Kinetics-Controlled Composition Profile of Semiconductor Alloy Quantum Dots and Nanowires via Growth Mode

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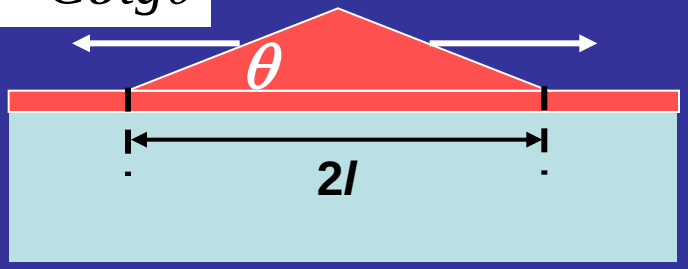
Support: DOE-BES, CAO Group

Island Nucleation on a Flat Surface

$$f = C\varepsilon tg\theta$$

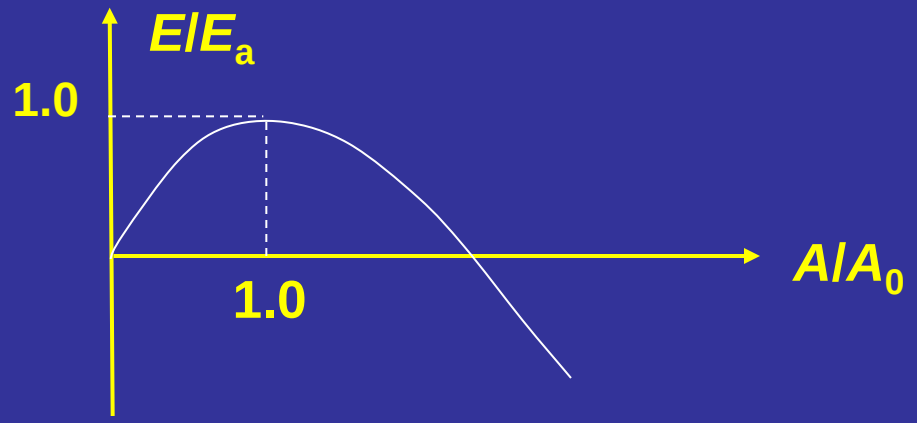


$$E = 2\Gamma A^{1/2} tg^{1/2}\theta - (3/2)\varepsilon_0 A tg\theta$$

$$\varepsilon_0 = c\varepsilon^2; \quad \Gamma = (\gamma_f \sec\theta - \gamma_w)(tg\theta)^{-1}$$

$$A_0 = (4/9)(\Gamma/\varepsilon_0)^2 (tg\theta)^{-1}$$

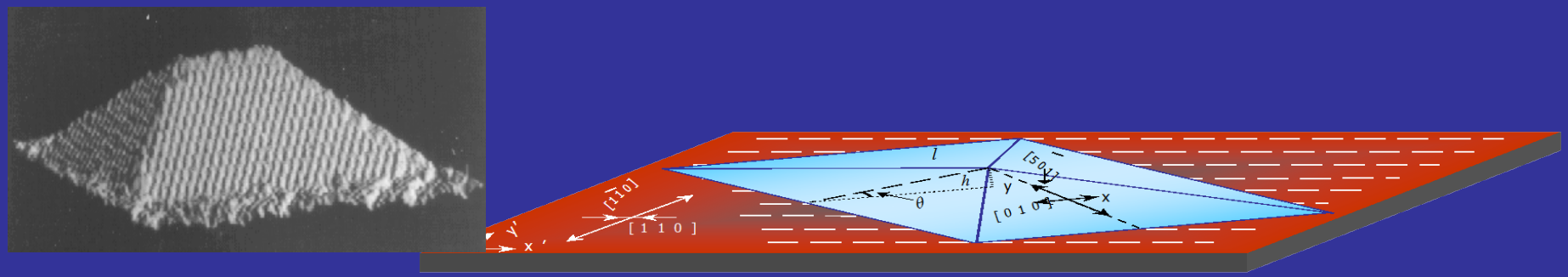
$$E_a = (2/3)(\Gamma^2/\varepsilon_0)$$



3D solution: $$E = 4\Gamma V^{2/3} tg^{1/3}\theta - 6C\varepsilon^2 V tg\theta$$

Tersoff & Legoues, PRL, 72, 3570 (94)

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



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

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

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

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

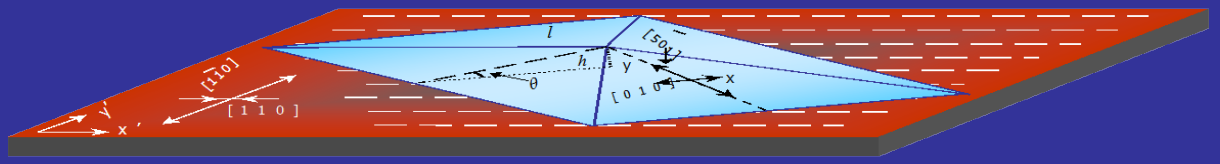
$$c' = F_\perp^2(1-\nu)/2\pi G_{Si}$$

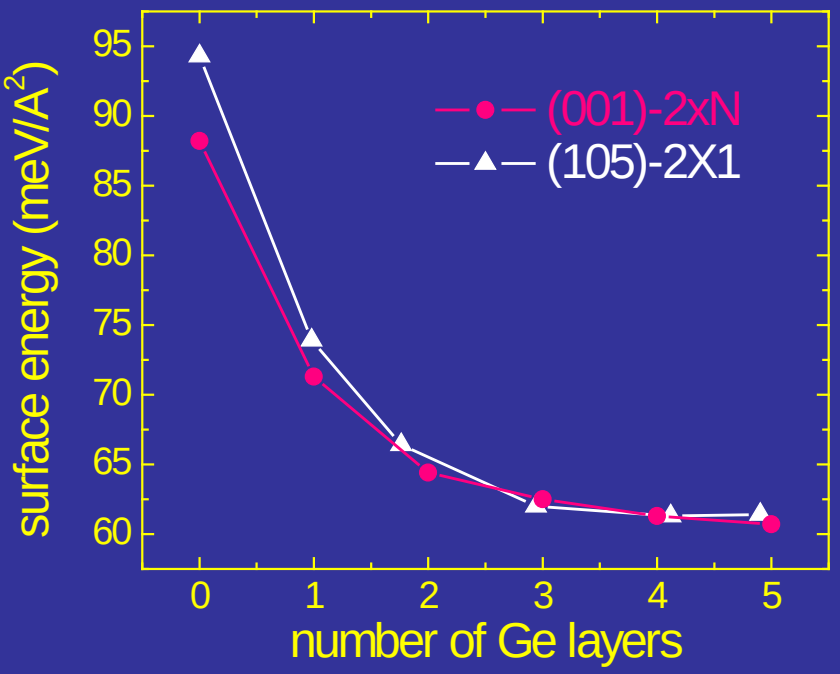
γ_h : converged Ge/Si(105) surface energy

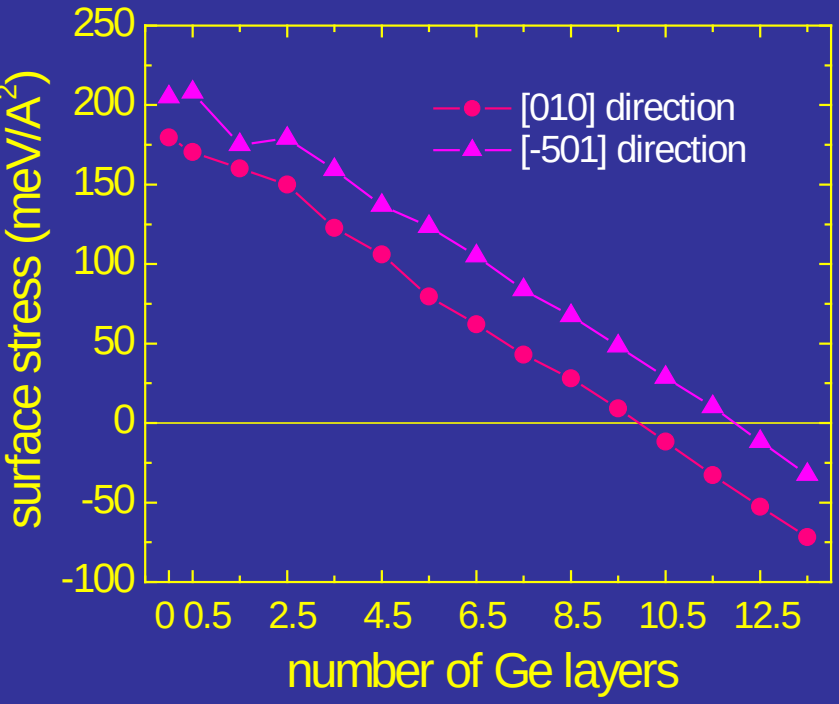
γ_w : Ge/Si (001) surface energy of 4 and 5 layers Ge deposition

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

First-principles: Surface Energy/Stress

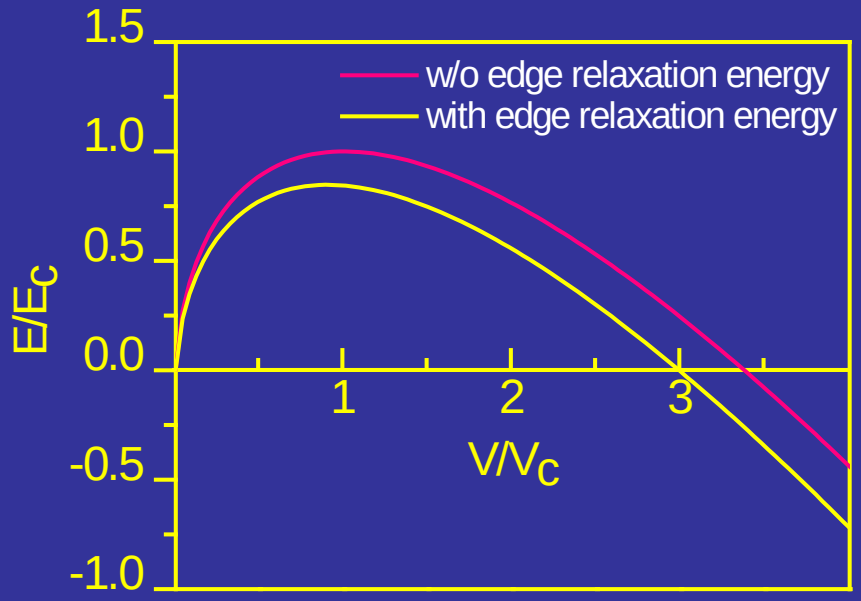






PRL, 94, 176103 (05); PRB 72, 125415 (05)

Quantitative Prediction: Critical Size/stability (first-principles + continuum)



$h_c \approx 4\Gamma / 9c$

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

Pure Ge hut:

h_c ~ 16Å; 6800 atoms

25% Ge SiGe alloy hut:

h_c ~ 216Å; 2.3×10^7 atoms

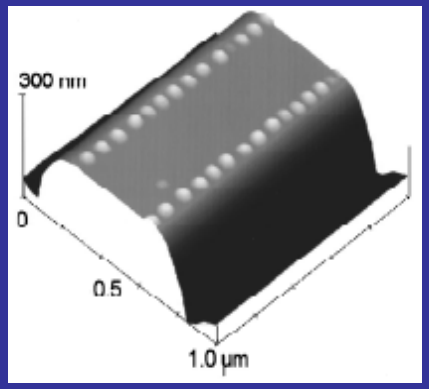
Implication on formation mechanism:

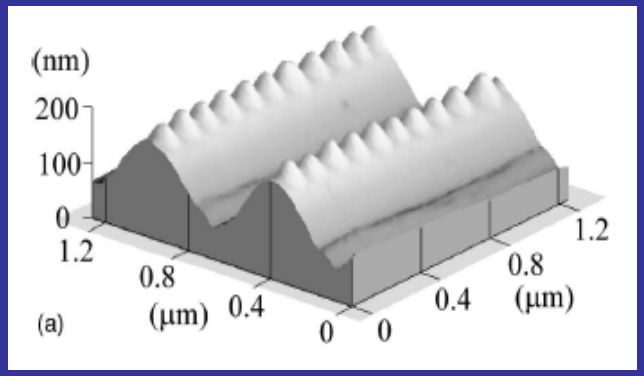
- too large via nucleation
- non-faceted "pre-pyramids"

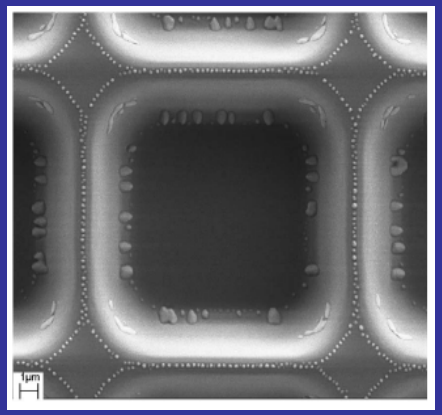
(continuum mounds or stepped islands)

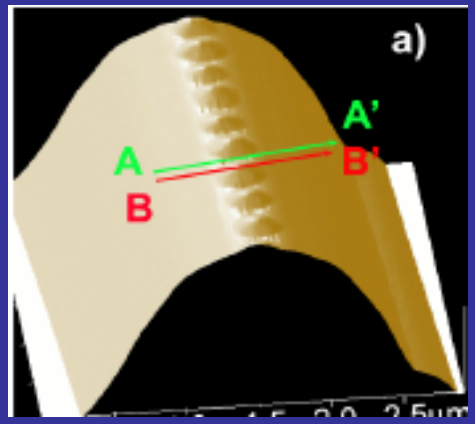
Lu & Liu, PRL, 94, 176103 (05)

Directed Self-Assembly of Strained Islands on Patterned Substrate







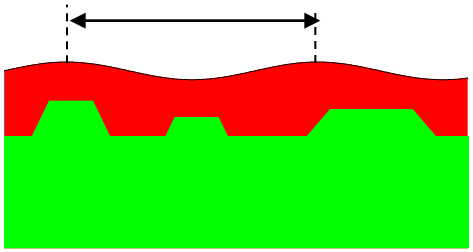


Kamins and Williams, APL 71, 1201 (97); Jin, *et al.*, APL 75, 2752 (99); Zhong, *et al.*, APL 82, 445 (03); Yang, *et al.*, PRL 92, 0255502 (04).

Morphological Instability on Patterned Substrate?

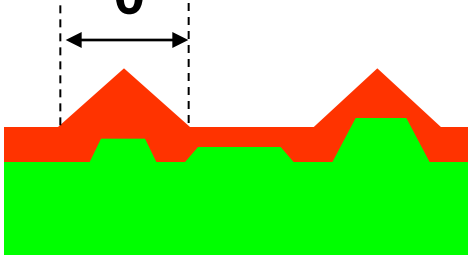
Surface undulation

λ_c=?

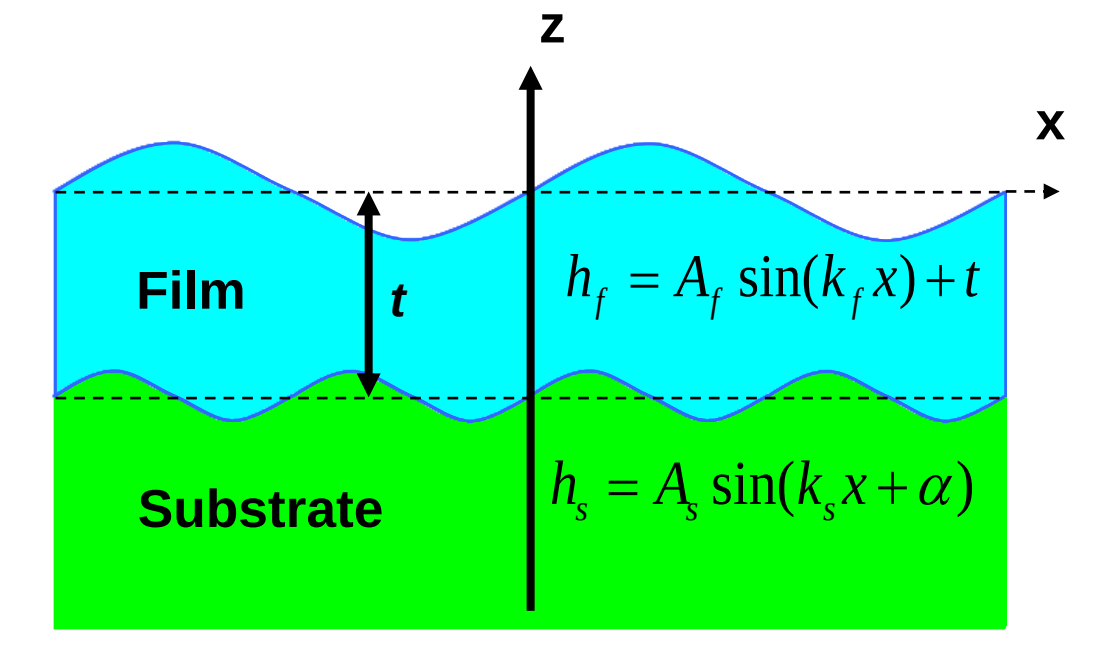


Island formation

l_0 =?



