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Effect of cluster size on Cu/Au(111) epitaxy

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Abstract. Investigations of the size effect on the epitaxy when a Cu cluster was softly deposited onto Au(111) were performed using molecular dynamics, combining the tight-binding interaction potential with electron–phonon coupling. These studies reveal that epitaxy can be obtained more easily for small clusters than for the large ones after deposition. The critical cluster size to obtain epitaxy depends strongly on the incident energy and ambient temperature. Moreover, the initial structure of the cluster is also responsible for epitaxy. Here, it is shown that the lattice distortion in the cluster–substrate interface is the most serious compared with the distortion in other layers.

1. Introduction

During the last few decades, a wealth of information has been obtained on the structures and properties of free clusters as functions of their size, and how their characteristics differ from the bulk have been approached [1]. Recently, renewed efforts on the preparation and understanding of the structures and properties of the clusters deposited onto a surface have been undertaken to find a way of forming nanostructured materials with a well defined shape and number of atoms. A few techniques (e.g. ionized cluster beam deposition (ICBD) [2], high energetic cluster beam deposition (HECBD) [3] and low energy cluster beam deposition (LECBD) [4]) have been developed to achieve this goal. Understanding the deposition process and the subsequent behaviours of the cluster on a surface is an essential first step for this purpose. After years of extensive and intensive investigations, both experimentally and theoretically, the preliminary conclusions can now be drawn that after deposition the structures and morphologies of a cluster depend strongly on the ambient temperature, initial translation energy and the orientations of the cluster and the substrate [5–9]. However, despite these fruitful studies, cluster deposition remains largely an art. Experimentally, there usually exists a size distribution for the deposited clusters [10]. A question occurs as a necessity: does the distribution influence on the structure and morphology of nanostructured materials after cluster deposition? Additional efforts are thus essential to elucidate the role of the different sizes in the cluster deposition from microscopic viewpoint.

In the paper, we will focus mainly on this issue in the case of the heteroepitaxial system Cu/Au(111), using molecular dynamics (MD) simulations. The reconstruction at the surface of Au(111) was not accounted for and its possible roles during cluster–surface interactions are thus overlooked in the present study and will be sought for at a later date.

2. Methods and models

2.1. The model and methods

In this work we simulated the process of the Cu cluster deposited on Au(111) using a realistic many-body potential based on the second moment approximation of the tight-binding scheme (TB-SMA), where the cohesive energy of an atom i can be written as

$$E_i = \frac{1}{2} \sum_j V(\mathbf{R}_{ij}) - \left[\sum_j \Phi(\mathbf{R}_{ij}) \right]^{1/2}. \quad (1)$$

The first term typically represents the repulsive potential and Φ can be interpreted as the sum of the squares of the hopping integrals within the tight-binding approach. \mathbf{R}_{ij} is the distance between atoms i and j . The potential functions are constructed as a series of cubic splines and the interaction range is limited just beyond the third-neighbour distance [11]. The potential has been applied successfully to investigate the structure, phase diagram of the noble metal alloys [11] and clusters assembled materials formed by depositing Au clusters on Au(111) in agreement with experiment [12].

As shown in [9], as a consequence of the impact of a cluster on a substrate, two factors should be considered in heating up the system. First, the cluster will transfer its translation energy to the substrate and directly contributes to the heating of the ionic system. This process lasts for a few picoseconds. Second, when the system evolves towards thermodynamic equilibrium, the ionic system couples with the electron. The characteristic coupling time is temperature dependent. For the gold crystal, the time is equal to 20 ps at 300 K. Since the clusters here are small compared with the substrate, the electron-phonon coupling is approximated to be entirely governed by the substrate properties.

The classical equation of motion was integrated by using velocity Verlet algorithm and the integration time step is 2×10^{-15} s.

2.2. The simulation system

The cluster size ranges from 13 to 1058 atoms. The initial cluster was cut in a large fcc single copper crystal and was thermalized up to equilibrium at a temperature of 500 K, in the meantime the linear and angular momenta were eliminated. The approach to equilibrium was monitored through the total energy of the cluster. Then these clusters are cooled down by means of simulated annealing to 0 K at a rate of 5 K ps⁻¹. We have calculated the average configuration energy per atom in the cluster at 0 K. Figure 1 shows that this is nearly linear function of $N^{-1/3}$ (N is the number of atoms in the Cu cluster), consistent with droplet model [1(a), 13], which makes it certain that a plausible energy minimum has been reached.

The morphologies and the structures of the clusters were examined by a direct visualization, central radial distribution function and a pair correlation function (not shown here). It is found that the cluster is of a fcc structure when it contains more than 200 atoms and other clusters are amorphous except for these clusters: Cu₁₃, Cu₅₅, Cu₁₃₅ and Cu₁₄₇, which are icosahedral. The structures of the Cu clusters are now still controversial issues and other possible structures of copper clusters were not considered here [1(a)].

