

Dimer Shearing as a Novel Mechanism for Cluster Diffusion and Dissociation on Metal (100) Surfaces

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Using bond-counting arguments and embedded-atom calculations, we establish the crucial importance of dimer shearing in metal (100) submonolayer epitaxy. This process provides the easiest pathway for diffusion of compact clusters of sizes 4, 6, and 8, and introduces a rich variety of localized cluster dynamics. A combination of the dimer shear motion and the traditional mechanism of sequential motion of individual atoms provides a better interpretation of the oscillatory behavior of cluster mobility with cluster size. This combination also defines a new set of critical cluster sizes that are likely to be selected in epitaxial growth. [S0031-9007(96)00442-5]

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Many recent studies have been aimed at providing microscopic mechanisms of crystal growth, whose nonequilibrium nature is usually characterized by growth kinetics. The phrase growth kinetics encompasses all atomic processes taking place during growth. Examples include adatom diffusion on terraces and over steps, as well as nucleation, aggregation, migration, and dissociation of unstable and/or stable clusters. These are among the elemental and crucially important rate processes determining the growth mode of a given system. Of particular note is metal-on-metal systems. In such systems, recent studies have shown that even very large clusters can have significant mobility at moderate temperatures [1–3]. Smaller clusters are expected to move even faster; therefore their mobility could play a more important role in influencing the growth characteristics of such systems.

The focus of this work is on the migration and dissociation of relatively small metal clusters on metal (100) surfaces. We notice that essentially all microscopic models developed in extensive previous studies of cluster diffusion and dissociation in metal (100) epitaxy have been based on the central assumption that cluster dynamics results from sequential motion of *individual* adatoms [4–13]. Here we show that this prevailing assumption is in fact incorrect or at least incomplete in many cases. Specifically, we use simple bond-counting arguments and detailed quantitative calculations to establish the importance of a collective atomic process, *shear motion of a dimer* belonging to a compact cluster. This previously overlooked process turns out to provide the most effective pathway for diffusion and dissociation of some clusters, as shown on several fcc (100) surfaces. Besides diffusion and dissociation, this process also introduces a rich variety of localized cluster dynamics. A combination of the dimer shear motion and the traditional mechanism of sequential motion of individual atoms provides a better interpretation of the oscillatory behavior of cluster mobility with cluster size. This combination also defines a new set of critical cluster sizes that are likely to be selected in epitaxial growth.

We first present a qualitative description of the dimer shear motion, and the corresponding bond-counting arguments favoring this process. In the traditional mechanism of sequential motion of individual atoms, diffusion of a compact tetramer shown in Fig. 1(a) must be initiated by first placing atom 1 one step ahead, involving the breakage of *two* nearest-neighbor (nn) bonds [see Fig. 1(b)]. The activation energy E_{2b} for this process is relatively high. After this rate-limiting step, if the rest of the cluster follows the motion of atom 1, then the event leads to diffusion of the tetramer. Alternatively, we should expect the process from Figs. 1(c) and 1(d), induced by a shear motion of the two dimers that constitute the tetramer, to be considerably easier than that from Figs. 1(a) to 1(b), because in reaching Fig. 1(d) only *one net* nn bond needs to be broken. The activation barrier E_s for this collective process can be significantly lower than E_{2b} if the bond switching (breaking of the 2-3 bond and reforming of the 2-4 bond) happens simultaneously near or right at the transition state. Similarly, dimer shearing could be an important process contributing to the diffusion and dissociation of any other cluster which has a lone dimer along its edge.

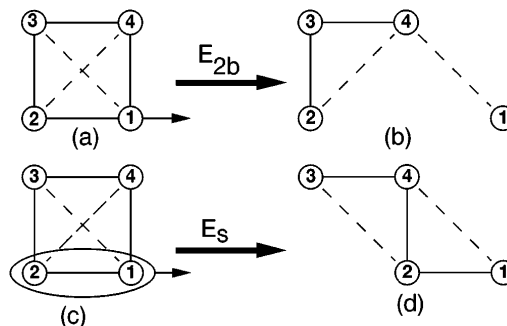


FIG. 1. A comparison of two competing mechanisms leading to the diffusion or diffusion of a tetramer (a),(b) by double bond scission: (c),(d) by a shear motion of a dimer. The solid and dashed lines represent nearest-neighbor and next-nearest-neighbor bonds, respectively.

