Atom Condensation at Lattice Steps and Clusters

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The deposition of individual Ir atoms on an Ir(111) surface with a central iridium cluster on it has been observed in the field ion microscope. Around Ir clusters of both 12 and 59 atoms at $T=20$ K there is an empty zone, ~2 nearest-neighbor spacings wide, in which condensed atoms are not found. From quantitative measurements of the distribution of adatoms over the surface it appears that atoms from the vapor striking this region skitter over the surface, even at $T \sim 20$ K, and are collected at cluster edges. Atoms from the vapor striking the cluster condense without damage to the cluster.

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During the last decade, a start has been made in visualizing the behavior of individual atoms during the growth of crystals from the vapor by relying on molecular dynamics simulations [1]. Actual experimental information, however, has been limited. So far, only a few of the atomic processes contributing to growth have been examined on the atomic level [2]. Here we wish to report the first observations of individual metal atoms from the vapor condensing at steps on a metal surface—one of the events contributing to the overall growth process.

Over the last thirty years, experiments have established that metal atoms from a thermal source, condensing on their own lattice at a low temperature, are immobilized close to the point of impact [3]; this is also the conclusion reached in recent molecular dynamics simulations [4]. The expectation therefore is that condensation should be reasonably uninteresting for understanding growth. The initial distribution of condensing atoms over a surface mirrors the flux of atoms from the gas phase. The few atoms striking steps can incorporate there; if the surface is at a reasonable temperature, however, atoms condensing on terraces can diffuse over the plane, and eventually may also reach growth sites at steps. Inasmuch as steps constitute only a small fraction of the total surface, it is these diffusing adatoms which make the dominant contribution to the growth current [5].

The many recent studies of growth [6] done with the scanning tunneling microscope (STM) do not serve to validate this picture, as single adsorbed atoms are not seen. STM experiments revealing adatoms have been done on a related phenomenon, the condensation of xenon on a cold Pt(111) surface. Weiss and Eigler [7], working with a special low-temperature instrument, observed xenon accumulating at crystal steps and other defects, but not at normal lattice sites, in agreement with molecular dynamics simulations of rare gas collisions with metal surfaces. These suggest that the weakly held xenon atoms bound over long distances before dissipating sufficient energy to the substrate to equilibrate [8,9]. Comparable experiments on the condensation of metal atoms on their own lattice are not available.

In our studies we have concentrated on the deposition of iridium atoms on the close-packed (111) plane of iridium, kept at ~20 K, a temperature at which diffusion of iridium over the surface is frozen in. Observations of individual atoms condensing on the surface are made by field ion microscopy, using techniques and equipment standard in our laboratory [10,11]. A cluster of the selected size is created on Ir(111) by pulsed field evaporation of atoms from the edges of the plane. Onto this starting surface, illustrated in Fig. 1(a), atoms are then evaporated from a resistively heated iridium wire, ~5 cm away and maintained at ~2500 K for a time interval long enough to deposit on average one atom. After every evaporation, the surface is imaged by slowly raising the applied voltage (over a period of ~3 sec). If an atom has indeed been deposited, as, for example, in Fig. 1(b), its position is recorded. In any event, the applied potential is subsequently raised to a level at which adatoms field evaporate, restoring the surface to its original state and making it ready for another deposition. This procedure is followed even if no adatom is visible under stan-

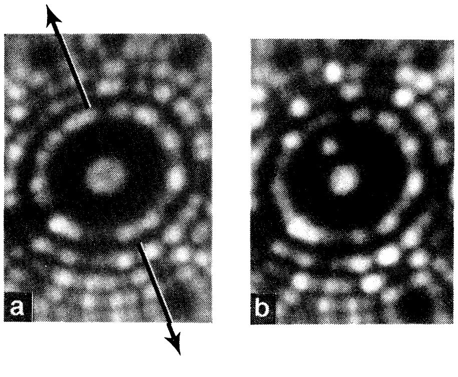

FIG. 1. Field ion image of Ir(111) with Ir_{12} cluster at the center. (a) Surface after formation of cluster by field evaporation. Arrows give projection of atom stream onto the (111) plane. (b) Same surface, after deposition of a single iridium atom onto the (111) plane at $T \sim 20$ K.

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dard conditions, to reveal atoms that might conceivably have been obscured by the local surface geometry.

It should be noted that, under normal imaging conditions, iridium adatoms are stable on Ir(111) and remain in their binding site even under prolonged observation. Only on raising the voltage $>12\%$ above normal are changes sometimes apparent: Just prior to field evaporation (at 14% above the normal imaging voltage), adatoms in fcc sites occasionally change over to an adjacent hcp site. Under normal conditions we obtain a reliable view of the location of iridium adatoms on the surface. A few hundred cycles of atom deposition, observation, and adatom removal are enough to create a map of the binding sites on the surface, and to note the occupation of the different sites. A few atom layers are then removed by field evaporation, to eliminate even traces of contamination that might have accumulated; a new cluster is created in the center of the plane, and the surface is ready for another round of deposition studies.