The gold substrate consisted of 12 layers, exposing two (111) surfaces, with 360 atoms in each layer and it was periodically repeated in the two directions parallel to the (111) surface (i.e. $[1\bar{1}0]$ and $[11\bar{2}]$). Boundary damping at the bottom of the substrate was employed to mimic a semi infinite medium [9]. Prior to the cluster deposition, the substrate was equilibrated to the desired temperature. The initial translation energy (incident energy) of the cluster ranges from 0.0 to 1.0 eV/atom, which is characteristic of LECBD. The clusters were deposited from a

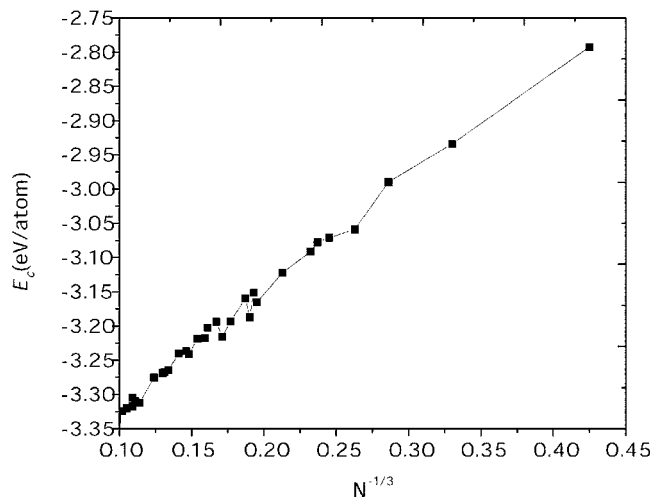


Figure 1. The configuration energy E_c as a function of $N^{-1/3}$ for a stable cluster at 0 K (N is the number of atoms in the cluster Cu).

randomly incident position and orientation at 300 K and the initial distance of the cluster from the surface of the substrate was chosen in such a way that the distance between the cluster atoms closest to the Au(111) surface is just shorter than the potential cutoff. The equilibrium was checked through the time evolution of kinetic energy and of the total energy of the Cu/Au system and it is believed to be achieved when there are no significant temporal variations in the kinetic and total energy. Starting with the initial conditions, as shown in [9], the temperature of the system will firstly be just above the expected temperature of 300 K, resulting from the translation energy of the cluster, and then will decrease asymptotically down to 300 K in 20 ps, as predicted by electron–phonon coupling. By far longer than this time, the system took at least 150 ps to reach a reasonable thermal equilibrium. The process of the evolution of the system is described concretely in [9].

3. Results and discussions

There are several ways of identifying epitaxy. The simplest is perhaps to visualize directly the structure. This was done and one part is presented in figure 2, which shows the equilibrium configurations obtained after the Cu cluster was deposited on Au(111) with different incident energies between 0.0 and 1.0 eV/atom as well as different cluster sizes (three representative ones) at 300 K. It is easy to see that the layer by layer in the cluster with respect to the substrate is visible for Cu201/Au(111) in the case of three incident energies (figure 2(1)), for Cu531/Au(111) at incident energies of 0.25 and 1.00 eV/atom (figures 2(2-b) and 2(2-c)), for Cu683/Au(111) only at an incident energy of 1.00 eV/atom (figure 2(3-c)), which implies that there might be epitaxy for these clusters after deposition. It is worth mentioning that *epitaxy* is different from *coherence*[†]. On the other hand, dislocation (figure 2(2-a)) or misorientation (figure 2(3-a)) with Au(111) surface may appear in these clusters with no observable layer by layer. Epitaxy can be ruled out of the two cases. In particular, after deposition at an incident energy of 0.25 eV/atom, the Cu683 cluster exhibits partially layer by layer with the

[†] Webster's Dictionary defines *epitaxy* as 'the growth on a crystalline substrate of a crystalline substance that mimics the orientation of the substrate' from [14].

