Observation of Two Diffusion Modes of a Re-Ir Dimer-Vacancy Complex on the Ir(001) Surface and Their Diffusion Mechanisms

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A Re-Ir dimer-vacancy complex can be formed on an Ir(001) surface when the surface is heated to ~240 K with a Re atom vapor deposited on it. Above ~210 K, the geometrical center of this complex can displace by one step of the substrate by an exchange displacement of its Ir atom with a substrate Ir atom. This mechanism confines the movement of the complex to four nearest-neighbor sites of the substrate lattice. Only above ~235 K can the complex move out of these four sites by a combined hopping-exchange mechanism. Above ~280 K, the Re-Ir dimer can dissociate. Upon dissociation, the Re atom will combine with the vacancy and self-diffusion of Ir will then occur.

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Surface diffusion is a subject of considerable current interest. Understanding the mechanisms of surface diffusion is a key to understanding the atomic steps involved in the epitaxial growth of thin films, in crystal growth, in surface reconstruction, in crystal shape changes, in point alloying of the top surface layer, and in many other surface phenomena involving the transport of atoms [1]. Recent theoretical [2] and experimental investigations [3] have found that on the fcc (001) surfaces of metals, self-adsorbed atoms (adatoms) diffuse along the ⟨100⟩ directions by an atomic-exchange-displacement mechanism instead of making atomic hops between adjacent binding sites as established for many metallic systems in earlier field-ion microscope (FIM) studies. During the exchange displacement, the adatom and the replaced substrate atom move in concert as illustrated in Fig. 1. No investigations of diffusion of metal adatoms on the Pt and Ir(001) surfaces, including heterosystems, have directly observed a dimer-vacancy configuration as illustrated in Fig. 1(b), which is therefore only a transient configuration rather than a metastable intermediate state. However, we have found recently that a Re-Ir dimer-vacancy complex can be formed on a clean (1×1) Ir(001) surface by depositing a Re atom on the surface and then heating the surface to ~240 K [4]. Upon heating again to this temperature, this dimer can rotate by 90°. All these are shown in Fig. 2. If the temperature exceeds 280 K, it may dissociate. Once it dissociates, the Re atom will combine with the vacancy to become a substitutional atom. The replaced Ir adatom will diffuse elsewhere by the exchange-displacement mechanism [3(b)]. The potential barrier heights for the formation and dissociation of the dimer-vacancy complex have been measured to be 0.65 ± 0.05 and 0.95 ± 0.07 eV, respectively. An impor-

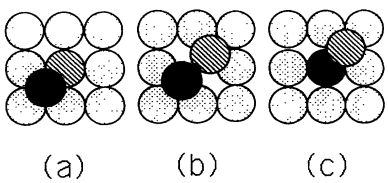

FIG. 1. In the exchange mechanism of adatom diffusion the adatom displaces a substrate atom and moves with it in the diagonal direction of the surface unit cell. Only for Re/Ir(001) is the intermediate dimer configuration found to be metastable. Note the geometrical center of the complex coincides with the original position of the displaced substrate atom.

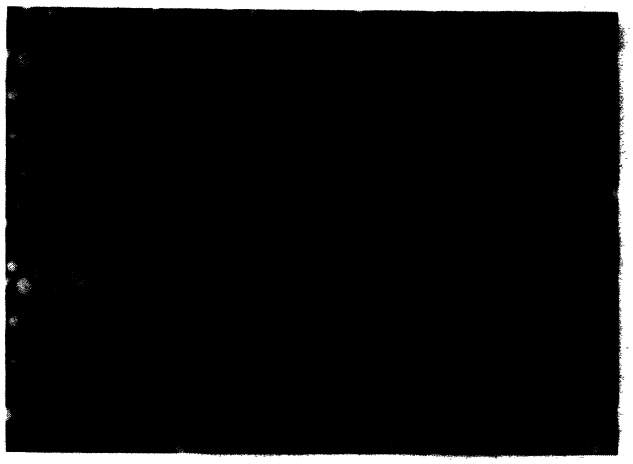

FIG. 2. (a) Two Re adatoms are deposited on an Ir(001) surface. (b) Two Re-Ir dimer-vacancy complexes are now formed. (c)–(f) show surface diffusion of these complexes. To enhance the visual effect, two complexes are deliberately formed on a surface. To avoid complicated mutual interactions, for collecting quantitative diffusion data, only one complex is formed on a surface.

