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Scaling behavior of one-dimensional Pt chains migration on Pt(110)–(1 × 2) surface

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Abstract

Based on the leapfrog diffusion mechanism, the atomic processes of one-dimensional Pt clusters diffusion on the anisotropic Pt(110)–(1 × 2) surfaces are studied with kinetic Monte Carlo simulations. Our results show that the temperature-dependent cluster displacement rate R agrees quite well with the experimental data from scanning tunneling microscopy. In addition, it is found that the scaling exponent α , which is associated with the scaling relation $R(L) \sim L^{-\alpha}$, is temperature dependent. As the temperature increasing, the exponent α increases linearly. © 2000 Elsevier Science B.V. All rights reserved.

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Cluster diffusion on metal surface is of fundamental important for the microscopic understanding of crystal growth, epitaxy growth of thin film, and other surface phenomena [1–19]. Recently, a lot of theoretical and experimental studies have been done in this field. Various microscopic atomic mechanisms have been proposed such as the interface gliding [1,2], the movement of dislocations [2–4], and the diffusion along the cluster edges [5–8], as well as atom evaporation and condensation [9–11]. The dependence of diffusivity on the cluster size is a crucial point, and has been extensively studied. A seminal study by Voter [12] shows that there exists a scaling law

between the diffusion coefficient D or the displacement rate R of the clusters and the cluster side length L

$$D(L) \sim R(L) \sim e^{-E_L/k_B T} L^{-\alpha} \quad (1)$$

where α is a scaling exponent, k_B is the Boltzmann constant, T is the substrate temperature, and E_L is the effective energy barrier for cluster diffusion. It has been found that the scaling exponent α depends on the cluster diffusion mechanism [13–16]. For example, if the island motion is caused by the evaporation and condensation limited diffusion mechanism (EC mechanism), then $\alpha = 1$; if the island motion is terrace-diffusion limited (TD mechanism), then $\alpha = 2$; if the island moves as a result of atom diffusion along the island periphery (PD mechanism), then

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$\alpha = 3$ [16]. These models predict integer exponents for the highly simplified or limited cases of small metal clusters diffusion on isotropic metal surfaces. In fact, non-integer scaling behaviors or size-dependent scaling exponents have been observed in several Monte Carlo simulations [14,17] and in experiment [18]. However, much less is known about the diffusion of small clusters on surfaces such as Pt(110)–(1 × 2) where the diffusions of atoms and clusters are expected to be anisotropic.

Recently, by using atom-resolved, time-lapsed scanning tunneling microscope (STM), Linderoth et al. [19] observed a novel diffusion process for one-dimensional platinum cluster on an anisotropic Pt(110)–(1 × 2) surface. This phenomenon is very interesting since the migration of Pt clusters is purely 1D and restricted to the troughs between the close-packed Pt rows (see Fig. 3 in Ref. [19]). It is found that cluster can migrate through a leapfrog mechanism. The schematic diagram is shown in Fig. 1. The end atom of the cluster crawls up to the top of the cluster, migrates over the cluster, and drops down again to the opposite end. The activation barriers for the ascending and descending adatom motion can be estimated from a quantitative analysis of the STM data. However, in the STM studies, the clusters typically consist of 3–6 atoms and the substrate temperature ranges from 334 K to 382K. It is found that in such a temperature region the influence of the cluster length on the cluster diffusivity is expected to be negligible [19]. This means that the diffusivity $D(L)$ or the displacement rate $R(L)$ is nearly inde-

pendent on the cluster length L which leads the scaling exponent α approaching to zero. The leapfrog diffusion mechanism is also studied by Montalenti and Ferrando [20] with molecular dynamics methods, but the scaling behaviors about the displacement rates are not concerned in their work. Our goal in this paper is to know whether the influence of the cluster length on the diffusivity is negligible or not as the substrate temperature increases, and what scaling behavior exists in the leapfrog diffusion mechanism. We know there is no experimental or theoretical report on that subject.

In this paper, based on the leapfrog mechanism, the atomic processes of one-dimensional Pt clusters diffusion on the anisotropic Pt(110)–(1 × 2) surfaces are studied with kinetic Monte Carlo simulations. From our results we find that the atomic leapfrog processes make the cluster diffusion similar to a one-dimensional random walk. The diffusivity D or the displacement rate R can be obtained from the mean-square displacement. A temperature-dependent cluster displacement rate is found which is in good agreement with the experimental results. We explain the reason why the influence of cluster length on the displacement rate is negligible at lower temperature. As temperature increasing the effect of the length on the displacement rate becomes more and more important (see following). As a result, we obtain a power-law dependence of the displacement rate R on the cluster length L , i.e., $R(L) \sim L^{-\alpha}$. Moreover, we find a linear relation between the scaling exponent α and the temperature T in the range of 320–850 K.

