Surfactant-mediated layer-by-layer homoepitaxial growth of Cu/In/Cu(100) and Ag/Sb/Ag(111) systems: A theoretical study

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Two typical surfactant-mediated homoepitaxial metal systems, Cu/In/Cu(100) and Ag/Sb/Ag(111), are studied by using first-principles calculations and a kinetic Monte Carlo method. Our results confirm the validity of the model that Zhang and Lagally suggested for Cu/In/Cu(100) system. A repulsion model is proposed for the Ag/Sb/Ag(111) system where surface-substitutional Sb atoms repel diffusing Ag adatoms. The layer-by-layer growth for Ag/Sb/Ag(111) system is achieved with a repulsion model in kinetic Monte Carlo simulation. By comparing the two different growth models, the importance of the additional barrier $\Delta E$ and effectiveness of two ways of reducing $\Delta E$ are confirmed in determining film morphology. [S0163-1829(98)00815-7]

I. INTRODUCTION

Over the last few years, many experiments have shown that the shape of films grown on solid surfaces can be appreciably altered by the presence of small amounts of surfactants.1–7 Smooth Ge films can be grown on the Si(100) surface preadsorbed by a monolayer of As, Sb, or Te (Refs. 1–4) while films grown on the clean surface are rough. It has also been observed that the presence of Sb on Ag, O on Pt, or In on Cu can induce layer-by-layer homoepitaxial growth at conditions typical for island growth in the systems.5–7 In these studies, the term surfactant refers to a monolayer or a submonolayer of foreign atoms on the surface. The classical definition of surfactant is a substance that lowers surface tension, thereby increasing spreading and wetting properties.8 Currently a surfactant is accepted to be a generic agent promoting two-dimensional (2D) layer-by-layer (LBL) growth as opposed to three-dimensional (3D) island growth for a special crystal face.9

A detailed understanding of the mechanisms involved in the surfactant-mediated growth for both semiconductor and metal systems in heteroepitaxy and homoepitaxy is not only of fundamental interest, but also has technological importance. The growth of thick, low-defect films with abrupt interfaces and smooth layers is an essential requirement for many modern electronic device applications.

In the present study we restrict our discussion to metal-on-metal homoepitaxial growth. Zhang and Lagally suggested a general model (ZL’s model) for metal systems.8 ZL’s model is based on the inequality $V_{A-A} > V_{A-S} > V_{S-S}$ connecting the adatom-adatom, adatom-surfactant, and surfactant-surfactant bond strengths ($A$ denotes adatom, $S$ surfactant). In this paper, two typical surfactant-mediated homoepitaxial metal systems, Cu/In/Cu(100) and Ag/Sb/Ag(111), are studied by using first-principles calculations and the kinetic Monte Carlo method. Our results confirm the validity of ZL’s model for Cu/In/Cu(100) homoepitaxial system. For the Ag/Sb/Ag(111) homoepitaxial system, a repulsion model based on first-principles calculations is proposed where surface-substitutional surfactant Sb atoms repel deposited Ag atoms and affect their migrations and nucleations. Kinetic Monte Carlo simulation results are in good agreement with experiments. These results confirm the importance of the additional barrier $\Delta E$ in determining film morphology.

This paper is organized as follows. Section II contains a brief description of the first-principles calculations we used, ZL’s model, our repulsion model, and the simulation method used. In Sec. III we present our results and detailed discussion and conclude in Sec. IV.

II. MODEL AND METHOD

A. Calculation of binding energies and diffusion barriers

In this paper, a discrete variational $X_a$ (DV-$X_a$) method is used in the calculation of various binding energies and diffusion barriers in Cu/In/Cu(100) and Ag/Sb/Ag(111) systems. The DV-$X_a$ method we used is a first-principles molecular cluster approach based on local-density-functional (LDF) theory. The matrix elements of the Hamiltonian and overlapping are evaluated by a numerical integration technique on a grid of about 1200 points per atom. In the DV method, the atomic wave functions $\phi$ are generated numerically from same LDF solutions for the free atoms and are used as basis functions. The molecular wave functions and eigenvalues are determined using the self-consistent charge to the potential. More details of this method have been given in Ref. 11. The frozen-core approximation is used for Cu, In, Ag, Sb, except that the Cu $3d$, In $4d$, Ag $4d$, and Sb $4d$ electrons are treated fully in the self-consistent iterations.
The Hedin-Lundqvist exchange-correlation terms are adopted in the potential. This cluster approach has proved to be a very good one in studying adsorption on transition metal surfaces.10 In the present calculations, model clusters of Cu25 and Ag24 are adopted to simulate the flat (100) surface of Cu and (111) surface of Ag (see Fig. 1). Thus a natural first step is to calculate the adsorption of In and Sb on Cu(100) and Ag(111) surface, respectively. We investigate the different adsorption sites described in Sec. III A. The adsorption energies of an adatom is defined as

