Atomic Aggregation Processes in the Early Stages of Pt/Pt(111) Growth*

ZHUANG Guo-Ce(庄国策)[1,2] ZHU Xiao-Bin(朱晓斌)[1] WANG Wei(王炜)[1]
[1]National Laboratory of Solid State Microstructure and Department of Physics, Nanjing University, Nanjing 210093
[2]Department of Physics, Yancheng Teacher's College, Yancheng, Jiangsu 224002

(Received 3 December 1999)

The atomic aggregation processes in the early stages of Pt/Pt(111) growth are studied by using kinetic Monte Carlo simulations. Our results show that the average neighbor coordination number of the atoms in a cluster is a function of temperature, agreeing well with the experiment observations of scanning tunneling microscopy. The influence of diffusion barriers of various atomic processes on the morphology of islands is also studied. Different morphologies of the islands (dendritic, fractal, or compact islands) are found.

PACS: 68.35.Fx, 61.16.Ch

Adatom diffusion on metal surfaces is of fundamental importance in the microscopic understanding of crystal growth, epitaxial growth of thin films, and other surface phenomena.[1-6] Recently, the surface growth of Pt atoms on a Pt(111) surface has been widely studied both experimentally and theoretically.[7-12] Field-ion microscopy (FIM) is often used to observe the surface diffusion process directly, and the technique has led to the discovery of many atomic diffusion mechanisms. By using scanning tunneling microscopy (STM) measurements, the static surface morphology of a film can be easily obtained.[2] Theoretically, through understanding of the various atomic processes, one can study the morphology of the surface growth by the kinetic Monte Carlo (KMC) method. In order to interpret a variety of experimental results, the mechanism of adatom diffusion and aggregation in addition to diffusion-limited aggregation (DLA) must be included. Hohage *et al.*[9] presented a kinetic Monte Carlo model including not only the diffusion of free adatoms but also that of adatoms with one neighbor binding at the edge of islands. Their simulations successfully modeled the experimental observations at low temperature. However, at relative high temperatures, the simulation data are lower than those of experiments. In their simulations, the diffusion of atoms with more than two neighbor coordination bindings was not included, from which we expect that they may largely affect the island morphology as the substrate temperature increases.

In our simulations, the Pt atoms are deposited at randomly chosen positions on the $L\times L$ lattice sites with a constant deposition rate F. All the free adatoms and the atoms along island edges with less than three neighbor coordination bindings are chosen randomly, and each of them attempts to surmount an energy barrier to have one lattice migration. If an edge atom is bonded with three or more atoms in the island, it will stick to the island immovably. In Fig. 1, we summarize some of the diffusion processes of an adatom in a (111)-type substrate. The diffusion barrier for each process is characterized by E_i, where i (i = 0,1,2) is the number of in-layer nearest neighbors before the jump. Two kinds of diffusion along the island edge must be distinguished, *i.e.*, the diffusion along an A-type edge (see process E_{1a} or E_{2a}) and a B-type edge (process E_{1b} or E_{2b}). Along an A-type edge, the atom will diffuse along a smooth surface, while along a B-type edge, the diffusion of the atom at the island edge must pass through a bridge, which has a little higher barrier.

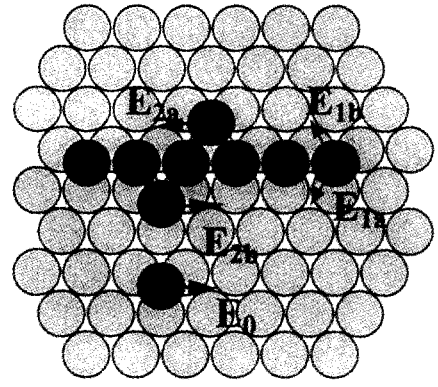

Fig. 1. Illustration of elementary diffusion processes of Pt on Pt(111) substrate. The diffusion barrier for each process is characterized by E_i, where i ($i = 0, 1, 2$) is the number of in-layer nearest neighbors before the jump. The processes can take place at both A-type and B-type steps.

