Chapter 3 Computational design of semiconductor systems

- Overview of Epitaxial Growth
- Self-Organized Growth of Semiconductor Quantum Dots
- Thin Film Growth on Flat or Vicinal Substrates
- Doping Engineering of Semiconductors
- Diluted magnetic semiconductors (DMS)

Overview of Epitaxial Growth

Some Basic Concepts in Heteroexpitaxial Growth

- **Stable vs. Unstable Growth**
- **Strain & Stress**
- **ATG (Asaro-Tiller-Grinfeld) Instability**
- **SK (Stranski-Krastanov) Growth**

Stable Growth vs. Unstable Growth

- **Stable Growth**

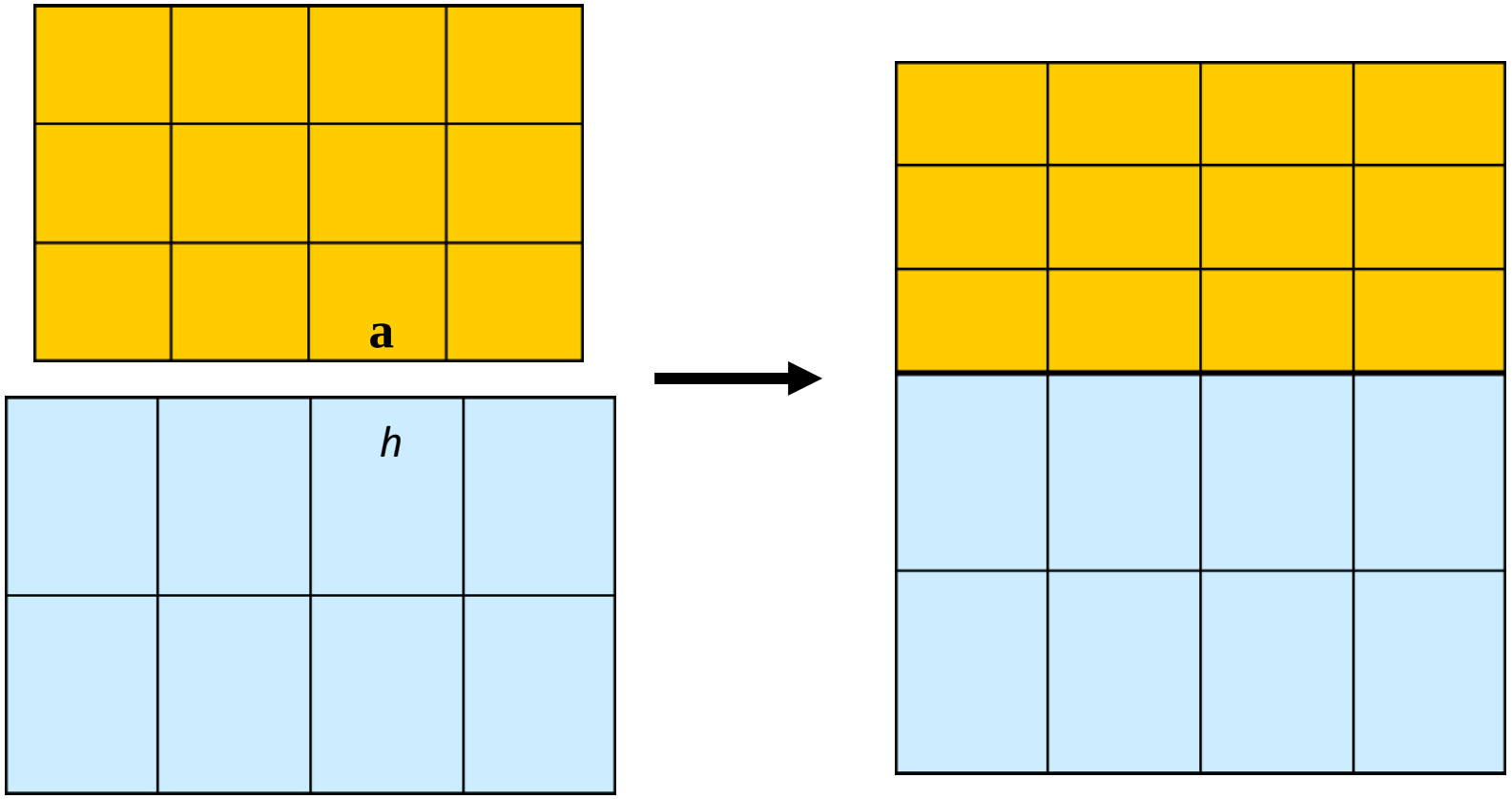
A growth system (nonequilibrium) is stable if the system has built-in error-correction mechanisms to preserve its inherent characteristic properties, such as the overall dimensionality, structural phase, or symmetry.

- **Unstable Growth**

A growth system is unstable if any fluctuation or error can be amplified in subsequent growth.

Morphological instability causes dimensionality d to change.

Strain & Stress



- **Strain energy accumulates in an epitaxial film due to lattice mismatch.**
- **Film is under stress.**

Lattice Mismatch

- Lattice constant in film : a
- Lattice constant in substrate: h
- Relative lattice mismatch $\varepsilon=(a-h)/h$

Strain in Epitaxial Systems

- **Lattice mismatch leads to strain**
  - Heteroepitaxy: A/B
  - Ge/Si has 4% lattice mismatch
  - AlSb/ InAs: 1.3% lattice mismatch
  - GaAs/InAs: 7%
- **Device performance affected by strain**
  - band-gap properties
- **Relief of strain energy results in geometric structures**
  - Quantum dot arrays

Three Growth Modes in Heteroepitaxy (A/B)
(Bauer, 1958)

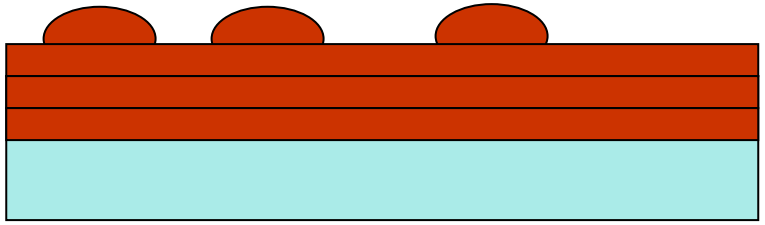
(a) 2D or layer-by-layer

(Frank - Van der Merwe)

$\Delta\gamma = \gamma_o + \gamma_i - \gamma_s < 0$

(b) 2D followed by 3D islanding

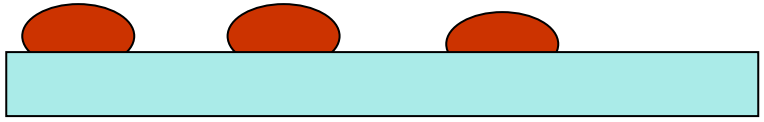
(Stranski - Krastanov)



$\Delta\gamma \sim 0$

(c) 3D islanding

(Volmer - Weber)



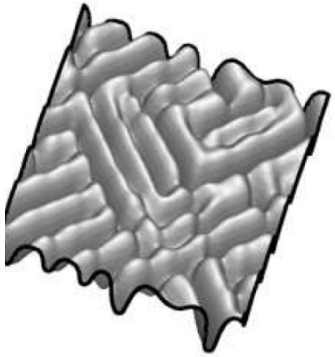
$\Delta\gamma > 0$

ATG Instability

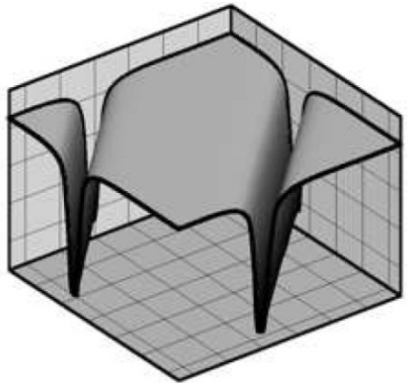
The **ATG** (**Asaro-Tiller-Grinfeld**) instability is an elastic instability, which is often encountered during molecular beam epitaxy. If there is a mismatch between the lattices of the growing film and the supporting substrate, elastic energy will be accumulated in the growing film. At some critical thickness, the free energy of the film can be decreased if the film breaks into isolated islands, where the tension can be relaxed laterally. The critical height depends on *Young's moduli (E and ν)*, *mismatch* size (ε), and *surface tensions* (γ).

M. Grinfeld, Sov. Phys. Dokl. **31**, 831 (1986)

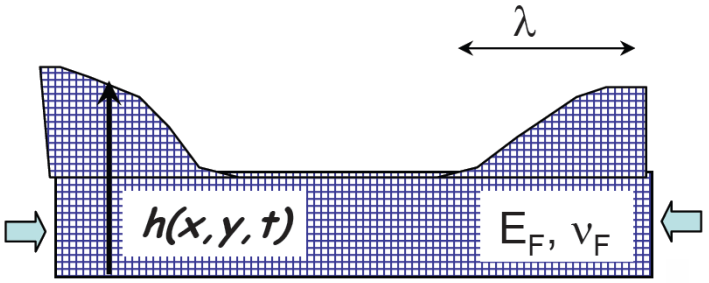
R. Asaro and W. Tiller, Metall. Trans. **3**, 1789 (1972).



Asaro-Tiller-Grinfeld (ATG) Model: Balance between **surface strain** (destabilizing) and **curvature** (stabilizing)



Asaro-Tiller-Grinfeld (ATG) Instability



$$\frac{\partial h(x,y,t)}{\partial t} = D\nabla^2\mu$$

Chemical potential energy with surface curvature κ

Surface energy — Elastic energy

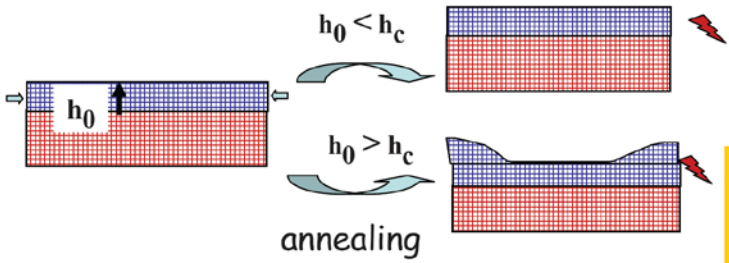
$$\mu = \gamma(h)\kappa + \gamma'(h) + \mathcal{E}[h(\mathbf{r})]$$

Wetting potential

Typical length $\lambda = \gamma/E_0 \sim 200\ nm$ for $Si_{0.8}Ge_{0.2}$, where E_0 is the flat film energy density.

