Simulation of surfactant effects on the growth of metal homoexpitaxial Sb–Ag/Ag(111)*

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A kinetic Monte Carlo simulation is performed in order to study the effect of Sb atoms as a surfactant on the growth of Ag on Ag(111). In our model the repulsive mechanism in which the surfactant Sb atoms repel diffusing Ag adatoms, and the exchange mechanism between Ag and Sb atoms, are considered. Our simulations show that the effects of Sb atoms for Ag/Ag(111) growth system are mainly to increase the chances for Ag atoms to overcome the Ehrlich–Schwoebel barrier both in the interlayer growth and along the edge diffusion. The influence of the coverage of Sb atoms and substrate temperature on the growth of Ag/Sb/Ag(111) is discussed.

Keywords: surfactant, repulsive, exchange, Monte Carlo simulation

PACC: 6855, 6840, 6890

1. Introduction

Many experiments and theories over the last few years have shown that the shapes of islands and the growth mode can be greatly altered by predepositing a sub-monolayer of surfactant on the metal surface,[1−15] for example, Sb atoms deposited on Ag(111),[1−3,8−10] O on Pt(111)[4] or Cu(111),[5] and In on Cu(100)[6] can induce layer-by-layer (LBL) homoepitaxial growth under typical conditions for multilayer (3D) growth in the system. If we are able to control the shapes of islands and the growth mode, we will be in a position to "design" surfaces with particular mechanical, electrical, magnetic, or chemical properties. A detailed understanding of the mechanism involving surfactant-mediated growth for metal systems in homoepitaxy is not only of fundamental interest but also of technological importance.

There are a large number of proposals for the mechanisms in Ag/Sb/Ag(111) growth system in literature.[1−3,7−10] Vegt *et al.*[1] found in their x-ray diffraction study on pre-cover with 0.2 monolayer of Sb, that an LBL growth behaviour was observed at temperatures between 225 K and 375 K. They suggested that Sb acted as a surfactant and, due to the fact that Sb atoms were adsorbed at the island edges, the barrier of Ag moving over step edges decreased and the inter-layer transport was enlarged. They found Sb atoms also to act as nucleation centres for Ag islands.[1] Georg *et al.*[9] reported that the density of the nucleus was observed to be enhanced in the presence of Sb atoms and this effect may be inferred as the mechanism for surfactant-induced LBL growth.[9] According to the results in Ref. [1], Vrijrnoeth *et al.*[2] suggested two main origins of LBL growth in Ag/Sb/Ag(111) using scanning tunneling microscopy (STM): one is that Sb atoms lower the mobility of Ag adatoms on terraces, thereby growing islands; the other is that Sb atoms lower the mobility along the step edges, thereby inducing dendritic island shapes. They emphasized that both effects were conducive to smoother growth but neither was sufficient for LBL growth.[2]

Savrina *et al.*[3] found in *ab initio* calculations that the mobility of Ag adatoms was reduced in the vicinity of Sb atoms. As a result, the increased Ag island densities cause the transition to LBL growth.[3] Jiang *et al.*[8] proposed a (1+1)-dimensional model for Ag/Sb/Ag(111) based on Savrina *et al.*'s calculations. In their model, the repulsions between surface-substitutional Sb atoms and deposited Ag atoms and the Ag–Sb exchange process were considered. Their simulation results emphasized the importance of an additional barrier in the Ag/Sb/Ag(111) growth mode.[8] Though the (1+1)-dimensional model is sufficient for a qualitative description, it fails to describe the 3D island morphologies and it is different from real thin-film growth. Zhang and Lagally[10] suggested a general model for metal systems that was

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based on the inequality $V_{A-A} > V_{A-S} > V_{S-S}$ connecting the adatom–adatom, adatom–surfactant, and surfactant–surfactant bond strengths. In their model, both the A–S exchange process and step crossing were necessary for S atoms to act as a good surfactant.[10] To understand the effect of Sb atoms on Ag/Ag(111) growth, a model in which a realistic growth model and physical parameters are used is needed.