$$E_{\text{adatom}} = -(E_t - E_{\text{clean}} - E_{\text{atom}}),$$

with $E_t, E_{\text{clean}}, E_{\text{atom}}$ being the total energies of the adsorbate-covered cluster, of clean one, and of the free atom. The vertical positions of the adsorbates are optimized by maximizing the binding energy of the cluster. The substrate sites have been frozen unless specially needed. The binding energies of various dimers on Cu(100) and Ag(111) surfaces are calculated and described in Sec. III A. The binding energy of a dimer on the surface is given by

$$E_b = E_{\text{dimer}} - (E_{\text{adatom}}^1 + E_{\text{adatom}}^2),$$

where $E_{\text{dimer}}$ is the total adsorption energy of the dimer on the surface, and $E_{\text{adatom}}^1, E_{\text{adatom}}^2$ are the adsorption energies of one adatom in a dimer. A dimer is said to be binding if the binding energy is positive in sign. The larger the binding energy, the more stable the dimer. For the Ag/Sb/Ag(111) system, the interaction between surface-substitutional Sb and the on-surface Ag atom nearby is calculated by varying the distance between them while their vertical positions are both optimized.

The diffusion barriers are given by the difference between the highest energy obtained in a saddle-point configuration and the energy in the initial situation. We adopt Cu33 and Ag33 clusters to simulate the stepped Cu(100) and Ag(111) surfaces in the calculation of those energy barriers concerning steps. For the calculation of Cu-In or Ag-Sb exchange barriers we used Feibelman’s method where a Cu or Ag adatom replaces a substrate In or Sb atom, as the latter becomes an adatom in a nearest-neighbor fcc site.12

B. Zhang and Lagally’s model for the Cu/In/Cu(100) system

Zhang and Lagally proposed a model for metal systems based on the assumption that $V_{A,S} > V_{A,S} > V_{S,S}$. In this model, the A-S exchange and push-out exchange processes are main action mechanisms of the surfactant for metal systems. They are shown in Fig. 2. In ZL’s model, the A-S exchange mechanism is the dominant process through which the surfactant atoms are lifted to avoid being buried. Whenever an S atom is about to be buried in a layer by an A atom on top, incorporation of the A atom into the layer by exchanging with the S atom is highly probable [see Fig. 2(a)]. Such an A-S exchange process can ensure that surfactants segregate effectively so that they continue to affect the growth mode of successive growing layers.

Another important process is push-out exchange process [see Fig. 2(b)]. For an A atom stepping down at an S-terminated step, a push-out exchange process can be favored over a direct “rollover” process.

For the Cu/In/Cu(100) system, our calculated results show that ZL’s basic assumption is satisfied ($V_{Cu-In} > V_{Cu-In} > V_{In-In}$). In the ZL’s (1 + 1)-dimensional simulations, they used a set of model parameters that are not relevant for the real Cu/In/Cu(100) system. In this paper we do our simulations with ZL’s model by using a set of real barriers of the Cu/In/Cu(100) system.

C. Our repulsion model for the Ag/Sb/Ag(111) system

Our calculated results show that ZL’s basic assumption is not satisfied in the Ag/Sb/Ag(111) system ($V_{Ag-Ag} < V_{Ag-Sb}$). Thus a new model is needed for the Ag/Sb/Ag(111) system. According to our results and Oppo et al.’s,13 Sb atoms preferably stay at surface-substitutional sites (see Table I), and surface-substitutional Sb atoms repel diffusing Ag atoms. We propose a repulsion model for the Ag/Sb/Ag(111) system. In our repulsion model, the Ag-Sb...
TABLE I. Adsorption energies of In, Sb on Cu(100) and Ag(111) for two adsorption sites. $E$ is the adsorption energy, $h$ is the vertical height of the adatom from Cu(100) and Ag(111) surfaces.

