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Structure and diffusion of small Ir and Rh clusters on Ir(001) surfaces

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Abstract

It is known that Ir adatoms diffuse on Ir(001) surface by atomic-exchange mechanism, whereas Rh adatoms diffuse on this surface by atomic-hopping mechanism. The question is how about their clusters, and how the mechanisms can affect their diffusion behavior and energetics. Using the field ion microscope, we have measured diffusion parameters of individual Rh and Ir adatoms and small clusters on Ir(001) surfaces. We also show how the activation energy changes as a function of the cluster size and shape. From the probability of observing different atomic configurations during diffusion, different diffusion mechanisms are investigated. By considering the energetics of different atomic processes, it appears that atomic-exchange is still favored for Ir dimers. But for clusters larger than trimers, the exchange mechanism is no longer favored. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

In epitaxial growth, deposited atoms can interact not only with the substrate, but also with one another. As a result, clusters of various sizes can be formed. Both the diffusion behavior and thermal stability of clusters can affect the mechanism of epitaxial growth through critical cluster size and diffusion kinetics. Understanding how individual adatoms and small atomic clusters move across the surface is therefore essential for developing atomic models for epitaxial and crystal growth. It may also shed light on adatom–adatom and adatom–substrate interactions. Through field ion microscope (FIM) studies, a considerable amount of experimental information is already available on the mechanisms and energetics of single-atom diffusion [1–3]. The migration behavior of small clusters on metal surfaces has also been studied experimentally [4–23] and theoretically [24–29]. Many questions, however, remain. In dimer diffusion, from a molecular-dynamics (MD) simulation [28], the activation barrier for Ir dimers is found to be higher than that for single adatoms, but an embedded-atom method (EAM) concludes differently [29]. Unfortunately, no experimental data are available. Contributions of dimer diffusion to growth phenomena have been investigated earlier. It is found to have only a minor effect for growth of Pt islands on Pt(111) [13], while it is important for growth of Pt islands on Pt(001) since the diffusion barrier of dimers of this system is found to be less than that of single-atoms [30]. An interesting question is whether or not these findings are also valid for other fcc metals. Also

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self-diffusion of dimers on some fcc(001) surfaces has been predicted to occur by atomic-exchange mechanism [28–30], but no experimental data are available for self-diffusion on Ir surfaces. Here from the probabilities of observing different atomic configurations of dimers as well as the energetics of various atomic processes, we will try to answer the question of whether or not dimer diffusion occurs by atomic-exchange.

On another property of clusters, stable 1D-chain configurations have been observed on some symmetric fcc(001) surfaces, such as Pt/Pt(001) and Ir/Ir(001) [16,17]. An interesting question is how the stable 1D-chain and 2D-island configurations affect cluster migration. Cluster shape can change during migration, especially for systems where the energy difference between stable structures and metastable structures is very small. For such clusters, the majority of displacements of the center of mass of the clusters can come from the shape change. In a recent FIM study [21–23], plots of the measured activation energy of surface diffusion as a function of the cluster size show a strong correlation between the mobility and the shape of the small clusters. The effect of shape change on the cluster diffusion has not been understood. Here we also report a measurement of the activation energy for surface diffusion of individual Rh and Ir adatoms and clusters on Ir(001) and study how the activation energy is affected by the cluster size and especially the shape. In addition, island mobility is known to be closely related to the early stages of thin-film growth [31]; we briefly discuss the relation of our results to the growth.

