Direct Observation of Substitutional-Atom Trapping on a Metal Surface

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(Received 21 October 1993)

Field ion microscope observations show that individual Rh adatoms on the Rh(100) surface are trapped in the four lattice sites adjacent to an Ir substitutional atom intentionally embedded into the surface. The activation barrier for the Rh adatom to escape from the impurity trap is 0.95 eV, considerably higher than the self-diffusion barrier on the defect-free surface (0.83 eV). The activation barrier to move between the four equivalent trap sites is 0.76 eV. The increased binding along with a higher Rh desorption field at the trap sites imply a stronger Ir-Rh bond compared to Rh-Rh.

PACS numbers: 61.16.Fk, 66.30.Jt, 68.35.Fx

The ability to achieve atomically smooth surfaces during crystal and epitaxial growth processes is becoming increasingly more important as scientists and engineers attempt to create new materials by controlling growth at the atomic level. Although it is often assumed that uniform, layer-by-layer growth is realized when the rate of diffusion across single crystal terraces exceeds the rate of nucleation events [1], there is indirect evidence that isolated surface defects can serve as nucleation sites and inhibit uniform growth [2]. However, little direct information is available on how diffusing atoms interact with surface defects. This Letter reports a field ion microscope (FIM) investigation of how one such defect, namely, a single, substitutional impurity atom, influences surface self-diffusion on an otherwise atomically perfect single-crystal plane. Since many surface phenomena do not follow what is expected from bulk thermodynamic properties, it is not possible to anticipate the influence of such impurities without experiment. In this study the location of the impurity atom within the top layer of surface atoms is identified unambiguously, and its presence is shown to act as a strong trap for an adatom migrating at or near room temperature.

In view of the numerous contributions made by the FIM to our understanding of diffusion and clustering phenomena on surfaces [3], it is somewhat surprising that there has been only one previous FIM surface diffusion study dealing specifically with the subject of impurity atom trapping. In 1977 Cowan and Tsong [4] used the FIM to study the interaction of a migrating W atom with substitutional Re atoms on the (110) plane of a W-3%Re alloy. By contrasting diffusion on the alloy surface with diffusion on the (110) surface of pure W, they concluded that there was an attractive interaction of 90 meV between the diffusing W adatom and Re substitutional atoms at their closest equilibrium separation. They also noted a smaller, repulsive interaction at the second closest separation.

The main reason for the limited number of FIM studies dealing with impurity atom trapping is the difficulty in producing a single substitutional atom with an atomically well-defined single-crystal plane. In the study mentioned above [4], the authors relied on a statistical distribution of Re atoms in the dilute alloy to produce a few isolated impurities in the surface layer. Identification of the substitutional atom was based on the observation of a noticeable increase in the frequency of observation of the diffusing atom at specific surface sites and a meaningful correlation of these sites with the location of field-evaporation-resistant atoms (presumed to be Re) in the surface layer.

The investigation reported here differs from this earlier work in that the substitutional atom (Ir, in this case) is intentionally embedded into the surface layer of the substrate (Rh). The embedding process relies on the substitutional or "exchange" mechanism observed in previous investigations of atom diffusion on other fcc(110) and (100) surfaces [5]. The unique aspect of the Ir/Rh(100) system is that, after exchange, the displaced Rh atom does not perform the usual random walk across the surface, but is confined to move about the four sites neighboring the substitutional Ir adatom. The exchange process thus provides a convenient method to generate both a substitutional impurity atom and a self-diffusing adatom, an ideal situation for the investigation of impurity atom trapping. A somewhat similar phenomenon was observed for Re adatoms on the Ir(100) surface [6], but in this system, rather than producing an embedded impurity atom, the Re atom combined with an Ir surface atom to form a dimer-vacancy complex.

