Size reduction of the barrier and liner stack for copper interconnects is a major bottleneck in further down-scaling of transistor devices. The role of the barrier is to prevent diffusion of Cu atoms into the surrounding dielectric, while the liner (also referred to as a seed layer) ensures that a smooth Cu film can be electroplated. Therefore, a combined barrier+liner material that restricts the diffusion of Cu into the dielectric and allows for copper electro-deposition is needed. In this paper, we have explored barrier+liner materials composed of 1 and 2 monolayers (MLs) of Ru-passivated epsilon-TaN and Ru doped epsilon-TaN and focus on their interactions with Cu through the adsorption of small Cu clusters with 1-4 atoms. Moreover, different doping patterns for Ru doping in TaN are investigated to understand how selective doping of the epsilon-TaN surface influences surface stability. We found that an increased concentration of Ru atoms in the outermost Ta layer improves the adhesion of Cu. The strongest binding of the Cu atoms was found on the 100% Ru doped surface followed by 1 ML Ru passivated surface. These two surfaces are recommended for the combined barrier+liner for Cu interconnects. The closely packed arrangements of Cu were found to exhibit weak Cu-slab and strong Cu-Cu interactions, whereas the sparse arrangements of Cu exhibit strong Cu-slab and weak Cu-Cu interactions. The Cu atoms seem to bind more favourably when they are buried in the doped or passivated surface layer due to the increase in their coordination number. This is facilitated by the surface distortion arising from the ionic radius mismatch between Ta and Ru. We also show that the strong Cu-Cu interaction alone cannot predict the association of Cu atoms as a few 2D Cu clusters showed stronger Cu-Cu interaction than the 3D clusters, highlighting the importance of Cu-surface interactions.
The role of Ru passivation and doping on the barrier and seed layer properties of Ru-modified TaN for Copper Interconnects

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Size reduction of the barrier and liner stack for copper interconnects is a major bottleneck in further down-scaling of transistor devices. The role of the barrier is to prevent diffusion of Cu atoms into the surrounding dielectric, while the liner (also referred to as a seed layer) ensures that a smooth Cu film can be electroplated. Therefore, a combined barrier+liner material that restricts the diffusion of Cu into the dielectric and allows for copper electro-deposition is needed. In this paper, we have explored barrier+liner materials composed of 1 and 2 monolayers (MLs) of Ru-passivated $\epsilon$-TaN and Ru doped $\epsilon$-TaN and focus on their interactions with Cu through the adsorption of small Cu clusters with 1-4 atoms. Moreover, different doping patterns for Ru doping in TaN are investigated to understand how selective doping of the $\epsilon$-TaN surface influences surface stability. We found that an increased concentration of Ru atoms in the outermost Ta layer improves the adhesion of Cu. The strongest binding of the Cu atoms was found on the 100% Ru doped surface followed by 1 ML Ru passivated surface. These two surfaces are recommended for the combined barrier+liner for Cu interconnects. The closely packed arrangements of Cu were found to exhibit weak Cu-slab and strong Cu-Cu interactions, whereas the sparse arrangements of Cu exhibit strong Cu-slab and weak Cu-Cu interactions. The Cu atoms seem to bind more favourably when they are buried in the doped or passivated surface layer due to the increase in their coordination number. This is facilitated by the surface distortion arising from the ionic radius mismatch between Ta and Ru. We also show that the strong Cu-Cu interaction alone cannot predict the association of Cu atoms as a few 2D Cu clusters showed stronger Cu-Cu interaction than the 3D clusters, highlighting the importance of Cu-surface interactions.

PACS numbers: Valid PACS appear here
Keywords: Copper interconnects, barrier + liner material, density functional theory

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I. INTRODUCTION

The scaling of interconnects has become the most serious limiting factor in the downsizing of complementary metal oxide semiconductor (CMOS) devices, as shown schematically in Fig. 1.\textsuperscript{1,2} While Cu performs extremely well as the interconnect metal, it requires a conductive diffusion barrier to prevent migration of Cu atoms into the dielectric and a liner material (also referred to as a seed or adhesion promoter or glue layer) to allow for successful electroplating of Cu films.\textsuperscript{3–7} The first diffusion barriers used were Ta and Si$_3$N$_4$.\textsuperscript{4,8–11} A wide variety of materials has been studied as alternative barrier materials in order to drive scaling and performance.\textsuperscript{12–17} Most of these materials are binary or ternary materials involving refractory metals, such as Ta, Mo and Os.\textsuperscript{18–23} Less work has been undertaken to find good liner materials. Most of the experimental work focuses on studying a liner material in combination with a particular diffusion barrier. For example, He and coworkers\textsuperscript{24} studied the effect of using a Co liner instead of the traditional Ta liner in conjunction with a TaN barrier. Performance of the liner materials was judged by studying SEM and STEM images and determining the presence or absence of line voiding and the Cu seed coverage. Shimizu et al studied ALD growth of Co(W) as a combined barrier+liner material and evaluated the films grown based on their diffusion coefficient\textsuperscript{25}, while Yang et al use Ru(Ta) in combination with a TaN barrier and were able to show enhanced wettability and gap-fill compared to Ta.\textsuperscript{26} To test different barrier as well as liner materials, van der Veen et al studied Ru and Co liners in combination with both TaN and MnN barriers, focusing in particular on examining the gap-fill performance as well as the electromigration and resistivity performance of the different material combinations.\textsuperscript{27}

Cheng and coworkers carried out a detailed theoretical study of various transition metals as potential liner materials on δ-TaN (1 1 1) and derived criteria based on adhesion energies that allow the prediction of a suitable liner material for a given system. For an ideal liner material on a given diffusion barrier the following three criteria were proposed\textsuperscript{28}:

1. Metal agglomeration on the liner material is prevented when the adhesion energy of the metal to the liner is stronger than the adhesion of the metal to the substrate. The substrate in this case would be the barrier material.

