Computer simulation of surfactant-mediated thin film growth*

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Abstract. A novel model consisting of basic micro-processes has been developed on the basis of the classic diffusion theory. It is first time that the concept of exchange rate has been introduced and the growing process of surfactant-mediated epitaxial thin-film growth has been simulated with Kinetic Monte Carlo (KMC) technique. The results of simulation found that the exchange reaction of RLA model is a combination of the basic micro-processes. The majorities of exchange are not complete position exchange and the exchange rate doesn’t always equal one. Both surfactant atoms and adatoms would diffuse from one layer to another. The diffusion happens mostly between single atoms and the diffusing atoms increase with substrate temperature.

1. Introduction

During of thin film growing, it is found that the growth characteristics with surfactant-mediated would be completely opposite from the non-surfactant situation. The investigations of the abnormal effects become a focus of film growth field in recent years[1-3]. Up to date, the studies for the mechanism of thin film growth with surfactant-mediated are not perfect. Among the numerous models, Reaction Limited Aggregation (RLA) [4-6] model successfully explains abnormal effects found in experiments. However, the basic principle of RLA model is different from that of DLA (Diffusion Limited Aggregation) [7-9] model. In RLA model the nucleation is affected mainly by exchange reaction, but in DLA model the nucleation is affected by diffusion reaction.

The key of RLA model is the exchange reaction and there are three basic presuppositions in RLA model. First, the adatoms could become a stable nucleation centre after conquering a larger potential and exchanging position with the surfactant atoms. Secondly, to become a portion of the stable island, the adatoms that deposite subsequently conquer also a larger potential and exchange position with the surfactant atoms. The last assumption is that only exchanged atoms could constitute form the island.

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namely the island locating in surfactant layer is stable. Basing on the first and second assumptions, exchange must be satisfied with the following qualifications:

(i) At the beginning, exchange must happen between nuclei (at least two atoms) and it is impossible that exchange happens between single atoms.
(ii) Exchange is the exchange of position, i.e. complete exchange.
(iii) The number of adatoms equals to one of surfactant atoms during exchange process.

The thin film growth is the result of atom diffusing and congregating at all, the micro-mechanism of exchange reaction in RLA model is not reported hitherto. In this paper, on the basis of diffusion theory we have simulated the mechanism of thin film growth with surfactant-mediated and investigated emphatically the essence of exchange reaction.

2. Description of simulator

It is known that the growth of thin film is due to atom diffusing and congregating. Basing upon diffusion theory and basic micro-processes, we advanced a novel three-dimensional model which consists of:

(1) A atom deposits on the substrate.
(2) A single atom diffuses on the surface of substrate.
(3) The diffusing atom encounters another and then both of them nucleate.
(4) The diffusing atom is captured by the existent island.
(5) The atom locating at the edge of island detach island at a certain probability.
(6) The atom locating at island edge retains bonding with island and removes along island edge.
(7) After diffusing, the atom deposited directly on island falls on the substrate again.
(8) The adatoms nucleate on a island.

The novel model does not comprise the exchange reaction of RLA model. By analyzing, we generalize the basic micro-processes of film growth into three classes:

(i) The incident atom deposits on the growing surface and is attached, called absorption event.
(ii) All kinds of atoms diffuse on the growing surface, called diffusion event.
(iii) The adatoms detach from the growing surface, called evaporation event. In fact, this process could be incorporated into a special kind of diffusion events.

After generalization, the novel model comprises not only all kinds of processes mentioned but also others, such as corner diffusion, layer-to-layer diffusion and so on.

The absorption rate of atoms is given by the number of incident atoms per unit time and the absorption event consists of:

(i) An incident atom deposits at a lattice site on the growing surface.
(ii) If the site has three atoms as nearest neighbors (stable site), the incident atom sticks and occupies this stable site, otherwise it will diffuse to one of the nearest or the next near vacant sites. If the site is not stable, the incident atom will continue to diffuse until it finds a stable site or evaporates from the growing surface. The whole process was regarded as one event.

The related effects caused by the atom diffusion were considered in the model. As illustrated in fig.1, since atom A has only two nearest neighbors, it will diffuse to a stable site. As a result, the site of atom B is no longer a stable site, it will diffuse to another stable site too, and so will atom C. Though different from the normal diffusion, it was regarded as one event rather than three events.

The diffusion rate of a single adatom was defined as the probability of a diffusion jump per unit time and is given by the Arrhenius-type expression

$$r = v_0 \exp \left( - \frac{\Delta E}{k_B T} \right)$$

where $v_0$ is the frequency of atom vibrations and it is assigned a value of $v_0 = (2\pi k_B T)/h$, $k_B$ the Boltzmann constant, $T$ the substrate temperature and $\Delta E$ the activation energy.
The evaporation rate was calculated as the same as the diffusion rate, but the final target site is that without any neighbors.

