Cluster size and substrate temperature affecting thin film formation during copper cluster deposition on a Si (001) surface*

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The soft deposition of Cu clusters on a Si (001) surface was studied by molecular dynamics simulations. The embedded atom method, the Stillinger–Weber and the Lennar–Jones potentials were used to describe the interactions between the cluster atoms, between the substrate atoms, and between the cluster and the substrate atoms, respectively. The Cu_{13}, Cu_{55}, and Cu_{147} clusters were investigated at different substrate temperatures. We found that the substrate temperature had a significant effect on the Cu_{147} cluster. For smaller Cu_{13} and Cu_{55} clusters, the substrate temperature in the range of study appeared to have little effect on the mean center-of-mass height. The clusters showed better degrees of epitaxy at 800 K. With the same substrate temperature, the Cu_{55} cluster demonstrated the highest degree of epitaxy, followed by Cu_{147} and then Cu_{13} clusters. In addition, the Cu_{55} cluster showed the lowest mean center-of-mass height. These results suggested that the Cu_{55} cluster is a better choice for the thin-film formation among the clusters considered. Our studies may provide insight into the formation of desired Cu thin films on a Si substrate.

Keywords: copper cluster, deposition, epitaxy, diffusion

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1. Introduction

Copper is a promising material to replace aluminum alloys for the next generation metallization of ultra-large scale integrated (ULSI) circuits due to its low electrical resistivity and high performance in withstanding electromigration.[1] In the past several decades, the deposition of Cu on a Si surface has attracted considerable research interest.[2–4] Scanning tunneling microscopy (STM) has been widely used to study the surface phenomena and correlate the structures to the experimental conditions.[5–8] However, the STM study of deposition has only provided information about the cluster size and the approximate distribution on the substrate surface. Little is known about the dynamics and the structure of the cluster.[9] The interaction between the atoms in the cluster and in the substrate surface is essential in charactering the deposition and diffusion process for the thin-film growth, which involves a sequence of steps leading to the center-of-mass displacement and the configurational change of atoms within the cluster.[8–10] In addition, the metal/semiconductor interface is widely used for ohmic contacts. The investigation on the configuration is significant for microelectronic devices.

The epitaxial growth of Cu layers on a Si substrate has been investigated experimentally in several studies.[11,12] For example, the epitaxial growth and the interfacial interaction of Cu thin films deposited in ultrahigh vacuum on a Si substrate have been studied.[13] Researchers have investigated the morphological and the structural properties of the epitaxial Cu/Si(001) structure to provide a better understanding of the characteristics related to the magnetism of ultrathin films.[14] Thin films of Cu have been deposited on Si(100) substrates by using neutral cluster beams (NCB) and ionized cluster beams (ICB), where the atomic diffusion and the interface reaction be-

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tween Cu and Si in the as-deposited and the annealed films at different temperatures were investigated.[15] Reliable methods for the deposition and growth of clusters on various substrates are being sought for microelectronics applications.[16−18] So far, experiments can only provide statistical information, such as the cluster size and the approximate distribution of clusters on the substrate, without much detail of the deposition dynamics. Molecular dynamics (MD) simulation is a useful tool for atomistic scale understanding of the cluster/substrate morphology and the diffusion process.

MD simulations can provide rich information, such as epitaxy, reconstruction, mixing of deposited and substrate atoms, as well as the sputtering process and the substrate damage at different ion incident energies and substrate temperatures. Many works on the cluster deposition with the MD simulations have focused on the interaction of metal clusters and metal surface atoms. For instance, in a study of the effects of cluster size and substrate temperature on the homoepitaxial deposition on a Au (001) surface, it was found that a small cluster size and a high substrate temperature favored the epitaxial recrystallization of the clusters.[19] The MD simulation was used to investigate the size effect on the epitaxy when a Cu cluster was softly deposited on the Au (111) surface.[20] The study revealed that the epitaxy formed more easily for smaller clusters than that for larger ones. It was also shown that the lattice distortion at the cluster–substrate interface was most significant compared to the other layers. Another study considered the deposition of three different Cu clusters on a Cu (001) substrate with temperatures between 300 K and 1000 K.[21] The results indicated that the epitaxial growth improved when the substrate temperature was raised within a certain range, and the degree of epitaxy of small clusters was higher than that of larger clusters. The effects of cluster size, substrate temperature, and incident kinetic energy during the soft deposition of Cu and Au clusters on the Cu (001) surface were investigated using MD simulations.[22] The effects of substrate size and temperature were also observed in the deposition of Cu cluster on a Cu (010) surface.[23] Several studies considered the deposition of Cu clusters on a Cu (111) surface and investigated the roles of impact energy and cluster size.[24] For nonmetals, some works focused on the Si system. For instance, the Stillinger–Weber (SW) potential has been employed to investigate the formation a Si film growing on a Si surface.[25] The study showed the conditions under which the film might grow toward an amorphous or crystalline structure.