<table>
<thead>
<tr>
<th>Adatom</th>
<th>Adsorption site</th>
<th>$E$ (eV)</th>
<th>$h$ (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In/Cu(100)</td>
<td>Hollow site</td>
<td>3.42</td>
<td>3.42</td>
</tr>
<tr>
<td></td>
<td>Surface-substitutional site</td>
<td>3.63</td>
<td>1.60</td>
</tr>
<tr>
<td>Sb/Ag(111)</td>
<td>Hollow fcc site</td>
<td>3.07</td>
<td>4.46</td>
</tr>
<tr>
<td></td>
<td>Surface-substitutional site</td>
<td>4.37</td>
<td>2.00</td>
</tr>
</tbody>
</table>

exchange process and the repulsive interaction between surface-substitutional Sb atoms and deposited Ag atoms are main action mechanisms of surfactants Sb. They are shown in Fig. 3. The A–S exchange process is a necessary condition for surfactant-mediated LBL growth, which is confirmed from our calculated results below, so it exists in both of these two growth models.

For unannealed surfaces, most preadsorbed Sb atoms occupy on-surface sites at the beginning of deposition. Due to $V_{Ag-Sb} > V_{Ag-Ag}$, after Ag atoms are deposited, Sb atoms will be centers of nucleation of deposited atoms. After small islands centering about Sb atoms are formed, the repulsion effect of substitutional Sb atoms begins to be put into action. The Ag atoms landing on small islands will diffuse to edges of the islands and step down rapidly due to the repulsion. Thus a smooth first layer is grown and an almost uniformly distributed repulsion network of surface-substitutional Sb atoms is formed. From the second layer on, the repulsion network starts to go into effect. For annealed surfaces, preadsorbed Sb atoms occupy surface-substitutional sites and build a repulsion network at the beginning of deposition.

When deposited Ag atoms enter this network, it will be repelled by Sb atoms around it. In a given time, the distance traveled by Ag walkers is diminished greatly, that is to say, the terrace diffusion barrier $E_{surf}$ is increased on average. It is the repulsive interaction and network that lead to this increase and enhanced island density. Our simulated results also show that the growth mode of Ag/Sb/Ag(111) depends on Sb coverage; this proves that an increase of $E_{surf}$ is the global effect of the surfactant network. For the interacting system, there are many microscopic diffusion barriers; the value of the measured diffusion barrier $E_{surf}$ must result from some complex average of all of them, and does not refer to any microscopic process in particular. In our present model, we focus on the qualitative property of $E_{surf}$.

For the Ag/Sb/Ag(111) system, we use the repulsion mechanism during the whole growth process (up to about 12 ML thick). Based on our calculated results, the repulsion energy between the surface-substitutional Sb and on-surface Ag nearby is approximately equal to $(0.8/\rho^2)$ eV, where the distance $\rho$ is 1, 2, or 3, corresponding to three neighboring sites of Ag adatoms (nearest, next nearest, and third nearest), otherwise is zero. The difference $E_f - E_i$ is calculated where $E_i(E_f)$ is the interaction energy of an adatom Ag with all the surface-substitutional surfactant Sb atoms nearby when an adatom Ag is at its location before (after) a jump. So in the presence of the surfactants Sb, the energy barrier $e$ for an adatom Ag diffusing on terraces, which is calculated from the intersection point between harmonic potential wells center on adjacent sites, is defined as

$$e = e_0 + (E_f - E_i)/2 + (E_f - E_i)^2/16e_0,$$

where $e_0$ is the energy barrier for an adatom Ag diffusing on terraces without surfactants Sb.

**D. Simulation method**

We consider a solid-on-solid model growing on an $L$ one-dimensional substrate with periodic boundary conditions. The $h(x,t)$ represents the height of the surface at the one-dimensional substrate at positions $x$ and $t$. Surfactants are precovered over the substrate with uniform random distribution. Atoms are deposited randomly on the surface at a constant rate and deposition of a single atom at position $x$ increments the height by unity. In a single time step, a small number of atoms are deposited randomly on the surface, and all the atoms including surfactants on the surface are allowed to hop to nearest-neighbor empty sites.

Here we use the time-dependent Monte Carlo method (TDMC) to simulate growth processes. Because an atom hops in each time-dependent Monte Carlo cycle, TDMC can overcome the “rare event problem.”

