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Step-facilitated dissociation of small metal clusters: A molecular-dynamics study

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The motion of small Pt clusters at a step edge on the Pt(111) surface was studied by molecular-dynamics simulations using the corrected effective-medium theory. It was found that interlayer diffusion of the clusters proceeds via dissociation and consecutive single-atom exchanges with the edge atoms, rather than hopping over the edge as a unit. The dissociation and the exchanges occur in a coherent way. We therefore propose that surface defects, like steps or large vacancy pits, may facilitate cluster dissociation via incorporation of the cluster atoms into the edges.

Mass transport of adatoms and adatom clusters, both intralayer and interlayer, plays a crucial role in determining the nucleation and growth properties of metal-on-metal epitaxial growth. Revealing the detailed atomic processes involved in the transport is helpful in understanding the mechanisms responsible for the smooth layer-by-layer growth under various experimental conditions, particularly at low temperatures.[1] Although great efforts have been devoted to this particular subject during the past several years, many fundamental questions related to metal-on-metal growth remain unanswered.[2]

Small metal clusters are mobile on metal surfaces at moderate temperatures.[2,3] There appears to be an increasing recognition that the mobility and dissociation of these clusters must be taken into account in order to characterize correctly the properties of nucleation and growth.[4,5] For the following two reasons, taking these into consideration may become more important when clusters are near step edges. First, the fate of a cluster at a step edge influences the growth mode. In fact, there has been a speculative suggestion that the potential-energy barrier (PEB) for interlayer mass transport may not exist for a cluster as it does for a monomer.[2] If true, a cluster could diffuse easily over the step edge and promote smooth growth. Second, field-ion microscopy (FIM) has been extensively applied to study the diffusion of adatom and small adatom clusters. Often in a FIM experiment clusters were found to disappear from terraces at relatively high temperatures.[6,7] An important question is the mechanism by which the clusters disappear. More specifically, one would like to know if the clusters dissociate first into single adatoms, which subsequently step down to a lower surface layer, or if the clusters diffuse over the edge as a coherent group. In their experimental study of Pd/Ta(110),[7] Schwoebel and Kellogg have claimed that small Pd clusters, *as a unit*, diffused over the step edges. However, experimental work on this is very limited, presumably due to technical difficulties imaging both the step edge and the clusters simultaneously.

To our knowledge, a theoretical study of clusters *at step edges* has not been done. Molecular-dynamics (MD) simulation has been proven to be a useful tool that in many cases provides detailed atomic information complementary to experimental results. In this paper, MD simulations were carried out to treat the motion of small Pt clusters at a step on the Pt(111) surface. This system has shown rich variation in growth mode (e.g., the reentrant growth[1(a)]) and a recent study has suggested that small Pt clusters are highly mobile on the Pt(111) surface.[8] From the present study, it will be seen that the motion of these clusters at step edges is more interesting and complicated than was suggested in Ref 7. Also, it will become clear that incorporation into step edges may provide an efficient mechanism for cluster dissociation.

We used the corrected effective-medium (CEM) theory[9] in its simplest framework, the MD/MC-CEM method,[10] which was developed particularly for molecular-dynamics and Monte Carlo calculations of large systems. The interaction energy of a system containing N atoms is given by

$$\Delta E(\{A_i\})=\sum_{i=1}^{N} \Delta F_{EXLM}(A_i;n_i)+\tfrac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N} V_c(i,j), \qquad (1)$$

where n_i is the "jellium" electron density surrounding atom A_i and $\Delta F_{EXLM}(A_i;n_i)$ is the "effective" embedding function for atom A_i. $V_c(i,j)$ is the Coulomb interaction between atoms A_i and A_j. This non-self-consistent density-functional theory incorporates some many-body effects appearing in metal systems, but requires less than twice the computational demands of a pairwise-potential model. During the past several years, the MD/MC-CEM theory has been applied extensively to the study of metal surfaces and clusters.[11] In general, this theory provides a reasonable description of the many-atom system.[10] For the Pt/Pt(111) system considered here, the theory gives a diffusion barrier for bridge hopping of 0.08 eV,[12] which is lower than the experimental value of 0.25 eV.[13] However, since we discuss in the present paper the relative barriers of different mechanisms for the motion of Pt clusters at step edges, we expect that the trend predicted by the present theory should be reliable. Experimental validation would be desirable.

