Growth and Pattern Formation for Epitaxial Surfaces

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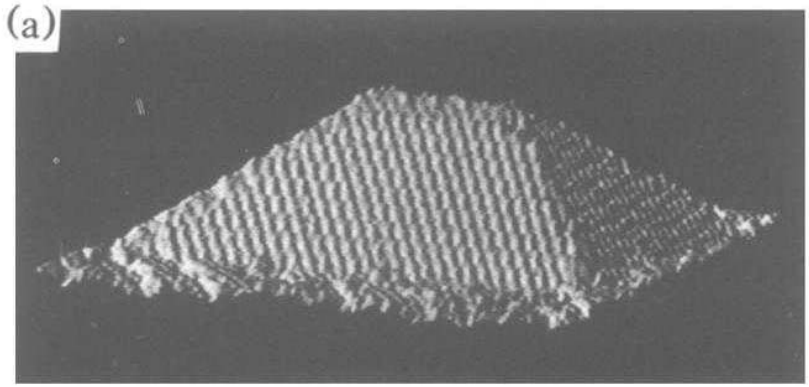
Outline

- Strain in epitaxial systems
  - Leads to structure
  - Quantum dots and their arrays
- Atomistic strain model
  - Lattice statics model
  - Lattice mismatch
- Numerical methods
  - Algebraic multigrid (AMG)
  - Artificial boundary conditions (ABC)
- Application to nanowires and nanocrystals
  - Step bunching instability
- Summary

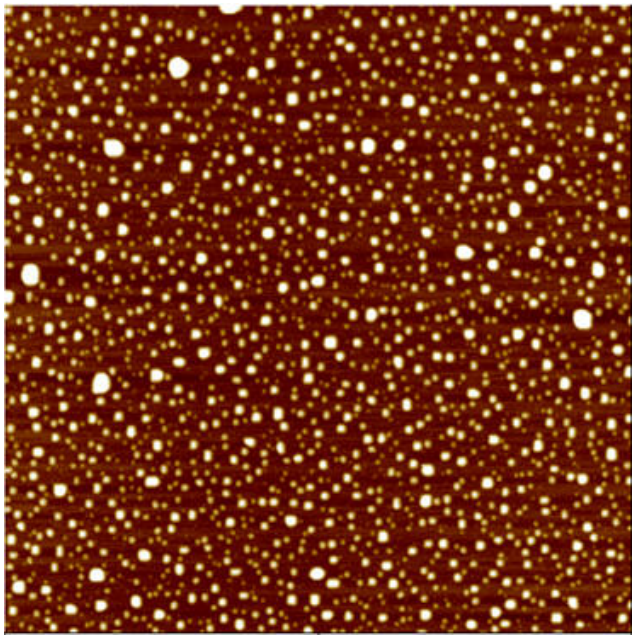
Strain in Epitaxial Systems

- Lattice mismatch leads to strain
  - Heteroepitaxy
  - E.g., Ge/Si has 4% lattice mismatch
- Relief of strain energy can lead to geometric structures
  - Quantum dots and q dot arrays

Quantum dots and Q Dot Arrays



Ge/Si, Mo et al. PRL 1990

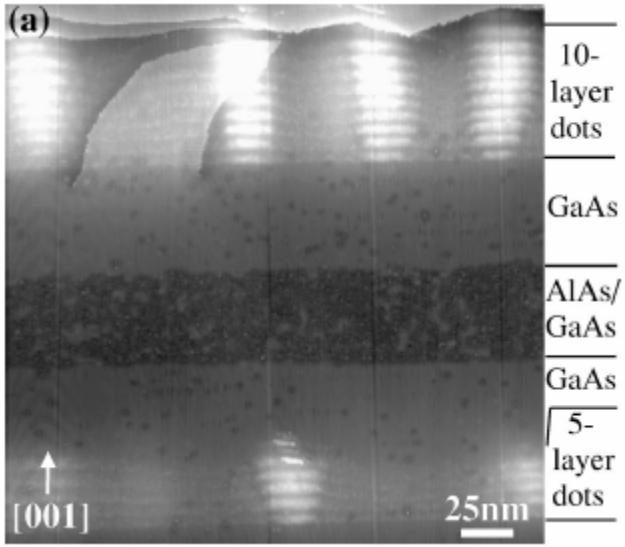


$Si_{.25}Ge_{.75}/Si$, $(5\ \mu m)^2$
MRSEC, U Wisconsin

Directed Self-Assembly of Quantum Dots

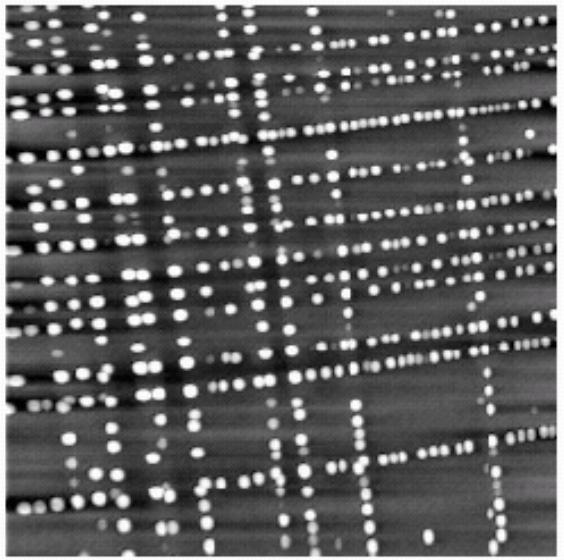
- Vertical allignment of q dots in epitaxial overgrowth (left)
- Control of q dot growth over mesh of buried dislocation lines (right)

$Al_xGa_{1-x}As$ system



B. Lita et al. (Goldman group), APL **74**, (1999)

GeSi system



H. J. Kim, Z. M. Zhao, Y. H. Xie, PRB **68**, (2003).

In both systems strain leads to ordering!

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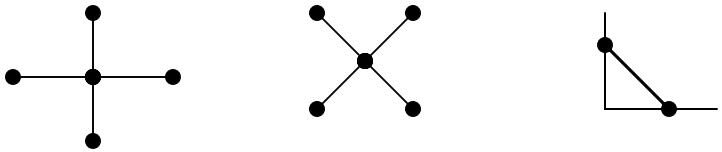
Atomistic Modeling of Strain in Thin Films

- Lattice statics for discrete atomistic system,
  - minimize discrete strain energy (Born & Huang, 1954)
  - Application to epitaxial films, e.g.
    - E.g., Stewart, Pohland & Gibson (1994), Orr, Kessler, Snyder & Sander (1992),
- Idealizations
  - Harmonic potentials, Simple cubic lattice
  - General, qualitative properties
    - Independent of system parameters
  - Computational speed enable additional physics & geometry
    - 3D, alloying, surface stress
- Atomistic vs. continuum
  - atomistic scale required for thin layer morphology
    - strain at steps
  - continuum scale required for efficiency
    - KMC requires small time steps, frequent updates of strain field

