PHYSICAL REVIEW B VOLUME 47, NUMBER 23 15 JUNE 1993-I

Dynamical behavior and energetics of the Ir(001) surface

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(Received 18 January 1993)

An atomic view of the dynamical behavior of the Ir(001) surface is presented. The atomic processes involved in the dissolution of the surface layer are isolated and their mechanisms and energetics are studied quantitatively. Above 400 K, lattice-step atoms can move along the steps, mostly along the $\langle 110 \rangle$ steps, and step atoms can also dissociate to the terraces. By diffusion, dissociation, and reabsorption of step atoms, an equilibrium shape of the surface layer can be achieved, which, around 400 K, is a square with its four sides parallel to the $\langle 110 \rangle$ closely packed atomic-row directions. Step atoms dissociate from edge sites, kink sites, ledge sites, and recessed sites with a comparable probability; thus the dissociation is not orderly and the steps are roughened above ~ 500 K. We measure the diffusion energy of ledge-site atoms along the $\langle 110 \rangle$ lattice steps to be 0.62 eV. This diffusion occurs by atomic hopping; for comparison, self-diffusion on the (001) terrace occurs by atomic replacement in the $\langle 001 \rangle$ directions. The dissociation energy of edge-site atoms and other step atoms are measured to be 1.35 ± 0.08 and 1.40 ± 0.07 eV, respectively. The line-energy density of the $\langle 110 \rangle$ step is $(3.2 \pm 0.5) \times 10^{-10}$ J/m and the self-adsorption energy is 6.37 ± 0.09 eV. We also find hollow clusters and "spongelike" two-dimensional surface layers on the Ir(001) surface.

I. INTRODUCTION

A solid surface is by no means static. At low temperatures, lattice vibration occurs but atoms are confined to their own sites. When the solid is heated to high temperature (but is still much lower than the melting point), surface atoms will start to dissociate from their lattice sites and diffuse around the surface. Not only the morphology of the surface may change from a well-ordered phase to a rough phase, if the crystal is small enough and the atom mobility is sufficiently high, the crystal can also reach its equilibrium crystal shape (ECS). These are subjects of considerable current interest.[1] In this study, we report an atomic resolution microscope study of the dynamical behavior of the Ir(001) surface. Our motivation is twofold. First, we are interested in the two-dimensional (2D) analogs of the phenomena of surface diffusion, surface roughening, and sublimation, etc. of the three-dimensional (3D) crystal. Second, we are interested in finding the detailed elementary atomic processes involved in the dynamical behavior of surfaces and studying their mechanisms as well as their energetics. We believe that only through a detailed sorting of these elementary atomic processes and quantitative studies of their mechanisms and energetics that first-principle theories of the dynamical behavior of solid surfaces can eventually evolve. From the practical side, as the structures in high-tech materials gradually reduce in size, their surface-atom-to-bulk-atom ratio will gradually increase. The dynamical behavior of these surfaces will become an important issue in the thermal stability and useful lifetimes of these material structures.

II. EXPERIMENT

In this study, the field ion microscope (FIM) is used.[2] FIM study of adatom behavior is an established technique. Detailed experimental procedures can be found in the literature.[3] In this experiment we pay great attention to the vacuum condition of the system and the cleanliness of the sample tip. The FIM is repeatedly baked and vacuum processed to reach a vacuum in the low 10^{-11}-Torr range. Before a tip is used for an experiment, it is repeatedly bombarded with Ne ions in the field emission mode, carefully annealed to 1500 K, and then low-temperature field evaporated. The tip temperature is controlled by joule heating of the tip mounting platinum loop using an electronic-controlled pulsed power supply. The tip temperature can be raised in less than 0.1 s to a prespecified value without overshoot. The heating periods used are in the range of 1 to 60 s. The wire coil adatom deposition source is thoroughly degased at the deposition temperature before it is used for the experiment. For the image gas, only Vyco-glass diffused helium is used to avoid contamination of the surface by the impurities in the image gas. This type of experiment involves tens of thousands of FIM images, which are either taken with a high-resolution video recorder or sometimes taken photographically. Atomic positions are mapped by an image digitizer.

When a (001)-oriented Ir tip is field evaporated at low temperature to a nearly hemispherical shape, (001) atomic layers form concentric rings as shown in Fig. 1. Except for a few zone line decorated atoms near the central parts of the $\langle 110 \rangle$ steps, there are basically two types of

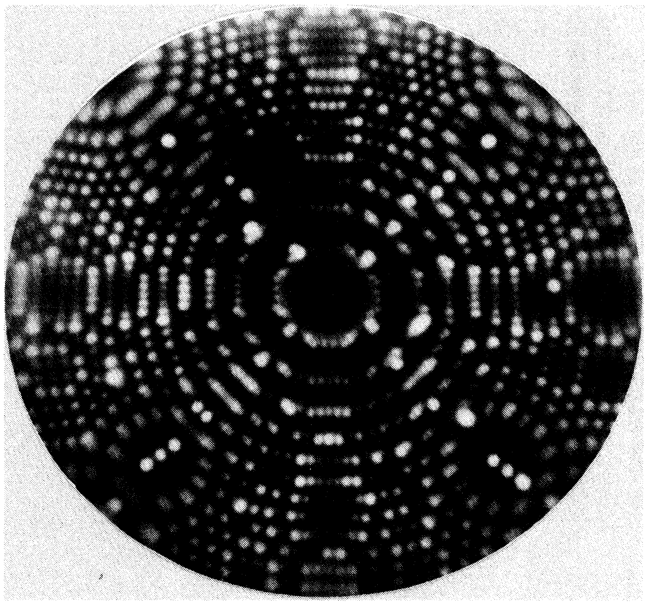


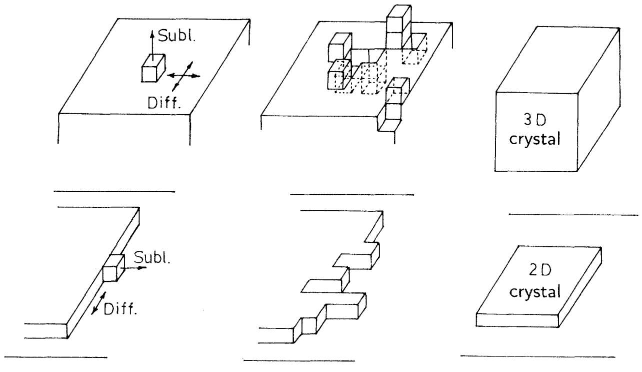
FIG. 1. A field ion micrograph of a (001)-oriented Ir tip. The concentric rings are formed by (001) surface layers. Each ring represents a surface layer.

