Molecular-dynamics study of transient-diffusion mechanisms in low-temperature epitaxial growth

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This paper investigates the transient-diffusion process in low-temperature epitaxial growth of thin-film Cu on the Cu(100) surface with molecular-dynamics simulations. By using a hybrid tight-binding-like potential, we have classified and made a quantitative comparison for the various transient-diffusion motions occurring during deposition. The statistics indicate that the impact cascade-diffusion mechanism plays a noticeable role in promoting atomic mobility. And the observed diffraction-intensity oscillations show that a quasi-layer-by-layer growth in the initial stage may take place for temperatures as low as 100 K. [S0163-1829(98)06308-5]

I. INTRODUCTION

In recent years, the growth mechanisms of thin metal films at very low temperature have attracted much experimental and theoretical attention.[1–7] Normally, it was thought that significant adatom diffusion stemming from high substrate temperature is necessary to get smooth film growth such as evaporation deposition. However, diffraction-intensity oscillations observed in reflection high-energy electron diffraction[1] (RHEED) and He-atom beam scattering experiments[8] suggested a smooth layer-by-layer growth for temperatures as low as 80–100 K, where the thermally activated diffusion seems unable to account for the observed surface mobility. To explain these interesting results, two models, ''transient mobility'' and ''downward funneling,'' were proposed. In the ''transient mobility'' model, Egelhoff and Jacob[1] suggested that the deposited atoms could skip across the surface before resting in an adsorption site due to the release of the latent heat of condensation. This idea provides some reasonable explanations, but the occurrence of such transient mobility is currently disputed.[4,9] In another explanation of ''downward funneling,'' Evans *et al.*[4,10,11] proposed that the small growing three-dimensional islands could not adsorb the incoming atoms on their steep sides, and thus the incoming atoms funneled downhill to the flat layers closer to the substrate.

In order to get a better understanding of the microscopic characteristics of the complicated growth phenomena, molecular-dynamics (MD) simulation is obviously an effective technique to study those short-term processes. Moran, Schuller, and Ramirez[12] used the MD method with a modified Lennard-Jones potential to simulate the intensity oscillations in RHEED and He-atom beam scattering. Gilmore and Sprague[5] conducted MD simulations on the growth of Cu and Ag onto Ag(001) surfaces and they observed transient processes at 300 K. For a realistic low-temperature deposition process, it is conceivable that these and other complicated transient motions should occur simultaneously, therefore it is necessary to ascertain whether those transient motions really occur in the initial stage of depositions and to make a quantitative comparison for the relative importance of these mechanisms, as well as to study their temperature effect. Those are the main tasks of this work. It is worthwhile to indicate that the actual film growth especially at higher temperatures is dominated by the thermal diffusion process, which cannot be described properly by the present MD technique. However, the MD studies do provide insight into transient processes, and at low temperatures, say 100 K, those transient motions will play a noticeable role in promoting the atomic diffusion mobility and evolution of surface morphology instead of the thermal diffusions.[5,3,8,13]

In this paper, we present systematic microscopic investigations of the transient diffusion processes occurring during evaporation deposition by MD simulations on the growth of thin film Cu onto a Cu(100) surface. In order to observe the details of the transient-diffusion motions, we have developed a computer code, which is able to identify and record all kinds of the transient motions. Meanwhile, the simulated diffraction-intensity oscillations[12] are utilized to monitor the evolution of the epitaxial growth.

Cu-Cu interactions are described via a hybrid potential by combining the Moliere potential with the tight-binding-like potentials, which includes the many-body effects and can reproduce satisfactorily many bulk and surface properties of pure Cu metals, Cu clusters, as well as its alloys.[14–18]

II. MODEL

The Cu(001) substrate modeled in the simulations consists of ten layers with one static on the bottom and nine movable atomic layers containing 98 atoms each. Periodic boundary conditions are applied in the lateral directions. 200 Cu atoms (about two layers) are deposited for each run randomly normal to the substrate with the initial kinetic energy

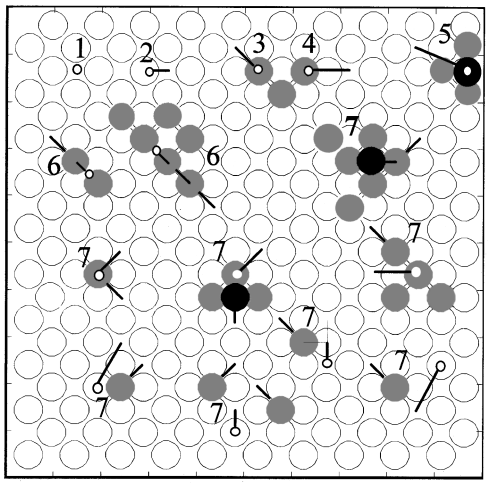

FIG. 1. Schematic representation of the different types of transient diffusion motions observed during deposition. 1 stands for ADJ1 (see text for the details), and 2 for ADJ2, 3 for DF1, 4 for DF2, 5 for DF3, 6 for ICD1, 7 for ICD2. The larger open circles stand for the substrate atoms. The larger gray and dark solid circles are for adatoms in the first and second layers from the substrate surface, respectively. The smaller open circles designate the impinging sites of impacting atoms.

