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Density Function Theory Study of Copper Agglomeration on the WN(001) Surface

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We report a first-principles study of copper agglomeration on the WN(001) surface using density functional theory. Small copper cluster formation was explicitly examined by calculating the minimum energy pathways, yielding detailed information on the adsorption structures and energies. The results show that copper agglomeration is a competitive process against surface wetting and agglomeration may occur under typical atomic layer deposition (ALD) conditions.

1. Introduction

Atomic layer deposition techniques (ALD)[1] have been recognized as the preferred method for developing highly conformal, extremely thin copper films that serve as interconnects in semiconductor devices.[2,3] Unfortunately, the high copper diffusivity in insulators and silicon substrate was found to degrade device performance, and thus thin diffusion barriers are needed to prevent copper diffusing.[2] Transition metal nitrides are currently the most intensively studied barrier materials.[4] In this respect, tungsten nitride (WN) is the preferred candidate due to its attractive properties as a highly refractory material with excellent mechanical and chemical properties.[5] Furthermore, ALD WN at a thickness of 1.5 nm proved to be good barriers for copper diffusion at temperatures up to 600 °C.[6] However, it was observed that copper tends to agglomerate in most diffusion barriers.[2] It is apparent that the interplays between the WN layer and the copper layer trigger the agglomeration process under typical ALD conditions, leading to island formation of copper films. As a result, the resistivity of the copper film increases significantly. Unfortunately, to date, the detailed agglomeration processes are still poorly understood. In the present work, we report first-principles studies on the mechanisms of copper agglomeration on the WN(001) surface by explicitly examining small cluster formation of copper atoms on the substrate. Various agglomeration routes were explored by calculating the minimum energy pathways, yielding detailed information on the adsorption structures and energies as well as energy barriers of cluster formation. We show that copper clustering is a competitive process against atomic wetting and agglomeration could occur under typical ALD conditions.

2. Computational Details

We choose the WN(001) surface to represent the barrier layer using a slab model, which contains four layers alternating with tungsten and nitrogen with the top layer being nitrogen (Figure 1a and 1b). The selected unit cell includes 32 W atoms and 32 N atoms with the cell parameters taken from the crystal structure of WN followed by full structural relaxation excluding the cell constant along the surface normal. The distance between adjacent slabs is set to 24 Å, large enough to prevent effective interaction between slabs. The bottom two layers are kept fixed and the top two layers as well as the Cu adatoms are fully relaxed. The electronic structure calculations were carried out using density functional theory (DFT) under the generalized gradient approximation as proposed by Perdew−Wang[7−9] and implemented in the SIESTA simulation code.[10] We employed the norm-conserving pseudopotentials to describe the core electrons, and the valence electrons are described by the double-ζ numerical basis set augmented with polarization functions. A 200 Ry energy cutoff is proven to yield sufficiently accurate results.[11,12] The spin polarization scheme was used to deal with the electronically open-shell system. The Brillouin zone integration was performed using the Monkhorst and Pack scheme with $2 \times 2 \times 1$ *k*-points. Calculations with $2 \times 2 \times 2$ and $4 \times 4 \times 2$ *k*-points were also performed for dimer formation on the WN(001) surface and the results were found to virtually identical to those calculated with $2 \times 2 \times 1$ *k*-points. Structural optimization was conducted using the conjugate gradient algorithm without symmetry constraints. To test the computational accuracy, we calculated the cohesive energy of bulk copper, which yielded a value of 3.54 eV in good agreement with the experimental value of 3.49 eV. The first principles molecular dynamics (MD) simulation was performed for 7 ps with a time step of 1 fs at 500 K to understand the dynamic behavior of a Cu atom on the barrier surface in a canonical ensemble using the Nose thermostat for temperature control.

