

(Morphology = Shape)

Morphological evolution of single-crystal ultrathin solid films

Mikhail Khenner

Department of Mathematics, Western Kentucky University

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Motivations: Physics & Technology on Nanoscale

Physics of Crystal Growth and Technology:

Lab growth of high-quality thin solid films and crystals is extremely challenging since it takes place in very tough environments such as high temperatures (up to 1000 C and higher) and high local stress levels (MPa range)

Despite more than 30 years of experimental, theoretical, and modeling work, the growth mechanisms are not well understood, and experimental methods are not sufficiently developed, which prevents the transition of many long-imagined applications from the growth experiment stage to a nanoscale semiconductor device-building stage

Example: Formation of single-crystal, defect-free, nanometer-sized “islands” from the initially continuous grown film
(*Stranski-Krastanow heteroepitaxial thin film growth*)

Motivations, continued: Physics & Technology on Nanoscale

Flat film



Figure: Flat, single-crystal semiconductor film ($Si_{1-x}Ge_x$ on Si) grown by MBE or CVD to height h_0 .

and then, suddenly, ...

Instability and pattern formation

Motivations, continued: Physics & Technology on Nanoscale

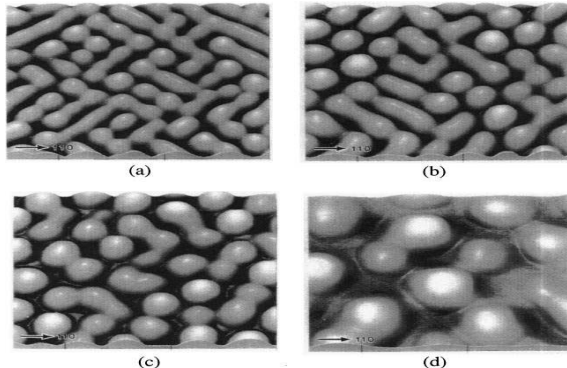


Figure: AFM images of 10nm-thick $Si_{0.82}Ge_{0.18}/Si$ alloy films. The images reveal evolving and coarsening surface patterns on samples annealed at 850 C for (a) 1 min, (b) 5 min, (c) 20 min, and (d) 2 h, respectively (from [1]).

Motivations, continued: Physics & Technology on Nanoscale

The ultimate goal is to grow uniform, defect-free superlattices of nicely-shaped crystal islands (pyramids, domes, rectangular, etc.). That is, methods of shape and order control must be perfected.

And, factors influencing **pattern formation and pattern coarsening** must be fully understood.

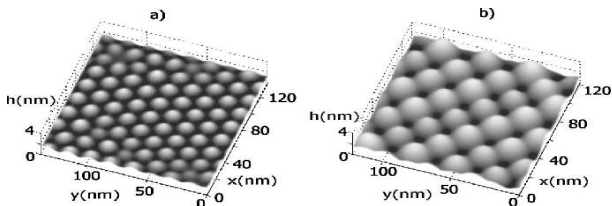


Figure: Computer simulation results of a mathematical model (from [2]). (a) Stationary hexagonal lattice; (b) Stationary square lattice. **This is MUCH better than the best experiments to-date!**

Models of thin films are often formulated in terms of high-order, heavily nonlinear evolution PDEs that have some unusual properties, such as unstable and non-differentiable solutions. This calls for nonstandard methods of analysis and solution that are interesting in their own right.

Modeling paradigms

- Atomistic, say Molecular Dynamics-type methods: very computationally expensive, limited to a few thousand atoms
- Continuum: explained in this talk, usually provide qualitative information only
- Mixed atomistic-continuum: state-of-the-art multiscale methods

We use continuum approach as follows

PDE-based initial-boundary value problem for the **film height function** is formulated based on available physical information

For a film above $x, y : 0 \leq x \leq X, 0 \leq y \leq Y$:

$h = h(x, y, t)$ and the IBVP has the form

$$h_t = F(h, h_x, h_y, h_{xx}, h_{yy}, \dots)$$

+ the initial condition: $h(x, y, 0) = h_0(x, y)$

+ the boundary conditions, for instance:

