 J. Phys. Chem. C **2008,** *112,* 9798–9802

Ab Initio Molecular Dynamics Simulation on the Aggregation of a Cu Monolayer on a WN(001) Surface

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Received: December 21, 2007

We present a first-principles simulation study of copper aggregation on a WN(001) surface. Copper cluster formation energies and activation barriers were systematically evaluated, and the results indicate that these energies do not significantly vary with cluster size if the cluster grows two dimensionally. Moderately higher activation barriers but more favorable thermochemical energies are required for growing three dimensional clusters on the substrate. Ab initio molecular dynamics simulations were performed to examine the dynamic behavior of a copper monolayer originally commensurate with the WN substrate at several atomic layer deposition (ALD) operating temperatures as well as at room temperature. The results reveal that the copper film undergoes substantial agglomeration on the WN(001) surface at ALD operating temperatures, which is consistent with experimental observations, whereas the copper monolayer remains largely stable at room temperature.

I. Introduction

The continued trend of shrinking feature size of logical devices has generated increasing interests in developing novel materials for semiconductor applications.[1] Design and development of a new generation of interconnect materials that are more reliable with higher conductivity to replace the conventional aluminum-based interconnect is a subject of extensive research.[2] Copper, in particular, has been widely accepted to be the preferred interconnect material due to its lower electrical resistivity and higher electromigration resistance than those of aluminum.[3] However, the high diffusivity of copper in silicon was found to degrade device performance.[4] To prevent copper diffusion, diffusion barriers using TaN or WN are required.[3,5,6] It has been widely recognized that atomic layer deposition is the preferred technology for depositing the copper seed layer for the future generation of logical devices.[7] Unfortunately, Cu films were found to agglomerate on diffusion barrier surfaces at typical atomic layer deposition (ALD) operating conditions, forming Cu islands on the surfaces that lead to a decrease of conductivity.[8] Fundamental understanding of Cu agglomeration processes on barrier surfaces is of essential importance to ensure successful applications of ALD technology. In this paper, we report an ab initio molecular dynamics (MD) simulation study on Cu agglomeration on WN(001) surface. We show that a well aligned Cu film on WN(001) remain stable at near ambient temperatures but can undergo a substantial agglomeration process at a typical ALD operating condition. Despite the fact that Cu aggregation on barrier layer surfaces has been experimentally observed, the present study represents the first comprehensive first-principles-based simulations to reveal the underlying mechanism that dictates the agglomeration processes.

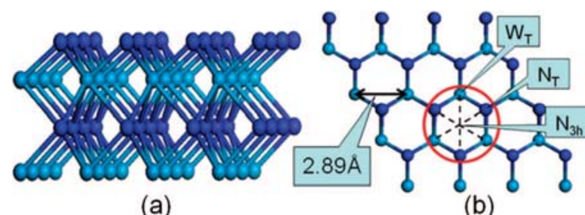

Figure 1. Structure of the WN(001) surface; (a) side view; (b) top view.

In a recent paper, we attempted to address the Cu agglomeration mechanisms by examining lowest energy pathways of small cluster formation on a WN(001) surface. Our results suggest that Cu surface clustering is a competitive process against surface wetting.[9] However, the key issue of whether a Cu thin film would agglomerate at an ALD operating condition was not addressed. The main purpose of the present study is to understand the dynamic behavior of Cu thin films on WN(001) in a typical temperature range of an ALD process. Specifically, we wish to further investigate the minimum energy pathways that lead to growth of small Cu clusters on a WN(001) surface upon diffusion of a few Cu atoms and to examine whether the agglomeration of a Cu thin film is dynamically possible at a typical ALD operating condition. For clarity, the concept of agglomeration in the present case specifically means that Cu atoms adsorbed on the WN(001) surface break the covalent bonds formed with the surface N atoms in favor of forming Cu−Cu metallic bonds, leading to formation of Cu clusters on the diffusion barrier surface.