In this paper, a full kinetic Monte Carlo simulation is presented to study how Sb atoms affect the growth of Ag/Ag(111) and to discuss the effects of the coverage of Sb θ_M and substrate temperature T on the growth mode in Ag/Sb/Ag(111) system. Our model gives a new insight on how Sb atoms act as a surfactant on the growth of Ag/Ag(111) and the simulation results are in good agreement with the experimental results.[1,2,16]

2. Simulation model

The kinetic Monte Carlo model used in the present paper is based on Savrina *et al.*'s calculations,[3] and it is more exact than that proposed by Jiang *et al.*[8] The repulsive mechanism proposed here is based on first-principles calculations,[3] in which surfactant Sb atoms repel deposited Ag atoms and affect their migrations and nucleations. The exchange mechanism[10] between Sb atoms and Ag adatoms is another main feature in our model and it is possible to incorporate the Ag atoms into the layer by replacing them with the Sb atoms when an Sb atom is about to be buried in a layer with an Ag adatom on top.

The simulations were carried out on a 100×100 fcc (111) substrate. First, the Sb atoms were deposited on the Ag(111) substrate. Pre-adsorbed Sb atoms occupy the fcc hollow sites and they do not aggregate to form clusters because the bond strength between Sb–Sb is very small. Next, we started to deposit Ag adatoms onto the Sb-preoccupied surface. Sb atoms act as nucleation centres of deposited Ag atoms. After small islands that are centred around the Sb atoms are formed, the repulsive effect of surface-substitution Sb atoms begins. The Ag adatoms landing on small islands will suffer this repulsive force. The force F is the repulsive interaction between surface-substitution Sb and Ag adatoms. Based on the first-principles calculation results presented by Jiang *et al.*,[8] the expression of F is expressed as

$$F = 0.8/\rho^2 \text{ (eV)}, \tag{1}$$

where ρ is the distance, whose values are 1, 2, and 3 corresponding to three neighbouring sites of Ag adatoms. In the simulation, the repulsive energy barrier of a diffusing Ag adatom is calculated to be[8]

$$E_{rep} = a(0.8/1) + b(0.8/4) + c(0.8/9) \text{ (eV)}, \tag{2}$$

where $a = 1$, $b = 1$ and $c = 1$ if the next-nearest site, the third-nearest site and the fourth-nearest site beneath the diffusing Ag adatom each have an Sb atom, otherwise $a = 0$, $b = 0$ and $c = 0$.

Surface migrations of Ag adatoms are modeled as a nearest-neighbour hopping process, whose hopping rate is in the Arrehnius form

$$D = D_0 \exp(-E/k_B T), \tag{3}$$

where D_0 is the vibration frequency of a surface adatom and assumed to be a constant ($= 10^{12}$ s^{-1}); k_B is Boltzmann's constant, T is the surface temperature and E is the energy barrier to hop. The energy barrier E is composed of three parts: the diffusion barrier[17] E_d for terrace diffusion, the ES barrier[18,19] for interlayer diffusion, and the repulsive barrier E_{rep}.[3,8] There are six in-layer nearest-neighbouring sites around a diffusing Ag adatom on the fcc (111) surface. The difference $(E_f - E_i)$ is calculated where $E_i(E_f)$ is the energy of Ag adatom before (after) a jump. The possibility for Ag adatom to hop into the nearest sites is decided based on the difference $(E_f - E_i)$.

When a diffusing Ag is just on top of an Sb atom and can overcome the exchange barrier E_{ex}, it will be dropped onto the site beneath. On the other hand, the Sb atom will be lifted to the above site. That is an exchange process between Sb and Ag, with the exchange rate in the Arrehnius form[20]

$$D_{ex} = D_0 \exp(-E_{ex}/k_B T). \tag{4}$$

The Ag adatoms will stop diffusing if one of the nearest-neighbouring sites has a deposited Ag adatom or Sb atom. That does not mean that they are dead; Ag adatoms that stick to an island will diffuse along the island boundary until they find sites where the number of nearest-neighbouring sites is more than three. The diffusion rate along the boundary of a half-dead Ag adatom is expressed in the Arrehnius form[20]

$$D_{edge} = D_0 \exp(-E_{edge}/k_B T), \tag{5}$$

where E_{edge} is the energy barrier when Ag atoms diffuse along the island edge. We suppose that E_{edge} is related to the number of the nearest-neighbouring deposited Ag adatoms and Sb atoms in our model. The E_{ag} and the E_{sb} correspond to the diffusion barrier

for an Ag adatom having one nearest-neighbouring Ag adatom and Sb atom respectively.