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tant question is whether or not a heterodimer-vacancy complex is stable enough to diffuse on the surface without dissociation and if it is then by what mechanisms. Because of the interesting dynamical behavior of this complex, it is an ideal model system for studying the exchange diffusion and exchange alloying of heterosystems. In this Letter we present a study of the detailed atomic steps involved in the surface diffusion of this complex. This, as far as we are aware, is the first time surface diffusion of a system consisting of adatoms and a vacancy in the substrate has been studied.

The present experiment was performed using an UHV FIM [5] with a base pressure in the lower 10^{-11} Torr range. The experimental methods are similar to earlier FIM studies of adatom behavior, thus will not be repeated here. During a heating period when atomic movements can occur, the applied field is turned off. Each heating period is 20 s. A diffusion step is observed only every few periods. Images are taken either photographically or with a VCR video camera equipped with a pc base image digitizer, and only after the surface has already cooled down to ~30 K when the applied field will not induce any change of the surface. As shown earlier, the structure of the underlying lattice can be revealed by mapping the rest sites of a diffusing adatom [1(d)]. The position of the geometrical center (gc) of a dimer, or a complex, can be mapped to a precision only slightly less than for an adatom, about ± 0.5 Å [3(b)].

The experiment consists of mapping the position of the gc of the Re-Ir dimer and also recording its orientation after each heating period. From such data all displacements and the accompanying orientation changes as well as visited site lattices are derived. We conclude from low temperature data that there are two distinctive modes of diffusion of the Re-Ir dimer-vacancy complex. One mode, which will be referred as the α mode, can occur above ~210 K. It shows three features. First, if the gc displaces to a nearest-neighbor (nn) site of the substrate lattice, then it is accompanied by a change of the dimer orientation by 90°. If the gc displaces in a diagonal direction of the substrate unit cell, no change of the dimer orientation is observed. Second, when only this mode of diffusion occurs, the gc is confined to the four sites of a unit cell of the substrate lattice. Third, these four sites surround the original adsorption site of the Re before the complex is formed. The other mode, which will be referred as the β mode, can occur only above ~230 K. It involves a displacement of the gc by either the nn distance of the substrate lattice, or the diagonal distance of the unit cell, or larger distances. If the displacement is the nn distance, then the dimer does not change its orientation. If it is in the diagonal direction of the unit cell, an orientation change will occur. For clarity, all the smallest displacements and their accompanying orientation changes of the observed α mode and β mode are tabulated in Table I. When diffusion occurs by the β mode, the dimer can diffuse anywhere on the surface without being confined locally. As can be seen from Table I, from the displacements of the gc in combination with the orientation changes of the dimer, the α mode and β mode can be distinguished without uncertainties. At low temperatures the α mode dominates. For example, out of a total of nearly 250 observations at ~220 K, the gc of the complex rarely moves out of the four confined nn sites. Figure 3(a) shows data taken at ~220 K, which contain ~120 observations of the α mode, where the geometrical center is confined to four sites of a (1×1) cell of the substrate lattice, or only the α mode occurs. At higher temperature, both modes can occur. Figure 3(b) shows a visited site lattice taken at ~245 K from a total of 186 observations which is the (1×1) lattice of the substrate. Now the complex can escape from the discussed confinement.

Mechanisms consistent with all the observed features

TABLE I. Experimentally observed diffusion modes.