$h(0, y, t), h(X, y, t), h(x, 0, t)$ and $h(x, Y, t)$

Physical factors: Epitaxial Stress

1. Compressive or tensile stress generated by lattice mismatch of the film and the substrate

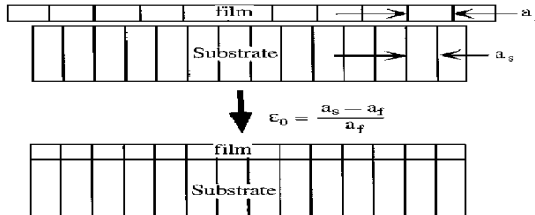


Figure: A heteroepitaxial thin-film structure. The mismatch between the lattice parameters of the film and substrate is accommodated by a (compressive) elastic stress in the film (from [1]).

Physical factors, continued: Surface diffusion I

2. Diffusive mass transport of **adatoms** along the film surface.

Owing to the small length scales and high-T environment, diffusive mass transport along the film surface is very fast and causes the *morphology* (= shape) of the film surface to evolve continuously with time

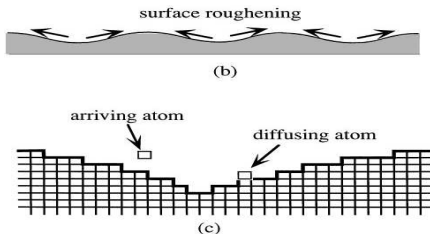


Figure: Continuum and atomistic view of surface diffusion (from [1]).

Physical factors, continued: Surface diffusion II

The surface diffusion process is governed by a **surface chemical potential** $\mathcal{M} = \mathcal{M}_\gamma + \mathcal{M}_e + \mathcal{M}_w + \dots = \mathcal{M}(h, h_x, h_y, \dots)$, where

γ : surface energy density;

e : elastic energy density; w : wetting energy density

Gradients of \mathcal{M} drive the diffusion flux along the surface:

$$j = -\nabla \mathcal{M}(h, h_x, h_y, \dots) \text{ (thermodynamic Fick's law)}$$

Thus surface height changes above the xy -domain

$$x, y : 0 \leq x \leq X, 0 \leq y \leq Y$$

Planar film is in **unstable equilibrium**, because:

In equilibrium the diffusion flux vanishes,

$$j = -\nabla \mathcal{M}(h, h_x, h_y, \dots) = 0 \rightarrow \mathcal{M}(h, h_x, h_y, \dots) = \text{const.}$$

Solution of the last (static) PDE gives **nontrivial** equilibrium surface shape $h(x, y)$. Here value of *const.* depends on film volume and boundary conditions.

Physical factors, continued: Surface diffusion III

\mathcal{M}_γ and \mathcal{M}_w are easy to model since they are **local** quantities (defined on the film surface)

\mathcal{M}_e is very difficult to model since it is **non-local**: must solve the elasticity problem for deformations and stresses in the bulk of the film, then take the solution on the film surface $h(x, y, t)$ (*which is itself the problem unknown*) \rightarrow a *free-boundary problem*

The free-boundary elasticity problem consists of certain PDEs for deformations and stresses in the film and in the substrate, and the boundary conditions on all surfaces, including the film-substrate interface and the (unknown) film surface.

FYI: Mathematical definition of a *free-boundary problem*: A problem for certain field variables Z_1, Z_2, \dots, Z_n on domain D such that the boundary conditions for Z_1, Z_2, \dots, Z_n are posed on the boundary of D whose shape and position are unknown and must be found as part of solution for Z_1, Z_2, \dots, Z_n .

Physical factors, continued: Anisotropy of surface energy density I

Since the film surface is the geometrical boundary of the crystalline solid, it inherits some properties of the crystal lattice - most importantly, the short- and long-range order in the arrangement of atoms.

Thus a surface is a collection of finite-size atomic planes, called **facets**. Each facet has distinct surface energy, which is different from the surface energy of another facet with different *orientation*.

3. Thus if γ stands for the surface energy of the *entire* 3D surface, then $\gamma = \gamma(\theta(x, y), \phi(x, y))$, where θ and ϕ are two angles of the *unit normal* to the surface at point (x, y) .