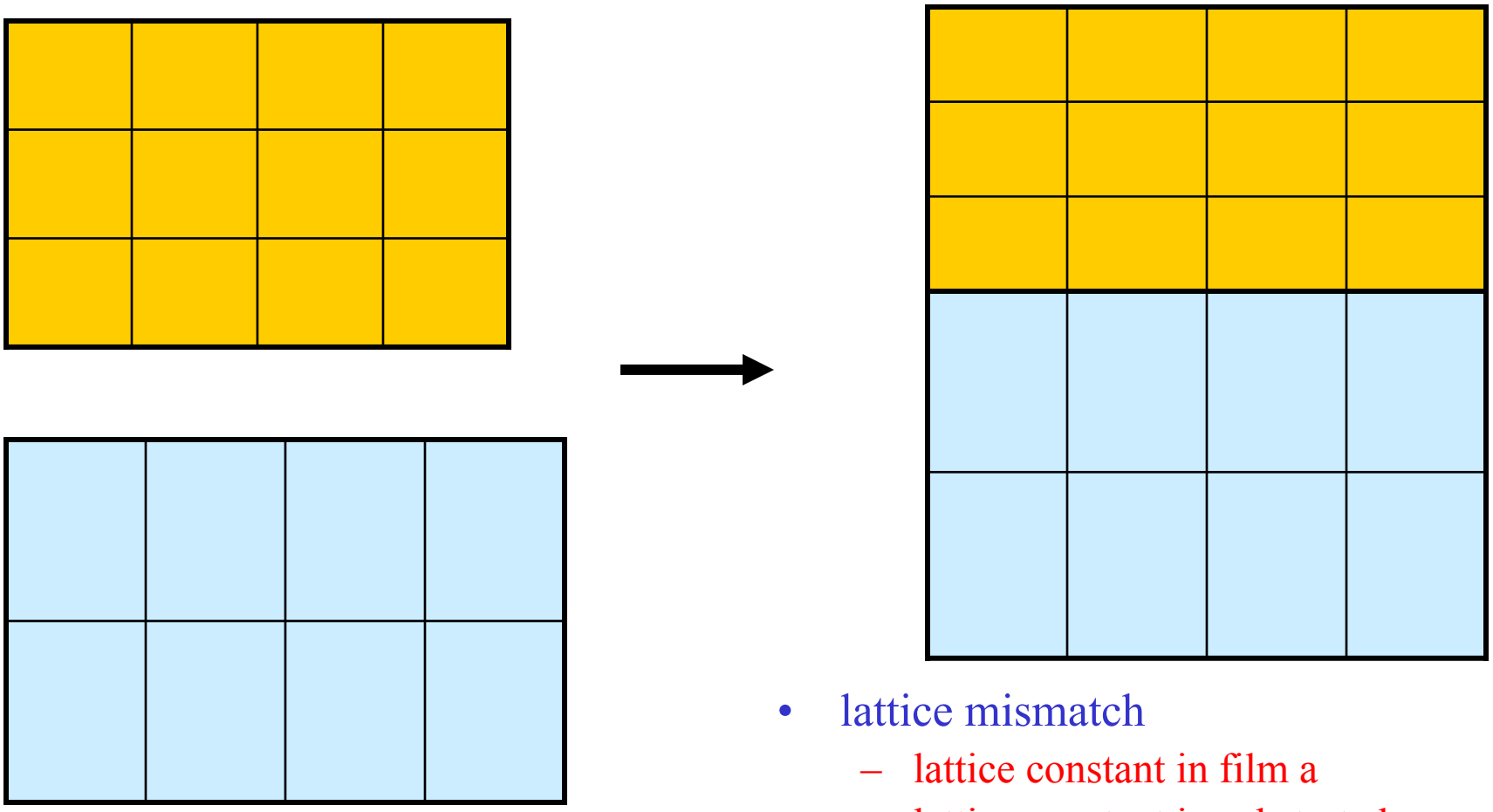
Microscopic Model of Elasticity with Harmonic Potentials

- Continuum Energy density
  - isotropic $E = \lambda(S_{xx} + S_{yy})^2 + \mu(S_{xx}^2 + S_{yy}^2 + 2S_{xy}^2)$
  - cubic symmetry $E = \alpha(S_{xx}^2 + S_{yy}^2) + \beta S_{xy}^2 + \gamma S_{xx} S_{yy}$



- Atomistic Energy density
  - Nearest neighbor springs
    $$E = k(S_{xx}^2 + S_{yy}^2)$$
  - Diagonal springs
    $$E = \ell\,(S_{xx} + 2S_{xy} + S_{yy})^2 + \ell\,(S_{xx} - 2S_{xy} + S_{yy})^2$$
  - Bond bending terms
    $$E = mS_{xy}^2$$
- Elastic equations $\partial_u \mathsf{E}\,[u] = 0$

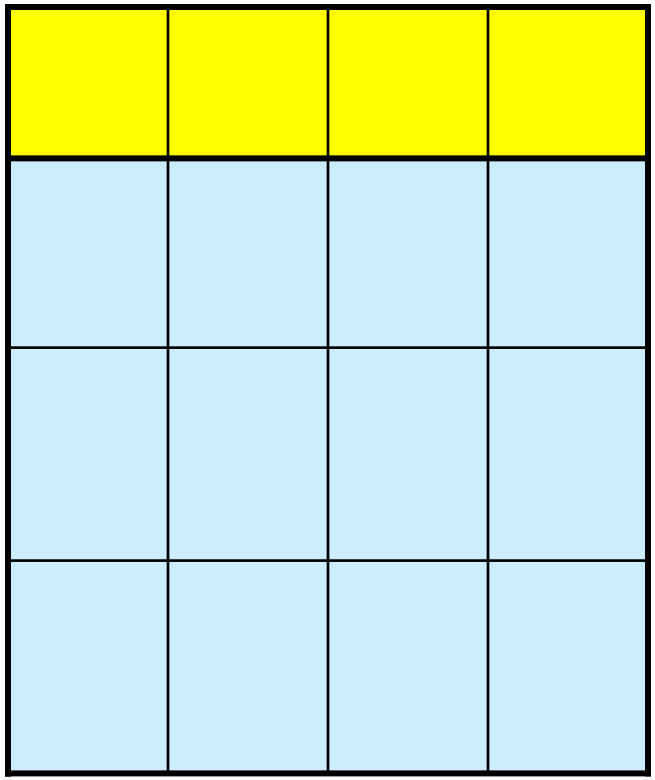
Strain in an Epitaxial Film Due to Lattice Mismatch



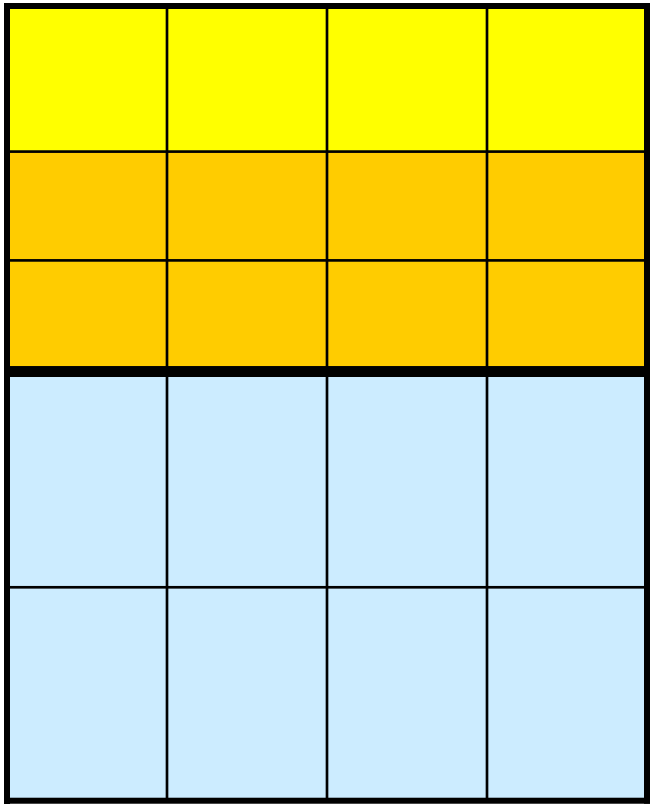
- lattice mismatch
  - lattice constant in film a
  - lattice constant in substrate h
  - relative lattice mismatch $\varepsilon=(a-h)/h$

