Atomic View of the Upward Movement of Step-Edge and In-Layer Atoms of Ir Surfaces

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The behavior of adatoms, step-edge atoms, and in-layer atoms at high temperature plays an important role in determining the growth mode of epitaxial thin films and crystals, the crystal shape change, and the morphology of crystal surfaces. From a direct field ion microscope observation, we find that around 500 K an edge atom of the Ir(111) step can ascend the step to the upper terrace as well as dissociate to the lower terrace. The activation barrier height for the ascending motion is measured to be 1.51 ± 0.10 eV, whereas the dissociation barrier is $\sim 1.6 \pm 0.2$ eV. Surprisingly, we also find that in-layer atoms can jump up to terrace sites, thus forming adatom-vacancy complexes, at unexpectedly low temperatures.

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The behavior of diffusing adatoms at lattice steps is known to play an important role in determining the growth mode of crystals and epitaxial thin films from the vapor phase, and the morphology of crystal surfaces at high temperature [1,2]. From a variety of studies, the generally accepted view is that when an adatom encounters a descending step, it either will be reflected or will descend the step by either hopping or atomic exchange and then be incorporated into the step. Likewise, when an adatom encounters an ascending step, it will be incorporated into the step edge. Field-ion microscopy (FIM) experiments that show most diffusing adatoms encountering a descending step of the bcc W (110) and (112) surfaces are reflected [3,4]. However, for the fcc Pt and Ir (001) and (111), the descending steps do not reflect diffusing adatoms. Instead, adatoms will descend the step and be incorporated into the step edges [5]. For the Ir(111) surface [2], W adatoms can incorporate into the Ir(111) step edges by either hopping or atomic exchange depending on the size of the Ir(111) island. The behavior of adatoms at the step edges can account for the two-dimensional and three-dimensional island growth as well as the reentrant growth during molecular beam epitaxy on metal surfaces [6]. A Monte Carlo simulation using the behavior of adatoms at the steps can explain various morphologies of crystal surfaces observed in STM studies of molecular beam epitaxy [7]. A simple argument tells us that the behavior of step-edge atoms at the temperature where they can detach from the step edges should play an equally important role. A step-edge atom may dissociate from the step to the lower terrace, or it may ascend the step to the upper terrace. It is interesting to note that without this latter capability a crystal can only flatten and thus cannot change it shape from a metastable one to the equilibrium one. Dominance of this latter process will favor 3D growth from the vapor phase. In this FIM study of effects of step edges on diffusing adatoms, we surprisingly discover that above 500 K step-edge atoms of the Ir(111) surface can ascend the step to the upper terrace as well as dissociate to the lower terrace. Even more surprising is that at about the same temperature in-layer atoms can also jump up to terrace positions, thus creating adatom-vacancy pairs at the terrace.

Detailed experimental procedures in FIM study of atomic processes on metal surfaces are well documented [8]. We again take great care in the vacuum processing. Before an experiment, the tip is first bombarded with neon ions and then flashed to 1500 K. The system is then subjected to a 3-day bake-out during which the tip and its heating loop and potential leads are degassed at ~1000 K. The tip is then further flashed to 1500 K for 2 min in low, 10^{-11} torr, vacuum and field evaporated at ~30 K. The image gas used is Vycor-glass-diffused helium from a research grade helium bottle. Tip heating is done by an electronically controlled pulsed power supply with a rise time of less than 0.2 s without overshoot. Unless otherwise stated, each heating period is 10 s. Even under such elaborate procedures, every 2 h the image gas is pumped out and the tip is flashed again in the low, 10^{-11} torr, vacuum and new image gas is readmitted.

An Ir(111) layer formed by low temperature field evaporation is nearly circular in shape and therefore contains edges of different atomic structures. Around 480 to 500 K, the layer shape can change by diffusion of step edge atoms along the step without detaching frequently to the terrace, or the number of atoms in the layer can be conserved. If this number is carefully controlled beforehand by field evaporation and vapor deposition [9] to fit a perfect hexagon, i.e., 7, 19, 37, 61, 91,... for Ir islands on the Ir (111), this shape is formed after annealing for a sufficiently long period of time. These numbers can be called the ideal numbers for this system. The equilibrium shape of this 2D crystal at this temperature is therefore a perfect hexagon which consists of *A*-type and *B*-type steps of equal length.