It is known that the diffusion rate of adatoms has an Arrhenius dependence on the substrate temperature: $D = \nu_0 e^{-E_d/kT}$,[7] where ν_0 is the attempt frequency, T is the substrate temperature, k is Boltzmann's constant, and E_d is the diffusion energy barrier. For various kinetic processes and for different neighbor coordination bindings, the diffusion barriers are different. Physically, the diffusion barrier for

*Supported by the National Natural Science Foundation of China under Grant No. 19604006, and the Outstanding Young Researchers Foundation of the National Natural Science Foundation of China under Grant No. 19625409.

an atom is mainly determined by the interactions between this atom and surrounding atoms, and which is increased as the neighbor coordination number increases. On the other hand, we should distinguish the difference between A-type and B-type edge diffusions. Thus, from comparison with some experimental results,[8] the diffusion barriers for various processes are chosen to have values $E_0 = 0.26\,\text{eV}$, $E_{1a} = 0.29\,\text{eV}$, $E_{1b} = 0.37\,\text{eV}$, $E_{2a} = 0.56$,eV, $E_{2b} = 0.71\,\text{eV}$. The attempt frequency is 10^{12}s^{-1}. The deposition rate is set as $F = 3.3\times10^{-3}\,\text{ML/s}$. All the simulations are performed for a 400×400 lattice. It is noted that in the early stages of the surface growth, the probability of an atom falling on an existed island is very small, so that the interlayer processes are not included in our simulations.

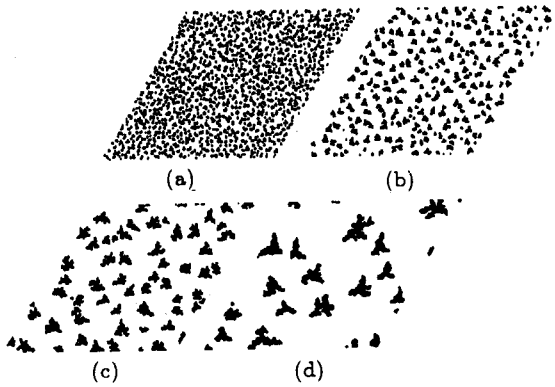

Fig. 2. KMC results for the morphology of the Pt(111) surface for a coverage of 0.1 at four different substrate temperatures: (a) $T = 140\,\text{K}$; (b) $T = 180\,\text{K}$; (c) $T = 220\,\text{K}$; (d) $T = 270\,\text{K}$. The system size is an $L\times L = 400\times400$ lattice.

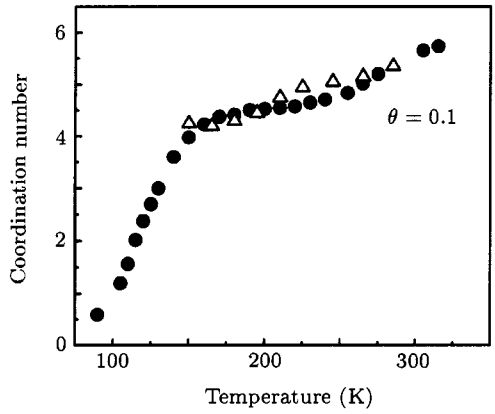

Fig. 3. Average coordination number as a function of substrate temperature. The circles are our simulation results and the hollow triangles are STM experimental results from Ref. 9.

Figure 2 shows the simulated island structures after deposition of a 0.1 monolayer of Pt on Pt (111) at four different low temperatures. We can see that the islands are dendritic. When the substrate temperature is low, the diffusion of an atom is slow. Thus, before it meets an existed island or adatom, another adatom will be deposited on the substrate. The average island number is large and the average size of the islands is small (see Fig. 2(a)). Because it is not easy for the adatom to diffuse along the island edge at low temperature, the branch of the island is very thin. From Fig. 2 we can see that as the temperature increases, the island size increases while the number of islands decreases (see Fig. 2(d)). However, although the island is dendritic, the thickness of the island branches is different at different substrate temperatures. That is, when the temperature is low the branches are thin, and when the temperature is high they are thick. At a much higher temperature, it is found that the morphology of the islands is compact (not shown here). In addition, due to the difference between the diffusion barriers along A-type and B-type edges, we can see that the dendritic islands are asymmetric (see Fig. 2(d)). These results fit the observations of island morphologies obtained by the STM experiments.[2]

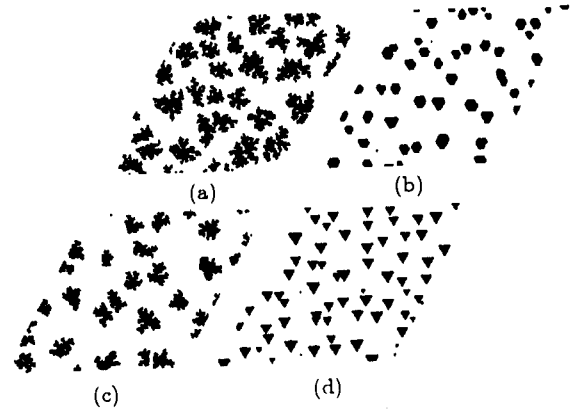

Fig. 4. Morphology of the islands on a Pt(111) substrate with different barrier parameters. (a) DLA-like growth, with an infinite barrier for atom diffusion along island edges; (b) the case when an atom at the island edges has a lower diffusion barrier than that of an adatom on the substrate; (c) the case when the A-type and B-type diffusion barriers are equal; (d) morphology of islands with extreme corner diffusion anisotropy.

