Energetics of surface atomic processes near a lattice step

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(Received 9 March 1998)

An atomic step of a solid surface can act as not only a reflective or nonreflective boundary but also as an atom-trapping boundary. Using the field ion microscope, we have probed in detail the behavior of Ir adatoms at and near the steps of Ir(001) and Ir(111) surfaces. Activation barrier heights of various atomic processes at step boundaries and the atom-trapping strengths of step-edge sites have been measured. These two surfaces exhibit entirely different step properties. At the terrace near the steps of Ir(111), an empty zone of adatom occupation is found the width of which depends on the terrace size. The difference in the reflective barrier heights of A-type and B-type step edges of Ir(111) layers is also derived. [S0163-1829(98)05528-3]

I. INTRODUCTION

Solid surfaces have many lattice steps. In epitaxy, aggregation of deposited atoms into islands or clusters during their diffusing can create many additional atomic steps. Atomic step boundaries will or will not reflect and trap diffusing atoms and molecules. Steps can therefore have a profound effect on surface phenomena where transport of atoms or molecules, or surface diffusion, across the surface is involved.[1] Such phenomena include surface reconstruction, crystal shape change, surface-enhanced chemical reactions, growth of crystals and epitaxial films, and so on. In a field ion microscope (FIM) study of random walk diffusion for tungsten adatoms on tungsten surfaces, Ehrlich and Hudda[2] noticed that these adatoms were reflected by step boundaries. Possible effects of such reflection boundaries to atom transport and growth phenomena were discussed by Schwoebel.[3] Using the single-atom tracing and mapping technique, Tsong observed that an adatom could also cross the step boundary and be trapped in a step-edge site near room temperature.[4] Wang and Tsong[5,6] measured the extra-barrier heights of several $5d$ transition metal adatoms at bcc $W(110)$ steps to be ~ 0.2 eV. Scanning tunneling microscope (STM) measurements find similar barrier heights for Pt/Pt(111) and Ag/Ag(111).[7] The importance of reflective property of steps to epitaxy has recently been emphasized and studied in detail.[8–10]

Other important parameters of a step are the trapping strengths of different step-edge sites. Burton, Cabrera, and Frank considered step-edge sties to be perfect sinks for incoming atoms that could produce step flow in standard nucleation and growth theory of epitaxy.[11] Recently Chen and Tsong, and Fu *et al.* found that the detachment of step-edge atoms of Ir(001) and (111) surfaces can already occur at relatively low temperatures of a few hundred K,[12–14] thus step-edge sites are not perfect sinks even at relatively low temperatures. In order to understand the nature of growth processes at different temperature ranges, it is important that we have the energetics data and consider both the atom-reflection and atom-trapping properties of the steps simultaneously. Most studies of thin-film epitaxy were performed on fcc metals, but only very limited amount of energetics data are available for fcc metals.[15] Here, we report a detailed quantitative measurement of the reflection barrier heights at step boundaries and the atom trapping strengths of step edge sites of fcc Ir(001) and (111) surfaces. FIM data are obtained under very-well-defined experimental conditions, thus data interpretations are often straightforward, or without the need of extensive theoretical modeling. Base on our data, we will then discuss briefly how the growth structure can be affected by various step barriers for Ir/Ir(001) and (111).

II. METHODS AND RESULTS

A. Reflective steps

Before presenting our experimental results, we would like to define a few terms. We will call the "descending" side of a step the α side and the "ascending" side the β side. The physical shape of the step is not as important as the potential energy surface of the atom-surface interaction near the step. A point of greater symmetry is the step-edge site, which is usually an atom-trapping site. In Fig. 1, a potential-energy diagram near the step is shown where, for simplifying our discussions, we will include only the more important barriers of various atomic processes. ΔE_b, ΔE_e, E_b, E_α, and E_β are important parameters that determine the step properties. They are also what this experiment measures. E_b and ΔE_b are the barrier height and the extra-barrier height for a diffusing adatom to cross the α step, E_α and E_β are the barrier height for a step-edge atom to detach to the α and β side, and ΔE_e is the extra strength of the binding energy of a step-edge atom compared to an adatom.

