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H Lei[1] and Y-J Tang

Research Center of Laser Fusion, China Academy of Engineering Physics, PO Box 919-987,
621900 Mianyang, People's Republic of China

E-mail: hailelei@yahoo.com

Abstract
The effect of stress due to the lattice misfit in the Cu/Au interface has been
studied by carrying out molecular dynamics simulations. Results show that the
stress can induce stacking faults to relieve the stress.

1. Introduction

To date, there are three main cluster deposition techniques known to obtain cluster-assembled
materials (CAMs). They are the ionized cluster beam deposition (ICBD) [1], high-energetic
cluster beam deposition (HECBD) [2] and low-energy cluster beam deposition (LECBD) [3]
techniques. The former two techniques do not generally lead to nanostructured materials but
to films similar to those obtained by the atomic deposition, with some specific properties.
LECBD is suitable for growing nanostructured materials. By depositing the clusters with low
energies that are far smaller than the binding energy of an atom in the cluster, no fragmentation
of the clusters is expected upon impact on the substrate. As a precursor to LECBD for forming
CAM, it is essential to understand the process of cluster deposition and, consequently, the
structure of the cluster on a surface. Our previous research has elucidated the time evolution
of cluster deposition and the effects of temperature and incident energy on the deposition
[4]. Some research has been carried out to explore the process of cluster deposition and the
effects of parameters such as temperature, cluster size and deposition velocity of a cluster on
the morphology and structure of a CAM. However, the structure of a cluster deposited on the
substrate via the LECBD is poorly understood at the atomic level.

Although considerable efforts have been made to understand surface structures, little
is known about the hetero-interface structure. Recent experimental and theoretical studies
showed a heterophase interface reconstruction between Ag(111) and Ru(0001) to relieve the
stress [5]. A Moiré structure has frequently been observed in many cases, where the two jointed
layers at the interface have the same symmetry but different lattice constants or rotations [6]. In
this paper, molecular dynamics (MD) simulations were carried out to investigate the structure
of the cluster, especially the interfacial layer, obtained by LECBD for a copper–gold system.

[1] Author to whom any correspondence should be addressed.

We focus on understanding the effect of stress due to the lattice mismatch between the cluster and the substrate on the structure of the cluster layer.

2. The model and methods

In our MD simulations, we used 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

$$E_i = \frac{1}{2} \sum_{j \neq i} V(\mathbf{r}_{ij}) - \left[\sum_{j \neq i} \Phi(\mathbf{r}_{ij}) \right]^{1/2}. \tag{1}$$

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 [7]. The potential has been applied successfully to investigate the structure and the phase diagram of the noble metal alloys [7] and the cluster-assembled materials formed by depositing Au clusters on Au(111) in agreement with the experiment in [8]. The simulated Au(111) substrate consisted of 12 atomic layers with 360 atoms per layer in the [111] direction exposing two (111) surfaces and was periodically repeated in the two directions parallel to the (111) surface plane (i.e. [1$\bar{1}$0] and [11$\bar{2}$]) so that it is effectively infinite in the two directions. Copper clusters with different numbers of atoms were softly deposited on the Au(111) surface at room temperature. Simulations of cluster deposition onto the substrate were carried out in the same way as in [4]. After deposition, the Cu–Au system was either cooled down to 0 K or was heated to higher temperatures and then cooled down to 0 K. It was found that a three-dimensional (3D) cluster on the Au(111) substrate would collapse via the so-called solid-on-solid settling mechanism and form a 2D structure when a high-enough temperature is reached [9]. In spite of different thermal treatments, the first layer of the Cu cluster (adjacent to the substrate surface) is of the same structure as shown in section 3. It will be discussed in more detail below.

