

Molecular Dynamics Study on Deposition Behaviors of Au Nanocluster on Substrates of Different Orientation

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ABSTRACT

Effects of the substrate orientation on the homo-epitaxial rearrangement of the deposited Au cluster were studied by molecular dynamics (MD) simulation using embedded-atom method (EAM) potential. (011), (001), and (111) low indexed surfaces were used as a substrate with clusters of 321, 1055 or 1985 atoms at 300 K. When the cluster has 321 atoms, the epitaxial rearrangement of the cluster was achieved by collective motion of the cluster atoms irrespective of the substrate orientation. However, the cluster has more than 1055 atoms, the deposition behaviors drastically changed and was affected by the substrate orientation. The (011) substrate has the lowest degree of epitaxy. As the symmetry of the substrate increase from (011) to (111) orientations, the epitaxial rearrangement was improved.

Keywords: molecular dynamics, cluster deposition, substrate orientation, homoepitaxy, charged cluster model

1 INTRODUCTION

Based on experimental and theoretical analyses of the CVD diamond films, Hwang et al. [1-3] suggested the charge cluster model (CCM), where the diamond films grow not by an atomic unit but by a cluster unit. In the model, nanometer-sized charged clusters form spontaneously in the gas phase and become the major flux for film growth. Because of Coulomb repulsion arising from charge, the clusters do not coagulate easily. During the deposition process, they maintain their nanometer size and are suspended like colloidal particles in a solution. Later, the growth mechanism of the CCM was applied to silicon CVD [4-6], zirconia CVD [7, 8] and the thermal evaporation coating of gold [9].

Since this new paradigm of the thin film growth mechanism was first suggested, we were confronted with the critics on the existence of such hypothetical clusters in the thin film reactor. Recently, the existence of these clusters was experimentally confirmed in diamond CVD [10, 11], silicon CVD [4], zirconia CVD [8] and thermal

evaporation coating of gold [9]. Such clusters have been also confirmed during evaporation coating of copper, silver, aluminum, platinum and tungsten in our on-going study. Spontaneous generation of charged clusters appears to be very general in the thin film reactors.

As the existence of the charged clusters have been confirmed in many thin film processes, now it becomes important to confirm the epitaxial rearrangement of the cluster and to understand the dynamics of the cluster deposition. Since it is practically impossible experimentally to make *in-situ* observations of epitaxial recrystallization of individual clusters, we showed this behavior by molecular dynamics (MD) study for gold cluster deposition [12-14], where the small cluster is more favorable for epitaxial recrystallization than the larger one. The correlation between the film microstructure and the processing condition implies that the epitaxial recrystallization is favored not only by the small size of clusters but also by the high deposition temperature. For example, the quality of diamond films increased with increasing substrate temperature as well as decreasing methane concentration, which decreases the cluster size.

The present study is motivated to examine the epitaxial deposition behavior of clusters predicted by the CCM using MD simulations. The effects of the substrate orientations were studied to expand our understanding of the cluster deposition phenomena. In this simulation, several sized clusters were deposited onto low index substrate surfaces of (011), (001), or (111) orientations. For reliability of the MD simulations, we used the embedded atom method (EAM) potential [15, 16], which is known to work relatively well with face-centered metals such as gold.

2 COMPUTATIONAL MODELS AND SIMULATIONS

The Au (001), (011), and (111) surfaces were prepared as a substrate, respectively. The substrate dimension was $31a_0 \times 31a_0 \times 4a_0$, where a_0 is the equilibrium bulk lattice constant of Au at 300 K. Au atoms filled the substrate as a

face-centered-cubic with a prescribed lattice parameter. The substrate was subject to a periodic boundary condition in a direction parallel to the deposition surface (x and y direction in this calculation). To mimic the bulk behavior of the substrate, the position of atoms in two bottom layers of the substrate was fixed. Spherical crystalline clusters containing Au atoms from 321 to 1985 were prepared by cutting the perfect face-centered cubic (fcc) lattice, respectively. 321-atom and 1985-atom clusters correspond to 2.3 nm and 4 nm of diameter, respectively. The EAM potential developed by Oh and Johnson [17] for Au atom was used. The cut-off distance of the EAM potential was 5.7 Å. An MD time step was 4 femtoseconds (fs).

