Electric Field Inhibition and Promotion of Exchange Diffusion on Pt(001)

G. L. Kellogg
Sandia National Laboratories, Albuquerque, New Mexico 87185

(Received 17 September 1992)

Direct observations of a Pt adatom migrating on the Pt(001) plane in the presence of an externally applied electric field show that a positive field raises, and a negative field lowers, the activation barrier for the adatom–substrate-atom exchange process. At field strengths of 1.5 V/Å and above, inhibition of the exchange mechanism is sufficient to change the diffusion mode from exclusively exchange displacements to a mode that includes hops. The effect of the electric field is explained by an electron-transfer process which changes the bonding of the adatom to neighboring surface atoms.

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

Recent theoretical and experimental investigations have shown that there are two mechanisms by which adsorbed atoms (adatoms) may diffuse across the (001) surface of fcc metals [1,2]. Instead of making hops between adjacent binding sites (conventional diffusion), adatoms on certain surfaces find it energetically favorable to push a neighboring atom out from the underlying metal (the substrate) and take its place within the top layer of surface atoms. The displaced surface atom becomes a new adatom and continues the migration process. This process has become known as either the exchange, replacement, or substitutional mode of surface diffusion. First observed on corrugated fcc (011) surfaces [3], exchange-mediated diffusion on atomically smooth fcc (001) surfaces has attracted considerable recent attention, both as an alternative mechanism for atom transport across surfaces and as a possible means for surface alloying in heteroepitaxial growth.

In this Letter I report an experimental investigation which shows that the rate at which exchange displacements occur on fcc (001) surfaces can be significantly altered by an externally applied electric field. Field ion microscope (FIM) measurements show that a positive electric field (i.e., a positive tip potential) inhibits and a negative field promotes the diffusion of a Pt adatom on Pt(001) by exchange displacements. The effects are observable at field strengths of ~0.5 V/Å, corresponding to an induced surface charge of 0.56 C/m^2 or about 0.1 electron/(surface atom). At sufficiently high positive fields inhibition is so strong that the diffusion mode changes from one consisting exclusively of exchange displacements to one including ordinary hopping displacements. The ability to control both the diffusion rate and the *transport mechanism* with an externally applied field suggests that it should be possible to alter crystal and epitaxial growth modes, for example, in electrochemical environments or by the addition of electropositive and electronegative adsorbates during more conventional growth processes.

The experimental methods used in this investigation follow closely those reported in earlier studies of Pt diffusion of Pt(001) under field-free conditions [2,4]. The details relating to sample preparation, field ion imaging, and surface diffusion measurements can be found in a recent review [5] and these earlier articles. Briefly, the procedure involves taking "snapshots" of a Pt adatom as it moves across an atomically smooth (001) crystal plane. The snapshots are taken with the sample at 77 K, where the adatom is immobile. Adatom motion occurs during 30-sec heating intervals when the sample is warmed from 77 K to temperatures in the range 160–284 K. The imaging voltage is reduced to a preset value during the heating intervals. The electric field strength is determined from the applied voltage by calibration against the known [6] evaporation field of Pt (4.8 V/Å). The series of snapshots is used to determine both the mean-square displacement of the adatom and the map of binding sites visited by the adatom. The activation barrier for diffusion is determined from the measured mean-square displacements and temperature, and the diffusion mode (exchange versus hopping) is inferred from the site-visitation maps as discussed below.

The inhibition of self-diffusion on Pt(001) by a positive electric field is seen qualitatively in a simple experiment involving heating cycles starting at 175 K. Under field-free conditions, the adatom displaces, on the average, about once per diffusion interval. (The measured mean-square displacement is 14.8 Å^2.) If an electric field of 0.5 V/Å is applied during the heating intervals without changing any other conditions, the motion completely stops. Increasing the temperature to above 200 K while keeping the field at 0.5 V/Å causes the diffusion process to resume. This indicates that the positive electric field increases the activation barrier for exchange diffusion. By increasing the temperature and field together, while maintaining a relatively constant diffusion rate, the field dependence of the activation energy is determined. In this investigation the effect of field strengths in the range from 0.5 to 2.25 V/Å was examined.

A similar experiment demonstrates the promotion of exchange diffusion by a negative field. At 160 K and zero applied field, a Pt adatom makes only two displacements in fifty heating cycles, which corresponds to a mean-square displacement of 0.61 Å^2. However, when an elec-

TABLE I. Diffusion parameters for self-diffusion on Pt(001).