Critical Wavelength on a Wavy Substrate

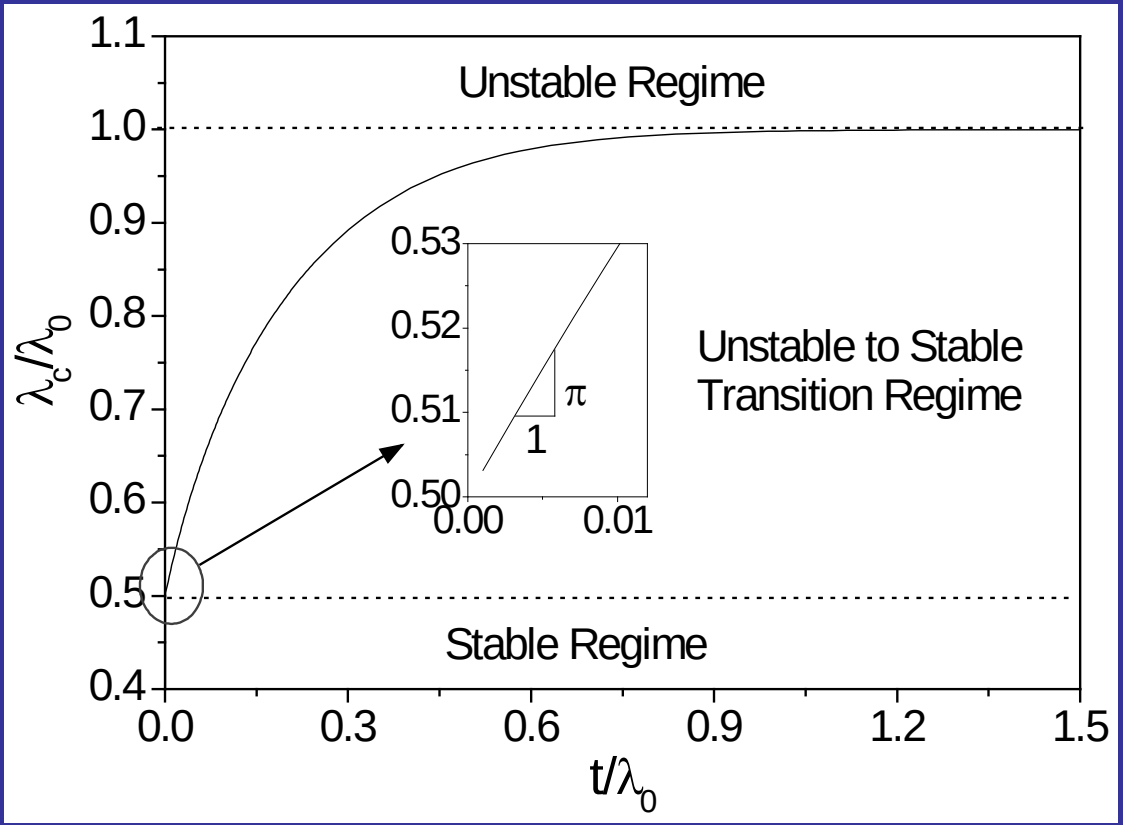


$$\sigma_{xx} = \sigma - 2\sigma A_f k_f \sin(k_f x) + 2\sigma A_s k_s e^{-k_s t} \sin(k_s x + \alpha)$$

$$\lambda_c (1 + e^{-2\pi t/\lambda_c}) = \lambda_0$$

Wang, *et al.*, JAP 104, 054301 (08)

Dependence of Critical Wavelength on Film Thickness



$$\lambda_c\left(1+e^{-2\pi\, t/\lambda_c}\right)=\lambda_0$$

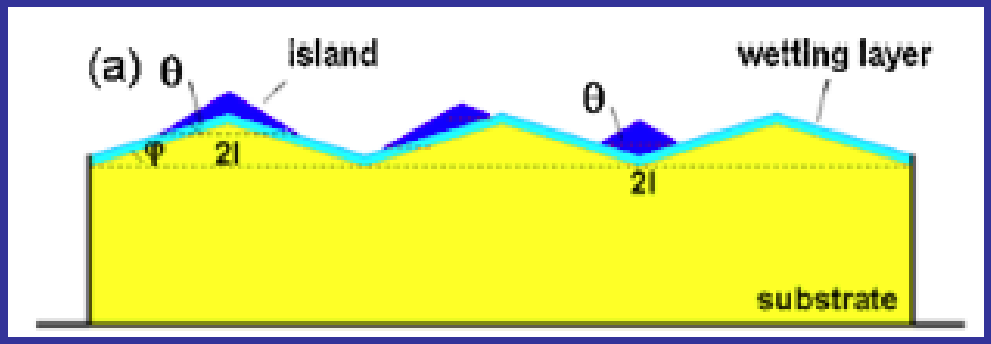
$$t\to 0,\ \lambda_c\to\lambda_0/2$$

$$t<<1,\ \lambda_c\cong\lambda_0/2+\pi t$$

$$t\to\infty,\ \lambda_c\to\lambda_0$$

Wang, *et al.*, JAP 104, 054301 (08)

Island Nucleation on Faceted Surface



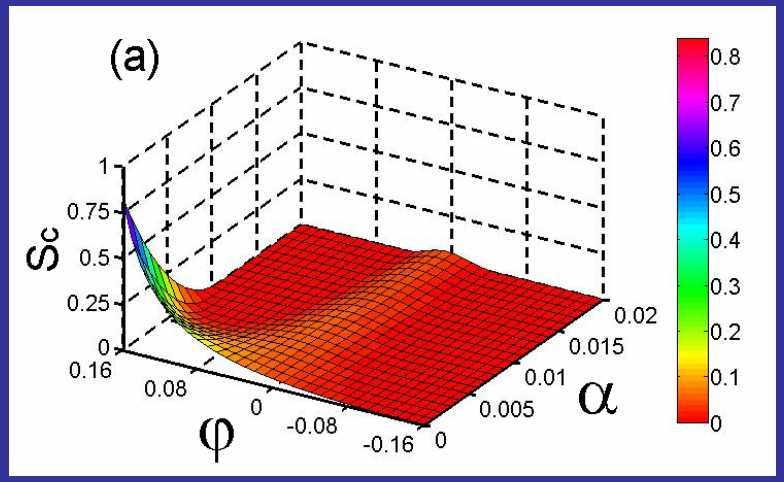
$$E = -\varepsilon_0 S(\tan\theta - \tan\varphi) + 2\Gamma S^{1/2}(\tan\theta - \tan\varphi)^{1/2}$$

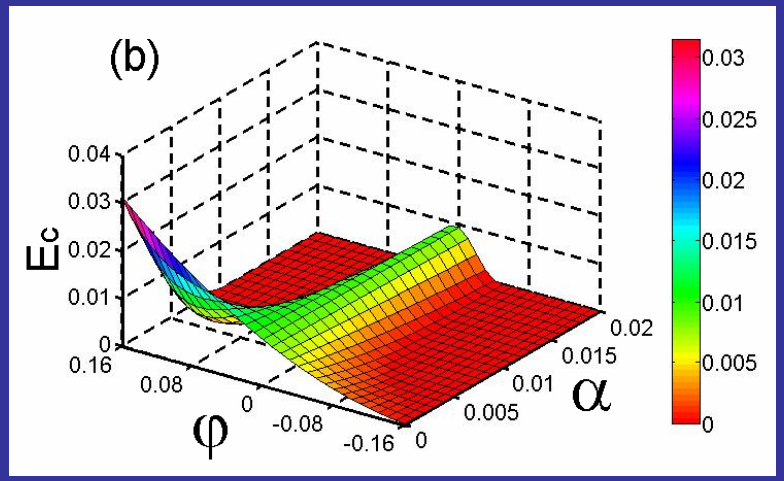
$$S_c = (\Gamma/\varepsilon_0)^2(\tan\theta - \tan\varphi)^{-1}$$

$$E_c = \Gamma^2/\varepsilon_0$$

$$\Gamma = (\gamma_f \sec\theta - \gamma_w \sec\varphi)(\tan\theta - \tan\varphi)^{-1}$$

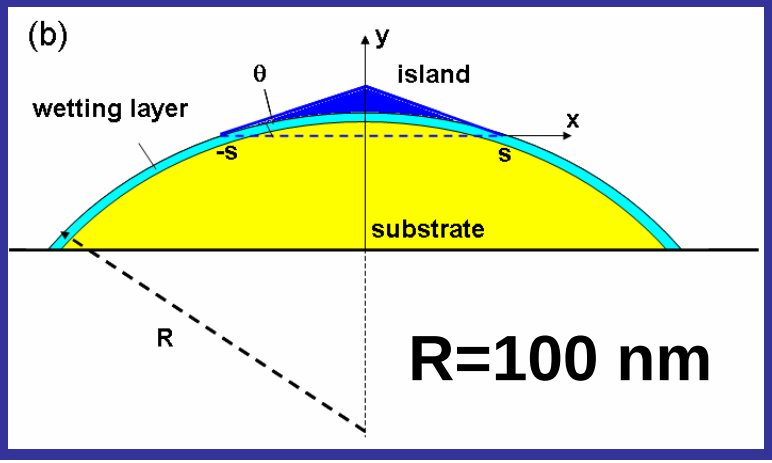
$$\gamma = \gamma_0[1 - \alpha\cos(n\varphi)]$$

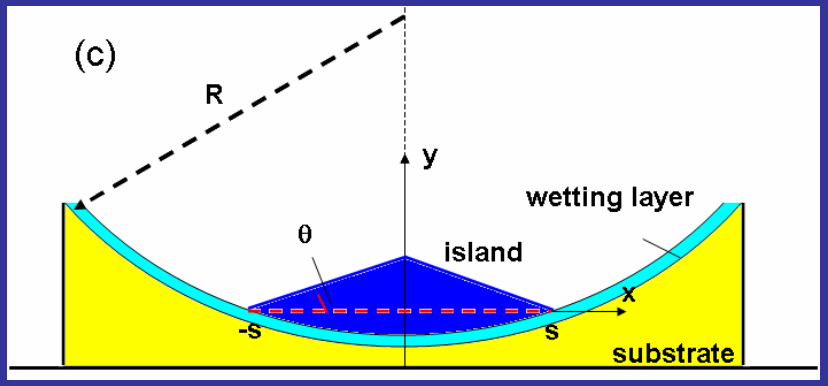


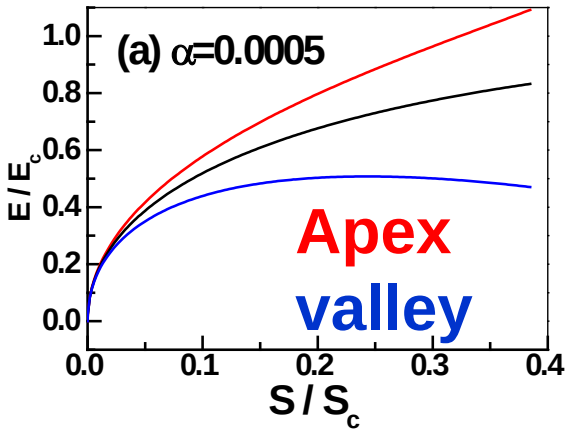


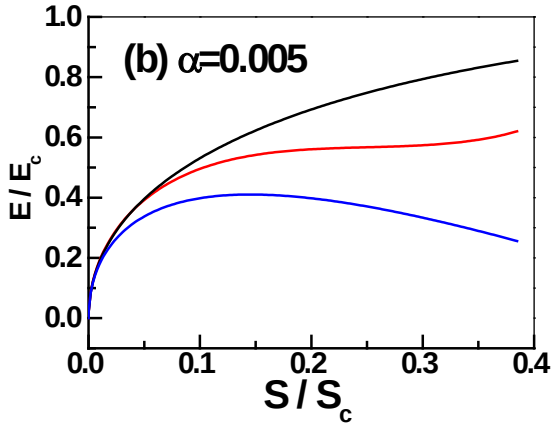
Hu et. al. *PRL* 101, 216102 (08)

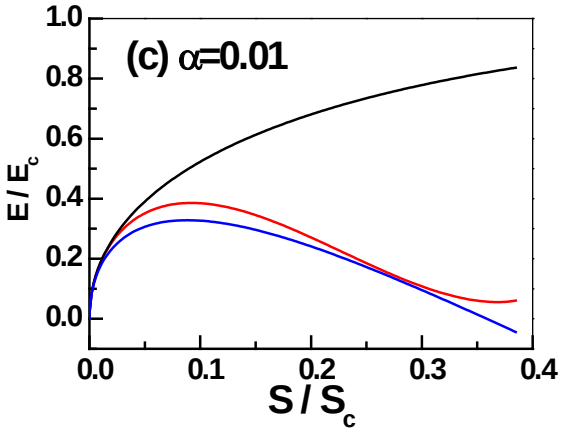
Island Nucleation on Curved Surface





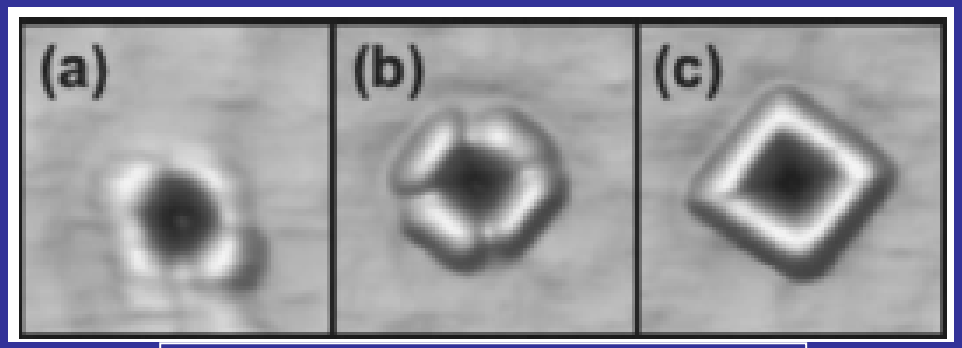




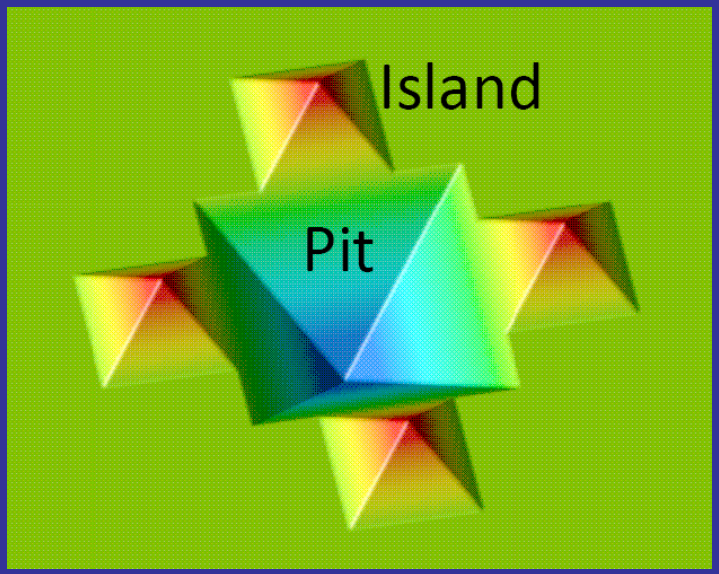


Hu et. al. *PRL* 101, 216102 (08)

Heterogeneous Nucleation of QDMs



Gray et al. PRB 72,155323(05)



$$E = (4\Gamma V^{2/3}\tan^{1/3}\theta - 6\varepsilon_0 V) + E_{pi} + E_{ii1}/2 + E_{ii2}$$

