Edge Diffusion during Growth: The Kink Ehrlich-Schwoebel Effect and Resulting Instabilities

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The morphology of surfaces of arbitrary orientation in the presence of step and kink Ehrlich-Schwoebel effects (SESE and KESE) during growth is studied within the framework of a model in which steps are continuous lines, and is illustrated by a simple solid-on-solid model. For vicinal surfaces KESE induces an instability often stronger than that from SESE. The possibility of stable kink flow growth is analyzed. Fluctuations can shift the stability threshold. KESE also induces mound formation. [S0031-9007(99)09023-7]

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Control of surface morphology during molecular-beam epitaxy (MBE) is of immense technological interest. One may want to produce either atomically flat or nanostructured surfaces. Small energy barriers can affect growth properties dramatically. In recent years, numerous papers have focused on the instabilities induced by the step Ehrlich-Schwoebel effect (SESE)—an asymmetry in energy barriers favoring the attachment of atoms arriving at a step from the lower side. This Letter concerns the analogous, largely unstudied (exceptions include Refs. [1–3]), kink Ehrlich-Schwoebel effect (KESE) for atoms diffusing alongside step edges near kinks or corners, and, more generally, to the consequences of diffusion along the steps in growth models.

SESE influences surface morphology during growth in three main ways: (a) It induces an uphill current, destabilizing nominal surfaces [4]. (b) Vicinal surfaces with large enough slope m become *stabilized* [5] against step bunching because the uphill Schwoebel current $j_s(m)$ is a decreasing function. (c) Steps suffer a morphological instability of the Mullins-Sekerka type [6]: the Bales-Zangwill (BZ) instability [7].

The essential features of (a) and (b) can be analyzed by evaluating $j_s(m)$ [8,9]. Politi and Villain (PV) [8] (whose notation we often follow) have shown that growth from nominal surfaces should lead to mounds and cracks. Investigation [9–11] of the BZ instability on vicinal surfaces showed that, following the initial instability leading to ripples, a secondary instability occurs resulting ultimately in mounds.

KESE can also destabilize or stabilize steps by the 1D analog of (a) or (b), the latter (b) leading to *kink* flow. We include possible nucleation of kinks, neglected in an earlier study of (b) [1], and the role of crystal symmetry (specifically, the fourfold symmetry of a simple cubic crystal). We show that the morphological instability of steps is typically driven more by KESE than SESE. We then determine the range of step orientations that are stable during growth. Finally, we show that KESE can also lead to mound formation.

On a vicinal surface, the ith step is a continuous line $z_i(x,t) = i\ell + \zeta(x,t)$, with ℓ the mean terrace width. We assume unit lattice spacing throughout. At low enough temperature T, detachment from the steps becomes negligible [12,13]. At the steps, mass conservation implies

$$\partial_t \zeta = F_s - \partial_x J, \tag{1}$$

where F_s [more generally $F_s(x)$] is the incoming flux of atoms from both adjoining terraces. Capital-letter variables denote properties along the step edge, while lowercase variables relate to the conventional quantities in one dimension higher. We can decompose the mass current J along the step: $J = J_k + J_e + J_n + J_{SB}$, where J_k is a possibly destabilizing current coming from the KESE, J_e, J_n are stabilizing contributions, and J_{SB} breaks the front-back symmetry of the steps [8].