2. The liner material will not agglomerate when the adhesion of the liner on the substrate
FIG. 1. The issues associated with the interconnect bottleneck and the solution proposed in this study.

is stronger than the adhesion of the metal on the substrate.

3. It is important that the liner material does not diffuse into the metal. This is prevented so long as the adhesion of the liner to the substrate is stronger than the adhesion of the metal to the liner material.

For example, using these criteria, they were able to accurately predict that when using Al as the liner material, Al atoms would diffuse into the Cu layer, as it failed to meet the third of their three criteria. The adhesion energy between Cu and Al layers was stronger than that between Al and TaN and thus diffusion occurred.

Currently, a tri-layer stack of TaN/Ta/Cu is being used as the barrier, liner and interconnect layers in industry. While this functions well at larger length scales, it is not practical for smaller sizes at the 14nm node and smaller, as indicated in Fig. 1. The three layers of material become increasingly difficult to grow in the high aspect ratio interconnect vias us-
ing standard methods such as physical vapour deposition (PVD), which can cause pinch-off or blocking of the via. In addition, the volume which the barrier/liner stack can occupy, without the volume available for Cu deposition becoming too small, decreases with each technology node.\textsuperscript{30-32} While there has been some success growing these films using atomic layer deposition (ALD)\textsuperscript{33} and atomic layer etching (ALE)\textsuperscript{34}, two layers of material take up too much of the available volume in the interconnect via, leaving no room to electroplate Cu.\textsuperscript{32} In addition, Cu has a propensity to form 3D nanoclusters\textsuperscript{35-37} rather than a thin film and Cu resistivity strongly increases at these length scales.\textsuperscript{30,31} This means that an alternative material is needed in order to overcome this interconnect bottleneck and drive scaling below the 14nm node.

In our previous work, we studied the behaviour of Cu atoms and Cu dimers on Ru-passivated and low percentage of Ru atom doped $\epsilon$-TaN in detail, to examine fundamental aspects of Ru-TaN as a combined barrier+liner material and the fundamental interactions with Cu.\textsuperscript{38} The (1 1 0) surface of $\epsilon$-TaN exhibited the lowest surface energy, offered the highest resistance toward Cu association and oxidized the adsorbed Cu atoms. In that article, we also characterized Ru-passivated and Ru-doped TaN(1 1 0) surfaces using a (1×4) surface supercell with 1 and 2 Cu atom adsorption. Our conclusion was that Cu adsorbed more strongly on both Ru passivated and Ru doped surfaces as compared to the clean surface, with the strongest adsorption on the passivated surfaces. On the other hand, the Ru-doped surfaces offered higher resistance towards the diffusion and association of Cu atoms as compared to the Ru passivated surfaces. However, the doped TaN(1 1 0) surface model considered only 8% Ru doping (1 atom per supercell) in the surface layer. In the present study, we extend that work using a larger supercell to model the TaN surface with 1 and 2 monolayer (ML) Ru passivation and a range of Ru doping contents, namely 25%, 50%, 75% and 100%, in the outermost Ta layer with different distributions of Ru dopants and adsorption of up to four metal atoms. Such a structure can be fabricated with an ALD process using Ta and Ru precursors and nitrogen plasma.\textsuperscript{39,40} We believe that the results of this simulation work will be of value to experimentalists to grow materials with suitable Ru content to prepare a combined barrier-liner material that promotes Cu deposition.
II. METHODS AND COMPUTATIONAL SETUP

All calculations reported in this paper are based on spin polarized density functional theory as implemented in VASP v5.4.\textsuperscript{41} The exchange-correlation contribution to the electronic interaction is approximated by Perdew-Burke-Ernzerhof (PBE) generalized gradient (GGA) exchange-correlation functional.\textsuperscript{42} In this paper, the valence electronic configuration of Ta, N, Ru and Cu atoms used are $6s^25d^3$, $2s^22p^3$, $4d^75s^1$ and $3d^{10}4s^1$, respectively. The valence electrons are expanded in a plane wave basis set with an energy cutoff of 400 eV, while the core electrons are described by projector augmented wave (PAW) potentials.\textsuperscript{43,44}

The description of the bulk $\epsilon$-TaN and the TaN (1 1 0) surface used in this study are already published elsewhere.\textsuperscript{38,45} The clean TaN (1 1 0) surface used in this study is a 5 layered ($2 \times 8$) supercell with 240 Ta and 240 N atoms. (see Fig. 2) In each layer there are 48 Ta and 48 N atoms, and 64 Ru atoms fit in 1 ML of Ru to passivate TaN. The bottom two layers of the slab are kept frozen in all the calculations to represent the bulk. The dimensions of the slab supercell model used in this study are 18.1 Å $\times$ 23.4 Å $\times$ 30.5 Å. A vacuum of 18.7 Å 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, a vacuum of 16.4 Å and 14.4 Å are present. These vacuum thicknesses were found sufficient to isolate the two slab surfaces.

