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ABSTRACT

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 ϵ -TaN and Ru doped ϵ -TaN and focused 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 ϵ -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 the 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 favorably 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.

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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.^{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.^{3–7} The first diffusion barriers used were Ta and Si₃N₄.^{4,8–11} A wide variety of materials has been studied as alternative barrier materials in order to drive scaling and performance.^{12–17} Most of these materials are binary or ternary materials involving

refractory metals, such as Ta, Mo, and Os.^{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 co-workers²⁴ studied the effect of using a Co liner instead of the traditional Ta liner in conjunction with a TaN barrier. The 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 atomic layer deposition (ALD) growth of Co(W) as a combined barrier + liner material and evaluated the films grown based on their diffusion coefficient,²⁵ while Yang *et al.* used Ru (Ta) in combination with a TaN barrier and were able to show enhanced wettability and gap-fill compared to Ta.²⁶ To test

FIG. 1. The issues associated with the interconnect bottleneck and the solution proposed in this study.

different barriers 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.²⁷

Han and co-workers 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: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 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.²⁹ While this functions well at larger length scales, it is not practical for smaller sizes at the 14 nm 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 using standard methods such as physical vapor 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.^{30–32} While there has been some success growing these films using atomic layer deposition (ALD)³³ and atomic layer etching (ALE),³⁴ two layers of materials take up too much of the available volume in the interconnect via, leaving no room to electroplate Cu.³² In addition, Cu has a propensity to form 3D nanoclusters^{35–37} rather than a thin film, and Cu resistivity strongly increases at these length scales.^{30,31} This means that an alternative material is needed in order to overcome this interconnect bottleneck and drive scaling below the 14 nm node.

In our previous work, we studied the behavior of Cu atoms and Cu dimers on Ru-passivated and low percentage of Ru atom doped ϵ -TaN in detail to examine fundamental aspects of Ru–TaN as a combined barrier + liner material and the fundamental interactions with Cu.³⁸ The (1 1 0) surface of ϵ -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 $\times$ 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 toward 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.^{39,40} In addition, we study up to four Cu atom clusters to explore possible dimensionality changes with Ru content. 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 v5.4.⁴¹ The exchange–correlation contribution to the electronic interaction is approximated by the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) exchange–correlation functional.⁴² In this paper, the valence electronic configuration of Ta, N, Ru, and Cu atoms used is $6s^2 5d^3$, $2s^2 2p^3$, $4d^7 5s^1$, 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.^{43,44}

The description of the bulk ϵ -TaN and the TaN (1 1 0) surface used in this study is already published elsewhere.³⁸ The clean TaN (1 1 0) surface used in this study is a five layered (2×8) supercell with 240 Ta and 240 N atoms [see Fig. 2(a)]. 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 $18.1 \times 23.4 \times 30.5 \text{ \AA}^3$. 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, a vacuum of $16.4 \text{ \AA}$ and $14.4 \text{ \AA}$ is present. These vacuum thicknesses were found to be sufficient to isolate the two slab surfaces.

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

$$E_{\text{bind}} = (E_{\text{int.sys.}} - (E_{\text{bare}} + nE_{\text{Cu-atom}}))/n\text{Cu}. \quad (1)$$

Here, $E_{\text{int.sys.}}$ is the total energy of the relaxed interacting system where $n\text{Cu}$ 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 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

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

We compute E_{bind^*} , which is the binding energy of the Cu_n cluster relative to a gas-phase Cu_n cluster,

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

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

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

FIG. 2. Panels (a)–(g) show 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. Ta, N, and Ru atoms are shown in gold, light blue, and purple, respectively. On the clean surface, the fivefold adsorption site coordinated by 3 Ta and 2 N is marked with “A.”

The doping energy per dopant is computed as

$$E_{\text{dope}} = \frac{E_{\text{total}} - (E_{\text{clean}} + n \times (E_{\text{Ru-atom}} - E_{\text{Ta-atom}}))}{n}, \quad (5)$$

where 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. 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 Figs. 2 and 3. The clean TaN surface and TaN with 1 and 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

Figs. 2(a)–2(g), respectively, while Fig. 3 shows the various dopant distributions studied with 50% doping, which will be discussed in detail in Sec. III B and Sec. I of the supplementary material. 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 labeled 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(d), the Ru atoms are preferentially arranged as far as possible from each other. On the Ru^{50} surface in Fig. 2(e), the doped Ru atoms form horizontal zigzag chains on the surface. The Ru atoms are randomly arranged on the Ru^{75} surface in Fig. 2(f) 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 69×10^9 , 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 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^{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 Figs. 2 and 3 is 4.23 nm^2 .

FIG. 3. Relaxed atomic structures for ten different Ru doping distributions in the Ru^{50} TaN (1 1 0) surface are shown in panels (a)–(j). The ratio of S:F type Ru atoms (see Sec. III B) is shown, as well as the doping energy per Ru atom for each surface.