Linear Analysis

$$h(x,y,t) = h_0 + \delta h \cdot e^{ikr+\alpha t}$$
$$\alpha = -c_w k^2 + |k|^3 - k^4$$
$$\gamma(h) = \gamma[1 + c_w \exp(-h/\delta)]$$

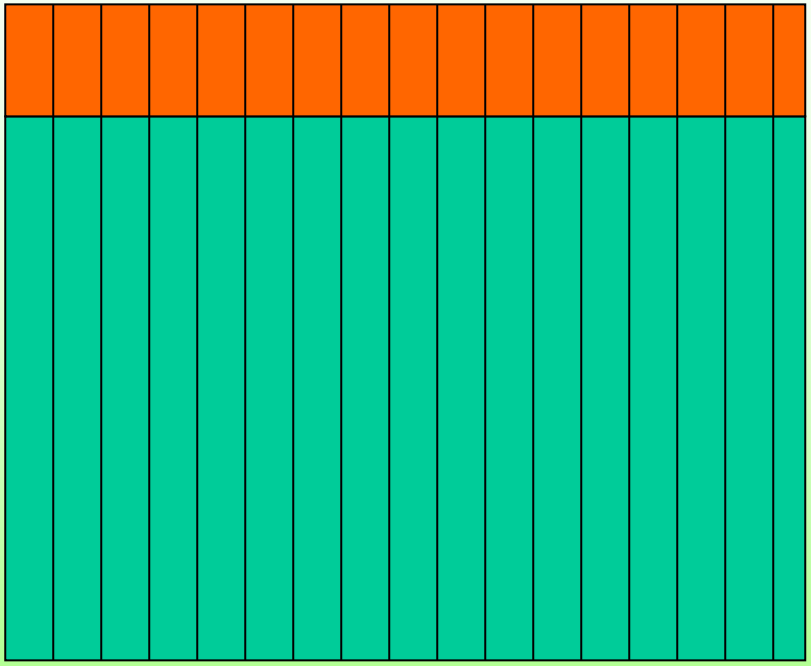


Flat film stable for $h_0 < h_c$

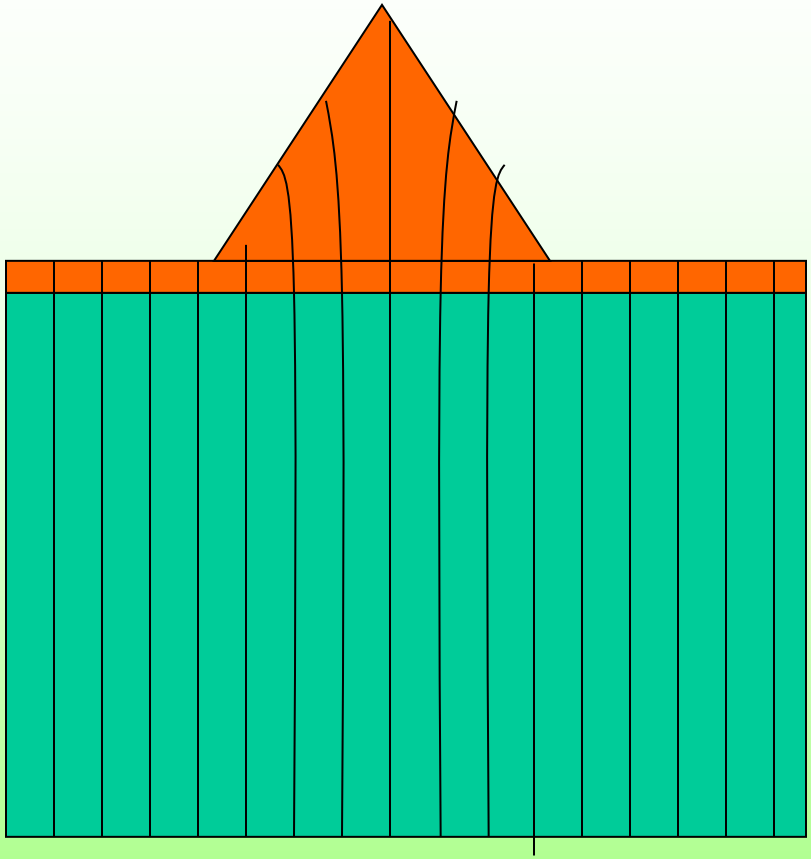
Wetting-ATG instability for $h_0 > h_c$

What evolution ?
Finite-time Singularity … ?

Stressed film



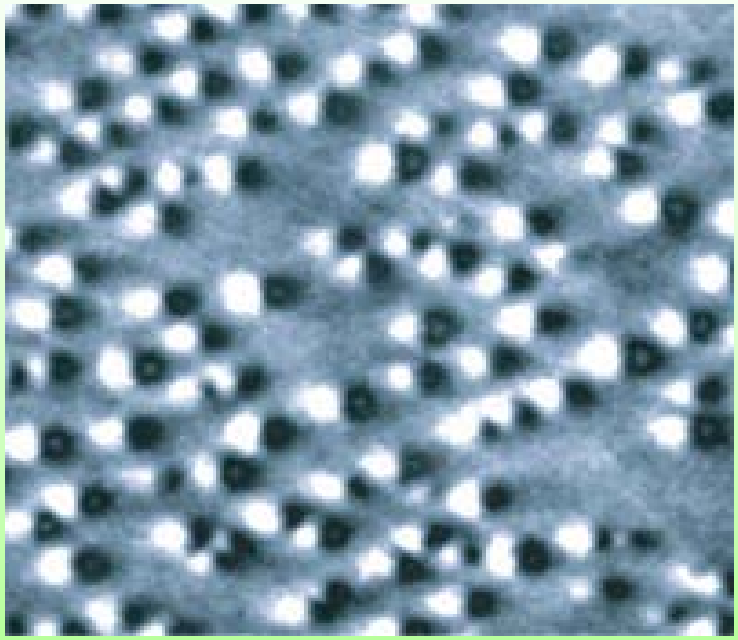
Partial relaxation

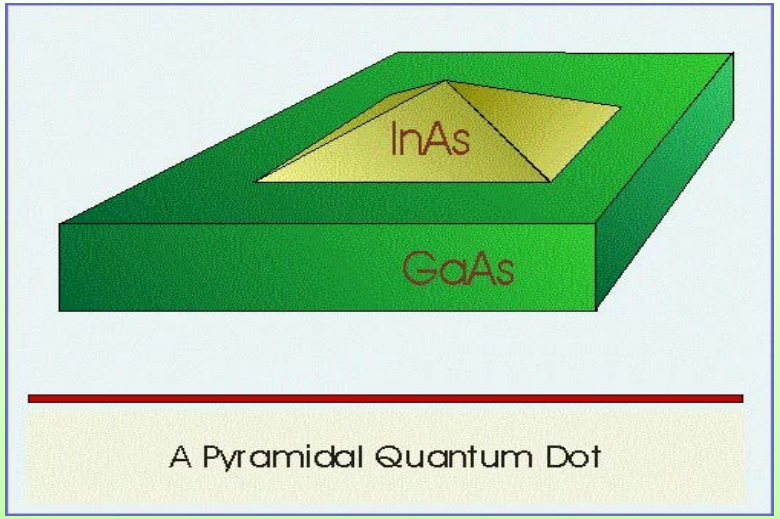


Narrow size observed InGaAs/GaAs, InAs/InP, InAS/InGaAs, ……

ATG Intability (Asaro-Tiller, 1972 -Grinfeld, 1986)
also named Stranski–Krastanov (SK) growth

Quantum dot formation





- Pyramid-shaped quantum dots can be grown from indium, gallium, and arsenic.
- Each dot is about 20 nanometers wide and 8 nanometers in height.

Self-Organized Growth of Semiconductor Quantum Dots

Good Review Articles:

1. V. A. Shchukin & D. Bimberg, Spontaneous ordering of nanostructures on crystal surfaces, Rev. Modern Phys. 71, 1125-1171 (1999).

2. C. Duport, C. Priester, J. Villain, Equilibrium shape of coherent epitaxial clusters, in: Z. Y. Zhang, MG Lagally (Eds.), Morphological Organization in Epitaxial Growth and Removal, World Scientific Series on Directions in Condensed Matter Physics, 1997, p. 73.

Self-Organized Formation of Nanostructures in Strained Thin Films

Courtesy of

Feng Liu, Professor & Chair
Department of Materials Science and Engineering
Center for Computational Design of Nano-Materials
University of Utah, Salt Lake City, UT

Self-Organization

Atomic Scale --- minimizing chemical bonding energy

self-organization of atoms and molecules
(crystal growth, fractal formation)

Nano Scale --- minimizing elastic strain energy

self-organization of islands (quantum dots)
and steps (quantum wires)