$\varepsilon_0=\sigma^2(1-\nu^2)/\pi Y$ is the strain energy density,
$\Gamma=\gamma(\sec\theta-1)tg^{-1}\theta$ is reduced surface energy density.
E_{pi} is the strain interaction energy between pit and island.
E_{ii1} is the strain interaction energy between two opposite islands.
E_{ii2} is the strain interaction energy between two adjacent islands.

$$E_{pi} = -\frac{16\varepsilon_0 V_p \cdot V_i}{3\cot\theta\left(V_p^{1/3} + V_i^{1/3}\right)^3}$$

$$E_{ii1} = \frac{2\varepsilon_0 V_i^2}{3\cot\theta\left(V_p^{1/3} + V_i^{1/3}\right)^3} \qquad E_{ii2} = \frac{4\sqrt{2}\varepsilon_0 V_i^2}{3\cot\theta\left(V_p^{1/3} + V_i^{1/3}\right)^3}$$

Setting:

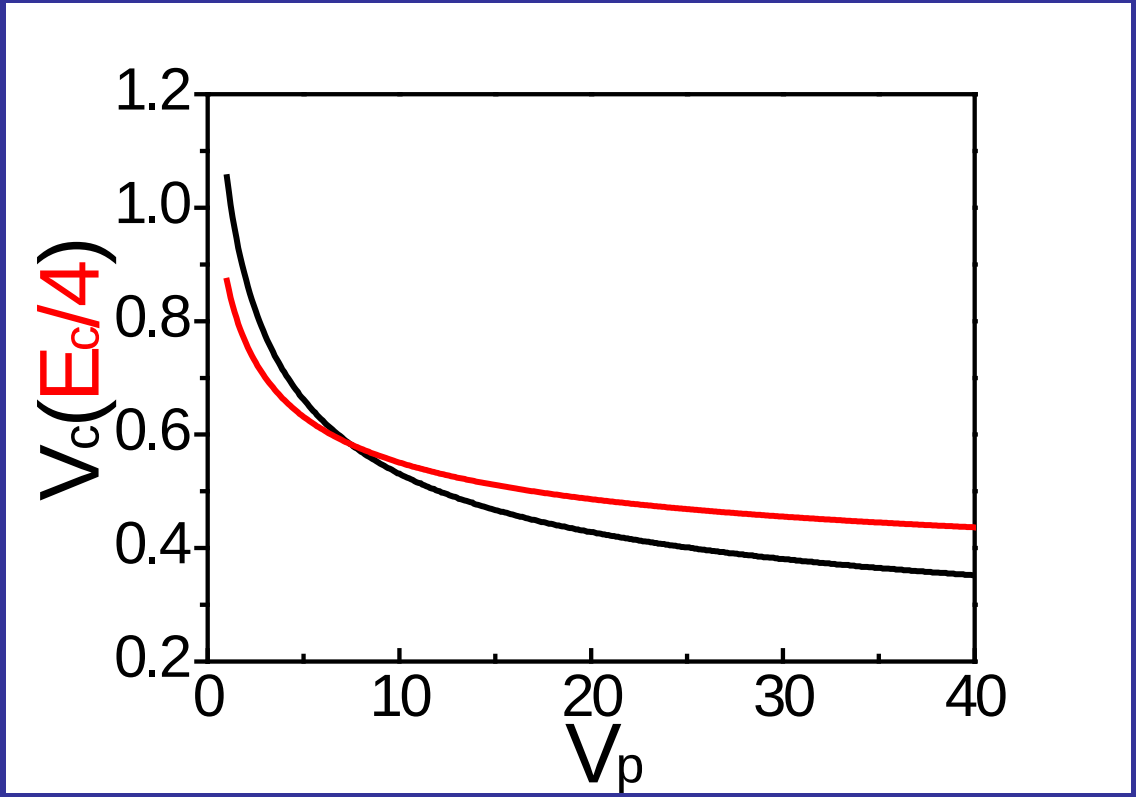
$$E_c^0 = \frac{1}{3}\frac{(4\Gamma)^3}{(9\varepsilon_0)^2}\cot\theta$$

$$V_c^0 = \left(\frac{4\Gamma}{9\varepsilon_0}\right)^3 \cot^2\theta$$

$$E = (3V_i^{2/3} - 2V_i) - \frac{16V_p \cdot V_i}{9(V_p^{1/3} + V_i^{1/3})^3} + \frac{V_i^2}{9(V_p^{1/3} + V_i^{1/3})^3} + \frac{4\sqrt{2}V_i^2}{9(V_p^{1/3} + V_i^{1/3})^3}$$

in units of E_0^c and V_o^c

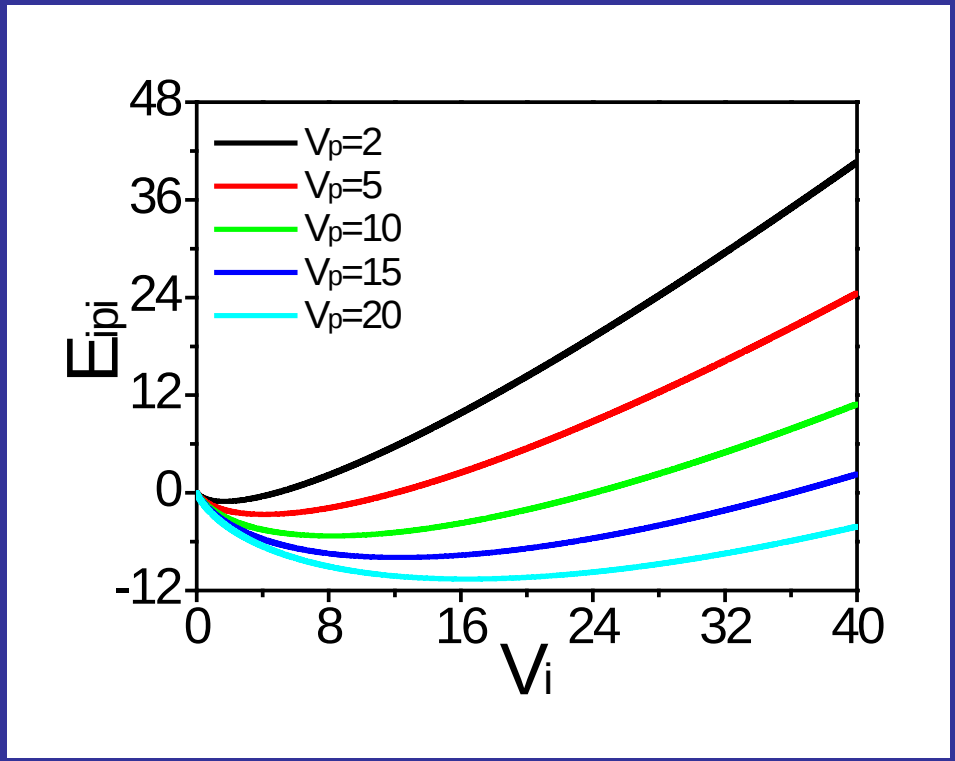
Nucleation Barrier and Critical Size of QDMs



Islands prefer to nucleate next to a pit to form QDM.

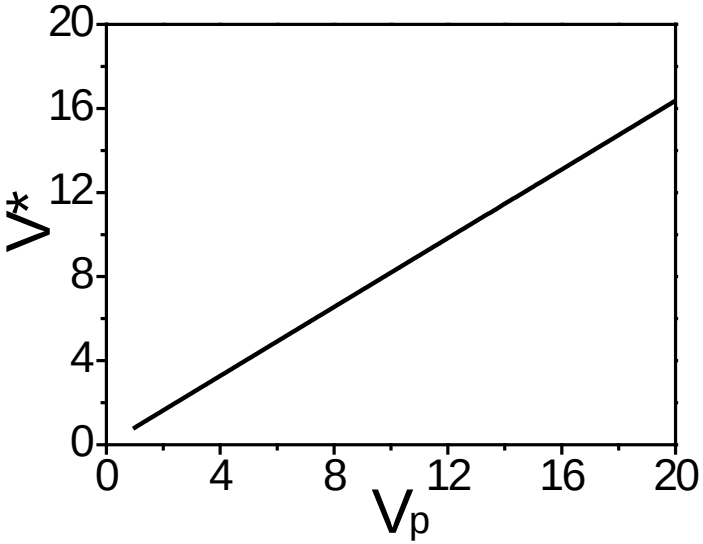
Self-Limited Growth

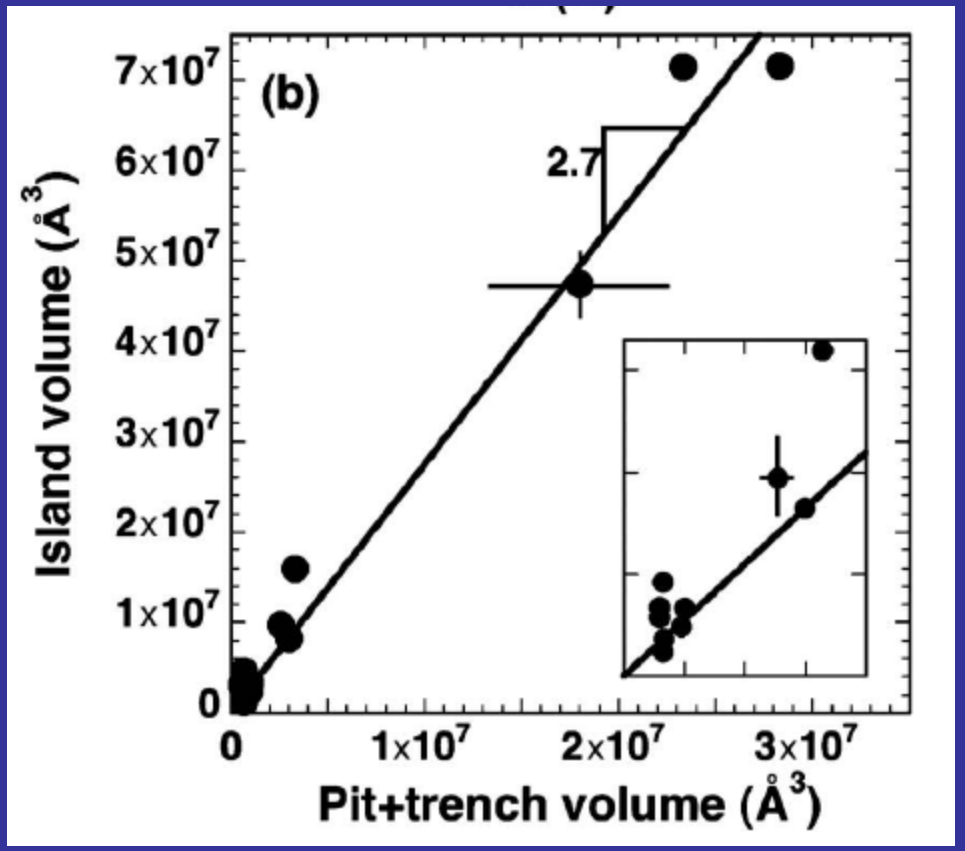
$$E_{\text{ipi}} = -\frac{16V_p \cdot V_i}{9(V_p^{1/3} + V_i^{1/3})^3} + \frac{V_i^2}{9(V_p^{1/3} + V_i^{1/3})^3} + \frac{4\sqrt{2}V_i^2}{9(V_p^{1/3} + V_i^{1/3})^3}$$



Critical volume V* at minimum E_{ipi}

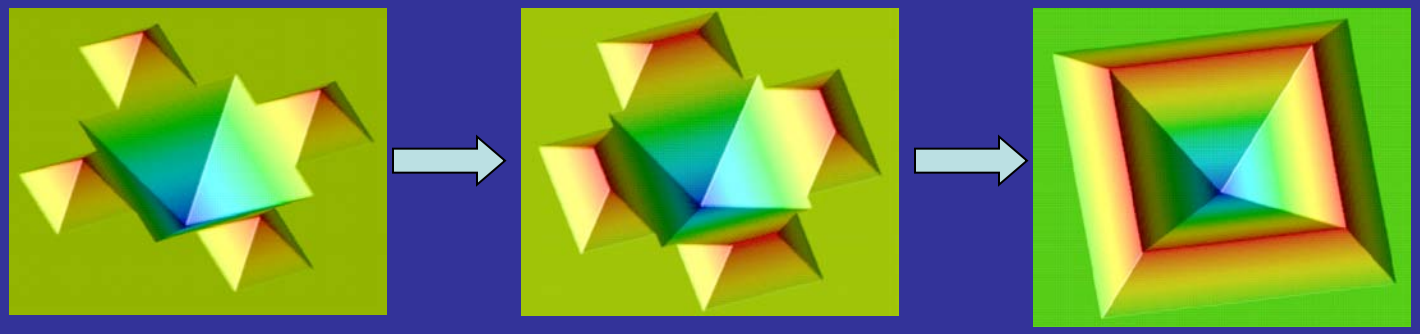
V* vs. V_p: linear





Gray. et al. PRB 72,155323(05)

Island Elongation



$$E = -2\left[s\ln et + t\ln es\right] - \frac{\frac{8}{3}l_p^3\left(st + \frac{1}{3}e^{1-\frac{2\Gamma}{\varepsilon_0 h}}\right)}{\left(l_p + \frac{s + e^{\frac{1}{2}-\frac{\Gamma}{\varepsilon_0 h}}}{2}\right)^2 e^{\frac{1}{2}-\frac{\Gamma}{\varepsilon_0 h}}} + \frac{(1+4\sqrt{2})\left(st + \frac{1}{3}e^{1-\frac{2\Gamma}{\varepsilon_0 h}}\right)^2}{16\left(l_p + \frac{s + e^{\frac{1}{2}-\frac{\Gamma}{\varepsilon_0 h}}}{2}\right)^2}$$

Tersoff and Tromp, *PRL* 70, 2782 (93)

A Simple Theoretical Model

predicting the effect of strain on surface diffusion

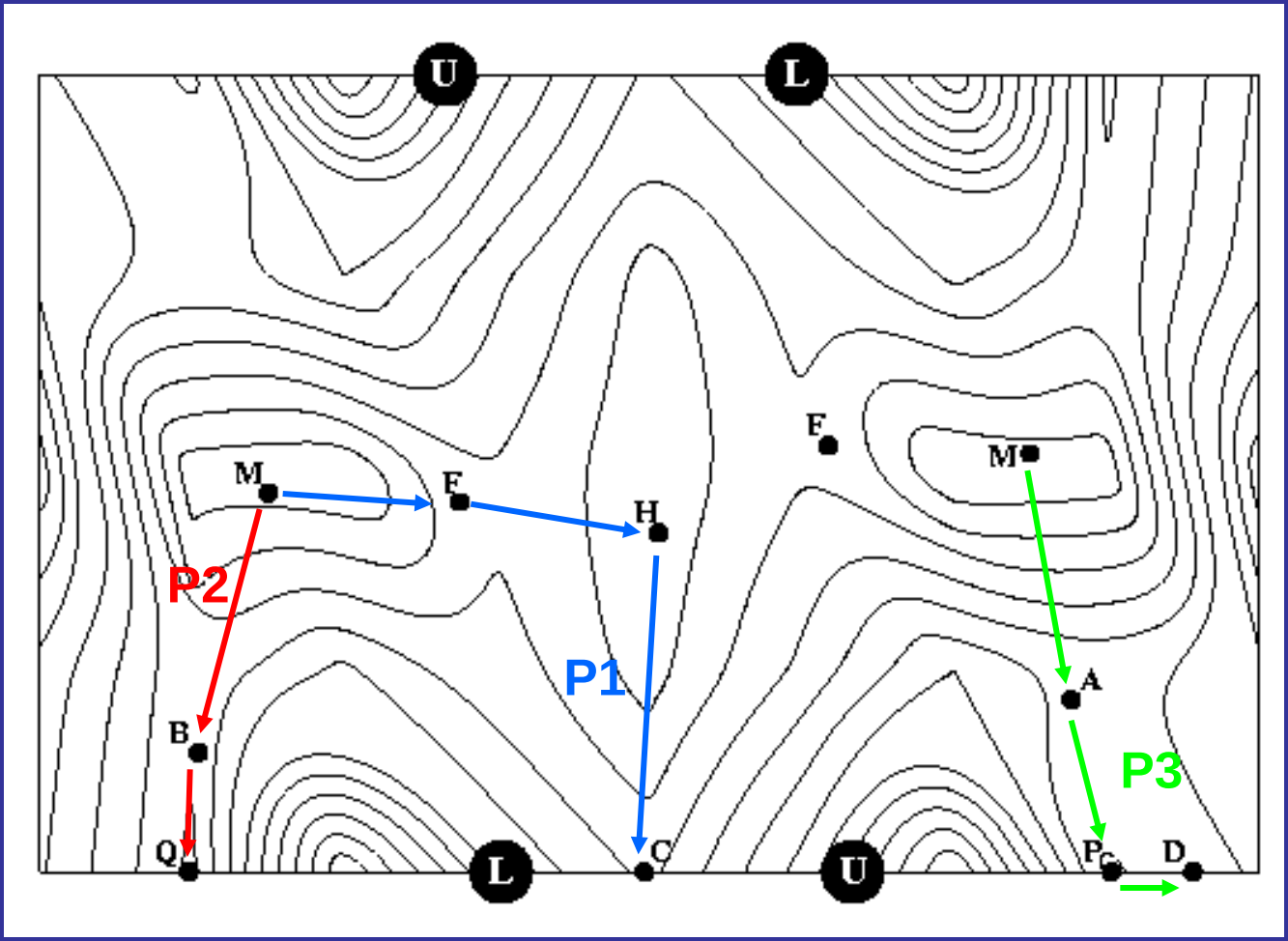
$$E_b^0 = E_s - E_m$$

$$E_b(\varepsilon) = (E_s - E_m) + A\,(\sigma_s - \sigma_m)\varepsilon$$
$$= E_b^0 + A\,(\Delta\sigma)\varepsilon$$

