Ru binds to site B as well. Similar to the (1 1 1) surface, the Cu and Ru adatoms are reduced to some degree at this surface as evident from the valence charges reported in Table A2.

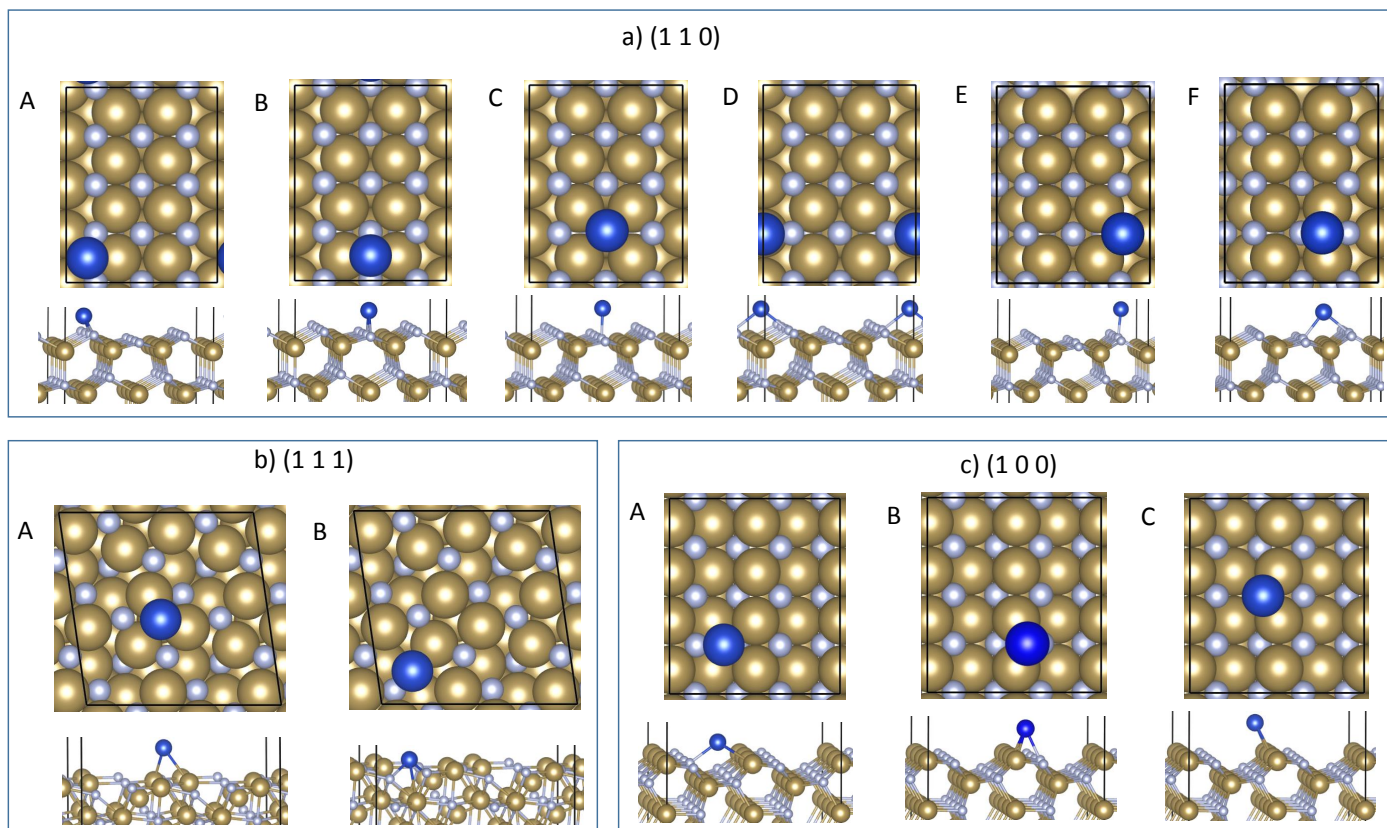


Figure A6: Panels a), b) and c) shows the top and perspective side views of the Cu/Ru adatoms at unique stable binding sites on the (1 1 0), (1 1 1) and (1 0 0) surfaces of ϵ -Ta₂N₃, respectively. The Ta and N atoms are shown in ochre and light blue, respectively. The adatom (Cu or Ru) is shown in blue.

Table A2: Average distances, valence electronic charge and binding energies of Cu and Ru adatoms on the low index surfaces of ϵ -TaN along with activation energies involved in the inter-minimum hopping of the adsorbed Cu and Ru adatoms. $d(X-Y)$ gives the average bond distance between the neighbouring X and Y species in the corresponding minimum geometries. $Q(X)$ gives the average valence electronic charge of atom X according to the Bader charge partitioning scheme. The '=' sign indicates that the activation energy is the same for both forward and reverse hops. (') next to A or B indicates that it is a symmetry equivalent site along the trench at the surface, while a (") refers to a symmetry equivalent site across the trench as shown in Figure 1 in Chapter 4.

Surface	Sites	Cu-Cu	Ru-Ru	Cu-N	Ru-N	Cu-Ta	Ru-Ta	Q(Cu)	Q(Ru)	E_{bind} [eV/ads.]	Pathway	$E_{\text{activation}}$ [eV]
1 Cu/Ru adatom												
(1 1 0)	A		1.9		1.9	2.8	2.6	10.5	7.8	-2.82	A=A'	0.69 1.49
	B	2.1	2.1	2.0	2.0	2.6	2.6	10.5	7.6	-2.04	B=B'	0.13 0.98
	C	1.8	-	-	-	3.2	-	10.5	-	-1.92	A-B	1.37 2.09
	D	2.1	2.1	-	-	2.4	-	10.4	-	-2.13	B-A	0.59 0.82
	E	1.8	1.8	-	-	2.6	-	10.5	-	-2.12		
	F	2.0	2.0	1.9	1.9	2.7	2.6	10.4	7.6	-2.25		-3.85
(1 1 1)	A	3.2	3.2	2.8	2.8	2.6	2.4	11.4	8.7	-2.80	A-B	0.85 1.88
	B	2.0	2.0	2.0	2.0	2.5	2.4	11.2	8.4	-3.21	B-A	1.26 2.37
(1 0 0)	A	2.1	2.1	2.1	2.1	2.7	2.6	11.1	8.3	-3.26	A=A'	0.50 0.68
	B	-	2.1	2.1	-	-	2.4	-	8.3	-	A-C	0.12 0.36
	C	3.1	3.1	3.1	3.1	2.6	2.4	11.2	8.5	-3.22	C-A	0.08 0.03
											C-B	- 0.23
											B-C	- 0.25
											C-A"	1.04 -
											A"-C	1.08 -
											B-A"	- 0.92
											A"-B	- 1.23

A2.4.2: 2 Cu/Ru on TaN

On the (1 1 0) surface, the first adatom is placed at site A and the other adatom is placed at one of the following sites: B (AB), C (AC), D (AD), E (AE), F (AF), A'' (AA''), on top of the adatom at site A (AA-top), A' adjacent to A (AA'c) and A' away from A (AA'a). The binding energies per adatom are in the range of -2.41 eV to -2.98 eV for Cu and -4.14 eV to -5.04 eV for Ru. Comparing the above results to the 1 adatom case, we do not find a significant increase in the binding energies per Cu atom even though the two adatoms are close to each other in several minimum geometries. Therefore the adatom-adatom interaction must be very low. The most favourable binding is observed when the Cu or Ru atoms are adsorbed at sites A and A'' (AA'') which are located adjacent to each other on the (1×4) supercell of TaN (1 1 0) surface and the least favourable binding is observed when the Ru adatoms are adsorbed on top of one another at site A (AA-top) and when Cu adatoms are adsorbed at sites A and B. Similar to the 1 adatom case, the Ru and Cu adatoms are oxidized at all sites on this surface

On the (1 1 1) surface, another geometry is considered where the two adatoms are placed on top of each other at site B (BB-top), however, this geometry is found to be unstable for both Cu and Ru adatoms and reverted to A2B. The associated state (B2A) is found to be unstable in the case of Cu adatoms.

On the (1 0 0) surface the first adatom is placed at site A and the other adatom is placed at the following sites: B (AB), C (AC), on top of the adatom at site A (AA-top), A' close to A (AA'c) and A' away from A (AA'a). The binding energies per adatom are in the range of -3.00 eV to -3.37 eV for Cu and -5.18 eV to -5.74 eV for Ru. Vertically stacked Cu/Ru adatoms at site A (AA-top) are found to be unstable and relaxed to AC. The associated state AA'c is the most favourable 2 atom site for Cu adatoms whereas the separated state AA'a is the most favourable for Ru adatoms. The Cu adatom remains metallic at site A and reduced at site C while the Ru adatom shows mild reduction at all sites.

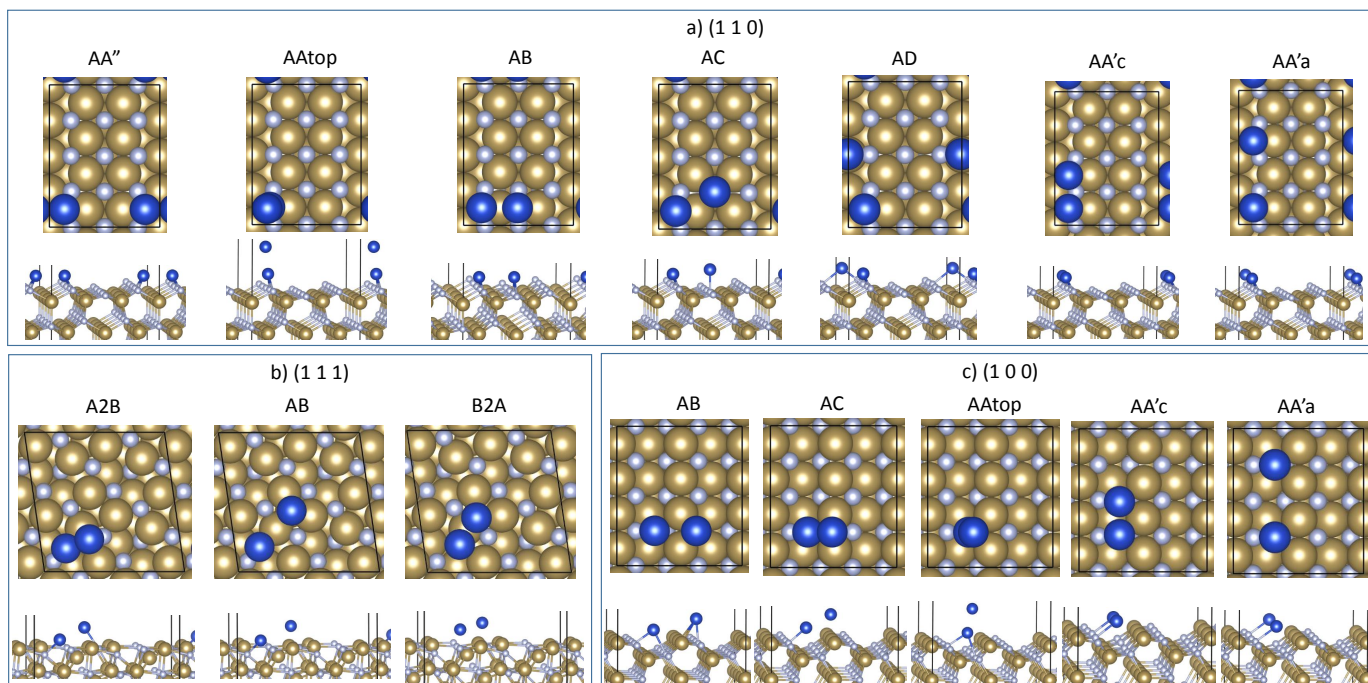


Figure A7: Geometries of 2 adatoms (Cu/Ru) at the unique 2 atom binding sites at the low index surfaces of ϵ -TaN. Here A2B represents the geometry where the adatom at A moved towards the adatom at site B and vice-versa. AA'c and AA'a represents 2 atom sites where the adatoms are close to each other and distant from each other, respectively. The Ta and N atoms are shown in ochre and light blue, respectively. The adatom (Cu or Ru) is shown in blue.

Table A3: Average distances, valence electronic charge and binding energies of Cu and Ru adatoms on the low index surfaces of ϵ -TaN along with activation energies involved in the inter-minimum hopping of the adsorbed Cu and Ru adatoms. d(X-Y) gives the average bond distance between the neighbouring X and Y species in the corresponding minimum geometries. Q(X) gives the average valence electronic charge of atom X according to the Bader charge partitioning scheme. The '=' sign indicates that the activation energy is the same for both forward and reverse hops. (') next to A or B indicates that it is a symmetry equivalent site along the trench at the surface, while a (") refers to a symmetry equivalent site across the trench as shown in Figure 1 in Chapter 4.

Surface	Sites	Interatomic distance [Å]				Q		E _{bind} [eV/ads.]		Pathway		E _{activation} [eV]	
		Cu-Cu	Ru-Ru	Cu-N	Ru-N	Cu-Ta	Ru-Ta	Q(Cu)	Q(Ru)	Cu	Ru	Cu	Ru
2 Cu/Ru adatom													
(1 1 0)	AB	2.9	2.4	2.0	2.0	2.8	2.9	10.5/10.5	7.6/7.5	-2.41	-4.50		
	AC	-	-	-	-	-	-	-	-	-	-		
	AD	4.6	-	2.0	-	2.7	-	10.5/10.5	-	-2.42	-		
	AE	-	-	-	-	-	-	-	-	-	-4.79		
	AF	4.7		1.9		2.8		10.5/10.5	7.8/7.6	-2.45	-4.31		
	AA''	2.4	2.4	2.0	2.0	2.8	2.8	10.6/10.6	7.7/7.5	-2.98	-5.04		
	AA-top		2.1		2.8		3.7		7.6/7.9	-	-4.14		
	AA'c	2.9	2.9	2.0	2.0	2.9	2.8	10.5/10.5	7.9/7.7	-2.70	-4.95	0.73	1.32
	AA'a	5.8	5.8	1.9	1.9	2.8	2.7	10.5/10.5	7.7/7.7	-2.77	-4.81	0.57	1.60
										AA'a-AA'c			
										AA'c-AA'a			
(1 1 1)	AB	3.8	4.0	2.5	2.6	2.6	2.4	11.2/11.3	8.4/8.7	-3.04	-5.37	0.20	0.16
	BB-top	-	-	-	-	-	-	-	-	-	-	0.06	0.47
	B2A	-	2.6	-	2.9	-	2.4	-	8.5/8.6	-	-4.94	-	0.93
	A2B	2.4	2.4	2.0	2.0	2.7	2.6	11.0/11.1	8.3/8.2	-2.96	-5.53	-	0.07
										AB-A2B			
										A2B-AB			
										AB-B2A			
										B2A-AB			
(1 0 0)	AB	-	2.8	-	2.1	-	2.6	-	8.2/8.1	-	-5.18		
	AC	2.3	2.4	2.7	2.6	2.8	2.9	10.8/11.2	8.0/8.6	-3.00	-5.47		
	AA-top	-	-	-	-	-	-	-	-	-	-		
	AA'c	2.7	3.0	2.1	2.0	2.7	2.7	11.0/11.1	8.3/8.2	-3.37	-5.64	0.48	0.64
	AA'a	5.9	5.8	2.1	2.1	2.7	2.7	11.1/11.1	8.3/8.3	-3.25	-5.74	0.71	0.43
										AA'a-AA'c			
										AA'c-AA'a			

A.2.5: Bader Charge Analysis

The Cu and Ru adatoms adsorbed on the (110) surface of ϵ -TaN are oxidized while those adsorbed on the (111) and (100) surfaces are partially reduced. To understand this behaviour, we performed Bader charge analysis and compared the charges of the surface atoms on a bare low-index surfaces with those when Cu/Ru adatoms are adsorbed at the A site on the respective surfaces in Figure A8. Comparing the charges on the bare surfaces (the top value on each atom) we clearly find that the (110) surface has the most oxidized Ta atoms and the most reduced N atoms. The average valence charge of Ta atoms on the (110) surface is 3.2, whereas this value is increased to 3.6 and 3.45 on the (111) and (100) surfaces. On the other hand the average valence charge of N atoms on the (110) surface is 6.3, which increases to 6.46 and 6.45 on the (111) and (100) surfaces, respectively. Therefore, when the Cu/Ru atoms are adsorbed on the (110) surface, the already oxidized S type Ta atoms gain electrons from them. The N atoms also gain electronic charge from the Cu adatom but not from Ru. This could be because of the larger electron affinity value of Cu (1.235) than Ru (1.046).

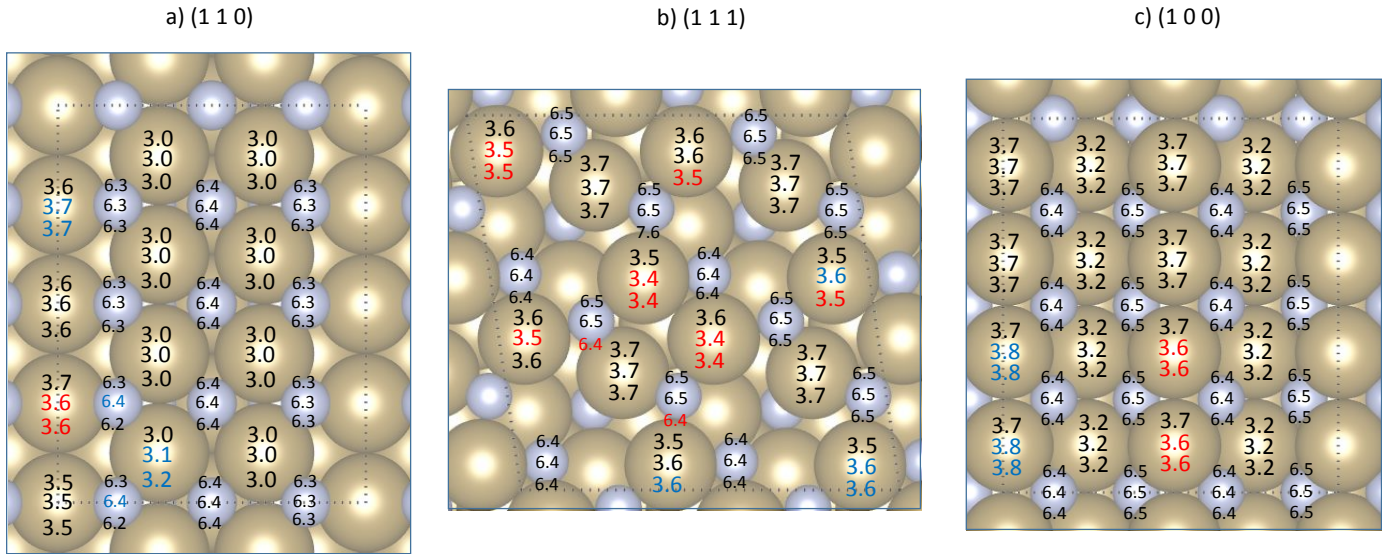


Figure A8: Bader charges of surface atoms on the low index surfaces of ϵ -TaN. There are three numbers listed for each surface atom. The number at the top is for the bare surfaces and the number in the middle and bottom is for the same surface where a Cu and Ru atom is adsorbed at the A site, respectively. Numbers in red indicate a decreased charge compared to the bare surface, numbers in blue indicate an increased charge.

On the (111) surface, clearly the surface S' type Ta atoms bound to Cu are further oxidized. This is probably due to their under coordination with N atoms as compared to the (110) surface. A similar observation is also made in the case of the (100) surface. However the charge transfer is smaller on the (100) surface as compared to the (111) and (100) surfaces. Moreover, on the (111) surface the charge transfer seems to be de-localized as compared to the (110) and (100) surfaces. There is also a high degree of corrugations and irregularities on the (111) surface as compared to the other two surfaces.

The surface charges on the doped surfaces compared to the bare surface show that doping causes the surface to become even more oxidised. Ru in RuS is the more oxidised than in RuF, indicating why RuS might be more reactive, but why

RuF is more energetically stable. See Figure A9.

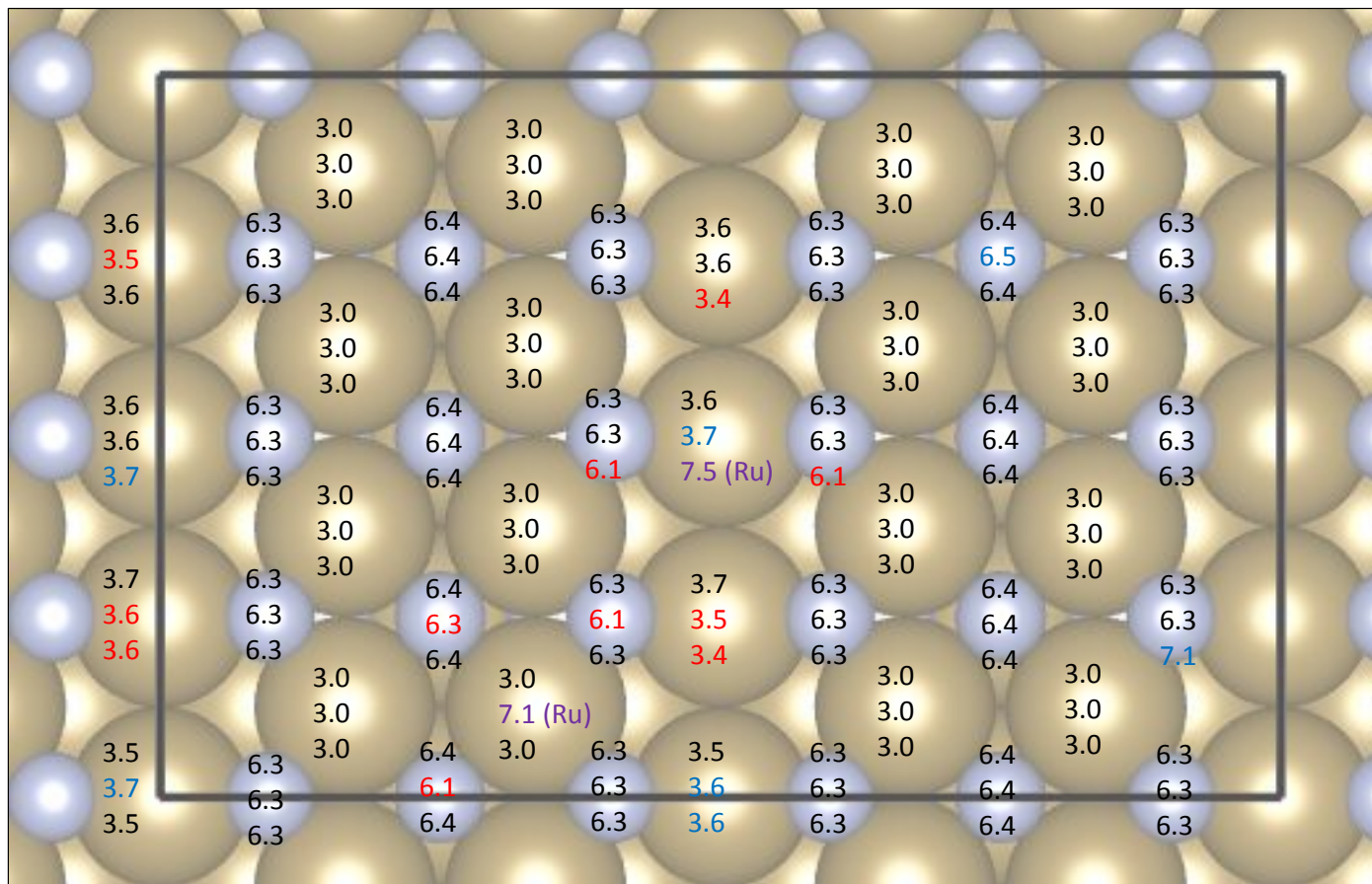


Figure A9: Bader charges of the surface atoms on the 2x4 supercell. The number at the top is for the bare surface, the second number is for RuS surface and the bottom number is for RuF surface. Charges of respective Ru atoms are shown in purple and labeled Ru. Numbers in red indicate a decreased charge compared to the bare surface, numbers in blue indicate an increased charge.

Comparing charges on 2x4 and 1x4 supercells shows that the electronic effect of doping is localised to those N and Ta atoms in direct vicinity of Ru. See Figure A10.

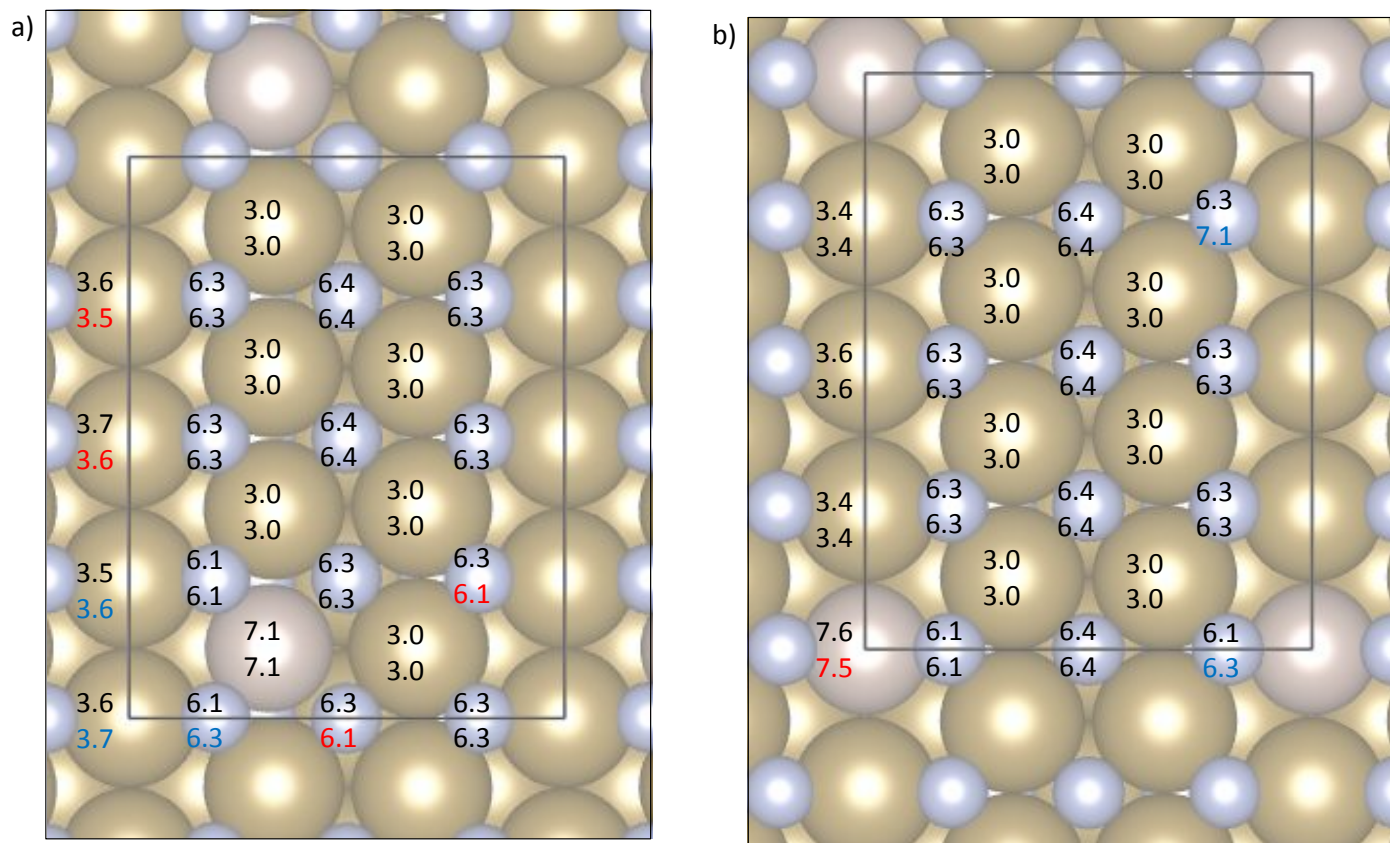


Figure A10: Bader charges of the surface atoms on the a) RuS and b) RuF 1x4 supercells. The number at the top is the charge on the 1x4 surface, the number at the bottom is the charge on the 2x4 surface. Red indicates the charge on the 2x4 surface is lower than on the 1x4 surface, blue indicated an increased charge.

A2.6: Density of States

From Bader charge partitioning analysis, we found that the Cu/Ru adatoms were oxidized on the (110) surface while they were reduced on the (111) and (100) surfaces. To understand this better, we compared the partial DOS of the adsorbed Cu/Ru atoms as shown in Figure A11. The total DOS plots of the bare surfaces are given in the first row and the PDOS plots of Cu and Ru adatoms at the most favourable site on these surfaces are shown in the second and third rows, respectively. From the second row in the case of the (1 1 0) surface, we clearly find significant DOS of Cu in the conduction band separated from the valance band by a gap of approximately 1.5 eV which indicates oxidation. Whereas, on the (111) and (100) surfaces we do not find significant DOS beyond the Fermi level which indicates a reduced Cu adatom. Similar to the copper case, the Ru adatom at the (1 1 0) surface has significant DOS beyond the fermi level indicating oxidation, however, its DOS at Fermi level is non zero which is in contrast with PDOS of Cu. PDOS plots of Ru on the (111) and (100) surfaces have a non zero DOS at the Fermi level which also extends into the conduction band suggesting a metallic nature.

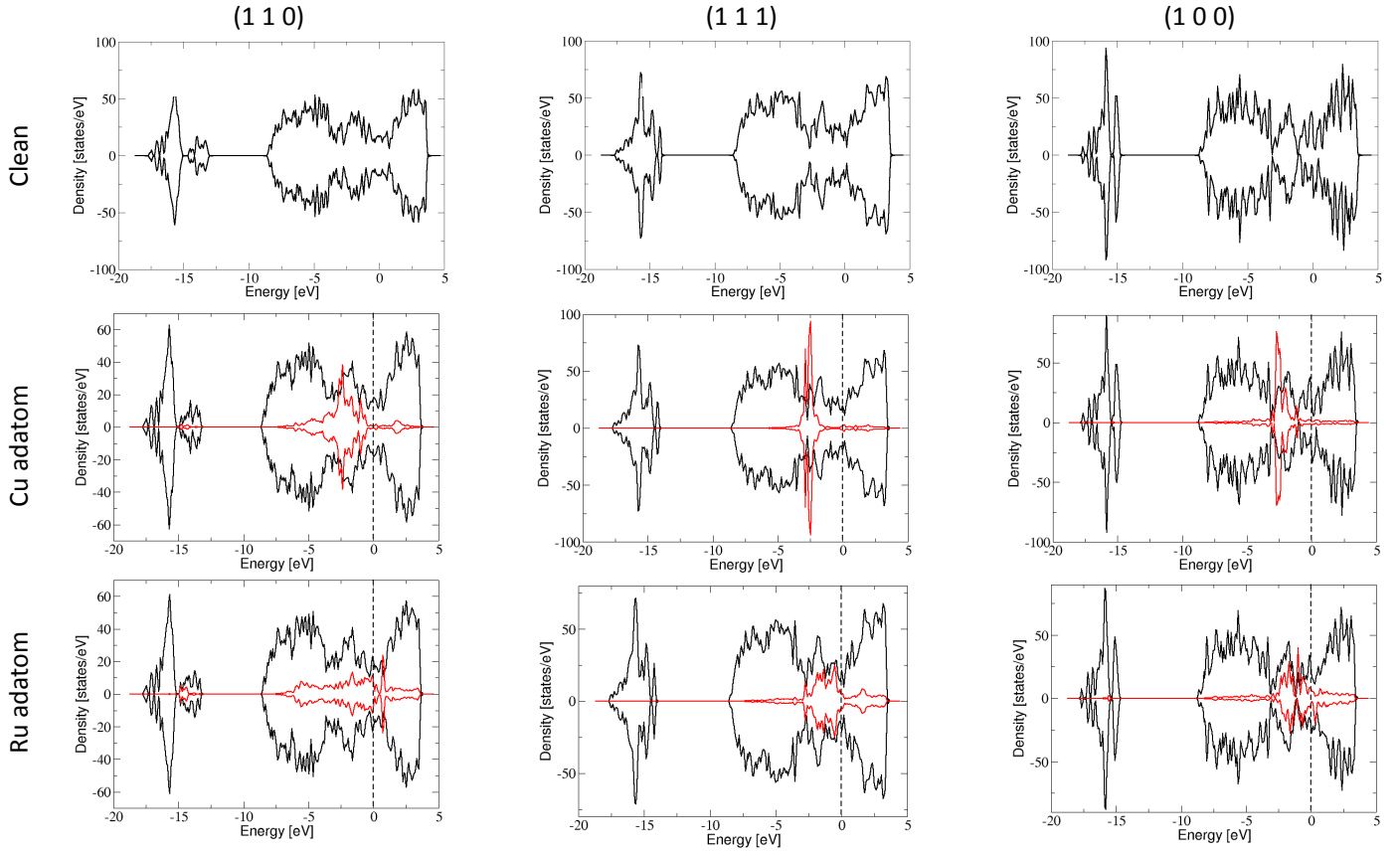


Figure A11: Total DOS of the bare TaN surfaces, total DOS of Cu/Ru adsorbed at the most favourable site on the TaN surfaces, and PDOS of Cu/Ru adatoms. The PDOS plots of Cu and Ru are shown in red and are scaled by a factor of 10.

A2.7: Cu on Ru passivated TaN

Several Ru atoms are first adsorbed on the TaN (1 1 0) surface as shown in Figure A12a-f so as to obtain a model of the saturated surface and the corresponding binding energies per adsorbed Ru atom are plotted in Figure A12g. From the geometries in Figure A12a-c, where 3-9 Ru atoms are adsorbed, we find that the adatoms preferentially bind at sites A, A' and B on the TaN (1 1 0) surface. As the coverage increases to 12 Ru/supercell, the adatoms at site B are displaced to the atop N site adjacent to B and initiate the formation of a closely packed structure. At a coverage of 16 Ru per supercell, where one monolayer of Ru is coated on the surface, we find a hexagonal packing of the Ru atoms. Two monolayers of Ru coverage is obtained at 32 Ru per supercell as shown in Figure A12f where a fully formed HCP surface of Ru is visible. From Figure A12g we observe that the binding energy per Ru increases up to 6 Ru adsorption and then decreases with additional Ru atoms as they begin to associate on the surface. This trend will continue until the binding energy reaches the cohesive energy of bulk Ru (6.8 eV). At 3 adatom adsorption the Ru adatoms are oxidized, similar to the 1 and 2 adatom cases discussed earlier, with valence charges in the range of 7.5 - 7.7. This range increases to 7.6 - 7.8 at 6 Ru adsorption and 7.7 - 7.9 at 9 and 12 Ru adsorptions. At 1 ML coverage, the Ru adatoms are less oxidized, with valence charges in the range of 7.8 - 8.1. At 2 ML coverage, the bottom layer of Ru atoms are slightly oxidized with the valence charge in the range 7.7 to 7.9 while the top layer is metallic with the valence charge between 8.0 and 8.1.

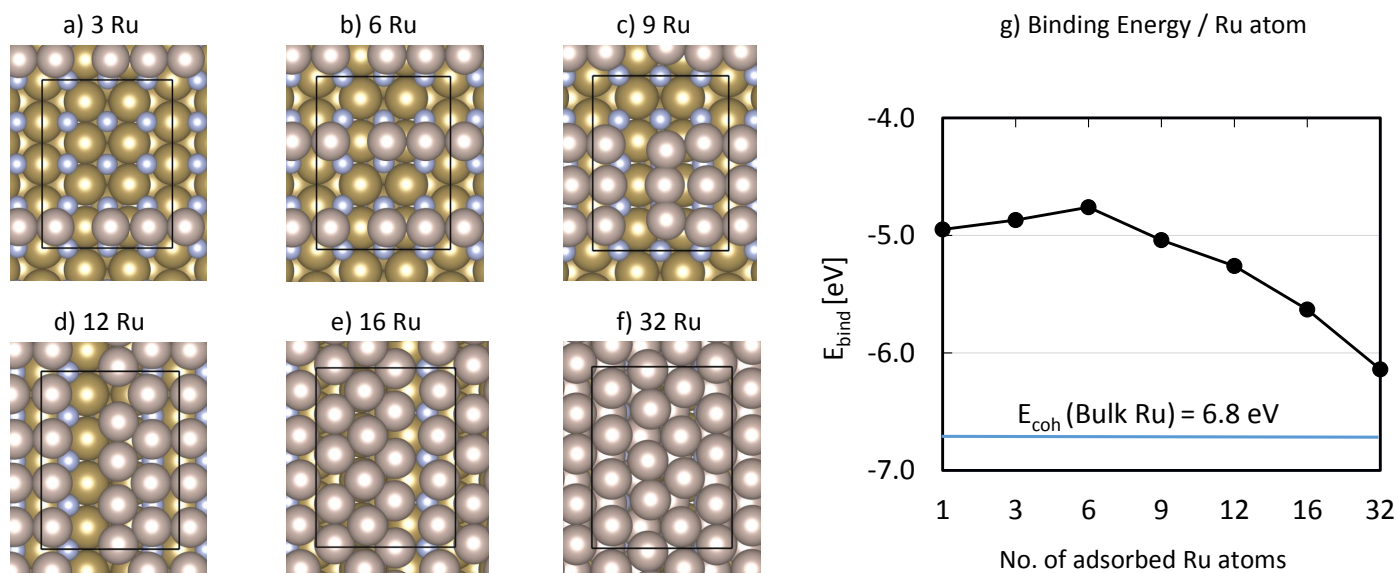


Figure A12: Panels a)-f) show minimum geometries representing Ru passivated TaN (1 1 0) surface. The graph in panel g) shows the binding energy per Ru atom adsorbed on the TaN (1 1 0) surface. The blue line indicates the cohesive energy of Ru in bulk state. The Ta, N and Ru atoms are shown in gold, light blue and silver, respectively.

Three stable binding sites (A, B and C) are found for a Cu adatom at the 1 ML of Ru passivated TaN(1 1 0) surface (Figure 6 in Chapter 4) and the corresponding binding energies are listed in Table A4. Site A is a wide 3 fold site above a sub-surface N atom, site B is another wide 3 fold site above a sub-surface Ta atom and site C is a two fold site. The binding energies are within the range of -3.2 eV to -3.5 eV where the strongest binding is seen at site B and the weakest

binding at site A. Moreover the binding energies are also moderately lower than on the bare (1 1 0) surface suggesting the favourable aspect of Ru passivation. We did not find significant changes in the valence charge of the adsorbed Cu atom which indicates that there is no significant electron transfer between the Cu adatom and the Ru layer and Cu remains metallic. On the 1 ML passivated surface, the geometries at A_{exch} and C_{exch} have the highest binding energies, whereas the geometry at B_{exch} has comparable binding energy to that of the on-surface adsorption. The forward activation energies for the exchange diffusion are significantly larger than for the reverse process and also considerable larger than that of the on-surface diffusion.

On the 2 ML of Ru passivated TaN(1 1 0) surface, four unique stable binding sites for 1 Cu adsorption (A, B, C and D) are found as shown in Figure 6c and the corresponding binding energies are listed in Table A4. The binding energies are in the range of -3.13 eV to -3.44 eV, which are comparable to the 1 ML Ru passivated surface. The two fold Ru coordinated site A is found to be the most favourable followed by B, C and D, each of which are three fold coordinated by Ru atoms. Similar to the 1 ML case, there is no significant charge transfer between the Cu and Ru atoms. As the next step, adsorption of 2 Cu is investigated where the first Cu is placed at the most favourable binding site (site B) and the second Cu is placed at sites A, C, D, B' and A' (we use combined site notation BA, BC, BD, BB' and BA' to represent the 2 atom adsorption site). From Table A4 we find that the binding energies per Cu adatom are in the range of -3.48 eV to -3.60 eV. Compared to the 1 Cu adsorption case, we find that the binding energies have decreased slightly, probably due to the additional Cu-Cu interaction and associated surface rearrangements. We found the geometry at site BB' to be the most favourable where the Cu atoms are at a distance of 2.47 Å.

Table A4: Binding energies and activation energies for the diffusion of Cu adatoms on 1 and 2 ML of Ru passivated TaN (1 1 0) surfaces. A '-' for the E_{bind} indicates that the respective geometry is found to be unstable and a '-' for $E_{\text{activation}}$ indicates that we could not find a transition state connecting the minima.

Adatoms	Sites	Q(Cu)	E _{bind} [eV]	d(Cu-Cu) [Å]	Pathway	E _{activation} E [eV]	
						Forward	Reverse
1 ML Ru							
1 Cu	A (3 fold atop N)	10.9	-3.24		A-B	0.01	0.21
	B (3 fold atop Ta)	11.0	-3.44		B-C	0.45	0.37
	C (2 fold)	10.9	-3.35				
	A _{exch}	10.8	-2.51		A-A _{exch}	0.84	0.11
	B _{exch}	10.8	-3.12		B-B _{exch}	0.72	0.41
	C _{exch}	11.0	-2.71		C-C _{exch}	1.03	0.38
2 Cu	BB'	11.0/11.0	-3.60	2.5			
	BA	11.0/11.0	-3.48	2.6	BB' - BA	0.44	0.20
	BC	11.0/10.9	-3.49	2.9	BB' - BC	0.48	0.24
	BB''	11.0/10.9	-3.52	5.2	BB' - BB''	0.35	0.18
2 ML Ru							
1 Cu	A (2 fold)	11.0	-3.44		A-B	0.46	0.44
	B (3 fold wide)	11.0	-3.42		A-C	-	-
	C (3 fold hcp)	10.9	-3.18		A-D	-	-
	D (3 fold hollow)	10.9	-3.13				
	A _{exch}	11.0	-2.41		A-A _{exch}	1.93	0.89
	B _{exch}	11.0	-2.07		B-B _{exch}	2.19	0.83
	C _{exch}	11.0	-2.17		C-C _{exch}	1.39	0.38
	D _{exch}	11.0	-2.22		D-D _{exch}	-	-
2 Cu	AA'	11.0/10.9	-3.43	2.7			
	AB	11.0/11.0	-3.43	2.5	AA' - AB	0.20	0.19
	AC	11.0/10.9	-3.35	2.4			
	AB'	10.9/11.0	-3.31	4.8	AA' - AB'	0.30	0.06
	AC'	11.0/10.9	-3.30	4.6	AA' - AC'	-	-

A2.8: Cu on Ru-doped TaN

The activation energies for each migration pathway are shown in Table A5. For reference the binding energies and charges that are presented in Chapter 4 are included again. Further, the geometries of all stable adsorption sites can be found in Fig. A14, A15 and A16.

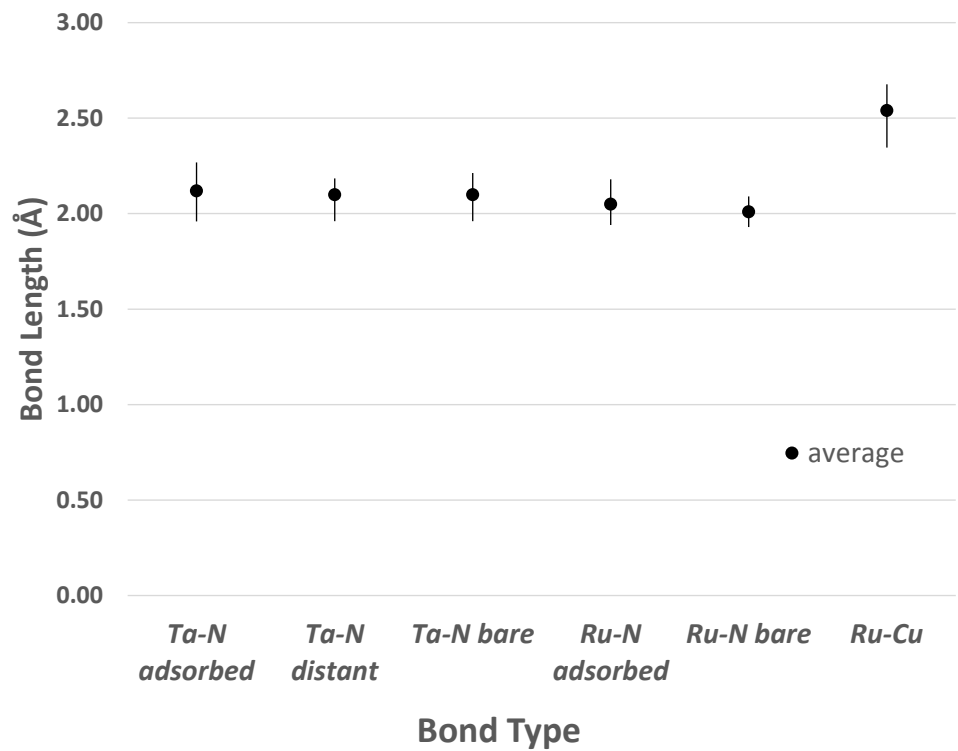


Figure A13: Average, maximum and minimum bond lengths measured. These values are based on measurements from Cu adsorption on both RuS and RuF surfaces. "Ta-N adsorbed" are bonds where N is directly bound to Cu at an adsorption site, "Ta-N distant" are bonds at an equivalent site on the surface away from the adsorption site and "Ta-N bare" was measured on a clean, doped surface. Similarly, "Ru-N adsorbed" are measured on a doped surface where Cu atoms have adsorbed and "Ru-N bare" was measured on the clean, doped surface.