From the surface geometries given in Fig. 2, we find that only the Ru^{75} surface is clearly distorted upon relaxation. This is due to the increase in Ru–Ru interactions as a result of having more Ru neighbors per Ru dopant and the shorter Ru–N distances compared to TaN. While the Ru^{100} surface has the highest number of Ru neighbors per Ru dopant, it shows an undistorted high symmetry structure in Fig. 2(g), which is likely a local minimum. A distorted, lower symmetry structure of the Ru^{100} surface can be obtained through the adsorption of a single Cu atom, which upon relaxation strongly distorts this surface, as shown in Fig. 4(b). 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/Ru dopant. The smaller ionic radius of the Ru atom [$(1.78 \text{ \AA})^{45}$] as compared to the Ta atom [$(2.00 \text{ \AA})^{45}$] is the primary origin of this distortion, and we can clearly see recesses [in Fig. 4(c)] 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 Sec. II of the [supplementary material](#). However, a similar distortion is also found on the Ru^{50} surface on adsorbing two or more Cu atoms, which will be discussed in Sec. III C 1. The surface distortion upon Cu adsorption was smaller on the Ru^{25} and Ru^{75} 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 the 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 Sec. II.

FIG. 4. Top and side views of the relaxed Ru^{100} Ru-doped TaN (1 1 0) surface before Cu adsorption are shown in (a), after the Cu adsorption in (b), and after the removal of the adsorbed Cu atom in (c).

B. 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 ten 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 and is compared with doping energies of the other Ru^x surfaces in Table S1 and Fig. S1 of the [supplementary material](#).

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 ($2.00 \text{ \AA}$).⁴⁵ 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. 5.

In our previous work,³⁸ 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 threefold coordinated with N, and S-type sites are sixfold coordinated with N. Ru doping at the F-site is more favorable than doping at the S-site.³⁸ We find that a higher level of S-site doping relative to F-site doping correlates with a less favorable surface. 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 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. This likely arises due to the presence of some F-site doping as opposed to no F-site doping in Ru^{50-1} . The Ru^{75} surface originally has an S:F ratio of 24:12. However, due to the significant rearrangement, the surface underwent during relaxation, and there are no longer unambiguous S and F sites. In fact, coordination environments other than three- and sixfold 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 favorable 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. Furthermore, 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 favorable 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 have higher energies. Overall, surface stability and,

FIG. 5. Examples of the recesses formed on various surfaces are shown in panels (a)–(i). All but the top layers of the surface slab were removed to make the recesses clearly visible.

thus, reactivity are found to be most affected by the S:F ratio, rather than the exact distribution of Ru atoms. The effect this change in stability has on the behavior of Cu adatoms is the subject of future work.

C. Adsorption of single Cu 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, as shown in Fig. 2. At least, one of the Cu atoms is adsorbed at the fivefold site [marked with A on the clean surface in Fig. 2(a)] coordinated by 3 Ta (Ru if doped) and 2 N atoms, which is the most stable site for Cu adsorption on the bare surface.³⁸ 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 a more detailed study of the stability of larger 2D and 3D Cu structures on Ru-modified TaN surfaces.

A Cu atom on the clean (2×8) TaN $(1\ 1\ 0)$ surface adsorbs at the fivefold 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 the 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 S2 of the [supplementary material](#) shows the relaxed geometries of the different surfaces with one adsorbed Cu atom at the fivefold site.

In Fig. 6, 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 Fig. 6(a)], 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 represents geometries where every Cu atom in the arrangement is bonded to at least one other Cu atom. In all structures, the notation (Cu_x^{far}) means that Cu atoms are separated, with up to $12\text{ \AA}$ between them. In the case of Cu_3 and Cu_4 , the templates [in Figs. 6(b) and 6(c)] include triangles for Cu_3 , a rhombus and tetrahedron for Cu_4 , and linear structures for both.

1. Adsorption and stability of Cu_n nanoclusters on TaN and Ru-modified TaN

The most stable adsorption geometries of Cu_n nanoclusters ($n = 2, 3$, and 4) on the different surfaces are shown in Fig. 7, and the other geometries are given in Figs. S3–S5 of the [supplementary material](#). 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 the Ru^{50} surface, as shown in Fig. 7(e). The tetragonal closely packed 3D arrangement, $\text{Cu}_4^{\text{c-tet3D}}$, was the most favorable only on the clean surface, while the flat configurations of Cu_4 are favored by all the other surfaces. This already suggests a preference to 2D Cu on the Ru passivated and Ru doped surfaces. The other 3D

FIG. 6. Template arrangements of 2, 3, and 4 atom nanoclusters showing the location of the Cu atoms adsorbed on the surfaces shown in Fig. 2 are given in panel columns (a)–(c), respectively. 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.

arrangement, $\text{Cu}_3^{\text{c-tri3D}}$, resulted in a 2D structure on the Ru passivated and Ru^{100} surfaces (see Fig. S4 of the [supplementary material](#)). In contrast, the $\text{Cu}_4^{\text{c-tet3D}}$ arrangement remained stable, though not the most favorable, 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 Fig. S6 of the [supplementary material](#).