Previous studies of cluster deposition have focused on either Cu clusters on a Cu or Au substrate, or the interaction between the Si clusters and a Si substrate. The important dynamics of Cu clusters on the Si substrate is little explored, such as the surface reconstruction mechanism, the transfer of kinetic energy, and the epitaxial degree of cluster on the surface. In this paper, we use MD simulations to investigate the interaction dynamics between the cluster and the substrate. We quantitatively characterize the effects of cluster size and substrate temperature in terms of the history of the kinetic energy, the center of mass of the cluster, and the degree of epitaxy.

2. Computational scheme

2.1. Atomic interaction potentials

Simulating a system of thousands of atoms directly by first-principles or quantum mechanics calculations is still beyond today's computational capability. Instead of solving the Schrödinger equation, the MD simulation uses constructed semi-empirical models of classical interaction between atoms and solves the Newton equation. This approach allows the fully dynamic simulation of large three-dimensional systems. In this study, we use the effective MD simulation code LAMMPS, which stands for the Large-scale Atomic/Molecular Massively Parallel Simulator.

Many-body potentials have been widely adopted to accurately account for the interaction between metal atoms. The embedded atom method (EAM) with its empirical many-body potential energy functions has been widely used to compute static and dynamical properties of metallic systems, such as Au, Cu, Ag, Pt, and their alloys.[26] In this work, we use the EAM potential with a cutoff radius of $R_{\rm c}^{\rm Cu} = 4.95$ Å to describe the Cu–Cu interaction. The parameters are those in Ref. [27]. The SW potential with a cut-off radius of $R_{\rm c}^{\rm Si} = 3.77$ Å is used to describe the Si–Si interaction. Following Ref. [28], we take $\varepsilon = 2.1683$ eV, which scales with the cohesive energy; $\sigma = 2.0951$ Å, which scales with the lattice

constant; $\lambda = 21.0$, which is a scaling factor that stabilizes the tetrahedral structure; $\cos\theta_0 = 0.3333$, which is the ideal tetrahedral angle; and $\gamma = 1.20$, $a = 1.80$, $A = 7.049556277$, $B = 0.6022245584$, $p = 4.0$, and $q = 0.0$, which are the control parameters fitted to the experiment.[29]

In the previous studies, the classical Lennar–Jones (LJ) potential has been used to describe the interaction between the cluster and the substrate atoms. For instance, in a study of film growth at low incident energy with various conditions of substrate temperature and incident angle, the LJ potential was used to describe the deposition of Ni atoms.[30,31] The LJ potential was successfully used for the interaction of Cu–C atoms to study the low energy deposition of Cu nano-clusters on graphite substrates.[32,33] The Cu–C interaction was repulsive at least to several coordination shells surrounding the carbon atoms. The repulsive part of the interaction might be fitted by any functional form. The fitted potential had to possess the parameters to reproduce the experimentally measured properties.[32,33] The Cu–C interaction and the determination of the parameters for the LJ potential have been investigated both experimentally and theoretically.[33] The parameters for the LJ potential to describe the Cu–C interaction were obtained. It was confirmed that the LJ potential is apt to reflect the quantitative properties of Cu–C. In our MD simulation, we focus on small displacements of the host atoms and approximate them in the framework of elastic interaction. Following the previous studies on the Cu–C system, we use the LJ potential to describe the interaction of Cu–Si atoms. This approach allows us to capture the main features of the deposition process. From the combination rule, we take $\varepsilon_{\alpha\beta} = \sqrt{\varepsilon_{\rm Si}\varepsilon_{\rm Cu}}$, $\sigma_{\alpha\beta} = (\sigma_{\rm Si} + \sigma_{\rm Cu})/2$, and $R_{\rm c}^{\alpha\beta} = \left(R_{\rm c}^{\rm Si} + R_{\rm c}^{\rm Cu}\right)/2$, where $\varepsilon_{\rm Si} = 2.1683$ eV and $\varepsilon_{\rm Cu} = 0.4096$ eV scale with the cohesive energy, $\sigma_{\rm Si} = 2.0951$ Å and $\sigma_{\rm Cu} = 2.3380$ Å scale with the lattice constants of Si and Cu, respectively.[34] These parameters give $\varepsilon_{\alpha\beta} = 0.942$ eV and $\sigma_{\alpha\beta} = 2.217$ Å to account for the Cu–Si interaction with a cut-off radius of $R_{\rm c}^{\alpha\beta} = 4.36$ Å.