The Pt system was modeled by six fcc(111) atomic layers. All atoms are allowed to move except those in the lowest two layers, which were fixed to mimic the infinite bulk lattice template. Each square-shaped layer is 17 atoms long on a side. Periodic boundary conditions were applied in the two directions parallel to the surface. A step of monolayer depth was produced by removing all atoms in one half of the top layer. The resulting system is shown in Fig. 1 and contains

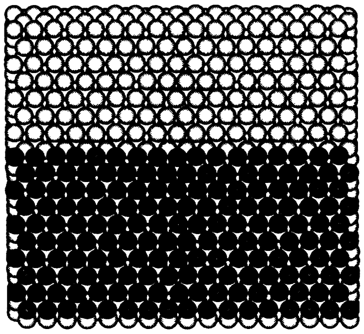

FIG. 1. A top view of the model system used.

about 1700 atoms in total. The step shown in Fig. 1 is the one where the PEB for interlayer mass transport was found to be the lowest for monomers (0.05 eV).[14]

Prior to MD simulations, values for the PEB of interested processes were obtained by performing minimum-energy-path calculations[15] and they were used later for comparison with MD results. In MD simulations, small Pt clusters, ranging from dimer to heptamer and to decamer, were initially placed at the descending step edge. The system was first thermalized at a desired temperature for a few picoseconds and then the trajectories of adatoms were followed. In the following we will describe our results briefly, with those obtained for dimers being emphasized. A more detailed presentation may be found in a forthcoming paper.[12]

We start with a dimer on a flat Pt(111) terrace since theoretical and experimental data are available for comparison. In our model, a Pt dimer occupies two nearest-neighbor fcc hollow sites of threefold symmetry. The energy barrier for dimer dissociation, $\mathrm{Pt}_2(a) \rightarrow \mathrm{Pt}(a) + \mathrm{Pt}(a)$, is 0.71 eV and exceeds 1.0 eV for larger clusters, $\mathrm{Pt}_n(a) \rightarrow \mathrm{Pt}_{n-1}(a) + \mathrm{Pt}(a)$, where a indicates an adsorbate. Therefore, dissociation of Pt clusters is very unlikely if the temperature is not too high. In our extensive MD simulations of dimer diffusion on terraces at 600 and 900 K, we never observed a single example of thermally activated dimer dissociation. These clusters, however, dissociate much more easily at step edges, as will become clear later.

For dimer diffusion on terraces, our model predicted correctly the two distinctive classes of motion: a fast so-called intracell motion and a slow intercell motion.[3] This difference was noted by Wang and Ehrlich in their FIM study of Ir_2/Ir(111) (Ref. 3) and has led them to propose that dimer diffusion occurs by two jumps of individual atoms, during which the dimer "bond" is stretched and hence leads to a large barrier for intercell motion. The PEB from our model is 0.12 eV for the intercell motion but only 0.03 eV for the intracell one. However, neither the minimum-energy path nor the MD simulations showed evidence for the bond stretching, contrary to the experimental proposal and in favor of the theoretical studies of the effective-medium theory[8] and the embedded-atom method approach.[16] The former work,[8] however, did not predict any difference between the intracell and intercell motion. We think that the stretching bond picture may not be appropriate to explain the large barrier for intercell motion. More detailed discussion of this will be given elsewhere.[12]

The self-diffusion coefficient for a dimer D_s can be obtained from the long-time behavior of the mean-squared displacement evaluated directly from the MD trajectories. The D_s values obtained at various temperatures yielded a dynamical barrier (the activation energy) of about 0.16 eV.[12] This number is considerably larger than the PEB for intercell motion, 0.12 eV, because the substrate nuclei do not follow the motion of the adsorbate dimer adiabatically. (This should not be confused with electronic nonadiabaticity.) This conclusion results from a detailed investigation of the trajectories for the dimer center-of-mass motion, which will be presented in Ref. 12.