The energy barriers used in the model simulation are consistent with the measured results and the calculated results.[8,16] The diffusing barrier for an Ag adatom on the Ag(111) surface is $E_{\rm d} = 0.10$ eV and the Ehrlich–Schwoebel (ES) barrier in Ag/Ag(111) system is ES = 0.15 eV.[16] The energy barrier for the Ag–Sb exchange process is $E_{\rm ex} = 0.35$ eV.[8] The diffusing barrier for an Ag adatom to have one nearest neighbour, Ag or Sb, is $E_{\rm ag} = 0.24$ eV[8] or $E_{\rm sb} = 0.29$ eV,[8] respectively.

3. Results and discussion

Figures 1(a) and 1(b) show the simulation morphologies of Ag on Ag(111) without and with Sb atoms in our model with the surface temperature $T = 225$ K and flux $F = 0.0167$ ML/s respectively. As we have seen, the typical morphology of multilayer growth is shown in Fig. 1(a) and after the deposition of five monolayers (MLs) of Ag more than eight layers are exposed. Pre-depositing 0.08 ML Sb in Ag/Ag(111) results in the LBL growth shown in Fig. 1(b), which is consistent with the experimental results.[1,2]

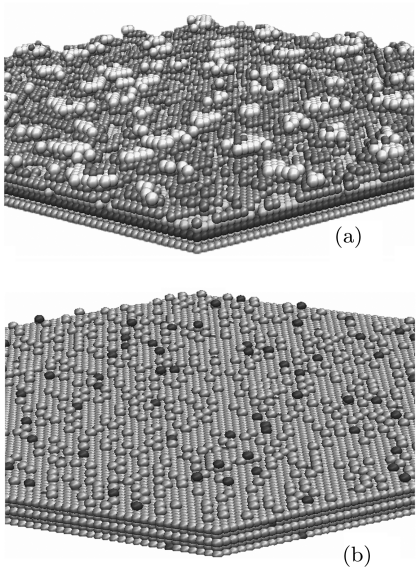


Fig. 1. Surface morphologies obtained after growing about 5.1 ML of Ag atoms (a) without Sb atoms and (b) with $\theta_M = 0.08$ ML pre-occupied under other identical growth conditions $T = 225$ K, $F = 0.0167$ ML/s. The black spheres represent Sb atoms and the grey spheres denote Ag adatoms in figure (b); the spheres of different colours in figure (a) represent Ag atoms in different layers.

In order to accurately determine the growth mode during multilayer Ag/Ag(111) thin film growth, the surface roughness as a function of coverage is calculated. The surface roughness is defined as[20,21]

$$\omega = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(h(x_i) - \bar{h})^2}, \tag{6}$$

where n is the total number of deposited atoms, $h(x_i)$ is the height of the thin film at the position of x_i and $\bar{h}$ is the average height of the thin films, which is given by $\bar{h} = (1/n)\sum_{i=1}^{n} h(x_i)$.

Figure 2 shows the coverage dependence of surface roughness of Figs. 1(a) and 1(b). The roughness of Fig. 1(a) grows with the coverage indicating a 3D growth mode. Obviously, when the roughness oscillates with the coverage in Fig. 2, it shows the LBL growth mode. When Ag adatom reaches the surface that is pre-occupied with Sb, it will meet an Sb atom and stop to form an island with the Sb atom. When a new Ag adatom reaches the island, it will easily overcome the ES barrier to fall from the island because the island is small enough and the Ag adatom has more opportunities to cross over.[22] Furthermore, the repulsive effect between the incoming Ag and the Sb adatom in the island will help the Ag adatom fall from the island. Our simulation results show that the LBL growth mode of the first layer is due to the enhanced density of nuclei by pre-occupied Sb atoms instead of the repulsive effect in our model. That is to say, the coverage of Sb, θ_M, plays a real role in the growth mode of the first layer.