To derive ΔE_b, the extra barrier height of the α step, we need to know the average number of times a diffusing adatom on a finite plane encounter the step boundary $\langle N_b \rangle$ during a heating period of length τ at a given temperature. For a general shape of a two-dimensional (2D) island,[5]

$$\langle N_b \rangle = g \langle N \rangle,$$

where $\langle N \rangle$ is the average number of atomic jumps during the heating period, g is the geometrical factor of the island size and shape. $g = 1/M$ for a linear (1D) lattice of M sites, $g \sim 2l/\pi R$ for a circular plane of radius R, and $g \sim (l/\pi)[(1/a)+(1/b)]$ for an elliptical plane of major and
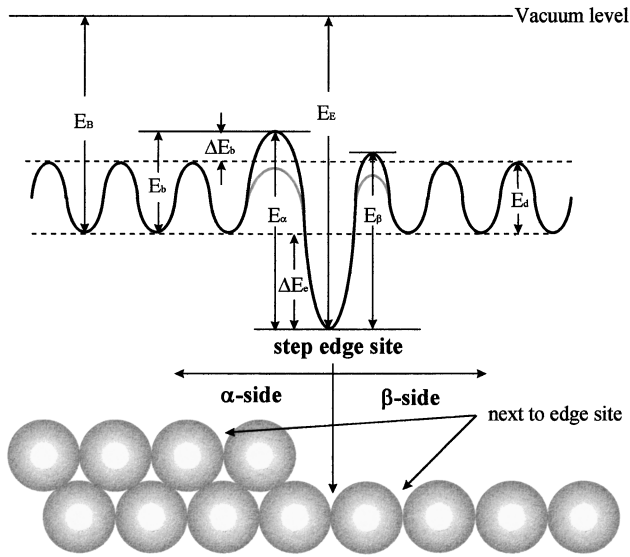
FIG. 1. Potential-energy diagram illustrating atom-substrate interaction near a step. The step-edge site is taken to be the reference point. E_B and E_E are, respectively, the binding energy of an atom in the adsorption site at the terrace and in the step-edge site. One notices also $E_\alpha = E_b + \Delta E_e$. ΔE_b is the extra-barrier height that an adatom has to overcome to reach the step-edge site from the α side; ΔE_e is the extra well that an edge atom has to overcome to detach the step-edge site to the α side or β side.

minor axes a and b. The probability P_b for an adatom to overcome a plane boundary within a heating period is related to $\langle N_b \rangle$ and ΔE_b by

$$P_b/(1-P_b) \sim \langle N_b \rangle \exp[(-\Delta E_b)/kT]$$
$$= g \nu_0 \tau \exp[-(E_d + \Delta E_b)/kT],$$

where the approximation sign accounts for the assumption that the number of paths for moving over the boundary is the same as the number of paths for moving inwards, or moving away from the boundary toward the middle of the plane. Thus by measuring P_b and plotting $ln[P_b/(1-P_b)]$ versus $1/T$, one obtains a straight line of the slope $-(E_d + \Delta E_b)/k$, and the intercept $ln(g\nu_0\tau)$. Comparing with diffusion energy E_d, the extra activation barrier at the plane edge ΔE_b can be determined.

1. Reflective barriers of Ir(111) and Ir(001) surfaces

We measure the terrace diffusion barriers of individual Rh or Ir atoms on Ir(100) surface first. Results for the diffusion parameters of Ir/Ir(001) and Rh/Ir(001) are shown in Fig. 2. Data and barrier heights of step boundaries for Rh/Ir(001), Ir/Ir(001) and Ir/Ir(111) we have obtained are shown in Fig. 3. The barrier height of an Ir adatom to cross the α step of Ir(001) is found to be slightly lower than that of terrace diffusion, 0.72 ± 0.08 versus 0.74 ± 0.02 eV. On the other hand, the barrier height of Rh adatom to cross the α step of Ir(001) is slightly higher than that of terrace diffusion, 0.84 ± 0.08 versus 0.80 ± 0.08 eV. A very surprising finding is the barrier height for an Ir adatom to cross the α step of Ir(111) is twice as high as that for terrace diffusion,[16] 0.41 ± 0.03 versus 0.21 ± 0.03 eV. For Ir/Ir(111) and Rh/Ir(001), the barrier to cross the α-step edge is represented by the dark line in Fig.
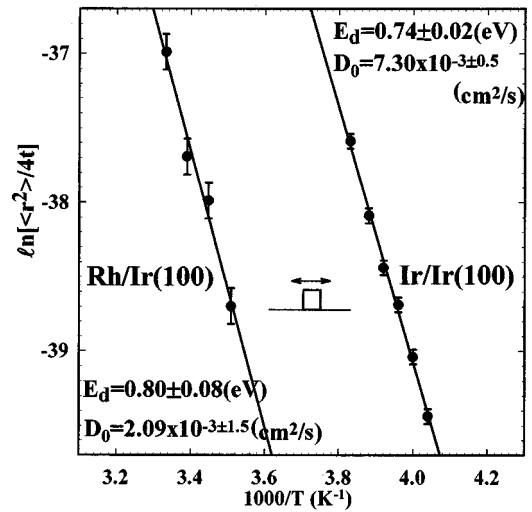