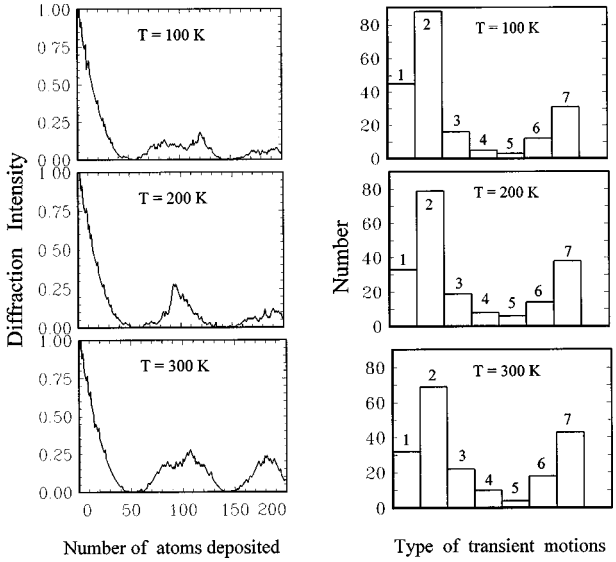

FIG. 2. The figures on the left side show the diffraction intensities as a function of the number of deposited atoms at different substrate temperatures. The figures on the right side give the numbers of the various transient diffusion motions to occur during deposition. 1–7 stand for the types of the transient motions as in Fig. 1. The incident Cu atom energy is 0.1 eV impinging on the Cu(001) substrate with 98 atoms per layer. The deposition rate is 1 atom/1 ps.

of 0.1 eV per atom and deposition rate of 1 atom/1 ps. The temperature of the system is controlled by rescaling the velocity of the atoms in the second through ninth layers from the surface in each time step (2 fs). The motion of the top-layer atoms is determined only through the interactions with other atoms and Newtonian mechanics. This arrangement ensures that the film and substrate are able to cool back to the desired substrate temperature before subsequent atoms impinge on the surface. This atom-velocity-rescaling method has often been used in recent MD simulations[12,14,19,20] to prevent any possible artificial heating of the surface due to the assumed deposition rate much higher than experiments. Three substrate temperatures, 100, 200, and 300 K, are studied, respectively.

In our simulations, transient-diffusion processes are defined as the motion of the impact atom from the time it first interacts with the surface until it localizes into an adsorption site and the motion of the adatom from one adsorption site into another adsorption site. Most typical transient-diffusion motions observed during deposition are shown in Fig. 1 and illustrated as follows.

ADJ mode: direct deposition. The adatom impinges on a locally smooth surface area with no step nearby, and the atom simply moves to a closer fourfold-hollow (4fh) adsorption site. No impact-driven motion of the adatoms already on the surface takes place. ADJ1 (ADJ2) refers to the lateral moving distance being less (larger) than a quarter of the lattice constant.

DF mode: downward-funneling transient motion. The impact site is near an atomic step and a downward-funneling-like transient motion takes place for the incident atom. No impact-driven motion occurs for the adatoms already on the surface. DF1, DF2, and DF3 refer to that the lateral moving distances of the incident atom are in the ranges of 0.35–0.7, 0.7–1.0, and 1.0–1.5 lattice constants, respectively.

ICD mode: impact cascade diffusion. The impacting atom knocks out at least one adatom already on the surface. ICD1 (ICD2) refers to that the incident atom takes (does not take) the place of the dislodged atom.

III. RESULTS AND DISCUSSION

The observed diffraction intensities as a function of the number of deposited atoms are shown in Fig. 2 for the three substrate temperatures. The intensity oscillation is observed at the temperature of 100 K, and becomes relatively strong at 300 K. Those observations are in good agreement with the MC simulations.[10] We note that in the recent experiments on the growth of Cu onto Cu(100) (Ref. 8) and Ag onto Ag(100) (Ref. 3) surface, the oscillations were also reported for temperatures as low as 100 K.