steps, namely the ⟨100⟩ and ⟨110⟩ steps, available for performing experiments. When the tip is heated to over 400 K, step atoms can start to diffuse along the step. Step atoms can also dissociate to the terraces above ~430 K. We find that the descending steps of the (001) layers are nonreflective to diffusing Ir adatoms. Also an Ir adatom, when encountering a step, will be absorbed into the step. Below 600 K, up-step diffusion of Ir adatoms is rarely found. Thus when the tip is heated to over ~430 K, an adatom dissociated from a step will either be reabsorbed or fall off the step of the next surface layer and be absorbed into this step. Thus by annealing beyond this temperature, the top surface layer can only reduce in size gradually and eventually disappears completely. The second layer and those that follow will gradually increase their size, and the tip will gradually become duller. It is with this particular behavior of the Ir(001) surface in the tip blunting process that we can isolate the top surface layer for studying how the Ir(001) layer dissolves and the atomic processes and energetics involved in this dissolving process.

III. RESULT AND DISCUSSIONS

A. 2D and 3D analogs

Before discussing our experimental result, it is worthwhile to explain very briefly some of the two-dimensional and three-dimensional analogs of surface diffusion, sublimation or desorption, surface roughening, ECS, etc., as illustrated in Fig. 2. Consider first surface diffusion. The surface of a 2D crystal, which is a surface layer, is the lattice steps. Thus the 2D analog of surface diffusion of a 3D crystal is diffusion of ledge atoms along the lattice steps. Sublimation in the 2D layer corresponds to dissociation of step atoms to terrace sites. The 2D analog of the roughening of a surface is the roughening of a lattice step which can occur either by diffusion of step atoms along the step or by dissociation or absorption of atoms at the step and the terrace. There are subtle differences between step roughening and surface roughening. For the fcc (001) surface, step roughening will produce surface roughening of the (11n) and (10n) surfaces for $n > 1$, but not the (001) surface itself. Finally, the equilibrium crystal shape at a given temperature is the equilibrium shape of the surface layer. In this study we are trying to study the elementary atomic processes involved in these phenomena and their mechanisms and energetics. Because of the reduced dimensionality, a microscopic understanding of these phenomena may become easier.



(a) Sublimation & Diffusion (b) Roughening (c) ECS

FIG. 2. 2D analogs of some surface phenomena of a 3D crystal. (a) Sublimation and surface diffusion. (b) Surface roughening. (c) Equilibrium crystal shape.

B. Diffusion of ledge atoms

For the Ir(001) surface, there are basically two types of steps, i.e., the ⟨100⟩ and ⟨110⟩ steps. All other steps, as well as "kinked steps" (the 2D analog of faceted surfaces), can be considered to be different combinations of these two types of steps. A few examples of their geometrical structures are shown in Fig. 3. On a step, there are different types of atoms. A convenient but nontrivial distinction is to separate step atoms into four types, namely ledge atoms, edge atoms, kink atoms, and recessed atoms. Ledge atoms are the 2D equivalent of adatoms while recessed atoms are the 2D analog of interior atoms of a surface layer. Therefore the 2D analog of adatom diffusion is diffusion of ledge atoms. This is the simplest type of solid-state diffusion where there is no need to create the diffusing atoms; such a creation will need additional formation energy. The ⟨110⟩ steps are formed by closely packed atomic rows whereas atoms at the ⟨100⟩ steps are not closely packed. We find that diffusion of ledge atoms along the ⟨110⟩ steps can start to occur around 240 K; a few images of this diffusion are shown in Fig. 4. Diffusion of ledge atoms along the ⟨100⟩ steps, however, can occur only at temperatures when ledge atoms and other steps atoms can already dissociate from the steps to the terraces. It is therefore difficult to study diffusion of

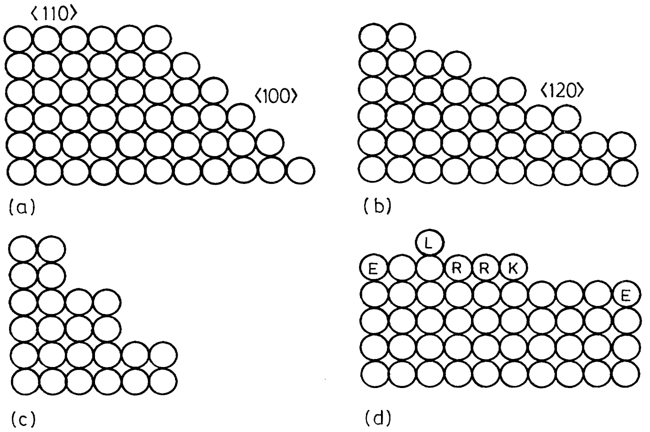


FIG. 3. (a) Geometrical structures of the ⟨110⟩ and ⟨100⟩ steps of the fcc (001) surface layer. (b) The ⟨120⟩ step. Each unit of this step consists of one unit of the ⟨100⟩ step and one unit of the ⟨110⟩ step. (c) A kink step of the ⟨110⟩ type, but parallel to the ⟨100⟩ step. (d) *L* is the ledge atom, *E* the edge atoms, *K* the kink atom, and *R* the recessed atoms.

ledge atoms along the ⟨100⟩ steps. We present here a quantitative study of the diffusion behavior of ledge atoms along the ⟨110⟩ steps.