Table A5: Binding Energies of Cu on Ru-doped TaN(1 1 0), as well as the activation energies for facile diffusion on the surface. The forward direction for activation energies indicates Cu moving away from Ru, while the reverse indicates Cu moving towards Ru. Q(Cu) is the charge on the Cu atom adsorbed to a doped surface, where there are two adatoms the charges are separated by a "/"

No.	Cu	Ru doping site	Cu adsorption site	E _{bind} [eV]			Q(Cu)	Migration Pathway	E _{activation} E [eV]	
				doped 1x4	doped 2x4	bare 2x4			Forward	Reverse
1	RuF		A	-2.88	-2.92	-2.80	10.5	A-A'	0.80	0.73
			B	-2.02	-2.09	-2.02	10.5	A-A''	0.40	0.38
			C	-1.88	-1.94	-1.90	10.6	A-B	1.42	0.56
			D	-2.56	-2.63	-2.13	10.4	B-B'	0.14	0.10
			E		-2.14		10.5			
2	RuS		AA''c		-3.12	-3.03	10.5/10.6	AA'c-AA'a	0.70	0.66
			AA''a		-3.34	-2.79	10.5/10.5			
			AB		-3.21	-2.42	10.6/10.5			
			AC				10.6/10.5			
	RuF		AD		-3.05	-2.42	10.5/10.4			
			AA''c		-3.03	-3.03	10.5/10.6	AA'c-AA'a	0.60	0.72
			AA''a		-2.88	-2.79	10.5/10.5			
			AB		-2.51	-2.42	10.5/10.5	-		

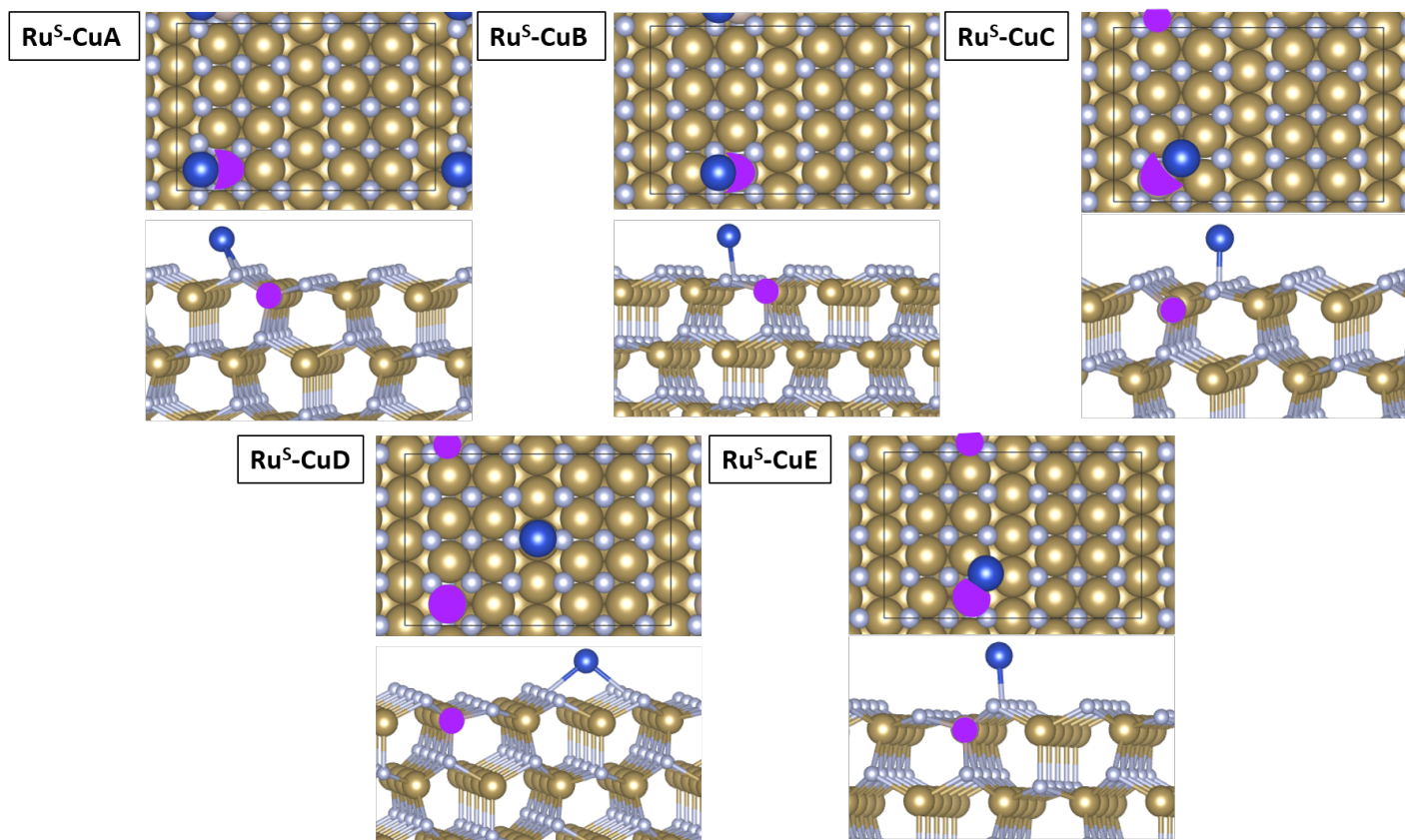


Figure A14: The adsorption geometries of 1 Cu atom on RuS-doped TaN(1 1 0). The Ta, N, Ru and Cu atoms are shown in ochre, light blue, purple and blue, respectively.

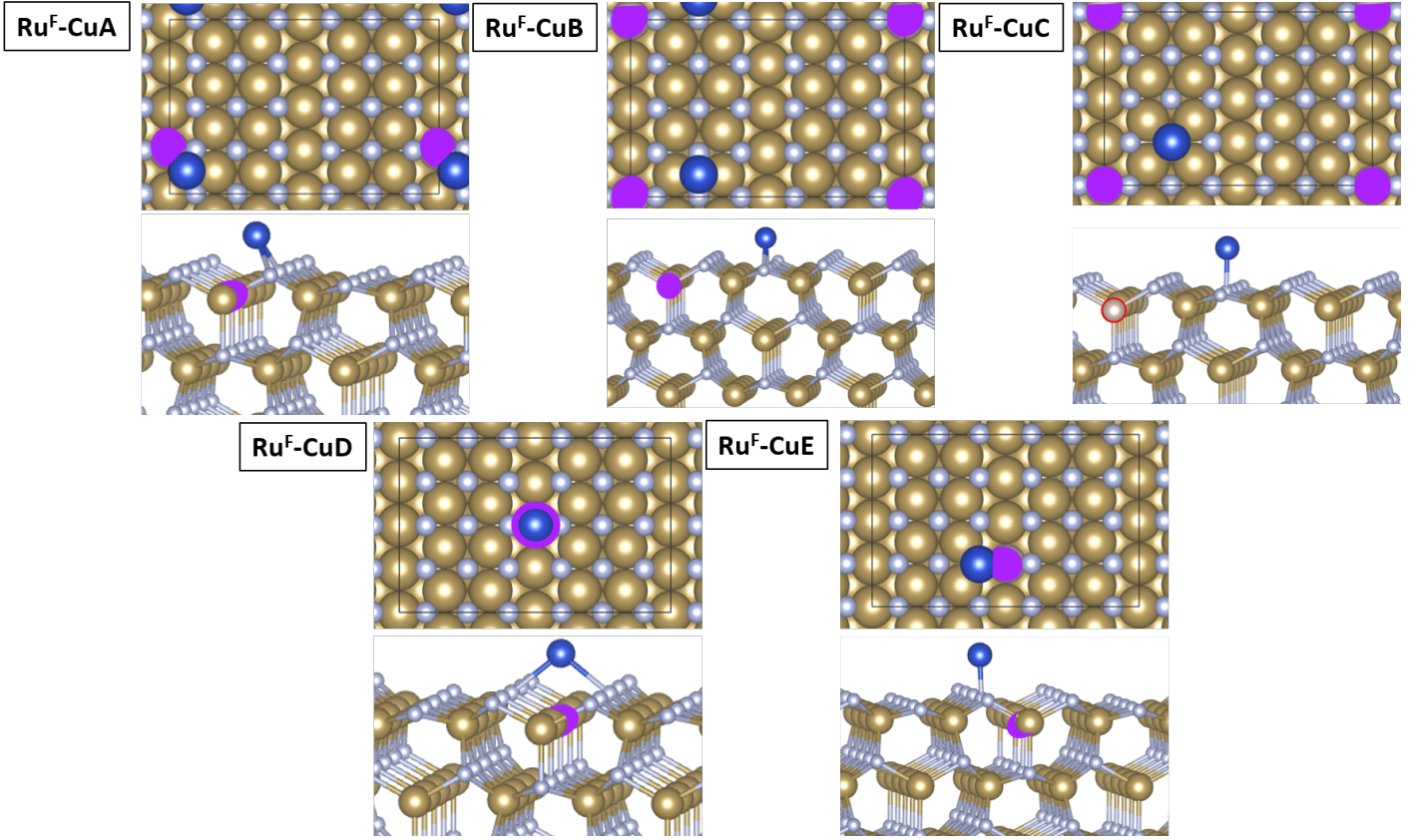


Figure A15: The adsorption geometries of 1 Cu atom on RuF-doped TaN(1 1 0). The Ta, N, Ru and Cu atoms are shown in ochre, light blue, purple and blue, respectively.

A2.9: Doping Arrangements

The doping energy per dopant is computed as

$$E_{\text{dope}} = \frac{E_{\text{total}} - (E_{\text{clean}} + n \times (E_{\text{Ru-atom}} - E_{\text{Ta-atom}}))}{n} \quad (1)$$

in which n is the number of Ru dopants in the surface layer. $E_{\text{Ta-atom}}$ and $E_{\text{Ru-atom}}$ are the energy of a single Ta and Ru atom in vacuum, respectively. E_{total} is the total energy of the relaxed doped surface and E_{clean} is the total energy of the clean TaN(1 1 0) surface.

We chose the 50% Ru-doped surface to study the effect of dopant distribution in the surface. A total of 10 surfaces were created, including both symmetric distributions, and less ordered, asymmetric structures, as shown in Fig. 3 of the main paper. To understand the stability of each distribution, the doping energy (Eq. 5) was computed for each surface and they are also compared with doping energies of the other Ru^x surfaces in Table A6 and Fig. A17. The doping energy reflects the relative energy needed to create the doped surface layer of the TaN (1 1 0) surface and can thus be used as a way of discovering a trend in surface stability. The purpose of this analysis is to examine a range of distributions of Ru dopants in the TaN (1 1 0) surface, while the actual incorporation of the dopants would be undertaken through atomic layer deposition (ALD), in which the final structure and distribution of Ru dopants is not necessarily the thermodynamically

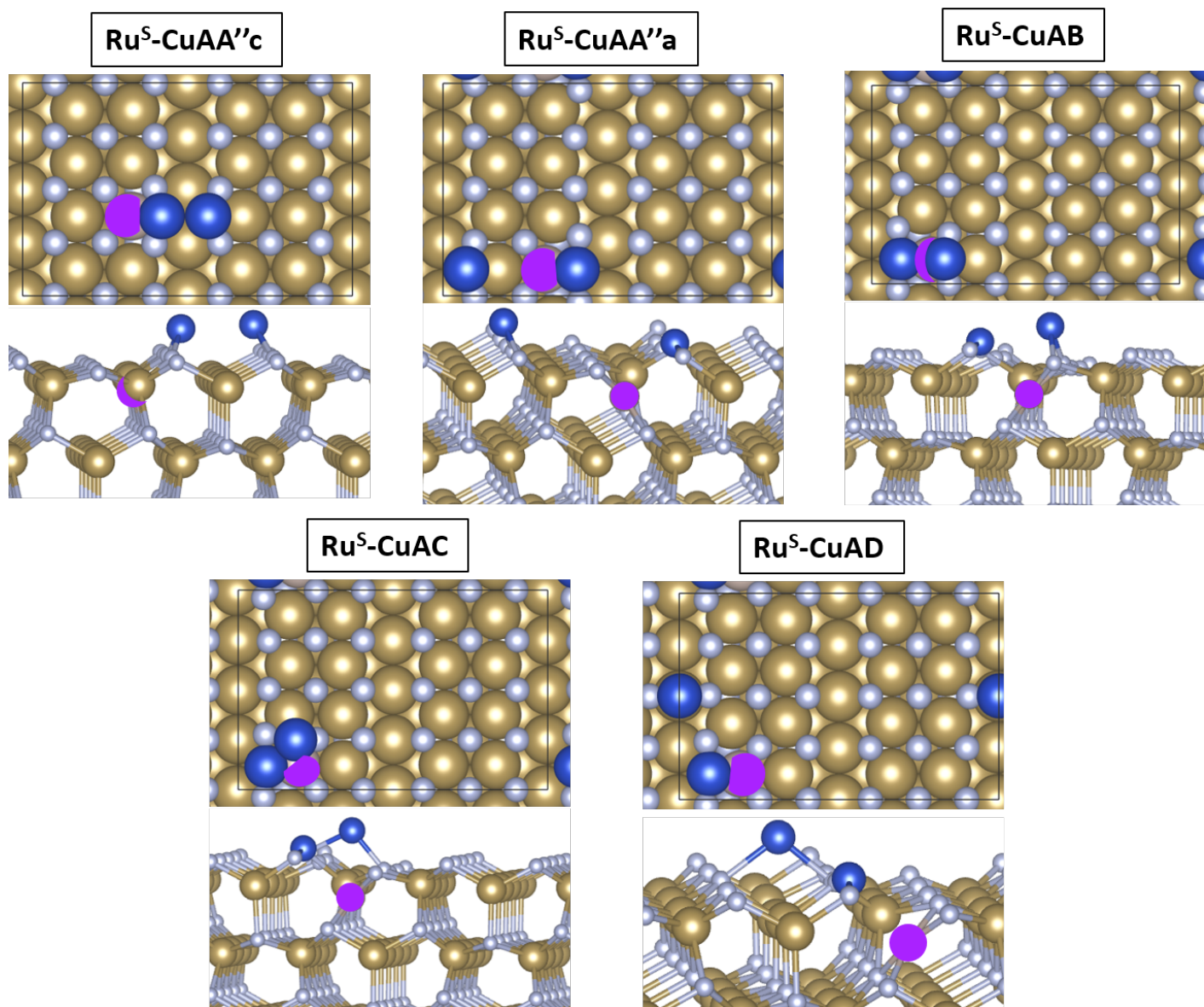


Figure A16: The adsorption geometries of 2 Cu atoms on RuS-doped TaN(1 1 0). The Ta, N, Ru and Cu atoms are shown in ochre, light blue, purple and blue, respectively.

most stable. These doping energies are plotted in Fig. A17 and they are also compared with doping energies of the other Ru^X surfaces in Table I of the SI.

Whether Ru atoms are clustered or more distributed over the surface layer appears to have no significant impact on the doping energy. However, there is a particular effect on the surface structure in the doped layer that can be clearly observed. Some surface rearrangement occurs and recesses tend to be formed where Ru atoms are adjacent to each other, due to the smaller atomic radius of Ru ($1.78\text{\AA}$) compared to Ta ($2.00\text{\AA}$). [3] Such recesses are found in all surface structures, although different arrangements show some variations in the amount of recesses present. The size of the recess depends on the overall environment and an increase in Ru-Ru interactions leads to larger recesses, with the exception of the bare Ru^{100} surface, where the recesses are very regular due to the high symmetry of the structure. Consequently, it is to be

Table A6: Doping energies for the different surfaces studied.

Surface	E_{doped} (eV/Ru)
100d	3.99
75d	3.57
50d-1	4.52
50d-2	3.91
50d-3	3.86
50d-4	3.97
50d-5	3.69
50d-6	3.61
50d-7	3.49
50d-8	3.45
50d-9	3.35
50d-10	3.30
25d	3.91

expected that Cu atoms will be more prone to bury into a recess on those surfaces where they are larger or more frequent. Examples of some of the recess structures formed are shown in Fig. 5 in the main paper.

In our previous work, [4] we found that there were two different doping sites on the surface, due to the two different types of Ta atoms in TaN. F-type sites are 3-fold coordinated with N and S-type sites are 6-fold coordinated with N. Ru doping at the F-site is more favourable than doping at the S-site. [4] We can see this effect in Fig. A17 as a higher level of S-site doping relative to F-site doping correlates with less favourable stability of the doped surface. By varying the doping pattern in the Ru^{50} surface through changing the ratio of S-type to F-type dopants in the surface, we can explore how the distribution of Ru influences the stability, which is important for a film with surface Ru doping that would be prepared by ALD. The high S-site doping in the Ru^{50-1} surface gives it the largest doping energy of all the surfaces studied, followed by the Ru^{100} surface. Interestingly, the Ru^{100} surface has an even higher proportion of S-site doping compared to the Ru^{50-1} surface, with an S:F ratio of 32:16. The relatively more favourable doping energy of 3.99 eV/Ru likely arises due to the presence of some F-site doping as opposed to no F-site doping in Ru^{50-1} . With an S:F ratio of 8:4, the Ru^{25} surface also has quite a large doping energy of 3.91 eV/Ru.

The Ru^{75} surface originally has an S:F ratio of 24:12. However, due to the significant rearrangement the surface underwent during relaxation there are no longer unambiguous S and F sites. In fact, coordination environments other than 3- and 6-fold can be observed for Ru atoms in this surface. This rearrangement upon doping could explain, why this surface has a lower doping energy than the Ru^{25} surface. Some of the more favourable Ru^{50} surfaces, in particular Ru^{50-5} and Ru^{50-6} , have doping energies close to the Ru^{75} surface, showing that the energy required per Ru to replace each of the 36 Ta atoms (24S:12F) in the Ru^{75} structure is as low as that required to replace 24 Ta (12S:12F) atoms in a Ru^{50} structure. In fact, the most favourable doping energy is observed for the Ru^{50-1} surface, showing that the doping energy is significantly affected by the dopant distribution. The doping energy and the S:F ratio of dopants are compared in Fig. A17, to more clearly illustrate the relationship between the S:F ratio and the doping energy of each dopant distribution.

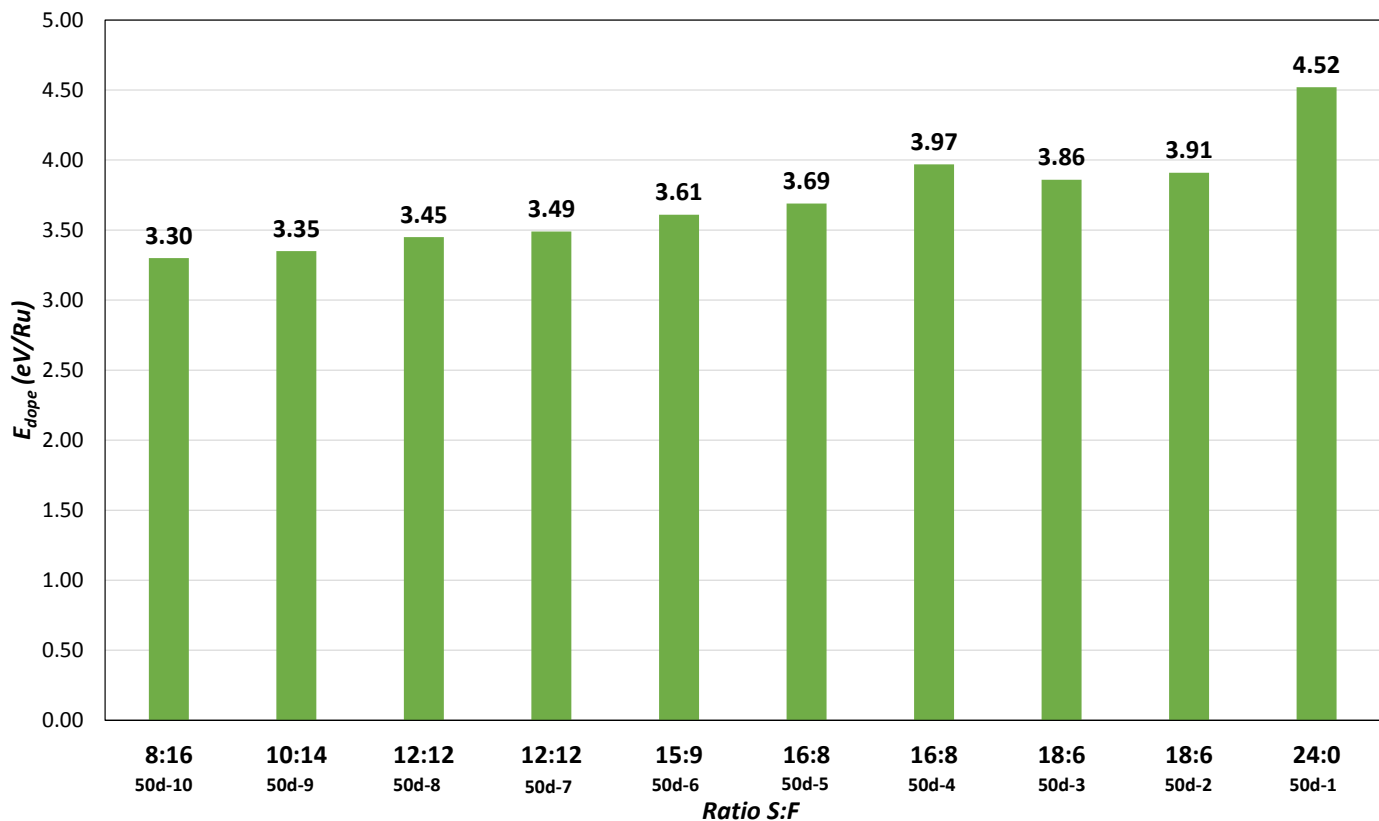


Figure A17: Effect of the ratio of S:F sites for 50% Ru doping in TaN(1 1 0) on the doping energy for Ru⁵⁰.

There is one exception, in that structure Ru⁵⁰⁻⁴, with a ratio of 16S:8F and a doping energy of +3.97 eV, does not follow this overall trend. Although it has an S:F ratio of 16:8, the doping energy is 0.28 eV/Ru larger than that of structure Ru⁵⁰⁻⁵, which has the same 16S:8F ratio. For all other structures with the same S:F ratios this difference is <0.10 eV/Ru. Further, structures Ru⁵⁰⁻² and Ru⁵⁰⁻³ have a larger amount of S-site Ru atoms with a ratio of 18:6, which should make them less stable, but they have a more favourable doping energy than structure Ru⁵⁰⁻⁴ instead. The origin of this is probably due to the high symmetry present in the Ru distribution in structure Ru⁵⁰⁻⁴. Such structures with high symmetry although stable, tend to have higher energies, indicating that they are local minima, as discussed for the Ru¹⁰⁰ doped surface earlier. However, this surface (Ru⁵⁰⁻⁴) did not distort on single Cu adsorption, as opposed to the Ru¹⁰⁰ surface, possibly due to the relatively lower Ru-Ru coordination number. Overall, surface stability and thus reactivity, are found to be more affected by the S:F ratio, rather than necessarily the exact distribution of Ru atoms in general. The effect this change in stability has on the behaviour of Cu adatoms is the subject of future work.

A2.10: Copper adsorption

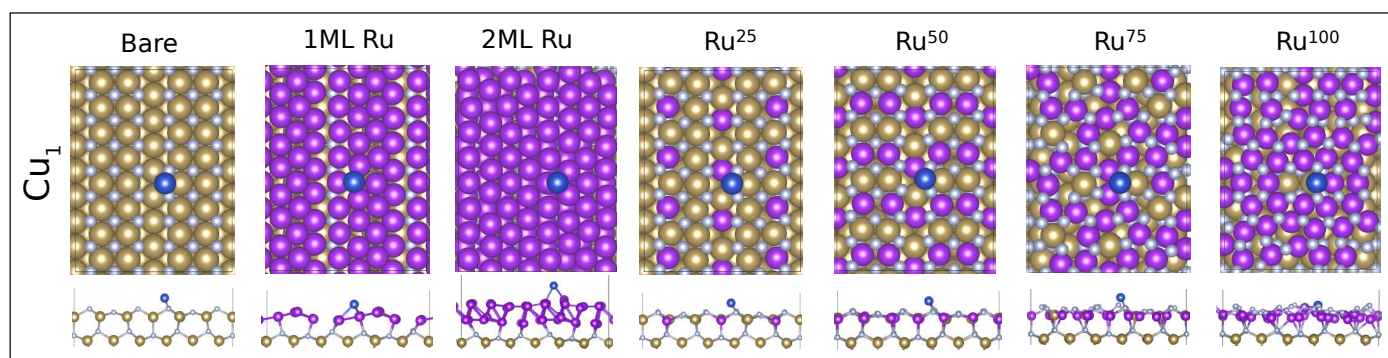


Figure A18: Relaxed geometries of the different surfaces with one adsorbed Cu atom at the 5-fold site.

A2.11: All Adsorption Geometries

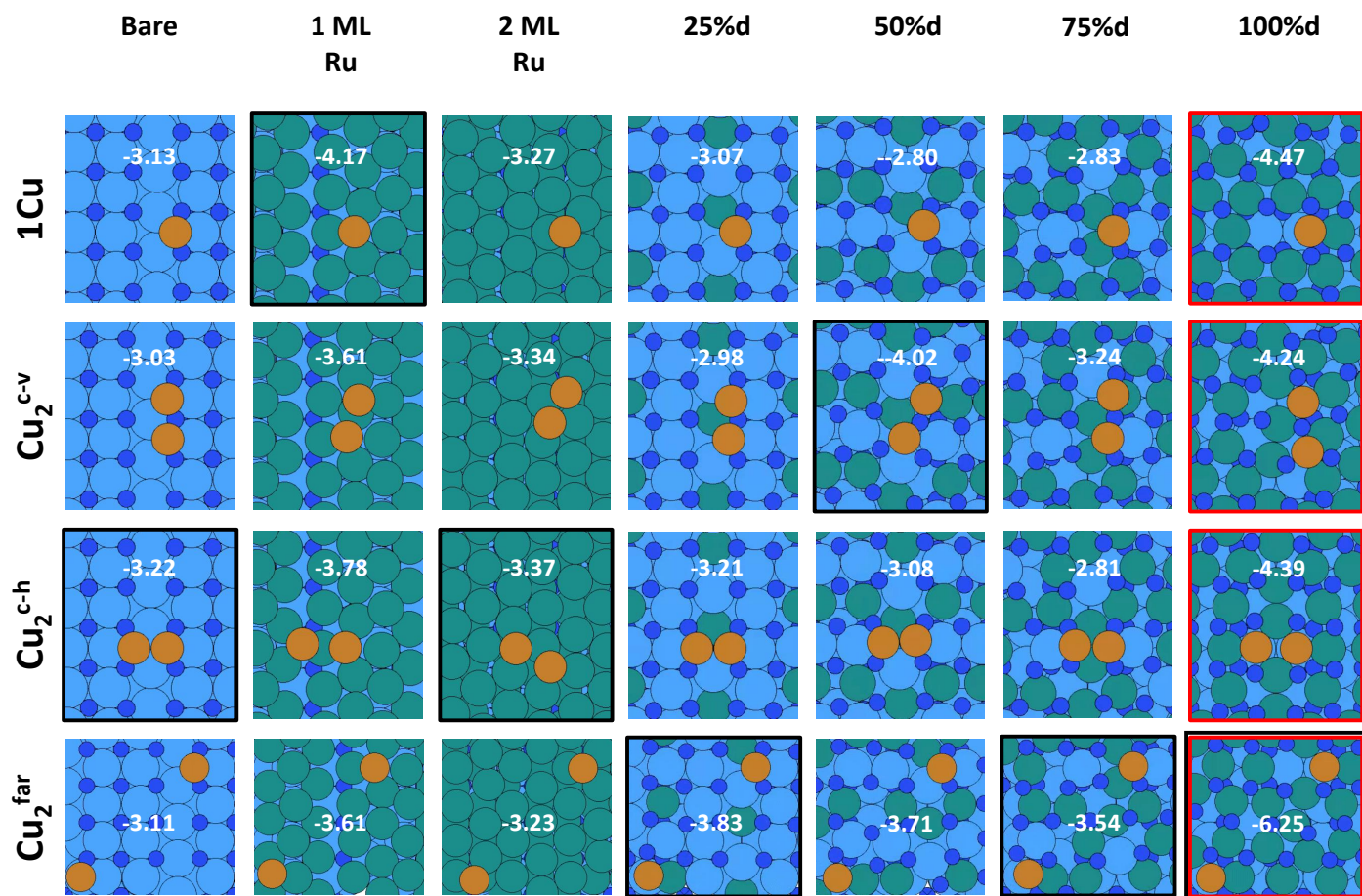


Figure A19: Minimum energy geometries of 1 and 2 Cu adsorbed on the different surfaces. Here the Ta, Ru, N, Cu atoms are represented by spheres colored in light blue, green, dark blue and brown, respectively

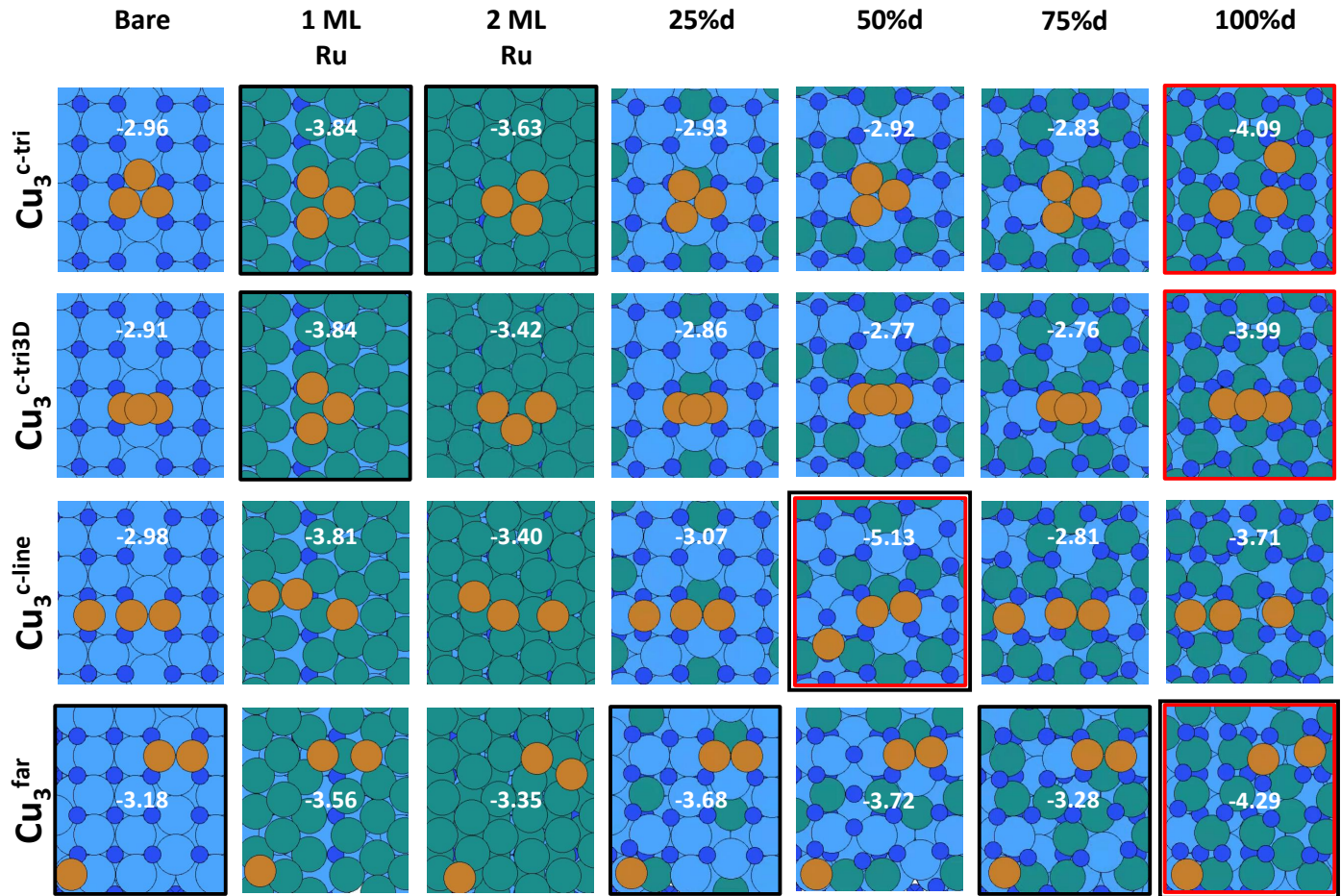


Figure A20: Minimum energy geometries of 3 Cu adsorbed on the studied surfaces. Here the Ta, Ru, N, Cu atoms are represented by spheres colored in light blue, green, dark blue and brown, respectively

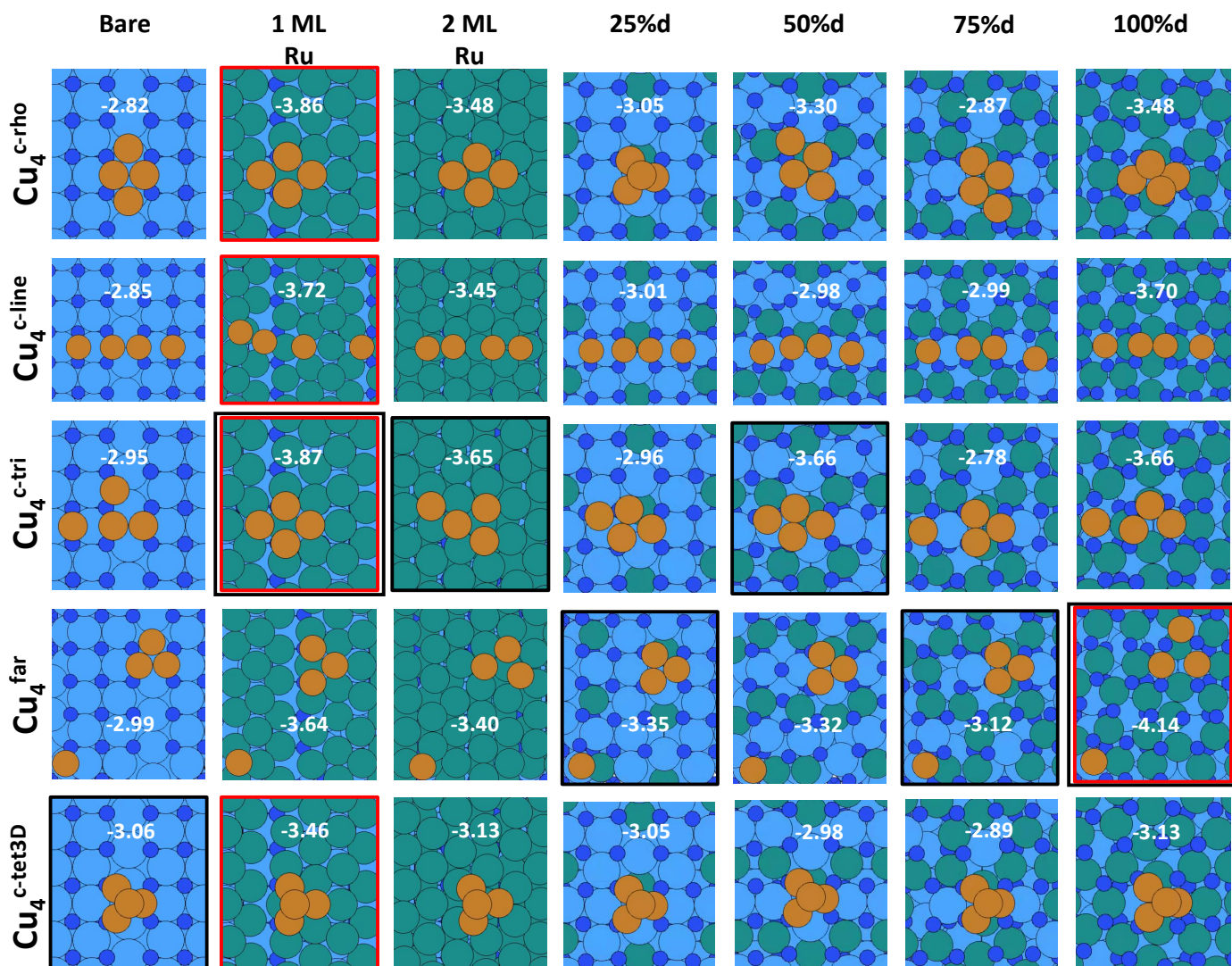


Figure A21: Minimum energy geometries of 4 Cu adsorbed on the studied surfaces. Here the Ta, Ru, N, Cu atoms are represented by spheres colored in light blue, green, dark blue and brown, respectively

A2.12: 2D to 3D Rearrangement in Ru²⁵ Surface

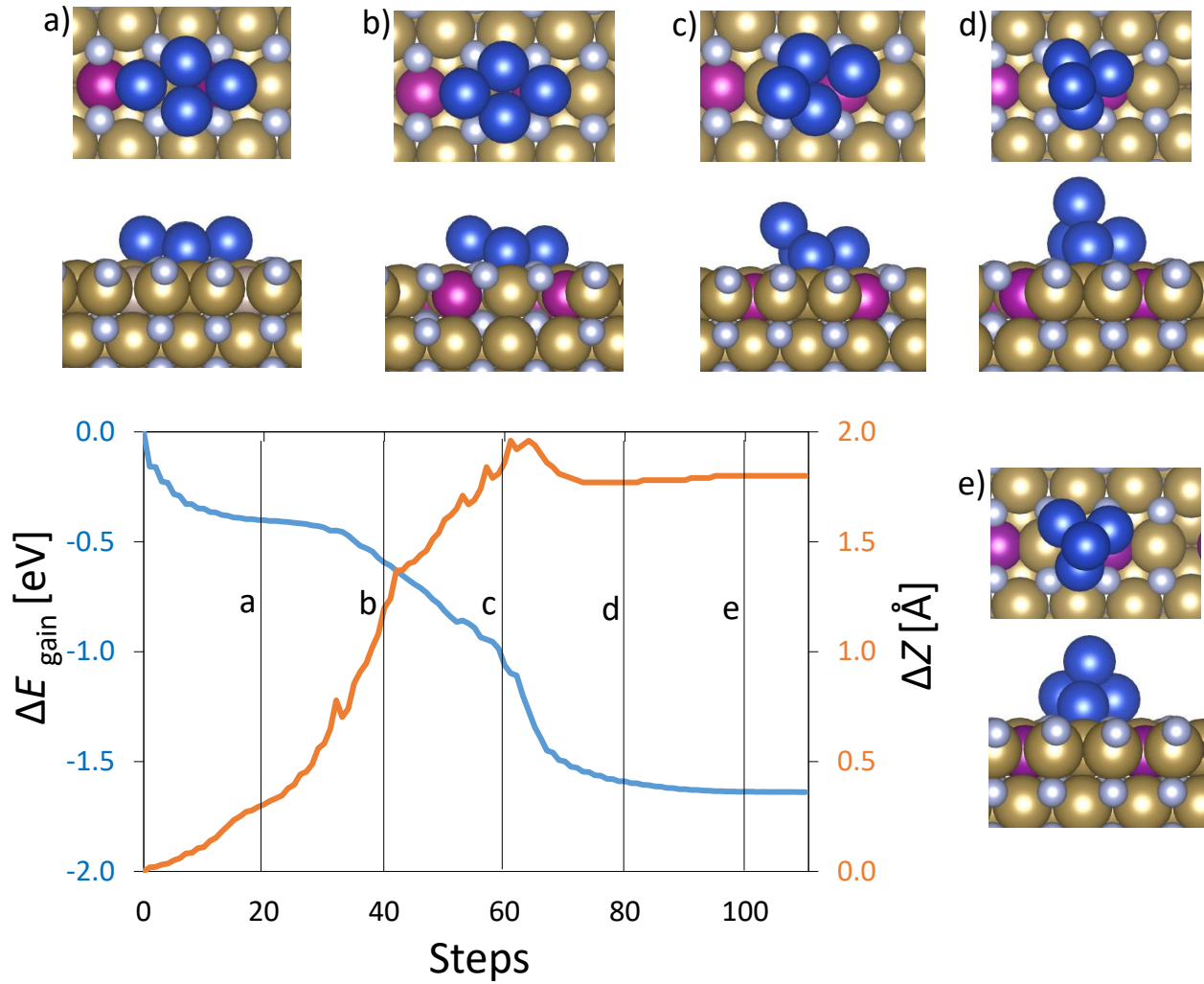


Figure A22: Top and side views of geometries extracted from $\text{Cu}_4^{\text{c-rho}}$ cluster relaxation trajectory on 25% doped surface. The graph shows the energy gained in this process (ΔE_{gain}) and the associated Z distance change (ΔZ) of the migrating Cu atom. From the geometries in this figure, we could clearly see the Cu atom in the left (a) lifting off from the surface and hopping on to the neighbouring Cu atoms via the bridge site (b-c-d) and reaching the apex 3-fold site in the end (e). We find from the graph a correlation between the overall energy gain and the increasing Z-distance of the migrating Cu atom. It is interesting to see that the migrating Cu atom was initially bound to a surface Ru atom (Cu-Ru bond), which is a stronger bond as compared to the Cu-Ta bond on the clean surface. Therefore, the preference to a 2 layered 3D Cu cluster on the Ru²⁵ surface suggests that this surface, with no Ru-Ru surface bonds, will promote aggregation of Cu into 3D clusters rather than wetting, indicating that the Cu-Ru interaction at low Ru concentration is not strong enough to promote the stability of this arrangement.

A2.13: Description of the Binding Energies

Cu binding energies reported in this paper are computed per atom from:

$$E_{\text{bind}} = (E_{\text{int.sys.}} - (E_{\text{bare}} + nE_{\text{Cu-atom}}))/n\text{Cu}. \quad (2)$$

Here, $E_{\text{int.sys.}}$ is the total energy of the relaxed interacting system where n Cu atoms are adsorbed on the respective TaN surface, E_{bare} refers to the relaxed energy of the corresponding bare surface and $E_{\text{Cu-atom}}$ is the total energy of an isolated Cu atom. Therefore, E_{bind} also includes the Cu-Cu interaction. $n\text{Cu}$ is the total number of Cu atoms in the adsorbed nanocluster. For certain doped surfaces, the adsorption of the Cu atoms distorted the surface atomic arrangements. Therefore we compute E_{surf} which refers to the single point energy of the relaxed interacting system with the copper atoms removed. E_{surf} would be almost similar to E_{bare} if the surface distortion is minimal. For some surfaces we found the difference between these two terms, termed as surface rearrangement energy (E_{SR}), is large. Therefore, to make a fair comparison of the Cu binding energies computed at different surfaces, we removed this E_{SR} contribution from E_{bind} . Thus the above equation becomes

$$E_{\text{bind}} = (E_{\text{int.sys.}} - (E_{\text{surf}} + nE_{\text{Cu-atom}}))/n\text{Cu}. \quad (3)$$

We compute $E_{\text{metal-substrate}}$, which is the binding energy of the Cu_n cluster relative to a gas-phase Cu_n cluster.

$$E_{\text{metal-substrate}} = (E_{\text{int.sys.}} - (E_{\text{surf}} + E_{\text{Cu-cluster}}))/n. \quad (4)$$

Here, $E_{\text{int.sys.}}$ and E_{surf} are the same as in Eq. 1, while $E_{\text{Cu-cluster}}$ refers to the single point energy of the Cu-cluster isolated from the TaN surface. Now, an estimate of the Cu-Cu interaction energy can be computed from

$$E_{\text{interact}} = E_{\text{bind}} - E_{\text{metal-substrate}}. \quad (5)$$

Table A7: A summary of the minimum and maximum Cu-Cu and Cu-slab distances for all arrangements of Cu_n nanocluster on bare and 100d surfaces.

Surf	cluster	Arrangement	d(Cu-Cu) [Å]		d(Cu-slab) [Å]		E_{bind}	$E_{\text{metal-substrate}}$	$E_{interact}$
			min	max	min	max	[eV]	[eV]	[eV]
Clean	2 Cu	C-v	2.93	2.93	1.73	1.73	-3.03	-2.37	-0.66
		C-h	2.43	2.43	1.7	1.7	-3.22	-2.2	-1.02
		far	12.59	12.59	1.71	1.71	-3.11	-3.11	0.00
	3 Cu	C-tri	2.41	2.45	1.76	2.22	-2.96	-1.75	-1.21
		C-tri3D	2.33	2.47	1.83	3.81	-2.91	-1.69	-1.22
		C-line	2.46	5.62	1.68	1.71	-2.98	-2.14	-0.84
	4 Cu	far	2.42	12.53	1.7	1.71	-3.18	-2.48	-0.7
		C-rho	2.43	4.22	1.8	2.12	-2.82	-1.27	-1.54
		C-line	2.5	8.98	1.67	1.71	-2.85	-2.15	-0.7
		C-tri	2.44	5.69	1.69	1.73	-2.95	-2.1	-0.85
		far	2.41	13.25	1.71	2.21	-2.99	-2.08	-0.91
		C-tet3D	2.38	2.48	1.81	3.99	-3.06	-1.71	-1.35
Ru^{100}	2 Cu	C-v	3.7	3.7	0.71	1.17	-4.25	-3.49	-0.76
		C-h	2.96	2.96	0.53	0.55	-4.39	-3.33	-1.06
		far	12.69	12.69	0.62	0.62	-6.25	-6.25	0.00
	3 Cu	C-tri	3.43	5.5	0.77	1.61	-4.09	-2.87	-1.22
		C-tri3D	2.49	3.83	0.66	2.26	-3.99	-2.76	-1.22
		C-line	2.68	6.54	0.58	1.71	-3.71	-2.83	-0.88
	4 Cu	far	3.51	12.83	0.83	0.94	-4.29	-3.6	-0.69
		C-rho	2.33	3.46	0.58	2.93	-3.48	-2.12	-1.36
		C-line	2.38	8.95	0.48	1.71	-3.7	-2.94	-0.76
		C-tri	2.39	6.16	0.45	2.08	-3.66	-2.13	-1.53
		far	3.13	13.98	0.56	1.52	-4.14	-3.23	-0.92
		C-tet3D	2.34	2.83	0.95	3.43	-3.13	-1.77	-1.36

Table A8: A summary of the minimum and maximum Cu-Cu and Cu-slab distances for all arrangements of Cu_n nanocluster on 75d and 50d surfaces.