Cu binding energies reported in this paper are computed per atom from:

\[ E_{\text{bind}} = \frac{(E_{\text{int.sys.}} - (E_{\text{bare}} + nE_{\text{Cu-atom}}))}{n\text{Cu}}. \]  \hspace{1cm} (1)

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, $E_{\text{bare}}$ 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, $E_{\text{bind}}$ 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 $E_{\text{surf}}$ which refers to the single point energy of the relaxed interacting system with the copper atoms removed. $E_{\text{surf}}$ would be almost similar to $E_{\text{bare}}$ if the surface distortion is minimal. For some surfaces we found the difference between these two terms, termed as surface rearrangement energy ($E_{\text{SR}}$), is large. Therefore, to make a fair comparison of the Cu binding energies computed at different
surfaces, we removed this $E_{SR}$ contribution from $E_{\text{bind}}$. Thus the above equation becomes

$$E_{\text{bind}} = \frac{(E_{\text{int.sys.}} - (E_{\text{surf}} + nE_{\text{Cu-atom}}))}{nCu}. \quad (2)$$

We compute $E_{\text{bind}^\ast}$, which is the binding energy of the Cu$_n$ cluster relative to a gas-phase Cu$_n$ cluster.

$$E_{\text{bind}^\ast} = \frac{(E_{\text{int.sys.}} - (E_{\text{surf}} + E_{\text{Cu-cluster}}))}{n}. \quad (3)$$

Here, $E_{\text{int.sys.}}$ and $E_{\text{surf}}$ 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

$$E_{\text{Cu-Cu}} = E_{\text{bind}} - E_{\text{bind}^\ast}. \quad (4)$$

The doping energy per dopant is computed as

$$E_{\text{dope}} = \frac{E_{\text{total}} - (E_{\text{clean}} + n \times (E_{\text{Ru-atom}} - E_{\text{Ta-atom}}))}{n} \quad (5)$$
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. $E_{\text{total}}$ is the total energy of the relaxed doped surface and $E_{\text{clean}}$ 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 Ru dopants.

III. RESULTS

In this section we discuss the different Ru passivated and Ru doped surfaces and the role of the distribution of the dopants in the outermost Ta layer. We then describe the adsorption energetics and structures of Cu nanoclusters with 2, 3 or 4 atoms on these Ru-modified TaN surfaces.

A. Ru Passivated and Ru Doped TaN Surfaces

The (Ru)TaN (1 1 0) surfaces used in this study are shown in Fig. 2 and Fig. 3. The clean TaN surface, TaN with 1 & 2 monolayer (ML) of Ru and Ru doped TaN surfaces with 25%,
FIG. 2. Top and side views of the relaxed atomic structures of the various surfaces. 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'.

50%, 75% and 100% Ru content in the outermost Ta layer are shown in Fig. 2, while Fig. 3 shows the various dopant distributions studied with 50% doping, which will be discussed in detail in Section III B. 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 Fig. 3 are labelled in the order they appear in Fig. 3, as Ru$^{50-n}$ where n=1-10.

For the Ru$^{25}$, Ru$^{50}$ and Ru$^{75}$ surfaces, Fig. 2 shows one arrangement for the distribution of Ru dopants after relaxation. On the Ru$^{25}$ surface shown in Fig. 2, the Ru atoms are
preferentially arranged as far as possible from each another. On the Ru\textsuperscript{50} surface in Fig. 2, which is also the Ru\textsuperscript{50−4} surface in Fig. 3, the doped Ru atoms form horizontal zig-zag chains on the surface. The Ru atoms are randomly arranged on the Ru\textsuperscript{75} surface after relaxation. We can clearly see from the side view of this surface a high degree of rearrangement of the surface layer atoms. In terms of the number of structures for Ru-doped TaN, there are approximately $69\times10^9$, $32\times10^{12}$ and $69\times10^9$ 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 Fig. 2, are to be understood as representative arrangements. However, to study more possible arrangements of the Ru doping sites we use the example of the Ru\textsuperscript{50} 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 Fig. 2 and 3 is 4.23 nm\textsuperscript{2}.

From the surface geometries given in Fig. 2, we find that only the Ru\textsuperscript{75} surface is clearly 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 Ru\textsuperscript{100} surface has the highest number of Ru neighbours per Ru dopant, it

FIG. 3. Relaxed atomic structures for different Ru doping distributions in the Ru\textsuperscript{50} TaN(1 1 0) surface.
FIG. 4. Top and side views of the relaxed Ru

shows an undistorted high symmetry structure in Fig. 2 which is likely a local minimum. A distorted, lower symmetry structure of the Ru surface can be obtained through adsorption of a single Cu atom, which upon relaxation strongly distorts this surface, as shown in Fig. 4. The surface retained the distortions upon relaxation after the removal of the Cu atom and it 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) as compared to the Ta atom (2.00 Å) is the primary origin of this distortion and we can clearly see recesses (in Fig. 4) caused by this distortion that will potentially trap Cu atoms, which in turn could act as nucleation points for the Cu film growth. However, whether this phenomenon will promote Cu wetting or Cu agglomeration is the subject of a further study that is beyond the scope of the present investigation. 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 Fig. 1 of SI. However, a similar distortion is also found on the Ru surface on adsorbing two or more Cu atoms which will be discussed in a later section. The surface distortion upon Cu adsorption was smaller on the Ru and Ru 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 energy calculation as
described in the methods section.

B. Effect of Dopant Distribution on Surface Stability

We chose 50% surface doping 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. To understand the stability of each distribution, the doping energy (Eq. 5) was computed for each surface. 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 most stable. These doping energies are plotted in Fig. 5 and they are also compared with doping energies of the other Ru\textsuperscript{X} surfaces in Table I of the SI.

![Graph](image)

FIG. 5. Effect of the ratio of S:F sites for 50% Ru doping in TaN(1 1 0) on the doping energy for Ru\textsuperscript{50}.

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 rearrange-
ment 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). 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 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. 6.