We have measured displacement distributions of ledge atoms along the ⟨110⟩ steps at several temperatures ranging from 246 to 284 K, as shown in Fig. 5. The lengths of the heating periods were adjusted to avoid long-distance displacements. Also, as the size of the steps used for our measurement is very small, only 10–20 atomic distances, so that atomic resolution can be achieved in the FIM, we collect data only for those cases where the starting position of the ledge atom is near the central section of the step or the ledge atom is still far away from the edge of the step. In the same diagrams we also show theoretical displacement distributions[4] calculated using the experimentally measured mean-square displacements, and with the assumption that only nearest-neighbor atomic jumps can occur. We find that, except for the data taken at 246 K, which agrees well with the theoretical distribution, all other experimental data indi-

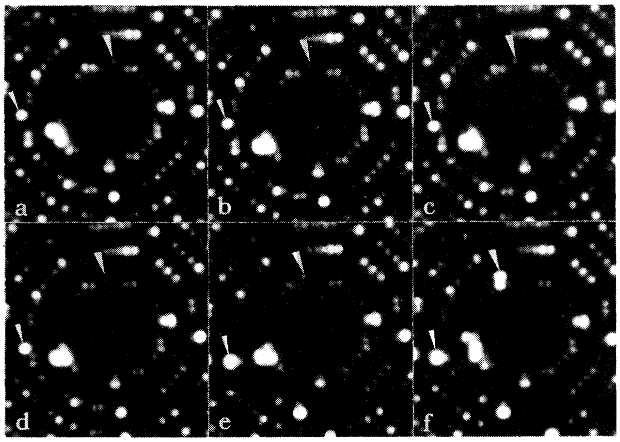


FIG. 4. FIM images showing the 1D random-walk diffusion of ledge atoms along the ⟨110⟩ steps. Ledge atoms tend to stick to the end site of the steps. Arrows point to the diffusing ledge atoms.

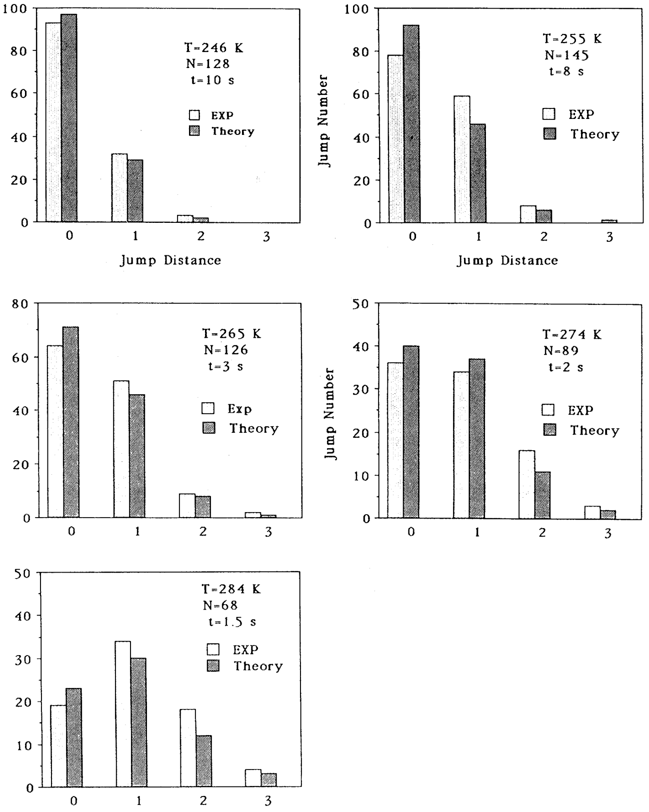


FIG. 5. Displacement distributions for the diffusion of ledge site atoms along the ⟨110⟩ steps, taken at five different temperatures. The jump distance is measured in numbers of sites.

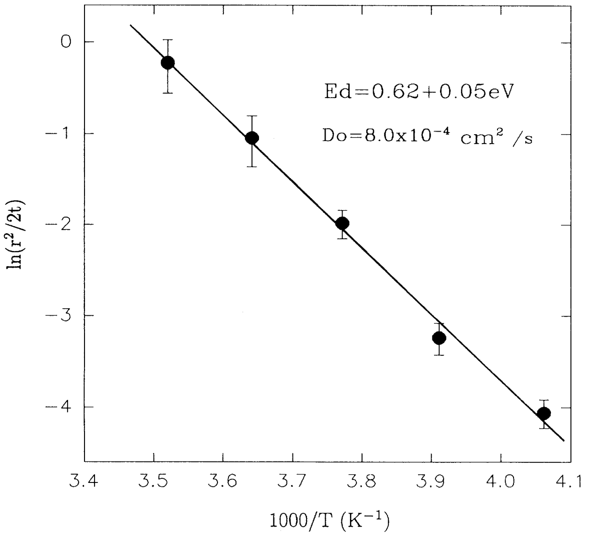


FIG. 6. An Arrhenius plot for the diffusion of ledge atoms along the ⟨110⟩ steps of the Ir(001) surface.

cate that a detectable fraction of the jumps reaches beyond the nearest neighbors. Although theoretical equations are available for other jump-length distributions such as an exponential jump-length distribution, there is a complication which refrains us from using such analyses, as will be clear later. From these experimental data, we also obtain an Arrhenius plot shown in Fig. 6. From this plot, the activation energy and preexponential factor of ledge-atom diffusion along the ⟨110⟩ steps are derived to be $E_d=0.62\pm0.05$ eV and $D_0=8\times10^{-4.0\pm0.8}$ cm^2/s. Since this diffusion is along the closely packed atomic-row direction, there is no likelihood that the diffusing ledge atom will replace either an atom at the recessed site of the step or an atom in the underneath layer. The diffusion should occur by atomic hopping. For comparison, diffusion of Ir adatoms on the Ir(001) surface occurs by atomic replacement, and the atomic jumps are in the ⟨100⟩ directions.[5] The activation energy is 0.84 ± 0.05 eV, or 0.22 eV higher than diffusion of ledge atoms along the ⟨110⟩ steps.

