Effects of Short-Range Attraction in Metal Epitaxial Growth

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The effects of short-range attraction in metal epitaxial growth are studied. Our results indicate that even at normal incidence, the short-range attraction of depositing atoms to step edges can significantly increase the selected mound angle and surface roughness for typical energies used in epitaxial growth. Our results also lead to a picture of the process of deposition near step edges that is quite different from the standard downward funneling picture. Results for the dependence of the uphill current on incident atom kinetic energy and substrate temperature are also presented.

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Understanding and controlling the evolving surface morphology of epitaxial thin films is of immense technological interest [1]. Examples include semiconductor heterostructures and quantum dots, metal conducting films, and magnetic films for applications in electronic and optoelectronic devices. Depending on the application, one may wish to produce either atomically flat or nanostructured surfaces. However, in each case, the performance depends critically on the surface morphology as well as on the underlying film structure.

One particularly important process controlling the evolution of the surface morphology is the accommodation of incoming atoms deposited near steps. For example, in metal epitaxial growth, the energy of condensation of depositing atoms is believed to lead to “downward funneling” (DF) [2], i.e., atoms deposited beyond the edge of a step “funnel” to the bottom terrace while atoms deposited on the “uphill” side go to the upper terrace. Such processes lead to a downhill current which tends to stabilize the surface. In the case of unstable growth [due either to an Ehrlich-Schwoebel (ES) barrier [3] to the descent of diffusing atoms at steps, or to step-adatom attraction [4,5] or to step-edge diffusion [6]] the resulting balance between uphill and downhill currents leads to slope selection [7]. Analytical calculations [5] indicate that the surface current and selected mound slope depend strongly on the “bias” for atoms landing near a step.

Recent experiments and molecular dynamics (MD) simulations of epitaxial growth also highlight the importance of understanding the deposition process in epitaxial growth. For example, recent experiments by van Dijken *et al.* [8] indicate that at grazing incidence the long-range van der Waals attraction of the surface to incoming atoms can lead to steering and shadowing effects which dramatically alter the surface morphology. Furthermore, recent MD simulations of Ag/Ag(100) growth at low temperature [9] demonstrate that even at normal incidence steering may affect the surface morphology, particularly at low incident kinetic energy. However, while a variety of simplified models have been used to describe the deposition process in kinetic Monte Carlo (KMC) simulations—ranging from the assumption that incoming atoms move to the lowest-energy site within a given incorporation radius [10] to the assumption of downward funneling [2,11–13], the dynamics of adatom deposition at steps and the effects of short-range attraction on the surface morphology are still not well understood.

In this Letter, we present the results of molecular dynamics simulations of Cu/Cu(100) growth which were carried out in order to measure the effects of short-range interactions on the deposition of atoms near step edges and the resulting effects on the surface current and surface morphology. Surprisingly, we find that even at normal incidence, the short-range attraction of incoming atoms to steps can lead to a significant uphill current which significantly increases the selected mound angle and surface roughness for typical energies used in epitaxial growth. Our results also lead to a picture of the process of deposition near step edges which is significantly different from the standard downward funneling picture. In particular we find that for typical incident energies in epitaxial growth, significant effects of the short-range attraction occur both *after* as well as *before* the atom has collided with the step and lost its kinetic energy of condensation. Our observation of similar results for Ag/Ag(100) growth indicates that such effects are likely to be generally important in metal epitaxial growth.

In order to determine the effects of short-range attraction at normal incidence we have carried out MD simulations of adatom deposition at a single (011) step on the Cu (100) surface. In order to test the dependence of our results on the potential used, our simulations were carried out using both a Lennard-Jones (LJ) copper potential [14] of the form $\phi(r) = 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6}]$ (where $\epsilon = 0.4093$ eV and $\sigma = 2.3377$ Å) as well as a more realistic embedded atom method (EAM) potential which takes into account many-body effects [15]. In order to minimize finite size effects, a system size of ten and one-half layers was used, with each layer consisting of a terrace of 10 atoms by 6 atoms, while periodic boundary conditions

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were assumed along each terrace direction. The top three and one-half layers underwent constant-energy MD while the bottom four layers were fixed. In order to equilibrate the substrate and absorb the energy of condensation of incoming atoms, the middle three layers of the system underwent constant temperature (Langevin) MD [16]. Simulations were carried out over a range of incident kinetic energies in order to study the dependence on the incident energy.