Diffusion mode	Step	Displacement in [110] dir.	Displacement in [110] dir.	$\Delta\theta$ (deg)
α mode	α_1	+1	+1	0
	α_2	+1	0	90
	α_3	0	+1	90
	α_4	No change		
β mode	β_1	0	+2	90
	β_2	0	+1	0
	β_3	−1	+2	0
	β_4	−1	+1	90

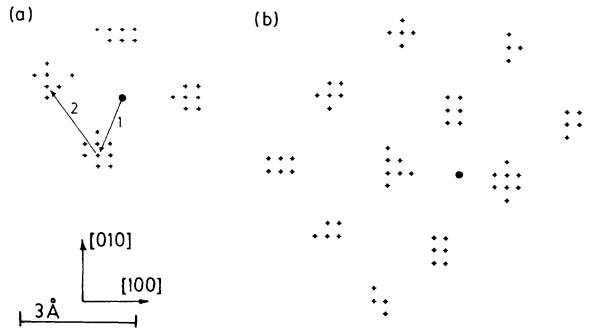

FIG. 3. (a) A visited site lattice of the geometrical center of a Re-Ir dimer-vacancy complex at ~210 K. The original position of the Re adatom before forming the complex is noted by the dot. (b) A visited site lattice of a complex at ~245 K. In these figures, each cross represents the position of the gc of the dimer after a heating period. The distance between two nearest crosses represents the limit of resolution of the image digitizer used. Note that many of the crosses are visited repeatedly by the gc of the dimer but for clarity these data are omitted here. The spread of the crosses within a cluster indicates the spatial resolution of the FIM with the pin pointing out the rest sites of the Re-Ir dimer.

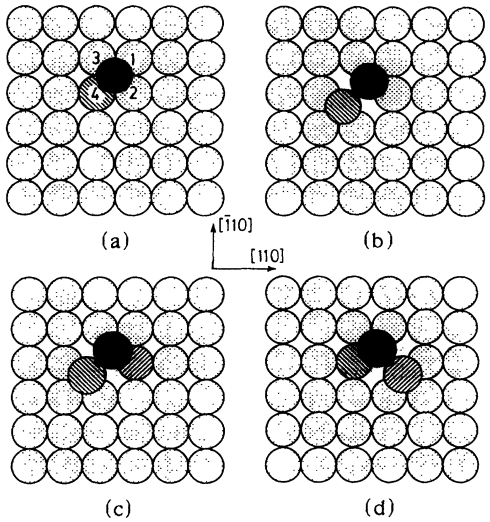

FIG. 4. This figure illustrates the mechanism of the α mode. (a) A Re adatom can displace any one of the four lattice atoms 1, 2, 3, and 4. (b) Atom 4 is displaced out of its site. (c),(d) The gc of the complex displaces toward the right by one step by exchange displacement with atom 2, resulting in the occurrence of the α_2 step. With this mode, the complex cannot move out of a unit cell of the substrate.

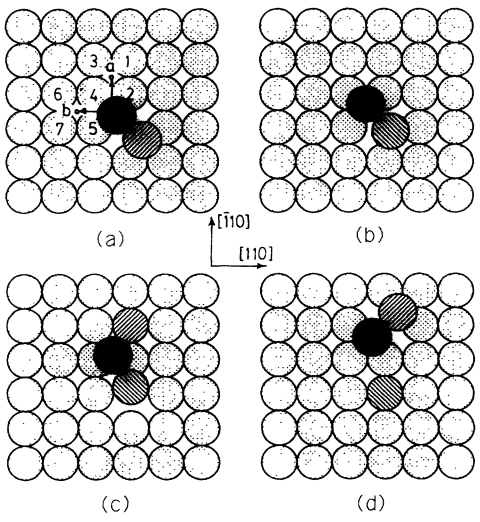

FIG. 5. This figure illustrates the β mode of diffusion. (a) shows that the Re atom in the dimer can hop either to a or to b. If it hops to a, then a substrate atom, either 1, 2, 3, or 4, will be displaced out of the substrate. If it hops to b, then either 4, 5, 6, or 7 will be displaced out of the substrate. (b)–(d) give an example of the Re atom hopping to a and then atom 1 is displaced out of the substrate, or the β_1 step occurs. One can figure out the other three displacements of the gc and orientation changes of the dimer as listed in Table I. Hopping of the Re atom along path b will produce similar steps.