Before deposition of the clusters at 300 K, both cluster and substrate were equilibrated with an assumption of Boltzmann distribution for initial velocity distribution of Au atoms for 400 picoseconds (ps). After the equilibration the cluster was brought to each Au surface within the cut-off distance of 5.7 Å. The orientation of clusters was chosen randomly. After being brought within the cut-off distance, the cluster was spontaneously attracted to the substrate surface by a strong attractive force. After landing of a cluster on the substrate, only the substrate was thermostated at the prescribed temperature. The total MD time in the cluster deposition was 4 ns.

3 RESULTS AND DISCUSSION

3.1 Deposition onto Au (001) Substrate

Fig. 1 shows morphologies of the deposited clusters of three different cluster sizes on the Au (001) substrate after 320 ps of deposition at 300 K. As shown in Fig. 1(a), nearly all the atoms of the 320-atom cluster rearranged to epitaxial relation with the substrate. The dynamic evolution of the cluster ended at 24 ps. After 24 ps, the morphology was hardly changed, showing {111} facets tilted 35.2° with the (001) substrate.

On the contrary, in the case of 1055-atom cluster shown in Fig. 1(b), a planar defect characterized as a $\Sigma 3$ boundary was evolved during the rearrangement process. The twin boundary was not observed before deposition. To check the generality of the twin formation phenomenon, several clusters with random orientation were deposited on the substrate. The twin was always observed in all cases. From the detailed analysis of the snapshots of the 1055-atom cluster with time evolution, the twin boundary was initially generated at the right bottom of the cluster with the development of a (001) facet at the right bottom.

Fig. 1(c) shows the morphology of the deposited cluster of 1985 atoms. In this case, the epitaxial rearrangement of the cluster atom with the (001) substrate was not observed except in the contact region with the substrate. The orientation of the upper part of the cluster was the same as that of the free cluster. Most atoms in the cluster were not

affected by the substrate and maintain their original identity. The morphology of the deposited cluster was similar to that of the “contact epitaxy”, which was proposed by Yeadon et al. [18]. In their results, the nanosized clusters showed contact epitaxy at an early stage of the deposition on the substrate. And they proposed that the epitaxial relation should be induced by the nanoparticle sintering process, which is a substantially slow process compared with the collective motion of the cluster atoms.

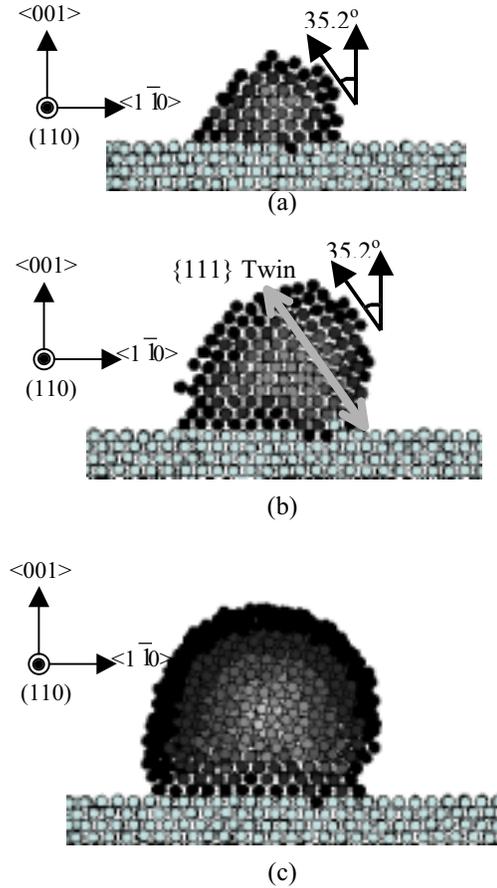


Fig. 1. (110) plane view morphologies of deposited Au clusters of (a) 321, (b) 1055 and (c) 1985 atoms on the Au (001) substrate at 300 K after 320 ps of deposition.