The selected unit cell structure shown in Figure 1c exhibits three possible adsorption sites for copper: the two atop sites of the W and N atoms (W_T and N_T) and the center of the hexagon formed by 3 N and 3 W atoms alternatively in a chairlike configuration (site N_{3h}). The adsorption energy of the copper atoms is defined by

$$E_{ad} = -[E(Cu_n + WN) - E(Cu_n) - E(WN)] \qquad (1)$$

where $E(Cu_n + WN)$, $E(Cu_n)$, and $E(WN)$ represent the total energies of the WN substrate with a Cu cluster in the chosen unit cell, the Cu cluster and the surface itself, respectively.

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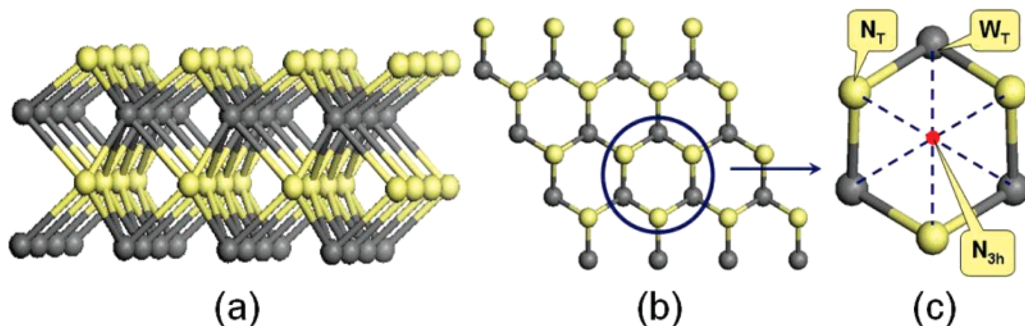

Figure 1. Structure of WN substrate: (a) Side view. (b) Top view. (c) Three possible adsorption sites, the two atop sites of the W and N atoms (site W_T and N_T) and the center of hexagon formed by 3 N and 3 W atoms alternatively in a chairlike configuration (site N_{3h}).

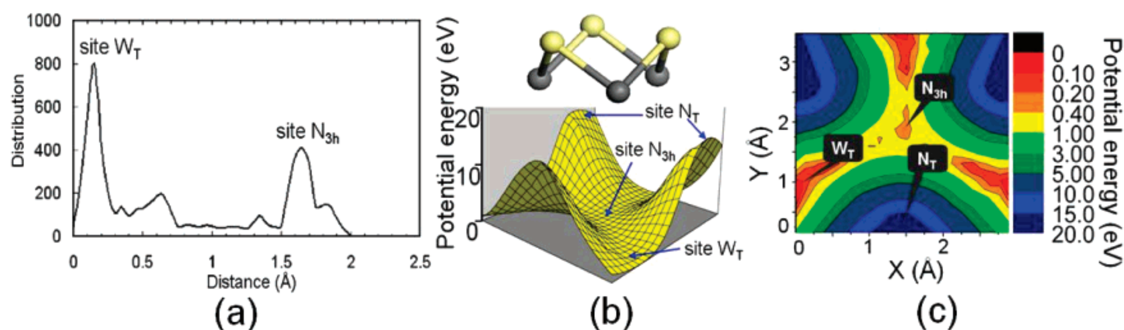

Figure 2. Deviation distance distribution and potential energy surface of Cu on WN(001) surface: (a) deviation distance distribution, (b) 3D view of potential energy surface, and (c) 2D view.

3. Results and Discussions

We first studied a single copper atom on the surface at the three adsorption sites identified in Figure 1c, yielding the adsorption energy of 4.94 eV at W_T, 3.77 eV at N_T and 4.91 eV at N_{3h}. Adsorption at W_T is only slightly more favorable than at N_{3h}, implying that the Cu atom can be essentially stabilized at both sites. At site N_{3h}, The Cu atom resides at the 3-fold hollow site formed by 3 N atoms with a Cu−N bond distance of 2.014 Å and charge transfer occurs from the Cu atom to the N atoms, suggesting a strong covalent bonding interaction. At site W_T, the Cu atom interacts with the nearby 3 N atoms similar to at site N_{3h}; In addition, the Cu atom also resides on top of the W atom at the second layer with a bond distance of 2.520 Å, and significant electron density was found between these two atoms. This indicates a metallic bonding between Cu and W, which gives rise to an additional contribution to the bonding and thus makes adsorption at this site more stable.

