Experimental Observation of Ballistic Atom Exchange on Metal Surfaces

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A ballistic (nonthermal) exchange process between vapor-deposited atoms and surface atoms is observed by field ion microscopy. A small fraction (11%) of Ir atoms impinging on a Rh(100) surface held at 77 K embed themselves into the surface layer during condensation. Observation of exchange at temperatures well below those required for thermal exchange (330 K) indicates that it is possible for an atom to transfer some of its energy of condensation into motion along the surface. The fact that only 11% of the atoms undergo exchange implies that the transfer is inefficient.

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The condensation of vapor-deposited atoms onto solid surfaces is an important phenomenon in the growth of crystals and epitaxial thin films. Of particular interest is the process by which an atom transfers its energy to the crystal lattice during condensation. When an atom from a thermal evaporation source at a high temperature T_s impinges on a surface at much lower temperature, it must give up energy associated both with its thermal kinetic energy and its energy of condensation. The thermal kinetic energy (kT_s) amounts to only a few tenths of an eV and is small in comparison with the energy of condensation, which is of the order of several eV. For most adsorbate-substrate combinations, the activation energy required for an atom to diffuse across a surface is also quite small in comparison to the condensation energy. This raises an interesting question: Can an atom use a portion of its condensation energy to make displacements parallel to the surface? If so, atoms could move across a surface at substrate temperatures well below those required for thermally activated diffusion. The existence of this effect, referred to as transient or ballistic mobility, has been a subject of considerable controversy in recent years [1–10].

Although convincing evidence in favor of transient mobility has been obtained for noble gas adsorption on metal surfaces [1], the issue is still unresolved for metal atoms on metal surfaces. In reflection high energy electron diffraction (RHEED) studies of various metals deposited on the (100) surfaces of Cu and Ag, Egelhoff and Jacob [2] observe intensity oscillations at 77 K, indicating layer-by-layer growth at temperatures below the onset of thermally activated diffusion. They attribute the layer-by-layer growth to transient mobility of the condensing atoms. Intensity oscillations implying layer-by-layer growth are also observed in low energy electron diffraction (LEED) studies of Pt on Pd(100) at 80 K by Flynn, Evans, and Thiel [3]. However, this group explains the oscillations in terms of a model in which atoms simply hit and stick, but with the additional requirement that atoms must adsorb in completed fourfold hollow sites. This and other models [4] suggest that observations of RHEED and LEED intensity oscillations at low temperatures are not, in themselves, sufficient to prove the existence of transient mobility.

Investigations of transient mobility by field ion microscopy (FIM) are also inconclusive. Although it is not possible to actually observe atoms as they condense from the vapor phase (the high electric field ionizes atoms in the gas phase before they can adsorb), one can gain information on the condensation process from the distribution of atoms after deposition. FIM experiments of W atoms deposited on the atomically rough regions of W field emitters conducted in the 1960s [11,12] suggest rapid localization of the condensing atoms. These observations, however, do not exclude the possibility of short-range diffusion of incoming atoms. More recently, Wang and Ehrlich [6] report investigations of Ir atoms deposited on a smooth Ir(111) surface at 20 K. They find that adsorption occurs randomly over the two types of threefold adsorption sites (the normal fcc lattice sites and the hcp fault sites). In contrast, when atoms diffuse across the surface at temperatures above the onset of thermal motion (104 K), they are observed in the hcp sites 86% of the time. From these observations they conclude that the atoms deposited at 20 K are localized at the point of impact. However, it is not obvious why an atom could not move across the surface during condensation and still accommodate rapidly with sufficient energy to produce a random distribution of sites. In fact, in more recent studies the same authors [7] find that Ir atoms deposited near an Ir cluster on Ir(111) are funneled in towards the cluster, even at 20 K. This indicates either the presence of atom mobility at temperatures well below the onset of thermal motion or a huge (unphysical) distortion in the surface potential near the cluster leading to thermal diffusion at 20 K.