The binding energies (E_{bind}) for all the arrangements on all the surfaces are plotted in Fig. 8 and are also listed in Tables S2–S5 of the [supplementary material](#). The binding energies including the contribution from Cu–Cu interaction are plotted in Figs. 8(a) and 8(b), and those without the Cu–Cu interaction are plotted in Figs. 8(c) and 8(d). As expected, one could find 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 shows stronger Cu–slab binding compared to clean TaN (1 1 0) and the 2 ML Ru passivated TaN surfaces [Figs. 8(a) and 8(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 Figs. 8(b) and 8(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 favorable Cu_2 and Cu_4 arrangements, respectively [see Figs. 8(b) and 8(d)], on the Ru^{100} surface, showing that wetting, even with a small number of atoms, could be promoted on the Ru doped surfaces.

$\text{Cu}_3^{\text{c-line}}$ on the Ru^{50} surface was the most favorable 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 favorable configuration on the Ru^{50} surface. From the side views of these most favorable arrangements in Figs. 7(d)–7(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. To summarize, the most favorable configurations of Cu adsorption appear on the doped surfaces, which offers 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. 9. The strongest overall $E_{\text{Cu-Cu}}^{\text{avg}}$ 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 neighbors. 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 and have the most favorable $E_{\text{Cu-Cu}}$ 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 $E_{\text{bind}*}^{\text{avg}}$, as per Eqs. (2) and (3), 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 clean TaN surfaces. We noted that in our previous publication,³⁸ 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 Cu–slab interaction. For all surfaces, including the clean surface, the Cu_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

FIG. 7. Geometries of bare, 1 and 2 ML Ru passivated, Ru^{25} , Ru^{50} , Ru^{75} , and Ru^{100} surfaces that provide the most favorable binding energy for the Cu_n nanocluster ($n = 2, 3$, and 4) adsorption are shown in panel columns (a)–(g), respectively.

would promote wetting over association. However, we know that the clean TaN surface promotes Cu association; this is not 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/surface supercell) for all geometries of the clean, 1 ML Ru passivated, Ru^{25} , and Ru^{75} surfaces, while it is negative for all geometries of the 2 ML Ru passivated and Ru^{100} surfaces (see Table S6 of the [supplementary material](#) for individual energies). A positive E_{SR} indicates that the undistorted surface is more favorable 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 Ru^{100} in Table I is -24.66 eV. This is the main reason to exclude this contribution in the E_{bind} calculations. Ru^{50} is not included in the above discussion because it showed negative E_{SR} for some arrangements and positive values for the others (Table S6 of the [supplementary material](#)). However, when the values are negative, they are very large in magnitude compared to the positive values in Table I. Large values of E_{SR} are always associated

with the formation of recesses on the surface due to the association of the doped Ru atoms. On the doped surfaces, the distorted surface geometries are favorable only in Ru^{50} and Ru^{100} surfaces. However, for the Ru^{100} surface, the favorable distortion was observed for all of the Cu_n arrangements but not so for the Ru^{50} surface. Specific Cu_n arrangements such as $\text{Cu}_2^{\text{c-v}}$, Cu_2^{far} , $\text{Cu}_3^{\text{c-v}}$, and all of Cu_4 clusters except the $\text{Cu}_4^{\text{tet3D}}$ arrangement are found to trigger the distortion in this surface. This could be due to the unique “zigzag” arrangement of the Ru dopants on the surface.

Table S7 of the [supplementary material](#) summarizes the most and least favorable arrangements of the Cu_2 , Cu_3 , and Cu_4 nanoclusters on the respective surfaces. From this table, the “far” arrangement has the most favorable Cu–slab interaction (E_{bind^*}), and although it has the least favorable 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 the formation of 3D-like structures.

FIG. 8. 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.

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. However, 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 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.

FIG. 9. 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.