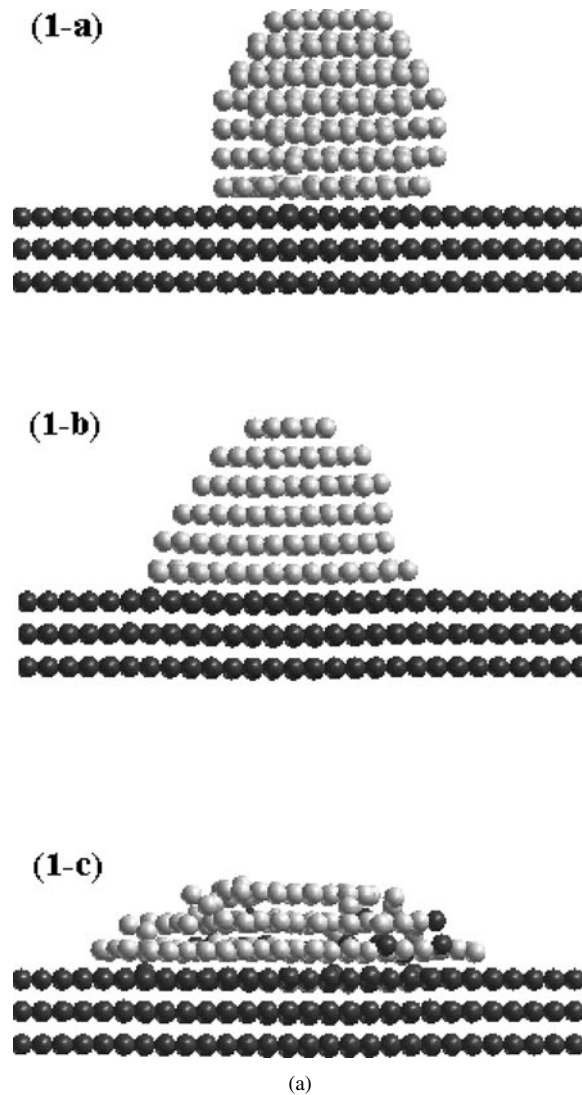


Figure 2. Configurations of three representative Cu clusters with respect to the substrate Au(111) after complete equilibrium achieved at 300 K three different incident energies ((a) 0.0 eV/atom, (b) 0.25 eV/atom and (c) 1.00 eV/atom): (1) Cu201 cluster, (2) Cu531 cluster and (3) Cu683 cluster. In each diagram, only part of topmost three layers of the substrate and the whole cluster layers are plotted. The darker circles denote the gold atom and lighter circles denote the copper atoms.

Au(111) surface at the cluster–substrate interface and other three-dimensional (3D) blocks (figure 2(3-b)). As a result, a grain boundary may be formed in the cluster.

The pair correlation function, $g(r)$, of the layer by layer along the [111] direction is used to observe the detail in obtaining epitaxy. Only the layer in the cluster closest to the Au(111) surface is displayed in figure 3, and others are available. These peaks, which can appear in the $g(r)$ of a (111) plane of gold, are located, as shown in inset of figure 3, at $\sqrt{2}/2a$, $\sqrt{6}/2a$, $\sqrt{2}a$, $\sqrt{14}/2a$ and so on (where a is the lattice constant of gold). If epitaxy takes place after deposition, this condition must be met: that each peak in the $g(r)$ of the cluster should be located at the position corresponding to that of each peak in the $g(r)$ of the (111) plane of gold

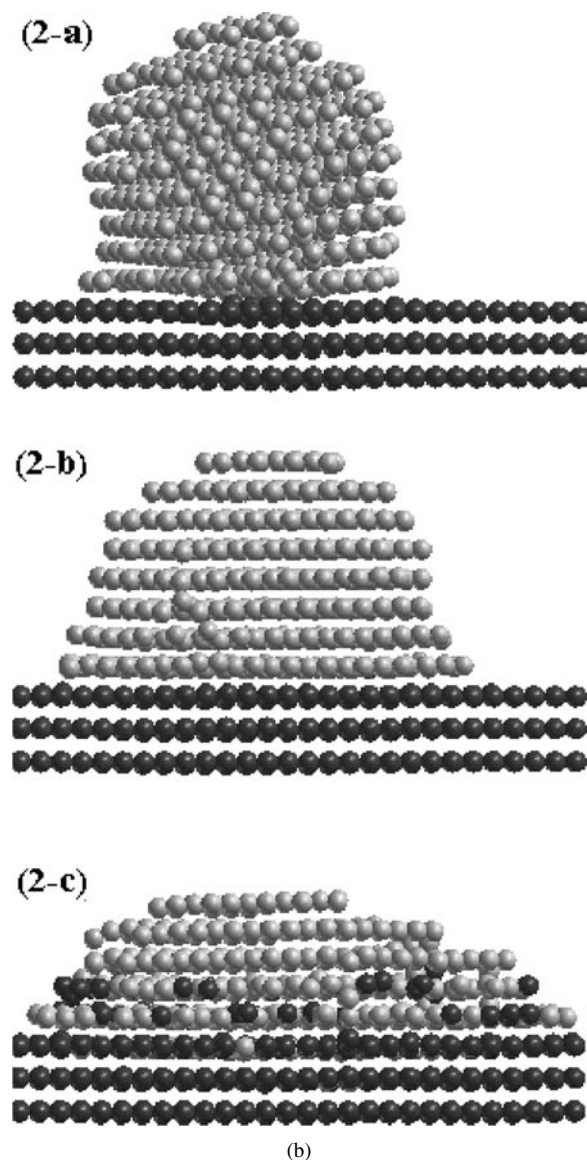


Figure 2. (Continued)