In our previous work, 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. We can see this effect in Fig. 5 as a higher level of S-site doping
relative to F-site doping correlates with less favourable stability of the doped surface. By

FIG. 6. Examples of the recesses formed on various surfaces. All but the toplayer of the surface
slab were removed to make the recesses clearly visible.
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. 5, to more clearly illustrate the relationship between the S:F ratio and the doping energy of each dopant distribution.

There is one exception, in that structure Ru$^{50-4}$, 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 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, structures 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 due to the high symmetry present in the Ru distribution in structure Ru$^{50-4}$. Such structures with high symmetry although stable, tend to have higher energies, indicating that they are local minima, as discussed for the Ru$^{100}$ doped surface earlier. However, this surface (Ru$^{50-4}$) did not distort on single Cu adsorption, as opposed to the Ru$^{100}$ 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.

C. Adsorption of single Cu atoms and 2, 3 and 4 atom Cu Nanoclusters

In this section, we study the adsorption of a single Cu and Cu$_n$ nanoclusters with $n = 2, 3$ and 4 atoms on the doped and passivated TaN surfaces given in Fig. 2. We aim 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 a more detailed study of the stability of 2D and 3D Cu structures on Ru-modified TaN surfaces to be presented in a later work. For this paper, we examine different arrangements of 2, 3 and 4 atom Cu clusters adsorbed on the different TaN (1 1 0) surfaces, described in the previous section, in which at least one of the Cu atoms is adsorbed at the 5-fold site (marked with A on the clean surface in Fig. 2) coordinated by 3 Ta (Ru if doped) and 2 N atoms, which is the most stable site for Cu adsorption on the bare surface.

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 Eq. 2. 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. Fig. 1 of SI shows the relaxed geometries of the different surfaces with one adsorbed Cu atom at the 5-fold site.

In Fig. 7, 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, two configurations in which
FIG. 7. Cluster templates showing the location of the Cu atoms adsorbed on the surfaces shown in Fig. 2. The label "c" stands for "clustered", i.e. each Cu atom binds to at least one other Cu atom.

the Cu-Cu bond axis is oriented in either a vertical (Cu\textsubscript{2}^c−v) or horizontal (Cu\textsubscript{2}^c−h) direction relative to the surface are chosen. The 'c' in the notation represent geometries where every Cu atom in the arrangement is bonded to at least one other Cu atom. In the third structure, the two Cu atoms are isolated from one another (Cu\textsubscript{2}^far), with ca. 12 Å between them.

In the case of Cu\textsubscript{3}, we have considered 4 templates. In two of these templates the Cu
atoms form a triangle, of which one is a flat 2D arrangement (Cu\textsuperscript{-tri\textsubscript{3}}) with all Cu atoms binding to TaN surface. The other triangle arrangement has one Cu atom bridging the other two Cu atoms oriented away from the surface, resulting in a 3D arrangement (Cu\textsuperscript{-tri\textsubscript{3D}}). The third template has the three Cu atoms in a linear configuration (Cu\textsuperscript{-line\textsubscript{3}}), parallel to the surface in horizontal direction, and the final structure has one of the Cu atoms isolated from an adsorbed Cu\textsuperscript{2−h} (Cu\textsuperscript{far}). We have used 5 template structures for adsorption of a Cu\textsubscript{4} nanocluster. Four of these are 2D arrangements in which the Cu atoms are arranged as a rhombus (Cu\textsuperscript{-rho\textsubscript{4}}), a horizontal linear chain (Cu\textsuperscript{-line\textsubscript{4}}), an extended triangle in which the fourth atom is adjacent to the base of the triangle (Cu\textsuperscript{-tri\textsubscript{4}}) and a Cu\textsuperscript{-tri\textsubscript{3D}}+Cu cluster with the fourth Cu atom isolated from the others (Cu\textsuperscript{far}). In the fifth template, the Cu atoms are arranged in a 3D tetrahedral fashion (Cu\textsuperscript{-tet\textsubscript{3D}}). There are two 3D arrangements (Cu\textsuperscript{-tri\textsubscript{3D}} and Cu\textsuperscript{-tet\textsubscript{3D}}) and 10 2D arrangements. All the cluster templates shown in Fig. 7 are adsorbed on each of the 7 surfaces shown in Fig. 2 and the geometries are relaxed.

**Adsorption and Stability of Cu\textsubscript{n} Nanoclusters on TaN and Ru-modified TaN**

The most stable adsorption geometries of Cu\textsubscript{n} nanoclusters are shown in Fig. 8 and the other geometries are given in Figs. 2, 3 and 4 in the SI. In general, the closely packed configurations of Cu are predominantly preferred on the Ru passivated surfaces while the sparse 'far' arrangement is mostly preferred on the doped surfaces with the exception of Ru\textsuperscript{50−4} surface which we will discuss later. The tetragonal close packed 3D arrangement, Cu\textsuperscript{-tet\textsubscript{3D}}, was the most favourable only on the clean surface while the flat configurations of Cu\textsubscript{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, Cu\textsuperscript{-tri\textsubscript{3D}}, resulted in a 2D structure on the Ru passivated and Ru\textsuperscript{100} surfaces (see Fig.3 in SI). In contrast, the Cu\textsuperscript{-tet\textsubscript{3D}} arrangement remained stable 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 Cu\textsuperscript{-rho} arrangement on the Ru\textsuperscript{25} surface resulted in the 3D Cu\textsuperscript{-tet\textsubscript{3D}} arrangement on relaxation as shown in Fig. 9. 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
FIG. 8. Surface geometries that provide the most favourable binding energy for Cu$_n$ nanocluster adsorption.

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 Ru$_{25}$ 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.