are proposed here. For the α mode, each jump of the complex involves an exchange replacement of the Ir atom in the dimer with a substrate Ir atom as illustrated in Fig. 4. From this figure and from Table I, it is easy to see that with this mechanism, four different steps α_1, α_2, α_3, and α_4 can occur which will exhibit all the three observed features of the α mode. For the β mode, a possible mechanism involves an atomic hopping of the Re atom to a nn site and an exchange replacement of the Ir with another substrate atom as illustrated in Fig. 5. From this figure and from Table I, one can easily figure out that this mechanism agrees with all the observed features of the β mode, including that if the diffusion occurs exclusively via the α mode, then the visited sites of the geometrical center should form only one primitive cell of the (1×1) surface of the substrate, and if diffusion occurs also via the β mode, then the visited site lattice should be the (1×1) surface net of the substrate without being confined to one unit cell. For the β mode, other mechanisms can also be consistent with all the observed features. For example, if one assumes the β_4 step to be the real diffusion step, then the other steps β_1, β_2, and β_3 can be generated as combinations of β_4 and α_1, α_2, and α_3. It appears that theoretical insights may be needed to decide without any doubt the mechanism for the β mode.

With the above explanations, it is clear that the two modes of diffusion can be separated from the displacements of the gc in combination with the orientation changes of the dimer even if both modes occur within a heating period (of course the heating periods still have to be short enough that only one atomic jump is observed for a few heating periods). For example, a repeat of the α_1 or α_2 step twice will result in a diagonal displacement with no change in the orientation, thus will not be confused with the β_4 step. However, since within the narrow temperature range from 210 K to 280 K, formation of the dimer-vacancy complex, the two different modes of diffusion, and dissociation of the complex can all occur, it is very difficult to determine accurately the activation energies of these two surface diffusion modes. Nevertheless we have succeeded in measuring the rates of occurrence of the α and β modes as a function of the temperature. The frequency factors ν_0 and the activation barrier heights E_d in the rate equation $N=\nu_0\tau\exp(-E_d/kT)$ of the two modes can be derived from the Arrhenius-like plots shown in Fig. 6. From these plots we obtain the activation barrier heights and frequency factors to be 0.60 ± 0.07 eV and $2.0\times10^{12.0\pm1.5}$ s^{-1} for the α mode, and 0.73 ± 0.07 eV and $2.6\times10^{13.0\pm1.5}$ s^{-1} for the β mode. In a two-dimensional random walk [1], the diffusion coefficient D_s is given by $D_s=D_0\exp(-E_d/kT)$. The diffusivity D_0 is given by $D_0=\nu_0 l^2/4$ where l is the jump distance. For the α mode, $l^2=2.8^2$ Å^2; thus $D_0=4\times10^{-4.0\pm1.5}$ cm^2/s. For the β mode, $l^2\simeq4\times2.8^2$; thus $D_0\simeq2\times10^{-2.0\pm1.5}$ cm^2/s. For the α mode, the gc can never move out of the four nn sites. The simple random walk theory is valid only if the measurement is done

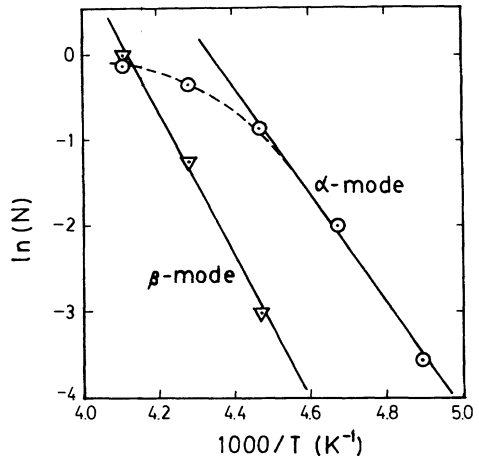

FIG. 6. Arrhenius-like plots obtained for the two modes of diffusion.

in such a way that only one displacement is observed for every several heating periods of observation. When the temperature goes up above ~230 K, this condition is hard to meet, and $\ln(N)$ should saturate quickly, in good agreement with our data.