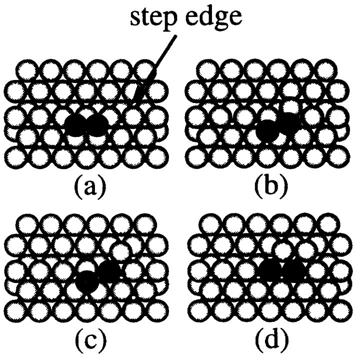

FIG. 2. A sequence of geometries along the minimum-energy path for Pt_2 interlayer diffusion: initial (a); two intermediate (b)-(c); final (d). A top view of a small part of the first two layers is shown.

At step edges, the motion of small Pt clusters is more complicated and their fate is very diverse. First, we calculated the PEB for a dimer diffusing along, away from, and over a descending step, again by finding the minimum-energy path for each process. The values are 0.11 eV for diffusing along (i.e., parallel to) the step edge and 0.10 eV for diffusing away from (i.e., perpendicular to) the edge. By comparison to the corresponding PEB of 0.12 eV for dimer diffusion on a terrace, we can state that dimers are not only unlikely to be trapped at the step but that diffusion away from the step may be faster than diffusion to the step. In addition, we found a very high barrier of 1.47 eV for a dimer to hop directly over the edge as a unit.

It is well known that the interlayer diffusion of a monomer at a step edge may occur via the so-called displacement-exchange mechanism.[17] Such a mechanism was also examined here for dimers. We found that the PEB for dimer exchange, as a unit, with two adjacent edge atoms is still high. However, our calculation suggested a minimum-energy path by which the exchange proceeds via essentially two single-atom exchanges. A sequence of geometries along the path is shown in Fig. 2. The corresponding PEB is much reduced, resulting in the value of 0.18 eV. It is surprising that this one-by-one exchange has the lowest barrier, in view of the fact that the dimer bond is broken during this process (i.e., dissociation of the original dimer is involved).

Our dynamical simulations were consistent with the above adiabatic responding surface picture but showed much richer variations. We simulated 100 independent trajectories, each starting by placing a dimer at the step edge. Different random number seeds were used in the simulations, giving different initial configurations of the system. It would have

TABLE I. Classification of the 100 MD trajectories according to the dimer locations at the end of each trajectory. The number in parentheses is the PEB from minimum-energy-path calculations for the corresponding process.

Incorporates onto lower layer 29 trajectories			Remains on upper layer 71 trajectories		
Single exchange	Double exchange	Multiple exchange	Diffuse along step	Diffuse away from step	Remain at initial site
16	10	3	17	51	3
(0.18 eV)	(0.18 eV)		(0.11 eV)	(0.10 eV)	

been most desirable to perform the simulations at room temperature, around which many interesting phenomena have been observed in homoepitaxial metal growth.[1] Such a temperature, however, would not be very feasible for simulations of a large number of trajectories, given the PEB of 0.18 eV, which implies that interlayer diffusion of dimers happens on a nanosecond scale at room temperature. Instead of running for nanoseconds, we have chosen to use a higher temperature (600 K) and run each trajectory for a shorter period (50 ps). We expect that the qualitative features discussed here will persist at lower temperatures.