FIG. 2. Arrhenius plots for diffusion of Ir and Rh adatoms on Ir(001) surface.

1. The steps are reflective. For Ir/Ir(001), the barrier is represented by the gray line. The step is nonreflective. This difference may arise from different atomic mechanisms for an adatom to cross the α step. An Ir adatom diffuses on an Ir(001) terrace by atomic exchange.[17] At the step, an adatom may cross the step by pushing a substrate atom out by one step, and by taking its site as shown in Figs. 4(a)–(c). Our present experiment finds that for Rh/Ir(001), terrace diffusion is by atomic hopping. An adatom may cross the step by hopping over a bridge site at the step edge. This barrier is slightly higher than that of terrace diffusion, since when the adatom is at the bridge site, there is no substrate layer atoms at the other side of the step. We note that even if step boundaries are reflective, the extra barrier height for crossing an α step is very small, only a small fraction of the barrier of terrace diffusion. The only exception we have found so far is Ir/Ir(111). For this system, the barrier height for crossing the
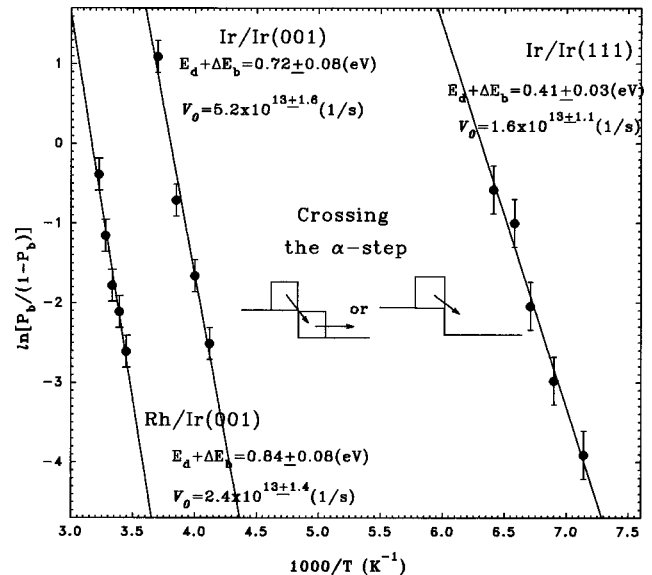

FIG. 3. A determination of $(E_d + \Delta E_b)$ for Ir adatoms to step down the Ir(001) and (111) step and Rh adatoms to step "down" the Ir(001).
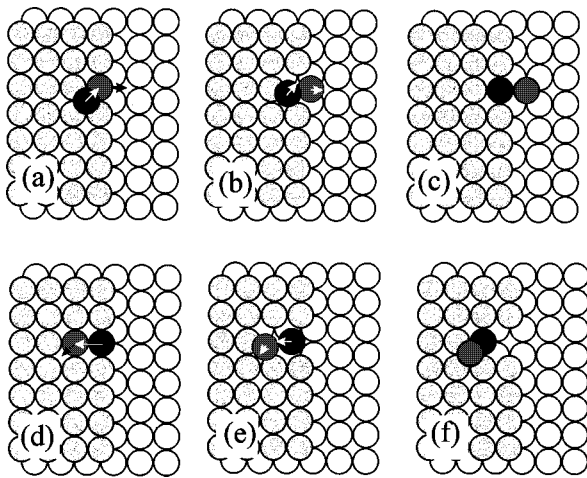
FIG. 4. (a)–(c): Schematic drawings illustrating the exchange mechanism of descending. (d)–(f): schematic drawings illustrating the exchange mechanism of ascending. The sample is fcc(001) surface of top view. The gray circles indicate the top-layer atoms, the white circles indicate the second layer, and the arrows indicate the direction of motion.