The specific procedure used to create the Ir impurity trap site on Rh(100) is illustrated in the series of field ion micrographs shown in Fig. 1. The images, obtained following the standard methods used in FIM surface diffusion studies [3], were recorded with the sample at 77 K. Figure 1(a) shows a single Ir adatom on top of the Rh(100) surface. The Ir adatom was deposited from a deposition source located a few cm from the tip. By raising the voltage applied to the Rh tip, it was found that Ir adatoms on Rh(100) are resistant to field desorption (i.e., the removal of surface atoms by an external electric field [7]) up to the evaporation field of the Rh substrate plane. The desorption field strength for Ir is therefore quite different from that for Rh adatoms on Rh(100), which desorb at approximately 75% of the substrate evaporation field. As shown in previous investigations, such a large

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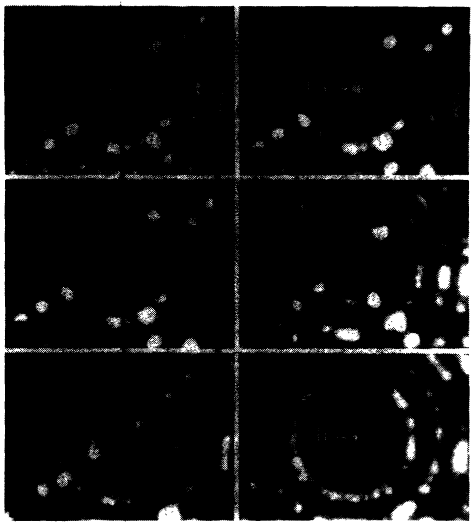

FIG. 1. Field ion micrographs illustrating the method used to generate Ir impurity atoms within the Rh(100) plane as discussed in the text. The images were recorded in 2×10^{-4} Torr Ne at 77 K.

difference in desorption fields can be used to distinguish between different types of adatoms on the surface [8].

Figure 1(b) shows the same surface after the sample was heated to a temperature of 330 K (with the imaging voltage turned off) for a period of 30 sec and recooled to 77 K. Although there is still an adatom at about the same location on the surface, careful analysis of the images indicates that a displacement of one nearest neighbor distance occurred during the heating interval. The adatom in Fig. 1(b) was observed to desorb at an electric field strength approximately 85% of the substrate evaporation field. The fact that the evaporation field of the adatom after heating corresponded to neither the desorption field for Ir nor that for Rh caused some initial confusion in the interpretation of the results. However, it will be shown below that the adatom in Fig. 1(b) can be identified as Rh, generated by an Ir-Rh exchange process. Figure 1(c) shows the Rh substrate after field desorption of the Rh adatom.

Direct confirmation of the Ir-Rh substitutional process is provided by the subsequent micrographs in Figs. 1(d)-1(f). These images show the Rh surface at various stages of field evaporation. The process of field evaporation removes atoms from the edge of the plane inward [7] giving rise to the decrease in diameter of the inner ring of spots seen in Figs. 1(d) and 1(e). It is clear in Fig. 1(f) that when the Rh(100) top-layer atoms are removed completely, an individual adatom remains on the surface. From its resistance to field desorption, the adatom is identified as Ir. It is possible to repeat the above sequence over and over. Each time the surface is heated to at least 3000 K, the Ir adatom substitutes itself into the top layer of Rh atoms, and each time the Rh surface is field evaporated, the Ir adatom reappears.

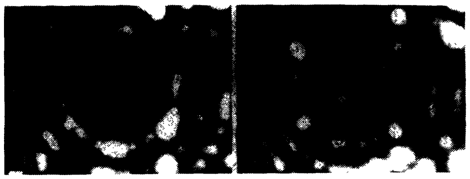

FIG. 2. Field ion micrographs illustrating the trapping of a Rh adatom by an Ir substitutional atom. (a) White dots superimposed on the Rh(100) plane correspond to the coordinates of a diffusing Rh adatom after each of 242 heating cycles at 255-260 K. (b) Field evaporation of the Rh(100) plane reveals an Ir substitutional atom below the four trap sites shown in (a).

An interesting observation related to the above exchange process was the occasional occurrence of Ir-Rh substitution at the base sample temperature of 77 K. In a few cases (approximately one in ten) a deposited Ir adatom embedded itself into the surface without any heating. This was surprising because once an Ir atom was deposited *on top* of the surface, it would remain there until the sample temperature was raised to at least 300 K. A possible explanation for exchange at 77 K is that some of the energy released in the condensation of the atom onto the surface is transferred to the energy required for exchange. The process may be related to the question of transient mobility, a subject of considerable controversy in recent years [9].

