Problems in growth and instabilities of microscopic steps on monocrystalline surfaces: The effects of anisotropic step energy (tension)

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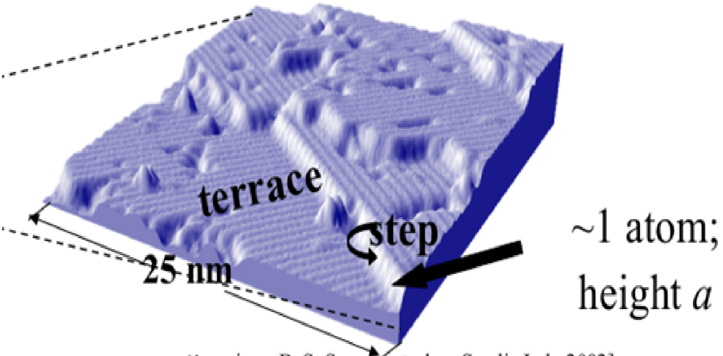
- Molecular Beam Epitaxy (MBE) is widely used to grow various semiconductor or metal nanostructures (quantum dots, wells, wires, etc.)
- If the substrate on which the crystal grows is a *vicinal (misoriented) surface*, then for metals or semiconductors the growth proceeds in step-flow mode
- *Anisotropy of step energy, or tension* (a dependence on orientation) has been shown to have a major effect on step morphology (Y. Saito and M. Uwaha, 1996). However, these authors considered weak anisotropy only. In this work, analysis is extended to **strong anisotropies**.



[Imaging : B. S. Swartzentruber, Sandia Lab, 2002]

Introduction, part II

Introduction to Step Dynamics and Step Instabilities 3

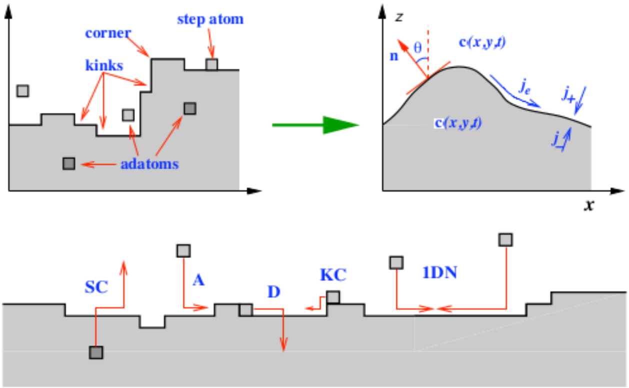


FIGURE 2. Atomic processes at a step: Attachment (A) and detachment (D) of terrace atoms; step crossing (SC); kink crossing (KC); and one-dimensional nucleation (1DN). As in Fig.1, the upper terrace is shaded.

(From: J. Krug (2004))

Let the step profile be $z = h(x, t)$

Introduction, part III

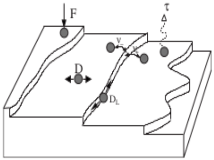


FIG. 4. Summary of various atomic processes on a vicinal surface. Deposition (with a flux F), diffusion (with D as the diffusion constant), desorption (with rate $1/\tau$), and step attachment or detachment (with rate $\nu_\pm$ from each side) is shown. D_L represents the line diffusion along the step.

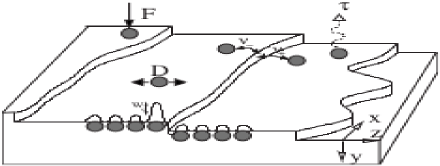


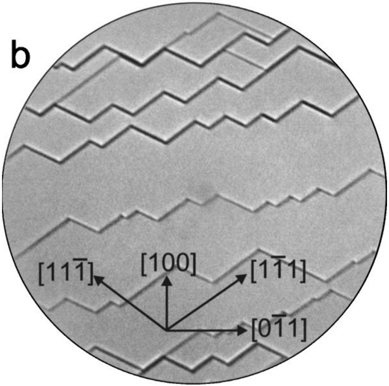
FIG. 10. Schematic view of a vicinal surface. D is the diffusion constant, F is the deposition flux, τ is the desorption time, and $\nu_\pm$ are step attachment coefficients from the lower and upper sides, respectively. The potential barrier to jump over the step is denoted as W_s.