Surf	cluster	Arrangement	d(Cu-Cu) [Å]		d(Cu-slab) [Å]		E_{bind} [eV]	$E_{\text{metal-substrate}}$ [eV]	$E_{interact}$ [eV]
			min	max	min	max			
Ru^{75}	2 Cu	C-v	3.16	3.16	1.69	1.7	-3.25	-2.82	-0.43
		C-h	2.46	2.46	1.69	1.89	-2.81	-1.73	-1.08
		far	12.05	12.05	1.07	1.67	-3.54	-3.54	0.00
	3 Cu	C-tri	2.35	2.43	1.87	2.44	-2.84	-1.62	-1.22
		C-tri3D	2.34	2.45	1.83	3.92	-2.76	-1.53	-1.22
		C-line	2.46	6.34	1.18	1.92	-2.81	-2.09	-0.72
	4 Cu	far	2.47	12.16	1.03	1.9	-3.28	-2.59	-0.69
		C-rho	2.38	4.28	1.92	2.44	-2.87	-1.35	-1.52
		C-line	2.47	7.95	1.17	2.1	-2.99	-2.12	-0.86
		C-tri	2.35	6.37	1.17	2.43	-2.78	-1.23	-1.55
		far	2.35	12.14	1.08	2.44	-3.12	-2.2	-0.92
		C-tet3D	2.38	2.45	1.83	4.03	-2.89	-1.53	-1.35
Ru^{50}	2 Cu	C-v	3.29	3.29	0.9	1.4	-4.02	-3.5	-0.51
		C-h	2.39	2.39	1.5	1.66	-3.08	-2.06	-1.02
		far	12.17	12.17	1.03	1.82	-3.71	-3.71	0.00
	3 Cu	C-tri	2.37	2.4	1.73	2.22	-2.92	-1.7	-1.22
		C-tri3D	2.34	2.45	1.79	3.8	-2.77	-1.55	-1.22
		C-line	2.46	6.4	0.75	1.73	-5.14	-4.43	-0.71
	4 Cu	far	2.43	12.52	0.85	1.81	-3.72	-3.04	-0.68
		C-rho	2.39	4.46	1.58	2.29	-3.3	-1.76	-1.54
		C-line	2.56	8.5	1.62	1.86	-2.98	-2.41	-0.57
		C-tri	2.36	4.36	1.89	2.43	-3.66	-2.71	-0.96
		far	2.37	12.07	1.04	2.18	-3.32	-2.4	-0.91
		C-tet3D	2.38	2.5	1.77	3.92	-2.98	-1.62	-1.36

Table A9: A summary of the minimum and maximum Cu-Cu and Cu-slab distances for all arrangements of Cu_n nanocluster on 25d and 1 ML Ru passivated surfaces.

Surf	cluster	Arrangement	d(Cu-Cu) [Å]		d(Cu-slab) [Å]		E_{bind}	$E_{\text{metal-substrate}}$	$E_{interact}$
			min	max	min	max	[eV]	[eV]	[eV]
Ru ²⁵	2 Cu	C-v	2.81	2.81	1.6	1.79	-2.98	-2.95	-0.02
		C-h	2.41	2.41	1.57	1.57	-3.21	-2.61	-0.6
		far	12.11	12.11	1.08	1.56	-3.83	-3.83	0.00
	3 Cu	C-tri	2.36	2.41	1.73	2.23	-2.93	-2.53	-0.39
		C-tri3D	2.34	2.45	1.77	3.76	-2.86	-1.77	-1.09
		C-line	2.44	5.57	1.57	1.77	-3.07	-2.45	-0.62
	4 Cu	far	2.41	12.19	1.08	1.58	-3.68	-3.48	-0.2
		C-rho	2.37	2.48	1.73	3.93	-3.05	-1.82	-1.23
		C-line	2.47	8.76	1.59	1.77	-3.01	-2.34	-0.67
		C-tri	2.34	4.42	1.68	2.2	-2.96	-1.98	-0.98
		far	2.36	12.12	1.08	2.23	-3.35	-2.96	-0.39
		C-tet3D	2.38	2.49	1.73	3.93	-3.05	-1.77	-1.28
1 ML Ru	2 Cu	C-v	2.93	2.93	1.47	2.28	-3.61	-3.06	-0.54
		C-h	3.13	3.13	1.39	1.57	-3.78	-3.27	-0.51
		far	11.81	11.81	1.42	2.2	-3.61	-3.61	0.00
	3 Cu	C-tri	2.46	2.99	1.51	1.64	-3.84	-2.71	-1.13
		C-tri3D	2.46	2.99	1.52	1.64	-3.84	-2.7	-1.14
		C-line	2.77	6.06	1.07	2.33	-3.81	-3.19	-0.61
	4 Cu	far	3.3	11.65	1.42	2.2	-3.56	-3.32	-0.24
		C-rho	2.48	4.1	1.5	1.67	-3.86	-2.48	-1.39
		C-line	2.75	8.89	1.13	2.33	-3.72	-3.33	-0.39
		C-tri	2.48	4.07	1.45	1.65	-3.87	-2.51	-1.36
		far	2.46	12.09	1.51	2.22	-3.64	-2.79	-0.85
		C-tet3D	2.41	2.68	1.62	3.58	-3.46	-2.12	-1.34

Table A10: A summary of the minimum and maximum Cu-Cu and Cu-slab distances for all arrangements of Cu_n nanocluster on 2 ML Ru passivated surface.

Surf	cluster	Arrangement	d(Cu-Cu) [Å]		d(Cu-slab) [Å]		E_{bind}	$E_{\text{metal-substrate}}$	$E_{interact}$
			min	max	min	max	[eV]	[eV]	[eV]
2 ML Ru	2 Cu	C-v	2.54	2.54	2.08	2.38	-3.34	-2.45	-0.89
		C-h	2.88	2.88	1.75	1.91	-3.37	-2.66	-0.7
		far	12.46	12.46	2.22	2.4	-3.23	-3.23	0.00
	3 Cu	C-tri	2.57	2.88	1.62	1.91	-3.63	-2.55	-1.08
		C-tri3D	2.47	3.66	1.74	2.49	-3.42	-2.31	-1.1
		C-line	2.56	6	1.73	2.13	-3.4	-2.69	-0.71
	4 Cu	far	2.85	11.27	1.67	2.27	-3.35	-2.9	-0.44
		C-rho	2.48	4.11	1.73	2.15	-3.48	-2.04	-1.43
		C-line	2.51	8.84	1.63	2.36	-3.45	-2.45	-0.99
		C-tri	2.56	5.12	1.67	1.86	-3.65	-2.36	-1.29
		far	2.56	12.85	1.71	2.28	-3.4	-2.61	-0.78
		C-tet3D	2.41	2.58	2.18	4.18	-3.13	-1.79	-1.34

A2.14: E_{SR} Values for All Geometries

Table A11: E_{SR} values for all arrangements on all surfaces in eV.

Cu	Arrangement	E_{SR} [eV]						
		Bare	1 ML Ru	2 ML Ru	25d	50d	75d	100d
1Cu	5-fold	0.53	0.42	-1.29	0.28	0.04	0.19	-27.3
2 Cu	C-v	0.84	0.35	-1.23	0.67	-3.51	1.3	-27.22
	C-h	0.61	0.49	-1.43	0.58	0.54	0.5	-21.27
	far	0.78	0.43	-0.32	0.71	-6.84	0.93	-23.88
3 Cu	C-tri	0.43	0.63	-0.84	0.38	0.36	0.63	-23.54
	C-tri3D	0.49	0.62	-1.09	0.28	0.14	0.23	-22.6
	C-line	0.72	0.46	-1.05	0.82	0.75	0.68	-24.08
	far	0.87	0.52	-1.12	1.02	-5.96	1.25	-23.27
4 Cu	C-rho	0.82	0.89	-1.12	0.48	-11.74	1.03	-24.79
	C-line	1.36	0.74	-0.16	1.44	-5.85	1.85	-25.27
	C-tri	1.27	0.82	-0.74	0.52	-3.42	0.59	-24.11
	far	0.95	0.67	-1.11	0.83	-7.24	1.1	-25.81
	C-tet3D	0.4	0.55	-1.23	0.48	0.43	0.48	-27.46

A2.15: Most and Least Favourable Arrangements

Table A12: Arrangements with the most favourable $E_{\text{metal-substrate}}$ and E_{interact} on the surfaces.

Surface	$E_{\text{metal-substrate}}$					
	Most favourable			Least favourable		
	2 Cu	3 Cu	4 Cu	2 Cu	3 Cu	4 Cu
clean	far	far	c-line	c-h	c-tri3D	c-rho
1 ML Ru	far	far	c-line	c-v	c-tri, c-tri3D	c-tet3D
2 ML Ru	far	far	far	c-v	c-tri3D	c-tet3D
25%d	far	far	far	c-h	c-tri3D	c-tet3D
50%d	far	c-line	c-tri	c-h	c-tri3D	c-tet3D
75%d	far	far	far	c-h	c-tri3D	c-tri
100%d	far	far	far	c-h	c-tri3D	c-tet3D

Surface	E_{interact}					
	Most favourable			Least favourable		
	2 Cu	3 Cu	4 Cu	2 Cu	3 Cu	4 Cu
clean	c-h	c-tri, c-tri3D	c-rho	far	far	c-line
1 ML Ru	c-v	c-tri, c-tri3D	c-rho	far	far	c-line
2 ML Ru	c-v	c-tri3D	c-rho	far	far	far
25%d	c-h	c-tri3D	c-tet3D	far, c-v	far	far
50%d	c-h	c-tri, c-tri3D	c-rho	far	far	far
75%d	c-h	c-tri, c-tri3D	c-tri	far	far	c-line
100%d	c-h	c-tri, c-tri3D	c-tri	far	far	c-line

A2.16: Individual Cu-Slab distances

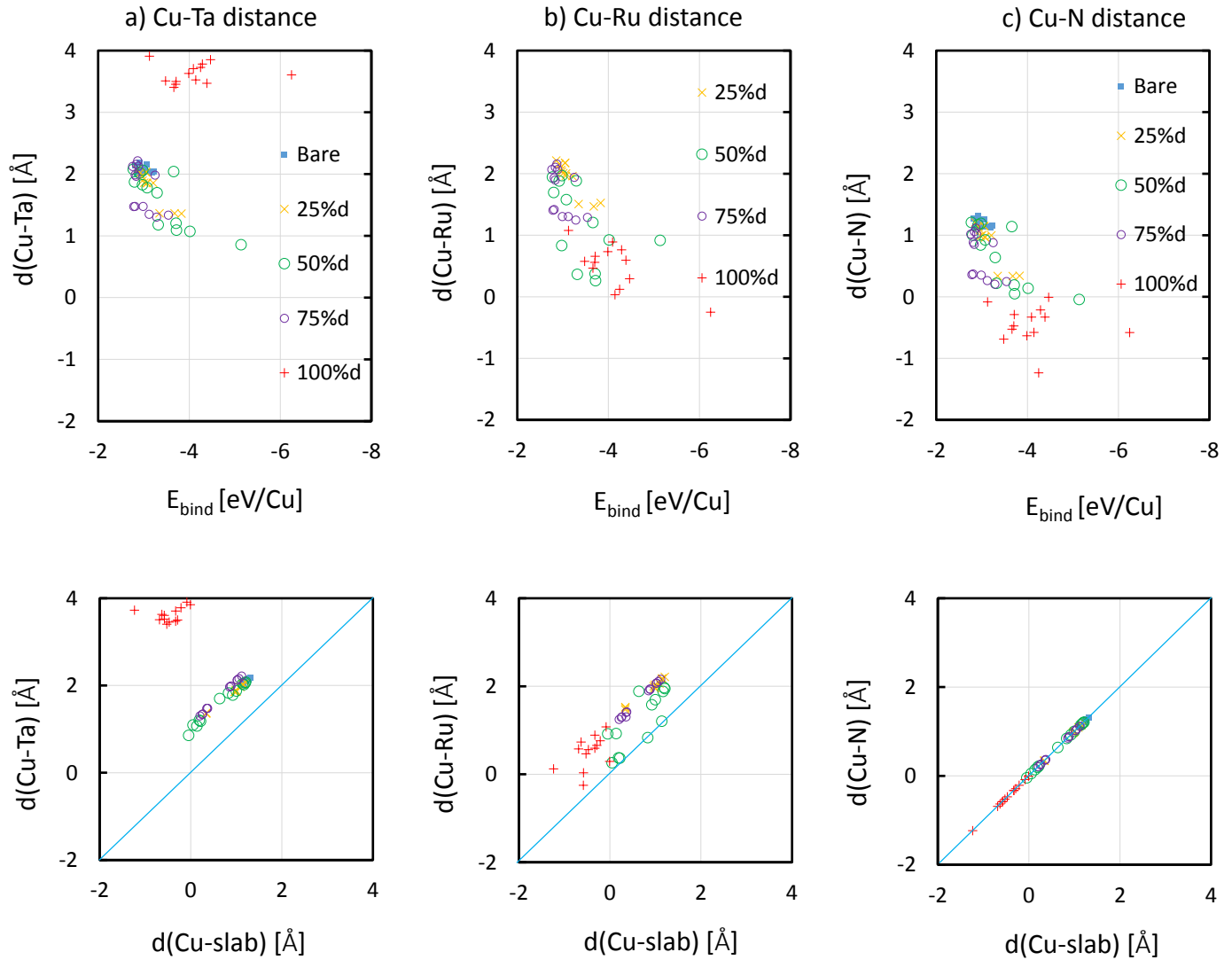


Figure A23: Scatter plots of the shortest $d(\text{Cu-X})$, where $X = \text{Ta}, \text{Ru}, \text{N}$, with respect to the binding energy are shown in panels a), b) and c), respectively.

Figure A23 details data on the difference bondlengths measurements that were made. The bottom plots in the panels show the correlation between the individual $d(\text{Cu-X})$ and the shortest overall $d(\text{Cu-slab})$, defined in Fig.21a of Chapter 4. As expected, the trend in these plots shows that the binding energy becomes more negative with a decrease in the distances. This figure also includes correlation plots comparing the $d(\text{Cu-X})$ ($X = \text{Ta}, \text{Ru}, \text{N}$) with the overall $d(\text{Cu-slab})$ given in Fig.21b, Chapter 4. From the correlation plots, we find that Ta is the farthest atom (along Z) from Cu in all the arrangements. The $d(\text{Cu-Ta})$ on Ru^{100} surface is longer than on the other surfaces since the full substitution of Ta with Ru means that the nearest Ta atoms are in the second layer of the slab. In some arrangements on the Ru^{50} and Ru^{100} Ru surfaces, $d(\text{Ru-Cu})$ is the shortest (those along the 45° line). These are the cases where the Cu atom is buried into the recess formed by the doped Ru atoms. However, in almost all cases, the $d(\text{Cu-N})$ is the shortest which is evident

from all the data points lying along the correlation line in panel c. The $d(\text{Cu-X})$ measurements on the Ru passivated surfaces are not shown, as the $d(\text{Cu-Ta})$ and $d(\text{Cu-N})$ values are much larger on these surfaces and do not add much to the discussion. However, the minimum distances on the passivated surfaces plotted in Fig.21b in Chapter 4 are between Cu and Ru atoms. Among the two passivated surfaces, shorter distances are reported for the 1 ML surface owing to the fact that the Ru layer on this surface is not closely packed as in the 2 ML surface and a trough is clearly visible in the 1ML structure in Fig.13b in Chapter 4 that could trap the Cu atoms. On some Cu arrangements, the $d(\text{Cu-Ru})$ value is near zero on the 1 ML passivated surface.

A3: Supplementary Information for Chapter 5

A3.1: Results and Discussion for Cu_{29} on Ru^{50-1} , Ru^{50-4} and Ru^{75}

This section of the appendix discusses the adsorptions of Cu_{29} on Ru-TaN not included in the main chapter. Figure A24 shows the 0K and 500K structures of Cu_{29} on two different Ru^{50} surfaces with varying Ru distribution and on Ru^{75} . Ru^{50-1} has Ru dopants only at site S (6 coordinate) and Ru^{50-4} has dopants at both site S and F (3 coordinate). An overview of geometries after 5 ps of MD at 300 K, 500 K and 800 K for Ru^{50-1} , Ru^{50-4} and Ru^{75} is shown in Figure A25.

Due to the large gaps formed in the Ru^{50-1} surface, we observe migration of several Cu atoms into the surface layer during relaxation. Only one Cu atom moves up to form begin the S+1 layer, while the overall structure remains flat. However, after 5 ps at 300 K we observe that an S+1 layer has been formed, with some Cu atoms remaining embedded in the Ru-TaN layer and some Ru atoms beginning to move out of the surface, as illustrated by the plot in Figure A26(a). Interestingly, the interaction with the surface wins out at 500 K, where study of the z-plot shows no atoms displaced by more than 1 Å, even though the geometry of the cluster is not entirely flat. Figure A26(b) also indicates that two Cu atoms have penetrated into the surface layer by up to -3 Å. The only other surface where we observe atom displacements of this magnitude is the Ru^{100} surface. A similar displacement of only one atom also occurs at 800 K (see Figure A26(c)). At this temperature there are once again atoms displaced to form the beginnings of an S+1 structure. The Cu structure formed is relatively disordered and lacks the distinctly faceted morphology observed in particular for TaN and Ru^{25} . Careful observation of the geometry shows that several Ru atoms begin to migrate out of the surface at 500 K and 800 K. This exchange between Ru and Cu is likely why the Cu atoms show such a large displacement, as was observed for Ru_{100} . Due to the close proximity of Ru dopants in this surface and area of pseudo 100% doping is created, which explains why Ru and Cu are beginning to mix in a similar fashion. Despite this, there is very little change to the morphology of Cu_{29} throughout the different MD simulations.

On the Ru^{50-4} , Cu shows a similar structure to that observed on Ru^{25} and Ru^{50-10} . Interestingly, with 2 atoms displaced to more than 1 Å, the geometry obtained at 300 K has more atoms which migrated into a new layer than those obtained at 500 K and 800 K (see Figure A26(d), (e) and (f)). This also means that this surface shows the least displacements of atoms at any temperature of the different Ru doped surfaces. Additionally, even though this surface does not have many large recesses, 3 to 4 Cu atoms are incorporated into the surface layer at all temperatures. The analysis of geometry and atom displacements shows that this surface behaves very similarly to Ru^{50-10} . Although Ru^{50-1} and Ru^{50-4} were not selected for more detailed study, the results obtained from both surfaces show that as long as the Ru atoms do not cluster together in the surface to form large areas of 100%-doping like areas and instead a relatively even distribution of dopants is ensured, any Ru^{50} surface is likely to inhibit the formation of further layers in the Cu structure without compromising on thermal stability.

Due to the disordered structure of the Ru^{75} surface there are many available sites for Cu atoms to migrate into the surface layer. This is evident in the migration of several atoms by up to 2 Å from their location after relaxation, as

seen in Figure A26(g), (h) and (i). Additionally, atoms migrate upwards to join the S+1 layer, although study of the geometry indicates that no S+2 layer is formed. The combination of the Cu atoms incorporating into the surface and some atoms migrating upwards in the same area of the structure most likely caused the gap in the Cu₂₉ cluster visible in Figure A24(c). Additionally, it appears that the atoms are kept somewhat apart due to incorporation into the surface. However, at 800 K, it becomes clear that for Ru⁷⁵, Ru atoms become too densely concentrated in areas of the surface and just like for Ru⁵⁰⁻¹ and Ru¹⁰⁰, we observe an exchange of Cu atoms with Ru and N atoms, atoms do not incorporate as deeply into the surface.

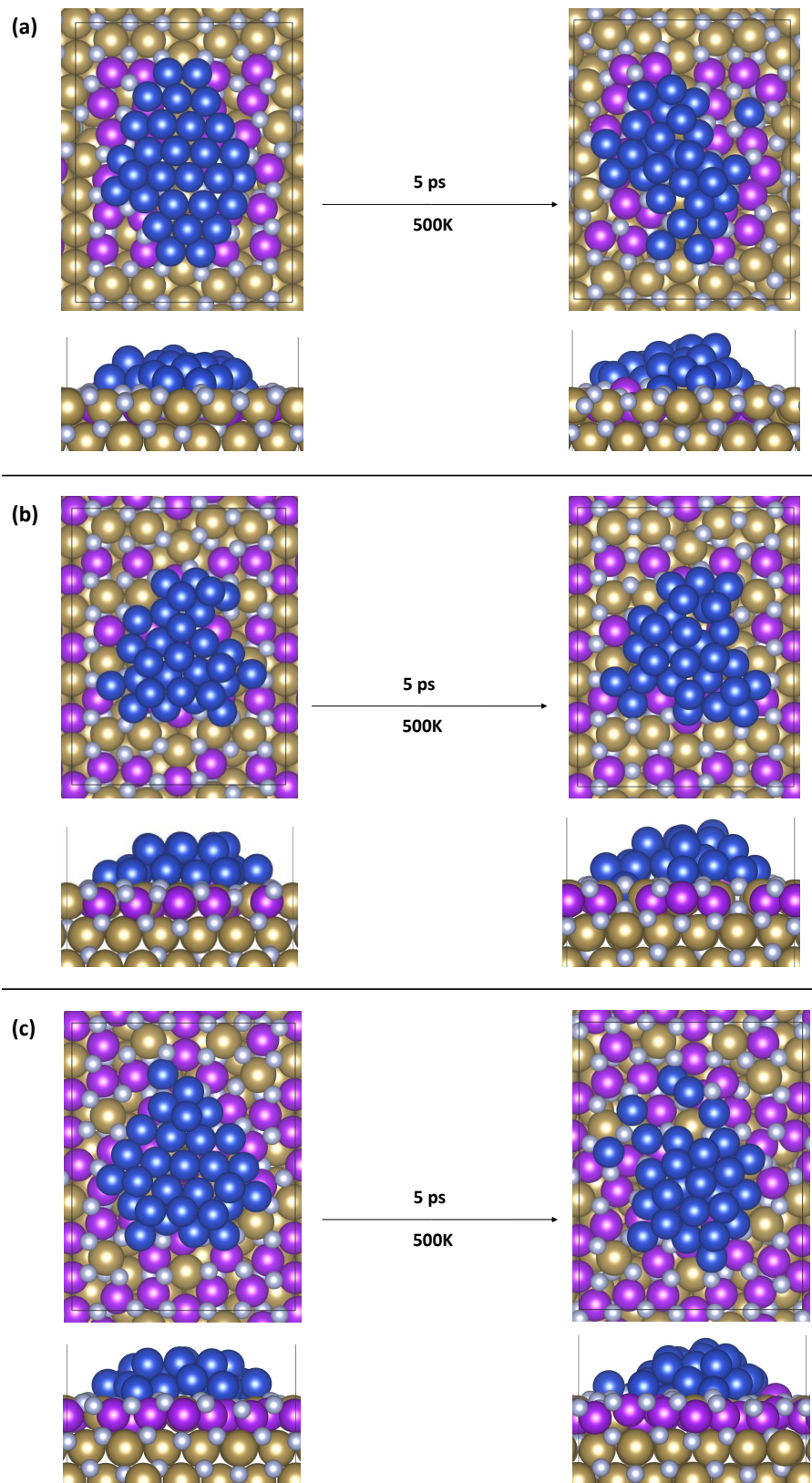


Figure A24: Structures of Cu_{29} obtained after relaxation and 500 K MD on a) Ru^{50-1} , b) Ru^{50-4} and c) Ru^{75} .

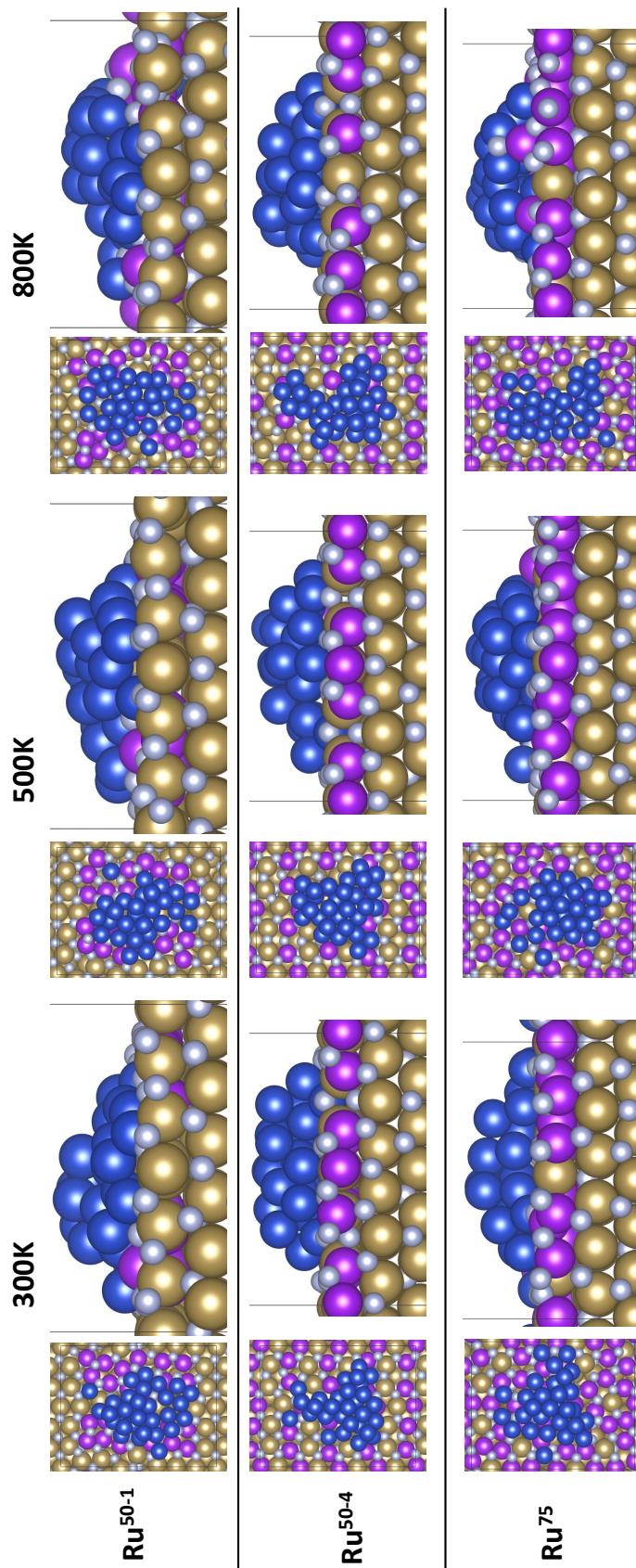


Figure A25: Geometries obtained after 300 K, 500 K and 800 K MD runs for Ru^{50-1} , Ru^{50-4} and Ru^{75} .

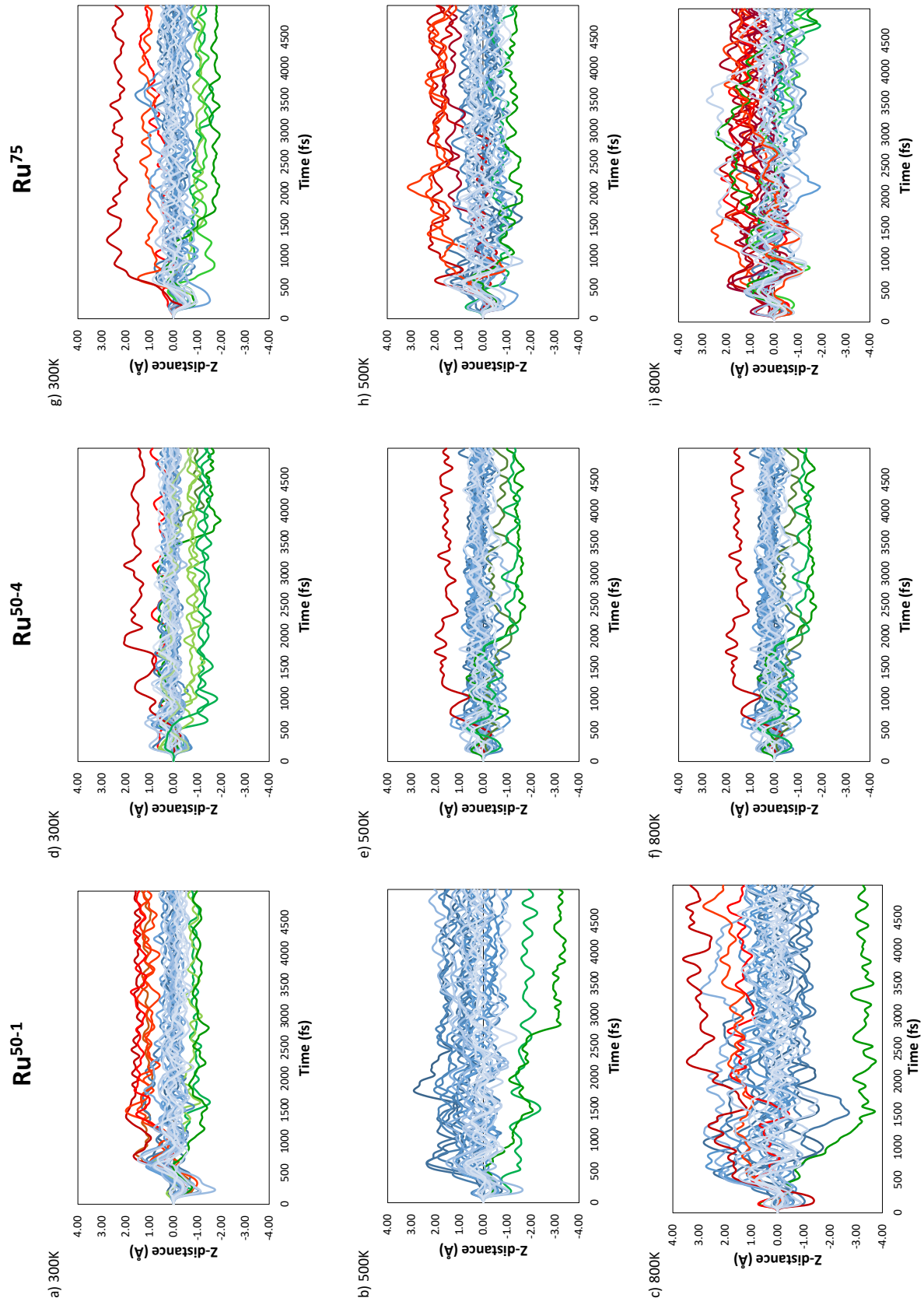


Figure A26: Change in Z-position with respect to time for Cu_{29} on Ru^{50-1} , Ru^{50-4} and Ru^{75} .

A3.2: Overview of MD Results

Figure [A27](#) shows top and side views for all geometries obtained after MD runs at 300 K, 500 K and 800K for the Ru-TaN surfaces discussed in the main chapter.

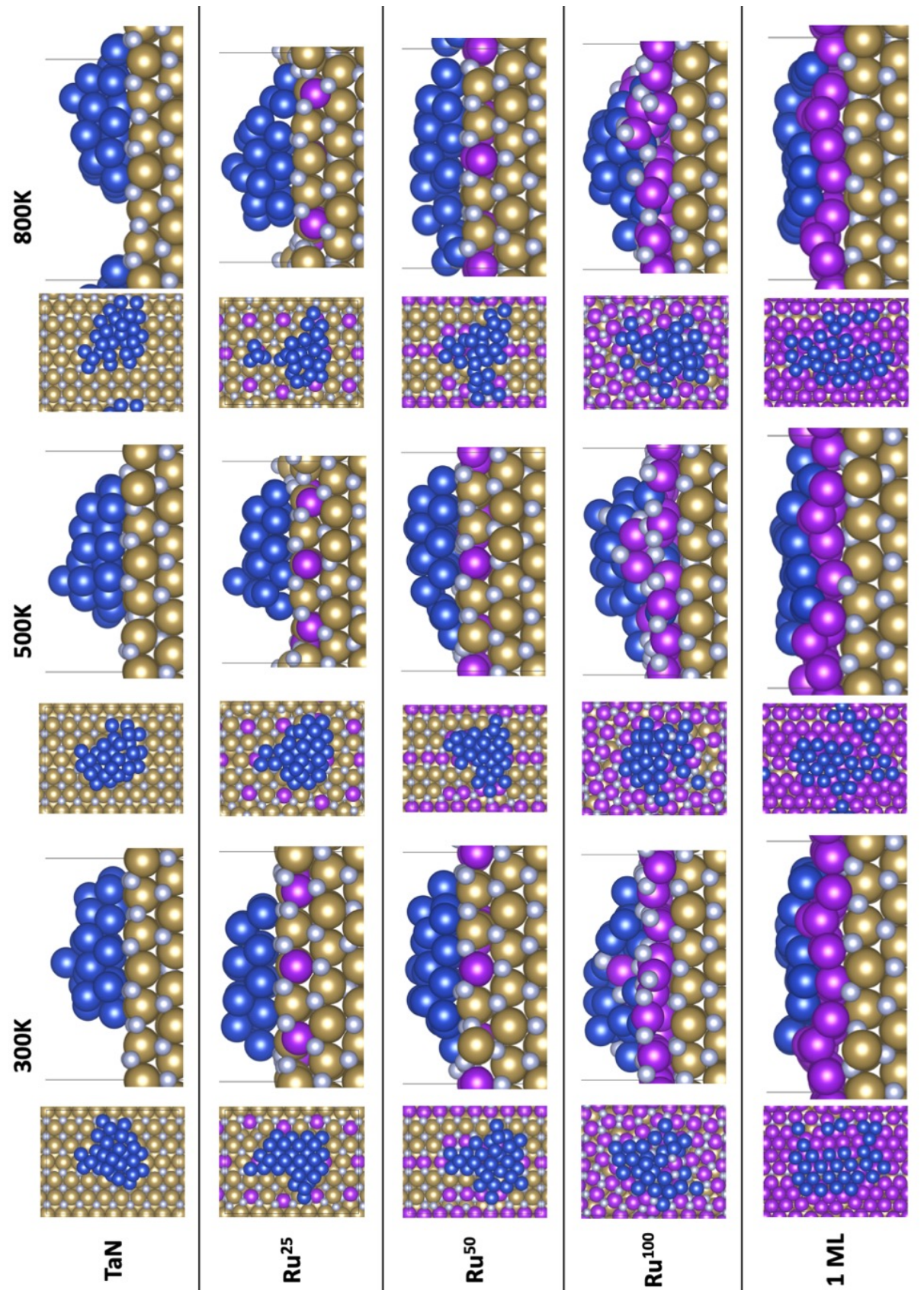


Figure A27: Geometries obtained after 300 K, 500 K and 800 K MD runs for TaN, Ru²⁵, Ru⁵⁰, Ru¹⁰⁰ and 1ML passivated TaN.

A3.3: DOS Plots and Bader Charges

In general, atoms bound to the surface are more strongly oxidized than any other Cu atoms, with computed Bader charges ranging from 10.5 to 10.9 electrons. Cu atoms solely bound to other Cu atoms once again remain metallic. Those atoms that are slightly elevated from the surface layer, but not fully in a $S+1$ layer remain metallic. Atoms incorporated into the surface layer are found to be more oxidized than atoms on the surface, with computed charges of 10.4 to 10.6 electrons.

DOS plots, Figure A28, and Bader charge analysis show that 1 ML Ru-modified TaN is metallic, and copper also remains metallic. Copper atoms that are directly bound to the surface are partially oxidised, with computed Bader charges between 10.6 and 10.9 electrons. Atoms in the second layer of the cluster are metallic, with computed Bader charges of 11.0 electrons. For the 1ML passivated surface Bader analysis shows that Cu atoms remain metallic. This indicates that there is no charge transfer between the Cu adatoms and the Ru atoms in the passivation layer.

The DOS of Ru²⁵ and Ru⁵⁰, as shown in Figure A28, shows a very weak contribution from the Cu d orbitals, in contrast to the much stronger contribution from the Ru d orbitals. This is unexpected, as there are less Ru atoms in the system than Cu atoms and as the number of Ru atoms is doubled for Ru⁵⁰. Similarly, to the bare surface, the atoms bound to the surface are slightly oxidised with computed Bader charges of around 10.8 electrons, while atoms in the second layer have remain fully metallic.

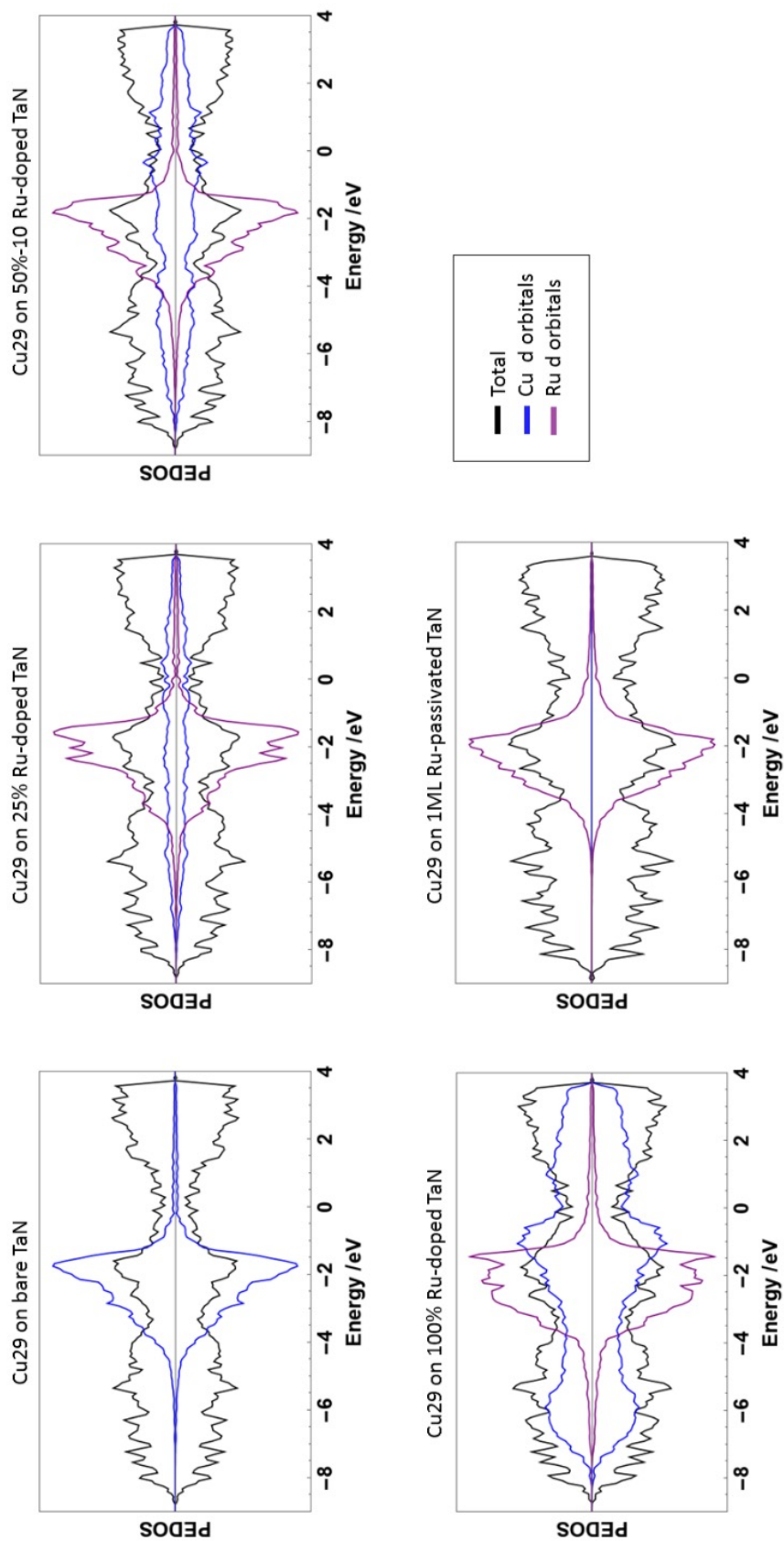


Figure A28: Density of State plots for all Cu_{29} adsorptions. The Cu and Ru contributions have been multiplied by 5 for easier comparison.

A4: Supplementary Information for Chapter 6

A4.1: Relaxed Geometries of Cu_n on W-TaN surfaces

A4.1.1: Single Atom Adsorption

Single Cu atom adsorptions on the various W-doped TaN surfaces are shown in Figures [A29](#) to [A32](#).