The incoming atoms make an angle of $\sim 45°$ with the (111) plane; the projection of the atom stream on the surface is roughly along ⟨231⟩, as indicated in the field ion image in Fig. 1(a). Throughout the experiments the metal surface is kept at ~ 20 K. Electric fields are imposed only when the surface is actually imaged. During atom deposition, the (111) plane is therefore in an essentially field-free environment, but it is surrounded by helium image gas. However, the pressure is so low, $<5\times10^{-5}$ Torr, that iridium atoms from the evaporator reach the (111) surface without collision. Moreover, at ~ 20 K and in the absence of applied fields, the fraction of the surface covered with helium is entirely negligible [12]. Collisions occur with a bare surface.

The distribution of iridium atoms on the flat terrace around Ir$_{12}$, derived from more than a thousand deposition cycles, is summarized in Fig. 2. It is immediately obvious that the deposited atoms are *not* distributed uniformly over the terrace, as expected if condensing atoms were localized on impact with the cold surface. Around the central cluster, there is a zone $\sim 2\frac{1}{2}$ nearest-neighbor spacings l deep, in which *no* atom is ever observed. At the cluster edges we see a much larger number of atoms accumulated at each site than present at terrace sites: The average number is 10 times higher than on the terrace. On top of the cluster the number of atoms per site appears comparable to that deposited on the terrace. It is worth noting that in all our observations the cluster of 12 iridium atoms maintains its structure throughout the depositions, despite the fact that incident atoms have a mean kinetic energy of ~ 10 kcal/mol, and the energy of condensation of Ir on Ir(111) amounts to ~ 135 kcal/mol. This energy appears to be dissipated very effectively into the lattice, leaving the cluster intact.

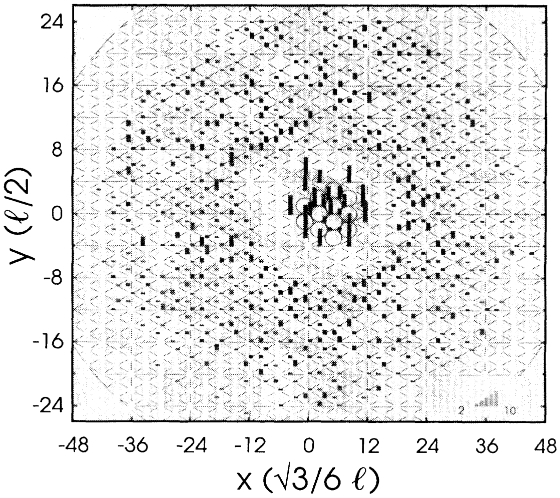

FIG. 2. Distribution of iridium atoms condensed on Ir(111) at $T\sim 20$ K with central cluster of 12 iridium atoms on it. hcp binding sites are at intersections of grid lines. Height of bars indicates population on sites; calibration is given at lower right. The maximum plane diameter is $26l$.

A simple picture can account for the results in Fig. 2: Atoms striking the flat terrace or the cluster condense rapidly close to the point of impact. However, atoms striking the region immediately around the cluster skitter over the cold surface, and eventually may come to rest at the cluster edge. The edge sites thus collect atoms that originally landed in the empty zone, which acts as a catch basin for atoms, draining to the edges. The traditional picture of condensation thus has to be modified. Even at low surface temperatures, at which ordinary diffusion over the crystal is not possible, the region immediately around a cluster can supply atoms to the steps.

These effects are not specific to clusters of 12 atoms. Deposition has also been studied on much larger clusters, containing 59 atoms, the sides of which more closely approximate ordinary lattice steps. The distribution of iridium atoms over the surface, including the central cluster, is shown in Fig. 3; to bring out the details more clearly, the population on top of the cluster is plotted on a larger scale. Just as in the experiments with a much smaller cluster at the center, there is a zone around Ir$_{59}$ in which no atoms are found. The width of this zone is somewhat smaller, amounting to $\sim 2l$. However, the qualitative trends for deposition on and around this larger cluster are similar to what has been found for Ir$_{12}$. The average occupation of the sites on top of the cluster is again comparable with the number per terrace site. Sites at the cluster edge are much more heavily populated; the average number of atoms per edge site in these experiments is 8.9, compared to 0.9 for terrace sites. It appears that atoms striking the region immediately around the cluster are not captured there. They are redistributed over the surface, and some find their way to the cluster edges, where they are trapped. Just like the smaller cluster, Ir$_{59}$ suffers no apparent structural change during the deposition, except for the addition of an occasional atom from the gas phase.