C. Binding strength along a step

One of the unusual behaviors we have noticed for ledge-atom diffusion along the ⟨110⟩ step is that a diffusing ledge atom tends to be trapped at an end of the step. We therefore measured the occupation numbers of a ledge atom in different sites of a very small ⟨110⟩ step consisting of nine sites during diffusion at 280 K. This small size is chosen to improve the statistics of the site occupation numbers. The occupation numbers are shown in Fig. 7(a). The slight asymmetry is produced by the lack of a true global equilibrium because of the very large sticking probability at the two end sites compared to all other sites and the still limited number of experimental measurements even though we have made about 1000 observations with one ledge atom. This is about the practical limit one can experiment with one ledge atom. As the two ends are completely equivalent for the ⟨110⟩ step of the fcc (001) surface, we take the averages of the equivalent sites from both sides and derive the relative binding energies of these sites according to their Boltzmann factors. These binding energies are shown in Fig. 7(b). From this set of data we conclude that within the uncertainty of the measurement, about ±5 meV, the binding strength of a ledge atom at the ⟨110⟩ step is fairly uniform, except at the last two end sites, which are 57±5 and 21±5 meV larger than the rest of the sites. Since our diffusion data of ledge atoms were taken on steps of very small size, it is difficult to avoid the effect of the nonuniform binding strength of step sites. A ledge atom near the central region tends to jump toward the edge. This may affect the jump-length distribution. The jump lengths observed in this experiment that are slightly longer than theoretical ones based on nearest-neighbor jumps may be partly produced by this effect; at least it is difficult to distinguish this effect of a chemical potential gradient from a true thermal effect.

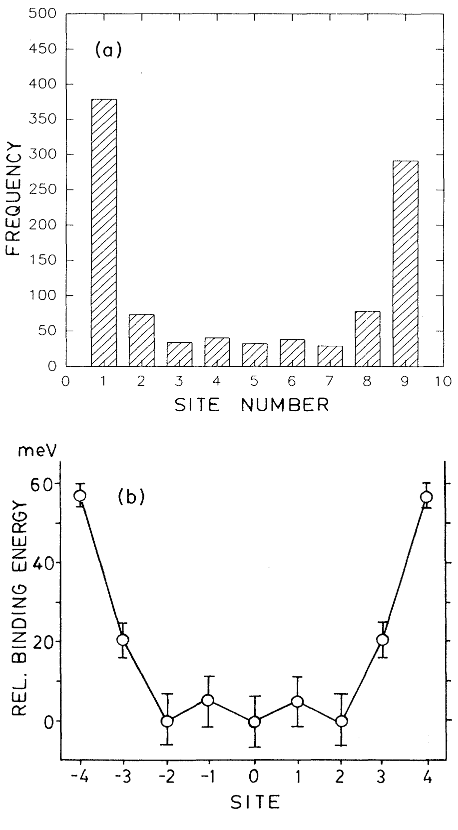


FIG. 7. (a) Site occupation numbers, or frequencies of occupation, of a ledge atom along a ⟨110⟩ step of nine atoms length at 280 K. (b) Relative binding energies of the ledge atom at the nine sites of the ⟨110⟩ step. The binding energy at the center site is used as the reference level.

D. Dissociation and adsorption energies

In the tip blunting process, when the tip is heated to high temperature, one can expect the top surface layer of the tip apex to become disordered and dissolve eventually. The question is whether a surface has to go through disordering to dissolve and what the atomic processes involved in the dissolution are. If pair energies are additive, as assumed in most chemistry and materials science literatures, then one can expect that, at least at low temperatures, atoms will dissociate from the steps in an ordered sequence, first from edge sites, followed by kink sites, etc., or the atomic rows at the steps are gradually removed one by one starting from two edges, as illustrated in Fig. 8. In reality, we find that for the Ir(001) layer,

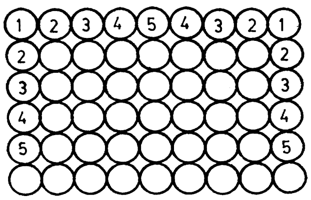


FIG. 8. Expected orderly sequence of dissociation of step atoms if bond energies are pairwise additive.

when the temperature is below $\sim$400 K, mostly only edge atoms are found to dissociate to the terraces, and the steps remain fairly smooth (see Fig. 9). Above $\sim$440 K, atoms start to dissociate from edge sites, ledge sites, kink sites, and recessed sites with a comparable probability, as shown in Fig. 10 where a small (001) layer eventually dissolves completely. In other words, the dissociation energies of atoms in all these sites are comparable; thus the dissociation is not orderly above $\sim$440 K and the steps are roughened. In 3D crystals, it is generally believed that there is a well-defined roughening transition temperature for the surfaces.[6] We find that for the steps of the Ir(001), roughening of steps occur around 440 K, but there is no clear-cut temperature where the steps start to roughen. Roughening of the steps occurs by dissociation of step atoms from different types of sites to terraces with comparable probabilities. We rarely observe atoms to dissociate to the layer above. An interesting theoretical question is whether a 1D step, or the surface of a 2D crystal, should also exhibit a well-defined roughening transition temperature. A 1D crystal may exhibit less collective effects than 2D and 3D crystals.