We first consider a step whose average orientation is [100]. Because of KESE, atoms landing on straight, close-packed parts of a step (1D "terraces"—viz. flat [100] edges) attach more often to an up kink than to a down kink. We can calculate the resulting mass current along the step, in the up-kink direction, using discrete rate equations. Each step adatom jumps with equal rate $f_0 \exp(-W_d/k_BT)$ in either direction. An additional attachment barrier (kink Schwoebel barrier) is introduced when jumping down kink, giving jump rate $f_0 \exp(-W_s/k_BT)$. If an atom lands directly on a kink site, it attaches there directly, and does not contribute to J. The stationary mass current along [100] edges of length L is $J_k^{\text{discrete}} = (F_s/2)(L-1)L_s/(L_s + L)$, where $L_s \equiv \exp(\Delta) - 1$ is the kink Schwoebel length, and $\Delta \equiv (W_s - W_d)/k_BT$. In the continuum description of the surface, the 1D step "slope" (denoted hereafter "twist") relative to the [100] direction is (locally) $M \equiv \partial_x\zeta$. In analogy to PV, we account for nucleation of new edges by writing $N \simeq |M| + L_c^{-1}$ for the step density, L_c being the characteristic length of an edge above which nucleation occurs. L_c, whose twist dependence is neglected here [8], depends on L_s and the flux F_s incident on [100] steps via [8] $L_c^4(1 + 6L_s/L_c) = 12D_s/F_s$, where D_s is the diffusion constant along $\langle 100\rangle$ edges. Then

$$J_k = \frac{F_s}{2}\,\frac{(1-|M|)L_s}{[1 + L_s(|M| + L_c^{-1})]}\,\frac{M}{(|M| + L_c^{-1})}. \tag{2}$$

Equation (2) differs from the result of PV by the factor $(1-|M|)$: J_k vanishes for $|M| = 1$ [14].

Equation (2) holds for $|M| \leq 1$. When $|M| > 1$, adatoms attach to the step on [010] edges. A contribution to the current is obtained if the atom attaches to the kink above it (cf. Fig. 1):

$$J_{k2} = \frac{F_s^{\perp}}{4} \frac{(1 - |M|)M}{L_s + |M|} \qquad (|M| > 1). \qquad (3)$$

This current is destabilizing but *vanishes* for strong KESE (large L_s). $F_s^{\perp}$ designates the flux of atoms incident on [010] edges. Nucleation on such steps is neglected since $F_s^{\perp}$ is small for large $|M|$ due to step crowding.

There are very few calculations of the energy barriers needed to estimate the kink Ehrlich-Schwoebel barrier, virtually none for semiconductors. For late transition metals, this barrier is 0.1 eV on {001} [12] and {111} [15] surfaces and 0.02 eV on Al{111} [13]; we find $L_s \approx 50$ at 300 K, and $L_s \approx 2$ at 1000 K on late transition metals (respectively, $L_s \approx 1.2$ and 0.3 for Al {111}). In MBE the typical incoming flux $F \simeq 1$ monolayer/sec (ML/s). Taking $D_s \sim 10^6$–10^8 s^{-1} and $\ell = 10$, so that $F_s \approx F\ell \approx 10$ ML/s, we find $L_c \simeq 100$. In the following, we consider arbitrary values of L_s and L_c, emphasizing $L_s < L_c$, the weak-KESE case.

The second contribution to the current J_e comes from the stabilizing effect of step stiffness $\tilde{\gamma}(M)$ (via the Gibbs-Thomson formula): $J_e = -(D_M c_{eq}^s / k_B T)\partial_s(\tilde{\gamma}\kappa)$; κ is the step curvature, s is the arclength, c_{eq}^s is the equilibrium concentration of adatoms at the step edge, and D_M is the macroscopic diffusion constant of an atom along a kinked step. For a step with kink density N, we have $D_M = D_s/(1 + NL_s) \approx D_s/[1 + (|M| + L_c^{-1})L_s]$, using the nucleation-based estimate for N. This leads to

$$J_e = D_M \frac{\partial_x}{(1 + M^2)^{1/2}} \left(\frac{\Gamma(M)\partial_x M}{(1 + M^2)^{3/2}} \right), \qquad (4)$$

where $\Gamma(M) \equiv c_{eq}^s \tilde{\gamma}(M)/k_B T$.