Figure 1 shows typical snapshots (top and side views) of an atom deposited near an (011) step on the Cu (100) surface with incident kinetic energy $K_i = 0.1$ eV at an initial distance $x = 0.3a_1$ beyond the step edge (horizontal line) where a_1 is the nearest-neighbor distance. The top two pictures correspond to the initial state, while the bottom two pictures show the final state 2.4 ps later, after the atom is adsorbed on the surface [17]. As can be seen, due to the short-range attraction the adatom is attracted to the top terrace rather than the lower terrace as would be expected in the case of downward funneling.

In order to quantify these effects we have measured the probability P_{up} that an atom deposited at normal incidence within a window of width $a_1/2$ (see Fig. 2) reaches the top terrace as a function of incident kinetic energy K_i. The system was first equilibrated at the desired temperature and the average position of the step edge was determined. Atoms were then deposited with the desired initial kinetic energy from an initial distance just above the potential cutoff and for each deposition the trajectory of the incoming atom was recorded. To obtain good statistics, 2500 depositions randomly distributed within the window were carried out for each value of K_i. To investigate the possible dependence on the substrate temperature, our EAM simulations were carried out at three different temperatures ($T = 1$, 100, and 300 K) while the LJ simulations were at $T = 100$ K.

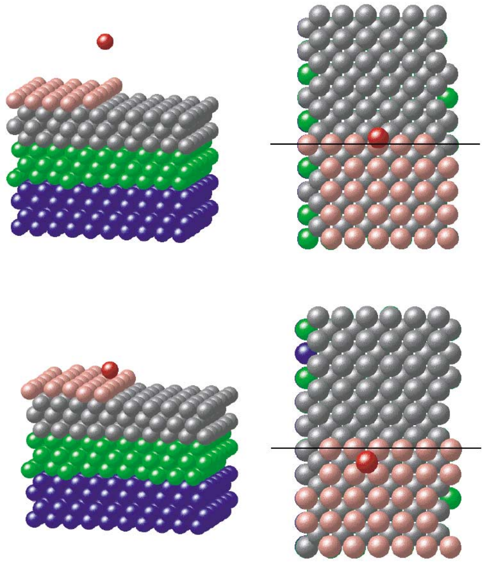

FIG. 1 (color online). Snapshots (side and top views) of MD simulations (LJ potential) of deposition near a monatomic step with substrate temperature $T = 100$ K.

Figure 3 shows our results for the uphill funneling probability P_{up} as a function of the incident atom kinetic energy K_i. In the absence of short-range attraction the geometrical downward funneling picture holds and therefore one expects $P_{\mathrm{up}} = 0$. However, as shown in Fig. 3, due to the short-range attraction there is significant uphill funneling even for an incident kinetic energy corresponding to the average value $\bar{K}_i = 2k_B T_m \simeq 0.23$ eV (where $T_m = 1356$ K is the melting temperature of copper) expected in copper epitaxial growth. We have also obtained similar results for Ag/Ag(100) at $T = 300$ K (dotted curve). These results indicate that the standard downward funneling picture must be significantly modified to take into account the effects of short-range attraction.

Also shown in Fig. 3 are our results for the LJ copper potential ($T = 100$ K) for two different values of the potential cutoff distance ($r_{\mathrm{cut}} = 2.0\sigma$ and $r_{\mathrm{cut}} = 3.2\sigma$). As might be expected, for the larger cutoff the uphill funneling probability is somewhat larger than for the smaller cutoff. However, the good agreement between the LJ and EAM results indicates that the degree of uphill funneling does not depend strongly on the details of the potential. In this connection, we note that the smaller LJ cutoff is the same as in the EAM potential, and in this case the two results are particularly close. Elsewhere we have shown [18] that the correct magnitude of the long-range van der Waals attraction for copper is actually significantly smaller than in our copper LJ potential, thus justifying the shorter cutoff. These results also imply that the long-range attraction can be neglected at normal incidence [18].

We now consider in more detail the dynamics of incoming atoms approaching a step edge. Figure 4 shows the x coordinate (distance from step edge) for three typical trajectories (solid upper curves) corresponding to an atom with an initial kinetic energy typical of epitaxial Cu growth ($K_i = 0.20$ eV). Also shown for comparison is a fourth trajectory (dashed curve) with significantly

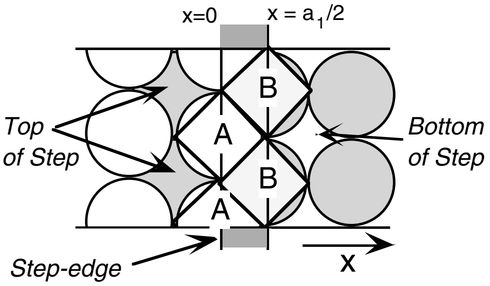

FIG. 2. Schematic showing deposition window ($0 < x < a_1/2$) near an (011) step used in MD simulations. Squares labeled A and B indicate capture zones used in KMC simulations.

