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First-Principles Simulations of Conditions of Enhanced Adhesion Between Copper and TaN(111) Surfaces Using a Variety of Metallic Glue Materials**

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Particle aggregation and film agglomeration have been among the main technical hurdles for solid-state thin film development and have been observed in many semiconductor and catalytic systems.[1–7] In heterogeneous catalysis, particle aggregation leads to reduction of effective surface area and degradation of catalytic performance.[1,8–10] On semiconductor surfaces, film agglomeration may give rise to electric short, electron migration, and device degradation.[6,11,12] Prevention of these effects presents a great technical challenge and has been one of the most active research areas in recent years.[12–19] One approach towards reducing surface agglomeration is to insert a thin interfacial layer, often referred to as a "glue layer", between the substrate and the adlayer of concern. Herein, we report three necessary fundamental conditions for a glue layer to be effective in promoting adhesion of a thin-film material to the substrate and to suppress agglomeration of the film at the interface. Copper agglomeration and adhesion enhancement on a TaN(111) surface, which was found to be the preferred orientation upon physical vapor deposition (PVD) growth,[20] will serve as the model system to demonstrate the theoretical approach. First-principles simulations were utilized to predict adhesion strength of various glue layer formulations. This approach allows us to make objective comparison of interaction energies between film interfaces and a set of performance criteria for material selection that augments empirically driven material selection processes, which have been largely trial-and-error in experiments to date.

TaN has been used effectively as a barrier to prevent diffusion of the copper metal interconnect into the insulating dielectric and ultimately into the gate dielectric of CMOS-based transistors (CMOS = complementary metal oxide semiconductor). Atomic layer deposition (ALD)[6] is a powerful thin-film deposition technique that provides atomistic control over deposition to support the continued scaling of the TaN barrier with a copper seed layer for advanced-generation CMOS devices. However, seed-layer copper agglomeration on the TaN surfaces has been a bottleneck in the development of this approach. Numerous attempts have been made to stabilize the copper thin film against agglomeration directly on the barrier with limited success.[18,19,21] Recently, Kim et al. proposed to insert a thin ruthenium layer between the copper film and the TaN substrate to enhance copper adhesion.[18] The concept was also demonstrated for a Cu/WN interfacial system.[12] Unfortunately, a Ru-based process is expensive, and thus its applications are limited. Herein, we show that first-principles simulations are capable of providing quantitative information to aid material selection to allow broad applications of glue-layer-based technology using ALD.

The TaN(111) surface is described by a slab model containing four alternating layers of tantalum and nitrogen, with nitrogen on top (Figure 1). In between slabs, there is a vacuum of approximately 24 Å. The nitrogen-terminated TaN(111) surface can be obtained by means of PVD[20] or by nitriding the Ta-terminated surface with N_2 gas.[22] To simplify the calculations, only monolayers or bilayers of copper and glue materials were included in our studies. We note that in practice the glue layer can be made as a monolayer or a bilayer, and the copper seed film can also be made ultrathin (less than 1.0 nm) using the ALD technique.[12,23] The selected

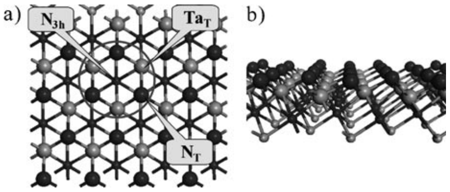

Figure 1. The structure of the TaN(111) surface. a) Top view, b) side view.

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rectangular unit cell contains 32 Ta and 32 N atoms in addition to atoms of copper and glue layers, up to 128 atoms total. All atoms, except those of the bottom two layers of TaN(111), and the surface cell parameters were fully optimized. The calculated surface cell parameters are $a = 12.416$ Å and $b = 10.753$ Å. Density functional theory (DFT) with the Perdew–Burke–Ernzerhof exchange–correlation functional was used in the spin-polarized electronic structure calculations.[22,24–27] The adhesion energies of metal layers were evaluated using Equation (1):

$$E_{\mathrm{ad}} = -[E(\mathrm{sub} + n\mathrm{M}) - E(\mathrm{sub}) - nE(\mathrm{M})]/n, \tag{1}$$

where E(sub+nM), E(sub) and E(M) are the total energies of M on substrate, substrate, and metal atom (M), respectively, and n is the number of atoms on the metal film. Upon full structural relaxation, the dynamic behavior of the Cu film and glue layer on the TaN(111) surface was simulated using ab initio molecular dynamics (AIMD) at a typical ALD process temperature of 500 K for 5 ps with a time step of 1 fs.[28–30]

