Diffusion of Pd adatoms and stability of Pd overlayers on the (011) surface of Pt

G. L. Kellogg
Sandia National Laboratories, Albuquerque, New Mexico 87185
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Field-ion microscopy has been used to examine the migration of individual Pd atoms and the stability of Pd overlayers on the (011) surface of Pt. Pd atoms are found to migrate within the $[0\bar{1}1]$ surface channels in the temperature range 207–235 K with an activation energy of 0.58 ± 0.05 eV. Cross-channel displacements are not observed. Clusters of Pd atoms on Pt (011) form stable (1×1) structures at temperatures below 300 K and do not reconstruct to the "missing-row" structure. Pd adatoms deposited on top of (1×1) Pd overlayers are found to diffuse in channel at a temperature of 167 K.

I. INTRODUCTION

Previous field-ion-microscope (FIM) studies of single-atom diffusion and surface reconstructions on fcc(011) single-crystal planes have yielded interesting results.[1–9] In 1978, Bassett and Webber[1] discovered that a Pt adatom migrating on a Pt(011) plane makes displacements in directions both parallel and perpendicular to the close-packed $[0\bar{1}1]$ atomic rows. The activation barrier for diffusion across the atomic rows (channel walls) was found to be the same as the activation barrier for diffusion within the surface channels. Based on this observation, they suggested that the observed cross-channel displacements were not due to the hopping of atoms over channel walls, but resulted from an exchange process in which the adatom pushes a channel wall into an adjacent surface channel and takes its place. That such exchange processes actually occur was subsequently confirmed by Wrigley and Ehrlich[2] in an atom-probe investigation of W atoms on the Ir(011) plane and, more recently, by Kellogg[3] in a FIM study of Pt atoms on the Ni(011) plane. These results have led to the general consensus that, as Bassett and Webber originally suggested, cross-channel displacements observed in self-diffusion on Pt(011) are due to exchange-type processes.

In the same article, Bassett and Webber[1] also reported that cross-channel displacements were observed for self-diffusion on Ir(011) surfaces (an observation confirmed by several subsequent FIM studies[2,4]) and suggested that there may be a connection between the unusual diffusion behavior of Pt and Ir and the fact that macroscopic (011) surfaces of Pt and Ir are reconstructed under equilibrium conditions. The reconstructed (011) surfaces of Pt and Ir are known to have a (1×2) periodicity which arises from a missing-row structure.[10] The possible connection between exchange displacements and the reconstruction of the surface was supported by the earlier observation[5] that surface diffusion on the Rh(011) surface, which does not reconstruct, is quite normal, i.e., cross-channel displacements are not observed. Subsequent studies of self-diffusion on Ni(011) by Tung and Graham,[6] however, showed that cross-channel displacements do not necessarily correlate with a missing-row reconstruction. Exchange displacements were found to take place on Ni(011), but the macroscopic surface does not reconstruct thermally.[10]

The primary motivation for the present investigation was to examine further the connection between the diffusion behavior of single atoms on fcc (011) surfaces and the tendency of these surfaces to reconstruct. The system studied was Pd on Pt(011). Although the results for Ni(011) indicate that the occurrence of cross-channel displacements does not necessarily result in a missing-row reconstruction, it is still possible that such displacements are involved in the transformation of those surfaces that do reconstruct. Self-diffusion of individual atoms has been examined on only two fcc (011) surfaces known to reconstruct (viz. Pt and Ir) and cross-channel displacements are observed on both of these surfaces. Cross-channel displacements may, therefore, be necessary but not sufficient condition for the missing-row reconstruction. If exchange-type displacements are involved in the formation of missing-row structures, it could help resolve questions raised in the past concerning mass transport during the reconstruction process.[11]

It is worth noting that the field-ion microscope is ideally suited to investigate this type of correlation. Cross-channel displacements are easily detected in single-atom diffusion studies and transformations from bulk-terminated to missing-row structures can be directly observed. Previous FIM experiments[7,8] have shown that (1×1) clusters of Pt atoms on Pt(011) transform to missing-row structures at temperatures of 300–350 K. Similar results are found for Ir on Ir(011) at higher transformation temperatures (500–700 K).[4,9] It is therefore possible to examine single-atom diffusion and surface reconstructions on the same crystal surface.