Above 500 K, other atomic processes can also occur for step-edge atoms. They can dissociate to the lower terrace or ascend the step to the upper terrace. What is most interesting and surprising is that the detachment

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of step-edge atoms can be achieved by both ascending the step to the upper terrace or dissociation to the lower terrace with nearly the same probability. Figure 1 shows an example of the ascending motion of a step-edge atom. In these pictures, successive images of a surface layer after preparing by field evaporation and then heated to 510 K for 20 s are shown. In Fig. 1(a), a layer with a vacancy at the step edge can be seen. After another heating period, the length of the heating period is chosen to observe less than one ascending atomic jump of step-edge atoms of the entire layer, an adatom appeared on the terrace near the step edge of the upper terrace. Upon field evaporating this adatom, we find a new vacancy in the step edge at the upper step. All the other step-edge atoms of this layer remain intact. Thus an edge atom has ascended the step as illustrated in the line drawings. From the images, it is not yet possible to identify the mechanism of the ascending motion, i.e., whether the step-edge atom ascends by an atomic hopping or by an atomic exchange displacement. At a slightly higher temperature, ~530 K, we find an even more interesting result; i.e., in-layer atoms can be promoted to adatom positions on the upper terrace. An example is shown in Figs. 2(a) and 2(b). Unfortunately, the vacancy created in the Ir(111) layer cannot be seen unless it reaches the step edge when the layer is gradually reduced in size by field evaporation, and, even then, it is difficult to reproduce the image clearly. But this atomic process can be seen much more clearly for other surfaces. At the Ir(113) surface, an adatom vacancy created at 450 K for 30 s can be seen much more clearly as shown in Figs. 2(c) and 2(d). The adatom-vacancy complex can recombine as well as dissociate. Upon recombination, the adatom will disappear. Upon dissociation, the adatom will diffuse elsewhere. It is impossible to trace its movement since the speed of adatom diffusion is very high at the temperature when the complex can dissociate. But the vacancy can still be seen if the layer is gradually reduced in size. An example is shown in Fig. 2(d). The possible mechanisms of these upward movements are illustrated in Fig. 3. From the data alone, we cannot decide whether direct atomic hopping or atomic exchange displacement is responsible for the ascending motion of step-edge atoms. The fact that an in-layer atom can move up to the upper terrace indicates, however, that step-edge atoms most probably move up by atomic hopping also.

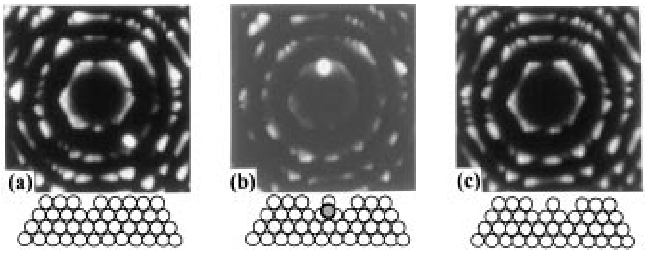

FIG. 1. (a) A layer of Ir(111) after some heating at 510 K. (b) In another heating to 510 K for 20 s, an adatom is found to sit near an upper terrace edge. (c) After field evaporating this adatom, a new vacancy at the step is found. Because of the image contrast, these structures can be clearly seen only in the original films, but these events are illustrated by the line drawings shown.

The activation barrier height of the ascending motion of step-edge atoms at the Ir(111) layer, E_{as}, can be measured by using the following equation:

$$p_{\mathrm{as}} = \nu \tau N_{\mathrm{edge}} e^{-E_{\mathrm{as}}/kT}, \qquad (1)$$

where p_{as} is the probability that the ascending motion of an edge atom is detected in a heating period of length τ, ν