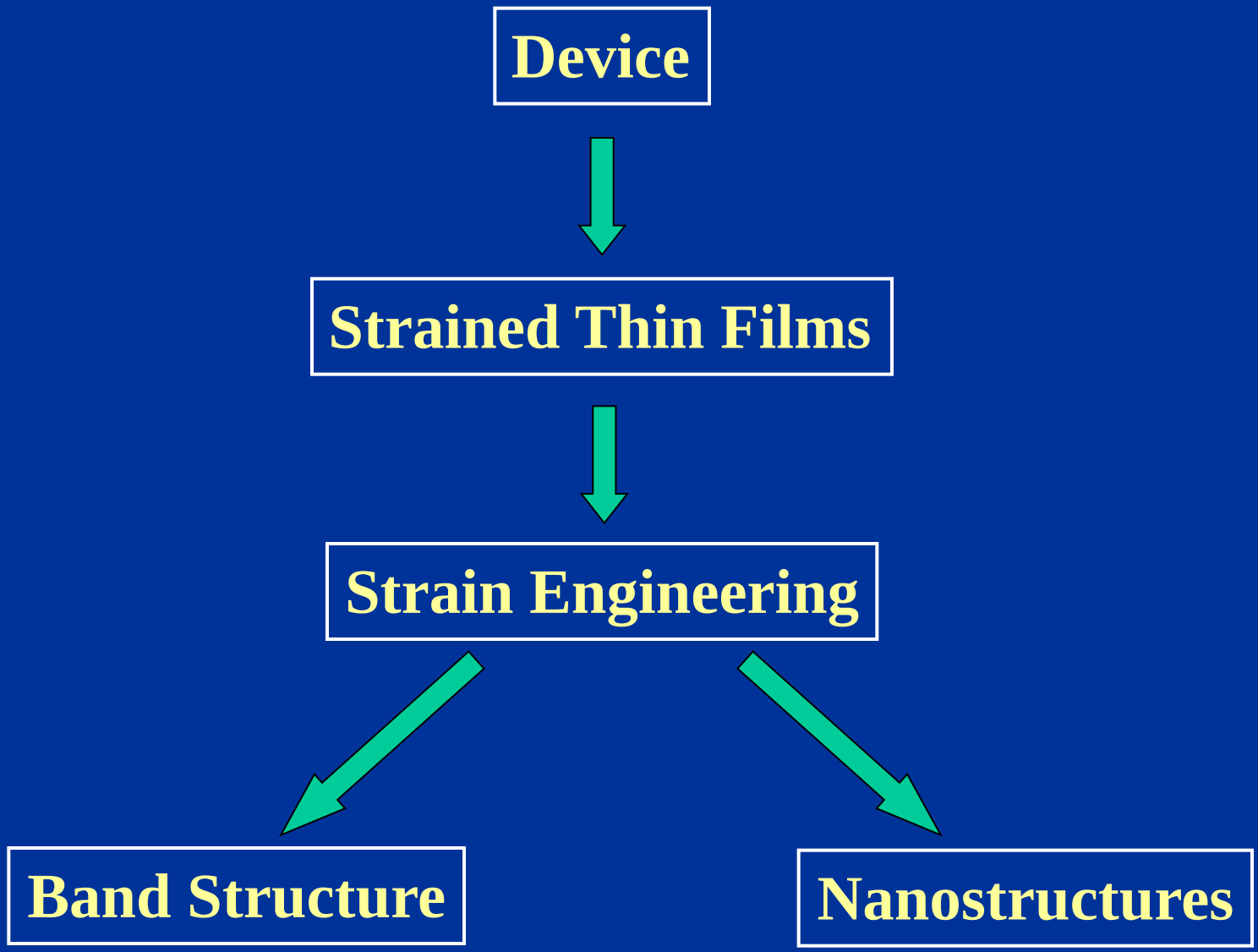
Why Strain Induced Self-assembly?

Length Scale of Self-Assembly

Crystal --- Atomic Scale --- Chemical bonding

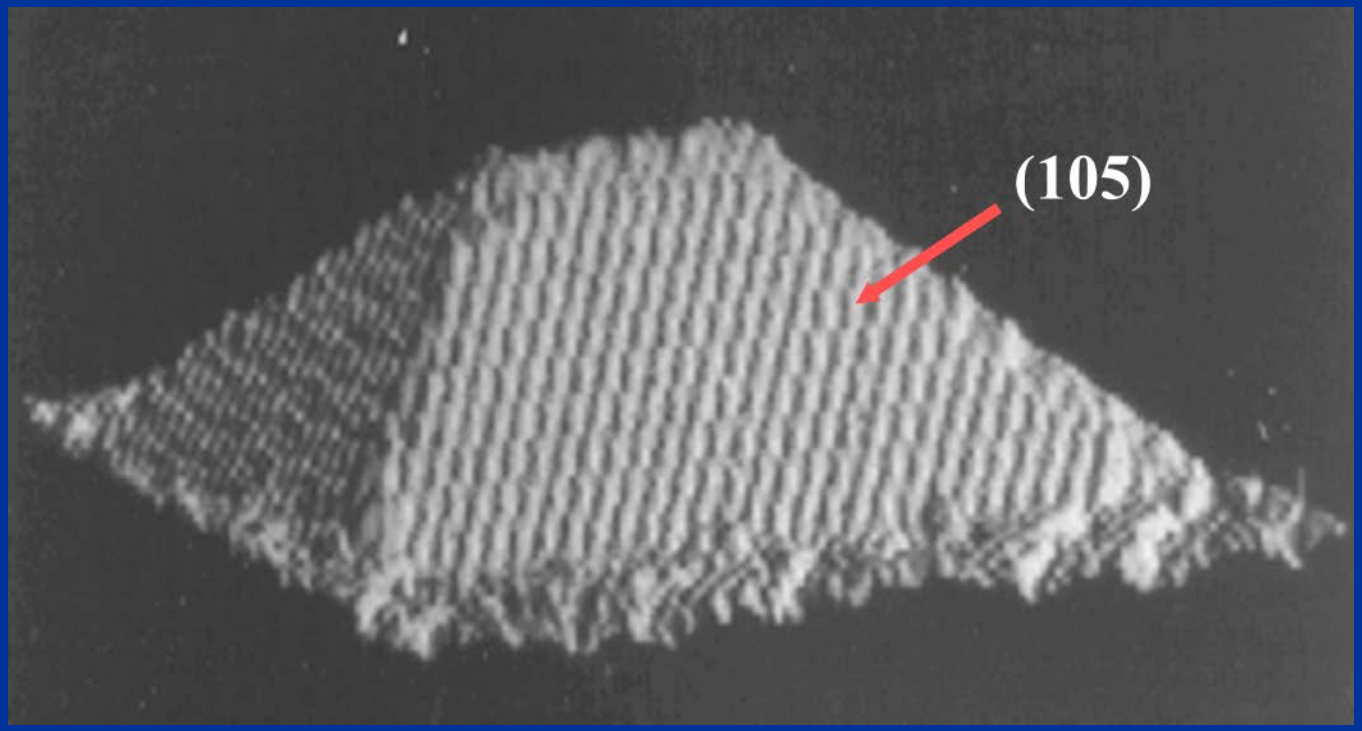
Nanostructure --- Nanoscale --- Elastic Force

"Strain"


Device
Strained Thin Films
Strain Engineering
Band Structure
Nanostructures

STM Image of Ge Island on Si(001)

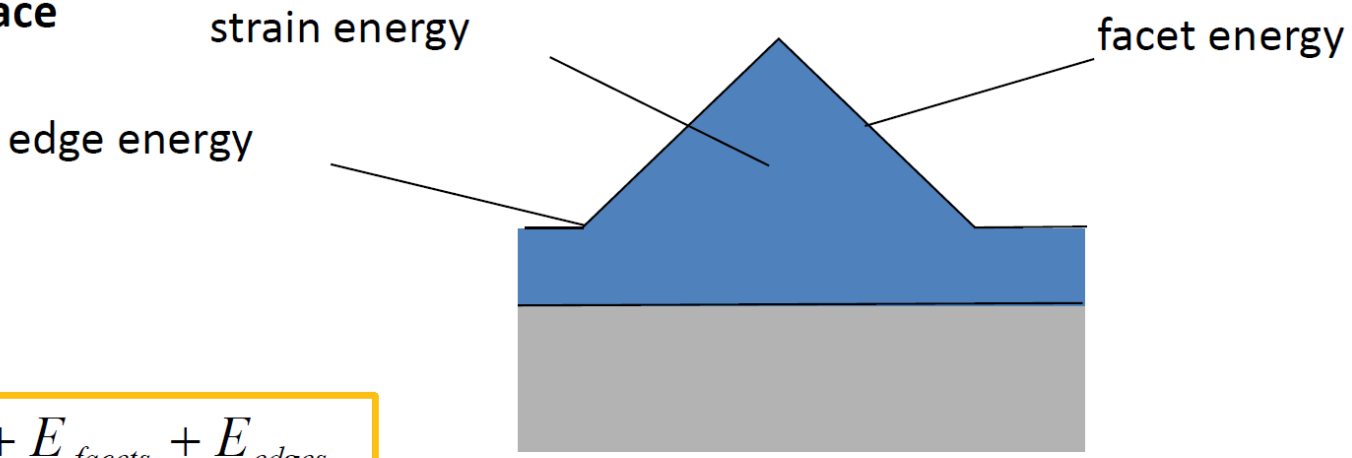
Mo et al., PRL 1990



Equilibrium coherent island shape

Contributions to total energy of isolated island (thermodynamics)

→ **strain and surface**



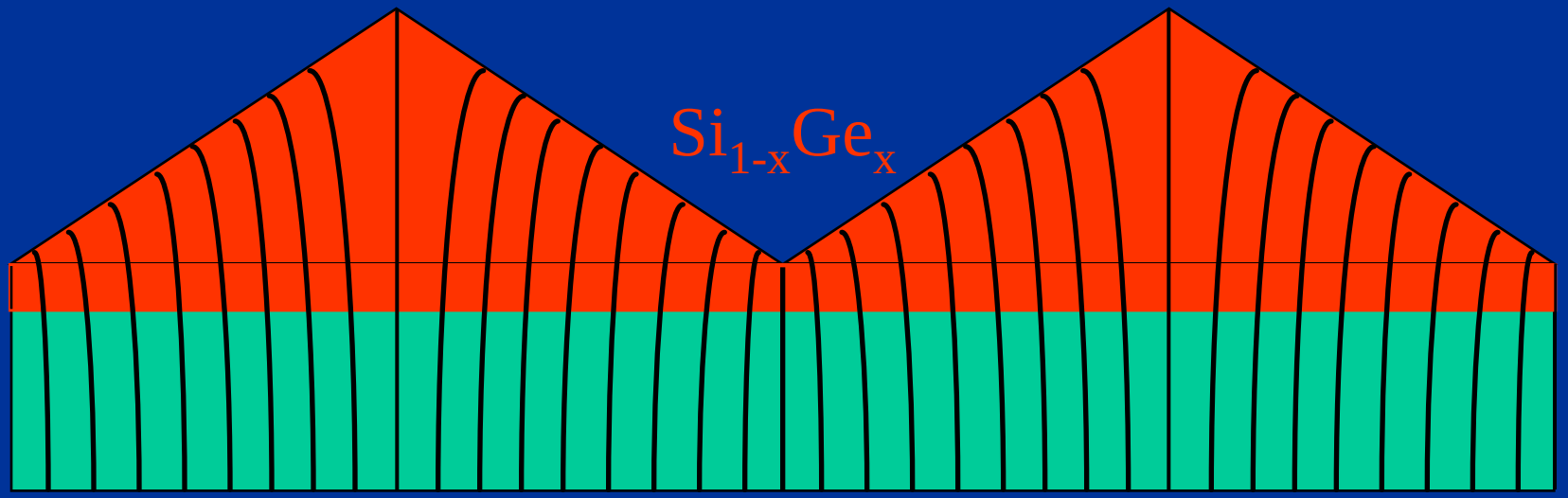
$$E_{island} = E_{strain} + E_{facets} + E_{edges}$$

$$E_{strain} \propto V_{island} \propto h^3, \quad E_{facets} \propto A_{facets} \propto h^2, \quad E_{edges} \propto L_{edges} \propto h$$