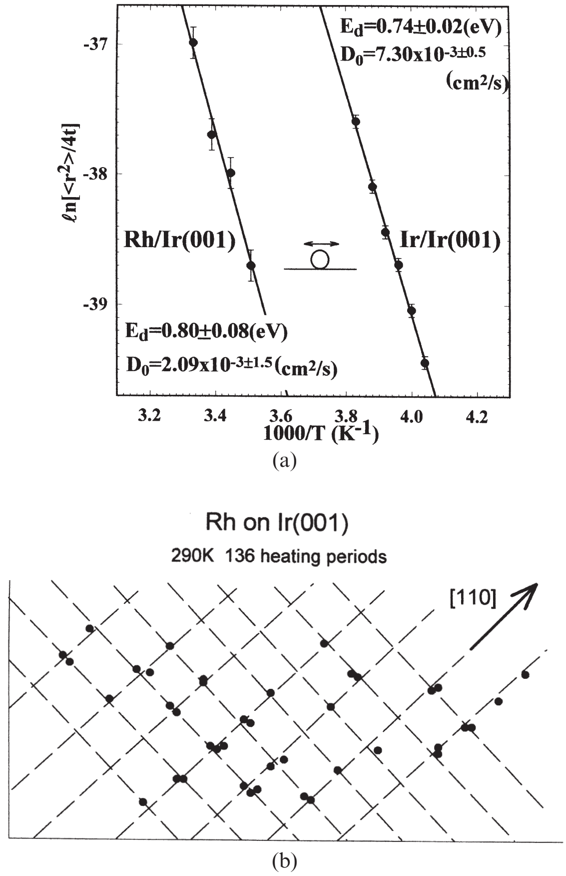
2. Experimental

All observations are made in an atomic resolution FIM. The instrumentation has already been described in detail elsewhere [1–3]. The procedures used in this investigation are the same as those used in our past FIM studies. Using a procedure first practised in 1972 [5], in this experiment we also strictly control the number of atoms in a cluster. In vapor deposition of atoms on the terrace of a sample, atoms are randomly distributed. Annealing the surface causes these single atoms to coalesce into clusters. Field evaporation can be used to reduce the number of atoms in a cluster. By repeating the procedure, a cluster of any given size can be prepared. For larger Ir clusters, preparation by coalescence of single atoms is more difficult than by terminating field evaporation right before the final collapse of the topmost surface layer. Heating is done by electronic controlled pulsed current power supply which can heat up the tip mounting loop in less than 0.5 s. Each heating period is 10 s in this experiment. When we refer to mean-square-displacement of a cluster, we always refer to the center-of-mass of the cluster.

3. Results and discussion

3.1. Single adatoms

Parameters for terrace diffusion of single Ir adatoms, or monomers, on Ir(001) have been measured before [32]. To be consistent in experimental conditions with our present study of diffusion of Ir clusters and Rh adatoms and clusters, in this study we also measure the diffusion parameters of individual Rh and Ir adatoms on Ir(001) surfaces. Fig. 1a shows Arrhenius plots for single adatom diffusion for Ir/Ir(001) and Rh/Ir(001). Interesting features are as follows. (1) A visited site mapping of a diffusing Rh adatom gives a (1×1) surface net as shown in Fig. 1b, thus Rh adatom diffuses on Ir(001) surface by atomic-hopping. Ir adatoms are already known to diffuse on Ir(001) surface by atomic-exchange, or the site visitation map is a $c(2\times2)$ surface net of the substrate [32,33]. (2) Rh has a lower cohesive energy than Ir (5.75 eV/atom vs. 6.94 eV/atom), one can therefore expect Rh atoms to have a lower activation barrier of surface diffusion than Ir adatoms. Our result shows a reversed order because of the very different diffusion mechanisms of the two systems. Atomic-exchange diffusion can occur for some systems because of its lower activation barrier compared with that for atomic-hopping. (3) Rh atoms have a slightly smaller atomic radius than Ir atoms, one would expect Rh atoms to exchange more easily with substrate Ir atoms. The fact that this does not occur implies that the effect



(a)

(b)

Fig. 1. (a) Arrhenius plots for diffusion of Ir and Rh adatoms on Ir(001) surface. (b) A site-visitation map for Rh on Ir(001) surface. This is a (1 × 1) surface net. It indicates that the diffusion mechanism for Rh on Ir(001) is atomic-hopping.

of atomic interaction is far more important than the size effect in determining the diffusion mechanism. Our result also indicates that at Ir(001) surface the strength of Rh–Ir bond is smaller than that of Ir–Ir bond.

3.2. Dimers

For both Ir_2 and Rh_2 on Ir(001), they are found to be more stable in the close-packed configuration than the configuration with the two atoms occupying the next-nearest-neighbor sites of the substrate. Frequent changes between two equivalent [110]-oriented configurations (nearest-neighbor sites) occur, but dimers oriented along the [100]-type directions (next-nearest-neighbor sites) have never been observed. This result clearly indicates that the nearest-neighbor (n-n) bond is attractive whereas the second n-n bond is either much less attractive or even repulsive. This is consistent with earlier experimental [18–20] and theoretical results [29].

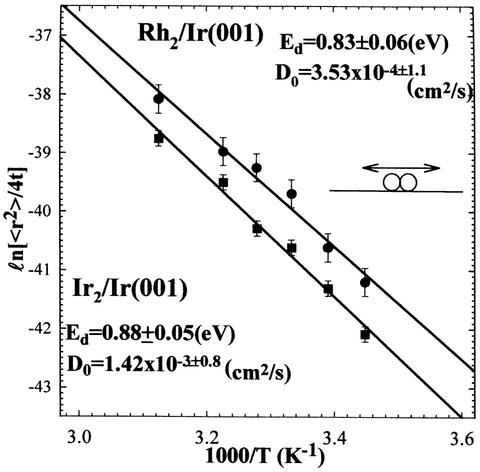


Fig. 2. Arrhenius plots for diffusion of Ir and Rh dimers on Ir(001) surface.