II. Computational Method

The WN(001) surface is described with a slab model containing four alternating layers with W and N with N on top

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10.1021/jp802979b CCC: $40.75 © 2008 American Chemical Society
Published on Web 06/07/2008

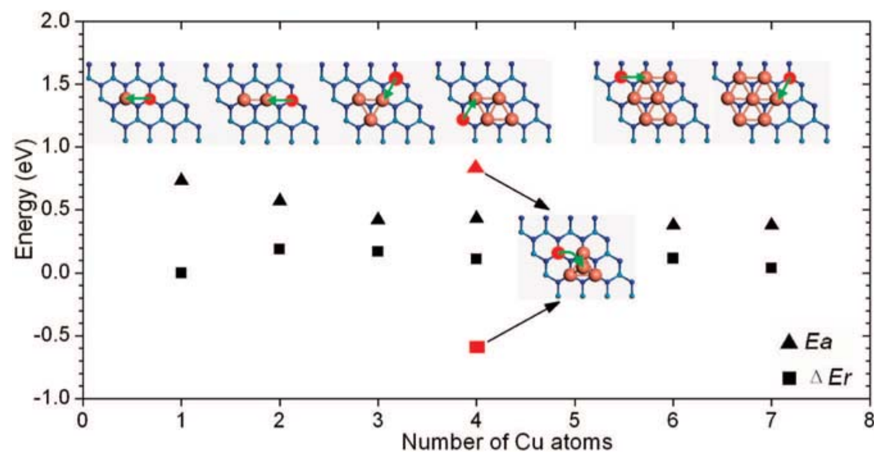

Figure 2. The calculated reaction energies and activation barriers of Cu_n ($n = 1-7$) cluster formation on the WN(001) surface. (The red square and triangle represent the reaction energy and activation barrier of tetrahedron formation on the surface, respectively.) The optimized structures of Cu_n ($n = 1-7$) are also shown in the figure, the red balls represent the initial position of the Cu atoms, and the green arrows indicate the pathways.

TABLE 1: The Calculated Average Mulliken Charge Transferred from Cu Atom to the WN(001) Surface*

number of Cu atoms	1	2	3	4	6	7	16
charge transfer (e/atom)	0.966	0.833	0.738	0.685	0.640	0.613	0.469

* The average charge transfer from Cu atom to the WN(001) surface of Cu tetrahedron is 0.546.

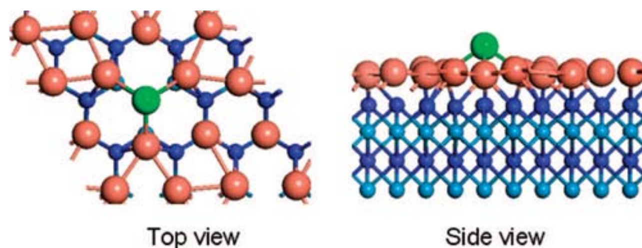

Figure 3. The optimized structure of 17 Cu atoms adsorb on the WN(001) surface. The green atom stands for the additional Cu atom.

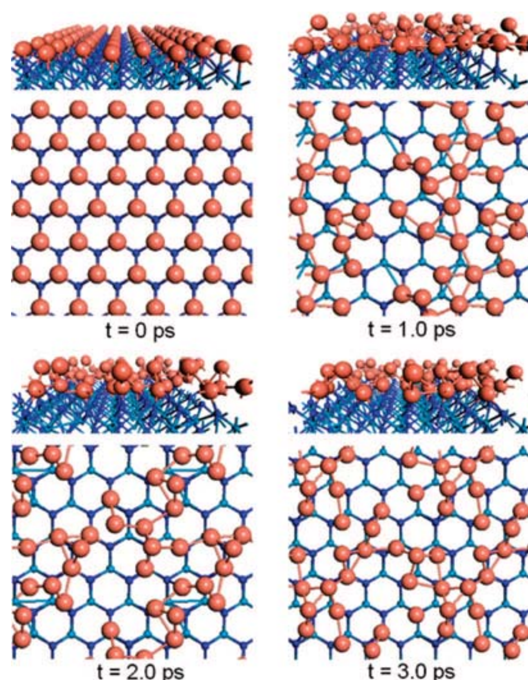

Figure 4. Snapshot of the MD trajectory.