(for example, figures 3(1), 3(2-b), 3(2-c) and 3(3-c)). Pronouncedly there are several extra peaks in the $g(r)$ of the Cu531 cluster after deposition with an incident energy of 0.0 eV/atom (figure 3(2-a)) and in Cu683 after deposition with incident energies of 0.0 and 0.25 eV/atom (figures 3(3-a) and 3(3-b)), compared to that in the $g(r)$ of a (111) plane of gold, and so epitaxy cannot possibly take place in these cases. The position of each peak in the $g(r)$ for the cluster shifts down a small amount (about 12%) relative to that for the gold substrate to suggest atomic spacing in the cluster after deposition is not fully strained up to that of the gold. Indeed, calculating the nearest-neighbour distance in each layer with an Au(111) surface indicates that the lattice of the part of the cluster adjacent to the substrate has been strained to

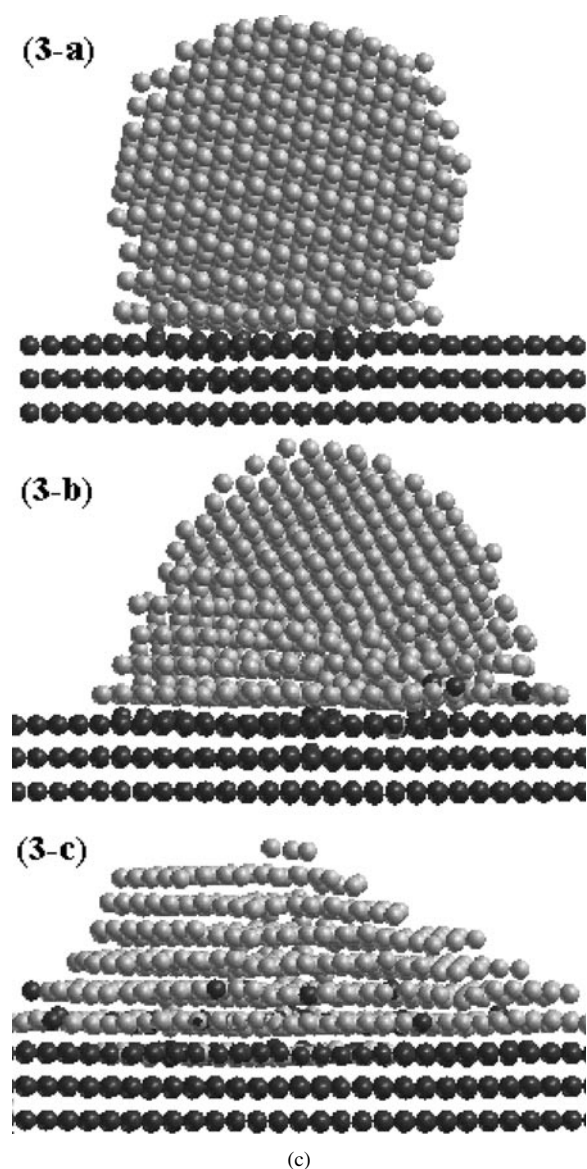


Figure 2. (Continued)

try to match the Au(111); its value is larger than that of the bulk copper (2.556 \AA), but smaller than that of gold (2.889 \AA), which confirms that the cluster cannot be coherent with the lattice of the Au(111) substrate even though full epitaxy may occur. This result is plausible since the substrate potential acting on the cluster (i.e. Cu–Au interaction) and the lateral interaction of the cluster (i.e. Cu–Cu interaction) are comparable. Systematically, the nearest-neighbour distance in the cluster decreases far from the cluster–substrate interface.

Comparing the $g(r)$ layer by layer in the cluster with that of a (111) plane of gold (figure 3) and combining direct snapshots in figure 2 with a viewpoints from above layer by layer, which ought to consist of a hexagonal structure similar to that of the (111) plane of gold