(From: C. Misbah et al. (2010))

Example system

MBE growth of refractory metals (niobium, molybdenum, tantalum, tungsten, and rhenium)

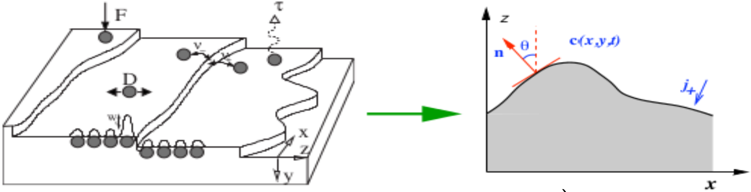
These metals are extraordinarily resistant to heat and wear



(Growth of Nb on Nb(001) substrates; from: M. Ondrejcek *et al.* (2002))

Notice distinct faceting of steps (light lines: individual steps; dark lines: step bunches)

Formulation of one-sided model, part I



(From: C. Misbah et al. (2010); adapted from J. Krug (2004))

Let C: atomic concentration; $z = h(x,t)$: the step profile

$$D\nabla^2 C - \tau^{-1} C = -F,$$

$$z = h(x,t):$$

$$C = C_{eq}\left[1 + \frac{\Omega}{k_B \bar{T}}\left\{\tilde{\beta} - \bar{\delta}(|\alpha|)\left(\frac{\kappa^2}{2} + \frac{\kappa_{ss}}{\kappa}\right)\right\}\kappa\right]$$

$$z \to \infty: \quad C = \tau F$$

$$v_n \equiv h_t \cos\theta = \Omega D\left(\nabla C_{|z=h(x,t)} \cdot \mathbf{n}\right), \quad \cos\theta = \left(1 + h_x^2\right)^{-1/2},$$

$$\mathbf{n} = \left(-h_x \cos\theta, \cos\theta\right), \quad \kappa = \frac{-h_{xx}}{(1+h_x^2)^{3/2}}, \quad \frac{\partial}{\partial s} = (\cos\theta)\frac{\partial}{\partial x}$$

Formulation of one-sided model, part II

$$\beta = \beta_0(1 + \alpha\cos 4\theta), \quad \text{(good model for fcc-crystals)}$$
$$\tilde\beta \equiv \beta + \beta_{\theta\theta} = \beta_0(1 - 15\alpha\cos 4\theta), \quad |\alpha| \geq \mathbf{1/15}$$

α is the anisotropy strength, $\bar\delta$ is the regularization parameter

$$z = h(x,t): \quad C = C_{eq}\left[1 + \frac{\Omega}{k_B\bar T}\left\{\tilde\beta - \bar\delta(|\alpha|)\left(\frac{\kappa^2}{2} + \frac{\kappa_{ss}}{\kappa}\right)\right\}\kappa\right]$$

This b.c. has the highly nonlinear *regularization term*; κ is the step curvature.

Reg. term IS REQUIRED when the *step energy* β is **strongly anisotropic** and therefore the *step stiffness* $\tilde\beta < 0$ for some orientations: $|\alpha| \geq \mathbf{1/15}$

Negativity of $\tilde\beta$ for some θ signals that the corner has formed at this orientation on the *equilibrium* crystal shape; in the dynamical situation, this corresponds to the evolution PDE becoming backward parabolic; thus it is ill-posed and unstable to short-wavelength perturbations. Inclusion of the *regularization term* restores well-posedness of the evolution PDE by imposing small radius of curvature at the corners; see A.A. Golovin *et al.* (1998)

Saito-Uwaha model for weak anisotropy ($\tilde{\beta} > 0 \; \forall \; \theta$), part I

Longwave perturbations ($0 < k < k_c$) are known to be the most dangerous in the isotropic and weakly anisotropic cases

$$
\begin{aligned}
x &= \epsilon^{-1/2} X, \; t = T_0 + \frac{T_2}{\epsilon^2}, \\
h &= \epsilon H_1(X, T_0, T_2) + \epsilon^2 H_2(X, T_0, T_2) + \ldots, \\
C &= C_0(X, z, T_0, T_2) + \epsilon C_1(X, z, T_0, T_2) + \epsilon^2 C_2(X, z, T_0, T_2) \ldots
\end{aligned}
$$