TABLE I. 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 Eq. (2), $E_{\text{bind}+}^{\text{avg}}$ is the average of the binding energies calculated as per Eq. (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, and 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)	$E_{\text{SR}}^{\text{avg}}$ (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

2. Influence of Cu–Cu and Cu–slab distances on the stability of Cu_n adsorption

In Figs. 8(b) and 8(d), we highlighted the examples Cu₂^{far} on the Ru¹⁰⁰ surface and Cu₃^{c-line} on the Ru⁵⁰ 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 Fig. 10(a), with the results plotted in Fig. 10(b). 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 (Cu₃^{c-line} on Ru⁵⁰ and Cu₂^{far} on Ru¹⁰⁰), and these are the same two arrangements marked in Figs. 8(b) and 8(d). In these structures, at least one of the Cu atoms is buried in the surface [indicated by the negative $d(\text{Cu-slab})$ in Fig. 10(b)] resulting in a higher

coordination and increased binding. Even though there exists a data point below −1.0 Å in the case of the Ru¹⁰⁰ surface (Cu₂^{c-v} arrangement), it still has a less favorable binding energy than the marked arrangements.

The reason for lower $d(\text{Cu-slab})$ in the Cu₂^{c-v} arrangement when compared to the Cu₂^{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 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, $d(\text{Cu-Ta})$, $d(\text{Cu-Ru})$, and $d(\text{Cu-N})$, as shown in Figs. S7(a)–S7(c) of the [supplementary material](#), 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.

FIG. 10. 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. 11. Bar charts (a)–(c) compare the binding energy differences ΔE_{bind} , ΔE_{bind^*} , and $\Delta E_{\text{Cu-Cu}}$, respectively, per adsorbed Cu adatom on all the studied doped surfaces with respect to the clean surface. ΔE_{bind} is calculated using Eq. (6).

Furthermore, the average $d(\text{Cu-slab})$ is also listed in Table I 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 the 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 S2–S5 of the supplementary material and also discussed in detail in Sec. VIII of the supplementary material. 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 favorable E_{bind} .

When analyzing 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 favorable binding energy. In contrast, only on the bare surface, a short Cu–slab distance and a short Cu–Cu distance are associated with favorable 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

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 favorable binding energies compared to the Ru^{50} surface (see Fig. 8 and Table I). To understand this observation better, the individual binding energy differences between the doped

surfaces and the clean surface

$$\Delta E = E^{\text{Ru}^x} - E^{\text{Clean}} \quad (6)$$

for E_{bind} , E_{bind^*} , and $E_{\text{Cu-Cu}}$ are plotted in Figs. 11(a)–11(c), 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 the Cu–Cu interaction. This less favorable binding to the surface could promote the 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 the topic of our future research.

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 four 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 the 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 develop a combined barrier + liner material that can facilitate the further downsizing of device interconnects. Twelve different arrangements of Cu₂, Cu₃, and Cu₄ 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 Ru⁵⁰ surface showed us that the surface stability is largely dependent 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 favorable 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. Furthermore, 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 three 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 Ru⁷⁵ surface, all modified TaN surfaces show enhanced Cu-slab interactions compared to the clean TaN (1 1 0) surface. The outlying behavior 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 favorable $E_{\text{bind}}^{\text{avg}}$, $E_{\text{bind}*}^{\text{avg}}$, and $E_{\text{Cu-Cu}}^{\text{avg}}$ values are observed for the Ru¹⁰⁰ 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 favorable 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 favorable binding energy, indicating that Cu atoms prefer to be separated on these surfaces. The same was not true on the clean surface, where favorable binding was associated with shorter Cu-Cu distances, showing a possible preference toward the 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 favorable 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/atom⁴⁶).
2. For wetting to be preferred over association, the Cu-slab binding energy must be more negative than the Cu-Cu interaction energy ($E_{\text{bind}*}^{\text{avg}} < E_{\text{Cu-Cu}}^{\text{avg}}$) and $E_{\text{bind}}^{\text{avg}} < -3.49$ eV/atom.

On all surfaces, including the clean surface where we know that Cu associates, we found $E_{\text{Cu-Cu}}^{\text{avg}} > E_{\text{bind}*}^{\text{avg}}$ and the value of $E_{\text{Cu-Cu}}^{\text{avg}}$ was much more positive than the bulk cohesive energy of Cu (for example, on the Ru¹⁰⁰ surface $E_{\text{Cu-Cu}}^{\text{avg}} = -0.90$ eV and $E_{\text{bind}*}^{\text{avg}} = -3.22$ 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 $E_{\text{Cu-Cu}}$ than the corresponding $E_{\text{bind}*}$. It was surprising to see the Cu₄^{c-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 condition 2 (including the clean surface), only 2 surfaces, namely, the 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. 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 favorable 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 favor 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.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for additional information on (a) doping arrangements, (b) 1 Cu adsorption geometries, (c) 2–4 Cu nanocluster adsorption geometries, (d) 2D to 3D transformation pathway, (e) list of various binding energies, (f) list of structural rearrangement energies, (g) most and least favorable arrangements, and (h) individual Cu–slab distances.

AUTHOR'S CONTRIBUTION

S.K.N. and C.-L.N. are contributed equally to this work.

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- ⁴⁶C. Kittel, *Introduction to Solid State Physics* (Wiley, 2004).