Diffusion parameters of Ir_2 and Rh_2 on Ir(001) are derived from plots shown in Fig. 2. What is most interesting is that, unlike individual Rh and Ir adatoms where the activation energy is higher for Rh than Ir, the diffusion barrier for Ir_2 is actually higher than that for Rh_2. Our result does not agree with the theoretical conclusion that the diffusion barrier for dimers is lower than that for single atoms, as predicted by EAM calculation [29]. The higher barrier for dimers predicted by MD simulation [28] is consistent with our result. Previous observations with FIM show that Pt dimers on Pt(001) or Rh(001) diffuse faster than the corresponding single adatoms, but the Rh dimers on Rh(001) diffuse slower than the corresponding single adatoms [21–23,30]. Among these systems, the diffusion mechanism of Pt/Pt(001) and Ir/Ir(001) is atomic-exchange while that of Rh/Rh(001), Rh/Ir(001), and Pt/Rh(001) is ordinary atomic-hopping. These results clearly indicate that the lower barrier in dimer diffusion of some systems is not necessarily a consequence of an

Table 1
Upper part lists the probabilities of observing reoriented displacements for Ir_2 and Rh_2. Lower part lists those of observing different diffusion steps for Ir_2. a is the lattice constant

Dimers	Temperature range (K)	Observed diffusion behavior	Probability (no. of observations)	Possible step
Ir_2	290–310	Reoriented displacement $\Delta \boldsymbol{r} = a/2$	85% (88)	1. Fig. 4a
Rh_2	290–310	Reoriented displacement $\Delta \boldsymbol{r} = a/2$	56% (81)	2. Fig. 4b
Ir_2	300–320	Reoriented displacement $\Delta \boldsymbol{r} = a/2$	50% (170)	Fig. 4a or b
		Pure displacement $\Delta \boldsymbol{r} = a/\sqrt{2}$	19% (65)	Fig. 4c
		Pure displacement $\Delta \boldsymbol{r} = a/\sqrt{2}$	6% (20)	Fig. 4d
		Pure displacement $\Delta \boldsymbol{r} = a$	12% (40)	1. Fig. 4f 2. Fig. 4f
		Others	13% (47)	Combine more than one elementary step

atomic-exchange mechanism. That the barrier is reduced by a weakened interaction with the substrate [27] may be the reason, but this may not be applicable to all systems.

It is, unfortunately, not yet possible to determine the diffusion mechanism for Ir dimers by a direct method as in the case of single adatom diffusion, but a detailed analysis of probabilities of observing different cluster configurations during diffusion can provide a very reliable conclusion. Table 1 lists some of our results. The probabilities of observing different diffusion steps at the temperature range 290–310K for Ir_2 and Rh_2 are listed in the upper part of Table 1. Fig. 3 shows FIM images of an Ir dimer where its orientation has changed during a diffusion step. Fig. 4 shows model of several possible elementary atomic steps which give the observed displacements and orientation changes. The term elementary here means these steps involve the least number of atomic jumps possible, and any other displacement can be considered a combination of these elementary steps. From Table 1, one finds that the orientation change of Ir_2 is more frequent than Rh_2. Diffusion by translation for Ir_2 is rarely observed below 300 K, but becomes more frequent at higher temperature. This indicates that diffusion steps with an orientation change are energetically favored for Ir_2. An orientation change can occur in two elementary diffusion steps, namely Fig. 4a and b. Fig. 4a shows a mechanism where one atom exchanges with a substrate atom. The same displacement and orientation change can also be produced by a hopping mechanism as shown in Fig. 4b. The intermediate state, having a configuration of two atoms occupying next-nearest-neigh-

