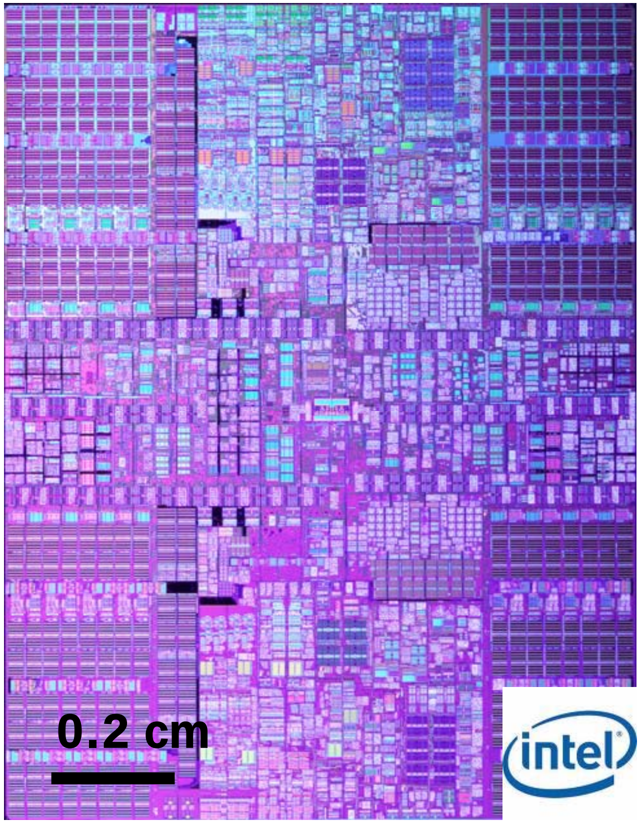
Frontiers in
Nanoscale Science I

Incredibly Shrinking Transistor
Semiconductor Nanostructures
Quantum Transport
Molecular Electronics

Frontiers in Nanoscale Science I

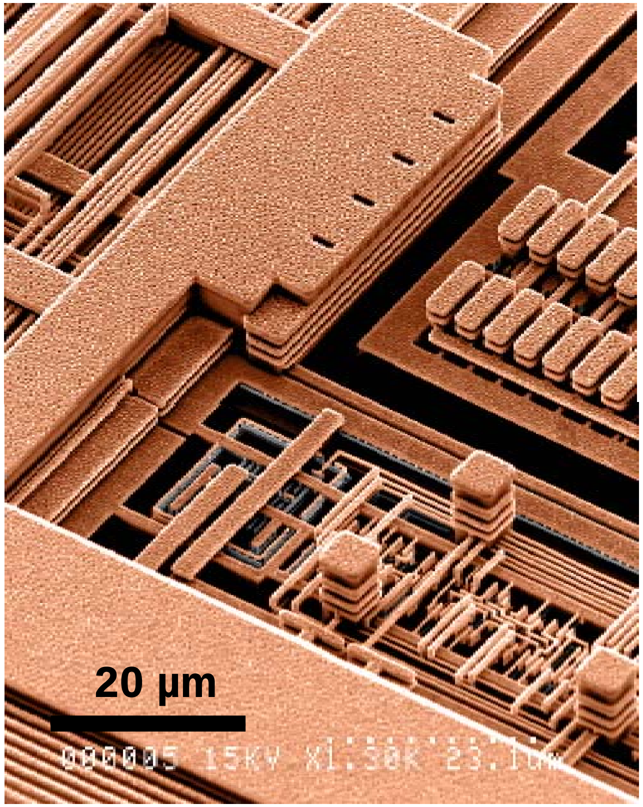
Incredibly Shrinking Transistor

Integrated Circuits



CPU as of 2008

~ 800 million transistors



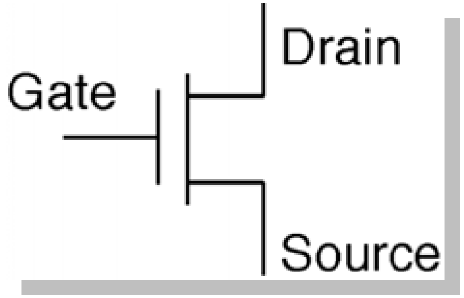
metal lines in a CPU

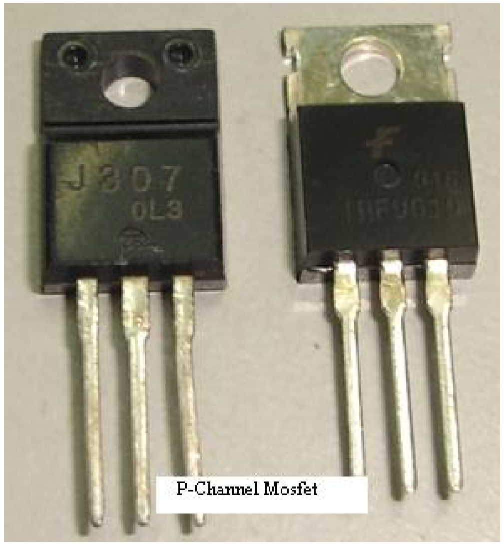
Transistor

- fundamental active electronic component of digital circuits
- *three* terminal device
- does 2 functions:
    1. *switch* – 0 / 1 → perform logic
    2. *gain* – amplifies digital signals

common form – field-effect transistor (FET)

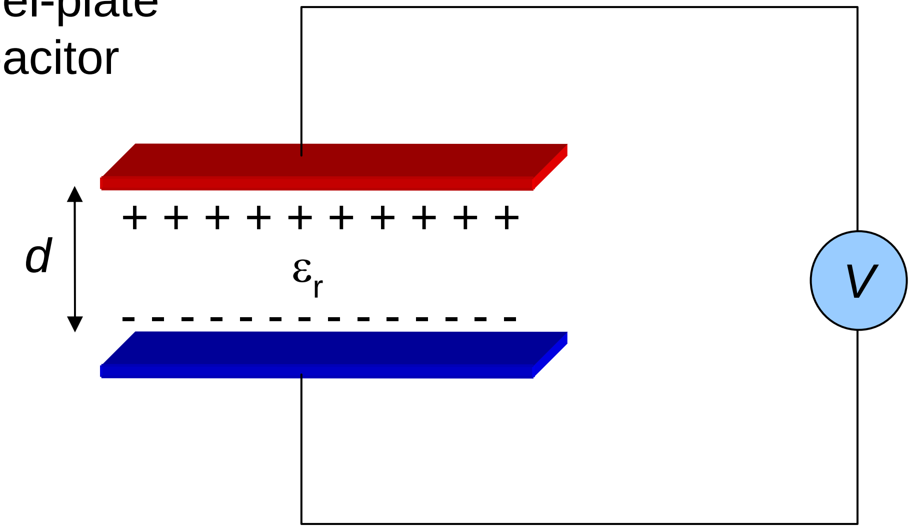
FET - symbol





Concept of Capacitance

parallel-plate capacitor

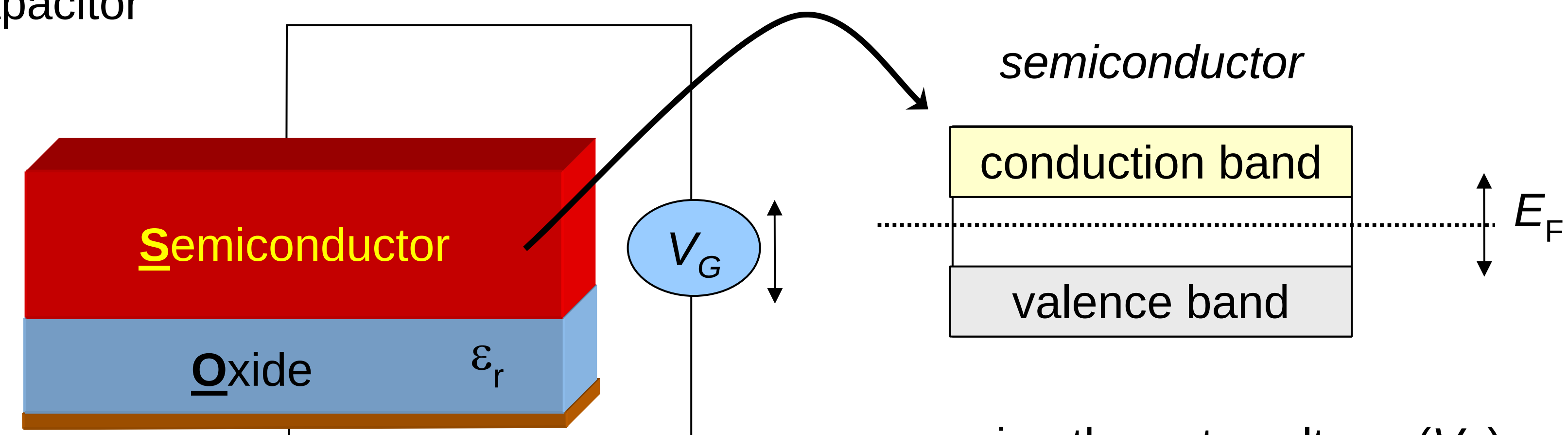


$$\Delta Q = C\,\Delta V$$

$$C = \varepsilon_0 \varepsilon_r A / d$$

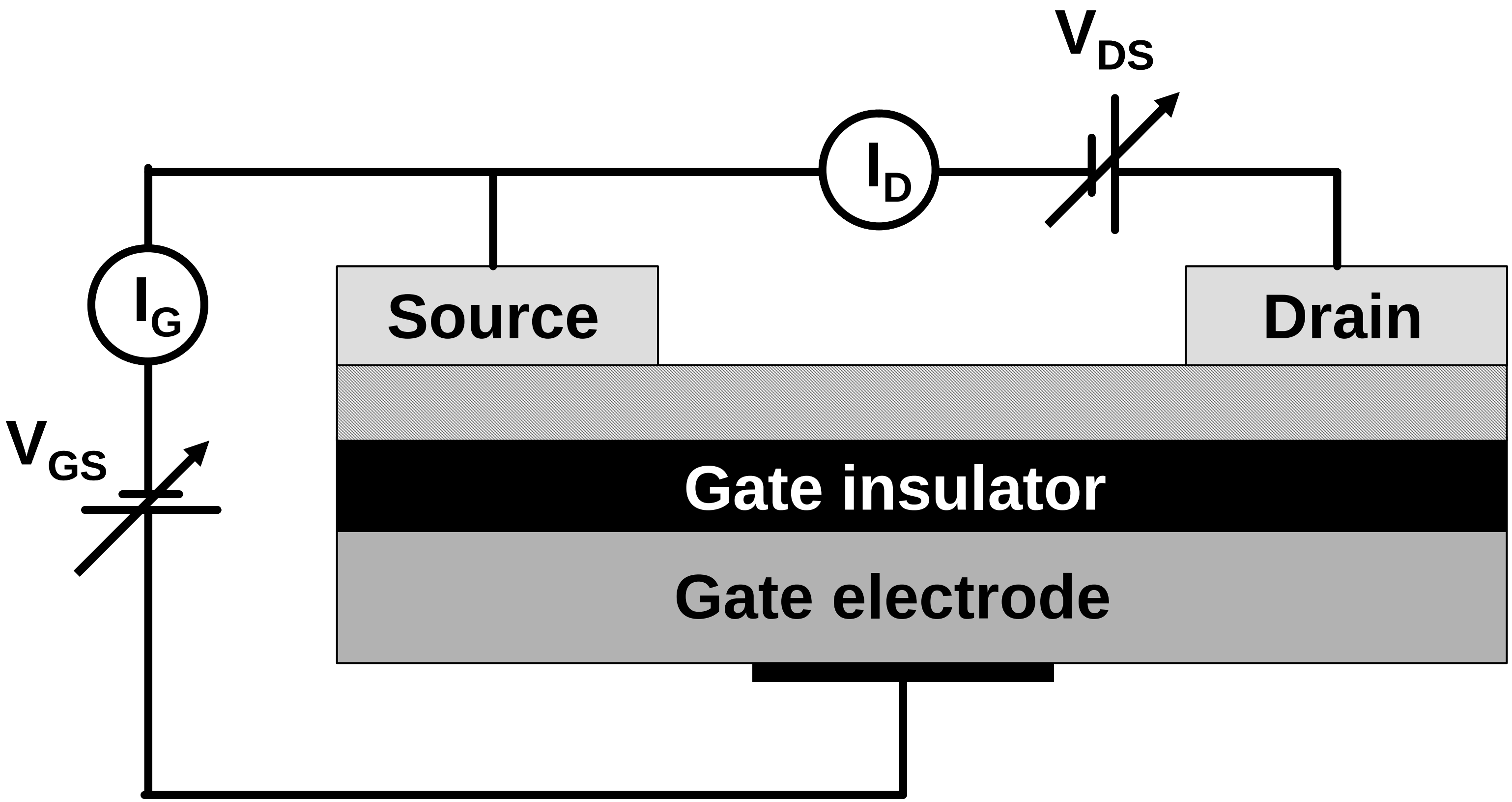
A – cross-sectional area of the plates
Q – Charge
ε – dielectric constant

MOS capacitor

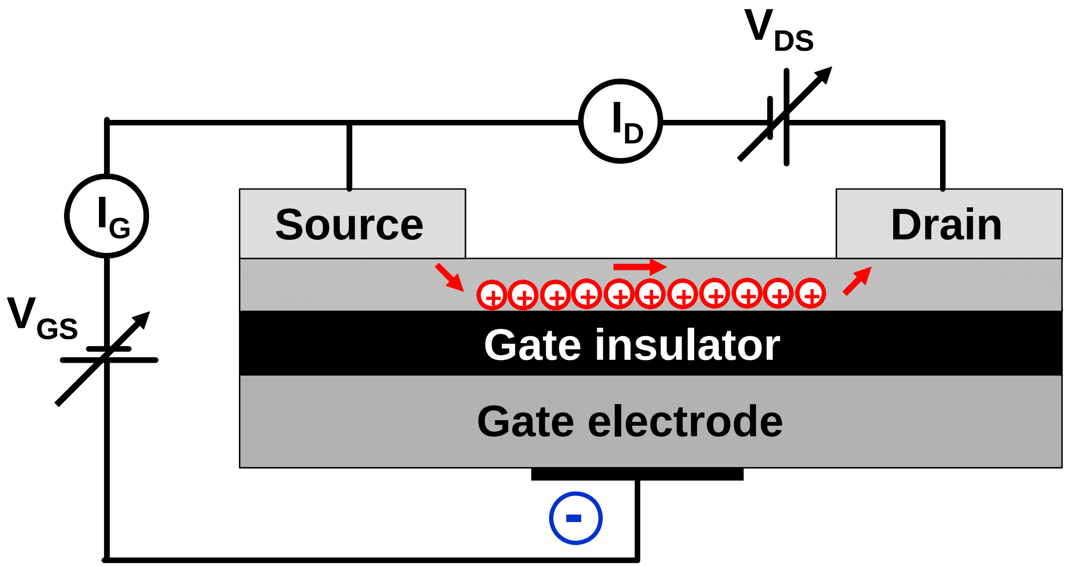


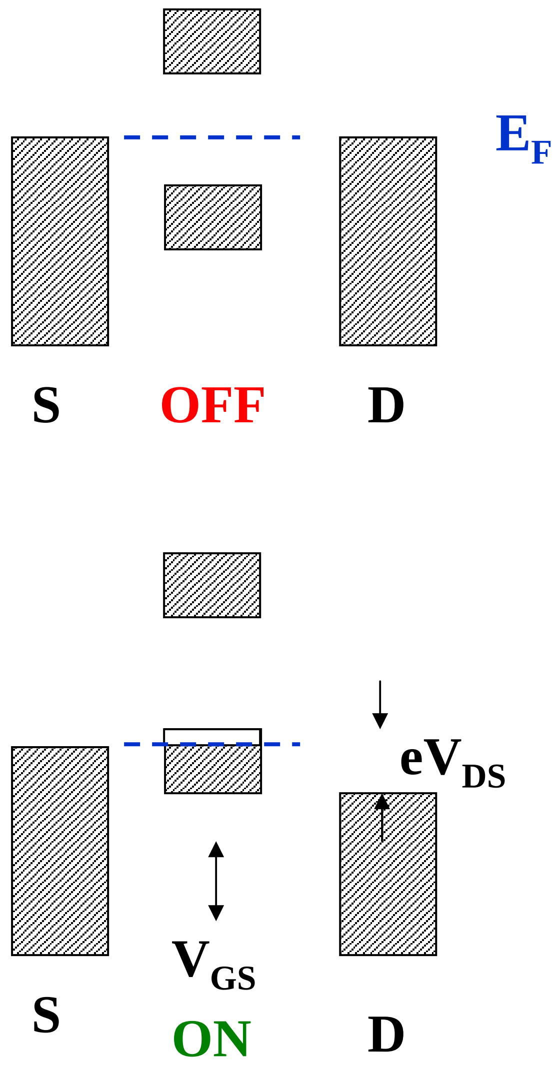
varying the gate voltage (V_G) leads to shift in Fermi level (E_F)

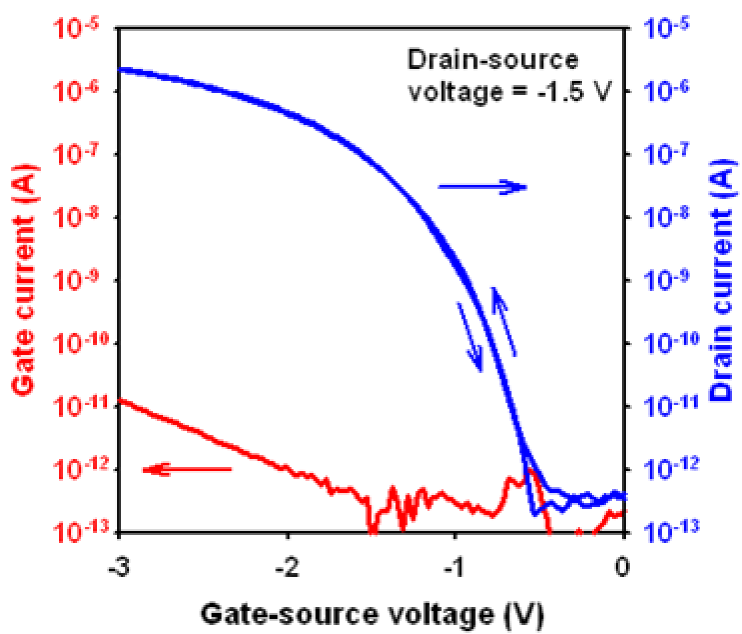
How does a modern field-effect transistor work ?



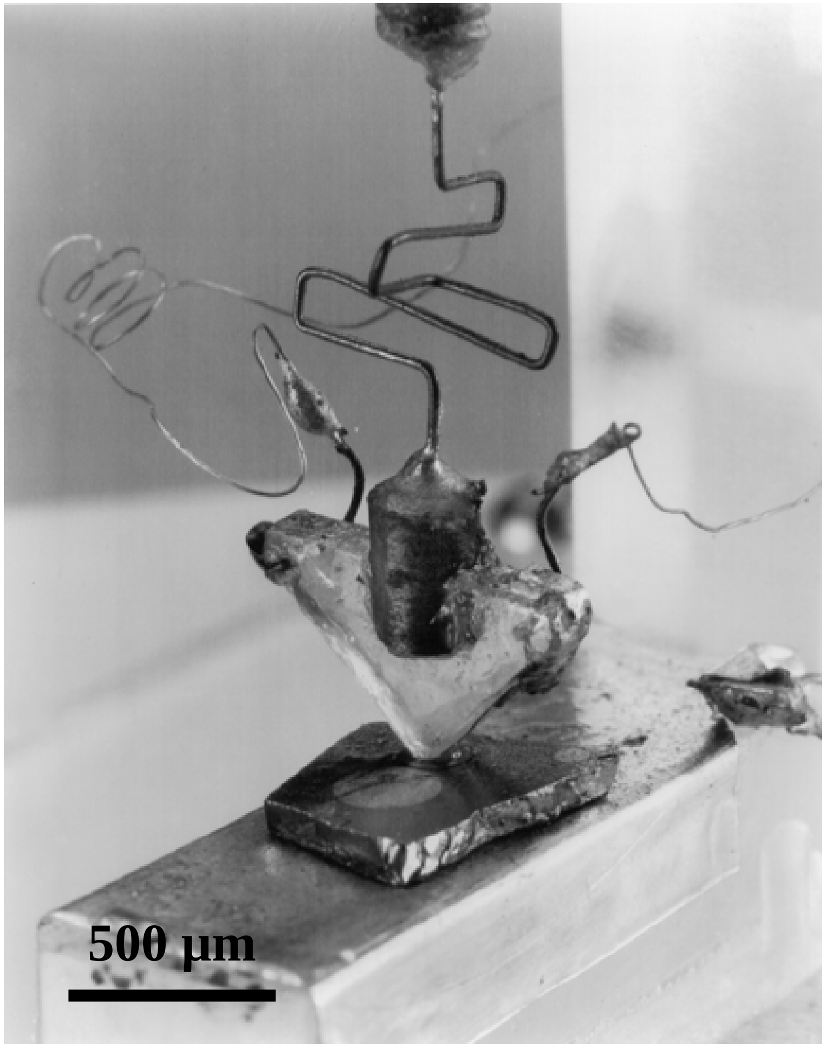
How does a modern field-effect transistor work ?



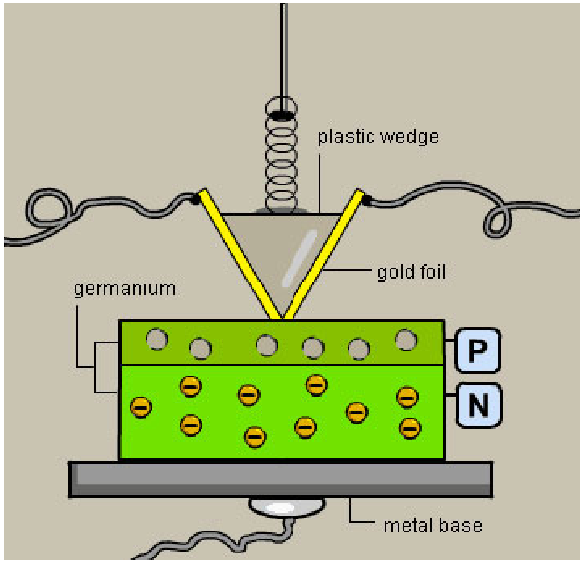


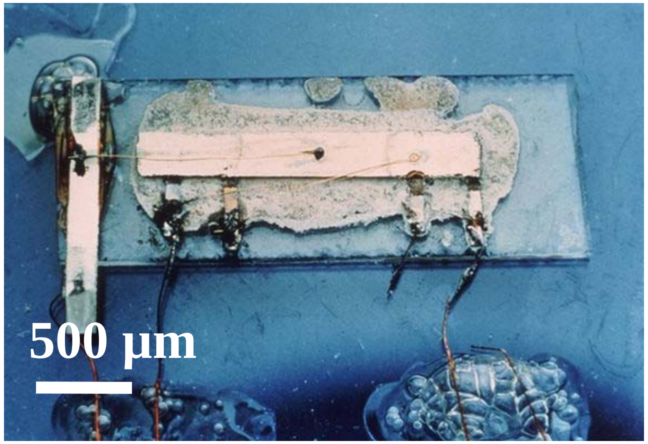


The beginning….



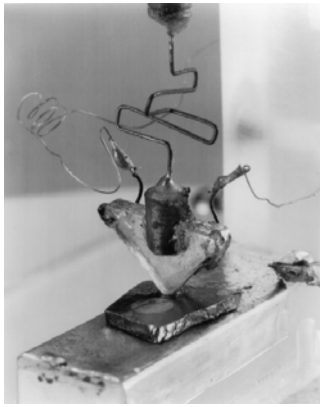
W.B. Shockley, J. Bardeen and W. H. Brattain, Bell Labs 1947

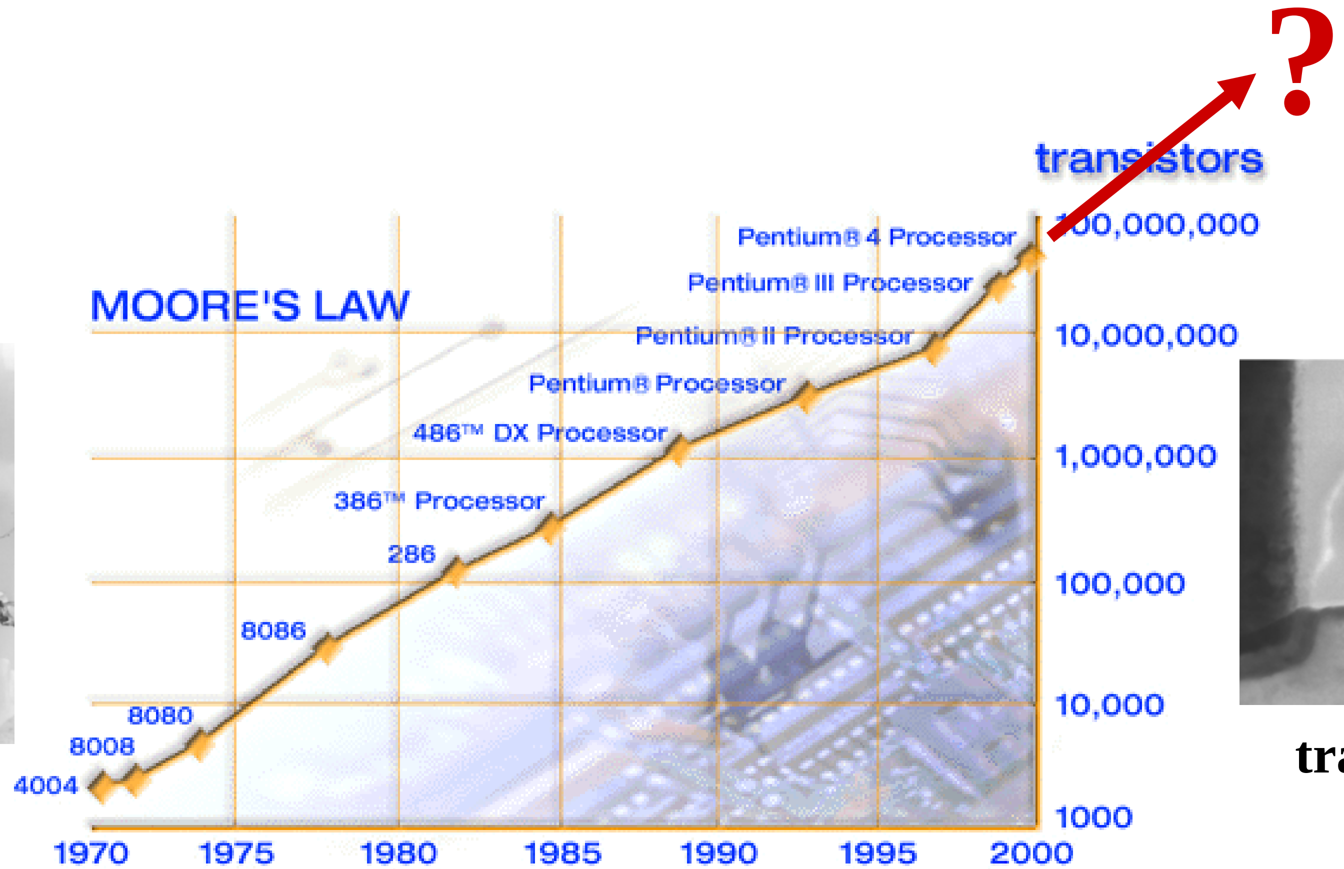


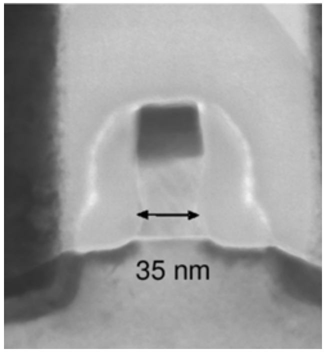


J. Kilby The first working integrated circuit

The incredible shrinking of the transistor


transistor
1947

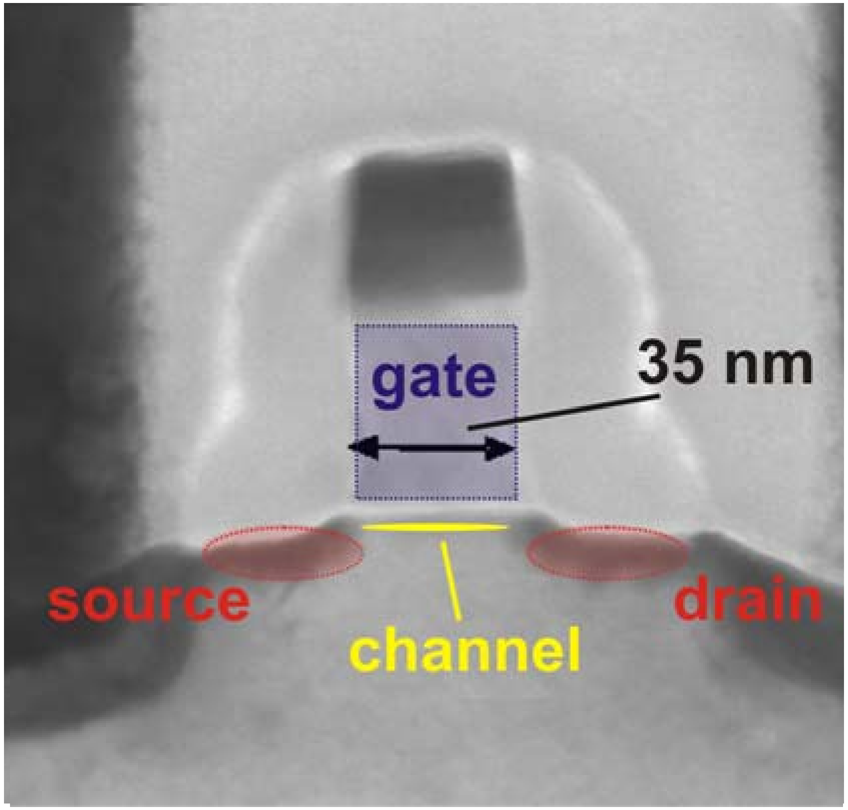




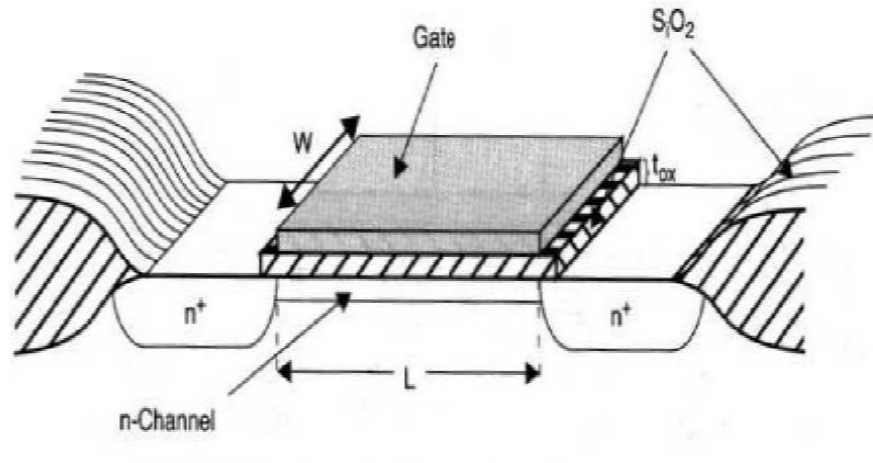
transistor
2005

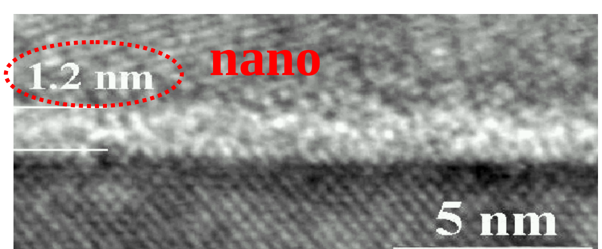
→ **Shrinking of parts of the transistor to atomic dimensions**

