Mathematical model of electromigration-driven evolution of the surface morphology and composition for a bi-component solid film

Mikhail Khenner, Mahdi Bandegi

Department of Mathematics, Western Kentucky University

SIAM-SEAS, University of Alabama at Birmingham, March 22, 2015

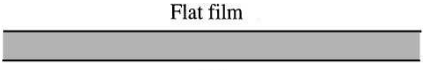
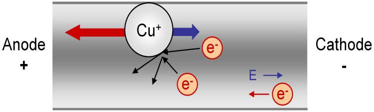


Figure : Single-crystal, metallic film grown on a substrate by MBE or CVD.

Surface electromigration: *Drift* of adatoms on **heated crystal surfaces** of metals in response to applied DC current, due to the *momentum transfer* from electrons to adatoms through scattering $\leftrightarrow$ "Electron wind"

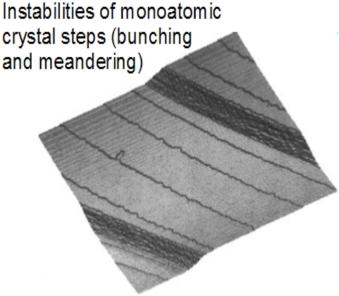


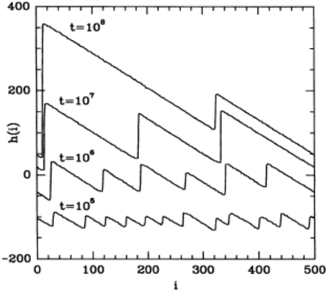
Adatom = mobile, adsorbed atom or ion

Continuum theory of surface dynamics on length scales much larger than the interstep distance: Krug & Dobbs'1994, Schimschak & Krug'1997

If the electric field is horizontal (along planar, unperturbed surface), then:

1. Facet orientations are first established locally,
2. Further evolution proceeds through a coarsening process

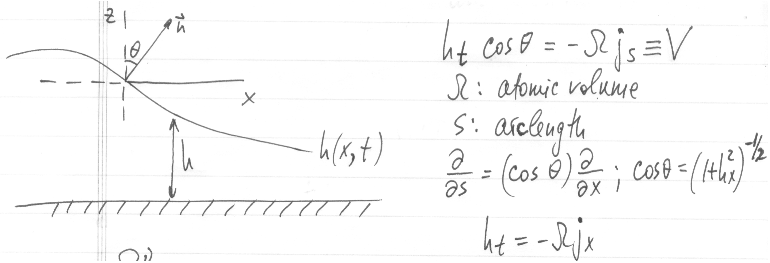




Facet size (hill-to-hill distance) $X \sim t^n$, where $n \approx 0.25$

Each facet = many monoatomic crystal steps

Introduction: Morphological evolution of a single-component surface (W.W. Mullins'57-65)



$j = -\frac{\nu}{kT} DM(\theta)\,(\mu_s + qE\cos\theta)$: adatoms flux on the film surface when **E** is along the x-axis

$DM(\theta)$: anisotropic diffusivity of the adatoms (surface orientation-dependent), where $M(\theta)$ is the *mobility*

$\mu(s) = \Omega\gamma\kappa$: the chemical potential (Mullins'57)

The model for a bi-component surface

$$h_t = V/\cos\theta, \quad V = -\Omega\left(\frac{\partial J_A}{\partial s} + \frac{\partial J_B}{\partial s}\right),$$

where J_A and J_B are the surface diffusion fluxes of the components A and B:

$$J_i = -\frac{\nu D_i}{kT} M_i(\theta) C_i(s,t)\left[\frac{\partial \mu_i}{\partial s} + qE\cos\theta\right], \; i = A, B$$

Here $C_A(x,t)$ and $C_B(x,t)$ are the dimensionless surface concentrations of adatoms A and B, defined as products of a volumetric number densities and the atomic volume. Then,

$$C_A(x,t) + C_B(x,t) = 1.$$

$$\mu_i = \Omega\gamma_i\kappa + kTln\frac{C_i}{1-C_i} \approx \Omega\gamma_i\kappa + -2kT + 4kTC_i,$$

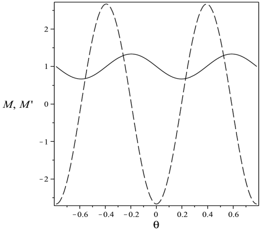
when the "mixture" contribution is linearized about $C_i = 1/2$.