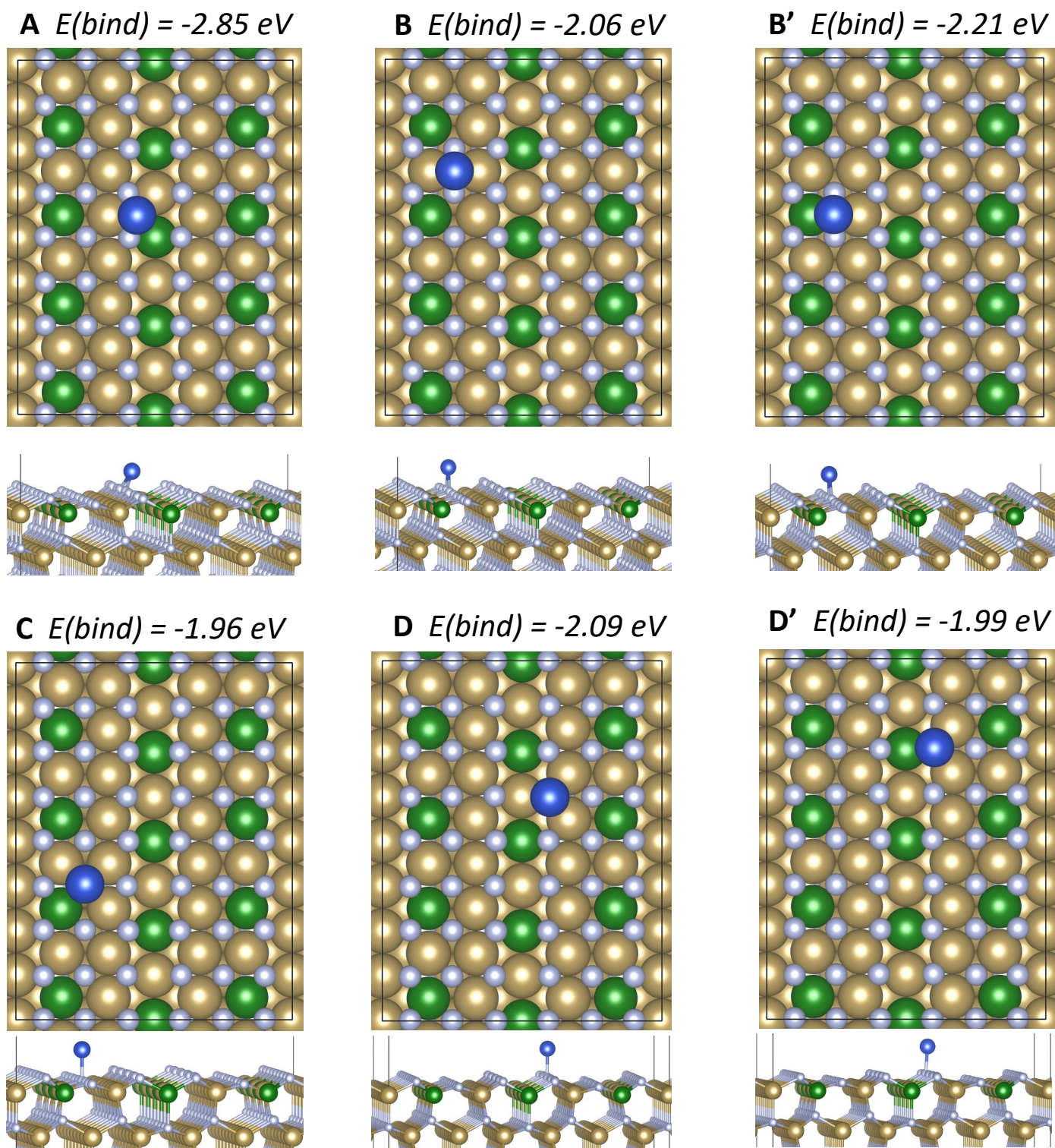
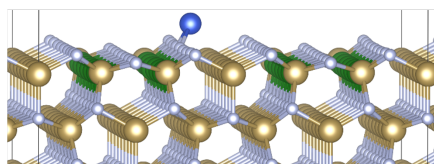
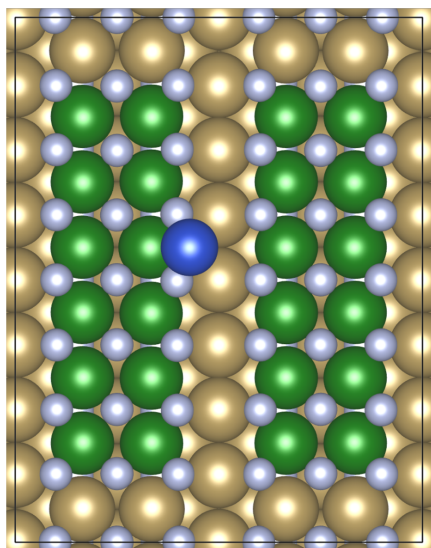
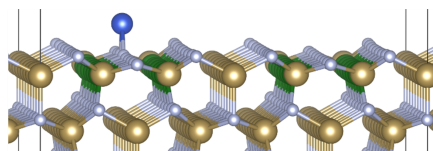
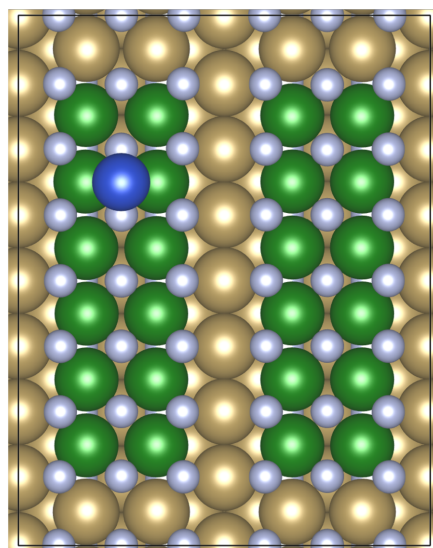


Figure A29: Adsorption of a single Cu atom at the unique adsorption sites on W²⁵

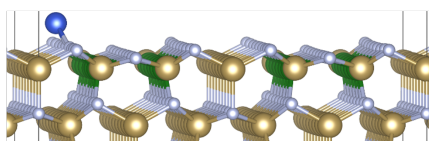
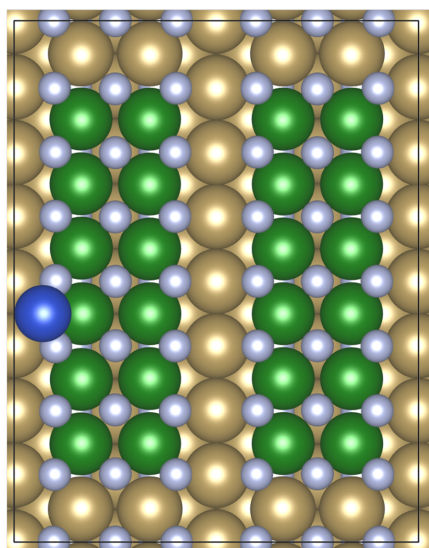
A $E(\text{bind}) = -2.57 \text{ eV}$



B $E(\text{bind}) = -1.96 \text{ eV}$



C $E(\text{bind}) = -2.57 \text{ eV}$



D $E(\text{bind}) = -1.65 \text{ eV}$

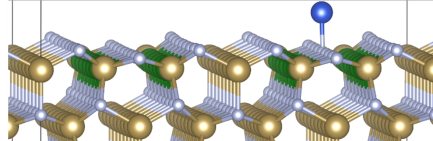
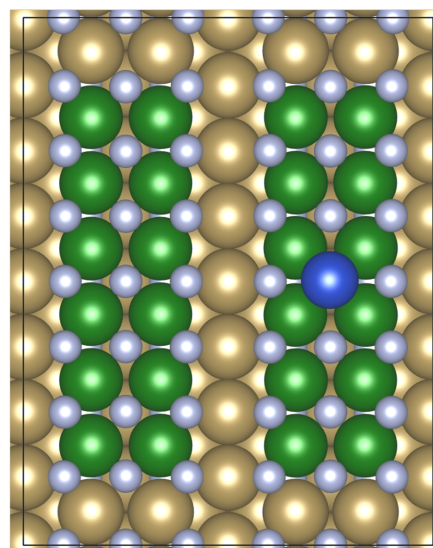
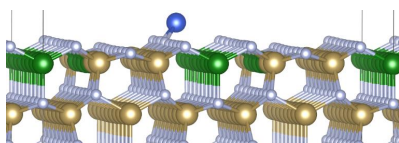
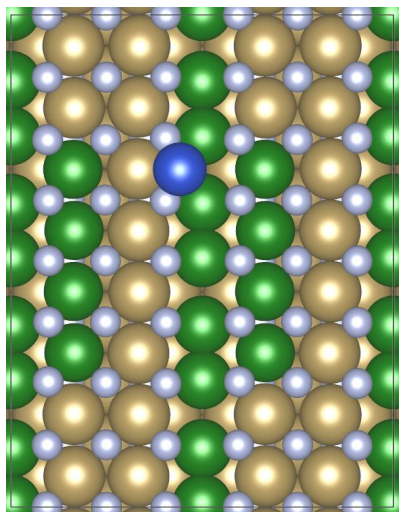
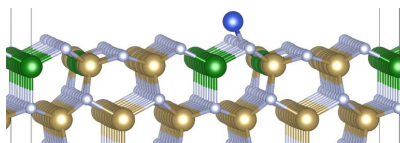
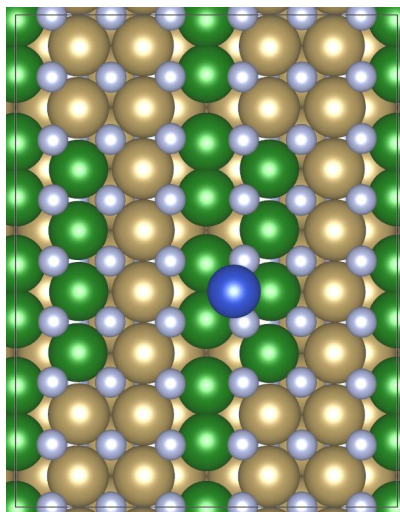


Figure A30: Adsorption of a single Cu atom at the unique adsorption sites on W^{50-S} . The original C geometry relaxed to an A site, as seen in the panel labelled C.

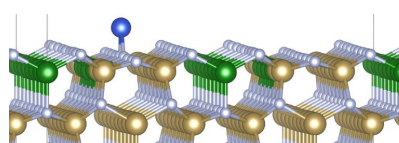
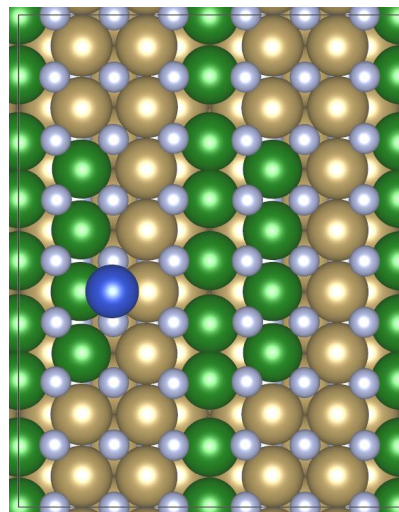
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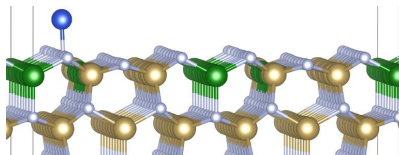
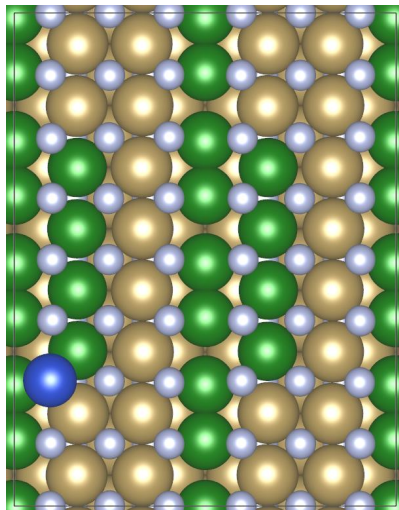
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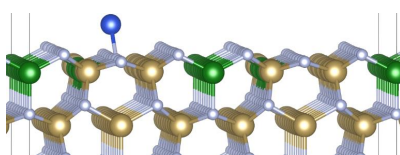
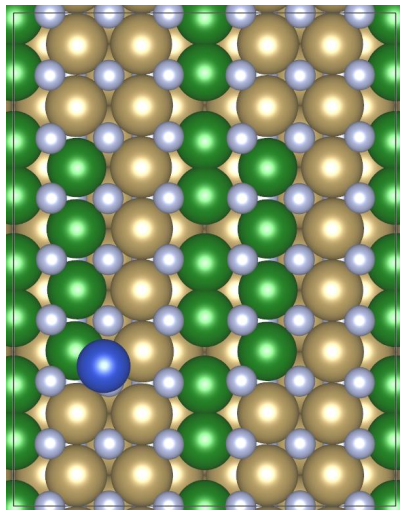
B $E(\text{bind}) = -2.00 \text{ eV}$



C $E(\text{bind}) = -2.69 \text{ eV}$



D $E(\text{bind}) = -2.71 \text{ eV}$



D' $E(\text{bind}) = -1.78 \text{ eV}$

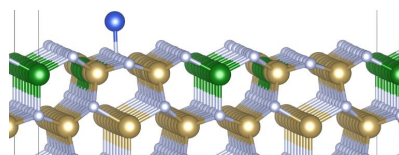
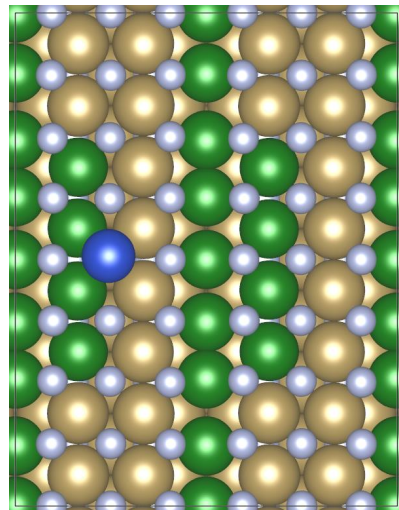
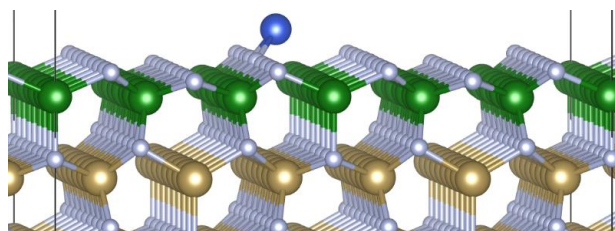
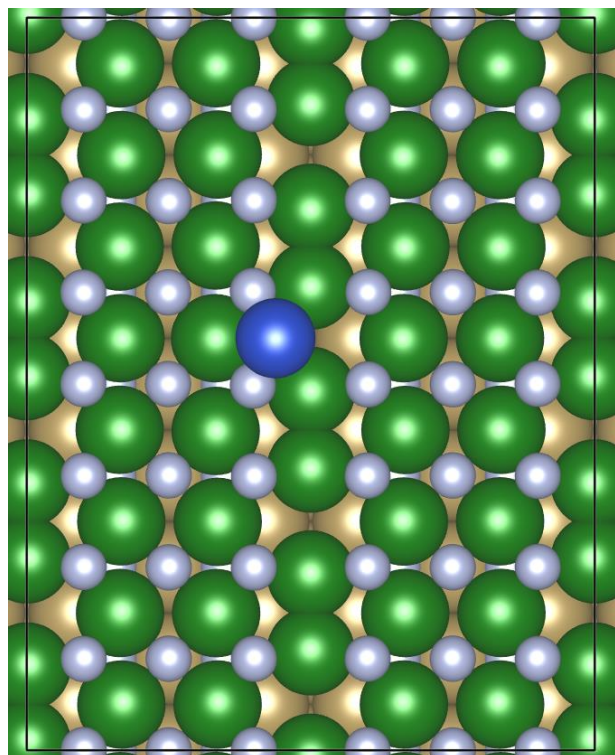


Figure A31: Adsorption of a single Cu atom at the unique adsorption sites on W^{50-F}

A $E(\text{bind}) = -3.94 \text{ eV}$



B $E(\text{bind}) = -3.36 \text{ eV}$

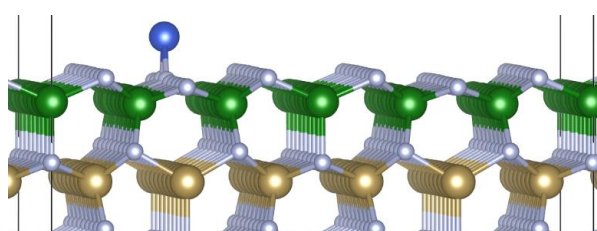
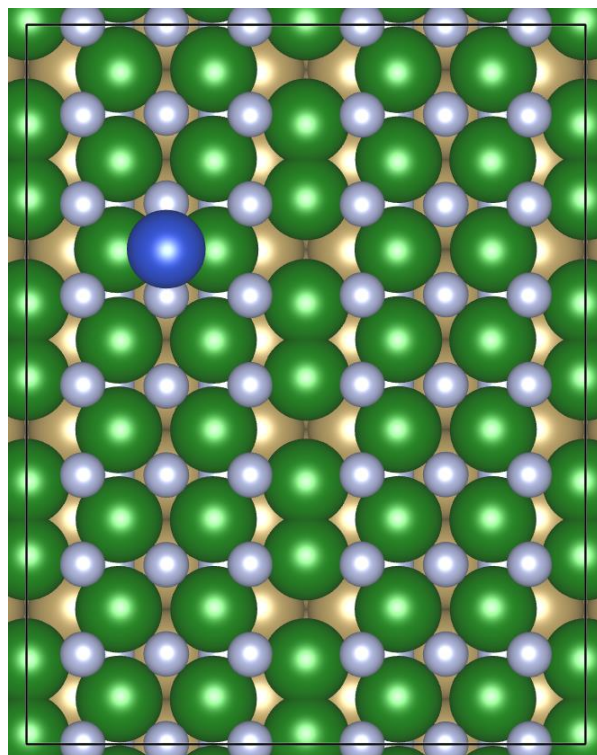


Figure A32: Adsorption of a single Cu atom at the unique adsorption sites on W^{100}

A4.1.2: Two and Four Atom Adsorption

Cu_2 and Cu_4 adsorptions on the different W-doped TaN surfaces are shown in Figures [A33](#) to [A36](#).

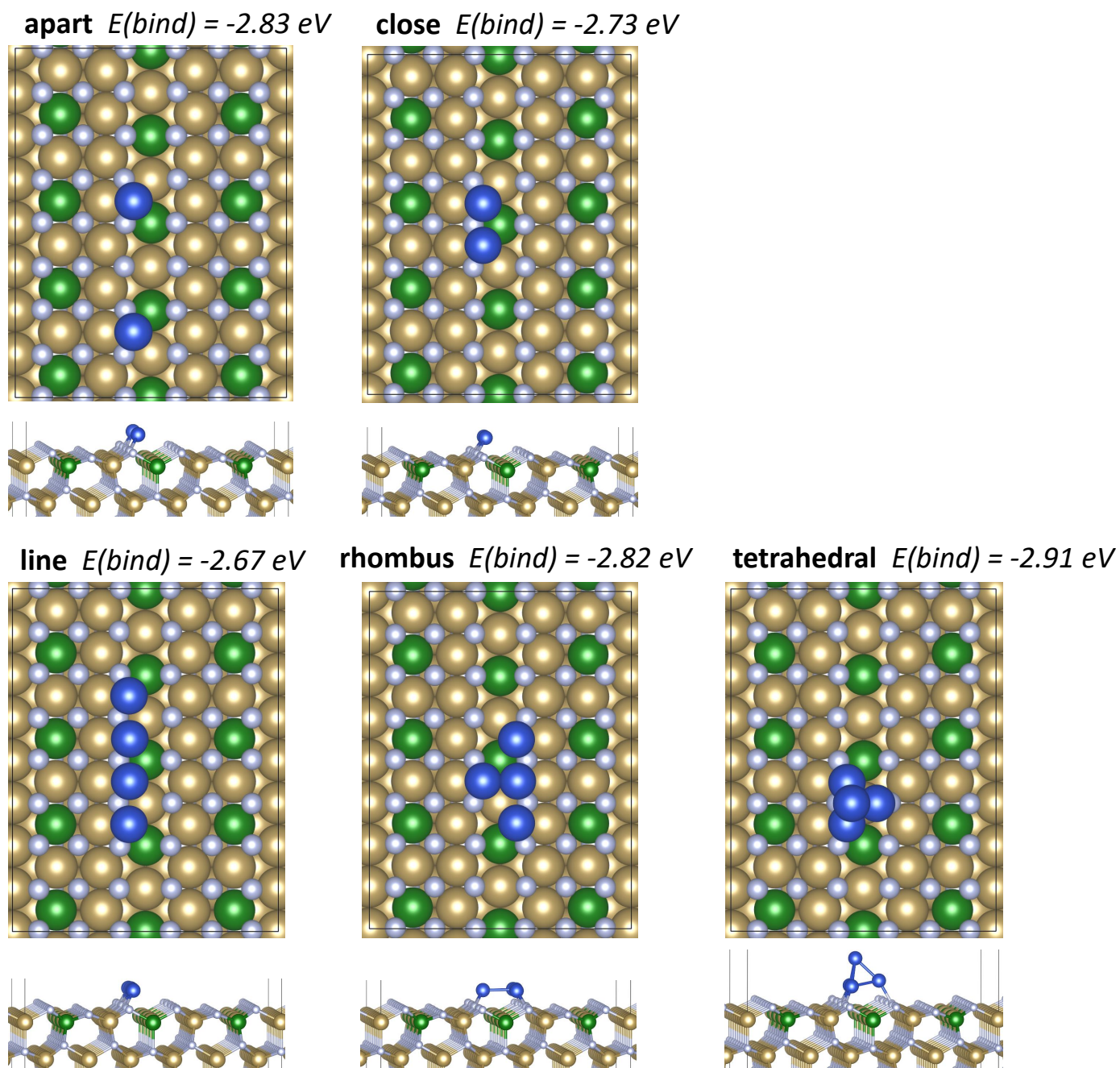
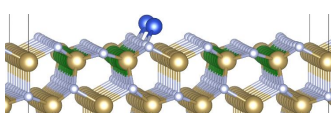
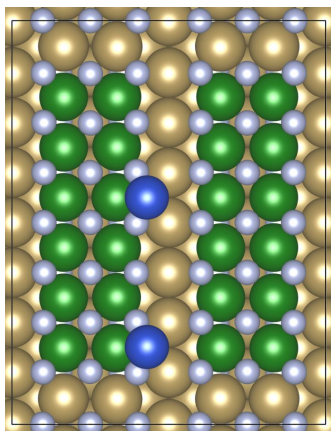
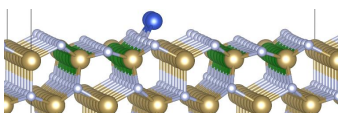
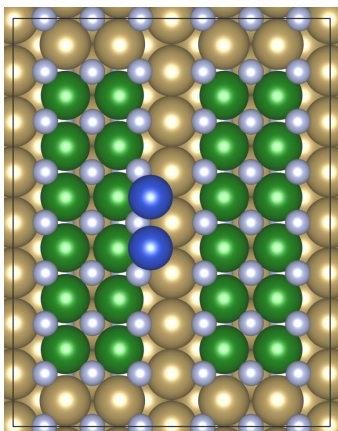


Figure A33: Adsorption of two and four Cu atoms in various configurations at the most favourable adsorption site on W^{25}

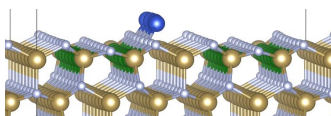
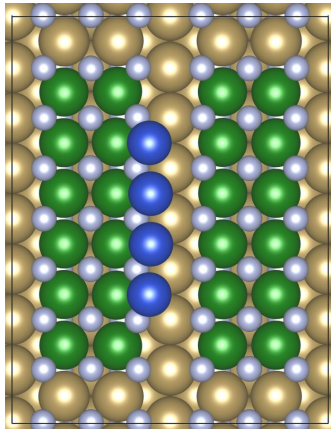
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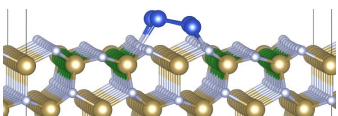
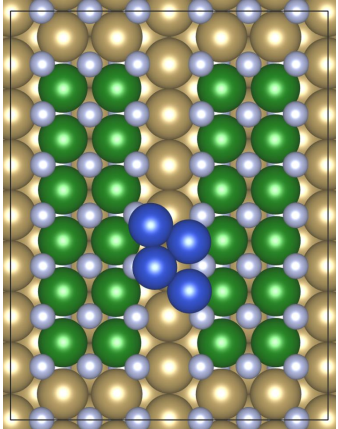
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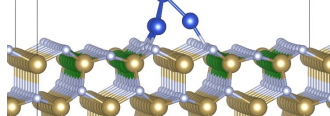
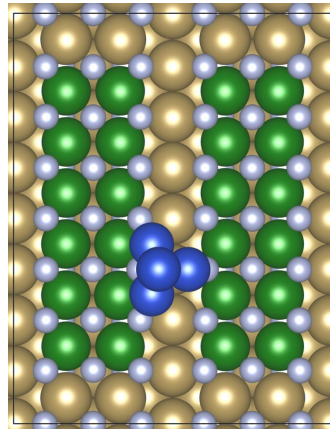
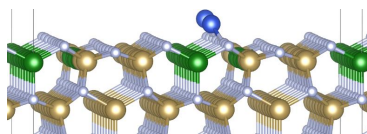
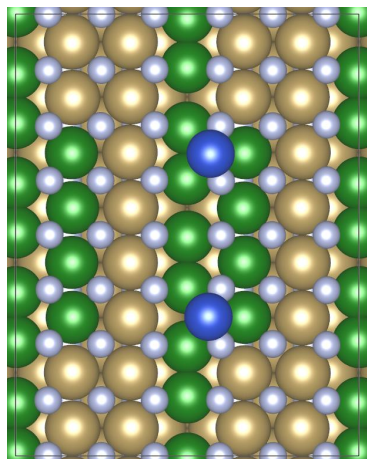
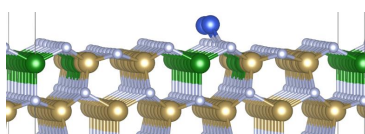
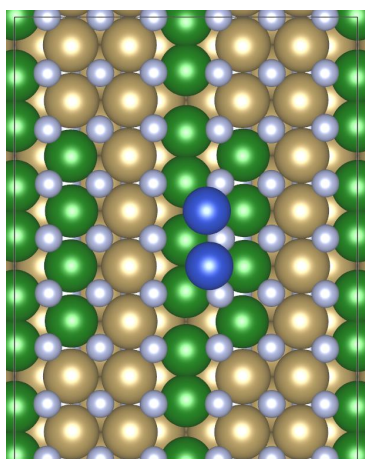


Figure A34: Adsorption of two and four Cu atoms in various configurations at the most favourable adsorption site on $\text{W}_{50}\text{-S}$

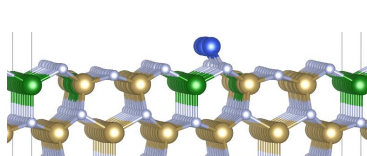
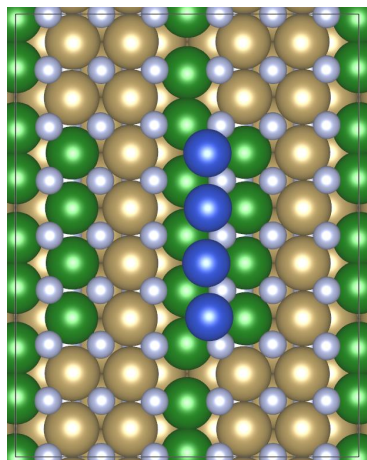
apart $E(\text{bind}) = -2.99 \text{ eV}$



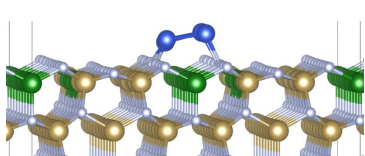
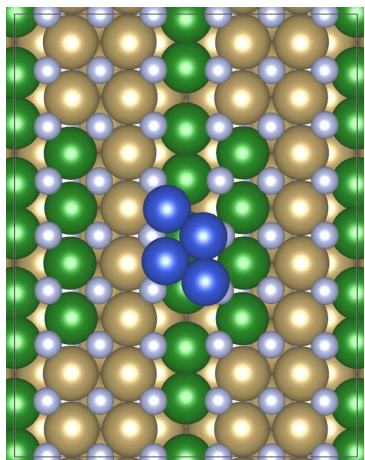
close $E(\text{bind}) = -3.97 \text{ eV}$



line $E(\text{bind}) = -2.66 \text{ eV}$



rhombus $E(\text{bind}) = -3.50 \text{ eV}$



tetrahedral $E(\text{bind}) = -2.87 \text{ eV}$

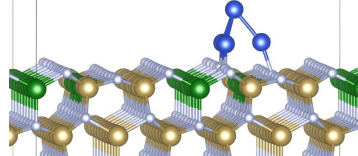
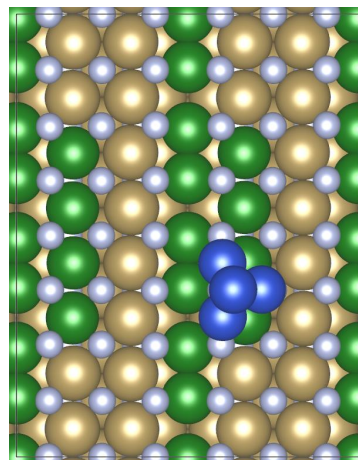
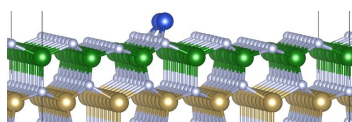
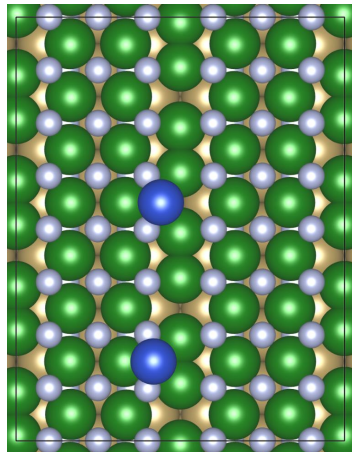
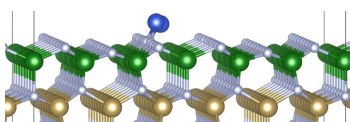
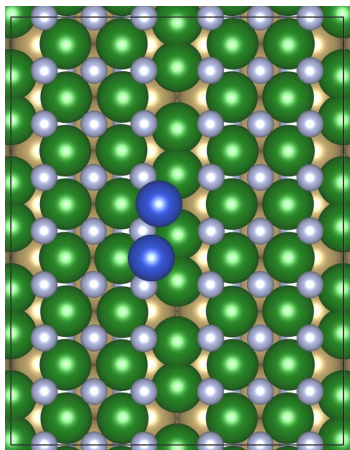


Figure A35: Adsorption of two and four Cu atoms in various configurations at the most favourable adsorption site on $\text{W}_{50-\text{F}}$

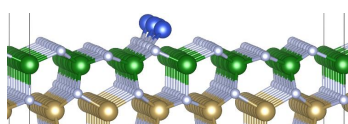
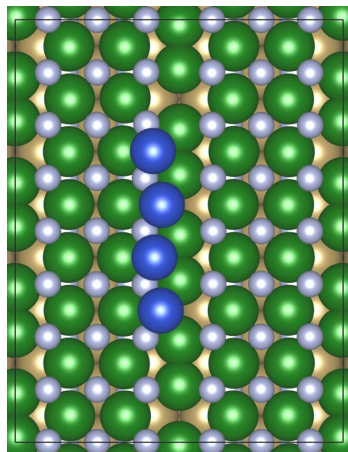
apart $E(bind) = -3.10 \text{ eV}$



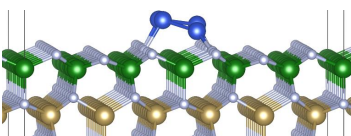
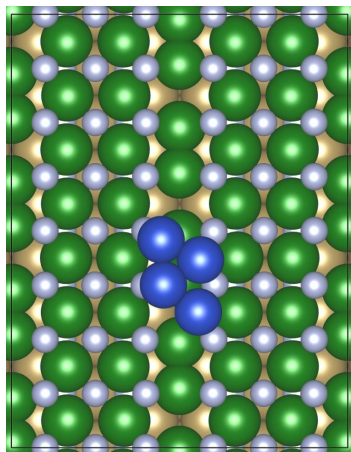
close $E(bind) = -3.06 \text{ eV}$



line $E(bind) = -2.67 \text{ eV}$



rhombus $E(bind) = -3.60 \text{ eV}$



tetrahedral $E(bind) = -3.03 \text{ eV}$

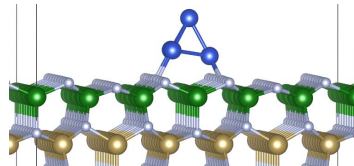
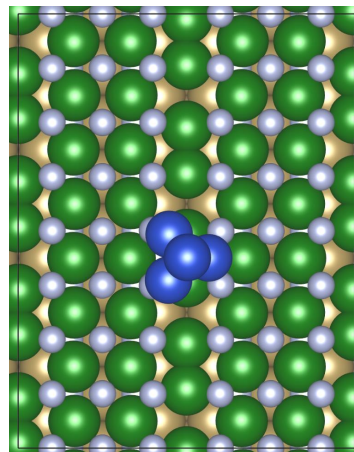


Figure A36: Adsorption of two and four Cu atoms in various configurations at the most favourable adsorption site on W^{100}

A4.2: Density of States of Cu_n on W-TaN

Partial density of states (PDOS) plots for all Cu adsorptions on W-doped TaN are shown in Figures A37 to A44. All Cu and W contributions have been multiplied by a factor of 5 for easier viewing.

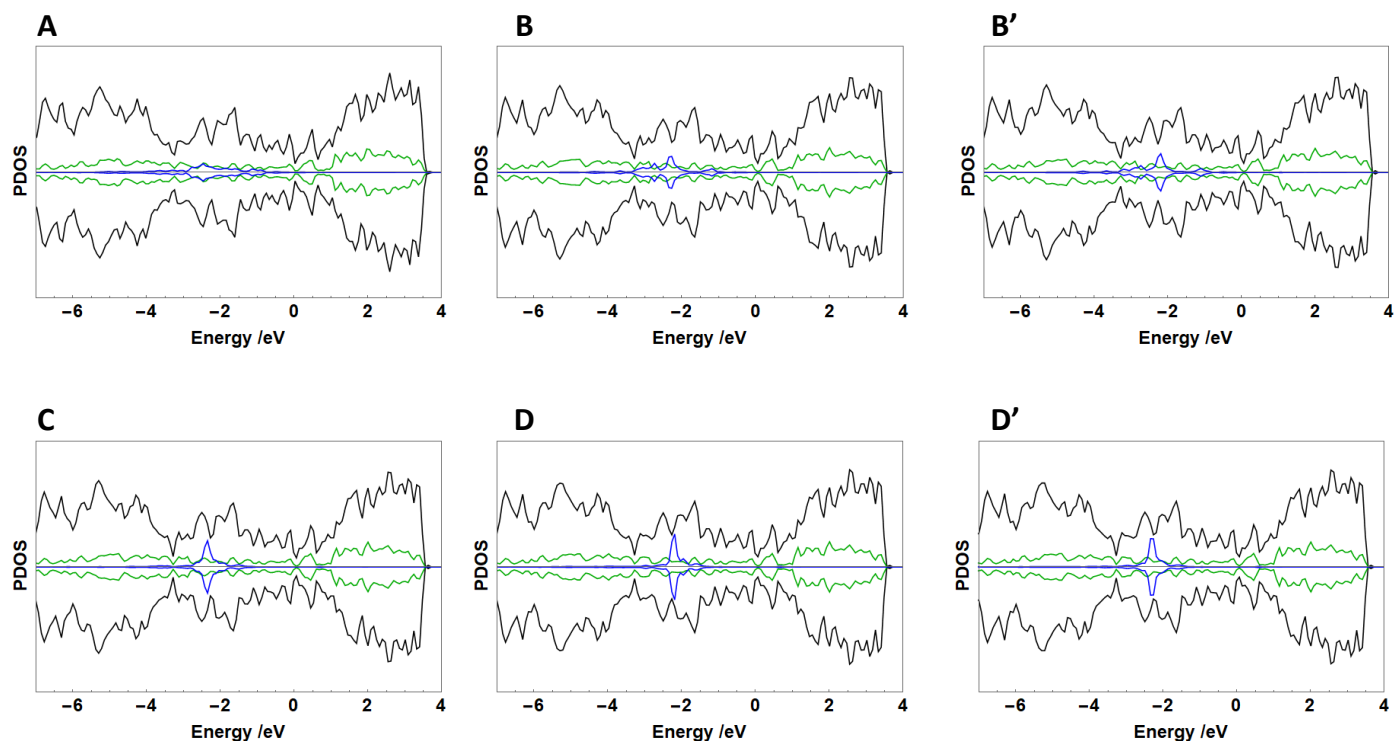


Figure A37: PDOS of single Cu adsorption on W₂₅. Black - total DOS, green - W d-orbital contribution, blue - Cu d-orbital contribution.

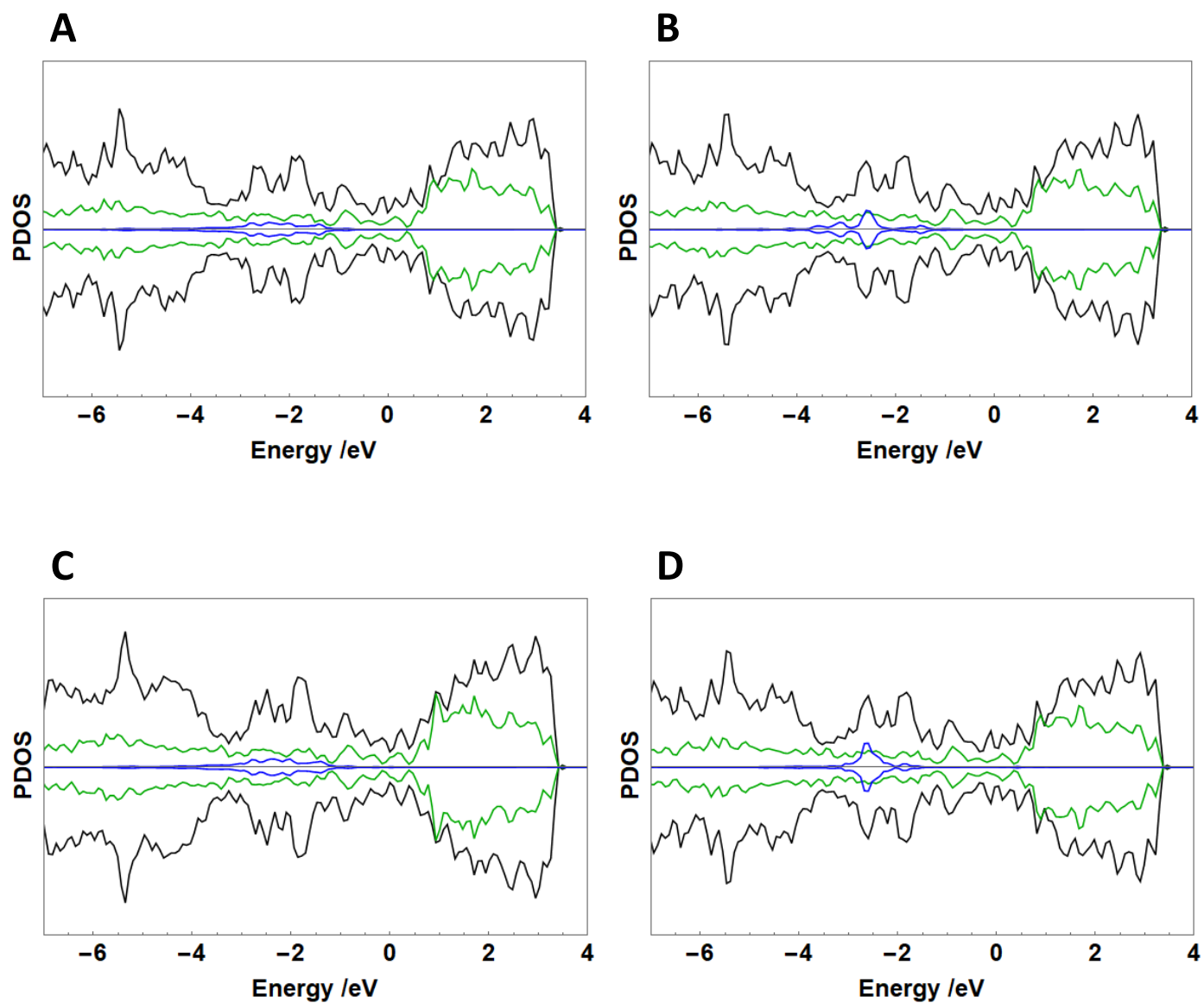


Figure A38: PDOS of single Cu adsorption on W^{50-S} . Black - total DOS, green - W d-orbital contribution, blue - Cu d-orbital contribution.

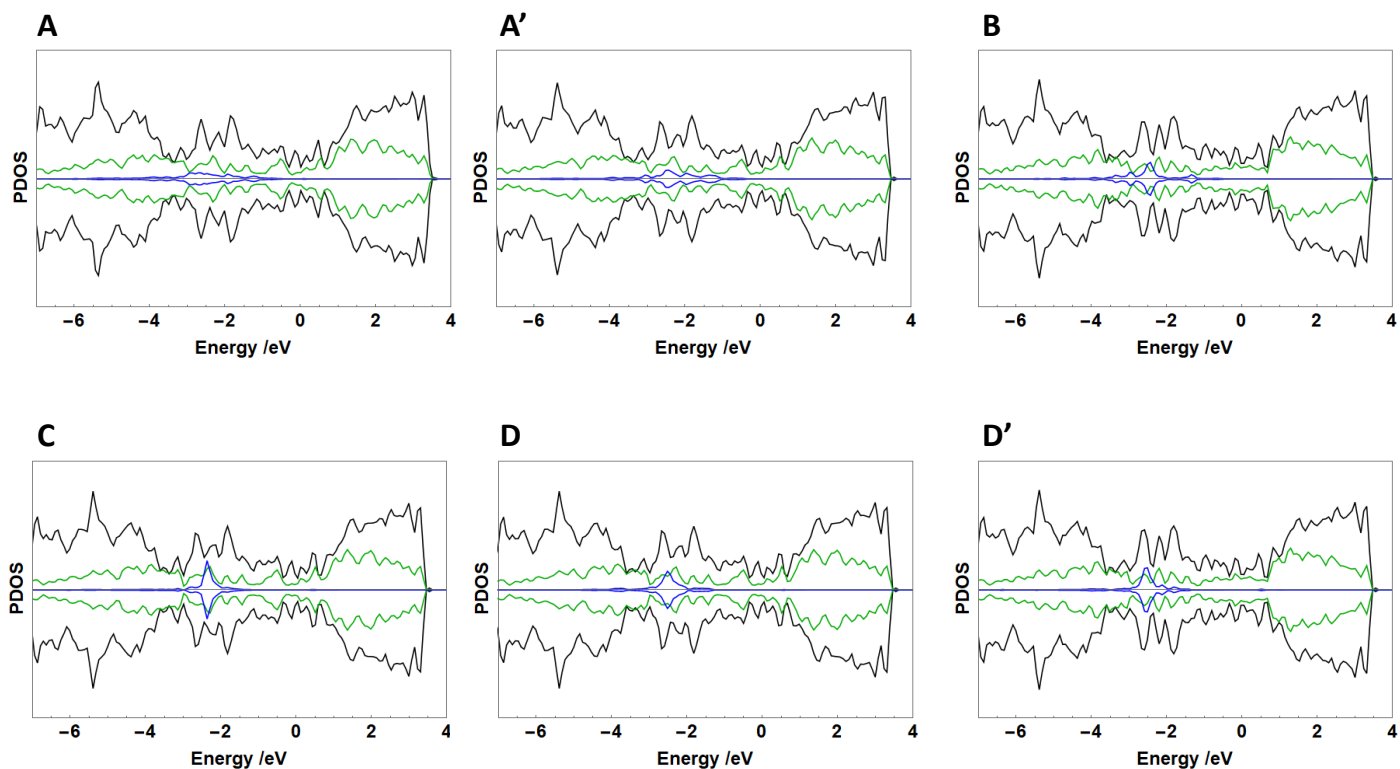


Figure A39: PDOS of single Cu adsorption on W^{50-F} . Black - total DOS, green - W d-orbital contribution, blue - Cu d-orbital contribution.

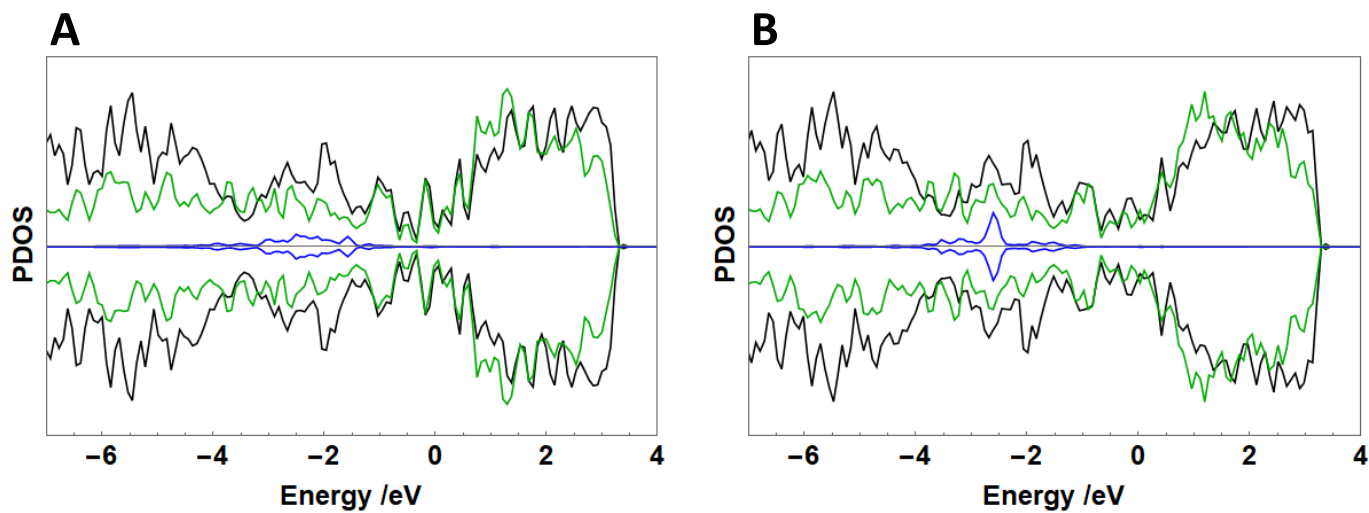


Figure A40: PDOS of single Cu adsorption on W^{100} . Black - total DOS, green - W d-orbital contribution, blue - Cu d-orbital contribution.

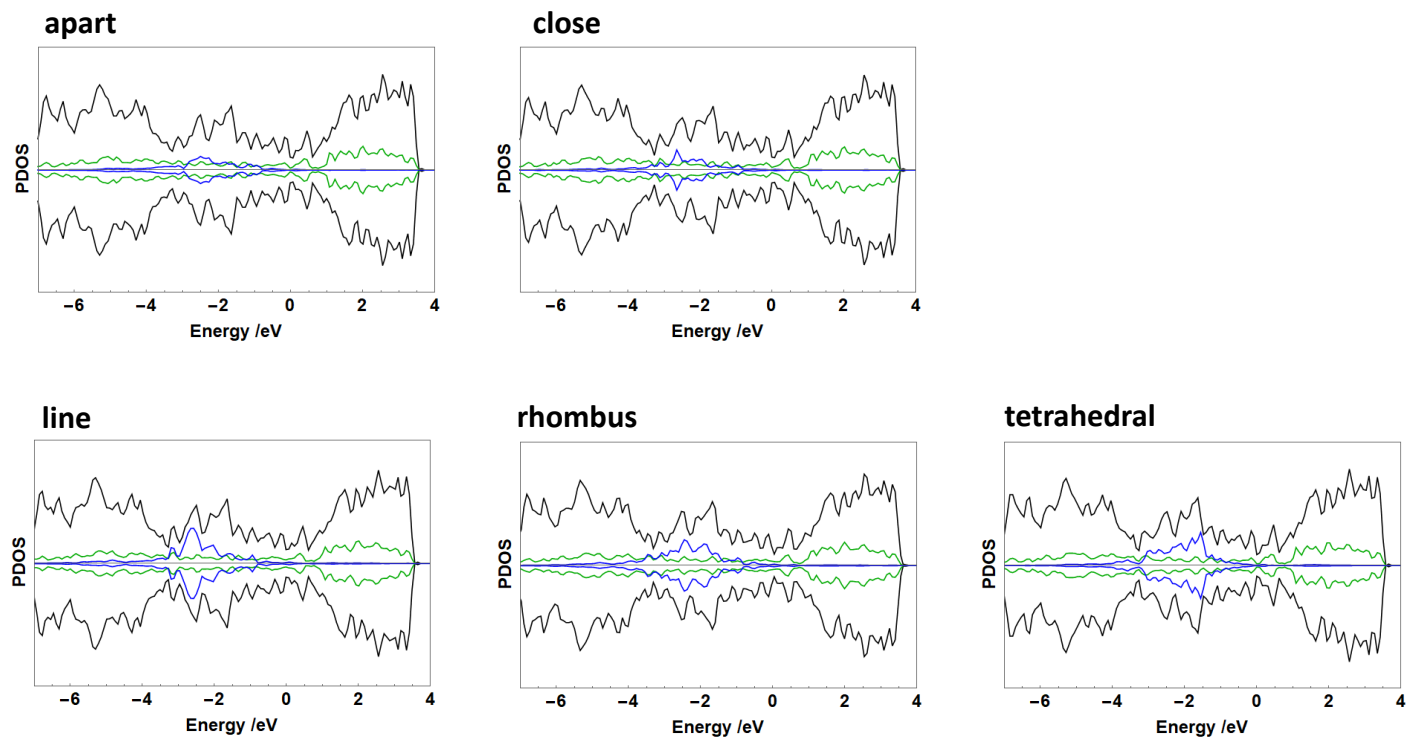


Figure A41: PDOS of Cu_2 and Cu_4 adsorptions on W^{25} . Black - total DOS, green - W d-orbital contribution, blue - Cu d-orbital contribution.