Since h is assumed $\mathcal{O}(\epsilon)$, that expansion results in the *weakly nonlinear* evolution PDE for the step profile: the *weakly anisotropic Kuramoto-Sivashinsky equation (waKS)* (Y. Saito and M. Uwaha, 1996)

$$
\begin{aligned}
h_t &= -\frac{1}{2}(1 - 8Ah_x^2)h_{xx} - \frac{3}{8}h_{xxxx} + \frac{1}{2}h_x^2, \\
A &= \alpha_{su}\epsilon^2, \quad \alpha_{su} \geq -1/2 \Leftrightarrow |\alpha| \leq \mathbf{1/15} \Leftrightarrow \tilde{\beta} > 0
\end{aligned}
$$

The PDE we derive is valid for large step deformations and for strong anisotropies, and it is more nonlinear and complicated than the waKS equation

Saito-Uwaha model for weak anisotropy, part II

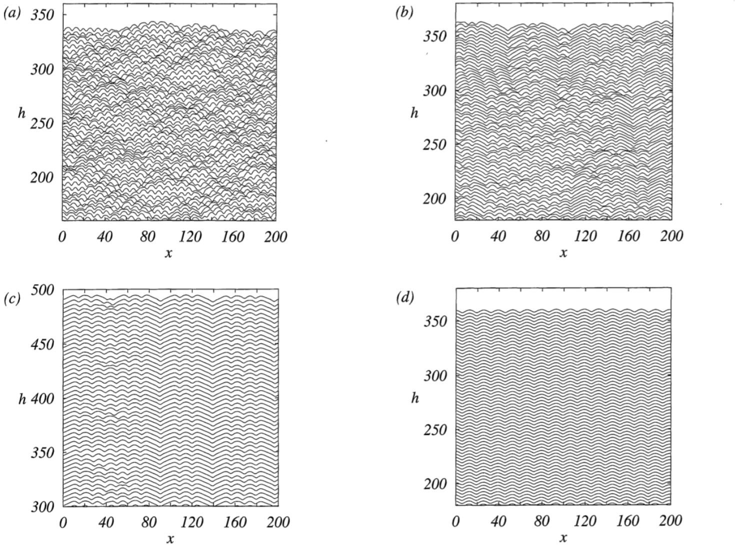
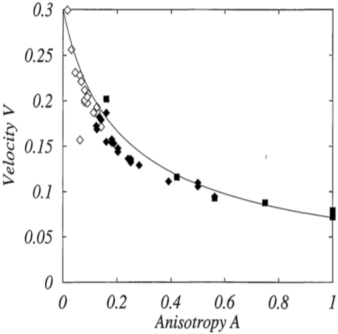


Fig. 1. Time evolution of a step profile with a stiffness anisotropy (a) $A = 0$ (isotropic), (b) $A = 0.2$, (c) $A = 0.5$ and (d) $A = 1.0$.

From: Y. Saito and M. Uwaha (1996)



From: Y. Saito and M. Uwaha (1996)

Implicit in the derivation is that straight step is long-wave unstable when:

$$F > F_c = F_{eq}\left(1 + \frac{2\Omega\beta_0}{x_s k_B \bar{T}}\right) > F_{eq}, \text{ since } \beta_0 > 0; \text{ here } x_s = (D\tau)^{1/2},$$

$F_{eq} = C_{eq}/\tau$: the equilibrium flux (sufficient for steady growth of **straight** step)

Notice independence of F_c on anisotropy strength !