The leapfrog mechanism in our simulations is shown in Fig. 1. An end atom in the chain is promoted from its position in the missing-row trough up to a position on the next crystal plane formed by the remainder of cluster and the two surrounding close-packed rows. From this site, it diffuses to the other end of the chain which results in one lattice displacement of the cluster. For the end atom to be promoted to the top of the cluster, it has to surmount the activation barrier E_{up} . Once promoted to the upper plane, the adatom resides in a metastable state with a given barrier E_0 for single atom diffusion on the cluster. Then it should pass an increased activation barrier E_{down} in order to descend from the cluster. All relevant single atomic processes in the migration of the cluster can be mapped out. The rate

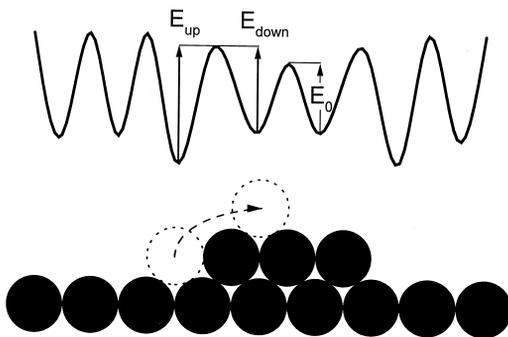


Fig. 1. The schematic diagram of the model of leapfrog diffusion mechanism. The curve describes the energy barriers for single adatom diffusion.

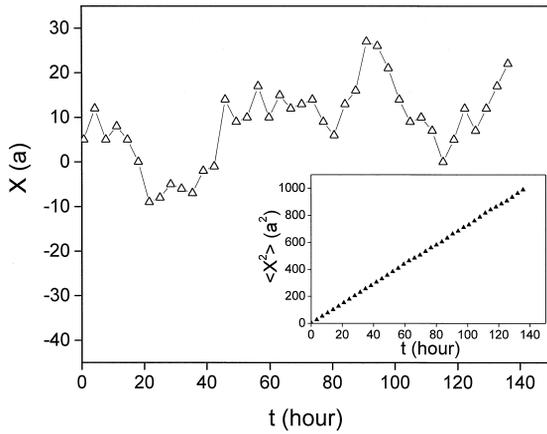


Fig. 2. A example of the records of the position of the four atoms chain after each 3.5 hours. a is the lattice constant of platinum. The inset gives the mean-square displacement, which is averaged from 10^3 runs.

for each atomic hopping can be given by the transition state theory

$$\nu_i = \nu_0 e^{-E_i/k_B T} \quad (2)$$

where E_i is the activation energy for diffusion. For all single atom jumps, the prefactor ν_0 is chosen as $\nu_0 = 10^{11} \text{ s}^{-1}$. The value of E_{up} and E_{down} are estimated to be 0.91 and 0.70 eV respectively from the STM studies [19], and the barrier for single-atom diffusion E_0 is chosen as 0.60 eV [20]. The clusters in our simulations are consisted of 3–7 atoms. Comparing with the average time for one lattice displacement of the cluster the mean lifetime of an atom in the metastable state is very short. Thus, the probability of two end atoms crawl to the cluster at the same time is expected to be negligible.

After giving a set of energy barriers for the individual atomic jumps, we can make kinetic MC simulations on the migration of Pt chains. Fig. 2 shows an example of the displacement of a four-atom chain at temperature $T = 350 \text{ K}$. Initially, the center of the chain is situated at $x = 0$ when $t = 0$. We record the position of the center of the chain at every other 3.5 hours. From Fig. 2 we can see that the displacement of the chain increases or decreases randomly. After an average of more than 10^3 runs, we obtain the time dependence of the mean-square displacement $\langle x^2 \rangle$ and find a good linear relation between $\langle x^2 \rangle$ and t (see the inset in Fig. 2). Accord-

ing to the theory of random walk [21], the diffusivity D or the displacement rate R can be obtained from the mean-square displacement from the equation

$$\langle x^2 \rangle = Nl^2 = 4Dt \quad (3)$$

where $N = Rt$ is the mean jump numbers of the cluster during time interval t , and l is the root-mean-square jump distance. R is the displacement rate which means the average number of the chain displacement caused by the leapfrog mechanism during one second. In our simulations we set $l = a$, with a being the lattice constant of platinum. From the slope of the line in the inset of Fig. 2 we obtain the displacement rate is $R \approx 2 \times 10^{-3} \text{ s}^{-1}$ at temperature $T = 350 \text{ K}$, which is closely similar to the data from STM experiment result.