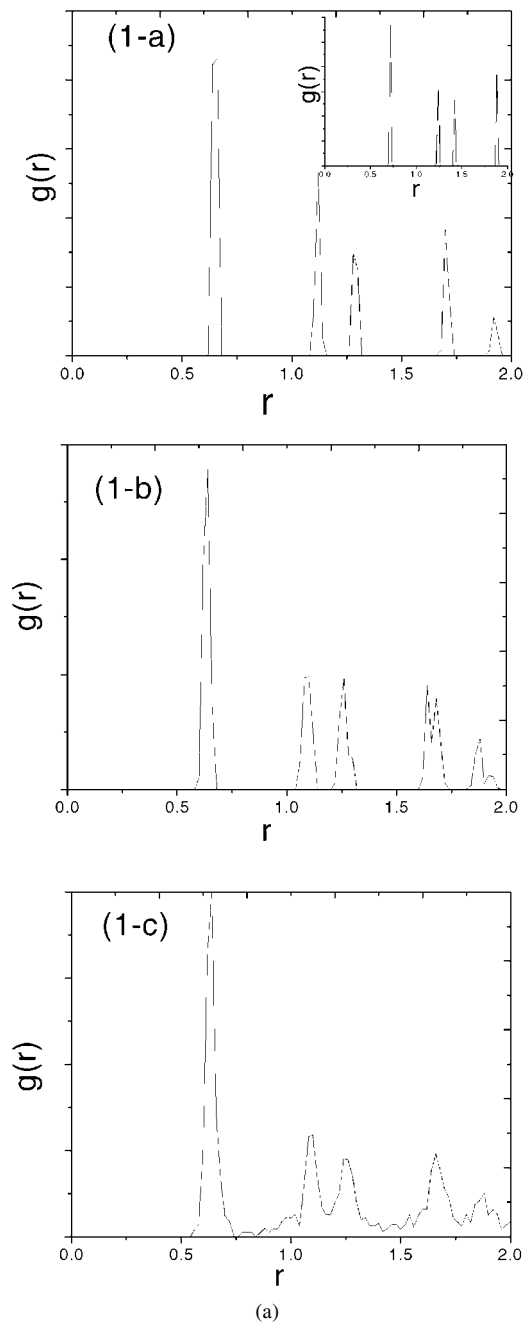


Figure 3. Corresponding to figure 2, the pair correlation function $g(r)$ measured in the layer closest to the substrate with a thickness of half the lattice constant of gold, which can ensure that one layer can just be contained when there are obvious layers. The PCF in other cluster layers is similar to this. r is in the units of the lattice constant of gold and $g(r)$ is in arbitrary units. In inset of (1-a) is the pair correlation function of a (111) plane of gold.

if epitaxy achieved, we found that epitaxy always occurs for Cu201/Au(111) in the three cases considered; for Cu531/Au(111) there is no epitaxy when the initial translation energy is

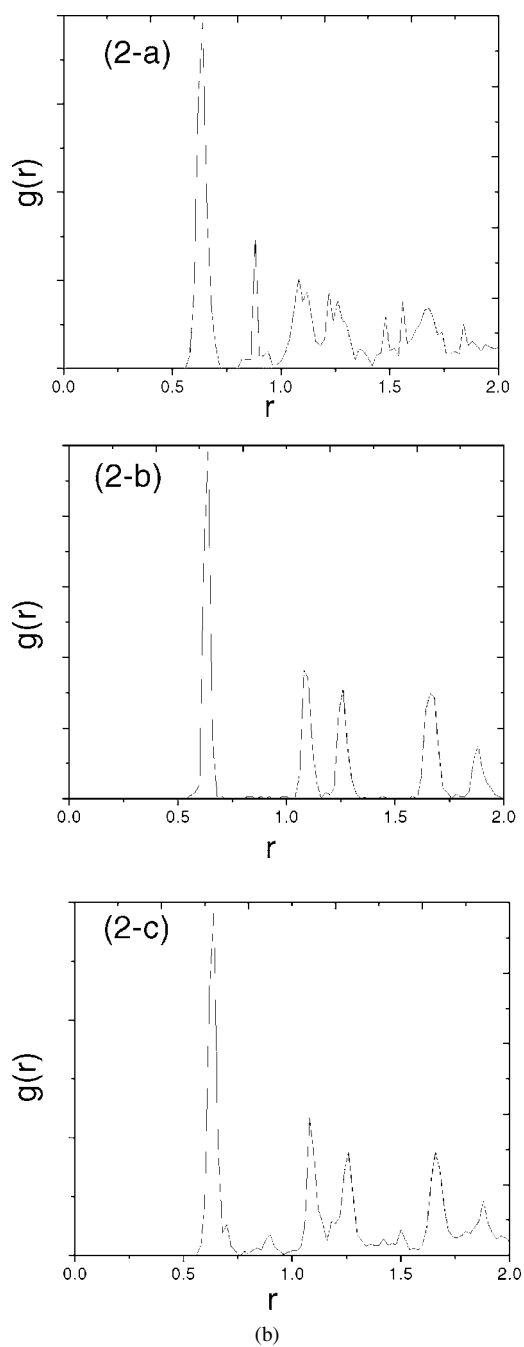


Figure 3. (Continued)

0.00 eV/atom, while epitaxy can be observed when this energy reaches 0.25 and 1.00 eV/atom; for Cu₆₈₃/Au(111) it is only this energy of 1.00 eV/atom that can induce epitaxy.