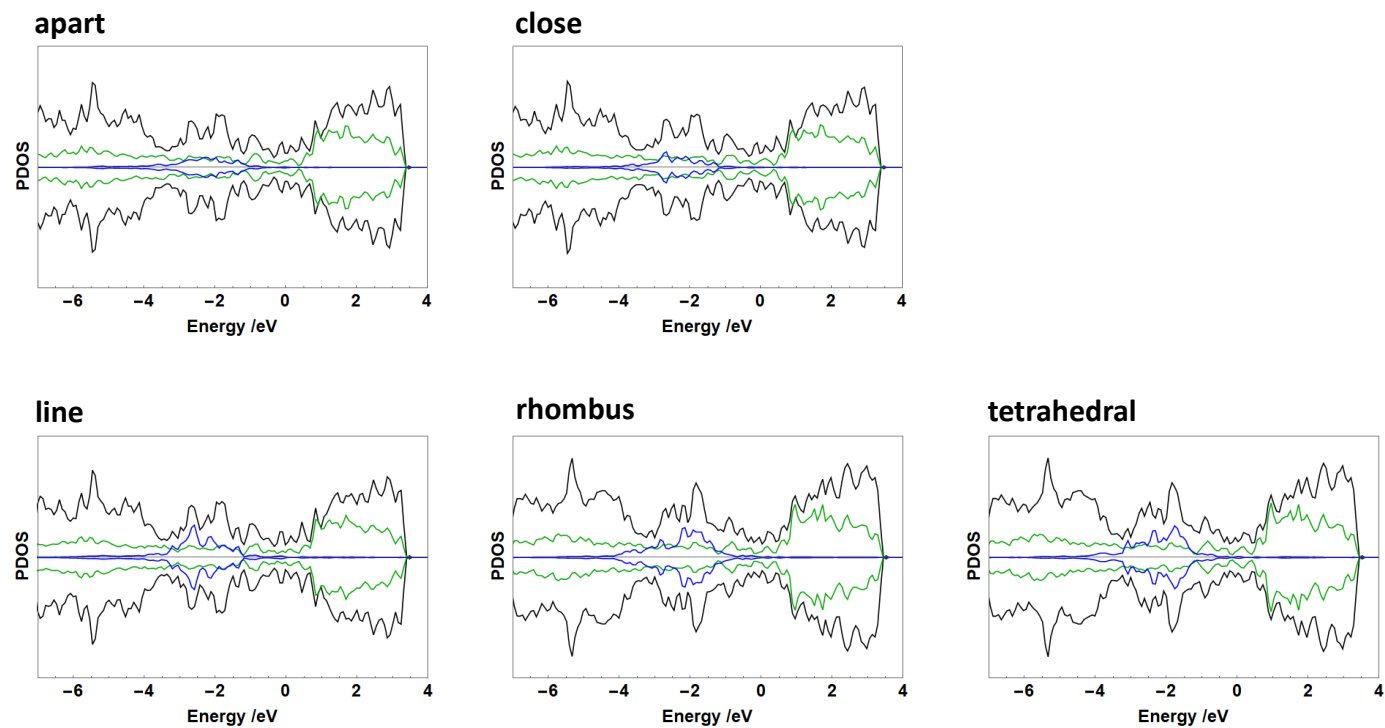


Figure A42: PDOS of Cu_2 and Cu_4 adsorptions on W^{50-S} . Black - total DOS, green - W d-orbital contribution, blue - Cu d-orbital contribution.

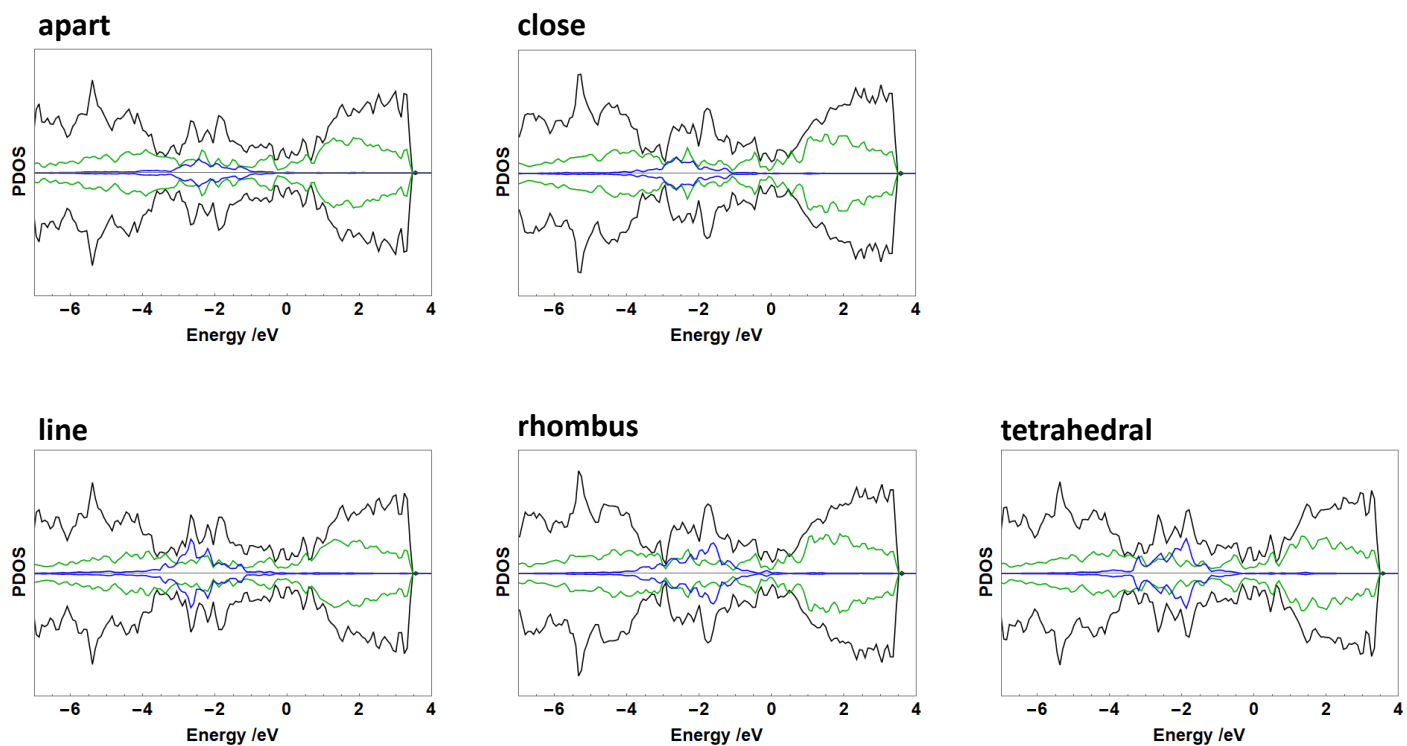


Figure A43: PDOS of Cu_2 and Cu_4 adsorptions on W^{50-F} . Black - total DOS, green - W d-orbital contribution, blue - Cu d-orbital contribution.

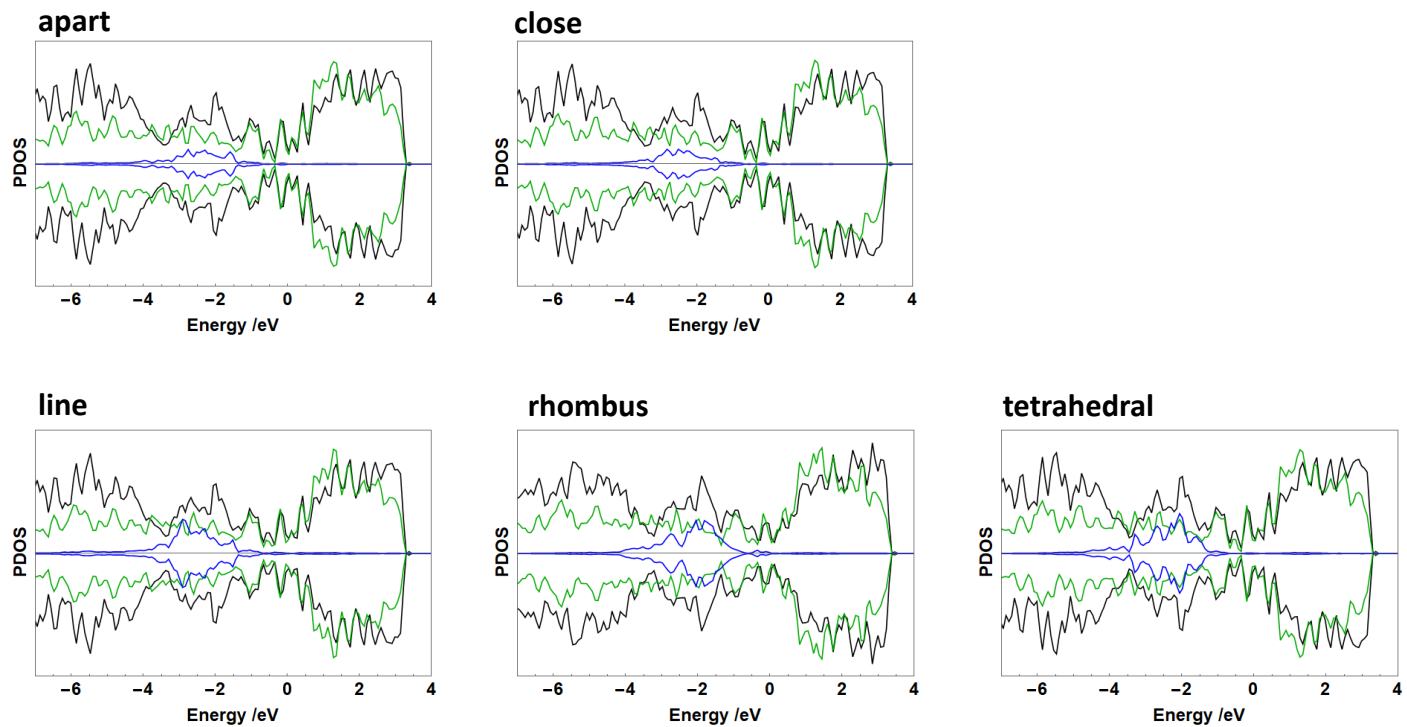


Figure A44: PDOS of Cu_2 and Cu_4 adsorptions on W^{100} . Black - total DOS, green - W d-orbital contribution, blue - Cu d-orbital contribution.

A4.3: Bader Charges of Cu_n on W-TaN

Table A13: Computed Bader charges (Q) for all Cu_n geometries on W-doped TaN. Cu has 11 valence electrons.

Surface	Geometry	$Q_{\text{Cu}1}$	$Q_{\text{Cu}2}$	$Q_{\text{Cu}3}$	$Q_{\text{Cu}4}$
W^{25}	A	10.5			
	B	10.5			
	B'	10.5			
	C	10.5			
	D	10.4			
	D'	10.5			
	close	10.5	10.5		
	apart	10.5	10.5		
	line	10.5	10.6	10.5	10.6
	rhombus	10.7	10.6	10.5	10.5
	tetrahedral	10.7	10.6	10.6	11.1
$\text{W}^{50-\text{S}}$	A	10.5			
	B	10.4			
	C	10.3			
	D	10.4			
	close	10.6	10.6		
	apart	10.5	10.5		
	line	10.6	10.6	10.6	10.7
	rhombus	10.7	10.8	10.7	10.7
	tetrahedral	10.7	10.6	10.6	11.0
$\text{W}^{50-\text{F}}$	A	10.5			
	A'	10.4			
	B	10.5			
	C	10.5			
	D	10.5			
	D'	10.5			
	close	10.5	10.5		
	apart	10.4	10.5		
	line	10.5	10.6	10.5	10.6
	rhombus	10.8	10.7	10.6	10.7
	tetrahedral	10.7	10.6	10.6	11.0
W^{100}	A	10.6			
	B	10.5			
	close	10.6	10.5		
	apart	10.5	10.4		
	line	10.5	10.6	10.6	10.5
	rhombus	10.7	10.8	10.8	10.7
	tetrahedral	10.6	10.7	10.7	11.0

A4.4: Relaxed Geometries of Cu_n on Co-doped TaN

A4.4.1: Single Cu adsorption

Single Cu atom adsorptions on the various Co-doped TaN surfaces are shown in Figures A45 to A48.

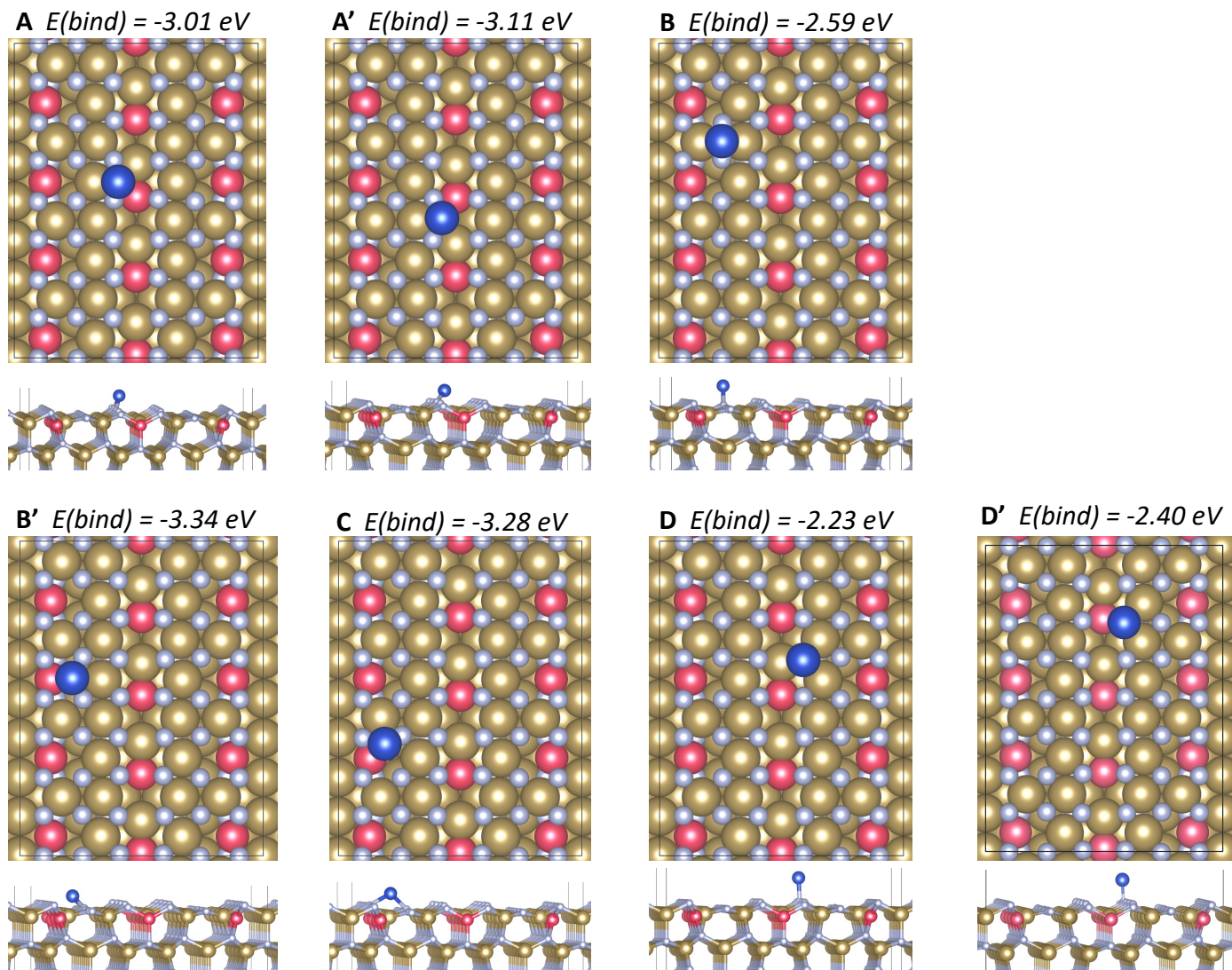


Figure A45: Adsorption of a single Cu atom at the unique adsorption sites on Co^{25}

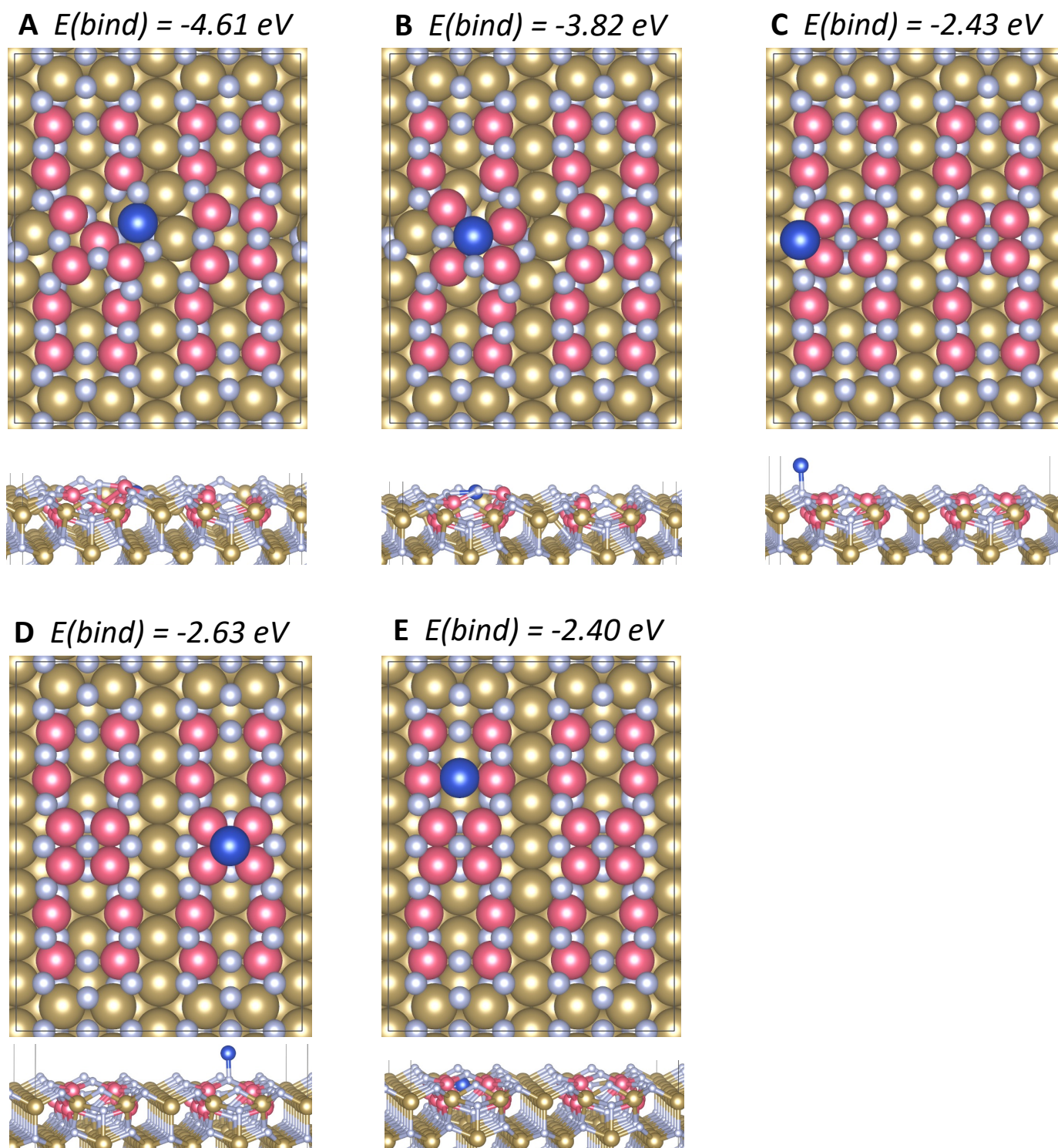
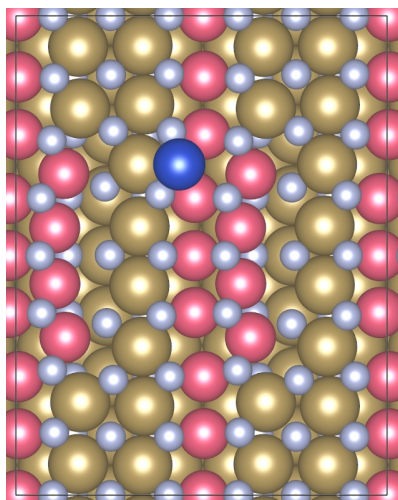
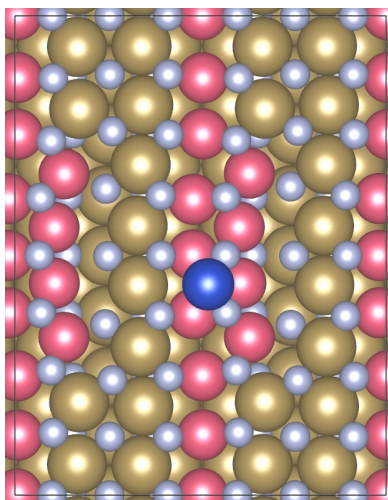


Figure A46: Adsorption of a single Cu atom at the unique adsorption sites on Co^{50-S}

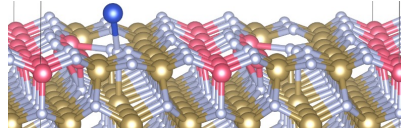
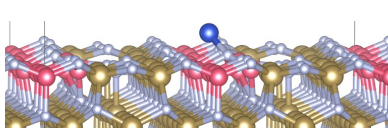
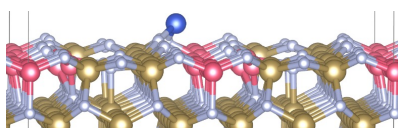
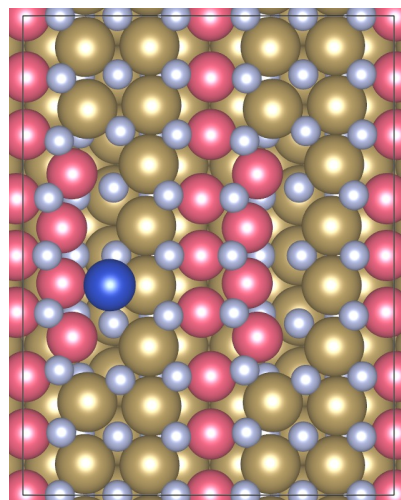
A $E(\text{bind}) = -3.73 \text{ eV}$



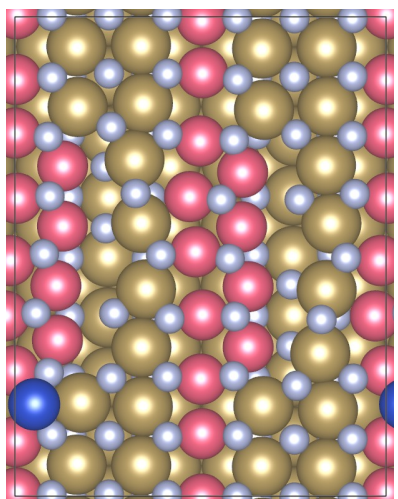
A' $E(\text{bind}) = -2.81 \text{ eV}$



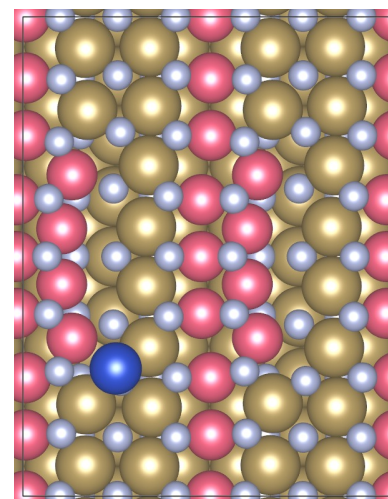
B $E(\text{bind}) = -4.53 \text{ eV}$



C $E(\text{bind}) = -3.55 \text{ eV}$



D $E(\text{bind}) = -2.38 \text{ eV}$



D' $E(\text{bind}) = -4.04 \text{ eV}$

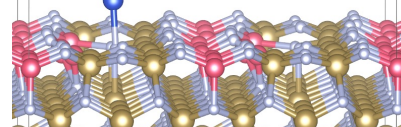
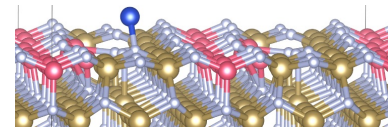
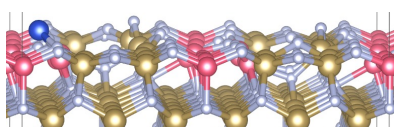
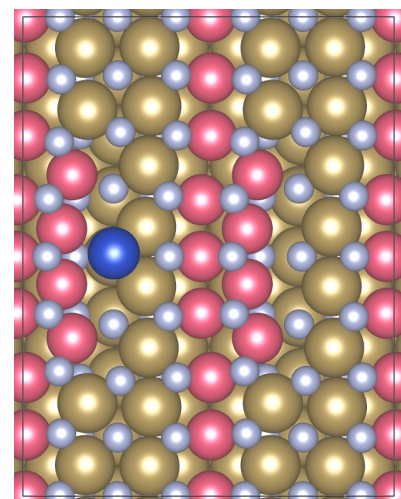
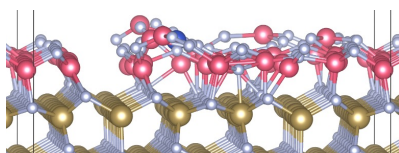
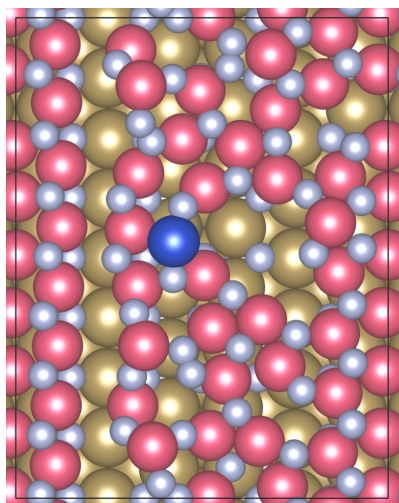
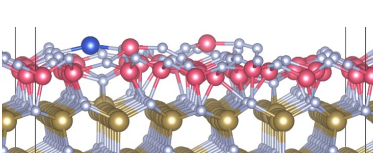
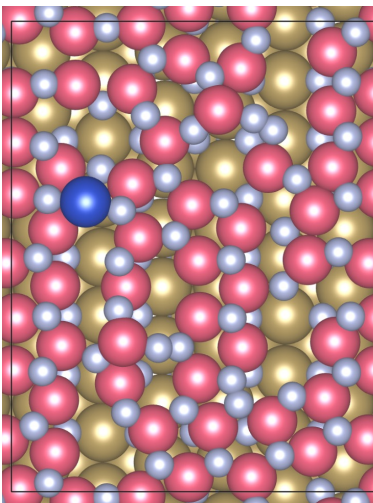


Figure A47: Adsorption of a single Cu atom at the unique adsorption sites on Co^{50-F}

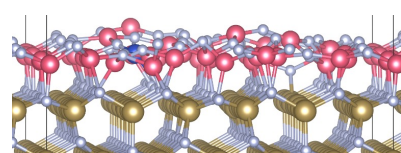
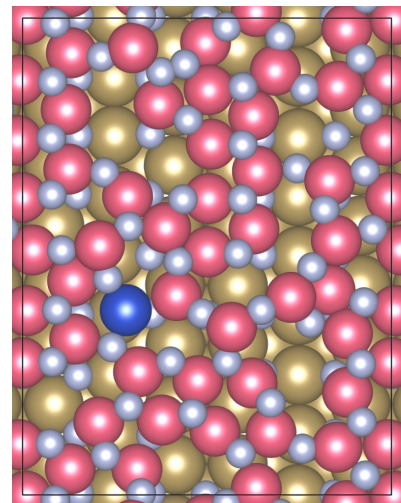
A $E(\text{bind}) = -4.56 \text{ eV}$



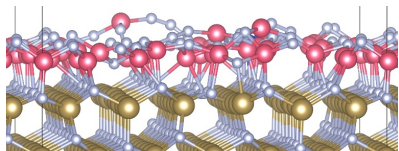
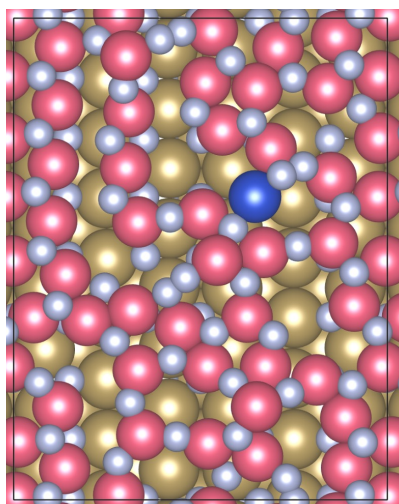
B $E(\text{bind}) = -3.93 \text{ eV}$



C $E(\text{bind}) = -4.76 \text{ eV}$



D $E(\text{bind}) = -3.68 \text{ eV}$



E $E(\text{bind}) = -3.51 \text{ eV}$

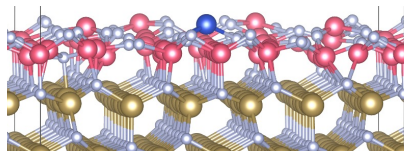
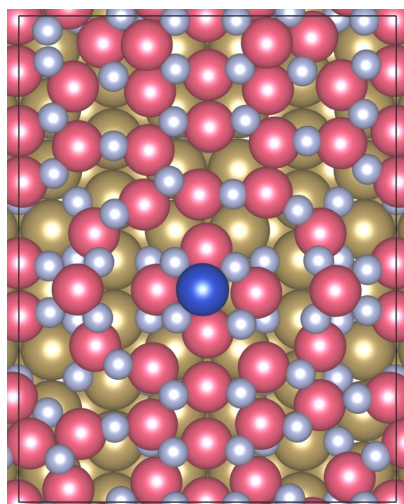


Figure A48: Adsorption of a single Cu atom at the unique adsorption sites on Co²⁵

A4.4.2: Two and Four atom adsorption

Cu₂ and Cu₄ adsorptions on the different Co-doped TaN surfaces are shown in Figures A49 to A52.

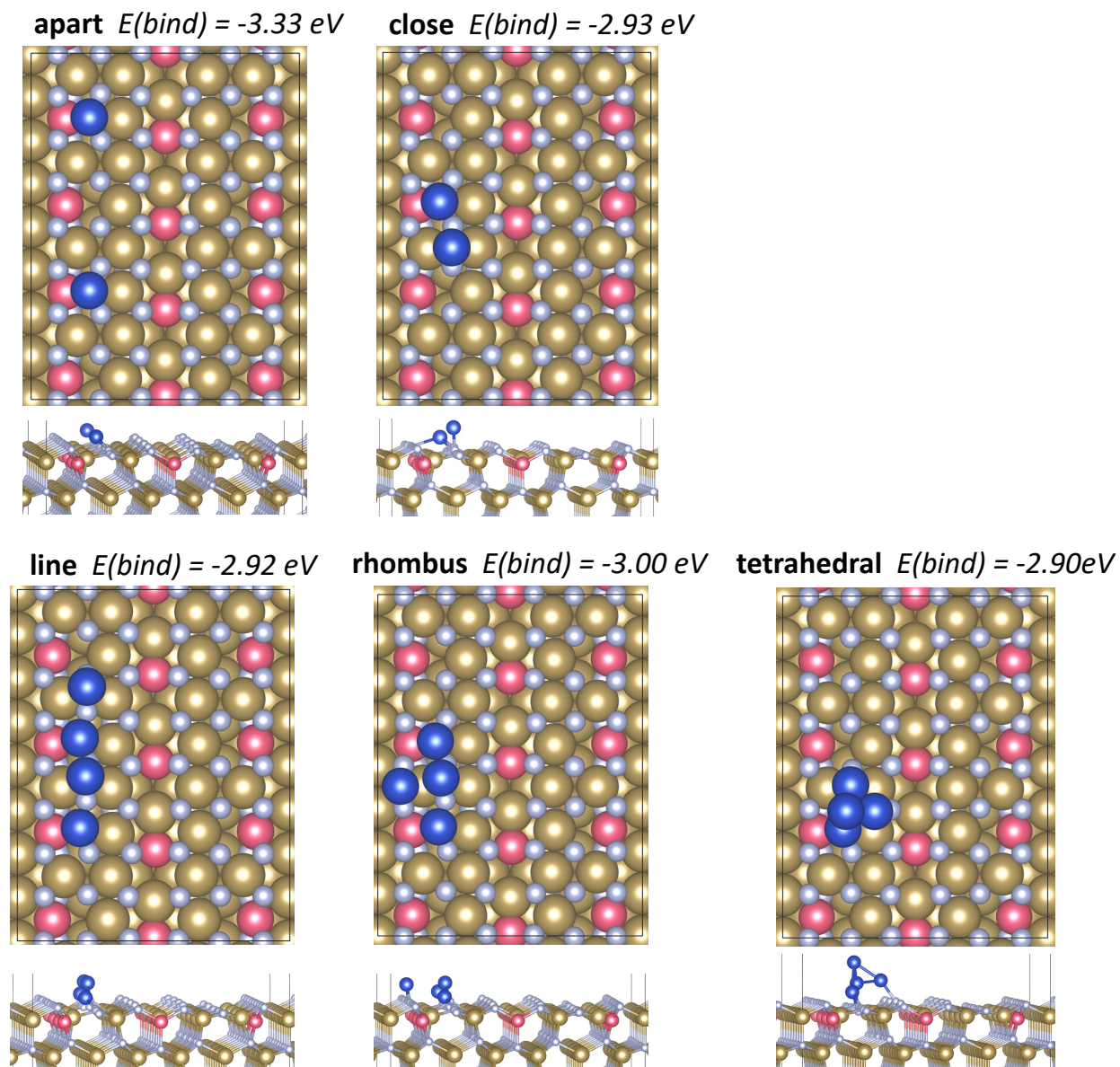


Figure A49: Adsorption of two and four Cu atoms in various configurations at the most favourable adsorption site on Co²⁵

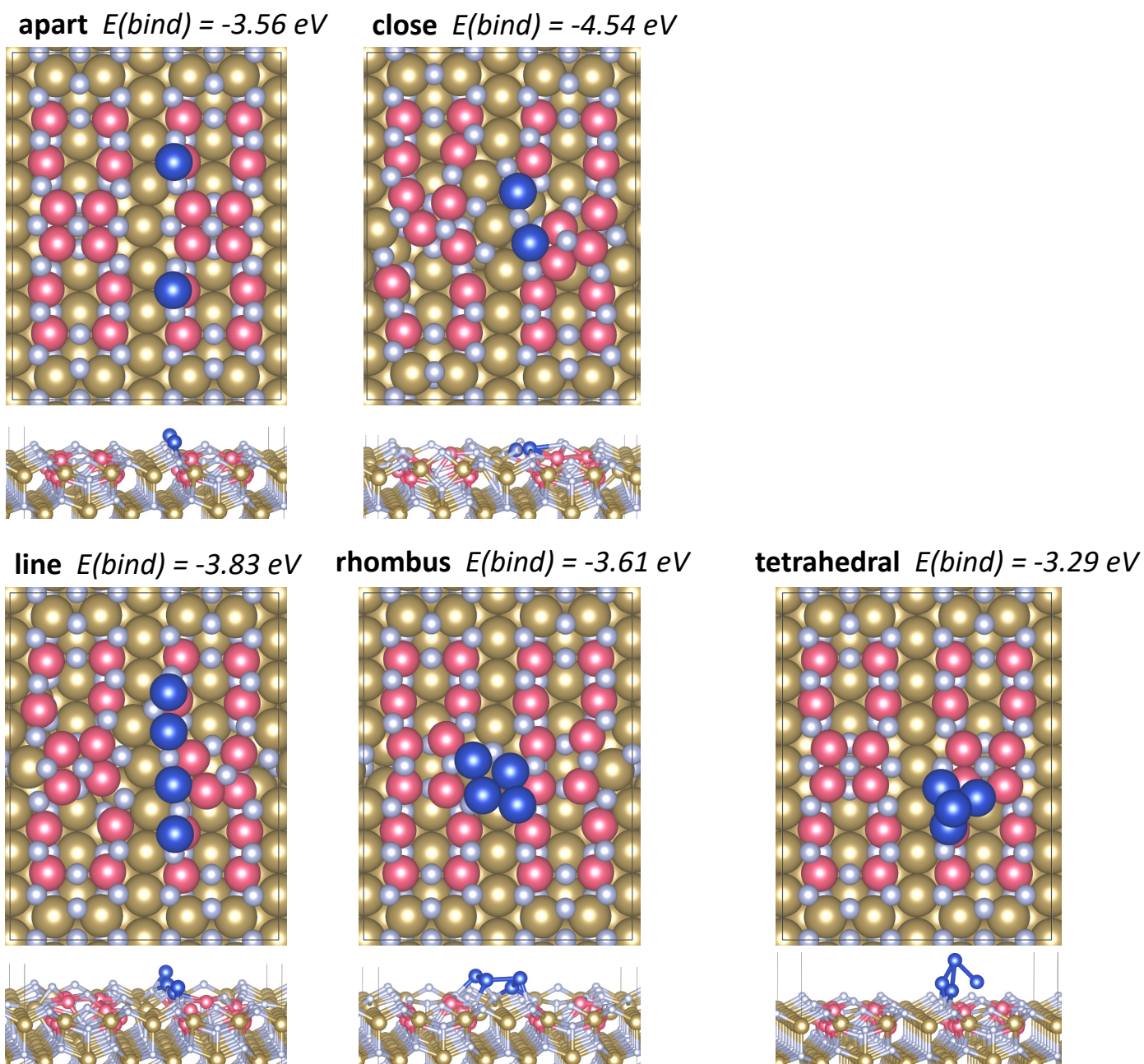
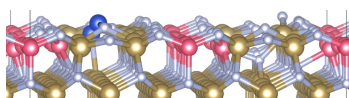
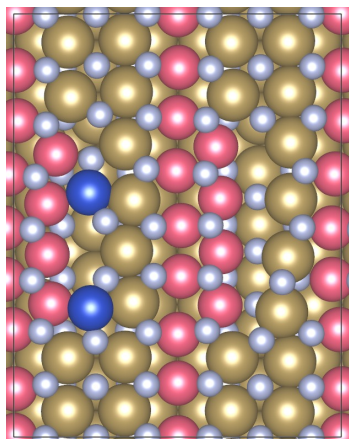
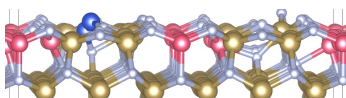
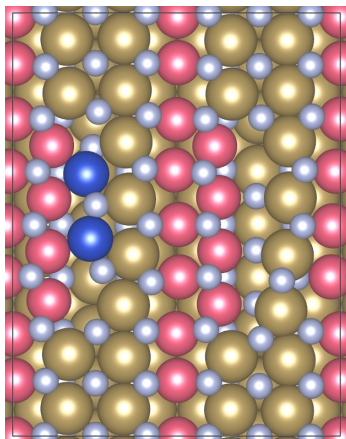


Figure A50: Adsorption of two and four Cu atoms in various configurations at the most favourable adsorption site on Co^{50-S}

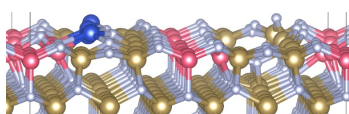
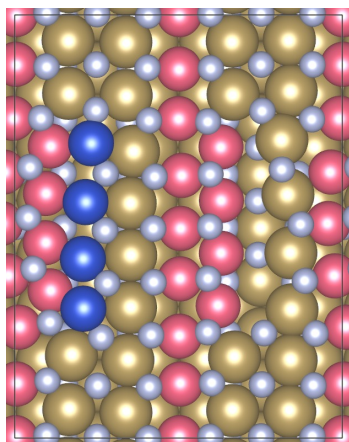
apart $E(\text{bind}) = -4.59 \text{ eV}$



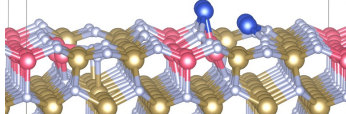
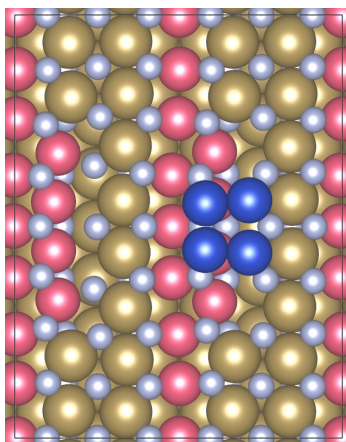
close $E(\text{bind}) = -6.18 \text{ eV}$



line $E(\text{bind}) = -4.82 \text{ eV}$



rhombus $E(\text{bind}) = -3.69 \text{ eV}$



tetrahedral $E(\text{bind}) = -3.26 \text{ eV}$

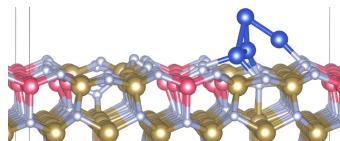
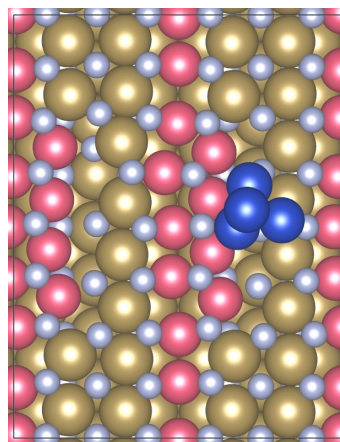


Figure A51: Adsorption of two and four Cu atoms in various configurations at the most favourable adsorption site on Co^{50-F}

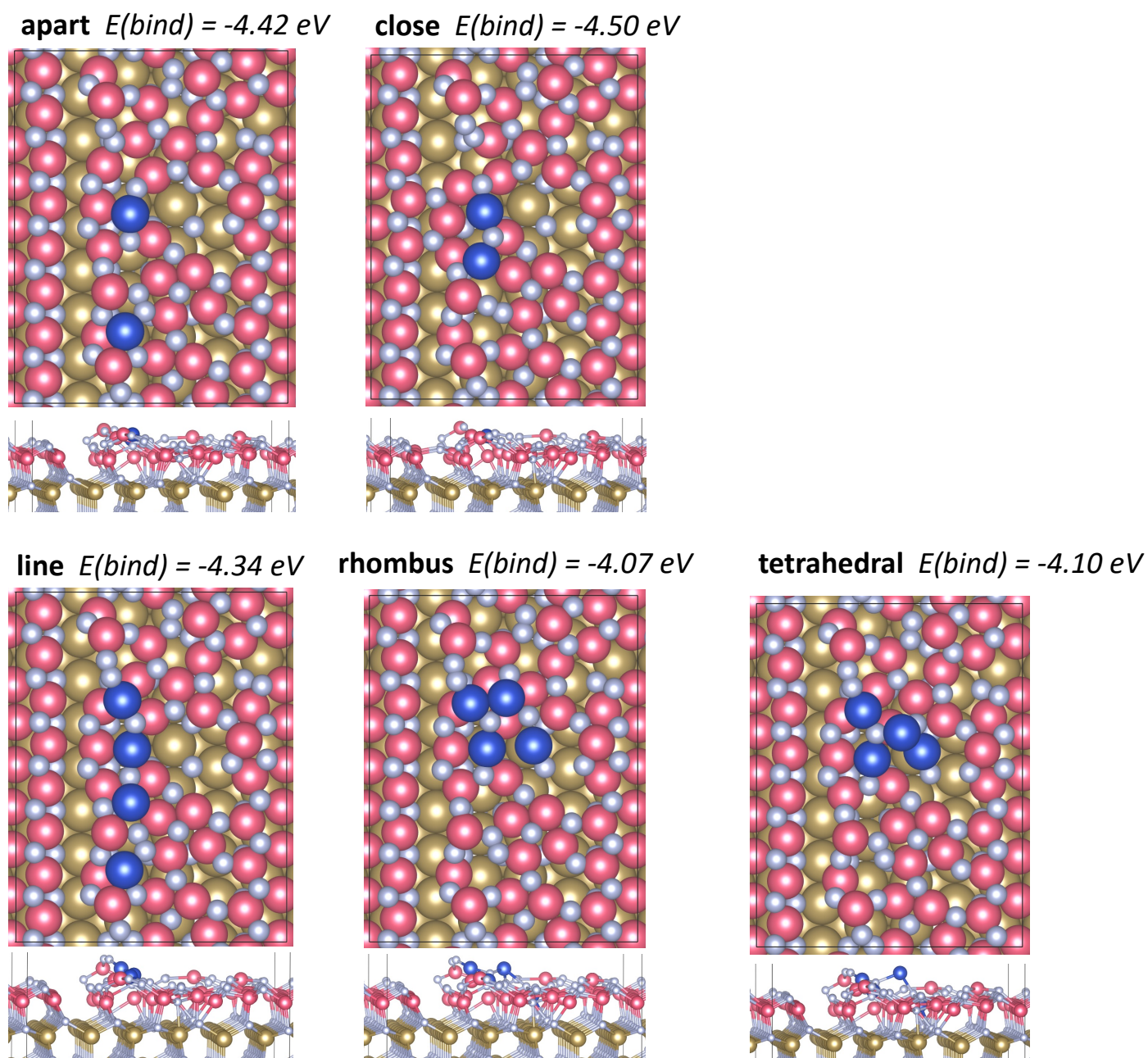


Figure A52: Adsorption of two and four Cu atoms in various configurations at the most favourable adsorption site on Co^{100}

A4.5: Density of States for Cu_n adsorptions on Co-doped TaN

Partial Density of States (PDOS) for all Cu_n adsorptions on Co-doped TaN are shown in Figures A53 to A60. All Cu and Co contributions have been multiplied by a factor of 5 for easier viewing.