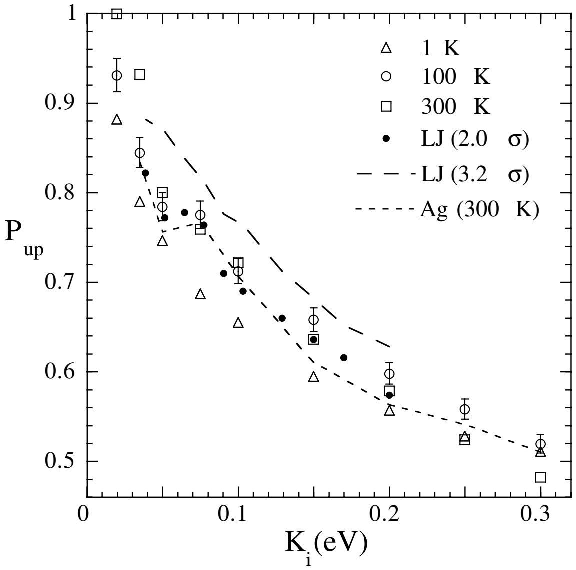

FIG. 3. Dependence of uphill funneling probability $P_{\rm up}$ on incident kinetic energy K_i for deposition at a Cu (011) step. Open symbols correspond to EAM potential. Statistical error bars are shown for 100 K EAM results. EAM results for a Ag (011) step are also shown (dotted curve).

lower initial kinetic energy ($K_i = 0.05$ eV). Because of the short-range attraction the atoms are "steered" towards the step edge. However, in all four cases the atoms collide with the step (i.e., feel the repulsive interaction) before reaching the step edge corresponding to $x = 0$. For example, for an initial distance $x_i = 0.25a_1$ beyond the step edge and $K_i = 0.20$ eV (middle solid trajectory), the depositing atom begins to feel the repulsive interaction at a distance $x \simeq 0.18a_1$ (vertical dotted line) corresponding to the peak in the kinetic energy curve. The depositing atom then pushes the step downwards, losing its kinetic energy of condensation in the process. It then bounces slowly off the step as the step rebounds upwards, and is then attracted over the step edge to the top terrace via the short-range attraction. A similar process can be seen for the other three cases in which the deposited atom lands on the upper terrace. These results show clearly that the effects of the short-range attraction *after* it collides with the step are just as important as the effects of steering in explaining the large value of the uphill funneling probability.

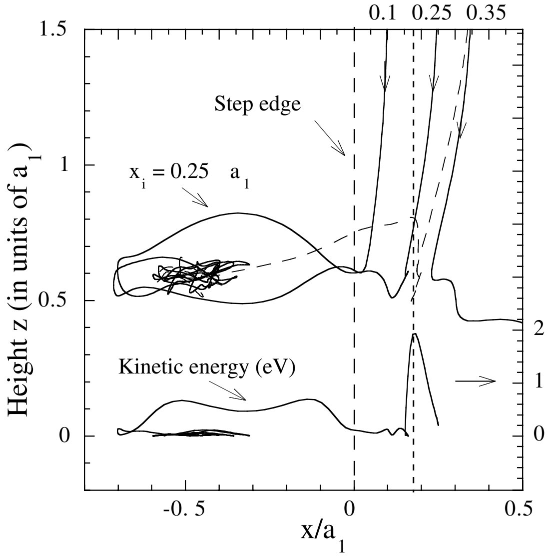

FIG. 4. Trajectories of incoming atoms deposited near a Cu (011) step ($T = 100$ K) with $K_i = 0.20$ eV obtained using EAM potential (solid curves). Kinetic energy curve corresponds to middle solid trajectory ($x_i = 0.25a_1$) while vertical dotted line indicates collision with step. Dashed trajectory corresponds to $K_i = 0.05$ eV. Time interval for all trajectories is 2.4 ps.

The results in Fig. 4 also suggest the existence of a critical distance $\delta(K_i)$ such that for $x_i < \delta(K_i)$ the deposited atom will almost always end up on the top terrace, while for $x_i > \delta(K_i)$ the deposited atom will land on the lower terrace. For $K_i = 0.20$ eV, we find $\delta \simeq 0.30a_1$ which implies $P_{\rm up} \simeq 2\delta/a_1 \simeq 0.6$ in good agreement with our results in Fig. 3, while for $K_i = 0.05$ eV, we find $\delta \simeq 0.4a_1$.