α-step edge is twice as high as that of terrace diffusion. But even so, step crossing can already occur at a temperature around 200 K. We must clarify that the above measurements are the average effect. For a more detailed consideration, the extra barrier for crossing an α step is, in fact, sensitive to the atomic arrangements of the steps and also the step-edge effect is very long range as described below.

2. Effect of atomic configuration to reflective α steps of Ir(111)

There are two different types of steps of Ir(111), i.e., A-type (having a {100} edge-atom configuration) and B-type (having a {111} edge-atom configuration) steps. It is conceivable that these two types of steps may have different reflective barrier heights, since their atomic configurations are different. Lower onset temperature for an atom to cross B-type steps has been reported[18] whereas theoretical prediction sug-
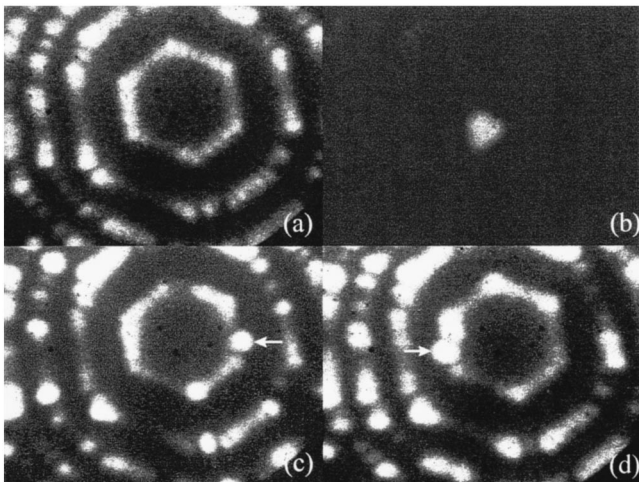

FIG. 5. Field ion images showing (a) a perfect hexagon shaped island, (b) a deposited adatom, and (c) the adatom to have crossed the α step of an A-type step, and (d) of a B-type step.
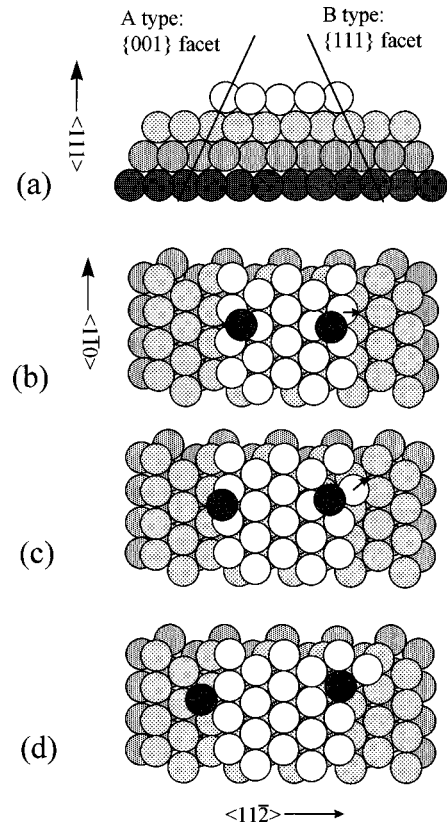

FIG. 6. (a) Schematic representations of A-type and B-type step edges (side view). (b)–(d): Schematic drawings illustrating the possible mechanism of descending to A-type or B-type step edges (top view).

