

Surface Self-Diffusion on Pt(001) by an Atomic Exchange Mechanism

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Field-ion microscopy has been used to map the surface sites visited by an individual Pt adatom migrating at 175 K on the Pt(001) plane and to determine its activation energy for surface diffusion. Atomic displacements are found to occur only in the [100] or [010] directions. A surprisingly low activation energy of 0.47 eV is measured. These results are consistent with a model in which the diffusion occurs by an adatom-substrate exchange mechanism. This mechanism is predicted theoretically for self-diffusion on Al(001).

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The mechanism by which metal atoms diffuse on a metal surface is of fundamental importance in processes such as a crystal growth and epitaxy. Migration of an atom from an adsorption site to the edge of an island is one of the basic steps in the growth process. In the conventional picture of surface diffusion on metals, atom migration takes place by a series of displacements over the minimum in the potential barrier between adjacent binding sites. Direct observations of atomic displacements with the field-ion microscope (FIM) are consistent with this sample hopping mechanism for a variety of bcc and fcc adatom-substrate combinations.¹

Only on the (001) surfaces of the fcc metals Pt, Ir, Ni, and Al is there evidence that the surface diffusion of metal atoms on metal surfaces proceeds by any other mechanism.²⁻⁵ On these surfaces, displacements across the close-packed [011] rows of atoms are believed to occur by an exchange mechanism, in which the adatom replaces a substrate atom in the channel wall, leaving the lattice atom to continue the diffusion process. This replacement process has been demonstrated unambiguously for W adatoms on Ir(001) in an atom-probe field-ion microscope investigation by Wrigley and Ehrlich.³ The relatively low activation barriers for cross-channel displacements of other atoms on the (011) surfaces of Pt, Ir, Ni, and Al suggest that the same mechanism applies whenever cross-channel displacements occur. Until the present work, however, diffusion by an exchange mechanism had not been considered for metal-atom diffusion on relatively smooth surfaces such as the fcc(001).

In this paper we present the results of a FIM investigation of Pt diffusion on the Pt(001) plane in which the migration is shown also to occur by an adatom-substrate exchange mechanism. Unlike cross-channel diffusion on the fcc(011) surfaces where the exchange is with a protruding channel-wall atom whose coordination is relatively low, on the (001) plane the exchange takes place with a nominally eightfold-coordinated substrate surface atom. Surprisingly, this exchange process occurs at temperatures as low as 175 K.

Place-exchange-mediated self-diffusion on a fcc(001) surface was originally proposed for the case of Al.⁶ First-principles calculations for Al(001) show that the

loss of coordination from 4 to 2, as an Al adatom proceeds from a fourfold hollow site to a transition-state bridge site, results in a substantially higher barrier for diffusion than a concerted displacement in which the transition state comprises two Al atoms adsorbed symmetrically above a surface-layer site vacated by one of them. The reason for the lower barrier is that in this state both of the (trivalent) Al's form three strong, covalent bonds. Of course, these arguments cannot be applied directly to Pt. However, as discussed further below, the fact that Pt favors low formal valencies may make the energy balance for Pt similar to that for Al.

The experiments were performed in an all-metal, ultrahigh-vacuum, field-ion microscope.⁷ The background pressure in the system after several bakeouts at 280°C and extensive vacuum processing was 2×10^{-11} Torr. The imaging gas was neon, purified by diffusion through a heated Vycor bulb and exposure to a Zr getter foil. An internal channel plate was used for image intensification. The Pt tip was prepared from 0.005-in.-diam polycrystalline wire and was electropolished to a fine point in a molten solution of NaNO₃ and NaCl.⁷ The tip surface was cleaned by a combination of thermal annealing at approximately 400°C, neon-ion bombardment, and field evaporation. The sample temperature was raised from its base value of 77 K by the standard resistive-heating methods used routinely in field-ion-microscope studies of surface diffusion.⁸

Single Pt atoms on the Pt(001) plane were generated by controlled field evaporation of the substrate. In this process atoms are removed from the edge of the plane inward, one atomic layer at a time.⁷ Small clusters of Pt atoms were obtained by stopping the field evaporation process when just a few atoms in the topmost layer were left. The clusters were broken apart by heating the tip to 250 K. Individual atoms from the dispersed clusters were removed by additional field evaporation until a single atom remained.