The trajectories were grouped into two sets according to the dimer location at the end of the simulations: those incorporating into the step edge and those staying on the upper terrace. It was found that there were 29 and 71 trajectories in the two groups, respectively (Table I). The ratio of these two numbers, 0.41, is significantly larger than what could be estimated from transition-state theory, $\exp\{-(0.18-0.12)\ \mathrm{eV}/(k_B\ 600\ \mathrm{K})\}\sim 0.31$. This is because the PEB value of 0.12 eV underestimated the dynamical barrier.[14] Among those 71 trajectories staying on the upper terrace, 17 diffused along the step edge, 51 diffused away from the edge, and 3 stayed at the edge, displaying only intracell motion (translational and rotational motion within the same hexagonal cell).[12]

Incorporation of dimers onto the lower layer (i.e., the remaining 29 trajectories) occurs only via the displacement-exchange mechanism. The exchange process is complicated. We observed single-, double-, and multiple-atom exchanges in 16, 10, and 3 trajectories, respectively (Table I). In a single-atom exchange, one of the dimer atoms displaces an edge atom, leaving the other on the upper terrace where it eventually diffuses away from the step. The original dimers were dissociated in this process. One example of the final geometry is shown in Fig. 3(a). In a double-atom exchange, both dimer atoms incorporate into the step edge but sequentially. The time separation between the two exchanges varies from 0.5 to over 10 ps. The spatial separation between the atomic sites where the two exchanges occur varies as well. The two consecutive exchanges may happen at a same atomic site at the edge [Fig. 3(b)], or at two nearest-neighbor sites [Fig. 3(c)], or at two sites separated from each other [Fig. 3(d)]. In a multiple-atom-exchange process, two dimer atoms incorporate into the step edge but *more than two* edge atoms are involved in the displacement. As an example of this process, a sequence of points along a MD trajectory is shown in Fig. 4. Such a multiple-atom exchange was also observed in a MD study of deposition process,[11(b)] but there it was induced by adatom adsorption.

Clusters with 3–7 atoms and a 10-atom cluster at the step edge were also studied. For each size, ten trajectories were monitored for 50 ps each. Since we expect the PEB to be larger than that for a dimer, we performed the simulations at 900 K for these larger clusters. We found these to be similar to dimers described in the foregoing paragraphs: clusters incorporate into step edges through dissociation and exchanges of individual adatoms with the edge atoms. This was mostly seen for clusters up to six atoms. Within the time period of the simulations, we observed only one exchange event for the 7-atom cluster and none for the 10-atom cluster. This is most likely due to the two-dimensional (2D) cluster structure we chose, a compact hexagon, in which each atom has at least three cluster atoms as its nearest neighbors. Such a cluster is particularly stable.[14]

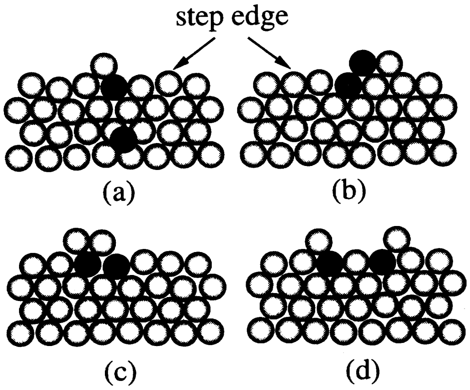

FIG. 3. Final geometries of single- (a) and double- (b)–(d) atom-exchange processes, taken from MD simulations. A top view of a small part of the first layer is shown.

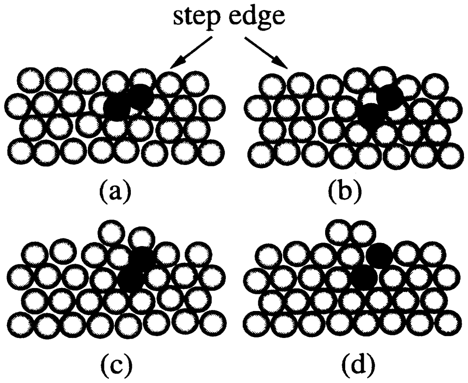

FIG. 4. Same as Fig. 2 except for a MD trajectory showing multiple-atom exchanges. A top view of a small part of the first layer is shown.