Field (V/Å)	Temperature (K)	Cycles	$\langle r^2 \rangle$ (Å^2)	E_d (eV)	Site map
−0.44	160	40	20.5 ± 4.7	0.44	$c(2\times2)$
0	175	100	14.8 ± 3.2	0.48	$c(2\times2)$
+0.50	212	50	26.0 ± 4.0	0.57	$c(2\times2)$
+0.75	224	50	33.9 ± 13	0.60	$c(2\times2)$
+1.00	230	68	18.6 ± 7.0	0.63	$c(2\times2)$
+1.25	243	42	32.9 ± 8.5	0.65	$c(2\times2)$
+1.50	265	23	12.9 ± 4.0	0.73	(1×1)
+1.75	265	55	3.69 ± 0.9	0.76	(1×1)
+2.00	284	42	7.67 ± 3.1	0.80	(1×1)
+2.25	278	16	19.9 ± 6.0	0.76	(1×1)

tric field of −0.44 V/Å is applied, the adatom begins to move in nearly every heating cycle. The measured mean-square displacement with the negative field on is 20.5 Å^2 (a 34-fold increase). A negative field therefore lowers the barrier for exchange displacements. Unfortunately, the accessible range of electric fields in the negative direction is severely limited by the onset of field electron emission, which is observed at a field strength of approximately −0.5 V/Å. As a result, the diffusion barrier in the presence of a negative electric field was determined at the single field strength of −0.44 V/Å.

The measured mean-square displacements and relevant diffusion data at ten different electric field strengths are listed in Table I. The activation energy of diffusion calculated from these values are also listed in the table and plotted in Fig. 1. At the higher field strengths and temperatures, adatom loss by migration off the plane was frequent and gathering statistics over a wide temperature range at a given field became impossible. For this reason the activation barriers were determined at a single temperature from the standard Arrhenius equation [5] with the assumption of a constant prefactor of 1×10^{-3} cm^2/sec. Although this value is now widely accepted for adatom diffusion under field-free conditions [7], there is an obvious concern that the prefactor may be influenced by an electric field. This concern is somewhat alleviated by the observation that, under field-free conditions, the prefactor for exchange displacements [including Pt on Pt(001)] has been found to be the same as that for hopping displacements [2,4]. If such a dramatic difference in the diffusion mechanism does not influence the prefactor, a continuously increasing electric field, whose effect is to change the mode from exchange to hopping (see below), is expected also to have a small effect on the prefactor.

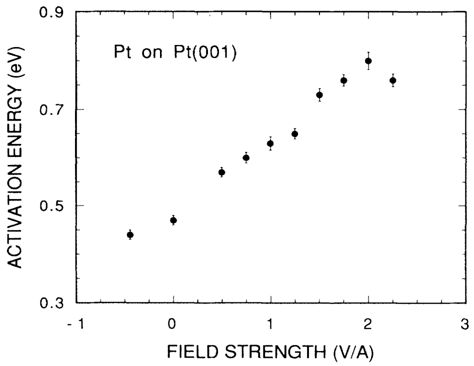
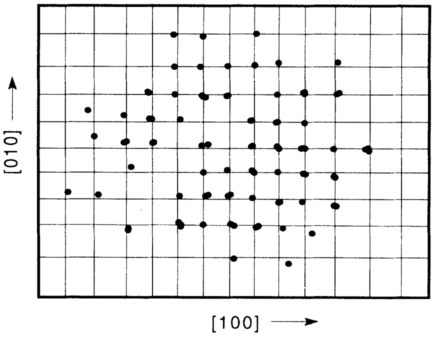


FIG. 1. A plot of the activation energy of surface diffusion for an individual Pt adatom on the Pt(001) plane as a function of the applied electric field.

The last column in Table I lists the periodicity of the site-visitation maps for each of the conditions of field and temperature examined in this study. It has been shown in previous studies that the diffusion mode (exchange versus hopping) for an adatom on an fcc (001) surface can be inferred from maps of the sites visited by the adatom as it moves across the surface [1,2,4]. The key consideration which allows one to differentiate between the two modes is that exchange displacements and hopping displacements take place along different directions. Exchange displacements involve the concerted movement of an adatom and a surface atom along a diagonal direction between fourfold hollow sites. On fcc (001) surfaces the diagonals correspond to the [100]-type directions. Hopping displacements, in which an adatom crosses over a twofold bridge site, occur along the [110]-type directions. Viewing the (001) surface as a checkerboard, displacements along [100]-type directions (exchange displacements) correspond to moves between squares of the same color, whereas displacements along [110]-type directions (hopping displacements) correspond to moves between adjacent squares of different colors. If the motion proceeds exclusively by exchange displacements, then only half of the available binding sites are visited and the map of sites is a square pattern with sides parallel to [100]-type directions [periodicity $c(2\times2)$]. If hopping displacements occur then all of the sites are accessible to the diffusing adatom and the map is a square pattern with sides parallel to [110]-type directions [periodicity (1×1)].

