

# Effects of short-range attraction in unstable metal (110) epitaxial growth: Molecular dynamics simulations for Cu, Ag, and Al

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The results of molecular dynamics simulations of the process of adatom deposition near steps for Cu(110), Ag(110), and Al(110) surfaces are presented in order to determine the effects of short-range (SR) attraction on the surface current and selected mound angle during unstable epitaxial growth. Our results indicate that, in qualitative agreement with previous work on metal (100) and (111) surfaces, for [001] steps the short-range attraction of depositing atoms to step edges can significantly increase the selected mound angle for typical energies used in epitaxial growth. In contrast, for the case of deposition near  $[1\bar{1}0]$  steps, due to geometric effects the effects of short-range attraction are significantly weaker. As a result the overall “uphill funneling” probability  $P_{av}^{110}$  is essentially the same as in the absence of SR attraction. Predictions for the selected mound angles along [001] and  $[1\bar{1}0]$  steps are also presented for the case of irreversible growth with a large Ehrlich-Schwoebel barrier. Our results are also compared with recent experimental results in which anisotropic hut clusters with (111) and (100) facets have been observed. While our results are in qualitative agreement with experimental observations that the selected mound slopes are typically larger for [001] steps than for  $[1\bar{1}0]$  steps, they also indicate that the effects of short-range attraction are not sufficient to explain the large-angle facets observed in Al/Al(110) growth at 400 K, thus confirming that in this case other effects such as uphill diffusion at step edges must play an important role.

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## I. INTRODUCTION

Understanding and controlling the evolving surface morphology of epitaxial thin films is of immense technological interest.<sup>1</sup> One particularly important process controlling the evolution of the surface morphology in epitaxial growth is the accommodation of incoming atoms deposited near steps. For example, in metal epitaxial growth, the process of deposition of atoms near step edges has traditionally been described by downward funneling (DF),<sup>2</sup> 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 downward funneling 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<sup>3</sup> to the descent of diffusing atoms at steps, or to step-adatom attraction,<sup>4,5</sup> or to step-edge diffusion<sup>6</sup>—the resulting balance between uphill and downhill currents leads to slope selection.<sup>7</sup> Analytical calculations<sup>5</sup> indicate that the surface current and selected mound slope depend strongly on the bias for atoms landing near a step.

Recently, we have shown<sup>8,9</sup> that for metal (100) and (111) epitaxial growth, the short-range attraction of depositing atoms to step edges can lead to significant deviations from the simple downward funneling (DF) picture.<sup>2</sup> In particular, we found that, due primarily to the effects of short-range attraction after the depositing atom has “collided” with the step and lost its kinetic energy of condensation, as well as partly to the effects of steering before colliding with the step, atoms deposited near step edges are significantly more likely to land on the upper terrace than predicted by DF. As a result, in the case of unstable growth due to an ES barrier, the short-

range attraction leads to a significant uphill current which significantly increases the selected mound angle and surface roughness for typical deposition energies used in epitaxial growth. By comparing kinetic Monte Carlo simulations of Cu/Cu(100) growth at  $T=160$  K with experiments we were also able to show that the magnitude of the effects measured in our molecular dynamics simulations can quantitatively explain both the observed (113) facets as well as the enhanced surface roughness at this temperature. Similar results were found for Ag/Ag(100) as well as for metal (111) surfaces.<sup>9</sup> In addition, for the case of irreversible growth with a large ES barrier, we have recently derived a simple analytical expression for the surface current and selected mound slope which is valid for arbitrary crystal geometry.

Here we consider the effects of short-range attraction on the deposition of atoms near steps and on the mound instability in metal fcc (110) homoepitaxial growth. This is of particular interest because the formation of anisotropic structures and/or ripples has been observed in Ag/Ag(110) and Al/Al(110) growth over a wide range of temperatures<sup>11,12</sup> and is also believed to occur in other metal (110) systems. In addition, the existence of a striking faceting instability characterized by the formation of anisotropic “nanocrystals” with well-defined (111) facets along the ripples and (110) facets at the ends has recently been observed in Al/Al(110) growth at  $T=400$  K.<sup>12</sup>

Recently, the formation of such high-angle facets in Al/Al(110) growth has been explained by the existence of adatom ascending processes (e.g., uphill diffusion) for atoms at  $[1\bar{1}0]$  and  $[100]$  ascending steps. One-dimensional kinetic Monte Carlo simulations<sup>13</sup> of Al/Al(110) growth with uphill

diffusion at steps have also been carried out which support this picture. However, in these simulations, the effects of downward funneling<sup>2</sup> and/or of short-range attraction were not taken into account. Therefore, it is of interest to investigate to what extent these effects may modify and/or enhance the kinetic instability observed in these experiments.