The dissociation energy of step atoms can be determined from a measurement of the dissociation time as a function of temperature. In the case of edge atoms, we can pinpoint the atom which dissociates during a particular heating period, as seen in the FIM images of Fig. 9. The dissociation time τ of edge atoms as a function of temperature can be measured precisely by focusing our attention on *each* of these edge atoms. An Arrhenius-type plot, $\ln(1/\tau)$ vs $1000/T$, for the dissociation of edge atoms is shown in Fig. 11(a), and it is linear as expected. From the plot, we find the dissociation energy to be 1.35 ± 0.07 eV and the time constant to be $2.5\times10^{-13.0\pm1.0}$ s. For other step atoms at the temperature where dissociation can occur, step atoms in different sites dissociate with a comparable probability and there is no ordered sequence. We therefore cannot determine the lifetime of atoms in different sites of the steps. Instead, we can determine the average dissociation energy of step atoms by measuring the dissolution time of a surface layer of the same size as function of temperature. A set of the data is shown in Fig. 11(b). From the slope of this plot the average dissociation energy of step atoms is found to be 1.40 ± 0.07 eV and the time constant of the rate equation is $2.4\times10^{-10\pm0.7}$ s. Two experimental facts can be noticed: First, the dissociation energy of edge site atoms is only 0.05 ± 0.09 eV lower than that of other step atoms. Second, kink-site atoms, ledge-site atoms, and recessed-site atoms have almost the same dissociation energy. Since, in the dissolution of the surface layer, the rate limiting step should be the dissociation of those atoms with the largest dissociation energy, we have to conclude that the dissociation energies of different step atoms cannot differ more than $0.05\pm0.09=0.14$ eV. Thus, within an uncertainty of $\pm(0.05\pm0.09)$ eV, the dissociation energies of all these step atoms are 1.40 eV, or more accurately with an uncertainty of $\sim(0.05^2+0.07^2)^{0.5}=0.09$ eV after considering the statistical error of the measurement. That a recessed atom with three nearest-neighbor (NN) surface bonds has a dissociation energy, or binding energy to the step, only 0.05 eV larger than an edge atom with two NN surface bond is unexpected, which points to a possible nonadditivity of bond energies on a metal surface.

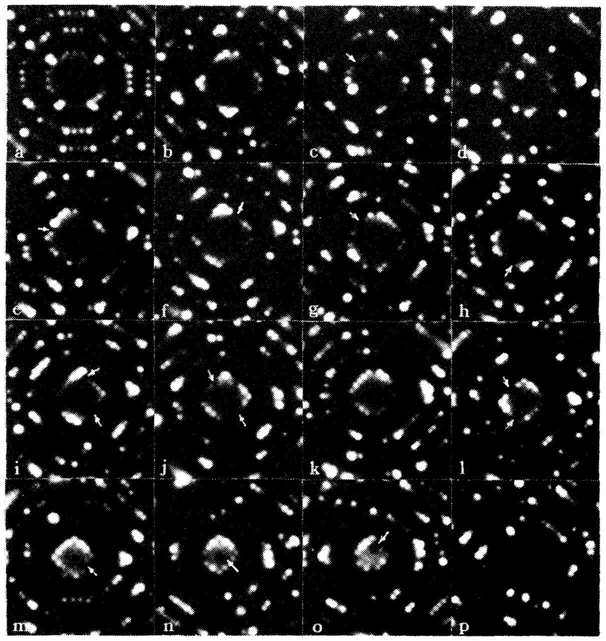


FIG. 10. Above $\sim$430 K, dissociation of step atoms to terraces is not very orderly. Atoms in kink sites, recessed sites, etc., can dissociate to the terraces as easily as ledge or edge atoms. Only in very rare cases are atoms found to dissociate to the layer above, as seen in (d). Arrows point to some of the recessed sites where steps atoms have dissociated. When the surface layer is reduced to contain only about 20 atoms, closing of a recessed site at the step by an interior atom, thus forming a vacancy inside the layer, often occurs, as seen in (n). Between two images is a heating period of 60 s at 570 K.

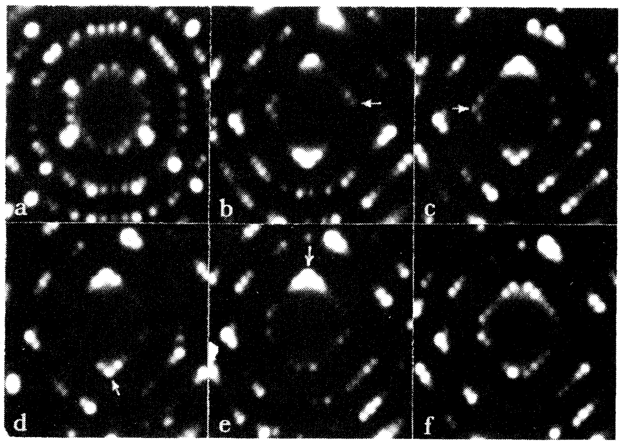


FIG. 9. At 420 K, a nearly circular Ir(001) layer is first changed into a square as shown in (a) and (b) by diffusion of step atoms along the steps. The images are slightly deformed because of the poor symmetry of the tip shape. Arrows point to the edge atoms which dissociate within the next heating period.