Deformation of Surface due to Intrinsic Surface Stress

Surface stress included by variation of lattice constant for surface atoms

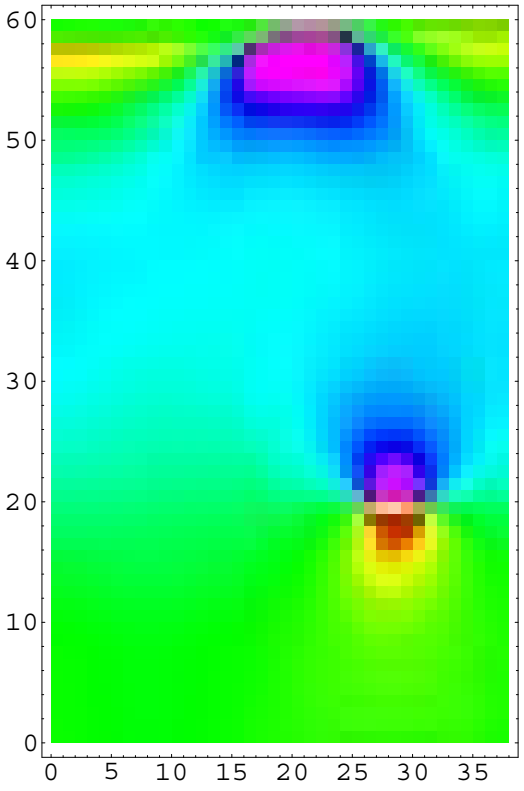


No misfit in film

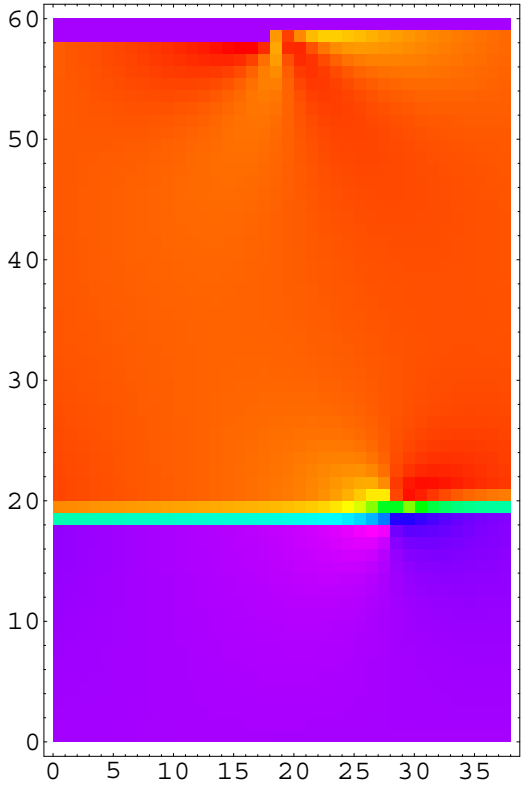


film misfit

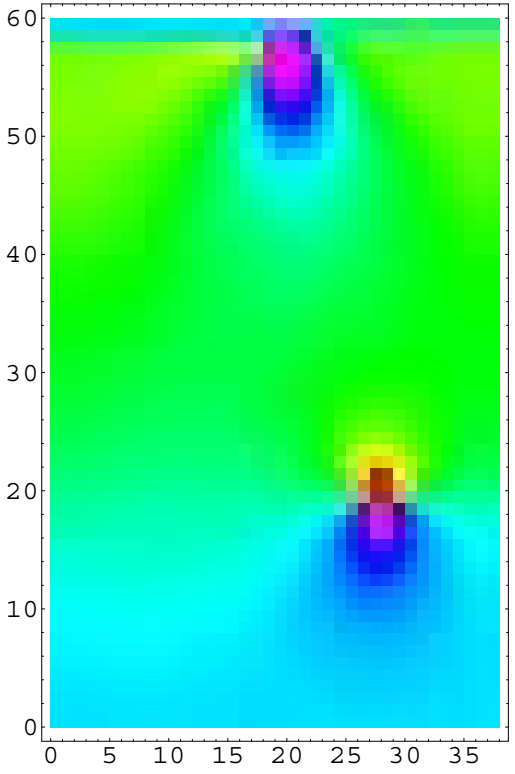
Strain Tensor
Step with No Surface Stress



S_{xx}

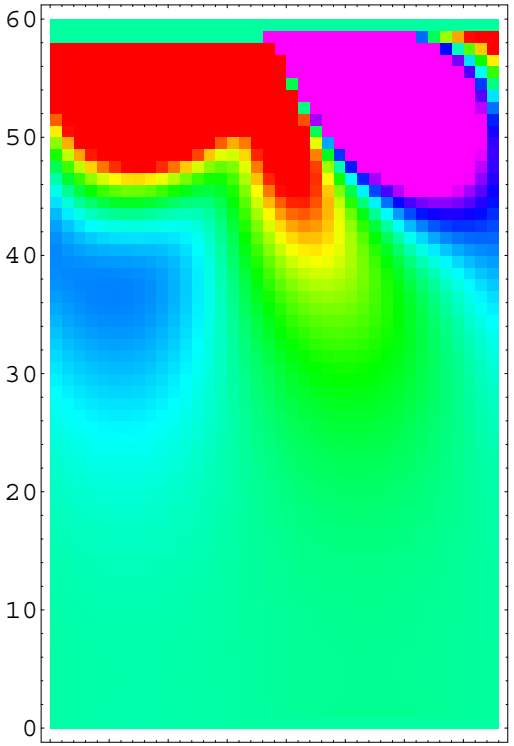


S_{xy}

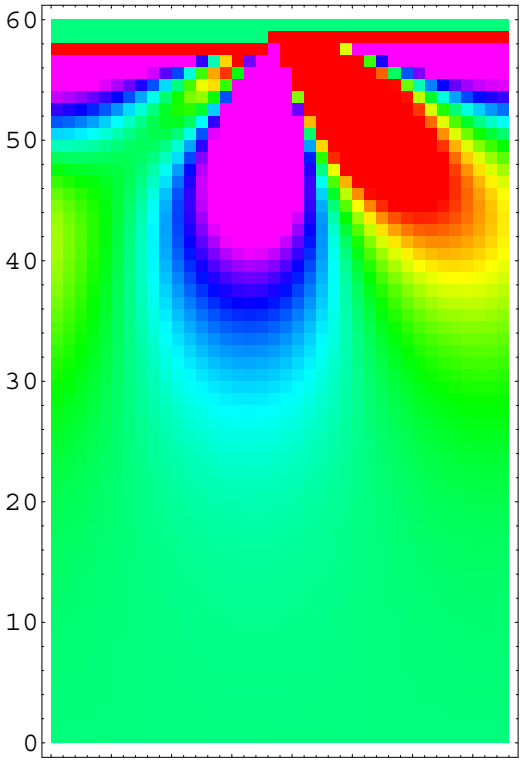


S_{yy}

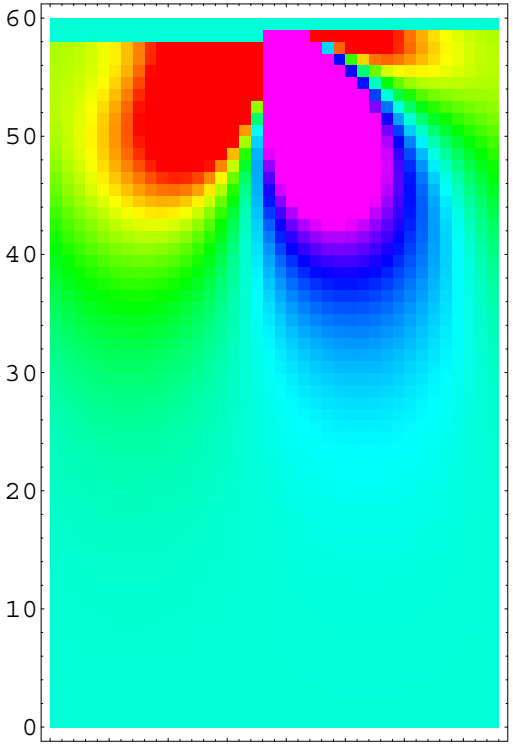
Strain Tensor
Step with Surface Stress
No lattice mismatch



