STEP INSTABILITIES DURING THIN-FILM EPITAXIAL GROWTH

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Summary The surface of a thin crystalline film consists of flat terraces separated by atomic steps. During step-flow growth, adsorbed atoms (adatoms) diffuse on terraces until they attach to steps, causing them to migrate. Two modes of morphological instability are observed: bunching, which leads to regions of high step density separated by wide terraces, and meandering, whereby steps become wavy. A quantitative understanding of the mechanisms underlying the onset and evolution of step instabilities is necessary for the nanoscale patterning, via self assembly, of crystalline surfaces. Experiments indicate that bunching and meandering coexist on metallic and semiconductor stepped surfaces, in contrast to the predictions of the standard Burton–Cabrera–Frank (BCF) model. Herein, a thermodynamically consistent (TC) generalization of the BCF theory that resolves this apparent paradox is presented. In particular, it will be shown that bunching and meandering occur simultaneously whenever the equilibrium adatom coverage exceeds a critical value and are driven by energetics rather than kinetics of step flow.

INTRODUCTION

At the nanoscale, the surface of a thin crystalline film consists of flat terraces separated by atomic steps. During epitaxial growth in the step-flow regime, adatoms diffuse on the terraces until they reach the steps where they incorporate into the bulk by attaching to kinks. By altering its configuration, the attachment of adatoms to a step causes its lateral migration. The collective motion of steps results in the net growth of the underlying film in the epitaxial direction. The diffusion of adatoms can be accompanied by desorption and their attachment to steps by some detachment onto the terraces. Two modes of morphological instability have been experimentally observed. The first mode, step bunching, results in the segregation between regions of high step density (step bunches) and wide terraces. The second mode, step meandering, designates the evolution of step configurations from straight to wavy.

BCF MODEL, EHRLICH–SCHWOEBEL BARRIER, STEP INSTABILITIES

At an intermediate scale, between atomistic and continuum, step-flow growth has been modeled using ideas that trace back to the seminal work of Burton, Cabrera and Frank [1]. In the quasistatic limit, the adatom density ϱ obeys the equation

$$D\Delta\varrho + F - \frac{\varrho}{\tau} = 0, \tag{1}$$

with D the diffusion coefficient, F the deposition flux, and τ the desorption time. Letting $\mathbf{n}$ denote the unit normal to the step, (1) is supplemented by the jump conditions

$$\pm D(\nabla\varrho)^{\pm}\cdot\mathbf{n} = K_{\pm}(\varrho^{\pm} - \varrho_{\rm eq}), \tag{2}$$

where K_+ (K_-) is the adatom hoping rate from the lower (upper) terrace onto the step edge and the step equilibrium adatom density $\varrho_{\rm eq}$ is related to the step chemical potential $\mu^{\rm s}$ through $\varrho_{\rm eq} \simeq \varrho^*_{\rm eq}(1 + k_{\rm B}^{-1}T^{-1}\mu^{\rm s})$, with $k_{\rm B}$ the Boltzmann constant, T the absolute temperature, and $\varrho^*_{\rm eq}$ the equilibrium adatom density of the staight step. The step chemical potential is given by the Gibbs–Thomson relation

$$\mu^{\rm s} = -\varrho_{\rm b}^{-1}\tilde{\psi}^{\rm s}\kappa, \tag{3}$$

where $\varrho_{\rm b}$ is the bulk density, κ is the curvature of the step and, letting ϑ be the angle between $\mathbf{n}$ and an in-plane reference axis and $\psi^{\rm s}(\vartheta)$ be the step free-energy density, $\tilde{\psi}^{\rm s} = \psi^{\rm s} + \partial^2\psi^{\rm s}/\partial\vartheta^2$ is its stiffness. Finally, the step velocity V satisfies the condition

$$\varrho_{\rm b}V = D[\![\nabla\varrho]\!]\cdot\mathbf{n}, \tag{4}$$

with $[\![\nabla\varrho]\!] = (\nabla\varrho)^+ - (\nabla\varrho)^-$ the jump in the adatom density gradient across the step.

It is generally accepted that adatom attachment to the step from the upper terrace is hindered by an energetic barrier higher than that which characterizes attachment from the lower terrace. This asymmetry in the step attachment kinetics is captured by the so-called Ehrlich–Schwoebel (ES) effect, viz., $K_+ > K_-$. Importantly, linear stability analyses of (1)–(4) in one space dimension show that *the ES effect is stabilizing against step bunching*. To account for experimental evidence that steps bunch, an extraneous mechanism is needed, above and beyond the diffusion of adatoms on terraces and their attachment to steps: pinning impurities; adatom electromigration; elastic interactions between steps; chemical coupling between adatom species; etc. Further, *the ES effect is known to destabilize against step meandering* (Bales & Zangwill [2]). Step bunching and meandering appear therefore to be a priori mutually exclusive. However, experiments on copper and silicon vicinal surfaces exist that indicate that these two modes of step instability occur simultaneously (cf., e.g., Néel et al. [3]). This discrepancy between theoretical predictions and experimental observations leads to an apparent paradox of the standard BCF model that the present paper aims to resolve.