3. Results and discussion

Figure 1 shows a slab of the Cu/Au system. The slab is three-layer thick, parallel to the Au(111) surface. It shows a projection of the two topmost substrate-surface planes and the first copper plane adjacent to the Au(111) surface. As shown in figure 1, a different stacking is always observed in the first layer of Cu (FCC and HCP stacking regions) for all the cases. The domain walls between the two regions are along the ⟨110⟩ direction. It is known that the in-plane stress due to the lattice mismatch often exists in the heteroepitaxial interface. The stress can be relaxed either by elastic strain or by forming misfit dislocations, which leads to a commensurate or an incommensurate interface, depending on the substrate potential acting on the epitaxial layer, the lateral interaction potential and the amount of lattice mismatch. The lattice mismatch between the isolated Cu cluster and the Au(111) substrate is more than 12%, while the interaction energies of Cu–Cu and Cu–Au are very close; so an incommensurate interface is preferable, as shown here. The result is in agreement with the experimental observation about Ag on Pt(111) [10], where the second Ag monolayer becomes stable by forming a trigonal incommensurate network to relieve the stress and the domain walls between the FCC and HCP regions, same as the present simulations, are along the ⟨110⟩ direction as the
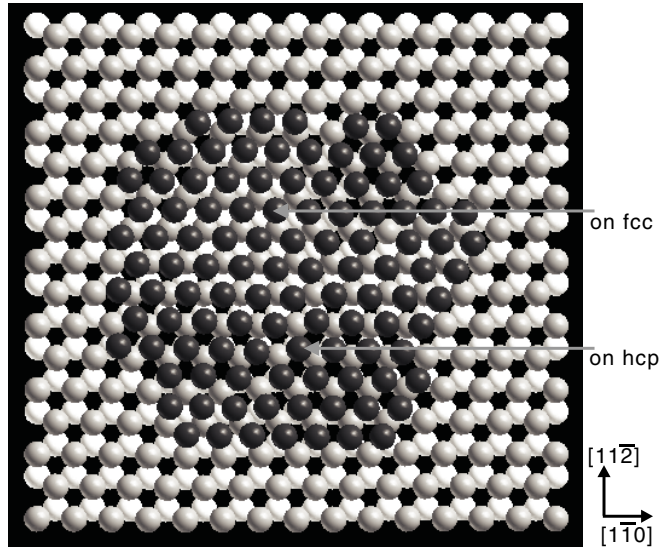
Figure 1. A typical slab of three (111) atomic layers in the final configuration after copper cluster deposition on the Au(111) surface via the LECBD technique. The top two layers of the Au(111) substrate and the interfacial copper layer are shown. The white spheres represent Au atoms in the second topmost layer of the Au(111) substrate and the dark spheres denote Cu atoms.

atomic separation in the first Ag monolayer is significantly extended. This extension results in a commensurate (1 × 1) fashion on Pt(111) due to the strong Pt–Ag interaction.

The static simulations at 0 K indicate that the system with one Cu atom on the HCP site of Au(111) has a slightly higher energy (3.3 meV) than the system with one Cu atom on the FCC site of Au(111). Such a small energy difference may be the reason for the number of atoms on FCC sites in the Cu cluster layer at the Cu/Au interface being almost the same as the number of atoms on HCP sites of Au(111). Another feature of the Cu/Au interfacial cluster layer is that each stacking region (FCC or HCP) contains only 20–30 atoms or so. In order to explore the underlying mechanism, additional simulations were carried out. N copper atoms (2D) were initially put on perfect FCC or complete HCP sites of Au(111). The Au(111) substrate contains 12 atomic layers in the [111] direction with a total of $N_0 = 4320$ gold atoms. With a specific initial configuration as shown in the inset to figure 2(a), we have concentrated only on the possibility of a stacking transition from the FCC to the HCP region in the [11$\bar{2}$] direction. The Cu–Au system was relaxed at 0 K until the total energy of the system no longer varied with additional minimization steps. The total energy of the Cu–Au system was calculated and compared with each other,

$$\Delta E = -\frac{E_c^{\text{S}} - E_c^{\text{HCP}^N}}{N}.$$ (2)