(Figure 1, panels a and b). The selected unit cell contains 32 W and 32 N atoms, and the surface cell parameters were fully optimized ($a = b = 11.56$ Å, $\alpha = 120°$). Between slabs there is an approximately 24 Å vacuum space to prevent effective interaction between slabs. The bottom two layers are kept fixed, and the top two layers, as well as the Cu adatoms or Cu monolayer, are fully relaxed. Density functional theory (DFT) calculations under the generalized gradient approximation were performed using the exchange-correlation functional proposed by Perdew−Wang.[10–12] The norm-conserving pseudopotentials are used to represent the core electrons, and the valence orbitals are described by a double-ζ numerical basis set augmented with polarization functions with a cutoff energy of 200 Ry, which is sufficient to produce well-converged results.[13,14] The electronically open-shell system was treated with a spin polarization scheme. The Brillouin zone integration was performed using the Monkhorst and Pack scheme with $2 \times 2 \times 1$ k-points. Calculations with higher k-points ($4 \times 4 \times 2$) were also performed for dimer formation on the WN(001) surface, and the results were found to be virtually identical to those obtained with $2 \times 2 \times 1$ k-points. All structures were first optimized using the conjugate gradient algorithm, and the computational accuracy was tested by calculating the cohesive energy of bulk copper. The calculated cohesive energy is 0.05 eV higher than the experimental value of 3.49 eV, suggesting that the method used in the present study is reasonably accurate. Upon structural relaxation, we performed ab initio molecular dynamics (MD) simulations for duration of 3.5 ps with a time step of 1 fs at several typical ALD operating temperatures as well as room temperature for comparison purpose to study the dynamic behavior of a Cu monolayer on the barrier surface in a canonical ensemble using the Nosé thermostat for temperature control. The distributions of distances between atoms of interest were calculated after 1.0 ps simulation time. To test the reproducibility of the distance distributions, we extended the simulations time to 5.0 ps at 500 K and found that the main features in the distribution profiles remain unchanged. All calculations were carried out using the SIESTA simulation package.[15]

III. Results and Discussions

As shown in Figure 1b, there are three possible adsorption sites for Cu on WN(001), and we identified the 3-fold site labeled as W_T the energetically most favorable site for adsorp-

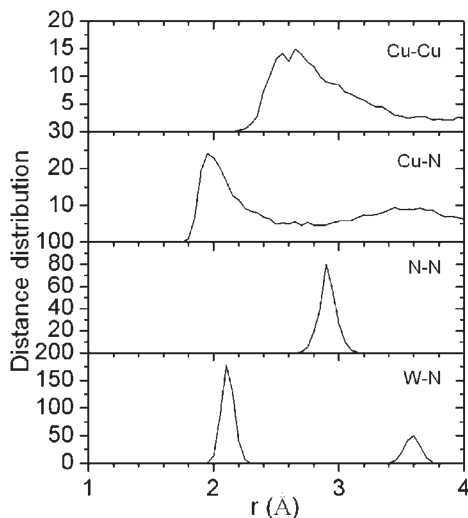

Figure 5. The calculated distribution of Cu−Cu, Cu−N, N−N, and W−N distances.