S_{xx}



S_{xy}

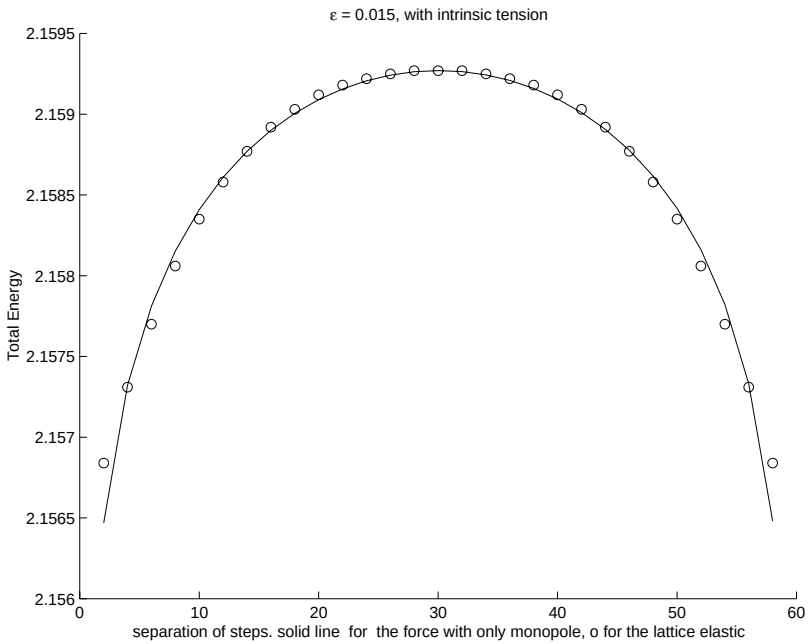


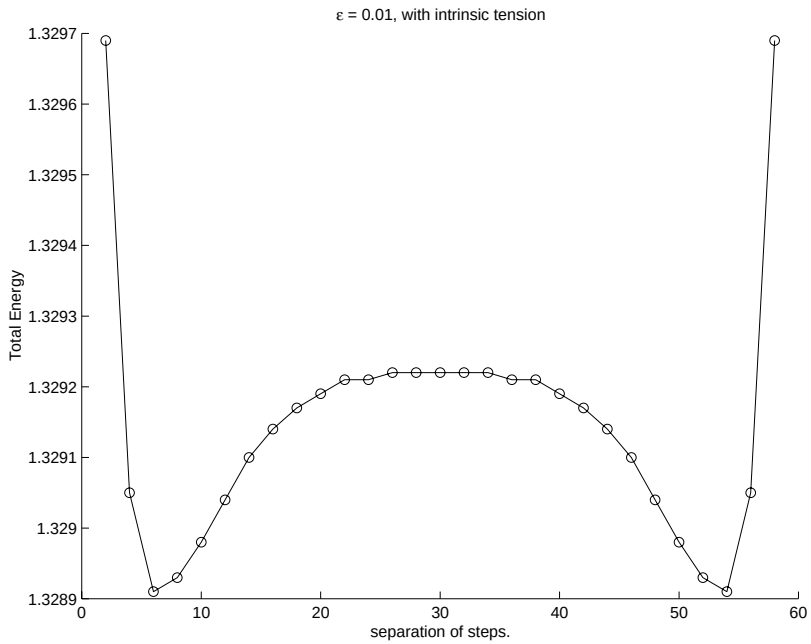
S_{yy}

Interaction of Surface Steps

- Steps of like "sign"
  - Lattice mismatch → step attraction
  - Surface stress → step repulsion

Energy vs. Step Separation





Step attraction due to lattice mismatch

Repulsion of nearby steps due to surface stress

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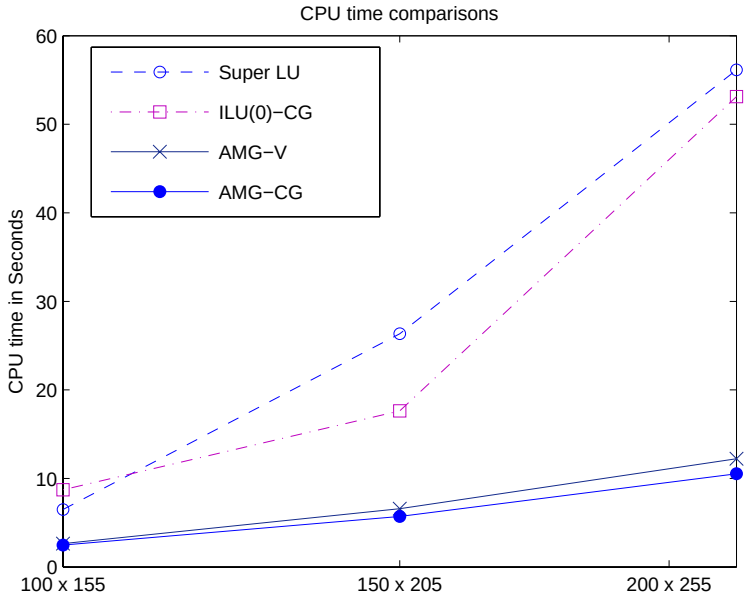
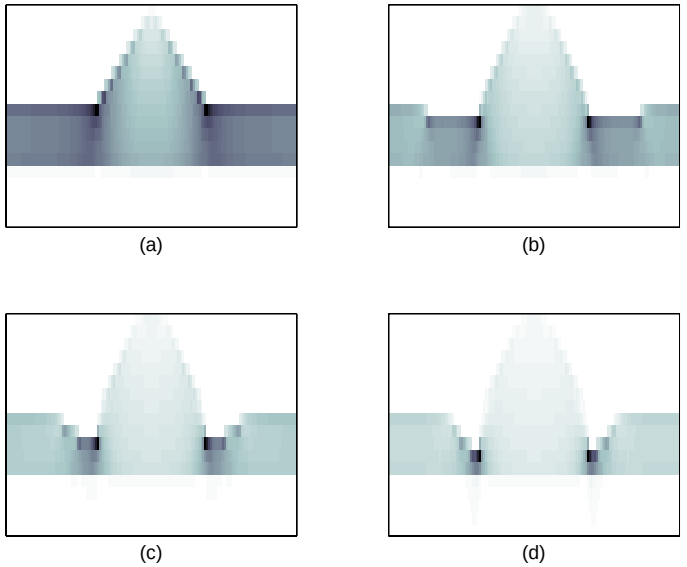
Numerical method for Discrete Strain Equations

- Algebraic multigrid with PCG
- Artificial boundary conditions at top of substrate
  - Exact for discrete equations
- 2D and 3D, MG and ABC combined
- Russo & Smereka (JCP 2006), Lee, REC & Lee (SIAP 2006), REC, et al. (JCP 2006)

Multigrid

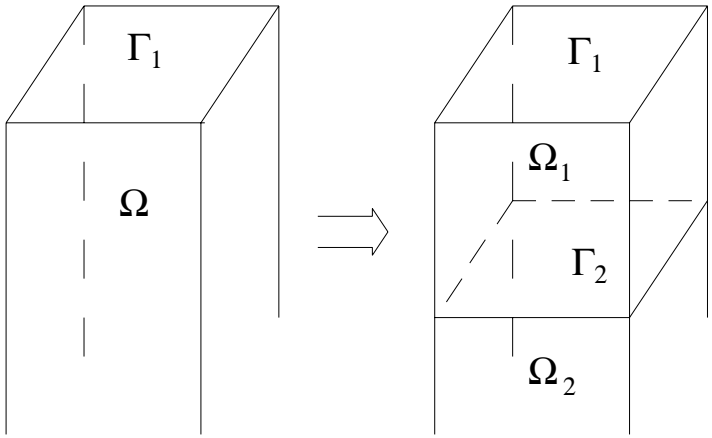


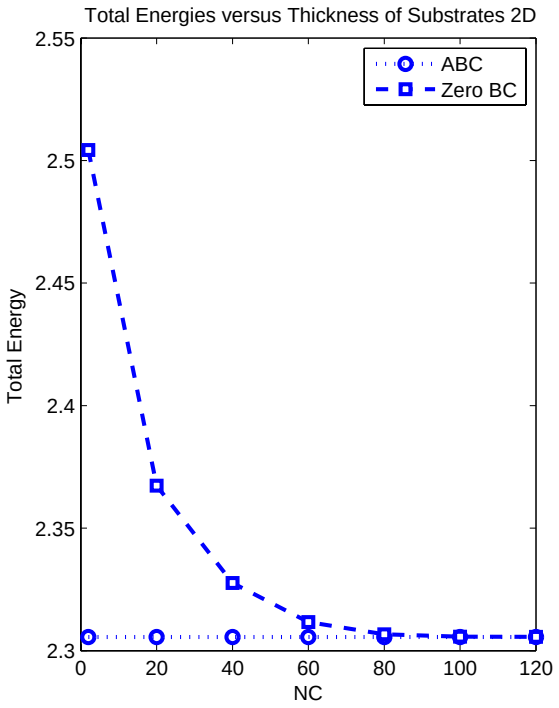
CPU speed (sec) vs. lattice size for strain computation in a 2D quantum dot system