Here we present the results of molecular dynamics simulations of the process of adatom deposition near steps for a variety of (110) metal surfaces including Cu(110), Ag(110), and Al(110), in order to determine the effects of short-range attraction on the surface current and selected mound angle. Somewhat surprisingly, we find that for the case of deposition on  $[1\bar{1}0]$  steps, the effects of short-range attraction are relatively weak. As a result the overall “uphill funneling” probability  $P_{av}$  is essentially the same as that predicted by downward funneling. However, for the case of  $[001]$  steps we find that the uphill funneling probability is significantly larger than the DF prediction. Using recently derived general expressions for the surface current and selected mound angle<sup>9</sup> which are valid for arbitrary crystal geometry in the case of a large ES barrier, we also obtain results for the maximum possible selected “mound” or “facet” angle in the absence of uphill diffusion and/or step detachment.

This paper is organized as follows. In Sec. II, we describe our molecular dynamics simulations. In Sec. III, we present our results along with an analysis of the selected slope for the case of large step barrier. Finally, in Sec. IV, we discuss our results in more detail and compare with recent experimental results for Al/Al(110).

## II. MOLECULAR DYNAMICS SIMULATIONS

In order to determine the effects of short-range interactions we have carried out molecular dynamics (MD) simulations of adatom deposition at both  $[001]$  steps [corresponding to (111) microfacets, see Fig. 1] and  $[1\bar{1}0]$  steps corresponding to (100) microfacets on the Cu(110), Ag(110), and Al(110) surfaces. As in previous work<sup>8,9</sup> our MD simulations were carried out using embedded-atom-method (EAM) potentials for Cu, Ag, and Al (Ref. 14) since they have been shown to be relatively accurate for a variety of metals.<sup>15</sup> We note that our previous results<sup>8</sup> for deposition near steps on Cu(100) also indicate that the effects of short-range attraction on the degree of “uphill funneling” are not overly sensitive to the details of the potential. In addition, we have recently shown<sup>10</sup> that for the case of Cu(100), there is relatively good agreement between the EAM model prediction for the potential energy surface near a step and the predictions of density functional theory calculations.

To include the possible effects of “knockout” of atoms on the upper terrace<sup>9</sup> as well as the effects of short-range attraction for atoms deposited beyond a step edge, we have measured separately the overall probabilities  $P_{up}$  ( $P'_{up}$ ) that an atom deposited within a window of size  $b$  ( $b'$ ) on the downhill (uphill) side of the step-edge lands on the upper terrace. For the case of  $[1\bar{1}0]$  steps we used  $b=b'=\sqrt{2}a_1$ , where  $a_1$  is the nearest-neighbor distance, corresponding to the “cross-channel” distance, while for the case of  $[001]$  steps we used

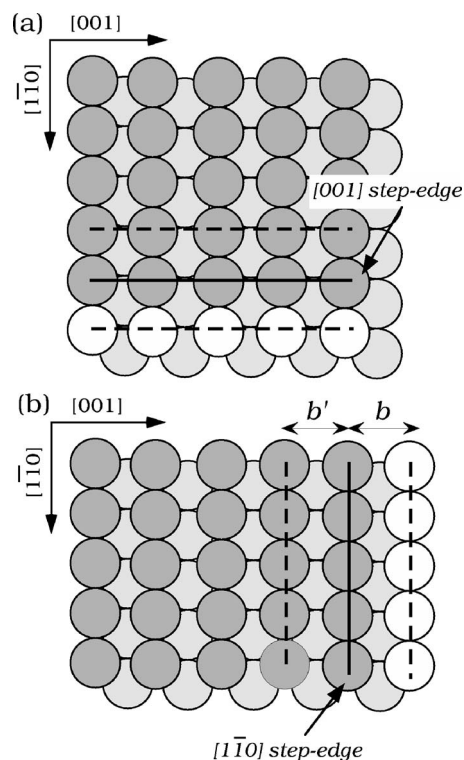


FIG. 1. Schematic (top view) of substrate configuration used in molecular dynamics simulations of deposition process near  $[001]$  and  $[1\bar{1}0]$  steps. Dark circles correspond to top 1/2 layer island while dashed circles correspond to attachment sites at step edge. Note that full layers below island (light gray circles) extend for another five to six rows beyond step edge (not shown) in the direction perpendicular to the step edge.