2.2. Molecular dynamics simulation

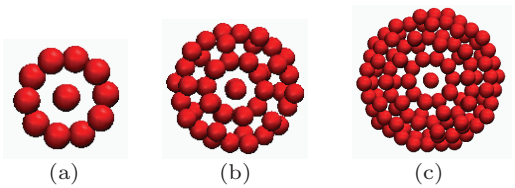
We consider a substrate of a diamond structural Si (001) fragment consisting of ten atomic layers in the vertical direction with a lateral dimension of $12a_0 \times 12a_0$, where a_0 is the lattice constant (about 5.431 Å). In our calculation cell, the top five layers of the substrate are used to account for the deposition, the middle three layers are a Berendsen thermostat, while the bottom two layers are fixed. Periodic boundary conditions are used in the two lateral directions parallel to the substrate surface. The fixed and the thermal bathed layers are not shown in the simulation results. The Newton equation of motion of the canonical ensemble (NVT) is integrated by using the velocity Verlet algorithm with a time step of 10^{-15} s. The calculation time is up to 40 ps for the Cu_{13} cluster and 60 ps for the Cu_{55} and Cu_{147} clusters.

The Cu clusters investigated are Cu_{13} (icosahedron structure), Cu_{55} (double-icosahedron configuration), and Cu_{147} (three-layer-icosahedron structure). Their configurations are shown in Fig. 1, which are in the global energy minimum states and process the high symmetry.[35] These configures correspond to the Mackay icosahedra made up of one, two, and three concentric shells with 13, 55, and 147 atoms, respectively.[36] In our simulations, the initial substrate temperatures before the impact of clusters are taken to be 0 K, 300 K, and 800 K, respectively. To consider the soft deposition, we place the clusters 5 Å above the substrate surface. The attractive force drives the cluster to approach the substrate. Three characteristic parameters are calculated to analyze the deposition behavior. First, we calculate the kinetic energies per atom of the cluster and the substrate as a function of time. Second, we calculate the structural parameter λ, which indicates the degree of epitaxy of a cluster on the surface. The expression is

$$\lambda = \frac{1}{2N_{\rm cluster}} \sum_{i=1}^{N_{\rm cluster}} \left(\cos\frac{4\pi x_i}{a_0} + \cos\frac{4\pi y_i}{a_0} \right), \quad (1)$$

where a_0 is the bulk lattice parameter of the substrate, and (x_i, y_i) are the coordinates of atom i in the plane parallel to the substrate surface. Finally, we calculate the mean heights of the substrate layers and the center of mass of the cluster. These parameters can provide information about how the cluster reaches and spreads on the surface as well as the relaxation of each

substrate layer.

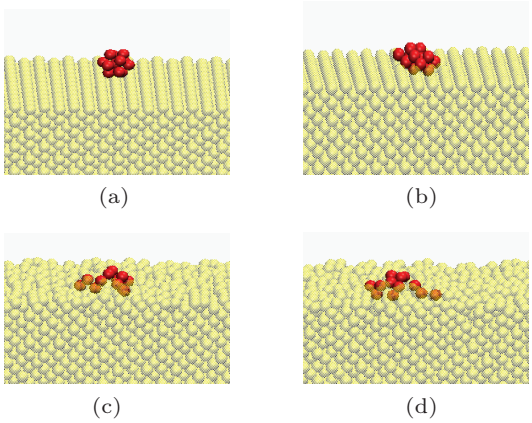


(a) (b) (c)

Fig. 1. (colour online) Initial configurations of (a) Cu_{13}, (b) Cu_{55}, and (c) Cu_{147} clusters.