If there are $N$ atoms in the system and the total number of possible transitions is $M$, for each transition type, the transition rate is $\omega_i$ ($i = 1, 2, \ldots, M$) where $\omega_i = \nu \exp(-e_{bi}/K_{B}T)$, where $e_{bi}$ is the energy barrier for $i$th transition type. We assume that there are $N_{bi}$ transitions of $i$th transition type, so a chosen transition type $j$ has relative rate $R_j$:

$$R_j = \frac{N_{bi} \exp(-e_{bi}/K_{B}T)}{\sum_i N_{bi} \exp(-e_{bi}/K_{B}T)}.$$  \hspace{1cm} (4)

At first the computer searches for all possible transitions in the system and calculates the corresponding $R$ by means of Eq. (4), and then generates a random number between zero and one. According to $\alpha$ and $R$, the energy barrier for the jump to be chosen will be determined. Then another random number $\beta$ can determine the jump in this transition type. That is to say, two random numbers determine a particular jump.

It is important to calculate the real time for studying dynamical behavior in Monte Carlo simulation. If we denote by $L$ the number of sites on the one-dimensional lattice, the mean time between the deposition of two atoms in our simulation is $T_d = T_0/L$, where $T_0$ is the time needed to grow a monolayer. A new method to calculate the real time was

![FIG. 3. Schematic picture of our repulsion model for the Ag/Sb/Ag(111) system. The force $F$ is the repulsive interaction between surface-substitutional Sb and Ag adatom. Sb atoms segregate by Ag-Sb exchange process. The empty circles represent Ag adatoms and dark circles represent Sb surfactants. For details, see text.](image_url)
TABLE II. Energy barriers for the Cu/In/Cu(100) system used in the model simulations. $N_i$ ($N_f$) is the number of in-layer nearest neighbors in the initial (final) state. Refer to Fig. 2 for Cu-In exchange and push-out exchange process.

<table>
<thead>
<tr>
<th>Diffusion type</th>
<th>$N_i$</th>
<th>$N_f$</th>
<th>Energy barrier (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cu/Cu(100)</td>
</tr>
<tr>
<td>Intralayer diffusion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diffusion on terrace</td>
<td>0</td>
<td>0</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>1 (Cu atom)</td>
<td>0</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>1 (In atom)</td>
<td>0</td>
<td>0.50</td>
</tr>
<tr>
<td>Diffusion to step</td>
<td></td>
<td></td>
<td>0.39</td>
</tr>
<tr>
<td>Dissociation from step</td>
<td></td>
<td></td>
<td>0.83</td>
</tr>
<tr>
<td>Interlayer diffusion</td>
<td></td>
<td></td>
<td>0.52</td>
</tr>
<tr>
<td>Cu-In exchange process</td>
<td></td>
<td></td>
<td>0.51</td>
</tr>
<tr>
<td>Push-out exchange process</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cross step directly</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

where $n$ is the total number of jumps in the time internal $T_d$.

In order to assess the relative importance of different processes in influencing the growth morphology, we have done various model simulations. For the Cu/In/Cu(100) system, the deposition rate is 0.01 monolayer per second (ML/s), the typical coverage of surfactants In $\theta_{\text{In}}$ is 0.08. For the Ag/Sb/Ag(111) system, the deposition rate is 0.02 ML/s, the typical coverage of Sb surfactants $\theta_{\text{Sb}}$ is 0.14. These parameters conform with the experiments. The surface temperature is 225 K in all model simulations. In the case of Sb on Ag(111), the Ag atoms grow in a layer-by-layer mode over the entire temperature range from 225 to 375 K; for Cu/In/Cu(100), LBL growth can be induced at 225 K. Since the interlayer mass transport will be enhanced as the growth temperature is increased, we choose the lowest temperature 225 K as the typical simulation temperature to test the various models. The vibrational frequency $\nu$ depends on the adatom mass and interatomic force constant. According to our calculated results, we choose $10^{13}$ s$^{-1}$ for Cu atoms [on the Cu(100) face], $10^{13}$ s$^{-1}$ for In atoms [on the Cu(100) face] $10^{12}$ s$^{-1}$ for Ag atoms [on the Ag(111) face], and $10^{12}$ s$^{-1}$ for Sb atoms [on Ag(111) face] in our (1+1)-dimensional simulations, respectively.

To characterize the quality of the growing surface, we measure the interface width $W(L,t)$: $W(L,t) = \sqrt{\langle h^2(x,t)\rangle - \langle h(x,t)\rangle^2}$, and the corresponding slope, $dW/dt$. So the relationship of $W(L,t)$ vs $t$ and $dW/dt$ vs $t$ can show the variation of surface flatness with the time $t$, which can indicate the growth mode.

