# Dislocation Mechanism for Island Diffusion on fcc (111) Surfaces

J. C. Hamilton, M. S. Daw,[*] and S. M. Foiles

*Sandia National Laboratory, Livermore, California 94550*

We describe a novel mechanism for diffusion of homoepitaxial 2D islands on fcc (111) surfaces by nucleation and motion of misfit dislocations. Embedded atom method molecular dynamics calculations show that this mechanism will compare favorably with edge running and simultaneous gliding for islands up to some tens of atoms in size. We suggest that this mechanism may facilitate diffusion of heteroexpitaxial strained overlayer islands containing dislocations in their lowest energy configurations.

The growth of thin films on surfaces occurs via deposition of adatoms or sputter deposition of clusters which coalesce forming islands and eventually films. The surface diffusion of single atoms and of islands is critical in thin film growth, since the kinetics of diffusion and the stability of various clusters determine the size and shape of the nucleating islands which grow into a film [1–5]. The diffusion of islands on surfaces can be observed using surface imaging techniques such as field ion microscopy (FIM), scanning tunneling microscopy (STM), and low energy electron microscopy (LEEM). Typically the islands can be imaged at intervals and changes in position or shape determined. However, it is difficult to image transition states because they are short lived. Thus the mechanism of island diffusion is typically inferred from indirect evidence such as the dependence of diffusion rate on island size or the changes in island shape associated with diffusion. Theoretical calculations such as the molecular dynamics calculations presented here allow short-lived transition states to be determined in a more direct way, albeit within the limitations of the potentials used to describe the atomic interactions.

Island diffusion on surfaces has been studied experimentally [6–9] and theoretically [10–14]. FIM is a relatively mature experimental technique commonly used to study island diffusion on surfaces. FIM allows "snapshots" of cluster configurations to be obtained before and after diffusion occurs. A major study of Ir diffusion on the fcc Ir(111) surface has been published by Wang and Ehrlich [6]. This study shows the atomic configurations of 2 to 13 atom clusters and proposed diffusion mechanisms which may be compared to the configurations and mechanisms observed in the present theoretical study. The generally accepted mechanism for diffusion of islands with more than a few atoms is an "edge running" of atoms around the island perimeter [13]. Evaporation and condensation of single atoms between the islands and a surrounding two dimensional gas has also been suggested to explain experimental observations [9]. Since the activation energy for moving an atom along the island perimeter should be smaller than that required to remove a single adatom from the island to an isolated site on the surface, edge running is considered the more likely mechanism in most cases.

The diffusion mechanisms discussed above involve jumps of single adatoms. In this Letter we consider island diffusion by collective mechanisms involving nearly simultaneous translation of atoms in the island. In particular, we describe a dislocation mechanism for diffusion of moderate-sized islands ($\sim$4 to 50 atoms) on fcc (111) surfaces. This mechanism involves simultaneous motion of a portion of the island from fcc to hcp sites creating a stacking fault for part of the island. The fcc and hcp sections of the island are separated by a misfit dislocation which runs from one side of the island to the other. This misfit dislocation can then move across the island as additional atoms shift from fcc to hcp sites. As a result of the nucleation and motion of the dislocation, all of the island atoms shift from fcc to hcp sites. (A similar process can then occur, translating the island atoms from hcp to fcc sites). The net result of these processes is island diffusion.

In our study of island diffusion we employed the embedded atom method (EAM) [15], which provides a simple potential allowing modeling of complex cooperative phenomena in metals. We performed EAM calculations demonstrating the dislocation mechanism for the diffusion of Ni islands on Ni(111), with island sizes ranging from 4 to 47 atoms. Two different sets of EAM potentials were used [16,17]. The qualitative results are similar for both potentials. The quantitative results presented here were calculated using the Voter-Chen potentials which yield bulk stacking fault energies in better agreement with experiment than do the Foiles-Baskes-Daw potentials. These runs were part of a larger study where we examined the diffusion of islands ranging from monomers to 47 atoms. The molecular dynamics calculations at temperatures from 400 to 1200 K ranged in length from 400 to 3000 psec. By use of a "movie" presentation of the results of the molecular dynamics runs, it was possible to identify a number of common jump mechanisms. The energies of transition states were then computed using EAM total energy calculations at 0 K to determine the barriers associated with various jump mechanisms.