The incredible shrinking of the transistor

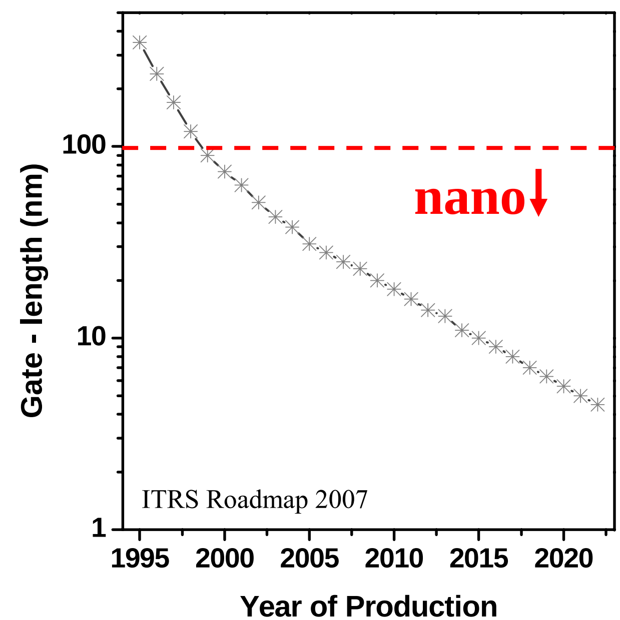


TEM image of a contemporary FET

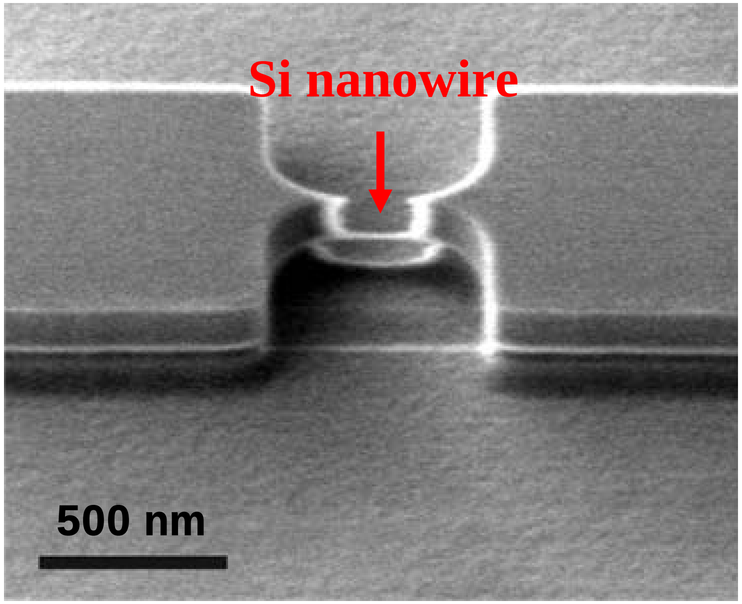


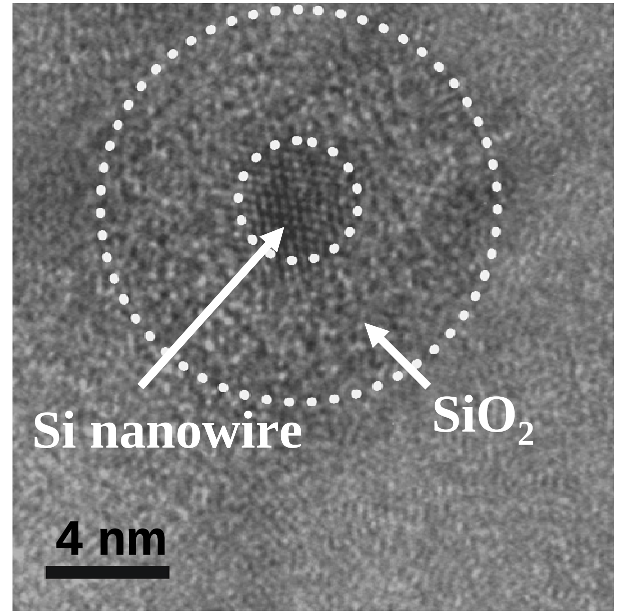


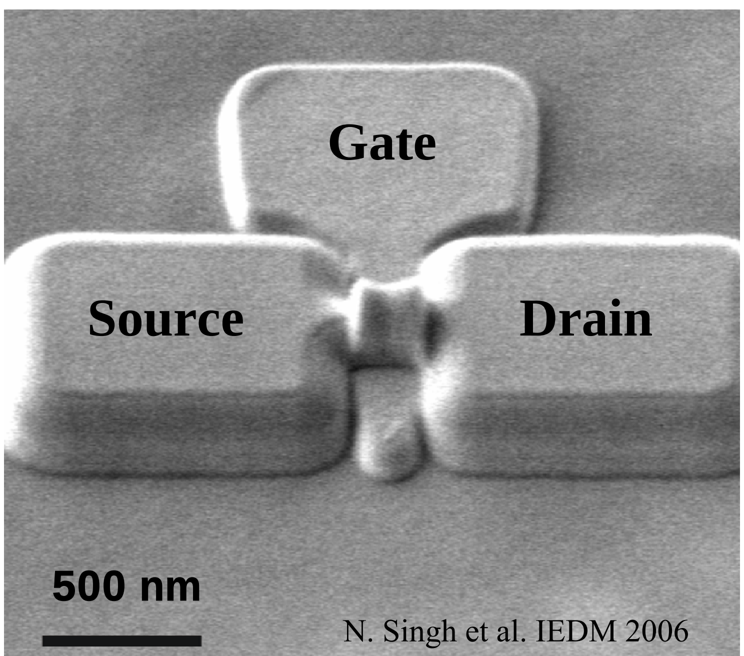
Electronmicroscope image of a SiO_2 **gate insulator**
LETI, CEA, France

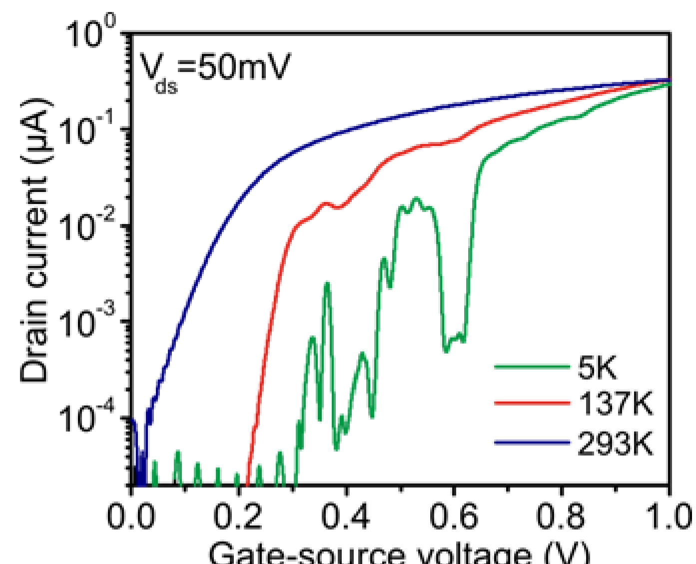


The incredible shrinking of the transistor – **future**

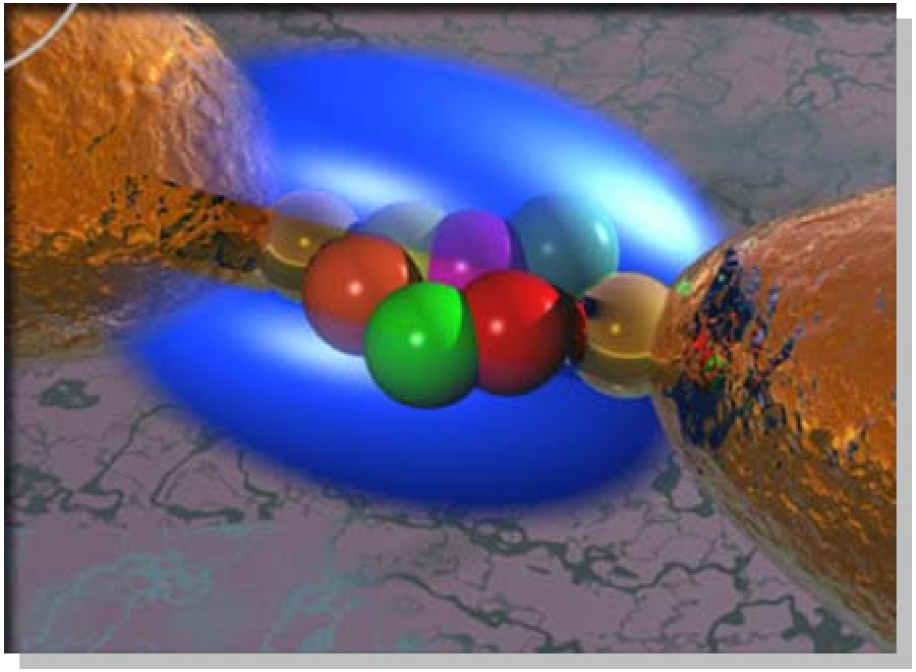


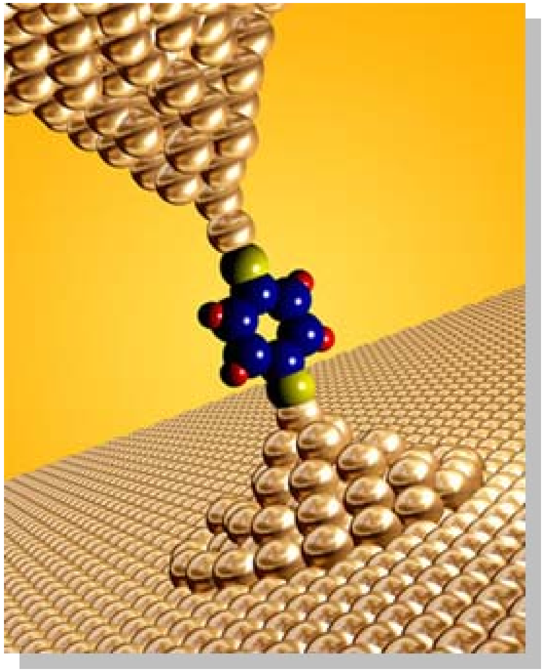






Molecular Electronics





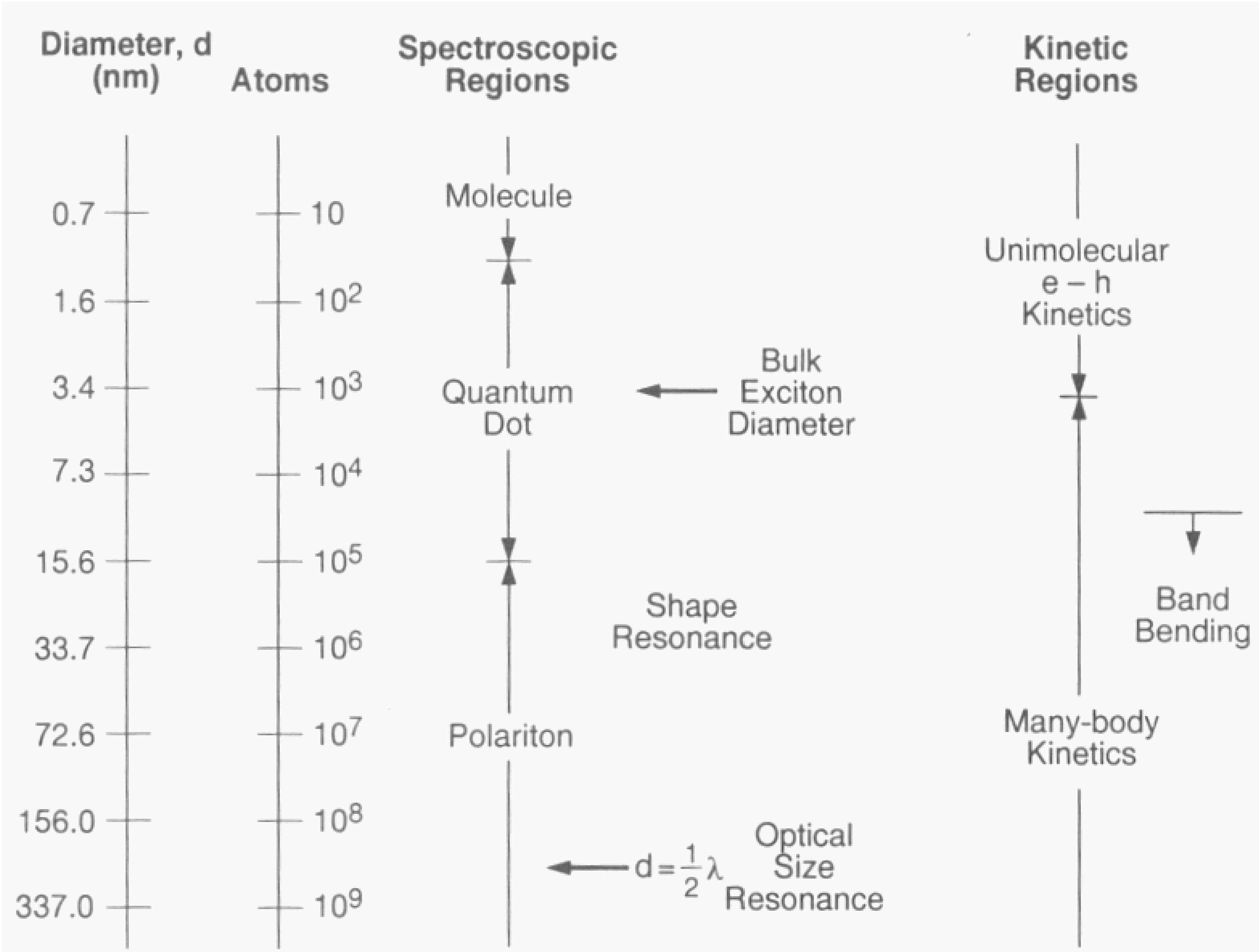
Frontiers in
Nanoscale Science I

Semiconductor Nanostructures

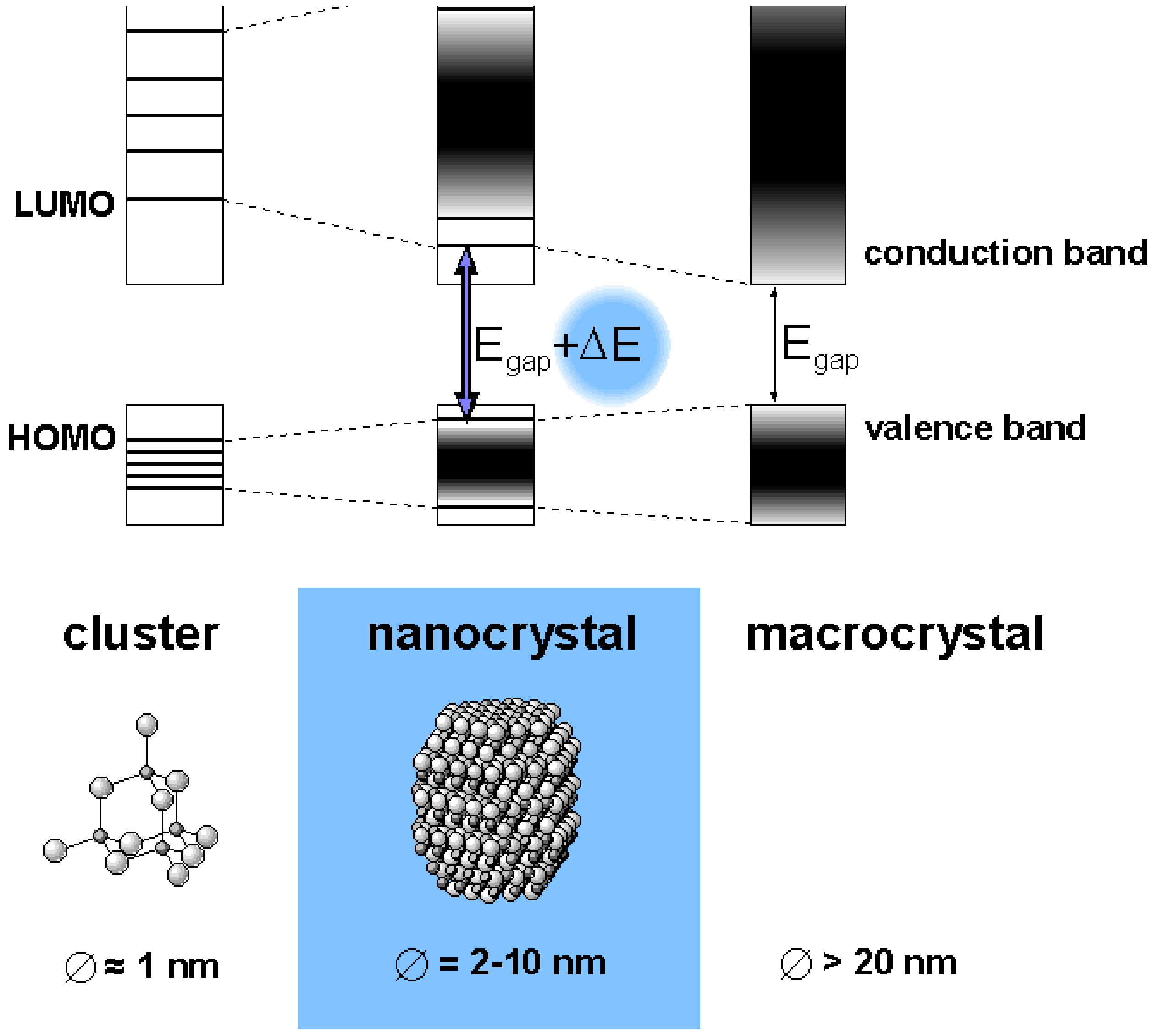
Semiconductor Nanostructures

- basics
- MBE quantum dots
- nanocrystals
- nanowires

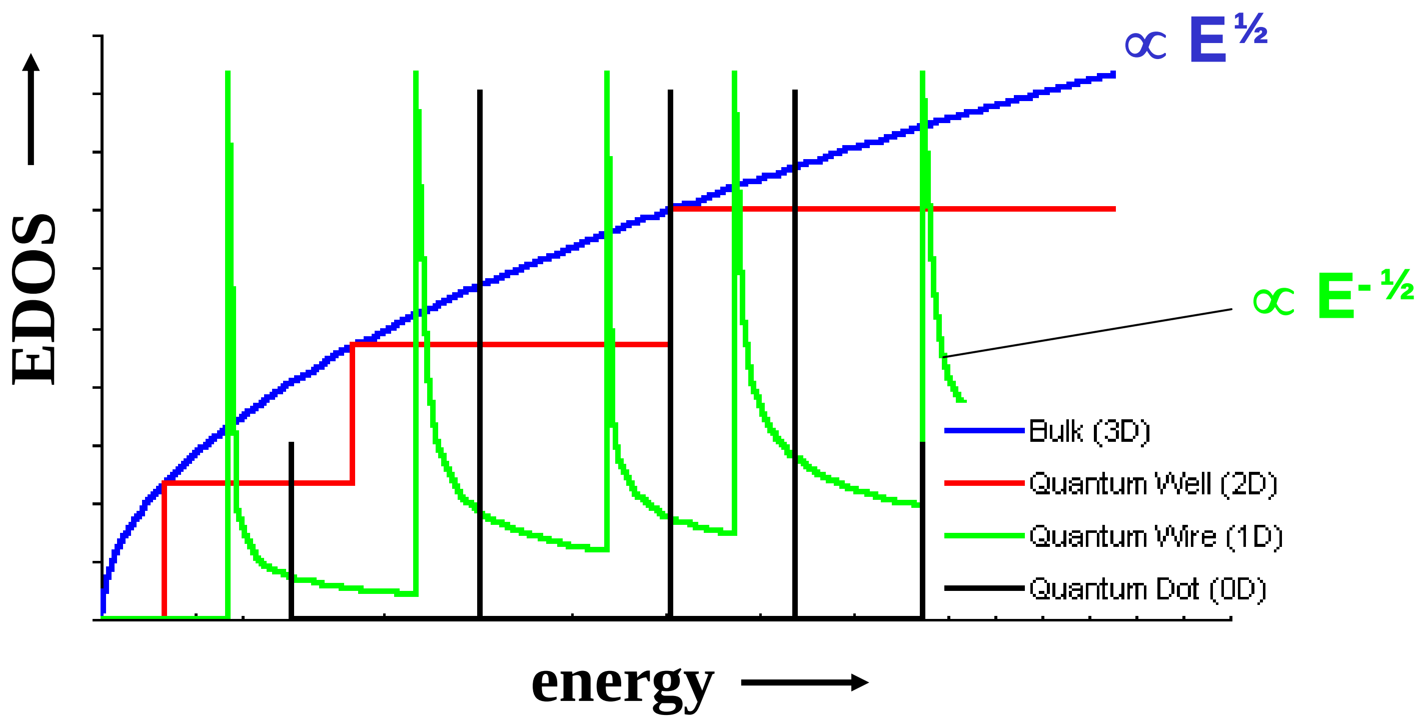
Size regimes



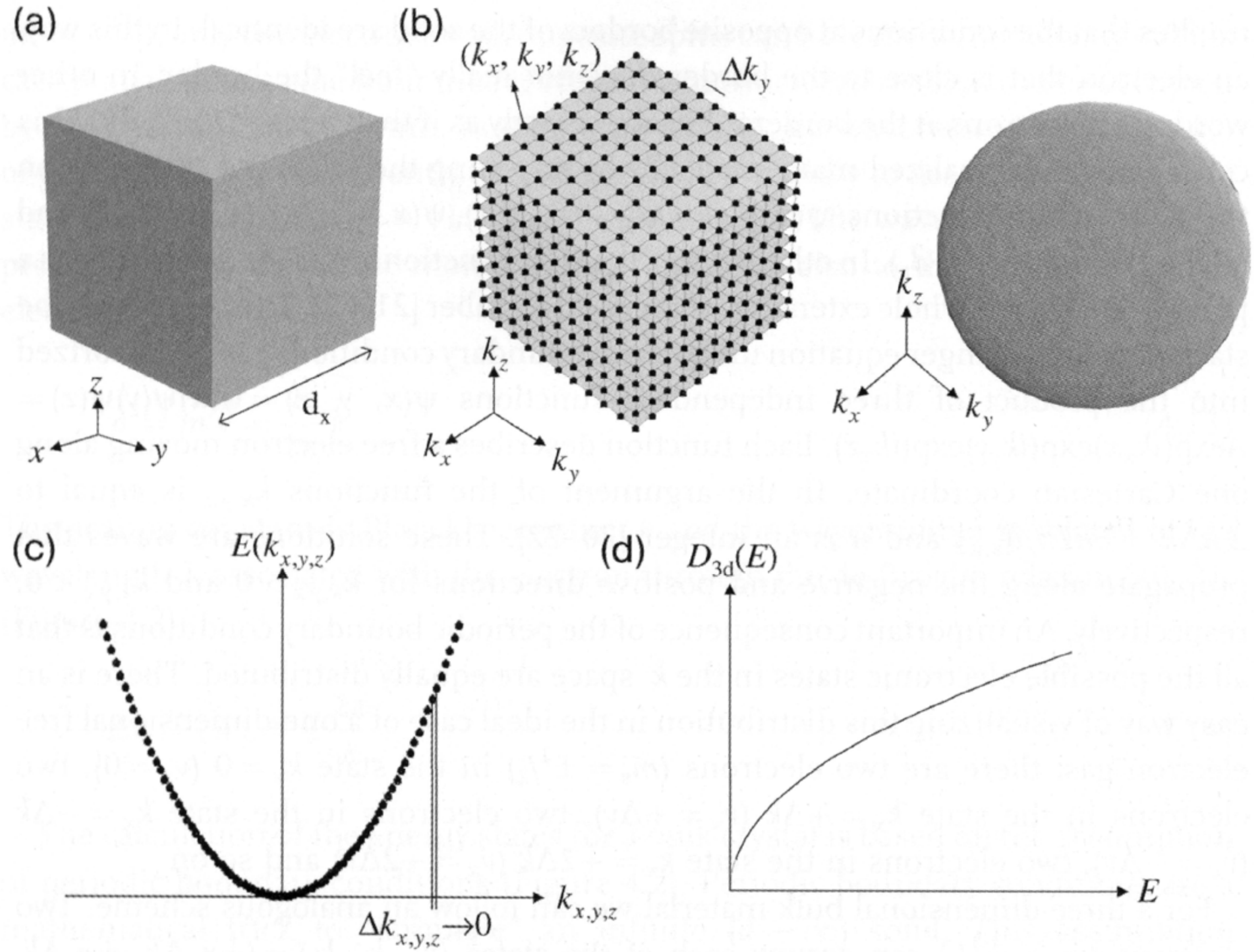
From solid state to molecules



Electronic density of states (EDOS)



