International Journal of Modern Physics B, Vol. 14, No. 4 (2000) 427–434

THE ATOMIC MOVING PROCESSES OF CLUSTER Ir_{18} DIFFUSION ON Ir(111)

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Received 12 July 1999
Revised 26 November 1999

The motion of peripheral atoms of an Ir_{18} cluster, which results in migration of the cluster on Ir(111), is studied by kinetic Monte Carlo simulations. Detailed moving processes of individual peripheral atoms of the cluster are proposed. Statistical average of staying times show that these atoms basically locate only at several energetical equilibrium positions, which makes the motion of atoms effectively in a form of jumping of dimer from one equilibrium position to another. The jumping of the dimers, which results in migration of the cluster, are further simulated by introducing effective energy barriers between these equilibrium positions. A temperature dependence of the diffusivity D for the migration of the cluster is in good agreement with the experimental results, which proves the suitable values of the effective energy barriers for the motion of the dimers.

PACS Number(s): 68.35.Fx, 05.40.+j, 66.30.Fq, 81.10.Aj

1. Introduction

Large cluster migration on metal surface is of fundamental important in processes such as crystal growth and epitaxy growth of thin film.[1−18] Recently, a lot of theoretical and experimental studies have been done in this field. Various microscopical atomic mechanisms have been proposed, such as the interface gliding,[1,2] the movement of dislocations,[2−7] and the diffusion along the cluster edges,[8−15] as well as atom evaporation and condensation.[10,16−18] All these mechanisms obviously are based on different experimental observations. For example, large Ag cluster moving on the Ag(100) surface at room temperature from scanning tunneling microscopy (STM) observations is believed due to the evaporation and condensation of adatoms at the periphery of the cluster.[10] Experiments on clusters of Ag atoms on Ag(111) surface also show similar phenomenon. To explore the atomic mechanism, the dependence of diffusivity on the cluster size is a crucial point, and has been extensively studied (see Refs. 15 and 18 and references therein).

Recently, by using field ion microscope (FIM), a series of direct observations of large Ir cluster diffusion on Ir(111) surface is made.[12−15] It is found that large Ir

cluster can move without evaporation and condensation of atoms when the cluster is warmed repeatedly for some time.[12,15] For compact hexagonal clusters, say Ir_7 (with 7 atoms) and Ir_{19} (with 19 atoms), on Ir(111), the clusters always retain their hexagonal shapes during the migration. The diffusivity and the activation energy of clusters on Ir(111) are obtained through quantitative measurements. A gliding of the whole cluster is believed to be the mechanism for the migration of such compact clusters.[15] Differently, for noncompact hexagonal clusters, e.g. Ir_{18} or Ir_{36}, the migration is found due to the moving of the peripheral atoms along the cluster edges. Detailed records of field ion images for Ir_{18} clusters show that the migration of the clusters after each heating interval always seems to involve the moving of two peripheral atoms with less number of nearest neighbor atoms from one equilibrium position to another. Since too long heating interval, 5 seconds, the detailed moving of these two atoms could not been observed. Thus the atomic mechanism for the migration of these noncompact clusters is only understood by an overall picture of the jumping of two peripheral atoms, or a "dimer".[12] What are the detailed atomic moving processes, or how do these peripheral atoms move along the edges of the cluster? Microscopically, with a suitable heating, the peripheral atoms should move step by step, i.e. from one lattice position to one of its nearest neighbors. That is, there may exist some intermediate states for their moving before they reach another equilibrium state. To have a more clear understanding for the microscopical mechanism of the diffusion of such noncompact cluster, in this paper we make a kinetic Monte Carlo (MC) study on the detailed moving processes of the peripheral atoms for various states. From our simulation results, we find that the average staying times of peripheral atoms for staying at the equilibrium states are larger than staying at the intermediate states. This can further be simplified as two atoms jumping together from an equilibrium position to another, i.e. a model of effective "dimer" jumping along the edges of the cluster. The cluster migration caused by such jumping of "dimers" are simulated through choosing proper effective energy barriers for the jumping of the dimers. The diffusivity D and the activation energy E_{D} are obtained, and are in good agreement with the experimental findings.[12–15]