We now consider the adsorption energy in self-adsorption on a terrace site E_b or the binding energy with the substrate in self-adsorption. Using the fact that in sublimation from a 3D crystal surface the desorption energy of kink-site atoms to free space is theoretically identical to the cohesive energy of the solid (this has recently been confirmed to an accuracy of ±0.2 eV with an experimental measurement of the ion energy distribution in low-temperature field evaporation[7]), and the energy diagram[8] shown in Fig. 12, we can now calculate the binding energy in self-adsorption at a terrace site to be $E_b = E_c + E_d - E_{\text{diss}} = (6.93+0.84-1.40)$ eV $= 6.37$ eV with an uncertainty of ~0.09 eV, where E_c is the cohesive energy, E_d is the activation energy in self-diffusion of adatoms, and E_{diss} is the dissociation energy of a kink-site atom to an adsorption site at the terrace. Thus the binding energy of an adatom having four nearest-neighbor bonds is only 0.56 ± 0.10 eV smaller than that of a kink-site atom having six nearest-neighbor bonds; this is again somewhat of a surprise. The binding energy of kink-site atoms of Ir is of course equal to the cohesive energy, or 6.93 eV. Our experiment shows that step atoms of the Ir(001) surface can dissociate to terraces at $\sim\frac{1}{6}$ and steps are no longer smooth at $\sim\frac{1}{5}$ the melting point of Ir.

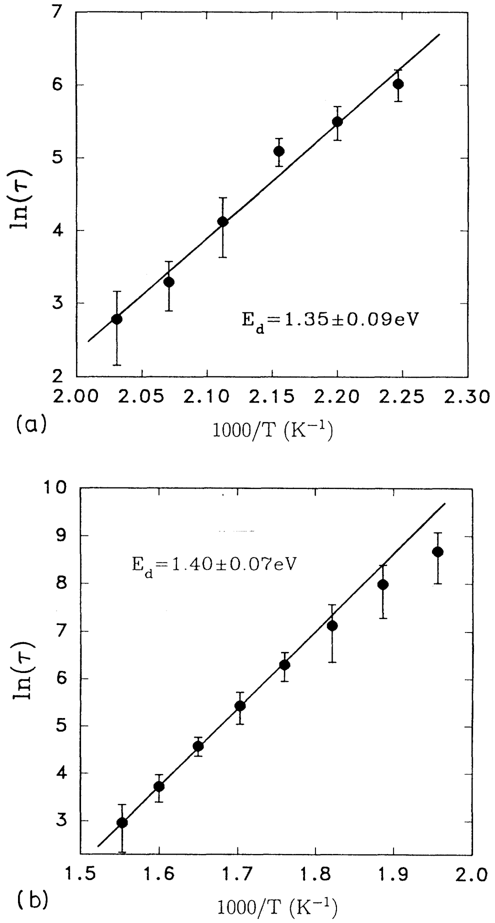


FIG. 11. (a) When the logarithm of the average lifetime of edge atoms is plotted against the inverse temperature, a linear plot is obtained. From the slope, the dissociation energy is found to be 1.35±0.09 eV and the time constant is found to be $2.5\times10^{-13.0\pm1.0}$ s. (b) A similar plot where τ now represents the average time for a surface layer to dissolve completely. From the slope of this plot, the average dissociation energy of step atoms is derived to be 1.40±0.07 eV. The time constant of this rate equation is $2.4\times10^{-10\pm0.7}$ s.

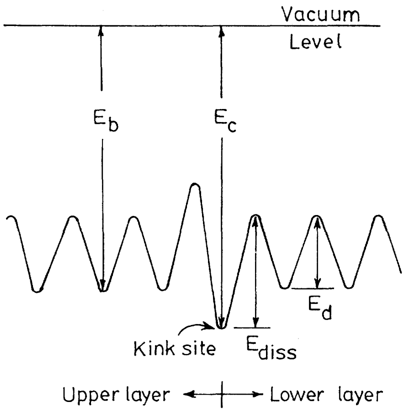


FIG. 12. A schematic potential-energy diagram showing the relationship between E_b, E_c, E_d, and E_{diss}. In this diagram we assume that the step is reflective to a diffusing adatom, which is not the case for Ir on the Ir(001). However, the relation is not affected by whether the step is reflective to or absorptive to a diffusing adatom.

E. Equilibrium crystal shape

Consider now the 2D ECS. In the 3D case, the ECS is determined by the polar angle dependence of the surface-energy density.[9] It can be predicted from a Wulff plot. A study of ECS can lead to a better understanding of the surface-energy anisotropy.[4] ECS is usually studied with microcrystals because there is the need to transport atoms from one place to another to achieve the shape. Because of this need and the relatively large size of the microcrystals, so far ECS has been studied only at very high temperatures. In principle, a study of the equilibrium crystal shape of a 2D crystal, or a surface layer, should make it easier to lead to a quantitative atomistic understanding of the atomic processes involved and their energetics than a 3D crystal because of the reduced dimensionality. Using an atomic resolution microscopy with a small surface layer, ECS can be studied at very low temperature, or only about $\frac{1}{6}$ of the melting point of the material. In the 2D case, the ECS is determined by the line-energy density of the lattice steps. In Figs. 10(a) and 10(b), we already showed that a nearly circular top (001) surface layer of an Ir field ion emitter, prepared by low-temperature field evaporation, is changed into an equilibrium crystal shape by the diffusion of lattice-step atoms. The shape change can already occur near ~420 K, or less than $\frac{1}{6}$ of the melting point of Ir. The ECS in this case is a square with its sides formed by the ⟨110⟩ closest-packed atomic rows. The "line tension" $\gamma(\theta)$ (or energy/length) should have deep cusps as shown in Fig.

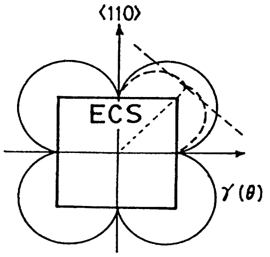


FIG. 13. The experimentally found equilibrium crystal shape of an Ir(001) layer is a perfect square with its steps parallel to the ⟨110⟩ directions. Therefore the step energy density polar plot should look like those shown either by the solid curve or the dotted curve.

