Atom Incorporation at Surface Clusters: An Atomic View

S. C. Wang and Gert Ehrlich
Materials Research Laboratory and Department of Materials Science and Engineering,
University of Illinois at Urbana-Champaign, Urbana, Illinois 61801
(Received 5 August 1991)

Observations have been made of the incorporation of single iridium atoms into ascending as well as descending steps at iridium clusters on Ir(111). At ascending steps, incorporation occurs once diffusion of adatoms becomes significant. At descending steps, it is more complicated, and proceeds differently on large compared to small (12-atom) clusters. The mechanism of incorporation has been tested in experiments with tungsten atoms. These reveal that incorporation at descending steps can occur by exchange of the adatom with a cluster atom rather than by simple jumps.

PACS numbers: 61.50.Cj, 68.35.Fx, 68.55.Ce, 68.55.Jk

In recent years there has been a growing realization that the atomic events at lattice steps play a vital role in affecting the growth of crystals from the vapor [1]. The standard view is that when an atom migrating over a crystal terrace strikes an ascending step, it will incorporate into it, as is illustrated in Fig. 1(a). In contrast, an atom approaching a descending step, as in Fig. 1(b), has to overcome an additional potential barrier to roll over the edge before it can attach itself to the step [2–5]. Comsa and co-workers [6–8] especially have emphasized the differences in incorporation at ascending and descending steps, and have explored how difficulties in accomplishing the former affect surface morphology. There is experimental evidence, derived from observations on individual atoms [9–12], that supports some aspects of the standard view of events at lattice steps. Theoretical estimates of the energetics of atoms at different positions at a step on a bcc (110) surface, by Jardin, Desjonquères, and Spanjaard [13], also fit this picture. However, there are suggestions that events at lattice steps may be much more complicated. For example, some time ago, Bassett [14] raised the possibility that during incorporation an adatom may exchange position with a lattice atom in the step, as in Fig. 1(c). Recent calculations by Nørskov [15], for atoms at descending steps on Cu(111), suggest that on this plane incorporation may occur by atom exchange. Inasmuch as little direct information is available about how atoms actually incorporate into a crystal, we have carried out a detailed study, using the field-ion microscope [16] to observe how individual atoms attach themselves to iridium clusters on an Ir(111) surface.

In Fig. 2(a), a cluster of 12 iridium atoms has been formed by controlled field evaporation [17–19] of a (111)-oriented iridium single crystal, and a single Ir atom has then been deposited, in Fig. 2(b), on the terrace adjacent to the cluster. Upon warming to $T \approx 100$ K, the normal temperature for diffusion on Ir(111) [20], the adatom migrates over the terrace in the absence of any applied fields [Fig. 2(c)]. After approaching the cluster, the adatom incorporates at the ascending step in Fig. 2(d). If the size of the cluster is increased, the sequence of events is still the same. It appears that incorporation at an ascending step occurs in accord with the standard view of crystal growth.

Things are quite different when an Ir atom is deposited on top of a cluster of 12 iridium atoms, as in the sequence in Fig. 3. Because of the extreme sensitivity of the imaging process to the electric field, only the adatom on top of the cluster is then visible in Fig. 3(b); nevertheless, the location of the adatom can still be traced. For the Ir atom to move from one position to another on top of the cluster requires a significantly higher temperature, $T \approx 120$ K, than on a flat terrace. Once the migrating adatom reaches a position at the cluster edge, it can incorporate at the step at the same temperature; the newly enlarged cluster then becomes visible again, as in Fig. 3(c).

Atoms deposited on larger iridium clusters, containing

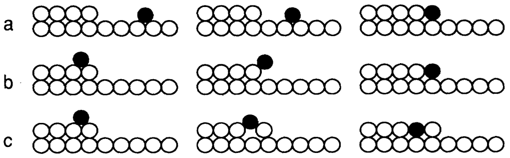

FIG. 1. Schematic view of atom incorporation at lattice steps. Incorporation (a) by diffusion of adatom to ascending step; (b) by atom jump into descending step; and (c) by adatom exchanging place with cluster atom.

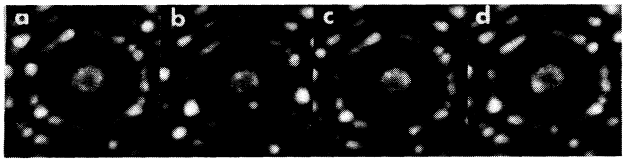

FIG. 2. Field-ion images of the Ir adatom incorporating at an ascending step of Ir_{12} on Ir(111). (a) Cluster formed by field evaporation. (b) Ir atom deposited on (111) terrace. (c) After diffusion at $T \approx 100$ K. (d) Incorporation into cluster.