To understand the relative stability and the mobility of the Cu atom at various sites on the barrier layer, we performed ab initio molecular dynamics simulations for a single Cu atom on the WN(001) surface in the chosen unit cell. Indeed, high mobility of the atom on the surface was observed. Initially, the Cu atom was placed at W_T followed by equilibration. We then defined the deviation of the Cu distance from its initial position and calculated the distribution of the deviation distance in the course of molecular dynamics. Figure 2a displays the calculated deviation distance distribution. It shows that the Cu atom mainly resides at W_T during much of the simulation time with significant deviation from its equilibrium position. The MD simulation shows that the atom can also travel to the less energetically favorable site N_{3h} with the highest probability around the center of 3-fold hollow site. It is interesting to observe that the Cu atom never moves to site N_T. To understand the dynamic behavior, we further scanned the potential energy surface of the Cu atom on the substrate and the results are shown in Figure 2, panels b and c. Indeed, the lowest energy site is near site W_T with the second lowest one at site N_{3h}; the potential energy at site N_T is the highest. These results provide useful physical insight into the dynamic behavior of Cu on WN(001) surface and explain why adsorption at site N_T was not observed in the MD simulation. In the following, we will focus our discussions of Cu agglomeration mostly on adsorption at site W_T.

To understand the mechanism of Cu agglomeration on the barrier layer, we first placed 2 Cu atoms at 2 W_T sites separated by another site W_T. One of the atoms then moves to the adjacent site W_T, as indicated in Figure 3a, along the pathway defined by the linear synchronous transit (LST)[13] using the initial and final structures. We subsequently calculated the potential energies along this pathway by minimizing the energy of all other degrees of freedom. The results are shown in Figure 3a. The calculated Cu−Cu distance is 2.692 Å, slightly larger than the bulk value of 2.556 Å. The calculation shows that the dimer formation process is slightly endothermic with the reaction energy of 0.19 eV and a moderate barrier of 0.57 eV. These results indicate that dimer formation can readily occur under the ALD conditions with a temperature in the range between 150 and 200 °C.

Next, we examine the trimer formation of Cu on the WN-(001) surface by moving a Cu atom at site W_T toward a dimer along two pathways shown in Figure 3, panels b and c, where the main optimized structural parameters are also shown. The calculations along the minimum energy pathways give trimer formation energies of 0.17 eV for path 1 and 0.25 eV for path 2, respectively, again slightly endothermic. The calculated barriers are 0.42 eV for path 1 and 0.72 eV for path 2, respectively. Obviously, path 1 is more favorable than path 2 both thermodynamically and kinetically. The reason is that the triangle formed in path 1 is more close-packed to maximize the Cu−Cu bonding. Our results indicate that the trimer