- V_{island} = island volume, A_{facets} = area of facets, L_{edges} = length of edges, h = island height . Hence…

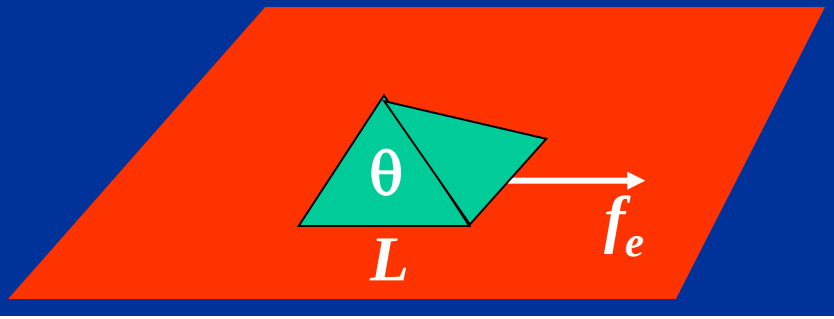
$$E_{island} = ah^3 + bh^2 + ch + d$$ ⟵ *a*, *b*, *c*, and *d* are constants → differentiate to find a minimum in energy = equilibrated shape, and hence an optimum island size

SK Growth: Mechanism of Strained Island Formation



$$\Delta E = a\Gamma(\theta)V^{2/3} - b\varepsilon^2 V$$

Continuum Theory of QD Formation Energy



$$E = 4\Gamma V^{2/3}\tan^{1/3}\theta - 6cV\tan\theta$$

surface **strain**

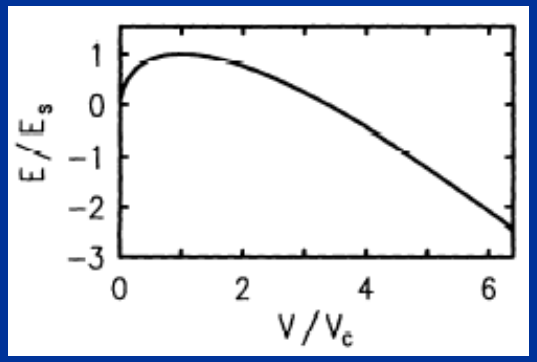
$\Gamma = \gamma_h csc\theta - \gamma_w cot\theta$ represents the increase of surface energy in presence of a wetting layer with γ_h and γ_w being energy per area of the hut and wetting-layer surface.

$V = h^3 cot^2\theta$ is the hut volume.

$c = (E_{Ge}\varepsilon)^2(1-\upsilon)/(2\pi G_{Si})$ with E_{Ge} and ε being the Young's modulus and the misfit strain of the Ge film, and υ and G_{Si} the Poisson ratio and shear modulus of the Si substrate.

J. Tersoff, PRL **72**, 3570 (1994); V.A. Shchukin, *et.al.* PRL **75**, 2968 (1995).

Equilibrium coherent island shape



- **Critical size for nucleation/formation?**
- **Stability for self-assembly?**

There are two possible mechanistic pathways of hut formation: One through a thermally activated **nucleation process** and the other through a **barrierless process involving faceted huts transformation** from nonfaceted prepyramids (mounds or stepped islands).

If huts form via the nucleation, there exists a critical size of nucleus, beyond which huts favor growth over decay. If huts form via the transformation, there exists a minimum size, beyond which huts become more stable than prepyramids.

Beyond Continuum Theory: First-Principles Based Modeling

First-principles calculation

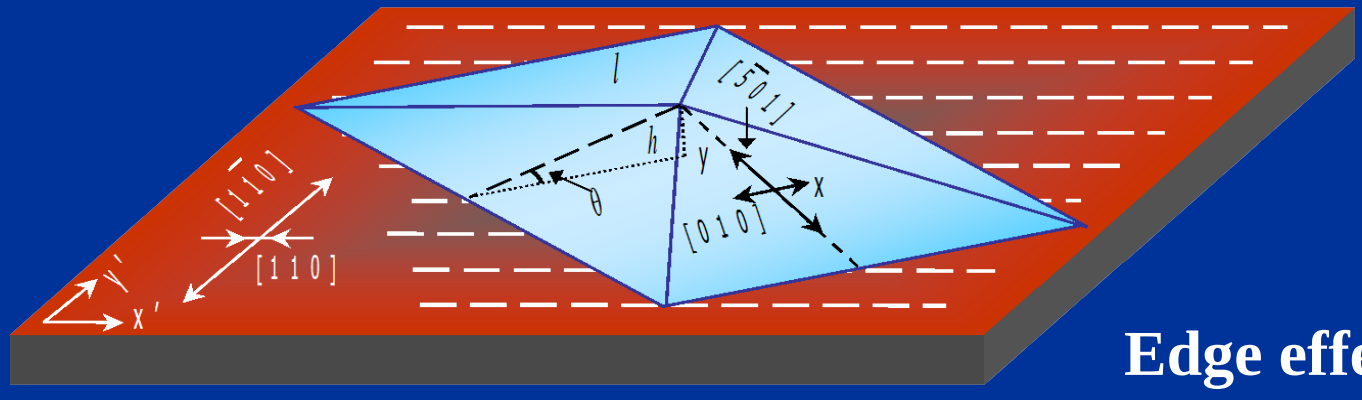
+

Continuum modeling

Previous difficulty:

- facet: high-index surface
- correct structure
- large supercell containing lots of atoms
- expertise in both first-principle and continuum method

(105)-faceted Ge Dot on Si(001)



Edge effect

$$E = 4\Gamma V^{2/3}\tan^{1/3}\theta - 6cV\tan\theta - 8C'V^{1/3}\cot^{1/3}\theta\ln(2V^{1/3}\cot^{1/3}\theta/a)$$

$$\Gamma = \gamma_h \csc\theta - \gamma_w \cot\theta$$

$$V \approx h^3\cot^2\theta$$

$$c = (M_{Ge}\varepsilon)^2(1-\nu)/2\pi G_{Si}$$

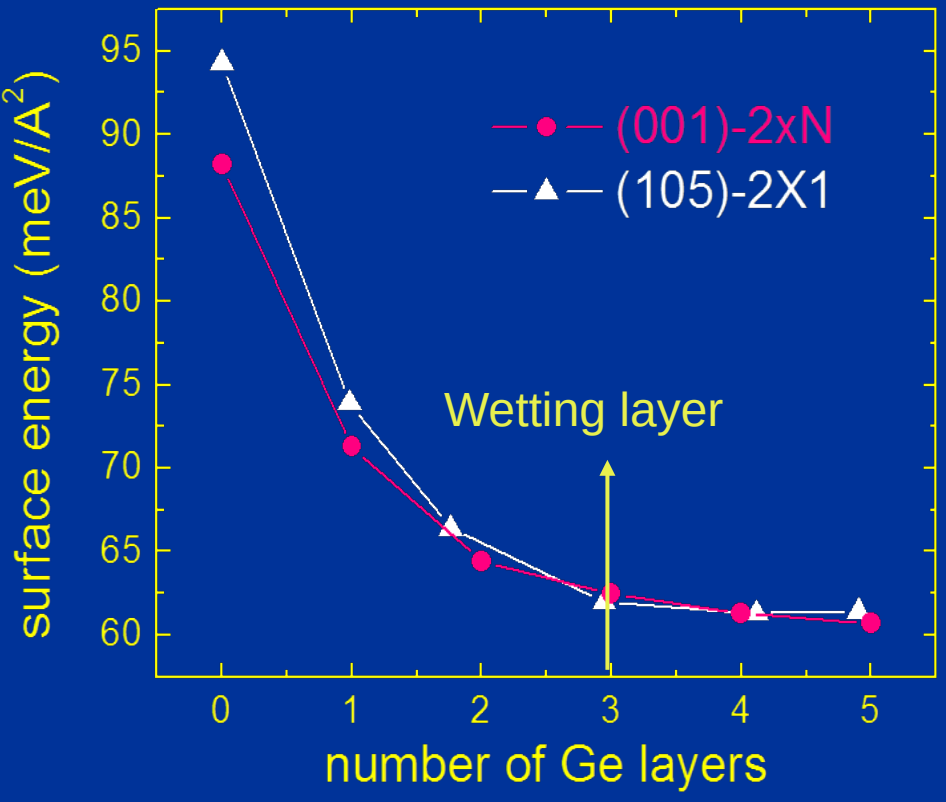
$$c' = F_\perp^2(1-\nu)/2\pi G_{Si}$$

γ_h : converged Ge/Si(105) surface energy

γ_w : Ge/Si (001) surface energy of 4 and 5 layers Ge deposition

$$F_\perp = \sigma_{xx}^h \cdot \cos\theta = 44.9$$

First-principles Surface Energy Calculation



one (001) layer ~ 2.55 (105) layers

- Become degenerate at ~3 ML, explaining

  formation of (105) facet

  3-4 ML of wetting layer thickness

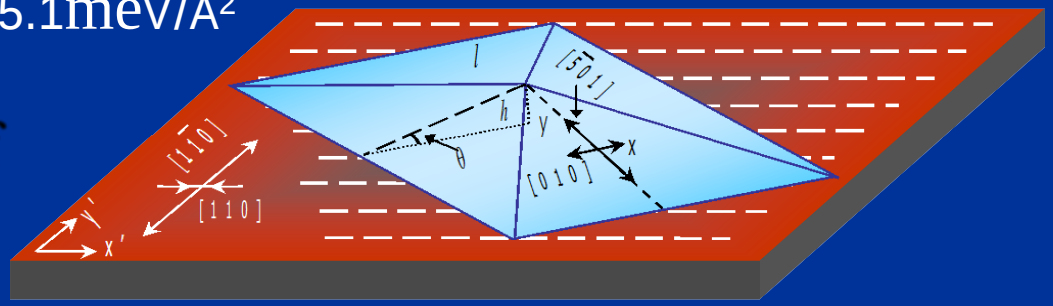
First-principles Surface Stress Calculation