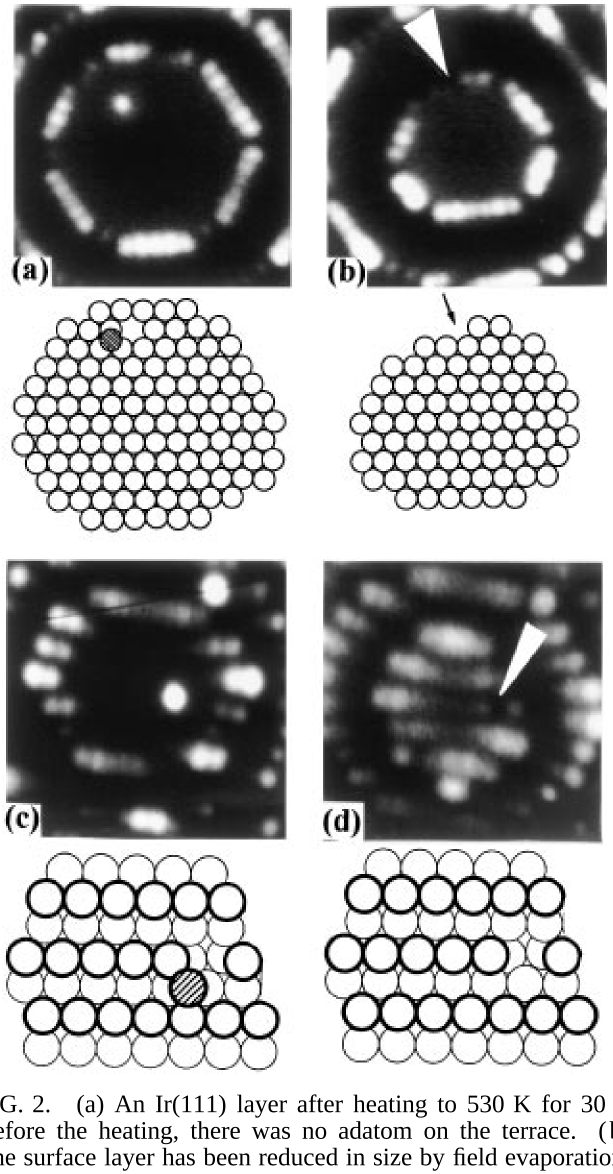

FIG. 2. (a) An Ir(111) layer after heating to 530 K for 30 s. Before the heating, there was no adatom on the terrace. (b) The surface layer has been reduced in size by field evaporation. Now at the digitized position of the adatom a vacancy can be found which is at the step edge pointed by an arrow. (c) After heating a (113) surface to 450 K for 30 s, an adatom is found on the terrace. (d) By gradual field evaporation, two vacancies are found in this surface layer, one of them (pointed to by an arrow) is at the neighbor site of the adatom as illustrated by the line drawings.

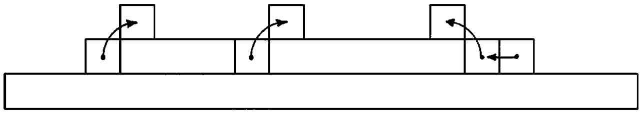

FIG. 3. Three possible mechanisms for the upward motion of step edge atoms and in-layer atoms.

is the frequency factor, and N_{edge} is the average number of step-edge atoms of the layers with which the data are taken. In our measurement, layers with N_{edge} in the range of 30 to 40, or about 35, were used and τ was 10 s. Our data, plotted in $\ln(p_{\mathrm{as}})$ vs $1000/T$, are shown in Fig. 4. From the slope and intercept of this plot, we derive E_{as} and ν to be 1.51 ± 0.10 eV and $3.1 \times 10^{11\pm1}\ \mathrm{s}^{-1}$, respectively. It is not yet possible to measure this energy in the upward movement of in-layer atoms.

The parameters of self-diffusion on the Ir(111) terrace have been measured earlier to be $E_d = 0.22$ eV and $D_0 = 9 \times 10^{-3}\ \mathrm{cm}^2/\mathrm{s}$ [5]. Observable diffusion of adatoms starts around 100 K. However, the adatom and the vacancy, created by the upward movement of the atom, interact rather strongly. The adatom-vacancy complexes created at the terrace start to move only above 200 K. The complexes can disappear by either dissociation or adatom vacancy annihilation above $\sim$250 K. For those near the step edge, their onset diffusion temperature is above $\sim$270 K, and even so their movements are dominantly along the step edge. Similar disappearance can occur above $\sim$300 K. Another phenomenon is the detachment of step-edge atoms to the lower terrace. An FIM emitter consists of concentric surface layers. For the small Ir(111), above 500 K, step-edge atoms can ascend the step as well as dissociate to the terrace; thus the size of the surface layer can change by heating. For the small top surface layer, the ascended atoms will descend again, but the chance of dissociated edge atoms to be reabsorbed is relatively small; therefore this top layer will gradually reduce in size. When the size is reduced to around 30 atoms, the layer as a whole can also diffuse [10] to the step edge and eventually be absorbed into it. Therefore it is very difficult to derive the dissociation barrier height of edge atoms. This energy can be derived from the temperature dependence of the dissociation time of the small top layer. We have measured the time for a layer of $\sim$100 atoms to reduce to $\sim$40 atoms as a function of temperature and plotted the data in an Arrhenius form as shown in Fig. 5. From the slope, the average dissociation barrier of step-edge atoms is found to be $\sim 1.6 \pm 0.2$ eV, very nearly comparable to the barrier height for ascending the step.