- Calculating adatom-induced surface stress on "unstrained surface"

Shu et al, *Phys. Rev. B*, 64, 245410 (01)

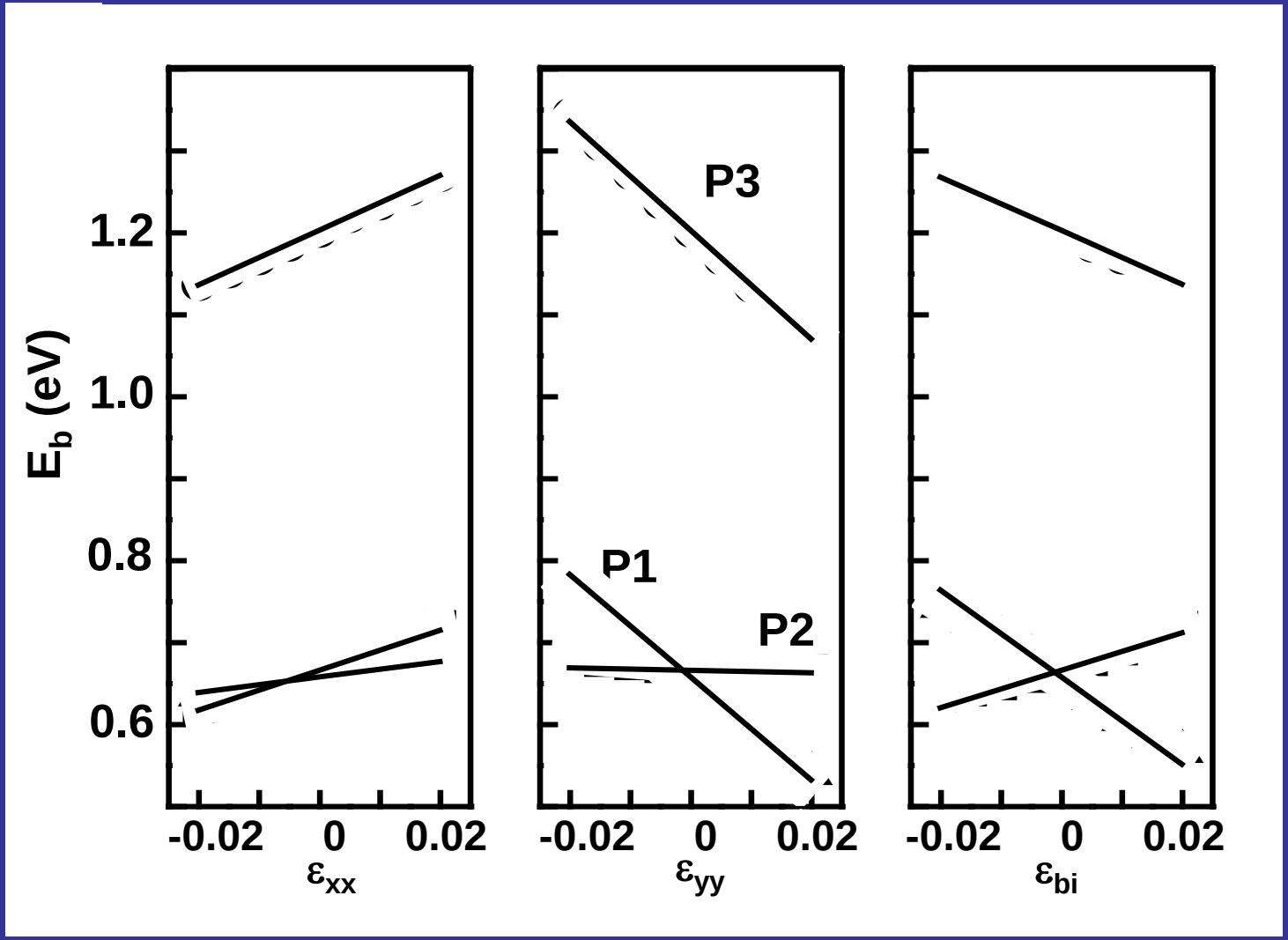
Potential-energy Surface on Unstrained Si(001) Surface



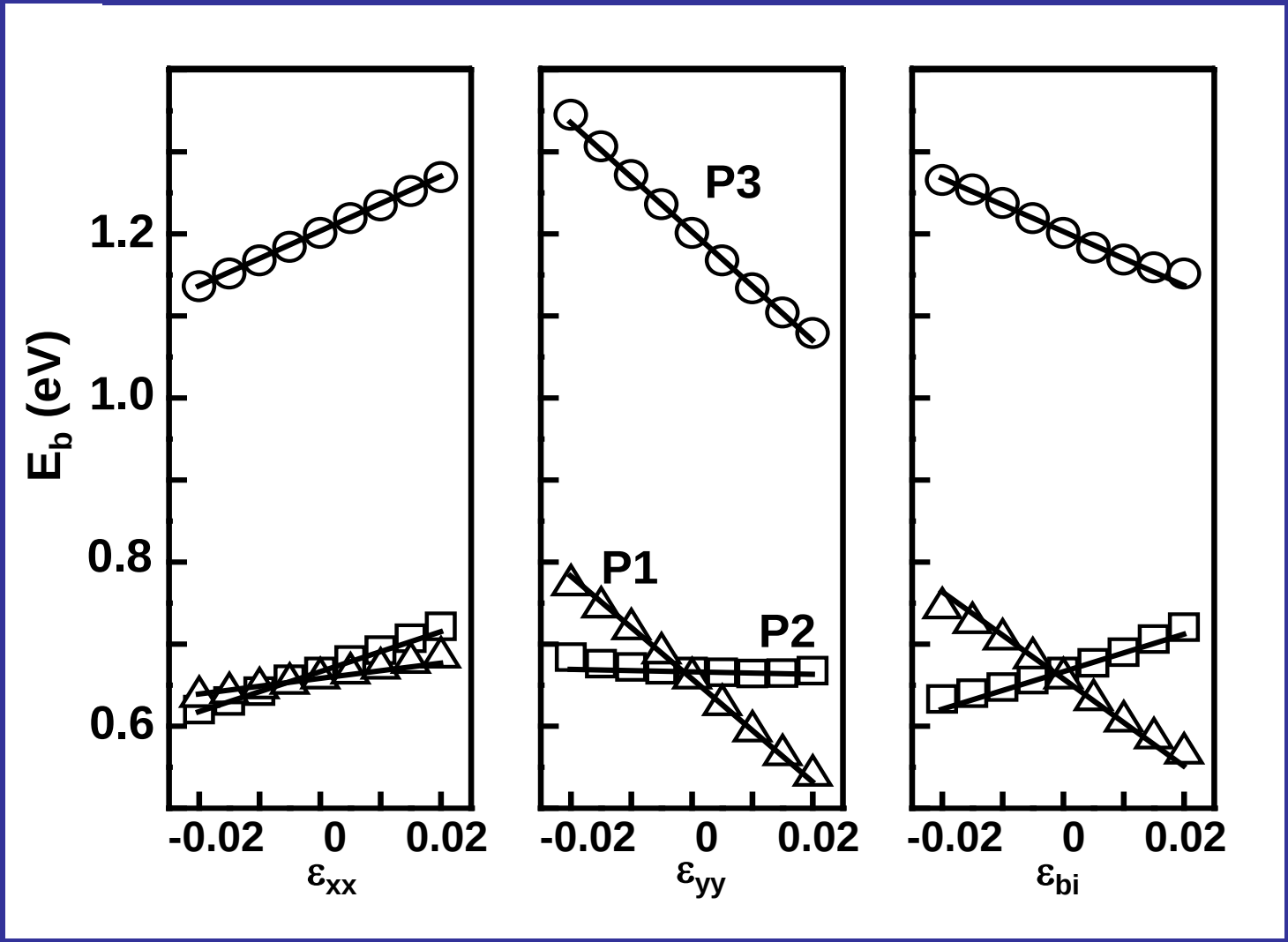
Adatom Diffusional Stress

	P1	P2	P3
$A(\Delta\sigma_{xx})$	0.94	2.43	3.32
$A(\Delta\sigma_{yy})$	-6.23	-0.15	-6.60
$A(\Delta\sigma)$	-5.29	2.28	-3.28

Predicted Dependence of Diffusion Barrier on Strain



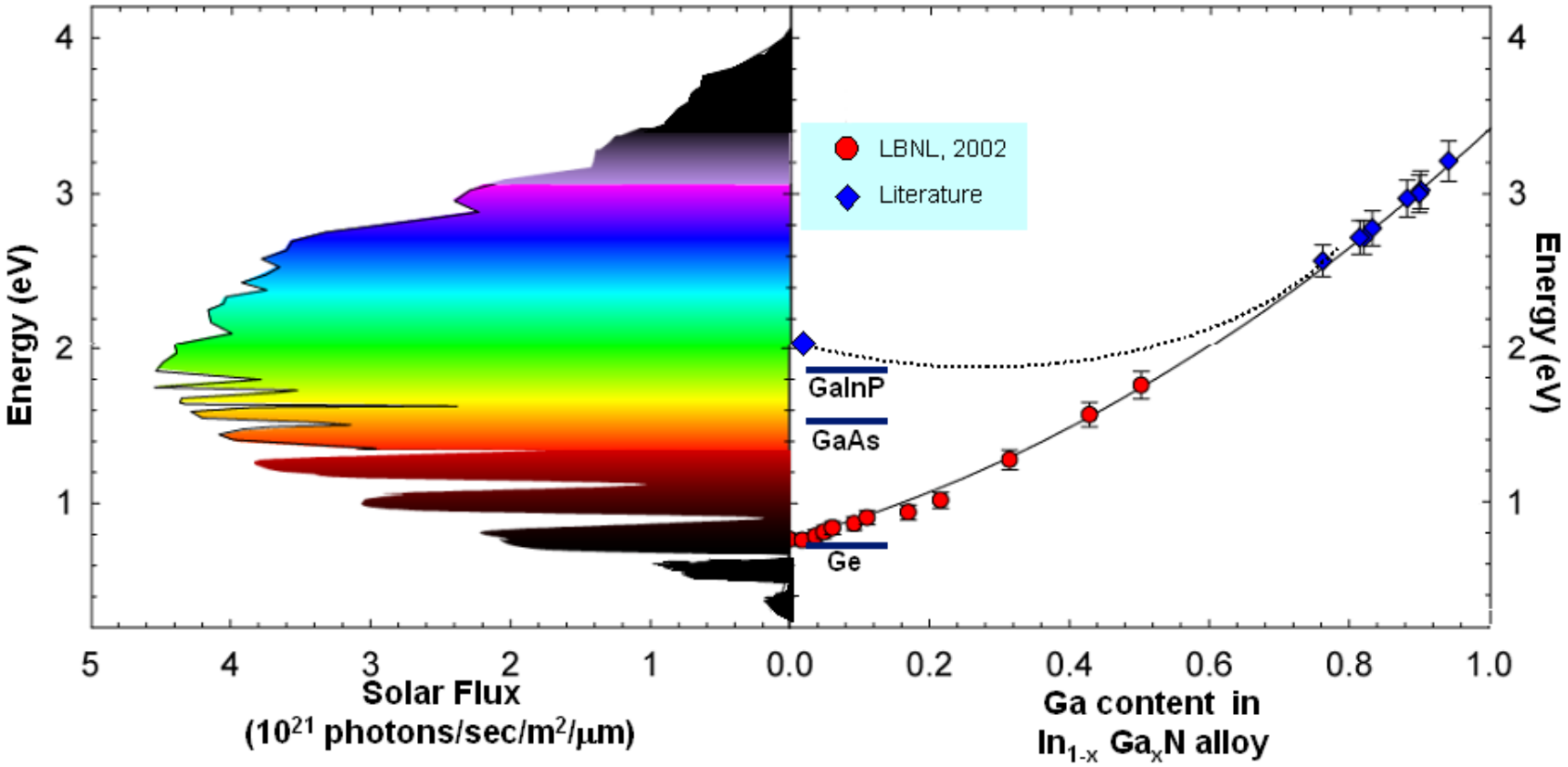
Calculated Dependence of Diffusion Barrier on Strain



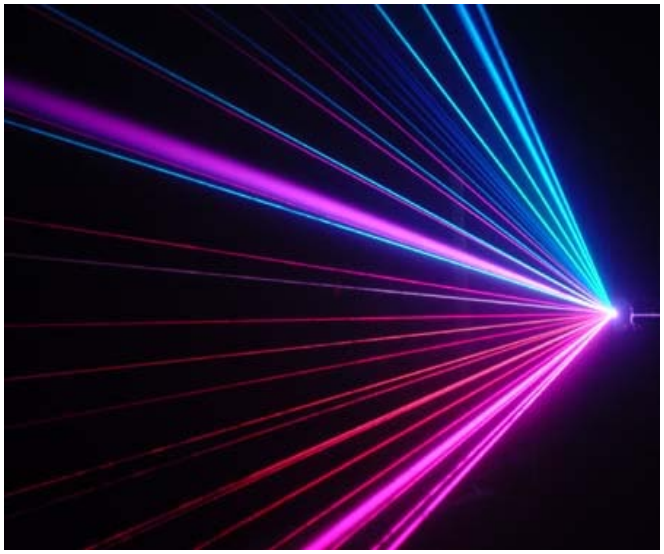
Shu et al, *Phys. Rev. B*, 64, 245410 (01)