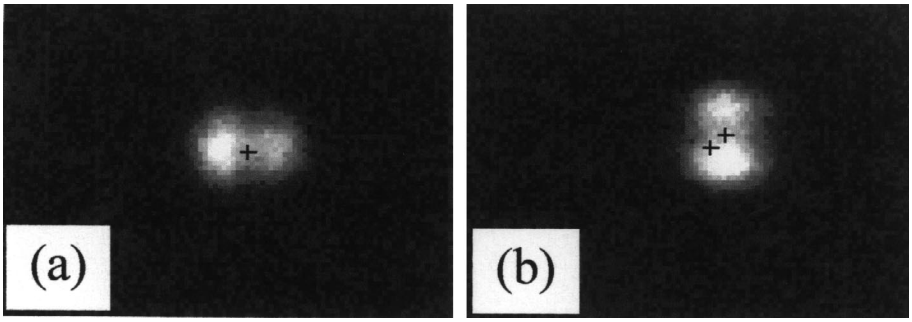


Fig. 3. FIM images of an Ir dimer diffusion at 300 K. The symbol "+" indicates where the center of mass of the dimer is. When a reorientation occurs, the center of mass also displaces by a distance $a/2$ in the ⟨100⟩-direction.

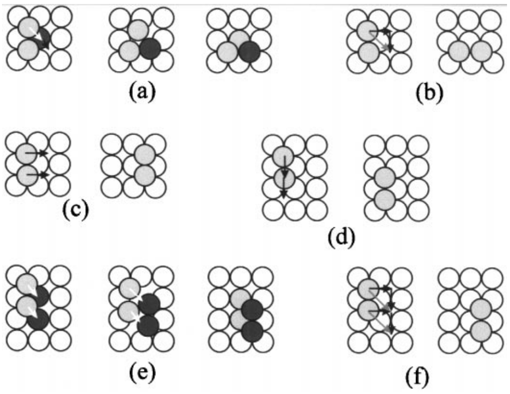


Fig. 4. Possible elementary steps which produce displacements and orientation changes in diffusion of Ir or Rh dimers on the Ir(001).

bor sites, has already been determined to have an energy 0.43 eV higher than the most stable nearest-neighbor configuration [20]. The difference in the activation energies of diffusion of Ir dimers and single atoms is only 0.14 eV. In addition, the MD simulation and EAM calculation both show a more than twice higher energy needed for Fig. 4b than for Fig. 4a [28,29]. We do not believe therefore that the atomic step of Fig. 4b can occur for Ir_2/Ir(001), or Ir_2 dimers diffuse most likely by the atomic-exchange mechanism shown in Fig. 4a. Of course, it is still possible that Ir_2 diffuses by concert rotational motion around a substrate atom, but this will have to lift the two Ir adatoms somewhat higher above the substrate. This may not be energetically feasible at low temperatures. The mechanism of Fig. 4b only occurs for systems where no exchange can occur, such as Rh_2 on Ir(001).

In the temperature range between 290 and 310 K, 15% of the time Ir dimers displace without changing their orientations. Their displacements are either $a/\sqrt{2}$ or a. Such displacements can occur by one of the steps shown in Fig. 4c–f, or by a proper combination of steps shown in Fig. 4. At the moment, we have no direct method for figuring out which of these steps is responsible for the observed displacements. We nevertheless can estimate the energy difference between the exchange mechanism of Fig. 4a and the other atomic steps. This difference is $\sim kT\ln(85/15)=0.04$ eV, a surprisingly small difference.

The atomic-exchange mechanism appears to be the favorable mechanism in diffusion of Ir_2 on Ir(001) surface, but not for diffusion of Rh_2 on Ir(001) for the following reason. If atomic-exchange occurs for Rh_2/Ir(001), the dimer would soon become Ir_2 after several diffusion steps, but the observed mobility does not find such a change. As we have already explained before, diffusion of single Rh adatoms does not occur by atomic-exchange because the Rh–Ir bond is weaker than the Ir–Ir bond, thus Rh dimers cannot diffuse by atomic-exchange either. Therefore, Rh_2 diffuses by hopping across the top site or two bridge sites as shown in Fig. 4b to produce an orientation change, most likely by two bridge sites. Intuitively, if diffusion occurs by atomic-hopping, then the energy barrier of reoriented displacement of Fig. 4b should be similar to that of translated diffusion of Fig. 4c. This is the reason why about half of the steps of Rh_2 are reoriented, and half are not reoriented.