Noticeable diffusion of Pt on Pt(001) in a 30-s time interval was detected at a temperature of 175 K. The image spot corresponding to the Pt adatom appeared to be quite large, making the substrate barely visible at field strengths low enough to image the Pt adatom

without its desorption. As reported earlier,² this situation made registry of the adatom with the substrate difficult to determine. Nevertheless, it was still possible to map out the surface sites accessible to the diffusing atom and to determine the lengths of the displacements during the heating interval. This was accomplished with a video camera held fixed with respect to the field-ion-microscope image. Field-ion images were recorded on video tape after each diffusion period. The recorded images were analyzed by marking the position of the adatom with a cursor generated by an x - y video digitizer. The coordinates of the atom positions were then transmitted to a microcomputer for analysis.

Diffusion data were collected for 300 heating periods at 175 K. A map of the sites visited by the adatom during diffusion (henceforth called the "diffusion-accessible" sites) is shown in Fig. 1. The grid appears to be somewhat distorted from the square pattern expected for diffusion on an fcc(001) surface. This distortion,

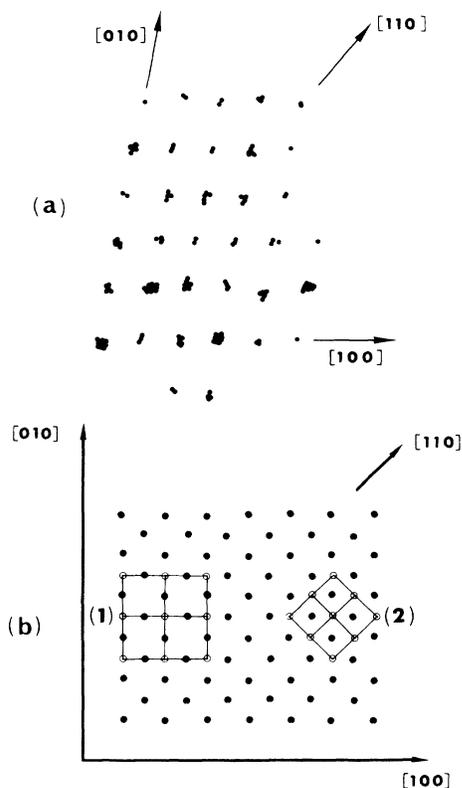


FIG. 1. (a) A map of diffusion-accessible sites for a Pt adatom diffusing on Pt(001) at 175 K. The mesh forms a slightly distorted square pattern with sides parallel to the [100] and [010] directions of the substrate plane. (b) A model of the fcc(001) plane. The solid circles represent substrate surface atoms and the open circles represent adatom binding sites. Pattern (1) shows the diffusion-accessible sites for migration confined to the [100] and [010] directions, i.e., motion along the surface diagonals. Pattern (2) shows the diffusion-accessible sites for bridge hopping.

which varies from tip to tip, is due to the nonuniform magnification of the field-ion microscope. A similar experiment (but with fewer diffusion cycles) on another tip resulted in a pattern with orthogonal axes. The important feature to note in Fig. 1(a) is that the sides of the "squares" in the grid are parallel to the [100] and [010] directions of the substrate surface. These directions are easily obtained from the symmetry of the various planes observed in the entire FIM image.

The mesh of diffusion-accessible sites shown in Fig. 1(a) can be used to determine the direction of the atomic displacements during migration, as illustrated in Fig. 1(b). In this figure the solid circles represent the substrate surface atoms and the open circles represent four-fold-binding sites. If atomic displacements are confined to the [100] and [010] directions, i.e., directions along the diagonals of the square surface lattice, the mesh of diffusion-accessible sites will correspond to pattern (1) in Fig. 1(b). The pattern is square, but only half of the binding sites are accessible to the diffusing atom. (The situation is analogous to moving on a checkerboard where only diagonal moves are permitted.) As a result, the sides of the square pattern are parallel to the [100] and [010] directions. On the other hand, if the diffusion takes place by hopping over the bridge sites, all binding sites will be accessible to the diffusing atom. The mesh of diffusion-accessible sites will again be a square grid, but in this case the sides of the squares will be parallel to the [110] and $[1\bar{1}0]$ directions. The mesh of sites for diffusion by the bridge-hopping process is shown as pattern (2) in Fig. 1(b). Clearly, the measured map of binding sites in Fig. 1(a) corresponds to the pattern (1) indicating that diffusion is always in the [100] or [010] directions. Displacements in these directions mean that the diffusing atom either goes directly over the top of a surface atom or replaces it in a concerted-displacement process.