In the same way, we make simulations on Pt clusters diffusion on Pt(110)– (1×2) surfaces at temperatures ranging from 320 to 390 K. Fig. 3 shows the cluster displacement rates versus inverse temperature. We make the simulations under two circumstances, 3 atoms and 6 atoms in the clusters, respectively. Compared with the data obtained from STM experiments, our simulations are in good agreement with the experimental results. From this figure we find that the simulation results with three atoms cluster are almost the same as that with six atoms cluster. This means that the influence of the cluster length on the cluster displacement rate is expected to

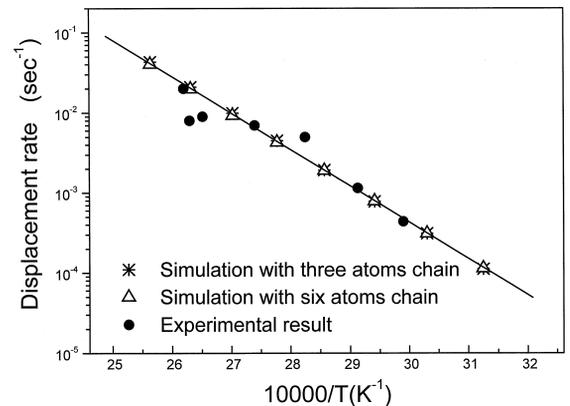


Fig. 3. Cluster displacement rates plotted versus inverse temperature from 320 to 390 K. The star points and the hollow triangular points are our simulation results, and the solid circle points are experimental results.

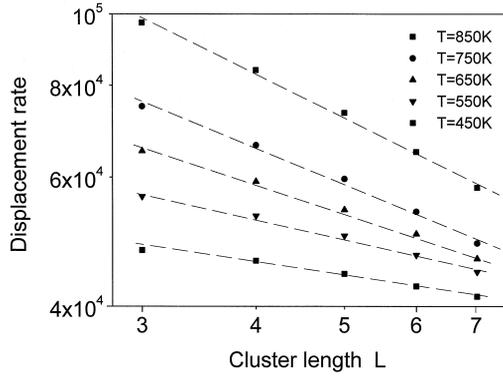


Fig. 4. The dependence of cluster displacement rate on cluster length for several different temperatures. The unit in vertical axis is 1 s^{-1} for $T = 850 \text{ K}$; 4 s^{-1} for $T = 750 \text{ K}$; 30 s^{-1} for $T = 650 \text{ K}$; 500 s^{-1} for $T = 550 \text{ K}$ and $3 \times 10^3 \text{ s}^{-1}$ for $T = 450 \text{ K}$.

be negligible. This is reasonable since the mean time τ for the cluster diffusing one lattice displacement, to a first approximation, is consisted of two parts: $\tau \approx \tau_1 + \tau_2$. Here, τ_1 is the average time of the end atom crawling to the cluster which is proportional to $\exp(E_{\text{up}}/k_{\text{B}}T)$, i.e., $\tau_1 \sim \exp(E_{\text{up}}/k_{\text{B}}T)$, and τ_2 is the average residence time for the atom on top of the cluster. The motion of the atom on top of the cluster is considered as a one-dimensional random walk in the range of $(0, L)$ with an edge energy barrier E_{down} . The mean time for the atom on top of the cluster is roughly dependent on the probabilities of two coherent events: random walking with a root-mean-square displacement L , and descending from the cluster with an edge barrier E_{down} . Thus, τ_2 is considered to be proportional to $\exp(E_{\text{down}}/k_{\text{B}}T)L^2$. At lower temperature, $\exp(E_{\text{down}}/k_{\text{B}}T)$ is a negligible quantity compared with $\exp(E_{\text{up}}/k_{\text{B}}T)$ (at $T = 350 \text{ K}$, for example, $\exp(E_{\text{down}}/k_{\text{B}}T)/\exp(E_{\text{up}}/k_{\text{B}}T) \sim 10^{-3}$), thus the average residence time at the metastable state τ_2 is negligible. This has also been observed in our simulations. For example, at $T = 350 \text{ K}$, the mean residence time for the atom on top of Pt chain is about 0.5 s , and the average time for one lattice displacement of the chain is near 500 s . The migration of the chain is dominated by the activation barrier E_{up} . Thus, the displacement rate R , which is the inverse of the mean time for one lattice displacement of the chain τ , i.e., $R = 1/\tau$, is only determined by $\exp(-E_{\text{up}}/k_{\text{B}}T)$ and is not associated with

