VOLUME 77, NUMBER 5 PHYSICAL REVIEW LETTERS 29 JULY 1996

Magic Size Effects for Heteroepitaxial Island Diffusion

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(Received 5 April 1996)

Activation energies for diffusion of small heteroepitaxial islands by nucleation and motion of a dislocation across the island are calculated using a Frenkel-Kontorova model. At "magic island sizes" the activation barriers for heteroepitaxial island diffusion are dramatically lowered. Total energy calculations and molecular dynamics simulations using the embedded atom method confirm the existence of a rapid diffusion process for two-dimensional islands. A signature of this process is a strongly temperature dependent activation energy for diffusion. [S0031-9007(96)00711-9]

PACS numbers: 68.35.Fx, 68.10.Jy, 68.35.Bs, 68.55.–a

Island diffusion is an important phenomena in the growth of thin films. The nucleation and diffusion of islands during deposition of adatoms plays a major role in determining island density, morphology, and eventually film structure. Most theoretical work to date has dealt with growth and diffusion of homoepitaxial or at least pseudomorphic islands. For such cases solid on solid models are appropriate and theories of growth [1–3] and diffusion [4–7] have been developed. The early stages of heteroepitaxial film growth in heteroepitaxial systems where dislocations can form are less well understood. Such growth is of great practical importance. There are a number of reports of rapid diffusion of heteroepitaxial islands in the literature [8–13].

The purpose of this paper is to examine diffusion of heteroepitaxial islands using the Frenkel-Kontorova (FK) model [14] and embedded atom method calculations (EAM) [15] to determine the activation energies for heteroepitaxial island diffusion by dislocation nucleation and motion. These models show dramatic minima in the activation energies as a function of island size. This implies that there are particular island sizes for which diffusion will be rapid. Using experimental tools for measuring heteroepitaxial island diffusion (field ion microscopy, scanning tunneling microscopy, and/or low energy electron microscopy), it should be possible to experimentally demonstrate the occurrence of this rapid diffusion for certain island sizes.

A soliton or dislocation mechanism for island diffusion has been proposed previously [14–16]. In this paper it is shown that diffusion by dislocation nucleation and motion is much more favorable for heteroepitaxy than for homoepitaxy. Quantitative calculations are reported in previously unexamined ranges of island misfit and size, where a dramatic reduction in activation energy for diffusion exists. Finally and most importantly, these calculations are extended to 2D systems showing that remarkably small activation energies can occur in realistic heteroepitaxial systems.

Before discussing the 2D calculations, it is instructive to examine the activation energies for the diffusion of small 1D islands in a 1D Frenkel-Kontorova model. The 1D Frenkel-Kontorova model represents the island atoms as moving in a periodic substrate potential, $V_{\mathrm{misfit}} = A[\cos(2\pi x) - 1]$. The interaction between two atoms located at x_{i+1} and x_i is $V_{\mathrm{strain}} = k(x_{i+1} - x_i - \varepsilon)^2/2$. The total energy is the sum over all of the island atoms,

$$E = \sum_{i=1,n} \frac{A}{2}[\cos(2\pi x) - 1] + \sum_{i=1,n-1} \frac{k}{2}(x_{i+1} - x_i - \varepsilon)^2 .$$

The length unit (lu) is the substrate lattice spacing, the equilibrium island bond length is ε, A is the periodic potential barrier, k is a spring constant, and n is the number of atoms in the 1D island.

In order to study the implications of this simple model for island diffusion on surfaces, the following parameters were used: $A = 100$ meV, $\varepsilon = 0.887$, and $k = 40000$ meV/lu^2. This corresponds to an overlayer with a lattice constant $\sim 11\%$ smaller than that of the substrate. Using numerical methods, the minimum energy configurations for 1D island sizes of 5, 6, 7, 8, 9, 10, and 11 atoms were determined. Energies of islands with a dislocation were calculated by constraining single atoms to remain at a peak in the substrate potential.

The results of this calculation for 9 atom island are shown in Fig. 1. The top panel shows the positions of the atoms in the substrate potential as the dislocation nucleates and moves across the island. For this island size and misfit, the dislocation-free configuration and the single-dislocation configuration have essentially the same energy. The dislocation-free configuration is labeled as having the dislocation position at 0.0 in units of island length. At 0.1, the dislocation is seen to nucleate at the left-hand side of the island. At 0.2, the dislocation is starting to move across the island. At 0.5, the dislocation is in the center of the island. This process continues until the dislocation leaves the right-hand side of the island at 1.0 (not shown). The net result of nucleating a dislocation and moving it all the way across the island is to move the