Simulations have been carried out for $L=600$ with various models and parameters. Multiple growth runs have been made for the same parameters but with different random number sequences, and results have been averaged together to reduce statistical fluctuations.

III. RESULTS AND DISCUSSION

A. Binding energies and diffusion barriers

For the adsorption of In on Cu(100) and Sb on the Ag(111) surface, we investigate three different adsorption sites including on-top, bridge, and hollow sites. Our calculated results show that the favorite adsorption sites are the hollow ones. For Sb/Ag(111), we also compare the fcc hollow site with hcp one, and find that the fcc hollow site is more stable. Surface-substitutional adsorption is also calculated. Table I shows the calculated results of on-surface favorite adsorption sites and surface-substitutional adsorption ones for In/Cu(100) and Sb/Ag(111), which are in agreement with other theoretical calculations. The binding energies of Cu-Cu, Cu-In, and In-In dimers on the Cu(100) surface are studied. Two configurations of these dimers including nearest-neighbor and next-nearest-neighbor separations on Cu(100) surface are considered. The vertical positions of two adatoms in a dimer are both optimized. The same procedure is done for those dimers on the Ag(111) surface. Our calculations show that the above dimers are most stable when they are at nearest-neighboring fcc sites. The binding energies of Cu-Cu, Cu-In, and In-In dimers on the Cu(100) surface are 0.63, 0.57, and 0.08 eV, respectively. Therefore, In atoms preferably stay among Ag islands and the assumption of ZL’s model is not satisfied in the Ag/Sb/Ag(111) system.

The various calculated migration barriers for Cu and In atoms on Cu(100) surface are summarized in Table II, which are used in our kinetic simulations. The terrace barriers for Cu adatoms and In surfactants on the Cu(100) surface are...
 TABLE III. Energy barriers for the Ag/Sb/Ag(111) system used in model simulations. $N_i$ ($N_f$) is the number of in-layer nearest neighbors before (after) a jump. Refer to Fig. 3 for Ag-Sb exchange process.

<table>
<thead>
<tr>
<th>Diffusion type</th>
<th>$N_i$</th>
<th>$N_f$</th>
<th>$E_{Ag/Ag}(111)$</th>
<th>$E_{Sb/Ag}(111)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intralayer diffusion</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diffusion on terrace</td>
<td>0</td>
<td>0</td>
<td>0.16</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>1 (Ag atom)</td>
<td>0</td>
<td>0.24</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>1 (Sb atom)</td>
<td>0</td>
<td>0.29</td>
<td>0.32</td>
</tr>
<tr>
<td>Diffusion to step</td>
<td></td>
<td></td>
<td>0.15</td>
<td>0.29</td>
</tr>
<tr>
<td>Dissociation from step</td>
<td></td>
<td></td>
<td>0.60</td>
<td>0.70</td>
</tr>
<tr>
<td>Interlayer diffusion</td>
<td></td>
<td></td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>Ag-Sb exchange process</td>
<td></td>
<td></td>
<td>0.31</td>
<td>0.44</td>
</tr>
<tr>
<td>Cross step directly</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

0.40 and 0.20 eV, respectively, which are consistent with experiments.\textsuperscript{17,18} The terrace barriers for a Cu adatom having one nearest neighbor, Cu and In, are 0.60 and 0.50 eV, respectively. The energy barrier for the Cu-In exchange process is 0.52 eV. It is small enough to ensure In surfactant’s segregation. The energy barrier for the push-out exchange process is lower than 0.30 eV, depending on geometric configuration of adatoms.\textsuperscript{22} In our simulations we choose 0.30 eV as a typical value. It is much smaller than the energy barrier for the Cu adatom crossing step directly, 0.51 eV. Note that the downstep barriers for Cu and In atoms used in our simulations are average values of two different downstep barriers, 100 and 110 steps.

The various calculated migration barriers for Ag and Sb atoms on the Ag(111) surface are summarized in Table III, which are used in our kinetic simulations. The terrace barriers for Ag adatoms and Sb surfactants on the Ag(111) surface are 0.16 and 0.29 eV, respectively, which are in agreement with other calculation and experiments.\textsuperscript{19} The terrace barriers for an Ag adatom having one nearest neighbor, Ag and Sb, are 0.24 and 0.29 eV, respectively. The energy barrier for the Ag-Sb exchange process is 0.35 eV. It is also small enough to ensure Sb surfactant’s segregation. Note that the downstep barriers for Ag and Sb atoms used in our simulations are average values of two different downstep barriers, 100 and 111 steps.

