Surface Diffusion Modes for Pt Dimers and Trimers on Pt(001)

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Field-ion-microscope observations and molecular statics calculations using embedded-atom-method potentials have identified the surface diffusion modes for Pt dimers and trimers on Pt(001). Dimers migrate by a series of displacements involving exchange between one of the dimer atoms and a substrate atom and have a lower activation barrier for diffusion than monomers. Trimer diffusion involves both exchange and hopping displacements and has an activation barrier comparable to monomers.

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The diffusion of single atoms and small clusters on atomically smooth single-crystal terraces is a crucial step in the nucleation and growth of metal overlayers on metal surfaces. The fundamental mechanism by which the atoms and clusters undergo individual displacements can have a major impact on the growth process. Recent theoretical [1,2] and experimental [3,4] investigations have established that the dominant mode for self-diffusion on certain fcc (001) surfaces is not the site-to-site hopping process which one would expect intuitively, but a process involving an exchange between the diffusing atom and a substrate surface atom. This process was first predicted theoretically for self-diffusion on Al(001) surfaces [1] and subsequently confirmed experimentally for self-diffusion on the (001) surfaces of Pt (Ref. [3]) and Ir (Ref. [4]). In the case of Pt, field-ion-microscope (FIM) observations [5] showed that the exchange process occurs at temperatures as low as 170 K. More recently, embedded-atom-method calculations have predicted that the exchange-mediated process is energetically favorable for self-diffusion on (001) surfaces of Pd, Pt, Au, and Al (Ref. [2]).

In this paper the diffusion mode for small clusters of atoms (dimers and trimers) is investigated both experimentally and theoretically. The fundamental question we address is whether dimers and trimers of Pt migrate on Pt(001) by the exchange process, by site-to-site hopping, or by some combination of the two. The activation barriers for the individual steps in the diffusion of dimers and trimers are determined and compared with the activation barrier for a single adatom.

The experimental technique used in this investigation was field-ion microscopy [6]. The details relating to sample preparation, surface imaging, and measurements of diffusion parameters can be found in a recent review [6] and publications concerning diffusion of single Pt atoms on Pt(001) (Refs. [3] and [5]). Briefly, the procedure involves taking "snapshots" of a Pt cluster (dimer or trimer) as it migrates across a perfectly smooth and clean surface. The snapshots are recorded at 77 K where the clusters are immobile. The migration is induced by raising the sample temperature during 30-sec time intervals when the imaging electric field is turned off. The series of snapshots are used to determine the mean-square displacement of the diffusing species at a given temperature and also to map out the binding sites visited by the center of mass of the dimer or trimer as it moves across the surface.

Theoretical descriptions of the displacement processes were obtained from molecular statics calculations. The interatomic forces were modeled using the embedded-atom method [7] (EAM), a form of potential that has proven quite successful in describing properties of fcc metals [8]. The Pt potential used here [9] was fitted to the bulk lattice constant, cohesive energy, elastic constants, vacancy energy, and the diatomic bond length and bond energy, exactly as described previously for other metals [9]. This fit predicts single-atom diffusion barriers that agree with FIM experiments to within 0.3 eV for each of five surfaces [2].

The Pt substrate was modeled using eight 50-atom layers with periodic boundary conditions in the two directions parallel to the surface. The top five layers were free to relax. After optimizing each geometry [2,10], the number of normal modes with a negative force constant was verified to be zero for a minimum and one for a saddle point. The barriers for the various displacement mechanisms are shown along with each of the converged geometries in Figs. 1, 2, and 4 for monomer, dimer, and trimer displacements, respectively.

The exchange mechanism for single atoms on fcc (001) surfaces involves the replacement of a substrate surface atom with the adatom in a concerted motion along a [100]-type direction [1,3], as indicated in Fig. 1(a). Experimental confirmation of this unusual displacement process was based primarily on binding-site maps obtained from FIM observations [3,4]. The pattern that results from displacements confined to [100]-type directions is a $c(2\times2)$ square pattern with sides parallel to [100] and [010] directions [3,4]. In contrast, for ordinary hopping over the twofold bridge sites [see Fig. 1(b)] the displacements are along [110]-type directions and the map of accessible binding sites is a (1×1) pattern with sides parallel to [110] and $[1\bar{1}0]$ directions. Binding-site maps for self-diffusion on both Pt(001) and Ir(001) surfaces [3,4] were found to be consistent with the adatom moving exclusively by the exchange mechanism.