If the displacements take place by hopping over a surface atom, one would expect a relatively high activation barrier for diffusion. However, we find the opposite to be true. The mean-square displacement measured from the 300 diffusion intervals at 175 K discussed above is 9.1×10^{-16} cm². With the assumption of the standard Arrhenius relationship for diffusion and a value of 10^{-3} cm² for the prefactor (consistent with a large body of FIM surface-diffusion data¹), the calculated activation energy for diffusion is 0.47 eV. This activation energy is significantly lower than that found previously² for self-diffusion on the (011), (113), and (133) planes of Pt, where the activation energy was found to range from 0.69 to 0.83 eV. Even if the diffusion were over bridge sites, a lower activation barrier on the (001) surface is unexpected because the (001) surface is more corrugated than any of these channeled surfaces in the direction of diffusion. It is also surprising that Pt atoms diffuse on Pt(001) at 175 K, whereas our preliminary experiments with the diffusion of Pd atoms on Pt(001) indicate that

Pd is immobile up to temperatures of ca. 265 K.⁹ Typically, a lower-melting-point element such as Pd would migrate at a lower temperature than a higher-melting-point element such as Pt. Based on this anomalously low activation barrier and the fact that a minimum diffusion barrier directly above a surface atom is physically unrealistic, we rule out the possibility that self-diffusion on Pt(001) occurs by hopping over surface atoms and conclude that the migration must be due to an adatom-substrate atom exchange process.

Theoretical support for this type of place-exchange diffusion on fcc(001) surfaces has been provided by recent first-principles calculations for Al adatoms on Al(001).⁶ The results of these calculations indicate that the barrier for place-exchange diffusion is lower than bridge hopping diffusion by several tenths of an eV. The replacement mechanism for diffusion on the fcc(001) plane, which is proposed as a result of these calculations, is illustrated in Fig. 2. The initial state with an adsorbed atom resting in a fourfold equilibrium site on the (001) plane is shown in Fig. 2(a). Interactions with the substrate cause the neighboring substrate atoms to relax out from their normal lattice positions. These relaxations are predicted theoretically by first-principles calculations¹⁰ for Al on Al(001) and recent embedded-atom-method calculations¹¹ for Pt on Pt(001). In the transition state, illustrated in Fig. 2(b), a substrate atom emerges from the surface plane to be replaced by what was originally the adatom. In this configuration each of the two atoms involved in the exchange forms three strong bonds, one to its fellow adatom and the other two to substrate atoms. Substrate symmetry only permits this configuration along [100] and [010] axes. The final state, illustrated in Fig. 2(c), is identical to the initial state except that the adatom now rests in a fourfold hollow diagonally across from the initial position.

The transition state illustrated in Fig. 2(b) corresponds to a low-energy state only if the threefold bonding of the two ad-Pt's sufficiently repays the cost of creating the surface vacancy. That creating a vacancy may not correspond to an overwhelming energetic cost is suggested by the facts that (1) Pt(001) irreversibly reconstructs at temperatures above 700 K,¹² (2) cluster nuclei on Pt(001) stabilize in unexpected configurations suggesting significant surface relaxations,^{11,13} and (3) Pt is typically not found in high-formal-valence states. The reconstruction of Pt(001) implies that the (1×1) surface is not the lowest-energy configuration and that energy can be gained by distorting it. Moreover, stable cluster configurations of Pt on Pt(001) are found to oscillate between chains and islands as the cluster increases in size from three to six atoms.¹³ Embedded-atom-method calculations predict these stable configurations only when surface relaxations are permitted. The directions of the calculated relaxations¹¹ are such to favor the exchange mechanisms shown in Fig. 2. Finally, the fact that Pt does not form many strong, directional bonds implies