3. Results and discussion

Figure 2 shows the initial configuration of a Cu_{13} cluster and the snapshots after 10 ps of deposition with different initial substrate temperatures. The cluster is released with zero initial kinetic energy in the proximity of the surface, and then the cluster–substrate interaction is switched on. Increasing temperature appears to cause more shape change of the cluster. The epitaxial area of the cluster on the surface also becomes larger, while the substrate demonstrates the increased surface roughness.



(a) (b) (c) (d)

Fig. 2. (colour online) The initial configuration (a) and the snapshots after 10 ps of a Cu_{13} cluster deposited on the Si substrate of different substrate temperatures ((b) $T = 0$ K, (c) $T = 300$ K, (d) $T = 800$ K).

The time evolutions of the kinetic energies per atom of the cluster and the substrate at 300 K and 800 K are shown in Fig. 3. The kinetic energy of the cluster grows as it moves toward the substrate. Once it reaches the surface, the cluster interacts with the substrate, diffuses, and finally equilibrates. In this process, the excess energy is absorbed by the substrate. We mark several main peaks and show the corresponding top views of the cluster configurations in the insets in Figs. 3(a) and 3(b). The sharp first peak at about 0.8 ps indicates that the cluster reaches the surface. After the impact, the cluster loses part of the kinetic energy and passes it to the substrate. Over time, the peak height decays quickly, suggesting that the cluster approaches an equilibrium state. The insets demonstrate how the cluster spreads on the surface and the evolution of the cluster configuration. Comparing the figures in Fig. 3, we find that the width of the curve (the time it takes for the kinetic energy to stabilize) is wider for the Cu_{147} cluster than that for the Cu_{13} cluster at the same temperature. The width of the curve for the Cu_{55} cluster is in-between, which is not shown. This trend can be understood in terms of the cluster size as well as the average binding energy per cluster atom, which increases with the number of atoms in the cluster.[35,37] For a larger cluster, it takes more time for the cluster/substrate interaction to break the bonds in the cluster and cause the cluster atoms to spread. For both Cu_{147} and Cu_{55} clusters, we find that the width of the curve is narrower at 800 K than that at 300 K. This trend is likely due to the accelerated diffusion at a higher temperature. This trend is less clear for the Cu_{13} cluster, where the thermal vibration is pretty strong due to the small cluster size. The transient time from an initially highly symmetric cluster to a stable structure on the substrate is very short. The process of deposition, diffusion, rearrangement, and equilibrium takes picoseconds.

Figure 4 shows how the mean height of the center of mass of the clusters evolves over time for different size clusters at 300 K and 800 K. For the relatively small Cu_{13} and Cu_{55} clusters, the substrate temperature appears to have little influence on the mean center-of-mass height of the clusters. Whereas the Cu_{147} cluster moves deeper along the deposition direction toward the substrate at 800 K than that at 300 K, as shown in Fig. 4(c). We can also identify an increase of the mean height at around 40 ps. This is because the Cu_{147} cluster is relatively large and has not reached equilibrium before 40 ps. At 40 ps, some atoms happen to find themselves in the locations that make the system energy lower. At 0 K, the mean heights of the centers of mass of the clusters are almost the same for all clusters.