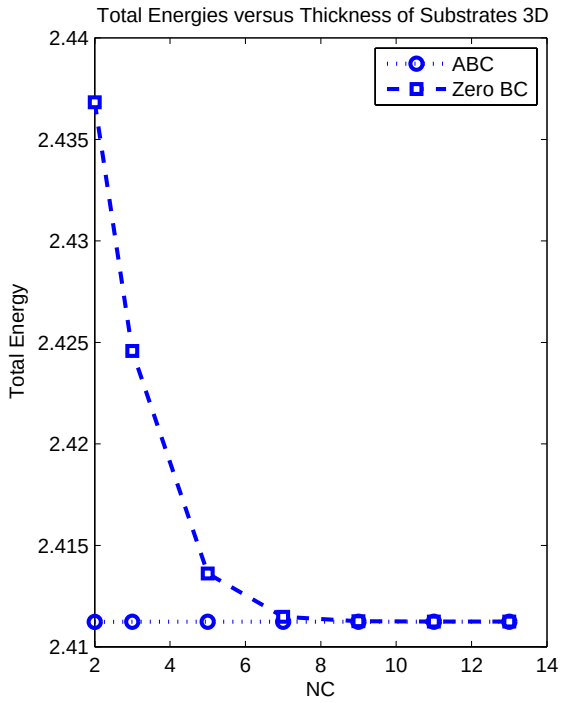


Strain energy density for 160 atom wide pyramid in 2D with trenches, for various trench depths

Artificial Boundary Conditions







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Nanowires

- Growth catalyzed by metal cluster (Au, Ti, …)
- Epitaxial
- Application to nano-electronics
- Stability difficulties

Ti-Nucleated Si Nanowires

Kamins, Li & Williams, APL 2003

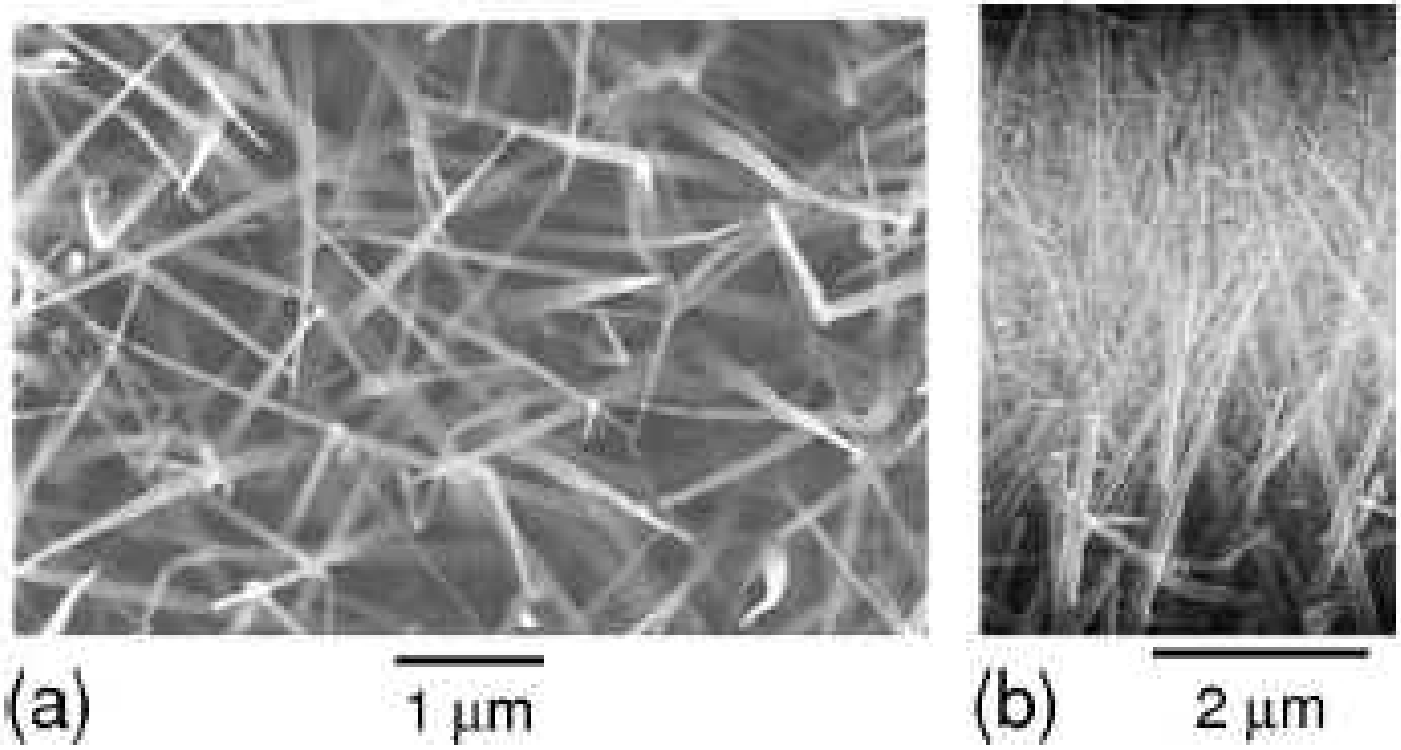
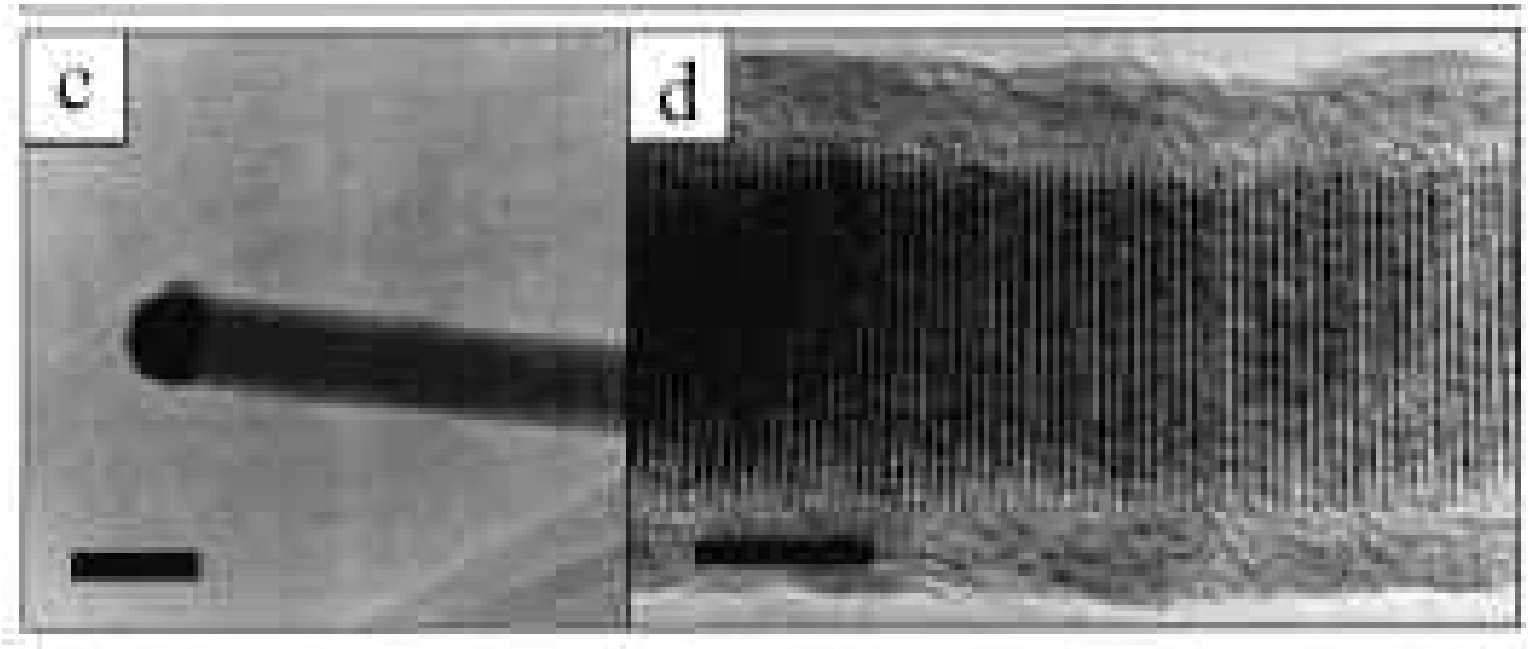


FIG. 1. (a) Plan-view and (b) cross-sectional scanning-electron micrographs of Ti-nucleated Si nanowires (60 min growth) after annealing in H_2 at 850 °C for 1 h.