$b=b'=a_1$  corresponding to the “in-channel” distance (see Fig. 1). We note that in preliminary simulations we found that if an atom is deposited at a distance larger than  $b$  ( $b'$ ) from the step edge, then the probability  $P_{up}$  ( $P'_{up}$ ) that it lands (remains) on the top terrace is 0 (1).

In order to minimize finite-size effects, a system size of 10.5 layers was used, with each full layer consisting of a terrace of 11 atoms by five atoms while periodic boundary conditions were assumed along each terrace direction. As in our previous simulations of metal (100) deposition,<sup>8</sup> the top three and one-half layers underwent constant-energy molecular dynamics, while the middle three layers of the system underwent constant temperature (Langevin) molecular dynamics,<sup>16</sup> and the bottom four layers were fixed. The Langevin layers were used to equilibrate the substrate and absorb the energy of condensation of incoming atoms. As shown in Fig. 1, in each case the top one-half layer consists of an island of size  $5 \times 5$  with either a  $[001]$  or a  $[1\bar{1}0]$  step.

In our simulations, the system was first equilibrated at the desired temperature ( $T=300$  K) 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. Simulations were carried out over a range of incident kinetic energies in order to study the dependence on the incident energy. To

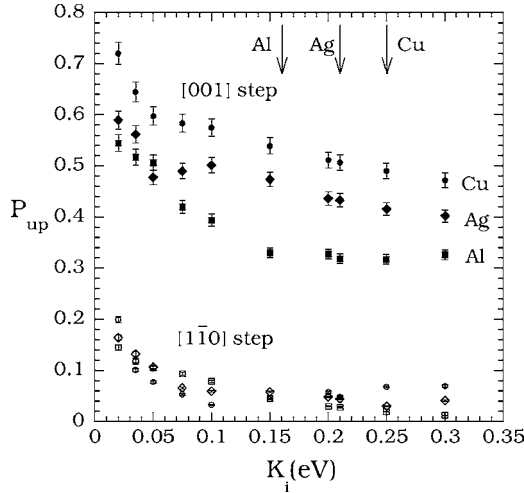


FIG. 2. Uphill funneling probability  $P_{up}$  of incoming atoms deposited within a window of width  $b$  beyond the step edge for [001] steps (filled symbols) and [110] steps (open symbols). Arrows indicate average thermal kinetic energy of deposited atoms in epitaxial growth.

obtain good statistics, 2500 depositions randomly distributed within each window were carried out for each value of the incident kinetic energy  $K_i$ .

### III. RESULTS

#### A. Uphill funneling probability $P_{up}$ for deposition beyond a step

Figure 2 shows a summary of our results for the uphill funneling probability  $P_{up}$  that an atom deposited in a region of width  $b$  beyond the step-edge lands on the upper terrace, as a function of the incident atom kinetic energy  $K_i$  for both [001] steps (filled symbols) and [110] steps (open symbols) on Cu(110), Ag(110), and Al(110). We note that in the absence of short-range attraction one expects  $P_{up}=0$  corresponding to downward funneling (DF). However, as shown in Fig. 2, for the case of [001] steps there is significant uphill funneling due to short-range attraction. In particular, for typical deposition energies in epitaxial growth (e.g.,  $2k_B T_m$  where  $T_m$  is the corresponding melting temperature) we find,  $P_{up[001]}^{Cu} \approx 0.48 \pm 0.02$ ,  $P_{up[001]}^{Ag} \approx 0.44 \pm 0.02$ , and  $P_{up[001]}^{Al} \approx 0.35 \pm 0.02$ .

The relatively large values of  $P_{up}$  for [001] steps may be explained by the geometry of the underlying substrate near the step as well as the relatively small deposition window size ( $b=a_1$ ). In particular, due to the relatively wide “channels” in the [110] direction, combined with the fact that it is relatively easy for a depositing atom to “push” an edge-atom down towards a “fourfold” hollow site in the layer below, atoms which collide with the step edge can “push” through relatively easily to the upper terrace. As a result, the combined effects of “steering” before the depositing atoms collides with the step edge, and of short-range attraction after the depositing atom has collided with the step edge and lost its “kinetic energy of condensation” can lead to relatively large values of  $P_{up}$ .