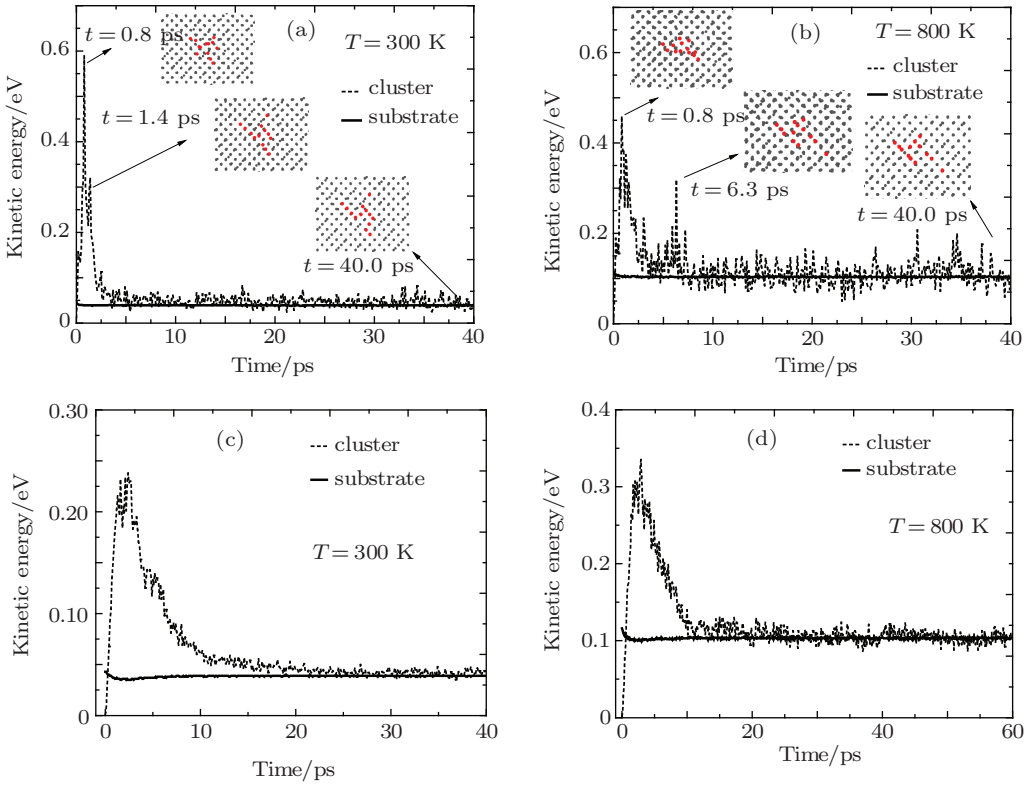


Fig. 3. (colour online) Evolutions of the kinetic energy per atom during the depositions of ((a), (b)) 13-atom and ((c), (d)) 147-atom Cu clusters at different substrate temperatures. The corresponding top view of the cluster is shown in the inset.

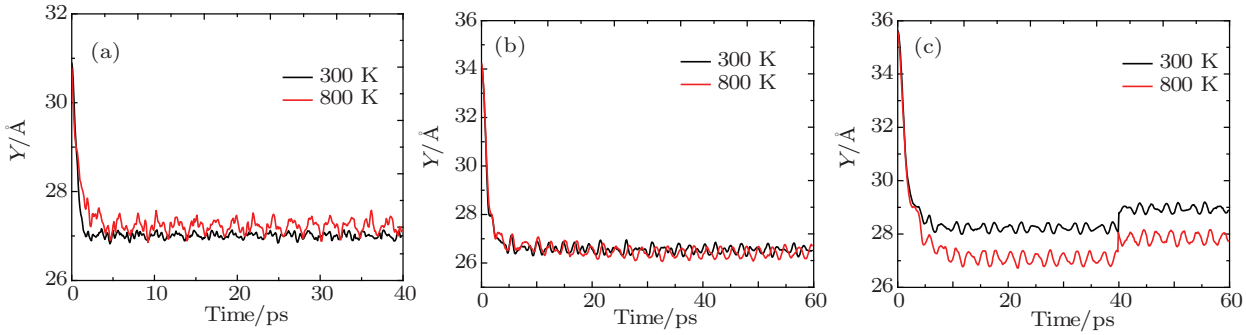


Fig. 4. (colour online) Developments of the mean centers of mass heights of the (a) 13-atom, (b) 55-atom, (c) 147-atom clusters at different substrate temperatures.

Figure 5 shows the degrees of epitaxy of clusters at different substrate temperatures. For all cluster sizes, the clusters have much higher degrees of epitaxy at 800 K than those at 300 K, since the cluster atoms diffuse more easily at a higher temperature. For the relatively large Cu_{147} cluster, the substrate temperature appears to have much stronger influence. Figure 6 demonstrates the effect of cluster size on the thin-film growth. At the same substrate temperature, the Cu_{55} cluster has a higher degree of epitaxy, as shown in Fig. 6. This might be relevant to that the number of atoms and the average binding energy of Cu_{55} are in the middle of the three kinds of clusters considered. The smaller Cu_{13} cluster vibrates strongly on the substrate. Part of the energy is associated with this vibration and therefore leads to a lower degree of epitaxy. On the other hand, the larger Cu_{147} cluster has more atoms. It vibrates weakly but also has a high average binding energy. It is more difficult for atoms to spread, leading to a lower degree of epitaxy. Compared with Cu_{13} and Cu_{55}, the Cu_{147} cluster moves much shallower along the deposition direction toward the substrate, as shown in Fig. 7. This behavior can be attributed to more atoms and the higher average binding energy that the Cu_{147} cluster has. The simulations suggest that using Cu_{55} clusters is a better option for thin-film deposition at 300 K and 800 K, followed by Cu_{147} and then Cu_{13}.