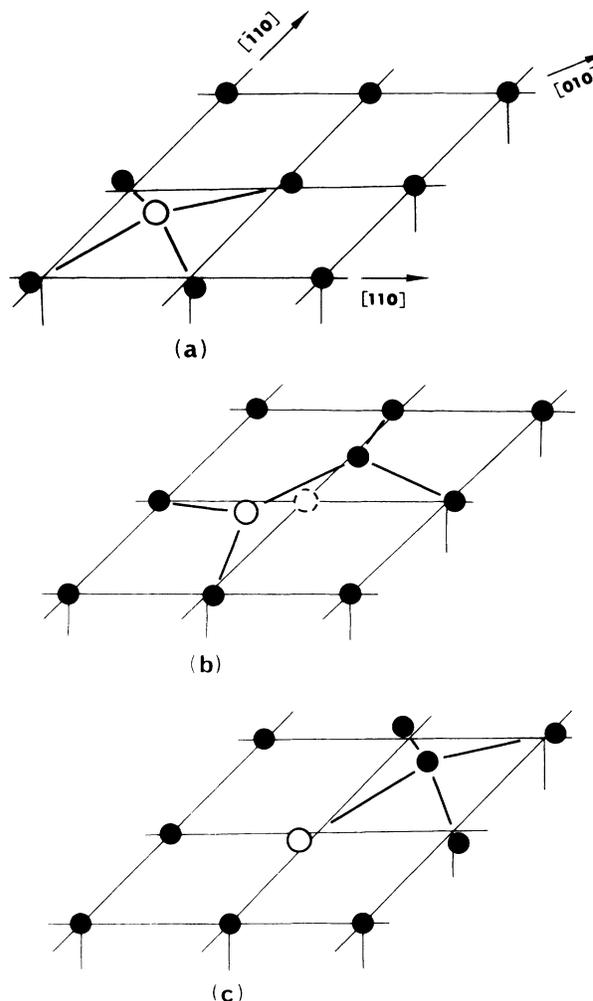


FIG. 2. A schematic of the proposed mechanism for diffusion by place exchange: (a) an atom in a fourfold hollow; (b) the transition state; (c) the final state. Details are discussed in the text.

that the eight "bonds" of a surface-layer Pt atom are sufficiently weak to permit replacing them with three stronger bonds.

The identification of an exchange mechanism for diffusion on a flat single surface such as fcc(001) at temperatures as low as 175 K has important implications in areas such as the fabrication of artificially layered structures, where atomically sharp interfaces may be required. For this reason it is of great interest to establish the conditions, quantitatively if possible, that determine whether ordinary hopping or a particular exchange mechanism will be preferred. At the present time, we only have a few measurements and a single calculation, which makes a phenomenological analysis dubious. FIM investigations of self-diffusion on Rh(001) have been reported by Ayrault and Ehrlich.⁸ In this case, the measured barrier, 0.88 eV, seems reasonable relative to other Rh planes. Thus, there is no reason to suspect exchange

diffusion, although the mesh of diffusion accessible sites explored by Rh was not reported. Concurrent with our work, Chen and Tsong¹⁴ report studies of self-diffusion on Ir(001), with conclusions essentially similar to ours for Pt, i.e., that exchange diffusion along [100] and [010] directions is preferred. Preliminary work in our laboratory for Pd diffusion on Pt(001) indicates that diffusion occurs via normal bridge hopping [the diffusion-accessible sites correspond to pattern 2 in Fig. 1(b)] with a reasonable activation barrier. However, for Ni on Pt(001) there is evidence for place exchange.⁹ Ni adatoms deposited with the tip at 77-K field desorb at field strengths where they are barely visible in an FIM image. However, if the surface is heated to 160 K or above after deposition of Ni, image spots appear on Pt(001) which resist field desorption up to the evaporation field of Pt adatoms. This suggests that deposited Ni atoms may displace substrate Pt atoms at 160 K and above. We speculate that this dependence of exchange-mediated diffusion on the chemical identity of the adatom arises from differences in the adsorbate-induced substrate relaxations mentioned above. However, the specific role of these relaxations remains to be explored both experimentally and theoretically.

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