Another stabilizing effect enters when M is small, due to the stochastic nature of nucleation. In the linear regime PV [8] showed $J_n \simeq K\partial_{xxx}\zeta$ ($\equiv K\partial_{xx}M$), which is valid only when $L_s \ll L_c$ (in which case $K = F_s L_c^4 = 12D_s$). In this limit, $J_e \simeq D_s \Gamma \partial_{xxx}\zeta$. In the simplest model, breaking bonds costs the kink energy ϵ. From experiments [16], $T_k \equiv \epsilon/k_B \sim 1000K$. At $T < T_k$, we find $\Gamma(0) \simeq \exp[-\epsilon/k_B T]/2 \ll 1$. Thus, $J_n \gg J_e$ when the mean local twist is near zero. When M is larger, nucleation is rare, due to the high kink density of steps, and J_e dominates. For stronger KESE, both D_M and K decrease, but the exact form of K is not known.

We add the current J to the usual Burton-Cabrera-Frank (BCF) model [17]. No desorption is allowed. Moreover, attachment of terrace adatoms to steps is irreversible, so that the equilibrium concentration on terraces vanishes. Thus, on the terraces and at the steps, respectively,

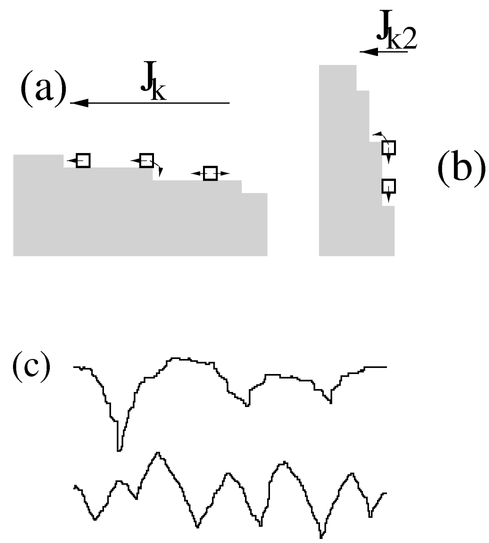

FIG. 1. (a) Schematic of the destabilizing step-edge current J_k [cf. Eq. (2)] due to KESE; (b) similar behavior of J_{k2} for highly twisted ($|M| > 1$) edges [cf. Eq. (3)]. (c) Shape of unstable steps on a vicinal surface from solid-on-solid simulations for parameters of set I (upper curve) and set II (lower curve) (see text).

$$\partial_t c = D\nabla^2 c + F, \qquad -D\partial_n c = \mp \nu_{\pm} c, \qquad (5)$$

where + (−) denotes the lower (upper) side of the step, while ∂_n indicates a derivative normal to the step. Invoking the customary quasistatic approximation, we take $\partial_t c = 0$. We also assume—as expected in most experiments—that attachment kinetics is instantaneous at the lower side: $\nu_+ = \infty$ (see Ref. [18] for the general case), and denote $l_s \equiv D/\nu_-$. In Eq. (1), $F_s = [-D\partial_z c]_+^-$. For steps of any average twist M_0, the contribution to J along the [100] and [010] directions are calculated, and projected along the corresponding step direction, at an angle $\tan^{-1} M_0$ from [100].

We next perform a linear stability analysis on the model, i.e., we perturb a regular train of straight steps by a small meander ζ, and determine its rate ω ($\zeta \sim e^{\omega t}$) of growth or decay. Since SESE induces a repulsion of diffusive origin between steps [10], the most unstable mode is when all steps meander in phase. Entropic repulsion (noncrossing of steps), important when $l_s \to 0$, also favors this in-phase mode. In the long wavelength $\lambda = 2\pi/k$ limit, we have

$$\omega = \frac{F\ell}{2} [(\ell^{-1} + l_s^{-1})^{-1} + g(M_0)]k^2 - Ak^4. \qquad (6)$$