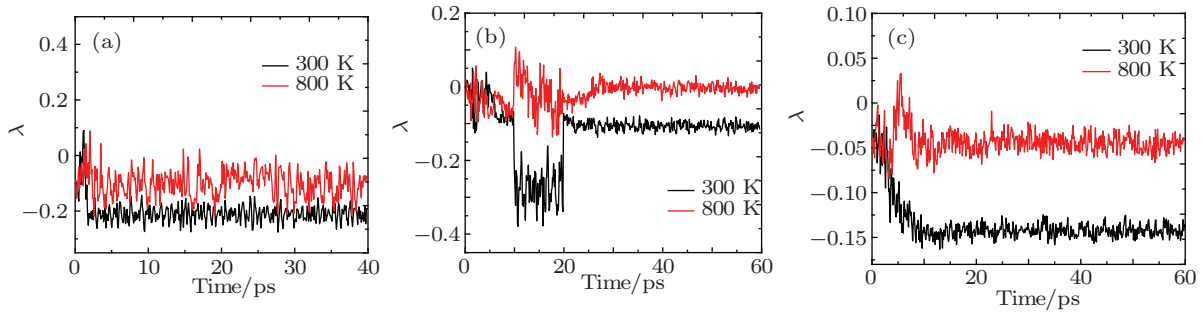


Fig. 5. (colour online) Developments of the structural parameter λ of (a) 13-atom, (b) 55-atom, (c) 147-atom clusters at different substrate temperatures.

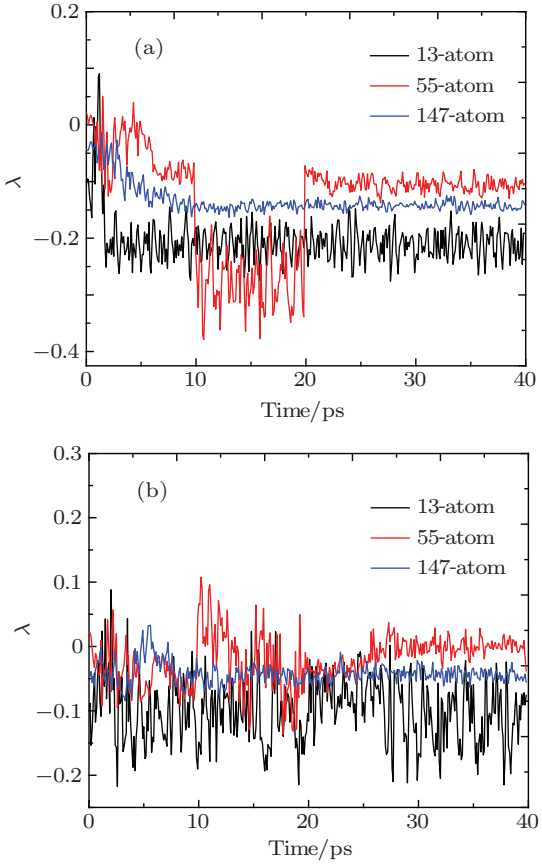


Fig. 6. (colour online) Developments of the structural parameter λ for different size clusters at (a) $T = 300$ K and (b) $T = 800$ K.

The morphology evolution of clusters is observed from both the top and the side in our simulations. Figure 8 shows the Cu_{55} clusters at 300 K and 800 K. The side view shows that the cluster evolves from an initial double-icosahedron structure to a flat layered structure. The top view shows that the cluster atoms spread over the substrate surface. The morphology at 800 K is similar to that at 300 K, but demonstrates a better degree of epitaxy. As suggested by Fig. 4(b), the mean center-of-mass height of the clusters shows no obvious difference at the two temperatures. Figure 9 shows the shape evolution of the Cu_{147} cluster. With more atoms, the cluster needs longer time to reach the equilibrium state. It also demonstrates a larger spreading area. Higher temperature enhances the spread of atoms. The side view shows a clear dome shape configuration in the middle of evolution, followed by the flat layered structure. From these figures, we can understand the detailed dynamics of how a cluster impacts the substrate and then spreads and diffuses over the substrate.