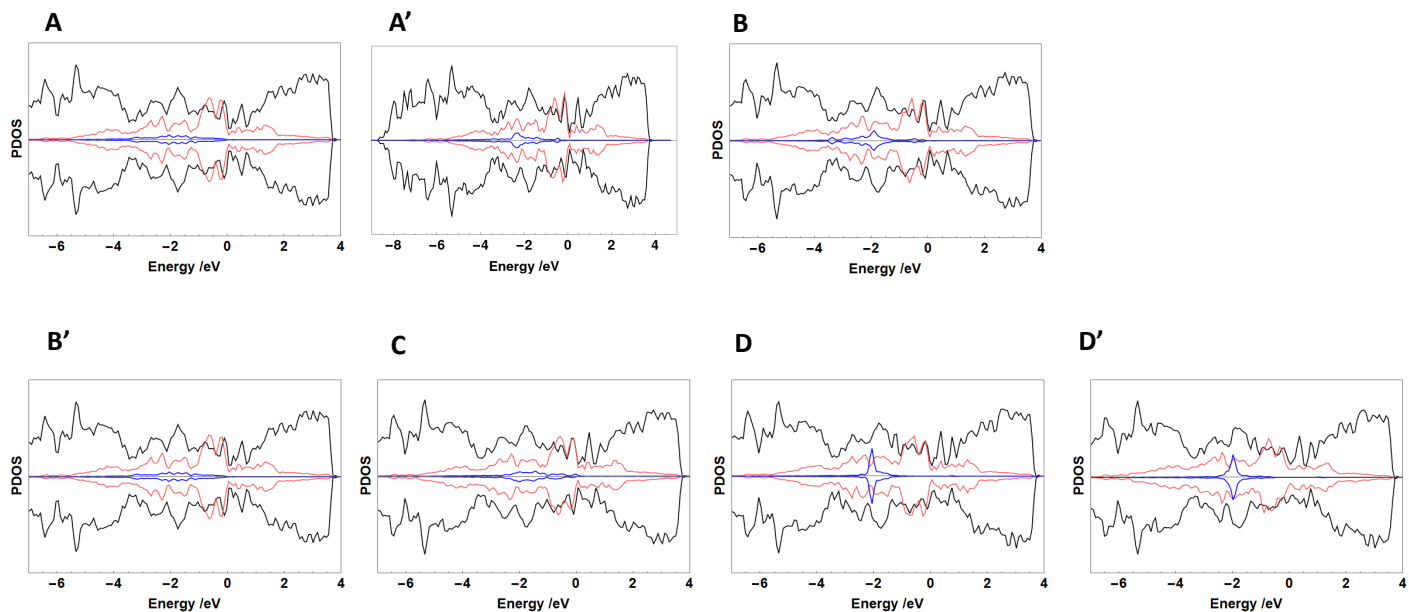


Figure A53: PDOS of single Cu adsorptions on Co^{25} . Black - total DOS, red - Co d-orbital contribution, blue - Cu d-orbital contribution.

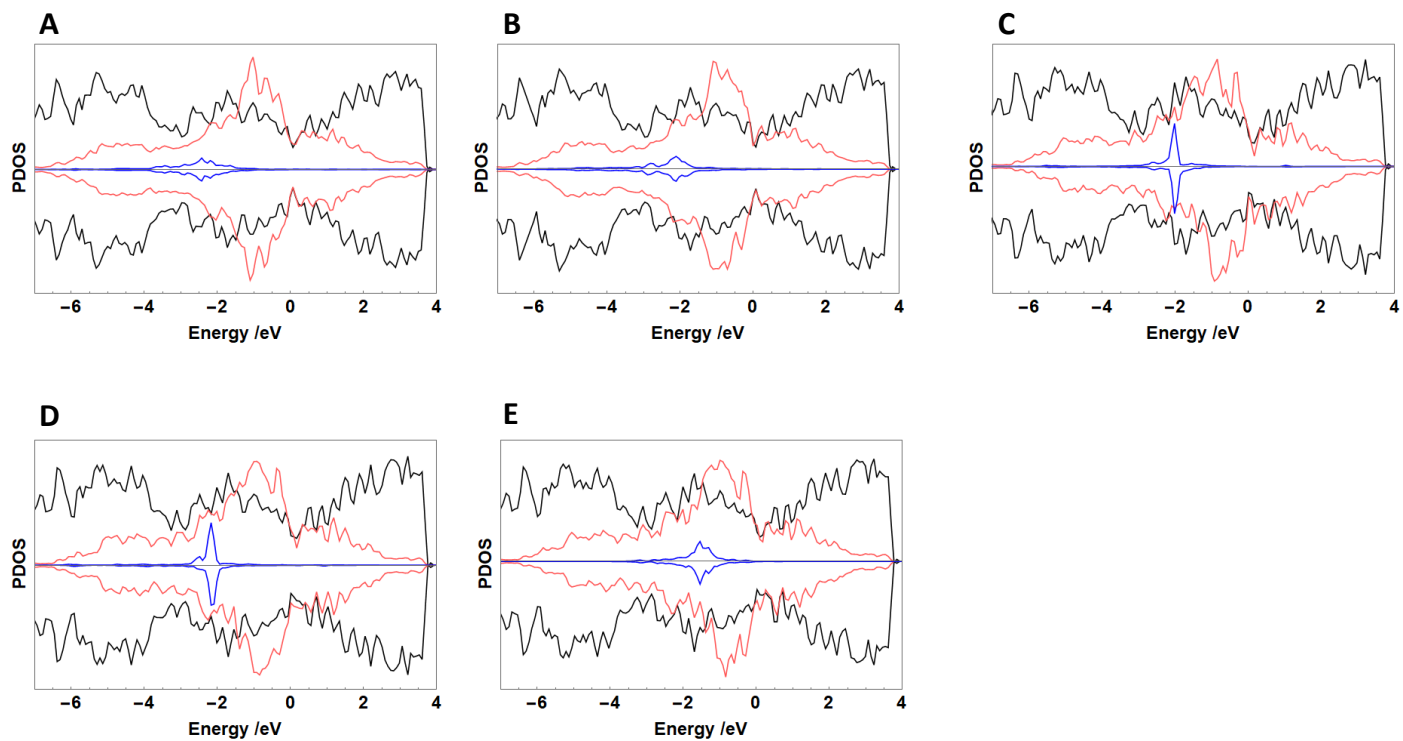


Figure A54: PDOS of single Cu adsorptions on Co^{50-S} . Black - total DOS, red - Co d-orbital contribution, blue - Cu d-orbital contribution.

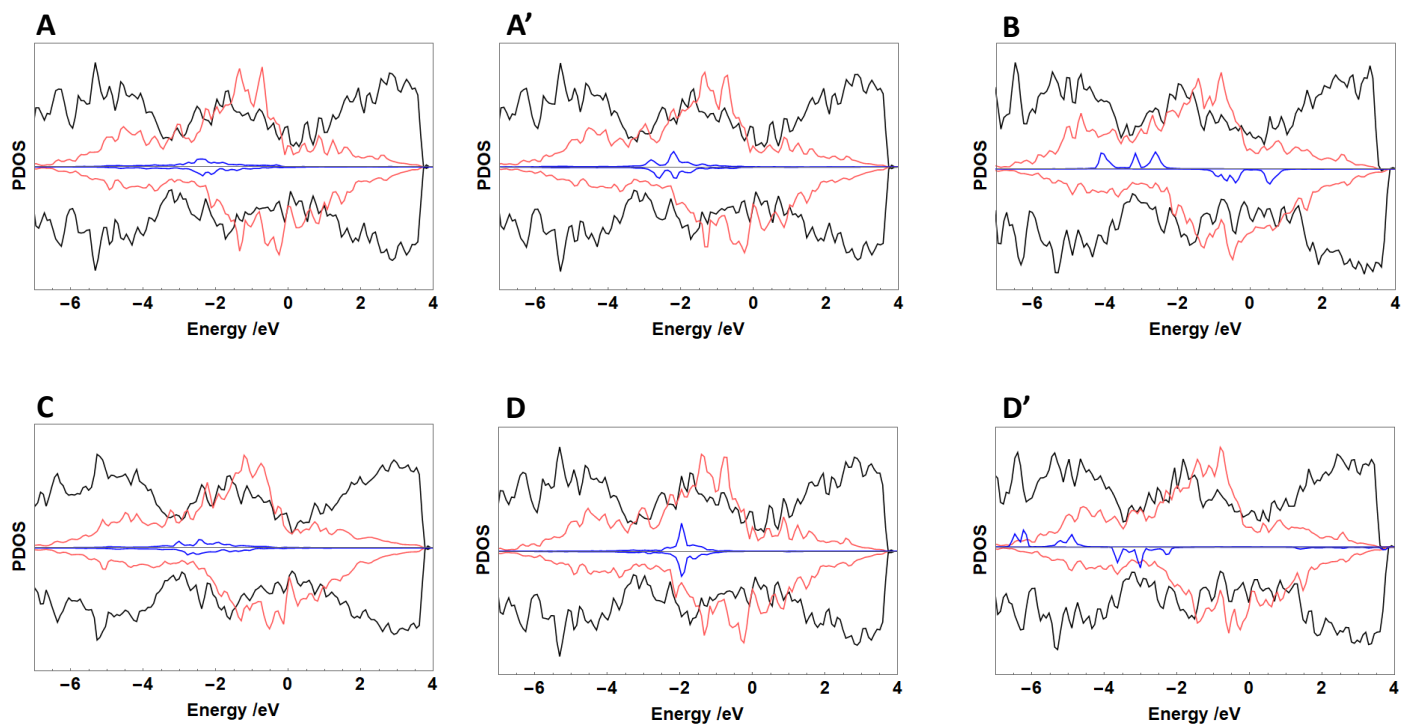


Figure A55: PDOS of single Cu adsorptions on Co^{50-F} . Black - total DOS, red - Co d-orbital contribution, blue - Cu d-orbital contribution.

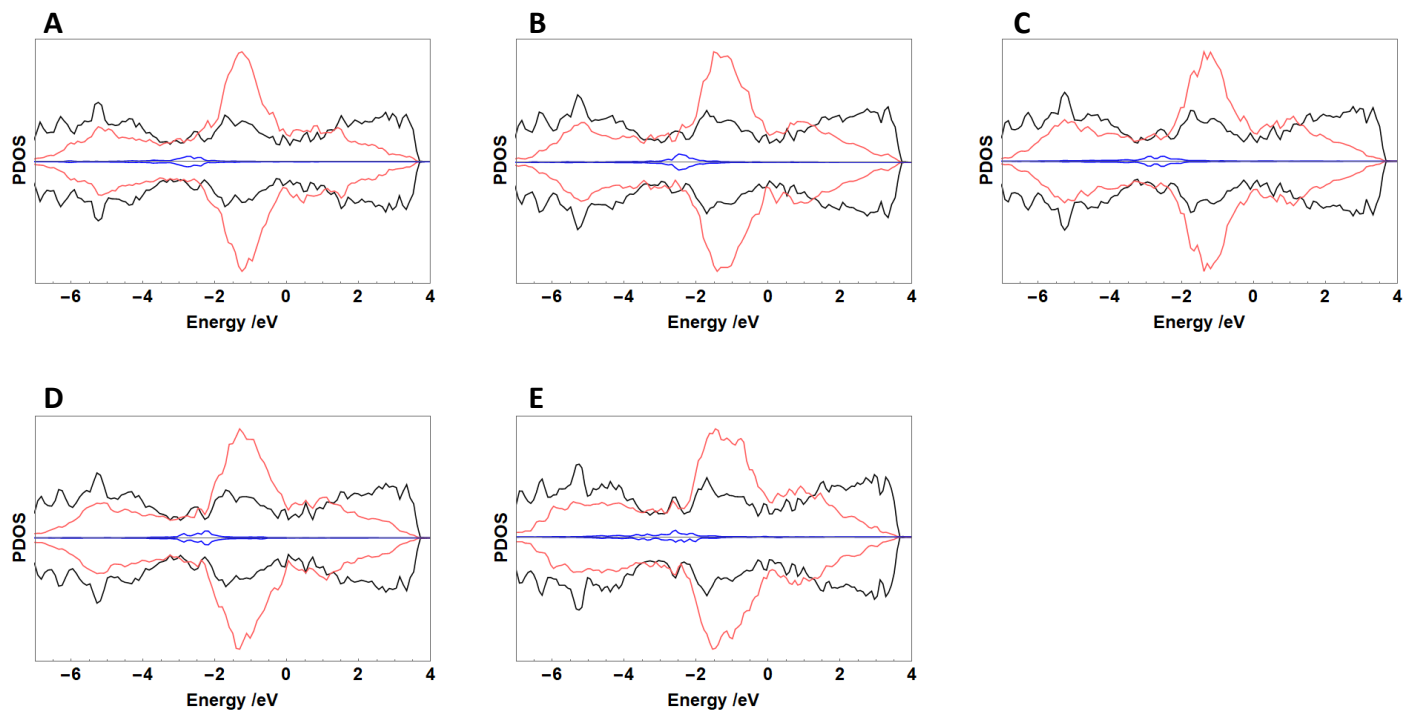


Figure A56: PDOS of single Cu adsorptions on Co^{100} . Black - total DOS, red - Co d-orbital contribution, blue - Cu d-orbital contribution.

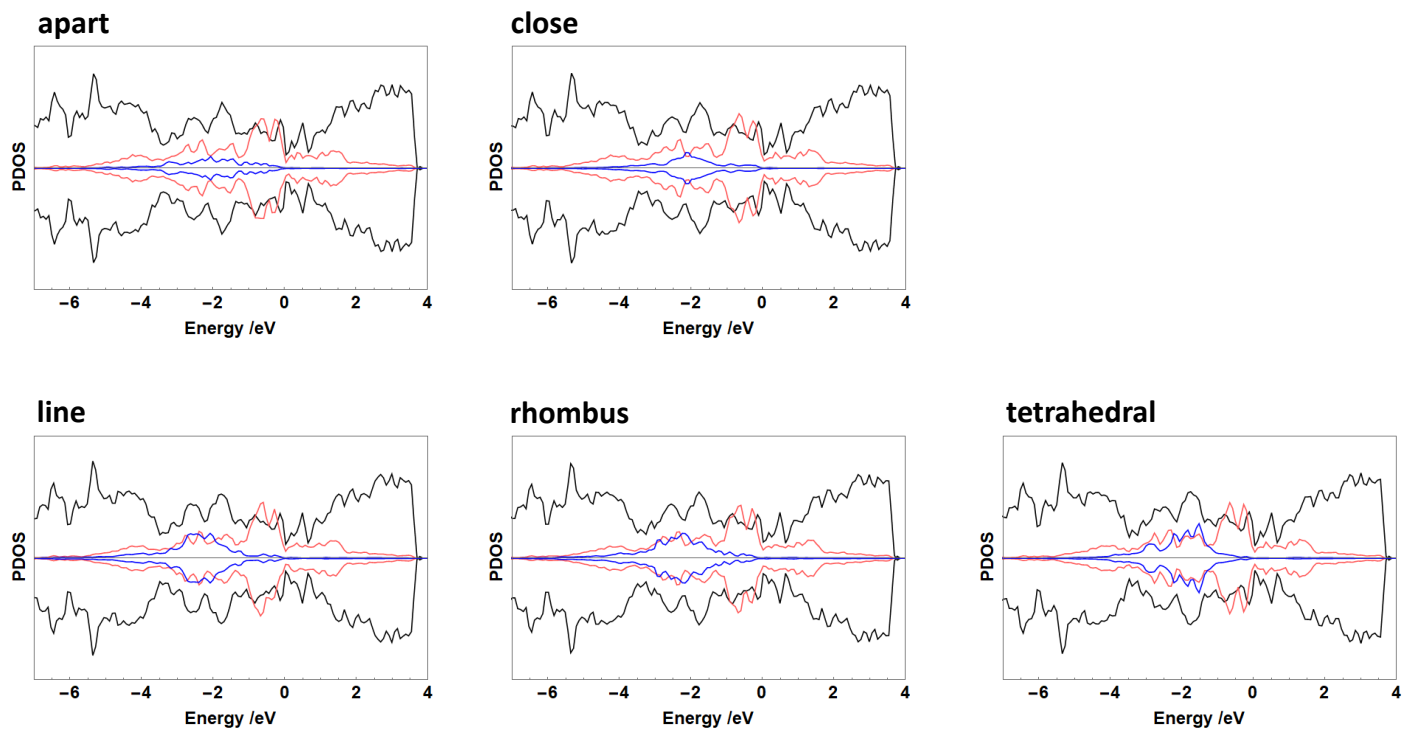


Figure A57: PDOS of Cu_2 and Cu_4 adsorptions on Co^{25} . Black - total DOS, red - Co d-orbital contribution, blue - Cu d-orbital contribution.

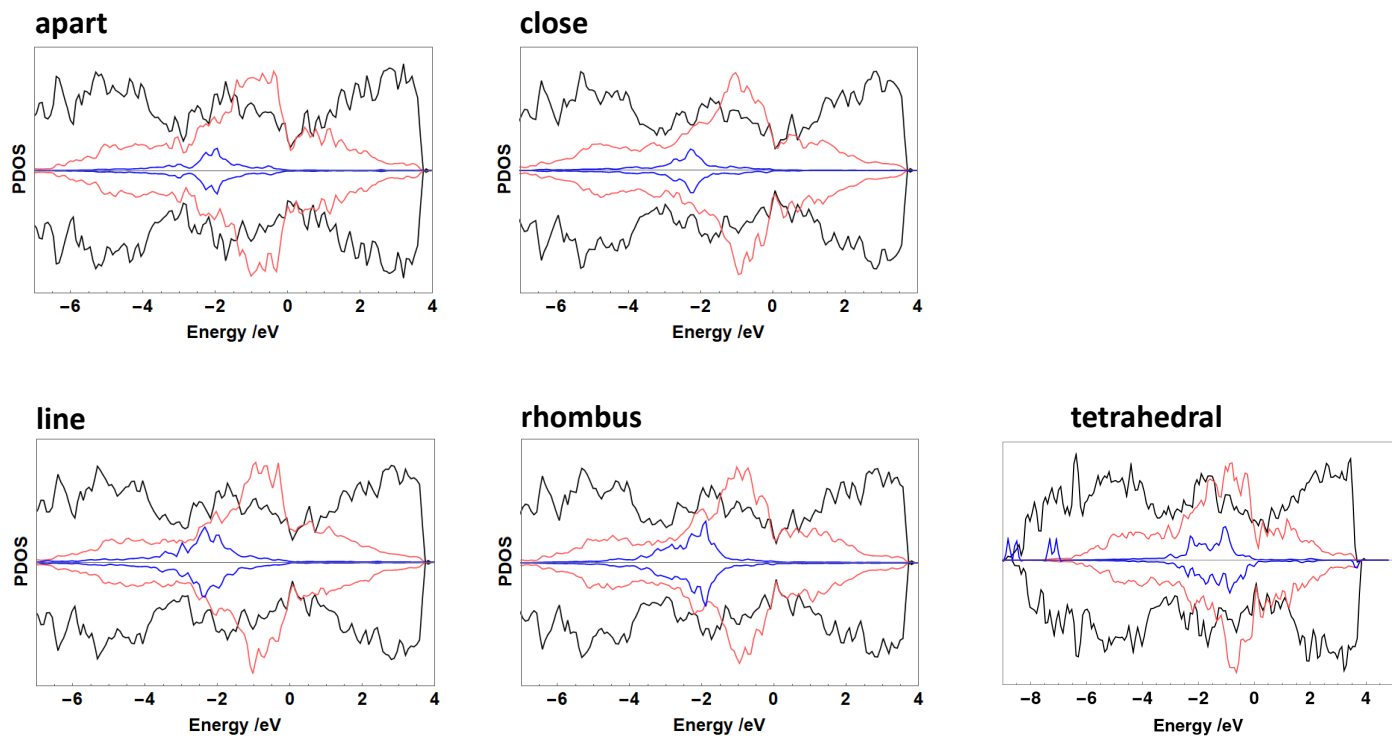


Figure A58: PDOS of Cu_2 and Cu_4 adsorptions on Co^{50-S} . Black - total DOS, red - Co d-orbital contribution, blue - Cu d-orbital contribution.

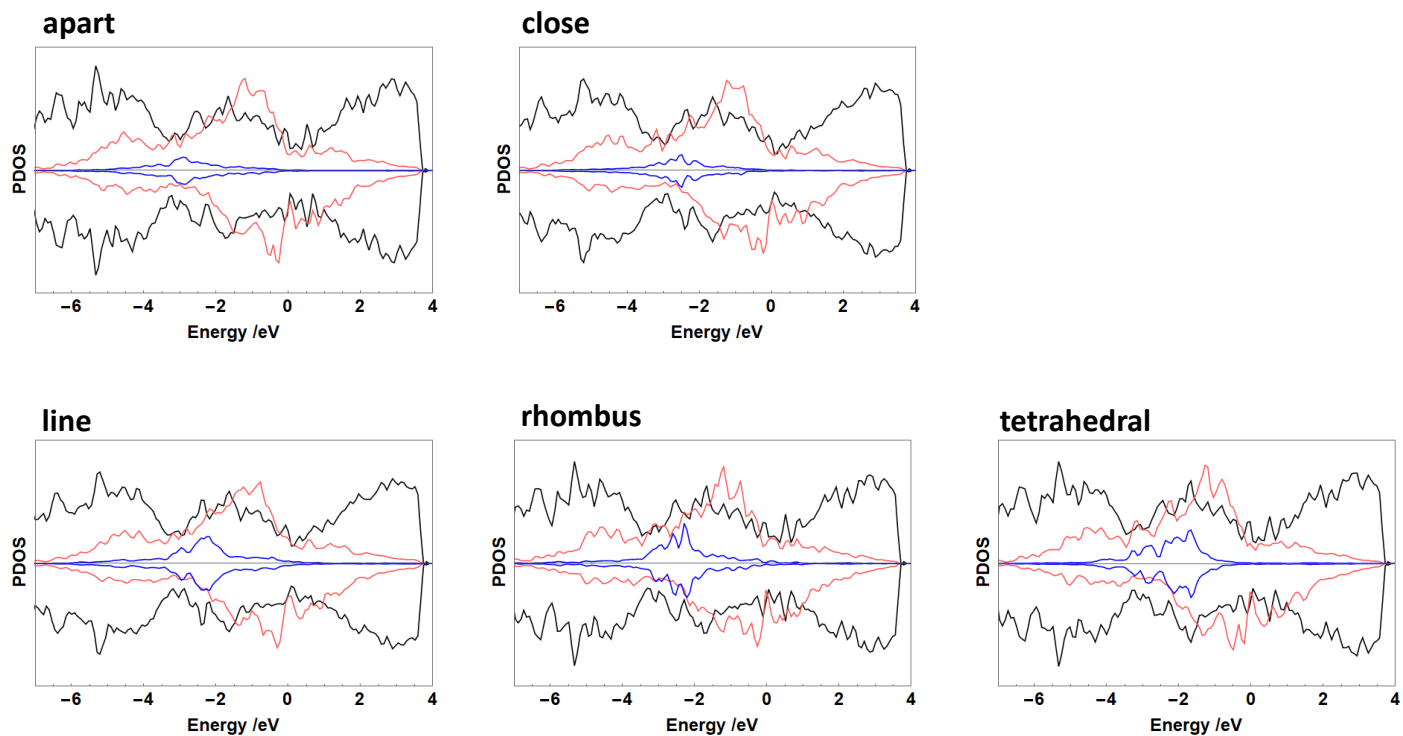


Figure A59: PDOS of Cu_2 and Cu_4 adsorptions on Co^{50-F} . Black - total DOS, red - Co d-orbital contribution, blue - Cu d-orbital contribution.

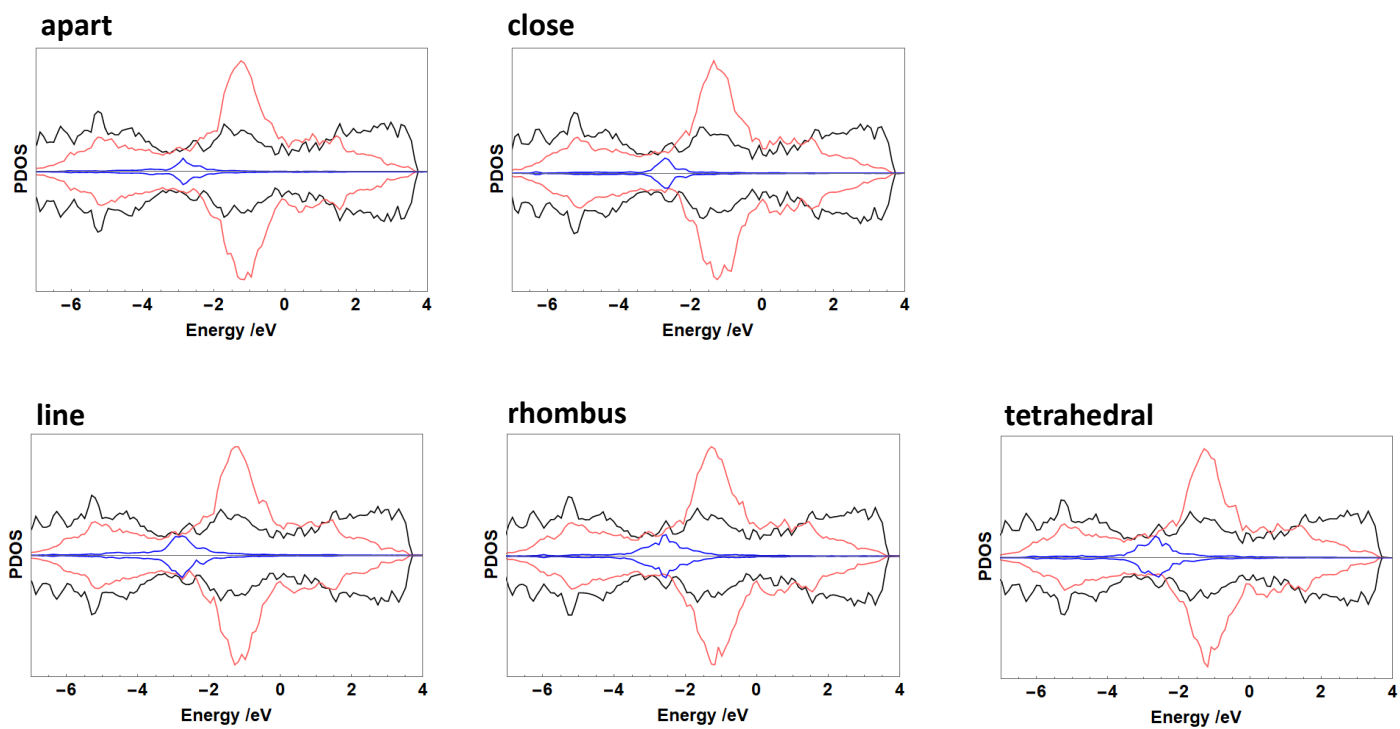


Figure A60: PDOS of Cu₂ and Cu₄ adsorptions on Co¹⁰⁰. Black - total DOS, red - Co d-orbital contribution, blue - Cu d-orbital contribution.

A4.6: Bader Charges of Cu_n adsorption on Co-doped TaN

Table A14: Computed Bader charges (Q) for all Cu_n geometries on Co-doped TaN. Cu has 11 valence electrons.

Surface	Geometry	$Q_{\text{Cu}1}$	$Q_{\text{Cu}2}$	$Q_{\text{Cu}3}$	$Q_{\text{Cu}4}$
Co^{25}	A	10.4			
	A'	10.4			
	B	10.4			
	B'	10.0			
	C	10.4			
	D	10.5			
	D'	10.5			
	close	10.4	10.5		
	apart	10.4	10.4		
	line	10.3	10.5	10.5	10.5
	rhombus	10.6	10.5	10.4	10.5
	tetrahedral	10.7	10.7	10.5	11.0
$\text{Co}^{50-\text{S}}$	A	10.5			
	B	10.5			
	C	10.5			
	D	10.6			
	E	10.8			
	close	10.4	10.4		
	apart	10.4	10.4		
	line	10.4	10.5	10.5	10.6
	rhombus	10.5	10.9	10.6	10.7
	tetrahedral	10.8	10.7	10.6	10.8
$\text{Co}^{50-\text{F}}$	A	10.4			
	A'	10.3			
	B	10.7			
	C	10.4			
	D	10.5			
	D'	10.6			
	close	10.5	10.5		
	apart	10.5	10.6		
	line	10.5	10.3	10.5	10.5
	rhombus	10.5	10.5	10.5	10.5
	tetrahedral	10.6	10.7	10.5	11.0
Co^{100}	A	10.4			
	B	10.3			
	C	10.3			
	D	10.3			
	E	10.3			
	close	10.4	10.4		
	apart	10.4	10.3		
	line	10.5	10.4	10.3	10.3
	rhombus	10.5	10.5	10.5	10.4
	tetrahedral	10.5	10.5	10.4	10.4

A4.7: Thermal Instability of Co^{50-S} and Co^{100}

Figure A61 shows the thermal instability of Co^{50-S} and Co^{100} as observed after 0.5 ps during a 500 K MD run.

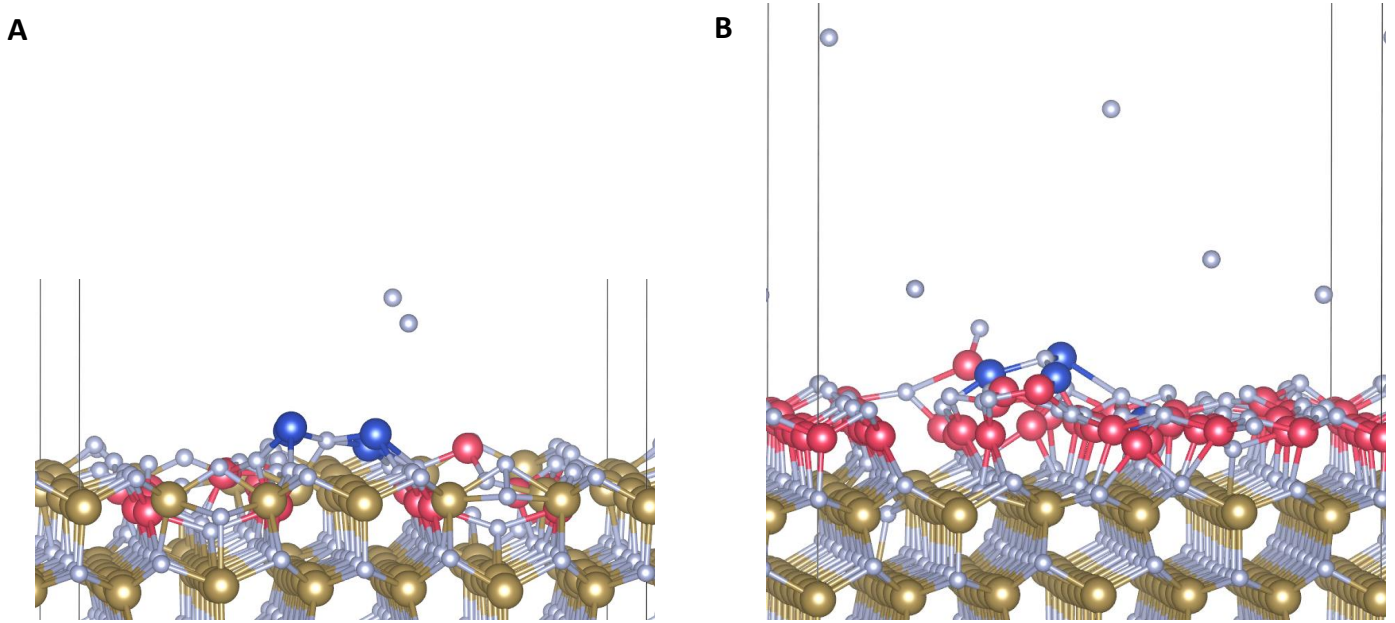


Figure A61: A: Cu₄ rhombus on Co^{50-S} after 0.5 ps at 500 K. B: Cu₄ rhombus on Co^{100} after 0.5 ps at 500 K.

A4.8: High-spin vs low-spin Co in Co-doped TaN

All calculations of Co doped surfaces are in the low-spin state by default. We tested the effect of imposing high spin using the adsorption of a Cu atom at site B' and the adsorption of a rhombus on Co^{25} as examples. The changed spin state has no effect on the geometry of either structure. There is a significant change in the adsorption energy for the single atom. With low spin the adsorption energy is -3.34 eV/atom, while high spin yields an adsorption energy of -0.90 eV/atom. The change in the adsorption energy is smaller for the rhombus adsorption, from -2.90 eV/atom for low spin to -2.29 eV/atom for high spin. As the adsorption energy remains negative for both adsorptions and there is no effect on the geometry we do not take the spin states into account for our analysis.

A4.9: Stable Co, W and Ru nitride stoichiometries

As discussed in Chapters 5 and 6, Ru^{100} , Co^{100} and Co^{50-S} show thermal instability during ab initio MD calculations, as well as strong surface distortion upon Cu adsorption. To gain further insight into the cause of these instabilities and distortions, we compare the different material properties of the relevant metal nitrides. Table A15 shows formation energies, types of unit cell and lattice parameters for selected Ta, Co, Ru and W nitrides. While the doped surfaces are expected to behave differently than the bulk metal nitrides, 100% doping creates a monolayer of metal nitride passivation

Table A15: Materials Data on various metal nitrides based on experimental crystal structures. *No experimental crystal structures are currently available for ruthenium nitrides. ^aLow-spin. ^bHigh-spin.

Metal Nitride	Formation Energy (eV/atom)	Unit Cell	Lattice Parameters (Å)	Metal Ionic Radius (Å)
TaN [6]	-1.36	hexagonal	a = b = 5.23, c = 2.93	0.72
RuN* [9]	0.07	cubic	a = b = c = 3.23	0.62
CoN [5]	-0.09	cubic	a = b = c = 3.01	0.55 ^a , 0.61 ^b
Co ₂ N [10]	-0.06	orthorhombic	a = 2.84, b = 4.29, c = 4.54	0.55 ^a , 0.61 ^b
WN [11]	-0.26	hexagonal	a = b = 2.88, c = 2.91	0.66
W ₂ N ₃ [8]	-0.32	hexagonal	a = b = 2.92, c = 15.84	0.66

on the TaN surface, which is constrained to the crystal packing of TaN. For this reason it is important to consider formation energies and lattice mismatch in order to understand how this passivation differs from the bulk nitride. For Ta, Co and Ru, the most stable nitride formed has a 1:1 stoichiometry. [5–7] For W, the nitride with the most favourable formation energy is W₂N₃. [8] However, W-doped TaN shows the best thermal stability compared to Co- and Ru-doped TaN. This indicates that the stable stoichiometries of the metal nitrides do not necessarily play a role in the stability of the various doped surfaces and in particular the 100% doped surfaces. There is a lattice mismatch between TaN and WN, however they have the same unit cell shape. It is therefore likely that the improved stability of W¹⁰⁰ is in fact a direct result of the similar ionic radius of W compared to Ta and the matching shape of the unit cell. Similarly, the distortions observed for Ru¹⁰⁰, Co¹⁰⁰ and Ru^{50-S} are most likely caused by the differences in ionic radius, as discussed in Chapter 4-6, as well as the different unit cell types, rather than the lattice mismatch.

A5: Supplementary Information for Chapter 7

A5.1: DOS Plots

Density of state plots for all Cu_n adsorptions are given below.

Shown below are density of state plots for all metal adsorptions on both pristine and defective MoS_2 .

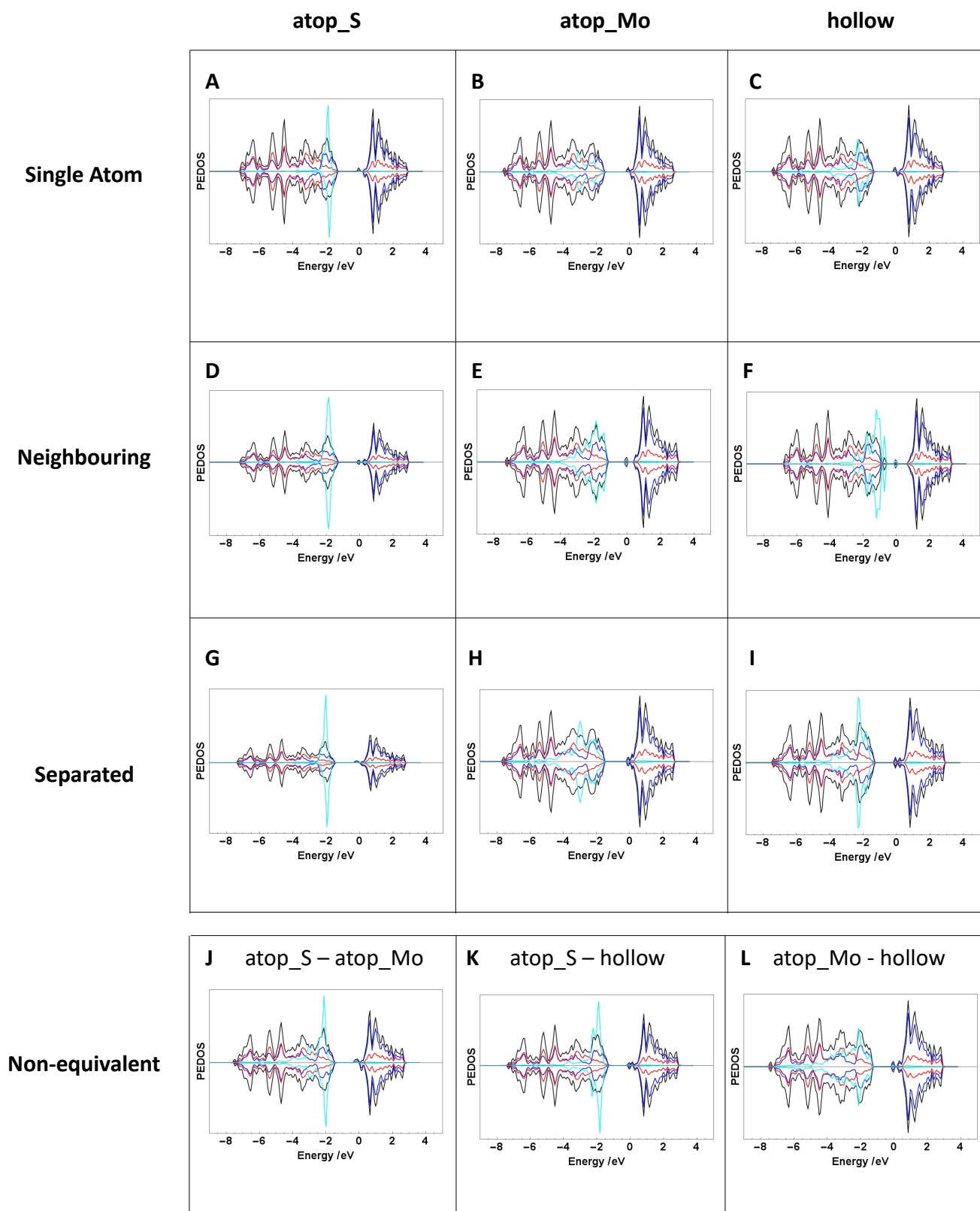


Figure A62: DOS plots of Cu₁ and Cu₂ adsorption structures. Black = total DOS, blue = DOS projected onto Mo d-orbitals, red = DOS projected onto S p-orbitals, cyan = DOS projected onto Cu d-orbitals. The contribution of the Cu d-orbitals has been increased by a factor of 5 for ease of comparison.

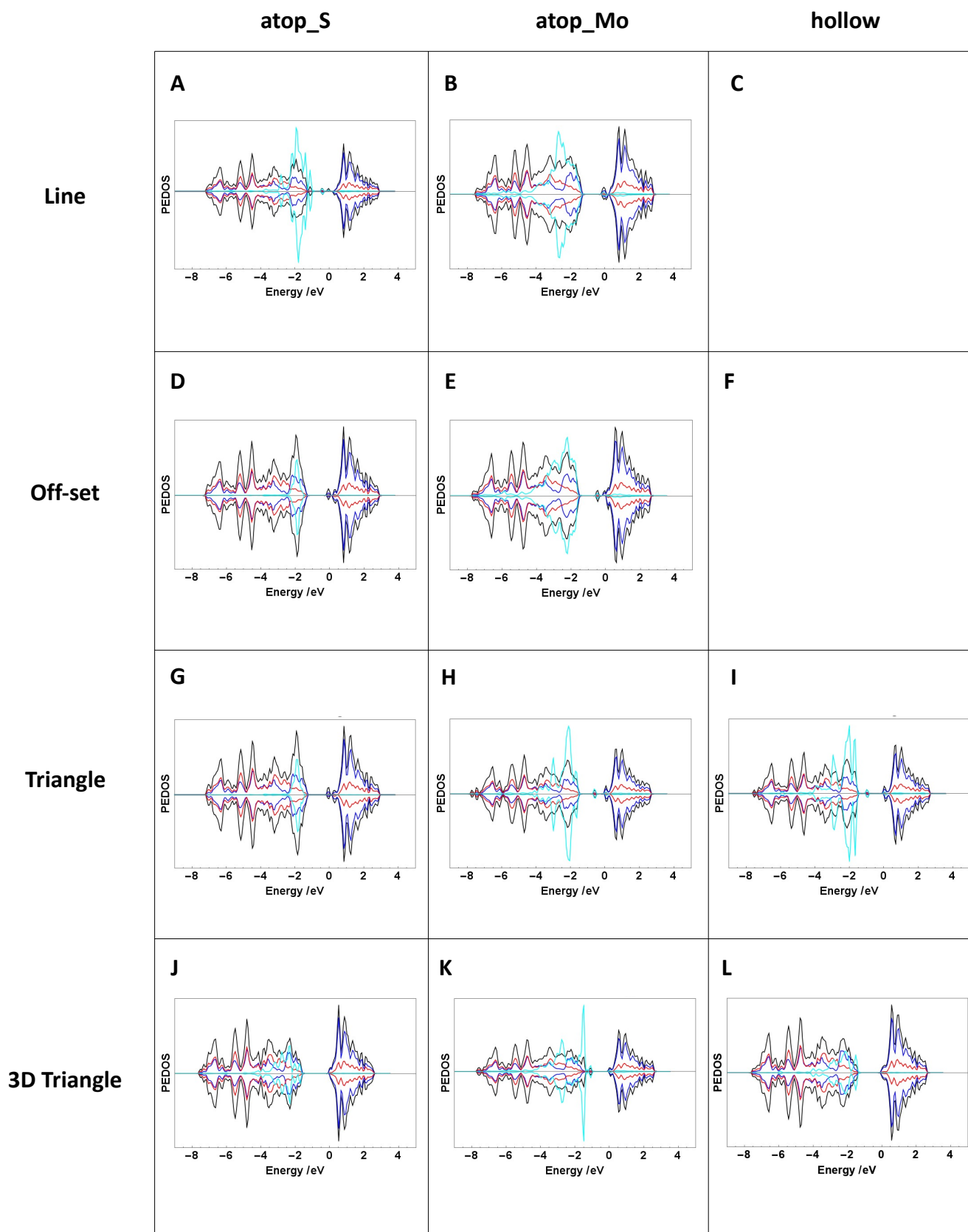


Figure A63: DOS plots of Cu_3 adsorption structures. Black = total DOS, blue = DOS projected onto Mo d-orbitals, red = DOS projected onto S p-orbitals, cyan = DOS projected onto Cu d-orbitals. The contribution of the Cu d-orbitals has been increased by a factor of 5 for ease of comparison.