Examples of site-visitation maps at two different field strengths and temperatures are shown in Fig. 2. The site map shown in Fig. 2(a) was compiled from 100 diffusion periods at 200 K and zero applied field. The pattern is

(a) F=0 V/Å T=200 K



(b) F=1.75 V/Å T=265 K

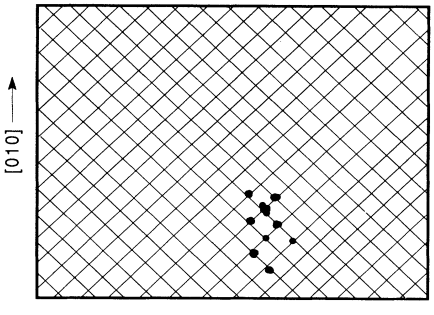


FIG. 2. Site visitation maps for a Pt adatom on Pt(001) for two conditions of field and temperature. (a) At zero field the periodicity is $c(2\times2)$ indicating diffusion by exchange. (b) At higher fields and temperatures the periodicity is (1×1) indicating the occurrence of hopping displacements.

square with sides parallel to the [100]-type directions [periodicity $c(2\times2)$]. This result is the same as reported previously [2] and indicates that diffusion occurs exclusively by the exchange mechanism. Figure 2(b) shows a map compiled from 55 diffusion cycles at a field strength of 1.75 V/Å and a temperature of 265 K. The pattern is square with sides parallel to [110]-type directions [periodicity (1×1)]. This result indicates that migration at 1.75 V/Å and 265 K includes ordinary hopping displacements. It does not mean that diffusion takes place exclusively by hopping, only that at least one hop has occurred during migration. In fact, a closer examination of the data indicates that hopping displacements are relatively infrequent under these conditions. In 55 diffusion cycles the adatom displaced 14 times. Of these displacements only four were between the two $c(2\times2)$ sublattices. Since the conditions were such that multiple hops were unlikely, it is clear that most of the displacements still occurred by the exchange mechanism. Only at higher field strengths and temperatures (2.25 V/Å and 278 K) did the fraction of hopping displacements become greater than exchange displacements (~60% hops).

As shown in Table I, the periodicity of site-visitation maps changes from $c(2\times2)$ to (1×1) at field strengths of 1.5 V/Å and temperatures of 265 K. The changeover from $c(2\times2)$ maps to (1×1) maps indicates that hopping displacements become energetically accessible at a temperature between 243 and 265 K. The activation barrier continues to increase with increasing field strength from 1.5 to 2.0 V/Å because the primary diffusion mode is still exchange (see above). The barrier reaches a maximum at 2.0 V/Å and then begins to decrease. This decrease is attributed to the fact that, as shown in previous studies of adatom diffusion on W(110) [8], hopping displacements are assisted by a positive electric field. Thus, above 1.5 V/Å, there are competing displacement processes: exchange displacements, which are inhibited by the field and hopping displacements, which are promoted by the field. The measured activation energies reflect the combination of the two displacement processes, dominated by exchange up to fields of 2.0 V/Å.

Although the above experiments have established that it is possible to control the rate of exchange displacements during self-diffusion processes by an externally applied electric field, the detailed mechanism by which this control is achieved is still an open question. It is generally agreed that the reason exchange displacements are preferred over conventional hops is that the adatom can maintain a higher coordination with the neighboring surface atoms by making a concerted displacement with a substrate atom [1,2]. In the case of self-diffusion on Al(001), the coordination geometry during the concerted motion is particularly attractive because Al is trivalent and the adatom can maintain three "bonds" as it undergoes an exchange displacement [1]. In order to hop over a twofold bridge site, the adatom must give up one of its bonds at a significant cost in energy. Although Pt and Ir are not trivalent, the enhanced coordination of the adatom during exchange displacements is believed to compensate for the energy required to create and fill a surface vacancy [2]. To understand how the exchange process is influenced by an external field, we need to ask how the electric field changes the bonding of the adatom with its neighbors during the displacement process.

It is known from studies of field evaporation that an external electric field at the site of a kink-site atom or an adatom induces charge transfer [9]. A positive electric field drains charge from the adatom, whereas a negative electric field adds charge to it. One explanation [10] for the inhibition of exchange displacements by a positive field is that this charge transfer changes the valence of the adatom such that the energy gain in making a concerted displacement is no longer sufficient to compensate for the cost in creating a surface vacancy. In the case of self-diffusion on Al(001), the applied field would change the valency from three towards two. Maintaining threefold coordination would no longer result in a significant energy gain. A valency of two would actually favor displacements over the bridge site further enhancing the hopping process (as observed in the experiments). However, it is not clear how this valency argument carries over to Pt and Ir, which are not trivalent. Even in the case of Al, the argument does not explain why a negative field would promote the exchange process.