From the experimental observations,[12] for the noncompact clusters, say an Ir_{18} cluster, it is found that there exists four energetically different forms at equilibrium, as shown in Fig. 1. In these four forms, there are 6 (for form I, II, and III) or 7 (for form IV) peripheral atoms having the least number of nearest neighbor atoms, i.e. 3 nearest neighbor atoms, while the total numbers of the nearest neighbors of the cluster are the same for all four forms. In forms I and II, the directions of the long edges of the cluster are on a {100} facet of the substrate (an A-type edge) and on a {111} facet (a B-type step), respectively. Along A-type edge, the atom will diffuse along a smooth surface, while along B-type edge, the diffusion of the atom at the cluster edge must pass through a *bridge*, which has a little high barrier. Differently, there exist six equivalent configurations for each form III and form IV. Therefore, there are totally fourteen energetically different configurations for an Ir_{18} cluster. The cluster shapes change from one configuration to another after

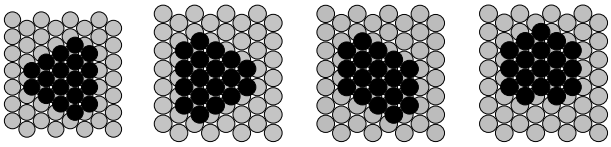

Fig. 1. Four nonequivalent forms of Ir_{18} cluster on Ir(111). There are one configuration for each form I and form II, and six equivalent configurations for each form III and form IV. But only one configuration is shown for each form (see Ref. 12) All these fourteen configurations have a same total number of nearest neighbor atoms, 78, and are the energetical equilibrium positions for the atoms in the cluster.

each heating interval, which results in the moving of the cluster on the substrate. Microscopically, this definitely involves the existence of some intermediate states. That is, once the cluster is warmed up, the peripheral atoms with less number of nearest neighbors will obtain energy, and will hop from their equilibrium positions to some metastable positions. After the stop of heating, these atoms will diffuse back to some certain equilibrium positions. Therefore, a series of overall changes of patterns shows that the migration of the atoms looks like a jumping of "dimer" from one position to another as found in the experimental observations.

2. Monte Carlo Simulation

In order to get a detailed understanding of the diffusion of cluster Ir_{18} in experimental conditions,[12] we map out one class of possible atomic processes in migration of the cluster. Figure 2 shows the microscopical atomic processes of the cluster transition between form I and III. The moving of the atoms are excited due to the heating. The concerted atomic motions of dimers are considered in our model. There are five metastable intermediate states (a, b, c, d and e) which have much higher energy than the equilibrium states I and III. The rate for each hopping i, say $a \to b$, can be given by the transition state theory

$$\nu_i = \nu_i^0 e^{-E_i/k_{\mathrm{B}}T} \tag{1}$$

where $E_i = E_{a\to b}$ is the activation energy, k_{B} is the Boltzmann constant and T is the substrate temperature. For all processes the prefactor ν_i^0 is chosen as $\nu_i^0 = 10^{12}$ sec^{-1}. Using a kinetic Monte Carlo algorithm the detailed atomic processes can be simulated. We start from one of the seven states in Fig. 2 randomly, the rate of hopping to a neighbor state is determined by Eq. (1). The activation energies E_i for various hoppings in our simulations are chosen from the model in Ref. 11 (see Fig. 2 in Ref. 11).[19] We record the MC steps (MCS) for the cluster being settled in each state within a certain long time interval, say 10^7 MCS. After running the MC simulations more than 100 different realizations, we obtain the statistics average of the percent of the staying times at each state as shown as the numerals below each configuration in Fig. 2. Almost all the settlements of the cluster are only at two