Nanowire

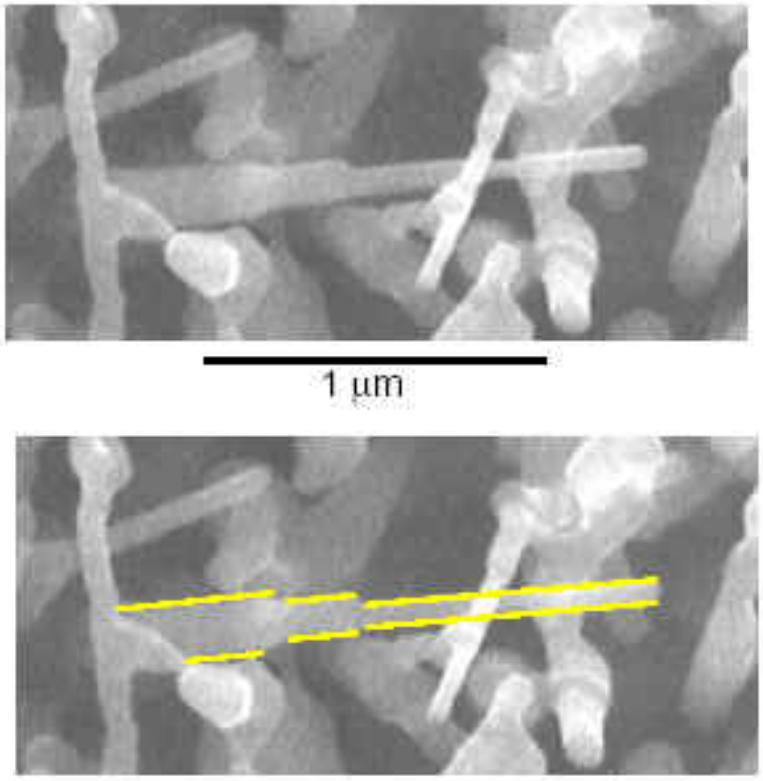


- InP wire
- 20nm Au cluster at tip
- Scale bar =5 nm
- Oxide coating, Not present during growth
- TEM

Gudiksen, Wang & Lieber. JPhysChem B 2001

Instability in Metal Catalyzed Growth of Nanowires

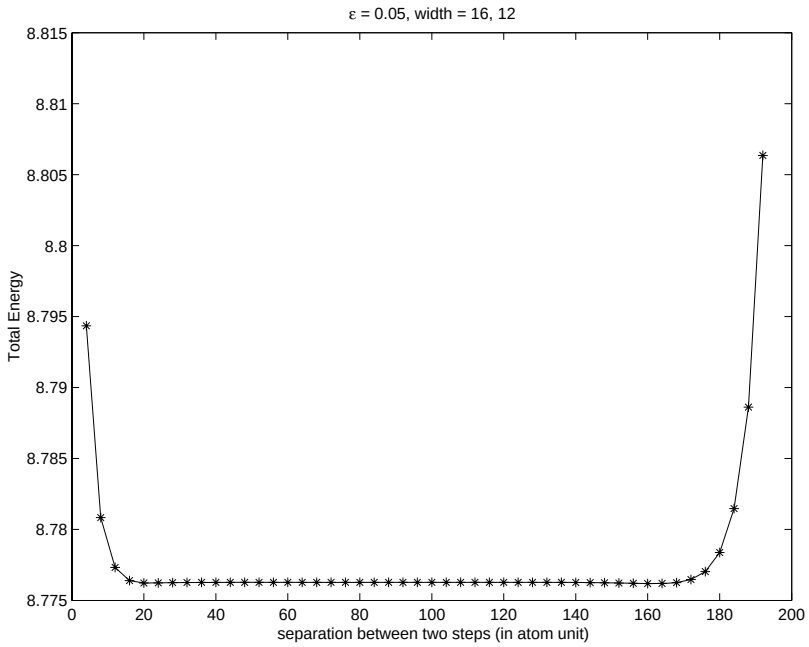
- Epitaxial structure
  - Tapered shape due to side attachment
- Instability at high temperature
  - Tapered shape → terraced shape
  - Step bunching



Kamins, Li & Williams, APL 2003

2D Simulation of Nanowires

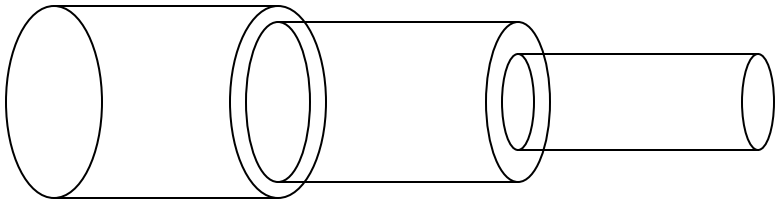
- 2 steps – looking for step bunching by energy minimization
- Model
  - Harmonic potential
  - Surface stress
- No step bunching in 2D



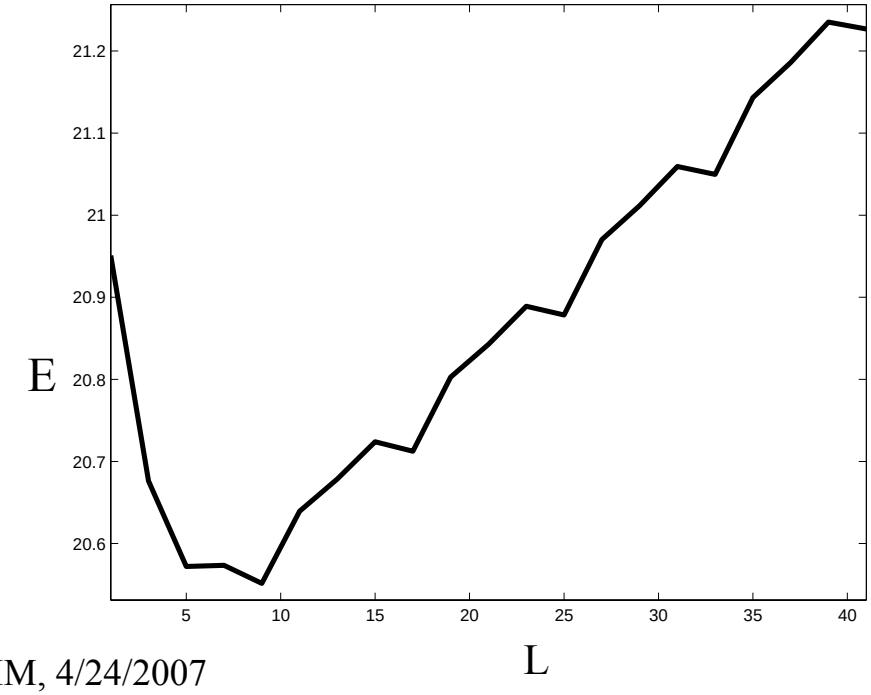
Strain Energy vs. distance between steps

3D Simulation of Interaction between Steps on Nanowires

- Homogeneous, epitaxial nanowire with surface stress
- Interactions of two steps
  - $r = R_1$ for $z<z_1$
  - $r = R_2$ for $z_1 < z < z_2$
  - $r = R_3$ for $z_2 < z$
  - $L= z_2-z_1$ = inter-step distance
  - z = axial distance, r = wire radius
- Energy minimum occurs for small L
  - Step bunching
- Results are insensitive to parameters
  - Step size ($R_1 - R_2$ or $R_2 - R_3$)
  - Surface stress
  - Wire radius, shape
- Lowest value of energy E occurs for small value of separation L
  - System prefers bunched steps