It is interesting to note the deposition of the clusters containing 13, 55, 135 or 147 atoms, since these clusters are icosahedral when they are free. In figure 4, the snapshots of the four

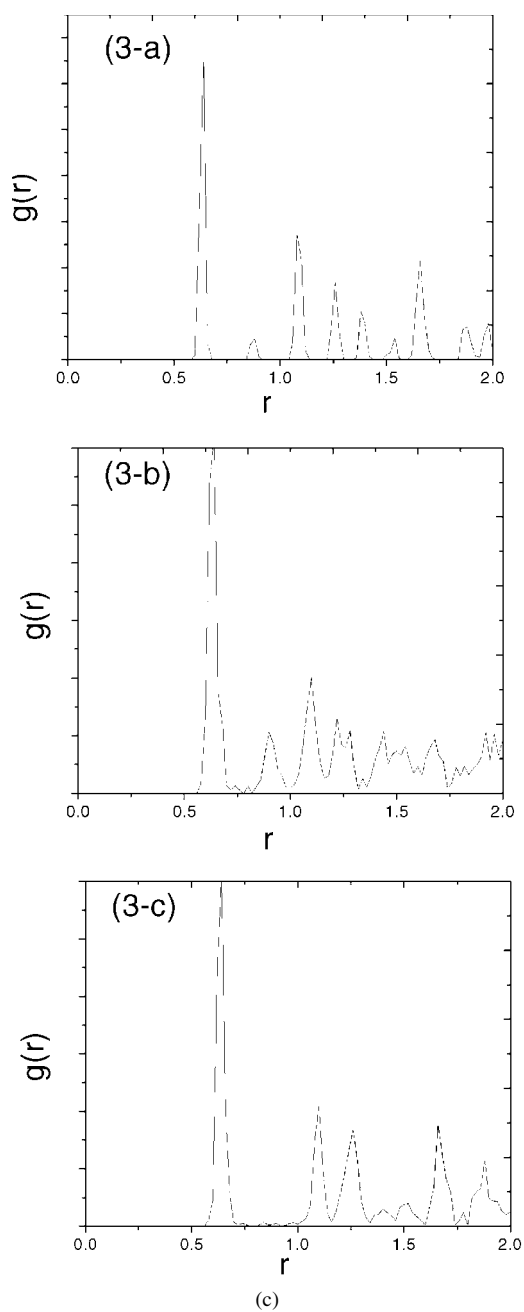


Figure 3. (Continued)

clusters after deposition with an incident energy of 0.0 eV/atom are displayed. As can be seen, there are obviously layer and layer with the Au(111) surface for the Cu13, Cu55 and Cu135 cluster layers; the interfacial layer of the Cu147 cluster tends flat to accommodate the lattice of Au (111) surface, while the others partially retain its icosahedral structure. Similar to the methods described above, we identified that for the Cu147 cluster there is no epitaxy, while

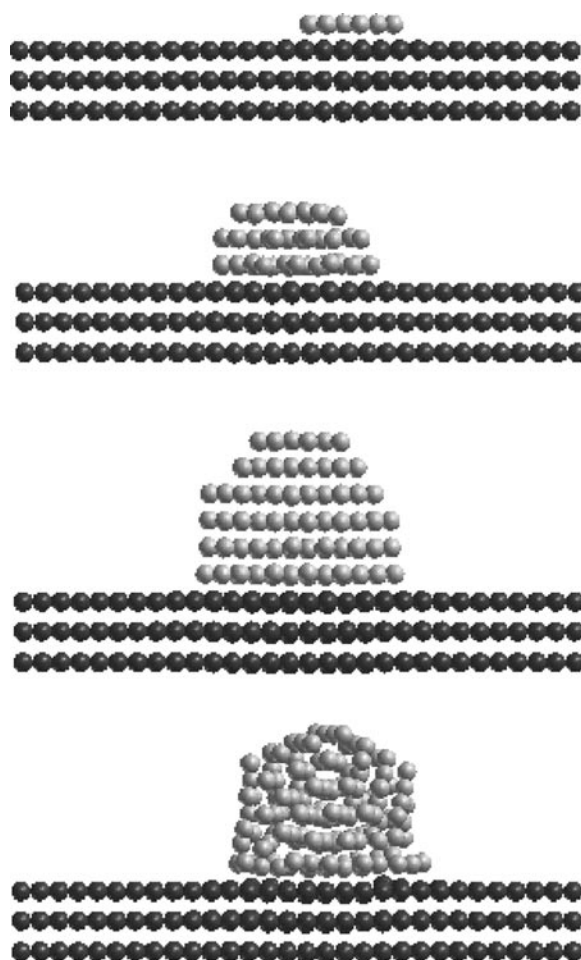


Figure 4. Configurations of the cluster–substrate system after deposition of the Cu13, Cu55, Cu135 and Cu147 clusters (from top to bottom) with an incident energy of 0.0 eV/atom at 300 K. In each diagram, only part of topmost three layers of the substrate and all the cluster layers are plotted. The darker circles denote the gold atoms and lighter circles denote the copper atoms.

for other three just there is. However, with higher incident energies of 0.25 and 1.00 eV/atom, the structures of these four clusters change from icosahedral to fcc like after the clusters are disrupted at the initial stage of deposition and then rearrange with respect to the substrate [9]. Epitaxy was also achieved when the Cu13 and Cu55 clusters of icosahedra were softly deposited on to Cu(001) [8].