Theoretical investigations of transient mobility on metal surfaces also yield conflicting results. Molecular dynamics simulations of growth using Lennard-Jones potentials [8] imply that there is some atom mobility even at $T_s = 0$. In contrast, simulations of condensation on fcc (100) surfaces using a variety of potential surfaces [9] and on Lennard-Jones fcc (111) planes [10] lead to exactly the opposite conclusion—atoms are localized upon impact.

In this paper I address two issues related to the question of transient or ballistic mobility. The first is whether or not an atom can transfer some of its condensation energy to motion parallel to the surface. The second concerns the efficiency of the energy transfer. The type of displacement under investigation differs from the conventional hopping displacements considered in the work discussed above. For certain combinations of metal adatoms and fcc (100) surfaces, isolated atoms on top of the surface find it energetically favorable to exchange with an atom in the surface layer rather than to hop across the surface [13–15]. In heteroepitaxial systems the exchange process leaves an unambiguous signature, i.e., a substrate atom on top of the surface and the exchanging atom embedded in the surface layer. In this investigation I use this signature to measure the probability of exchange displacements occurring during condensation at temperatures well below those required for thermally activated exchange. I refer to this phenomenon, which is closely related to transient or ballistic mobility, as *ballistic exchange.*

Direct observations of Ir-Rh(100) exchange processes are possible because Ir and Rh adatoms can be distinguished in the FIM by differences in their desorption fields [16]. At sufficiently high electric field strengths, atoms on a surface are ionized and removed. This process is known as *field desorption* for adsorbed atoms and *field evaporation* for substrate surface atoms. Field desorption of single atoms on low-index crystal planes usually occurs at field strengths much less than that required for field evaporation of the substrate. For example, Rh adatoms on Rh(100) desorb at about 75% of the substrate evaporation field. Ir adatoms, however, resist desorption up to the field at which evaporation of the Rh(100) surface commences. The difference in the desorption is attributed to a much stronger Ir-Rh bond strength compared to Rh-Rh [16]. This difference in desorption fields allows one to identify an adatom on Rh(100) as either a Rh or Ir adatom, even without atom-probe mass identification.

The thermally activated exchange process is illustrated by the field ion micrographs shown in Fig. 1. In Fig. 1(a) a single Ir adatom is adsorbed on top of a Rh(100) plane. This and all subsequent images are recorded with the substrate at 77 K. Figure 1(b) shows the same surface after heating it (with the applied field turned off) to a temperature of 330 K for 30 sec. Careful mapping of the atom's position indicates that it has made a displacement to a next-nearest-neighbor lattice position. More importantly, the desorption field for the atom seen in Fig. 1(b) is much lower than that for an Ir adatom. This indicates that the adatom in Fig. 1(b) is now a Rh adatom generated by an exchange process. Figure 1(c) shows the same surface after field desorption of the Rh adatom. The embedded Ir adatom cannot be seen in Fig. 1(c) because the FIM only images those atoms which protrude from the surface. Its presence, however, can be verified by using field evaporation to strip away the top layer of Rh(100) atoms. Figure 1(d) shows the surface after removal of one layer of Rh atoms. The Ir adatom, which does not desorb during removal of the Rh layer, reappears on top of the new Rh(100) surface, further confirming the exchange process. The onset temperature of 330 K indicates that the activation energy for the Ir/Rh(100) exchange process is ca. 0.90 eV. This estimate assumes that the standard Arrhenius relationship holds for exchange displacements and that the attempt frequency (Arrhenius prefactor) is of the order of 10^{12} sec^{-1}.

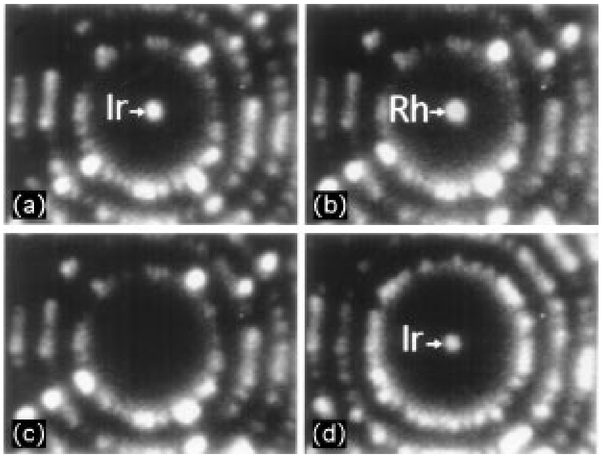

FIG. 1. Field ion micrographs illustrating thermally activated exchange of an Ir atom on Rh(100) as discussed in the text. Images recorded in 2×10^{-4} Torr Ne at 77 K.