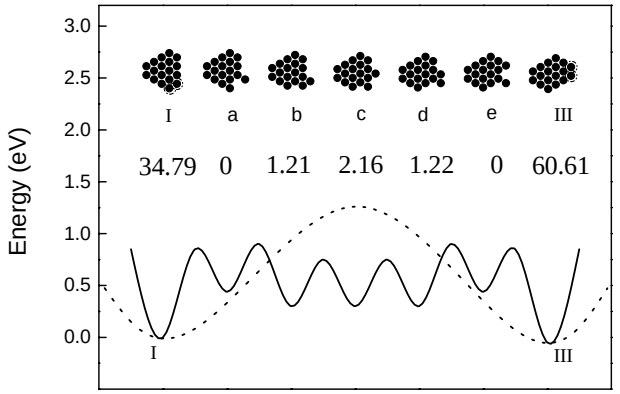

Fig. 2. The detailed moving processes of the periphery atoms from form I to III. *a*, *b*, *c*, *d* and *e* are five metastable intermediate states. A couple of atoms with dashed line circled is the dimer which migrates from one energetical position to another. The solid curve is the energy barriers for a single atom diffusion processes. The heights of the barriers and the depths of wells are all meaningful related to the choice for the values of activation energies of various processes. All the activation energies marked in the figure have units in eV. The dashed curve describes an effective energy barrier $E_{\rm eff}(\mathrm{I} \rightarrow \mathrm{III})$ for the "dimer" jumping. The numerals below each configuration indicate the percent of the average staying times at each configurations from the simulations.

states I and III; the intermediate metastable states from *a* to *e* only occupy very little part of the times. From this result we may conclude that the intermediate states can hardly be observed in experiments. This is because the intermediate shapes are of much higher energy than the stable states I and III and they exist just briefly before hopping to the energetical forms. Thus, the moving of two peripheral atoms looks like in a form of dimer which jumps from one position to another.

Due to the statistical and kinetical characteristic mentioned about, we may ignore the existence of the intermediate states. That is, we consider the jumping of dimers along the edges of the cluster. An effective energy barrier $E_{\rm eff}(\mathrm{I} \rightarrow \mathrm{III})$ is introduced to describe the dimer jumping. For example, in the jumping from form I to form III in Fig. 2, the dimer should jump from a short edge in form I of the cluster to the long edge on the right. In this process the dimer should cross a barrier of $E_{\rm eff}(\mathrm{I} \rightarrow \mathrm{III})$. The effective energy barrier $E_{\rm eff}$ can be estimated from the relation of $\nu = \nu^0 e^{-E_{\rm eff}/k_{\rm B}T}$, where ν is determined by the average rate of jumping from form I to form III in the individual atomic processes.

As dimers jumping along the cluster edges, the shapes of the cluster change among the four nonequivalent forms as shown in Fig. 1 (with fourteen different configurations). For a long interval of time, the changes of the cluster shapes make the center of the cluster move on the substrate. Figure 3 shows the schematic pictures of the migration of the cluster Ir_{18} and the effective energy barriers for each process of the dimer jumping. It is noted that for the symmetric jumping processes the effective energy barriers are assumed to be the same. For example, the marked dimer in form I has two positions for jumping, either to the right

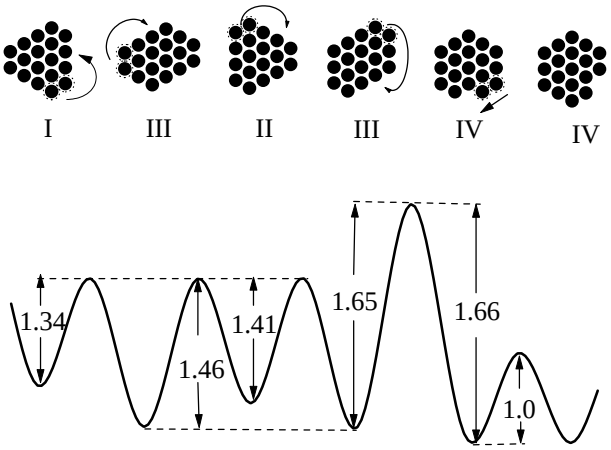

Fig. 3. Jumpings of the "dimers" between different forms. A couple of atoms with dashed line circled is the dimer which jumps from one energetical position to another. The movement is indicated by the arrow which shows the overall changes of the dimers. The effective energy barriers E_{eff} of several dimer jumping processes are marked. The exact values for the barriers come from the best fitting of the diffusivity with the experimental results in Fig. 5.

one or to the left one, i.e. both positions have the same probability and the same effective energy barriers $E_{\text{eff}}(\text{I} \rightarrow \text{III}) = 1.34$ eV. For four configurations of form III, there are only two different jumping processes for the dimers as shown in Fig. 3, i.e. one process with an effective energy barrier $E_{\text{eff}}(\text{III} \rightarrow \text{II}) = 1.46$ eV for the dimer jumping from form III to form II, and another process with an effective energy barrier $E_{\text{eff}}(\text{III} \rightarrow \text{IV}) = 1.65$ eV for the dimer jumping from form III to form IV.