B. Cu/In/Cu(100) homoepitaxial system

The simulation results for the Cu/In/Cu(100) system with ZL’s model are shown in Fig. 4, where we plot the interface width $W(L,t)$ as a function of the deposition time $t$. The surface temperature is 225 K.\textsuperscript{7} Curve (a) is for pure Cu-on-Cu(100) growth. The interface becomes increasingly rough as growth proceeds. In curve (b), the preadsorbed In atoms have a coverage $\theta_{In}=0.08$. The Cu-In exchange process is turned off but the push-out exchange process is turned on. The first layer is smooth. From the second layer, the interface becomes increasingly rough as growth proceeds. All surfactant In atoms have been buried within the first layer. In curve (c), the Cu-In exchange process is turned on but the push-out exchange process is not allowed. It is clear that the interface width is also increasing from layer to layer. Compared with curve (b), the interface width increases slowly, but shows no clear oscillation. In curve (d), the interface width $W(t)$ displays perfect oscillation indicating LBL growth where both the Cu-In exchange process and the push-out exchange process are turned on. After 18 layers are grown, about 23.3% of the preadsorbed In atoms have been buried in lower layers.

From the above results, it is obviously seen that ZL’s model can apply to the Cu/In/Cu(100) system. Surfactant In atoms induce LBL growth through segregation and push-out exchange processes. Comparing curves (b), (c), and (d), we know that neither of the two processes can induce LBL growth alone. In the Cu/In/Cu(100) system, the downstep barrier $E_{step}$ is reduced by push-out exchange process [exchange between In atoms at the edge of steps and Cu atoms on top of steps, see Fig. 2(b)]. The segregation process ensures In atoms can affect the growth mode of more than one
layer. If the segregation process is turned off, only one smooth layer (first layer) is obtained [see curve (b) in Fig. 4].

We have also investigated the effect of surfactant coverage for the Cu/In/Cu$_{100}$ system. Table IV lists the behavior of $W(t)$ and the values of $W$, $dW/dt$ after 8 layers of Cu atoms are deposited at different In coverages. Apparently, the values of $W$, $dW/dt$ at both $\theta_{\text{In}} = 0.01$ and 0.03 are much greater than the ones at $\theta_{\text{In}} = 0.06$. This indicates that the roughness of the interface will increase rapidly at too low coverage of In atoms. Clearly, if the surfactant coverage is too low, the push-out exchange process only exists in a few places, and cannot affect the whole growing terraces effectively. When the coverage of In atoms $\theta_{\text{In}} = 0.06$, nearly perfect LBL growth is also achieved.

Figure 5(a) shows the snapshot of the representative process of growth for curve (d) in Fig. 4 where only 80 columns are displayed (600 columns are used in our calculation). It is clearly seen that In atoms prefer to stay at the edges of steps and not many small islands are nucleated on the growing terraces. This result is in good agreement with experiments. This implies that LBL growth cannot be explained by an increased island density in the Cu/In/Cu$_{100}$ system.

C. Ag/Sb/Ag(111) homoepitaxial system

The simulation results for the Ag/Sb/Ag(111) system with our repulsion model are listed in Table V where we give the behavior of $W(t)$ and the values of $W$, $dW/dt$ after 8 layers of Ag atoms are deposited. The surface temperature is 225 K.

Scenario (a) is for pure Ag-on-Ag(111) growth. The interface becomes increasingly rough as growth proceeds. After 8 layers of Ag atoms are deposited, the interface width $W$ reaches 2.53. In scenario (b), the preadsorbed Sb atoms have a coverage $\theta_{\text{Sb}} = 0.14$, the Ag-Sb exchange process is turned off but repulsion between Ag and surface-substitutional Sb atoms is allowed. The interface becomes increasingly rough as growth proceeds. Only the first layer is smooth. All surfactant Sb atoms have been buried within the first layer. In scenario (c), the Ag-Sb exchange process is turned on but repulsion is not allowed. It is clear that the interface width is also increasing from layer to layer. Compared with scenario (b), the interface width increases slowly, but shows no clear oscillation. In scenario (d), the interface width $W(t)$ displays perfect oscillation, indicating LBL growth where both the

FIG. 4. The interface width $W(t)$ as a function of the deposition time $t$ for the Cu/In/Cu(100) system under different conditions. For every case, the surface temperature is 225 K. For (b)–(d), the In coverage $\theta_{\text{In}} = 0.08$, deposition rate is 0.01 ML/s, and $L = 600$. For details, see text.