The binding energies ($E_{\text{bind}}$) for all the arrangements on all the surfaces are plotted in Fig. 10 and are also listed in Tables II to V in the SI. The binding energies including the contribution from Cu-Cu interaction are plotted in Fig. 10(a) and 10(b), and those without the Cu-Cu interaction are plotted in Fig. 10(c) and 10(d). As expected, one could find
FIG. 9. Top and side views of geometries extracted from Cu$_4^{c-rho}$ cluster relaxation trajectory on 25% doped surface. The graph shows the energy gained in this process ($\Delta E_{\text{gain}}$) and the associated $Z$ distance change ($\Delta Z$) of the migrating Cu atom.

by comparing the above plots 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 show stronger Cu-slab binding compared to clean TaN (1 1 0) and the 2 ML Ru passivated TaN surfaces (Fig. 10(a) and 10(c)). This arises from the structure of the 1 ML 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 Fig. 10(b) and (d)), the Ru$_{100}$ surface (red data points) has the strongest Cu binding energy for all arrangements except in the cases of Cu$_3^{c\text{-line}}$ and Cu$_{4}^{c\text{-tri}}$ 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 Fig. 10), on the Ru$_{100}$ surface, showing that wetting could be promoted on the Ru doped surfaces. Cu$_3^{c\text{-line}}$ on the Ru$_{50}$ surface was the most favourable Cu$_3$ arrangement. It is to be noted that this arrangement
FIG. 10. The binding energies per adsorbed Cu adatom for all studied arrangements on the Ru passivated (a) and Ru doped surfaces (b) 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.

has the second least Cu-Cu coordination number among the considered Cu$_3$ nanoclusters following the Cu$_3^{\text{far}}$ configuration, which is the second most favourable configuration on the Ru$_{50}$ surface. From the side views of these most favourable arrangements in Fig. 8, 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. The minimum, maximum and average distances of Cu atoms from the slab is computed to support the above finding and are discussed in the next section. To summarise, 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 Eq. 4 are plotted in Fig. 11. The strongest overall $E_{\text{Cu-Cu}}^{\text{avg}}$ was observed for the Cu$_4^{c-rho}$ arrangement (-1.43 eV) where the Cu atoms form a closely packed structure, a rhombus, with each Cu atom having two closest
FIG. 11. Bar chart showing the Cu-Cu interaction energy contribution computed according to Eq. 4. The average Cu-Cu interaction energy per arrangement is also indicated above the bars.

Cu neighbours. Among the Cu$_2$ arrangements, Cu$_2^{c-h}$ has the shortest Cu-Cu distance and among the Cu$_3$ arrangements, Cu$_3^{c-tri3D}$ is the only 3D arrangement with maximum Cu-Cu coordination. For these reasons, the above arrangements have the most favourable $E_{\text{Cu-Cu}}$ in the Cu$_2$ and Cu$_3$ cases. The Cu atoms in Cu$_2^{\text{far}}$ arrangement are well separated from each other, which results in no Cu-Cu interaction and hence $E_{\text{Cu-Cu}}=0$. The Cu$_3^{\text{far}}$ arrangement has enhanced Cu-Cu binding as compared to the Cu$_2^{\text{far}}$ arrangement since there are at least 2 Cu atoms next to each other forming a Cu-Cu bond. As expected, this arrangement has the lowest Cu-Cu binding energy in Cu$_3$, followed by the Cu$_3^{c-line}$ and Cu$_3^{c-tri}$ arrangements. For the Cu$_4$ nanocluster, two arrangements, namely Cu$_4^{c-line}$ and Cu$_4^{\text{far}}$ have the weakest Cu-Cu interactions.

The average Cu binding energies ($E_{\text{bind}}^{\text{avg}}$ and $E_{\text{bind}^*}^{\text{avg}}$) and the average Cu-Cu interaction energies ($E_{\text{Cu-Cu}}^{\text{avg}}$) extracted from all 13 cluster adsorptions are listed in Table I. The strongest overall binding of Cu and Cu$_n$ ($E_{\text{bind}}^{\text{avg}}$ and $E_{\text{bind}^*}^{\text{avg}}$) is observed on the Ru$_{100}$ surface and the weakest overall binding is found on the Ru$_{75}$ and the clean TaN surfaces. We noted in our previous publication$^{38}$ 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 the clean TaN. While the average Cu-Cu binding energies were very similar on all the doped surfaces, the strongest $E_{\text{Cu-Cu}}^{\text{avg}}$ was found for the Ru$_{100}$ surface closely followed by Ru$_{75}$, Ru$_{50}$ and Ru$_{25}$ 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 Ru$_{100}$ surface offers the strongest Cu-Cu interaction as well as the strongest
TABLE I. Average values of binding energies and interatomic distances of Cu adsorbed on the studied surfaces are listed. \( E_{\text{avg}}^{\text{bind}} \) is the average of the binding energies calculated as per equation 2, \( E_{\text{bind}*}^{\text{avg}} \) is the average of the binding energies calculated as per equation 3, \( E_{\text{Cu-Cu}}^{\text{avg}} \) is the average Cu-Cu distance, \( E_{\text{SR}}^{\text{avg}} \) and \( E_{\text{SR}}^{\text{max/min}} \) are the average, minimum and maximum surface rearrangement energies and \( d_{\text{Cu-slab}}^{\text{avg}} \) is the average Cu-slab distance.