Our model for strong anisotropy ($\tilde{\beta} < 0$ for some θ), part I

Introduce "stretched" variable X, the "fast" time T_0 and the hierarchy of "slow" times T_2, $T_3, ...$:

$$x = \frac{X}{\epsilon}, \quad t = T_0 + \frac{T_2}{\epsilon^2} + \frac{T_3}{\epsilon^3} + ..., \quad \text{where} \quad \epsilon \ll 1$$

Also expand the concentration in powers of ϵ:

$$C = C_0(X, z, T_0, T_2, ...) + \epsilon^2 C_2(X, z, T_0, T_2, ...) + ...$$

Note: h(X,T) is not expanded, meaning large step deformations are allowed: $h(x,t) = \mathcal{O}(1)$

Substitute variables and expansions, collect the like powers of ϵ and obtain a sequence of coupled, exactly solvable problems at ϵ^0, ϵ^2, $\epsilon^4, ...$

At each order, a problem is an ODE boundary value problem: a 2nd-order ODE in z subject to two b.c.'s, one at $z \to \infty$ and another at $z = h(X)$

- Solve the BVP ODE problems at orders $\epsilon^0,\ \epsilon^2,\ \epsilon^3,\ \epsilon^4$
- Transfer to the reference frame moving in the $z > 0$ - direction with the speed of straight (unperturbed) step: $h_{T_0} = \Omega x_s \left(F - F_{eq}\right)$, where $F_{eq} = C_{eq}/\tau$ is the flux at the equilibrium, and $x_s = \sqrt{\tau D}$ is the diffusion length
- Combine the time derivatives:

$$h_t = \epsilon^2 h_{T_2} + \epsilon^3 h_{T_3} + \epsilon^4 h_{T_4}$$

- Introduce the original variable x; this eliminates ϵ^2, ϵ^3 and ϵ^4 from the PDE
- Make the PDE dimensionless by chosing x_s as the length scale and τ as the time scale

Our model, part III: Evolution PDE

Keeping same notations for dimensionless variables:

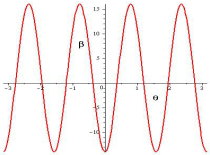
$$h_t = (m_1 - m_2)\, h_{xx} - m_3 h_{xxxx} + \frac{m_1 \mp m_2}{2} h_{xx} h_x^2 + m_1 \left(\frac{3}{2} h_x^4 - h_x^2 \right) \mp m_2 h_{xxx} h_x, \qquad (1)$$

$$m_1 = \frac{1}{2} (F_{eq} - F)\, \Omega \tau, \quad m_2 = \frac{F_{eq} \Omega^2 \beta_0 \tau}{k_B \bar{T} x_s} (15\alpha - 1), \quad m_3 = \frac{F_{eq} \Omega^2 \tau \delta(|\alpha|)}{k_B \bar{T} x_s^3} > 0$$

m_1 measures the deviation of the flux from the equilibrium value, m_2 measures the strength of the anisotropy, and m_3 measures the effect of the regularization (corner rounding)

$+ :\ \alpha \geq 1/15$

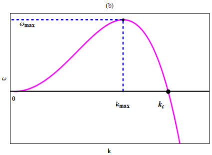
$- :\ \alpha \leq -1/15$ [will choose $+ \Leftrightarrow \alpha \geq 1/15$ in the analysis (stiffness $\tilde{\beta}$ is minimum in the growth direction $\theta = 0$)]



Our model, part IV: Analysis of the evolution PDE

- Straight step is long-wave unstable, iff

$$m_1 - m_2 < 0 \;\Leftrightarrow\; F > F_c = F_{eq}\left(1 - \frac{2\Omega\beta_0}{x_s k_B \bar{T}}(15\alpha - 1)\right)$$



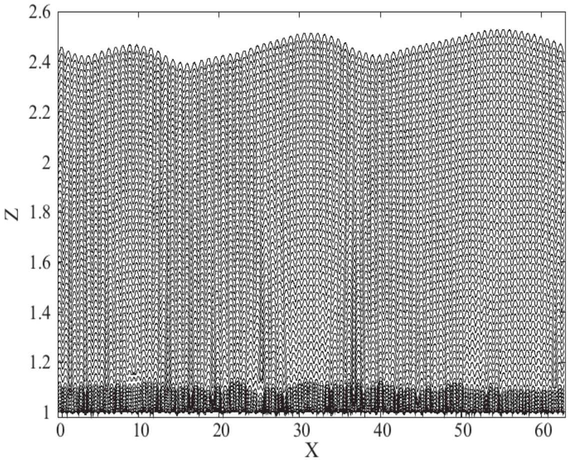
$$k_c = \sqrt{(m_2 - m_1)/m_3}, \quad k_{max} = k_c/\sqrt{2}, \quad \omega_{max} = (m_2 - m_1)^2/4m_3$$