The effect of change transfer in the case of self-diffusion on Pt(001) may be more subtle and related to the mechanism used to explain the different diffusion modes for Pt and Pd on Pt(001) [11]. It has been shown that, whereas Pt adatoms on the Pt(001) plane diffuse exclusively by exchange displacements, Pd adatoms on the same surface diffuse by ordinary hopping. The difference in the diffusion mode is attributed to a difference in the amount of relaxation of the neighboring substrate atoms induced by the adatom. Embedded atom method calculations indicate that the lateral relaxations induced by a Pt adatom are about 25% greater than those induced by a Pd atom [11]. The adatom-induced lateral relaxations are along [100]-type directions, the same direction adatoms move during exchange displacements. In other words, the relaxations provide an initial push in creating the vacancy for the exchange mechanism. The effect of a positive electric field in inhibiting the exchange process can be envisioned as making the relaxations around a Pt adatom more like those around a Pd adatom, i.e., the field-induced charge transfer lifts the atom off the surface and reduces the lateral relaxations. (This lifting is the precursor to field desorption in which the electric field actually detaches the adatom from the surface.) Consistent with the experimental observations, a negative electric field would then move the adatom closer to the surface, increase the lateral relaxations, and promote the exchange process.

It is clear that the above explanations are only speculative and detailed theoretical treatments will be required to understand field-induced inhibition and promotion of exchange displacements in depth. A comprehensive understanding of how electric fields affect surface diffusion is obviously quite important in view of the practical implications of this study mentioned above, i.e., the ability to control crystal growth processes with an electric field. Although the strengths of the fields used in this study are not typically achievable under standard growth conditions, they are routinely accessible in electrochemical environments, where recent studies [12] have shown that electric fields of magnitudes comparable to those used in this study can induce surface reconstructions. Even in the case of materials growth by more standard methods (vapor deposition, molecular beam epitaxy, etc.), it should be possible to simulate the effect of an electric field with electropositive or electronegative adsorbates. It is well known that small amounts of alkali adsorbates, which induce surface charges comparable to the external fields used in this study, can change the stability of different structures on fcc (011) surfaces [13]. First-principles theoretical calculations [14] provide compelling evidence that the difference in the stability is due to charge-transfer effects from the local fields induced by the adsorbates. The observation that electric fields of about the same magnitude strongly influence both the fundamental nature of surface diffusion processes and the stability of surface structures suggests a possible relationship between the two effects. A more detailed experimental and theoretical investigation of this relationship should be a fruitful area for further study.

The author acknowledges helpful discussions with P. J. Feibelman and J. E. Houston of Sandia National Laboratories. This work was supported by the U.S. Department of Energy under Contract No. DE-AC04-76DP00789.

[1] P. J. Feibelman, Phys. Rev. Lett. **65**, 729 (1990).

[2] G. L. Kellogg and P. J. Feibelman, Phys. Rev. Lett. **64**, 3143 (1990); C. Chen and T. T. Tsong, Phys. Rev. Lett. **64**, 3147 (1990).

[3] D. W. Bassett and P. R. Webber, Surf. Sci. **70**, 520 (1978); J. D. Wrigley and G. Ehrlich, Phys. Rev. Lett. **44**, 661 (1980).

[4] G. L. Kellogg, Surf. Sci. **246**, 31 (1991).

[5] T. T. Tsong, *Atom-Probe Field Ion Microscopy* (Cambridge Univ. Press, Cambridge, 1990), pp. 202–265.

[6] *Atomic-Probe Field Ion Microscopy* (Ref. [5]), p. 39.

[7] S. C. Wang and G. Ehrlich, Surf. Sci. **206**, 451 (1988).

[8] T. T. Tsong and G. L. Kellogg, Phys. Rev. B **12**, 1343 (1975); S. C. Wang and T. T. Tsong, Phys. Rev. B **26**, 6740 (1982).

[9] *Atom-Probe Field Ion Microscopy* (Ref. [5]), pp. 31–71.

[10] P. J. Feibelman (private communication).

[11] G. L. Kellogg, A. F. Wright, and M. S. Daw, J. Vac. Sci. Technol. A **9**,1757 (1991).

[12] X. Gao, A. Hamelin, and M. J. Weaver, Phys. Rev. Lett. **67**, 618 (1991).

[13] B. E. Hayden, K. C. Prince, P. J. Davie, G. Paolucci, and A. M. Bradshaw, Solid State Commun. **48**, 325 (1983); J. W. M. Frenken, R. L. Krans, and J. F. van der Veen, Phys. Rev. Lett. **59**, 2307 (1987).

[14] C. L. Fu and K. M. Ho, Phys. Rev. Lett. **63**, 1617 (1989).