Surface stress discontinuity:

<105> direction (normal to edge): 44.9 meV/A^2

<001> direction (parallel to edge): 5.1meV/A^2

Rotating the principal axes of wetting layer Ge/Si(001):



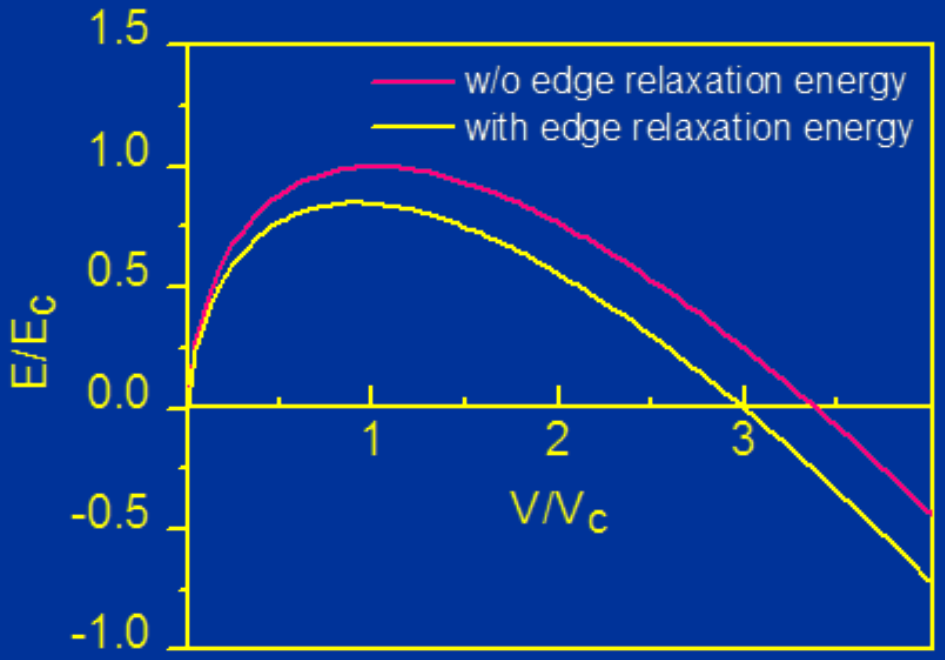
Ge/Si (001) (x', y') → (105) (x, y) ϕ : 45°

$$\begin{pmatrix} \sigma^w_{xx} \\ \sigma^w_{yy} \end{pmatrix} = \begin{pmatrix} \cos^2\phi & \sin^2\phi \\ \sin^2\phi & \cos^2\phi \end{pmatrix} \begin{pmatrix} \sigma^w_{x'x'} \\ \sigma^w_{y'y'} \end{pmatrix} = \begin{pmatrix} 0.5 & 0.5 \\ 0.5 & 0.5 \end{pmatrix} \begin{pmatrix} 79.1 \\ -5.3 \end{pmatrix} = \begin{pmatrix} 36.9 \\ 36.9 \end{pmatrix}$$

Isotropic !

It is interesting to see that, although the wetting-layer stress tensor is highly anisotropic in the original coordinate system, it coincidentally becomes isotropic after transformation.

Quantitative Prediction: Critical Size & Stability



$h_c \approx 4\Gamma / 9c$

$h_c \sim \varepsilon^{-2}$

Pure Ge hut:

$h_c \sim$ 16Å; 6800 atoms

$Si_{0.75}Ge_{0.25}$ alloy hut:

$h_c \sim$ 216Å; 2.3×10^7 atoms

No stable size !

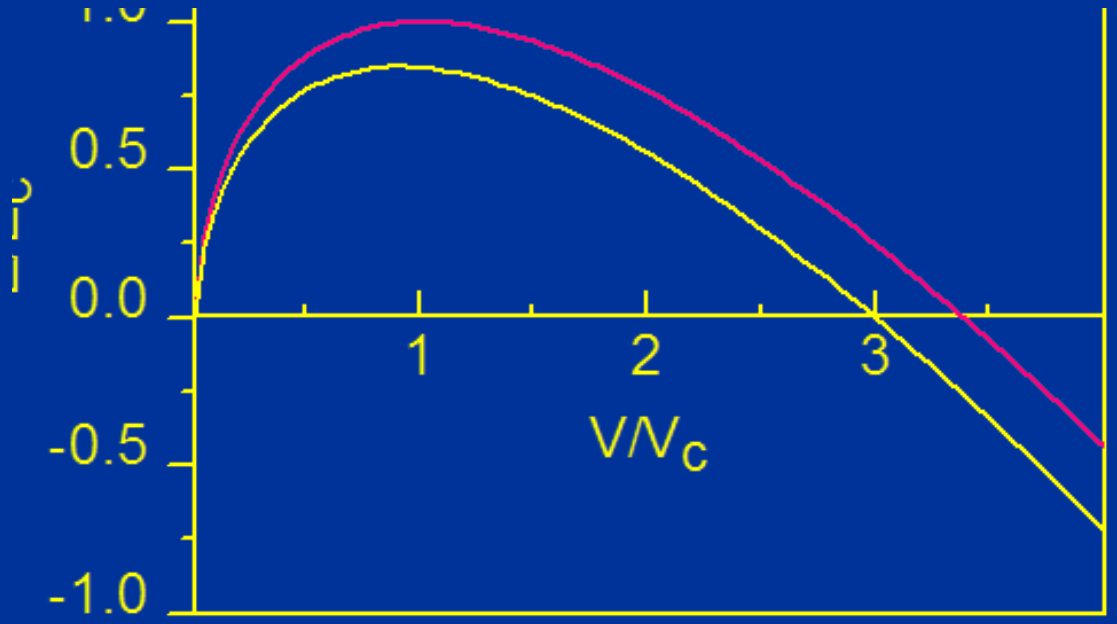
Formation mechanism:

- The hut is unlikely to form via nucleation mechanism because much too large thermal fluctuation involving too many atoms is required.

- non-faceted “pre-pyramids” : Before reaching so many atoms, other nonfaceted prepyramids shall form first as continuum mounds or stepped islands due to thermodynamic or kinetic surface roughening.

Quantitative Prediction: Stability

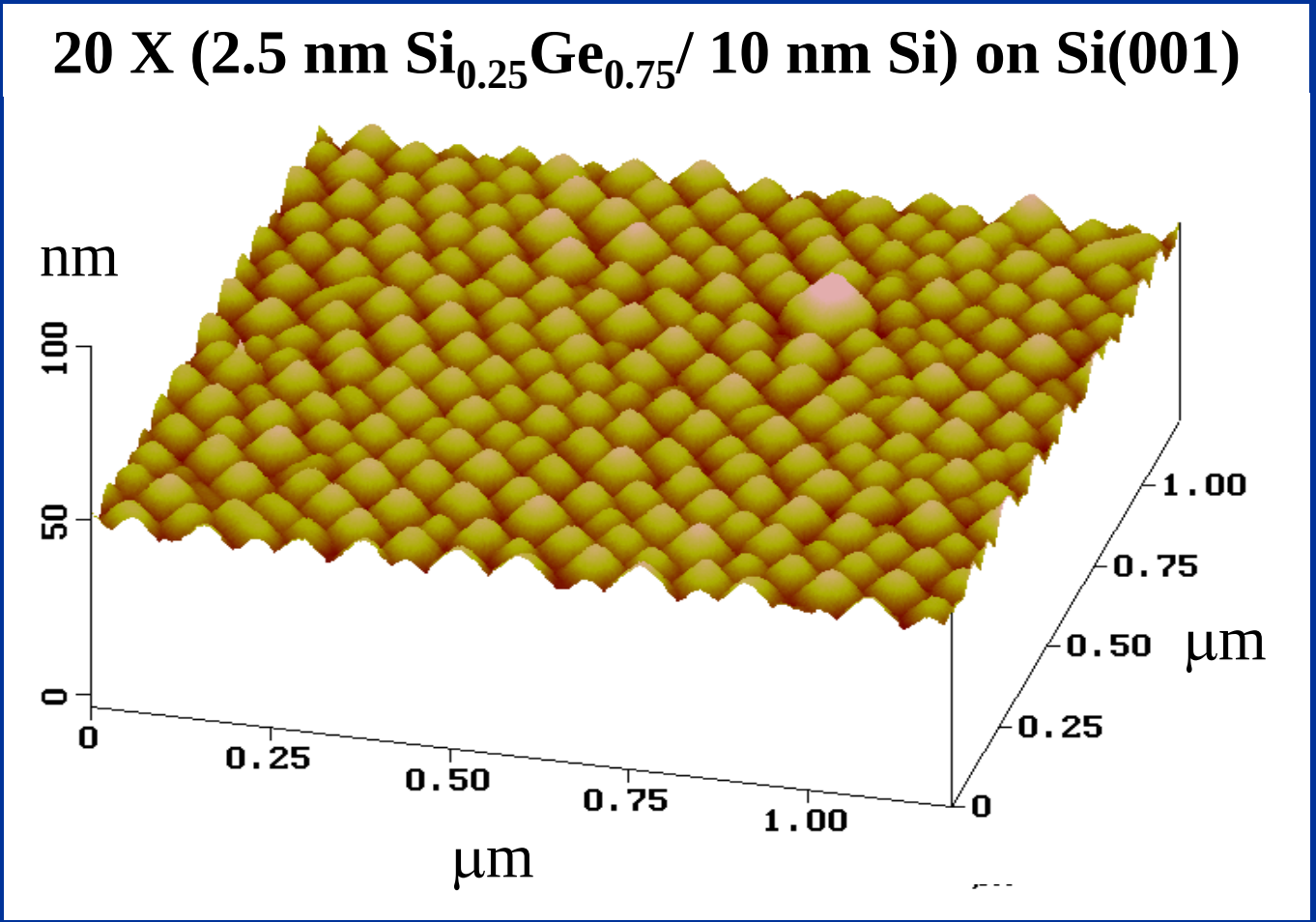
$$E = 4\Gamma V^{2/3}\tan^{1/3}\theta - 6cV\tan\theta - 8C'V^{1/3}\cot^{1/3}\theta\ln(2V^{1/3}\cot^{1/3}\theta/a)$$