| Surface | \( E_{\text{bind}}^{\text{avg}} \) [eV/Cu] | \( E_{\text{bind}*}^{\text{avg}} \) [eV/Cu] | \( E_{\text{Cu-Cu}}^{\text{avg}} \) [eV/Cu] | \( E_{\text{SR}}^{\text{avg}} \) [\text{eV}] | \( E_{\text{SR}}^{\text{max/min}} \) [\text{eV}] | \( d_{\text{Cu-slab}}^{\text{avg}} \) [\AA] | \( d_{\text{Cu-slab}}^{\text{max/min}} \) [\AA] |
|---------|---------------------------------|---------------------------------|---------------------------------|----------------------------|----------------------------|----------------|----------------|
| 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\textsuperscript{25} | -3.16                           | -2.59                           | -0.57                           | 0.65                       | 0.28/1.44                 | 1.88           | 3.93/1.08     |
| Ru\textsuperscript{50} | -3.41                           | -2.60                           | -0.82                           | -3.25                      | -11.74/0.04               | 1.81           | 3.92/0.75     |
| Ru\textsuperscript{75} | -2.98                           | -2.09                           | -0.89                           | 0.83                       | 0.19/1.30                 | 1.92           | 4.03/1.03     |
| Ru\textsuperscript{100} | -4.12                           | -3.22                           | -0.90                           | -24.66/27.46/-21.27        | 1.13                      | 3.43/0.45     |

Cu-slab interaction. For all surfaces, including the clean surface, the Cu\textsubscript{n}-slab interaction (\( E_{\text{bind}*}^{\text{avg}} \)) is much stronger compared to the Cu-Cu interaction (\( E_{\text{Cu-Cu}}^{\text{avg}} \)). Consequently, we might speculate that all surfaces should promote wetting over association to an extent. But we know that the clean TaN surface promotes Cu association, so the above cannot be the only criteria to predict Cu association.

The surface rearrangement energy, \( E_{\text{SR}} \), 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, Ru\textsuperscript{25} and Ru\textsuperscript{75} surfaces, while it is negative for all geometries of the 2 ML Ru passivated and Ru\textsuperscript{100} surfaces (individual energies shown in Table VI of SI and the maximum and minimum values, depending on Cu\textsubscript{n} binding mode, given in Table I). A positive \( E_{\text{SR}} \) 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. The average rearrangement energy is less than 1 eV per supercell for the first set of surfaces where the distorted surface is less favourable, but they are much larger for the second set where the bare surface model is only a local minimum. Particularly, note that the \( E_{\text{SR}}^{\text{avg}} \) value for Ru\textsuperscript{100} in Table I is -24.66 eV. This is the main reason to exclude
this contribution in the $E_{\text{bind}}$ calculations. Ru$^{50}$ is not included in the above discussion because it showed negative $E_{\text{SR}}$ for some arrangements and positive values for the others (Table VI of SI). But when the values are negative they are very large in magnitude compared to the positive values which is reflected in the negative $E_{\text{SR}}^{\text{avg}}$ reported in Table I. Basically the large values of $E_{\text{SR}}$ 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 found to be favourable only in Ru$^{50}$ and Ru$^{100}$ surfaces. However, for Ru$^{100}$ surface the favourable distortion was observed for all of the Cu$_n$ arrangements but not so for Ru$^{50}$ surface. Only a certain specific Cu$_n$ arrangements such as Cu$_2^{c-v}$, Cu$_2^{\text{far}}$, Cu$_3^{c-v}$ and all of Cu$_4$ clusters except the Cu$_4^{\text{tet3D}}$ arrangement are found to trigger the distortion in this surface. This could be due to the unique 'zig-zag' arrangement of the Ru dopants on the surface.

Table VII in the SI 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 ($E_{\text{bind}}$) 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 should 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 (Cu$_4^{c-tet3D}$) only on the 25% doped surface, but not on the other Ru-doped surfaces. Since this Cu$_4^{c-tet3D}$ 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 Cu$_4^{c-tet3D}$ arrangement has one of the lowest 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.
**Influence of Cu-Cu and Cu-Slab Distances on the Stability of Cu\textsubscript{n} adsorption**

In Fig. 10b and 10d, we highlighted the examples Cu\textsubscript{2}\textsubscript{far} on the Ru\textsuperscript{100} surface and Cu\textsubscript{3}\textsuperscript{c-line} on the Ru\textsuperscript{50} surface for showing the lowest E\textsubscript{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 Fig. 12a, with the results plotted in Fig. 12b. 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 as d(Cu-slab) throughout the text for clarity. There are only two data points beyond -5 eV (Cu\textsubscript{3}\textsuperscript{c-line} on Ru\textsuperscript{50} and Cu\textsubscript{2}\textsubscript{far} on Ru\textsuperscript{100}) and these are the same two arrangements marked in Fig. 10b and 10d. In these structures at least one of the Cu atoms is buried in the surface (indicated by the negative d(Cu-slab) in Fig. 12b) 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\textsuperscript{100} surface (Cu\textsubscript{2}\textsuperscript{c-v} arrangement), it still has a less favourable binding energy than the marked arrangements. The reason for lower d(Cu-slab) in the Cu\textsubscript{2}\textsuperscript{c-v} arrangement when compared to the Cu\textsubscript{2}\textsuperscript{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

![Diagram](image.png)

**FIG. 12.** 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 surf atom are in the same plane.
FIG. 13. Scatter plots of the shortest $d(Cu-X)$, where $X = Ta, Ru, N$, with respect to the binding energy are shown in panels a), b) and c), respectively. The bottom plots in the panels show the correlation between the individual $d(Cu-X)$ and the shortest overall $d(Cu-slab)$, defined in Fig. 12.