Information on mechanisms of diffusion can also be investigated with the displacement distribution function [34]. We have also measured the displacement distributions for diffusion of Ir_2 at different temperatures. It is known that the displacement distribution in discrete random walk is given by

$$W(x)=\exp(-\bar{N})I_x(\bar{N}),$$

where

$$I_x(\bar{N})=\sum_{k=0}^{\infty}\left(\frac{\bar{N}}{2}\right)^{(x+2k)}/k!(x+k)!$$

is the modified Bessel function of the first kind [35], and $W(x)$ represents the probability of making x times elementary jumps with the given average number of elementary jumps. Our experimental data are shown as shaded bars in Fig. 5. The error bars show these data are statistically significant. The unshaded bars are theoretical displacement distributions using experimental mean jump numbers and also assuming that only the elemental diffusing steps of Fig. 4a or b occur. These two elementary atomic steps produce the

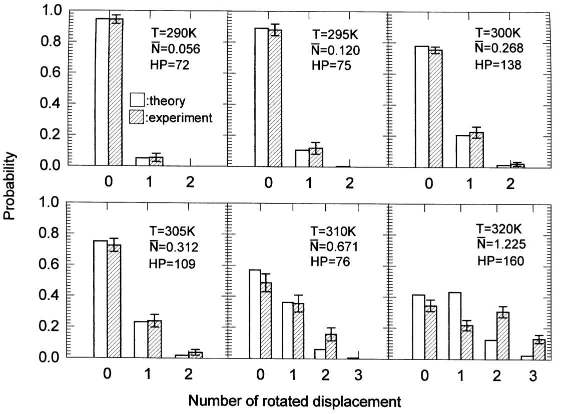


Fig. 5. The unshaded bars are theoretical displacement distributions using experimental mean jump numbers and also by assuming only the displacement step of Fig. 4a can occur. The shaded bars are experimental displacement distributions. The error bars show the statistical uncertainty. HP represents the number of heating periods.

same observable features, and thus cannot be distinguished from displacement distribution measurements alone. As one can see from Fig. 5, below 300 K, the experimental distribution functions agree nearly perfectly with theoretical displacement distributions. This result therefore supports the occurrence of either one or both of the two mechanisms. Earlier, from an energetic consideration, we have already argued in favor of the mechanism in Fig. 4a.

The higher the temperature from 300 K, the worse the agreement becomes, indicating that some other elementary atomic steps such as those shown in Fig. 4c–f can also occur. From Table 1, it can be seen that translated motion of Ir_2 dimers in the direction perpendicular to the dimer axis (Fig. 4c) is more frequent than that in the direction parallel to the dimer axis (Fig. 4d). These two steps can also be achieved by two rotated steps of Fig. 4a. However, if these two steps are produced by only steps of Fig. 4a, then steps of Fig. 4c and d should occur with the same probability. The fact our data listed in Table 1 do not show the same probability clearly indicates that these steps can occur also, or they are real elementary steps. Of course, the step of Fig. 4a is energetically highly favored compared with either the step of Fig. 4c or d. The EAM calculation of Chang et al. [29] is consistent with our result. Another question is whether the steps shown in Fig. 4e and f are elementary or not. If they are not, then it can easily be argued that the probability of observing steps with a displacement a should be much smaller than that with a displacement $a/\sqrt{2}$. Our data does not show this feature, thus either Fig. 4e or f should also be an elementary step. Obviously, Fig. 4f cannot be one since this step involves hopping of an atom over the apex site of a substrate atom which is energetically highly unfavorable.

Based on the probability analysis described, we can now conclude the following. (1) Atomic-exchange mechanism is energetically favored for diffusion of Ir dimers, thus it is the most likely mechanism pending on some unforeseen mechanisms. (2) When the temperature is raised, other mechanisms can start to occur due to the relatively small activation energy difference. We have also established from displacement distributions the occurrence of different elementary steps. When the number of atoms in the cluster is increased, many more possible mechanisms can occur. Determination of the activation energy of cluster diffusion by Arrhenius plots becomes more and more difficult, since beside the complicated structure changes, the size of facets available on a field ion emitter surface becomes a little too small for such a study.

3.3. *Trimers*

A small cluster with three or more atoms can have both a 1D and more than one 2D structures. Three-atom clusters (trimers) are the smallest clusters which can have 1D and 2D structures on the surface. Early studies found that 1D chain structure is more stable for Ir_3 on Ir(001). The relative pair interaction at three different bond lengths was derived from the relative binding energies of different structures [18–20]. Here we report observations of different diffusion behavior of Ir_3 and Rh_3 on Ir(001).