gests a higher barrier[19,9] if one considers an atom to cross the step by atomic hopping. A very careful and time-consuming experiment was performed to determine this difference. First, an island of perfect hexagonal shape was prepared by controlled deposition and field evaporation of atoms followed by annealing of the surface until it became a perfect hexagon[12] as shown in Fig. 5(a). Then, one Ir atom was deposited onto the hexagon shaped island as shown in Fig. 5(b). After several heating periods of 10 s each at 180 K, the adatom was found to have crossed the α step. We then check from which type of the steps, A step or B step, the adatom crossed the step. Figure 5(c) shows a case where the atom crossed an A-type step and Fig. 5(d) a B-type step. This unambiguous identification is possible because ledge atom diffusion can occur only above ~ 250 K,[13] whereas crossing of steps can occur already at 180 K. The time consuming nature of the experiment comes from the fact that we have to prepare a new island every time to avoid the existence of an irregular site at the ledge atom site of the step. In addition, if the number of deposited atoms is over one, whether they are on the top layer or the second layer, the results cannot be used. In this experiment, out of a total of 58 runs, the number of atoms crossing A steps is 18 and that of crossing B steps is 40. This result shows that B steps have a slightly lower reflective barrier than A steps by $\sim kTln(40/18) = 0.012$ eV. Although this difference is only 3% of the average reflective barrier height, it can be measured. The different reflective barrier heights of these two step types can be expected, since the step crossing mechanisms resulting from different atom
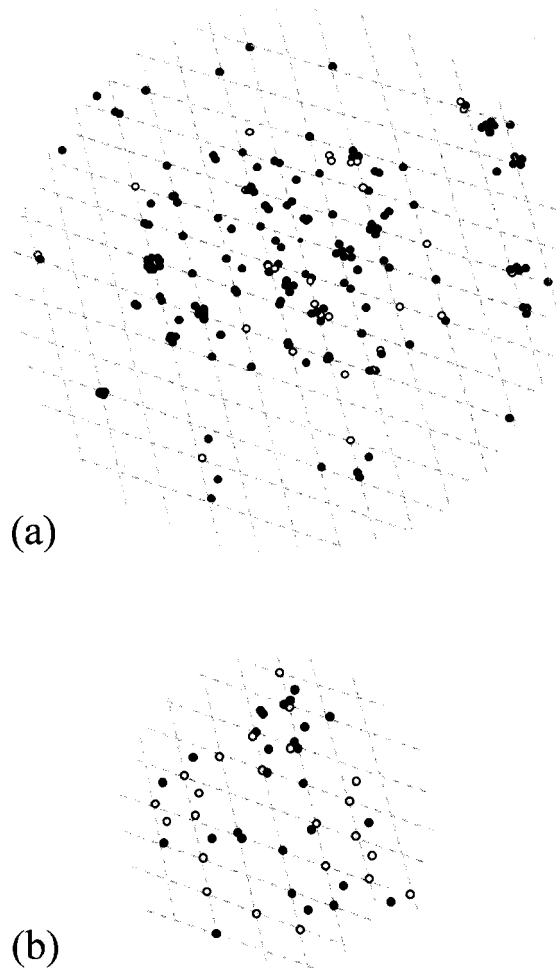
FIG. 7. Map of sites occupied by Ir atoms on an Ir(111) cluster. (a) ∼150 atoms, (b) ∼70 atoms. The back dash nets are hcp lattice nets. Black circles mark the location of the atom after diffusion. Gray circles identify atoms after deposition at ∼30 K. Only one atom is present on the cluster at any one time during mapping. In principle, all regions can be populated by condensing atoms.
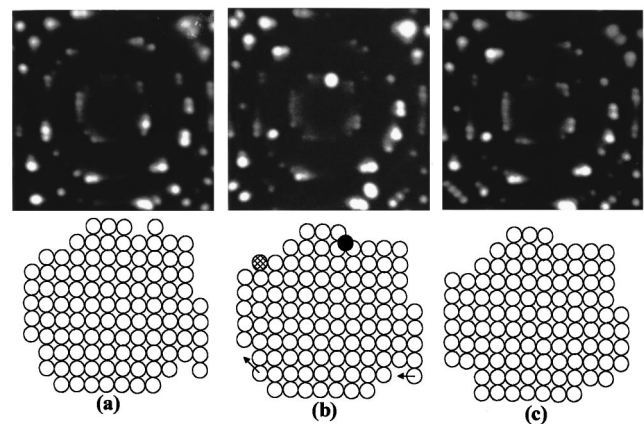

FIG. 8. Field ion images showing (a) A layer of Ir(001) after some heating at 400 K. (b) In another heating to 440 K for 10 s, an adatom is found to sit near an upper terrace edge. (c) After field evaporating this adatom, we can find the four atoms have reduced to three atoms in the upper side. I illustrate some events by the line drawings. ● indicates the upward moving atom. ⊗ indicates the dissociation atom. ⊙ indicates the atoms that diffuse along the step edges where the arrow indicates the direction of diffusion and the final sites.

configurations should be different, as illustrated in Fig. 6. The occurrence of exchange mechanism only at B-type steps has been found for W adatoms on 69-atom Ir(111) island.[18] MD/MC-CEM theory has also predicted an energy difference for different crossing mechanisms for fcc(111) surfaces for Pt(111) and Ag(111).[9] However, both of the mechanisms, and thus the energetics, should be sensitive to the material of the system, and direct comparison is difficult.