The positive A reflects stabilizing effects related to J_e and J_n. While $(\ell^{-1} + l_s^{-1})^{-1}$—the cutoff length associated with terrace diffusion—accounts for the destabilization due to SESE, the even function $g(M_0)$ describes the effects of KESE on stability:

$$g(M_0) = \frac{\partial}{\partial M} \left[\frac{1 - |M'|}{(1 + M'^2)^{1/2}(1 - M'M_0)(L_s^{-1} + L_c^{-1} + |M'|)} \left(\frac{M'}{L_c^{-1} + |M'|} + \frac{M_0}{2L_s} \right) \right]_{M=0}, \qquad (7)$$

with $M' \equiv (M - M_0)/(1 + MM_0)$. From its positive value at $M_0 = 0$ [cf. Eq. (8)], g plunges through the abscissa axis (at $M_0 = M_{\min} \ll 1$) to a relatively shallow minimum at $M_0 = M^*$ and then increases gradually toward a small negative value at $M_0 = 1$.

For the aligned case $M_0 = 0$, two instabilities occur simultaneously: (i) That of BZ [7] stems from preferred attachment of adatoms to step protuberances. Combined with the asymmetry of attachment, this leads to a morphological instability studied [7,9,10] for vicinal surfaces using the BCF model [17]. (ii) A novel instability comes from the up-kink (destabilizing) current induced by KESE—the 1D analog of the mound formation created by SESE. The latter dominates [cf. Eq. (6)] when

$$(\ell^{-1} + l_s^{-1})^{-1} < g(0) = L_c(L_c^{-1} + L_s^{-1})^{-1}. \quad (8)$$

With $L_c \approx 100$ and $L_s \approx 1\text{–}10$, Eq. (8) shows that only when the step spacing ℓ exceeds $10^2\text{–}10^3$ does the BZ instability dominate. Thus, the instability observed experimentally [19] on vicinal surfaces with $M_0 = 0$ is probably due to KESE. Equation (8) gives a lower limit for the range of relevance of the BZ instability. An upper bound comes from nucleation on terraces, which at low T is likely to occur for $\ell > 10^3$. Around $M_0 = 0$ (where $J_n \gg J_e$) the initial wavelength of the instability (starting from straight steps) will thus be determined by nucleation, not by line tension. For $L_s \ll L_c$, the most unstable wavelength is [8] $\lambda_u \simeq (L_c^3/L_s)^{1/2}$. With $L_c \approx 100$ and $L_s \approx 1\text{–}10$, we find $\lambda_u \approx 10^3\text{–}3 \times 10^2$. In the late stages of the instability, M_0 increases and J_e influences the unstable step profile.

For azimuthally misoriented vicinal steps ($M_0 \neq 0$), KESE may cause stable kink flow. The effective dynamic repulsion between kinks is the 1D analog of that which stabilizes step flow of vicinal surfaces [5,10]. If the position of a kink with respect to its (like-signed) neighbors fluctuates from an initial uniform distribution, the kink velocity increases or decreases to compensate. This phenomenon has already been studied by Aleiner and Suris [1] in the absence of nucleation of new kinks, and neglecting the discrete effects that intervene when $M \sim 1$.

A criterion for the existence of stable kink flow can be derived from linear analysis of our model. Small twists are always unstable due to the combined effects of the BZ and the KESE instabilities for $M_0 \sim 0$. Large twists (M_0 can always be chosen so that $|M_0| \leq 1$) are unstable if the stabilization due to KESE for $|M_0| = 1$ described in Fig. 3 (below) cannot overcome the BZ instability, i.e., if $(\ell^{-1} + l_s^{-1})^{-1} > g(1)$. Given $l_s > 1$, this criterion is always satisfied, and there is a finite range of stable twists centered around the most stable twist M^*.