Controlled Composition Profiles:
tuning the color

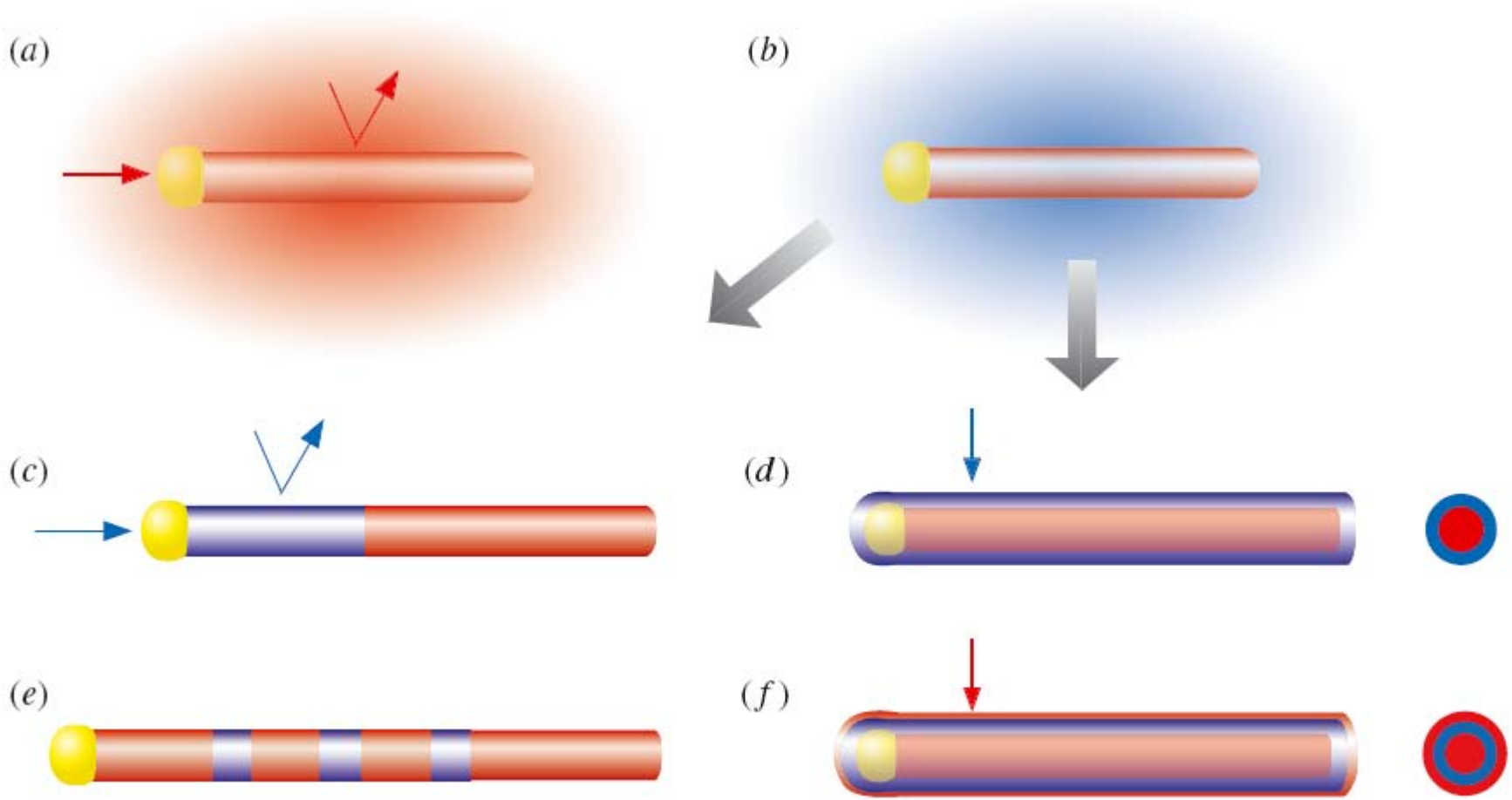
- The direct energy gap of $In_{1-x}Ga_xN$ covers most of the solar spectrum



Semiconductor Alloy QDs and NWs:
building blocks for nano optoelectronic devices



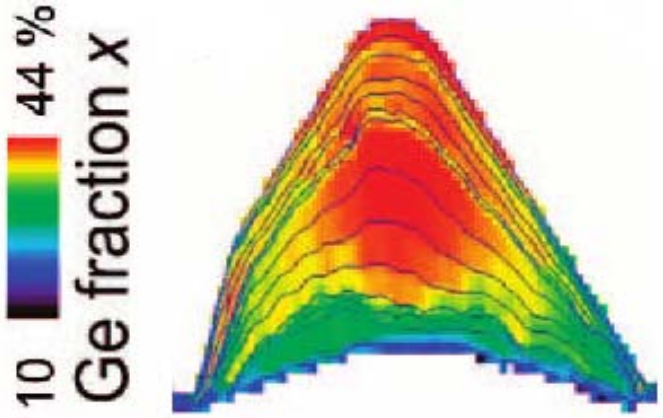
Experiment: sequential growth of axial superlattice and radial core-shell structure of NWs:



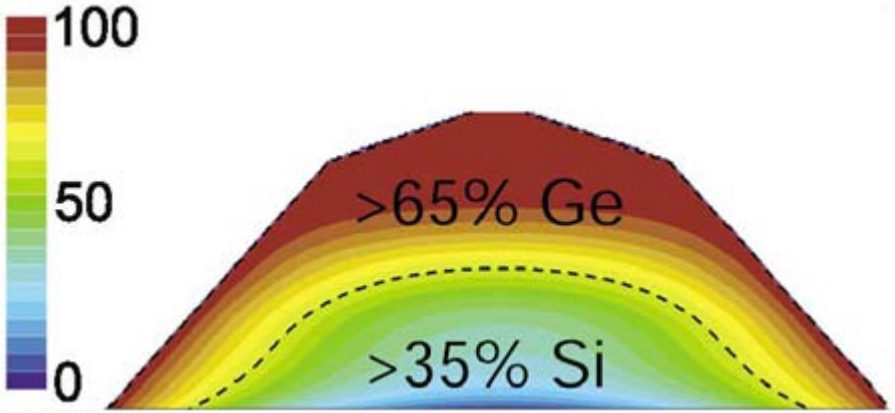
M. S. Gudiksen, *et al.*, *Nature*, **415**, 617 (2002)

Experiment: self-assembled core-shell QDs & NWs

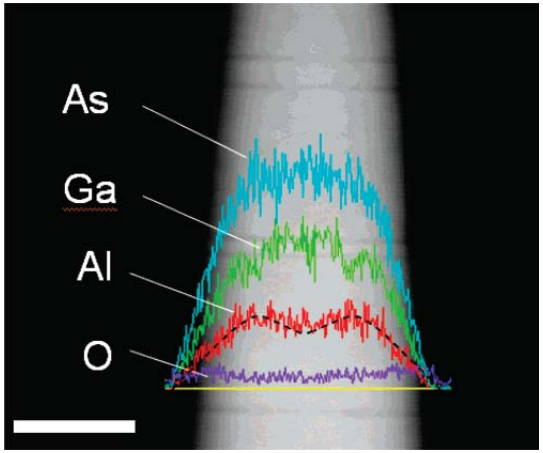
GeSi core-shell QD grown on Si with Ge rich core



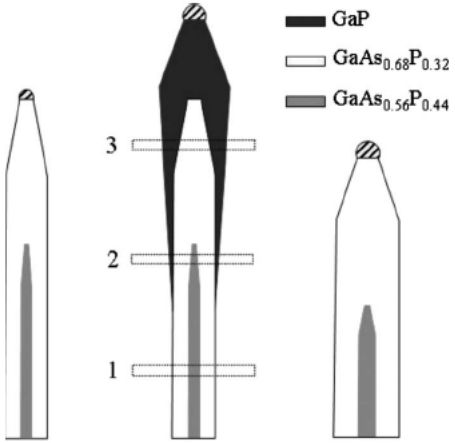
GeSi core-shell QD grown on Si with Si rich core



AlGaAs core-shell NW grown on GaAs with Ga rich core

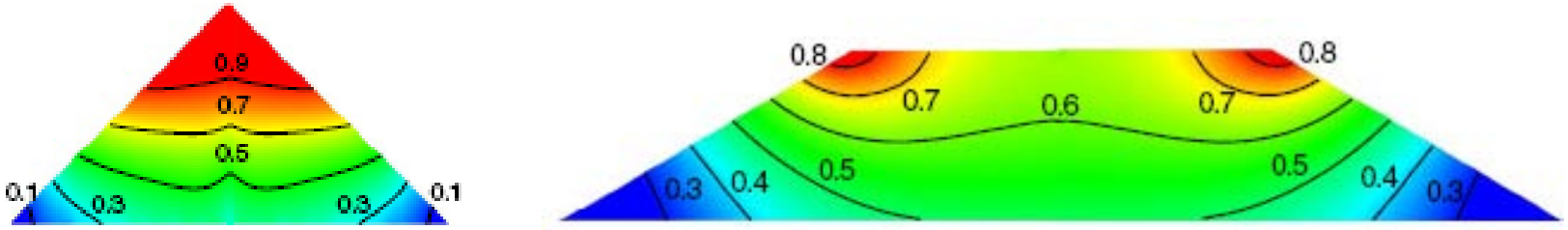


GaAsP core-shell NW grown on Si with P rich core

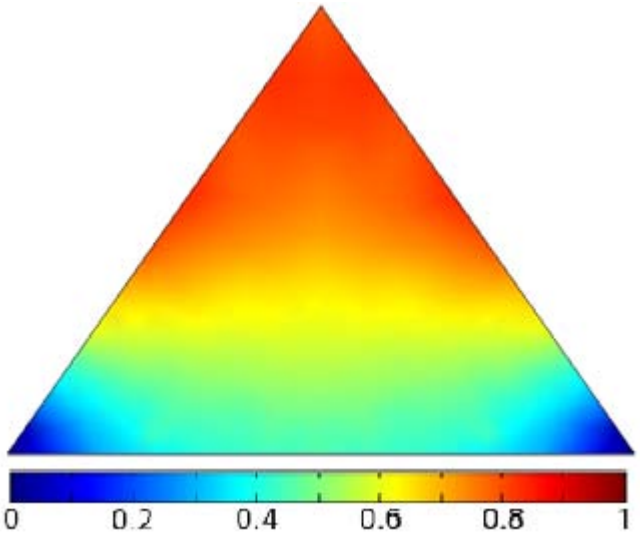


Rastelli, *et al.*, *Nano Letters*, **8**, 1404 (2008); Malachias, *et al.*, *PRL*, **91,** 176101 (2003); Chen, *et al.*, *Nano Letters*, **7**, 2584 (2007); Mohseni, *et al.*, *JAP*, **106**, 124306 (2009).

Theory: “equilibrium” composition profile



Finite Element result of equilibrium composition profiles in $A_{0.5}B_{0.5}$ QDs
Medhekar, *et. al*., *Phys. Rev. Lett.* **100**, 106104 (2008);



Monte Carlo result of composition profiles in $Ge_{0.6}Si_{0.4}$QDs
Medhekar, *et. al*., *Phys. Rev. Lett.* **100**, 106104 (2008);

Motivation: kinetics-limited composition profile

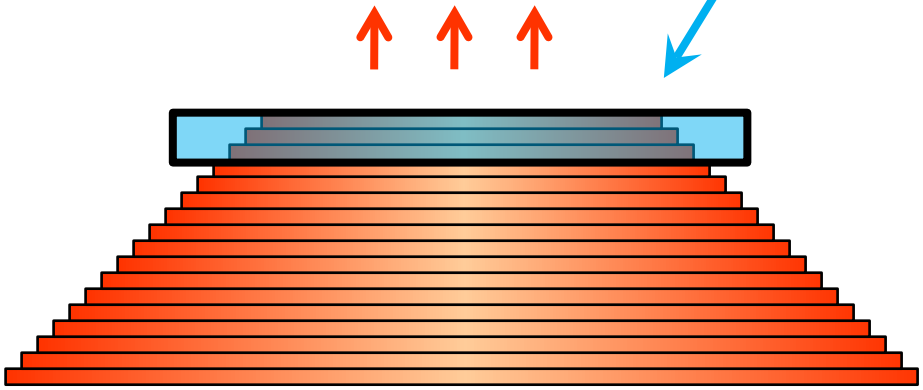
- Composition profile is determined by diffusion limited atom mixing.
- Equilibrium distribution is generally not expected for relatively large nanostructures, while local equilibrium is only established in the surface region (growth front).
  - Surface diffusion >> Bulk diffusion
- Kinetic growth mode controls the overall composition profile.
  - Layer-by-layer Growth vs. Faceted Growth

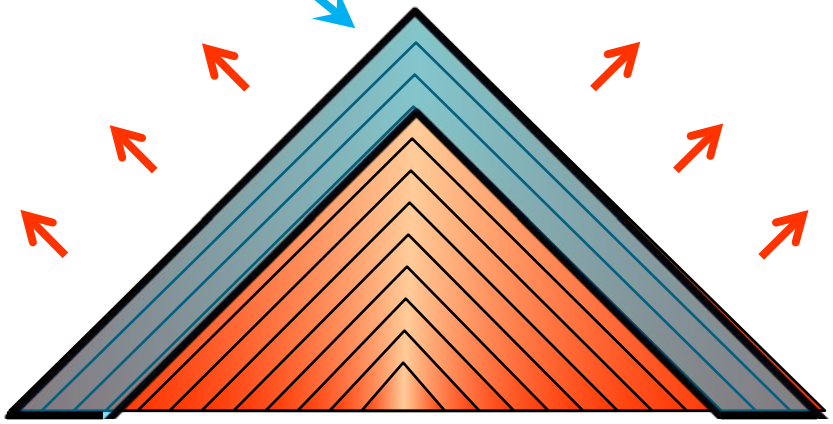
Growth Modes: local equilibrium of mixing

