# Step-Adatom Attraction as a New Mechanism for Instability in Epitaxial Growth

Jacques G. Amar and Fereydoon Family
*Department of Physics, Emory University, Atlanta, Georgia 30322*
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We show that short-range attraction of adatoms towards clusters and ascending steps leads to an instability towards mound formation in epitaxial growth. This instability is studied both analytically and via Monte Carlo simulations on bcc/fcc(100) surfaces. The origin of this instability in terms of second-layer nucleation and its implications for surface morphology and interpretation of recent experiments are also discussed. [S0031-9007(96)01674-2]

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The key to understanding epitaxial growth of materials is the identification and elucidation of processes which control the evolution and the morphology of the surface. Since atomic diffusion is the dominant dynamical process on the surface, much effort has been made to determine the rates of different atomistic diffusive processes on surfaces. For example, measurements of island nucleation, field-ion-microscopy (FIM) studies of atom migration, and theoretical calculations have all been devoted to the determination of energy barriers for diffusion on surfaces.

In detailed FIM studies of adatom diffusion on the Ir(111) surface, Wang and Ehrlich [1] have found that there exists a short-range attractive interaction between an adatom diffusing on a terrace and a cluster. In particular, adatoms within a few nearest-neighbor spacings from a cluster were found to diffuse rapidly towards the cluster. This attraction was found to be independent of cluster size and to lead to the rapid incorporation of adatoms near clusters and ascending step edges. The cause of this effect, which has also been observed in embedded atom calculations of diffusion barriers on metal (100) surfaces [2], is an alteration in the potential landscape in the vicinity of a cluster (see Fig. 1). Although it was pointed out that this effect increases the capture radius for a cluster, the consequences of this attraction on epitaxial growth have not been investigated. However, it has already been demonstrated [3,4] that the existence of a potential *barrier* for an adatom to diffuse from the top of a step to the layer below (often referred to as the Ehrlich-Schwoebel barrier or step barrier [5]) does lead to a morphological instability in epitaxial growth. The question is, does short-range step-adatom or cluster-adatom attraction also have consequences for the surface morphology in epitaxial growth?

In this Letter we discuss the effects of step-adatom attraction on the stability and evolution of epitaxial growth. We show that (in the absence of desorption) this effect causes an instability that leads to mound formation even in the absence of an Ehrlich-Schwoebel barrier. In particular, we present an analytic calculation which clearly indicates the existence of an instability due to step-adatom attraction. We also present the results of kinetic Monte Carlo simulations which verify the existence of this instability. Finally, we discuss the physical origin of this instability and its possible implications on the interpretations of various experiments.

In order to study the effects of step-adatom attraction on a specific model, we consider the stability of a bcc(100) [or equivalently fcc(100)] surface in the presence of step-adatom attraction. The choice of such a surface is motivated partly by the existence of a variety of experiments on (100) metal surfaces in which unstable growth leading to mound formation has been observed [6,7]. For simplicity we consider a quasi-one-dimensional model consisting of a regular stepped bcc(100) surface [corresponding to a $(1\ 0\ l)$ facet] with infinitely long straight steps along the [001] direction (see Fig. 1) with terrace length $l = 1/m$ (in units of $1/2$ the next-nearest-neighbor distance) where $l = 2j + 1$ and $j$ is the number of exposed rows in each (100) terrace and $m$ is the slope of the surface. We also assume irreversible attachment at ascending steps (site 0). Such a model is appropriate in the case of relatively straight steps when the mound size is significantly larger than the terrace size, and has previously been used [8] to study the critical temperature for mound formation in the case of a step barrier. We note that while our calculations correspond to a specific

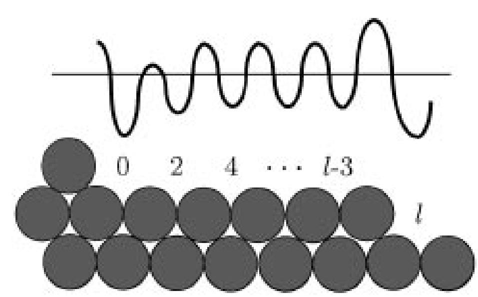


FIG. 1. Diagram showing stepped bcc/fcc (100) surface with slope $m$ (terrace width $l = 1/m$) and straight step edges along the (001) axis (side view). Even sites correspond to fourfold-hollow sites on terrace. Also shown is a schematic of the potential surface showing decreased potential barrier due to step-adatom attraction near the ascending step along with a possible step barrier at the descending step.

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crystal surface we expect the qualitative behavior not to depend on the details of the crystal geometry.