Quadrimer diffusion exhibits several features indicative of the diffusion mechanisms observed for larger clusters. Figure 1 shows the most common mechanisms observed
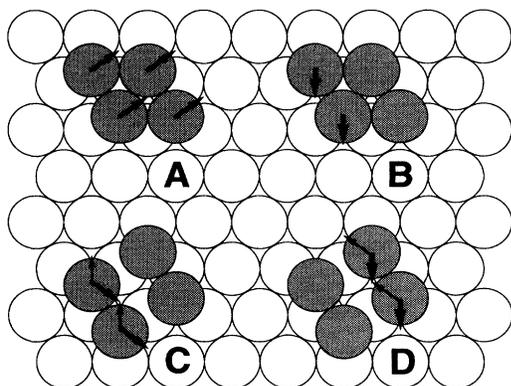
0031-9007/95/74(14)/2760(4)$06.00

FIG. 1. Mechanisms of diffusion for nickel quadrimer on Ni(111). In A a gliding mechanism is shown. The four nickel atoms move nearly simultaneously through the bridge sites in a parallel direction. In B and D a dislocation mechanism is shown. In B two of the atoms move nearly simultaneously through the bridge sites to produce an island with a dislocation C or D. There are four ways to relax the dislocation as shown by the four pairs of arrows in C and D.

TABLE I. Calculated activation energies for processes allowing diffusion of $Ni_4$ on Ni(111). these activation energies are maximum barrier heights from EAM total energy calculations at 0 K.

| Process | Activation energy (eV) |
|---|---|
| Simultaneous parallel translation of four atoms through bridge sites | 0.30 |
| Dislocation formation | 0.36 |
| Edge running | 0.58 |
| Detachment of monomer leaving trimer | 1.16 |

in molecular dynamics calculations for quadrimer diffusion. The most energetically favorable mechanism is for all four atoms to translate nearly simultaneously over the bridge sites in a "gliding" motion. This process is illustrated in Fig. 1 as A. For quadrimers, our molecular dynamics calculations also show another mechanism which we call a "dislocation" mechanism. Illustrated in Fig. 1 as B, this mechanism starts with nearly simultaneous parallel translation of two atoms from fcc to hcp sites. This translation of two atoms forms a dislocation (shown at the bottom of Fig. 1 as C or D). There are four ways to relax the strain associated with this dislocation by moving a pair of atoms, as shown by the four pairs of arrows in C and D. The light arrows in C simply return the cluster to its original configuration with no translation of the center of mass. The heavy arrows in C rotate the cluster and translate the center of mass by $\sqrt{3}a_0/6$, where $a_0$ is the nearest neighbor spacing. The light arrows in D also rotate the cluster and translate the center of mass by $\sqrt{3}a_0/6$. This cluster rotation has been observed experimentally for quadrimers on iridium [6]. The heavy arrows in D result in translation of the whole cluster by $\sqrt{3}a_0/3$. Our molecular dynamics calculations also show occasional occurrences of edge running for the quadrimers. At high temperatures, it is also possible for quadrimers to dissociate, forming trimers and single adatoms which will diffuse and then recombine producing a net motion of clusters (and changes in their size distribution).

In Table I, we compare the calculated energy barriers for these various transition states for the Ni quadrimer on Ni(111). A six layer nickel slab with four nickel adatoms was used. Energy minimization was used with appropriate initial configurations and constraints to calculate the total energy of the initial state and transition states. Since the transition states lie at saddle points on the total energy surface, they would be difficult or impossible to observe ex-

perimentally. For iridium clusters, however, a dislocation configuration similar to Fig. 1(c) has been observed experimentally [6]. We hypothesize that the observation is due to a metastable transition state that exists on iridium but not on nickel. In any event, the experimental observation of a dislocation structure for iridium quadrimers provides further confirmation for the dislocation mechanism for the diffusion proposed here. The rotations shown in Fig. 1 have also been observed experimentally.