the cluster length L . This leads to the length-independent displacement rate of the chain at lower temperature. However, as temperature increasing, the value of $\exp(E_{\text{down}}/k_{\text{B}}T)$ becomes more and more comparable to the value of $\exp(E_{\text{up}}/k_{\text{B}}T)$. This means that, at high temperature, the average residence time τ_2 for the atom on top of the cluster can not be neglected which is associated with the cluster length L . The cluster displacement rate is influenced by the length of the cluster at higher temperature. Therefore, there exists a temperature-dependent scaling relations between the displacement rate and the length of the chain.

In order to check our arguments and obtain a detail understanding of the scaling laws between displacement rate and chain length, we make further simulations on the diffusion of one-dimensional Pt chains at temperatures ranging from 450 to 850 K . We find that as the temperature is increased from 450 to 850 K gradually, the displacement rate of the chain becomes more and more dependent on the chain length. We plot the logarithm of the displacement rate $R(L)$ against the logarithm of the cluster length L in Fig. 4 for different temperatures. In order to show our results clearly, the units of the displacement rates in vertical axis of Fig. 4 are scaled with different factors for different curves (see the captions in Fig. 4). For each temperature, the straight line through the data points clearly indicates a power-law dependence of the displacement rate R on the cluster length L , i.e., $R(L) \sim L^{-\alpha}$. From the slopes of the lines the exponent α are obtained as follows: $\alpha = 0.18 \pm 0.01$ for $T = 450 \text{ K}$; $\alpha = 0.28$

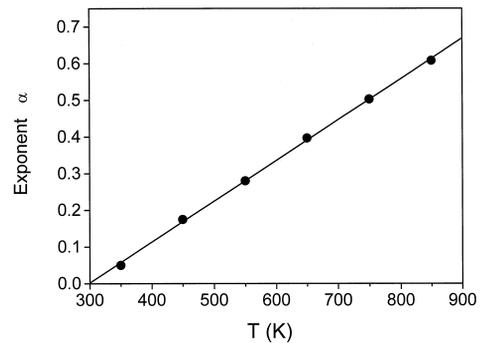


Fig. 5. The scaling exponent α plotted versus the temperature.

± 0.02 for $T = 550$ K; $\alpha = 0.40 \pm 0.02$ for $T = 650$ K; $\alpha = 0.50 \pm 0.02$ for $T = 750$ K and $\alpha = 0.61 \pm 0.02$ for $T = 850$ K, respectively. The dependence of the exponent α on the temperature T is shown in Fig. 5. We can see that as temperature increasing the exponent α increases linearly. This result indicates that, for the leapfrog diffusion of one-dimensional Pt cluster, as the temperature is higher than 350 K the influence of cluster length on the cluster diffusivity can not be neglected which leads to a length-dependent displacement rate and temperature-dependent scaling exponent α . Physically, the scaling exponent α depends on the competition between the average time of the end atom crawling to the cluster τ_1 and the average residence time on top of the cluster τ_2 for the atom. At higher temperature, τ_2 is comparable to τ_1 . This is quite different from the cases at lower temperature where τ_2 is a negligible quantity compared with τ_1 . Our result gives a novel scaling exponent for the one-dimensional leapfrog mechanism.

In summary, we have performed a kinetic Monte Carlo simulation study on one-dimensional diffusion of Pt chains on Pt(110)–(1 × 2) surfaces at temperatures ranging from 320 to 850 K. Our results show that the cluster displacement rates caused by the leapfrog mechanism are in good agreement with the STM experimental observations. Moreover, it is found that the influence of cluster length on the displacement rate is negligible at lower temperature and the displacement rate only depends on the temperature. However, as temperature increasing the effect of cluster length on displacement rate becomes more and more important. There exists a scaling law between the displacement rate and cluster length. We found that the scaling exponent α is temperature dependent. As temperature increasing the exponent α increases linearly.

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