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 $d(Cu-X)$ ($X = Ta, Ru, N$) with the overall $d(Cu-slab)$ given in Fig. 12b. From the correlation plots, we find that Ta is the farthest atom (along $Z$) from Cu in all the arrangements. The $d(Cu-Ta)$ 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 surface Ru atom. Since the N atoms are the top-most along the surface normal on the clean and doped surfaces (see Fig. 2), 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 $d(Cu-Ta)$, $d(Cu-Ru)$ and $d(Cu-N)$ as shown in Fig. 13a, 13b and 13c, respectively.
slab. In some arrangements on the Ru$^{50}$ and Ru$^{100}$ Ru surfaces, d(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(Cu-N) is the shortest which is evident from all the data points lying along the correlation line in Fig. 13c. The d(Cu-X) measurements on the Ru passivated surfaces are not shown, as the d(Cu-Ta) and d(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. 12b 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. 2 that could trap the Cu atoms. On some Cu arrangements, the d(Cu-Ru) value is near zero on the 1 ML passivated surface. Furthermore, the average d(Cu-slab) are also listed in Table I in which d(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(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(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 largest d(Cu-slab) is observed for the 2 ML Ru passivated surface at 2.06 Å. All the other surfaces had an average Cu-slab distance between 1.81 and 1.92. The maximum Cu-slab distance for all the surfaces is always for the top atom in the Cu$_4^{tet3D}$ arrangement, while the minimum Cu-slab distance is always for either one of the far arrangements or the c-line arrangements that have the lowest Cu-Cu coordination. The Cu-Cu and Cu-slab distances in each arrangement on each surface is provided in Tables II to V in the SI and also discussed in detail in the next section. The surfaces with the least d(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.

D. Effect of Doping on the Cu Binding Energies

Increased surface doping with Ru does not always result in enhanced Cu binding as the Ru\textsuperscript{75} surface did not produce more favourable binding energies compared to the Ru\textsuperscript{50} surface (see Fig. 10 and Table I). To understand this observation better, the individual binding energy differences between the doped surfaces and the clean surface

\[ \Delta E = E^{Ru^X} - E^{Clean} \] (6)

for \( E_{\text{bind}} \), \( E_{\text{bind}^*} \), and \( E_{\text{Cu-Cu}} \) are plotted in Fig. 14, in which we observe that for 7 out of 13 Cu arrangements on the Ru\textsuperscript{75} surface, the \( \Delta E_{\text{bind}} \) values are positive. This shows that the Ru\textsuperscript{75} surface is less reactive to Cu adsorption than the clean surface. In contrast, the Ru\textsuperscript{25} and Ru\textsuperscript{50} surfaces have 6 and 5 arrangements that have positive \( \Delta E_{\text{bind}} \) values. However, the maximum deviation is the largest with 0.41 eV/Cu in the case of Ru\textsuperscript{75} surface followed by 0.33 eV and 0.06 eV in the cases of Ru\textsuperscript{50} and Ru\textsuperscript{25} surfaces. On checking with the \( \Delta E_{\text{bind}^*} \) and \( \Delta E_{\text{Cu-Cu}} \) values, we conclude that this deviation for Ru\textsuperscript{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\textsuperscript{100} is the only doped surface that shows enhanced Cu binding for every Cu\textsubscript{\textit{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 would promote 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 the topic of our future research.
FIG. 14. Bar charts representing the various binding energy difference per adsorbed Cu adatom on all the studied doped surfaces with respect to the clean surface. $\Delta E_{\text{bind}}$ is calculated using equation 6.
IV. DISCUSSION

The first objective of this paper is to compare and characterize 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. The understanding gained from this will be extremely relevant to developing a combined barrier+liner material that can facilitate the further downsizing of device interconnects. 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 the surfaces show strong distortions due to the smaller atomic radius of Ru compared to Ta. This distortion causes the formation of recesses on the surface, with a large distance between atoms, which arises from the increased Ru-Ru attraction in the surface layer and the smaller Ru radius compared to Ta. Such a recess could act as a trap/anchor point for Cu seed layer formation. We also find such a recess 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.$^{38}$

Studying the effect of different dopant arrangements using the Ru$_{50}$ 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 ALD, surfaces with a high concentration of S-site Ru in the surface can be formed. Further, we found that all of the tested arrangements formed recesses in the surface layer due to the difference in atomic radii between Ru and Ta. These surface 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. As with the surface recesses formed on the surfaces
with different doping percentages, 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.

A decrease in surface stability with an increase in the concentration of Ru doping is observed due to replacing Ta atoms with Ru. With the exception of the Ru\textsuperscript{75} 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 probably due to the over-stabilization of this surface upon relaxation, which makes it less reactive to the adsorbed Cu atoms. The most favourable \( E_{\text{bind}}^{\text{avg}} \), \( E_{\text{bind}^*}^{\text{avg}} \) and \( E_{\text{Cu-Cu}}^{\text{avg}} \) values are observed for the Ru\textsuperscript{100} doped surface followed by the 1 ML passivated surface. \( E_{\text{Cu-Cu}}^{\text{avg}} \) is higher on the Ru passivated surfaces, more so on the 1 ML surface than the 2 ML surface, 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 Ru\textsuperscript{100} surface do not behave similarly. The Ru\textsuperscript{25} and Ru\textsuperscript{50} surfaces showed weaker average Cu-Cu interactions with respect to the clean surface, while the Ru\textsuperscript{75} and Ru\textsuperscript{100} 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.

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,** \( (E_{\text{Cu-Cu}}^{\text{avg}} < E_{\text{bind}^*}^{\text{avg}}) \) and **if \( E_{\text{Cu-Cu}}^{\text{avg}} \) reaches the cohesive energy of bulk copper (-3.49 eV/atom\textsuperscript{47}).**

2. For wetting to be preferred over association, the Cu-slab binding energy
must be more negative than the Cu-Cu interaction energy \( \langle E_{\text{bind}}^* \rangle < \langle E_{\text{Cu-Cu}} \rangle \) and \( \langle E_{\text{bind}}^* \rangle < -3.49 \text{ eV/atom} \).