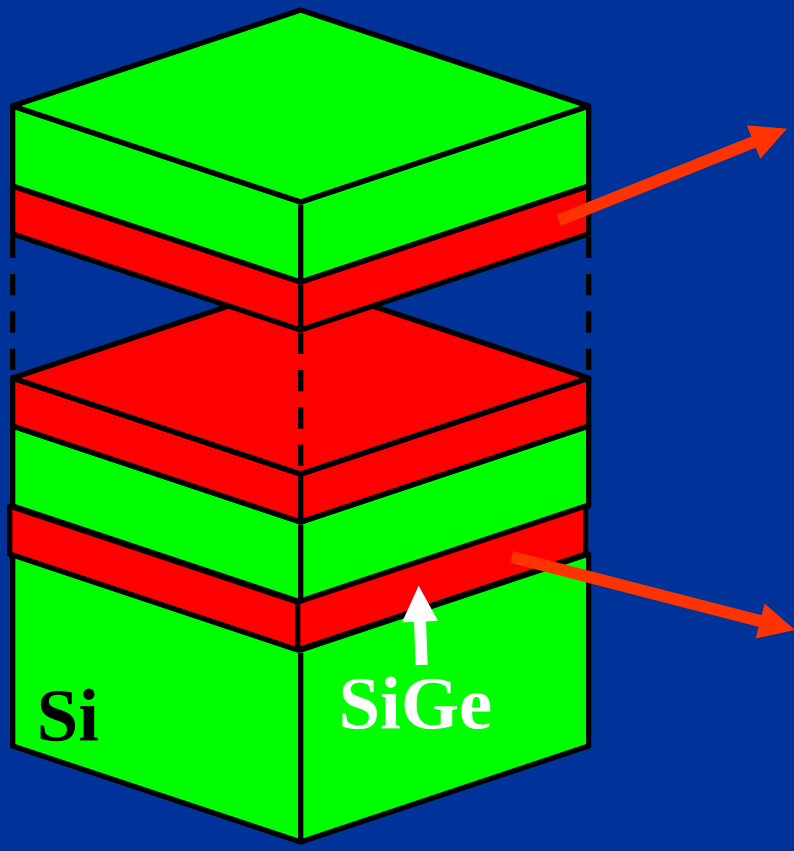
Edge effect is too small to induce stable island size !

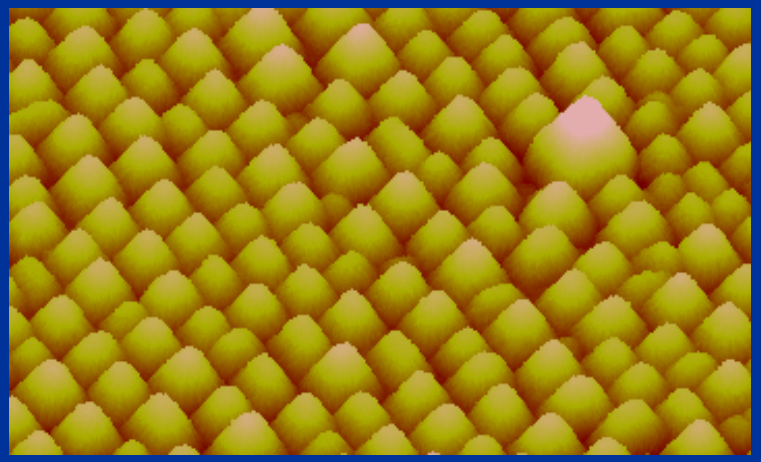
Lu & Liu, Phys. Rev. Lett., **94**, 176103 (2005)

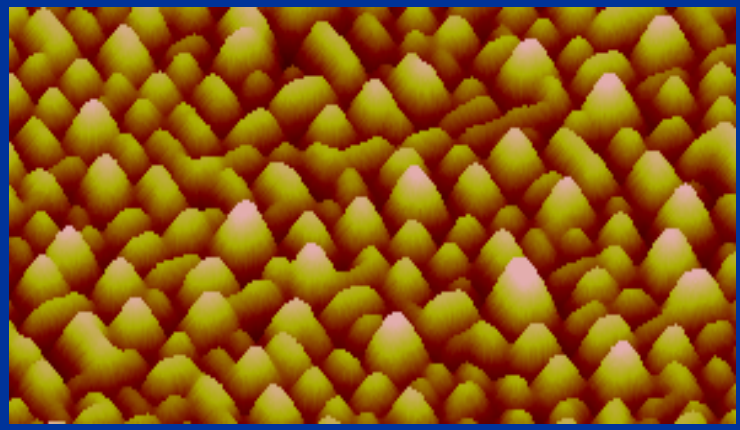
AFM Image of SiGe Islands in a Multilayer Film