The fact that the displaced Rh adatom does not field desorb at the field strength corresponding to Rh on Rh(100) can be attributed to its proximity to the substitutional Ir adatom. When the adatom is moved to a location away from the exchange site (see below), the measured desorption field is found to be 75% of the substrate evaporation field, consistent with Rh on Rh(100). Thus, there are three desorption fields associated with Ir and Rh on Rh(100): Ir adatoms on Rh(100), which desorb at electric fields very close to the substrate evaporation field F_{ev}; Rh adatoms on defect-free Rh(100), which desorb at 75% of F_{ev}; and Rh adatoms on Rh(100) in a site adjacent to an Ir substitutional atom, which desorb at 85% of F_{ev}. The difference in desorption fields for Rh at the two different types of sites suggests that the binding of a Rh atom is stronger at the sites adjacent to the substitutional Ir atom.

A more direct indication of trapping by the substitutional Ir atom is provided by the field ion micrographs shown in Fig. 2. Figure 2(a) shows an image of a bare Rh(100) substrate plane. Added to this image are small white dots corresponding to the coordinates of a self-diffusing Rh adatom, generated by the Ir-Rh substitutional procedure described above. The coordinates were obtained from digitized FIM images taken after each of 242 heating intervals. The sample temperature during the heating intervals ranged from 255 to 260 K. It is clear from Fig. 2(a) that the adatom is confined to four binding sites on the surface. Figure 2(b) shows the same surface after field desorption of the Rh adatom and field evaporation of the top layer of Rh(100) atoms. The adatom seen in Fig. 2(b) is identified as Ir, based on its desorption field as discussed above. Superposition of the two images indicates that the four sites visited by the Rh adatom are those adjacent to the Ir substitutional adatom. The confinement of self-diffusion to the four sites neighboring the Ir atom was found to persist over the temperature range from 250 to 320 K.

The activation barrier for displacements of the Rh adatom between the four sites surrounding the Ir atom can be obtained from the temperature dependence of the displacement rate. If the temperature is sufficiently low that multiple displacements are unlikely, then the conventional random-walk analysis used in FIM investigations of adatom diffusion across extended surfaces is applicable [3]. According to this analysis, the mean-square displacement of the adatom $\langle r^2\rangle$ is related to the activation energy E_d through

$$\langle r^2\rangle/\tau = 2\nu_0 l^2 \exp(-E_d/kT)\,, \qquad (1)$$

where τ is the diffusion time interval, ν_0 is the atomic vibrational frequency, l is the jump distance, k is the Boltzmann's constant, and T is the temperature. The prefactor term, $2\nu_0 l^2$, is often defined as D_0 and called the diffusivity. Equation (1) assumes zero activation entropy and single jumps between adjacent sites. The activation energy and diffusivity are obtained from the slope and intercept of an Arrhenius plot of $\ln(\langle r^2\rangle/\tau)$ vs $1/T$. Applying this analysis to displacements of Rh on Rh(100) in the vicinity of an Ir trap, the activation energy and diffusivity are determined to be 0.78 ± 0.10 eV and $2\times10^{-3\pm2}$ cm^2/sec, respectively. The large errors are the result of the narrow temperature range over which the experiments could be performed. A more reliable activation barrier can be obtained by assuming that D_0 is given by 1×10^{-3} cm^2/sec (consistent with a large body of FIM surface diffusion measurements [3]) and calculating the barrier at each temperature. With this procedure the activation energy at four temperatures in the range from 248 to 265 K is 0.76 eV to within 0.01 eV. Note that the assumed value of D_0 corresponds to an atomic vibrational frequency of $\sim10^{12}$ sec^{-1}.

As mentioned above, the Rh adatom remained trapped in the four sites adjacent to the Ir atom until the temperature during the diffusion intervals was increased to above 320 K. Once it detached, the Rh adatom performed an ordinary random walk across the surface. Analysis of the sites visited by the Rh adatom indicated diffusion on the defect-free surface takes place by ordinary hopping. From measurements of the mean-square displacement at 300 K and assumption of the standard D_0 mentioned above, the activation barrier was determined to be 0.83 ± 0.05 eV. This value is within the experimental error of earlier, more detailed measurements reported by Ayrault and Ehrlich [10].