These results indicate that, as previously observed for metal (100) and (111) surfaces,<sup>8,9</sup> for deposition on metal (110) surfaces the standard downward funneling picture must be significantly modified to take into account the effects of short-range attraction. Interestingly, and in contrast to our previous results for (100) and (111) surfaces, the values of  $P_{up}$  obtained for [001] steps are roughly proportional to the corresponding bulk melting temperatures ( $T_m^{Cu}=1357$  K,  $T_m^{Ag}=1235$  K,  $T_m^{Al}=933$  K). This is consistent with the fact that as was previously observed for metal (100) and (111) surfaces, the dominant effect of short-range attraction on uphill funneling is the attraction of the depositing atom to the step after it has collided with the step edge, and lost its kinetic energy of condensation.

In contrast, for atoms deposited near [110] steps, the overall uphill funneling probability  $P_{up[110]}$  is significantly lower. In particular, for typical deposition energies in epitaxial growth we find,  $P_{up[110]}^{Cu} \approx 0.070 \pm 0.005$ ,  $P_{up[110]}^{Ag} \approx 0.040 \pm 0.005$ , and  $P_{up[110]}^{Al} \approx 0.030 \pm 0.005$ . The relatively small values of  $P_{up}$  for atoms deposited beyond [110] steps may also be explained by the step geometry. In particular, the existence of relatively narrow “channels” between [110] step-edge atoms makes it difficult for atoms which collide with the step-edge to “push” through to the upper terrace, thus reducing the uphill funneling probability. This effect is enhanced by the fact that it is relatively difficult for a depositing atom to “push” an edge atom back over an “atop” site in the layer below (see Fig. 1). The relatively large deposition window size ( $b=\sqrt{2}a_1$ ) for [110] steps also tends to decrease the overall uphill funneling probability.

#### B. Uphill funneling probability $P'_{up}$ for deposition on the upper terrace

We now consider the probability  $P'_{up}$  that an atom deposited within a window of width  $b'$  on the upper terrace, remains on the upper terrace. Figure 3 shows a summary of our results for  $P'_{up}$  as a function of the incident atom kinetic energy  $K_i$  for both [001] steps (filled symbols) and [110] steps (open symbols) on Cu(110), Ag(110), and Al(110). As can be seen, in all cases relatively large values of  $P'_{up}$  ( $P'_{up} \geq 0.8$ ) are obtained thus indicating that “knockout” and/or exchange effects are relatively infrequent. However in contrast to the case of deposition beyond the step edge, in general the values of  $P'_{up}$  for [001] steps are somewhat larger than for [110] steps. This is consistent with the fact that the knockout process requires atoms to “detach” from the step and that atoms at the [001] step edge are more strongly bonded with the upper terrace than atoms at the [110] step edge. In addition, we note that as for the case of deposition beyond the step edge in general we find  $P'_{up[001]}^{Cu} > P'_{up[001]}^{Ag} > P'_{up[001]}^{Al}$ . In particular, for atoms deposited with average kinetic energy  $\bar{K}_i = 2k_B T_m$  beyond a [001] step we find,  $P'_{up[001]}^{Cu} = 0.95 \pm 0.01$ ,  $P'_{up[001]}^{Ag} = 0.93 \pm 0.01$ , and  $P'_{up[001]}^{Al} = 0.80 \pm 0.01$ . Similarly for atoms deposited beyond a [110] step we find,  $P'_{up[110]}^{Cu} \approx$



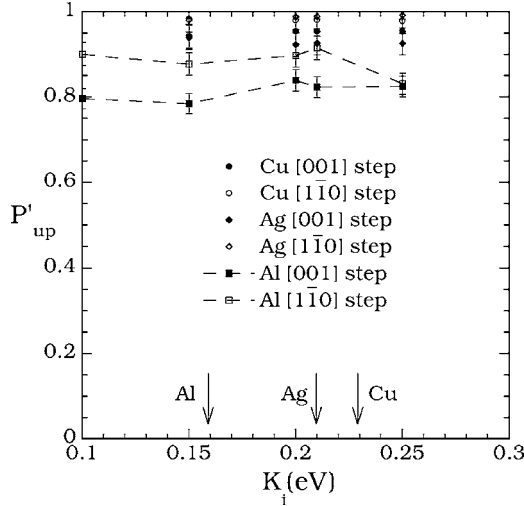


FIG. 3. Uphill funneling probability  $P'_{up}$  of incoming atoms deposited within a window of width  $b'$  on the uphill side of a step edge. Symbols are the same as in Fig. 2.