Layer by Layer Growth

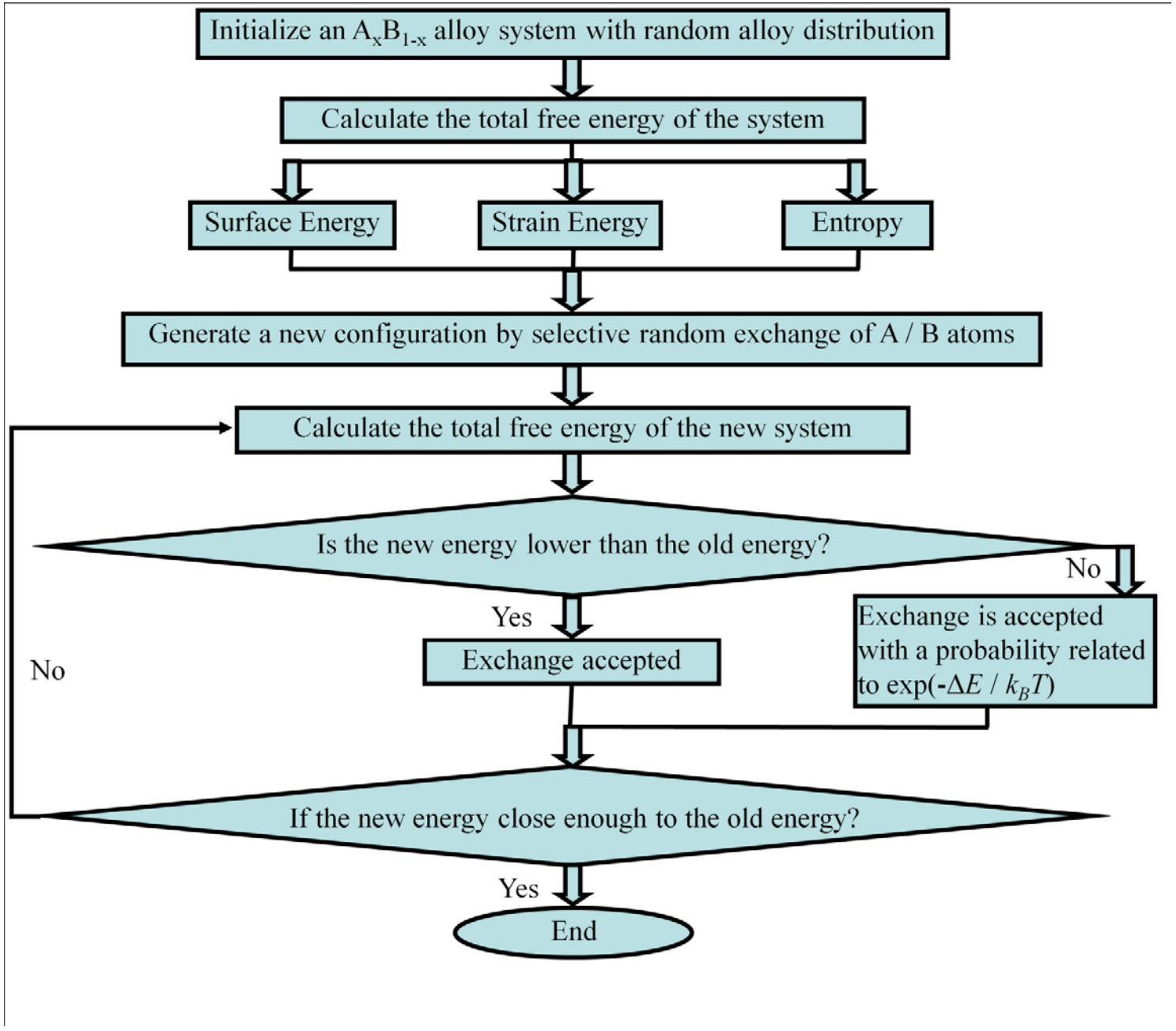
Faceted Growth

Surface diffusion depth (SDD) controlled mixing

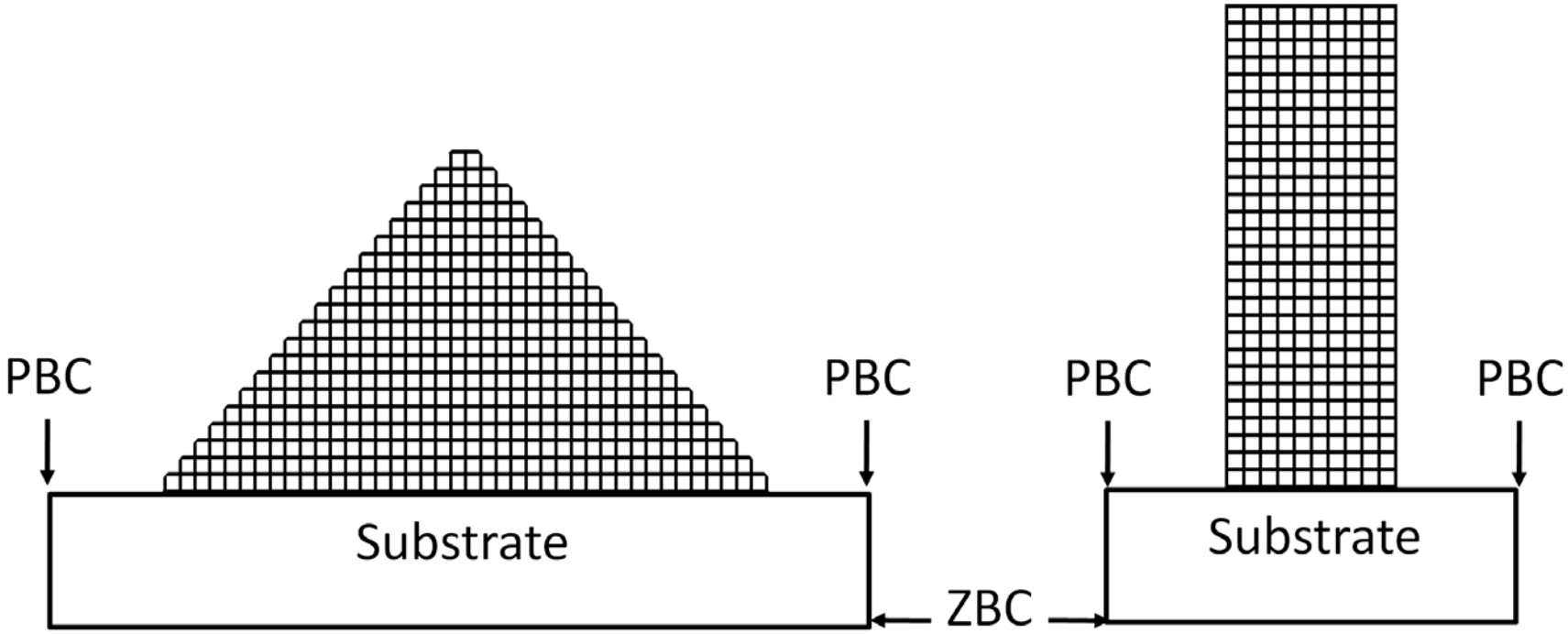




Algorithm of Simulation



Simulation Framework



$$G = H - TS,$$

$$H = E_s + E_{el}$$

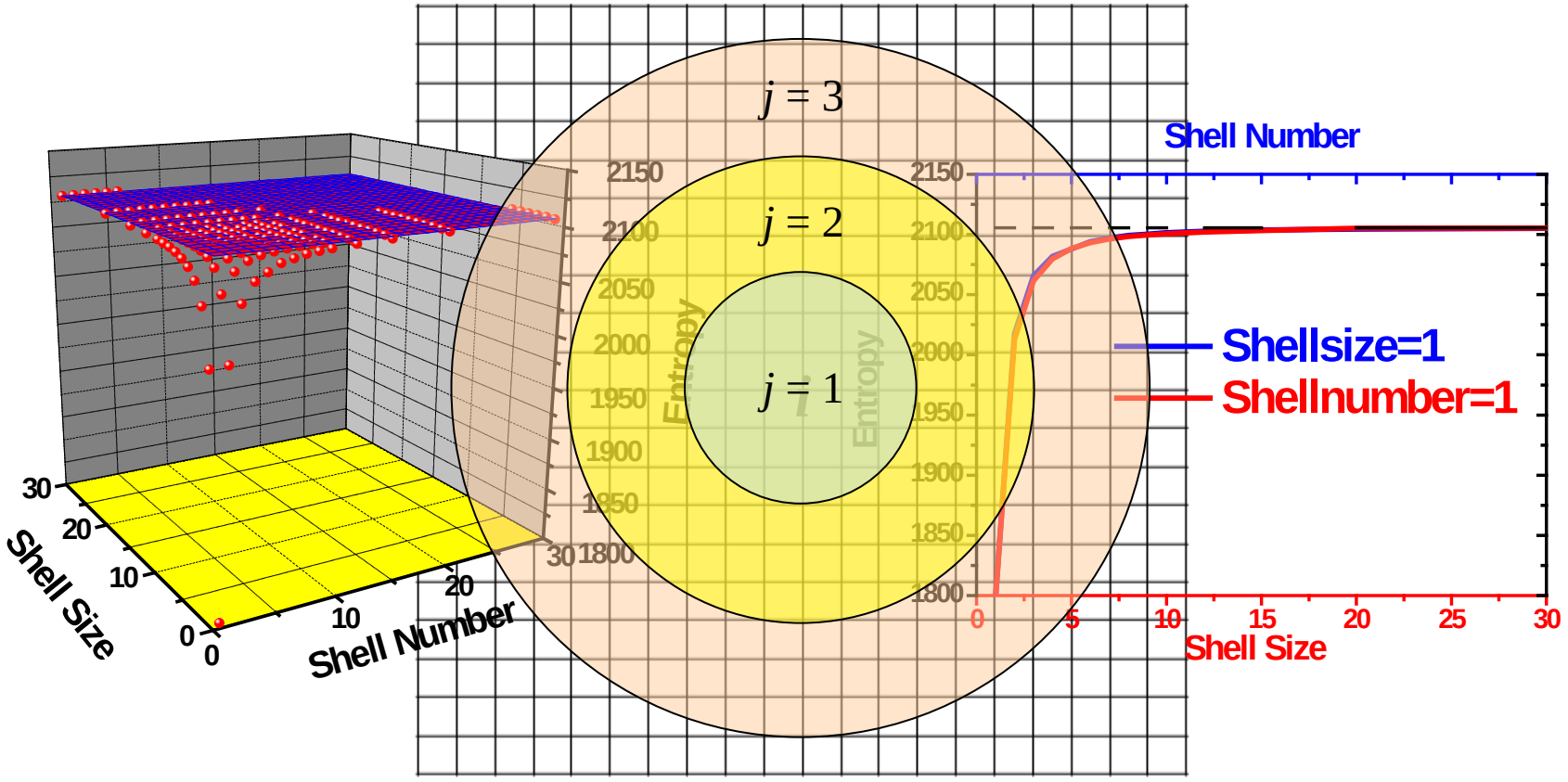
Entropy
Regular solution shell model

Surface energy
Bond-breaking model

Elastic energy
Atomistic strain Model

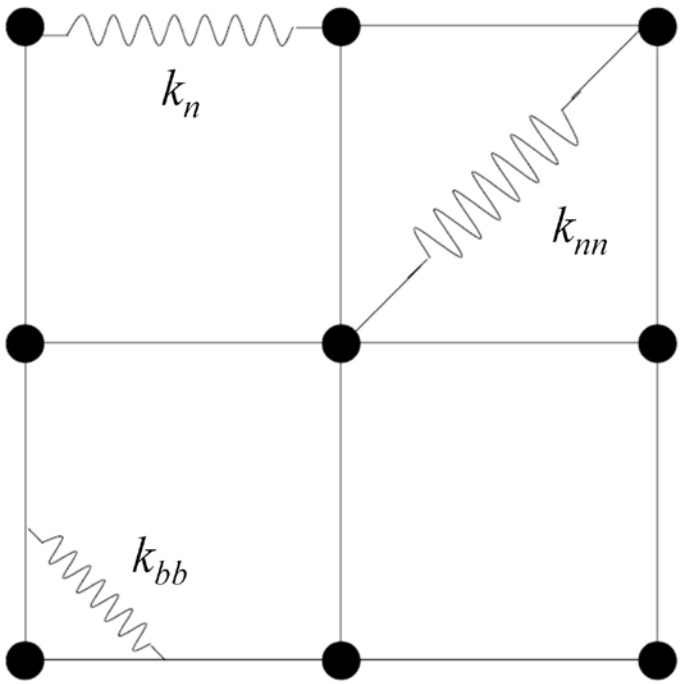
Entropy: regular solution shell model

$$S = \sum_{\text{Lattice } i=1}^{N} S_i = -k \sum_{\text{Lattice } i=1}^{N} \left\{ \frac{1}{n} \sum_{\text{Shell } j=1}^{n} \left[x_{ij} \ln\left(x_{ij}\right) + (1 - x_{ij}) \ln\left(1 - x_{ij}\right) \right] \right\}$$



Shell # = 3, Shell Size = 3

Strain Energy: atomistic stain model



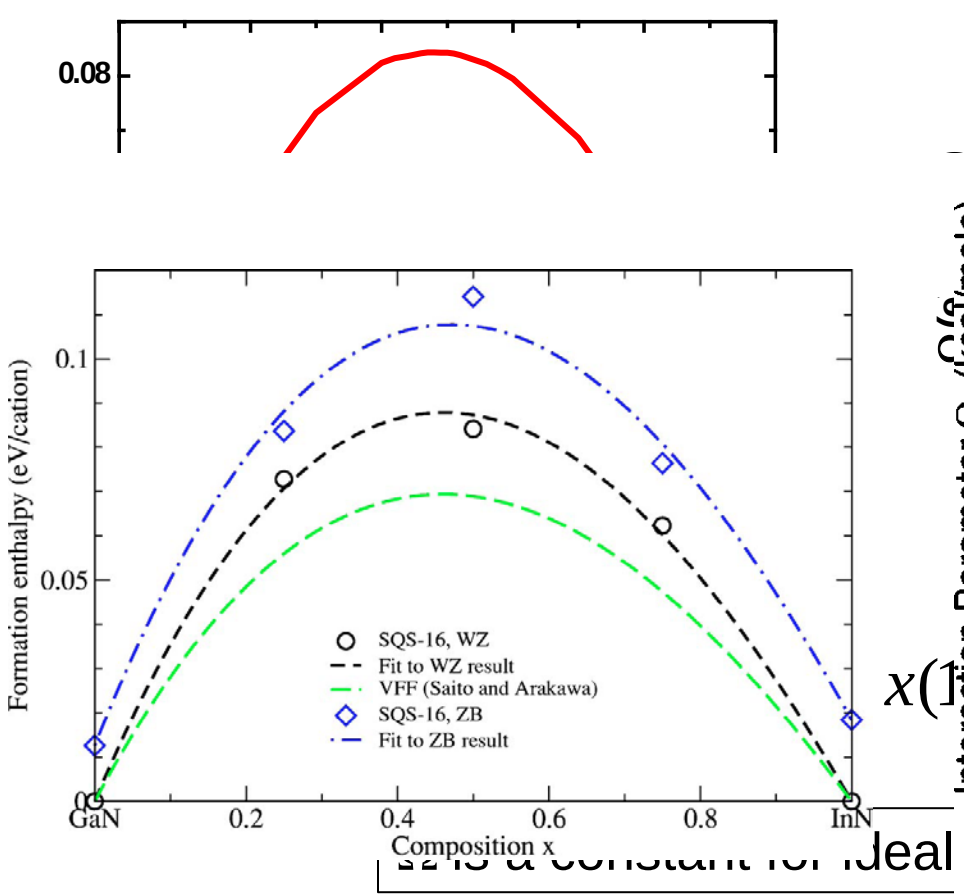
$$E_{el} = k_n\left(S_{xx}^2 + S_{yy}^2\right) + k_{nn}\left[\left(S_{xx} + 2S_{xy} + S_{yy}\right)^2 + \left(S_{xx} - 2S_{xy} + S_{yy}\right)^2\right] + k_{bb}S_{xy}^2,$$

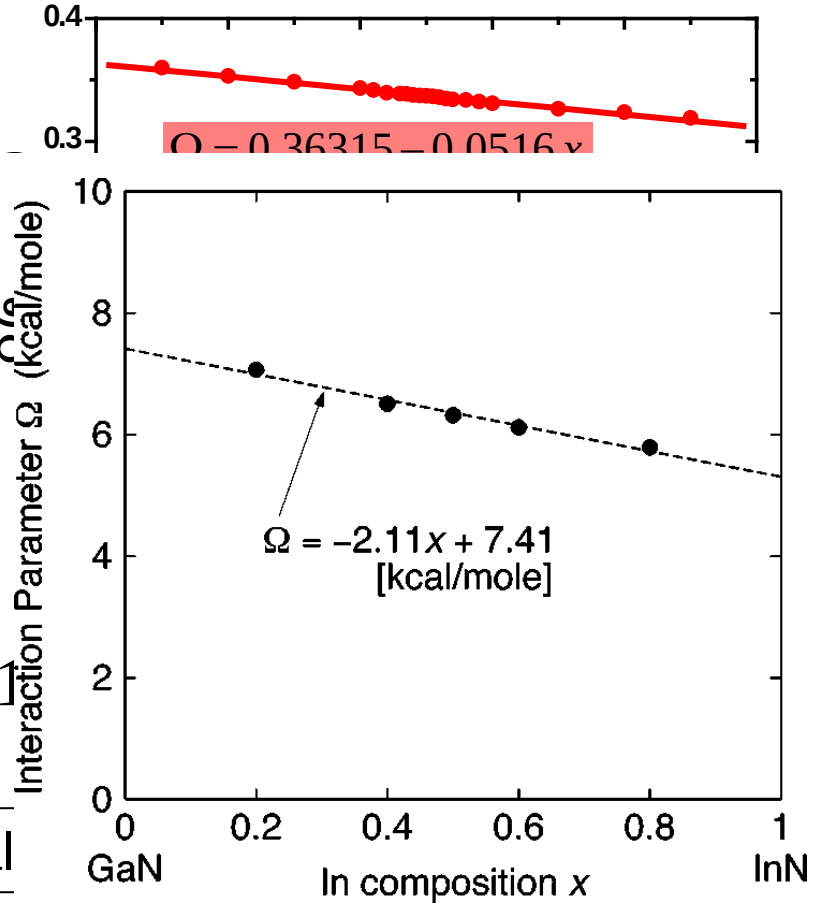
$$S_{kl} = \frac{1}{2}\left(\partial_k u_l + \partial_l u_k\right),\ \partial E_{el} \Big/ \partial \mathbf{u} = 0,\ \mathbf{u} \text{ is the displacement vector.}$$

Schindler, *et. al.*, *PRB*, **67**, 075316 (2003).