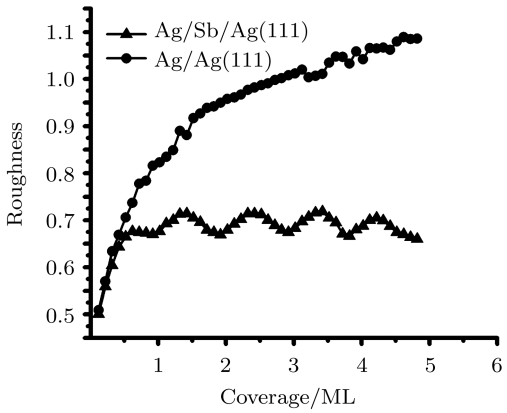


Fig. 2. Coverage dependences of surface roughness without and with Sb atoms pre-occupied.

As the island grows, several islands will coalesce into a bigger one and the new incoming Ag adatoms on the islands find more difficult to fall from the island and the second layer growth begins. To sustain the LBL growth, the repulsive effect of the second layer is still required. Sb atoms in the first layer will repel Ag adatoms when Ag atoms arrive at the second layer.

In a given time, the Ag atom travel distance is diminished greatly, that is to say, the diffusion of Ag atoms is restricted and slows down. So, as the new incoming Ag is deposited on the slowed one, it has more opportunities to overcome the ES barrier and fall down.[1] On the other hand, when the first layer is completed, some Sb atoms come up to the second layer by the exchange effect. That leads to the enhancement of island density and causes the Ag atom to fall easily. Both the repulsive effect and the exchange effect help the Ag atom overcome the ES barrier and result in LBL growth in our model.

The coverage of Sb atoms, θ_M, will affect the growth mode. Figures 1 and 2 show that when $\theta_M = 0.08$ ML, LBL growth in Ag/Ag(111) takes place. As the coverage of Sb decreases, the growth mode is changed as demonstrated in Fig. 3: the roughness grows when $\theta_M = 0.01$ ML and $\theta_M = 0.03$ ML, which is easy to understand. If the Sb atom coverage is lowered, the density of islands in the first layer is diminished. That is to say, Ag atoms find it more difficult to fall when the island is larger. On the other hand, as the number of Sb atoms reduces, the repulsive and exchange mechanisms are restricted. As a result, the layer transport is restricted and the growth mode turns to be 3D growth.

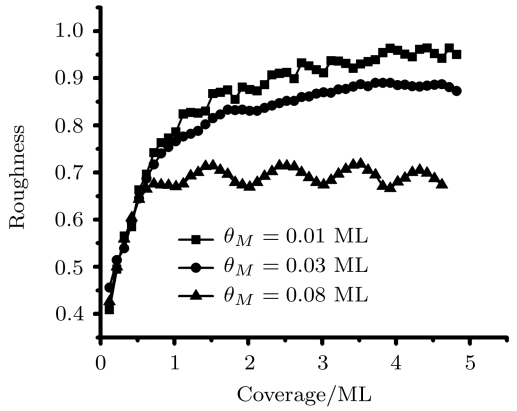


Fig. 3. Coverage dependences of surface roughness at $T = 225$ K with descending values of Sb coverage θ_M, i.e. $\theta_M = 0.08, 0.03$ and 0.01 ML.

We also check the growth mode of Ag/Ag(111) when the Sb coverage is increased. Figure 4 shows that the roughness oscillates with the coverage as the value of θ_M increases from 0.12 ML to 0.25ML except for the first layer. The vibration of the first layer disappears when $\theta_M = 0.18$ ML and $\theta_M = 0.25$ ML, indicating 3D growth of the first layer in our model. When pre-deposits give a higher coverage of Sb on the substrate, the density of islands increases and the distance between them descreases. As a result, larger islands form easily by coalescing and the density of islands diminishes rapidly. As we have discussed, that will prevent Ag atoms from falling when the islands become larger. So, when the first layer is growing, there are many Ag atoms that stop on the second layer. It is a different situation when Ag atoms are deposited on the third layer. Due to the lesser Sb coverage on the second layer by exchange mechanism, the smaller size of islands and the repulsive mechanism will help Ag atoms of the third layer overcome the ES barrier and fall down. For this reason, when θ_M is increased to 0.18 ML and 0.25 ML, the LBL growth begins from the second layer in our model. On the other hand, when the Sb coverage increases, the Sb adatoms buried therein increases.