In summary, we have found that the Re-Ir dimer-vacancy complex is stable with respect to surface diffusion on the Ir(001) surface in the temperature range 210–280 K. There are two distinctive modes of diffusion. Mechanisms consistent with these two modes are proposed though they may need to be further ascertained by theoretical studies. Despite the narrow temperature range in which these diffusion modes can occur, their jump rates and diffusion parameters are successfully derived but the accuracy is still somewhat limited. That the diffusion parameters and mechanisms of a heterodimer combined with a vacancy in the substrate can be studied in such atomic detail is a pleasant surprise to us. We believe it will shed some light on the diffusion behavior of more complex systems. The diffusion mechanisms of complex systems such as the one discussed here should also be of interest for theoretical studies [6].

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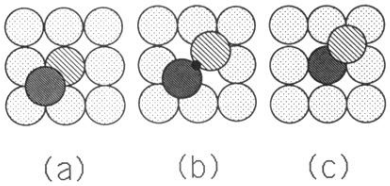

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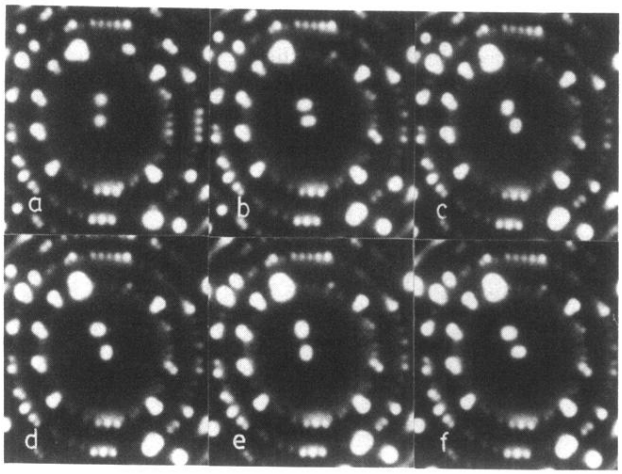

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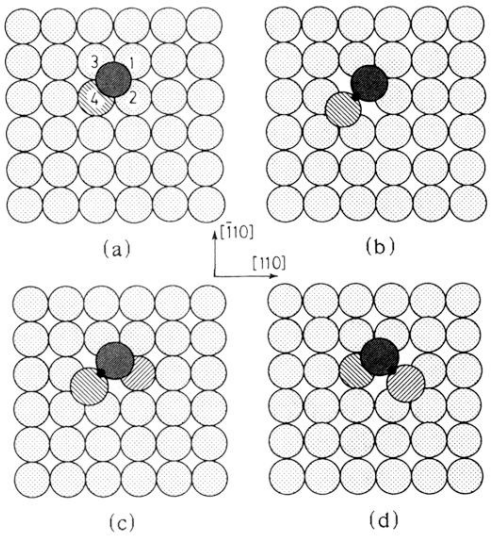

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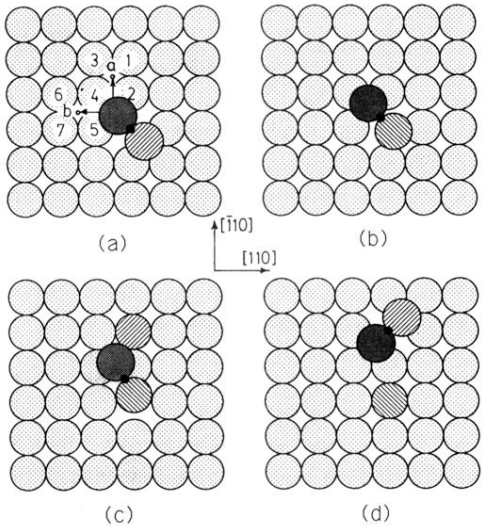

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