Formation Enthalpy and Interaction Parameter

atomistic stain model

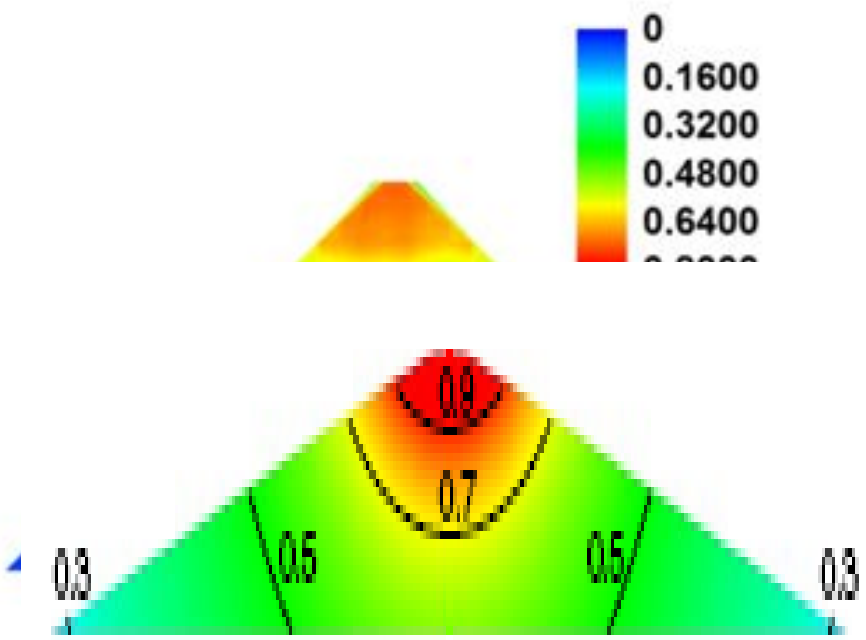


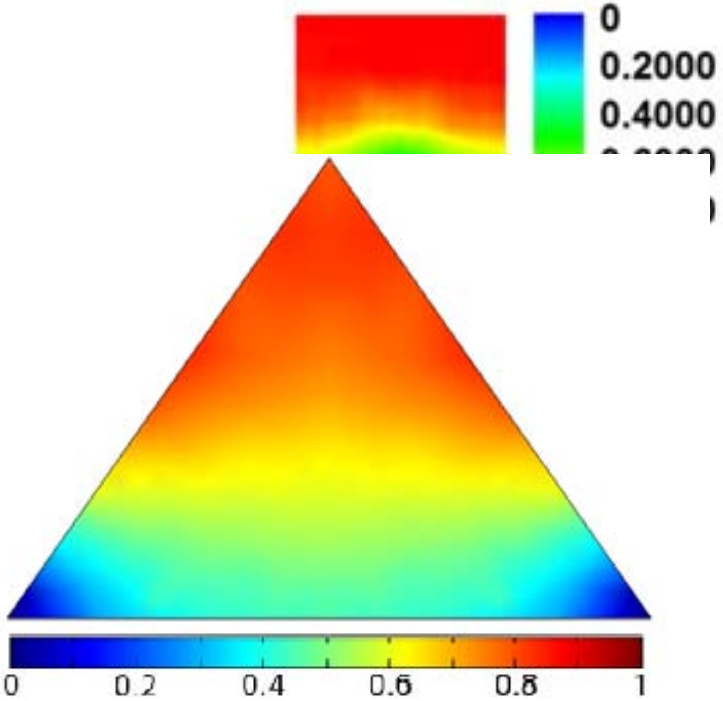


Gan, *et al.*, *Phy. Rev. B* **73**, 235214 (2006); Saito, *et al.*, *Phy. Rev. B* **60**, 1701 (1999)

Equilibrium Composition Profile

$In_{0.3}Ga_{0.7}N$ QDs and NWs on GaN substrate

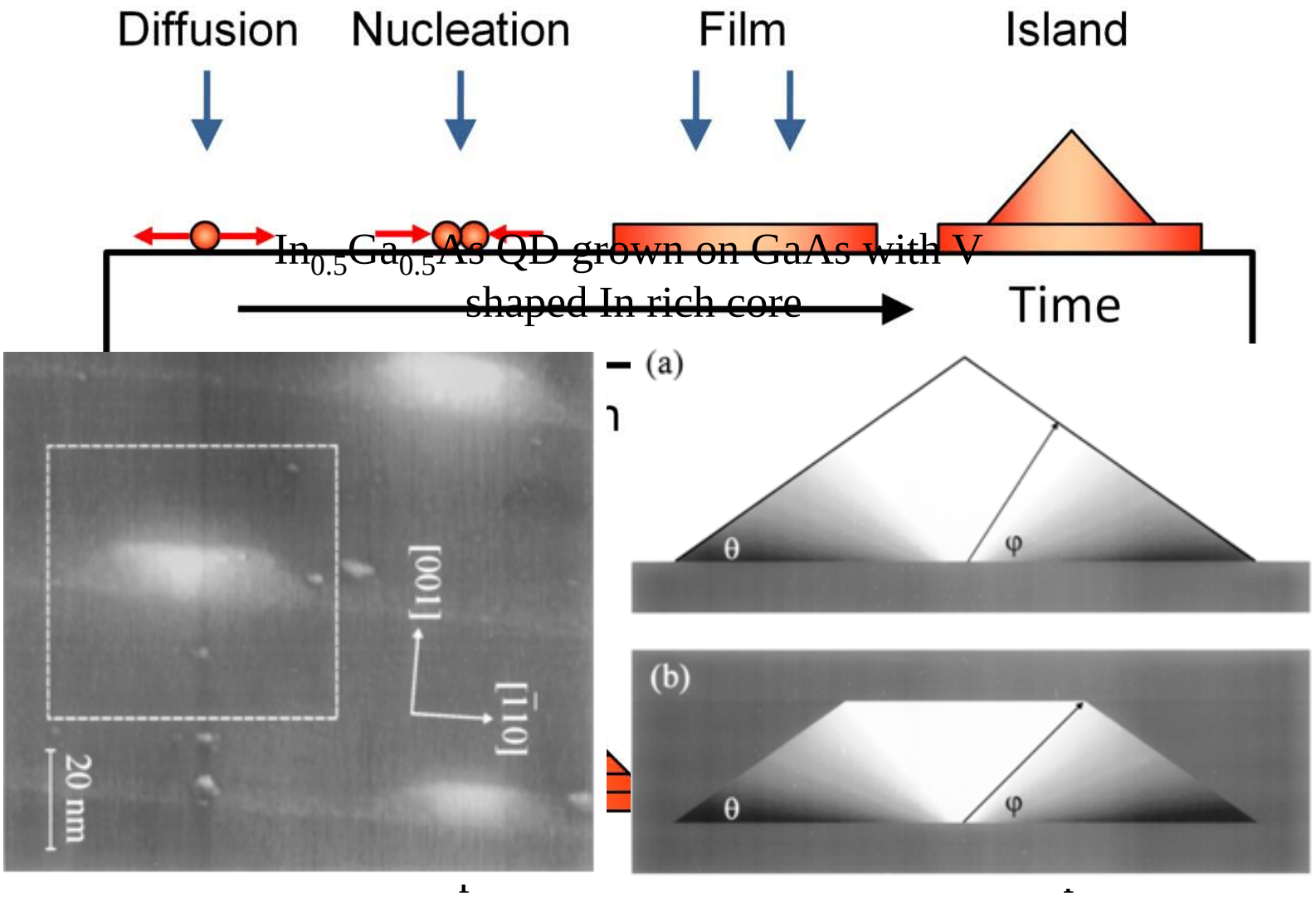




Medhekar, *et. al.*, *Phys. Rev. Lett.* **100**, 106104 (2008);

Uhlík *et. al.*, J. *Phys.: Condens. Matter* **21**, 084217 (2009).

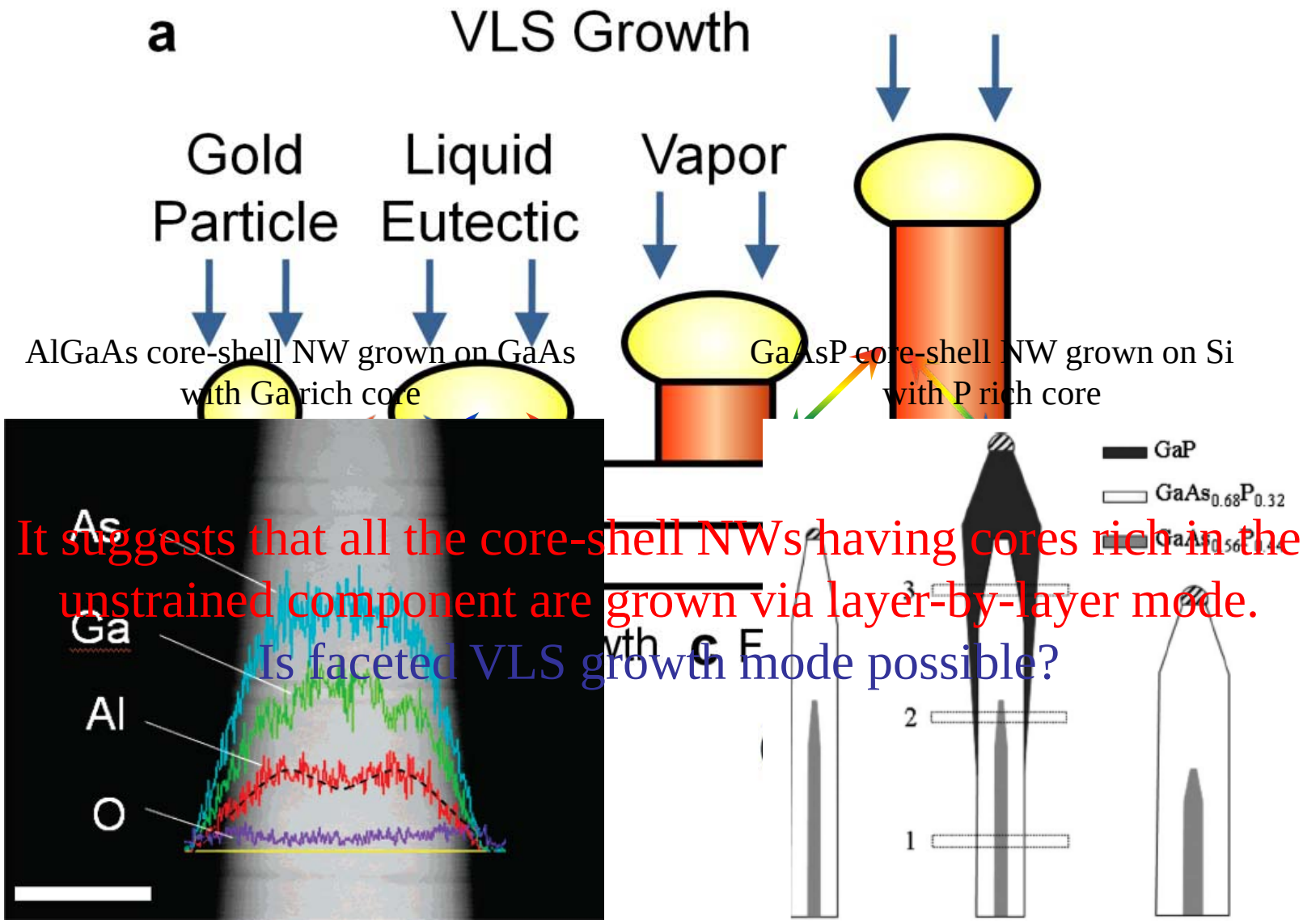
Kinetic Composition Profile of $In_{0.3}Ga_{0.7}N$ QDs



$In_{0.5}Ga_{0.5}As$ QD grown on GaAs with V shaped In rich core

Liu, Tersoff, Baklenov, Holmes, Jr., and Shih, *Phy. Rev. Lett.* **84**, 334 (2000).

Kinetic Composition Profiles of $In_{0.3}Ga_{0.7}N$ NWs

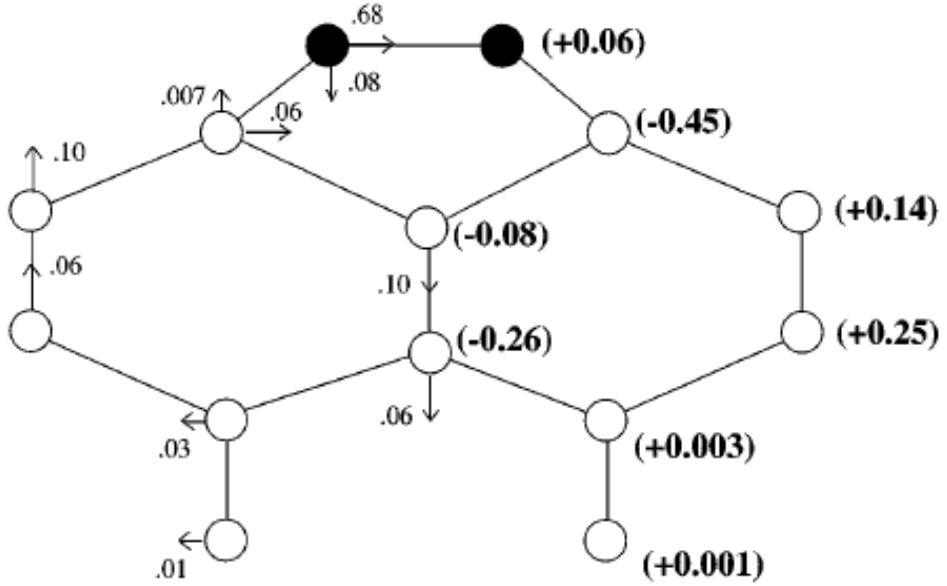


It suggests that all the core-shell NWs having cores rich in the unstrained component are grown via layer-by-layer mode.

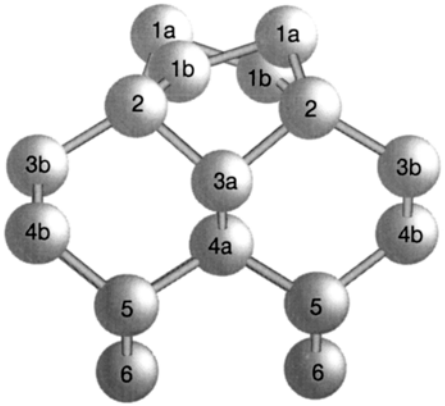
Is faceted VLS growth mode possible?

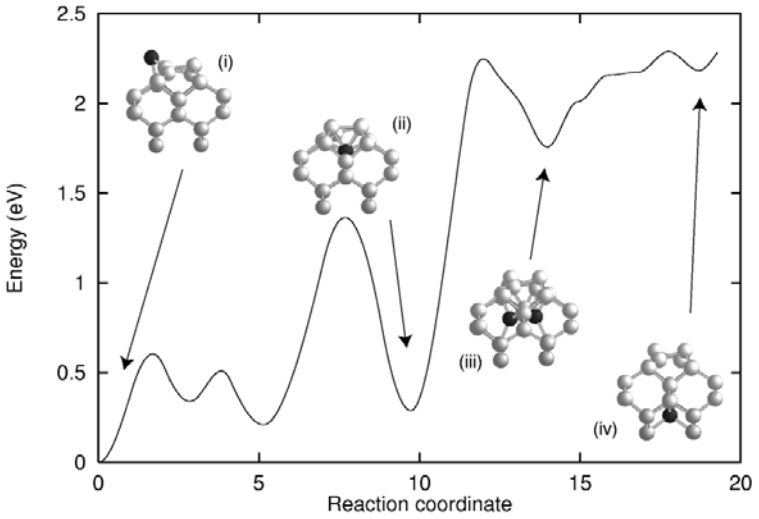
Chen, *et al.*, *Nano Lett.*, **7**, 2584 (2007); Mohseni, *et al.*, *JAP*, **106**, 124306 (2009).

Diffusion Depth up to Several Sub-Surface Layers



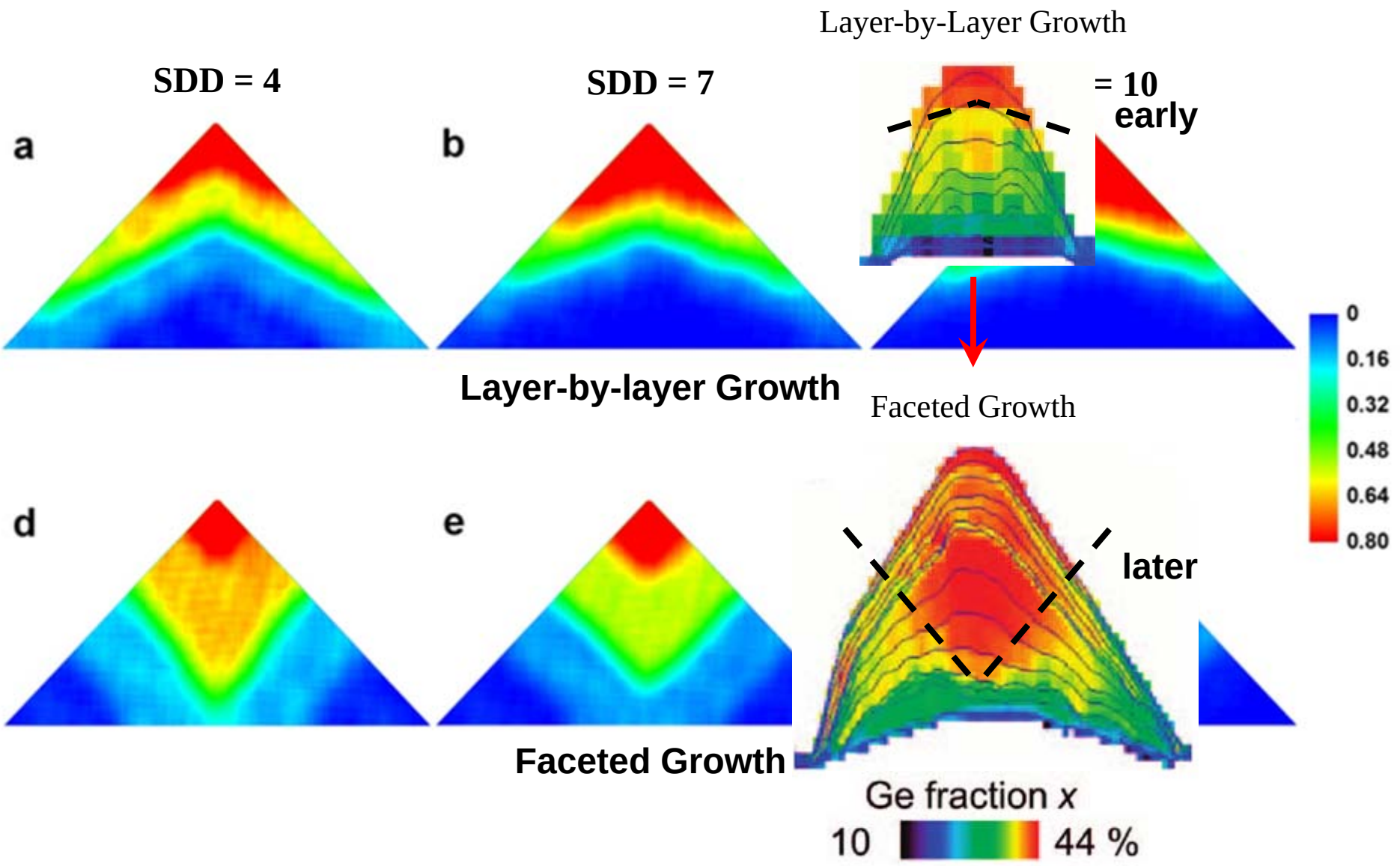
Liu & Lagally, *Phys. Rev. Lett.* 76, 3156 (1996).