Field ion micrographs illustrating the ballistic exchange process are shown in Fig. 2. Figure 2(a) is an image of a clean Rh(100) surface prepared by field evaporation at 77 K. Not one field-desorption-resistant atom (Ir) is observed during field evaporation of many tens of atomic layers. Figure 2(b) is an image of the same surface after deposition of Ir adatoms for 1 min. Measurements of the resistance drop across the Pt tip supporting loop (used for sample heating) indicate that the sample temperature does not increase above the base temperature of 77 K during deposition. A number of additional atoms (bright

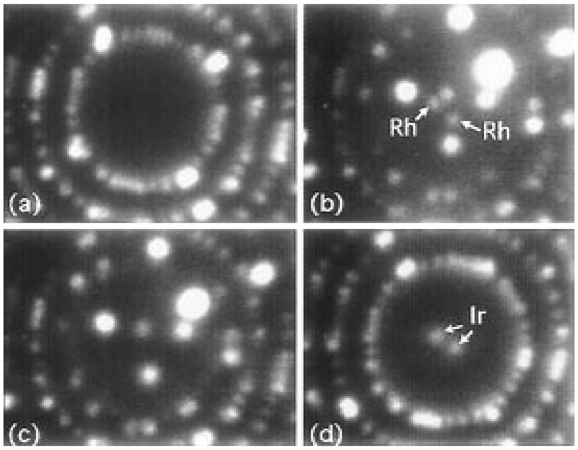

FIG. 2. Field ion micrographs illustrating ballistic exchange of two Ir atoms on Rh(100) as discussed in the text. Images recorded in 2×10^{-4} Torr Ne at 77 K.

spots) appear in Fig. 2(b), seven of which reside on the topmost Rh(100) plane. Note that the atoms near the edge of the plane in Fig. 1(b) appear quite large with respect to atoms at the center of the plane. In particular, the Ir atom in the upper right portion of the image is very close to the edge and appears exceptionally large. This phenomenon is well known in field ion microscopy [17] and is the result of a higher electric field near the plane edge. Two of the atoms in Fig. 2(b) are identified as Rh. This identification is based on their subsequent desorption as voltage is increased from 6.1 to 6.6 kV. Figure 2(c) shows the surface imaged at 6.6 kV with the two Rh adatoms removed. The remaining five adatoms (including the one at the very edge of the plane) are resistant to field desorption and are thus identified as Ir. Confirmation that the two adatoms identified in Fig. 2(b) are Rh atoms generated by an Ir-Rh exchange process is provided by the image shown in Fig. 2(d). This image shows the Rh(100) surface after removal of the five Ir adatoms and the top layer of Rh atoms. Two Ir atoms appear at locations associated with the two Rh adatoms shown in Fig. 2(b). Thus, in the sequence shown in Fig. 2, five Ir atoms land on top of the surface and two Ir atoms exchange into the surface during condensation at 77 K.

The fraction of Ir atoms that undergo ballistic exchange on Rh(100) was measured by repeating the above sequence of steps 37 times. A total of 275 Ir atoms were deposited during these 37 sequences. Of these, 30 atoms were observed to exchange into the substrate leading to a probability of exchange of 0.11. The accuracy of the measured probability is estimated to be 20%. Possible sources of error include not observing Rh adatoms near to brightly imaging Ir atoms (undercounting the total number of atoms deposited) and not observing exchanged Ir atoms in the Rh surface layer due to their desorption along with the Rh(100) layer (undercounting the number of exchanged atoms).