Because of statistical fluctuations, linearly stable steps will sample a wide range of twists, and so may reach the unstable region and develop instability. The new, more stringent stability criterion is that the twist variation needed to develop the instability should exceed the typical small-k twist fluctuations (calculated with Langevin formalism [10]) at M^*. When $l_s > 1$ this takes the following form:

$$(\ell^{-1} + l_s^{-1})^{-1} < l^* \equiv -g(M^*) - 2^{-3/2} g''(M^*)^{1/2}. \quad (9)$$

The g'' term in Eq. (9) gives the stochastic shift of the deterministic stability criterion (obtained with the g term alone). Since l^* is apparently always negative, steps are always unstable in the presence of SESE.

For vanishing SESE ($l_s < 1$) and $L_s > 1/2$, linear stability analysis shows steps are stable if $M > M_{\min}$ [where $g(M_{\min}) = 0$]. If $L_c, L_s \gg 1$, then $M_{\min} \simeq (L_c L_s)^{1/2}$. This threshold value increases due to fluctuations; mimicking Eq. (9) we find step stability when $M_0 > \tilde{M} \equiv M_{\min} + (1/2)[-g(M^*)]^{-1/2}$. In Fig. 2, $\tilde{M}$ is plotted as a function of L_c and L_s. In the limit of perfect KESE ($L_s \to \infty$, $L_c \to 0$), steps are unstable, as found in a 1D-model study of step-flow breakdown with perfect SESE [20]. When $M_0 = 1$ the projection of next-nearest-neighbor (NNN) hops along the [110] direction is twice as long as that of nearest-neighbor (NN) hops. Thus, for $L_s = 0$ (i.e., NN and NNN hop rates equal) the latter produces a smaller flux along the [110] direction, leading to a geometrical KESE-induced instability (with kinks along $\langle 100 \rangle$). More generally, when $M_0 = 1$ and $l_s = 0$, steps are unstable if $L_s < 1/2$.

For illustration, we discuss preliminary results of a simple solid-on-solid model: Atoms land randomly on the surface and cannot desorb. Possible hops are picked randomly and are realized with some probability p based on the following rules: (i) The number n of in-plane NN's of the atom cannot decrease. (ii) Atoms freeze once $n > 1$. (iii) When $n = 0$ (adatoms) only NN hops are allowed and $p = 1$. (iv) When $n = 1$ (step adatoms), $p = 1$ for NN hops and $p = \exp[-\Delta]$ for NNN hops.

Since we seek far-from-equilibrium properties, attachment to steps and to kinks can be taken as irreversible (thereby violating detailed balance and removing line-tension effects). The two stabilizing effects are kink flow and random nucleation. Since there is no step Schwoebel

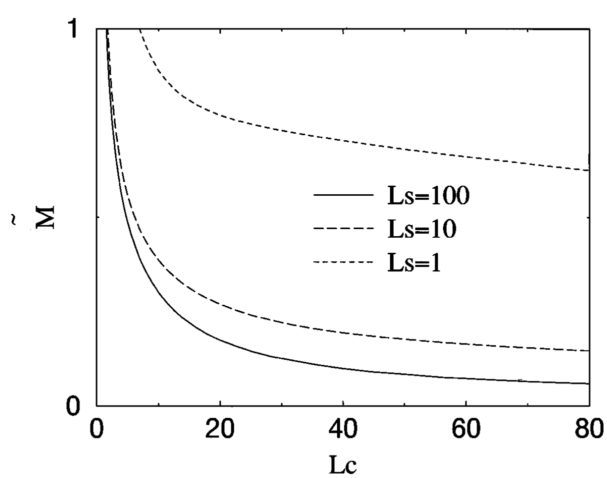

FIG. 2. $\tilde{M}$, the smallest stable twist without SESE, vs the nucleation length, for weak, moderate, and strong KESE.

barrier, steps can be unstable only for small M_0. We have checked this prediction for $F = 2 \times 10^{-4}$. With $\Delta = 2.5$, we have $L_s \simeq 11.2$ and $L_c \simeq 3.7$, implying $M_{\min} \simeq 0.18$. Thus, growth should be stable for $M_0 > \tilde{M} \simeq 0.7$. Simulations show that the steps are still unstable for $M_0 > M_{\min}$ and that step roughness decreases for $M_0 > 0.75$, corroborating predictions.