We first examined the adhesion of a copper monolayer on the TaN(111) surface. There are three possible adsorption sites for Cu on the surface, as labeled in Figure 1: on top of a N atom ($\mathrm{N_T}$), on top of a Ta atom ($\mathrm{Ta_T}$), and the three-fold site formed by top-layer N atoms with third-layer N atom underneath ($\mathrm{N_{3h}}$). The calculated adsorption energies of Cu on these sites are 2.24, 3.01, and 3.51 eV, respectively, indicating that the $\mathrm{N_{3h}}$ site is strongly preferred for Cu atoms. The Cu atoms adsorbed at other sites all shifted to the $\mathrm{N_{3h}}$ sites upon geometry optimization. Structurally, the Cu atoms are slightly embedded in the top N layer to take advantage of the interaction with the Ta layer and the third-layer N atoms. Compared with Cu adsorption on WN surfaces with adsorption energy of 4.94 eV,[31] the adsorption strength on TaN(111) is considerably smaller. Calculation of adhesion energy of a well-aligned Cu monolayer, commensurate with the TaN(111) substrate structure with Cu atoms anchored at the $\mathrm{N_{3h}}$ sites, yields 3.31 eV atom^{-1}, again significantly smaller than on WN surfaces (3.91 eV).[32] The results imply that Cu agglomeration would more readily occur on TaN than on WN surfaces. Indeed, our AIMD simulations suggest that a Cu monolayer on TaN(111) surface undergoes rapid aggregation to form surface islands at 500 K (Figure 2 a), similar to the behavior of Cu monolayers on WN surfaces.[32] A bilayer of Cu thin film on TaN(111) was also found to undergo rapid aggregation upon AIMD simulation at 500 K, suggesting that direct deposition of Cu seed layers on TaN(111) would not produce a smooth thin Cu film under ALD process conditions, regardless of the film thickness. The results are in excellent agreement with experimental observations.[6]

Recent studies using radio-frequency sputtering and ion-beam sputtering suggest that Ru can be utilized to develop a glue layer to enhance Cu adhesion on diffusion barrier surfaces with good conformity.[18,19] However, the underlying mechanism has remained poorly understood. We thus first examined the behavior of a Cu monolayer on the TaN(111) surface with a Ru monolayer inserted in between by performing AIMD simulations. Similar to Cu, Ru atoms are all preferentially adsorbed on the $\mathrm{N_{3h}}$ sites. The calculated Ru adhesion energy on TaN(111) is 4.92 eV atom^{-1}. The significantly higher adhesion energy for Ru on the TaN(111) surface gives rise to a well-aligned Ru monolayer, commensurate with the substrate structure. We subsequently studied copper adhesion on the Ru/TaN(111) surface. We found that the energetically most favorable location for a Cu atom is the three-fold hollow site formed by Ru atoms with a Ta atom underneath. The calculated Cu adhesion energy on Ru/TaN(111) is 4.56 eV atom^{-1}, significantly higher than Cu on TaN(111). Structural comparison with and without the Ru glue layer is shown in Figure 2. In contrast to the case without the glue layer, our AIMD simulations indicate that the Cu monolayer remains stable and does not agglomerate during the entire AIMD run, clearly demonstrating the critical role of the Ru glue layer in stabilizing the Cu film. The calculated Cu–Cu radial distribution function (RDF), shown in Figure 2 b, exhibits significant downshift from 3.1 to around 2.5 Å, which is the typical Cu–Cu bond distance of Cu clusters,[33] for Cu/TaN(111), while for Cu/Ru/TaN(111) the RDF is peaked at 3.1 Å, which is the distance between two adjacent $\mathrm{N_{3h}}$ sites. The results indicate that the Cu monolayer undergoes agglomeration to form Cu clusters on TaN(111) but remains stably commensurate with the structure of Ru/TaN(111). Figure 3 displays the calculated electron density difference of the Cu/TaN(111) and Cu/Ru/TaN(111) monolayers. For Cu/TaN(111), the adhesion is governed by electron transfer from Cu to the substrate. On Ru/TaN(111), Cu adhesion is enhanced by Cu–Ru metallic bonding.