tion of Cu atoms on a WN(001) surface at low coverage in a previous paper.[9] Before we present the MD results, we first examine the diffusion of Cu atoms to form clusters on the substrate for coverage up to 0.4375 ML, which allows us to gain useful insight into the energetics required for the cluster formation. The calculated thermochemical energies and activation barriers to move a Cu from a W_T site (red ball) to the designated site along the arrow direction are shown in Figure 2. The barrier to move a single Cu atom at zero coverage is 0.73 eV, which is rather moderate. However, it requires 0.19 eV thermochemical energy to form a dimer with a barrier of 0.57 eV; in the middle of the destination, the Cu atom "feels" the attraction of the nearby Cu atom and thus the barrier decreases. Similarly, the activation barrier further decreases as the number of Cu atoms increases, except for the tetrahedral configuration. The increase of the activation barrier for the tetrahedron structure arises from the stringent requirement to move the Cu atom from the surface to the top of the Cu triangle. As the cluster size increases, the average charge flowing from Cu clusters to the WN(001) surface decreases monotonically, as shown in Table 1, because the strengthened Cu−Cu bond in larger clusters reduces the tendency of charge transfer to the substrate.

The above results suggest that diffusion of Cu atoms on barrier surfaces is facile with moderate activation barriers and nearly neutral thermochemical energies at low to moderate coverage. Higher reaction barriers would incur when the Cu clusters grow three dimensionally, although such growth is thermodynamically more favorable due to stronger Cu cohesive energies. It is expected that these barriers can be readily overcome at ALD operating conditions.

We now examine the Cu monolayer on WN(001) surface by placing Cu atoms at the two adsorption sites labeled in Figure 1b as W_T and N_{3h}, which are the most stable sites for Cu, as shown in our previous paper.[9] The placement is commensurate with the substrate structure. Upon geometry optimization, Cu atoms adsorbed at the N_{3h} sites are all shifted to the W_T sites. The calculated adhesion energy of the monolayer, defined by $E_{ad} = -[E(\text{sub} + n\text{Cu}) - E(\text{sub}) - nE(\text{Cu})]/n$, is 3.91 eV/atom. The calculated Mulliken charge on Cu is 0.469 per atom, considerably smaller than that at low coverage.

The closest Cu−Cu distance in the commensurate Cu monolayer structure on the WN(001) surface is 2.89Å, which is considerably longer than the one in a copper crystal structure (2.56Å). However, the seemingly loose monolayer structure can not further accommodate more Cu atoms in the structure plane. Indeed, by placing an additional Cu atom in the selected unit cell in the same plane of the Cu monolayer followed by structural optimization, the extra Cu atom is squeezed out of the plane to reside on top of the 3-fold hollow site formed by the monolayer Cu atoms, as shown in Figure 3, where the extra Cu atom is highlighted in green. The results indicate that all energetically feasible adsorption sites for Cu atoms in the monolayer plane are fully saturated.

We next performed an ab initio MD simulation on the fully equilibrated surface with a Cu monolayer at 500 K, which is in a typical ALD operating temperature range. Figure 4 displays several selected snapshots of the MD trajectory. Initially, the Cu monolayer is well aligned and is commensurate with the substrate. Cu atoms are then quickly disassembled and move away from their equilibrium positions through surface diffusion upon MD run. At $t = 1$ ps, some of the Cu atoms start moving upward to grow three dimensionally. At $t = 3$ ps, the Cu atoms are aggregated together, forming surface islands, and the perfectly ordered monolayer structure becomes significantly disordered. Further MD runs prompt Cu atoms to continuously move, forming surface islands of various shapes, but no wetting of copper clusters on the surface was observed. The simulated dynamic behavior is in good agreement with experimental observations.[8]

Figure 5 displays the calculated distributions of Cu−Cu, Cu−N, N−N, and W−N distances. All peak positions for $r_{\text{Cu-Cu}}$ and $r_{\text{Cu-N}}$ are significantly shifted downward from their original positions in the ordered structure. In particular, the Cu−Cu bond distances are much shorter upon Cu agglomeration and are close to the Cu bulk value of 2.556 Å. The peak broadening reflects the structural disorder. Similarly, the Cu−N bond distances are substantially reduced from 2.15 Å to 1.96 Å as a result of moving Cu atoms from the W_T sites to form Cu clusters, which makes the distances between the Cu atoms and some of the N atoms shorter. The peak around 3.5 Å indicates the distance between the topmost Cu atoms and the surface N atoms. In contrast, sharp features in the distribution profiles of N−N and W−N distances are observed, and the peak positions are all around their original substrate positions in spite of slight broadening due to thermal motion, indicating that the barrier layer structures are hardly changed upon Cu agglomeration.