In this investigation, the diffusion of individual Pd atoms and the stability of (1×1) Pd overlayers on the Pt(011) surface were investigated. This study represents the first time that both the diffusion behavior of single atoms and the tendency towards reconstruction have been examined for a heterogeneous system. Pd on Pt is an interesting combination in that, although Pt surfaces tend to reconstruct and Pd surfaces tend to be stable, other properties of the two metals are quite similar. The lat-

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tice mismatch is less than 1% and they are continuously miscible in the solid state.[12] Low-energy electron-diffraction and Auger-electron-spectroscopy investigations[13,14] indicate that Pt films deposited on macroscopic Pd(110) surfaces form both (1×2) and (1×3) reconstructions with very interesting properties. However, similar studies have not been carried out for Pd on Pt(110), and the overlayer surface structure is not known.

II. EXPERIMENTAL METHODS

A general overview of field-ion microscopy and its applications can be found in a recently published book by Tsong.[15] The procedures used to generate individual adatoms on perfectly clean and smooth crystal surfaces and examine their diffusion behavior are described in Tsong's book and several review articles.[16] Here, I mention only a few experimental details relevant to the study of Pd on Pt. The Pt tips were prepared from 99.99% pure wire. They were electropolished in a molten solution of $NaNO_3$ and NaCl at 5 V (dc) to achieve a tip radius of 30–50 nm. The surfaces were cleaned with a combination of Ne ion sputtering, thermal annealing, and field evaporation. Field-ion imaging was carried out in a stainless-steel vacuum chamber having a background pressure of 3×10^{-11} Torr. The imaging gas was Ne, purified by diffusion through a Vycor bulb and exposure to a heated Zr foil. A liquid-nitrogen-cooled cold finger was used to cool the sample tips to their base temperature of 77 K. The temperature was raised from this base value by the standard resistive heating methods used routinely in FIM surface diffusion studies.[16] The deposition sources were coils made from 0.127-mm-diam Pd wire. An internal channel plate was used for image intensification. Images were recorded with the use of either a video camera and recorder system or a 35-mm still camera.

III. EXPERIMENTAL RESULTS

The diffusion of individual Pd atoms on the Pt(011) plane is illustrated by the series of field-ion micrographs shown in Fig. 1. The images were recorded with the sample at 77 K. Between each photograph the tip was heated to 220 K for 1 min with the imaging voltage turned off. The photographs in Fig. 1 are oriented such that the $[0\bar{1}1]$ direction is nearly horizontal. Small white dots have been superimposed on photographs 1(b)–1(d) to indicate the position of the atom in the previous photographs. No motion occurred between (a) and (b), but did take place between (b) and (c) and (c) and (d). From these photos, along with video images following hundreds of diffusion cycles in the temperature range from 207–235 K, it is concluded that diffusion of the Pd atom is one dimensional, i.e., the displacements are confined to within a single-surface channel. The lower limit of the temperature range is defined by the temperature at which the adatom is immobile and the upper limit by the temperature where it frequently migrates off the plane edge.

The mean-square displacement for the diffusing atom was obtained at five different temperatures within the 207–235-K range. The activation barrier was obtained

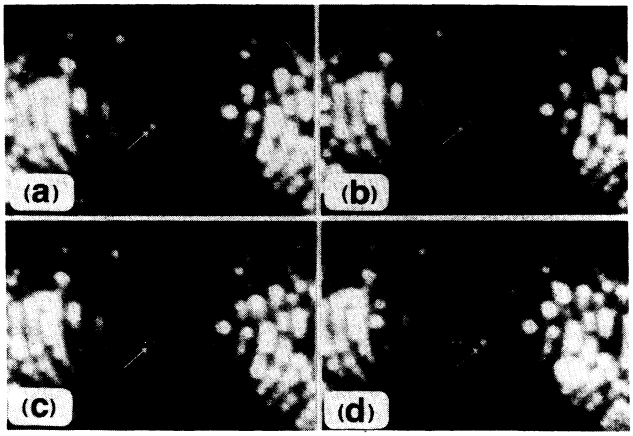

FIG. 1. A sequence of field-ion micrographs showing the migration of a Pd atom on the Pt(011) plane. The images were recorded with the tip at 77 K in 2×10^{-4} Torr Ne. Between each photograph the tip was warmed to a temperature of 220 K for 1 min. The small white dots in (c) and (d) indicate the adatom position in the previous images. Atom motion is confined to within a single $[0\bar{1}1]$ channel (the channels run horizontally on the photographs).