The step roughening exponent β ($\langle \zeta^2 \rangle^{1/2} \sim t^{\beta}$) has been determined for two sets of parameters. For $F = 10^{-4}$, $\Delta = 0.5$ (set I), we find $\beta = 0.3 \pm 0.05$; with $F = 2 \times 10^{-4}$, $\Delta = 5.0$ (set II), $\beta = 0.57 \pm 0.07$. Figure 1c depicts typical morphologies. The step skewness $\langle \zeta^3 \rangle / \langle \zeta^2 \rangle^{3/2}$ is ~ 1.0, and ~ 0.1, respectively, for sets I and II. The observed front-back asymmetry of step shape only for weak Schwoebel effect is well known [8] and is related to the mass current J_{SB} along the step. More novel is the shape of the mounds and their coarsening. In the weak KESE case (set I), cusps form after some transient period during which steps synchronize their phases. The cusps due to J_{k2} seem to prevent lateral coarsening. When KESE is stronger, a special twist $|M| \simeq 1.5$ [14] is selected, and coarsening is seen. It is unclear whether this regime is transient. The absence of groove formation in set II is related to a vanishing J_{k2} for strong KESE. As predicted above (for $l_s = 0$), an instability is also seen for $M_0 = 1$ and $L_s = 0$.

Even in the absence of SESE, mounds form at long times on vicinal surfaces (as in Refs. [9,10]); however, this limit can prove unattainable, especially for large m. Our simulations with $l_s = 0$, starting from a flat surface, do show mounds, which must be induced by the *kink* uphill current. To see how this occurs, consider a step stabilized by edge diffusion. With no diffusion or attachment bias, atoms landing on a vicinal surface attach to a step in an average position which is the landing site. Since the step meanders due to statistical fluctuations, the adatom will then drift in the uphill direction once it is attached, stabilizing the step, as depicted in Fig. 3. From this drift comes a mound-forming uphill current. Because of the geometrical KESE, mounds have square symmetry with straight steps along $\langle 100 \rangle$ ($\langle 110 \rangle$) when $L_s \ll (\gg)\ 1/2$.

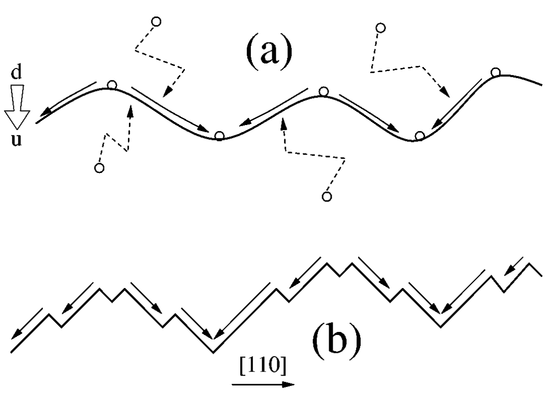

FIG. 3. Schematic showing the origin of the uphill kink Schwoebel current: (a) continuum with mass currents marked; (b) discretized.

In conclusion, we have investigated several consequences of edge diffusion during MBE on stepped surfaces with arbitrary azimuthal orientation. A strong instability appears on vicinal surfaces, over-riding the Bales-Zangwill instability. SESE prevents stable kink flow. Diffusion of atoms along the steps not only affects the morphological stability of the steps, but also can induce up-step mass current leading to mound formation. Nonlinear analysis of the model and extensive simulations are under way to investigate morphology and coarsening of the structures induced by these instabilities [18].

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Note added in proof.—Aspects of KESE have also been observed and studied in simulations by M. V. Ramana Murty and B. H. Cooper (to be published).

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