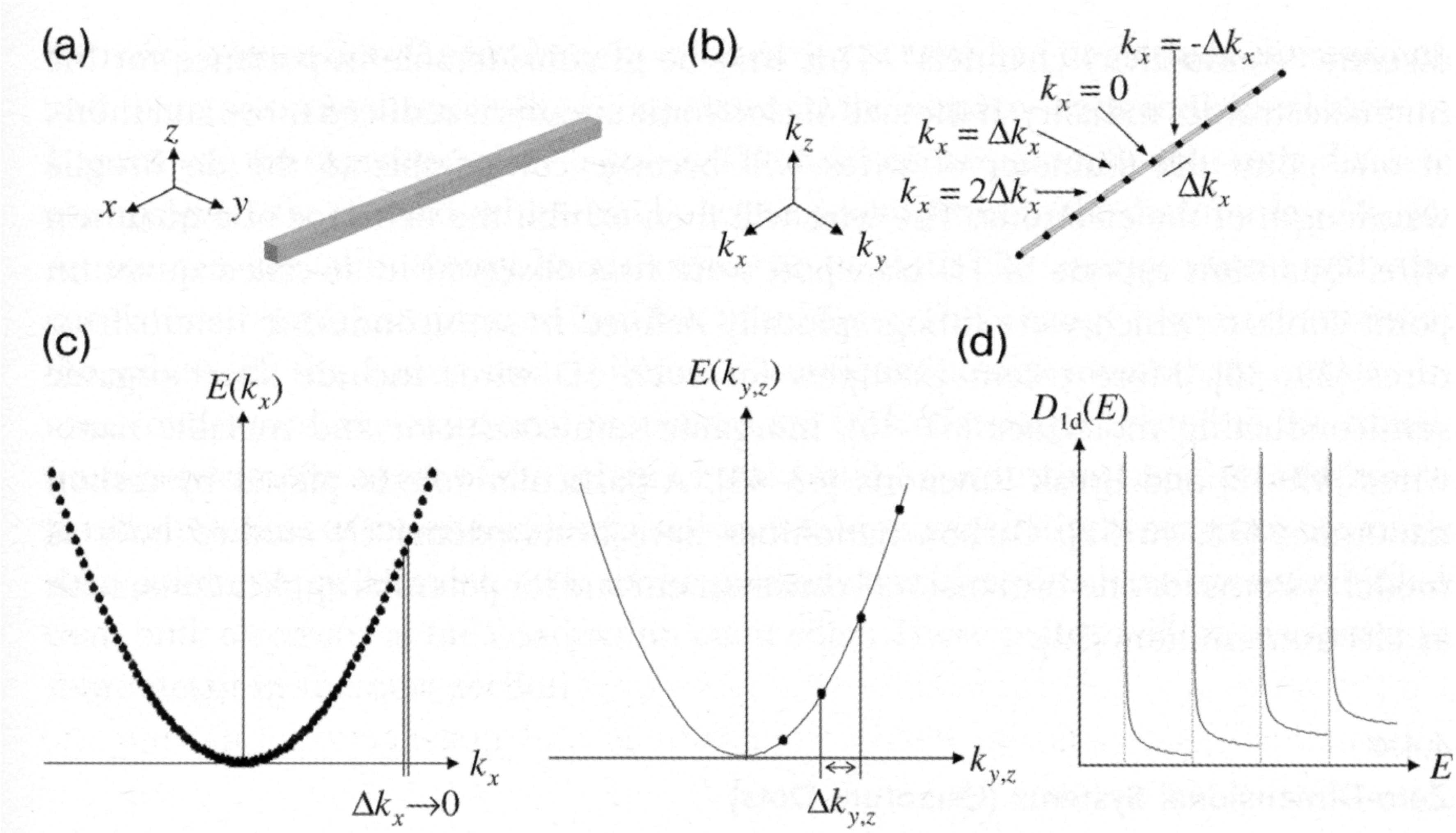
3D systems (bulk material)



$$D_{3D}(k) = \frac{\mathrm{d}N(k)}{\mathrm{d}k} \propto k^2$$

$$D_{3D}(E) = \frac{\mathrm{d}N(E)}{\mathrm{d}E} = \frac{\mathrm{d}N(k)}{\mathrm{d}k}\frac{\mathrm{d}k}{\mathrm{d}E} \propto E \cdot \frac{1}{\sqrt{E}} \propto \sqrt{E}$$

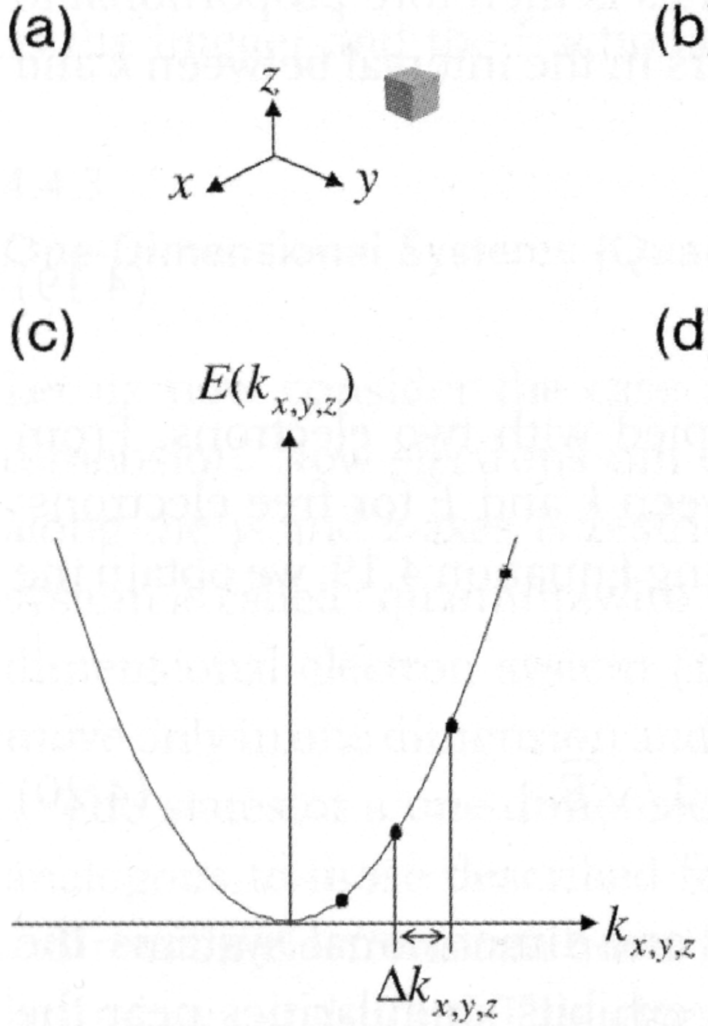
1D systems (nanowires)



$$D_{1D}(k) = \frac{\mathrm{d}N(k)}{\mathrm{d}k} \propto 1$$

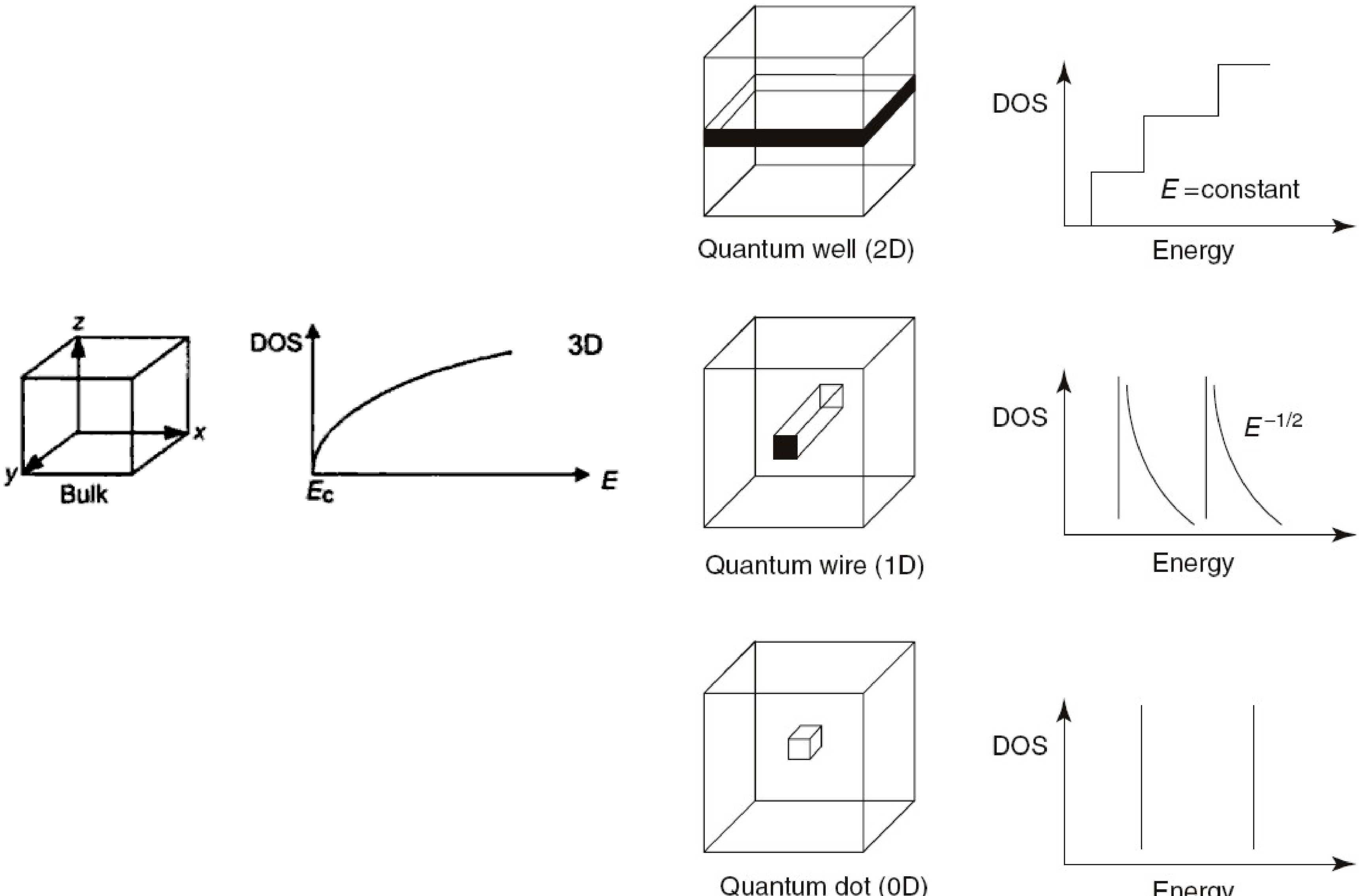
$$D_{1D}(E) = \frac{\mathrm{d}N(E)}{\mathrm{d}E} = \frac{\mathrm{d}N(k)}{\mathrm{d}k}\frac{\mathrm{d}k}{\mathrm{d}E} \propto 1 \cdot \frac{1}{\sqrt{E}} \propto \frac{1}{\sqrt{E}}$$

0D systems (quantum dots)

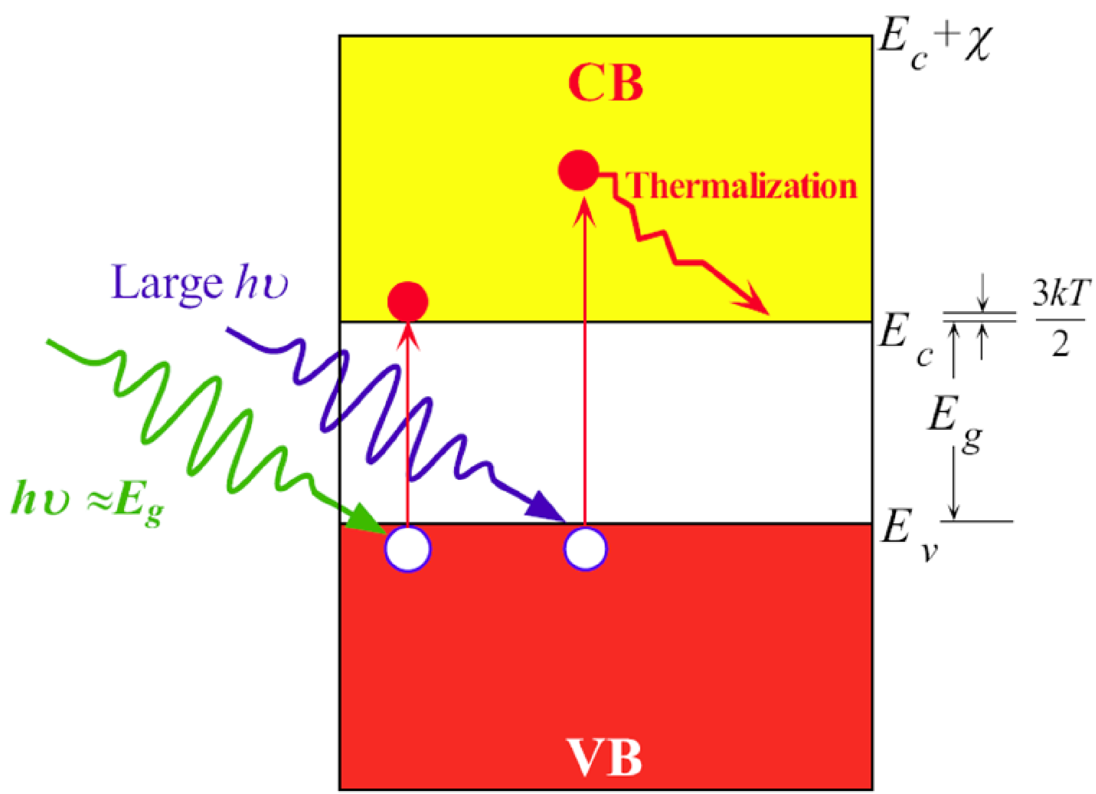


discrete level spectrum

Electronic density of states - Overview

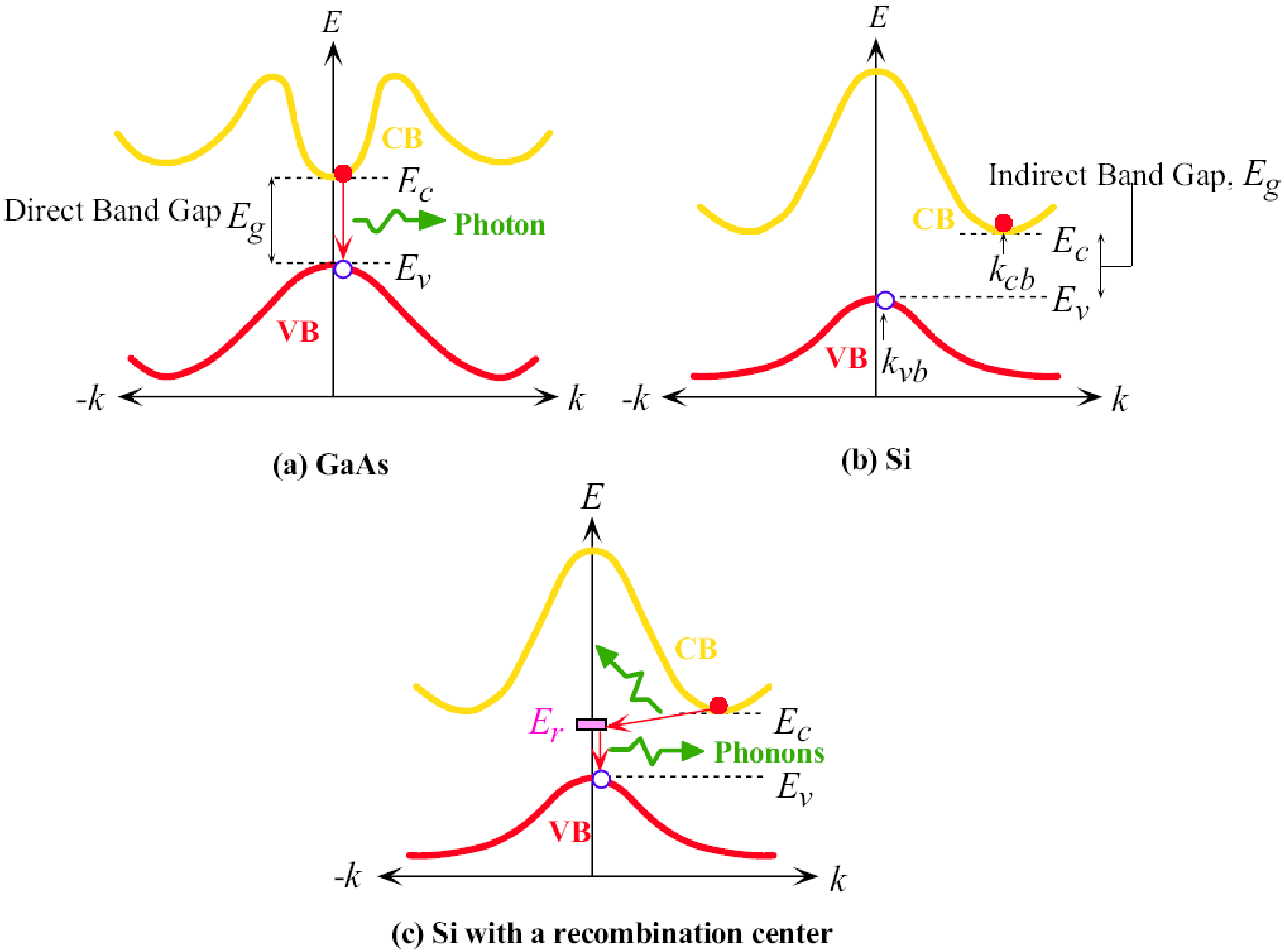


Band-to-band absorption



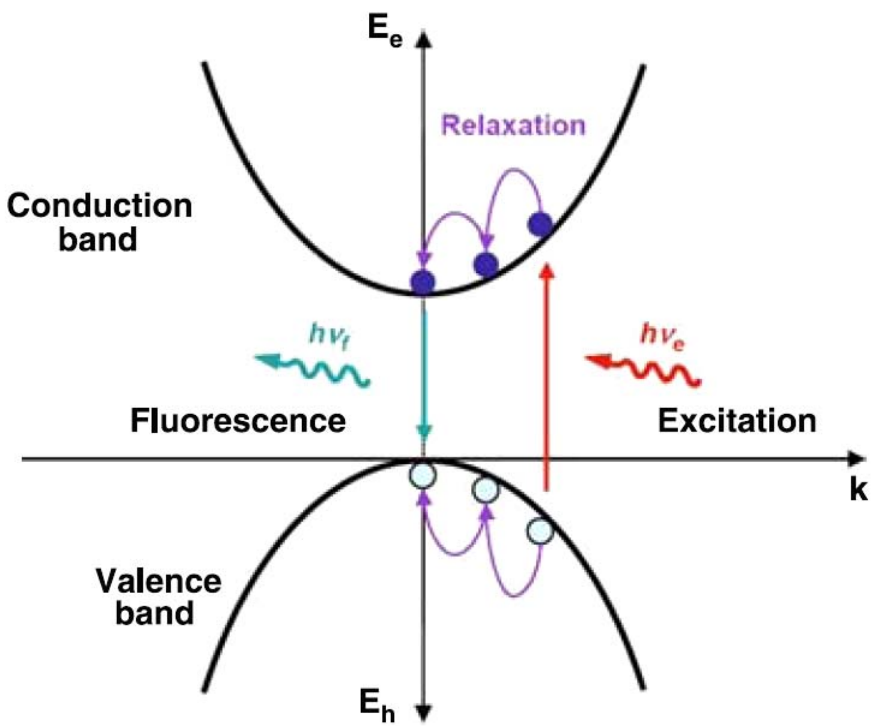
Optical absorption generates electron-hole pairs.
Energetic electrons must lose their excess energy to lattice vibrations until their average energy is $(3/2)kT$ in the CB.

Direct and indirect band gap materials



(a) In GaAs the minimum of the CB is directly above the maximum of the VB. GaAs is therefore a direct band gap semiconductor. (b) In Si, the minimum of the CB is displaced from the maximum of the VB and Si is an indirect band gap semiconductor. (c) Recombination of an electron and a hole in Si involves a recombination center.

Fluorescence



time dependence of excess carrier concentration: $\frac{d\Delta n}{dt} = -\frac{\Delta n}{\tau}$

τ … carrier lifetime

recombination rate $R = -\frac{d\Delta n}{dt} = \frac{\Delta n}{\tau}$

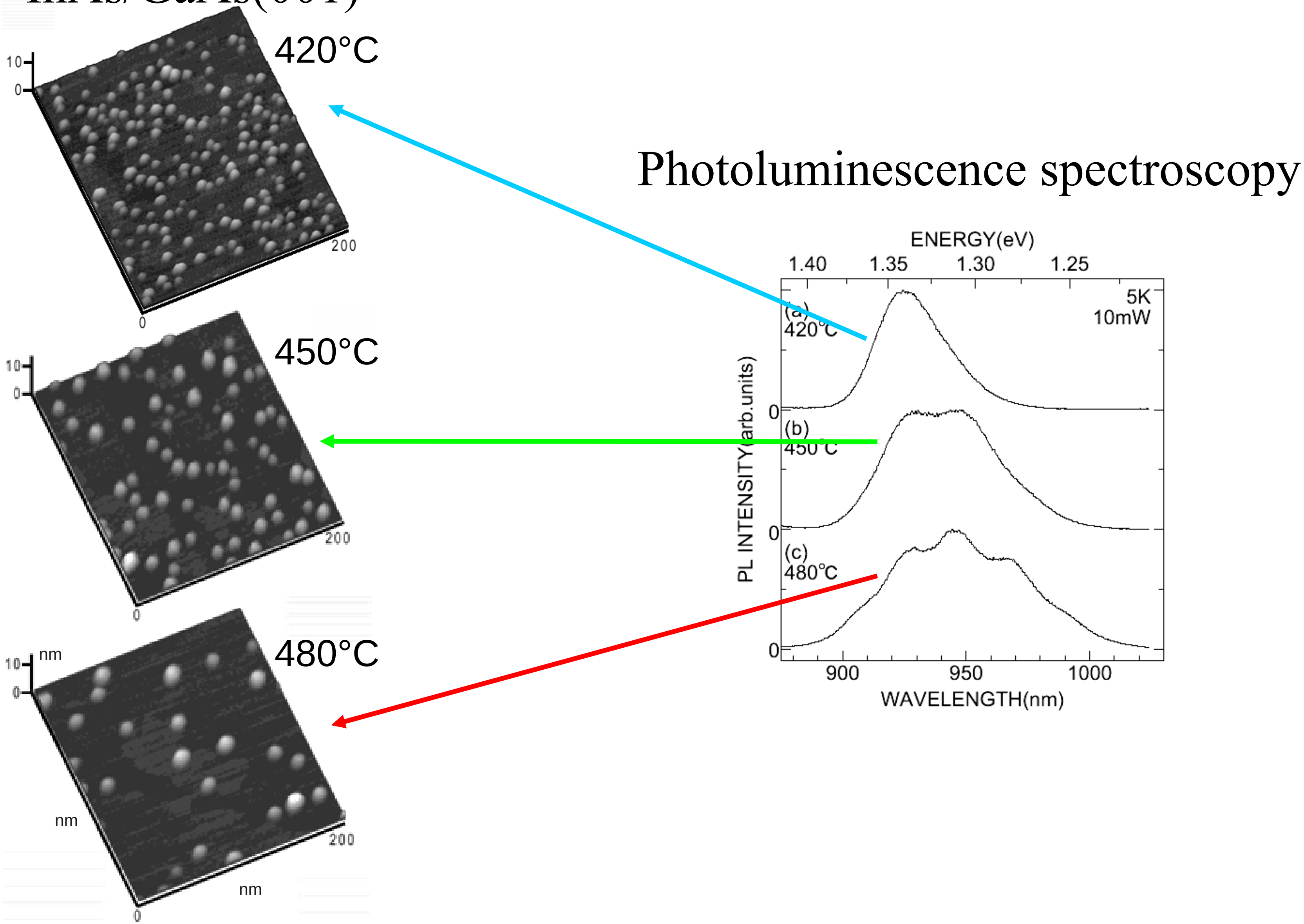
internal quantum efficiency $\eta_i = \frac{R_r}{R_r + R_{nr}}$

'r'… radiative
'nr' ..non-radiative

Quantum dots: Size dependence

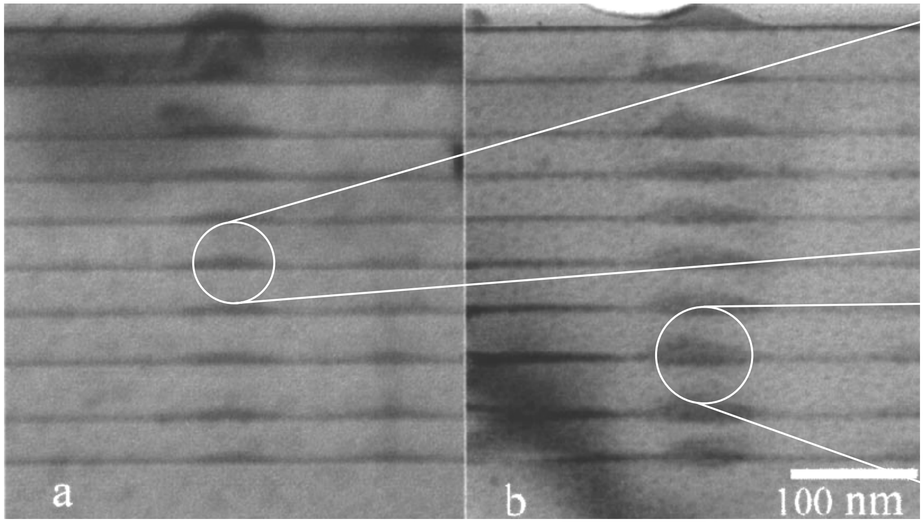
InAs/GaAs(001)

Photoluminescence spectroscopy

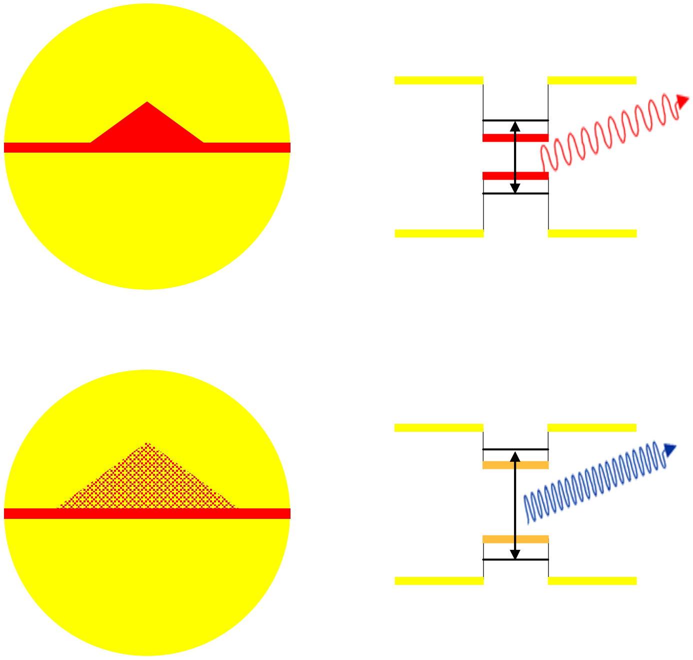


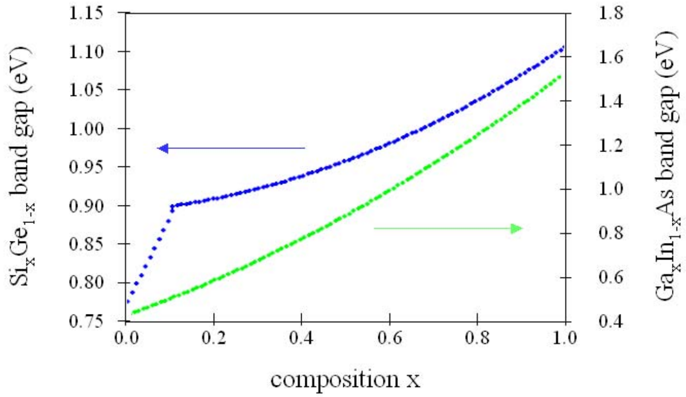
O. Suekane et al., JJAP **41**, 1022 (2002)