A key observation here is that interlayer diffusion of small 2D clusters proceeds via dissociation, as symbolized by $\mathrm{Pt}_n(a) \rightarrow \mathrm{Pt}_{n-1}(a) + \mathrm{Pt}(a)$. This contrasts, though for different systems, with the experimental suggestion that small clusters may diffuse over a step edge *as a unit.*[7] However, this suggestion was based on the fact that the clusters were stable on a flat terrace at relatively high temperatures.[7] This does not necessarily guarantee that they are also stable near step edges, particularly in recognition of the following important difference. On a flat terrace, dissociation of a cluster reduces the number of nearest-neighbor metal bonds. This will be energetically very costly. At a step edge, on the other hand, the reduction in the number of bonds may be compensated by creation of new bonds via incorporation of the cluster atoms into the edge. This is precisely what we have seen in MD simulations, where dissociation and the exchange process occur in a coherent way. We therefore propose that surface steps may facilitate cluster dissociation, which would be otherwise very difficult on a perfect terrace.

In summary, there exists a potential energy barrier for interlayer mass transport for clusters, which is actually much larger than that for monomers. Therefore, cluster interlayer diffusion is not expected to make significant contribution to the layer-by-layer growth at low temperatures. The incorporation of clusters into step edges is a quite complicated process and proceeds via dissociation and exchanges of single adatom with the edge atoms, rather than diffusing over the edge as a unit. We propose that surface defects, such as steps or large vacancy pits, may facilitate cluster dissociation via the interlayer-exchange mechanism.

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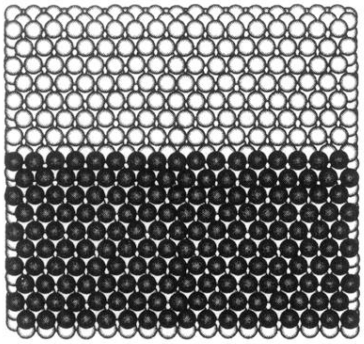

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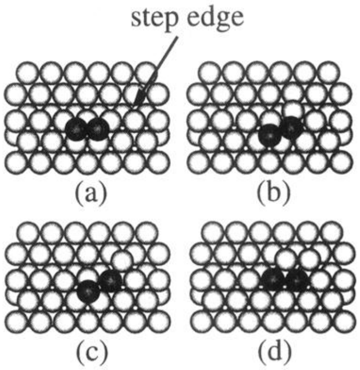

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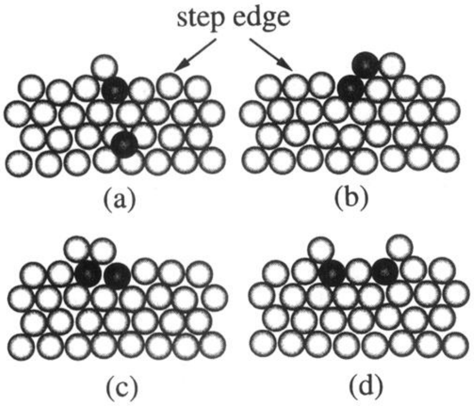

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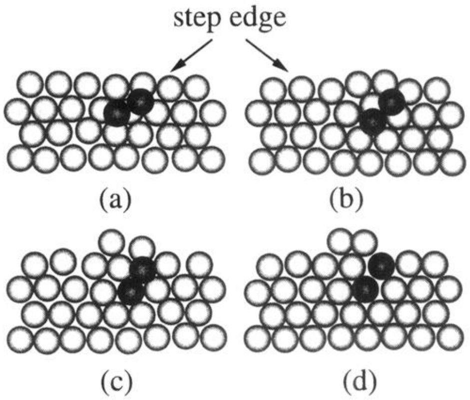

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