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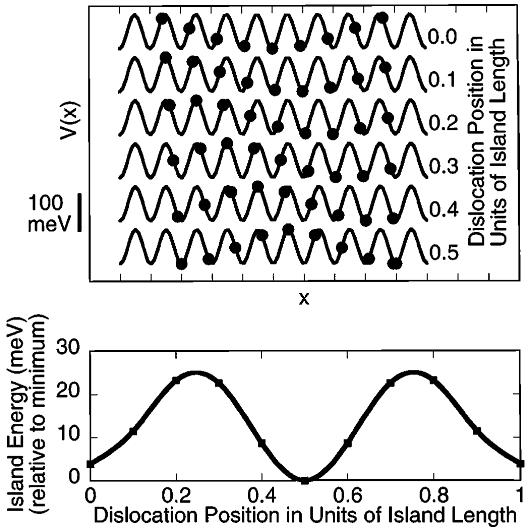

FIG. 1. Top panel shows positions of 9 atom island in substrate potential for one-dimensional FK model described in the text. Parameters for model are $A = 100$ meV, $\varepsilon = 0.887$, and $k = 40000$ meV/lu^2. The minimum energy configuration has no dislocation (labeled by dislocation position 0.0). The other configurations labeled by dislocation positions 0.1, 0.2, 0.3, 0.4, and 0.5 show a dislocation nucleating and moving across the one-dimensional island. Moving this dislocation all the way from the left to the right side of the island translates the island to the right by one lattice spacing. The bottom panel shows the energy of the island as a function of dislocation position. The energy is plotted relative to the energy of the minimum energy configuration.

island right by one lattice unit. The lower panel shows the energy of the island relative to the minimum energy configuration as the dislocation nucleates and moves across the island. The activation energy for this process is less than 25 meV even though the activation energy for a single atom diffusing in this potential is 100 meV.

In Fig. 2, the results of similar calculations for a range of island sizes are plotted. For each island size, the island energy (relative to the energy of the minimum energy configuration for that island size) is plotted as a function of dislocation position. There are two important features to be noticed in this figure. First, the minimum energy configuration for 7 or 8 atoms is dislocation free, whereas the minimum energy configuration for 10 or 11 atoms contains one dislocation centered at the middle of the island. Second, there is a dramatic minimum in the activation energy for diffusion as a function of island size. The activation energy for diffusion is smallest for the island size where the minimum energy configuration changes from zero dislocations to one dislocation. At this "magic" island size, the activation energy for heteroepitaxial island diffusion drops to one-quarter of the activation energy for single atom diffusion on this surface. The activation energy as a function of island size is plotted in the inset of Fig. 2. Since diffusion rates depend exponentially on activation energies, this magic size effect produces immense increases in diffusion rates at these magic sizes.

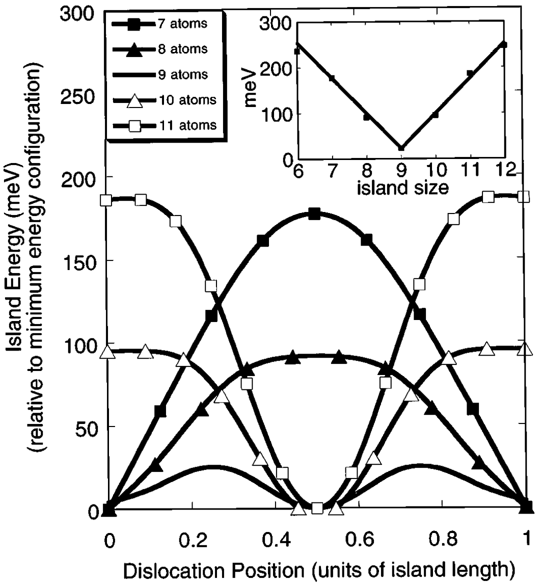

FIG. 2. The main graph shows the energy of various size islands moving in substrate potential. Calculations were performed using one-dimensional FK model with the same parameters as in Fig. 1. The activation energy for island diffusion by dislocation mechanism (inset graph) shows a dramatic minimum for island sizes of 9 atoms. This corresponds to the size where the minimum energy configuration changes from zero to one dislocation.

For a given island size, the activation energy for diffusion by this mechanism depends strongly on the misfit between the substrate and the overlayer lattice constants. Figure 3 shows the activation energy as a function of the misfit for a 9 atom island. In real heteroepitaxial systems, the misfit will generally be temperature dependent, due to differential thermal expansion of the substrate and overlayer. A temperature dependent misfit would imply a temperature dependent activation energy for island diffusion by this mechanism. I will demonstrate the existence of a temperature dependent activation energy using embedded atom method molecular dynamics simulations later in this paper.

In order to determine whether island diffusion by this dislocation mechanism will be important for real surfaces, it is essential to consider the problem in two dimensions. The 2D EAM model presented here is in qualitative agreement with the 1D FK model in that is shows a dramatic minimum in activation energy for diffusion at a magic island size where the minimum energy configuration changes from zero to one dislocation.