When N copper atoms are initially located on perfect FCC sites of Au(111), the S in equation (2) denotes FCC^N and the total energy of the Cu–Au system is E_c^{S}. When the copper atoms are initially on perfect HCP sites of Au(111), S denotes HCP^N and the total energy of the Cu–Au system is E_c^{HCP}. For convenient comparison among the Cu–Au systems with different Cu atoms, the difference in total energy is normalized by the number of atoms in the cluster. Since the internal energy is negative, equation (2) indicates that $\Delta E > 0$ if the Cu–Au system initially in the S state is more stable than HCP^N, otherwise $\Delta E < 0$. Figure 2(a) shows that
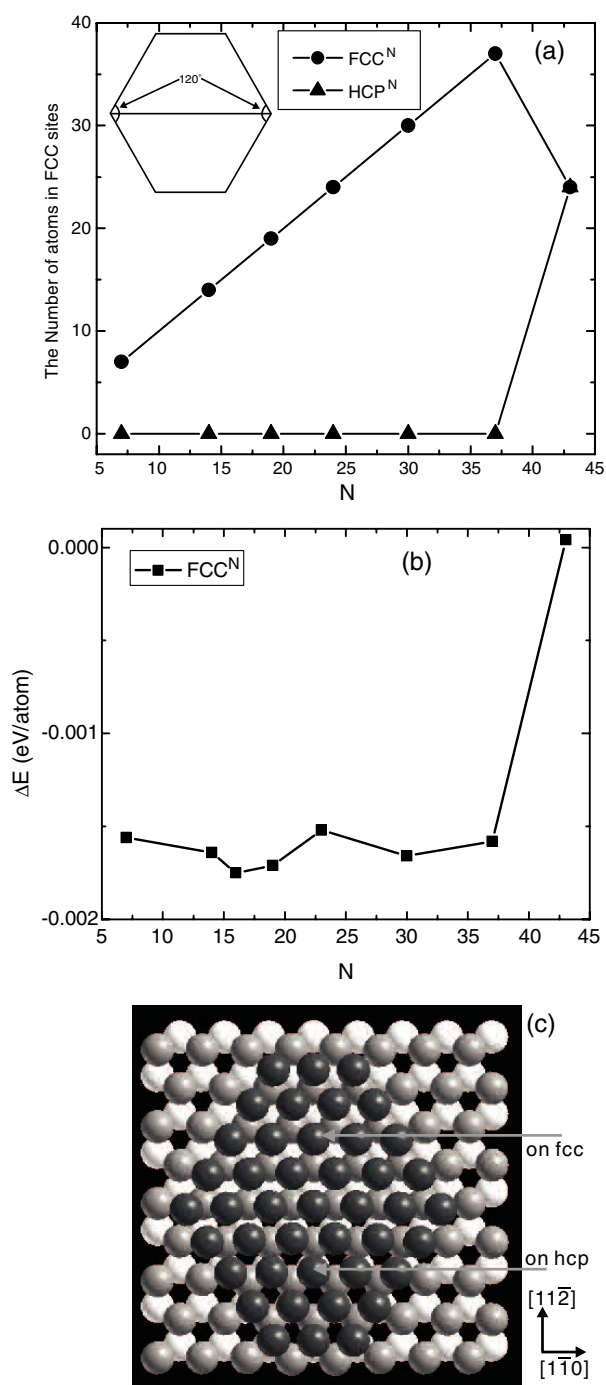
Figure 2. (a) The number of copper atoms on FCC sites of Au(111) and (b) the energy difference ΔE (see text) as a function of the number of Cu atoms. (c) A topview of Cu$_{43}$/Au(111) after full relaxation at 0 K. Two of the surface substrate layers and the interfacial copper layer are shown. The white spheres represent Au atoms in the second topmost layer of Au(111) and the dark ones denote Cu atoms. The initial configuration of the 2D Cu cluster on the Au(111) surface is shown in the inset of (a).
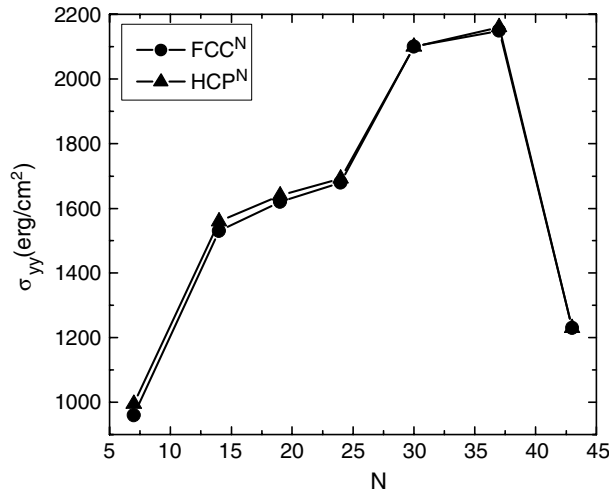
Figure 3. The stress σ_{yy} in the cluster varies with the number of Cu atoms on Au(111).