The above results lead to two important conclusions: (1) ballistic exchange does occur; i.e., it is possible for an atom to transfer some of its energy of condensation into motion parallel to the surface and (2) the fraction of atoms that actually undergo ballistic exchange is quite small. Although the results show unambiguously that there are metal systems for which atoms do not simply hit and stick during condensation, the investigation neither confirms nor disproves the existence of *extended* transient mobility on metal surfaces. In those sequences for which the images were photographed, the ejected Rh atoms were always observed adjacent to the embedded Ir atoms. There was no evidence of any long-range displacements in which an ejected Rh atom is found far away from the embedded Ir atom.

The measured probability of nonthermal exchange displacements provides some insight into the efficiency of energy transfer from the released energy of condensation to the exchange displacement. For this discussion, it is useful to define the various energies involved in the transfer process. The thermal kinetic energy of Ir atoms produced by a hot filament near its melting point of 2727 K is given by $kT = 0.23$ eV. The energy of condensation for Ir on Rh(100) is not known, but since Ir adatoms desorb at about the same electric field strength as Rh kink site atoms field evaporate, a reasonable approximation (to within 1 or 2 eV), is the Rh sublimation energy of 5.75 eV [18]. As discussed above, the activation energy required for exchange displacements is 0.90 eV.

To assess the efficiency of the energy transfer, one can calculate the expected probability of exchange using the above energies. For thermally activated displacements, the probability per attempt p that a displacement requiring an activation energy E_a occurs at a temperature T is given by the standard Boltzmann distribution

$$p = e^{-E_a/kT}. \tag{1}$$

If one substitutes $E_a = 0.90$ eV (activation energy of exchange) and $kT = 5.75$ eV (energy of condensation), the probability of an exchange displacement *per attempt* is 0.86. In metal-on-metal diffusion systems the attempt frequency is approximated by the atomic vibrational frequency ($\sim 10^{12}$ sec^{-1}) multiplied by a factor that accounts for the difference in entropy between the equilibrium configuration and the saddle configuration of the system [19]. From a large body of FIM data [20], one concludes that the entropy factor is negligible for hopping displacements (at least to within an order of magnitude). FIM studies of self-diffusion on Pt(100) [21] and Ir(100) [14], as well as calculations for self-diffusion on Cu(100) [22], suggest that the same holds for exchange displacements. Thus, if the energy transfer from condensation to exchange were totally efficient, 86% of Ir atoms condensing on Rh(100) would exchange in one atomic vibrational period. In three vibrations the probability would be essentially unity (0.997). Even if the condensation energy is assumed to be 3.0 eV instead of 5.75 eV, the probability per attempt is still quite high (0.74).

As noted above, the measured probability of Ir exchange during condensation on Rh(100) is only 0.11. This indicates that either thermal accommodation takes place in much less than one atomic vibration or that the transfer of energy from the heat of condensation to an exchange displacement is highly inefficient. Because accommodation in less than an atomic vibration is unphysical, one must attribute the low probability of exchange to an inefficient transfer of energy.

Why is the energy transfer to inefficient? Calculations have shown that thermally activated exchange displacements involve a concerted motion of the adatom and substrate surface atoms [23]. In order for exchange to occur by a concerted process, the atom must couple into the vibrational motion of the surface atoms. If a significant amount of energy is lost during the time needed to achieve this coupling, the energy available for exchange is much less than the full value of the condensation energy. In this case, kT in Eq. (1) is much smaller than the condensation energy leading to a lower probability of exchange. It is also conceivable that the condensing atom does not couple to the motion of the surface atoms at all and that ballistic exchange occurs via a completely different (e.g., direct collision) and higher energy path than thermal exchange. In this case, E_a in Eq. (1) is much larger than the activation energy for thermal exchange displacements, again leading to a lower probability of exchange. Another possibility is that the condensing atom bounds across the surface by ordinary hopping displacements losing energy with each displacement before becoming sufficiently localized for an exchange process to occur.

Obviously, the specific reason for the inefficient energy transfer cannot be discerned from the present experiments. this work clearly establishes that the phenomenon of ballistic exchange does take place and defines the probability of its occurrence for the system of Ir on Rh(100). A detailed description of the ballistic exchange mechanism and an explanation of the inefficient energy transfer will require further experimental and theoretical input.

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