Consequently, whether there is epitaxy or not after deposition for all the clusters considered can be determined, and is presented in figure 5. For convenience, the flag value is set as one if full epitaxy, otherwise, it is zero. We see, with an incident energy of 0.0 eV/atom, there is epitaxy for the cluster containing fewer than 531 atoms (except for the 147-atom cluster) while no epitaxy is found for the clusters with more than 531 atoms. Furthermore, the clusters undergo a structural transition from layer by layer with the Au(111) surface, in which each layer mimics the structure and orientation of the substrate surface, upto 3D blocks with increases in the cluster size. When the incident energy is increased, the critical size (here *the critical size*

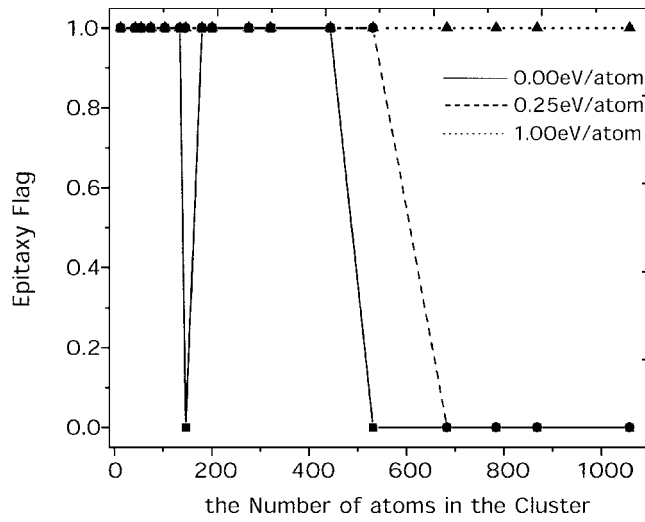


Figure 5. Epitaxy flags with the cluster size at three different incident energies. For convenience, the flag is set as one if epitaxy and otherwise zero.

refers to the dividing line of epitaxy and no epitaxy) tends to be larger; for an incident energy of 0.25 eV/atom, this is the cluster with 683 atoms or so. For 1.00 eV/atom all the clusters (size ranges from 13 to 1058 atoms) become epitaxial.

In order to explore to what degree the lattice in the cluster is distorted due to the cluster–surface interaction, we introduce intrinsic strain, which is defined as

$$\varepsilon = \frac{1}{N_{nn}} \sum_{i=1}^{N_{nn}} \frac{|d_{i,nn} - \bar{d}_{nn}|}{\bar{d}_{nn}} \quad (2)$$

where d_{nn} and \bar{d}_{nn} are the nearest-neighbour distances, and average nearest-neighbour distance, respectively. N_{nn} is the total number of nearest neighbours. Equation (2) shows that a larger distortion results in a larger ε .

In order to avoid the influence of the thermal vibration on the results, the intrinsic strain was measured in each atomic layer along the [111] direction after the cluster was deposited at 300 K and quenched quickly to 0 K. In figure 6 only one example is displayed, and it is found the distribution of the intrinsic strain is systematically the same for all the clusters after deposition. A marked character can be observed, such that the intrinsic strain is always largest at the cluster–substrate interface. With higher incident energies, the lattice distortion in the cluster becomes so serious that the intrinsic strain is substantially enhanced (figure 6(c)). Atoms exchange between the Cu cluster and Au(111) substrate when the incident energy is high enough, up to 1.00 eV/atom (see figure 2). These foreign atoms can change the local order in the cluster and contribute to the lattice distortion. It was also found that this exchange happens mainly at the initial stage of the cluster deposition, when the cluster collides with the substrate, and the number of atoms exchanged increases with the cluster size (figure 7); suggesting that a collective effect plays an important role in the cluster–substrate collisions.

Finally, to further explore effect of the cluster size on the epitaxy at the different temperatures, we carried out the same simulation with an incident energy of 0.0 eV/atom at 600 K. It is indicated that high temperature can enhance epitaxy with this incident energy and that the critical size increases from Cu531 at 300 K to Cu683, and for all of the four clusters, Cu13, Cu55, Cu135 and Cu147 cluster, the epitaxy is striking.

