Self-Diffusion on the Reconstructed and Nonreconstructed Ir(110) Surfaces

Chong-lin Chen
Physics Department, The Pennsylvania State University, University Park, Pennsylvania 16802

Tien T. Tsong[(a)]
Physics Institute, Academia Sinica, Nankang, Taipei, Taiwan 11529, Republic of China

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On the (1×1) Ir(110) surface the diffusion of single Ir adatoms is two dimensional; i.e., an adatom can diffuse along the $[1\bar{1}0]$ surface channel by atomic hopping as well as across the channel by atomic replacement. The energy needed for an Ir adatom to hop along the channel is 0.80 ± 0.04 eV, or 0.09 eV larger than needed to replace a lattice atom in the cross-channel jump. In contrast, Ir adatom diffusion on the (1×2)-reconstructed surface, with double-space $[1\bar{1}0]$ channels, is one dimensional; i.e., an adatom can only hop along these channels. The activation energy, 0.86 ± 0.03 eV, is higher than that for either cross-channel or along-the-channel diffusion on the nonreconstructed surface.

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Knowledge of surface diffusion[1] is essential to a detailed atomistic understanding of the mechanisms of many surface phenomena where a transport of atoms is involved. These phenomena include nucleation and growth of surface layers, thin films, and crystals, surface-atomic reconstructions, surface-enhanced chemical reactions, adsorption and desorption, etc. Although surface diffusion can be studied by many techniques, field-ion microscopy has the capability of obtaining quantitative information in atomic detail.[2] Many important surface phenomena, including the growth of epitaxial layers and crystals, occur at high temperatures where the surface is already reconstructed. Thus, quantitative data of surface diffusion on reconstructed surfaces are needed for understanding the transport of atoms in many surface phenomena. It is worthwhile to study quantitatively the difference in the diffusion behavior of atoms on reconstructed and nonreconstructed surfaces. We report here what is presumed to be the first field-ion-microscope comparative study of surface diffusion of Ir adatoms on both the (1×2)-reconstructed and the (1×1)-nonreconstructed Ir(110) surfaces.

At low temperatures, surface atoms are immobile. Metal surfaces produced by low-temperature field evaporation should have structures identical to those in the bulk, or the (1×1) structures, because of the very small field penetration depth.[3] To produce a (1×2)-reconstructed Ir(110) surface, the emitter surface has to be annealed at over 700 K in UHV.[4] The reconstructed surface is now well accepted as having a missing-row structure, or having alternating $[1\bar{1}0]$ atomic rows of atoms missing from the top layer of the surface. In other words, the reconstructed surface has closely packed $[1\bar{1}0]$ atomic rows separated by surface channels of ~7.6 Å in width. The underlying layer then returns to the (1×1) structure.

In theories of diffusion by a random lattice walk,[2] essential data are the atomic-jump directions, the jump-length distributions, the displacement distributions, and the temperature dependence of these distributions. We shall define a jump to represent an atomic displacement produced either by an atomic hop or by an atomic replacement of a substrate atom by the adatom. The length of each atomic jump cannot be directly observed by experiments, but information on the jump length, or more precisely the jump-length distribution, can be obtained by comparing the experimentally observed displacement distributions with those calculated from random-walk theories or generated from Monte Carlo simulations. For the nonreconstructed surface, the sites visited by an adatom can be mapped out using a video recorder and an image digitizer. We find that for the (1×2)-reconstructed Ir(110) surface, the image intensity of an adatom is much too dim for the video-recorded images to have a sufficient intensity and resolution; thus, we are unable to digitize the visited sites from the recorded images. Our analysis of the displacements and their distributions is done by taking photographs and mapping the displacements using substrate atoms as internal fiduciary marks. We find the diffusion of Ir adatoms on this surface is one dimensional; this photographic technique has a sufficient resolution for mapping the displacements. As the field-ion emitter surface is very small, we often have to perform the diffusion experiment on a facet having only one to a few double-width $[1\bar{1}0]$ atomic channels of the (1×2) surface.

The (1×1) Ir(110) surface has a rectangular unit cell of 2.7 Å×3.8 Å. It is composed of closely packed $[1\bar{1}0]$ atomic rows separated by surface channels of 3.8 Å width. On this surface, one can expect an Ir adatom to diffuse in one dimension by hopping along the $[1\bar{1}0]$ atomic channel. Experiments, however, find that the diffusion is two dimensional; i.e., the adatom can diffuse both along the surface channel and across the surface channels.[5] Figure 1 shows a few field-ion images demonstrating this 2D diffusion. Displacement distributions