the final number of Cu atoms on FCC sites of Au(111) after a long-time relaxation at 0 K is equal to N in the case of the initial FCC^N state and is zero in the case of the initial HCP^N state when $N < 43$. This implies that the long-time relaxation at 0 K cannot result in the transition of Cu atoms from FCC (or HCP) to HCP (or FCC) sites and the final state is the same as the initial state of the system. Because of the relationship between the bond strength and bond length among Cu–Cu, Cu–Au and Au–Au bonds, Cu atoms after relaxation cannot occupy accurately their initial positions even at 0 K. ΔE as a function of the number of Cu atoms in the 2D Cu cluster is shown in figure 2(b), indicating that the system initially in the HCP^N state is more stable than that initially in the FCC^N state when $N < 43$ or so. For N up to 43, the Cu–Au system with two different initial states has the same final structure as shown in figure 2(c), where about half the Cu atoms are on FCC sites and the other half are on HCP sites of the Au(111) surface after relaxation at 0 K.

In addition to the energy preference, the stress relief in the cluster layer is another reason why each stacking region (FCC or HCP) at the Cu–Au interfacial cluster layer contains only about 20–30 atoms. As mentioned above, in the limit of the specific initial configurations, only the diagonal stress σ_{yy} in the $[11\bar{2}]$ direction is important for the present purpose. The stress in the cluster can be calculated by [11]

$$\sigma_{yy} = -\frac{1}{V} \left[\sum_{i=1}^{N} m_i v_{i,y}^2 + \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i} \frac{y_{ij}^2}{R_{ij}} F_{ij} \right], \qquad (3)$$

where m_i is the mass of atom i and y_{ij} is the distance between atoms i and j in the $[11\bar{2}]$ direction. R_{ij} is the distance between atoms i and j and F_{ij} is the interaction force between atoms i and j. $V = \sum_{i=1}^{N} V_i$ and V_i is the volume assigned to atom i. The stress σ_{yy} as a function of the number of Cu atoms on the Au(111) surface is shown in figure 3. There was no significant difference in stress for the Cu–Au system initially in the FCC^N or HCP^N state. When $N < 43$, Cu atoms after relaxation completely occupy the FCC or HCP sites of the Au(111) surface determined by their initial states. The 2D Cu cluster accumulates the stress with increasing N ($N < 43$) until the stress reaches some critical value (about 2200 erg cm^{-2}; see figure 3). Such a large stress would force the transition of some copper atoms from FCC

(or HCP sites) to HCP (or FCC sites) in the $[11\bar{2}]$ direction so that the final Cu atoms partly occupy FCC and HCP sites. Through this transition, the large stress is relieved to a smaller value. The result indicates that stress is the driving force for the formation of a stacking fault.

4. Conclusion

In summary, we reported results of molecular dynamics simulations employing a classic tight binding potential, aimed at studying the effect of stress on the structure of the cluster deposited on a substrate in the case of the hetero-Cu–Au system. Since Cu atoms at the Cu/Au interface try to relieve the stress from the lattice mismatch between the Cu cluster and the Au(111) substrate and tend to take up the most stable sites due to the energy preference, two different stackings, FCC and HCP, always exist in the atomic layer of the clusters adjacent to the Au(111) substrate. The two stacking regions with about 20–30 atoms each are divided by domain walls, which are always in the $\langle 110 \rangle$ directions. Finally, it is worth noting that the Cu cluster and the Au substrate cannot mix with each other despite a large negative mixing enthalpy between Cu and Au atoms since all the processes were simulated at low temperatures or low kinetic energies. Under these conditions, the Cu and Au atoms cannot overcome the energy barrier to intermix with each other. As a matter of fact, for instance, the cluster deposition at a high temperature or at a high incident kinetic energy leads to a strong intermixture [4].

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