Guided Self-Assembly Using Multilayers

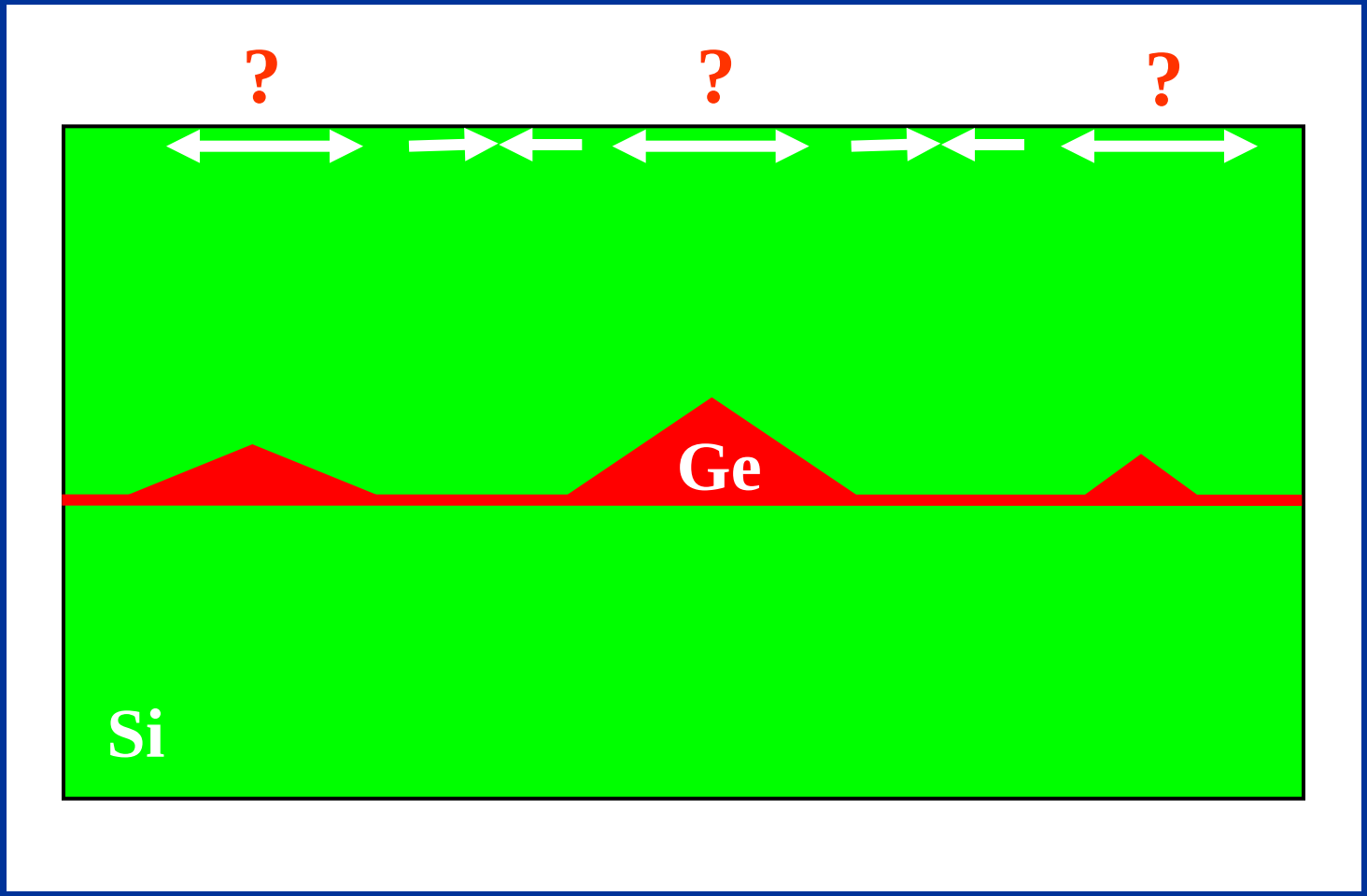




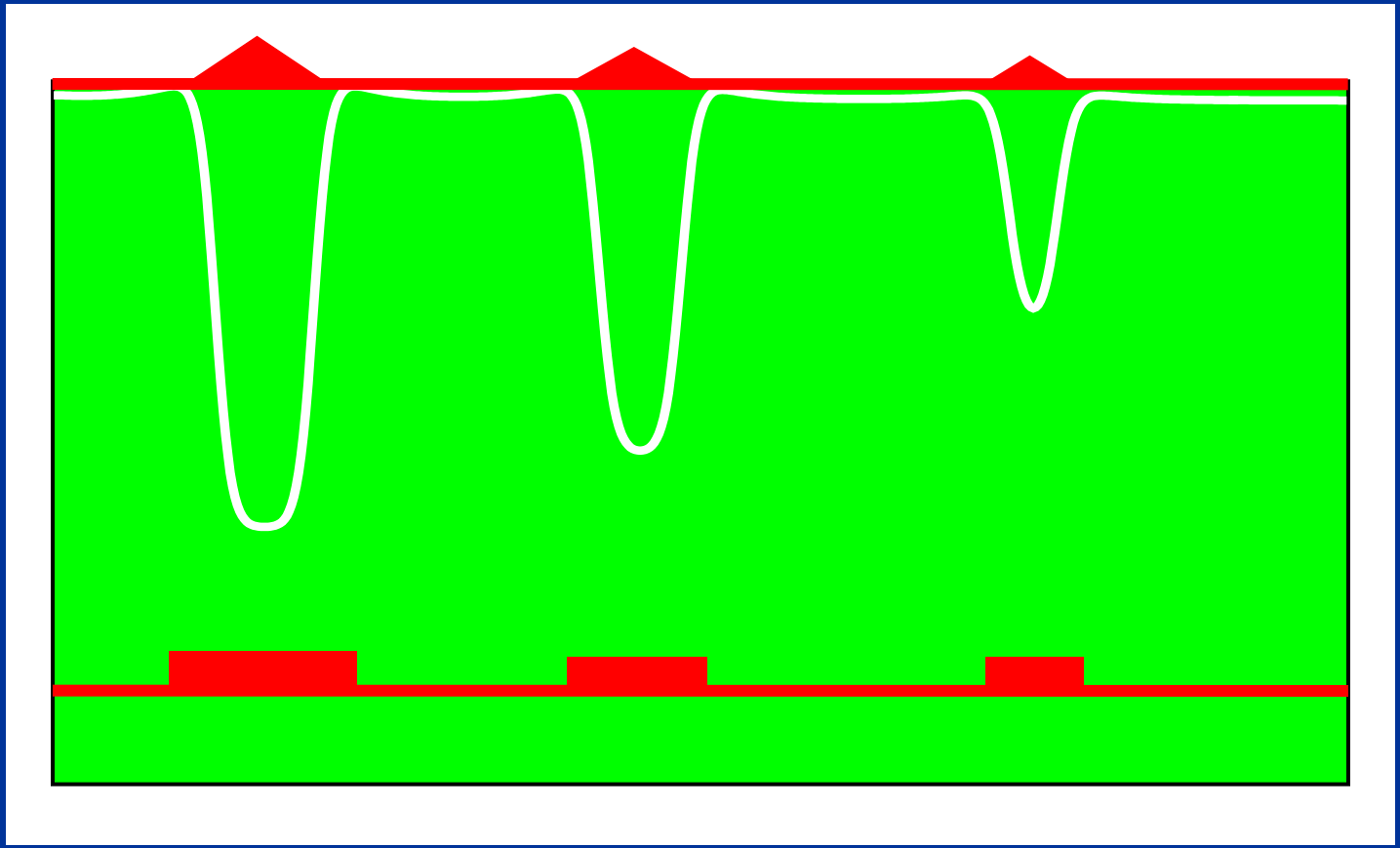


courtesy of M. Lagally

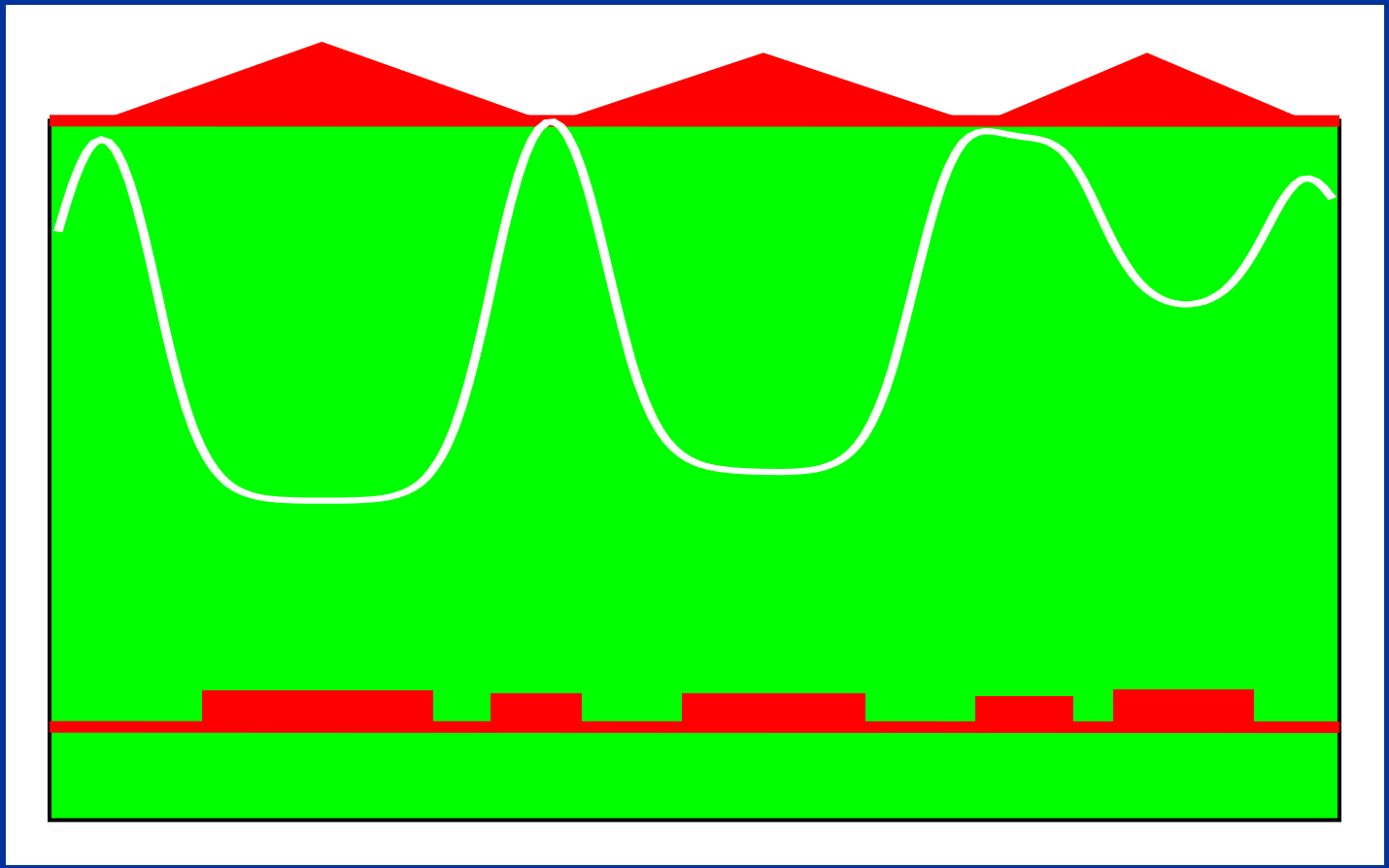
Island Formation in a Multilayer Film



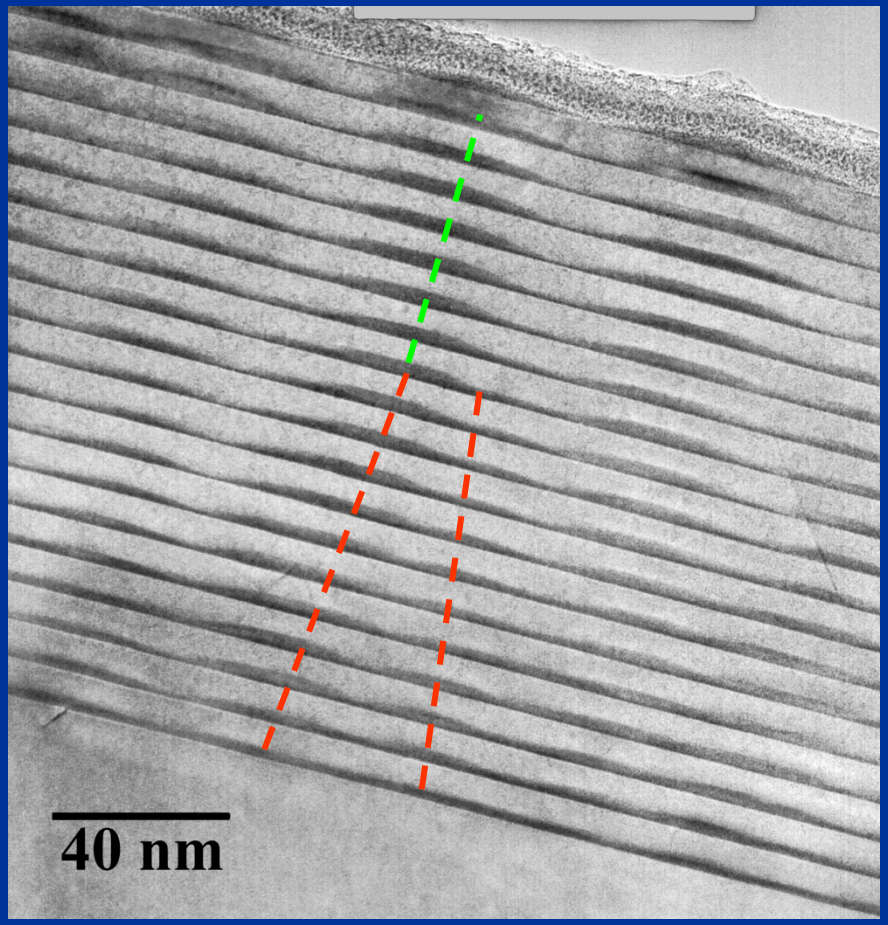
Surface Strain Field and Island Nucleation and Growth