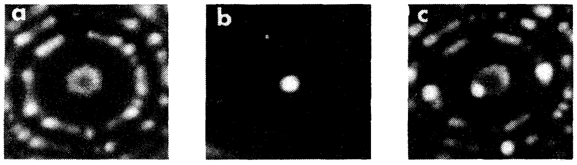

FIG. 3. Incorporation at descending step of Ir$_{12}$ (a) Cluster created by field evaporation. (b) After deposition, only the iridium atom on top of cluster is visible. (c) Ir atom incorporated into cluster step after heating to $T \approx 120$ K.

18 or more atoms, behave rather differently. On top of the cluster of 50 iridium atoms shown in Fig. 4(a), an Ir adatom diffuses at essentially the same temperature, $T \approx 100$ K, as on a (111) plane. Once it reaches a position at the edge, migration ceases and the adatom is trapped there. Only if the temperature is increased substantially, to $T > 150$ K, can the trapped atom escape; it does so by incorporating itself in the descending step, in preference to returning to other positions on top of the clusters. The conditions for incorporation are quite sensitive to the local atomic arrangement, which is sketched in Fig. 5(a). In conformity with the threefold symmetry of the (111) plane, neighboring edges alternate in their geometry, and can be either of type A, defined by the structure of the edge normal to [2$\bar{1}\bar{1}$], or of type B. Incorporation at an edge of type A, in Fig. 4(b), is initiated by warming the surface to ≈ 175 K; incorporation at a type-B edge, in Fig. 4(c), occurs at lower temperatures, after warming to only ≈ 160 K. This behavior has been reproduced in many experiments.

These observations reveal an incorporation process markedly different for atoms deposited on small and on large clusters, which should significantly affect nucleation of new layers. On the former, incorporation occurs at considerably lower temperatures, as soon as the adatom becomes mobile. On top of larger clusters, the migrating adatom is trapped close to the edge [21]; incorporation takes place at temperatures significantly above those required for diffusion. Such differences between small and large clusters have recently been postulated by Kunkel *et al.* [6] to account for their observations of layer-by-layer growth of Pt on Pt(111) in two quite separate temperature domains, but have not been previously observed. On the larger clusters, atomic behavior differs substantially from the traditional picture, which does not allow for trapping in the vicinity of a descending step. The differences from the standard view of incorporation can be understood in terms of the potential diagrams in Fig. 5(b). Still not clear is the reason for the significant dependence upon step orientation, or the mechanism of atom incorporation into a descending step. Does this occur by a simple atomic jump, as usually envisioned, or is it possible that the adatom changes place with one of the cluster atoms forming the edge?

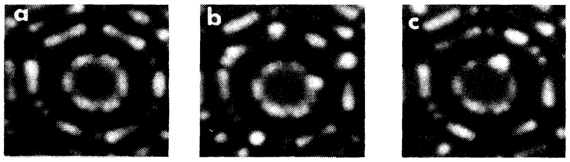

FIG. 4. Incorporation of Ir atom deposited on iridium cluster of 50 atoms. (a) View of initial cluster. (b) Incorporation at step of type A, after warming to $T \approx 175$ K. (c) Incorporation at step of type B, after warming to $T \approx 160$ K.

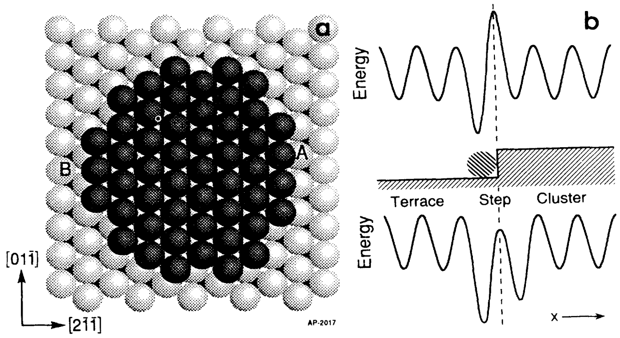

FIG. 5. (a) Schematic of cluster of 50 atoms on Ir(111), illustrating edges of type A and B. (b) Schematic potential diagrams for Ir atom moving toward a step. Top: Traditional view. Bottom: Potential consistent with present results.