We now consider the implications of uphill funneling due to short-range attraction on the evolution of the surface morphology in metal (100) growth. In previous work [5] expressions for the surface current and selected mound slope were derived for the case of irreversible growth as a function of the ES barrier $E_{\rm ES}$ as well as of the probabilities c_1 (c_2) that an adatom deposited within the square labeled A (B) in Fig. 2, will reach the bottom terrace. Using the fact that $P_{\rm up} = 3/2 - c_1 - c_2$ these expressions may be translated into the present notation. In particular, these results imply that for a moderate ES barrier (i.e., $E_{\rm ES}/k_BT \geq 2$), the selected mound slope for irreversible growth on an fcc (100) surface is given by $m_0 = \sqrt{2}/(4 - 2P_{\rm up})$. In the case of downward funneling ($P_{\rm up} = 0$) this implies $m_0 = \sqrt{2}/4$. In contrast, our MD simulations indicate that for Cu/Cu (100) growth, one has $P_{\rm up} \simeq 1/2$ which implies $m_0 \simeq \sqrt{2}/3$ corresponding to a (113) facet. This result is in good agreement with the experimental observation of mounds with (113) facets at $T = 160$ K in Cu/Cu(100) growth by Ernst *et al.* [19]. Thus, the experimental observation of (113) facets in Cu/Cu(100) growth at 160 K may be explained by the effects of the short-range attraction as observed in our simulations.

In order to further study the effects of short-range attraction in metal epitaxial growth, we have also carried out kinetic Monte Carlo (KMC) simulations of Cu/Cu(100) growth [20] at $T = 160$ K. Our KMC simulations were based on activation energies for adatom diffusion calculated using effective medium theory [21], and lead to parameters very similar to those recently obtained by Furman *et al.* [22] as well as to excellent

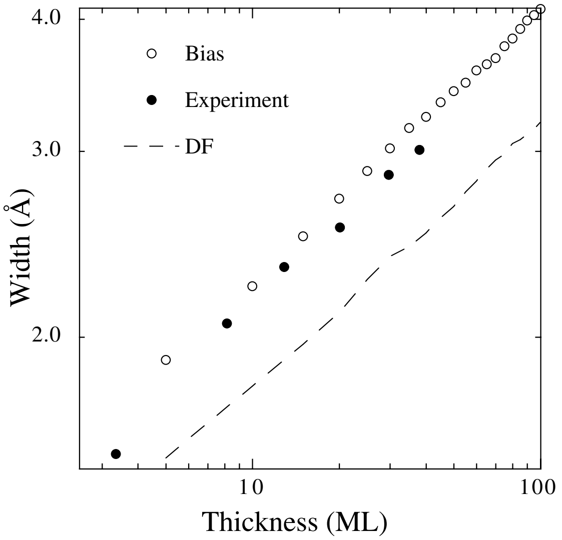

FIG. 5. Log-log plot of rms surface width as a function of coverage for Cu/Cu(100) growth (see text). Filled symbols correspond to experimental results from Ref. [19].

agreement with submonolayer experiments over the temperature range $T = 180$–300 K [20,22–24]. We note that in our KMC simulations at $T = 160$ K, the dominant processes are monomer and dimer diffusion and rapid edge-diffusion while there is a very weak dependence on the strength of the ES barrier.

Figure 5 shows a comparison between our KMC results for the rms surface width and the experimental results. As can be seen, for the case of downward funneling ($P_{\mathrm{up}} = 0$) the surface width is significantly smaller than in the experiment. However, by including a "bias" in our KMC simulations such that $P_{\mathrm{up}} = 1/2$ (open symbols), we obtain significantly better agreement. In contrast, including a significantly higher bias ($P_{\mathrm{up}} = 1$) leads to results which are significantly higher than experiment. Thus, we find that by including an amount of uphill funneling close to that predicted by our MD simulations, we obtain reasonable agreement with experiment.

In conclusion, we have shown that short-range attraction can play an important role in determining the surface morphology in metal epitaxial growth. In particular, in the presence of an ES barrier, uphill funneling at step edges can significantly enhance the surface current and selected mound angle. In KMC simulations we have also found that it can enhance the instability in the case of unstable growth due to step-edge diffusion [6].

In addition to its effects on unstable mound growth, uphill funneling due to short-range attraction may also play an important role in step-flow growth. For example, in the presence of an ES barrier, it can enhance the meandering instability, while in the case of step-bunching due to rapid edge-diffusion it can enhance the step-bunching instability. The similar magnitude of our results for Cu/Cu(100) and Ag/Ag(100) indicates that such effects are likely to be generally important, particularly when the step density is large, in metal epitaxial growth.

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