In order to include the effects of short-range step-adatom attraction in our calculation we assume that an adatom one step away from an ascending step (site 2 in Fig. 1) experiences a diffusion bias in which the probability ratio of a hop to the left (towards the step) versus a hop to the right is given by $R'$, where $R' > 1$ due to step-adatom attraction. Similarly, we consider the possibility of a step barrier by including a diffusion bias on an adatom at site $l - 3$ where the ratio of a hop to the left (away from the step) versus a hop to the right is given by $R$. Accordingly, our model can be mapped to a one-dimensional random walk between two absorbing barriers (sites 0 and $l$ in Fig. 1) with biased diffusion at site 2 due to step-adatom attraction and at site $l - 3$ due to a step barrier. We note that due to the crystal geometry adatoms are allowed to occupy only the fourfold-hollow sites corresponding to the even sites shown in Fig. 1, while freshly deposited atoms at a step edge (sites $l - 2$ and $l - 1$ in Fig. 1) are assumed to cascade with probability $c_1$ and $c_2$, respectively, to the lower step attachment site 0, and with probability $1 - c_1$ and $1 - c_2$ to the upper step. Typically, downward funneling [9] at a straight step edge implies that $c_1 = 1/2$ and $c_2 = 1$. Here we consider the more general case of arbitrary $c_1$ and $c_2$. This effect leads to a downward current which stabilizes the mound angle in the case of an instability [10].

In order to investigate the presence of an instability, we calculate the surface current $J$ as a function of the slope $m$. The existence of a negative (downhill) surface current for small slopes implies a positive surface tension and a stable surface, while a positive (uphill) surface current implies a negative surface tension and an unstable surface [3,11].

For a given slope $m$, the surface current per particle ($J$) may be estimated by multiplying the probability $m$ that an atom will be deposited at a given site by the average (signed) distance traveled before incorporation at an ascending or a descending step [12]. The total surface current may be divided into two contributions (see Fig. 1). The first contribution $[J_1 = -(2c_1 + c_2 - 1/2)m]$ comes from processes which lead to immediate attachment of a freshly deposited adatom at a step edge (sites 0 or $l$). The second contribution corresponds to those processes in which diffusion on the terrace takes place before attachment to a step edge and involves the probability $P_i = 1 - [2 + 2(i - 1)R']/[(l + 2R - 5)R' + 2]$ that a random walker deposited at site $2i$ will attach to the ascending step. Combining both contributions, we obtain

$$J = \frac{(2R - 1)R' - 2 + m(4 + 5R' - 2RR'[2(c_1 + c_2) + 1])}{2(R' + m[(2R - 5)R' + 2])}, \quad (m \leq 1/7). \tag{1a}$$

For larger slope, the distinction between the asymmetry parameter due to step-adatom attraction and due to a step barrier is no longer meaningful, and setting $R'$ equal to 1 and replacing $R$ by $R'$ in (1a) we obtain

$$J = \frac{(2R' - 3) + m(9 - 2R'[2(c_1 + c_2) + 1])}{2[1 + (2R' - 3)m]}, \quad (1/5 \leq m \leq 1/3). \tag{1b}$$

Equation (1) implies that for $R > 1/2$ there exists a critical value of the step-adatom attraction $R'_c = 2/(2R - 1)$ such that for $R' > R'_c$ the surface current is positive for small $m$ leading to a mound instability. We note that $R'_c$ is independent of the parameters $c_1$ and $c_2$ which control the funneling near a step edge. The reason is that the effects of these parameters vanish in the limit of small slopes. In particular, (1) implies that even without a step barrier ($R = 1$) step-adatom attraction with $R' > 2$ will lead to a mound instability.

From (1) the selected mound angle $m_0$ can be calculated by finding the value of the slope for which the current is zero [11]. In particular, in the absence of a step barrier ($R = 1$) but in the presence of strong short-range step-adatom attraction ($R' = \infty$), Eq. (1) implies that $m_0 = 1/[1 + 2(c_1 + c_2)]$. This is the same as was previously found for the case of a very large step barrier without step attraction [10]. We note that in the above calculation we ignored the possibility of islanding on a terrace. This leads to a finite diffusion length $\sigma$ which sets the initial length scale in the case of an instability. This also implies that for very small slope the surface current will be cut off by the diffusion length and will go to zero as $m$ goes to zero [13].