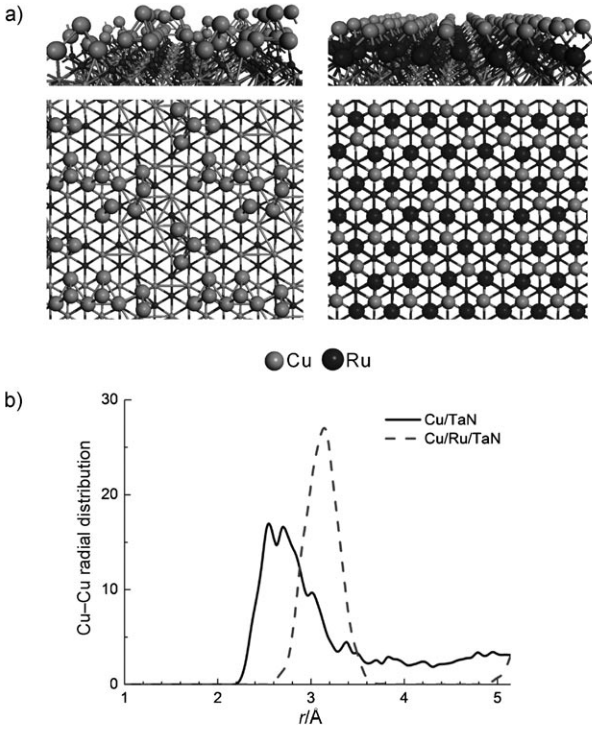


Figure 2. MD results of Cu/TaN and Cu/Ru/TaN surface at 500 K. a) Snapshots of Cu/TaN(111) (left) and Cu/Ru/TaN(111) (right). b) Cu–Cu radial distribution function.

In practice, the glue layer might be thicker than a monolayer, and it might be expected that the Cu monolayer

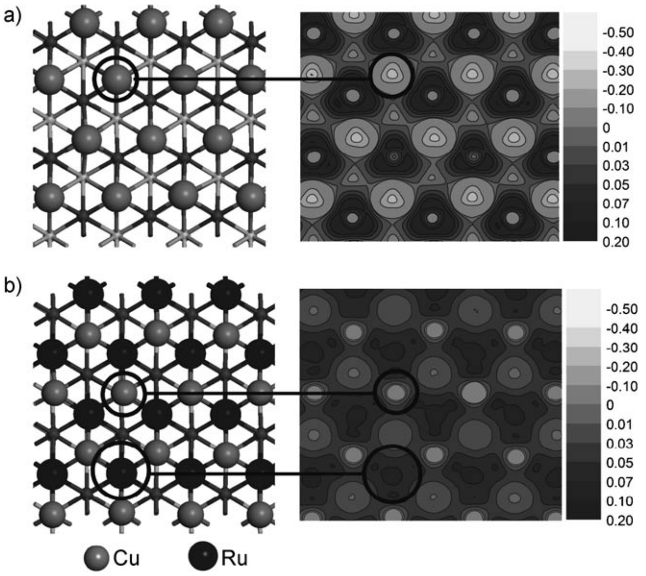
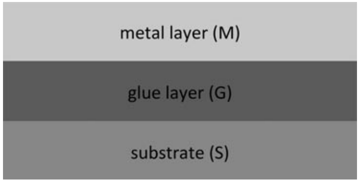


Figure 3. Electronic density difference for the a) Cu/TaN(111) and b) Cu/Ru/TaN(111) surfaces.

would behave differently. To address this issue, we performed calculations on a Cu monolayer on a slab of Ru(001) surface with four layers, which was reported to be the most stable surface for Cu adhesion.[34] The calculated Cu adhesion energy is 4.18 $\mathrm{eV\,atom^{-1}}$, slightly smaller than on a Ru monolayer on TaN(111) but still considerably higher than a Cu monolayer on TaN(111). In the AIMD simulation, the well-aligned Cu monolayer was found to remain nearly intact on the Ru slab. We next performed AIMD simulations on a monolayer and a bilayer of Cu thin films on a Ru bilayer commensurate with the substrate TaN(111) surface at 500 K. Again, no Cu agglomeration was observed in either case.

The above results clearly demonstrate the importance of the relative strength of adhesion forces at solid–solid interfaces. Fundamentally, three factors are critical for selecting the appropriate glue layer (G) for optimizing the interfacial interactions of the metal layer (M) with the substrate (S), as schematically shown below:



1. To prevent metal (M) agglomeration on a glue layer (G), the adhesion of the metal film on the glue layer (E_{MG}) must be stronger than on the substrate (E_{MS}), that is, $E_{MG} > E_{MS}$.
2. To prevent glue layer agglomeration on the substrate, the adhesion of the glue layer on the substrate (E_{GS}) must be stronger than the adhesion of the metal layer on the substrate (E_{MS}), that is, $E_{GS} > E_{MS}$.
3. To prevent the diffusion of glue layer atoms into the metal film, the adhesion of the glue layer on the substrate must be stronger than the adhesion of the metal layer on the glue layer, that is, $E_{GS} > E_{MG}$.

Obviously, Ru as the glue layer material satisfies all three conditions for Cu adhesion on TaN(111) surfaces. More importantly, first-principles simulation methods provide a unique advantage to quantitatively predict adhesion energies and to identify materials with appropriate binding strengths to improve solid-phase interfacial interactions.