from the standard Arrhenius analysis[16] and the results are shown in Fig. 2. Due to the limited statistics, the data plotted in Fig. 2 suggest non-Arrhenius behavior (or perhaps two activated regimes). However, the linearity of such plots is well established in past FIM studies[16] and it is, therefore, appropriate to assume a simple Arrhenius form. From the slope and intercept of the plot, the activation barrier and Arrhenius prefactor are determined to be 0.58 ± 0.05 eV and $3.5\times(10^{\pm1.2})\times10^{-3}$ cm^2/sec, respectively. The fact that the prefactor lies within the experimental error of the accepted value[16] of 10^{-3} cm^2/sec for metal-on-metal diffusion further justifies the assumption of Arrhenius behavior with a single activated regime.

The possible reconstruction of Pd overlayers on Pt(011) was examined by observing the thermal stability of small

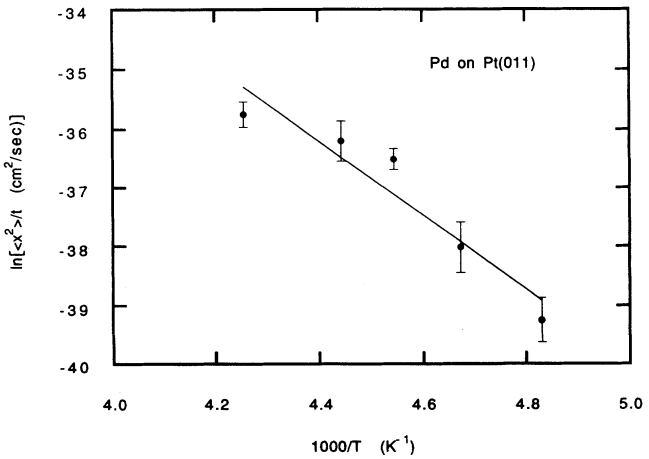

FIG. 2. An Arrhenius plot for the diffusion of Pd on Pt(011). The slope and intercept yield an activation energy of 0.58 ± 0.05 eV and a prefactor of $3.5\times(10^{\pm1.2})\times10^{-3}$ cm^2/sec.

Pd clusters in the FIM. The clusters were generated by depositing Pd with the tip at 77 K and subsequently warming it to 230 K. With a sufficient dose of Pd, this procedure resulted in a large (1×1) cluster on the Pt(011) plane. Low-temperature (77-K) field evaporation was then used to form smaller clusters. The evaporation field of Pd was found to be significantly less than that of Pt, so it was possible to field evaporate the Pd to the desired cluster size without affecting the Pt substrate. The structure of the clusters was determined to be (1×1), i.e., rows of Pd atoms appeared in adjacent rows of the underlying substrate. After a cluster was formed the surface was heated to determine if restructuring took place. The results were compared to Pt clusters produced by field evaporation of the substrate (011) plane.

The (1×1) structure of Pd clusters was found to be stable upon heating to temperatures of 300 K. Figure 3 shows FIM images of a small Pd cluster on Pt(011) before and after heating to 295 K for 1 min. The Pd cluster is unchanged by the heat treatment. In contrast, Fig. 4 shows FIM images of a small Pt cluster on the same surface before and after heating to the same temperature. Whereas the Pd cluster was unchanged at this temperature, the Pt cluster is seen to transform to a missing-row structure. When heated to temperatures higher than 300 K, the Pd clusters would break apart. Although there was some evidence that exchange between the Pd cluster atoms and the Pt substrate atoms occurred at these higher temperatures, missing-row structures were not formed under any conditions. It is therefore concluded that the missing-row structure is not the stable structure for Pd overlayers on the Pt(011) surface.