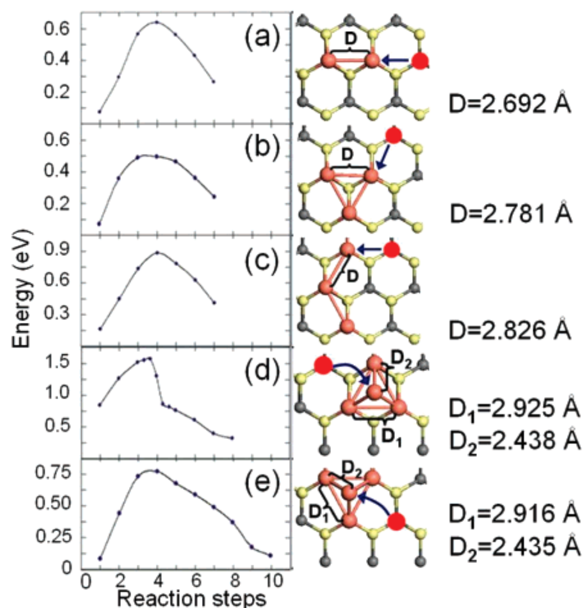

Figure 3. Evolution and final structures of Cu_n ($n = 2-4$) clusters on WN(001) surface: (a) migration path of two Cu atoms, (b and c) path 1 and 2 of three Cu atoms migration, and (d and e) path 1 and 2 of four Cu atoms migration. The red dots represent the initial position of the migration atoms and the blue arrows show the migration path.

formation is a competitive process compared to adsorption of a dimer and a single atom separately.

We further investigated the formation of a 3-dimensional Cu tetramer from a 2-dimensional diamond structure on the surface. The pathways are defined such that one of the atoms in the diamond structure climbs onto the top of the equilateral triangle along two directions: one from site W_T to site N_{3h} passing through site N_T (path 1, Figure 3d) and another from site W_T to site N_T through site N_{3h} (path 2, Figure 3e). The main geometry parameters of the fully optimized final structures are also indicated in these figures. The calculations along the chosen minimum energy pathways yield tetramer formation energies of -0.60 eV for path 1 and 0.023 eV for path 2, respectively. The calculated barriers are 0.83 eV for path 1 and 0.66 eV for path 2, respectively. The results indicate that path 1 is thermodynamically more favorable than path 2; however, kinetically the barriers appear to be higher than those of smaller clusters. The underlying reason is that to climb up onto the trimer the fourth Cu atom must pass through either site N_T (path 1) or site N_{3h} (path 2), which requires additional energy. In path 1, the Cu atom passes through the least energetically favorable site N_T, leading to a higher energy barrier than in path 2.

The cluster formation on the WN(001) surface results in strong Cu−Cu metal bonds. Figures 4a−c displays the calculated total electron densities for $n = 2-4$ for the lowest energy clusters on the surface. The contour plane was carefully chosen so that it is parallel to the surface and passes through the cluster atoms to maximize the visualization of electron density. One observes that a large electron density is distributed between Cu atoms in all cases. In particular, we note that for the tetramer on the surface a large electron density is localized around the center of the Cu atoms despite the fact that the electron density of the Cu atom on the top is only partially visualized. The difference between the total electron density and the superposition of the atomic electron density is shown in Figure 4d−f, which indicates the charge flow upon cluster formation. For