In order to verify the presence of a mound instability due to step-adatom attraction, we have carried out simulations for growth on a fcc/bcc(100) surface without a step barrier but with a short-range step-adatom attraction. As in previous simulations [10], adatoms are allowed to occupy only fourfold-hollow sites and diffuse (hop) over the bridge sites to nearby fourfold-hollow sites. Also as in previous studies [8,10], the simplest form of downward funneling corresponding to $c_1 = 1/2$ and $c_2 = 1$ was used. In our simulations, we assume a hopping rate for isolated adatoms on a terrace $D = D_0 e^{-E_a/k_B T}$ where $E_a$ is the activation energy. Although in our simulations we assume irreversible attachment to islands and ascending step edges, we also allow island relaxation by including edge diffusion of single-bonded atoms along the edges of islands and around kinks at a rate given by $D_e = De^{-E_e/k_B T}$. Simulations were carried out at room temperature for a variety of different deposition rates [corresponding to experiments on Fe/Fe(100) deposition [7,14]] including a *fast* deposition rate ($F = 0.51$ ML/sec) and a *slow* deposition rate ($F = 0.0257$ ML/sec) with $D_0 = 1.8 \times 10^{11}$ sec$^{-1}$, $E_a = 0.45$ eV, and $E_e = 0.1$ eV [15]. Step-adatom attraction was included by introducing a diffusion bias such that for an adatom one step away from a cluster or ascending step the ratio of the probability for hopping and bonding to the step edge versus the probability for hopping away from the step edge is given by $R'$.

Figure 2 shows a comparison of the surface morphology both with and without step-adatom attraction obtained after 100 layers have been deposited. As expected, without step-adatom attraction the surface has the usual self-affine-fractal morphology indicating no typical length scale or feature size [16]. However, in the presence of step-adatom attraction large mounds with a characteristic length scale are clearly visible, indicating the presence of an instability. As evolution proceeds, these mounds continue to coarsen and increase in size as in the case of the Erhlich-Schwoebel instability [4]. Analysis of similar images indicates that at late times the average mound slope is close to $1/4$ in agreement with the prediction of Eq. (1).

In order to further quantify these results we have calculated the circularly averaged height-height correlation function $G(r) = \langle \tilde{h}(\mathbf{0}) \tilde{h}(\mathbf{r}) \rangle_C$ where $h(\mathbf{r})$ is the height in layers at site $\mathbf{r}$, and $\tilde{h}(\mathbf{r}) = h(\mathbf{r}) - \langle h \rangle$, where $\langle h \rangle$ is the average film thickness or layer height. We also calculated the root-mean-square surface width $w = [G(0)]^{1/2}$. The average feature separation ($2r_c$) was estimated by calculating $r_c$, the position of the first zero crossing of $G(r)$. We also calculated the ratio $w/r_c$ which in the case of mound formation may be taken to be proportional to the tangent of the average mound angle. These results were also used to calculate values for the effective coarsening exponent $n$ ($r_c \sim \langle h \rangle^n$) and kinetic roughening exponent $\beta$ ($w \sim \langle h \rangle^\beta$) [16].

Figure 3 shows the aspect ratio $w/r_c$ as a function of film thickness corresponding to the growth conditions in Figs. 2(a) and 2(b). A finite saturation value of $w/r_c$ is indicative of mound formation while a small or decreasing value of $w/r_c$ is indicative of a self-affine surface. As can be seen, for the case of deposition *without* attraction to ascending steps the value of $w/r_c$ is very small in agreement with the morphology shown in Fig. 2(a). In contrast, inclusion of only a moderate amount of step-adatom attraction leads to a much larger mound angle ratio which increases with film thickness and appears to saturate at large thickness. The corresponding value of the mound coarsening exponent is $n \simeq 0.19$, which is consistent with that obtained in a variety of experiments and in previous simulations with a step barrier [10].

We have also studied the surface width as a function of film thickness corresponding to the growth conditions in Fig. 2. Without step-adatom attraction, the surface width is relatively small and there are large oscillations indicative of quasi-layer-by-layer growth. A power-law fit gives a small value of the kinetic roughening exponent $\beta$ ($\beta \simeq 0.11$) which is consistent with Edwards-Wilkinson, logarithmic behavior [17]. In the case of a moderate amount of attraction to ascending steps ($R' = 10$), the surface width is much larger and grows steadily with increasing film thickness, indicating an unstable growth. A fit over the range 10–100 ML gives an effective roughening exponent $\beta \simeq 0.4$ which is significantly larger than for the case without step-adatom attraction. The large value for $\beta$ is due to the increase in the mound angle in this regime as shown in Fig. 3 and is similar to what has been previously observed [10] in the case of an instability due to a weak step barrier.