The ability to produce stable (1×1) Pd monolayers on the Pt(011) surface also stimulated a preliminary investigation of Pd adatom surface diffusion on top of the Pd monolayers. After forming a Pd monolayer by the procedure described above, an individual Pd atom was deposited. Displacements of the adatom were observed on the overlayer at temperatures as low as 167 K, well below the onset of diffusion of Pd on the Pt substrate. The motion of the Pd atom was confined to within a surface channel of the Pd overlayer. Interestingly, the adatom did not migrate freely from one end of the channel to the other. Instead, the motion was restricted to within a few atomic sites of the center of the channel. If the temperature was raised by even a few degrees above 167 K, the adatom would disappear during the heating interval. It could not be determined whether the adatom migrated off the edge of the plane or became incorporated into the monolayer. Further investigations will be needed to explain this unusual behavior.

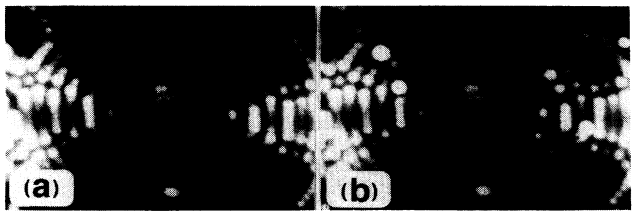

FIG. 3. Field-ion micrographs of a small Pd cluster on Pt(011). Between the photographs the tip was warmed to 295 K for 1 min. No restructuring of the cluster is observed.

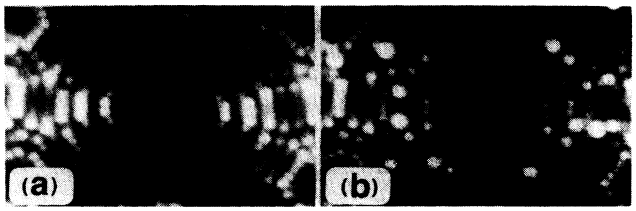

FIG. 4. Field-ion micrographs of a small Pt cluster on Pt(011). Between the photographs the tip was warmed to 295 K for 1 min. Restructuring to a missing-row structure is observed.

IV. DISCUSSION

The main conclusions from this study are that the diffusion of individual Pd atoms on the Pt(011) plane takes place by conventional hopping-type displacements along the surface channels and that small clusters are stable against reconstruction. As mentioned in the Introduction, there seems to be a correlation between the mode of single-atom self-diffusion on fcc(011) surfaces and the tendency of the surface to reconstruct. If the diffusion mode is exchange, the surfaces reconstruct. If the diffusion mode is conventional hopping, they do not. Here, the correlation is found to hold for the mixed-metal system of Pd on Pt. Apparently, self-diffusion on the (011) surface of Ni (and possible Al) remain the exceptions to this general rule.

Another trend which appears to be emerging from FIM studies of adatom migration is that the diffusion mode (exchange vs hopping) for an adatom is the same on the (011) and (001) surface of a given substrate. Recent theoretical[17,18] and experimental[19,20] studies have identified a diffusion mode on certain fcc(001) surfaces involving exchange between an adatom and a substrate surface atoms. Exchange displacements have been experimentally confirmed for self-diffusion on the (001) surfaces of Pt (Ref. 19) and Ir (Ref. 20) and for Pt on Ni(001).[21] As mentioned earlier, exchange (cross-channel) displacements are observed on the (011) plane for the same atom-substrate combinations. In this study, Pd atoms are found to migrate on Pt(011) by conventional hopping, the same as the mode found in a recent study of Pd on Pt(001).[22]

The observation that Pd overlayers on the Pt(011) plane do not reconstruct, whereas Pt overlayers on Pd(011) do,[13,14] suggests that it is the chemical composition of the outermost layer of atoms that determines the stable surface structure. A possible explanation for this effect has been offered by Fu and Ho,[23] who propose that the stable structure for the fcc(011) surfaces is controlled by the surface electron concentration. Their first-principles calculations indicate that a negative electric field of $\sim 10^7$ V/cm induces a surface charge of ~ 0.05 electron/surface atom and changes the stable structure of a Ag(011) surface from (1×1) to (1×2). This result nicely explains the promotion of the (1×2) reconstruction of $3d$ and $4d$ fcc(011) surfaces by electron donors