In order to confirm this expectation quantitatively, first-principle calculations [14] should be preferred in principle, but in practice are severely limited by computing power, particularly when diffusion of *sizable* clusters on *nonsimple* metal surfaces is concerned. Alternatively, we employ the embedded-atom method (EAM) [15], which provides a simple yet reasonable potential that allows exploration of various complicated cluster diffusion mechanisms on fcc (100) metal surfaces. In these calculations, the substrate is typically modeled by a slab of 12 layers with 128 atoms per layer. Atoms in the bottom three layers are fixed at their respective bulk positions, while atoms in the top nine layers plus those in the ad-cluster are free to move. Periodic boundary conditions are applied in the plane parallel to the surface. The potential energy surface along a given reaction path is mapped out by the standard approach: Increase the coordinate of the diffusing atom along the reaction path, then at each fixed increment of this coordinate fully relax all the other coordinates of the active atoms. When a diffusion process involves the shearing of a dimer, the coordinates of both atoms of the dimer are increased along the direction of motion, but only one of them is fixed in the relaxation step, allowing a free adjustment of the dimer bond length [16].

The results of activation energies for self-diffusion of compact clusters of sizes $i \leq 10$ on the (100) surface of Cu, Ag, and Ni are summarized in Table 2. We first call attention to the cases of $i = 4, 6,$ and 8 . For those compact clusters that have no single periphery atom, dimer shear motion is always an effective process to initiate cluster diffusion, consistently more favorable than the traditional mechanism of sequential motion of individual atoms. The difference in the activation energies, $E_{2b} - E_s$, is on the order of 0.1–0.15 eV for all the cases. Notice that the dimer shear motion defined here not only provides an easier pathway, its participation in cluster diffusion also significantly reduces the number of intermediate steps needed for a net displacement of a given cluster. One self-explanatory example is shown in Fig. 2. In Fig. 2(a), the diffusion of a compact Cu tetramer on Cu(100) is initiated by the shear motion of a dimer, followed by the shear motion of the remaining dimer. The whole displacement takes only two steps to complete. In contrast, the traditional pic-

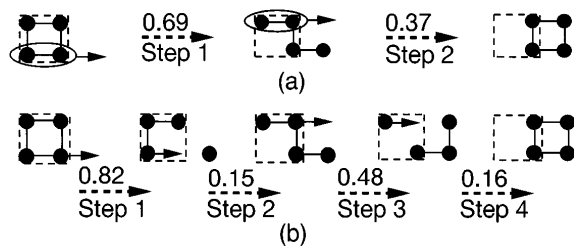


FIG. 2. Diffusion pathways for a tetramer (a) via dimer shearing and (b) via sequential motion of individual atoms. The dashed squares mark the original place of the tetramer. All the activation energies are in eV.

TABLE I. Atomic processes and the corresponding activation barriers (in eV) leading to the diffusion and/or dissociation of homoepitaxial clusters on the (100) surface of three fcc metals.

Cluster Geometry	Cu (100)	Ag (100)	Ni (100)
	0.503	0.478	0.632
	0.494	0.480	0.611
	0.501, 0.552	0.491, 0.503	0.621, 0.673
	0.688, 0.815	0.637, 0.723	0.842, 0.989
	0.551	0.510	0.675
	0.713, 0.835	0.658, 0.737	0.870, 1.008
	0.552	0.512	0.677
	0.758, 0.838	0.676, 0.740	0.918, 1.011
	0.857, 0.975	0.763, 0.903	1.051, 1.215
	0.554	0.516	0.678

ture shown in Fig. 2(b) based on sequential motion of single atoms [4] would require four steps for the same displacement. Clearly, the process shown in Fig. 2(a) will dominate the diffusion of the tetramer. This type of diffusion process is certainly also valid for compact clusters of sizes 6 and 8.

For clusters of sizes 5, 7, and 10 that have a single periphery atom outside a compact core, the traditional picture of cluster diffusion still applies. Namely, in order to induce a *net* displacement of the whole cluster, the easiest pathway is to place the periphery atom one step ahead via single bond scission, as shown in Table I. This traditional picture is also preserved for the more compact 3×3 cluster, because sliding of either a dimer or a collinear trimer out of this cluster is energetically more costly than simple placing a corner atom one step ahead via double bond scission.