$(R_1 , R_2 , R_3) = (3,4,5)$

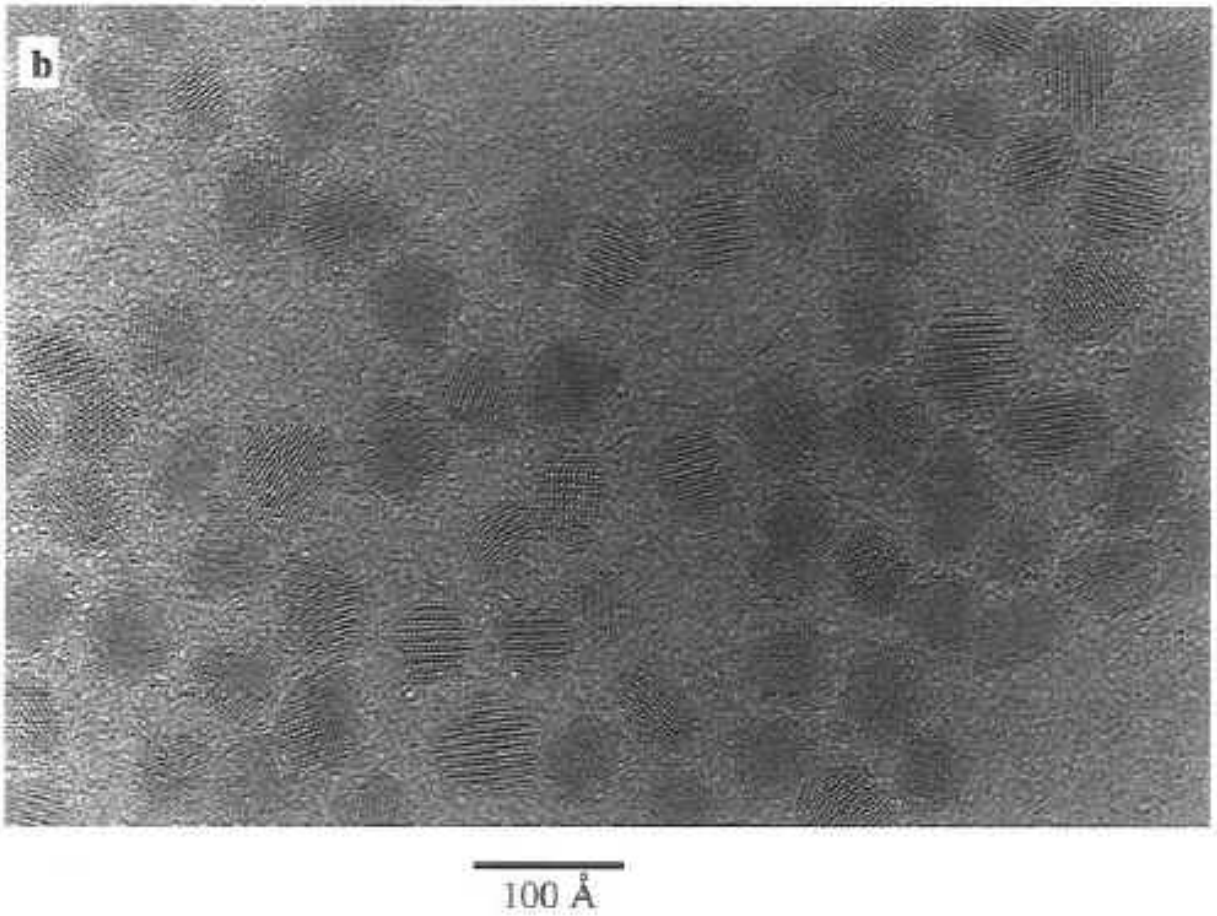


Nanocrystals

- Sphere or rod (diameter =10 - 50 nm)
- Coated by shell (thickness = 1 – 10 nm)
- Epitaxial structure
- Wide range of new properties and applications
- Difficulty with instability of shell due to strain

Epitaxial Nanocrytals

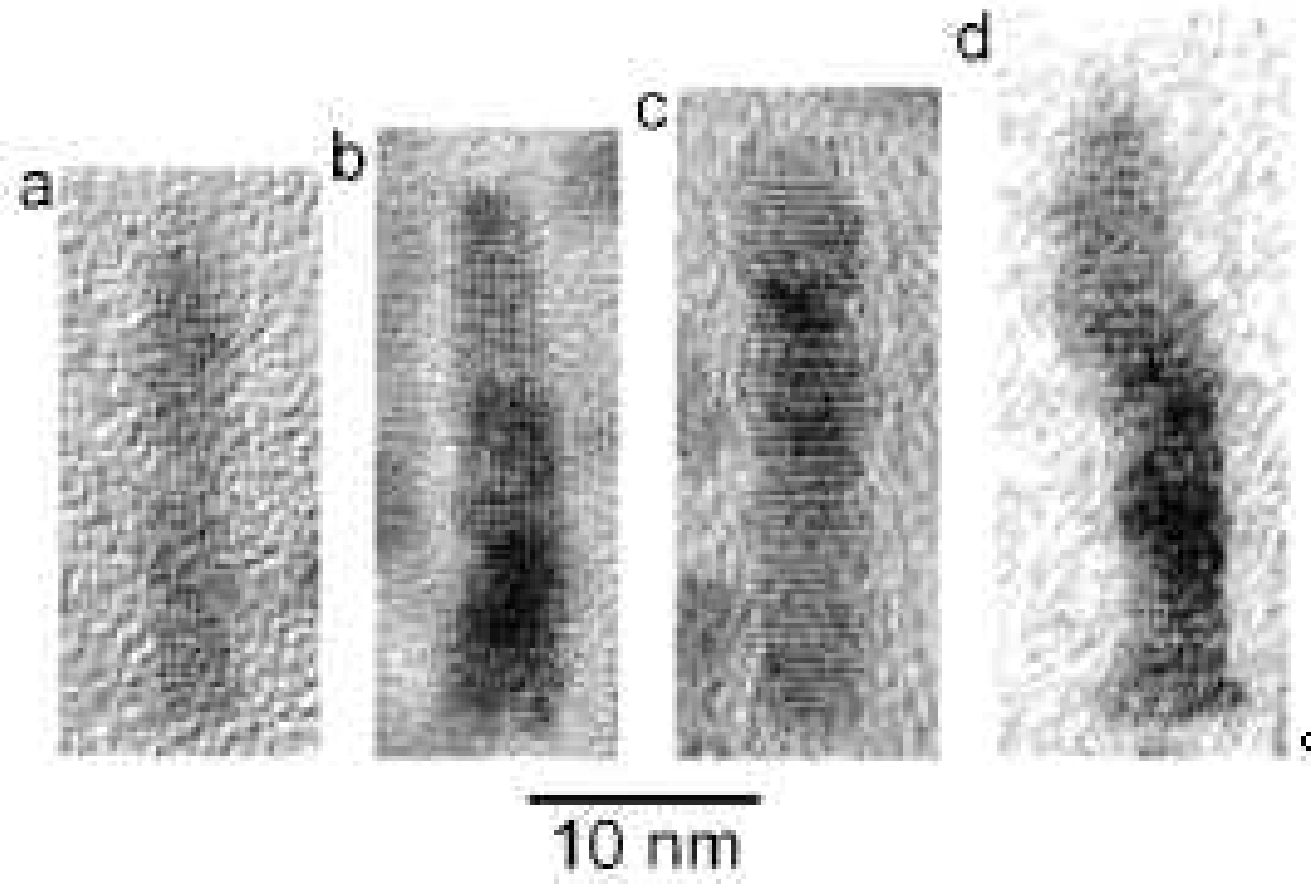
core/shell=CdSe/CdS R_{core}=34Å, R_{shell}=9Å



HRTEM

Peng, Schlamp, Kadavanich, Alivisatos. JACS 1997

Epitaxial Nanorods
core/shell=CdS/ZnS



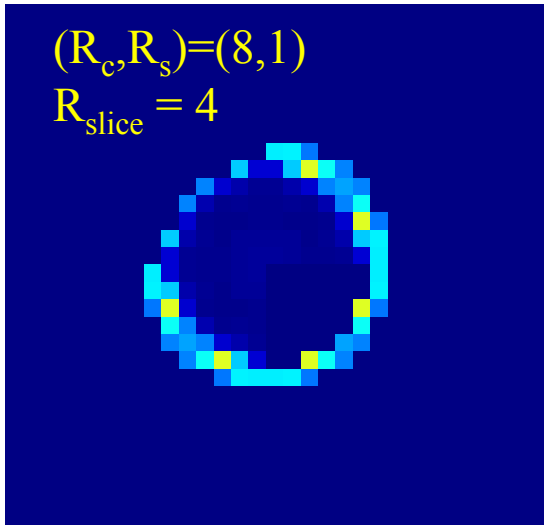
- Left to right Increasing shell thickness
- Epitaxial structure breaks down at larger shell size
- HRTEM