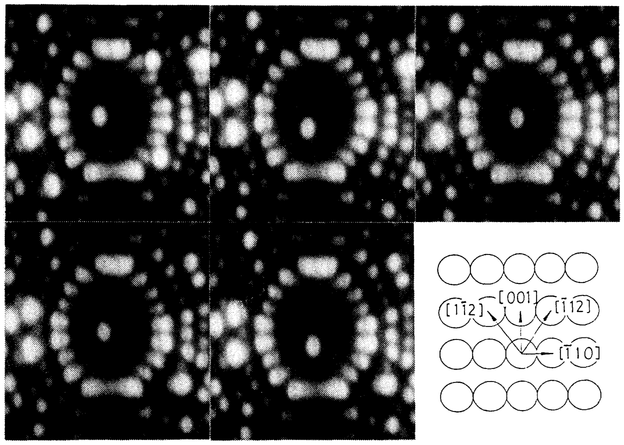

FIG. 1. Field-ion images showing 2D random-walk diffusion of an Ir adatom on an Ir(110) surface.

measured at four temperatures are shown in Fig. 2 as shaded bars. As one can see an adatom makes the cross-channel jump more often than the along-the-channel jump. The cross-channel diffusion of a W atom on the Ir(110) surface has been found to be achieved by an atomic replacement.[6] In view of this experiment and recent experiments for diffusion of Ir and Pt adatoms on the Ir and Pt (001) surfaces[7] and many theoretical calculations of diffusion of Al on Al (001) and (110) (Ref. 8) and Pt on Pt (001) and (110),[9] we believe that the cross-channel diffusion of Ir on Ir(110) is also achieved by an energy-exchanged atomic-replacement mechanism as shown in Fig. 3(a). A similar mechanism was also postulated for self-diffusion on the W(211) surface at low temperature.[10]

The displacement distributions agree best with those generated by a Monte Carlo simulation based on a mechanism where 80% of the jumps are in the $\langle 112\rangle$ direction and 20% of them are in the [001] direction. Also, all these jumps are only unit length of the visited-site lattice vectors. The Monte Carlo distributions are shown as open bars in Fig. 2. It can be shown that for the nearest-neighbor random walk with this mechanism we should have

$$\langle(\Delta x)^2\rangle = N_1 + N_2, \quad \langle(\Delta y)^2\rangle = N_2,$$

where N_1 and N_2 represent, respectively, the average numbers of the along-the-channel and cross-channel jumps within a heating period τ, and Δx and Δy represent, respectively, the displacements in the $[1\bar{1}0]$ and [001] directions within a heating period. Arrhenius plots for N_1 and N_2 are shown in Fig. 4. The energy needed for making an atomic replacement resulting in a cross-channel jump is found to be lower than that needed for making an atomic hop along the [110] surface channel, or 0.71 ± 0.02 vs 0.80 ± 0.04 eV. The diffusivity D_0 is slightly larger for the along-the-channel diffusion,

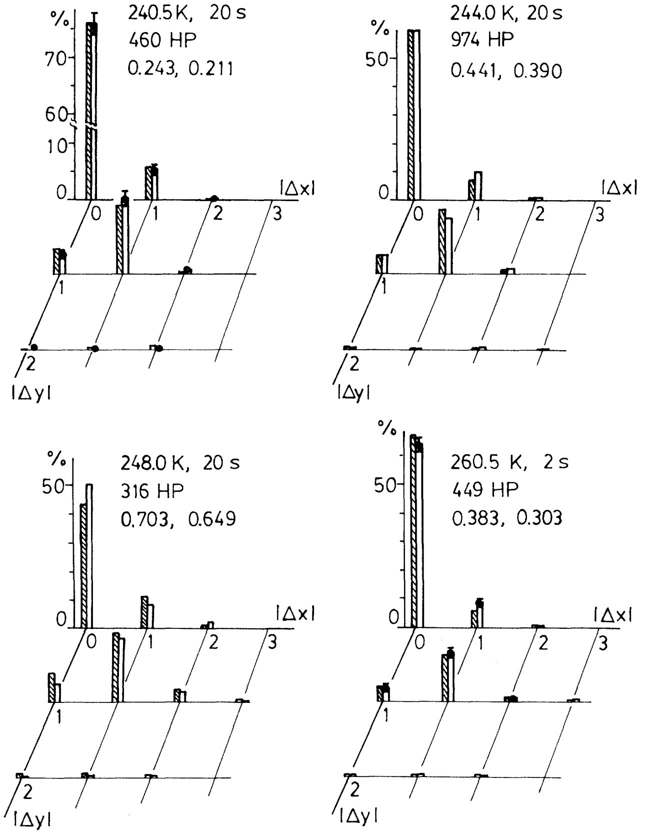

FIG. 2. Experimental 2D displacement distributions, shown as shaded bars. Monte Carlo distributions based on the mechanisms shown in Fig. 3(a) are displayed as open bars. x and y represent, respectively, the $[1\bar{1}0]$ and [001] directions. Temperature and τ are given for each distribution. HP denotes heating period. The last two numbers are the mean-square displacements in the x and y directions.