To further reveal the surface agglomeration structure, we display the heights of the surface atoms of the top three layers in Figure 6, normalized by the total number of MD steps, and compare them with the original heights of the atoms. The peak located around 2.8 Å indicates the W layer, that around 4.1 Å is for the N layer, and that around 5.5 Å stands for the Cu layer. At 500 K, despite slight broadening, the height of the W layer is rarely changed. However, the N layer is slightly pushed downward. Drastic broadening, ranging from 5.24 to 7.84 Å, for the Cu layer is readily visible. The first peak of the Cu layer represents the Cu atoms in contact with the substrate, and the second one stands for the topmost Cu atoms, almost 2 Å above their original positions. It is noteworthy that, despite the relatively short MD simulation time, we found that the main features displayed in Figures 5 and 6 do not appreciably change upon a 50% increase of simulation time.

Next, we performed the same ab initio MD simulations at two other ALD operating temperatures (450 and 550 K) as well as at 300 K for comparison purpose. The calculated distribution of Cu−Cu and Cu−N distances is displayed in Figure 7, and

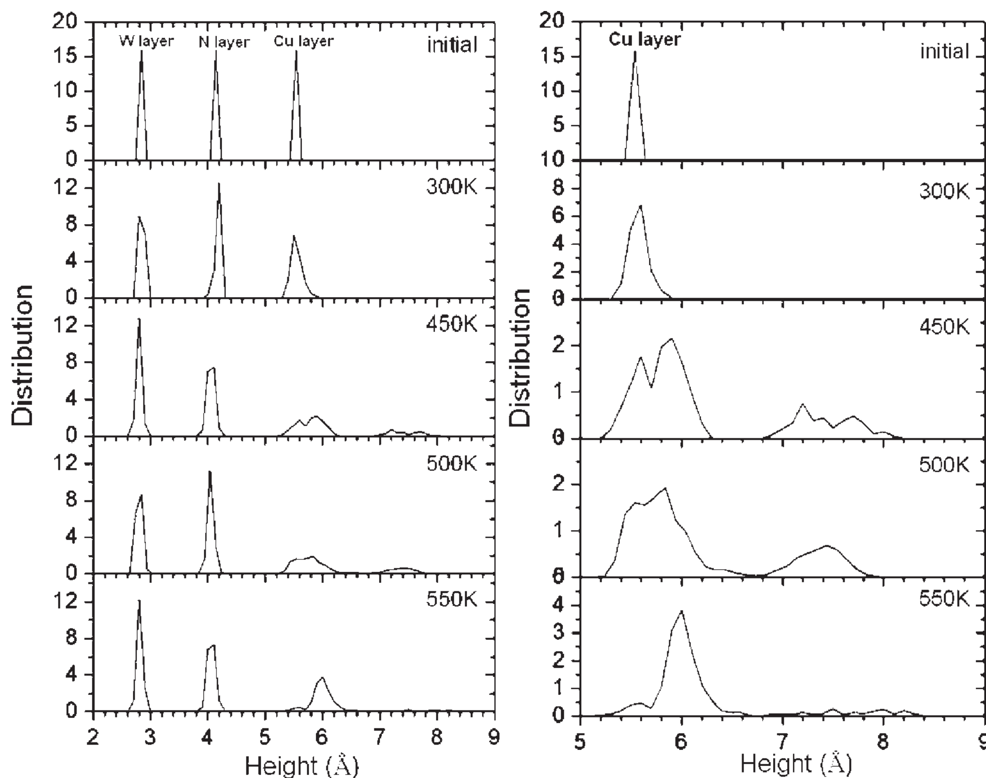

Figure 6. The height distribution of the top three layers (including the Cu layer) of the Cu/WN(001) surface.