Physical factors, continued: Anisotropy of surface energy density II

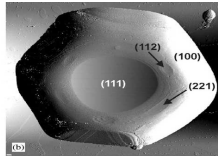


Figure: SEM image of micrometer-sized Pb crystal at room temperature (from [3]).

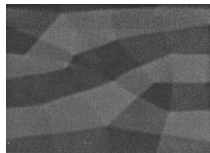


Figure: Faceted surface of a *film*. Facets appear as regions of uniform color (from [4]).

Physical factors, continued: Wetting energy

4. Energy of a long-range molecular repulsion or attraction between the atoms of the film surface and the atoms of the substrate surface

Long-range \equiv larger than atomic length: 0.1 - 10 nm

For some film-substrate materials interaction is repulsive \rightarrow film always covers the substrate everywhere: substrate can't get exposed. Example: SiGe alloy on Si

For other film-substrate materials interaction is attractive \rightarrow film tries to expose substrate. Example: Si on SiO₂ (silicon-on-insulator)

To account for W , the usual approach is to **allow surface energy to be a function of film thickness:**

$\gamma = \gamma(\theta(x, y), \phi(x, y), h(x, y))$. Then

$$\mathcal{M}_w \sim \frac{\partial \gamma}{\partial h}$$

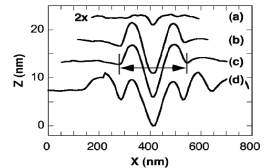
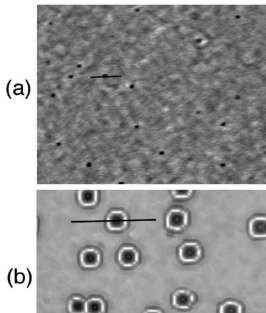
Stages of concept/modeling framework development

- Surface energy (including anisotropy), surface diffusion: 1950's and 1960's (William Mullins, Conyers Herring)
- Stress: 1970's and 1980's (Asaro, Tiller, Grinfeld, Srolovitz), 1990's (Spencer, Voorhees, Tersoff, Freund, Gao, Chiu)
- Wetting energy: 2000's (Ortiz, Golovin)

Also, alloy composition/segregation effects and uninterrupted film growth effects have been studied since 1990

Problem: Dewetting of silicon-on-insulator (Si on *amorphous* SiO₂)

AFM images at $t = 1$ h after the start of annealing at $T = 550\text{C}$.
(a) $h_0 = 5$ nm; (b) $h_0 = 20$ nm. (from [5]). **Pits form in the film !**



Problem: Dewetting of silicon-on-insulator, continued

How is pitting initiated and how it proceeds ? What are the factors influencing pit width and depth ? More generally, what are the factors influencing instability of Si surface ?

Great relief #1! Lattice mismatch of Si and SiO_2 is zero \rightarrow there is no epitaxial stress in the film $\rightarrow \mathcal{M}_e = 0 \rightarrow$ no need to solve the free-boundary elasticity problem. And, Great relief #2! Alloy composition/segregation effects are not present

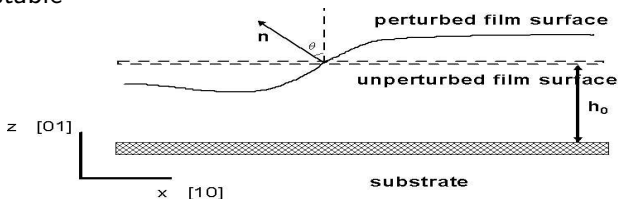
For simplicity let the film surface be one-dimensional \rightarrow
 $h = h(x, t)$ and $\gamma = \gamma(\theta, h)$

- General Linear Stability Analysis (GLSA): gives information on surface stability/instability with respect to **small perturbations** defined on $(-\infty, \infty)$
- GLSA is not very helpful in the case of a pit, since pit results from the evolution of a perturbation which is defined locally and perhaps is **large**. Need computer simulations of **nonlinear** model.