We carried out extensive molecular dynamics simulations with cluster sizes of 19, 27, 37, and 43 atoms. These calculations show that larger islands can diffuse by gliding and dislocation mechanisms similar to those described for quadrimers. For 19 atom clusters both gliding and dislocation mechanisms were observed at 1000 K. For a 27 atom cluster both gliding and dislocation mechanisms were observed at 1100 K. Figure 2 shows a single frame from the 1200 K, 43 atom island simulation showing diffusion by the dislocation mechanism. These temperatures were selected to allow one or more of these events to occur within a 0.5 nsec simulation time.

Figure 3(a) shows the energy-minimized structure for a misfit dislocation on a 19 atom island. The structure was calculated starting with the atoms in appropriate fcc and hcp sites. The adatoms at the two edges of the island parallel to the dislocation were constrained to move in the plane normal to the dislocation and the adjacent *substrate* atoms were constrained to move normal to the surface. This dislocation can move by simultaneous gliding of a whole row of atoms, as shown in Fig. 3(a). It can also move by a kink mechanism involving sequential motion of single atoms through the bridge sites. Formation and motion of kinks is a common mechanism for motion of bulk dislocations. Figure 3(b) compares the energies required to move the island by the gliding of the whole island, dislocation motion by simultaneous gliding of a row of atoms, and dislocation motion by formation and motion of kinks along the dislocation. The plotted points are the results of the EAM calculation; the lines are the models described in the next paragraph.

The energetic barriers shown in Fig. 3(b) can be approximated by a model in which the energy required to move an overlayer atom through the bridge site $E_{\text{glide}}$ is independent of its local environment. Similarly, the stacking fault energy $E_{\text{fault}}$, the dislocation line energy

$E_{\text{dislocation}}$, and the energy to create a kink in the dislocation $E_{\text{kink}}$ are independent of local environment. We express all these energies in units of eV/atom. We approximate an island of $N$ atoms by a circle of radius $r = a_0[(N/\pi)\sin(\pi/3)]^{1/2}$ centered at $x = 0$ and $y = 0$. The dislocation is a line parallel to the $y$ axis, located at position $x$ where $-r \le x \le r$. We considered two mechanisms for dislocation motion: motion as a straight dislocation parallel to the $y$ axis, and motion by formation and

motion of kinks. It takes $n$ steps for a dislocation to move across the island. The fraction of atoms transformed from the fcc to hcp sites is $f = (\varphi - \sin\varphi\cos\varphi)/\pi$, where $\varphi = \cos^{-1}(x/r)$. We retain only the first term in the Fourier series representing the energy barrier for moving an atom through the bridge site.

The energy barrier to move the island by gliding is

$$E_g(f) = NE_{\text{glide}}(1 - \cos 2\pi f)/2 + NE_{\text{stack}}f. \qquad (1)$$

The energy barrier to move the island by moving the dislocations by moving rows of atoms is

$$E_r(f) = E_{\text{dislocation}}L/a_0 + E_{\text{glide}}L/a_0\{\cos[n\pi(x/r + 1) + \pi)] + 1\}/2 + NE_{\text{stack}}f, \qquad (2)$$

where $L = 2r\sin\varphi$ is the length of the dislocation. The energy barrier to move the island by moving the dislocations by moving a kink is

$$E_k(f) = E_{\text{dislocation}}L/a_0 + E_{\text{kink}}g(x/r) = NE_{\text{stack}}f, \qquad (3)$$

where

$$g(x/r) = \begin{cases} 0 & \text{for } x/r = -1, \ -1 + 2/n, \ -1 + 4/n, \ -1 + 6/n, \ \ldots, \ 1, \\ 1 & \text{for all other } x/r. \end{cases}$$