To quantitatively compare the epitaxial rearrangement of the deposited clusters, a static structure factor [12] was used as a characterization tool for quantifying the degree of epitaxy. Fig. 2 shows the degree of epitaxy with the cluster size. As can be seen from Fig. 2, the smaller cluster shows a high value of the degree of epitaxy. The reason why the smaller cluster cannot achieve 100 % of the degree of epitaxy is due to the atomic motion at a finite temperature. When a perfect crystal at 0 K was considered, the crystal shows 100 % of the degree of epitaxy. As the cluster size increased, the degree of epitaxy degraded. This result

implies that there exists a size limit in the epitaxial rearrangement.

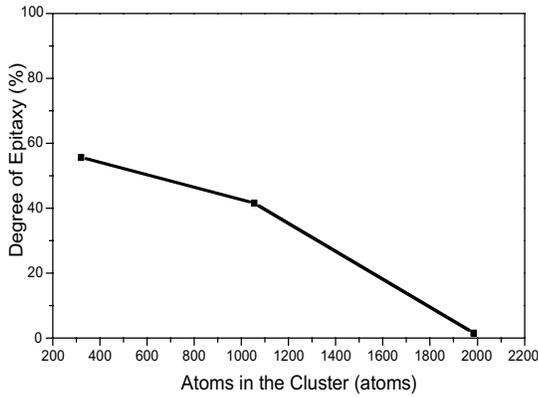


Fig. 2 The degree of epitaxy with the cluster size at 300 K on the (001) Au substrate.

3.2 Effect of substrate orientations on the deposition behavior.

Fig. 3 shows morphologies of the deposited 321-atom cluster onto various substrate orientations. As can be seen in the figure all the deposited clusters show a good epitaxial relation with the substrate. The analysis of the time evolution of the snapshots showed that the epitaxial rearrangement was completed after 25 ps of deposition for the three orientations. The fast epitaxial rearrangement of the 321-atom cluster was attributed to the collective motion of the cluster atoms, which was revealed by analyzing the snapshots of atomic configuration with time. The collective motion of the cluster atoms upon deposition was also reported by Hou[19] in all substrate orientations. In this case, the mechanism of epitaxial rearrangement of the cluster is not by the interaction with the substrate but by the collective motion of the cluster atoms.

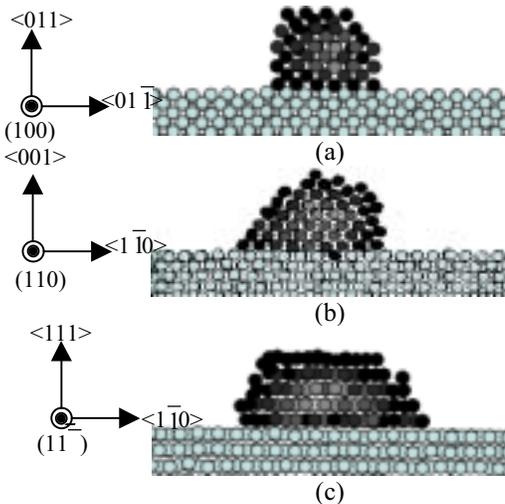


Fig. 3. Morphologies of the deposited 321-atom cluster at 300 K after 320 ps of deposition on on (a) (011) (b) (001) and (c) (111) substrates.

Morphologies of the 1055-atom clusters after 400 ps of deposition are shown in Fig. 4. The shapes of the 1055-atom cluster were drastically changed with the substrate orientation. Judging from their appearances, the morphology of the cluster on the (011) substrate was similar to that of Fig. 1(c). This result implies that the effects of the substrate were the smallest on the (011) substrate compared to other orientations. Only a small fraction of atoms in contact with the substrate shows an epitaxial relation with the substrate. The upper part of the cluster still maintains its original orientation. Though the surface energy of the (011) substrate was the highest among three low index surfaces, the epitaxial rearrangement of the cluster atoms was observed to be the worst. The morphologies of the cluster hardly changed from those of Fig. 4 for the used time limit of 1 ~ 2 nanoseconds (ns) of our MD simulation.