Problem: Dewetting of silicon-on-insulator, continued

Plan for GLSA:

- (i) Derive the nonlinear evolution PDE for $h(x, t)$ using the framework
- (ii) Perturb the surface about the equilibrium constant height h_0 by the perturbation $\xi(x, t)$, obtain PDE for ξ
- (iii) Linearize PDE for ξ and obtain linear PDE
 $\xi_t = F(\xi, \xi_x, \xi_{xx}, \dots)$
- (iv) Take $\xi = e^{\omega t} \cos kx$ and substitute in PDE $\rightarrow \omega(h_0, k, A)$. A is the anisotropy strength
- (v) Examine for what values of h_0, k, A the growth rate is positive or negative. $\omega < 0$: surface is stable; $\omega > 0$: surface is unstable



Problem: Dewetting of silicon-on-insulator, continued

Nonlinear evolution PDE in dimensionless form

$$h_t = B(1 + h_x^2)^{1/2} \frac{\partial^2}{\partial s^2} (\mathcal{M}_w + \mathcal{M}_\gamma), \quad \frac{\partial}{\partial s} = (\cos \theta) \frac{\partial}{\partial x}$$

$$\mathcal{M}_w = \frac{\partial \gamma(h, \theta)}{\partial h} \cos \theta = \left(\gamma^{(f)}(\theta) - G \right) e^{-h} \cos \theta$$

To obtain final form of \mathcal{M}_w , we used the **two-layer exponential wetting model**:

$$\gamma(h, \theta) = \gamma^{(f)}(\theta) + \left(G - \gamma^{(f)}(\theta) \right) e^{-h}$$

$$\gamma(h, \theta) \rightarrow \gamma^{(f)}(\theta) \text{ as } h \rightarrow \infty, \quad \gamma(h, \theta) \rightarrow G \text{ as } h \rightarrow 0$$

Also, for $\gamma(h, \theta)$ as shown above:

$$\mathcal{M}_\gamma = \left(\gamma^{(f)}(\theta) + \gamma_{\theta\theta}^{(f)} \right) \left(1 - e^{-h} \right) \kappa + G e^{-h} \kappa,$$

$$\kappa = -h_{xx} / (1 + h_x^2)^{3/2}; \quad \text{choose } \gamma^{(f)}(\theta) = 1 + A \cos 4\theta$$

$$\text{Finally, } \cos 4\theta = 8 (\cos^4 \theta - \cos^2 \theta) + 1, \quad \cos \theta = (1 + h_x^2)^{-1/2}$$

Problem: Dewetting of silicon-on-insulator, continued

Next, perturbation $\xi(x, t)$ of the equilibrium film height h_0 is introduced, the PDE is linearized, and ξ is taken in the form $\xi = e^{\omega t} \cos kx$

The perturbation growth rate, as derived:

$$\omega(h_0, k, A) = B \left[\left(\Lambda - (G + \Lambda)e^{-h_0} \right) k^4 - (G - 1 - A) e^{-h_0} k^2 - \Delta k^6 \right]$$

$$\Lambda = 15A - 1, \quad \Delta > 0 \quad \text{when anisotropy is strong: } A > 1/15$$

Surface-substrate interaction is attractive: $G < 1, G - 1 - A < 0$

Problem: Dewetting of silicon-on-insulator, continued

- If perturbation wavenumber $k > \max(k_c, k_c^{(u)})$, where

$$k_c = \sqrt{\Lambda/\Delta}, \quad k_c^{(u)} = \sqrt{-(G-1-A)/(G+\Lambda)},$$

then film of any thickness is stable

- If $k_c < k < k_c^{(u)}$, then film is stable if $h_0 > h_0^{(c_1)}$ and unstable otherwise, where

$$h_0^{(c_1)} = -\ln \frac{\Lambda k^2 - \Delta k^4}{G - 1 - A + (G + \Lambda)k^2}, \quad \text{typically } 2 - 4 \text{ nm}$$

- If $k_c^{(u)} < k < k_c$, then the film is stable if $h_0 < h_0^{(c_1)}$ and unstable otherwise → **typically seen in experiments**
- If $k < \min(k_c, k_c^{(u)})$, then the film of any thickness is unstable

Problem: Dewetting of silicon-on-insulator, continued

Computer simulations of a pit using the nonlinear evolution PDE

$$h_t = F(h, h_x, h_{xx}, \dots)$$

The initial condition:

$$h(x, 0) = 1 - d \exp \left[- \left(\frac{x - 5}{w} \right)^2 \right], \quad 0 \leq x \leq 10$$