In Eq. (3) we neglected the energy required to move the kinks by moving a single atom through a bridge site. This energy (equal to $E_{\text{glide}}$) should be negligible compared to the other energies involved. $E_{\text{glide}}$, $E_{\text{stack}}$, $E_{\text{dislocation}}$, and $E_{\text{kink}}$ are readily estimated using the EAM. Plots of Eqs. (1), (2), and (3) for $N = 19$ are in excellent qualitative agreement with the full EAM
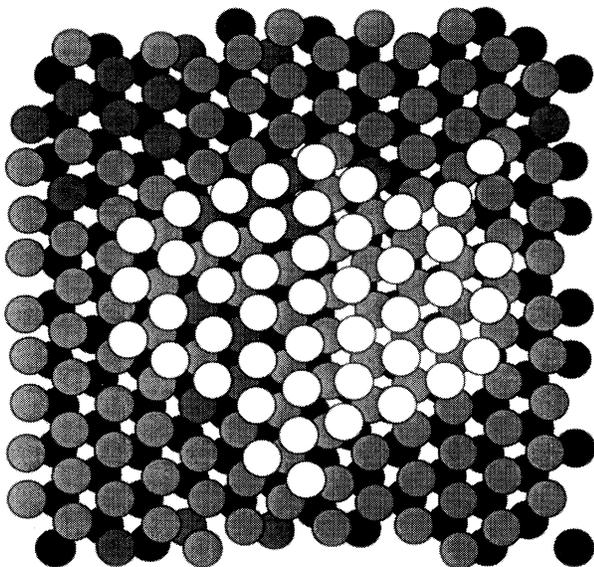


FIG. 2. Configuration from molecular dynamics simulation showing the diffusion of 47 atom island on Ni(111) at 1200 K by a dislocation mechanism. The third layer of substrate atoms is not shown in order to emphasize the difference between fcc and hcp sites for the adatoms. The left portion of the island sits in fcc sites while the right portion sits in hcp sites. A dislocation runs from top to bottom across the island. In the simulation, this diffusion nucleated at the right-hand side of the island and moved from right to left across the island as the island diffused to the right. The island started in fcc sites and finished in hcp sites after this dislocation processes occurred.

calculation, as shown in Fig. 3(b). These equations should be in even better agreement for larger islands, since edge effects will play a lesser role for such islands.

Equations (1), (2), and (3) allow us to compare activation energies for these mechanisms as a function of island size. For circular nickel islands on Ni(111) with $N < {\sim}20$, the gliding mechanism has the lowest activation energy. For ${\sim}20 < N < {\sim}100$, the dislocation motion by sequential gliding of rows of atoms has the lowest activation energy. For $N > {\sim}100$, dislocation motion by kink motion has the lowest activation energy. These results are consistent with the mechanisms observed in the molecular dynamics runs for the range of sizes examined. For elongated or fractal islands the dislocation mechanism is further favored, since the length of the dislocation would be reduced relative to a circular island of the same number of atoms.

A remaining question is the relative contribution to island diffusion by edge running versus the gliding and dislocation mechanisms discussed above. Gruber [18] gives a discussion of the bulk mobility of pores in a metal by surface diffusion which can be easily modified to treat the surface mobility of islands on a metal by edge diffusion. This gives the expression

$$D_s = 0.12D_p n^{-3/2},$$

where $D_s$ is the surface diffusion rate for the island, and $D_p$ is the diffusion rate for adatoms on the island perimeter. This equation is consistent with simulations [13,19]. Since the activation energy for edge running is independent of island size, while the activation energy for gliding and dislocation formation increases with island size, edge running will eventually dominate as island size increases. For the island sizes and temperatures considered here, the molecular dynamics simulations show that gliding and dislocation motion are more favorable than edge running. Some edge running is observed particularly for

(a)



(b)