The 2D problem poses the following important questions: (1) What is the minimum energy orientation of the dislocation line for an island? (2) How does the dislocation move (glide) across the island? Is a kink mechanism or simultaneous motion of a row of atoms more favorable? (3) What is the preexponential factor for the collective process of dislocation nucleation and motion? (4) Will the dependence of activation energy on misfit

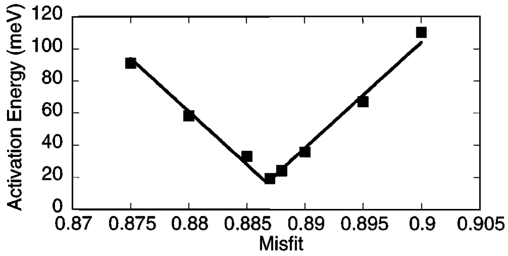

FIG. 3. Activation energy for diffusion of a 9 atom island as a function of substrate-island misfit, ε. Calculations were performed using one-dimensional FK model with $A = 100$ meV and $k = 40000$ meV/lu^2.

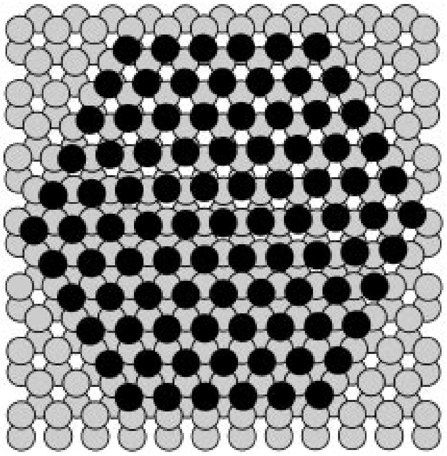

FIG. 4. Minimum energy configuration for 91 atom hexagonal silver island with dislocation on ruthenium (0001), calculated using EAM. A single dislocation runs across the island separating the lower fcc portion of the island from the upper hcp portion of the island.

(and thus temperature) be observable in real heteroepitaxial systems?

Based on numerous experimental observations of partial misfit dislocations in overlayers on close-packed surfaces, a close-packed surface was chosen as a case where dislocations in small islands would likely occur. This choice was also encouraged by molecular dynamics calculations of homoepitaxial island diffusion by a dislocation motion on Ni(111) [16]. As a contrast to the one-dimensional model I chose a model system with the island lattice constant larger than that of the substrate, specifically Ag on Ru(0001). This system shows partial misfit dislocations at submonolayer coverages [17] and thus represents a good candidate for island diffusion by a dislocation mechanism. It is important to emphasize that other heteroepitaxial systems having dislocations at submonolayer coverages should show similar phenomena.

The minimum energy configuration for a dislocation in a 91 atom Ag island on Ru(0001) determined using EAM is shown in Fig. 4. A single dislocation runs across the island separating the lower fcc portion of the island from the upper hcp portion of the island. The dislocation line is at an angle of ~15° from the horizontal. This angle reduces the number of atoms sitting in bridge sites relative to a configuration with a horizontal dislocation line. The bulk metals, dislocations are generally thought to move via extended kinks, ten or more atoms long [18]. Figure 4 is entirely consistent with this extended kink mechanism for dislocation glide. The activation energies for diffusion by dislocation nucleation and motion at 0 K were estimated as 681, 729, 457, 293, and 786 meV for diffusion of 19, 37, 61, 91, and 127 atom silver islands on ruthenium using the EAM.

In order to estimate preexponential factors, EAM molecular dynamics simulations were used to calculate diffusion rates for Ag islands and for Ag monomers on Ru(0001). For temperatures in the vicinity of room temperature, a 61 atom island was found to have a much larger diffusion rate than the 37 or 91 atom island. Apparently differential thermal expansion changes the magic island size from ~91 atoms at 0 K to ~61 atoms at 300 K. For diffusion of the 61 atom island at low temperatures, the total simulation time was 20 ns. For higher temperatures, the total simulation time was several ns. For the Ag monomers, the simulation time was a fraction of ns. The diffusion rates are plotted in the top panel of Fig. 5. The units are jumps between hcp and fcc per nanosecond. Assuming that the jumps are not correlated, these jump rates can be translated directly into diffusion constants. The plotted error bars are based on the assumption that the jumps obey Poisson statistics. At room temperature the diffusion of a monomer is only about 100 times faster than that of a 61 atom island. The molecular dynamics simulations clearly substantiate the existence of rapid diffusion at magic island sizes. Significantly, EAM molecular dynamics simulations using a smaller island (37 atoms) showed absolutely no jumps at room temperature during a 4 ns run. We note that the EAM tends to underestimate stacking fault energies. This will cause the EAM to overestimate diffusion rates for these islands. Again, this does not alter the existence of magic island sizes unless the stacking fault energies become so large as to preclude any transition state involving the island in a faulted configuration.