We implemented the simulation onto face-centered cubic (100) surface, the substrate is 50 × 50, and we adopted the periodic border condition. The surface of substrate atom A is surfactant S and the incident atom is atom A.

\[ V_{ij} = V_0 \exp\left(-\alpha \left( \frac{r_{ij}}{r_0} - 1 \right) \right) - 2 \exp\left(-\alpha \left( \frac{r_{ij}}{r_0} - 1 \right) \right), \]

where \( \alpha \) is a constant depending on the interaction range of atoms and \( V_0 \) is the interactional potential between the nearest neighbour atoms. In the simulating, we referred to the interaction potentials reported \[4\] and took \( V_{AA} = 0.87\text{ev} \), \( V_{AS} = 0.46\text{ev} \) and \( V_{SS} = 0.13\text{ev} \) respectively, \( r_{ij} \) is the distance between atoms \( i \) and \( j \), \( r_0 \) is the distance between the nearest neighbors, \( r_{ij}/r_0 \) is determined by the geometric relation of face-centered cubic structure. It has been demonstrated that Morse potential could reasonably represents the interaction between two atoms and easily calculates the potential change during the atom diffusion. The calculation of activation barrier was improved further on the basis of our previous methods \[10-12\]. In order to find the maximum activation barrier \( E_{\text{max}} \) between two atoms, we took 99 points \( P_i \) (\( i=1, 2, \ldots, 99 \)) on the line connecting the initial lattice site to the next jump target. We took another two points \( P_0 \) and \( P_{100} \), the distances from \( P_0 \) to the initial site and from \( P_{100} \) to the next jump target are 0.01 \( a \) (\( a \) is the lattice constant). The respective potentials are \( E_i \) (\( i=0 \) to 100), \( E_{\text{ini}} \) (potential in the initial site) and \( E_{\text{fin}} \) (potential in the next jump site). The total potential for each point of interest can be obtained by summing up the contribution from all atoms within a sphere of radius of 1.5\( r_0 \). \( E_{\text{max}} \) is the maximum of \( E_i \) (\( i=0 \) to 99), and \( E_{\text{fin}} \). The activation energy \( \Delta E \) is determined by taking the difference between \( E_{\text{max}} \) and \( E_{\text{ini}} \).

In this paper, we firstly introduced the concept of exchange rate in order to study the micro-mechanism of exchange reaction and defined it as

\[ s = \frac{n_2}{n_1}, \]

where \( n_1 \) is the numbers of surfactant atoms diffusing from surfactant layer to thin film surface, \( n_2 \) is the numbers of incident atoms diffusing from the film surface to surfactant vacant sites. It is obvious that the exchange rate equals to one forever according to RLA model.

3. Results and discussion

Figure 2 shows a snapshot of film morphology at the initial stage with surfactant-mediated at temperature of 300K and deposition rate of 0.32 lay./s, where the layers from 1 to 3 are substrate atoms.
and the layers from 4 to 5 are surfactant atoms, white and grey spheres represent respectively the incident and surfactant atoms.

Seen from the figure 2, a part of surfactant atoms diffuse to the surface and simultaneously some adatoms diffuse to the surfactant during film growing, and the majority of diffusion is layer-to-layer diffusion of single atom. A trace file was created during the simulation, which could record the initial and the next jump positions of every jump. By analyzing the trace file, we found that both surfactant and adatoms diffuse in the way of layer-to-layer with the interactions of atom kinetic movement and interactions between atoms. On one hand some surfactant atoms diffuse up to the surface and leave vacant sites. Because of the existence of vacants, the surfactant atoms diffuse constantly in the surfactant layers so that the vacant sites move continually too. On the other hand adatoms diffuses on the film surface and might arrive at one of the nearest neighbours of vacant site (in the deposited surface). Because of lower energy of vacant site, the adatom diffuses more easily down and holds the vacant in the surfactant and then forms a filled site. At the same time, if the surfactant atom, which diffused into the surface, diffuses to other nearest neighbors of the filled site (in the surface, but not the position where the adatom located before filling), and the exchange is called quasi-exchange. If the vacant site just diffuses to the position where the adatom located before filling, and the exchange is called complete-exchange. It was found that the most of layer-to-layer diffusions happen between single atoms during simulation trace. Although there might exist a few quasi-exchange and few complete-exchange of position, these exchanges are the combination results of basic micro-processes. The possibility, in which the adatom nucleates firstly and then occurs the quasi-exchange or complete-exchange of nuclei, is comparatively small.

The dependence of the number of diffusing atoms on substrate temperature is presented in Fig. 3. In this figure, both the surfactant atoms which diffuse upwards to surface and the adatoms which diffuse downwards to surfactant layer increase sharply with temperature increasing. But the tendency becomes obviously slow down while the temperature is higher than the valve (approximately 320K), and the valve might be the maximum saddle energy of layer-to-layer diffusion. Because the atom can not be activated effectively at low temperature and the most of atoms possess larger barrier while diffusing, the atom can but diffuse in the same layer. However, the movement becomes more and more acute with temperature increasing so that many atoms can climb over the saddle and cross through layer when the temperature arrives at the valve.

![Figure 3](image1.png)  
**Figure 3.** The dependence of atoms crossing layers on the substrate temperatures.

![Figure 4](image2.png)  
**Figure 4.** The dependence of exchange rate on the substrate temperature.
4. Conclusion

A three-dimensional kinetic Monte Carlo (KCM) technique has been developed for simulating surfactant-mediated epitaxial growth of thin film Cu. The following results are drawn:

1. The layer-to-layer diffusion is mostly the single atom diffusion during film growth. There might exist a few quasi-exchange and few complete-exchange of position, but these exchanges are combination results of basic micro-processes.

2. Both surfactant atoms and adatoms diffuse from one layer to another. The majority of diffusion is layer-to-layer diffusion of single atom and the atoms of layer-to-layer diffusion increase with the temperature increasing.

3. The layer-to-layer diffusion is not simple exchange of position, and not the exchange of 1:1. The surfactant atoms which diffuse into the surface is greatly more than the adatoms which diffuse into the surfactant, namely the exchange rate is much less than one. The exchange rate increases rapidly with temperature increasing and reaches the maximum at the valve, and then begins to decrease and tend to be stable.

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