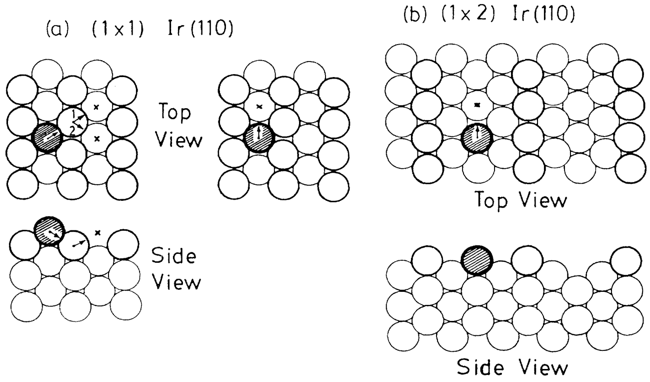

FIG. 3. (a) Three different atomic-jump directions in the diffusion of an Ir adatom on the (1×1) Ir(110) surface. The left-hand figure shows two different jump paths, 1 and 2, by the energy-exchanged atomic-replacement mechanism. The right-hand figure shows diffusion along the surface channel by the atomic-hopping mechanism. Crosses represent final sites. (b) The 1D diffusion along the double-width $[1\bar{1}0]$ surface channel of the (1×2) surface.

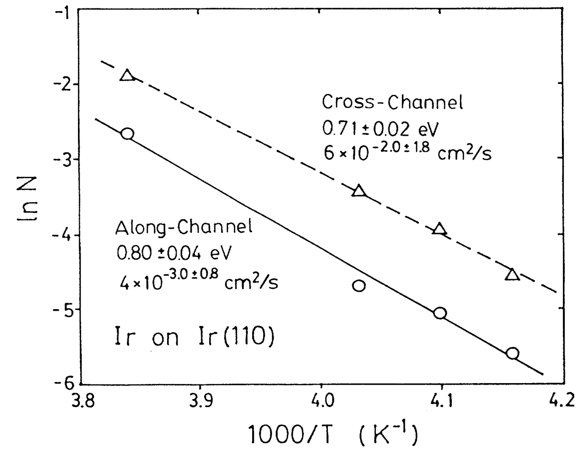

FIG. 4. Arrhenius plots for the cross-channel and along-the-channel diffusion of Ir atoms on the (1×1) Ir(110) surface. The activation energies and diffusivities are also listed.

$6\times10^{-2\pm1.8}$ vs $4\times10^{-3\pm0.8}$ cm²/s.

The (1×2)-reconstructed Ir(110) surface has closely packed $[1\bar{1}0]$ atomic rows forming surface channels of double width, or ~7.6 Å. In such a surface channel, the diffusion of Ir adatoms is found to be one dimensional, or adatoms can only hop along the $[1\bar{1}0]$ surface channels. Displacement distributions obtained at five temperatures are shown as open bars in Fig. 5. Shaded bars are theoretical distributions using an experimental mean number of jumps per heating period $\bar{N}$ based on a theory of discrete nearest-neighbor random walk. The experimental and theoretical distributions agree with each other to within the statistical uncertainties of the data. From the Arrhenius plot shown in Fig. 6, the activation energy E_d and the diffusivity D_0 for the atomic hopping are found to be $E_d=0.86\pm0.03$ eV and $D_0=1.2\times10^{-3\pm1}$ cm²/s, respectively. This activation energy is considerably higher than that for either the cross-channel or the along-the-channel diffusion on the nonreconstructed surface.

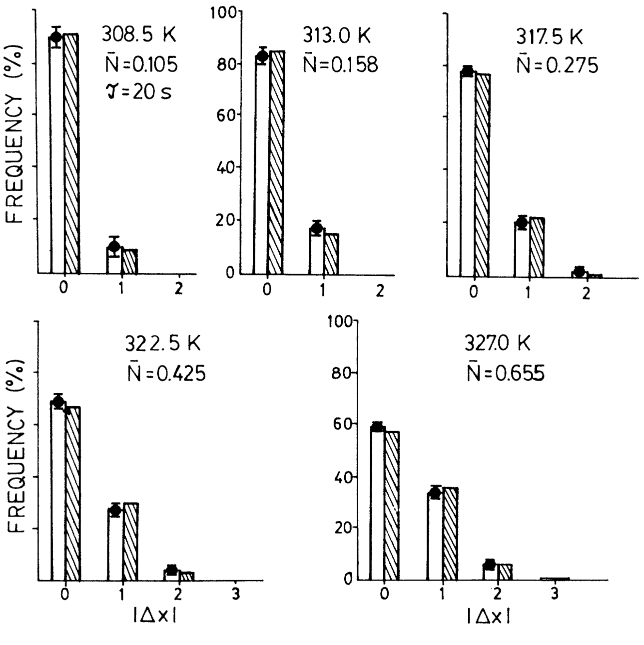

FIG. 5. Experimental 1D displacement distributions for an Ir adatom diffusing in the double-width $[1\bar{1}0]$ channel of the reconstructed Ir(110) surface, shown as open bars. Those from the discrete nearest-neighbor random-walk theory are shown as shaded bars.