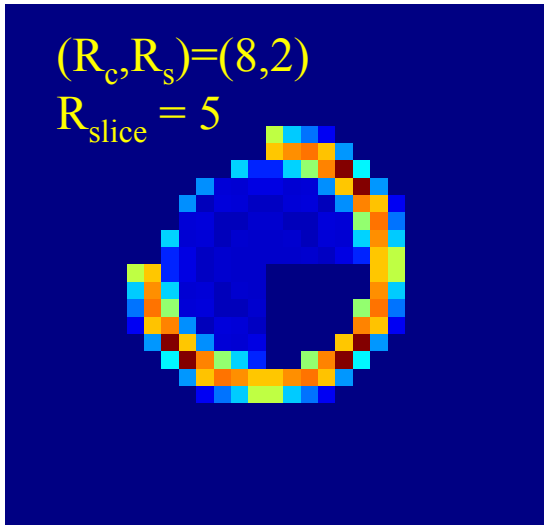
Manna,Sher, Li, Alivisatos. JACS 2002

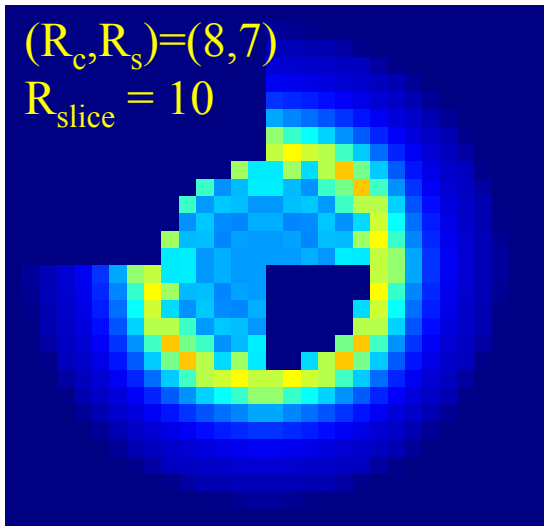
Simulation of Strain Field in Nanocrystals

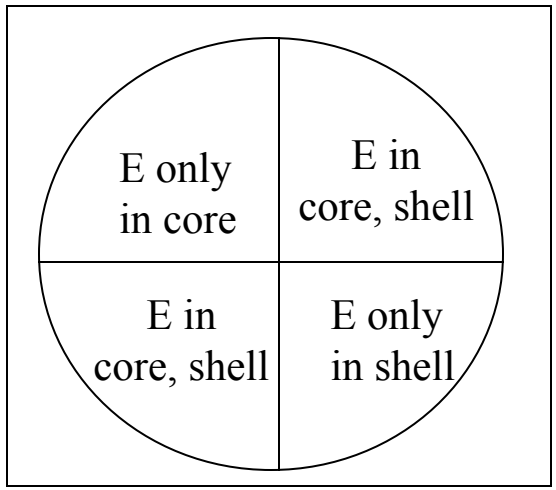
- Core $0 < r < R_{core}$
- Shell $R_{core} < r < R_{shell}$
- Strain model
  - Harmonic potential
  - Equal elastic parameters
  - lattice mismatch
  - No surface stress
- Max energy density occurs at critical shell thickness
- Critical shell thickness is at peak in photoluminescence
- Robust results: same in 2D, variation of parameters

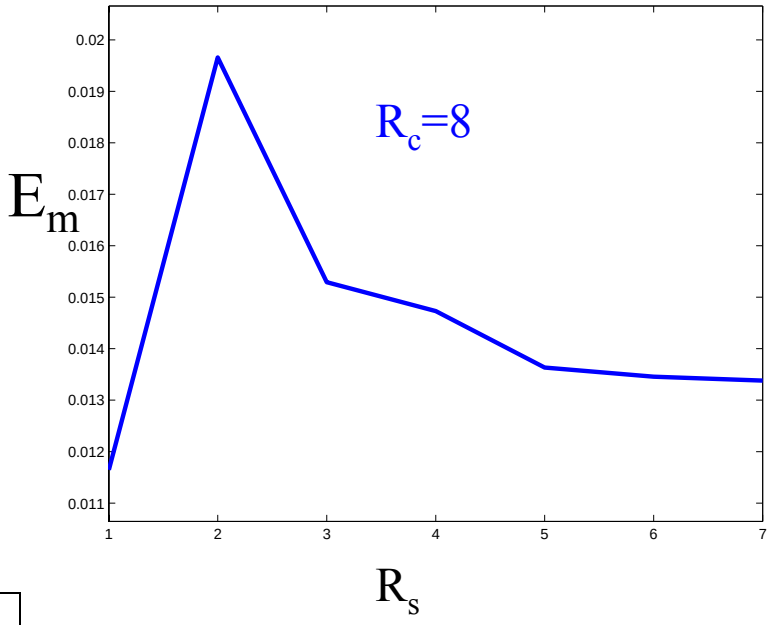
Energy Density for 3D Nanocrystal Showing Critical Shell Thickness











- Plots of E for 3 values of R_s
  - slice containing max of E
  - subcritical (R_s =1),
  - critical (R_s =2)
  - supercritical (R_s=7)
- Graph of E_m vs. R_s
- E=energy density, E_m=max(E)
- (R_c, R_s) = (core, shell) thickness

Comparison to Critical Size for Photoluminescence

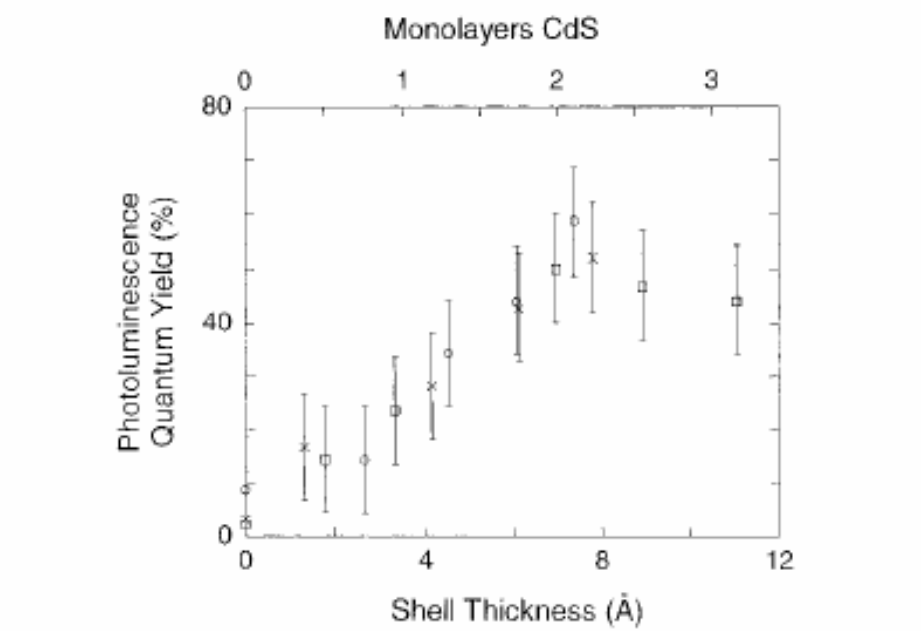


Figure 4. Photoluminescence quantum yield variation with shell thickness for three different core/shell syntheses starting with core diameters of 23 Å (circles), 34 Å (X's), and 39 Å (squares).

Peng, Schlamp, Kadavanich, Alivisatos. JACS 1997

Peak in photoluminescence is at same shell thickness as peak in elastic energy density

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- Strain model
  - Harmonic potential
  - Minimal stencil
  - Surface stress represented by variation in lattice constant
- Numerical methods
  - AMG
  - ABC
- Nanowires
  - Surface stress
  - No step bunching in 2D
  - Step bunching in 3D