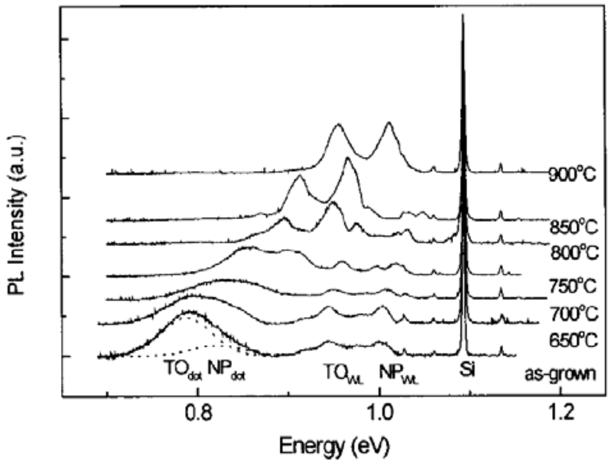
Composition dependence



as grown   annealed @ 900°C





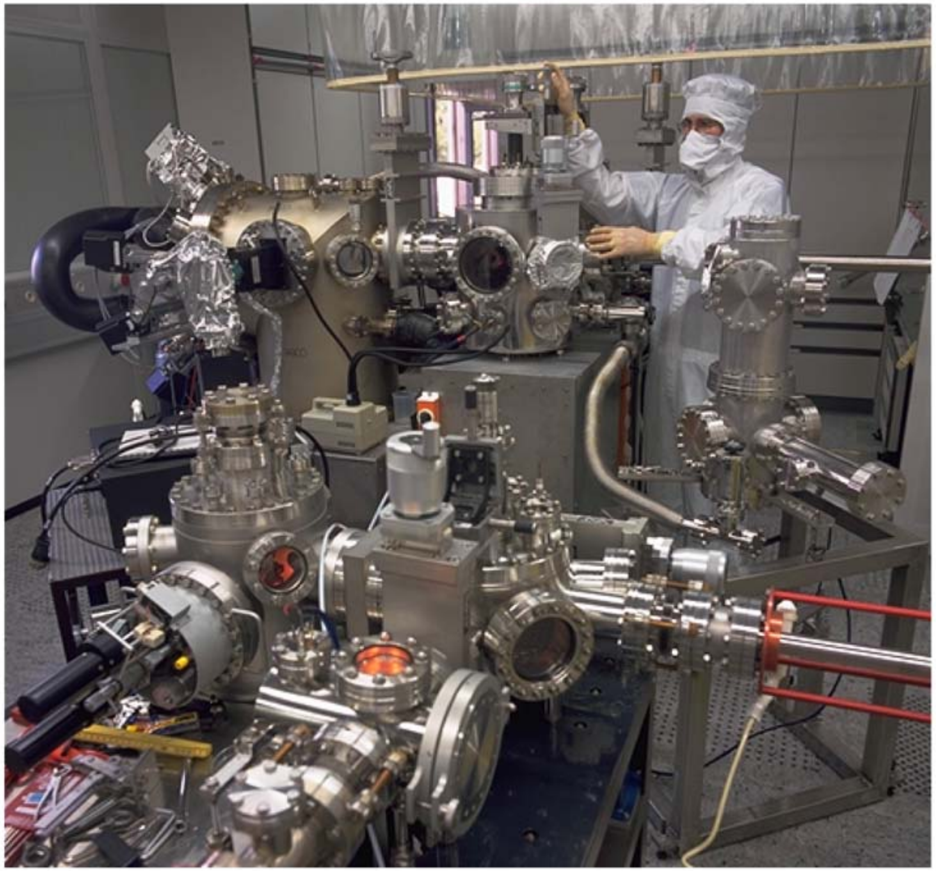


J. Wan et al., JAP **90**, 4290 (2001)

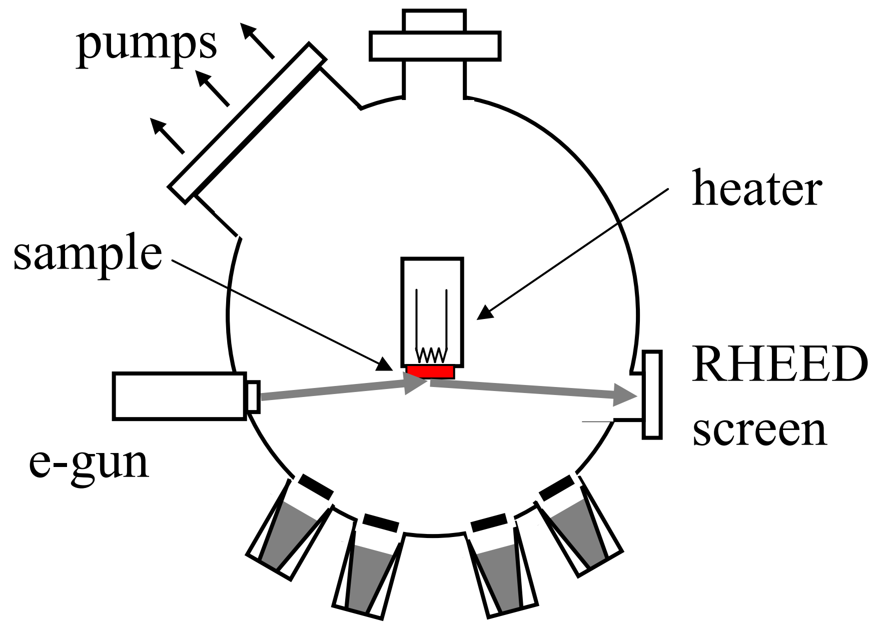
Semiconductor Nanostructures

- basics
- MBE quantum dots
- nanocrystals
- nanowires

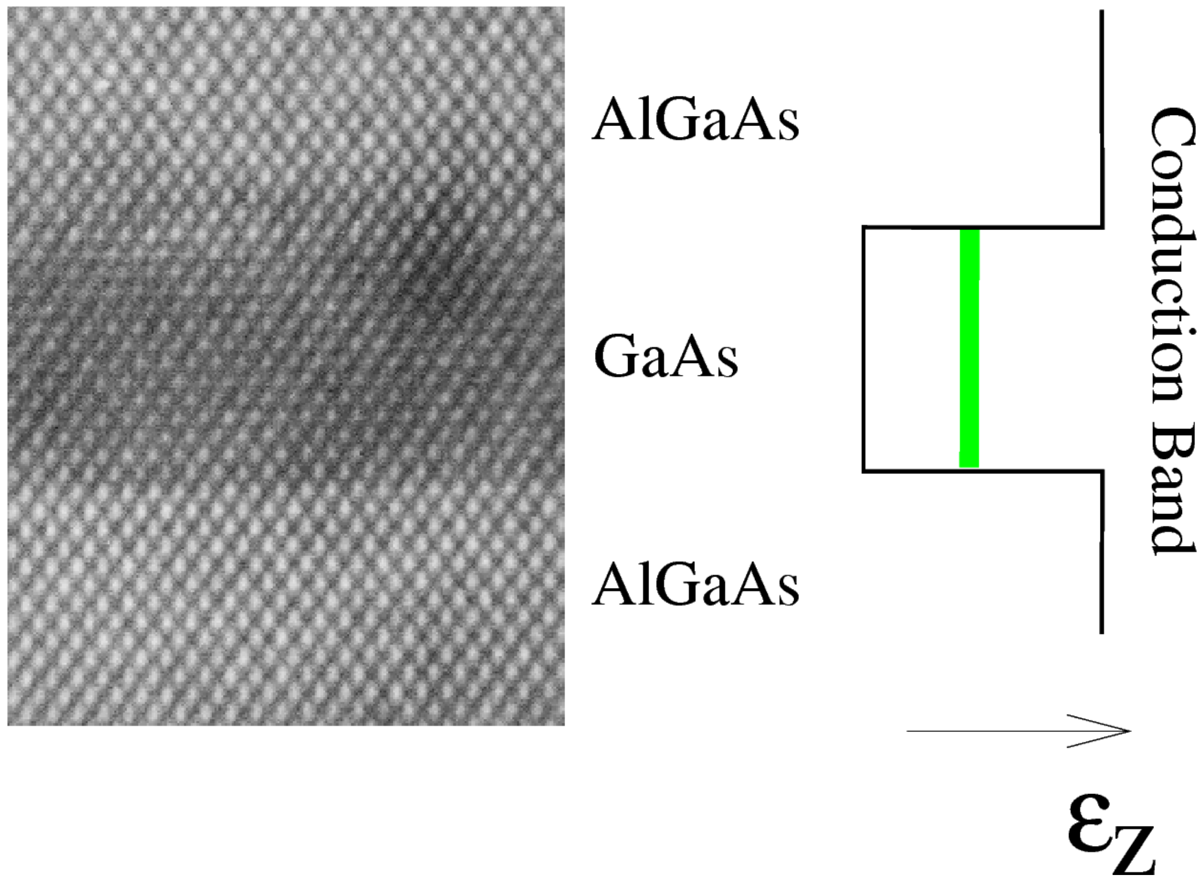
Molecular Beam Epitaxy (MBE) in UHV Chambers



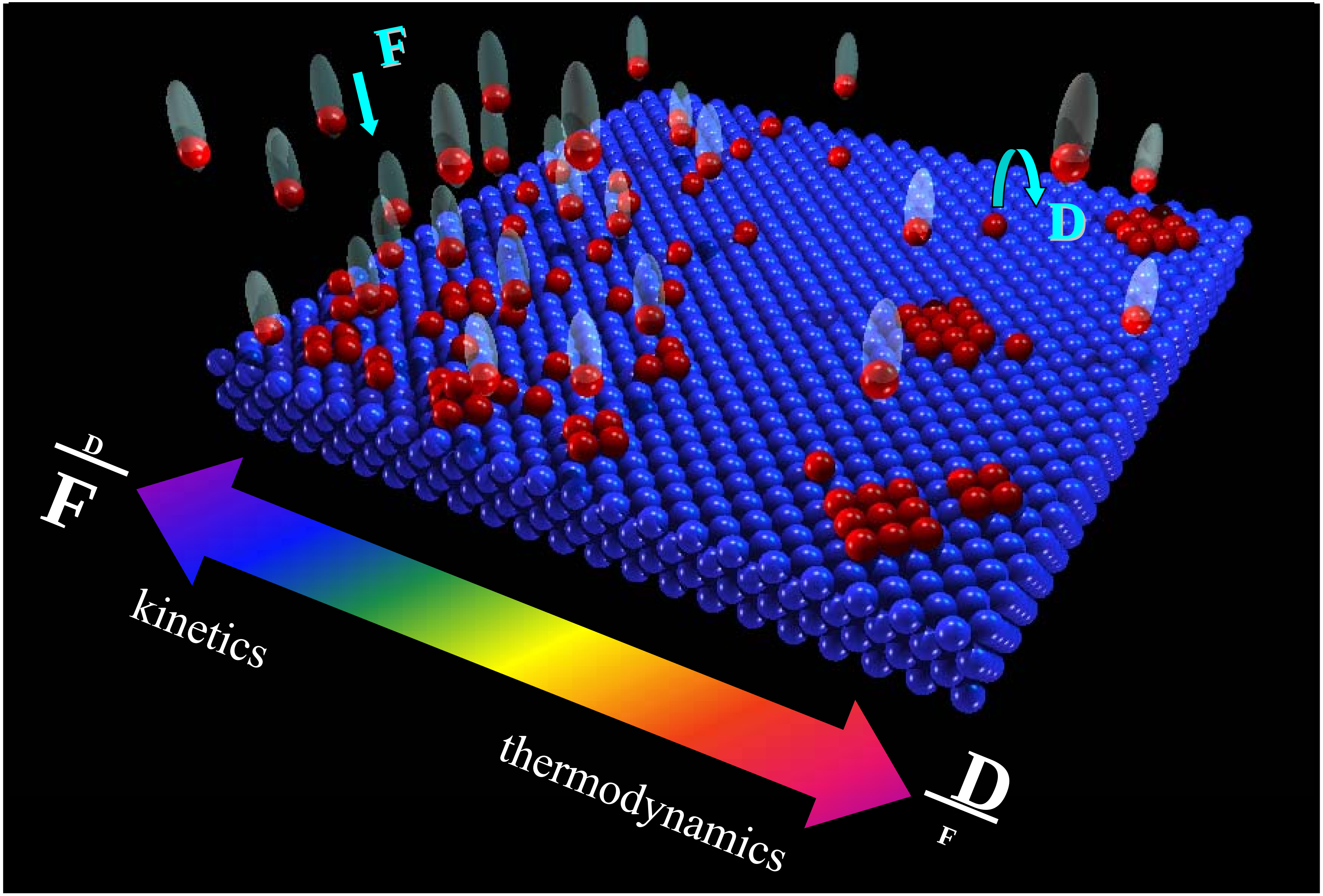
UHV: base pressure < 10^{-10} mbar
growth rate: 0.1 – 1.0 ML/s



Example: 2DES in a Quantum Well



Thin Film Growth



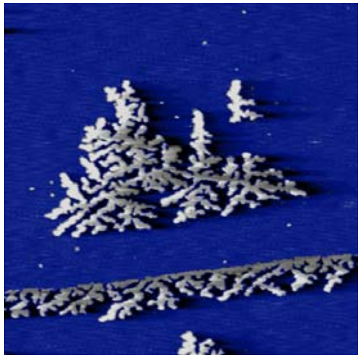
Self-Organized Growth at Surfaces

$\frac{D}{\mathbf{F}}$

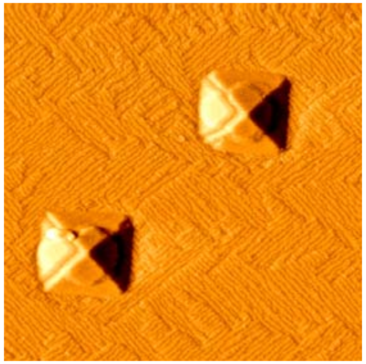
$\frac{\mathbf{D}}{F}$

kinetics

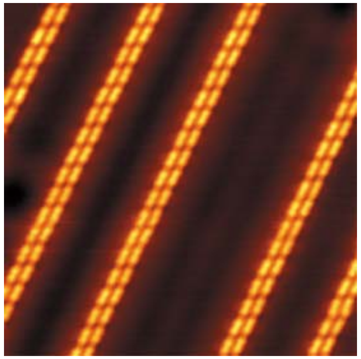
thermodynamics



metal epitaxy

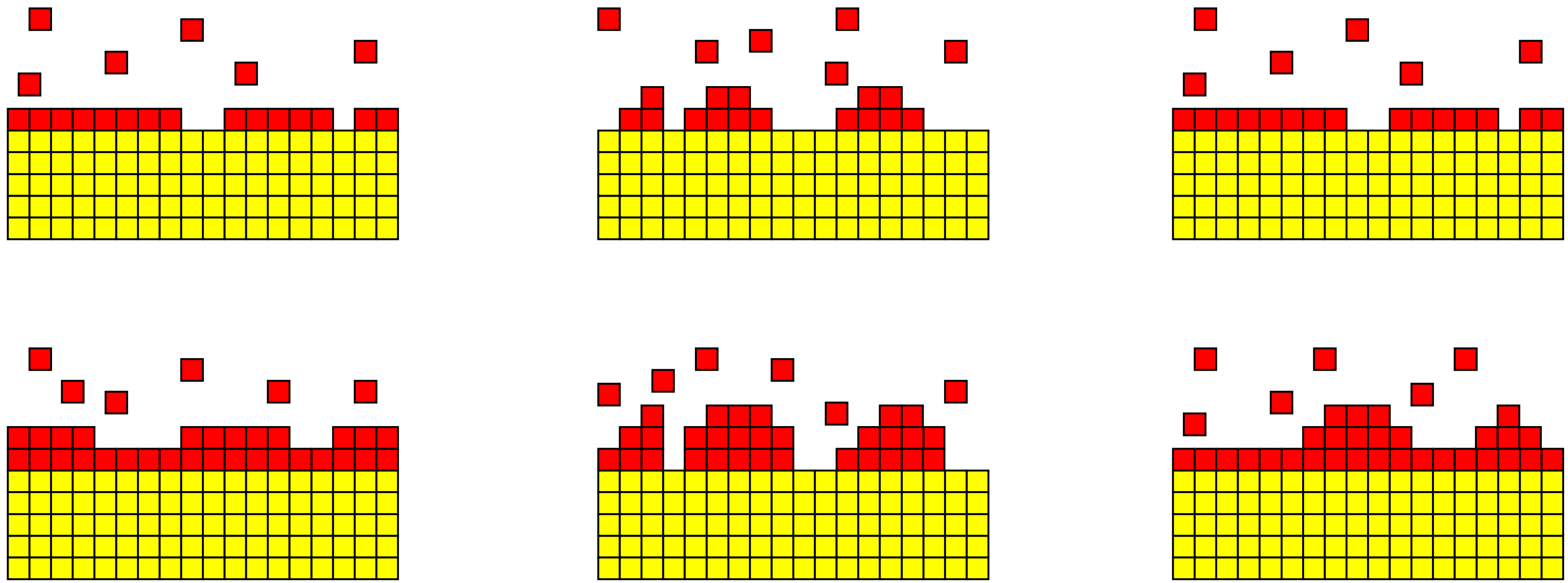


semiconductor
MBE



molecular
self-assembly

Growth modes



layer - by - layer growth
(Frank - van der Merve)

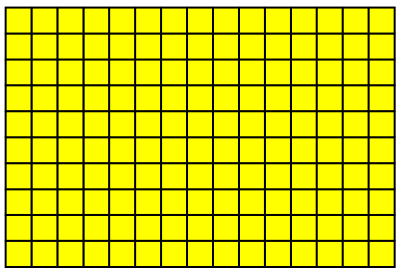
island growth
(Volmer - Weber)

layer - by - layer
+ island growth
(Stranski - Krastanov)

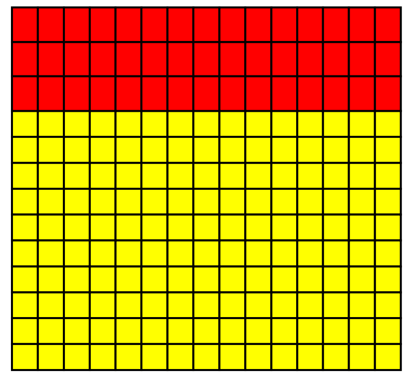
quantum dots

Stranski-Krastanov Growth of Semiconductor QDs

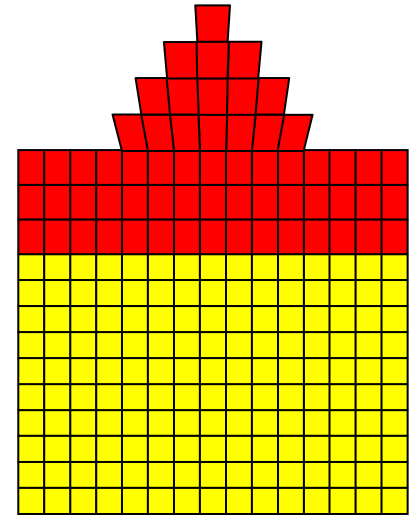
lattice constants: $a_A > a_B$



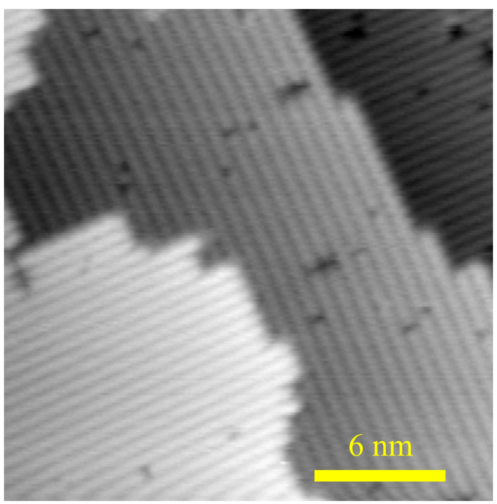
substrate



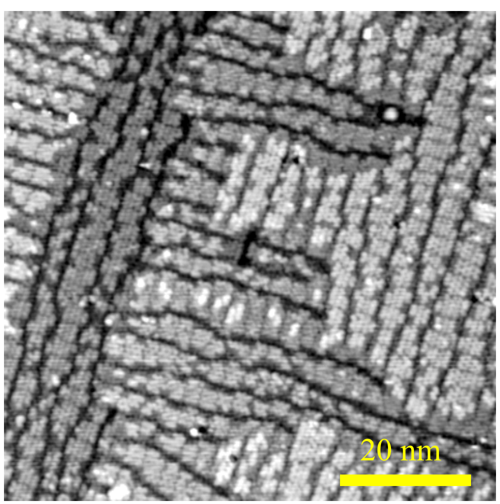
wetting layer



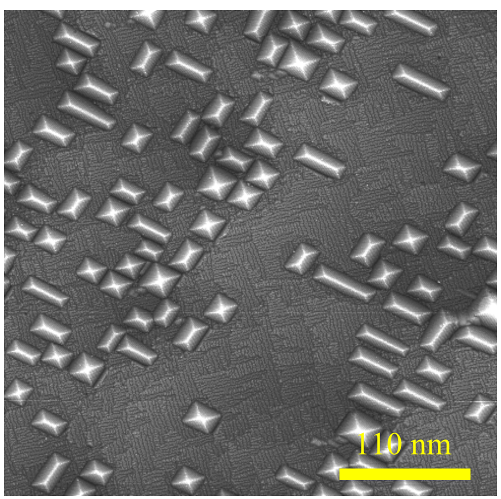
islands



Si(001)

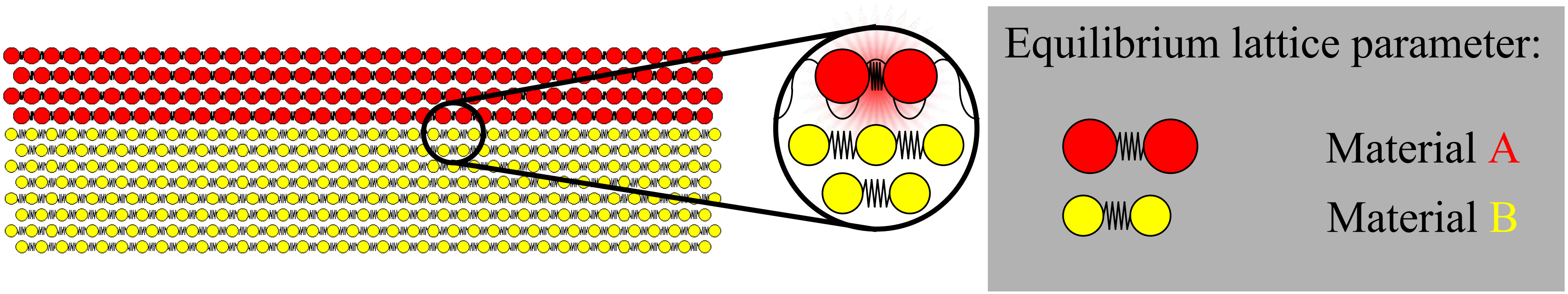


3ML Ge on Si(001)



6ML Ge on Si(001)

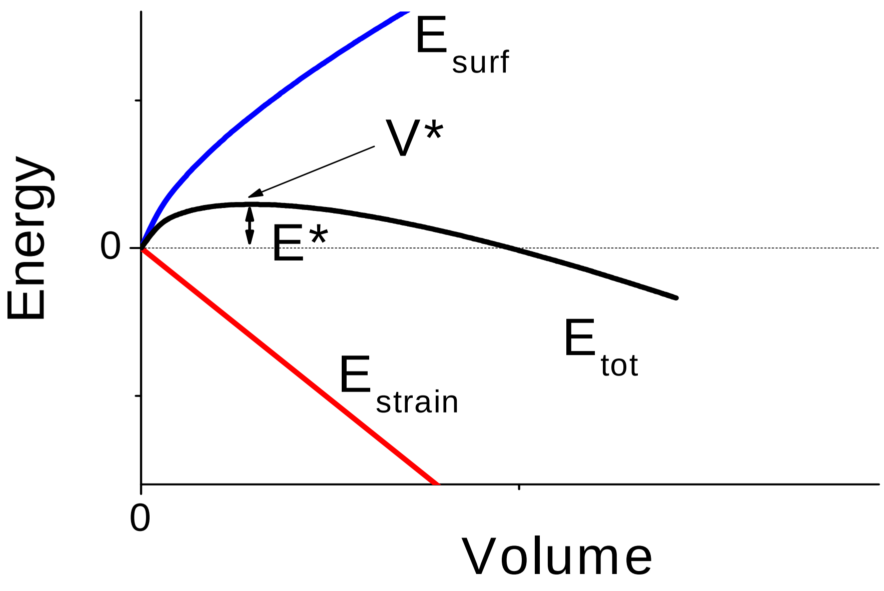
Stranski-Krastanov Growth



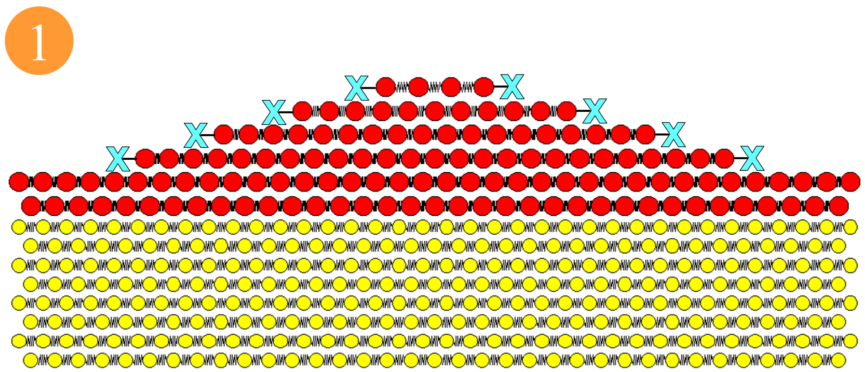
$$E_{tot} = E_{strain} + E_{surf}$$

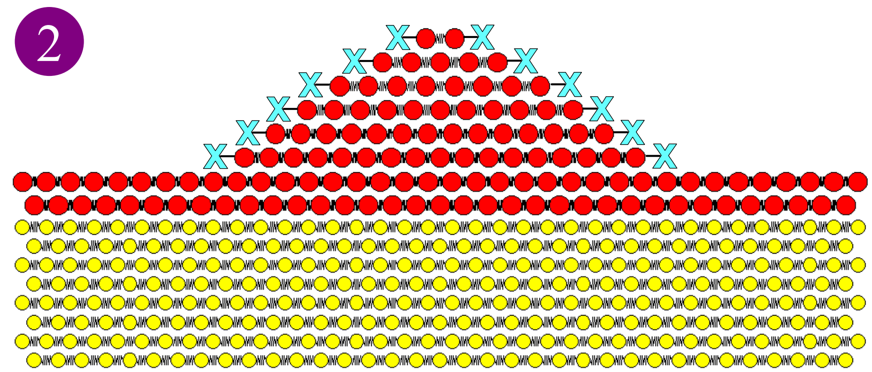
$$E_{strain} = -\alpha V$$

$$E_{surf} = +\beta V^{2/3}$$



Stranski-Krastanov Growth





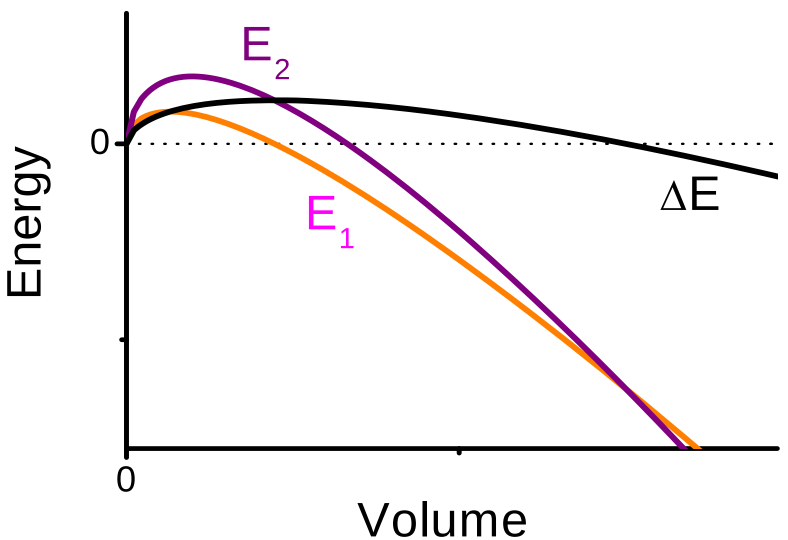
more strain energy
less surface energy

less strain energy
more surface energy

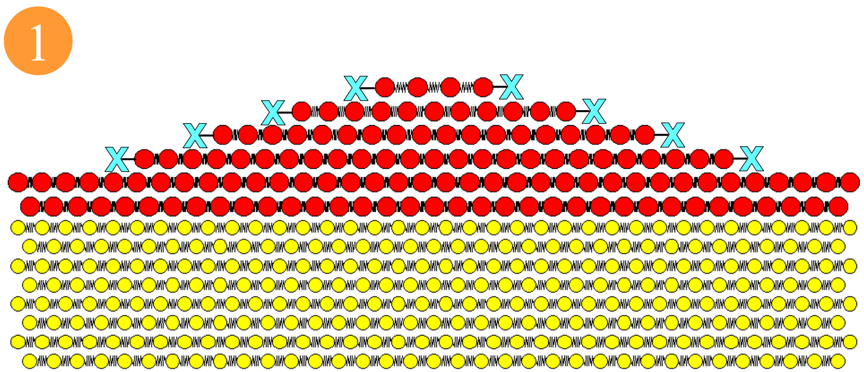
$$E_1 = -\alpha_1 V + \beta_1 V^{2/3} \;;\; E_2 = -\alpha_2 V + \beta_2 V^{2/3}$$