Table 2 lists measured mean-square displacements, and calculated activation barriers for Rh_3 and Ir_3 of different structures based on an approximation that D_0 is given by $1\times10^{-3}\,\mathrm{cm}^2/\mathrm{s}$. It is

Table 2
Measured mean-square displacements and activation barriers obtained for Rh and Ir clusters

Clusters	Structure	Temperature (K)	Mean-square displacement (Å^2)	Activation energy[a] (eV)	Number of observations	Average activation energy (eV)
Rh_3	2D	260	0.73	0.76	37	
		270	0.81	0.78	24	0.77
	1D	330	2.59	0.93	30	
		340	9.88	0.92	34	0.92
Ir_3	2D	280	0.88	0.81	25	0.81
	1D	370	1.59	1.06	70	
		390	2.44	1.10	160	1.09
Rh_4	2D	290	2.69	0.82	30	0.82
	1D	330	2.38	0.93	116	0.93
Ir_4	2D	300	1.42	0.86	13	0.86
	1D	380	1.38	1.09	136	
		390	3.11	1.09	90	1.09
Rh_5	2D	310	2.12	0.88	29	0.88
Ir_5	1D	380	1.03	1.10	105	1.10
Rh_6	2D	310	1.36	0.89	69	0.89
Ir_6	1D	390	2.06	1.11	25	1.11
Rh_7	2D	300	0.66	0.88	45	0.88
Rh_8	2D	310	0.93	0.90	123	0.90

[a] Calculated assuming $D_0 = 1 \times 10^{-3}$ cm^2/s.

most interesting to note that the activation energies for Ir_3 clusters to change shape or to migrate on Ir(001) are much higher than those for Rh_3. This behavior is already apparent for dimers but the difference there is much smaller. As further discussions will make clearer, the activation energies for diffusion of Ir clusters are always larger than those for Rh clusters, except for monomers, or single adatoms. This fact shows clearly that, except for single adatoms and Ir dimers, the atomic-exchange mechanism is not necessarily energetically favored for Ir clusters. Another interesting observation is that for diffusion of 2D Rh_3 clusters on Ir(001), the activation barrier is smaller than that for single Rh adatoms.

In Fig. 6, we show all possible elementary atomic steps which can produce the same orientation changes and displacements observed in the trimer diffusion. In diffusion of Ir and Rh 2D trimers, the mechanism shown in Fig. 6a has a much lower activation barrier. For Rh_3, the activation energy is even lower than that for single Rh adatoms. A molecular statistics calculation [30] may offer an explanation. Examination of the saddle-point geometry shows that the hopping atom is closer to the other two atoms of the trimer than it would be if it were in the saddle position in monomer diffusion. In fact, the hopping atom at the bridge site is four-fold coordinated with the other two atoms of the trimer present. This higher coordination at the saddle point during the trimer movement results in a decrease of activation energy. Table 2 shows that the diffusion temperature due to a 2D structure change is much lower than that for diffusion of a 1D cluster. The possible mechanisms of a 2D structure change are shown in Fig. 6a–b′. When the temperature is a little higher than 290 K, most of the observed 2D Ir_3 cluster diffusion events are produced by changing the structure from 2D to 1D. Possible mechanisms are shown in Fig. 6c and d.

To find out whether diffusion of Ir_3 is by atomic-exchange mechanism or not, one can use a binding site mapping for the center atom of the clusters. The observed (1 × 1) [not c(2 × 2)] pattern with sides parallel to the ⟨110⟩ directions indicates that atomic-exchange is not the only mechanism. At least, the atomic-hopping mechanism shown in Fig. 6a is also energetically accessible. In fact, atomic-exchange mechanism is not the energy

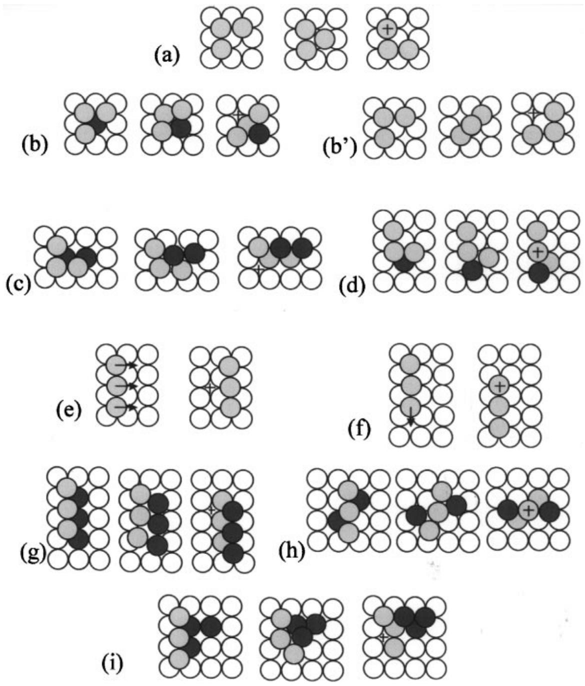


Fig. 6. Possible elementary atomic steps which can produce the same displacements and orientation changes observed in diffusion of Ir or Rh trimers on Ir(001) surface. Arrows indicate the directions of atomic motion, and crosses indicate the center atoms of trimers before the motion.