We have also carried out simulations with significantly larger as well as smaller values of the step-adatom attraction parameter. Interestingly, the kinetic behavior for $R' = 10^5$ is very similar to that for $R' = 10$, while the values of the mound angle ratio and mound angle are only slightly higher. This is in agreement with Eq. (1)

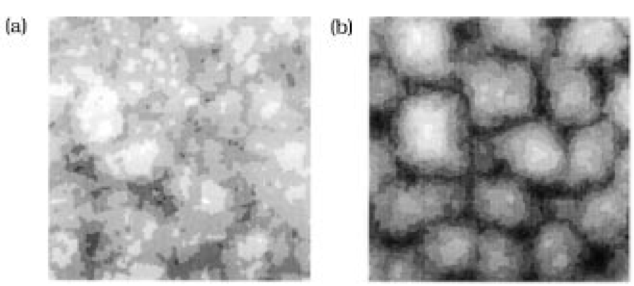


FIG. 2. Gray-scale plots ($128 \times 128$) of surface morphology obtained after 100 ML deposition without a step barrier ($R = 1$, $E_B = 0$) for the case of *fast* deposition. Pictures correspond to a portion of a $256 \times 256$ system. (a) No step-adatom attraction ($R' = 1$). (b) Step-adatom attraction with $R' = 10$.

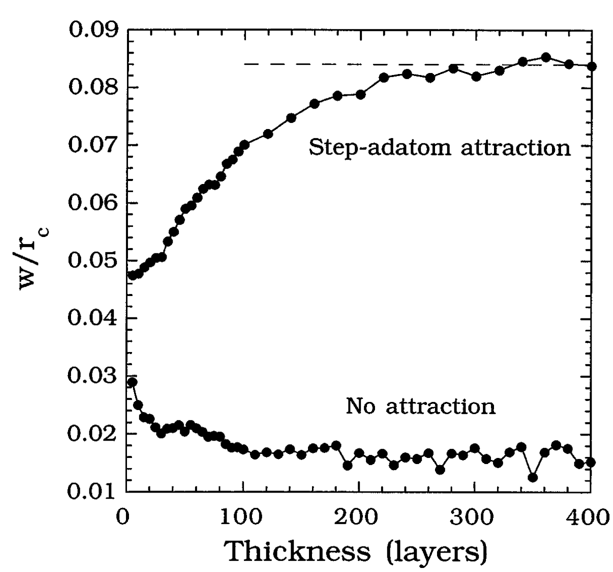


FIG. 3. Mound angle ratio $w/r_c$ as a function of film thickness with step-adatom attraction ($R' = 10$) and without step-adatom attraction ($R' = 1$).

which predicts a very weak dependence of $m_0$ on $R'$, for $R'$ significantly larger than $R'_c$. Simulations for smaller values of $R'$ indicate a critical value for mound formation ($R'_c \simeq 1.5$) which is close to but slightly lower than predicted by Eq. (1a).

What is the physical origin of the instability due to step-adatom attraction? As noted in Ref. [1], the existence of step-adatom attraction increases the island capture radius so that the first-layer island density is reduced. This leads to larger islands for a given coverage and enhances the probability of second-layer nucleation leading to multilayer growth and mound formation. This picture is confirmed by our simulations which show a reduction in the first-layer island density in the presence of step-adatom attraction. Our simulations also indicate that with decreasing deposition rate (increasing $D/F$) the relative reduction in the island density due to step-adatom attraction decreases. This implies that as the ratio of the diffusion rate to deposition rate increases, although the selected mound angle does not change, the rate of mound formation decreases.

We now consider the implications of step-adatom attraction on experiments in epitaxial growth. In general, we expect both the effects of a (positive or negative) step barrier and (attractive or repulsive) step-adatom interaction to be present. Therefore, effects which have in the past been ascribed to the step barrier may in fact be due to a combination of a step-barrier and step-adatom attraction. We note that consideration of the effects of step-adatom attraction may also lead to a new mechanism by which surfactants [18] may promote stable growth. In particular, the presence of surfactants may passivate some of the bonds at a step edge, leading to a decreased step attraction, or even repulsion at ascending steps. Such an effect can reduce or eliminate the instability due to step-adatom attraction or a step barrier and lead to layer-by-layer growth.

In conclusion, we have shown that the presence of step-adatom attraction leads to a new mechanism for instability in epitaxial growth. Our results indicate that such an effect may play a significant role in addition to the Ehrlich-Schwoebel barrier in determining surface morphology and in the interpretation of experiments.

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