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MODIFIED GIBBS–THOMSON RELATION

The Gibbs–Thomson relation (3) provides incomplete information about the step chemical potential insofar as it derives from the definition of μ^{s} as the variational derivative of a free-energy functional associated with the step. But, in computing the energetic cost of attaching an adatom to (or removing it from) a step, it is the *total* free energy, with contributions from the adjacent terraces and from the crystalline bulk, that needs to be considered. By computing the temporal rate of change of the total free energy and identifying μ^{s} with the conjugate of the step velocity V, we obtain the modified Gibbs–Thomson relation

$$\mu^{\mathrm{s}} = \varrho_{\mathrm{b}}^{-1}(\Psi_{\mathrm{b}} - [\![\omega]\!] - \tilde{\psi}^{\mathrm{s}}\kappa), \tag{5}$$

where Ψ_{b} is the free-energy density of crystallized adatoms and $[\![\omega]\!]$ denotes the jump in the adatom grand canonical potential. Note that there are two novel contributions to the step chemical potential, above and beyond that of the step ($-\varrho_{\mathrm{b}}^{-1}\tilde{\psi}^{\mathrm{s}}\kappa$): one from the bulk ($\varrho_{\mathrm{b}}^{-1}\Psi_{\mathrm{b}}$) and the other from the adjacent terraces ($-\varrho_{\mathrm{b}}^{-1}[\![\omega]\!]$).

THERMODYNAMICALLY CONSISTENT GENERALIZATION OF BCF

Away from equilibrium, the second law states that the thin crystalline film will tend to lower its free energy if dissipative mechanisms exist to do so. Here, these dissipative mechanisms are the diffusion of adatoms on terraces and their attachment to steps. We use the free-energy imbalance to restrict the constitutive relations that enter our thermodynamically consistent generalization of the BCF theory (1)–(4). Letting μ denote the adatom chemical potential, the resulting free-boundary problem consists of the equation

$$\frac{\partial \varrho}{\partial t} = M\Delta\mu + F - \sigma\mu \tag{6}$$

on the terraces, supplemented by the jump conditions

$$\pm\varrho^{+}V \pm M(\nabla\mu)^{\pm}\cdot\mathbf{n} = C_{\pm}(\mu^{\pm} - \mu^{\mathrm{s}}) \tag{7}$$

and the mass balance

$$\varrho_{\mathrm{b}}V = C_{+}(\mu^{+} - \mu^{\mathrm{s}}) + C_{-}(\mu^{-} - \mu^{\mathrm{s}}) \tag{8}$$

at the steps, where the step chemical potential μ^{s} is prescribed by (5). Here, M is the adatom mobility, σ is the desorption coefficient, and C_{+} (C_{-}) is the attachment coefficient to the step from the lower (upper) terrace. Note that, in contrast to (2) and as a result of the jump $[\![\omega]\!]$ in the adatom grand canonical potential in (5), the boundary conditions (7) couple the adatom diffusions on adjacent terraces. Equations (6)–(8), complemented by the modified Gibbs–Thomson relation (5), serve as the basis for the stability analysis that aims at reconciling theory with experiments.

COEXISTENCE OF STEP BUNCHING AND MEANDERING

Restricting attention to two-terrace periodic trains of rectilinear steps and allowing for small departures from local equilibrium, we derive a linear stability criterion for the onset of step collisions. In the absence of desorption, it states that step bunching occurs in the presence of the ES barrier ($C_{+} > C_{-}$) whenever the equilibrium adatom coverage $\Theta = \varrho_{\mathrm{eq}}/\varrho_{\mathrm{b}}$ exceeds a critical value Θ_{c} given by

$$\Theta_{\mathrm{c}} = \frac{\ell_{-} - \ell_{+}}{2(\ell_{-} + \ell_{+}) + \ell}, \tag{9}$$

where $\ell_{\pm} = M/C_{\pm}$ are kinetic lengths by which to measure the strength of the ES effect. Moreover, we show that *step collisions are driven by energetics rather than by the kinetics of step flow*. Specifically, the instability results from the competition between the standard BCF kinetics and an energetic correction that becomes dominant if the equilibrium adatom coverage is non-negligible (as is the case during, e.g., molecular beam epitaxy of GaAs semiconductor films). Finally, by performing the linear stability analysis in two space dimensions and in the limit when $C_{+} \to \infty$ and $C_{-} = 0$, we show that step meandering also occurs during growth, as expected. Hence, bunching and meandering instabilities can coexist in the presence of the ES effect, in accordance with experimental observations.

References

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