(e.g., alkali-metal atoms)[24–27] and the lifting of the (1×2) reconstruction of 5*d* fcc(011) surfaces by electron acceptors (e.g., CO, O).[28–32] The result is also consistent with the present observations, i.e., a 4*d* overlayer on a 5*d* substrate has less surface charge than the reverse situation leading to a (1×1) structure for Pd on Pt and a $(1\times n)$ structure for Pt on Pd.

A final observation emerging from this study is that an individual Pd atom migrating on a Pd overlayer on top of the Pt(011) plane has a lower barrier to diffusion than a Pd atom on the bare (011) substrate and its motion is confined to within the centermost portion of the plane. The lower barrier is consistent with the general observations that the second layer of atoms in a metal-on-metal system is more weakly bound than the first and that diffusion-activation energies typically scale with binding energies. That the atom is confined to the center of the plane is quite different than that which is usually observed for an adatom on a bare substrate. Normally, an atom diffuses from one edge of the plane to the other with a small reflection barrier at the plane edge. Here, the reflection barrier is found towards the center of the plane. This observation has important ramifications for the nucleation and growth of epitaxial films and will be the subject of future studies.

V. SUMMARY

The diffusion of atoms on the Pt(011) plane proceeds by ordinary hopping within the $[0\bar{1}1]$ channels in the temperature range 207–235 K. The activation barrier for diffusion is 0.58 ± 0.05 eV. Unlike Pt on Pt(011), small clusters of Pd atoms on Pt(011) do not reconstruct to the missing-row structure. The migration of Pd atoms on an overlayer of Pd occurs at much lower temperatures (167 K), but the atom is confined to within a few atomic sites of the center of the plane.

ACKNOWLEDGMENT

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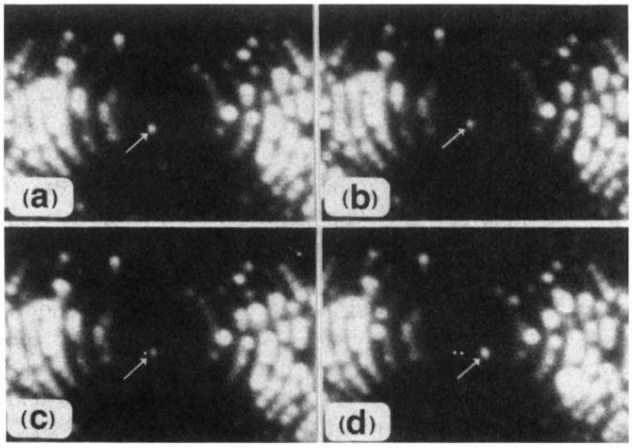

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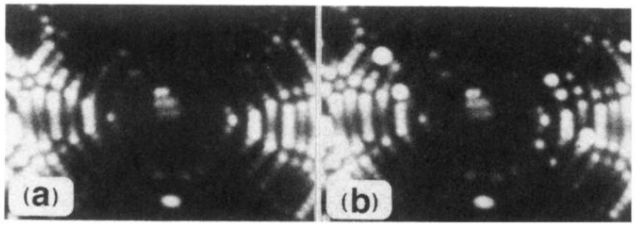
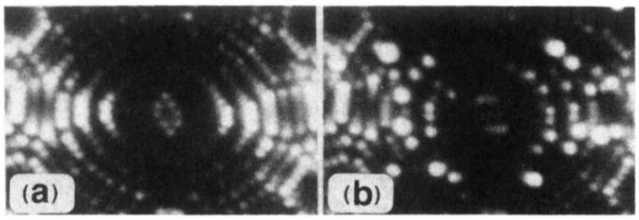


FIG. 3. Field-ion micrographs of a small Pd cluster on Pt(011). Between the photographs the tip was warmed to 295 K for 1 min. No restructuring of the cluster is observed.



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