3. Long-range effect of the step boundary

Another experiment shows the step boundary effect to extend at least 3–4 nearest-neighbor distances from the step edges. We have derived a visited site map out of 254 10s-heating periods of observations at 130 K. From the site map shown in Fig. 7(a), it is obvious that the site occupation number is not uniformly distributed over all the available sites. The occupation number is nearly zero for sites within a ring-shaped region of the island. For the rest of the sites, the occupation number is fairly uniform. This result is similar to what has been reported by Golzhanser and Ehrlich for Pt/Pt(111).[20] However, our result do not agree with that of Wang and Ehrlich for Ir/Ir(111).[21] They find no nonuniform

distribution of occupation probabilities for Ir/Ir(111). We believe this discrepancy arises from the very different sizes of Ir islands the two groups use, they use an Ir$_{59}$ cluster of much smaller size than our Ir$_{150}$ cluster. We also mapped the occupied sites using Ir$_{70}$ cluster as shown in Fig. 7(b), and find the empty zone to be much narrower and even ambiguous. The width of empty zone is obviously dependent on the terrace size. This observation shows the surface potential near a step is very complicated. The reflective barrier heights we have measured therefore represents effective barrier heights of α steps in reflecting diffusing adatoms.

B. The atom-trapping property of step-edge sites

When an adatom overcome the barrier at the rim of a step, it will reach a step-edge site. Likewise, when an adatom at a terrace diffuse to a β step, it will reach a step-edge site also. The question is how this adatom is going to behave. It may be trapped into a step-edge site, and then it may not. Obviously, it will depend on the system we are dealing with. In the past, step-edge sites are assumed to be perfect sinks in standard nucleation and growth theories. The important parameter of step-edge site is ΔE_e (see Fig. 1) which is also what we derive. This quantity affects the trapping strength of a step-edge atom regardless of which side of the step the step-edge atom detaches to. Detachment of step-edge atoms can go to either the α side (''ascending'' the step, barrier height E_α) or the β side (dissociation from step edges, barrier height E_β). A recent study by Fu, Tzeng, and Tsong[12,13] shows that step-edge atoms of Ir(111) can as easily detach to the α side as to the β side. We have now also measured the ascending barrier height for Ir(001). Figure 8 shows an example of the ''ascending'' motion at the step of Ir(001). Since an ''upper'' adatom ''descend'' by atomic exchange, the ''ascending motion'' should likewise be achieved by atomic exchange. A possible ascending mechanism for
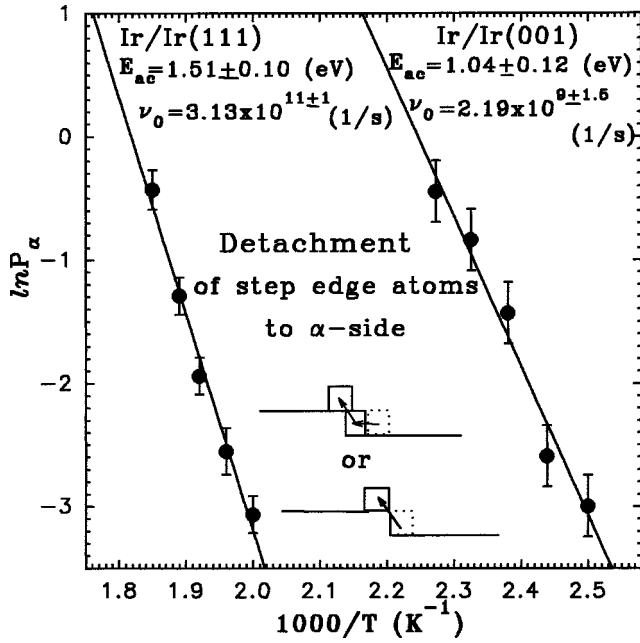
FIG. 9. Arrhenius-like plots for the detachment of step-edge atoms of Ir(111) and Ir(001) to the α side of the lattice step.