Incorporation by ordinary atom jumps and that by atomic exchange can be readily distinguished if the adatom is chemically different from the substrate. In the former process, illustrated in Fig. 1(b), the original atom appears attached to the lattice step. On the contrary, if incorporation involves atomic exchange, then a lattice atom will end at the step—the original adatom is buried inside, as in Fig. 1(c). The field-ion-microscope image reveals the location of individual atoms at the surface, but generally does not provide clues to the chemical identity. However, chemically different adatoms evaporate at different applied field; under favorable conditions, and after calibration, this may afford a simple means of establishing the chemical identity of different atoms at a sur-

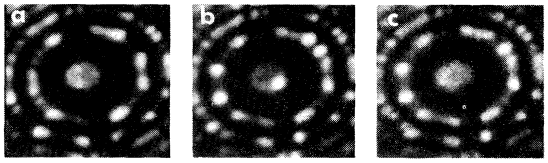

FIG. 6. Incorporation of W at descending step on Ir$_{12}$. (a) Bare cluster. W is deposited on this, and the temperature is raised to 220 K. (b) After incorporation; protruding atom stable at 10.7 kV. (c) After field evaporation of protruding atom at 11.3 kV; two adjacent atoms have also been removed from the cluster.

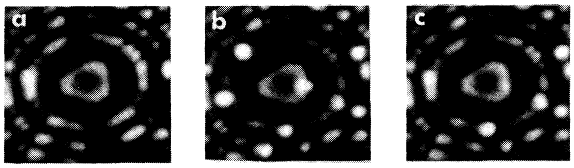

FIG. 7. Tungsten incorporation at type-A step on Ir_{33}. (a) Starting cluster. W atom is then deposited on cluster, and warmed to 220 K. (b) After incorporation at step of type A. (c) Protruding atom has been removed at 9.2 kV, which for this cluster is characteristic of W. Note that here and in Fig. 8 the tip diameter is smaller than in Fig. 6.

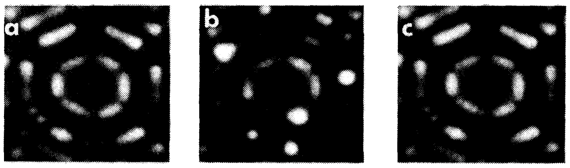

FIG. 8. Incorporation of W at step of type B on Ir_{69}. (a) Cluster formed by field evaporation. W is then deposited on it, and the temperature is raised to 220 K. (b) After incorporation at step of type B. (c) Protruding atom has been field evaporated at 9.8 kV, typical for Ir atom at step.

face [22].

In our experiments we have probed the fate of a tungsten adatom, deposited on top of an iridium cluster on Ir(111). To establish our ability to differentiate between iridium and tungsten adatoms attached to a cluster step, an iridium adatom is deposited on a terrace and is allowed to incorporate itself at an ascending cluster step. This protruding atom is then removed by field evaporation at ≈20 K, and the voltage required is noted. This procedure is repeated until the conditions for field evaporation of the iridium atom from all sites on the periphery have been mapped. A similar sequence determines the conditions for field evaporation of tungsten atoms. In our experiments on a cluster of 12 atoms, there is only a small variation (<0.1 kV) in the applied voltage of ≈11.3 kV necessary to remove an iridium atom from different positions on the periphery. However, the voltage to remove an iridium adatom from the cluster is consistently 5% (≈0.6 kV) higher than that for tungsten. As the evaporation voltage can easily be determined to much better than 1%, we have a reliable criterion for distinguishing the type of atom at a step.

To explore how incorporation of an atom takes place at a descending step, a tungsten atom is deposited on top of a cluster of 12 iridium atoms [Fig. 6(a)]. On warming the surface to 220 K, the atom migrates and finally disappears from the top; an atom is then seen attached to the step, shown in Fig. 6(b). After applying a voltage of 10.7 kV, sufficient to remove a tungsten atom from the cluster, the image remains unchanged—the protruding atom has *not* been removed. To field evaporate this atom requires a substantial voltage increase, to 11.3 kV, which corresponds to the conditions for removing an iridium atom. As is apparent from the image of the cluster, in Fig. 6(c), field evaporation then removes not only the protruding atom, but also two adjacent atoms in the cluster itself. That is expected if incorporation of the tungsten adatom occurs by exchange with a cluster atom. The atom attached to the step will then be iridium, and next to it in the cluster should be the incorporated tungsten atom. Once the protruding iridium atom has been removed, at a relatively high field, the tungsten atom is in a field which exceeds that required for its evaporation. It is therefore removed, leaving a single Ir atom at the edge, which field evaporates as well.