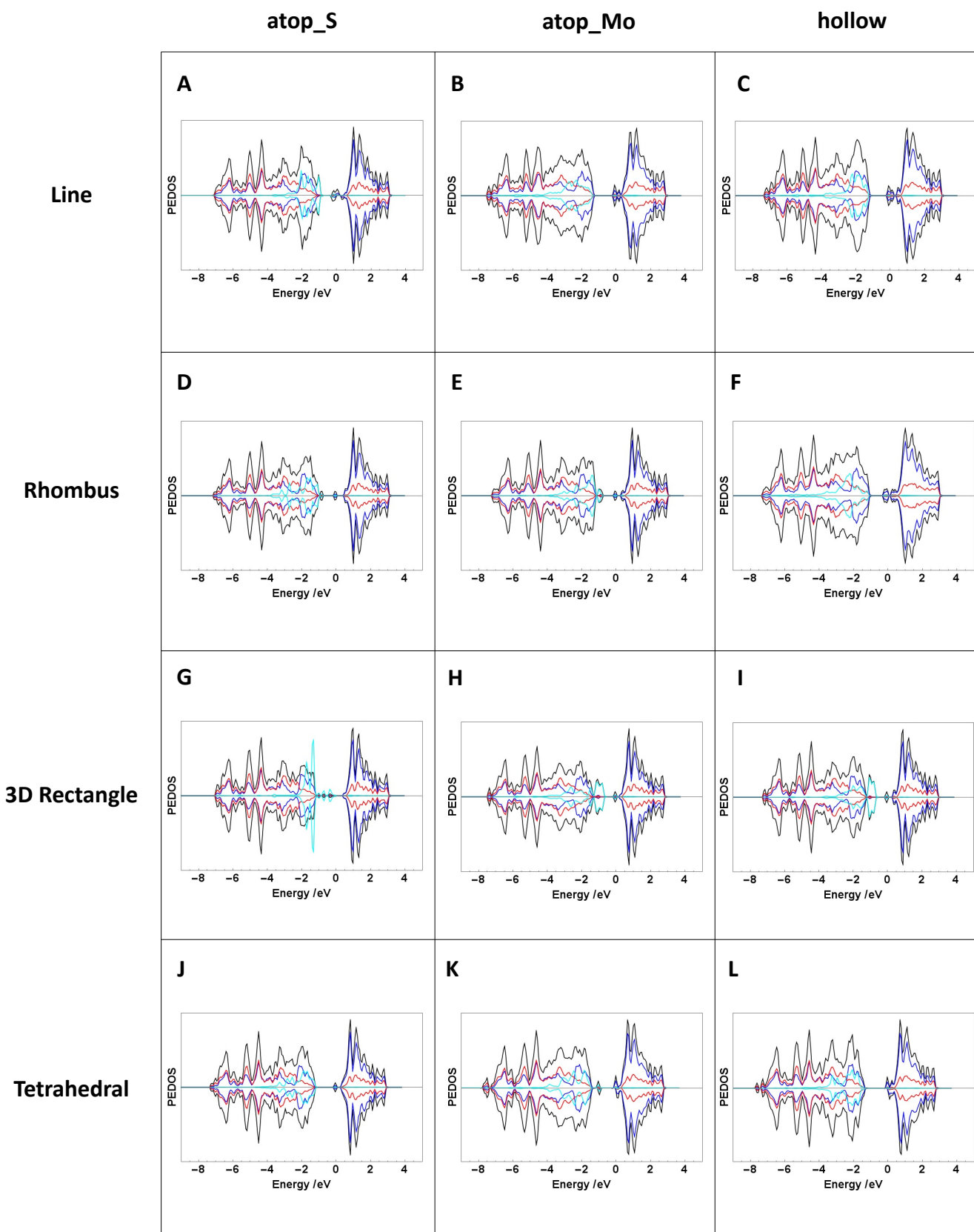


Figure A64: DOS plots of Cu₄ adsorption structures. Black = total DOS, blue = DOS projected onto Mo d-orbitals, red = DOS projected onto S p-orbitals, cyan = DOS projected onto Cu d-orbitals. The contribution of the Cu d-orbitals has been increased by a factor of 5 for ease of comparison.

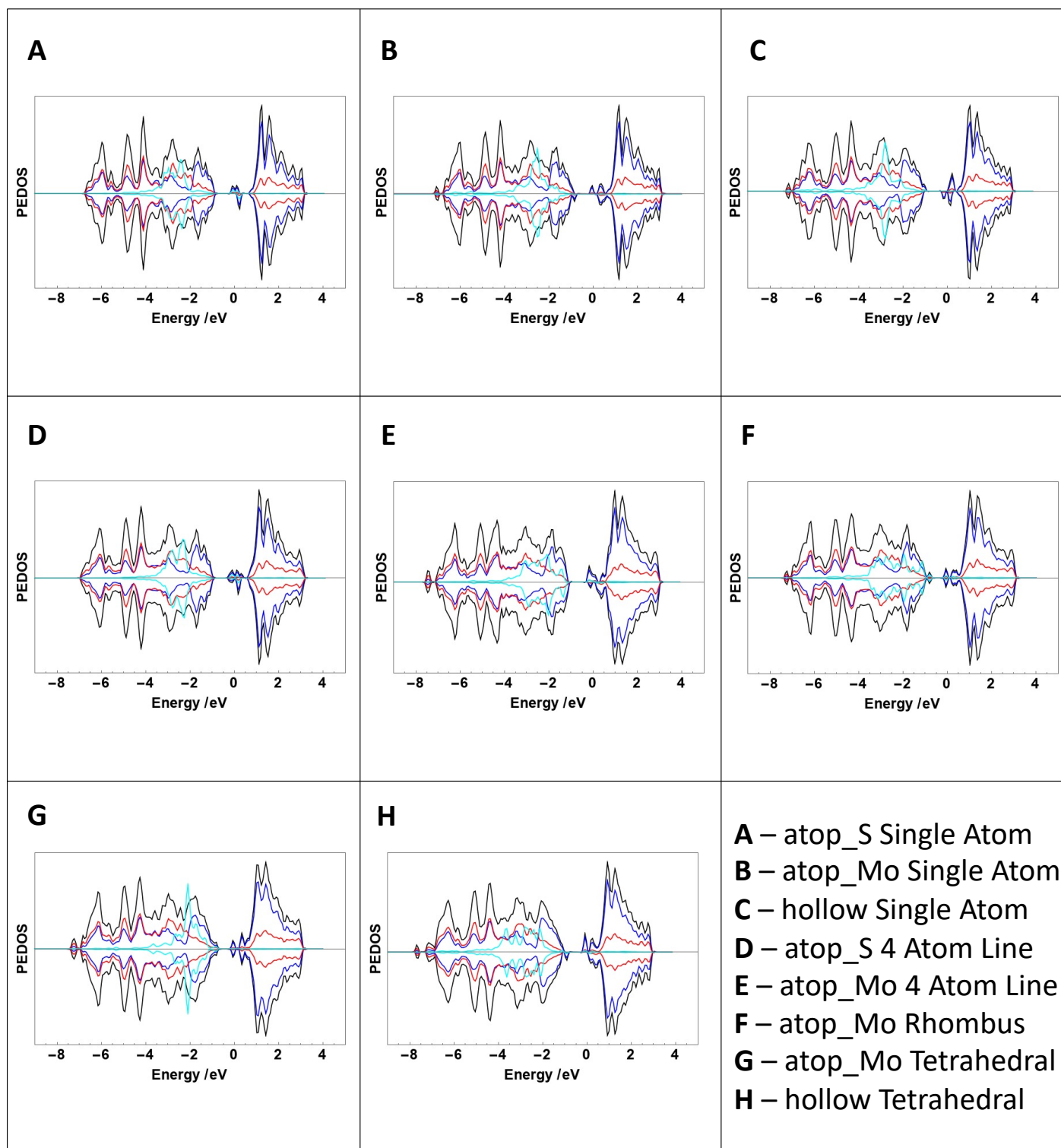


Figure A65: DOS plots of Cu_1 and Cu_4 adsorption structures on defective MoS_2 . Black = total DOS, blue = DOS projected onto Mo d-orbitals, red = DOS projected onto S p-orbitals, cyan = DOS projected onto Cu d-orbitals. The contribution of the Cu d-orbitals has been increased by a factor of 5 for ease of comparison.

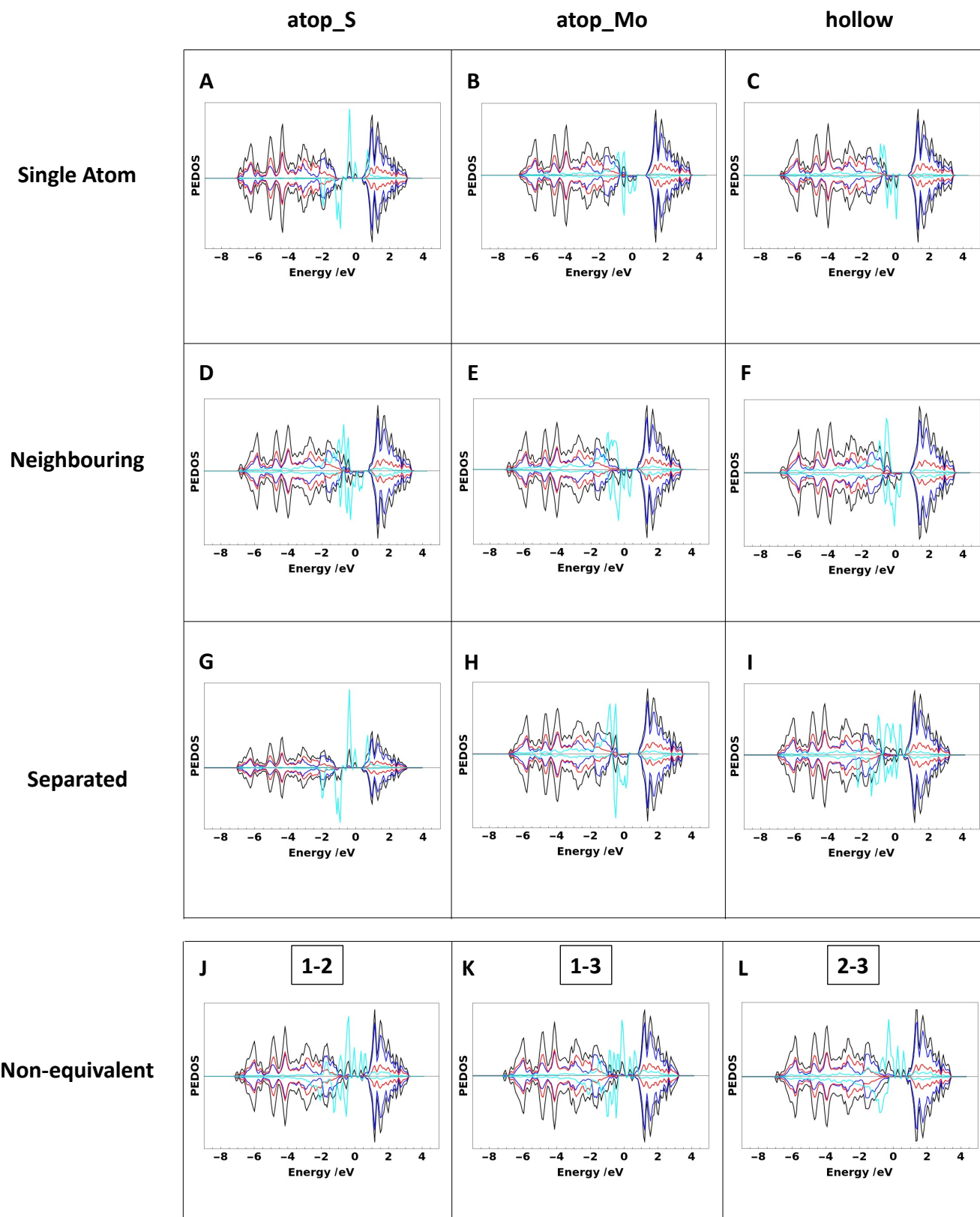


Figure A66: PEDOS for Co and Co₂ adsorption on MoS₂. Black - total DOS; blue - Mo d-orbital contribution; red - S p-orbital contribution; cyan - Co d-orbital contribution

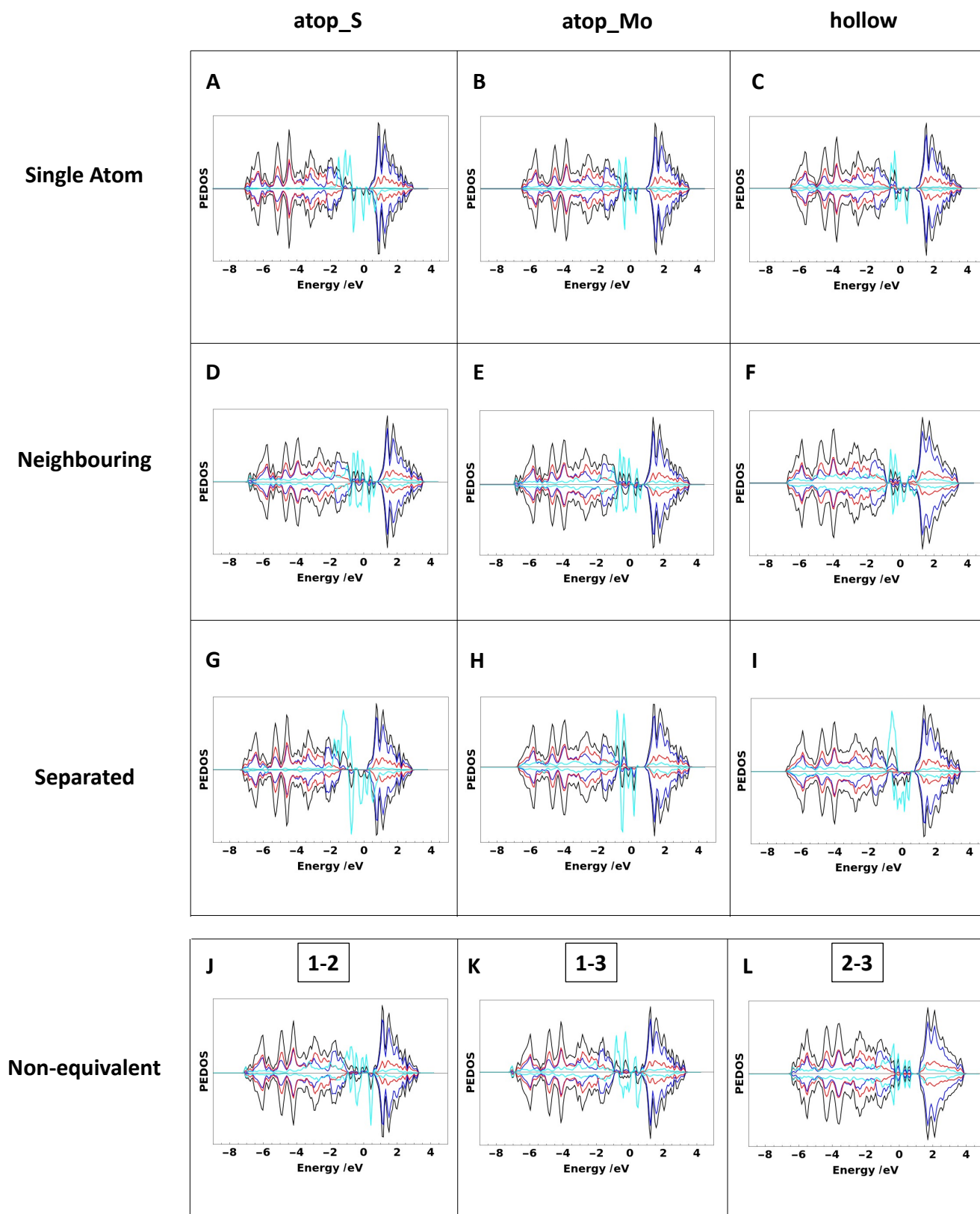


Figure A67: PEDOS for Ru and Ru₂ adsorption on MoS₂. Black - total DOS; blue - Mo d-orbital contribution; red - S p-orbital contribution; cyan - Ru d-orbital contribution

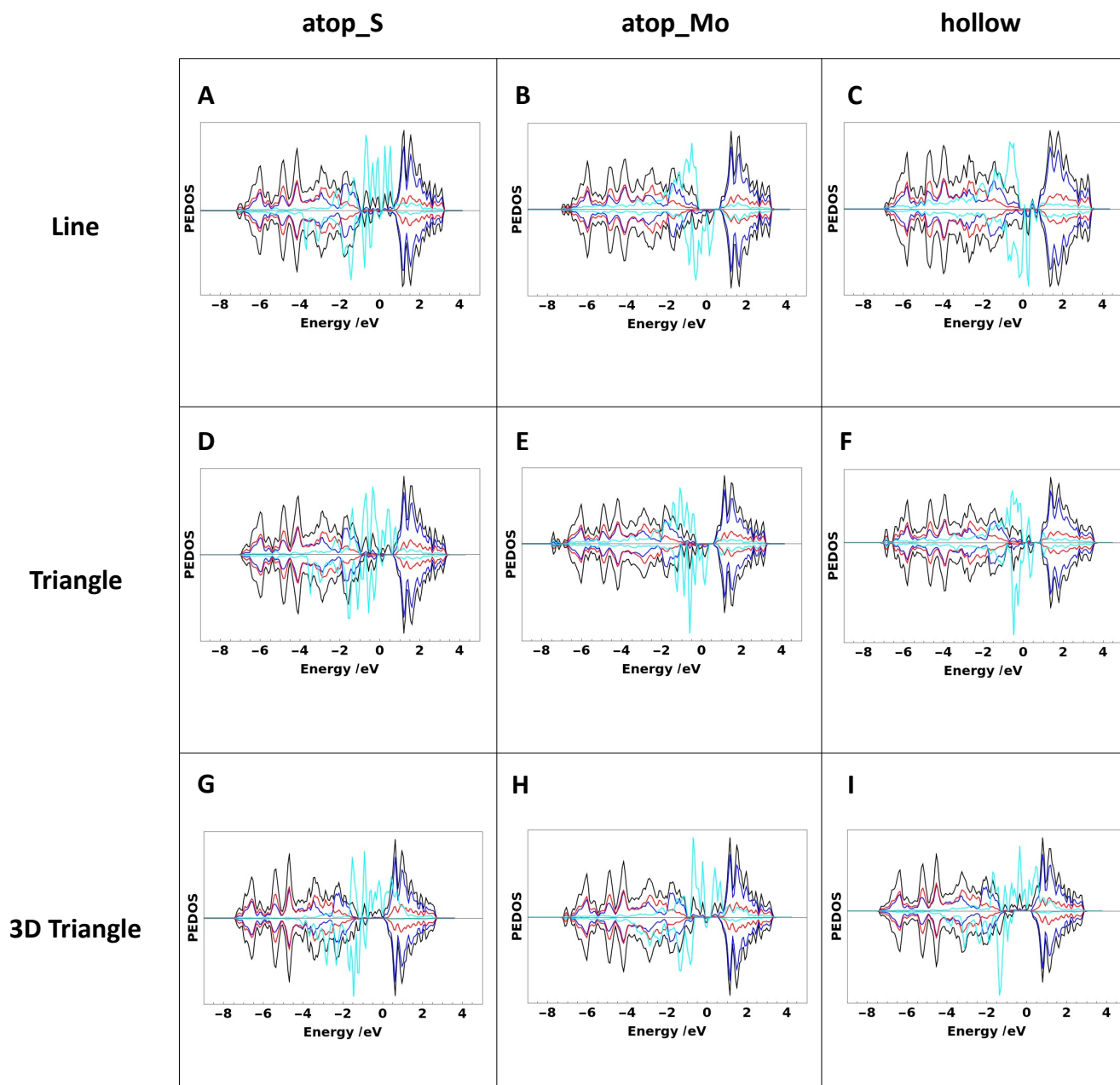


Figure A68: PEDOS for Co_3 adsorption on MoS_2 . Black - total DOS; blue - Mo d-orbital contribution; red - S p-orbital contribution; cyan - Co d-orbital contribution

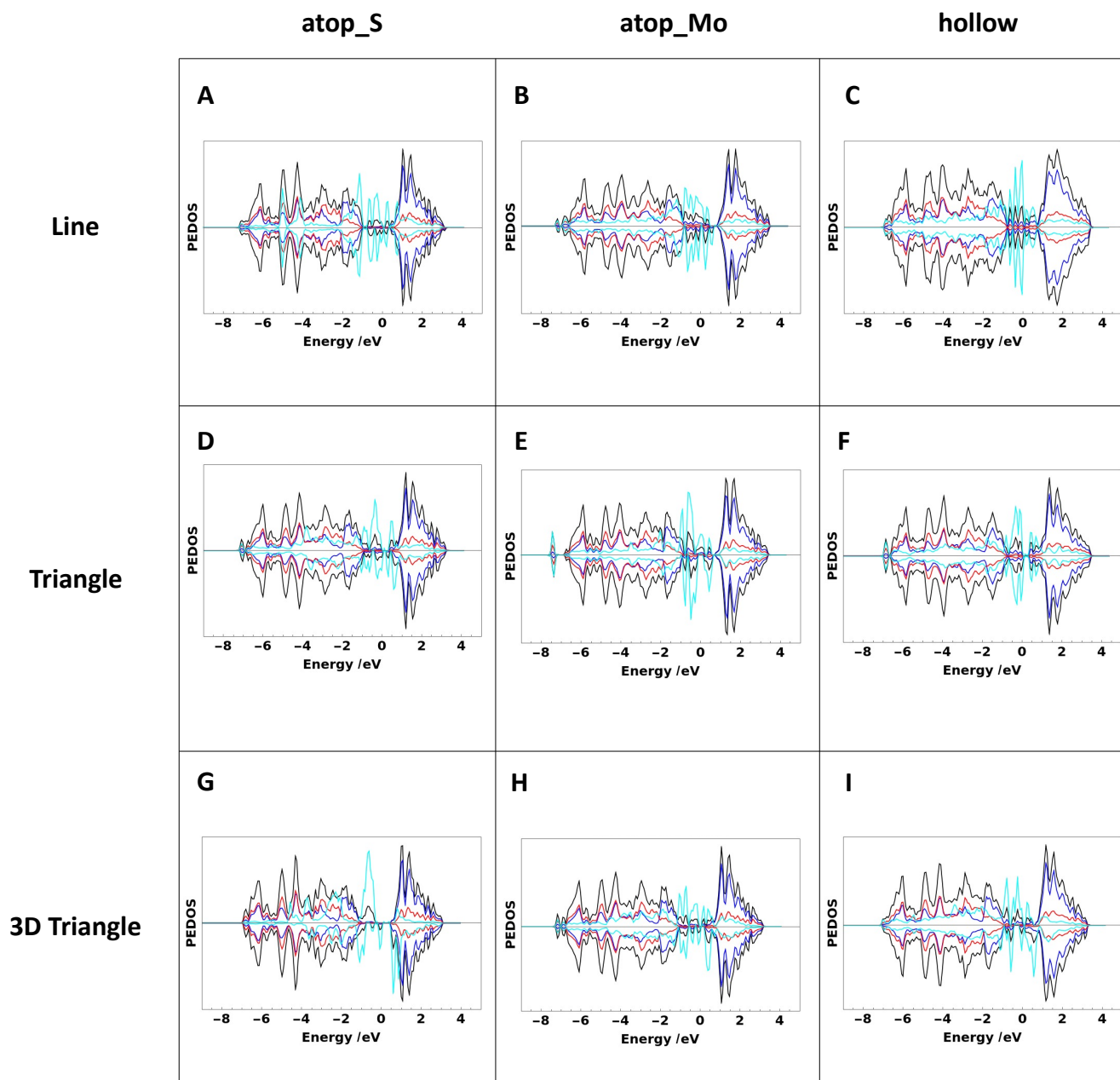


Figure A69: PEDOS for Ru_3 adsorption on MoS_2 . Black - total DOS; blue - Mo d-orbital contribution; red - S p-orbital contribution; cyan - Ru d-orbital contribution

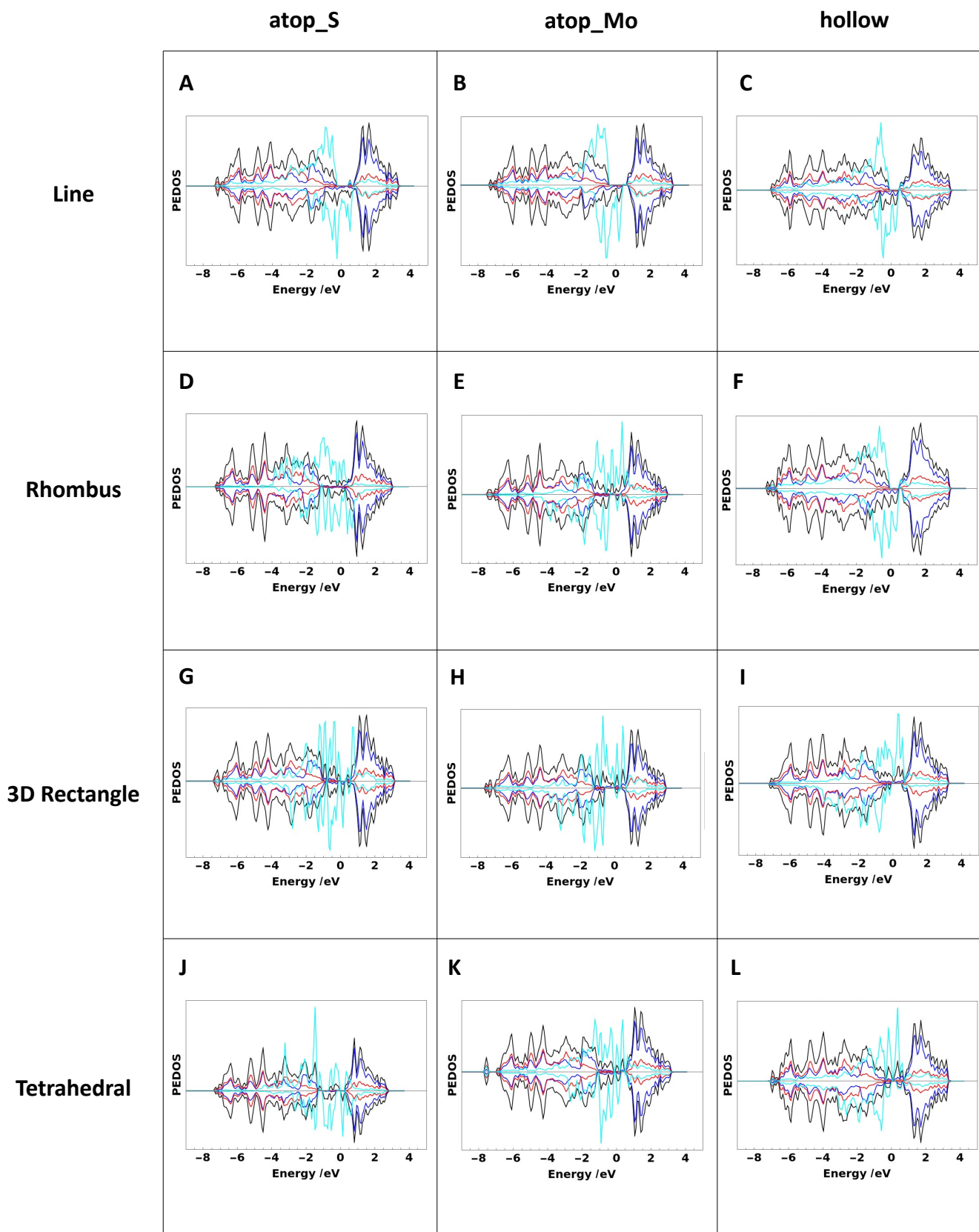


Figure A70: PEDOS for Co_4 adsorption on MoS_2 . Black - total DOS; blue - Mo d-orbital contribution; red - S p-orbital contribution; cyan - Co d-orbital contribution

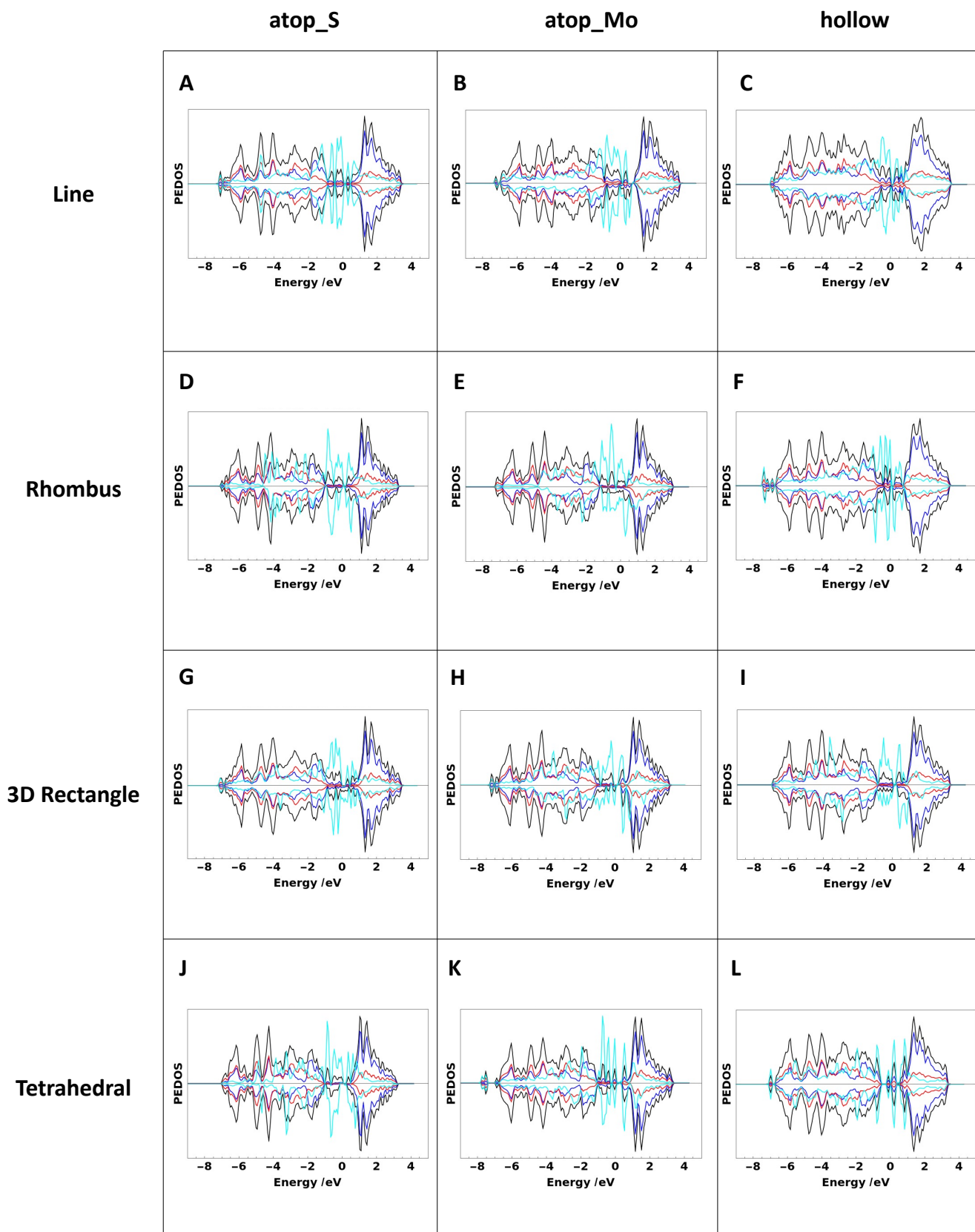


Figure A71: PEDOS for Ru₄ adsorption on MoS₂. Black - total DOS; blue - Mo d-orbital contribution; red - S p-orbital contribution; cyan - Ru d-orbital contribution

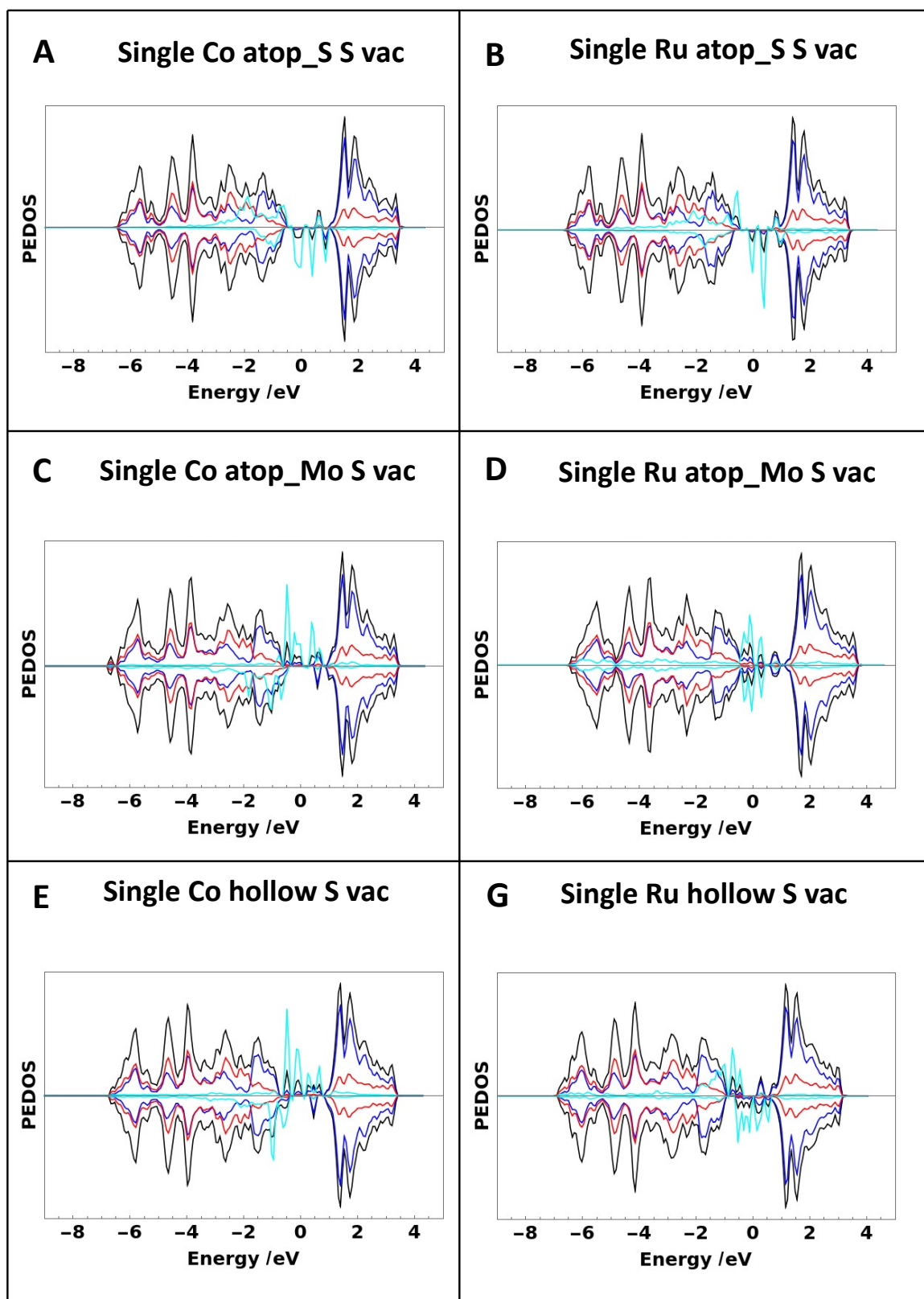


Figure A72: PEDOS for single Co and Ru atom adsorption on defective MoS₂. Black - total DOS; blue - Mo d-orbital contribution; red - S p-orbital contribution; cyan - metal d-orbital contribution

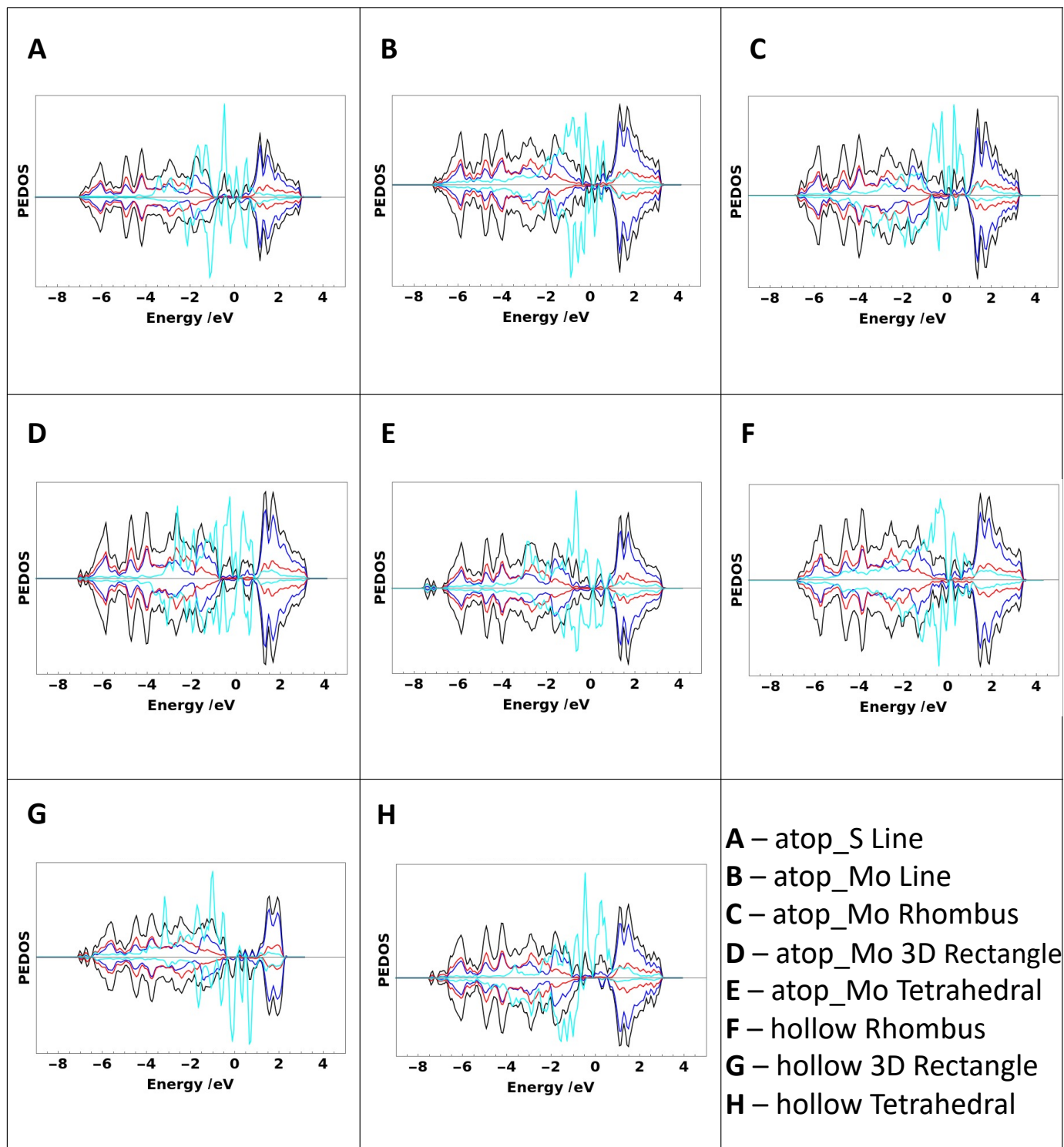
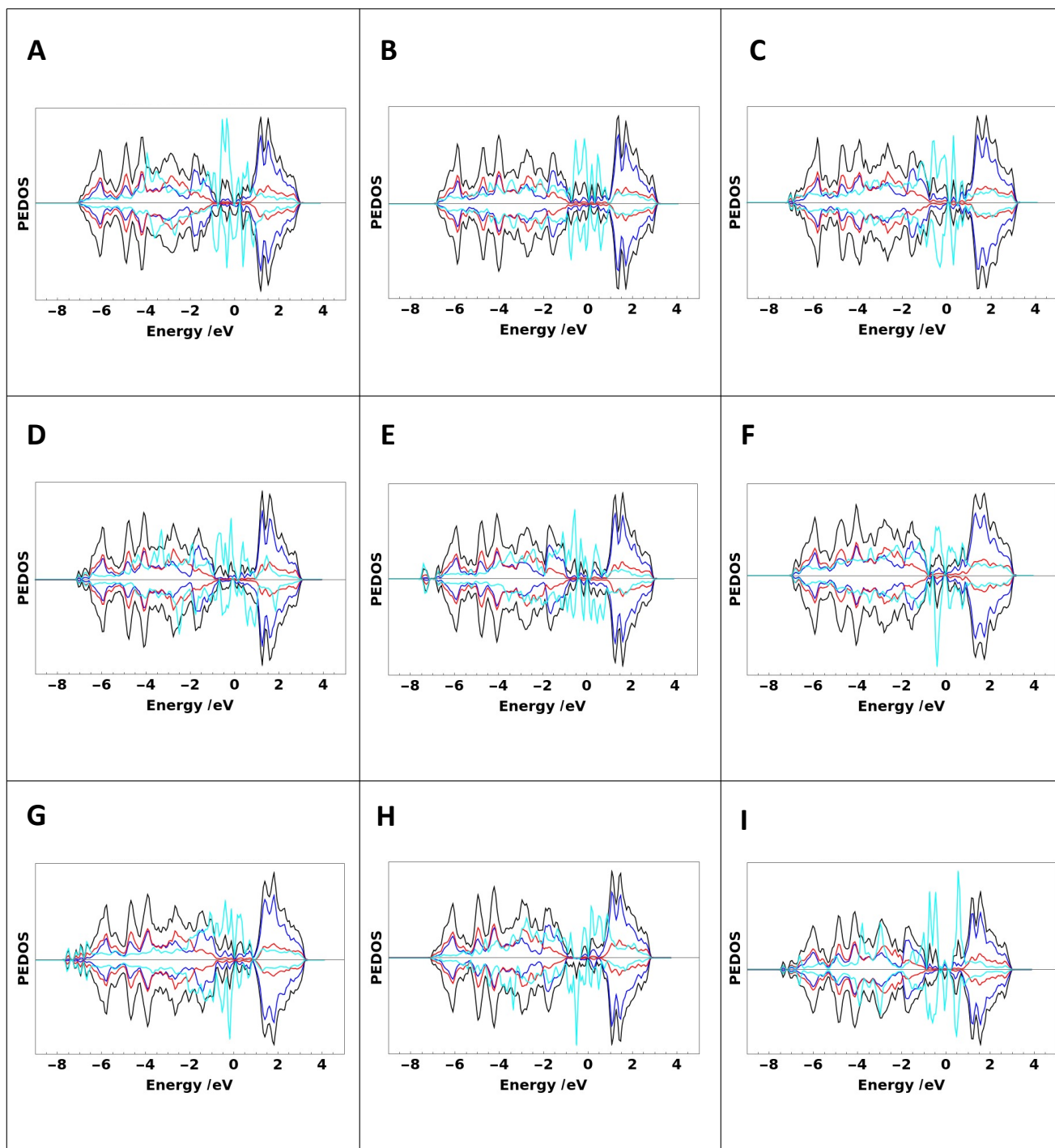


Figure A73: PEDOS for Co_4 adsorption on defective MoS_2 . Black - total DOS; blue - Mo d-orbital contribution; red - S p-orbital contribution; cyan - Co d-orbital contribution



- A** – atop_S Line
B – atop_Mo Line
C – atop_Mo Rhombus
D – atop_Mo 3D Rectangle
E – atop_Mo Tetrahedral
F – hollow Line
G – hollow Rhombus
H – hollow 3D Rectangle
I – hollow Tetrahedral

Figure A74: PEDOS for Ru_4 adsorption on defective MoS_2 . Black - total DOS; blue - Mo d-orbital contribution; red - S p-orbital contribution; cyan - Ru d-orbital contribution

A5.2: Bader Charges for Cu_n on pristine and defective MoS_2

Table A16: Computed Bader charge (Q) on each Cu atom for Cu_1 and Cu_2 on pristine MoS_2 . Cu has 11 valence electrons.

Site	Adsorption Configuration	Q(Cu.1)	Q(Cu.2)
atop_S	Single Atom	10.8	-
atop_Mo	Single Atom	10.6	-
hollow	Single Atom	10.6	-
atop_S	Neighbouring	10.8	10.8
atop_Mo	Neighbouring	10.7	10.7
hollow	Neighbouring	10.8	10.8
atop_S	Separated	10.9	10.9
atop_Mo	Separated	10.6	10.6
hollow	Separated	10.6	10.6
atop_S-atop_Mo	Non-equivalent	10.8	10.6
atop_S-hollow	Non-equivalent	10.8	10.6
atop_Mo-hollow	Non-equivalent	10.5	10.7

Table A17: Computed Bader charge (Q) on each Cu atom for different adsorption configurations of 3 Cu atoms on pristine MoS_2 . In 3D structures, Cu.1 and Cu.2 are interacting with the monolayer, while Cu.3 is at the apex of the triangle. Cu has 11 valence electrons.

Site	Configuration	Q(Cu.1)	Q(Cu.2)	Q(Cu.3)
atop_S	Line	10.8	10.9	10.9
atop_Mo	Line	10.6	10.8	10.6
hollow	Line			
atop_S	Off-set	10.8	10.8	10.8
atop_Mo	Off-set	10.6	10.7	10.7
hollow	Off-set			
atop_S	Triangle	10.8	10.8	10.8
atop_Mo	Triangle	10.7	10.7	10.7
hollow	Triangle	10.8	10.8	10.8
atop_S	3D Triangle	10.8	10.8	11.0
atop_Mo	3D Triangle	10.7	10.7	11.1
hollow	3D Triangle	10.72	10.7	11.0

Table A18: Computed Bader charge (Q) on each Cu atom for different adsorption configurations with 4 Cu atoms on pristine MoS₂. For the 3D rectangle configurations, Cu_1 and Cu_2 are interacting with the monolayer and Cu_3 and Cu_4 are adsorbed atop of Cu_1 and Cu_2. For the tetrahedron, Cu_4 is at the apex, while Cu_1, Cu_2 and Cu_3 are all interacting with the MoS₂ monolayer. Cu has 11 valence electrons.