This form of the "mixture" contribution implies a thermodynamically stable alloy, thus the natural surface diffusion acts to smooth out any compositional nonuniformities. On the other hand, the electromigration may be the cause of their emergence and development.

The anisotropic adatom mobility (Schimschak & Krug'1997):

$$M_i(\theta) = \frac{1 + \beta_i \cos^2\left[N_i(\theta + \phi_i)\right]}{1 + \beta_i \cos^2\left[N_i \phi_i\right]}, \quad \text{where}$$

N_i : the number of symmetry axes, ϕ_i : the angle between a symmetry direction and the average surface orientation, β_i : anisotropy strength.



PDE governing evolution of the surface concentration $C_B(s,t)$ (Spencer, Voorhees and Tersoff'93):

$$\delta \frac{\partial C_B}{\partial t} + \mathbf{C_B V} = -\Omega \frac{\partial J_B}{\partial s},$$

where δ is the thickness of the surface layer and quantifies the "coverage".

The dimensionless problem (using $[x] = h_0, [t] = h_0^2/D_B$)

$$\mathbf{h_t} = \frac{4}{mQ}\frac{\partial}{\partial x}\left\{\left(1+h_x^2\right)^{-1/2}\left[DM_A(h_x)(1-C_B)\left(R_A\frac{\partial \kappa}{\partial x} - \frac{\partial C_B}{\partial x} + F\right) + M_B(h_x)\,C_B\left(R_B\frac{\partial \kappa}{\partial x} + \frac{\partial C_B}{\partial x} + F\right)\right]\right\},$$

$$\frac{\partial \mathbf{C_B}}{\partial \mathbf{t}} = -\left(1+h_x^2\right)^{-1/2}\left[\mathbf{QC_Bh_t} - \frac{4}{m}\frac{\partial}{\partial x}\left\{\left(1+h_x^2\right)^{-1/2} M_B(h_x)\,C_B\left(R_B\frac{\partial \kappa}{\partial x} + \frac{\partial C_B}{\partial x} + F\right)\right\}\right].$$

Here the parameters are:

$$R_i = \frac{\Omega\gamma_i}{4kTh_0},\ F = \frac{\alpha\Delta Vq}{4nkT},\ Q = \frac{h_0}{m\Omega\nu},\ D = \frac{D_A}{D_B}.$$

This assumes:

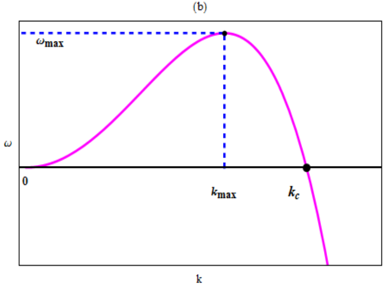
- $E = \Delta V/L$, where ΔV is the applied potential difference and $L = nh_0$ is the lateral dimension of the film ($n > 0$ is a parameter),
- $\delta = m\Omega\nu$, where $m > 0$ is a parameter; $\Omega\nu$ is *monolayer* thickness

(i) Perturb the surface about the equilibrium constant height h_0 by the perturbation $\xi(x,t)$, obtain PDE for ξ

(ii) Linearize PDE for ξ and obtain linear PDE $\xi_t = F(\xi, \xi_x, \xi_{xx}, \ldots)$

(iii) Take $\xi = e^{\omega t}\cos kx$ and substitute in PDE $\rightarrow \omega(h_0, k, R_i, n, m, D)$

(iv) Examine for what values of the parameters the growth rate is positive or negative. $\omega < 0$: surface is stable; $\omega > 0$: surface is unstable



Long-wave instability. k_c: the cut-off wavenumber; k_{max}: a wavenumber detected in experiment

LSA

- $h(x,t) = 1 + \xi(x,t),\ C_B(x,t) = C_B^0 + \hat{C}_B(x,t)$: the perturbations
- $\xi(x,t) = Ue^{\omega(k)t}e^{ikx},\ \hat{C}_B(x,t) = Ve^{\omega(k)t}e^{ikx}$, where $U,\ V$ are (unknown) constant and *real-valued* amplitudes
- $\omega = \omega^{(r)}(k) + i\omega^{(i)}(k)$
- Also expand: $M_i\left(h_x\right) = M_i(0) + M_i'(0)h_x$, where $M_i(0),\ M_i'(0)$ are the parameters