$$=0.98 \pm 0.01, P'_{up[110]}^{Ag} = 0.99 \pm 0.01, \text{ and } P'_{up[110]}^{Al} = 0.88 \pm 0.01.$$

Table I shows a summary of our results for the overall uphill funneling probability  $P_{av} = (P_{up} + P'_{up})/2$  for [001] and [110] steps on Cu(110), Ag(110), and Al(110). As can be seen, for the case of [001] steps, the overall uphill funneling probabilities are significantly higher than predicted by downhill funneling (DF). However, for the case of [110] steps, one has  $P_{av} \approx 1/2$  which is essentially the same as for downward funneling. Also shown in Table I are the corresponding mound slopes calculated using the expressions,<sup>9</sup>

$$m_0^{[001]} = \frac{1}{8(1 - P_{av})}, \quad (1a)$$

$$m_0^{[110]} = \frac{\sqrt{2}}{16(1 - P_{av})}. \quad (1b)$$

which were derived based on the assumption of a large ES barrier and in the absence of detachment from steps.

We note that in recent experiments on Al/Al(110) growth at 400 K, anisotropic hut clusters with large mound angles corresponding to  $m_0^{[001]} = 1$  [(100) facet] and  $m_0^{[110]} = 1/\sqrt{2}$  [(111) facet] were observed. Using Eq. (1), this corresponds to values of the overall uphill funneling probabilities ( $P_{av}^{[001]} = P_{av}^{[110]} = 7/8$ ) which are significantly larger than ob-

TABLE I. Overall uphill funneling probabilities  $P_{av}$  along with corresponding selected slopes calculated using Eq. (1) for the case of irreversible growth and large ES barrier.

	Cu	Ag	Al
$P_{av}^{[001]}$	0.72	0.69	0.58
$P_{av}^{[110]}$	0.53	0.52	0.46
$m_0^{[001]}$	0.44	0.40	0.30
$m_0^{[110]}$	0.19	0.18	0.16

tained in our simulations. This indicates that the large mound slopes observed in these experiments cannot be explained by the effects of short-range attraction but must be explained by other effects which are not included in Eq. (1) such as the existence of uphill diffusion of atoms at step-edges.<sup>13</sup> However, since the calculated barriers for uphill diffusion for Al(110) are relatively large, e.g., 0.60–0.67 eV,<sup>13</sup> at lower temperatures such “uphill diffusion” is likely to be inoperative. Accordingly, our results should be useful in explaining the observed mound slopes at such temperatures.

#### IV. CONCLUSION

We have presented the results of molecular dynamics simulations carried out in order to determine the uphill funneling probabilities for atoms deposited near step edges on the Cu(110), Ag(110), and Al(110) surfaces. As was previously found for the case of deposition on metal (100) and (111) surfaces,<sup>8,9</sup> our results for [001] steps indicate that the effects of short-range attraction can significantly enhance the degree of uphill funneling. As a result, the surface roughness and corresponding selected mound-angle can be significantly enhanced due to short-range attraction. However, due to geometric effects, for [110] steps the amount of uphill funneling is negligible. As a result, the total uphill funneling probability  $P_{av}$  for [110] steps is essentially the same as in the case of downward funneling. Thus, in the absence of detachment from steps and in the case of a large Ehrlich-Schwoebel barrier, one expects that the resulting mound slopes will be significantly larger for steps along the [001] direction than for steps along the [110] direction. This is in qualitative agreement with experimental results for Ag/Ag(110) (Ref. 11) and Al/Al(110) (Ref. 12) over a relatively large range of temperatures.

We have also compared the corresponding predicted mound slopes using Eq. (1), with experimental results for Al/Al(110) growth at 400 K in which anisotropic hot clusters with (111) and (100) facets were observed.<sup>12,13</sup> Our results indicate that while short-range attraction can enhance the kinetic instability for [001] steps, it is not sufficient to explain the large mound slopes [(111) facets] observed at 400 K. These results support the recent suggestion that some other process such as uphill diffusion at step edges<sup>13</sup> is likely to play an important role at this temperature. However, at somewhat lower temperatures for which the detachment of adatoms from step edges can be ignored, we expect that the effects of short-range attraction will play an important role in determining both the selected mound angle as well as the early stages of mound development in epitaxial growth.

#### ACKNOWLEDGMENTS

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