After giving a set of effective energy barriers for the jumpings between different forms, we can make kinetic Monte Carlo simulations for the migration of the cluster Ir_{18}. It is obviously that the simulation results are sensitive to the choice of the values of the effective energy barriers. In our model, the effective energy barriers are estimated by referring to the dimer moving processes in other systems, such as $E_{\text{eff}}(\text{I} \rightarrow \text{III}) = 1.34$ eV for dimer jumping from form I to form III, which is comparable to the STM results for ad-dimer diffusion on Si(100)[20] and the bond counting results in Ref. 21. However, the final selection of the exact values of the effective energy barriers in Fig. 3 comes from the best fitting with the experiments (see following). In our simulations, it is assumed that the rates for all the dimer jumping are also determined by the rate equation (1), but the activation energy E_i should be substituted by the effective energy barrier E_{eff}. By measuring the displacement Δx_i of each of the n atoms in the cluster, the displacement of the center of the mass Δx_c is obtained from $\Delta x_c = \sum_{i=1}^{n} \Delta x_i / n$. The mean-square displacement $\langle R^2 \rangle$ after a sufficient long time is obtained, then its statistical average by repeating 100 simulations.

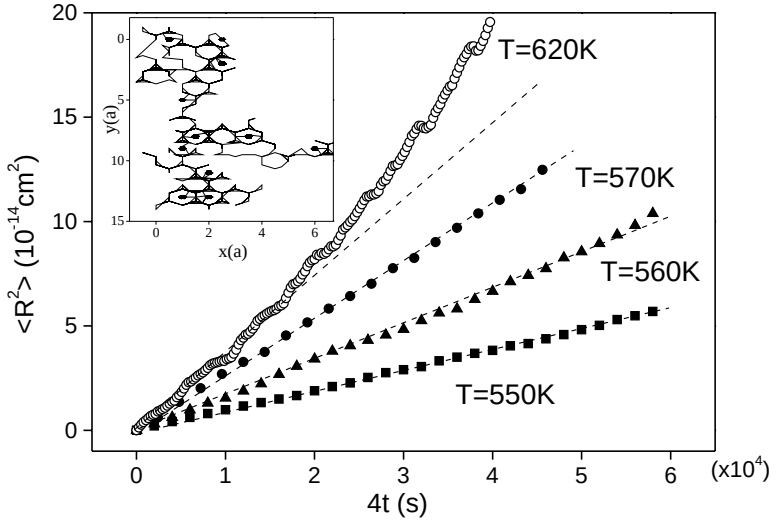

Fig. 4. The time dependence of the mean-square displacement $\langle R^2 \rangle$ for several different temperatures. From the slopes of the lines, the diffusivity D are obtained as: $D = 9.6 \times 10^{-19}$ cm^2/s for $T = 550$ K, $D = 1.75 \times 10^{-18}$ cm^2/s for $T = 560$ K and $D = 2.8 \times 10^{-18}$ cm^2/s for $T = 570$ K, respectively. The inset gives a trajectory of the centre of mass of a Ir_{18} cluster during its random walk at $T = 570$ K.

According the random walk theory,[22] the diffusivity D can be obtained from the mean-square displacement from the equation

$$\langle R^2 \rangle = NL^2 = 4Dt\,, \tag{2}$$

where N is the mean number of the dimer jumps during the diffusion interval t and L is the root-mean-square jump distance. The time dependence of the mean-square displacements for three different temperatures are shown in Fig. 4. The inset in Fig. 4 shows a trajectory of the centre of the mass of a cluster during its random walk in the temperature of 570 K. From this figure we can see that, in the range of 520–580 K, the straight lines through the data indicate a linear dependence of $\langle R^2 \rangle$ on the time t. From the slopes of these lines, the diffusivity D can be obtained as follows: $D = 9.6 \times 10^{-19}$ cm^2/s for $T = 550$ K, $D = 1.75 \times 10^{-18}$ cm^2/s for $T = 560$ K and $D = 2.8 \times 10^{-18}$ cm^2/s for $T = 570$ K, respectively. The dependence of the diffusivity D on various temperatures T from 520 K–580 K can be obtained similarly as shown in Fig. 5. One can see that the data obtained from simulations are in good agreement with the experimental results.[15] Naturally, from the Arrhenius equation $D = D_0 \exp(-E_{\rm D}/k_{\rm B}T)$, the values of the prefactor D_0 and the activation energy $E_{\rm D}$ for the migration of Ir_{18} cluster can be obtained as $D_0 = 7.4(\times 3.1^{\pm 1}) \times 10^{-4}$ cm^2/s and $E_{\rm D} = 1.62 \pm 0.05$ eV. They basically coincide with the experimental results $D_0 = 7.8(\times 4.5^{\pm 1}) \times 10^{-4}$ cm^2/s and $E_{\rm D} = 1.63 \pm 0.07$ eV. All our results indicate that the model of an effective dimer jumping along cluster edges describes the behaviour of the migration of cluster Ir_{18} very well