Summarizing the results obtained so far, we obtain a natural oscillatory behavior of the activation energy in the *rate-limiting* step of cluster diffusion with cluster size, as shown in Fig. 3. The oscillation magnitude in the range of $3 \leq i \leq 8$ is on the order of $E_s - E_b$, or about 0.15–0.20 eV, where E_b is the typical energy for single bond scission. This oscillation magnitude is considerably lower than the value of $E_{2b} - E_b$ defined in previous theoretical studies [4–6]. Note also that the activation energy for dimer diffusion is lower than that for monomer diffusion; the physical origin has been discussed some time ago [14].

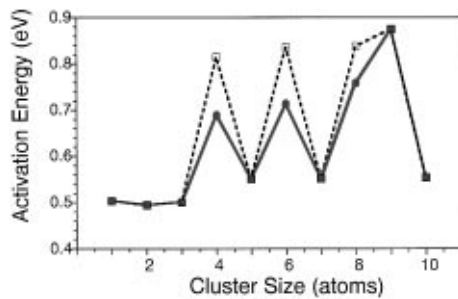


FIG. 3. A plot of the rate-limiting activation energy of surface diffusion for Cu clusters on Cu(100). The solid curve corresponds to the case where dimer shearing is active, where the dashed curve is obtained with the restriction of sequential motion of individual atoms.

The oscillatory behavior will most likely be washed out for very large clusters [1–4], but for small clusters it should be observable, as shown recently by Kellogg in an elegant experiment of cluster self-diffusion on Rh(100) [7]. Kellogg estimated the *effective* barrier for diffusion of a given cluster by following the displacement of the whole cluster as a function of time at a given temperature, and by assuming a common prefactor of 10^{12} hop attempts per second for all clusters of different sizes. The results were plotted in his Fig. 2. Strictly speaking, one cannot make a direct quantitative comparison between Fig. 3 of this work and Fig. 2 of Ref. [7], because of the differences in the elements and in the quantities plotted. Nevertheless, we do notice that the experimentally observed oscillation magnitude of about 0.1 eV is certainly much closer to $E_s - E_b$ than to $E_{2b} - E_b$.

Besides diffusion and dissociation, consideration of dimer shear motion also introduces interesting localized dynamics into some clusters. Two examples are shown in Figs. 4 and 5, both for the case of Cu. Figure 4 displays the reflection of a periphery atom located on one side of 2×3 compact core to the other side, included by only two steps of inner-cluster dimer shearing. The highest activation energy involved is only 0.45 eV. This barrier is much lower than the barrier of 0.75 eV to slide a dimer out of the cluster, and is also lower than the barrier of 0.52 eV for splitting the dimer. Notice that the intermediate configuration shown in Fig. 4(b), in which every atom is able to have at least two nearest neighbors, also happens to be the most stable configuration of all possible clusters of size 7. Figure 5 displays the rotational motion of a “corner vacancy” among the four corner sites of a compact octamer (a 3×3 cluster with one corner atom missing), again induced by inner-cluster dimer shearing.

Because the activation barrier for inner-cluster dimer shearing is typically lower than the rate-limiting activation barrier for net displacement of a cluster, the localized cluster dynamics as described above should be observed at a temperature below the onset of cluster diffusion. While

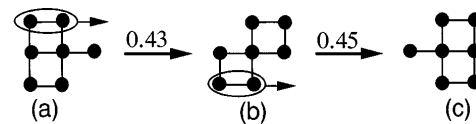


FIG. 4. Localized cluster dynamics: a periphery atom is effectively reflected from one side of the 2×3 core to the other side by two steps of dimer shearing.

the reflection of a periphery atom as shown in Fig. 4 is still to be verified experimentally, the rotation of a corner vacancy identical to those shown in Fig. 5 has actually been observed in Kellogg’s field ion microscopy studies of the localized dynamics of a Rh octamer on Rh(100) [7]. Furthermore, the rotation was indeed observed at a temperature lower than what was needed to activate net displacement of the octamer, though at that time the possible contribution of dimer shearing in inducing such rotational motion was not recognized [7].

The internal cluster dynamics shown in Figs. 4 and 5 can be viewed as being induced by dimer shearing along a short step. We expect dimer shearing to be a favorable process along a true step edge as well, as confirmed by our calculations on the (100) surface of Cu, Ag, and Ni. In particular, for every element, the energy barrier of dimer shearing along the ledge is always lower than the energy barrier to split the dimer at the ledge. Furthermore, the barrier for dimer shearing along the edge is expectedly higher than the barrier for single adatom diffusion along the edge, but is still lower than the barrier for adatom diffusion on a terrace. These conclusions qualitatively agree with the results of a recent study of Rh adatom and dimer diffusion on a stepped Rh(100) surface [17].