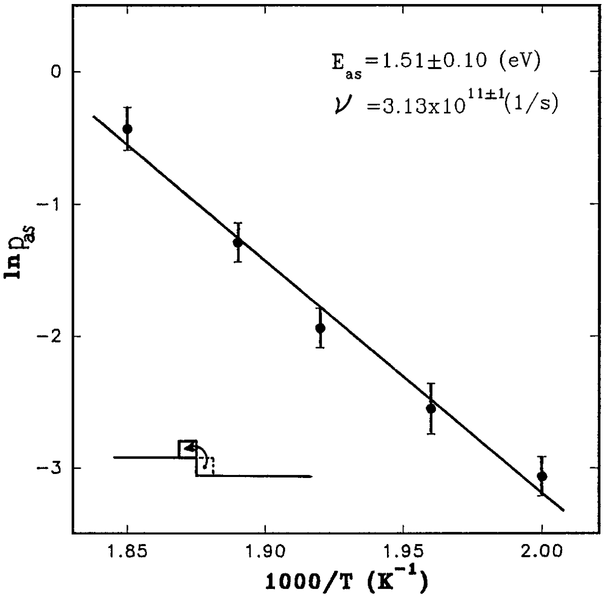

FIG. 4. Data of p_{as} are plotted in an Arrhenius form from which E_{as} is derived to be 1.51 ± 0.10 eV.

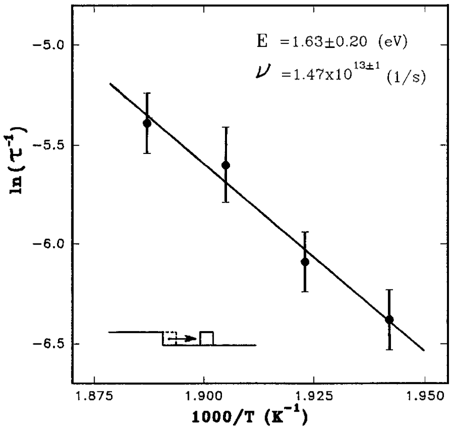

FIG. 5. The average dissolution time for an Ir layer of $\sim$100 atoms to reduce to $\sim$40 atoms is plotted in an Arrhenius form from which the average dissociation barrier of step-edge atoms is estimated to be $E_{\mathrm{dis}} \cong 1.6 \pm 0.2$ eV.

For the terrace of the top surface layer, no atoms can come from dissociation of edge atoms of the upper layers. On the other hand, for terraces of all other layers, atoms can come both from the dissociated atoms from the upper layers as well as from the ascended atoms of its own layer and the lower layers. One can therefore expect these layers to have many scattered adatoms on their terraces during these dynamic changes. This is indeed the case as seen in Fig. 6.

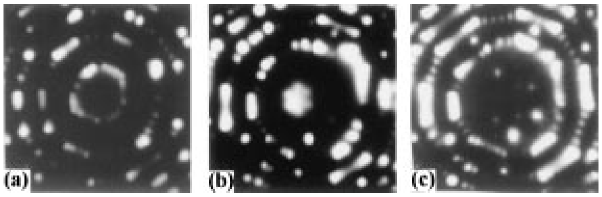

FIG. 6. FIM images showing that during the dissolution of the top surface layer all terraces are decorated with adatoms dissociated from step edges. They can be more clearly seen if these layers are gradually field evaporated.

In summary, we have observed the upward motion of step-edge atoms and have measured the activation energy of this motion. We have also observed the upward motion of in-layer atoms. Both of these upward motions of atoms should play an equally important role as the behavior of adatoms at the descending steps in the dynamic behavior of surface atoms on crystal surfaces as well as in determining the growth mode of epitaxial layers. The observed effects should also shed some light on the energetics of surface atoms, as well as step-step interactions [11]. These interactions are really produced by the exchange of step-edge atoms among different lattice steps, especially between two neighbor steps.

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