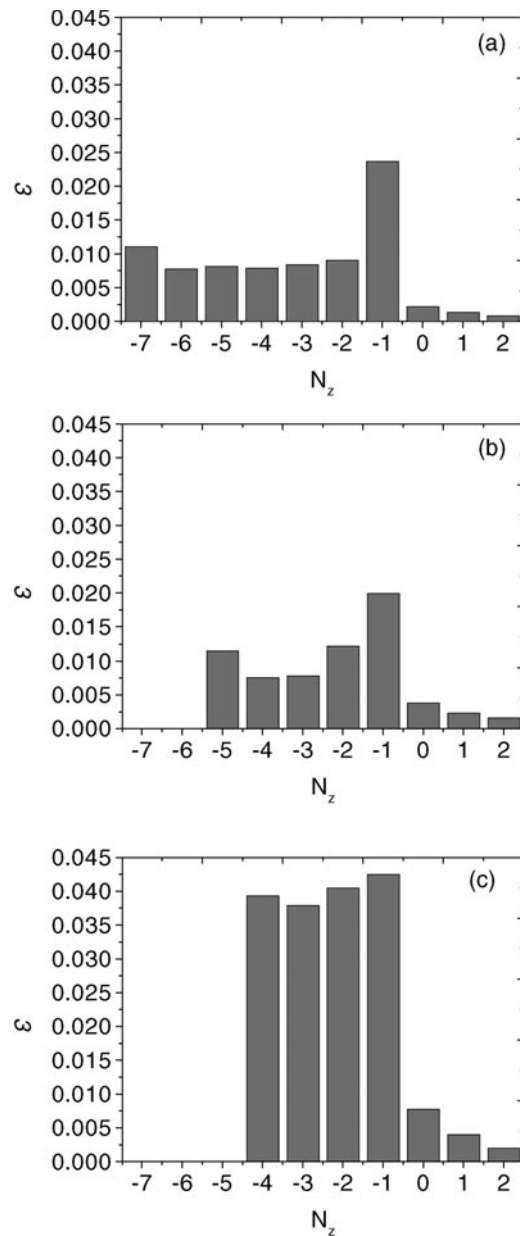


Figure 6. The distribution of the intrinsic strain along [111] of a typical example (here it is for the cluster with 201 atoms, other clusters have the same distribution as this). The incident energies are: (a) 0.0 eV/atom, (b) 0.25 eV/atom and (c) 1.00 eV/atom. N_z refers to number of layers along [111] ($N_z < 0$ for the cluster and $N_z \geq 0$ for the topmost three layers of the substrate).

4. Summary

In this paper, we reported results of MD simulations combining the tight-binding potential with the electron–phonon coupling, aimed at the investigation of the size effect of copper clusters on the epitaxy in the case of the heteroepitaxial system Cu/Au(111). There are two

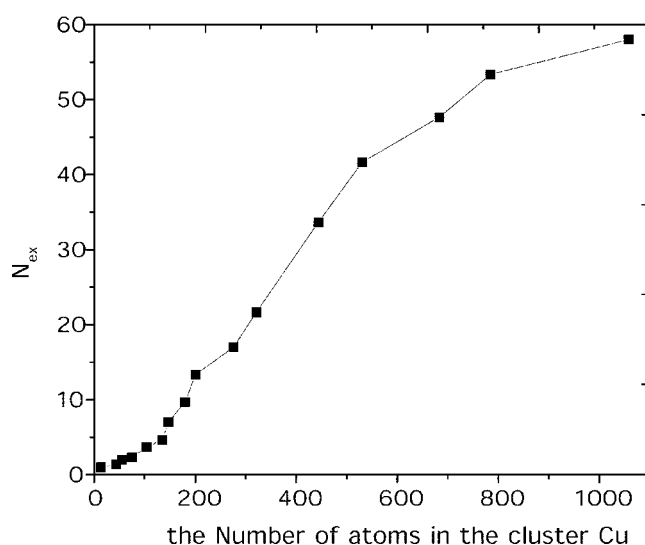


Figure 7. The number of atoms exchanged between a cluster and substrate as a function of the cluster size at an incident energy of 1.0 eV/atom.

main findings. (1) It is not easier to obtain epitaxy for larger clusters and so higher incident energies or temperatures are needed; when a cluster with a structure that is different to the substrate is deposited, it is comparatively difficult to obtain epitaxy. This implies that a barrier might exist to hinder the transition of the cluster from a icosahedral structure to fcc-like one. As a balance of the size effect and this barrier, epitaxy is not found for the deposition of the Cu147 cluster while it is for the Cu13, Cu55 and Cu135 clusters with a 0.0 eV/atom incident energy at 300 K. (2) The lattice distortion is largest in the cluster–substrate interfacial part of the cluster compared with other layers. Although the simulated timescales may be shorter than the relaxation time needed experimentally to reach equilibrium, and the simulation systems can possibly go into a metastable state, it is certain that the MD simulations proceed to give qualitative information on the tendency of the systems: whether it is ‘easy’ or not to obtain epitaxy from microscopic viewpoint. Further experimental work has been initiated to explore the issue macroscopically.

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