The activation barrier for dissociation from the impurity trap was determined by measuring the average time it took for the Rh adatom to detach from the four sites adjacent to the impurity atom. As discussed in previous articles [3], the dissociation time $t_{\rm dis}$, as a function of temperature T, is given by the expression

$$1/t_{\rm dis} = 2\nu_0 \exp(-E_{\rm dis}/kT)\,, \qquad (2)$$

where $E_{\rm dis}$ is the activation energy for dissociation and ν_0 and k are defined as in Eq. (1). In principle, the dissociation barrier can be determined from an Arrhenius analysis as described above for diffusion barriers. In practice, for Rh atoms bound to Ir impurities, the temperature range over which reliable dissociation times can be measured was too small to obtain a reasonable Arrhenius plot. However, by assuming that the frequency prefactor for dissociation from the trap is the same as the prefactor determined above for diffusion around the trap (i.e., 10^{12} sec^{-1}), the dissociation barrier can be obtained from the dissociation time at a single temperature. The dissociation times measured at 343 and 335 K were 40 ± 11 and 160 ± 60 sec, respectively, corresponding to an average activation barrier of 0.95 ± 0.02 eV.

The relative energetics corresponding to the self-diffusion on Rh(100) in the vicinity of an Ir substitutional impurity are shown in Fig. 3. The upper portion of the figure shows schematically a top view of the Rh(100) surface. The lightly shaded circles represent the top layer Rh atoms, the darkly shaded circle represents the Ir impurity, and the striped circle represents a Rh adatom. The lower portion of Fig. 3 shows a graph of the binding energy of the Rh adatom along the line AB of the schematic. The activation energies are the values obtained in the experiments reported above. Not shown on the figure is the possibility that the impurity atom could affect binding at sites beyond the closest trapping sites (i.e., smaller attractive or repulsive barriers may exist at the next closest sites to the impurity). Sufficient statistics could not be obtained to probe these interactions because self-diffusing Rh atoms typically migrated off the edge of the plane after detaching from the impurity site. In

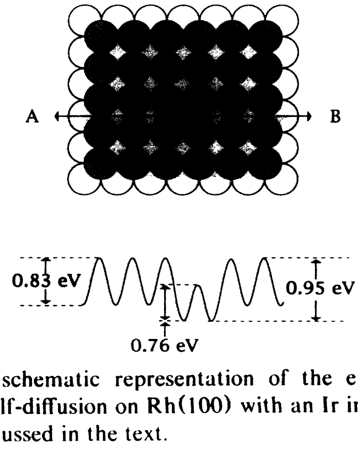

FIG. 3. A schematic representation of the energetics involved in Rh self-diffusion on Rh(100) with an Ir impurity trap. Details are discussed in the text.

several experiments, detached Rh atoms were observed to retrap at the impurity suggesting the absence of any significant repulsive interactions near the impurity.

Although the above experiments establish that Ir impurity atoms create strong trapping sites for a self-diffusing Rh adatom and provide quantitative measurements of the energetics involved in the process, the underlying physics of the trapping mechanism is subject to speculation. The noticeable increase in the desorption field for a Rh adatom at the Ir impurity site (three Rh-Rh bonds and one Rh-Ir bond) compared to Rh on Rh (four Rh-Rh bonds) and the further increase in the desorption field for an Ir atom on the Rh(100) surface (four Rh-Ir bonds) suggests that the Rh-Ir bond strength is significantly stronger than Rh-Rh. In fact, a simple analysis using pairwise additive bonds and assuming a larger Rh-Ir bond strength can qualitatively explain all of the observed field desorption and trapping phenomena [11]. However, a determination of whether the increased Rh-Ir binding strength is due to electronic interactions, lattice strain effects, or some other interaction will require more detailed theoretical calculations.