Let $\alpha \geq 1/15$, then:

- $F_c < F_{eq}$
- $F_c = 0$ at $\alpha = \alpha_c = 1/15 + r$, where $r = x_s k_B \bar{T}/30\Omega\beta_0$. Thus at $\alpha > \alpha_c$ any flux destabilizes the step. $r \sim 0.01 - 0.1$
- At $F > F_{eq} > F_c$ the step is unstable and grows (in the frame moving with non-zero speed h_{T_0}); similar to isotropic and weakly anisotropic cases
- At $F_c < F < F_{eq}$, the step is unstable and it grows; (no analog in isotropic and weakly anisotropic cases) ($h_{T_0} = 0$)

Computational results for strongly anisotropic PDE, part I

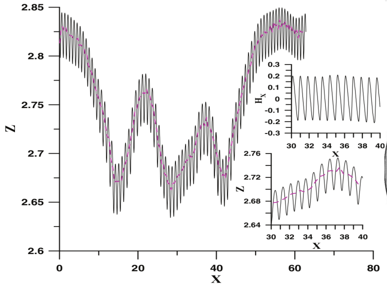
Random initial condition $h(x,0) = 1 +$ noise on the large domain $(0 \leq x \leq 100\lambda_{max})$, periodic b.c.'s

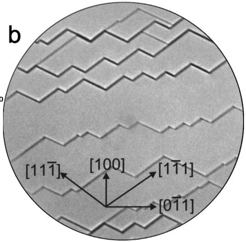


$\alpha = 1.6$, $F/F_{eq} = 2$; time increases from the bottom to the top

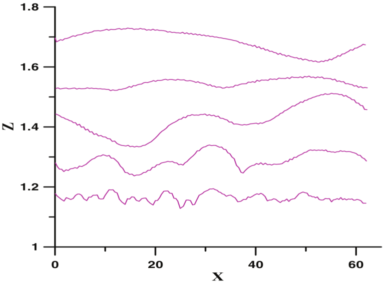
A quasi-steady state emerges: Hills and valleys ceased coarsening, but the long-wavelength median (envelope) perpetually coarsens

Computational results for strongly anisotropic PDE, part II



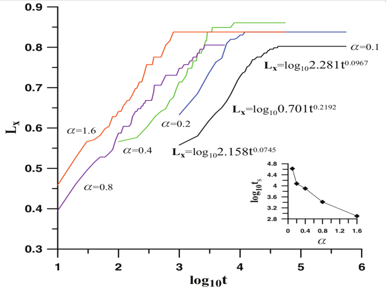


The quasi-steady state

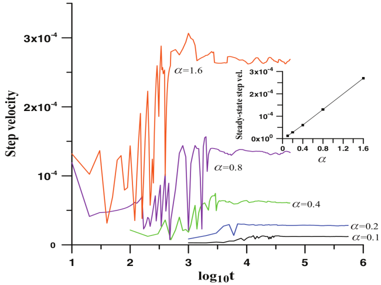


Coarsening of the long-wavelength median step position; time increases from the bottom to the top

Computational results for strongly anisotropic PDE, part III



Coarsening of the hill-and-valley structure for various α values



Step speed vs. the time for various α values

- A longwave PDE is formulated for the description of the strongly anisotropic step dynamics within the framework of a one-sided model
- The linear stability of a step depends not only on the strength of the adatoms flux from the terrace to the step, but also on the *strength of the step energy anisotropy parameter* α
- The critical atomic flux from the terrace that destabilizes the step is *less* than the equilibrium value, and it is even possible to destabilize the step by anisotropy alone by taking α large enough. That is, *the flux and the anisotropy complement each other in destabilizing the step.*

THE END

References

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