In agreement with the experimental observations, the

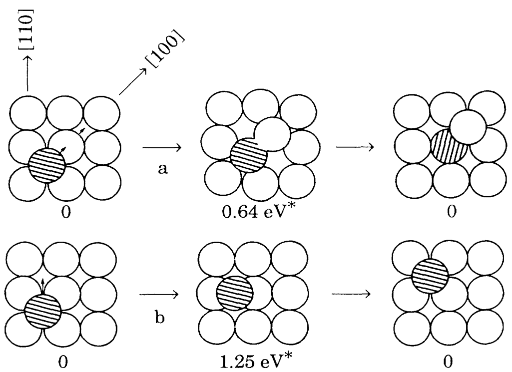

FIG. 1. Surface-normal (top) view of possible mechanisms for migration of a Pt monomer on Pt(001). (a) Exchange mechanism and (b) conventional hopping mechanism. The atom positions are from converged molecular statics calculations with energies listed for each geometry. Asterisks indicate saddle points for the diffusion process.

molecular statics calculations predict that monomer self-diffusion on Pt(001) proceeds by the exchange mechanism (see Fig. 1). Although the calculated barrier (0.64 eV) is high compared to the experimental value [3,5] (0.47 eV), the theory predicts that the exchange barrier is significantly lower than the hopping barrier.

For Pt dimers on Pt(001), FIM observations in the present investigation indicate that diffusion without dissociation takes place at a temperature of 175 K. The mean-square displacement of the center of mass in a 30-sec time interval, corrected for interactions with the plane edge (a reflection boundary), is 7.53×10^{-14} cm^2. During migration at 175 K, the orientation of the dimer changes frequently. In an experiment with 106 diffusion cycles at 175 K, the dimer axis is found to be oriented along the [110] direction 58 times and along the $[1\bar{1}0]$ direction 48 times.

It is surprising that the measured mean-square displacement for a Pt dimer migrating at 175 K is over 50 times greater than that for a single atom migrating at the same temperature [3]. If one assumes that the Arrhenius prefactors (also known as the diffusivity) for single-atom and dimer diffusion are the same [i.e., 1×10^{-3} cm^2 (Ref. [5])], the measured mean-square displacement yields an activation barrier for dimer self-diffusion on Pt(001) of 0.41 eV, which is 0.06 eV less than the single-atom barrier of 0.47 eV. Although dimer diffusion that is faster than the corresponding monomer diffusion has been observed previously in FIM studies of Re on W(112) [11], the diffusion mode was conventional hopping. First-principles calculations also indicate that the dimer barrier is lower than the monomer barrier for self-diffusion on Al(001) surfaces [12], but, again, the migration is assumed to occur via ordinary hopping. Our observation of a lower barrier for dimer diffusion on Pt(001) (where the monomer migrates by exchange) raises the interesting question as to whether this lower barrier occurs as a consequence of an exchange-type mechanism or because the dimer reverts to ordinary hopping and the barrier is reduced by a weakened interaction with the substrate [12].

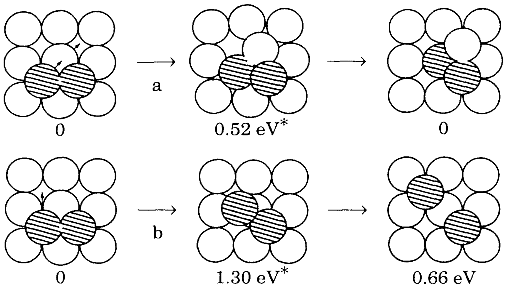

FIG. 2. Possible mechanisms for Pt dimer migration on Pt(001), plotted as in Fig. 1.