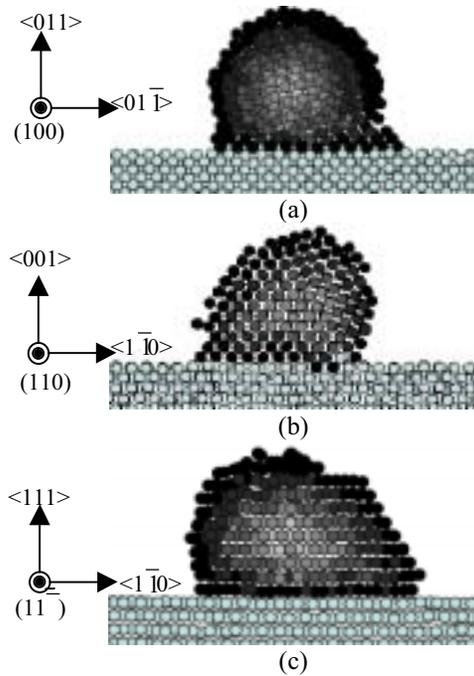


Fig. 4. Morphologies of the deposited 1055-atom cluster at 300 K after 320 ps of deposition on . (a) (011), (b) (001) and (c) (111) substrates.

When the substrate orientation was changed to <001> that has the next highest surface energy among three surfaces, the cluster evolves to nanograins with a $\Sigma 3$ twin boundary. After the formation of the twin boundary, the cluster morphology was hardly changed for 1 ns. As the excess energies of the surface facet and the twin boundary have relatively small, this morphology was considered as a metastable structure, which was maintained for the time limit of the MD simulation.

When the 1055-atom cluster was deposited onto the (111) substrate, the deposition behavior was different from those on (011) and (001) substrates, which was shown in

Fig. 4(c). Almost all the atoms in the cluster showed the epitaxial relation with the (111) substrate except the small fraction of misfit atoms in the upper left part of the cluster.

To compare the effect of the substrate orientation on the epitaxial rearrangement of the deposited cluster, the static structure factor was used. Fig. 5 shows the degree of epitaxy variation with the substrate orientation and the cluster size. In the 321-atom cluster deposition, all the clusters had high values of the degree of epitaxy. The smallest value for the (001) substrate might be caused by the formation of a surface misfit layer. When the 1055-atom clusters were deposited on the various substrates, the degree of epitaxy was drastically diverged. The (111) substrate showed the highest value of the degree of epitaxy, the (001) substrate showed the next and the (011) substrate showed the lowest value of the degree of epitaxy, as had been predicted by the snapshots of Fig. 4.

For the cluster of 1985 atoms, the (111) substrate still showed the highest degree of epitaxy, maintaining a relatively good epitaxial rearrangement. However, the (001) and (011) substrates did have very poor epitaxial relations with the substrate except the region where the cluster and the substrate were in contact. From these results, the (111) orientation is concluded to be the most favorable substrate in epitaxial rearrangement of the cluster.

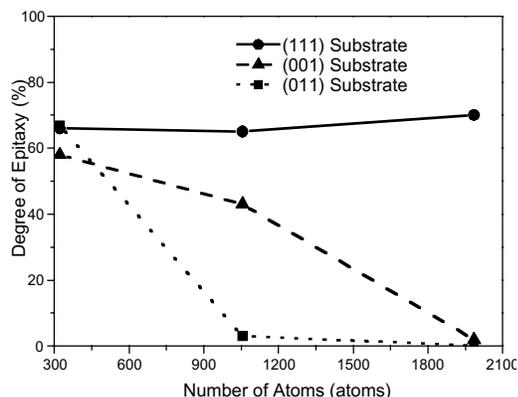


Fig. 5 The dependence of the degree of epitaxy on the substrate orientation and the cluster size.

4 CONCLUSION

Molecular dynamics simulations on the deposition behaviors with three different cluster sizes and substrate orientations were conducted. For a small 321-atom cluster, the epitaxial rearrangement of the cluster atoms could be achieved even at 300 K, irrespective of the substrate orientation by the collective motion of the cluster. For larger 1055-atom and 1985-atom clusters, the substrate orientation drastically changed the morphology of the deposited cluster. On a (011) substrate, no epitaxy was observed except the region where the cluster and the substrate were in contact. When the substrate was replaced by the high symmetry orientation, the degree of epitaxy was improved. In the case of (111) substrate, the 1985-atom

cluster still had a high value of the degree of epitaxy. The reason why the high symmetry surface has a high degree of epitaxy is under study.

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