Ir(001) is illustrated in Figs. 4(d)–(f). Data of both surfaces are shown in Fig. 9 for easy comparison and reference.

In this experiment, we measure the probability of an atom observed at the "upper" terrace, and derive the activation energy E_{ac}. Considering the fact that the "upper" terrace adatom is easily descending again, we perform the following correction to get E_α approximately. For detaching to the α side, the rates of ascending and descending motions, K_e and K_b, are given, respectively, by

$$K_e = n_b \nu_0 \exp(-E_\alpha/kT), \quad K_b = \nu_0 \exp(-E_b/kT),$$

where n_b is the number of step-edge atoms of the surface layer. Let the occupation probability at time t of the step-edge site and the upper terrace site be $p_e(t)$ and $p_\alpha(t)$, respectively. Then

$$p_\alpha(t) = [K_e/(K_b+K_e)]\{1 - \exp[-(K_b+K_e)t]\}.$$

Data interpretation is much more straightforward under two conditions, (1) when $(K_b+K_e)t$ goes to 0, $p_\alpha(t) \sim K_e t$

$= n_b t \nu_0 \exp(-E_\alpha/kT)$, thus the $\ln p_\alpha(t)$ versus $1/kT$ plot has a slope of $-E_\alpha$, and (2) when $(K_b+K_e)t \gg 1$, $p_\alpha(t) \sim K_e/K_b$, or the $\ln p_\alpha(t)$ versus $1/kT$ plot has a slope of $-(E_\alpha - E_b)$. Despite our considerable effort to use larger surface layers with a larger number of step-edge atoms, so that the chance of observing an ascended atom is greatly increased, the measurement is still very difficult. A detailed analysis shows that the energy we have derived, E_{ac}, should be $\sim (E_\alpha - \frac{1}{2}E_b)$ where E_α is the dissociation energy of a step-edge atom to the α side. In other words, $E_\alpha \sim (E_{ac} + \frac{1}{2}E_b)$. The barrier height to the β side (E_β) can be measured from the temperature dependence of the dissolution time of a finite-size plane.[14] Data for Ir(001) and Ir(111) have been reported in our earlier studies.[12–14] To facilitate our discussion, we summarize available experimental data for Ir/Ir(111) and Ir/Ir(001) in Table I. While the accuracy of a few of these measurements is still limited, these results already indicate that for a nonreflective α step, the "ascending" motion of a step-edge atom should be as easy as detachment to the same terrace as should be expected from Fig. 1. They are both affected by the same extra well depth ΔE_e.

In general, at the temperatures epitaxial growths are usually done, the more important step property is most likely the atom-trapping strength of step-edge sites. For α steps, even when they are reflective, the barriers are only 0.2 eV or less, much smaller than the activation energy of adatom diffusion. Thus the reflective property is effective only at a temperature close to the onset temperature of adatom diffusion. The only exception appears to be the (111) surface of some fcc metals where ΔE_b, though small, is still comparable to the activation energy of adatom diffusion. The atom-trapping strength ΔE_e, as estimated by $(E_\alpha - E_b)$, is ~ 1.3 eV for Ir(111) while it is less than ~ 0.7 eV for Ir(001) (See Table I). In other words, ΔE_e varies over a wide range for different systems. At high temperatures, all diffusing adatoms and atom clusters can reach step-edge sites regardless of whether they approach the step from the α or the β side, since the reflectivity is too small to be effective. Once they reach the step-edge sites, they can either be trapped there nearly permanently (almost perfect sinks), or they can detach to either the terrace at the α side or the β side depending on the materials of system, and also if the temperature is high enough. In other words, the upper layer atoms in 3D growth may come from the detached atoms, not really restricted to those from

TABLE I. Experimental data.