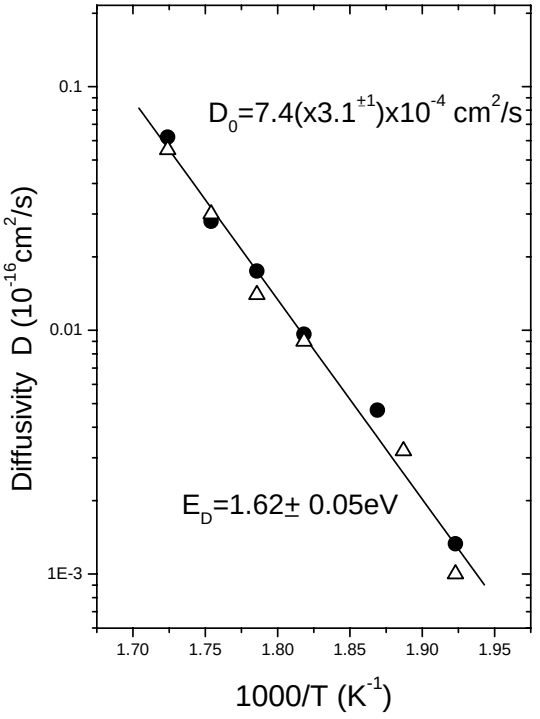

Fig. 5. Temperature dependence of the diffusivity D of Ir_{18} cluster migration on Ir(111) obtained from the mean-square displacements. The solid circles are our simulation results and the open triangles are experimental results cited from Ref. 15.

in temperature range from 520–580 K. In addition, the choice of the values of the effective energy barriers means the fit in with the real experimental situations. It is noted that as $T > 600$ K, the diffusivity D obtained from this model becomes far away from the straight line given by Arrhenius equation. As a matter of fact, the cluster Ir_{18} is less stable than its neighbor Ir_{19} and will be evaporated, when the substrate temperature is larger than 600 K. Finally, it is also worthy to point out that the mechanism of effective dimer jumping at the edges for Ir_{18} cluster may work similarly for the Ir_{36} cluster since its migration always involves the jumpings of three edge atoms. Therefore, it may be described by a trimer jumping along cluster edges.

3. Conclusion

We have made a study on the atomic processes in the migration of Ir_{18} clusters on Ir(111) surface based on kinetic Monte Carlo simulations. By examining the detailed atomic moving processes in the cluster edges, we study a model of jumpings of dimers along cluster edges with effective energy barriers in various jumping processes. Our simulation results show that both the diffusivity D and the activation

energy E_D for the migration of Ir_{18} cluster are in good agreement with the results from experimental observations. Our simulations may provide a general description for the jumping of periphery atoms in cluster migration.

Acknowledgment

One of the authors (W. Wang) acknowledges the support from the the National Natural Science Foundation (19604006), and the Outstanding Young Research Foundation of the National Natural Science Foundation (19625409).

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19. The choice of the values of E_i should be related to the diffusion process of the Ir atoms along the periphery of Ir cluster. However, on one hand, the exact values for various processes in Fig. 2 are not available from the literature. On the other hand, they are not so important for the simulations since we only need the relative staying times of all positions. The data used in Ref. 11 are good enough for our propose. In addition, we did some simulations by setting various values of E_i from Ref. 23 since the Pt atoms and Ir atoms are neighbors in the period table. The simulation results show that the detailed atomic processes are the same. From the average staying times and average rate of jumping, we obtained an effective barrier $E'_{\text{eff}}(\text{I} \to \text{III}) = 1.25$ eV which is close to the value from the best fitting (see text).
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