This results in the quadratic eqn. for $\omega^{(r)}(k)$:

$$\omega^{(r)}(k)^2 + \omega^{(r)}(k)\left[k^2 C_B^0\left(M_B(0)\left(1-\frac{m}{4}C_B^0\right) + \frac{M_A(0)}{4}mD\left(1-C_B^0\right)\right) + \frac{k^2}{Q}\left\{DFM_A'(0)\left(1-C_B^0\right) + FM_B'(0)C_B^0 + k^2 DR_A M_A(0)\left(1-C_B^0\right) + k^2 R_B M_B(0) C_B^0\right\}\right] + \frac{k^4}{Q}\left[DF\left(M_B(0)M_A'(0) + M_A(0)M_B'(0)\right)C_B^0\left(1-C_B^0\right) + k^2 D\left(R_A + R_B\right)M_A(0)M_B(0)\left(1-C_B^0\right)\right] = 0,$$

LSA, continued

And,

$$\omega^{(i)}(k) = \left[M_B(0) \left(1 - \frac{mC_B^0}{4} \right) + \frac{M_A(0)}{4} DmC_B^0 \right] kF.$$

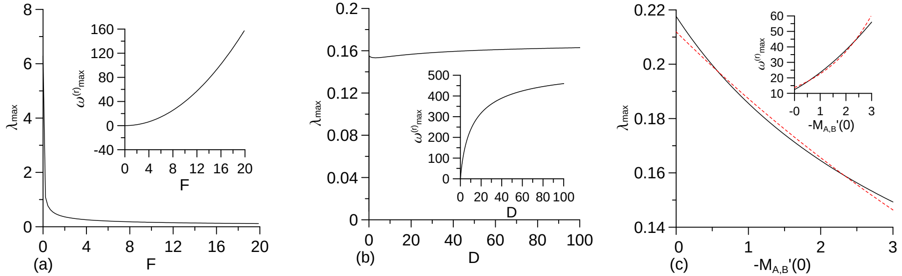
Thus the perturbations experience the lateral drift with the speed $v = |\omega^{(i)}(k)/k| \sim F$, which does not depend on k.

LSA, continued: analysis of $\omega^{(r)}(k)$

- The limit of vanishing surface layer thickness: As $\delta \to 0$ ($Q \to \infty$), $\omega^{(r)}(k) < 0$
- For finite Q, the longwave instability with

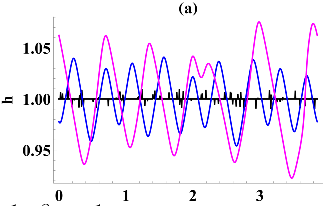
$$k_c = \left[F \left(1 - C_B^0\right) \frac{M_B(0) M_A'(0) + M_A(0) M_B'(0)}{M_A(0) M_B(0) \left(C_B^0 - 1\right) \left(R_A + R_B\right)} \right]^{1/2} \sim F^{1/2}$$

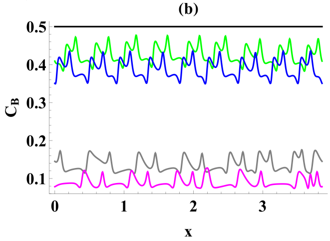
Note that $k_{max} \neq k_c/\sqrt{2}$; obtain $\lambda_{max} = 2\pi/k_{max}$ numerically



$\lambda_{max} \sim F^{-1/2}$, $\omega^{(r)}_{max} \sim F^2$; Dashed lines in (c): fits $\lambda_{max} = 0.212 \exp\left(0.123 M'_{A,B}(0)\right)$, $\omega^{(r)}_{max} = 13.8 \exp\left(-0.493 M'_{A,B}(0)\right)$.

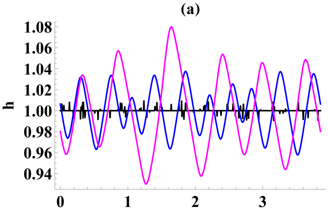
- Comp. domain $0 \le x \le 20\lambda_{max}$, initial condition:
  $h(x,0) = 1 +$ small random perturbation, $C_B(x,0) = 1/2$, periodic b.c.'s
- Perpetual coarsening $\rightarrow$ hill-and-valey structure $\rightarrow$ scaling law ?
- Most interesting nontrivial results for $\beta_A \neq \beta_B$