On all surfaces, including the clean surface where we know that Cu associates, we found \( \langle E_{\text{Cu-Cu}} \rangle > \langle E_{\text{bind}}^* \rangle \) and the value of \( \langle E_{\text{Cu-Cu}} \rangle \) was much more positive than the bulk cohesive energy of Cu (for example, on Ru\(^{100}\) surface \( \langle E_{\text{Cu-Cu}} \rangle = -0.90 \text{ eV} \) and \( \langle E_{\text{bind}}^* \rangle = -3.22 \text{ eV} \)). However, if we look at the individual energies, \( \text{Cu}_4^{c-\text{rho}} \) arrangement on the clean surface and \( \text{Cu}_4^{c-\text{rho}} \) and \( \text{Cu}_4^{c-\text{tri}} \) arrangements on the Ru\(^{75}\) surface have lower \( E_{\text{Cu-Cu}} \) than corresponding \( E_{\text{bind}}^* \). It was surprising to see the \( \text{Cu}_4^{c-\text{top3D}} \) arrangement, a simple model for associated Cu, to have \( E_{\text{bind}}^* < E_{\text{Cu-Cu}} \) 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 Ru\(^{100}\) 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. Based on the above observation, these two 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 Fig. 1, compared to the multi-layer stack that is currently in use\(^{29}\).

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 paper will be considered and this is the focus of ongoing work.
V. CONCLUSION

A first principles investigation of the stability and reactivity of Ru passivated and Ru-doped surfaces of ε-TaN(1 1 0) with respect to adsorption of 2-4 Cu clusters was conducted. 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. 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 above condition was satisfied for the 100% Ru doped surface and the 1 ML Ru passivated surface, which makes them top contenders for the combined barrier+liner material. Going forward, our next step is to study the stability of large 2D Cu films on these Ru passivated and Ru-doped surfaces.

ACKNOWLEDGMENTS

The authors would like to thank SFI-NSFC Partnership NITRALD (17/NSFC/2975) for project funding and the Irish Super Computing Center (ICHEC Project number: tiche087b) for the computer time.

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Electronic Supporting Information of 'Effect of Doping Vs Passivation of Ru on TaN Surfaces in the Barrier/Liner Properties of Copper Interconnects - A First Principles Study'\textsuperscript{a)}

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(Dated: 3 February 2020)

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FIG. 1. Relaxed geometries of the different surfaces with one adsorbed Cu atom at the 5-fold site.

| Surface | $E_{\text{doped}}$ (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                        |

TABLE I. Doping energies for the different surfaces studied
FIG. 2. 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.
FIG. 3. 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.
FIG. 4. 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.
### TABLE II. 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 | \(d(\text{Cu-Cu}) \, [\text{Å}]\) | \(d(\text{Cu-slab}) \, [\text{Å}]\) | \(E_{\text{bind}} \, [\text{eV}]\) | \(E_{\text{E}_{\text{Cu-Cu}}} \, [\text{eV}]\) |
|---------------------------|-------------------------------|-----------------------------|----------------|----------------|
| Clean 2 Cu                | min max | min max | \(E_{\text{bind}}\) | \(E_{\text{E}_{\text{Cu-Cu}}}\) |
| 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 |
| far                       | 2.42 12.53 | 1.71 1.71 | -3.18 -2.48 | -0.7 |
| 4 Cu                      | C-rho | 2.43 4.22 | 1.8 2.12 | -2.82 -1.27 | -1.54 |
| C-line                    | 2.5 8.0 | 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 |
| far                       | 3.51 12.83 | 0.83 0.94 | -4.29 -3.6 | -0.69 |
| 4 Cu                      | 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 |
| Surf cluster | Arrangement | \( \text{d(Cu-Cu)} \) [Å] | \( \text{d(Cu-slab)} \) [Å] | \( E_{\text{bind}} \) [eV] | \( E_{\text{bind}} \) [eV] | \( E_{\text{Cu-Cu}} \) [eV] |
|--------------|-------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 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           |
|               | far         | 2.47            | 12.16           | 1.03            | 1.9             | -3.28           | -2.59           | -0.69           |
| 4 Cu          | 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           |

| 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           |
|               | far         | 2.43            | 12.52           | 0.85            | 1.81            | -3.72           | -3.04           | -0.68           |
| 4 Cu          | 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 III.** 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] | $E_{\text{bind}}$ | $E_{\text{bind}}$ | $E_{\text{Cu-Cu}}$ |
|-------|---------|-------------|--------------|----------------|----------------|----------------|----------------|
|       |         |             | 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 |
|         | far    |             | 2.41 | 12.19| 1.08 | 1.58 | -3.68 | -3.48 | -0.2  |
| 4 Cu   | 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 |
|         | far    |             | 3.3  | 11.65| 1.42 | 2.2  | -3.56 | -3.32 | -0.24 |
| 4 Cu   | 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 IV. 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] | $E_{\text{bind}}$ [eV] | $E_{Cu-Cu}$ [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           |
|                          | far          | 2.85 11.27    | 1.67 2.27      | -3.35 -2.9      | -0.44           |
| 4 Cu 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           |

TABLE V. 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.
| Cu | Arrangement | Bare 1 ML | Ru 2 ML | 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 |

**TABLE VI.** $E_{SR}$ values for all arrangements on all surfaces
| Surface  | 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 |

$E_{bind^*}$

| $E_{Cu-Cu}$ | Most favourable | Least favourable |
|-------------|-----------------|------------------|
| Surface     | 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 |

TABLE VII. Arrangements with the most favourable $E_{bind^*}$ and $E_{Cu-Cu}$ on the surfaces
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