FIG. 5. Snapshots of representative process of layer-by-layer growth for the Cu/In/Cu(100) and Ag/Sb/Ag(111) epitaxial systems. (a) 6.52 Cu layers are grown for the Cu/In/Cu(100) system, $\theta_{\text{In}} = 0.08$, deposition rate is 0.01 ML/s; (b) 5.52 Ag layers are grown for the Ag/Sb/Ag(111) system, $\theta_{\text{Sb}} = 0.14$, deposition rate is 0.02 ML/s. Only 80 columns are displayed. The empty circles represent Cu or Ag adatoms, the dark circles represent In or Sb surfactants. $T = 225$ K, $L = 600$. 

Ag-Sb exchange process and repulsive interaction are turned on. After 10 layers are grown, about 62.8% of preadsorbed Sb atoms have been buried in lower layers.

From the above results, it is obviously seen that our repulsion model can apply to the Ag/Sb/Ag(111) system. Surfactant Sb atoms induce LBL growth through segregation and repulsive interaction mechanisms. Comparing scenarios (b), (c), and (d), we know that neither of the two mechanisms can induce LBL growth alone. In the Ag/Sb/Ag(111) system, the repulsive interaction between surface-substitutional Sb atoms and diffusing Ag atoms results in an increase of terrace barriers for Ag adatoms on average, so island density is enhanced. Enhanced island density can increase interlayer mass transport and induce LBL growth. The segregation process ensures Sb atoms can continue to influence the growth mode of successive layers. If the segregation process is turned off, only one smooth layer (first layer) is obtained.

We have also investigated the effect of surfactant coverage for the Ag/Sb/Ag(111) system. Table IV lists the behavior of $W(t)$ and the values of $W$, $dW/dt$ after 8 layers of Ag atoms are deposited at different Sb coverages. Apparently, the values of $W$, $dW/dt$ at both $\theta_{\text{Sb}}=0.01$ and 0.03 are much greater than the ones at $\theta_{\text{Sb}}=0.08$. This indicates that the roughness of the interface will increase rapidly at too low coverage of Sb atoms. Clearly, if the surfactant coverage is too low, an average increase in terrace barrier for Ag atoms is very small, island density can increase only a little. When the coverage of Sb atoms $\theta_{\text{Sb}}=0.08$, nearly perfect LBL growth is also achieved.

Figure 5(b) shows a snapshot of the representative process of growth for scenario (d) in Table V where only 80 columns are displayed (600 columns are used in our calculations). It is clearly seen that Sb atoms are surrounded by Ag atoms and many small islands are nucleated on the growing terraces. This result is in good agreement with STM observations. It implies that LBL growth can be explained by enhanced island density in the Ag/Sb/Ag(111) system.

### D. Additional barrier $\Delta E$ and surfactant mechanism

Now let us discuss the effects of surfactants in the above two metal systems, Cu/In/Cu(100) and Ag/Sb/Ag(111). A necessary condition for LBL growth is rapid interlayer mass transport. It is imaginable that surfactants must have enhanced interlayer mass transport in some way. In order to assess the interlayer mass transport during the growth quantitatively, Meyer et al., introduced a ratio factor $R_{0,C}/R_{1,C}$:  

$$
\left( \frac{R_{0,C}}{R_{1,C}} \right) = \left( \frac{h_0}{h_1} + \frac{2 \exp(\Delta E/kT)}{R_{1,C}} \right)^{1/2},
$$

where $R_{1,C}$ is the critical radius of the first-layer island (the radius of the first-layer island at the onset of second-layer nucleation), $R_{0,C}$, the measure of the spacing between the centers of first-layer islands, $h_0$ and $h_1$ are the hopping probabilities on the substrate and the first-layer island respectively, the additional barrier $\Delta E$ is the difference between the hopping barriers on the terrace and step edges, $\Delta E = E_\text{step} - E_\text{sulf}$ (see Fig. 6). The ratio $R_{0,C}/R_{1,C}$ is close to 1 for smooth growth and larger than roughly 1.5 for 3D island growth.