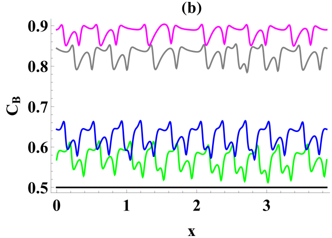




$\beta_A = 0.1,\ \beta_B = 1.$

x

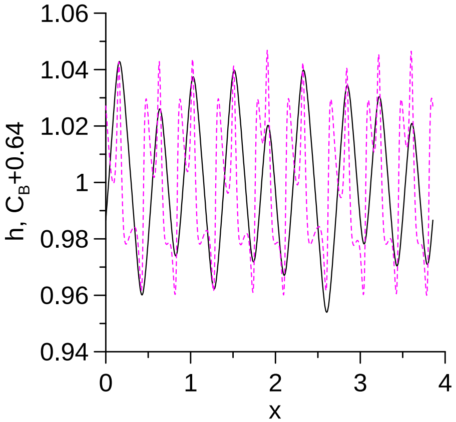




$\beta_A = 1,\ \beta_B = 0.1.$

x

Nonlinear surface dynamics, continued

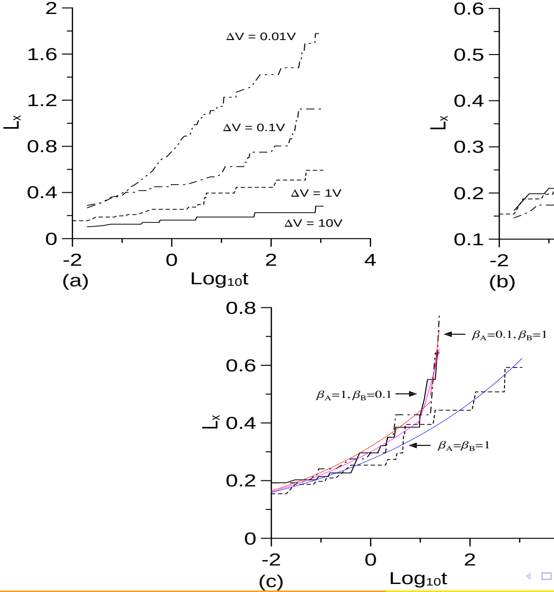


Concentration of B adatoms (dashed line) superposed over the corresponding surface shape (solid line). $\beta_A = 0.1,\ \beta_B = 1$.

Let L_x be the mean distance between neighbor valleys

Nonlinear surface dynamics, continued

Coarsening on the comp. domain $0 \le x \le 20\lambda_{max}$, periodic b.c.'s



Coarsening laws:

- vs. ΔV:

  $L_x^{(\Delta V=0.01V)} = 0.77t^{0.138}$, $L_x^{(\Delta V=0.1V)} = 0.46t^{0.126}$,
  $L_x^{(\Delta V=1V)} = 0.273t^{0.118}$, $L_x^{(\Delta V=10V)} = 0.156t^{0.074}$

- vs. D:

  $L_x^{(D=0.1)} = 0.205t^{0.138}$, $L_x^{(D=1)} = 0.273t^{0.118}$, $L_x^{(D=10)} = 0.29t^{0.104}$

- For $\beta_A = 0.1,\ \beta_B = 1$:

  $L_x^{(\beta_A=0.1,\beta_B=1)} = 0.318t^{0.143}$ for $0 \le Log_{10}t \le 1.22$,
  $L_x^{(\beta_A=0.1,\beta_B=1)} = 0.04t^{0.905}$ for $1.22 \le Log_{10}t \le 1.38$

- For $\beta_A = 1,\ \beta_B = 0.1$:

  $L_x^{(\beta_A=1,\beta_B=0.1)} = 0.3t^{0.135}$ for $0 \le Log_{10}t \le 1$,
  $L_x^{(\beta_A=1,\beta_B=0.1)} = 0.128t^{0.514}$ for $1 \le Log_{10}t \le 1.38$

Summary

- Found the long-wavelength instability coupled to the lateral surface drift. The drift is not present in the similar model for the one-component film
- The perturbations wavelength λ_{max} and the growth rate $\omega_{max}^{(r)}$ scale as $F^{-1/2}$ and F^2, respectively, where F is the applied electric field parameter
- λ_{max} sharply decreases when the derivatives of the diffusional mobilities increase
- If β_A differs significantly from β_B, the surface is enriched by one atomic component. The second component is absorbed into the solid
- Increase of ΔV makes the surface rougher (coarsening slows down)
- If β_A differs significantly from β_B, then there is a pronounced speed-up of coarsening at the late times (a factor of 4-6 increase in the coarsening exponent)

THANKS ![1]

[1] To appear in the special issue on modeling on nano- and micro-scale of *Mathematical Modelling of Natural Phenomena*, Ed. A.A. Nepomnyashchy