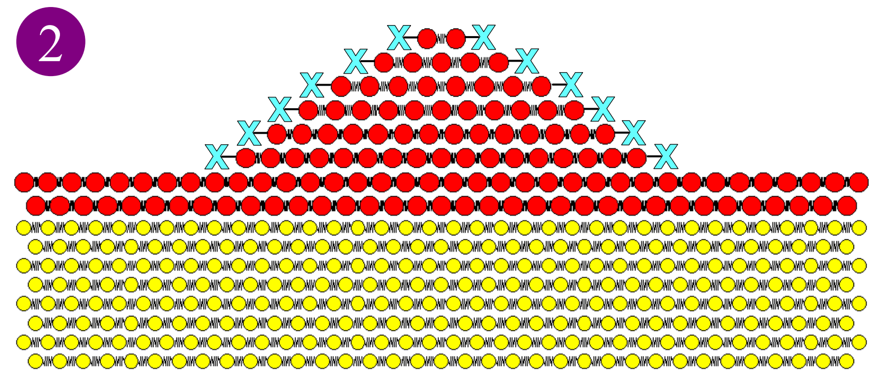
$\alpha_2 > \alpha_1$ $\beta_2 > \beta_1$

$$E_2 - E_1 = -(\alpha_2 - \alpha_1)V + (\beta_2 - \beta_1)V^{2/3}$$



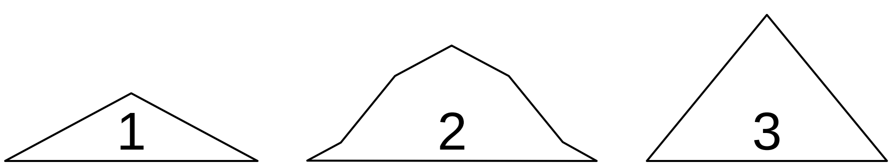
Stranski-Krastanov Growth

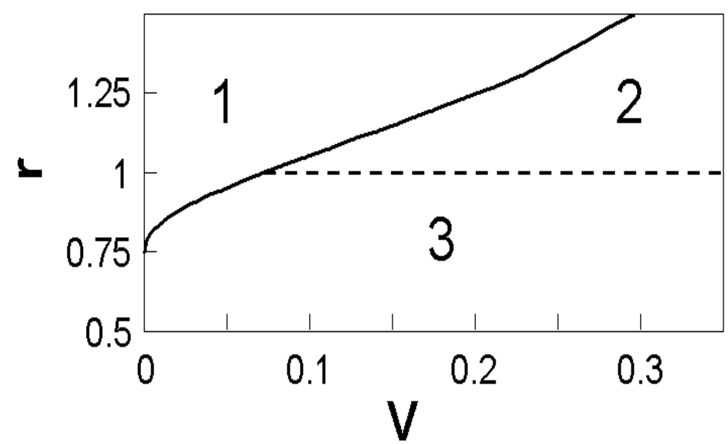




more strain energy
less surface energy

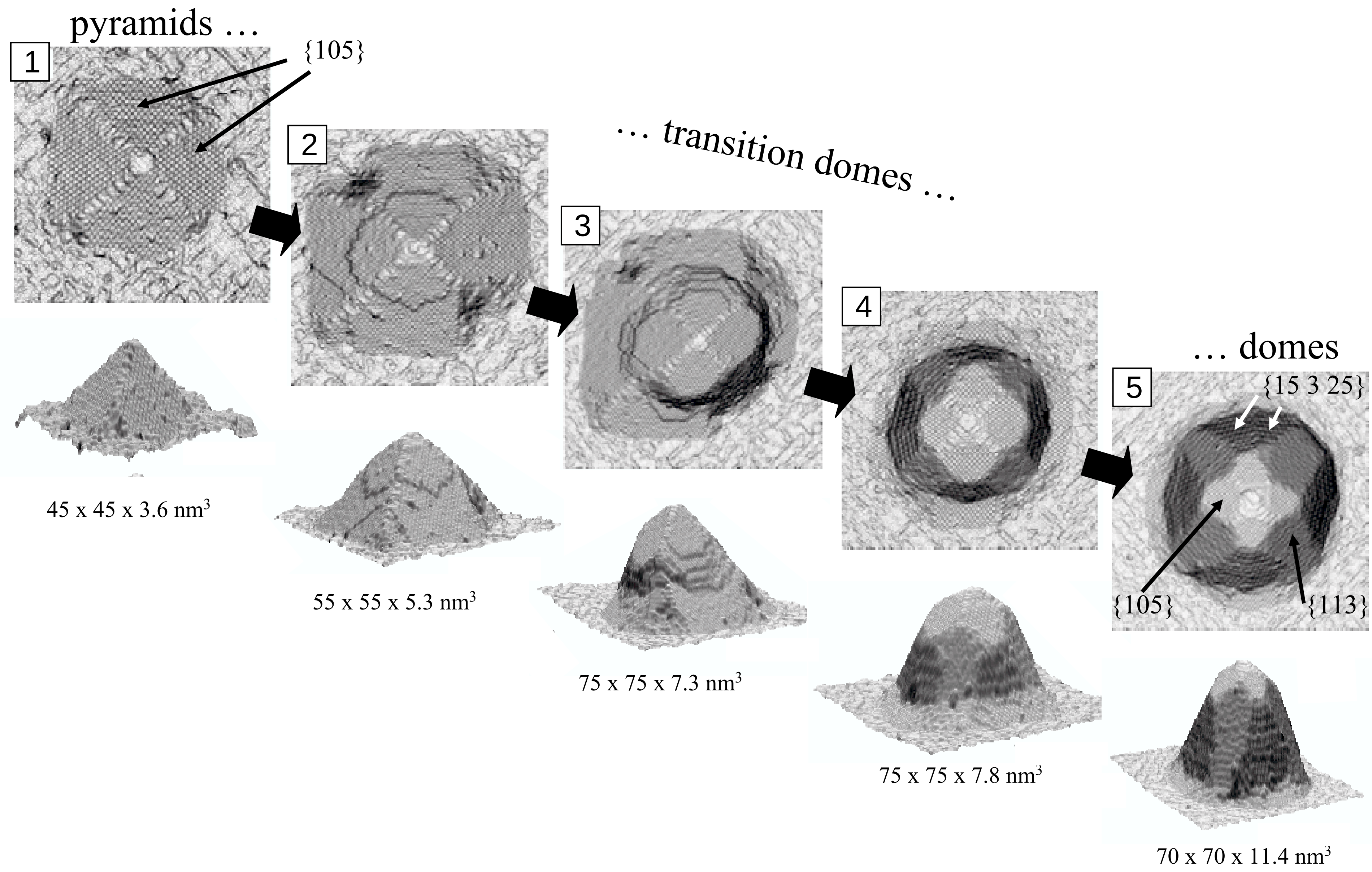
less strain energy
more surface energy



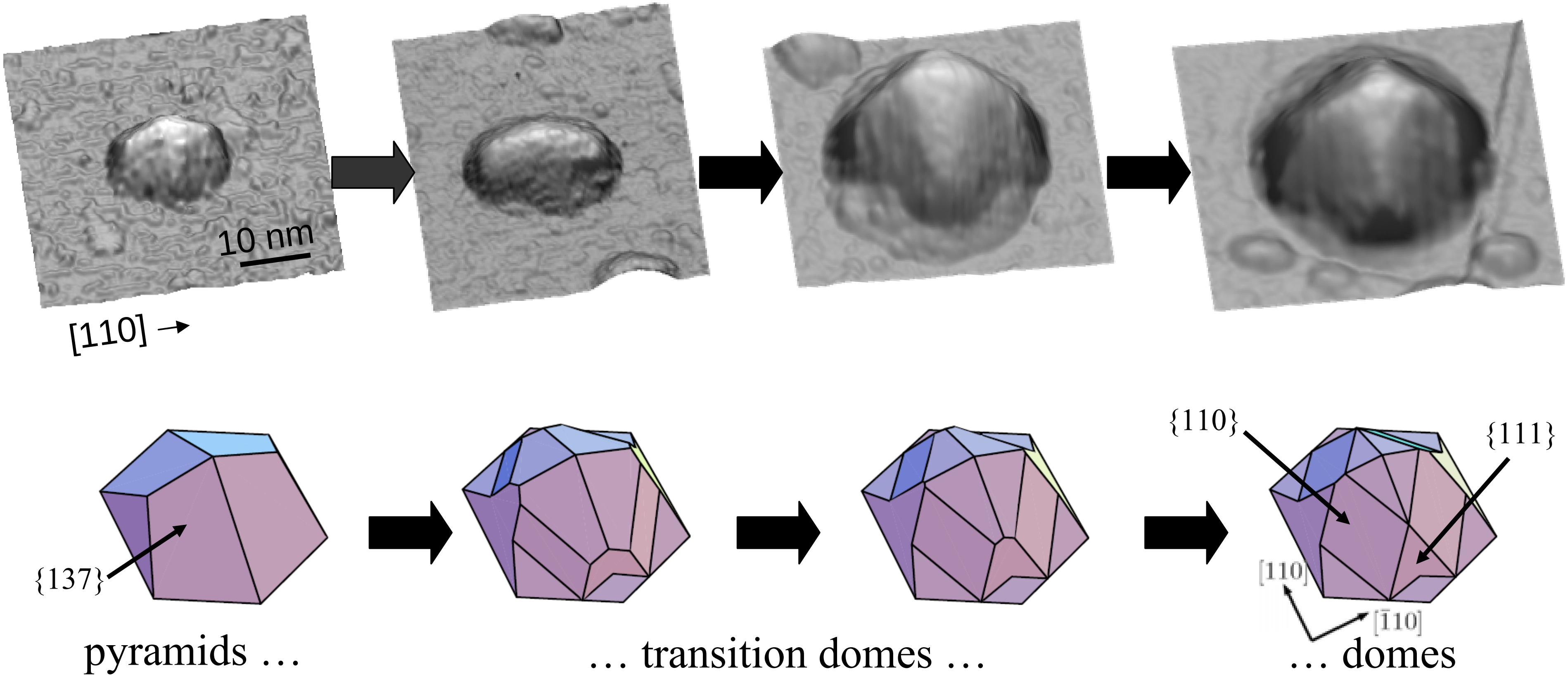


I. Daruka et al., PRL**87**, 2753 (1999); PRB**66**, 132104 (2002)

Pyramid-to-Dome transformation : Ge/Si(001)



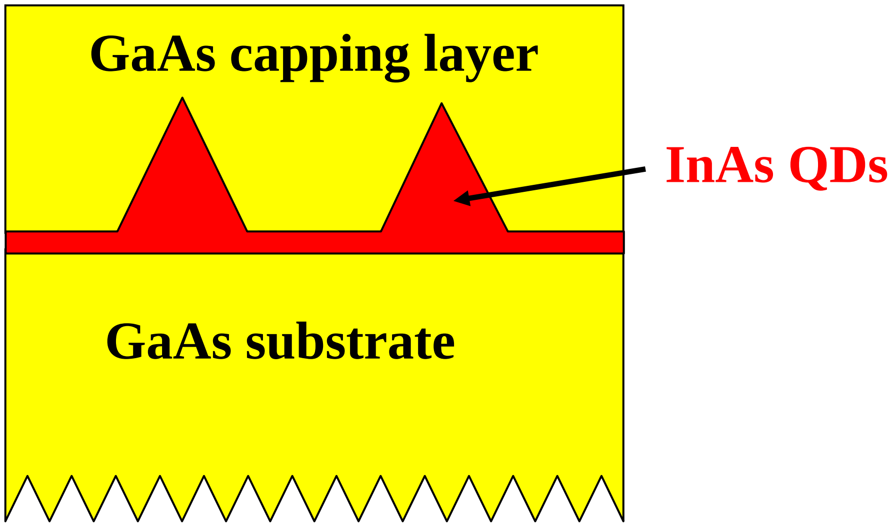
Pyramid-to-Dome transition : InAs/GaAs(001)

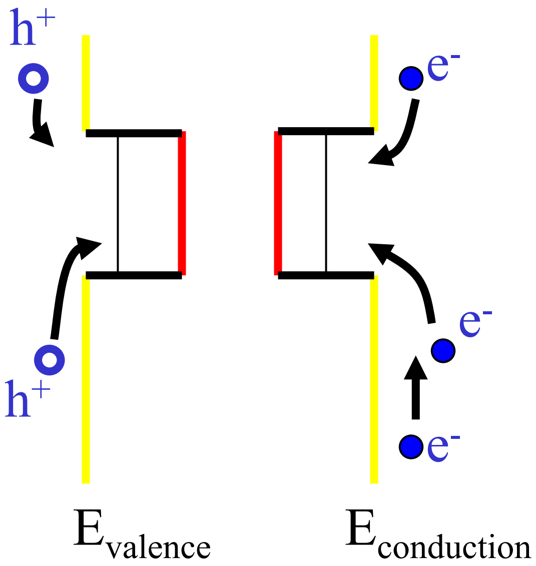


sucessive evolution of {110} and {111} facets at the expense of {137} facets
→ transformation pyramid to dome

PRB **73**, 205347 (2006)

Overgrowth: GaAs/InAs/GaAs(001)



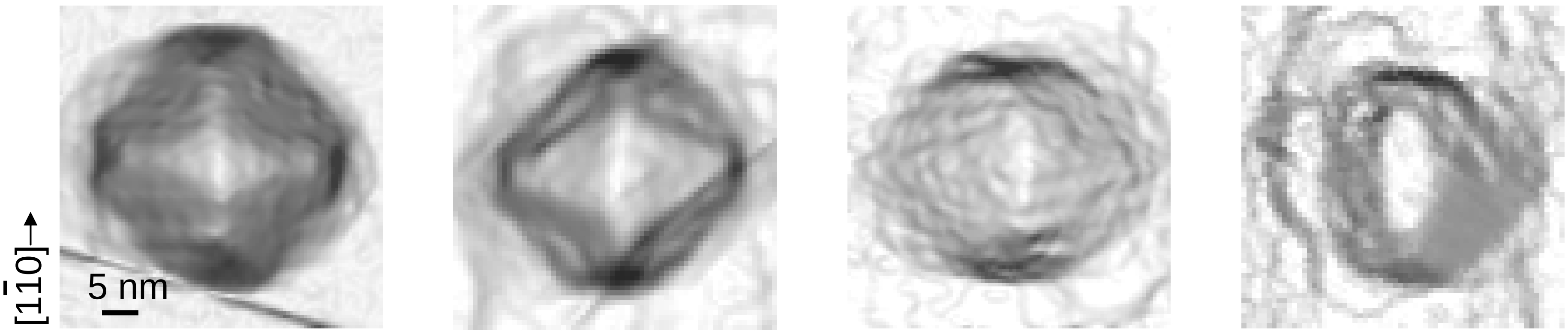


overgrowth of QDs:

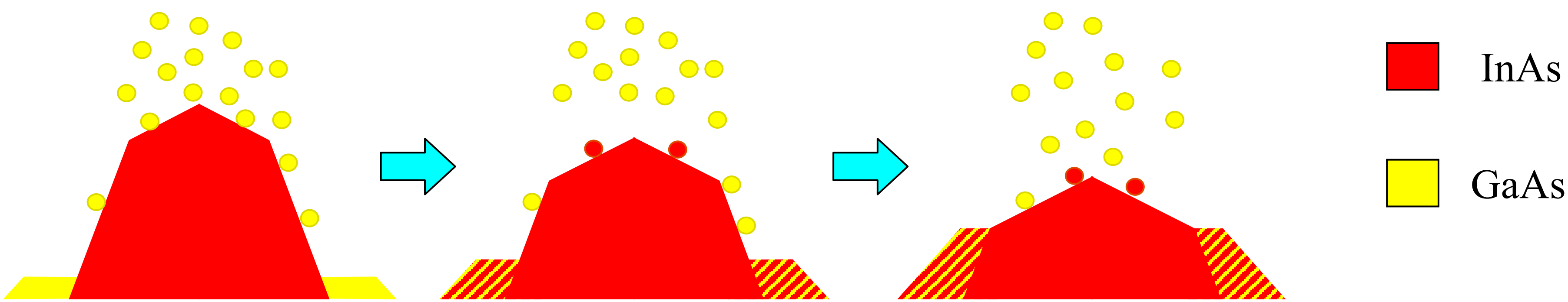
- protection of the surface: passivation of surface states
- bandgap discontinuity acts as a trap for the charge carriers
- capping layer effects the composition and morphology of the islands

High resolution analysis of the overgrowth

0 ML 1 ML 2 ML 3 ML



backward dome-to-pyramid transition



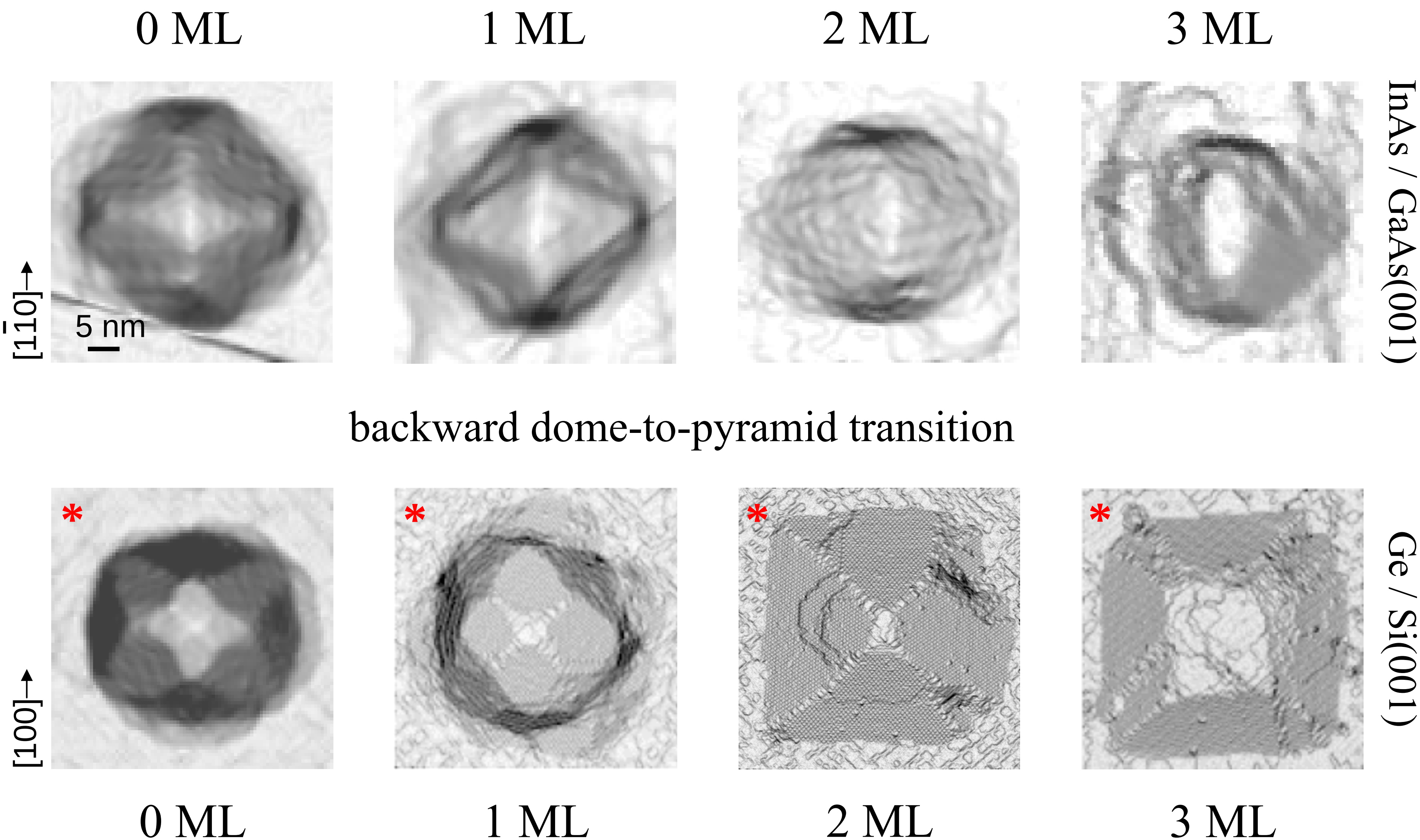
lattice mismatch
Ga out-diffusion

alloying
In out-diffusion

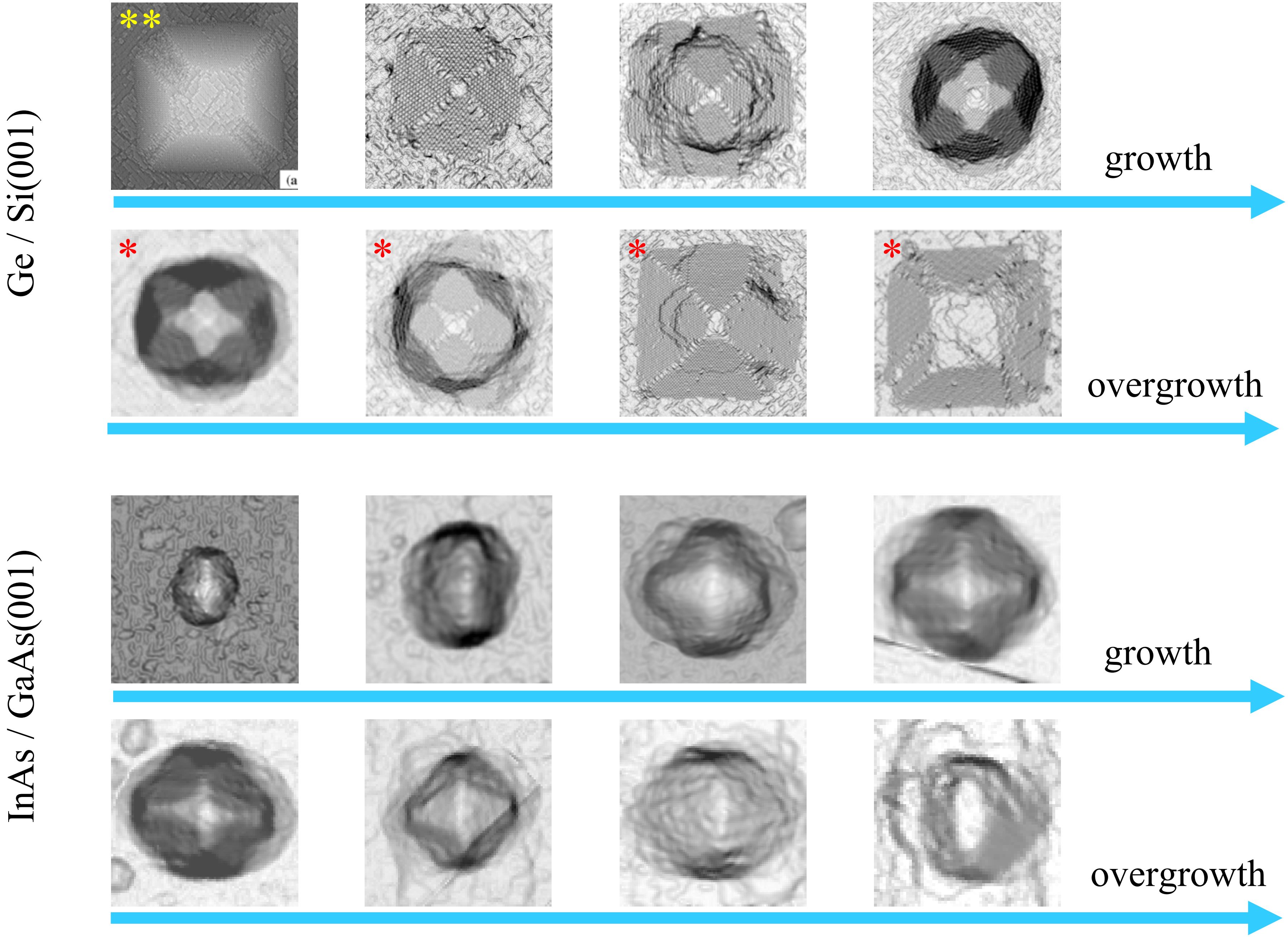
shape
transformation

PRL **96**, 226106 (2006)

High resolution analysis of the overgrowth

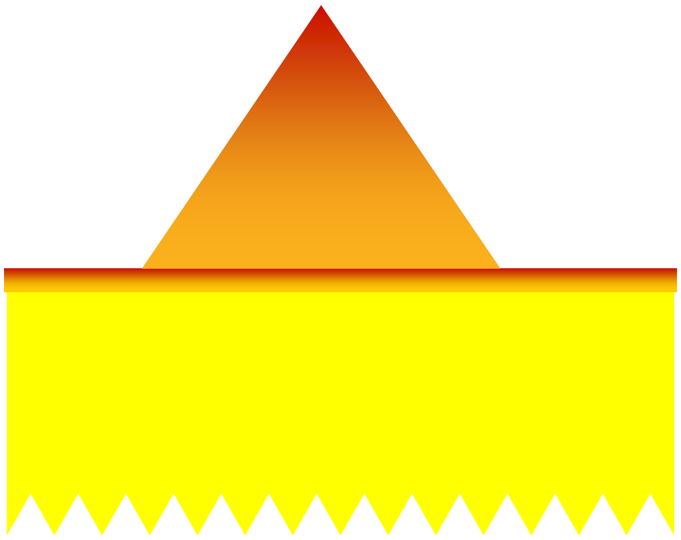


* A. Rastelli et al., PRL **87**, 256101 (2001)



* A. Rastelli et al., PRL**87**, 256101 (2001); ** J. Tersoff et al., PRL**89**, 196104 (2002)

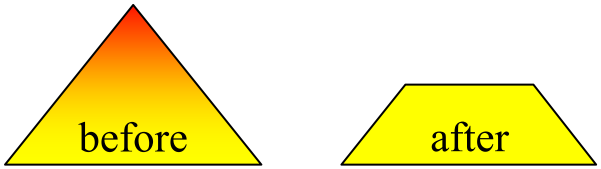
Quantum dot composition

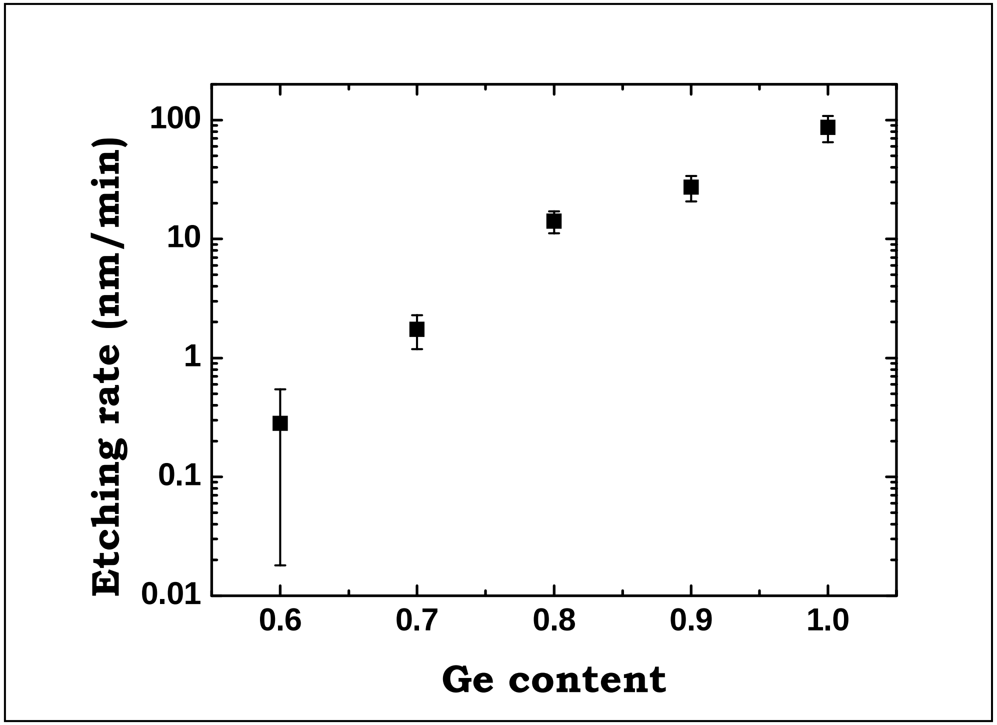


Determining intermixing by AFM

Indirect method: <u>Selective Chemical Etching</u>

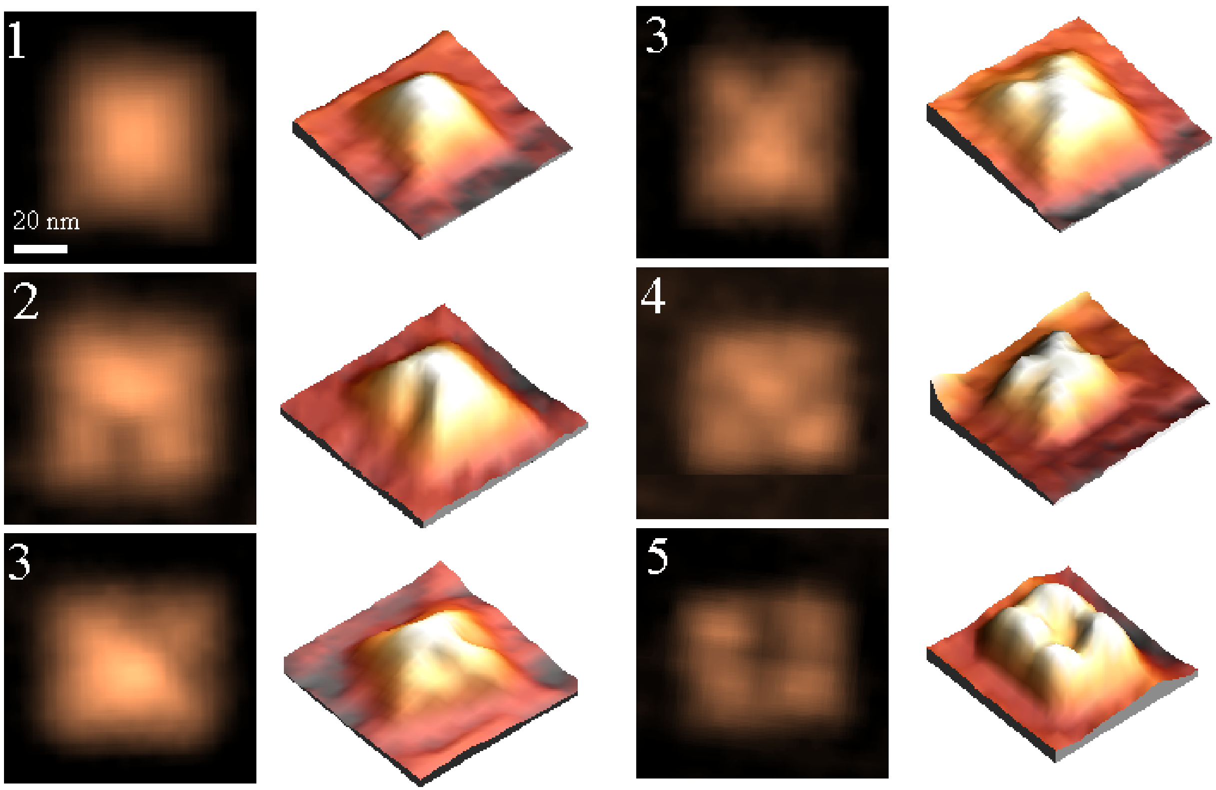
E.g.: etching $A_{1-x}B_x$
for $x \leq 20\%$