	System	
Parameter	Ir/Ir(001)	Ir/Ir(111)
Terrace diffusion (E_d)	0.74 ± 0.02 eV	0.21 ± 0.03 eV
Ledge atom diffusion ($E_{d,1}$)	$\langle 110 \rangle$ step: 0.62 ± 0.05 eV	A step: 0.82 ± 0.05 eV
		B step: 0.76 ± 0.05 eV
Barrier height to α side ($E_\alpha = E_{ac} + \frac{1}{2}E_b$)	$\sim 1.40 \pm 0.16$ eV	$\sim 1.72 \pm 0.12$ eV
Barrier height to β side (E_β)	1.40 ± 0.07 eV	1.63 ± 0.20 eV
Barrier height of α step ($E_b = \Delta E_b + E_d$)	0.72 ± 0.08 eV	0.41 ± 0.03 eV
Reflective barrier (ΔE_b)	-0.03 ± 0.08 eV	0.20 ± 0.03 eV
Extra trapping energy (ΔE_e)	0.68 ± 0.16 eV	1.31 ± 0.12 eV

the reflected atoms. The temperature needed even for a refractory metal such as Ir is only about 500–600 K. What our result shows here is the importance of the atom-trapping property of steps, which should play a crucial role in many atom transport phenomena.

III. SUMMARY

Ir(001) and Ir(111) exhibit totally different step properties as can be seen from data shown in Table I. For the (111), the activation energy of adatom diffusion is exceptionally low because of the very smooth surface corrugation. Adatom diffusion can occur already at ~ 100 K. Step-edge diffusion, on the other hand, can occur only above ~ 280 K. The extra-barrier height of the reflective α step is as high as the activation energy of adatom diffusion. In other words, only when the temperature is above ~ 180 K, adatom can cross the α step. The atom-trapping strength of step-edge sites is also very high of ~ 1.7 eV, thus step-edge atoms can detach to either the α side or the β side only above ~ 550 K. Ir(001) exhibits entirely opposite behavior. Adatom diffusion on Ir(001) can occur only above ~ 230 K, whereas ledge atom diffusion can occur already below 200 K. In addition, there is no reflective barrier for the α step, and the atom-trapping strength of step-edge sites is relatively small of only ~ 1.4 eV. In fact, around 450 K, not only atoms in step-edge sites can dissociate to both the α and β sides of the step, even ''in-layer'' atoms can ''ascend'' to the adatom site. These differences will reflect in very different growth behavior of these two surfaces. We will now give a few simple observations.

For Ir on both surfaces, when the temperature is well below 100 K, no diffusion can occur. The growth will be random condensation of atoms, or the morphology of the film will have a columnar fractal structure. For Ir/Ir(111), around 100 K, terrace diffusion of single atoms can occur but not ledge atom diffusion. α steps act as effective reflective boundaries, thus the growth is 3D and the island shape should be fractal as observed in other fcc(111) surfaces. As

the temperature is raised above ~ 250 K, the reflective barrier becomes less effective. If the deposition rate is low enough such that the chance of adatom aggregation is much smaller than their being incorporated into step edges, we can expect the growth to be 2D, otherwise 3D growth can be expected. When the temperature reaches above 300 K, ledge atom diffusion starts and the fractal island shape should disappear completely. When the temperature is further raised above 500 K, adatom and ledge atom diffusions are so rapid that they are no longer the rate limiting steps, cluster diffusion and atom trapping strength (i.e., whether the ascending and dissociation of the step-edge atoms can occur) will play the dominant role. For Ir/Ir(001), terrace diffusion cannot occur below 230 K, thus islands are formed by a ''hit and stick'' process. On the other hand, step-edge diffusion can occur around 200 K along $\langle 110 \rangle$ edges. Thus no fractal shaped 2D islands will ever be formed at any temperature. When the temperature is raised above 250 K, both terrace and step-edge diffusion can occur. In addition, α steps are nonreflective. Therefore, if atom deposition rate is low, the growth is expected to be 2D of compact islands. When the temperature is raised well above 450 K, ascending and dissociation of the step-edge atoms can occur at high rates because of the weak atom-trapping strength of steps and the surface may become less and less smooth.

Phenomena at lattice steps are quite sensitive to the chemical identity of the atoms and substrates, thus our results may not be directly applicable to some other systems. However, a study of mechanisms and energetics of surface atomic processes can provide us with basic knowledge needed to judge the more important parameters at a given temperature in growth and other phenomena involving transportation of atoms. Our data should also be useful for comparing with surface energetic calculations.[22]

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