Incorporation of tungsten has also been tested on larger clusters. Shown in Fig. 7 are experiments on a cluster of 33 Ir atoms. After incorporation of a tungsten atom at an edge of type A, shown in Fig. 7(b), the voltage to remove the adatom protruding from the periphery is low; field evaporation takes place under conditions typical for tungsten atoms. At this type of an edge, incorporation therefore occurs by a simple jump of the tungsten atom from the top of the cluster into a position at the step. When a tungsten adatom incorporates at an edge of type B, as is shown in Fig. 8 for an iridium cluster of 69 atoms, the adatom protruding from the cluster after incorporation can only be removed at a higher voltage characteristic of Ir atoms. At an edge of type B, incorporation therefore takes place by exchange of the tungsten adatom with one of the iridium atoms of the cluster [23].

These first experiments on the details of atom incorporation at steps reveal a rather different behavior for atoms on top of small and large clusters; they also indicate that for both, incorporation at descending steps may involve atom exchange. Our experiments establish this as the operative mechanism for tungsten atoms incorporating into small iridium clusters, and at edges of type B on larger clusters. It is at such edges that incorporation of iridium atoms occurs readily at low temperatures. We therefore believe that iridium also may incorporate by exchange, but for this there is no direct evidence. In any event, it is clear that atom incorporation at steps is much more interesting than envisioned in standard theories of crystal growth, and that the role of local geometry and the participation of exchange processes will have to be carefully explored.

This work was carried out with support from the Department of Energy under Grant No. DEFGO2-91 ER45439. We have received considerable help from M. F. Lovisa, D. Cowell Senft, and F. Watanabe.

---

[1] See, for example, E. Chason and B. W. Dodson, J. Vac. Sci. Technol. A 9, 1545 (1991).

[2] H. Bethge, in *Kinetics of Ordering and Growth at Surfaces,* edited by M. G. Lagally (Plenum, New York, 1990), p. 125.

[3] R. Kariotis and M. G. Lagally, Surf. Sci. **216**, 557 (1989).

[4] P. Bennema and G. H. Gilmer, in *Crystal Growth: An Introduction,* edited by P. Hartman (North-Holland, Amsterdam, 1973), p. 263.

[5] R. L. Schwoebel, J. Appl. Phys. **40**, 614 (1969).

[6] R. Kunkel, B. Poelsema, L. K. Verheij, and G. Comsa, Phys. Rev. Lett. **65**, 733 (1990).

[7] B. Poelsema, R. Kunkel, L. K. Verheij, and G. Comsa, Phys. Rev. B **41**, 11609 (1990).

[8] T. Michely, K. H. Besocke, and G. Comsa, Surf. Sci. **230**, L135 (1990).

[9] G. Ehrlich and F. G. Hudda, J. Chem. Phys. **44**, 1039 (1966).

[10] D. W. Bassett, C. K. Chung, and D. Tice, Vide **176**, 39 (1975).

[11] S.-C. Wang and T. T. Tsong, Surf. Sci. **121**, 85 (1982).

[12] H.-W. Fink and G. Ehrlich, Surf. Sci. **173**, 128 (1986).

[13] J. P. Jardin, M. C. Desjonquères, and D. Spanjaard, J. Phys. C **18**, 1767 (1985).

[14] D. W. Bassett, in *Surface Mobilities on Solid Materials,* edited by V. T. Binh (Plenum, New York, 1983), p. 63.

[15] J. K. Nørskov, in Proceedings of the Workshop on Self-diffusion at Metal Surfaces, Copenhagen, April 1991 (to be published).

[16] The techniques are those standard for our laboratory, described by S. C. Wang and G. Ehrlich, Surf. Sci. **206**, 451 (1988).

[17] H. J. Kreuzer, in *Chemistry and Physics of Solid Surfaces VIII,* edited by R. Vanselow and R. Howe, Springer Series in Surface Science Vol. 22 (Springer-Verlag, Berlin, 1990), p. 133.

[18] J. A. Panitz, in *Solid State Physics: Surfaces,* edited by R. L. Park and M. G. Lagally, Methods of Experimental Physics Vol. 22 (Academic, Orlando, FL, 1985), p. 349.

[19] E. W. Müller and T. T. Tsong, *Field Ion Microscopy Principles and Applications* (American Elsevier, New York, 1969).