It is clear from Eq. (7) that there exist multiple possibilities to decrease the value of $R_{0,C}/R_{1,C}$. In a pure system, $h_0 = h_1$, thus, the most efficient way to decrease the value of $R_{0,C}/R_{1,C}$ is to increase the growth temperature. Because low-temperature layer-by-layer growth is often desired, the next choice is to reduce $\Delta E$. There exist two ways to reduce $\Delta E$. One way is to reduce step-edge barrier $E_\text{step}$, the other is to increase the terrace barrier $E_\text{sulf}$. An increase of the terrace barrier $E_\text{sulf}$ will induce an enhanced island density. Apparently, either a reduced $E_\text{step}$ or an enhanced island density can enhance interlayer mass transport. Two surfactant-mediated LBL growth models listed in Sec. II B and Sec. II C are corresponding to the two ways reducing $\Delta E$, respectively. Therefore, additional barrier $\Delta E$ is an essential physical quantity in determining film morphology. In the Cu/In/Cut(100) system, surfactant In atoms preferably stay at edges of Cu islands and reduce step-edge barrier $E_\text{step}$ by exchange with Cu atoms on islands. In the Ag/Sb/Ag(111) system, surfactants Sb atoms preferably stay at surface-substitutional

![FIG. 6. Schematic diagram for Meyer’s ratio $R_{0,C}/R_{1,C}$ and potential diagram for adatoms. $R_{1,C}$ is the critical radius of the first-layer island; $R_{0,C}$, a measure of the spacing between the center of first-layer island. $\Delta E$ is the difference between the terrace barrier $E_\text{sulf}$ and step-edge barrier $E_\text{step}$. For details, see text.](image-url)
sites and repel Ag atoms approaching them. It is the repulsive interaction network that leads to an increase of average diffusion barriers for Ag atoms on terraces, $E_{\text{surf}}$, and enhanced island density. Our simulation result in Fig. 5(b) supports this expectation.

Our $(1+1)$-dimensional model is simple but enough for qualitative descriptions. For the Cu/In/Cu(100) system, due to $V_{\text{Cu-Cu}}>V_{\text{Cu-In}}$, In atoms prefer to stay at edges of Cu islands in one dimension as two dimensions. The only difference is the dimensionality of the island between one dimension and two dimensions. This does not affect the two important processes, exchange and push-out processes, during the growth of Cu/In/Cu(100). For the Ag/Sb/Ag(111) system, due to $V_{\text{Ag-Ag}}<V_{\text{Ag-Sb}}$, Sb atoms are centers of nucleation in one dimension as two dimensions, the only difference is also the dimensionality of the island. After deposited Ag atoms enter a two-dimensional repulsive network, they tend to avoid those repulsive centers Sb and aggregate to small islands between those Sb atoms. As in two dimensions, many small islands are formed between the surface-substitutional Sb atoms in our $(1+1)$-dimensional model. The island density $N$ satisfies the scaling relation $N \propto r^\lambda \exp(\beta E_{\text{surf}})$, where $r$ is the deposition rate. In two dimensions, $\lambda = 1/3$, and in one dimension $\lambda = 1/4$. Therefore, an increase of $N$ implies an increase of diffusion barrier $E_{\text{surf}}$ under the same growth conditions. From the above scaling relation, we can see that different dimensional models do not change the qualitative result of an increase of $E_{\text{surf}}$ on average, but quantitative descriptions are apparently different. Based on the above analysis, we can conclude that our $(1+1)$-dimensional model conforms with real growth process in a qualitative manner.

IV. SUMMARY AND CONCLUSION

We have studied two typical surfactant-mediated homoepitaxial metal systems, Cu/In/Cu(100) and Ag/Sb/Ag(111), using first-principles calculations and kinetic Monte Carlo simulations. Our results show that ZL’s model is suited to the Cu/In/Cu(100) system and our repulsion model is suited to the Ag/Sb/Ag(111) system.

For the Cu/In/Cu(100) system, surfactants in reduce the downstep barrier $E_{\text{step}}$ by the push-out exchange process at Cu island edges; for the Ag/Sb/Ag(111) system, surfactants Sb increase the terrace barrier $E_{\text{surf}}$ by the repulsive interaction network. In the two metal systems, surfactants In and Sb can segregate effectively, which is a necessary condition for surfactants.

Our calculated results also show that the additional barrier $\Delta E$ is an essential physical quantity in determining film growth mode. Only if $\Delta E$ becomes smaller will smooth growth be induced. Two ways to reduce $\Delta E$, either to reduce $E_{\text{step}}$ or increase $E_{\text{surf}}$, is proved to be effective equally.

It is noteworthy that $(1+1)$-dimensional simulation is relatively simple but enough for qualitative analysis. At present, we are performing $(2+1)$-dimensional simulations in order to get the deeper insight into the surfactant mechanisms.

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