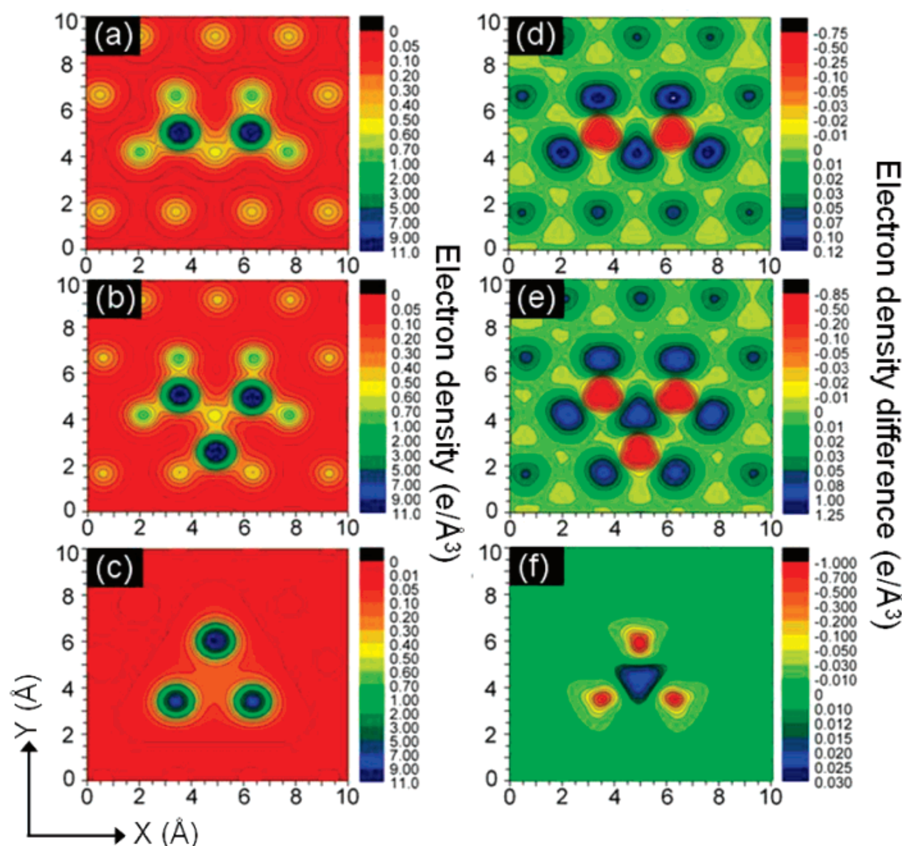

Figure 4. Calculated total electron density and the difference between the total electron density and the superposition of the atomic electron density for Cu_n ($n = 2-4$) for the lowest energy clusters on the WN(001) surface. The electron density is shown for (a) 2 Cu atoms, (b) 3 Cu atoms, and (c) 4 Cu atoms. The difference of electron density is shown for (d) 2 Cu atoms, (e) 3 Cu atoms, and (f) 4 Cu atoms.

the dimer and trimer, the Cu atoms lose electrons to the substrate with the neighboring N atoms serving as an electron acceptor. For the tetramer, however, the charge on the bottom three Cu atoms flows not only onto the nearby N atoms but also to the center of the tetramer to contribute to the cluster formation. Likewise, a fraction of electron from the top Cu atom also moves to the center of the tetramer, leading to strong Cu−Cu bonding.

4. Summary

We have conducted a series of first-principles studies to understand the mechanism of copper agglomeration on the WN-(001) surface by exploring the pathways from Cu adatoms to small copper clusters on the substrate. We first identified energetically most favorable adsorption sites for the copper atoms either as adatoms or as clusters. Subsequently, minimum energy pathway calculations were carried out. We showed that cluster formation on the chosen substrate is near thermo neutral and the calculated energy barriers are relatively moderate, suggesting that the copper cluster formation on the WN(001) surface is a competitive process compared with the formation of a conformal monolayer. This is consistent with experimental observations.[2] The calculated electron density maps of copper clusters indicate that strong Cu−Cu bonds are formed and partial charge transfer from copper atoms to the substrate. The results imply that the copper atoms on the surface could be considerably mobile under the ALD conditions, leading to the agglomeration of copper film. It was proposed recently that prior to deposition of Cu film on WN surfaces, a cobalt glue layer should be deposited to enhance the conformity of Cu layers.[2] Indeed, our DFT calculations on the adhesion of a Co atom on the WN-(001) surface gave a substantially higher adhesion energy for the Co atom than that of the Cu atom (6.34 eV vs 4.93 eV), indicating the strong interaction between Co and substrate. Moreover, the agglomeration behavior of Co on the WN(001) surface is also tested through the barrier calculations of Co dimer formation from two separated Co atoms. The primitive results give a much higher reaction energy of 0.58 eV and a barrier of 1.64 eV than those of Cu (0.19 and 0.57 eV, respectively). This explains why the Co may not agglomerate on the WN(001) surface. We plan to study the agglomeration behavior of Cu on WN surfaces using Co as a glue layer in our future research and will publish the results in due course.

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