The diffusion data for the Ag monomer shown in Fig. 5 are fit by a standard Arrhenius equation with a preexponential factor of 2160 jumps/ns, and an activation energy of 57 meV. The activation energy is in reasonable agreement with the bridge site energy and the preexponential has a reasonable value. The diffusion data for the 61 atom island, however, cannot be fit by a single activation energy and preexponential. I attribute this effect to a temperature dependent misfit between the Ag overlayer and the Ru substrate. The activation energy for island diffusion will depend on the misfit and thus on the temperature. By analogy with the results shown in Fig. 3, the activation energy was represented by

$$E(T) = E_{\min} + \gamma |T - T_{\min}| \,.$$

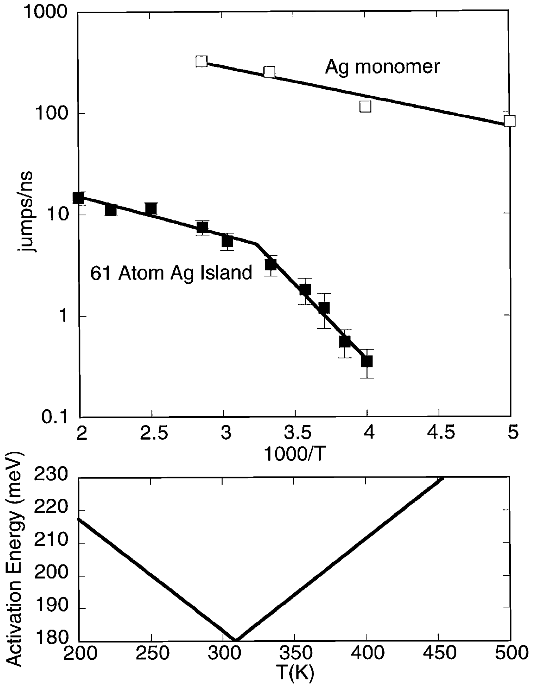

FIG. 5. The top panel shows the Arrhenius plot for diffusion of single Ag atom and for 61 atom Ag island on Ru(0001). The jump rates are counted from embedded atom molecular dynamics simulations. The error bars are calculated based on Poisson statistics. The 61 atom Ag island points are fit using *a single temperature independent preexponential factor and a temperature dependent activation energy* (plotted in the lower panel). Note that the upper panel has a reciprocal temperature x axis, whereas the lower panel has temperature as the x axis.

Here the misfit is assumed to be linear with temperature and that the activation energy for diffusion is assumed to be linear with the deviation of the misfit from an optimum misfit. $E_{\min}$ is the minimum activation energy which occurs at a temperature $T_{\min}$. γ is a coefficient giving the linear dependence of the activation energy on the magnitude of deviation of temperature, T, from $T_{\min}$. Assuming a constant preexponential factor the jump rate is $\nu = \nu_0 e^{-E(T)/kT}$ where ν_0 is the preexponential factor. The fit to the island diffusion data shown in the top panel of Fig. 5 was obtained by least squares fitting allowing $E_{\min}$, $T_{\min}$, γ, and ν_0 to vary. The minimum activation energy, $E_{\min}$, for the 61 atom island was 180 meV. The preexponential factor, ν_0, was 5400 jumps/ns. $T_{\min}$ was 309 K and γ was 0.343 meV/K. This temperature dependent activation energy, $E(T)$, is plotted in the lower panel of Fig. 5.

These numerical values for $E_{\min}$, $T_{\min}$, γ, and ν_0 should be regarded as only semiquantitative since the EAM is an empirical method. Nonetheless, they show several important points. First, they indicate that the preexponential factor for island diffusion by this dislocation mechanism is comparable to the preexponential factor for monomer diffusion. Second, they show that the concept of a very small activation energy for diffusion with a magic island size and misfit is valid. Finally, they emphasize the importance of a temperature dependent activation energy as an explanation for departures from a simple Arrhenius behavior for diffusion rates in these systems.

This paper offers a quantitative model allowing a prediction of heteroepitaxial island diffusion rates. The model predicts a magic size at which diffusion becomes quite rapid. This magic size is the size at which islands with and without a single dislocation are nearly degenerate in energy. The model shows a dependence of activation energy on substrate-island misfit and thus on temperature. I hope the present analysis will prompt more quantitative experimental studies of heteroepitaxial island diffusion rates as a function of island size. Finally, experimental measurements of island size distributions after growth should be sensitive to this effect since islands of the magic size should coalesce rapidly and thus rarely be seen in experiments.

I would like to acknowledge programming assistance and helpful conversations with Stephen M. Foiles. I also acknowledge valuable discussions with Norman C. Bartelt and Robert Q. Hwang.

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