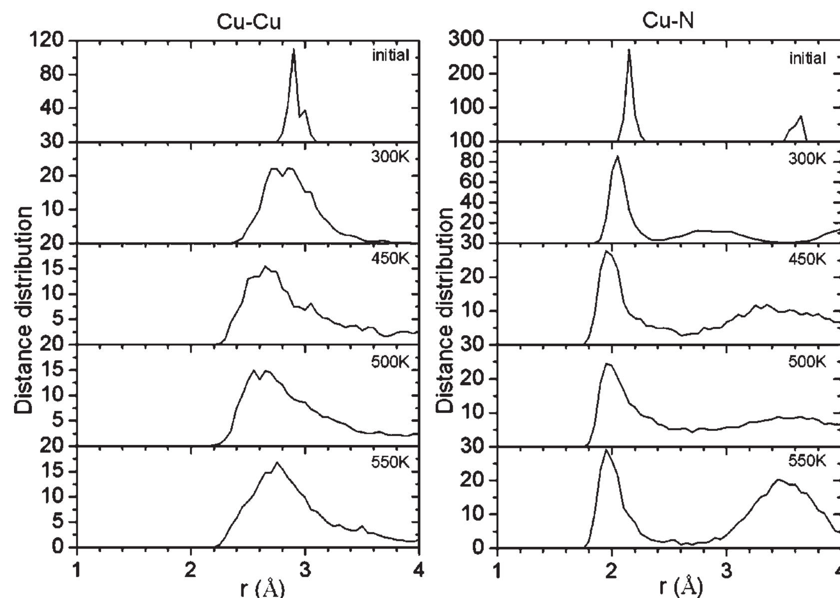

Figure 7. The calculated distribution of Cu−Cu and Cu−N distances at various temperatures.

the height distribution of the top three layers of the Cu/WN(001) surface is shown in Figure 6. Without exception, agglomeration of the Cu monolayer takes place at temperatures above 450 K. As expected, the agglomeration process occurs more significantly at higher temperatures as more Cu atoms shift away from their original positions to build surface clusters. In contrast, the Cu monolayer remains largely stable, although significant thermal motion around its original position is readily visible.

IV. Summary

We have performed extensive DFT calculations to investigate Cu adsorption on a WN(001) surface from zero coverage to a commensurate full monolayer to understand the agglomeration process of Cu atoms. It was demonstrated that Cu atom diffusion along the barrier surface is thermodynamically and kinetically facile due to the fact that the adhesion of Cu films on the substrate is weaker than the Cu−Cu bonding. Our results suggest that Cu island formation on the substrate requires only relatively moderate activation barriers with nearly neutral thermochemical energies. An Ab initio molecular dynamics simulation was then performed for a perfectly well-ordered Cu monolayer commensurate with the substrate surface at several ALD operating temperatures as well as at room temperature to examine the behavior of the Cu film on the barrier surface. Our simulation reveals that the Cu atoms undergo rapid agglomeration processes at ALD operating temperatures, forming three dimensional

clusters on the surface, whereas at room temperature the Cu thin film remains essentially stable. The results suggest that the adhesion of the Cu film on the barrier surface is relatively poor. Indeed, in view of the moderate Cu diffusion barriers and neutral thermochemical energies, it is not surprising that Cu agglomeration would occur on diffusion barrier surfaces, such as WN and TaN. The simulated agglomeration phenomena are in excellent agreement with experimental observations,[8] and the method utilized in the present study provides a possibility to design novel ALD processes to enhance Cu adhesion on diffusion barrier surfaces.

Acknowledgment. This work is partially supported by the National Natural Science Foundation of China under Grant No. 20703040 and Air Products & Chemicals, Inc.

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JP802979B