Unlike monomer diffusion on fcc (001) surfaces, the diffusion mode for dimers (with two atoms involved in the migration) cannot be inferred from a binding-site map. Both the exchange process indicated in Fig. 2(a) and the conventional hopping mechanism indicated in Fig. 2(b) (with a return to a close-packed dimer) will lead to the same binding-site map. To deduce the diffusion mode for Pt dimers on Pt(001), we consider the calculated energy barriers for the various displacement processes. Displacements involving the simultaneous hop of two dimer atoms are excluded based on high activation barriers (calculated to be > 2 eV). In addition, these types of displacements do not produce the observed changes in axis orientation. The conventional-hop displacement shown in Fig. 2(b) is also excluded based on its activation barrier (1.30 eV). An attempt to find the saddle point for simultaneous exchange of both atoms (to yield a dimer of two fresh atoms) was unsuccessful, but this barrier is also expected to be high. (Again, such displacements do not produce a change in orientation.) The exchange displacement shown in Fig. 2(a) is found to have the lowest calculated barrier by far (0.52 eV) and is the only displacement consistent with the measured value (0.41 eV). In further agreement with experiment, the calculated exchange barrier is seen to be less than the calculated exchange barrier for the monomer. We therefore conclude that the dimer migration takes place exclusively by the exchange mechanism shown in Fig. 2(a). Inspection of Fig. 2(a) shows that the reason for the lower barrier (compared to the monomer) is that the coordination number is higher for the migrating atom. Given that the average bond strength typically decreases with higher coordination number, weaker bonds are broken to form the dimer transition state.

For Pt trimers on Pt(001) FIM observations indicate that diffusion without dissociation can take place up to temperatures of 200 K. The observed configuration is always a chain oriented along either the [110] or $[1\bar{1}0]$ directions. Frequent changes in the orientation of the chain do occur, but the triangular configuration is not observed. This result is consistent with past FIM observations and EAM calculations which have shown that the linear configuration of a Pt trimer is more stable than the triangular configuration [13]. From the measured mean-square displacement of the center atom and the assumption of the standard prefactor mentioned above, the activation barrier for trimer diffusion is found to be 0.49 eV, only slightly larger than the single-atom diffusion barrier.

The map of binding sites for the center atom of the linear cluster is shown in Fig. 3. The map is a (1×1) pattern with sides parallel to [110]-type directions. A detailed analysis of the diffusion data indicates that the center atom makes frequent changes between the two $c(2\times2)$ sublattices during formation of the (1×1) pattern.

Figure 4 shows a number of possible steps which could be involved in the migration of a Pt trimer on Pt(001). Mechanisms involving the simultaneous transition of two or more atoms have been excluded, as they were determined in the dimer calculations to have much higher barriers. The single-atom exchange shown in Fig. 4(a) leads to the metastable triangular configuration which is expected to be an intermediate in the diffusion process. Given the accuracy of the calculations, the energy barrier for this process (0.65 eV) is consistent with the experimental value (0.49 eV). Figure 4(b) shows the reverse transition of Fig. 4(a) leading from the metastable triangular configuration back to the linear configuration. These same transitions could be accomplished via conventional hops, but the calculated barrier for hopping transitions (1.35 eV) is too high for hopping displacements to be considered.

It is obvious that a combination of the two exchange processes shown in Figs. 4(a) and 4(b) can produce a change in the orientation of the trimer, but no motion of its center of mass. If one allows the additional exchange process shown in Fig. 4(c), motion of the center of mass can occur, once the metastable triangle has been formed. The calculated energy barrier for this exchange is also sufficiently low to be consistent with the experimental observations. Thus, the calculations suggest that it is possible to obtain both center-of-mass motion and changes in orientation with only exchange-type processes. However, displacements of the type shown in Fig. 4(c), which lead to center-of-mass motion, are confined to [100]-type directions, exactly like the exchange process with single adatoms. Since displacements of the type shown in Figs. 4(a) and 4(b) do not result in center-of-mass motion, any combination of the displacements shown in Figs. 4(a)-4(c) will lead to a $c(2\times2)$ binding-site map with sides parallel to [100]-type directions, as was the case for a single atom [3]. Even allowing the simultaneous exchange of all three atoms in combination with those in Figs. 4(a)-4(c) results in a $c(2\times2)$ binding-site map. From Fig. 3, it is clear that the map of binding sites is a (1×1) pattern with sides parallel to [110]-type directions.