Surface Strain Field and Island Nucleation and Growth

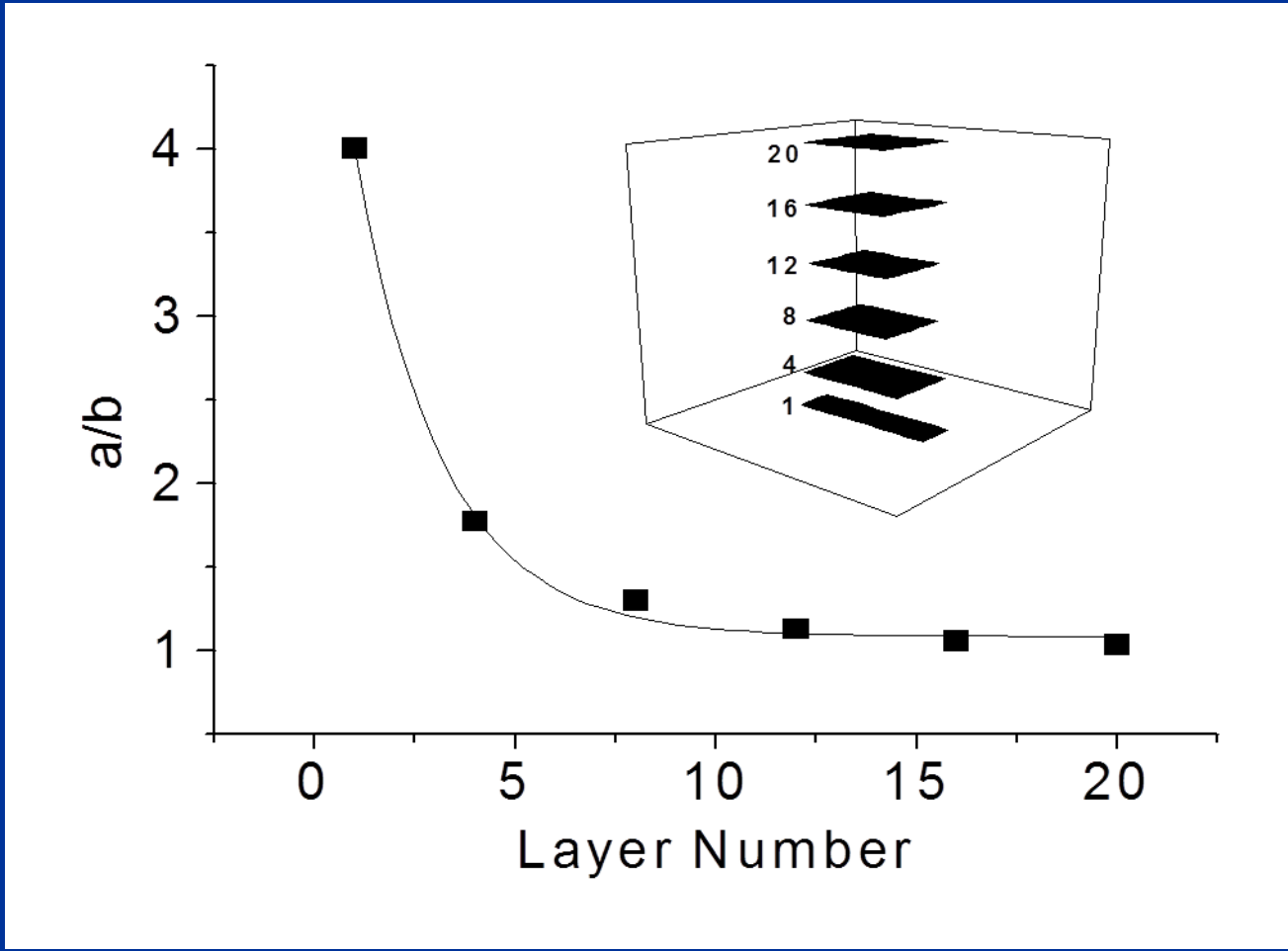


XTEM of SiGe islands in SiGe/Si Multilayers

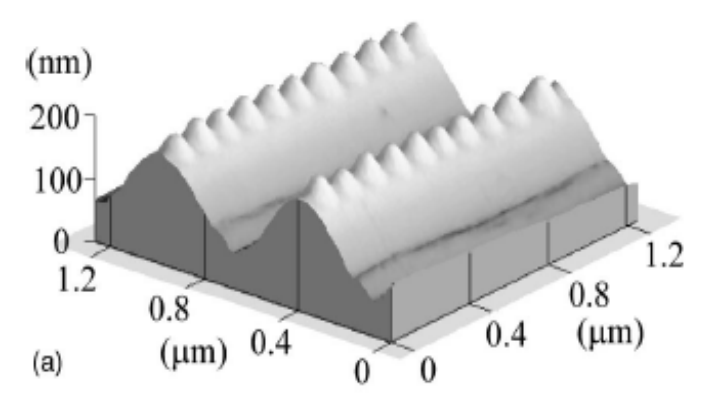


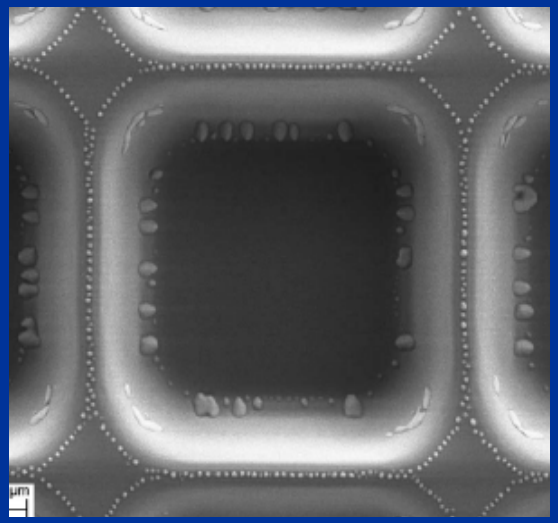
E.Mateeva et al., Appl. Phys. Lett. **71**, 3233 (1997)

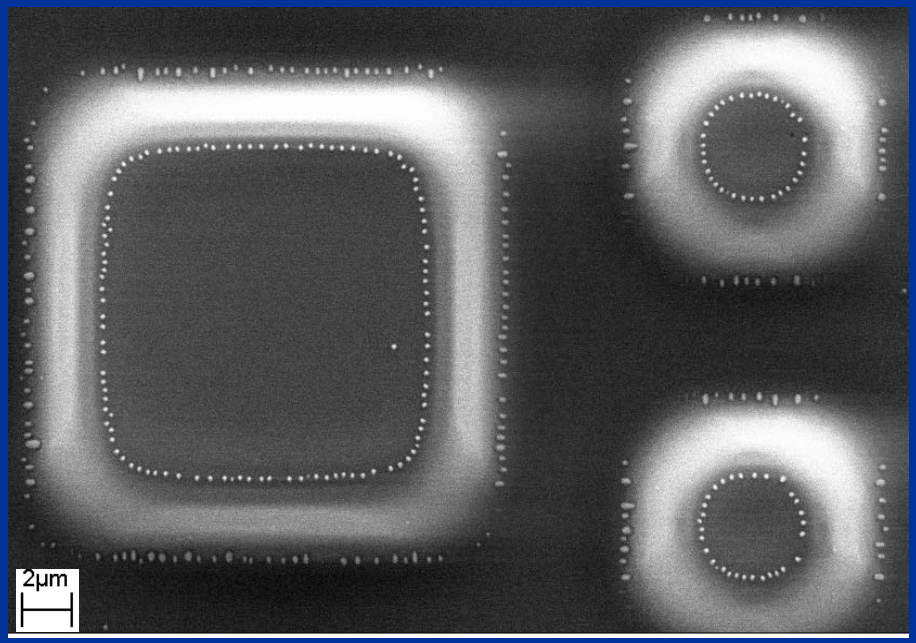
3D Simulation of Island Shape Transformation



A Hybrid Approach: Patterning + Self-assembly

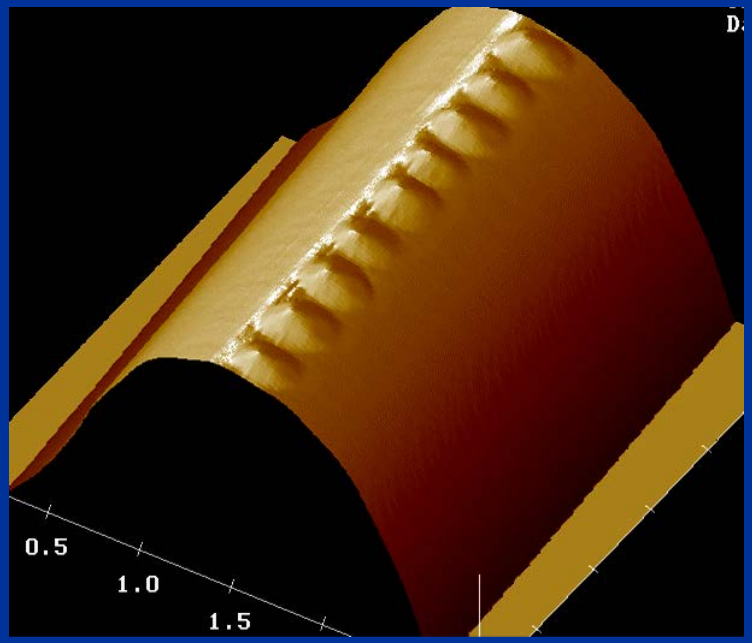


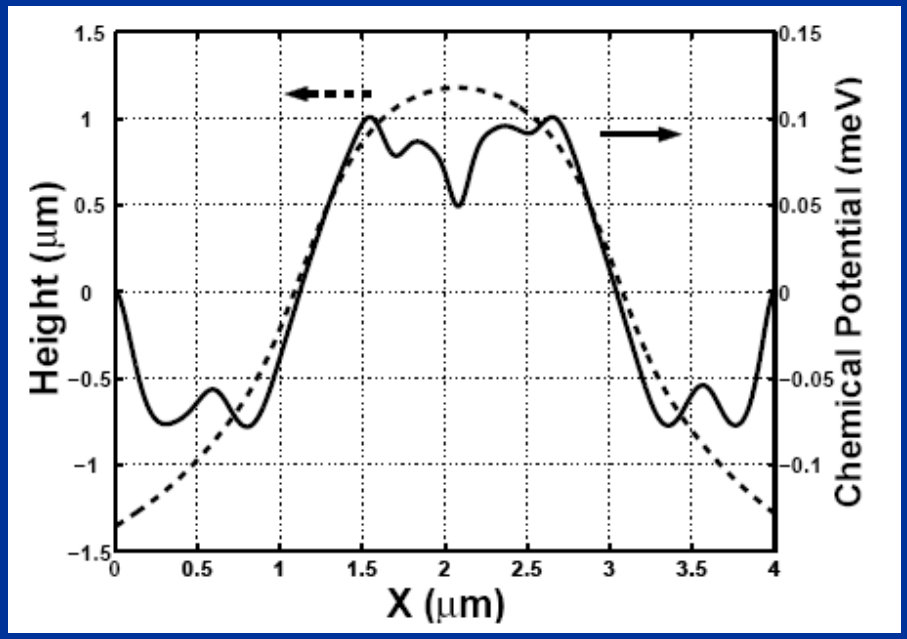




Jin, *et al.*, APL **75**, 2752 (99); Yang, *et al.*, PRL **92**, 0255502 (04)

Local-Strain-Mediated Chemical-Potential Control on Self-Assembly of Ge Quantum Dots





Yang, Liu, & Lagally, Phys. Rev. Lett., **92**, 025502 (04)