favored mechanism for Ir_3/Ir(001). Table 3 lists an analysis of the observed different probabilities. The results of Rh_3/Ir(001), where no atomic-exchange mechanism is expected, are used to compare with the results of Ir_3/Ir(001). No obvious difference between the behavior of Rh and Ir trimers indicates that there is no evidence of atomic-exchange mechanism in diffusion of Ir_3. For 2D trimers, if the exchange mechanism were energetically favored, the probability of diffusion step shown in Fig. 6b should be higher than that of Fig. 6a. That this is not the case shows the exchange mechanism is no longer favored for Ir trimers. The fact that the probability of atomic step shown in Fig. 6b is quite high may indicate that the atomic step shown in Fig. 6b′ can also occur. For 1D trimers, the probabilities of the occurrence of all the different diffusion steps are somewhere around 10–20%. There appears to be no particular energetically favored elementary atomic steps.

3.4. *Effects of size and shape in cluster diffusion*

Table 2 also lists the measured mean-square displacements and calculated activation energies for Ir_x ($x=4,5,6$) and Rh_y ($y=4,5,6,7,8$) clusters. If a chain remains a chain after diffusion, we list the cluster structure as 1D. Otherwise, we list the structure as 2D. Plots of the measured onset temperatures of diffusion and the calculated activation energies of diffusion as a function of cluster size are shown in Figs. 7 and 8. Interesting features

Table 3
Probabilities of different diffusion mechanisms for Ir_3 and Rh_3

Trimers	Temperature range (K)	Observed diffusion behavior[a]	Probability (no. of observations)	Possible step
2D Ir_3	270–290	As Fig. 6a	65% (13)	1. Fig. 6a
		As Fig. 6b	35% (7)	2. Fig. 6b or b′
2D Rh_3	260–280	As Fig. 6a	59% (24)	1. Fig. 6a
		As Fig. 6b	41% (17)	2. Fig. 6b or b′
1D Ir_3/Rh_3	380–400/330–350	Pure displacement $\Delta \boldsymbol{r}=a/\sqrt{2}$	17% (27)/13% (10)	Fig. 6e
		Pure displacement $\Delta \boldsymbol{r}=a/\sqrt{2}$	9% (14)/12% (9)	Fig. 6f
		Pure displacement $\Delta \boldsymbol{r}=a$	22% (35)/14% (11)	Fig. 6g or Fig. 6e and f
		Reoriented displacement $\Delta \boldsymbol{r}=0$	15% (24)/14% (11)	Fig. 6h by either exchange or hopping
		Reoriented displacement $\Delta \boldsymbol{r}=a/\sqrt{2}$	18% (28)/25% (19)	Fig. 6e and h or Fig. 6f and h
		Reoriented displacement $\Delta \boldsymbol{r}=a$	16% (25)/12% (9)	Fig. 6i or Fig. 6g and h
		Others	3% (5)/10% (8)	Combine more than two elementary steps

[a] a is a lattice constant.

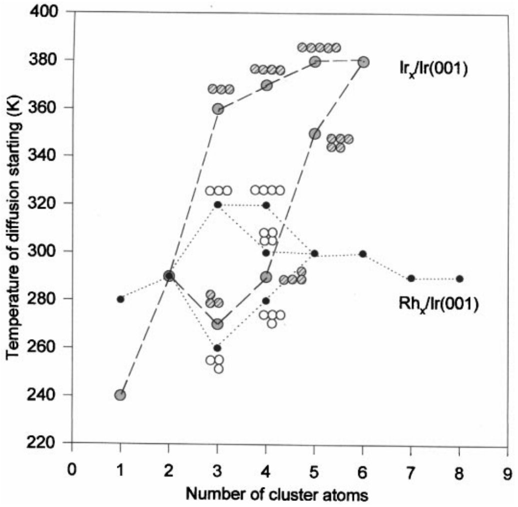


Fig. 7. Cluster structure specific onset temperature of diffusion versus the cluster size for Ir/Ir(001) and Rh/Ir(001).