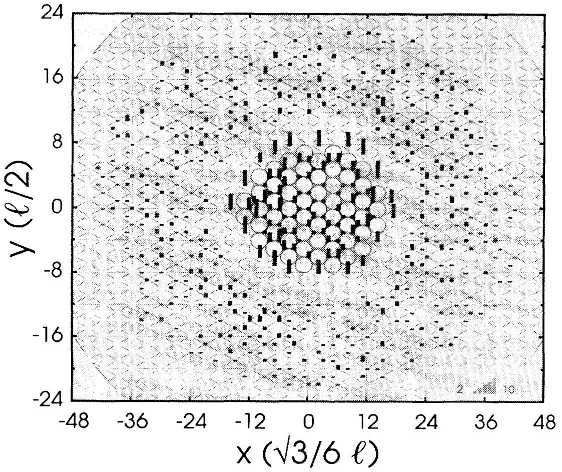

FIG. 3. Distribution of iridium atoms condensed on Ir(111) at $T \sim 20$ K with a central Ir_{59} cluster. Population of atoms on top of cluster is plotted on a scale twice normal. The maximum plane diameter is $24l$.

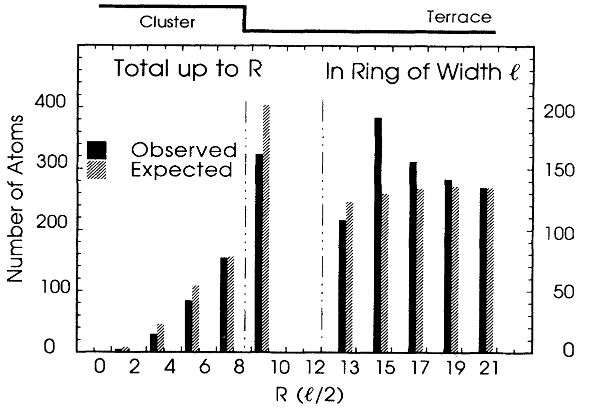

FIG. 4. Population of Ir atoms on Ir(111) with an Ir_{59} cluster at the center. Total number of atoms within a distance R from the center is plotted at left; shown at right is the population in a strip of width l at the indicated radius. Dashed lines indicate empty zone. The "expected" values are obtained on the assumption that atoms condense where they first land on the surface, except in the empty zone. l is the nearest-neighbor distance.

In order to quantify this view of the deposition process, we have also measured the distribution of atoms evaporated from the same source onto a (111) plane *without* a cluster on it. After adjusting for differences in the total number of atoms deposited on the flat surface and on the (111) with a cluster on it, we can compare the distribution observed on the latter with that expected if atoms localize immediately at a site close to the point of impingement. This is done in Fig. 4 for an Ir(111) plane with an Ir_{59} cluster at the center; the results for Ir_{12} are similar. The total deposited on top of the cluster is in excellent agreement with the assumption that all atoms striking the cluster condense on it. However, if we compare the number of atoms actually captured at cluster edge sites with the total that struck the empty zone, that is, the region from the cluster edge out to a radius $R = 6l$, we find that the observed number is significantly smaller than predicted from this picture. On the other hand, the number captured on terrace sites exceeds that predicted, with the disparity greatest around $7\frac{1}{2}l$. It follows that atoms striking the empty zone around the cluster must have some mobility, and are able to redistribute themselves over the surface. More than $\frac{2}{3}$ find their way to the cluster and become attached to its edges. The remainder end up on the terrace, heaped up one nearest-neighbor spacing away from the boundary of the empty zone.

The detailed behavior of atoms striking the cluster itself is not as easy to define. From the results in Fig. 3, it is clear that the distribution of condensed atoms is not uniform over the cluster—the average number of atoms is about twice as high at sites close to the cluster edge as in the interior. From previous observations of diffusion on the cluster we know that, close to the edge, adatoms are bound in considerably deeper wells than in the central regions of the cluster [13]. Atoms from the vapor making head-on collisions with cluster atoms may be preferentially scattered into these deep sites. However, alternative rationalizations, such as focusing of the incoming atoms by the cluster edges, cannot be ruled out. Nevertheless, it can be concluded that Ir atoms striking the cluster condense on top of it; they do *not* bury into the cluster, displacing a cluster atom to the outer periphery. The number of atoms observed on top of the cluster after atom condensation is not consistent with such a mechanism, nor with any significant transient diffusion over the edges.