Uberuaga, *et al.*, *Phys. Rev. Lett.* **84**, 2441 (2000).

The Effect of Sub-Surface Diffusion Depth



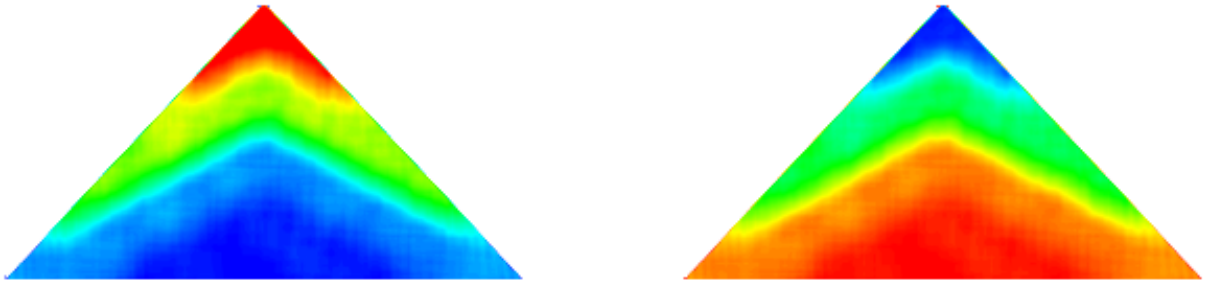
Rastelli, *et al.*, *Nano Lett.*, **8**, 1404 (2008);

The Effect of Substrate on Alloy Phase Separation

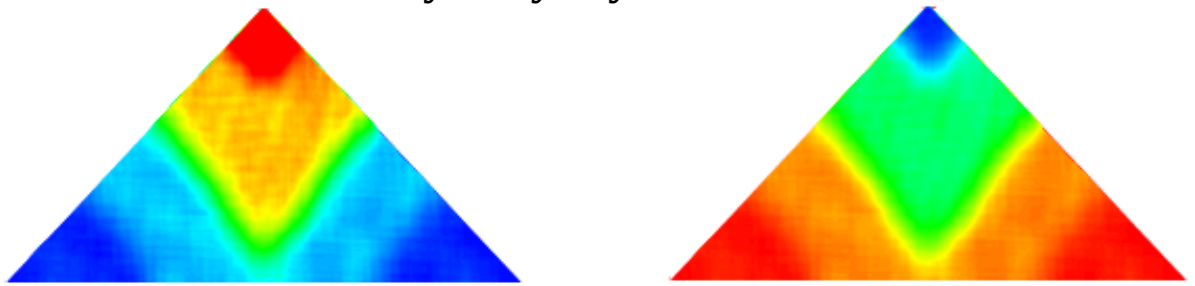
reversing the composition – InGaP (SDD=4)

$In_{0.3}Ga_{0.7}P$ on GaP

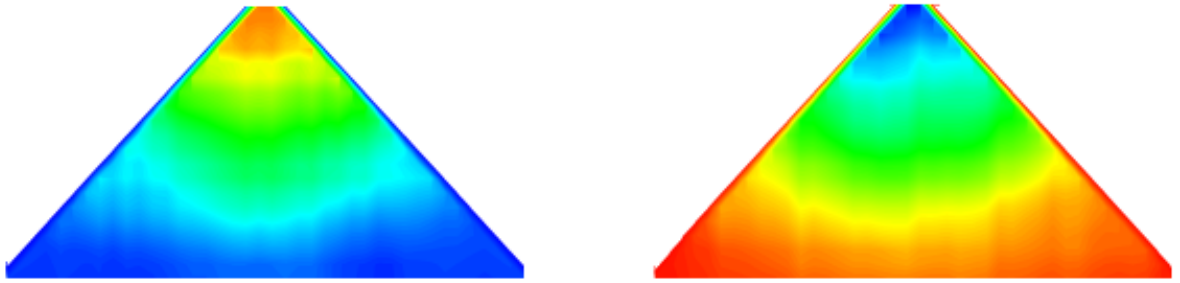
$In_{0.7}Ga_{0.3}P$ on InP



Layer-by-layer Growth



Faceted Growth

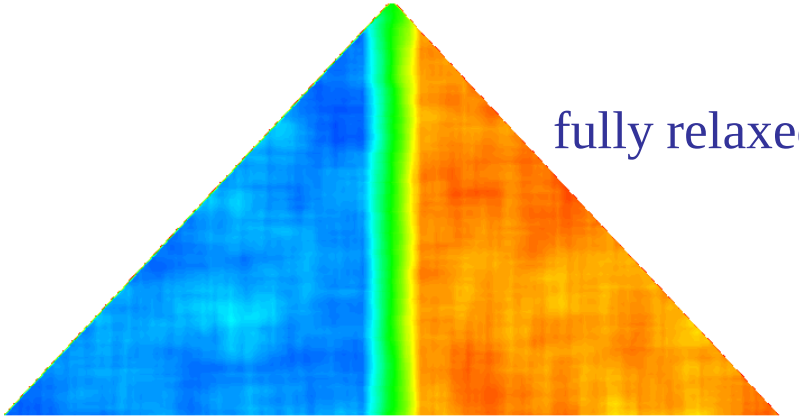


Equilibrium

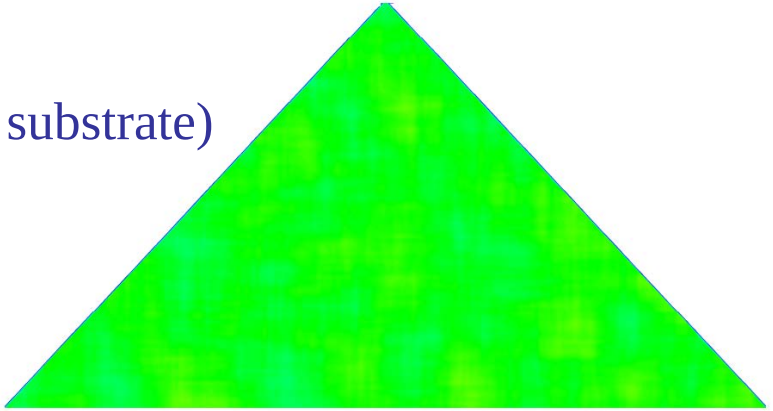
Suppressing Miscibility Gap by Growth

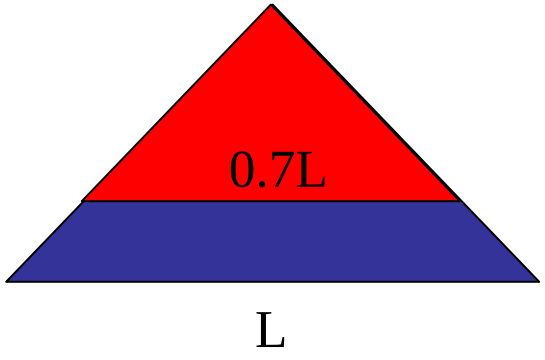
$In_{0.5}Ga_{0.5}N$ with miscibility gap

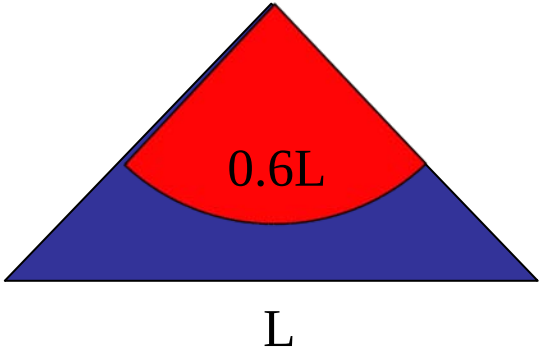
$Ge_{0.5}Si_{0.5}$ with no (small) miscibility gap

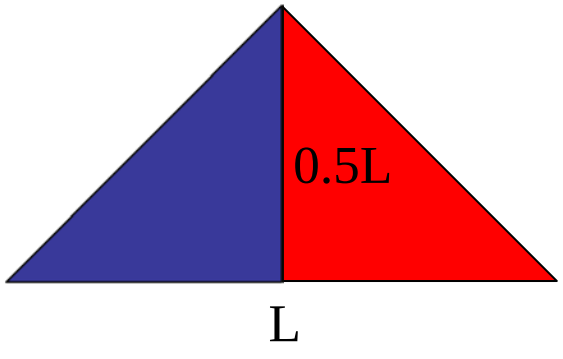


fully relaxed (no substrate)



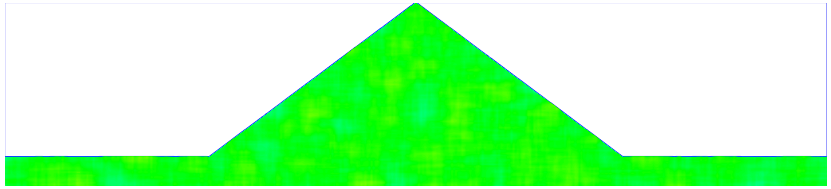




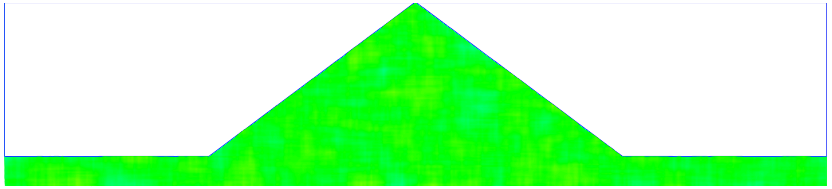


Suppressing Miscibility Gap by Growth Kinetics

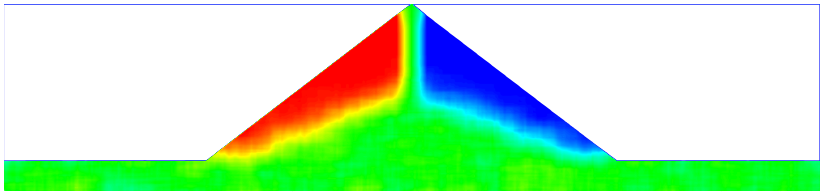
layer-by-layer growth of $In_{0.5}Ga_{0.5}N$ QD on $In_{0.5}Ga_{0.5}N$ substrate



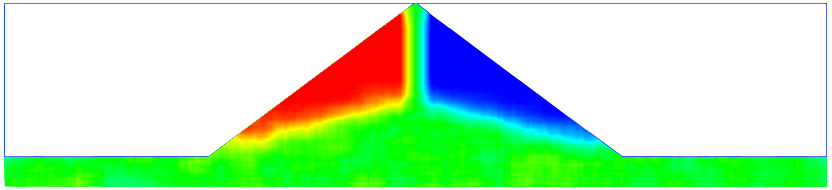
SDD = 1



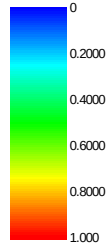
SDD = 4



SDD = 5



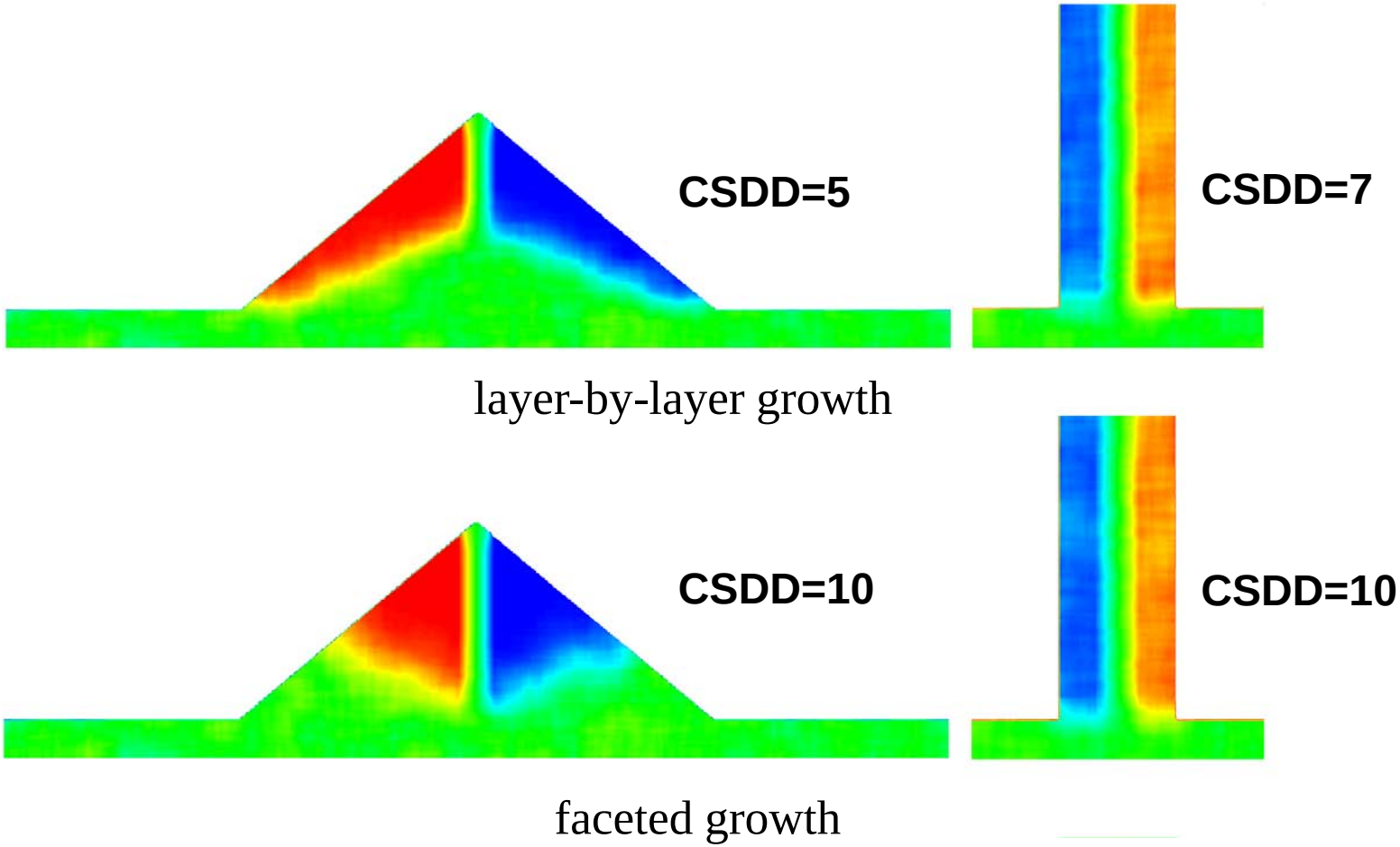
SDD = 7



Critical surface diffusion depth (CSDD) for mixing = 5
(misfit strain acts against phase separation)

Suppressing Miscibility Gap by Growth Kinetics

the effect of growth mode



Summary

- **The kinetics-controlled alloy composition profiles are distinctively different from the equilibrium composition profiles.**

- **There exists a striking correlation between the composition profiles of epitaxial strained semiconductor alloy QDs and NWs and the growth mode: layer-by-layer versus faceted.**

- **The layer-by-layer growth yields structures with cores rich in the unstrained component by lateral phase separation via strain relaxation; while the faceted growth mode yields structures with cores rich in the strained component by vertical phase separation via strain relaxation.**

- **Suppressing phase separation by selective growth substrate and kinetics**