The transient-diffusion motions of all the types described above have been observed for each substrate temperature, and Fig. 2 gives the mean numbers for every type of transient motion to occur in each run. It has been found that a significant transient motion, which is defined as the lateral moving distance being equal to or greater than 0.7 lattice constant, occurs only after the first few atoms are deposited. This shows that the significant transient motion primarily stems from the impacting atoms interacting with other adatoms already on the surface. And it is precisely those transient mechanisms that make possible the surface mobility of adatoms and the smooth film growth in the initial stage at such low substrate temperatures and low incident energy. This result is consistent with the simulations by Gilmore and Sprague.[5]

Now we proceed to make a comparison of the contributions from those transient motions to the surface mobility. The contribution of the ADJ mode seems to be trivial, although it takes a relatively larger fraction in the total depo-

sition events. Our simulations show that when an atom impinges on a locally smooth surface, e.g., a top site with more than four supporting atoms below, the atom is most likely to directly move to the closest 4fh adsorption site and no significant ''transient mobility'' suggested by Egelhoff and Jacob[1] is observed. The important transient-diffusion motions observed are the ICD mode and the DF mode. As exhibited in Fig. 2, the fraction of the ICD mode is almost twice that of the DF mode. This is because the downward funneling motion of impinging atoms is often accompanied by the impact-driven motion of adatoms already on the surface. For instance, when an atom impinges nearly on an island edge, most often the incident atom will not directly hop onto the lower layers over the island edge, but rather it drives the island atoms to ''diffusion outward'' or ''funnel downward,'' causing spreading of atoms in the layers closer to the substrate. All those kinds of motions are attributed to the ICD mode in the present statistics. Besides, each ICD motion can make a relatively larger contribution to the smoothness of the growing film compared with that of the DF mode as well as ADJ mode. ICD motion often has relatively larger lateral moving distance and, most important, can cause collapsing of 3D islands and spreading of adatoms on the monolayers. Therefore, the ICD mode mechanism plays an important role in contributing to the surface mobility of adatoms and quasi-layer-by-layer growth of the metallic thin film in the initial stage of low-temperature growth.

As for the temperature effect on the transient motions, it can be seen from Fig. 2 that the fractions of significant diffusion motions (ICD mode and DF mode) increase with increasing temperature, whereas that of the ADJ mode decreases. This is because at a higher temperature adatoms in a locally smooth island are more easy to activate by atomic impact. These phenomena in conjunction with the increased thermal-diffusion contribution explain the experimentally observed general trend, the improving smoothness of film growth when increasing the substrate temperature.

It should be mentioned that, concerning the ICD mode, there exists some controversy in the literature. The first limited MD studies for this system did not observe any ICD motion.[11] In the subsequent works, Halstead and DePristo performed extensive MD simulations[21] with fixed micropyramids fabricated on surface studying the impinging effect of incident atoms on those symmetric microstructures. These authors indicated that in their studied cases the knockout mechanisms are typically inoperative for low substrate temperatures. On the other hand, in the recent MD simulations of Cu and Ag on Ag(001) surface,[5] Gilmore *et al.* observed displacement, replacement, and activation of the existing adatom clusters with EAM potential. Also, the calculations of diffusion barriers and bonding energies by using the density-functional theory[22] and MC method[13] have found the two-atom exchange process near island edges favorable at low temperature, which is consistent with the ICD mode discussed here. Now by using the hybrid tight-binding-like potential and assuming that the velocity rescaling technique used does not corrupt the dynamics, this work not only demonstrates the existence of ICD mode, but also presents a quantitative idea about how frequent this motion occurs in the deposition process.

IV. SUMMARY

Due to intrinsic limitations, the MD simulations conducted here have been limited to studying the transient process of the low-temperature epitaxial growth of metal thin films. The thermally activated diffusion has not been included in this study, which can be regarded as a long-term process compared with the transient process and becomes even more important in determining the configuration of the deposited film with increasing the substrate temperature. By using the hybrid tight-binding-like potential and assuming a high deposition rate of atoms impinging on the modeled substrate mentioned above, the simulations have observed damped diffraction intensity oscillations for temperatures as low as 100 K, indicating quasi-layer-by-layer growth in the initial stage. Furthermore, we have examined the characteristics of the various transient diffusion motions, which underlie the surface mobility. The transient motions are classified into three categories, namely, the direct deposition (ADJ), downward-funneling (DF), and impact cascade diffusion (ICD). A quantitative comparison of those transient-diffusion motions to occur during deposition is given. It has been found that the major contribution to the surface mobility of adatoms in the initial stage comes from the interactions of the impact atoms with metallic adatoms already deposited on the surface, which make the stacks of deposited atoms on the surface (three-dimensional islands) unstable and easy to collapse and spread the adatoms to the monolayer. This is the impact cascade-diffusion mechanism discussed in the present work.

There are many questions left open to further discussion, such as the potential deviations from the true dynamics caused by setting the velocity-rescaling region below the surface layer, etc. We plan to study these questions in the future. We have also taken note of the reported abnormal variation of the diffraction-intensity oscillations with temperature[2,8] and the suggested explanation on this phenomenon.[13,23]

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