The thickness of the island branches can be described by the average neighbor coordination number of the atoms on the surface. By considering the mechanism of edge diffusions, we found that the average coordination number is a function of the substrate temperature. Figure 3 shows the dependence of the coordination number on the substrate temperature in the coverage of $\theta = 0.1$. Comparing with the STM observations in the range of 150 to 300 K, we see that the data points obtained from simulations are quite in agreement with the STM experimental results of Ref. 9. Generally, the coordination number increases as the substrate temperature increases. At very low temperatures, the adatom is nearly static on

the substrate, and almost no diffusion occurs after the atoms are deposited on the surface. However, as the substrate temperature increases, the diffusion rate of adatoms increases, the adatoms on the substrate will form an island, which will increase the average coordination number. As a result, it is expected that when the temperature is large enough, the island on the substrate will form a compact structure, in which the average coordination number approaches six. In Fig. 3, we can also see that there may exist a transition from the growth with thick branches to the growth with thin branches around $T = 150\,\mathrm{K}$, as the temperature decreases, which may be related to different dominating diffusion mechanisms and to different scaling behavior of the island size distributions. This will be discussed in detail elsewhere.

The island morphology is very sensitive to the barrier parameters. In the following, we analyse the influence of the energy barriers on the morphologies of the islands. If we only consider the single adatom diffusion, *i.e.*, the diffusion of adatoms along the island edge is not considered, we simulate the growth for the DLA mode. In this case, we choose all energy barriers to be infinite except for E_0. The simulation gives a fractal island, as shown in Fig. 4(a), which has been widely studied in Ref. 1. One can see that the branch of the island is too thin compared with experimental results. The coordination number is much lower than that of experiments, and at the same time, it is not sensitive to temperature. Therefore, the diffusion of adatoms along the island edge must be considered. In the simplest case, we assume that the atoms with one atom neighbor binding and two neighbor bindings can diffuse as easily as a single adatom. In this situation, it is easy for the adatom to find a place with large coordination number before another adatom attaches to the island, and we can expect that the island will be more compact. Figure 4(b) shows the morphology in such a situation. It is found that the island has a compact hexagonal structure, and the coordination number is about six. It is known that, in the (111)-type substrate, the morphologies of islands are asymmetric because of the difference between A-type and B-type diffusion. If such a difference is not considered, *i.e.*, the diffusion barriers of A-type and B-type diffusion are assumed equal, various symmetry morphologies can be obtained as shown in Fig. 4(c). This can be seen more clearly if one compares the islands of the asymmetric case (Fig. 2(c)) with those of the symmetric case (Fig. 4(c)). The coordination number is larger than that of the situation in which the asymmetry is considered. Nevertheless, in a rather limited situation, considering that the energy barrier of B-type diffusion is much larger than that of A-type diffusion, *i.e.*, B-type diffusion along an edge via a bridge cannot take place, the morphologies of the islands are quite different. Such asymmetry affects the morphology of the surface greatly. In Fig. 4(d), we have chosen a low diffusion barrier E_0 for the A-type diffusion, and a high enough diffusion barrier for the B-type. We observe clearly the compact triangular islands. This is in agreement with Ovensson's argument that the compact triangular islands are mainly determined by the corner diffusion anisotropy.[6] Therefore, the structures of the thin films are closely related to various diffusion barriers in the atomistic processes. The islands show different morphologies when different types of diffusion dominate the growth. However, through adjusting the barriers, the island morphologies and average coordination number change sensitively, and a lot of patterns can be observed corresponding to the experiments. Our simulation may be helpful for understanding the kinetic processes in actual thin film growth.

In conclusion, we have studied the atomic aggregation processes in the early stages of Pt/Pt(111) surface growth by KMC simulations. The morphologies of the islands have been studied at different substrate temperatures, and found to be compatible with the results of experiments. The average coordination number of the atoms on the surface is calculated as a function of temperature over a large range, which is in agreement with the island branch thickness measured by STM experiments. In addition, the influence of the barrier parameters on the island morphology has been analyzed, which gives more information about the atomic processes of the thin film growth.

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