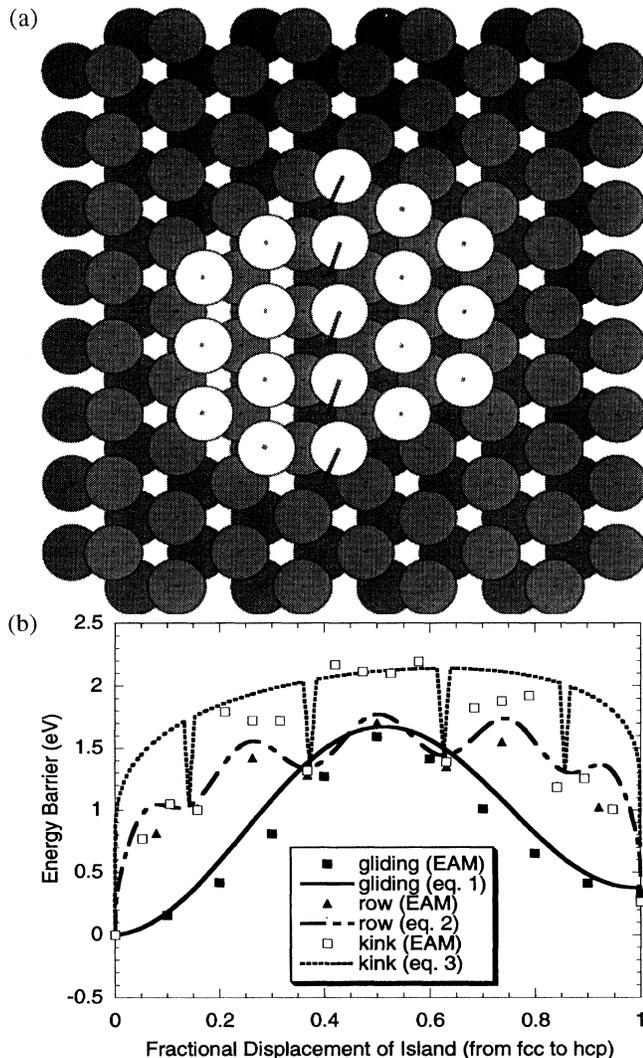Fractional Displacement of Island (from fcc to hcp)

FIG. 3. In (a) the lowest energy configuration of a metastable misfit dislocation for a 19 atom island on the (111) surface is shown. The arrows indicate motions of atoms into the bridge sites which allow motion of the dislocation. (b) shows the energy of the island as a function of the fractional displacement of the center of mass from the fcc to hcp sites. Three different diffusion mechanisms are considered. These are as follows: simultaneous motion of all the atoms through the bridge sites, gliding, dislocation nucleation and motion by a kink mechanism, and dislocation nucleation and motion by simultaneous translation of a row of atoms through the bridge sites. The points are the result of an EAM calculation; the lines are the result of the model discussed in the text.

the larger islands at higher temperatures, however, its contribution to overall island diffusion is less than that of the gliding and dislocation mechanisms.

This Letter describes a novel dislocation mechanism for island diffusion on fcc (111) surfaces. We note that dislocation mechanisms also play a role in the collapse of structures on surfaces [20]. For homoepitaxial systems, in particular, Ni on Ni(111), this mechanism is competitive with edge running in this range of island sizes and temper-

atures. The activation energy required to form this misfit dislocation for Ni on Ni(111) is relatively large (268 meV per atom). Consequently, relatively high temperatures are required for island diffusion. However, there are other (111) surfaces (e.g., gold) for which the lowest energy configuration of the surface includes misfit dislocations [21,22]. For islands with misfit dislocations in their lowest energy configurations (including heteroepitaxial systems), this dislocation mechanism might allow rapid diffusion of large clusters, much faster than predicted by edge running or evaporation and/or condensation of perimeter atoms. This fast diffusion could play an important role in thin film growth for these materials.

*Present address: Physics Department, Clemson University, Clemson, SC 29634

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