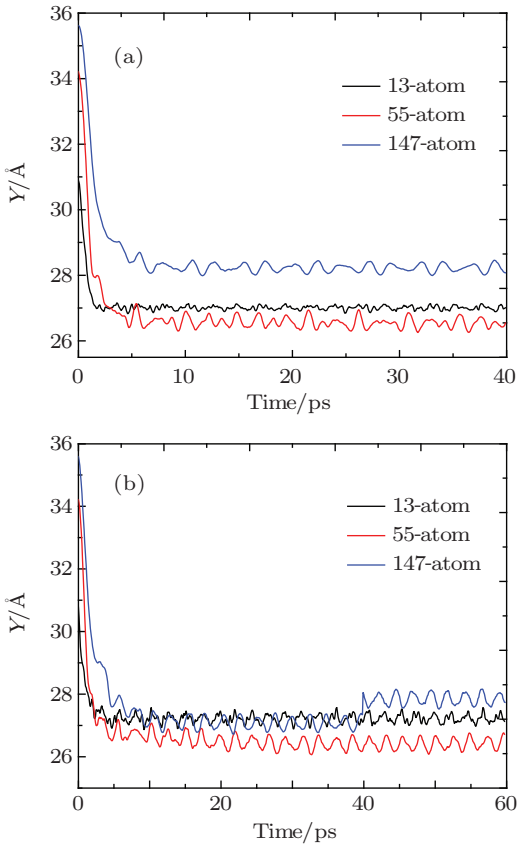


Fig. 7. (colour online) Developments of the mean center-of-mass height of the clusters for different size clusters at (a) $T = 300$ K and (b) $T = 800$ K.

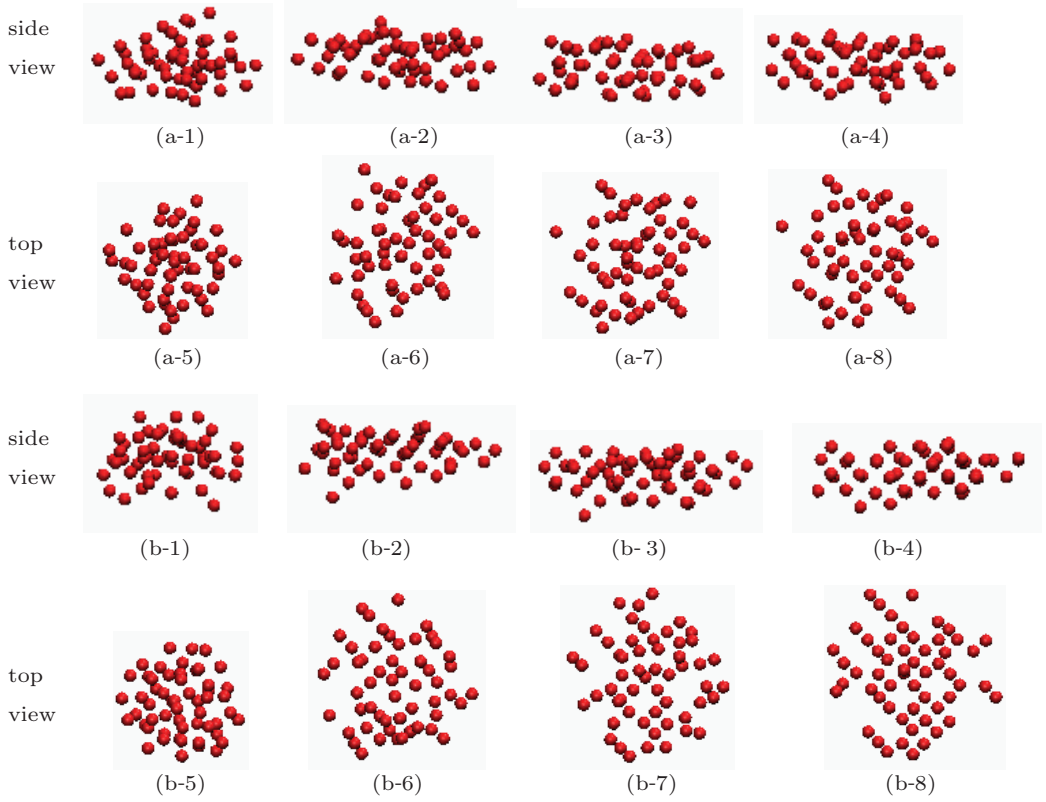


Fig. 8. (colour online) Morphology evolution of a Cu_{55} cluster at 1.5 ps, 2.5 ps, 4 ps, and 60 ps with the substrate temperatures of (a) 300 K and (b) 800 K.