Table 1 lists the calculated adhesion energies of several selected metals that are much less expensive than Ru and could potentially serve as glue layer materials for improving Cu adhesion on the TaN(111) surface. Without exception, all metal atoms preferentially reside on the N_{3h} site, and the monolayer is commensurate with the substrate structure. Of these metals, ruthenium and tantalum have been shown experimentally[18,19,21] to be suitable for effectively gluing Cu onto barrier surfaces, such as TaN(111). The calculated adhesion energies satisfy all three conditions required for Cu adhesion enhancement and are consistent with experimental observations. For nickel, the adhesion energy of Cu on Ni/TaN(111) is much weaker than that of Cu on TaN(111), indicating poor Cu adhesion on the surface. Indeed, the Cu monolayer undergoes drastic aggregation on the surface upon AIMD simulation, and attempts to use Ni as glue layer material to stabilize Cu thin films have never been successful experimentally. The calculated adhesion energies of aluminum on TaN(111) and Cu on Al/TaN(111) satisfy the conditions 1 and 2 but fail to match the condition 3, implying that Al could potentially diffuse into the Cu seed layer. To confirm the prediction, we performed an AIMD simulation on a Cu monolayer on Al/TaN(111). As expected, a few Al atoms break away from the TaN(111) substrate and penetrate into the Cu layer to form an Al–Cu alloy layer. Figure 4 displays a snapshot of the AIMD run and the height distribution of Cu and Al atoms. Al diffusion into the Cu layer is readily visible. The perfectly ordered original monolayer structure of Cu and Al (Figure 4b) becomes significantly disordered (Figure 4c). To further test the diffusivity of Al into the Cu film, we studied the interfacial adhesion properties of a Cu monolayer on an Al bilayer commensurate with the substrate TaN(111) surface. Again, the calculated

Table 1: The calculated adhesion energies of metal monolayers in eV per atom.

Surface	M/TaN	Cu/M/TaN
Cu	3.31	
Ru	4.92	4.56
Ta	7.91	5.07
Ni	4.04	2.98
Co	3.61	3.78
Al	4.01	4.25
Nb	5.30	4.96
Ti	4.21	3.75
Zr	6.56	4.28

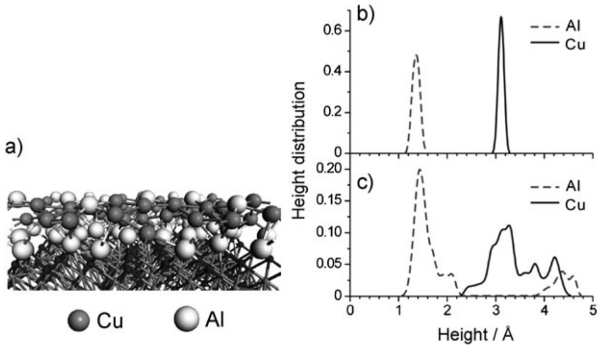


Figure 4. a) Snapshot of the Cu/Al/TaN(111) surface. b) Initial and c) equilibrium height distribution of the Cu/Al/TaN surface. The height of the top N layer was shifted to zero.

adhesion energies between the Cu and Al layers are higher than the adhesion energy between the Al and the TaN(111) surface ($E_{\text{Cu-Al}} = 4.28$ eV, $E_{\text{Al-TaN}} = 3.91$ eV). As expected, Al atoms in the glue layer were found to rapidly diffuse into the Cu films upon AIMD simulation at 500 K. A previous time-of-flight secondary ion mass spectrometry experiment[11] on physical vapor deposition of Al–Cu alloy seed layers onto TaN surfaces has identified Al diffusion into the Cu film upon annealing, and our simulation results are in excellent agreement with the experimental observations. The calculated adhesion energy of cobalt on TaN(111) shows marginal improvement over the adhesion energy of Cu on the surface. The conditions 1 and 2 are barely met, and condition 3 is not satisfied. We thus conclude that Co is not suitable to serve as a glue layer material for Cu adhesion on TaN(111). Finally, our calculations suggest that the adhesion energies of niobium, titanium, and zirconium all nicely satisfy the conditions 1–3, and we therefore predict that these metals should be well-suited as glue layer materials for improving Cu adhesion.

In summary, we have identified three fundamental conditions that can be used as a guiding principle for materials design and selection to improve interfacial adhesion of solid surfaces. These conditions are particularly useful for multilayer interfacial phenomena and facilitate rapid screening of material candidates for specific applications by first-principles quantum mechanical simulations. Using copper adhesion on TaN(111) surface with a variety of metals as glue layer candidates as an example, we have demonstrated that theoretical methods are capable of predicting the adhesion properties in excellent agreement with observed experimental phenomena. It is worth noting that the three fundamental conditions are necessary but not sufficient. The predicted adhesion phenomena need to be verified by ab initio molecular dynamics at the designated temperature and, ultimately, validated by experiments.

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