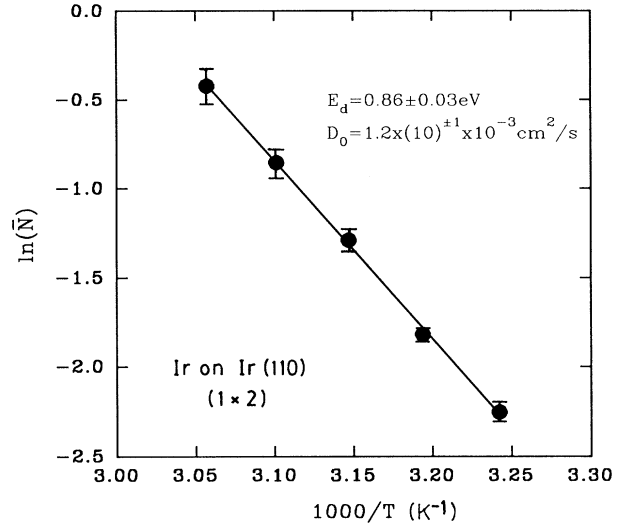

FIG. 6. Arrhenius plot for the 1D diffusion of Ir adatoms in the double-width surface channels of the (1×2) surface.

We can now represent the known mechanisms of surface diffusion with potential-energy diagrams shown in Fig. 7. For surfaces where no atomic reconstruction occurs such as the W (110), (112), and (123) and Rh (111), (311), (110), (331), and (110), and surfaces al-

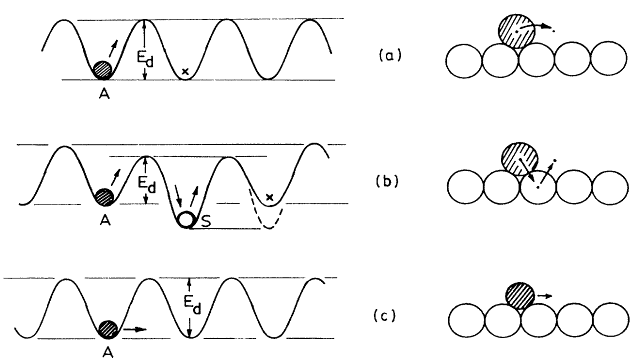

FIG. 7. Potential-energy diagrams for the three mechanisms of surface diffusion of single atoms as explained in the text.

ready reconstructed such as the (1×2) Ir(110), self-diffusion occurs by atomic hopping, as shown in Fig. 7(a). For surfaces where surface reconstruction can occur, such as the (1×1) Pt and Ir (001) and (110), a replacement of substrate atoms by self-adsorbed atoms often needs less energy than for the adatoms to hop a step, and the mechanism of surface self-diffusion occurs by an energy-exchanged atomic replacement, as illustrated in Fig. 7(b). For very light atoms such as H, D, and T, and most probably also for Li, Be, and B, surface diffusion can occur by an atomic tunneling as shown in Fig. 7(c). In this case, single adsorbed atoms cannot be localized by lowering the temperature of the surface. Thus, direct imaging of these atoms on a surface will be difficult.

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[a] To whom correspondence should be addressed. On leave from the Department of Physics, The Pennsylvania State University, University Park, PA 16802.

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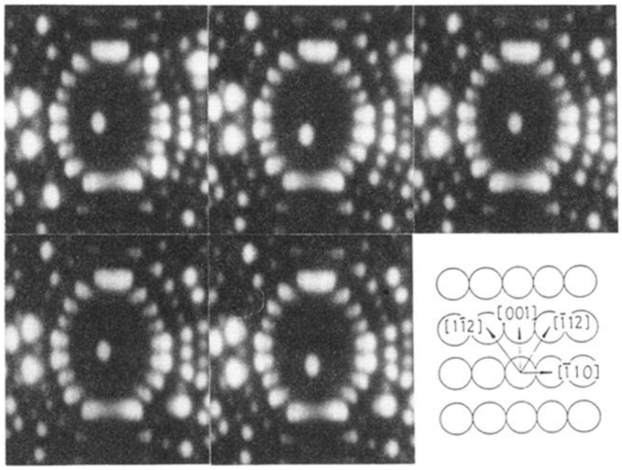

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