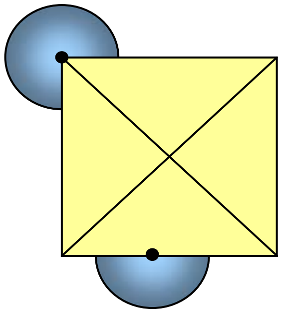




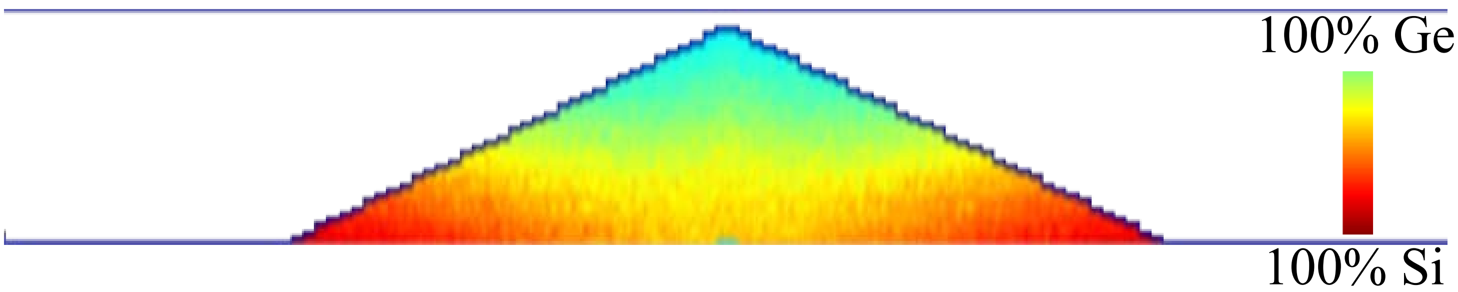
U. Denker et al., PRL **90**, 196102 (2003)

Composition profile of Ge/Si(001) pyramids

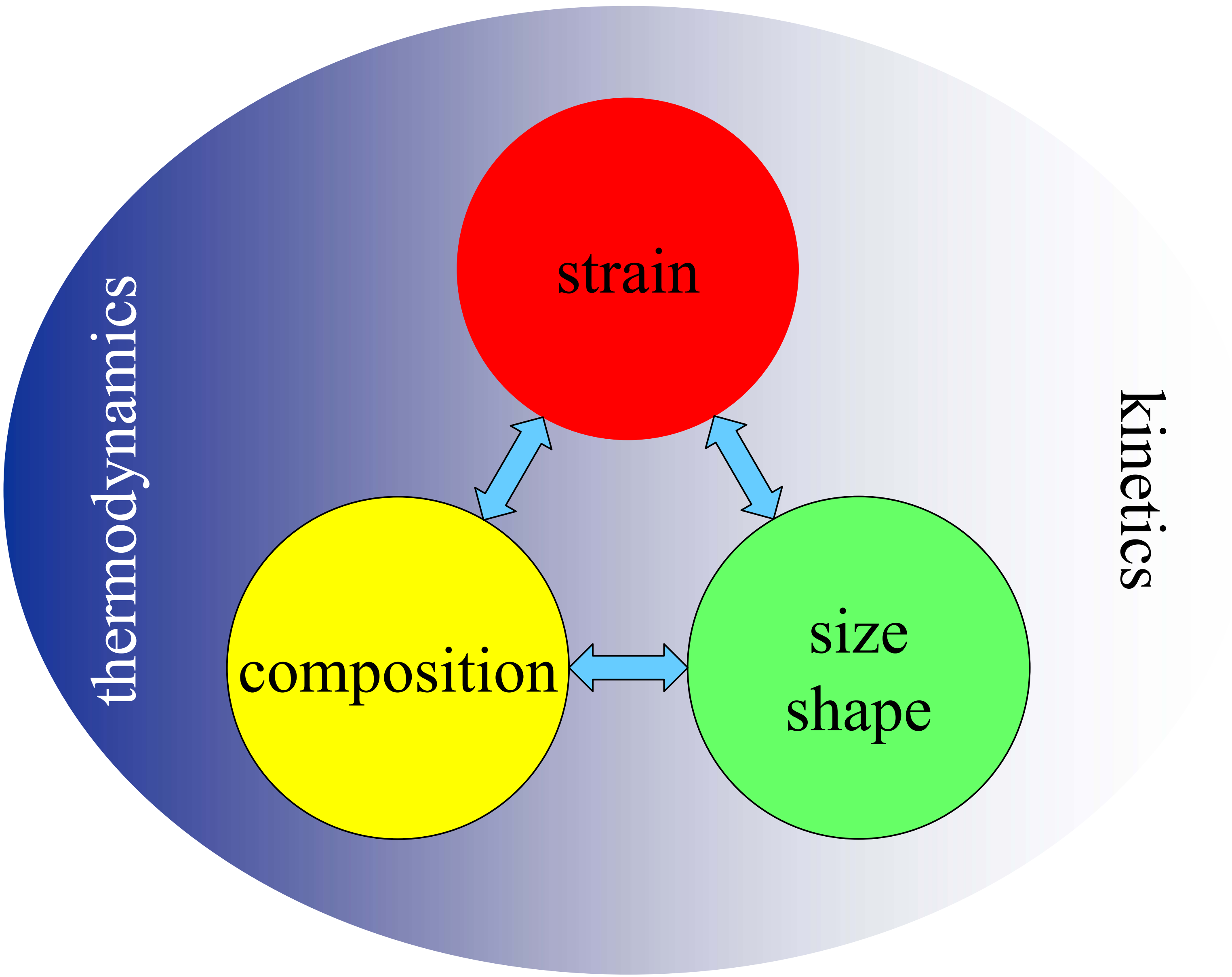




Si enrichment at the corners of the pyramids



Self – organized semiconductor quantum dots

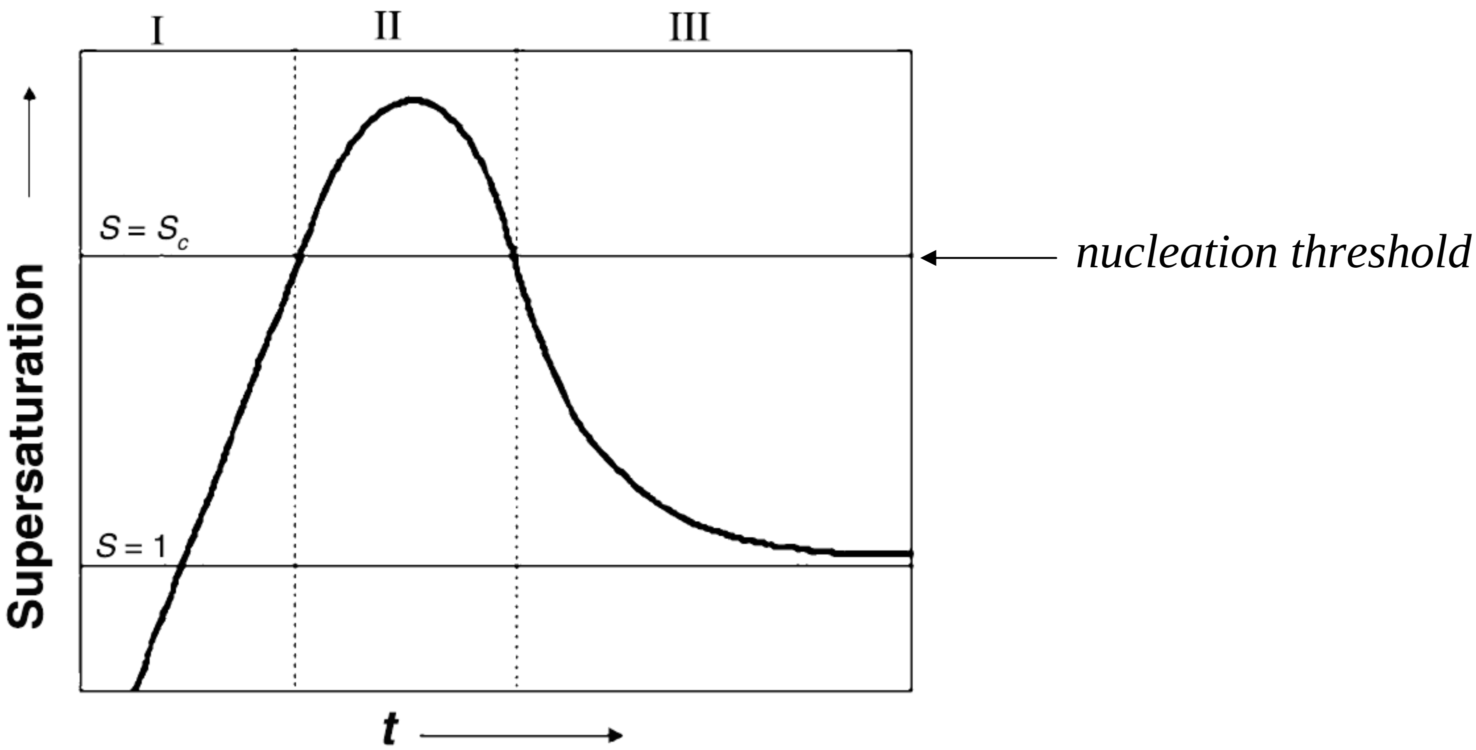


Semiconductor Nanostructures

- basics
- MBE quantum dots
- nanocrystals
- nanowires

Solution-based nanocrystal synthesis

Degree of supersaturation vs. reaction time (LaMer plot):

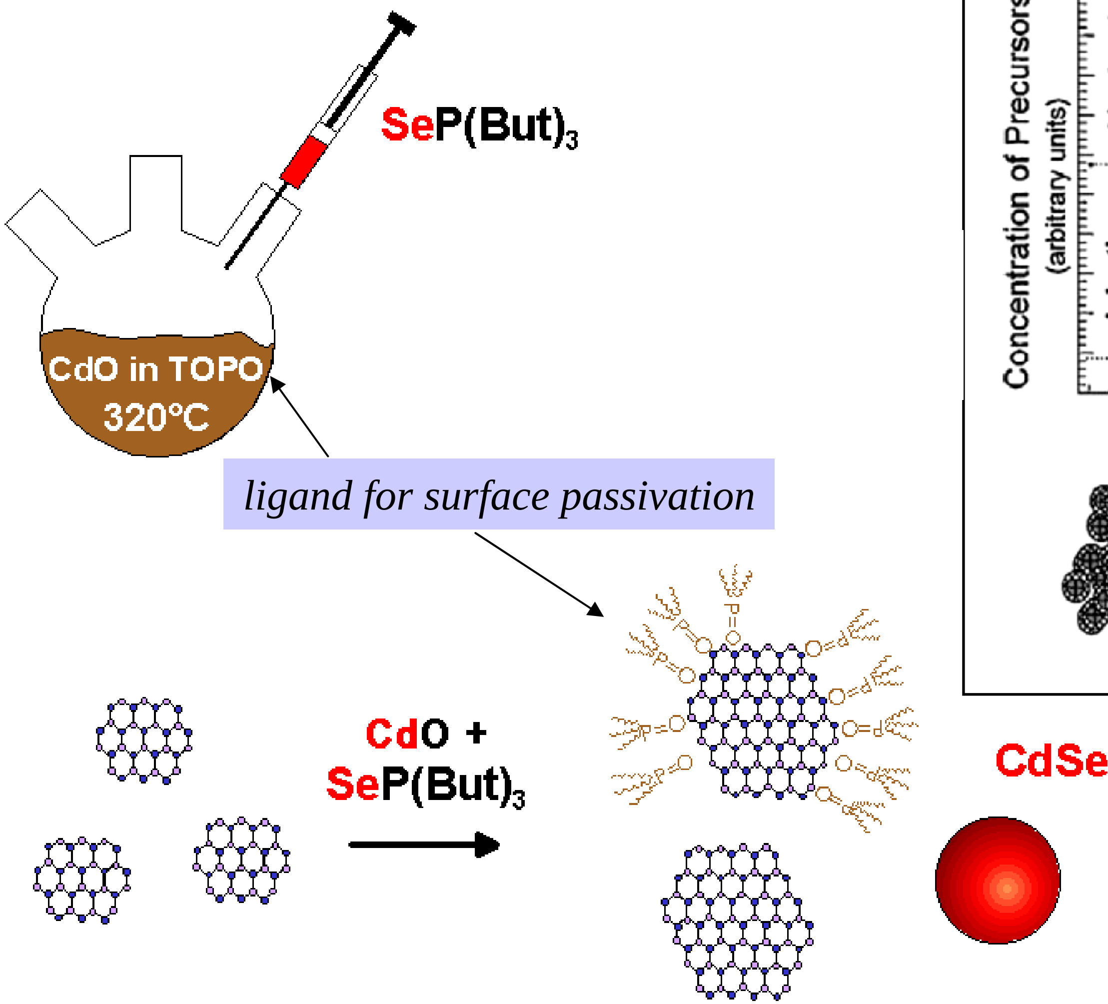


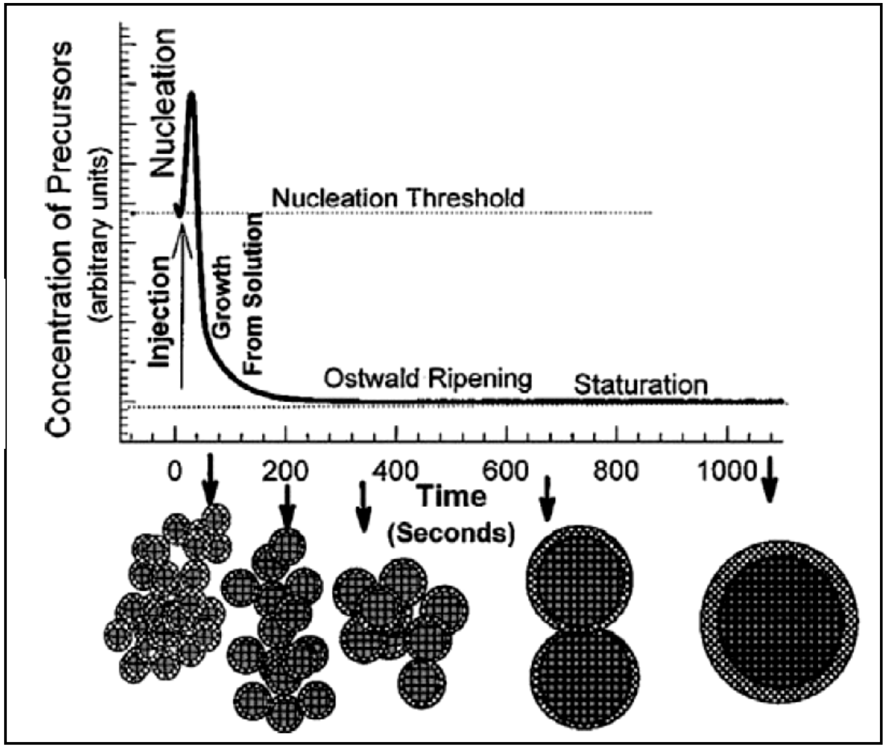
→ homogeneous nucleation requires temporal separation of nucleation and growth of the seeds.

hot injection method
(instantaneous nucleation)

heating-up method
(in situ formation of reactive species)

CdSe nanocrystal synthesis



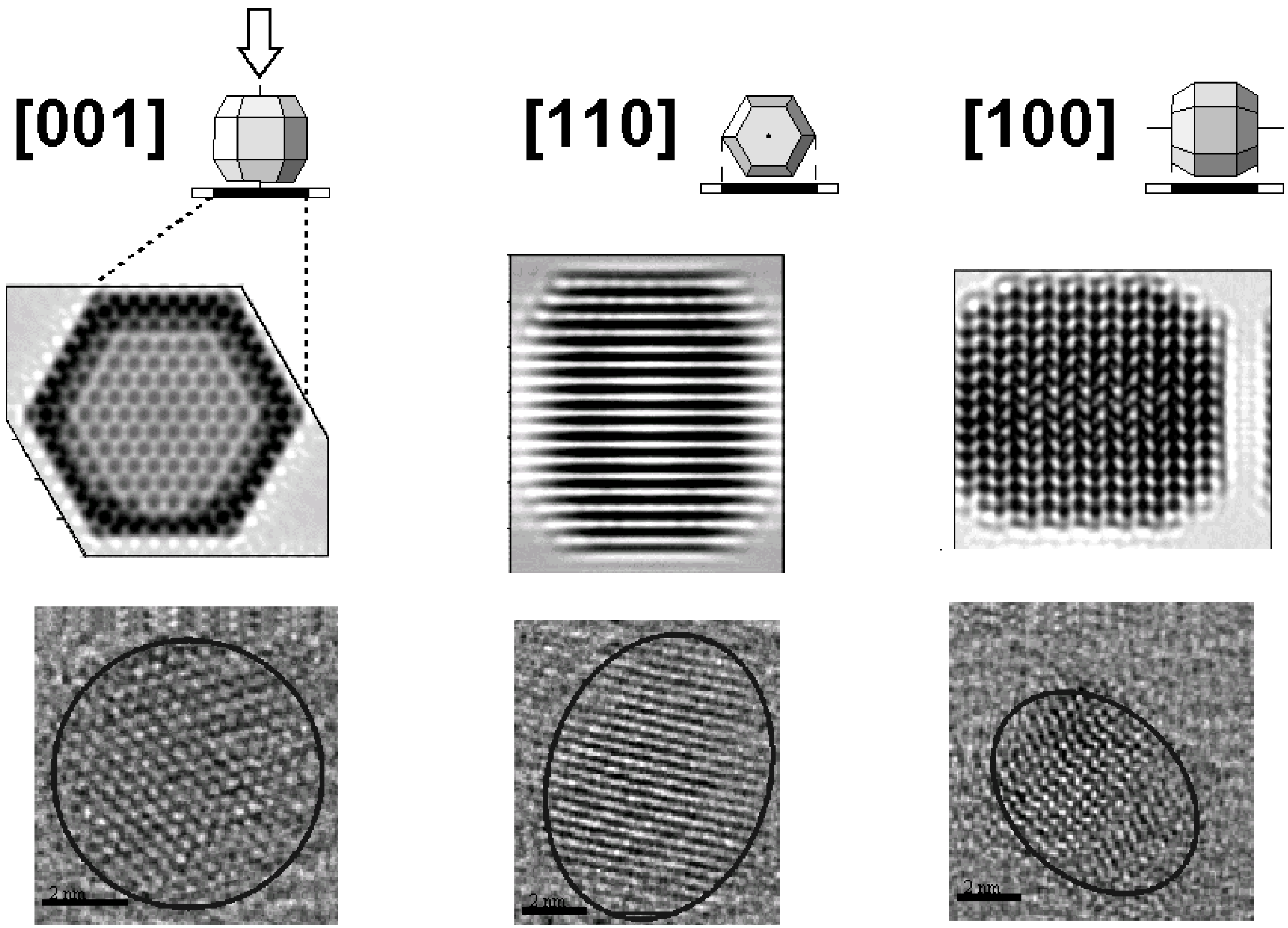


nucleation (320°C)

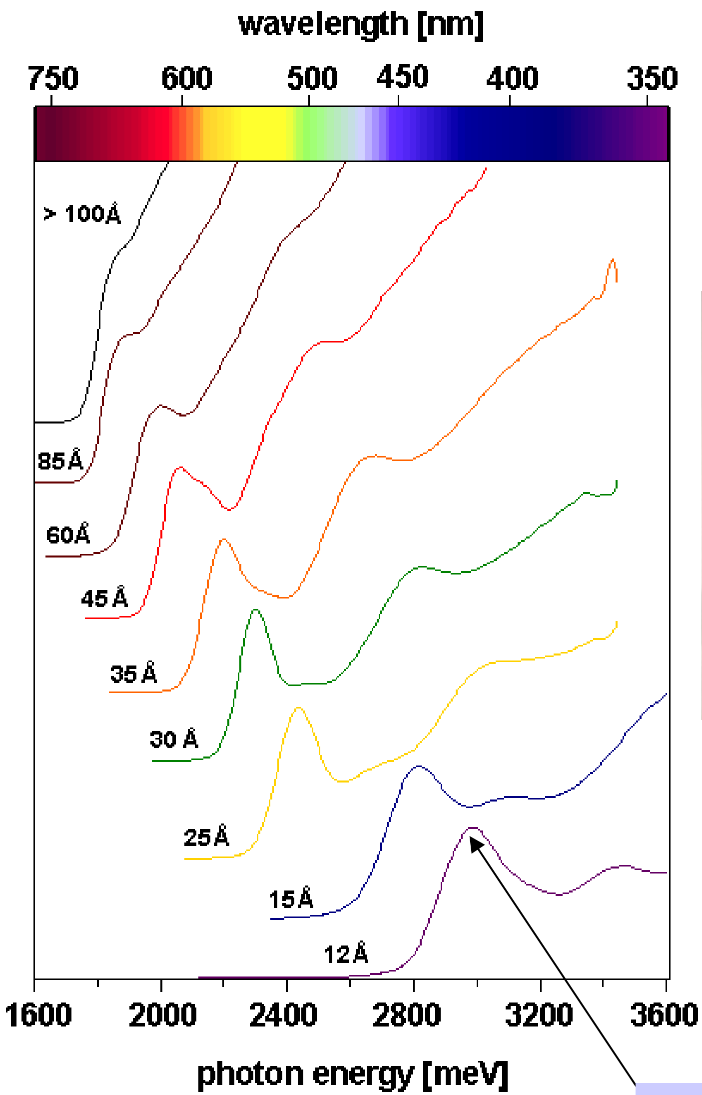
growth (250°C)

Microscopic structure

HRTEM images of hexagonal CdSe nanocrystals:

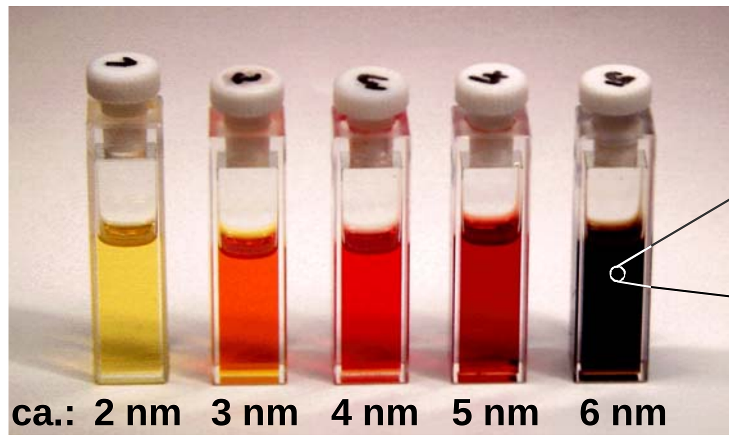


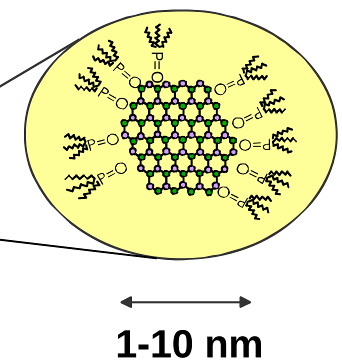
Size-dependence of optical absorption



excitonic peak

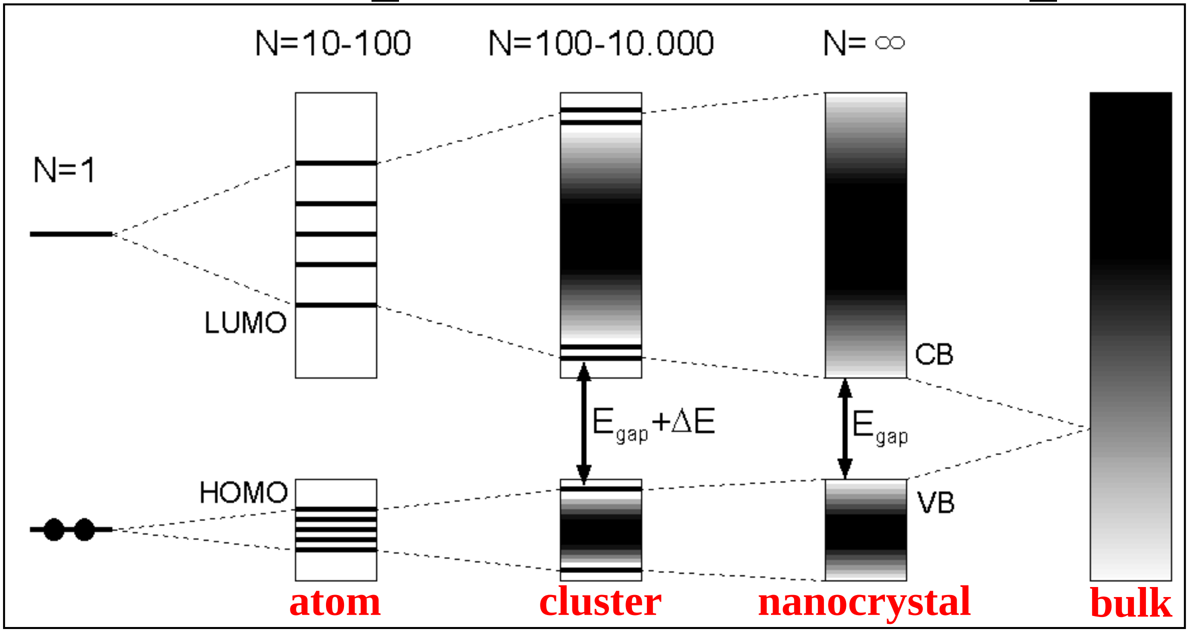
CdSe nanocrystals

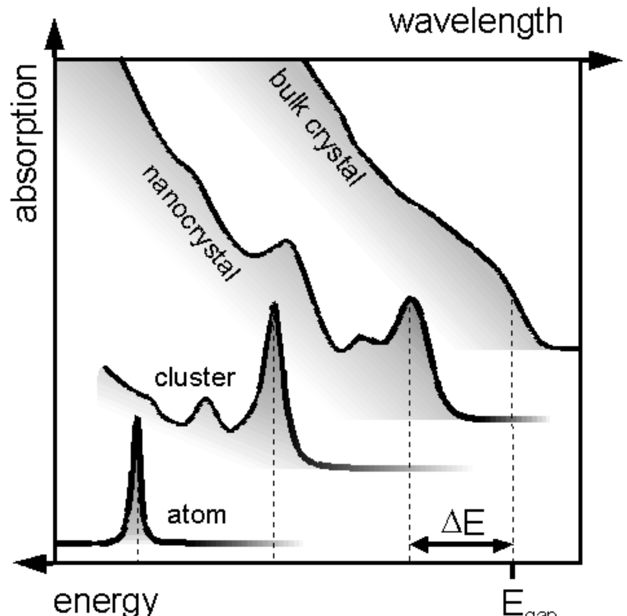




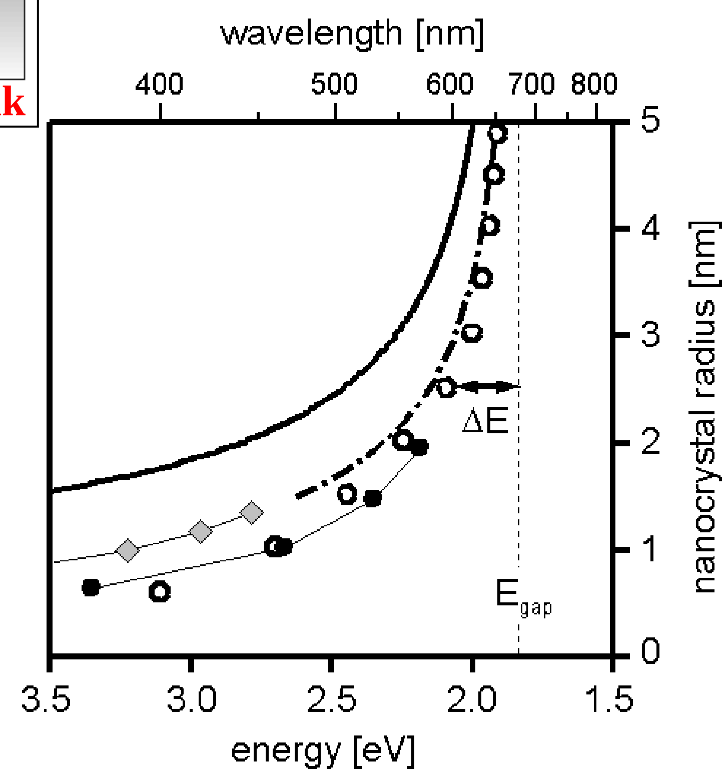
- very large molar extinction coefficients ($1\text{-}5 \times 10^6\ M^{-1}\ cm^{-1}$), ~ 10-50 times larger than that of organic dyes