The observed (1×1) pattern can be achieved if the transformation between triangular trimers shown in Fig. 4(d) (either by exchange or hop) is energetically accessible. A sequence of displacements (a), (d), and (b) will move the center atom of the chain in a [110]-type direction, which is required to produce the (1×1) pattern. However, it is difficult to imagine how a displacement of the type shown in Fig. 4(d) may be involved in the migration of the trimer because it requires either some less obvious exchange mechanism or a conventional hop, which is expected (based on the results for single atoms and dimers) to have a much larger activation barrier than the FIM value of 0.49 eV.

The molecular statics calculations offer an explanation.

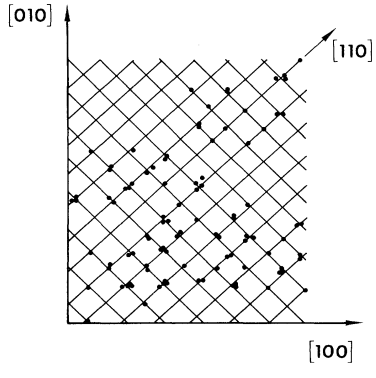

FIG. 3. Site visitation map for the center atom of a linear Pt trimer migrating on Pt(001). The map was compiled from FIM observations following 115 diffusion cycles at 186 and 202 K.

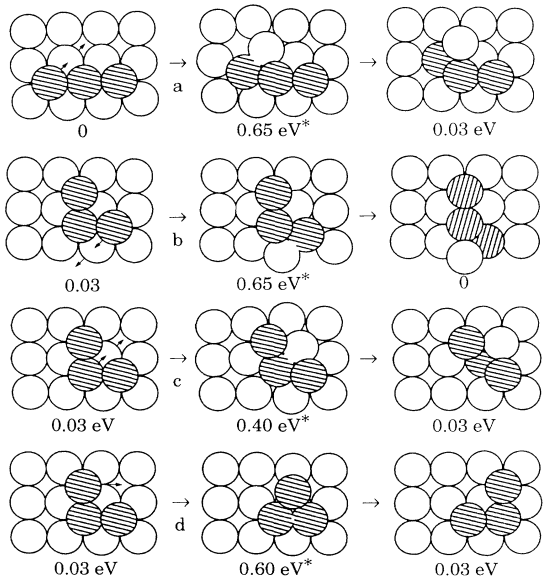

FIG. 4. Possible mechanisms for Pt trimer migration on Pt(001), plotted as in Fig. 1.

Whereas the conventional-hop displacements for the monomer, dimer, and linear trimer all have barriers above 1.2 eV (much higher than the exchange displacements), the transformation of the triangular trimer via the hop mechanism shown in Fig. 4(d) has a dramatically lower barrier (0.60 eV), which is comparable to the exchange-type displacements. Examination of the saddle-point geometry shows that the hopping atom is closer to the other two atoms of the trimer than it would be if it were in the unperturbed (monomer) saddle position. In fact, the hopping atom at the bridge site is fourfold coordinated when the other two atoms of the trimer are present. This higher coordination at the saddle during the trimer transformation results in an energy lowering of more than 0.65 eV. It is of fundamental interest that clusters of at least three atoms are required before hopping-type displacements are energetically accessible in the Pt on Pt(001) system.

In summary, it has been shown that Pt dimers migrate on Pt(001) by a series of displacements involving exchange with Pt substrate atoms and exhibit a slightly lower diffusion barrier than monomers due to higher coordination. Trimers are found to migrate by a combination of steps involving both exchange- and hopping-type displacements. Conventional hopping in the trimer is energetically accessible because of the higher coordination of the hopping atom at the saddle point.

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