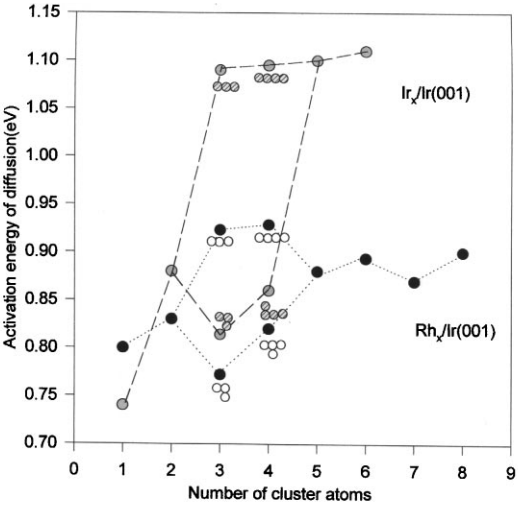


Fig. 8. Cluster structure specific activation energy of diffusion versus the number of cluster atoms for Ir/Ir(001) and Rh/Ir(001).

are the following. (1) Except for single adatoms, the diffusion barriers of Ir clusters are higher than those of Rh clusters. The reason is again due to the weaker Rh–Ir bonds. (2) In discussing center of mass displacement of a small cluster, we have to distinguish carefully that produced by a cluster structure change and that produced by a true displacement of all the cluster atoms. The displacements of 1D chain structures are the true displacements of the entire chain. The displacements of a 2D structure can usually be produced by the movement of one or two atoms along an atomic row forming the boundary of the cluster like that shown in Fig. 6a. This can occur at quite low temperatures. Often the 2D structures are less stable with respect to shape change than 1D structures. Only at a slightly higher temperature can frequent transformation of the structures from 2D to 1D occur, but not the reverse. The transformation of the structures is also the source of displacements of the cluster center of mass. If different sources of displacements are not carefully separated, the size dependence of cluster mobility will show an oscillatory feature [21–23], as that of Rh_5 to Rh_8 shown in Fig. 8, which may not be real in long distance diffusion. We control the temperature carefully to make the different kinds of diffusion steps distinguishable, and derive structure specific activation energies of different cluster shapes. We show only the differences in the onset diffusion temperature if the number of observations of a particular cluster shape is statistically insufficient for deriving the activation energy. (3) The diffusion barriers for 1D Ir trimers, tetramers, pentamers, and hexamers are found to be quite similar, suggesting a common rate-determining step in the migration process. The rate-determining step may be for a cluster atom to break from an end of the chain to become a free atom, since at only slightly higher temperatures than which they can start to diffuse, atoms at the two ends of the clusters can also start to dissociate, or detach from the clusters. (4) That the critical cluster size in nucleation and growth theory is dependent upon the temperature is generally recognized in the literature [36,37]. The results shown in Fig. 7 can be used to determine the temperature regime of the critical nucleus size in classical nucleation theory. In classical nucleation theory [36,37], the steady-state island density, N, which relates to the adatom diffusion constant D and the deposition flux F, is given by

$$N \sim \left(\frac{D}{F}\right)^{-P} \exp\left[\frac{E_i}{(i+2)k_B T}\right]$$

where $p=i/(i+2)$ is the growth exponent, i is the critical nucleus size defined by $i=s-1$ with s representing the minimum size of the stable island, E_i the cohesive energy of the critical-sized island, T the sample temperature, and k_B the Boltzmann constant. FIM experiments can be interpreted to show that the critical nucleus size, i, is dependent on the temperature. For Ir/Ir(001), a single dimer and all other larger islands are stable below 290 K, thus $i=1$ below this temperature. When the temperature is in the range 290–380 K, clusters with a size greater than 2 are stable, thus $i=2$. Since at ~440 K, step edge atoms of large clusters having over 100 atoms can start to dissociate from the clusters, no critical nuclear size really exists above this temperature. The cluster size distribution then depends on the average density of atoms on the terrace.

4. Summary

Diffusion of Rh adatoms and clusters on Ir(001) is found to proceed by atomic hopping. As to diffusion of Ir adatoms and clusters on Ir(001), single Ir adatoms are already known to diffuse by atomic-exchange. For dimers, the exchange mechanism, which can result in an orientation change in each elementary atomic step, appears to still be favored for Ir dimers. Our data clearly show, however, that other mechanisms can also occur at higher temperatures. For Ir trimers and larger clusters, there is no evidence that the atomic-exchange mechanism is either favored or occurs at all. The activation energies of diffusion for individual Rh and Ir adatoms and clusters on Ir(001) surfaces have been measured and analyzed. The size and shape dependence of cluster mobility is expected to play an important role in defining the nature of crystal and epitaxial growth processes at different temperatures. What we have presented here are phenomena on the atomic scale. How the behavior of single adatoms and clusters on the surface is related to standard macroscopic nucleation theories is a subject worthy of further investigations.

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