Size-dependence of optical absorption



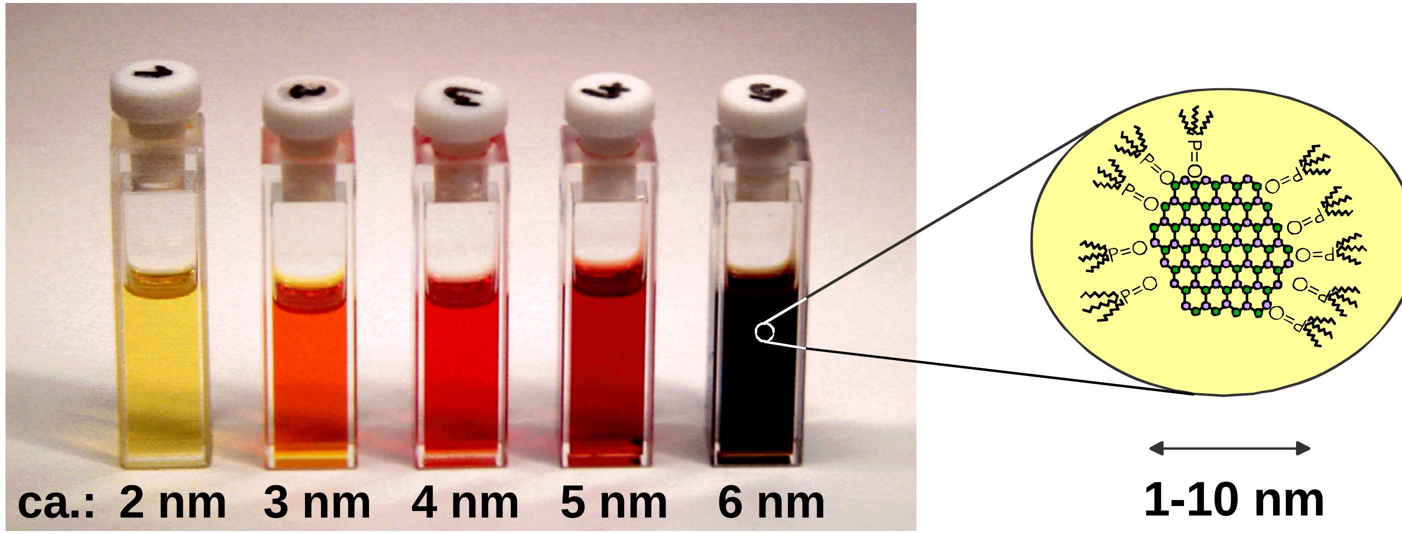


band gap as a function of nanocrystal size:

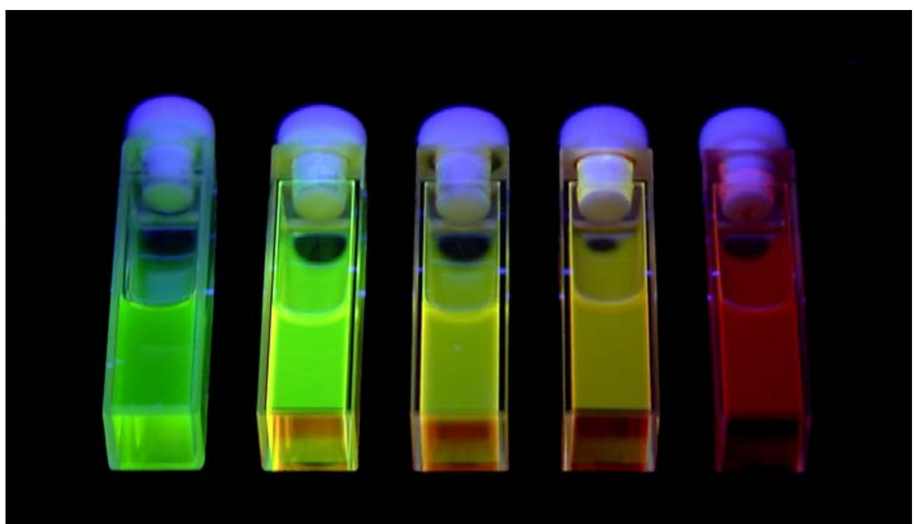


Colloidal CdSe nanocrystals

CdSe absorption

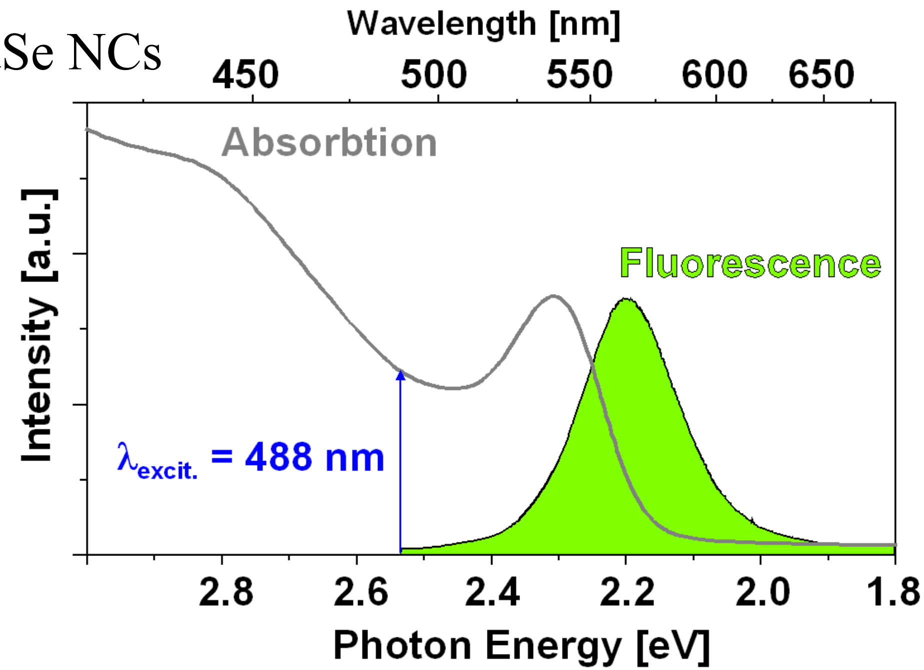


CdSe fluorescence



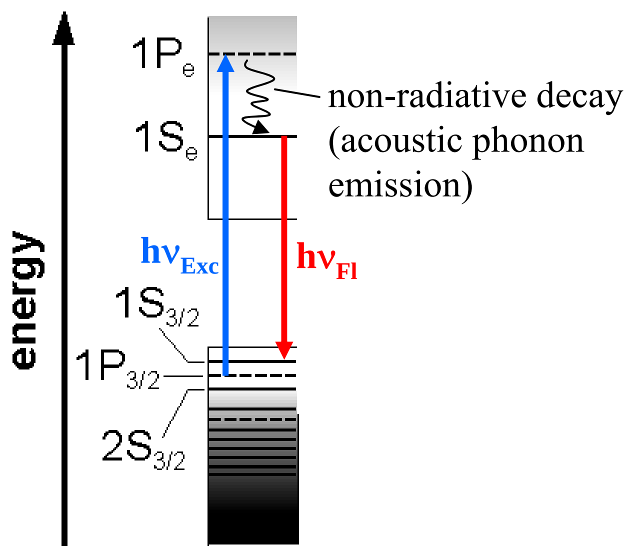
Fluorescence of nanocrystals

CdSe NCs

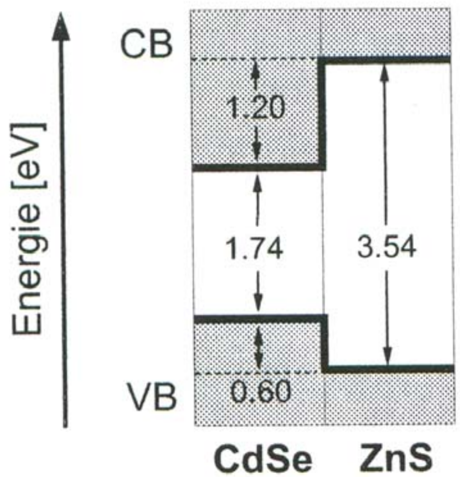


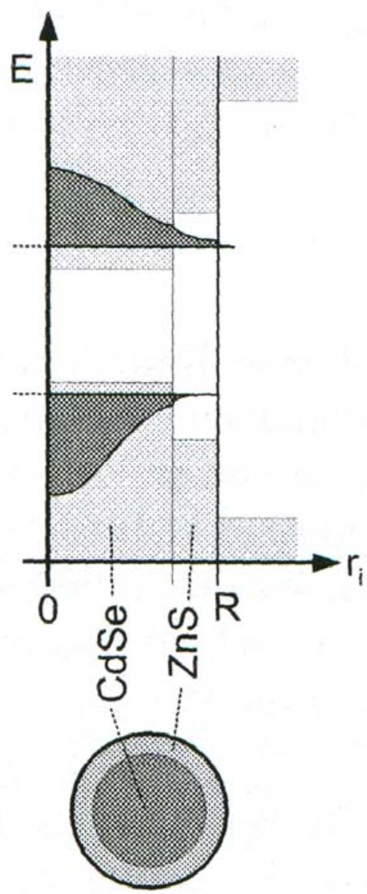
fluorescence quantum yield ranges between ~ 40 and 80%, depending on the influence of surface trap states

origin of pronounced Stark shift:



Core/shell nanocrystals (CdSe/ZnS)

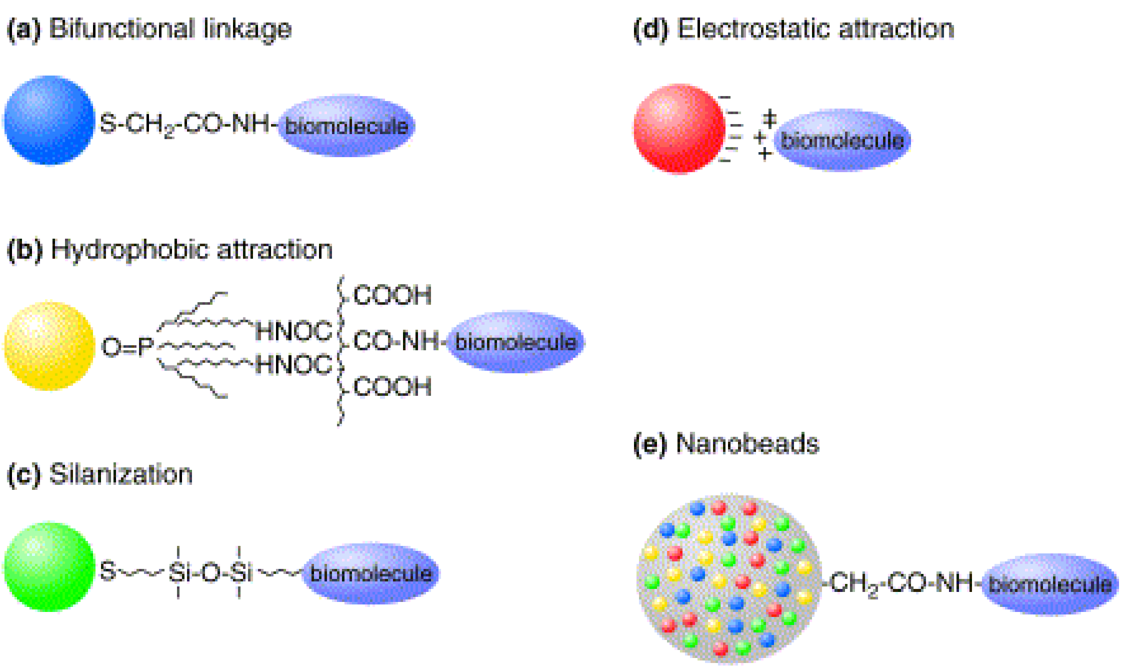




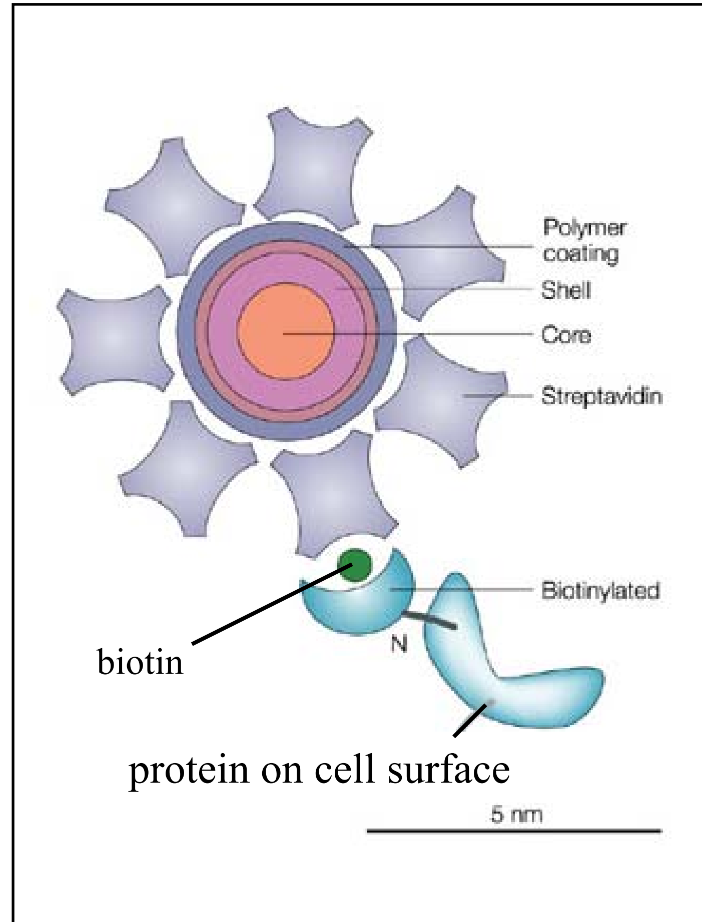
The larger gap ZnS shell confines the wavefunction of the CdSe core and reduces non-radiative exciton recombination at surface defects

SC nanocrystals as bio-labels

bio-conjugation strategies:



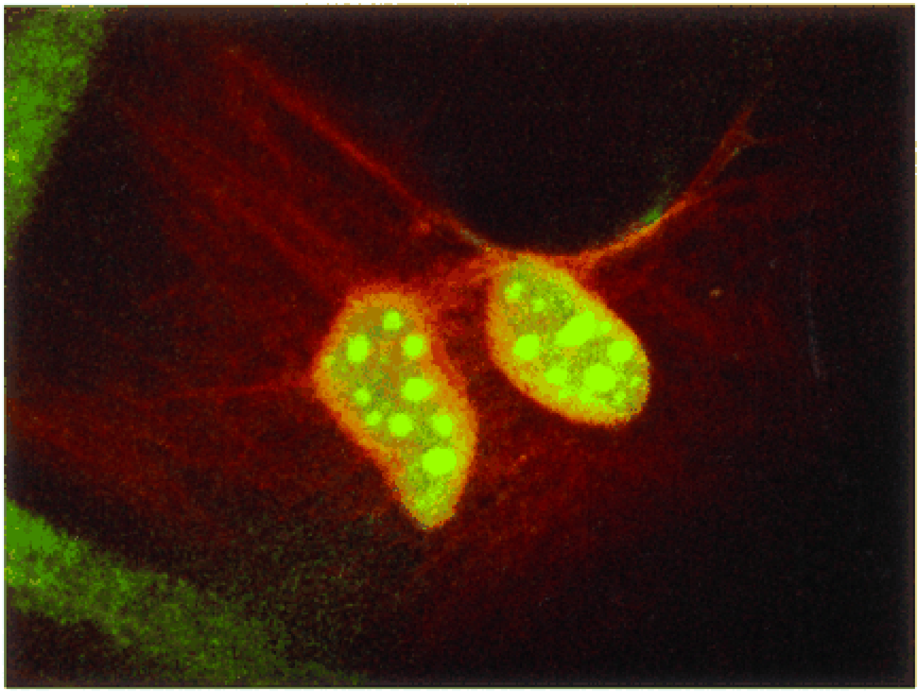
example:



core-shell nanocrystal
conjugated to streptavidin

A. Miyawaki et al., Nature Cell Biology 5, S1-S7 (2003).

SC nanocrystals as bio-labels



mouse fibroplast cells stained with CdSe-CdS core-shell particles of different size (2 nm core particles: green emission; 4 nm core particles: red emission)

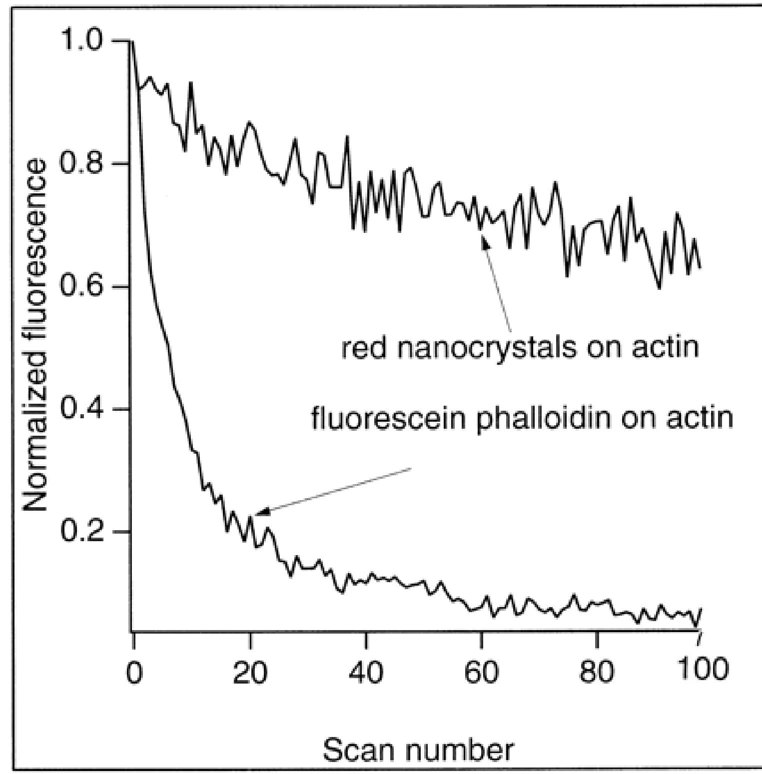
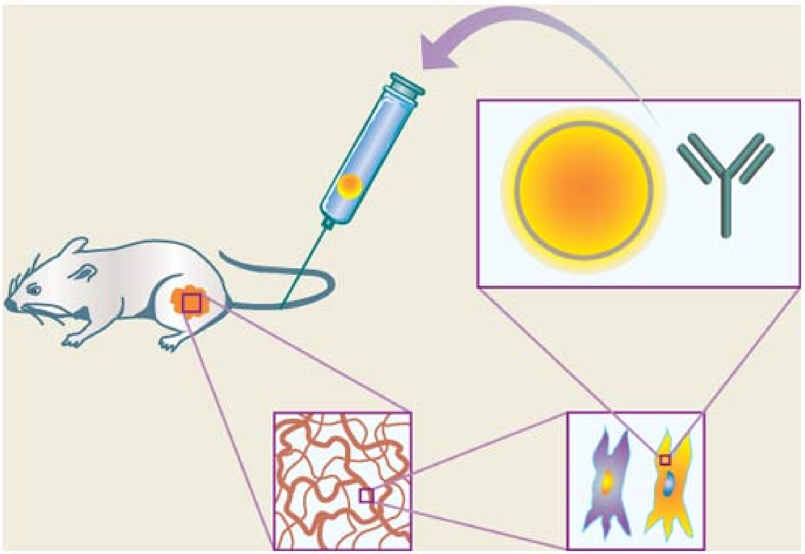
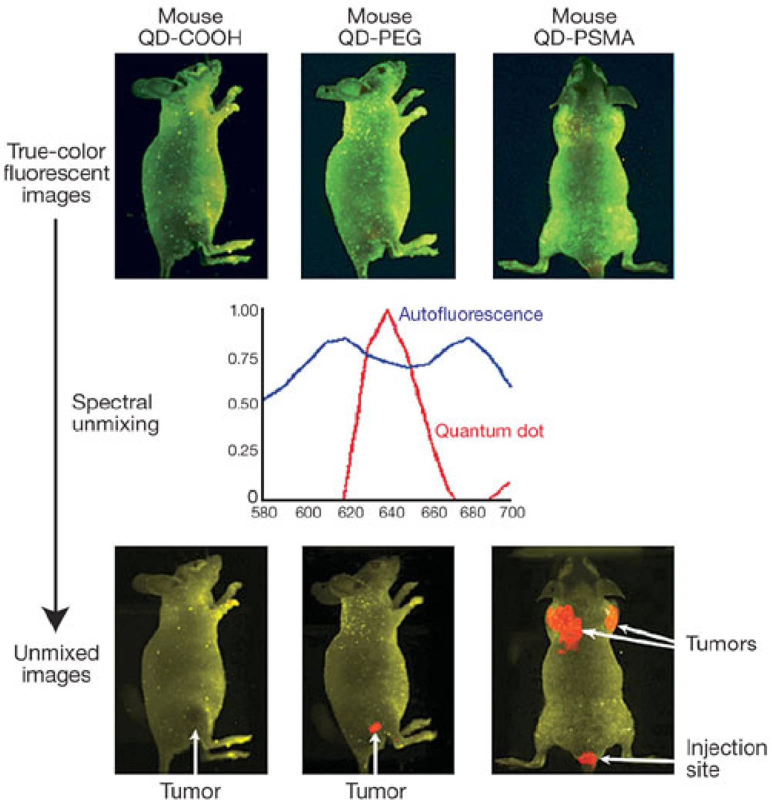


photo-stability comparison for actin fibres stained with fluorescent dyes or core-shell nanocrystals

M. Bruchez et al., Science 281, 2013 (1998).

In-Vivo Cancer Imaging with QD´s

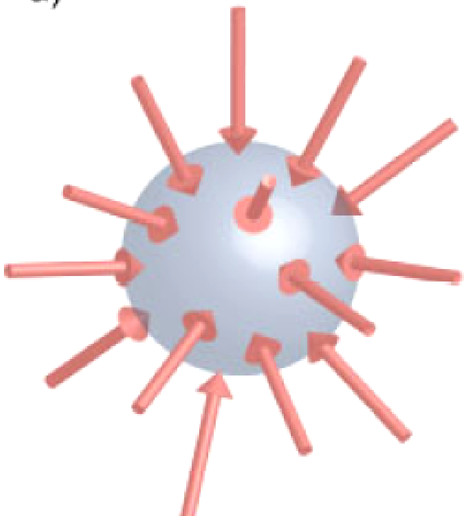




X. Gao et al.,Nature Biotechnology 22,969(2004)

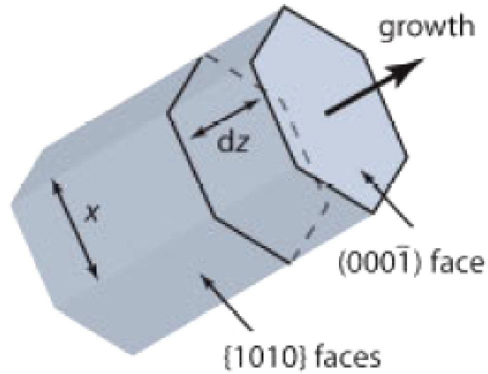
Shape control of NCs

a)



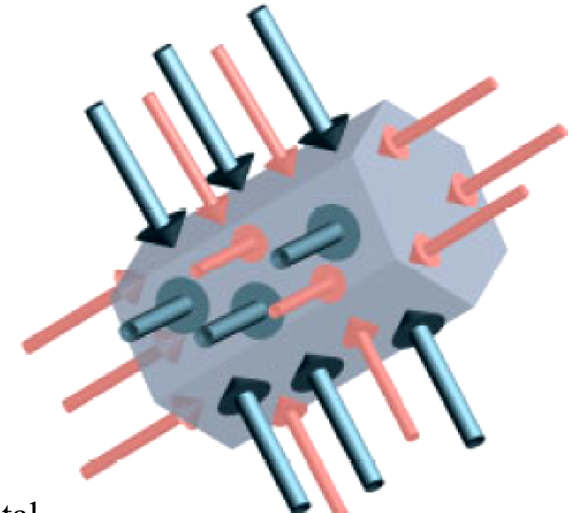
balanced surface tension by uniform ligand coverage

b)



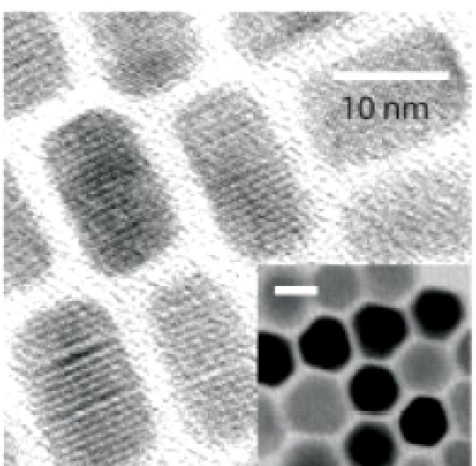
growth of a hexagonal nanocrystal along the c-axis

c)



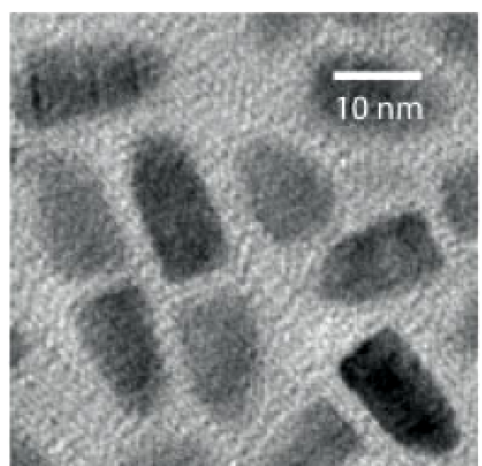
stabilization of rod-shape via non-uniform ligand coverage

d)



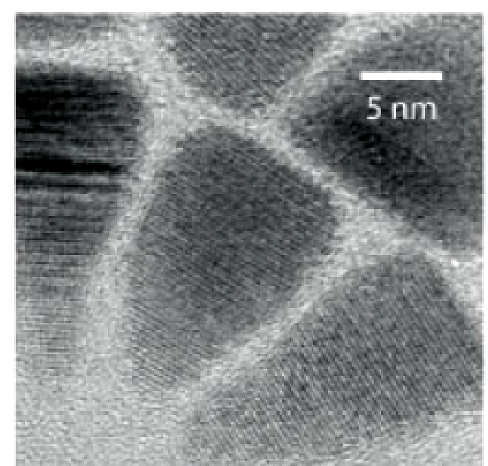
CdSe nanorods

e)



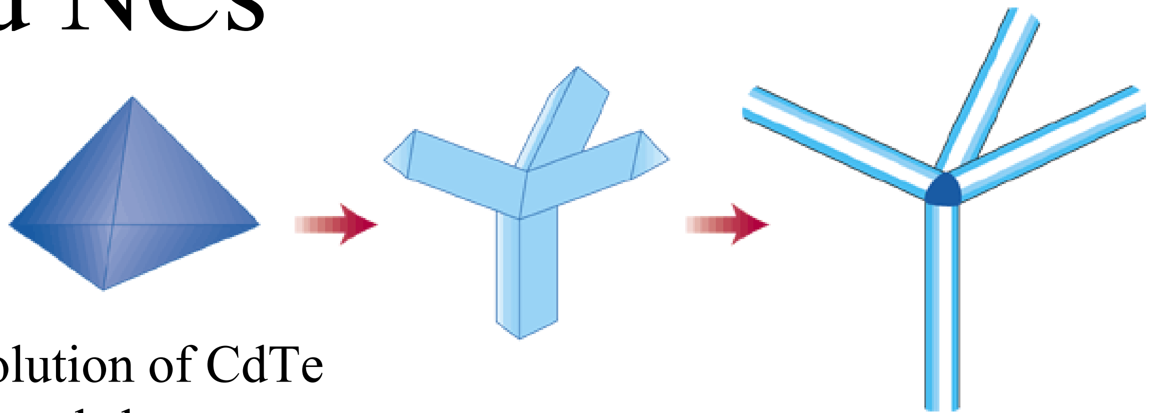
CdSe nanobullets

f)