Stimulated by the experimental work reported here, recent theoretical efforts [11] employing the embedded atom method (EAM) have been undertaken to examine the energetics associated with a Pt impurity atom embedded into a Pd(100) surface. The Ir-Rh system was not used for the calculations because the basic assumptions of the EAM limit its applicability primarily to the six noble and near-noble metals. The Pt-Pd system was chosen because these are the two elements to the immediate right of Ir-Rh in the periodic table. Qualitatively, the results from these calculations are the same as the Ir-Rh system, i.e., the Pt atom finds it energetically favorable to embed itself into the Pd surface and the barrier for Pd diffusion around the Pt impurity is significantly lower than for diffusion away from it. More detailed calculations are expected to provide insight as to the role of lattice relaxations in the trapping process and help probe the finer details of the surface potential surrounding the impurity atom.

A comprehensive understanding of the impurity trapping mechanism is of obvious importance in relation to the nucleation and growth processes mentioned in the introduction. It is often assumed that impurity atoms at or near the surface can serve as nucleation sites during crystal growth, but little is actually known about the nature or strength of such traps [2]. The information obtained in this investigation will provide useful input to growth simulation models. It should be mentioned that, in order for the impurity atom to serve as an actual nucleation site for subsequent island growth, additional atoms encountering the trapped adatom must become trapped as well. It is conceivable (although not likely) that the presence of one trapped atom would change the energetics of the trap site such that it would not bind additional atoms. To check this possibility, an experiment was performed in which several Rh-Ir trap sites were created on the same surface. The surface was then heated to 345 K to release some of the trapped Rh atoms. At this temperature, there was a relatively equal chance that the Rh would either remain trapped or detach from the trap site. Once an atom dissociated, the temperature was lowered to 300 K during the diffusion intervals. Occasionally the detached atom would diffuse to the location of another trapped atom and form a close-packed Rh-Rh dimer at the site of the impurity atom. The temperature at which the dimer became mobile (320 K) and at which it detached from the impurity trap (390 K) were significantly higher (by approximately 60 K) than the corresponding temperatures for a single trapped atom. Although the experiments need to be further quantified and extended to larger clusters, the current results provide compelling evidence that the Ir impurity atom does indeed serve as a nucleation site for island growth on the Rh(100) surface.

The author acknowledges helpful discussions with J. E. Houston, P. J. Feibelman, and A. F. Wright of Sandia National Laboratories. This work was performed at Sandia National Laboratories and supported by the U.S. Department of Energy under Contract No. DE-AC04-94AL85000.

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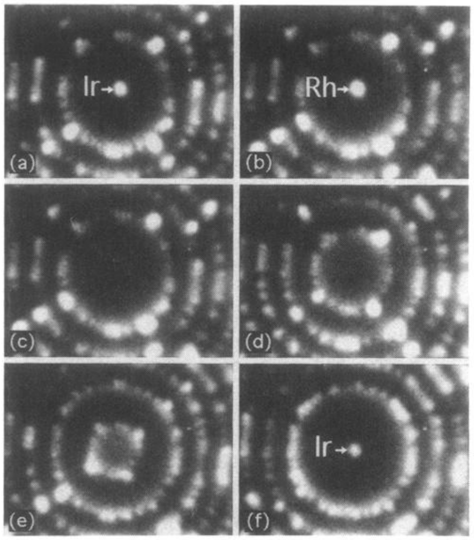

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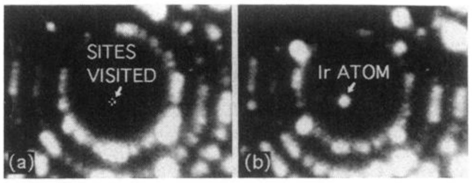

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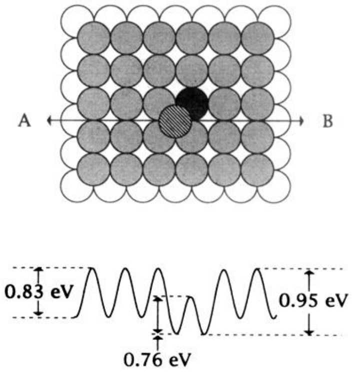

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