$d = 0.5$ (shallow pit) AND one of the following:

$w = 0.15$ (narrow pit), or

$w = 1$ (intermediate pit), or

$w = 2$ (wide pit)

Periodic b.c.'s at $x = 0$ and $x = 10$

$$G = 0.5, \quad A = 1/12, \quad B = 3.57 \times 10^{-3}$$

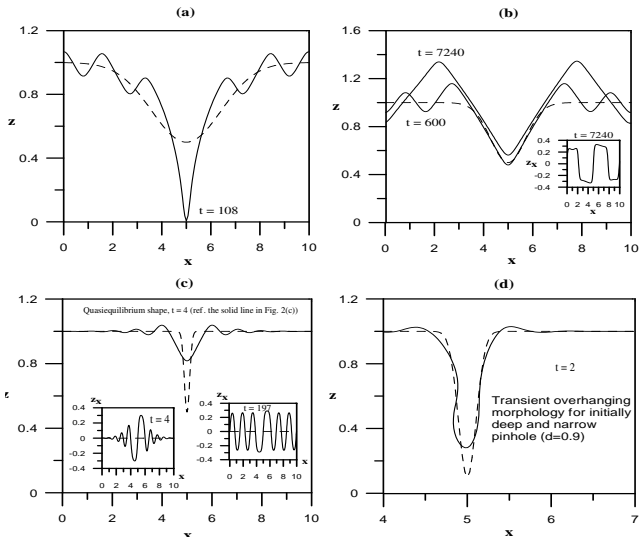
Problem: Dewetting of silicon-on-insulator, continued

Numerical method:

- PDE is discretized in x using the 2nd-order finite differences, time is left continuous \rightarrow large system of coupled ODEs in time (100 to 5000 ODEs)
- Use standard ODE solver to integrate the system in time

Problem: Dewetting of silicon-on-insulator, continued

Computer simulation results: Pit shapes



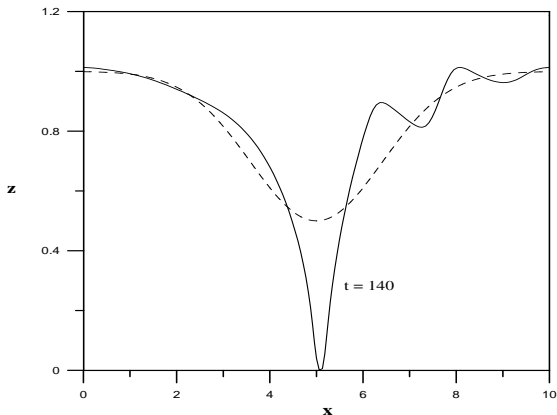
(a): $w = 2$, (b): $w = 1$, (c): $w = 0.15$

Problem: Dewetting of silicon-on-insulator, continued

Computer simulation results: Pit shapes

Rotate sample, expose different crystallographic orientation:

$$\gamma^{(f)}(\theta) = 1 + A \cos 4(\theta + \beta)$$



$$w = 2, \beta = 10^\circ$$

- ① H. Gao and W.D. Nix, "SURFACE ROUGHENING OF HETEROEPITAXIAL THIN FILMS", *Annu. Rev. Mater. Sci.* 1999, 29:173-209
- ② A.A. Golovin *et al.*, "Faceting instability in the presence of wetting interactions: A mechanism for the formation of quantum dots", *PHYSICAL REVIEW B* 70, 235342 (2004); B.J. Spencer *et al.*, "Morphological instability in epitaxially strained dislocation-free solid films: Linear stability theory", *J. Appl. Phys.* 73, 4955 (1993)
- ③ H.P. Bonzel, "3D equilibrium crystal shapes in the new light of STM and AFM", *Physics Reports* 385 (2003) 1-67
- ④ M. Rost, "Continuum models for surface growth", preprint
- ⑤ J.L. Gray *et al.*, "Kinetic size selection mechanisms in heteroepitaxial quantum dot molecules", *Phys. Rev. Lett.* 92, 135504 (2004)