So far we have not addressed the question of how to account for the existence of an empty zone around clusters, in which deposited atoms are not found. A similar zone has been previously observed in diffusion of adsorbed iridium atoms toward a cluster [14]. The region around a cluster of 12 atoms in which no atoms were found after diffusion is of the same extent as in the deposition experiments in Fig. 2. In the diffusion studies it was possible to rationalize the existence of an empty zone by invoking a small gradient in the adatom potential around clusters; this lowers the barrier to motion toward the cluster by a small fraction, $\sim \frac{1}{10}$ the normal diffusion energy, as suggested in Fig. 5. Once atoms diffusing over the terrace enter the empty zone they would be rapidly swept toward the cluster. Such an effect is certainly in keeping with the strain fields known to exist around lattice steps [15]. However, a *small* perturbation of the atomic potentials around a cluster is hard to reconcile with the phenomena observed in atom deposition. Atoms striking a binding site from the vapor are normally expected to condense at

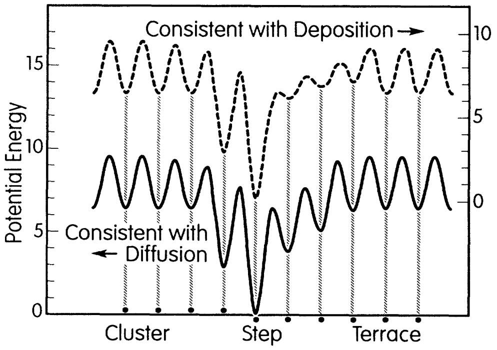

FIG. 5. Schematic of potential acting on adatom moving over a (111) plane with a central cluster. Bottom curve gives qualitative impression of potentials consistent with diffusion experiments [14]; curve at top suggests more severe alterations, which may account for atom behavior in condensation.

that site. The fact that in the empty zone they do *not* suggests a more profound modification of atomic potentials, such as sketched in Fig. 5.

For understanding crystal growth the most interesting result is the surprisingly large number of condensed atoms observed at cluster edges. These are atoms which must have struck the empty zone and been funneled to the cluster. This direct supply of atoms from the vapor to steps, even at low temperatures in the absence of surface diffusion, is an order of magnitude higher than expected, and under some conditions is competitive with the number of atoms supplied by diffusion over the surface. It appears that the alteration of atomic behavior in the vicinity of steps is quite significant and must be taken into account in modeling growth phenomena.

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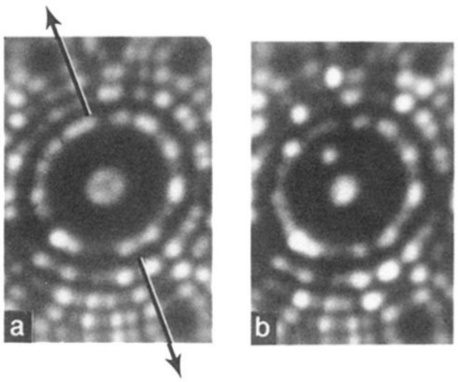

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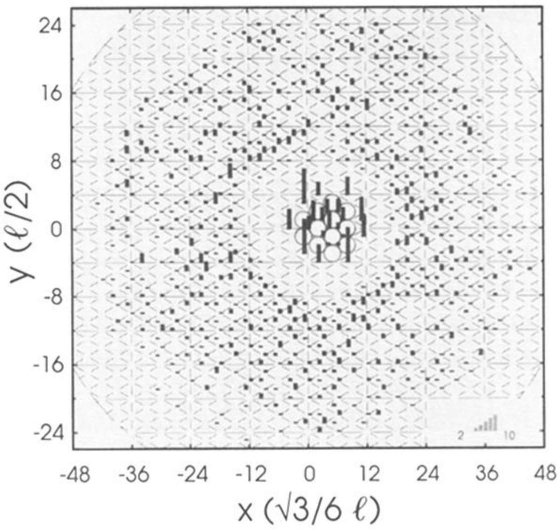

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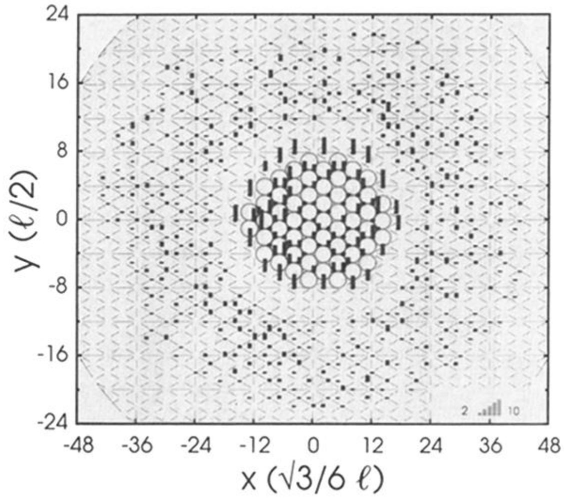

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