Site	Configuration	Q(Cu_1)	Q(Cu_2)	Q(Cu_3)	Q(Cu_4)
atop_S	Line	10.8	10.8	11.0	10.8
atop_Mo	Line	10.6	10.8	10.8	10.6
hollow	Line	10.6	10.8	10.8	10.6
atop_S	Rhombus	10.9	10.8	10.9	10.8
atop_Mo	Rhombus	10.8	10.9	10.8	10.8
hollow	Rhombus	10.6	10.8	10.8	10.6
atop_S	3D Rectangle	10.8	10.8	11.1	11.1
atop_Mo	3D Rectangle	10.7	10.7	11.1	11.1
hollow	3D Rectangle	10.7	10.7	11.0	11.0
atop_S	Tetrahedral	10.9	10.8	10.9	11.0
atop_Mo	Tetrahedral	10.7	10.7	10.7	11.1
hollow	Tetrahedral	10.7	10.7	10.7	11.0

Table A19: Computed Bader charge (Q) on each Cu atom for all Cu₁ and Cu₄ adsorption structures on the MoS₂ monolayer with an S vacancy. For the tetrahedral configuration, Cu_4 is at the apex, while the other three atom are interacting with the monolayer. The rhombus structure rearranged, Cu_1 here does not interact with the monolayer. Cu has 11 valence electrons.

Site	Configuration	Q(Cu_1)	Q(Cu_2)	Q(Cu_3)	Q(Cu_4)
atop_S	Single Atom	10.9	-	-	-
atop_Mo	Single Atom	10.5	-	-	-
hollow	Single Atom	10.5	-	-	-
atop_S	line	10.9	10.9	10.9	10.8
atop_Mo	line	10.8	10.8	10.7	10.6
atop_Mo	rhombus	11.1	10.8	10.8	10.5
atop_Mo	tetrahedral	10.7	10.7	10.7	11.1
hollow	tetrahedral	10.6	10.7	10.7	11.0

A5.3: Bader Analysis of Co and Ru structures on pristine MoS₂

A metallic Co atom has all 9.0 valence electrons, while an atom is considered oxidised when it has a Bader charge of less than 9.0 electrons. Similarly, metallic Ru has 8.0 valence electrons, and oxidised Ru will have a Bader charge of less than 8.0 electrons. Analysis of the Bader charges for Co adsorption shows that in general atoms bound to the MoS₂ ML are oxidised, while adatoms that are only bound to other Co atoms remain metallic. A single exception to this was observed for the tetrahedral configuration at site **hollow**. Here, the atop atom is slightly oxidised with 8.7 electrons. The base atoms for this structure are incorporated into the S layer, which could have caused a change to the charge distributions of this structure.

There is some variance in how strongly Co atoms are oxidised, depending on the adsorption site and particular configurations. This means the oxidation is directly influenced by the coordination of each atom, with some correlation between stronger oxidation (Bader charge ~ 8.5 electrons) and more favourable adsorption energies. Mo atoms are not electronically affected by the presence of Co. There are some changes to the oxidation state of S atoms around the adsorption site, but the difference is minimal, varying by ± 0.1 electrons, depending on the proximity to Co.

For Ru we find that atoms are slightly oxidised when adsorbing to the MoS₂ ML, with a Bader charge of around 7.6 to 7.8 electrons, compared to metallic Ru with 8.0 electrons. As the quantity of metal adatoms increases, atoms tend to be less oxidised, becoming more metallic in nature. Any Ru atom in a 3D configuration that is only adsorbed to other Ru atoms remains metallic with Bader charges of 7.9 to 8.0 electrons. As for Co, the exception to this is the tetrahedral configuration at site **hollow**. Here, three S atoms have moved out of the ML to form an Ru₄S₃ cluster with the adsorbed Ru₄ structure. With a Bader charge of 7.6 electrons we find that the atop Ru has become oxidised through its bond with S atoms. There are no changes to the Mo charges throughout the surface. S is affected by the presence of Ru more than by the presence of Co. Nearby S atoms gain less electrons (6.4 electrons) than those that have distorted from their original lattice position (6.6 electrons) to accommodate Ru adsorption. S atoms that have rearranged and formed Ru-S clusters are found to also be less reduced, typically with about 6.3 electrons, while there is no change to the charge of S atoms further away from the adsorption site (6.5 electrons). These changes in oxidation state are likely related to the coordination environment of the S atoms.

Table A20: Computed Bader charge (Q) on each Co and Ru atom for M₁ and M₂ configurations on pristine MoS₂. Co has 9 valence electrons and Ru has 8 valence electrons.

Site	Adsorption Configuration	Q(Co_1)	Q(Co_2)	Q(Ru_1)	Q(Ru_2)
atop_S	Single Atom	8.7	-	7.7	-
atop_Mo	Single Atom	8.5	-	7.6	-
hollow	Single Atom	8.5	-	7.6	-
atop_S	Neighbouring	8.6	8.6	7.8	7.7
atop_Mo	Neighbouring	8.6	8.6	7.7	7.8
hollow	Neighbouring	8.6	8.6	7.7	7.8
atop_S	Separated	8.8	8.8	7.8	7.8
atop_Mo	Separated	8.5	8.5	7.6	7.6
hollow	Separated	8.7	8.6	7.6	7.6
atop_S-atop_Mo	Non-equivalent	8.7	8.7	7.8	7.7
atop_S-hollow	Non-equivalent	8.7	8.7	7.8	7.7
atop_Mo-hollow	Non-equivalent	8.6	8.6	7.7	7.9

Table A21: Computed Bader charge (Q) on each Cu atom for different adsorption configurations of 3 Co and Ru atoms on pristine MoS₂. In 3D structures, M_1 and M_2 are interacting with the monolayer, while M_3 is at the apex of the triangle. Co has 9 valence electrons and Ru has 8 valence electrons.

Site	Configuration	Q(Cu_1)	Q(Co_2)	Q(Co_3)	Q(Ru_1)	Q(Ru_2)	Q(Ru_3)
atop_S	Line	8.7	8.8	8.7	7.8	7.9	7.8
atop_Mo	Line	8.6	8.6	8.6	7.8	7.8	7.7
hollow	Line	8.7	8.7	8.7	7.8	7.9	7.9
atop_S	Triangle	8.6	8.7	8.7	7.8	7.7	7.8
atop_Mo	Triangle	8.7	8.6	9.0	7.8	7.8	7.8
hollow	Triangle	8.7	8.6	8.7	7.8	7.8	7.8
atop_S	3D Triangle	8.8	8.7	9.0	7.8	7.8	8.0
atop_Mo	3D Triangle	8.7	8.7	9.0	7.7	7.8	7.8
hollow	3D Triangle	8.7	8.7	9.0	7.7	7.8	7.9

Table A22: Computed Bader charge (Q) on each Co or Ru atom for different adsorption configurations with 4 metal atoms on pristine MoS₂. The numbering convention is based on the geometry prior to relaxation. For the 3D rectangle configurations, M_1 and M_2 are interacting with the monolayer and M_3 and M_4 are adsorbed atop of M_1 and M_2. For the tetrahedron, M_4 is at the apex, while M_1, M_2 and M_3 are all interacting with the MoS₂ monolayer. Co has 9 valence electrons and Ru has 8 valence electrons.

Site	Configuration	Q(Co_1)	Q(Co_2)	Q(Co_3)	Q(Co_4)	Q(Ru_1)	Q(Ru_2)	Q(Ru_3)	Q(Ru_4)
atop_S	Line	8.6	8.7	8.7	8.7	7.8	7.9	7.8	7.8
atop_Mo	Line	8.6	8.6	8.6	8.6	7.8	7.8	7.7	7.74
hollow	Line	8.8	8.8	8.7	8.7	7.8	7.9	7.8	7.9
atop_S	Rhombus	8.8	8.8	8.8	8.8	7.8	7.9	7.9	7.9
atop_Mo	Rhombus	8.8	8.8	8.9	8.7	7.8	7.8	7.8	7.8
hollow	Rhombus	8.5	8.7	8.7	8.7	7.8	7.8	7.8	7.8
atop_S	3D Rectangle	8.7	8.7	8.7	9.0	7.8	7.8	7.9	7.9
atop_Mo	3D Rectangle	8.7	8.7	8.7	9.0	7.7	7.8	8.0	8.0
hollow	3D Rectangle	8.8	8.7	8.7	8.8	7.8	7.7	7.9	7.9
atop_S	Tetrahedral	8.8	8.8	8.8	9.0	7.8	7.8	7.8	8.1
atop_Mo	Tetrahedral	8.7	8.7	8.7	9.0	7.8	7.8	7.7	8.1
hollow	Tetrahedral	8.8	8.9	8.8	8.7	7.8	7.8	7.8	7.6

A5.4: Bader Analysis of Co and Ru structures on defective MoS₂

We find that the presence of the vacancy has a different effect on Co compared to Ru in terms of bader charges. A Co atom adsorbed at site **atop_S** and thus in the vacancy is less oxidised than on the pristine surface. In contrast, Ru adsorbed in the same manner is found to be more oxidised. Co adsorbed at site **atop_Mo** is more oxidised compared to adsorption at site **atop_Mo** on the pristine surface, while Co at site **atop_Mo** and Ru at sites **atop_Mo** and **hollow** have an oxidation state comparable to the same adsorptions on the pristine surface.

Atoms away from the vacancy tend to be more oxidised than those close to it. This is particularly noticeable for the rearranged rhombus configuration at site **atop_Mo**, where the fourth atom that is adsorbed away from the vacancy is more oxidised with 8.5 electrons, and the atoms near the vacancy are less oxidised with 8.8 and 8.7 electrons. A similar effect is observed for most configurations.

As for Co, the separated fourth atom that is adsorbed away from the vacancy is more oxidised than the other Ru atoms. S atoms that were displaced due to adsorption or have moved out of the ML and into the Ru cluster are slightly less reduced, including the S atom incorporated with Ru for the line configuration at site **hollow**, which has 6.4 electrons. The oxidation state of Mo is not affected by Ru adsorption.

The S atom that has moved out of the surface for the rhombus configuration at site **hollow** is less reduced than other S atoms, with 6.4 electrons, and S atoms surrounding the adsorption site are somewhat more reduced than others in the ML with 6.6 electrons. As on the pristine surface, the oxidation state of Mo atoms does not change, either from Co adsorption or the presence of the vacancy.

Site	Configuration	Q(Co.1)	Q(Co.2)	Q(Co.3)	Q(Co.4)	Q(Ru.1)	Q(Ru.2)	Q(Ru.3)	Q(Ru.4)
atop_S	Line	8.9	8.8	8.9	8.7	8.0	7.7	7.8	7.8
atop_Mo	Line	8.8	8.6	8.6	8.8	7.8	7.8	7.7	7.8
hollow	Line	-	-	-	-	7.7	7.9	7.8	7.9
atop_Mo	Rhombus	8.8	8.6	9.0	8.6	7.8	7.6	8.1	7.8
hollow	Rhombus	8.7	8.7	8.8	8.8	7.8	7.8	7.7	7.8
atop_Mo	3D Rectangle	8.7	8.7	8.9	8.9	7.7	7.7	8.0	8.0
hollow	3D Rectangle	8.6	8.6	9.0	8.6	7.7	7.8	7.9	8.0
atop_Mo	Tetrahedral	8.7	8.7	8.7	9.0	7.7	7.8	7.8	8.0
hollow	Tetrahedral	8.7	8.6	8.6	9.0	7.7	7.7	7.7	8.0

Table A23: Computed Bader charge (Q) on each Co or Ru atom for different adsorption configurations with 4 metal atoms on defective MoS₂. The numbering convention is based on the geometry prior to relaxation. For the 3D rectangle configurations, M.1 and M.2 are interacting with the monolayer and M.3 and M.4 are adsorbed atop of M.1 and M.2. For the tetrahedron, M.4 is at the apex, while M.1, M.2 and M.3 are all interacting with the MoS₂ monolayer.

A5.5: Charge Density Difference of Cu, Co and Ru structures on MoS₂

Changes to the charge density for a selection of adsorption geometries are shown in Figures A75, A76 and A77. The charge density differences were extracted from VASP output files using scripts available as part of the Bader charge partitioning scheme. [12, 13] The difference between the charge density of the total system and the sum of the charge densities of the MoS₂ ML and the adsorbed metal cluster can be determined with these and then visualised using VESTA.

The changes in charge density are localised around the adatoms and the Mo and S atoms in the immediate vicinity. Atoms that were found to be near metallic during the Bader analysis are also found to have somewhat less charge density compared to atoms that were oxidised. This is especially visible for the Ru₄ line configuration at site **hollow** (see Fig.A77E). Here, the four adatoms all have approximately 7.8 electrons which is reflected in the minimal charge density difference. It is also of note that for this configuration, there is significant distortion of the surrounding S atoms, which are slightly more oxidised compared to other S atoms in the ML. This can be observed in some small charge density differences around these S atoms, but overall, this particular configuration shows very little changes in charge density, as compared to the other structures. There is no distinct difference in how Co and Ru affect the charge density with adsorption to MoS₂.

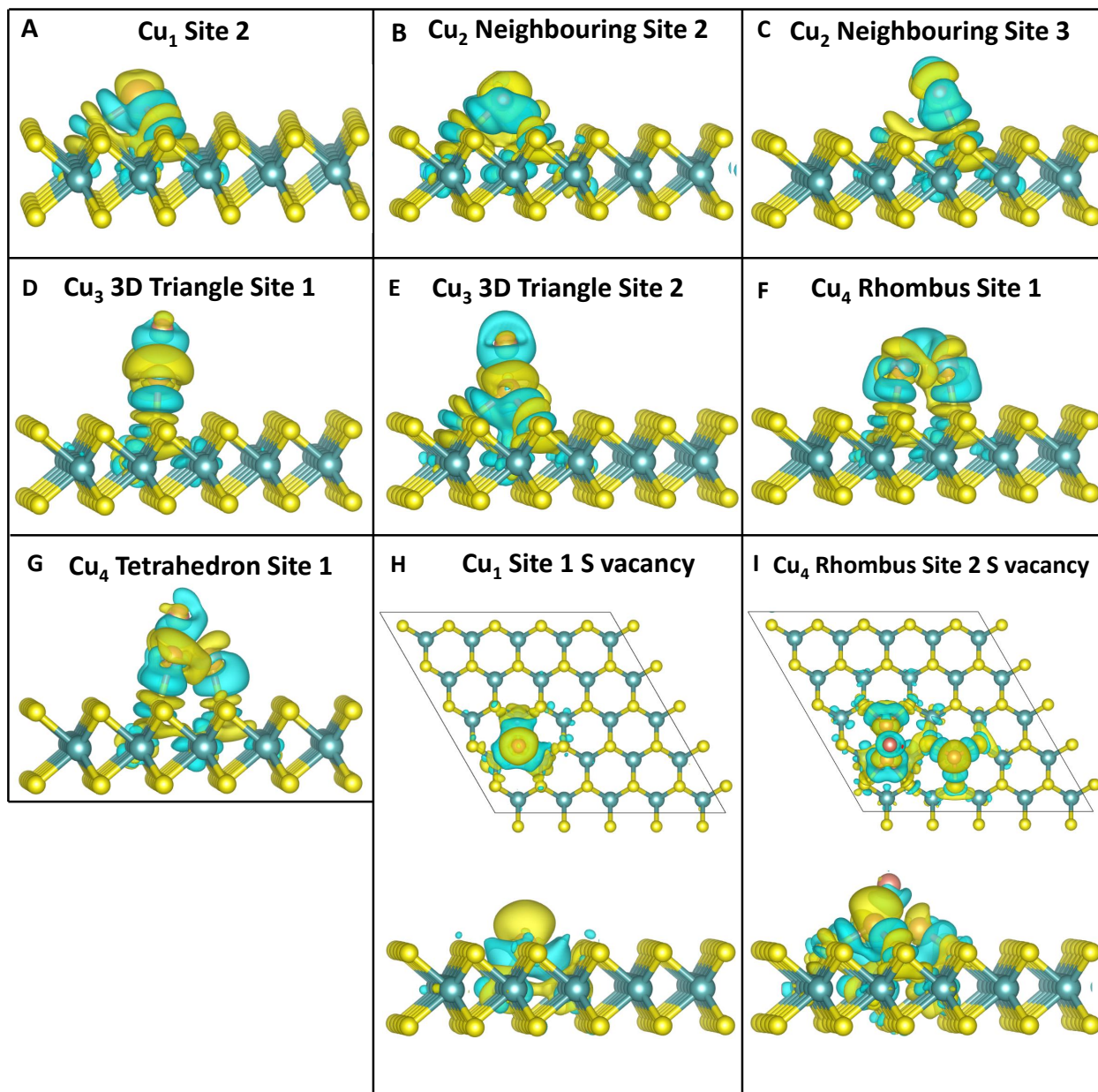


Figure A75: Charge density difference after adsorption of the most favourable Cu_n on pristine (A-G) and defective (H and I) MoS₂.

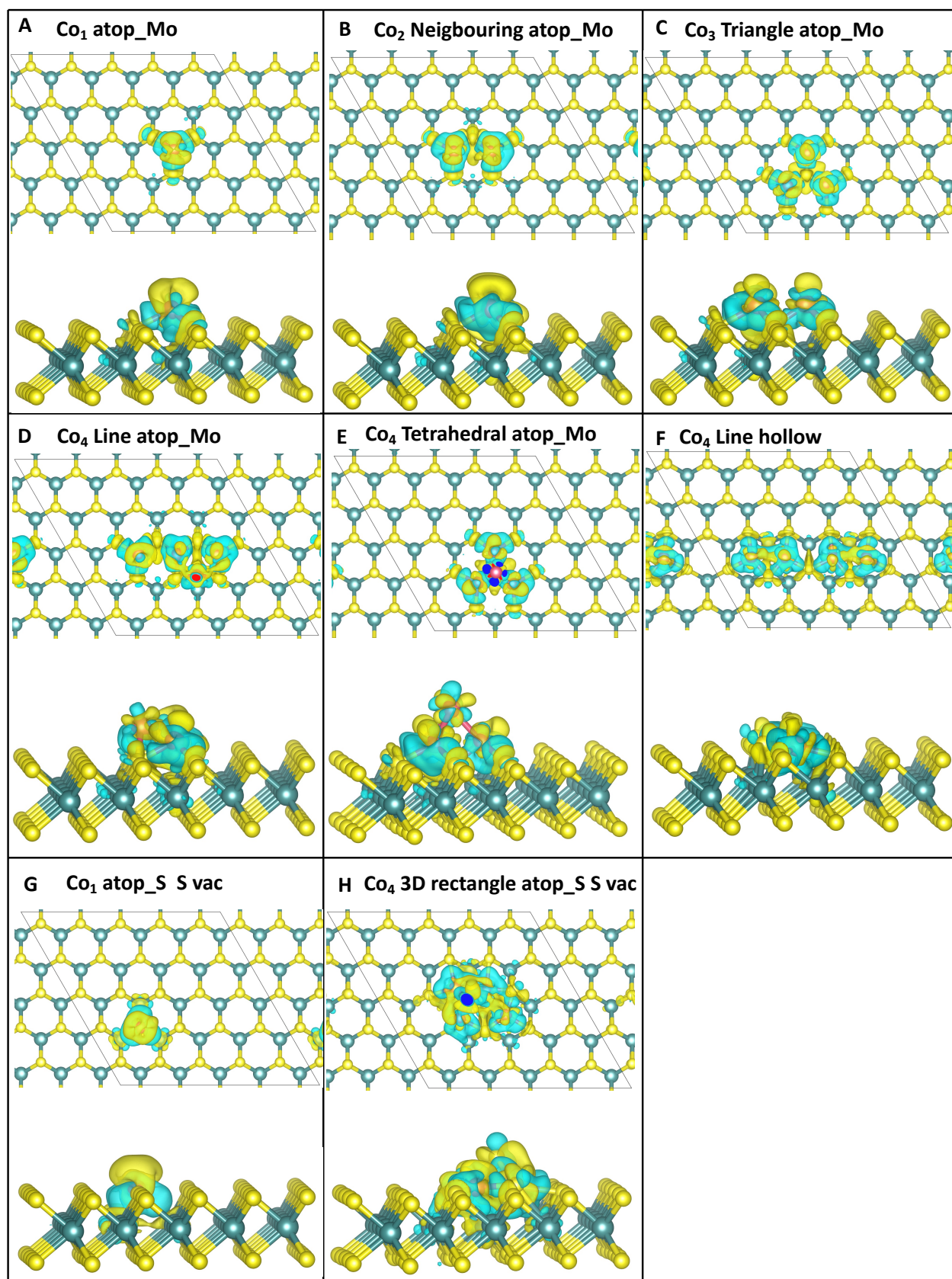


Figure A76: Charge Density Difference computed for most favourable Co adsorptions.

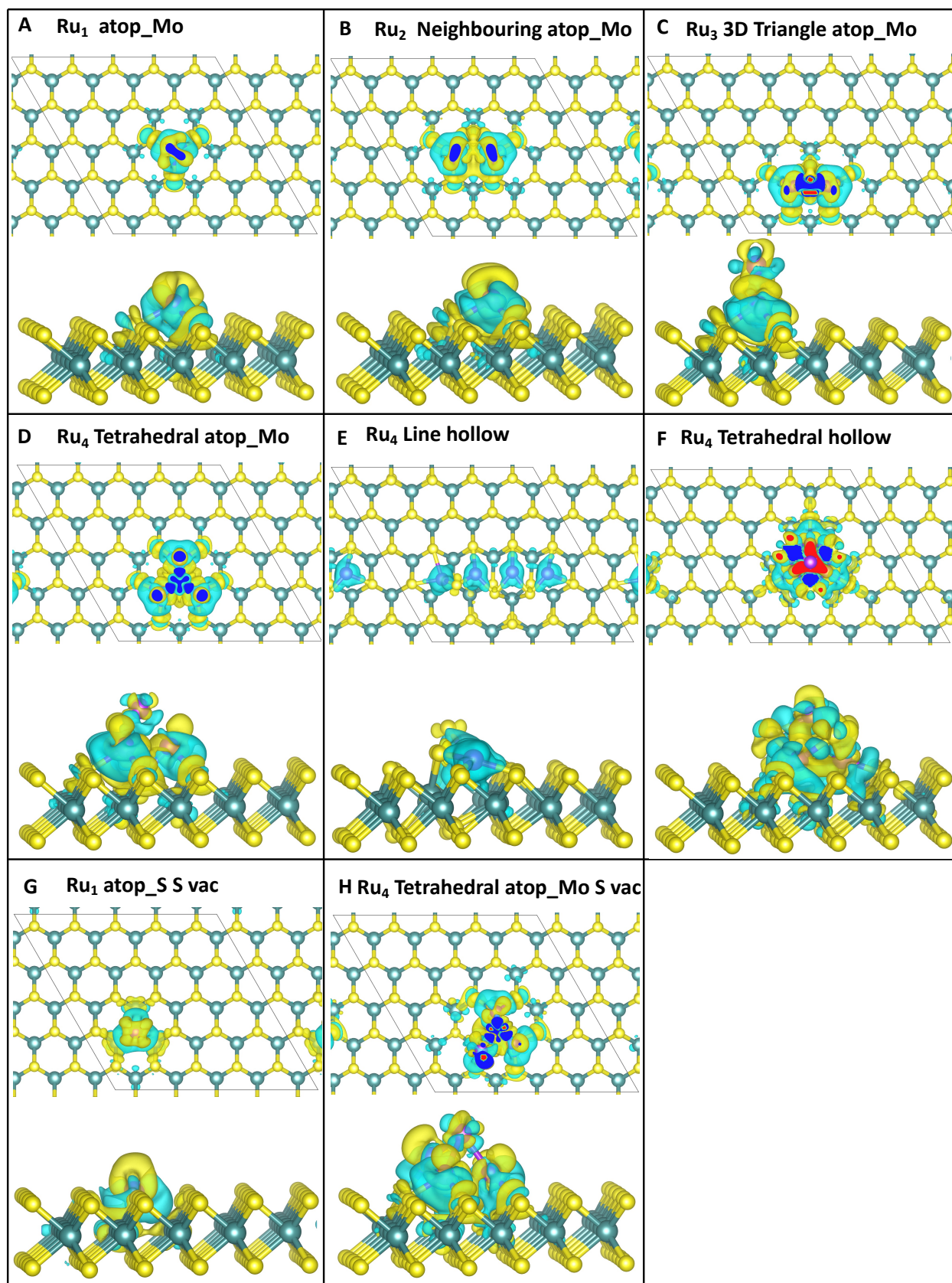


Figure A77: Charge Density Difference computed for most favourable Ru adsorptions.

A5.6: Cu atom repelled from ML

An example of a Cu atom that is repelled from the MoS₂ ML is shown in Fig. A78. This occurred during the relaxation of several Cu₄ structures on the MoS₂ monolayer with an S vacancy.

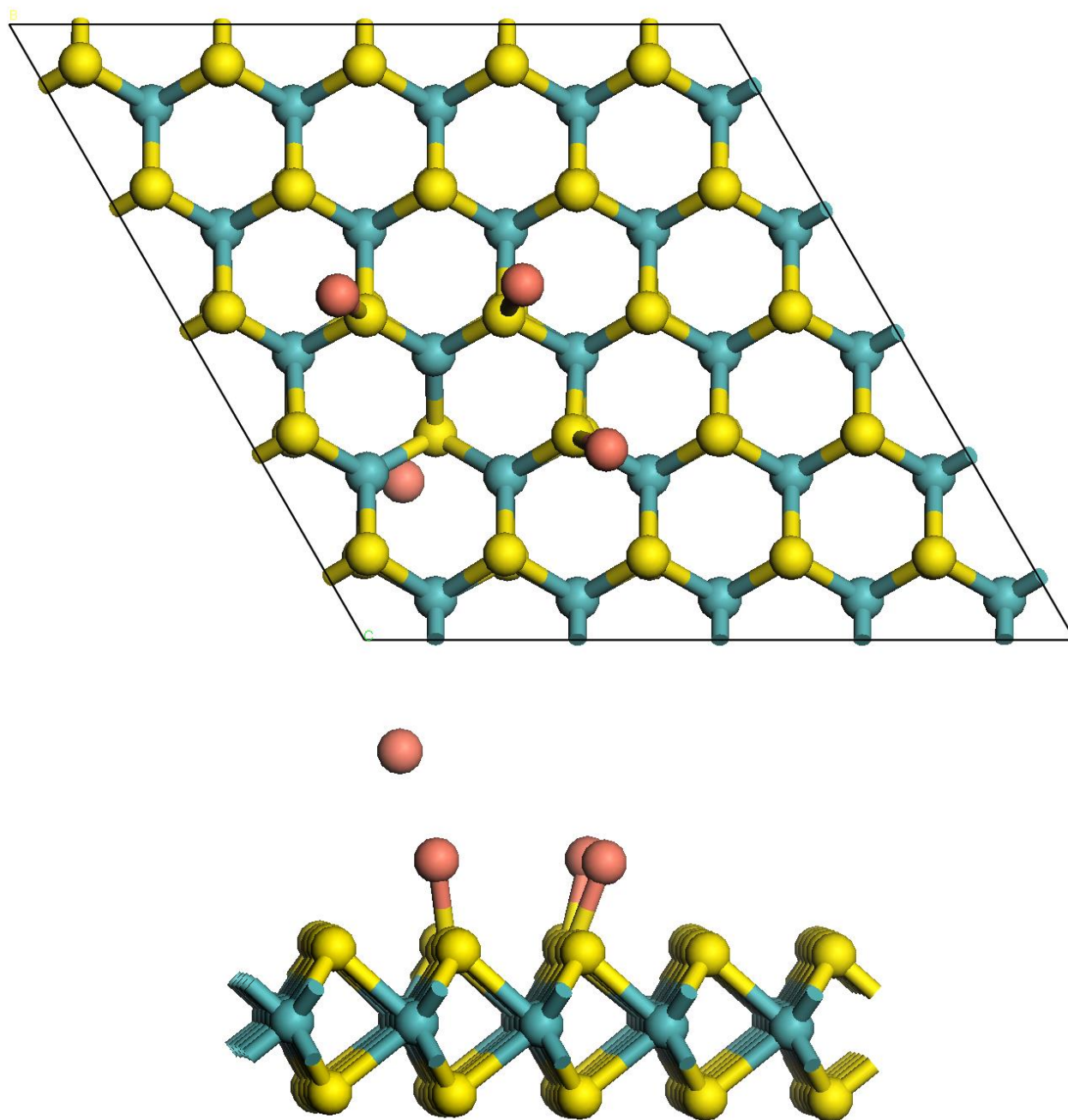


Figure A78: Cu atom is repelled from the surface during the geometry relaxation.

A5.7: Co and Ru Geometries on MoS₂

A5.7.1: Co₄ adsorption on pristine MoS₂

The other two configurations with atom migrations are the linear configuration at site **atop_S** and the 2D rhombus configuration at site **atop_Mo**. For the former, one of the atoms migrates from its location at site 1 to bridge between two S atoms half way between site **atop_Mo** and **hollow**, forming a triangle with two of the atoms (see Figure 13A, Chapter 7). For the latter, atoms migrate closer to each other during relaxation, with one atom at site **hollow**, another remaining at site **atop_Mo** and the third and fourth atom binding only to the other Co atoms and thus forming a 3D rhombus structure (see Figure 13E, Chapter 7). These rearrangements show that if Co atoms are close enough to each other that bonds can be formed, 3D clusters form that resemble a tetrahedron.

A5.7.2: Ru₄ adsorption on pristine MoS₂

Two of the atoms in the line configuration at site **atop_S** migrated to a site **hollow**, while the two atoms that were originally atop in the 3D rectangle configuration at site **atop_S** migrated to the ML and adsorbed at site **atop_Mo** on either side of the two base atoms, as shown in Figure 14A and G in Chapter 7. The latter structure is also the least favourable geometry for Ru₄, with an adsorption energy of -3.29 eV. Similarly to the migrations observed for its Co₄ counterpart, the rhombus configuration at site **atop_Mo** is distorted with one atom at site **hollow**, one remaining at site **atop_Mo** and the other two atoms slightly removed from their original position at site **atop_Mo** to allow for Ru-Ru bonding (see Figure 14E, Chapter 7). One of the atoms has also lifted away from the surface and is thus only bound to other Ru atoms.

A5.8: Addition Energies of Co and Ru structures on MoS₂

Calculating addition energies allows us to study the energy gain as more atoms are added to a structure. Due to the many rearrangements of configurations observed, the energy gain computed from Eq.4 also contains the energy gained from the rearrangement. We observe particularly large addition energies for structures such as the Co₄ line and 3D rectangle configurations, when rearrangements occur to realise a particularly favourable structure. Smaller addition energies are observed for rearrangements to a structure that is less favourable. Where no rearrangement occurs, the addition energies are of similar magnitude for different configurations, indicating that the variation arises only from the structure. For Ru adsorption, the range of addition energies observed is larger than for Co adsorption, as more rearrangements occur. While most of the major geometry rearrangements occurred for structures at site **hollow**, most of the variation in addition energy happens for adsorptions at site **atop_S**. The least favourable addition of -0.52 eV occurs when moving from the site **atop_S** Ru₃ triangle configuration to the site **atop_S** Ru₄ 3D rectangle configuration. This is likely caused by the Ru₄ structure migrating from its original configuration to a 2D formation, causing the overall energy gain to be quite small. Other less favourable addition energies are typically associated with structures that are somewhat distorted or

No. metal atoms	Configuration	Co E_{add}			Ru E_{add}		
		atop_S	atop_Mo	hollow	atop_S	atop_Mo	hollow
2	neighbouring	-	-6.29	-5.88	-	-4.97	-3.82
	separated	-4.19	-5.81	-5.90	-2.44	-3.92	-4.10
	non-equivalent	-6.91/-5.30	-6.54/-5.20	-4.29/-6.15	-5.52	-4.95	-2.97
3	line	-4.72	-6.12	-6.17	-7.13	-4.52	-5.74
	triangle	-4.18	-6.28	-6.21	-2.61	-5.06	-5.89
	3D triangle	-4.50	-6.06	-5.23	-7.56	-5.26	-5.58
4	line	-7.60	-6.18	-6.17	-4.89	-4.77	-5.80
	rhombus	-7.15	-5.33	-5.81	-10.75	-3.17	-4.09
	3D rectangle	-8.51	-7.17	-7.05	-0.52	-5.58	-5.40
	tetrahedral	-7.11	-6.88	-6.55	-11.11	-6.62	-5.58

Table A24: Computed addition Energies for each Ru and Co configuration ($M_{n-1} + M \rightarrow M_n$) using Eq.4. For the "non-equivalent" configurations for 2 metal atom adsorption, the column "site 1" has atoms at sites 1 and 2, "site 2" has atoms at 1 and 3 and "site 3" has atoms at 2 and 3.

have a less favourable binding energy such as the site **atop_Mo** Ru₄ rhombus configuration. Similarly, very favourable addition energies are associated with structures that form Ru-Ru bonds due to addition of a second atom, such as the transition from neighbouring atoms at site **atop_S** to the Ru₃ line at site **atop_S**, or simply where the addition of an atom yields a much more favourable structure as is the case for adding an atom to neighbouring atoms at site **atop_S** to create the Ru₃ 3D triangle at site **atop_S**. The two largest addition energies are observed for the addition of an atom to the Ru₃ triangle configuration at site **atop_S** to create the rhombus and tetrahedral configurations at site **atop_S**. These structures have addition energies of -10.75 and 11.11 eV, respectively. This is because the triangle configuration at site **atop_S** is the least favourable Ru₃ structure.

A5.9: Bondlengths of Co and Ru structures on MoS₂

A5.9.1: One atom adsorption

We find that for a single adatom, Co-S bonds are shortened to between 1.99 and 2.16 Å compared to 2.31 Å in bulk CoS₂, while Ru-S bonds are shortened to between 2.13 and 2.24 Å compared to 2.37 Å in bulk RuS₂. The shortest metal-S bonds are measured at site **atop_S**. Co-Mo distances are about 0.3 Å longer compared to 2.56 Å in bulk Co₃Mo. There are no Ru-Mo bonds for single atom adsorption, which is one possible origin for enhanced Co binding, compared to Ru. The length of Mo-S bonds is largely unaffected, with changes around 0.03 Å for sites **atop_S** and **atop_Mo** and of up to 0.1 Å for site **hollow**.

A5.9.2: Two atom adsorption

Co-Co bonds are between 2.26 and 2.34 Å long, depending on the adsorption sites, which is shorter compared to the Co-Co bulk length of 2.48 Å. As for single atom adsorption, Co-S atoms are shorter, particularly at site **atop_S**, and range between 1.99 and 2.16 Å. Co-Mo distances continue to be longer compared to the bulk. Mo-S bonds remain largely unaffected, deviating in lengths by -0.01 to +0.2 Å, and both shortest and longest bonds are typically measured for those configurations that have caused slight distortions to the ML. These are neighbouring adsorptions at site **atop_Mo**, adsorptions at site **atop_S** and **hollow** and adsorption at site **atop_Mo** and **hollow**, as shown in Fig. 9B, H and I, in Chapter 7.

Ru-S and Ru-Mo bonds tend to be shorter, compared to their bulk equivalents, and do not appear to be affected by adsorption site. Ru-S bonds range from 2.13 to 2.37 Å, compared to 2.37 Å in the bulk and Ru-Mo bonds range from 2.46 to 2.72 Å, compared to 2.71/2.76 Å in bulk RuMo. Variation within the measured Mo-S bonds are caused by distortions in the lattice structure, due to Ru adsorption. Bonds deviate from the bulk length of 2.42 Å by -0.3 to +0.2 Å.

A5.9.3: Three atom adsorption

Co-Co bonds were measured to range between 2.08 and 2.64 Å, compared to 2.48 Å in the bulk. The line configuration at site **atop_S** and the 3D triangle at site **atop_Mo** have a mixture of bonds on the shorter and longer end of the range, while the triangle at site **hollow** has only longer Co-Co bonds. For all other configurations, Co-Co bonds are on the shorter end of the range, indicating that Co₃ stability is not influenced by either presence or length of Co-Co bonds.

Co-S bond lengths can be longer or shorter than the bulk length of 2.31 Å, ranging between 2.08 and 2.36 Å depending on the adsorption structure. Most bonds are on the shorter end of the range, particularly for the 2D triangle structures, indicating a potential correlation between shorter Co-S bonds and less favourable structures. Longer bonds occur less frequently, but can be found for all three different adsorption structures.

The majority of Mo-S bonds are within 0.1 Å of the length in the bare ML, which is 2.42 Å. In structures with some surface rearrangements, Mo-S bonds tend to deviate from this near the adsorption sites, and can become somewhat longer compared to elsewhere in the ML, with an increase in length of up to 0.3 Å. These longer Mo-S bonds are also observed for the triangle configuration at site **atop_S** and the 3D triangle for site **atop_Mo**, even though no distortions are visible.

All Ru-Ru bonds measured here are shorter ranging from 2.29 to 2.52 Å, compared to 2.67 Å in the bulk. Ru-S bonds are overall slightly shorter, with some longer bonds measured for configurations with atoms that are quite close to each other, as well as the line configuration at site **hollow**, likely due to the ML distortions observed here. Lengths range between 2.14 and 2.49 Å, compared to 2.37 Å in the bulk. Once again, distortions in the ML are also reflected in some Mo-S bondlengths changes, although the overall deviation of -0.05 to +0.23 Å from the bare ML is quite small.

A5.9.4: Four atom adsorption

The majority of Co-Co bonds measured are shorter compared to bulk, by up to $-0.4 \text{ \AA}$. However, half of the Co_4 configurations also have Co-Co bonds that are longer compared to bulk, by up to $+0.3 \text{ \AA}$. In particular, this is the case for the various tetrahedral configurations, where due to the geometry some bonds are longer than others.

Co-S bonds are found to be either shorter or similar in length to the bulk length of $2.31 \text{ \AA}$, ranging from 2.06 to $2.31 \text{ \AA}$. with a single Co-S bond that is $2.54 \text{ \AA}$ long. This is measured for the 3D rectangle at site **hollow**, and has an increased length due to geometry distortions. Co-Mo distances are consistently longer than the bulk length of $2.55/2.56 \text{ \AA}$, with increases of up to $0.35 \text{ \AA}$. The majority of Mo-S bonds are the same lengths as the on a bare ML ($2.42 \text{ \AA}$) or slightly longer in a range up to $2.69 \text{ \AA}$, with a small number of bonds that are up to $0.04 \text{ \AA}$ shorter. The longer bonds are formed due to lattice distortions.

All Ru-Ru bonds measured for Ru_4 , are shorter than the bulk length of $2.67 \text{ \AA}$, in a range between 2.11 to $2.65 \text{ \AA}$. Similarly to what we observe for Co-S bonds, Ru-S bonds are overall shorter than in the bulk length of $2.37 \text{ \AA}$, with a few exceptions of longer bonds, in a range between 2.18 and $2.52 \text{ \AA}$. These longer bonds are measured for adsorptions at site **hollow** caused by the lattice distortions. Ru-S bonds at site **atop_Mo** are very similar in length to bonds in the bulk, a possible cause for favourable adsorption. Ru-Mo bonds in the bulk are either 2.71 or $2.75 \text{ \AA}$ long. For Ru_4 adsorption, Ru-Mo bonds are only formed at site **hollow** adsorptions and can be either shorter or longer than the bulk in a range between 2.55 and $2.82 \text{ \AA}$. The majority of Mo-S bonds is similar to or slightly longer than the bulk length of $2.42 \text{ \AA}$. Longer bonds were measured at site **hollow** and the shortest bonds were measured for site **atop_S**. The overall range was between 2.24 and $2.56 \text{ \AA}$.

A5.10: Co and Ru structures on Defective MoS_2

A5.10.1: Bondlengths

A5.10.1.1: Single atom adsorption

Both Co-S and Ru-S bonds are found to be shorter than the bulk of $2.31 \text{ \AA}$ and $2.37 \text{ \AA}$, respectively, for one adatom adsorption on the defective ML. Co-S bonds range between 2.02 and $2.05 \text{ \AA}$ and Ru-S bonds range between 2.18 and $2.28 \text{ \AA}$. Co-Mo distances are found to be slightly longer by up to $0.3 \text{ \AA}$ than the bulk of $2.55/2.56 \text{ \AA}$ for adsorption at site **atop_Mo** and **hollow**, while distances at site **atop_S** are shorter than the bulk by about $0.1 \text{ \AA}$. Ru-Mo bonds are only formed at site **atop_S** and range between 2.62 and $2.66 \text{ \AA}$, which is slightly shorter than the bulk of $2.71/2.76 \text{ \AA}$. As for other sites Mo-S bonds range within $0.1 \text{ \AA}$ compared to the bare surface of $2.42 \text{ \AA}$ with slightly longer bonds for Ru adsorption at sites **atop_Mo** and **hollow** and slightly shorter bonds at site **atop_S**.

A5.10.1.2: Four atom adsorption

Co-Co bonds are found to be overall similar to bulk of 2.48 Å, while the line configuration at sites **atop_S** and **atop_Mo** and the rhombus configuration at site **atop_Mo** all have slightly shorter Co-Co bonds ranging between 2.14 and 2.38 Å. Co-S bonds are shorter for adsorption at site **atop_S** and **atop_Mo**, ranging between 2.02 and 2.26 Å. For adsorptions at site **hollow**, we find both shorter bonds and slightly longer bonds than the bulk equivalent, ranging between 2.10 and 2.83 Å. Co-Mo distances vary widely depending on the geometry in question, as due to migration into the vacancy and metal incorporation into the S layer, some Co atoms are closer to Mo than others. Lengths range between 2.40 and 2.88 Å, with most on the longer end of the spectrum. Mo-S bonds remain within 0.1 Å of the bare ML, except for the typical elongations and contractions caused by ML distortions.

Ru-Ru bonds are found to be shorter than in Ru bulk of 2.67 Å, ranging between 2.14 and 2.60 Å. Ru-S bonds are overall very similar in lengths to the bulk ranging between 2.10 and 2.53 Å, which makes them slightly longer compared to the pristine surface where the majority of Ru-S bonds was found to be significantly shorter than in the bulk. Ru-Mo distances are mostly similar to bulk, however for configurations with Ru atoms in or near the vacancy site these distances tend to be shorter. The various bondlengths measured range between 2.60 and 2.83 Å. Mo-S bonds are unaffected and typically measured within 0.1 Å of the bare surface reference, as there are no significant lattice distortions for Ru adsorption on the defective ML.

A5.11: Impact of van der Waal's Interactions Co and Ru strucures on MoS₂

We compared the impact of applying vdW corrections for five Co and five Ru geometries. Nine of the ten structures tested showed no changes to geometry and a consistent increase of the binding energy by ca. 3 eV for Co and ca. 4 eV for Ru, as shown in Tables S2 and S3. The Co **atop_Mo** rhombus structure rearranges into a tetrahedral structure. Overall, there is no considerable impact on the geometries or energies of the Co and Ru clusters on MoS₂, indicating that they do not play a significant role in the system and can therefore be omitted.

Geometry	E _{bind} /Co[eV]	E _{bind} /Co[eV] with vdW	Changes with vdW
Line atop_Mo	-6.10	-9.71	None
Tetrahedron atop_Mo	-6.32	-9.83	None
Rhombus atop_Mo	-5.93	-9.86	Relaxed to tetrahedron
Line atop_Mo S vac	-6.22	-9.78	None
Tetrahedron atop_Mo S vac	-6.22	-9.68	None

Table A25: Binding energies without and with vdW corrections for selected Co structures.

Geometry	E _{bind} /Ru [eV]	E _{bind} /Ru [eV] with vdW	Changes with vdW
3D rectangle atop_Mo	-4.93	-8.43	None
Tetrahedron atop_Mo	-5.14	-8.68	None
Line hollow	-4.76	-8.31	None
Line atop_Mo S vac	-4.91	-8.54	None
Tetrahedron atop_Mo S vac	-4.95	-8.40	None

Table A26: Binding energies without and with vdW corrections for selected Ru structures.

A5.12: Magnetism of Co structures on MoS₂

We find that for single atoms, those Co atoms adsorbed at **atop_Mo** and **hollow** sites have a magnetisation of 1 μ_B , which is expected as Co has an uneven number of valence electrons. However, for a single atom **atop_S**, the magnetisation increases to 1.5 μ_B . This is most likely due to the single Co-S bond at this site, compared to the three Co-S bonds per Co atom at the other two sites. For two Co atoms this effect is balanced by the addition of a second **atop_S** atom, leaving both atoms with a magnetisation of 1 μ_B . Adsorption of atoms at separated sites or non-equivalent sites causes an unequal distribution of magnetic moments, although the total magnetisation remains at approximately 2 μ_B . For Co₃ and Co₄ clusters the magnetisation becomes quite complicated with large fluctuations in the total magnetism as well as the magnetism of individual atoms. There is no clear correlation between structure stability and magnetic moment. We also observe different distributions of magnetic moments for structures which relaxed to the same geometry. This could be a cause as to why these structures do not have the exact same binding energies.

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