We finally examine the role of dimer shearing in defining the sequence of clusters that is kinetically stable against atom detachment as one increases the surface temperature. We present our discussion in a hypothetical experiment. First, we prepare a surface filled with a

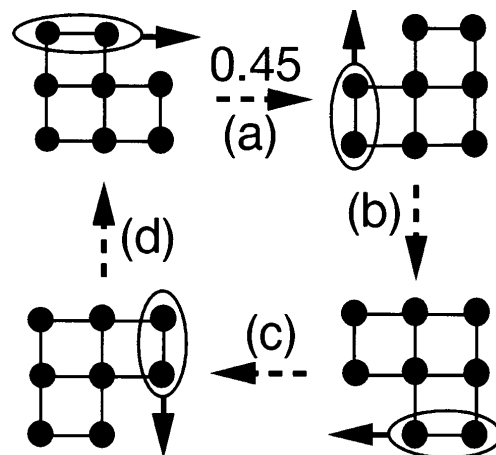


FIG. 5. Localized cluster dynamics: a corner vacancy is rotated among four corner sites, each time as a result of dimer shearing.

collection of clusters of varying size, predominantly in their most compact configurations. Then we increase the substrate temperature to several specific values, each time for the same duration. When the surface temperature is sufficiently low, a dimer formed on the surface is stable, as are all larger clusters. Therefore, the minimum size of the kinetically stable cluster is $i_{s,\min} = 2$. If the temperature is increased to the regime where single atom detachment is active but not dimer shearing, then only compact clusters without an extra atom at the periphery are stable. In this case $i_{s,\min} = 4$. If the temperature is further increased to the regime where dimer shearing is active but not double-bond scission, then only clusters with compact 3×3 structure are stable, because once a dimer shears out of a compact cluster of size 4, 6, or 8, atom detachment by single bond scission can take place. In this case, $i_{s,\min} = 9$, and most of the surviving clusters are at least three atoms wide. Finally, when the temperature is high enough to make double-bond scission an efficient process, then clusters of all sizes can be dissociated. In this regime, either one large cluster will be formed on an ideally flat surface, or, more realistically, all the clusters will join pre-existing steps.

In contrast, within the traditional picture of sequential motion of individual atoms, only two possible sizes are special: 2 and 4 [8–10,13]. If no bond can be broken, then a dimer is the smallest kinetically stable cluster; if only single-bond scission is active but not double-bond scission, then a compact tetramer is the smallest cluster. Once double-bond scission becomes active, no cluster is kinetically stable against dissociation. In particular, the regime $i_{s,\min} = 9$ is simply not allowed [13].

Extensive recent studies have dealt with the spatial and size distribution of clusters formed under various submonolayer growth conditions [8–13]. The focus has been mainly on uncovering the various scaling laws satisfied by the clusters. In defining such scaling laws, one central concept is the critical cluster size i_c , defined by $i_c = i_{s,\min} - 1$. For metal (100) epitaxial growth systems, previous discussions have been primarily restricted to the possibilities of selecting $i_c = 1$ or 3. Clearly, the inclusion of dimer shear motion will significantly increase the mobility of the clusters in the sizes between 4 and 8. Furthermore, dimer shearing also significantly reduces the kinetic stability of a compact tetramer against atom detachment, while it renders extra kinetic stability to a 3×3 cluster. Can the enhanced mobility of such sizable clusters introduce detectable modifications to the scaling laws? Can the possibility of the critical size $i_c = 8$ be realized in a real growth system? While further theoretical and experimental studies are called to possibly answer the first question, one recent experiment on Cu(100) submonolayer homoepitaxy [18] has already provided confirmative support to the second question.

In summary, we have established a simple yet crucially important atomic process, shear motion of a dimer belong-

ing to a compact cluster for cluster diffusion and cluster dissociation in metal (100) submonolayer epitaxy. Consideration of this process necessitates the reevaluation of many important dynamical processes in such systems. It provides the easiest diffusion pathway for some compact clusters, interprets better the oscillatory behavior of cluster mobility with cluster size, introduces a rich variety of localized cluster dynamics, and defines a new set of possible critical-sized clusters.

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Note added.—After the initial submission of this Letter we were informed that evidence for the existence of $i_c = 8$ has also been observed in Ni/Cu(100) submonolayer epitaxy [19].

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