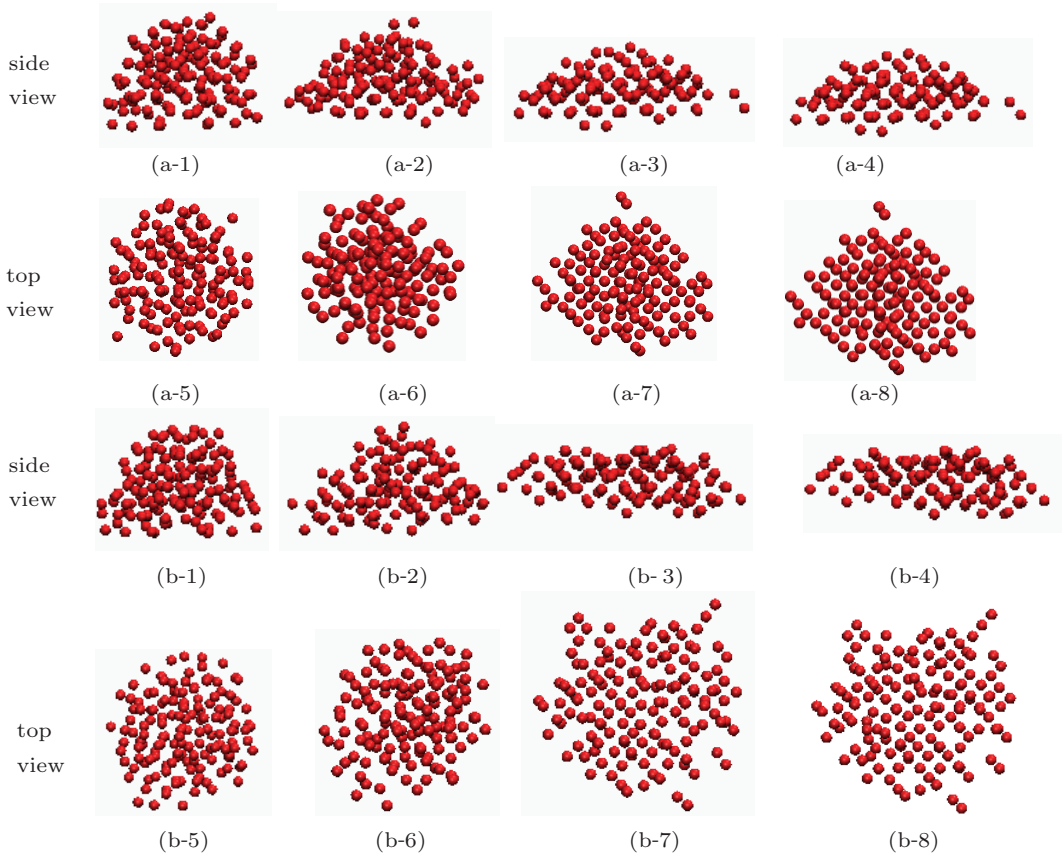


Fig. 9. (colour online) Morphology evolution of a Cu_{147} cluster at 1.5 ps, 2.5 ps, 40 ps, and 60 ps with the substrate temperatures of (a) 300 K and (b) 800 K.

4. Conclusion

We studied the deposition of Cu_{13}, Cu_{55}, and Cu_{147} clusters on a Si (001) surface with different substrate temperatures by MD simulations. The temperature we studied was far below the melting temperatures. Thus, we did not worry about the effects due to the large correlation lengths, which appeared during the first-order phase transitions. We calculated the kinetic energy per atom, the structural parameter, and the mean center-of-mass height of the clusters. We found that the substrate temperature had a significant effect on the Cu_{147} cluster in terms of its diffusion and epitaxy on the surface. For smaller Cu_{13} and Cu_{55} clusters, the substrate temperature in the range of study appeared to have little effect on the mean height and the degree of epitaxy. With the same substrate temperature, the Cu_{55} cluster demonstrated the highest degree of epitaxy, followed by Cu_{147} and then Cu_{13} clusters. Our simulations also demonstrated various cluster configurations during the evolution. These results implied that the cluster size and the substrate temperature can have important effects on the thin film growth.

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