13. At this temperature, the anisotropy of the step energy is too high to have steps other than the ⟨110⟩ steps present in the equilibrated layer. When the temperature is raised above 440 K, atoms start to dissociate from everywhere at the lattice step to the terrace, but the square shape is maintained. There is no clear-cut rounding of the corners, except a few missing edge atoms, which can be expected simply from the random dissociation of step atoms. This again indicates that the line-energy anisotropy of the steps of the Ir(001) surface is too high to allow the existence of an appreciable fraction of the steps to be anything other than the ⟨110⟩ type at a temperature where 2D sublimation of atoms can already occur. The line energy density γ of the ⟨110⟩ step should be given by $(E_{\text{diss}}-E_d)/l$, where l is the unit length of the step. Therefore $\gamma=\{(1.40-0.84)\pm0.09\}$ eV/2.8 Å, or $(3.2\pm0.5)\times10^{-10}$ J/m. The cohesive energy of the 2D crystal, or the difference in the binding energy of an atom in a kink site and that in a terrace site, is 0.56±0.09 eV.

F. Hollow 2D clusters

We report here observations of *hollow square and rectangular surface clusters and surface layers* during heating and surface layer dissolution experiment as shown in Fig. 14 for an eight-atom square cluster, a ten-atom rectangular cluster, and a "spongelike" surface layer. These hollow clusters are formed during the last stage of dissolution of a surface layer. Generally an atom at a recessed site is dissociated from a step thus creating a "vacancy" at the step. This vacancy is then filled by an atom from the interior of the cluster to form a hollow cluster. A hollow eight-atom square cluster has eight nearest-neighbor surface bonds. In comparison, an eight-atom cluster of a filled square with one corner atom missing has ten NN surface bonds [see Fig. 14(g)]. That the hollow one with eight bonds is thermally more stable than the filled one with ten bonds demonstrates convincingly the nonadditivity of bond energies at a metal surface. Therefore the generally believed nonadditivity of bond energies at metal surfaces is convincingly established through this observation of hollow 2D clusters. These hollow clusters are unstable with respect to surface diffusion, or dissociation often occurs during diffusion. In rare cases, a small (001) surface layer with a very large number of vacancies can be formed during the heating. Figure 14(f) is an example. That this spongelike small metal surface layer can be formed at ~780 K is interesting and it further demonstrates the complicated nature of atomic interaction on metal surfaces. It is possible that during the heating, this layer is disordered. Atoms settle into lattice sites only when it is quenched to low temperature. Unfortunately, FIM technique will not be able to answer this question.

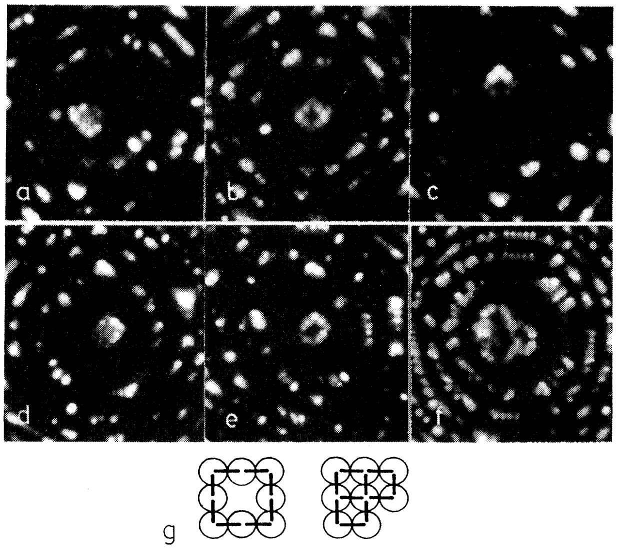


FIG. 14. (a)–(c) show how a small closed cluster of 11 atoms, after some diffusion and dissociation, ends up in a hollow 8-atom cluster. (d) and (e) show how a closed 12-atom rectangular cluster loses two interior atoms to the terrace to form a 10-atom hollow cluster. (f) shows a spongelike surface layer. (g) shows that the hollow 8-atom cluster has only 8 nearest-neighbor bonds, whereas a closed 8-atom cluster can have 10 NN bonds. Yet the hollow one is found to be energetically favored, or more stable.

ACKNOWLEDGMENT

This work was supported in prt by DMR of NSF and NSC of ROC (81-02080-M-001-19).

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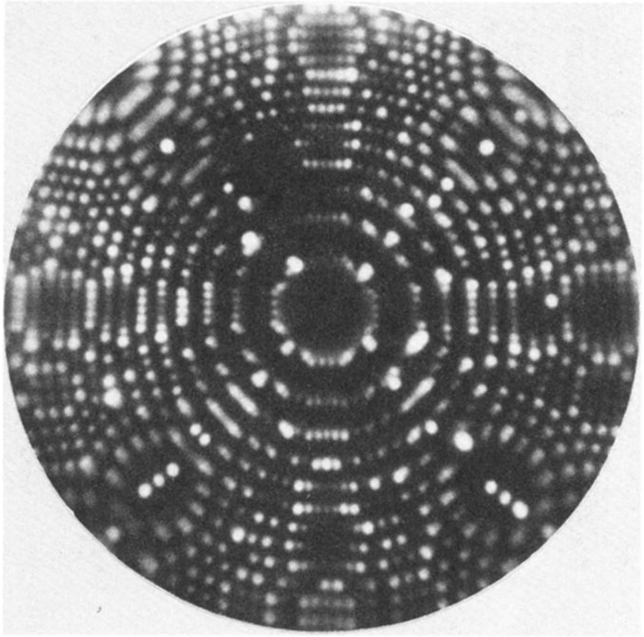

FIG. 1. A field ion micrograph of a (001)-oriented Ir tip. The concentric rings are formed by (001) surface layers. Each ring represents a surface layer.