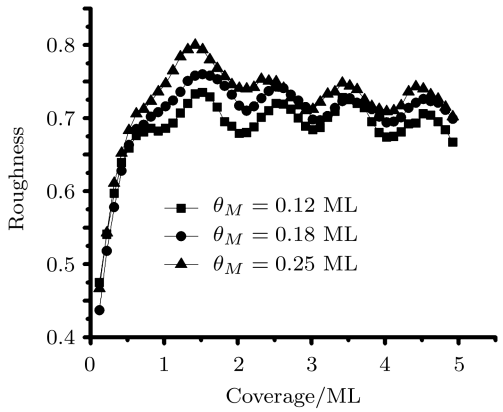


Fig. 4. Coverage dependences of surface roughness at $T = 225$ K for different values of Sb coverage θ_M, i.e $\theta_M = 0.12, 0.18$ and 0.25 ML.

As is known from Refs. [16] and [20], the substrate temperature can affect the growth mode in metal epitaxial growth. In an x-ray diffraction study, no LBL growth behaviour is observed for Ag on clean Ag(111) over the temperature range between 575 K and 175 K.[1,2]

Here, with 0.08 ML Sb atoms pre-covered on the substrate in our model, the LBL growth appears as the temperature increases from 200 K to 375 K as shown in Fig. 5. If temperature T increases from 375 K to 575 K, we speculate that the growth mode of Ag/Ag(111) is LBL, not only because the higher substrate temperature will result in smoother growth of thin film but also due to the effect of Sb on Ag growth in our simulation model.

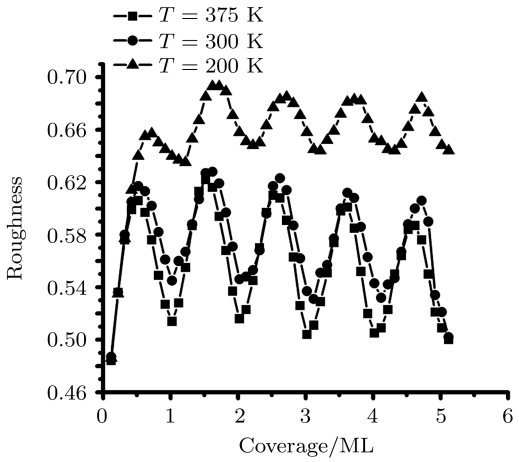


Fig. 5. Coverage dependences of surface roughness in Ag/Sb/Ag(111) growth at three substrate temperatures, i.e. $T = 200, 300$, and 375 K with $\theta_M = 0.08$ ML and $F = 0.0167$ ML/s.

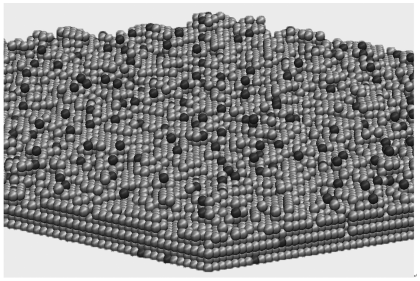


Fig. 6. Surface morphologies obtained after growing about 5.1 ML of Ag atoms without considering the effects of Sb atoms on edge diffusion in our Ag/Sb/Ag(111) growth model with $\theta_M = 0.08$ ML, $T = 225$ K, and $F = 0.0167$ ML/s. The black spheres represent Sb atoms and the grey spheres refer to Ag adatoms.