[20] S. C. Wang and G. Ehrlich, Phys. Rev. Lett. **62**, 2297 (1989).

[21] For such trapping on W(211), see H.-W. Fink and G. Ehrlich, Surf. Sci. **143**, 125 (1984).

[22] This approach has been previously proposed by D. W. Bassett and also by J. D. Wrigley (private communication).

[23] Field evaporation occurs differently if W incorporates at a corner position; it may then also be removed from the cluster.

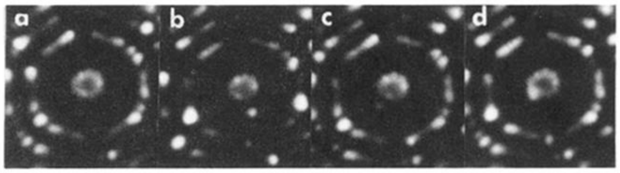

FIG. 2. Field-ion images of the Ir adatom incorporating at an ascending step of Ir_{12} on Ir(111). (a) Cluster formed by field evaporation. (b) Ir atom deposited on (111) terrace. (c) After diffusion at $T \approx 100$ K. (d) Incorporation into cluster.

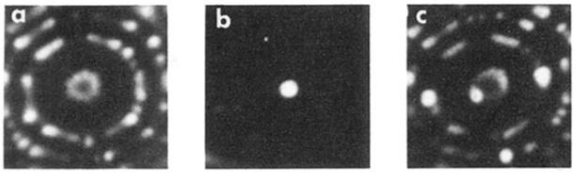

FIG. 3. Incorporation at descending step of Ir_{12} (a) Cluster created by field evaporation. (b) After deposition, only the iridium atom on top of cluster is visible. (c) Ir atom incorporated into cluster step after heating to $T \approx 120$ K.

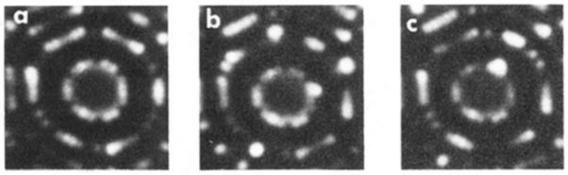

FIG. 4. Incorporation of Ir atom deposited on iridium cluster of 50 atoms. (a) View of initial cluster. (b) Incorporation at step of type A, after warming to $T \approx 175$ K. (c) Incorporation at step of type B, after warming to $T \approx 160$ K.

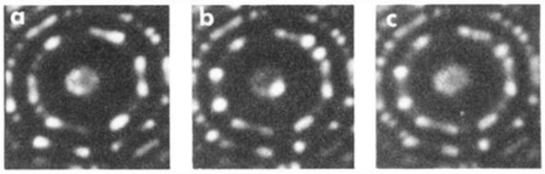

FIG. 6. Incorporation of W at descending step on Ir_{12}. (a) Bare cluster. W is deposited on this, and the temperature is raised to 220 K. (b) After incorporation; protruding atom stable at 10.7 kV. (c) After field evaporation of protruding atom at 11.3 kV; two adjacent atoms have also been removed from the cluster.

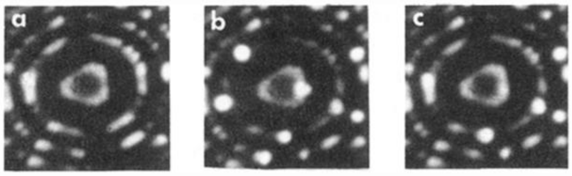

FIG. 7. Tungsten incorporation at type-A step on Ir_{33}. (a) Starting cluster. W atom is then deposited on cluster, and warmed to 220 K. (b) After incorporation at step of type A. (c) Protruding atom has been removed at 9.2 kV, which for this cluster is characteristic of W. Note that here and in Fig. 8 the tip diameter is smaller than in Fig. 6.

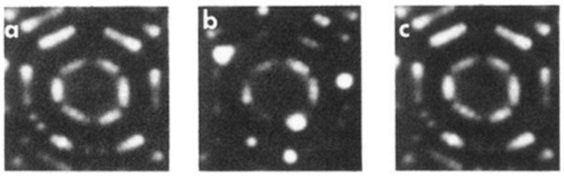

FIG. 8. Incorporation of W at step of type B on Ir_{69}. (a) Cluster formed by field evaporation. W is then deposited on it, and the temperature is raised to 220 K. (b) After incorporation at step of type B. (c) Protruding atom has been field evaporated at 9.8 kV, typical for Ir atom at step.