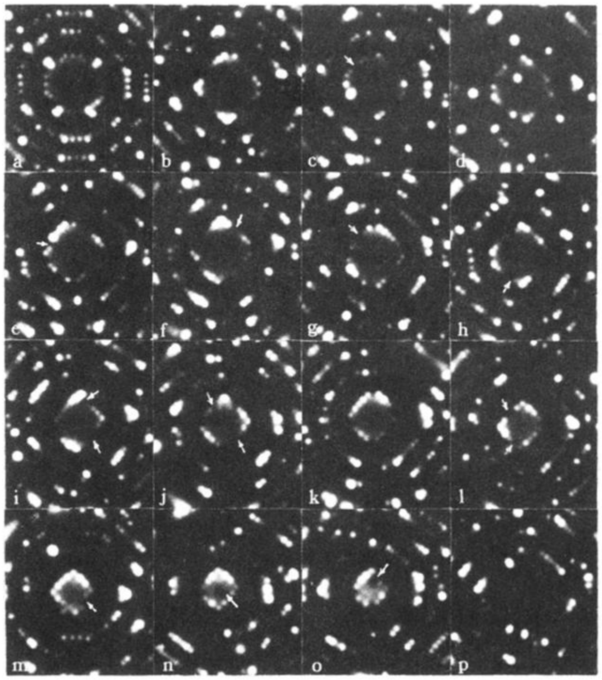

FIG. 10. Above ~430 K, dissociation of step atoms to terraces is not very orderly. Atoms in kink sites, recessed sites, etc., can dissociate to the terraces as easily as ledge or edge atoms. Only in very rare cases are atoms found to dissociate to the layer above, as seen in (d). Arrows point to some of the recessed sites where steps atoms have dissociated. When the surface layer is reduced to contain only about 20 atoms, closing of a recessed site at the step by an interior atom, thus forming a vacancy inside the layer, often occurs, as seen in (n). Between two images is a heating period of 60 s at 570 K.

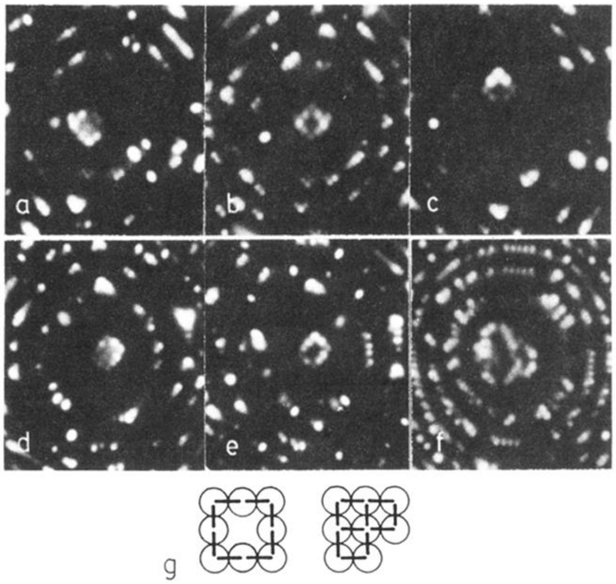

FIG. 14. (a)–(c) show how a small closed cluster of 11 atoms, after some diffusion and dissociation, ends up in a hollow 8-atom cluster. (d) and (e) show how a closed 12-atom rectangular cluster loses two interior atoms to the terrace to form a 10-atom hollow cluster. (f) shows a spongelike surface layer. (g) shows that the hollow 8-atom cluster has only 8 nearest-neighbor bonds, whereas a closed 8-atom cluster can have 10 NN bonds. Yet the hollow one is found to be energetically favored, or more stable.

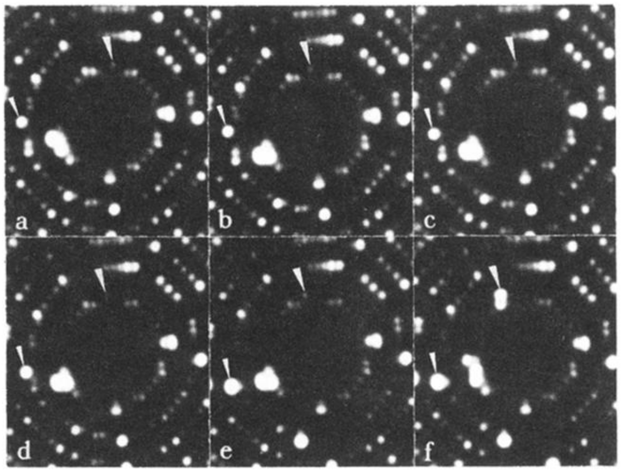

FIG. 4. FIM images showing the 1D random-walk diffusion of ledge atoms along the ⟨110⟩ steps. Ledge atoms tend to stick to the end site of the steps. Arrows point to the diffusing ledge atoms.

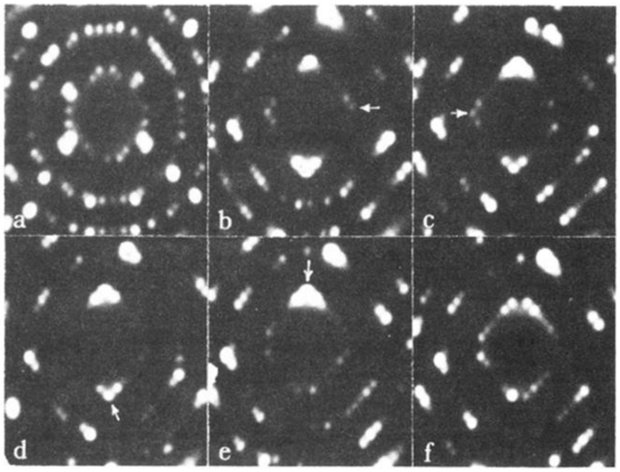

FIG. 9. At 420 K, a nearly circular Ir(001) layer is first changed into a square as shown in (a) and (b) by diffusion of step atoms along the steps. The images are slightly deformed because of the poor symmetry of the tip shape. Arrows point to the edge atoms which dissociate within the next heating period.