Finally, we discuss the surfactant effect on diffusion along the island edge in our model. As we have seen, a half-dead Ag needs to the overcome $E_{\rm edge}$ barrier when it diffuses along the island boundary. The $E_{\rm edge}$ is related to $E_{\rm sb}$ and $E_{\rm rep}$ in Ag/Sb/Ag(111) growth. As $E_{\rm sb} > E_{\rm ag}$,[8] Ag diffusion along the island edge will be slowed down when the nearest-neighbouring sites have Sb atoms. Moreover, if the half-dead Ag atom meets the repulsive barrier $E_{\rm rep}$, it will be pushed away from the island centre. That results in long and dispersal island edges. Both effects of Sb atoms on edge diffusion will cause the islands to be more irregular and fractal. That is another way to increase inter-layer transport in our Ag/Sb/Ag(111) growth model.[22] Figure 6 shows the surface morphology obtained at $\theta_M = 0.08$ ML, but it does not show the effects of Sb atoms on the edge diffusion. In contrast to Fig. 1(b), obviously, there is neither LBL growth nor 3D growth, and we think that it is more like an S–K growth model.

Figure 7 shows the coverage dependences of the surface roughness with and without the effects of Sb atoms on edge diffusion at $\theta_M = 0.08$ ML, $T = 225$ K, and $F = 0.0167$ ML/s. Clearly, the roughness grows when the effects of Sb atoms on edge diffusion are not considered in our model. Consequently, the effects of Sb atoms on edge diffusion resulting in more irregular and fractal island edge induce an important process in our Ag/Sb/Ag(111) growth model to obtain LBL growth.

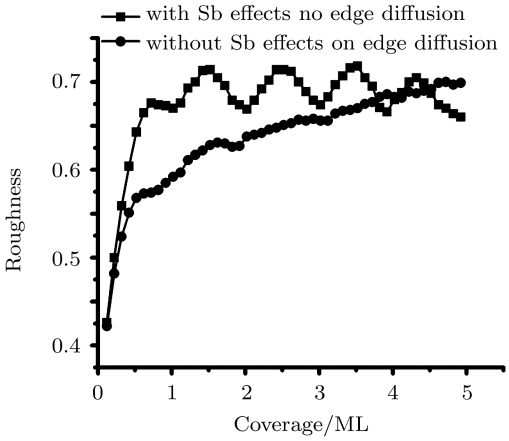


Fig. 7. Coverage dependences of surface roughness with and without effects of Sb atoms on edge diffusion at $\theta_M = 0.08$ ML, $T = 225$ K, and $F = 0.0167$ ML/s.

4. Conclusions

A kinetic Monte Carlo simulation model is presented to investigate the effect of Sb atoms as a surfactant in the Ag/Ag(111) growth system. The repulsive mechanism between Ag atoms and Sb atoms as well as the Ag–Sb atom exchange mechanism are the main processes considered in our model. Through the simulations we can obtain the following conclusions.

(i) One of the effects of Sb atoms in Ag/Ag(111) growth is to slow down the diffusion of Ag atoms; as a result, new incoming Ag atoms will have more chance to overcome the ES barrier and fall from the slowed Ag atoms. This is an important way to improve inter-layer transport.

(ii) The other effect of Sb atoms is to induce edge diffusion in Ag/Ag(111), thereby forming a long and irregular island boundary. Therefore, an Ag atom is more likely to cross over the edge. This is another way to improve inter-layer transport.

(iii) Both effects of Sb atoms in Ag/Ag(111) are necessary. Neither the slowed Ag nor the irregular boundary is enough to obtain the LBL growth in our model.

(iv) The growth mode of Ag/Sb/Ag(111) depends on the coverage of Sb, θ_M. If the value of θ_M is too low

the repulsive mechanism and the exchange mechanism to enhance inter-layer growth are restricted. However, if the value of θ_M is too high, the LBL growth will not exist at the beginning and will affect the quality of the thin film. The appropriate values of θ_M to obtain LBL growth in our model are in a range of 0.08 ML $\leq \theta_M \leq$ 0.14 ML.

(v) When substrate temperature T increases from 200 K to 375 K, pre-depositing 0.08 ML Sb atoms will change the growth mode of Ag/Ag(111) from 3D to LBL in our model.

There may be a critical value of Sb coverage to obtain a perfect LBL growth but we have not studied it precisely in our model. We will perform more simulations to get a deeper insight into the surfactant mechanisms. Our findings in this paper will be helpful for developing nanotechnology in film growth.

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