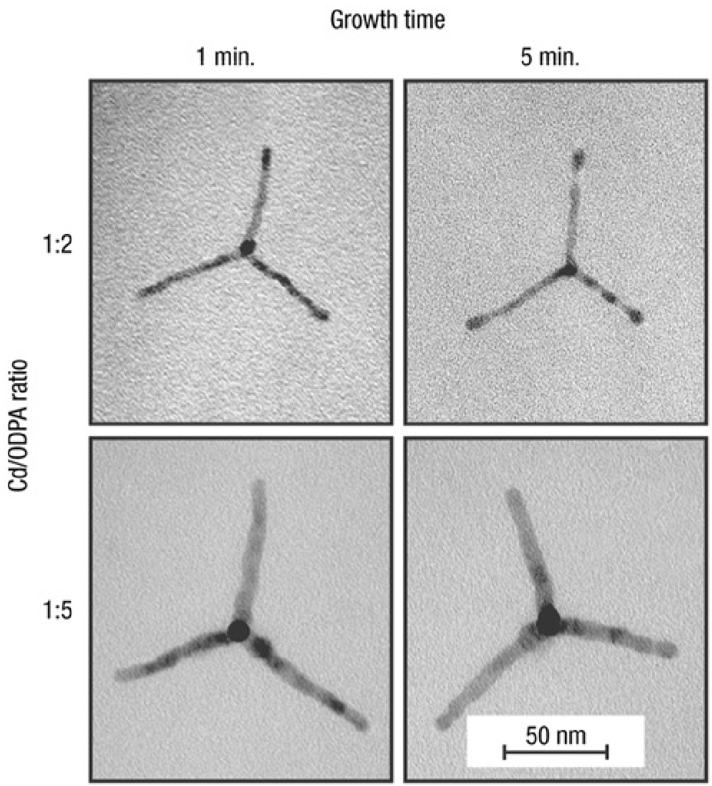


CdSe nanopyramids

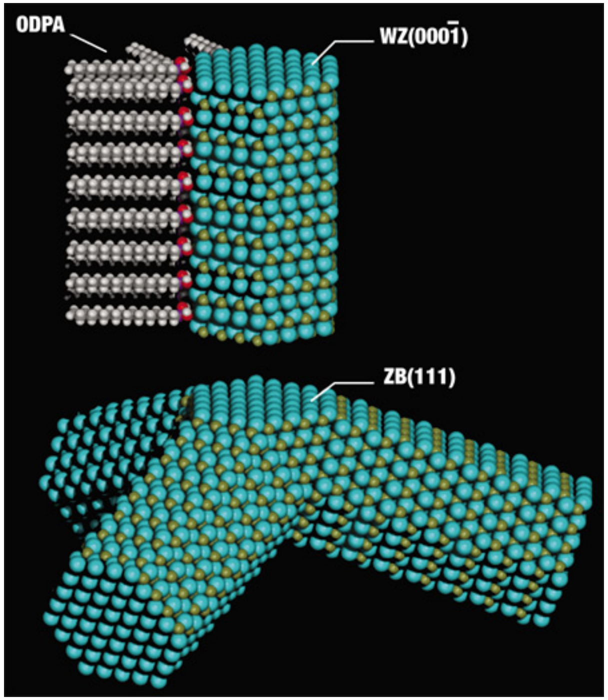
Branched NCs



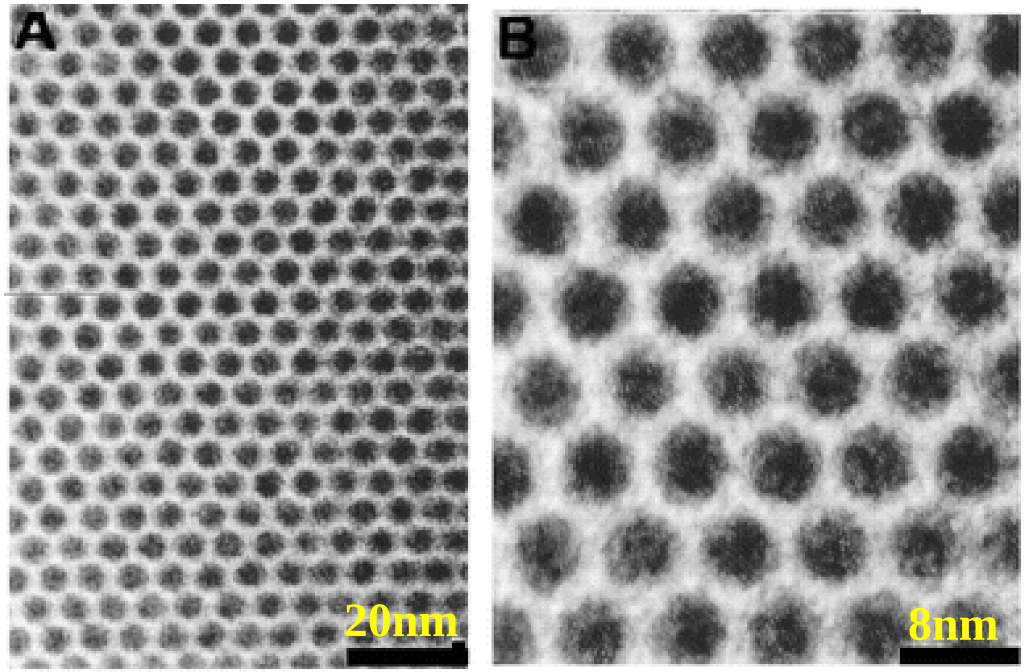
time evolution of CdTe tetrapod shape:



model of a CdTe tetrapod:



Ordered arrays of semiconductor NCs

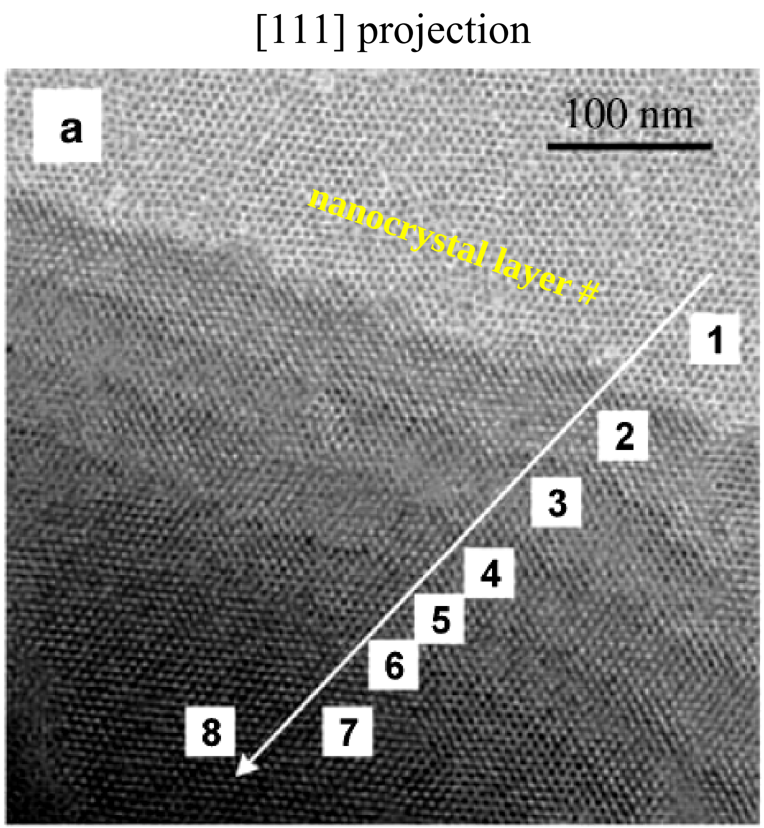


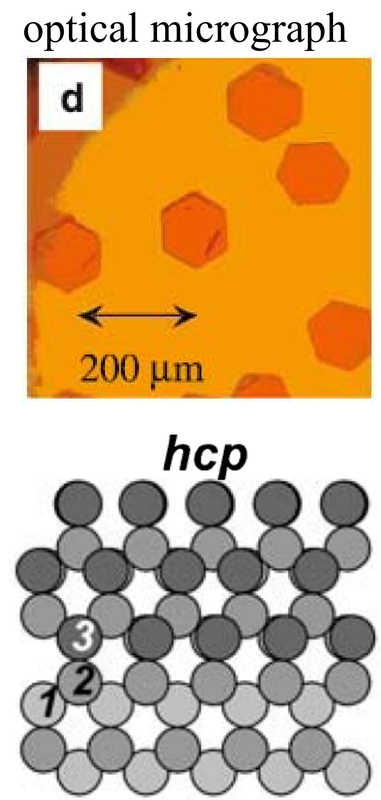
2D-array of CdSe nanocrystals (d = 4.8nm) on carbon grid

C.B. Murray et al., Ann. Rev. Mater. Sci. 30, 545 (2000).

Semiconductor NC 3D-superstructures

A *hcp* superlattice self-assembled from CdSe NCs:

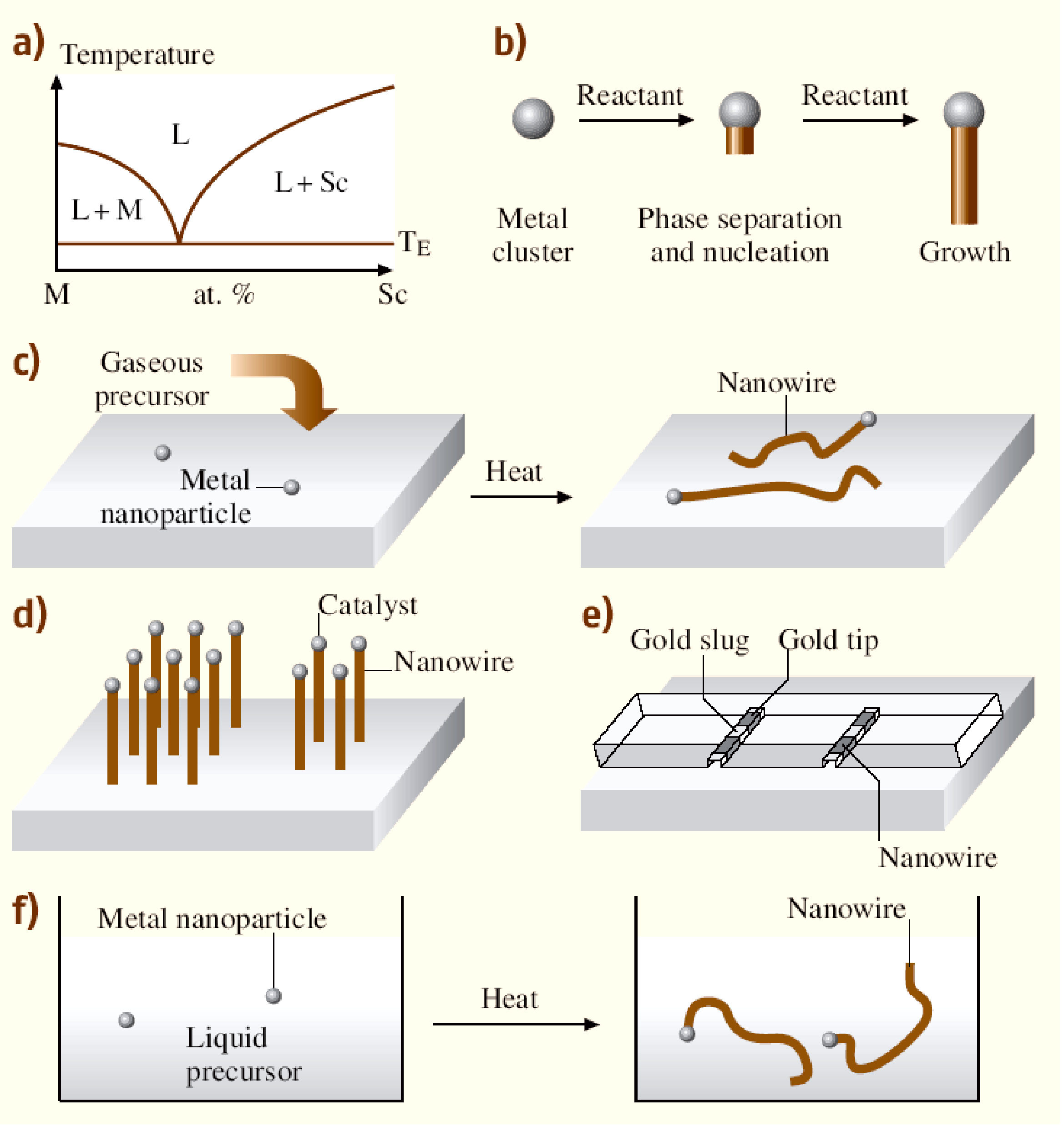




Semiconductor Nanostructures

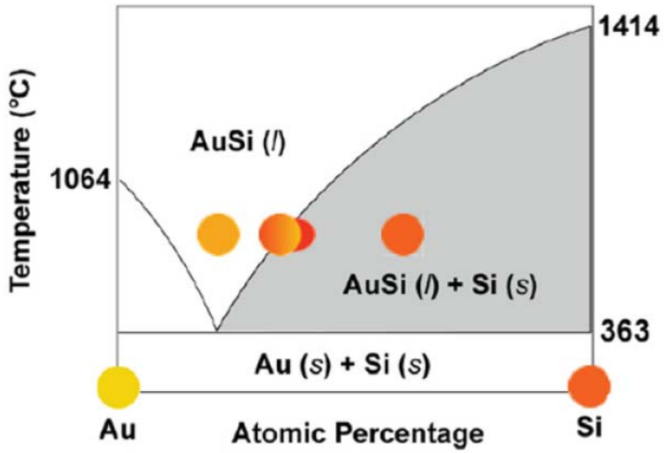
- basics
- MBE quantum dots
- nanocrystals
- nanowires

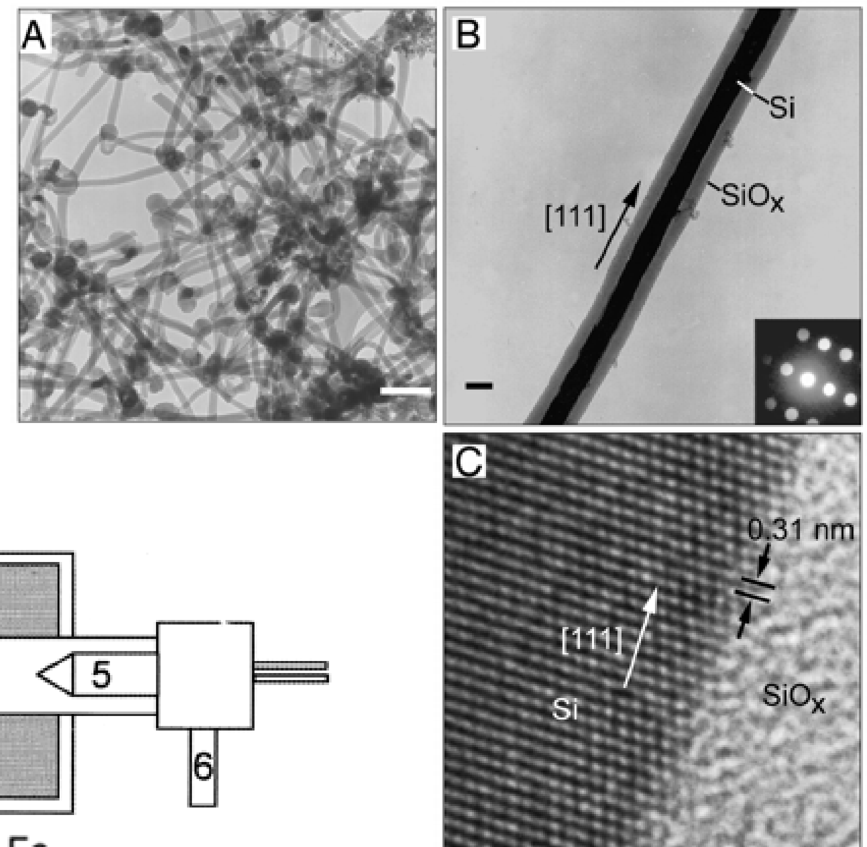
Synthesis methods - Overview

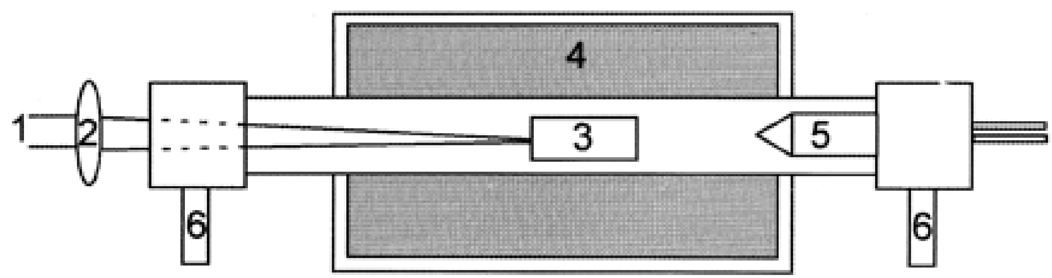


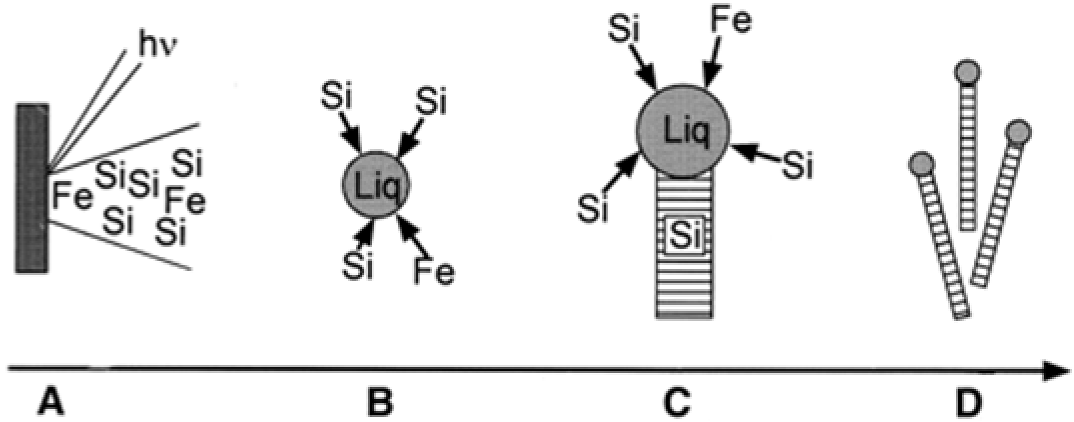
Vapor-liquid-solid growth mechanism

Si nanowire synthesis:

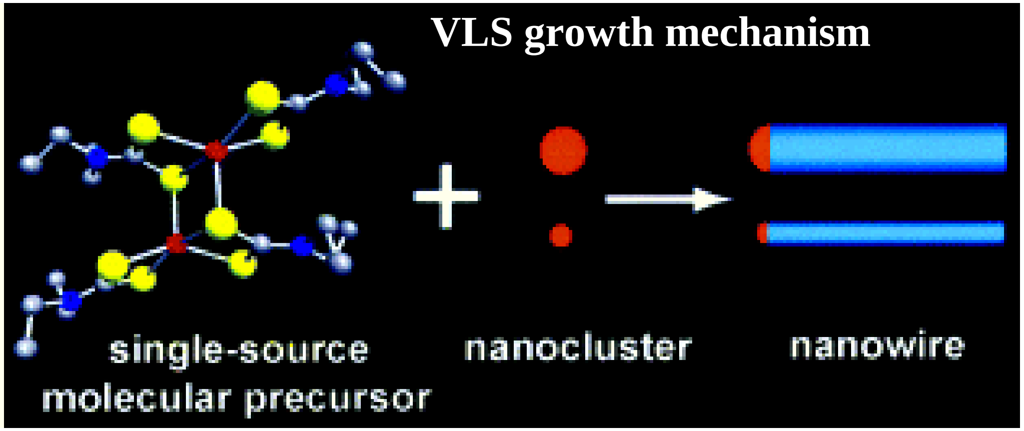




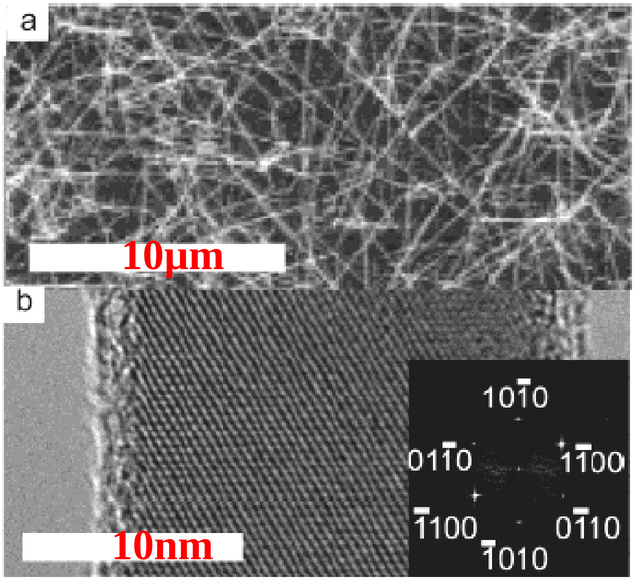




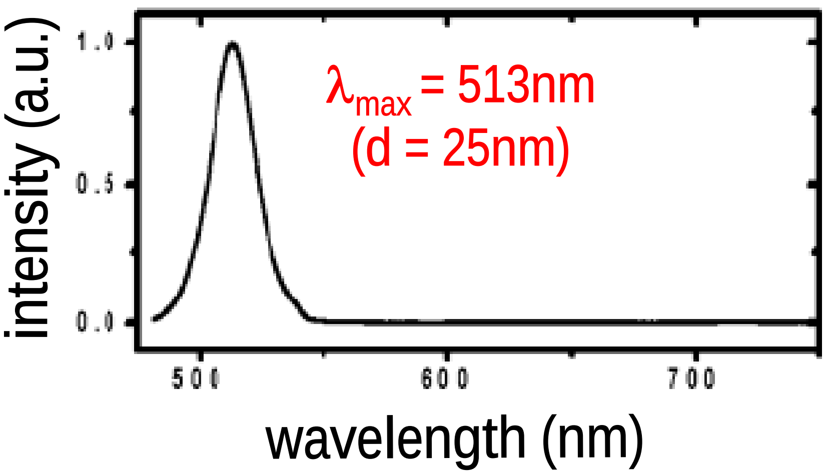
CdS NWs from molecular precursor



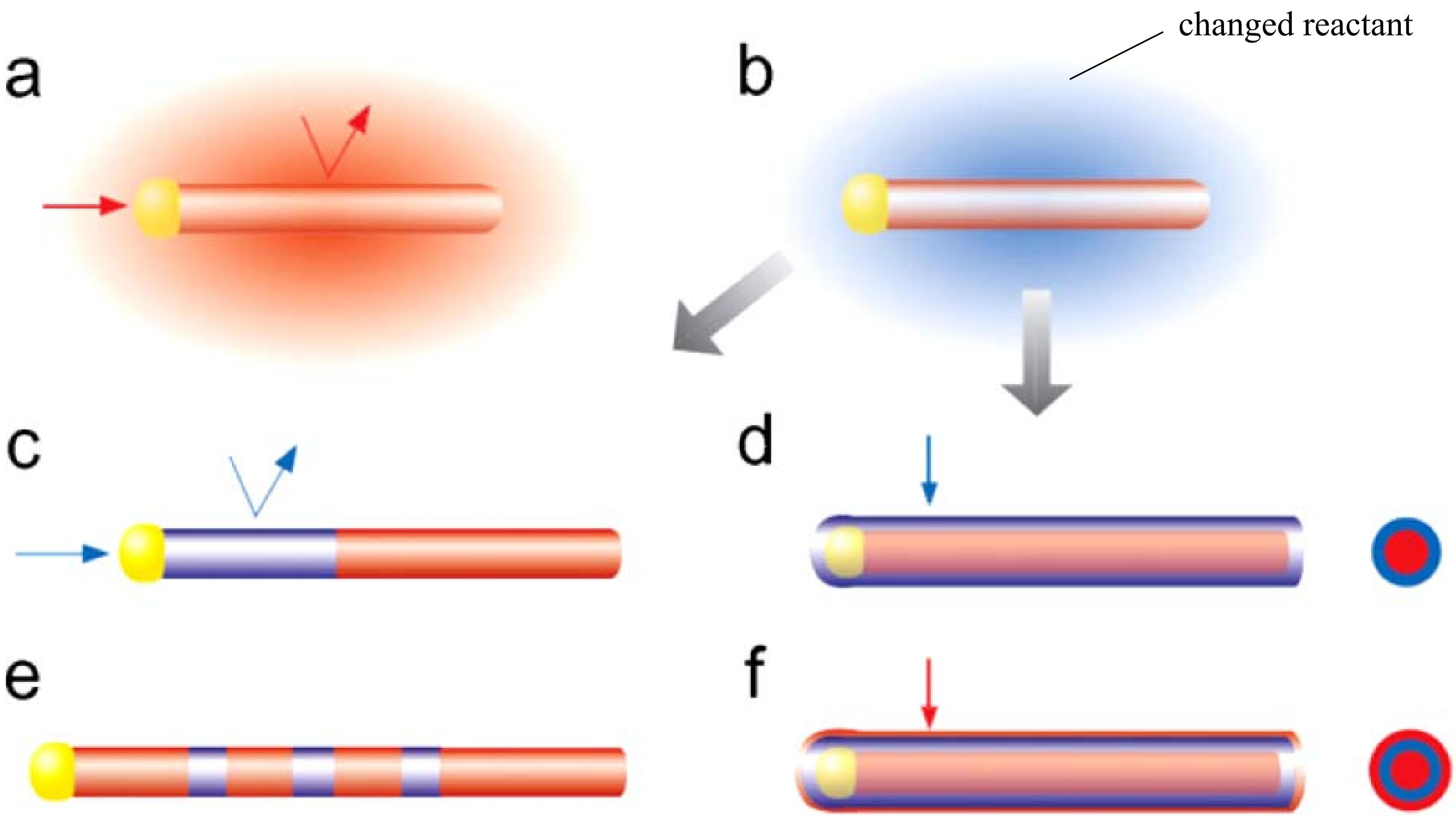
$Cd(S_2CNEt_2)$



photoluminescence (RT)



Nanowire heterostructure synthesis

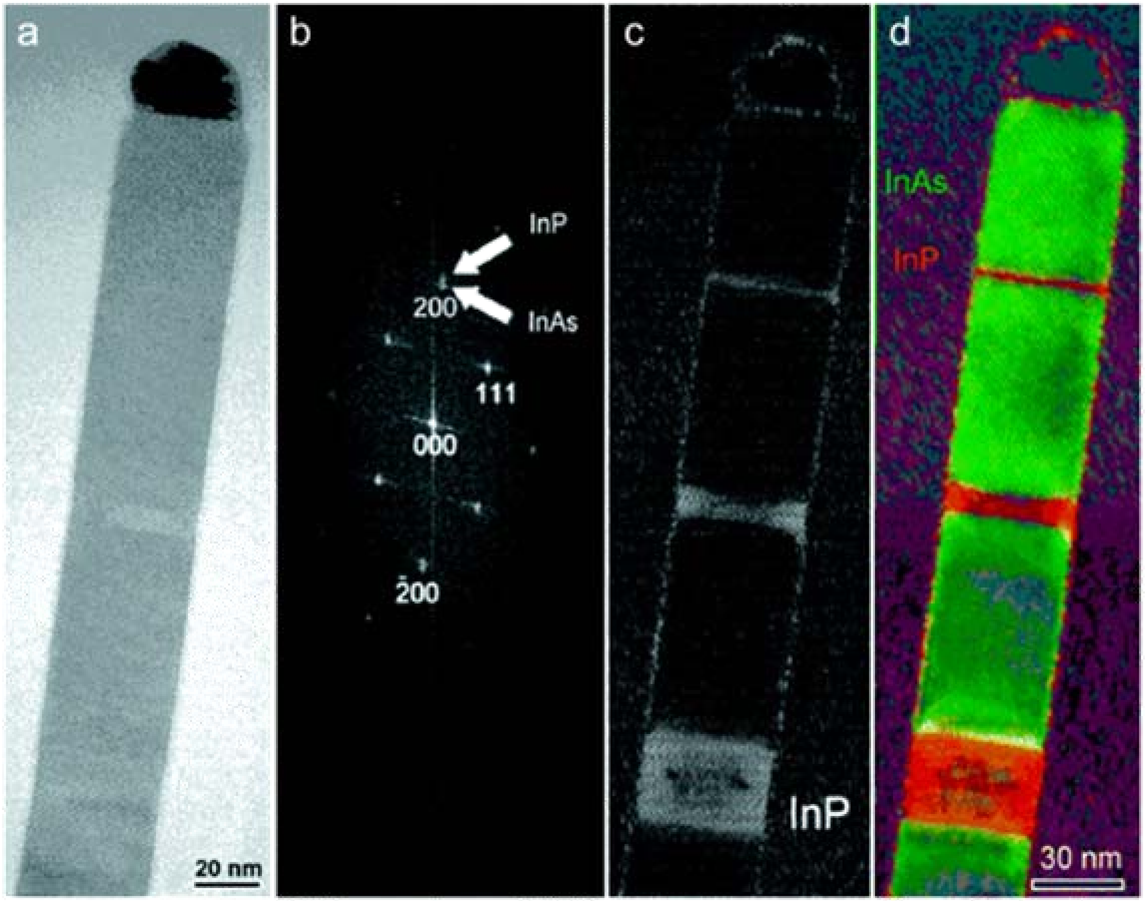


axial heterostructure growth

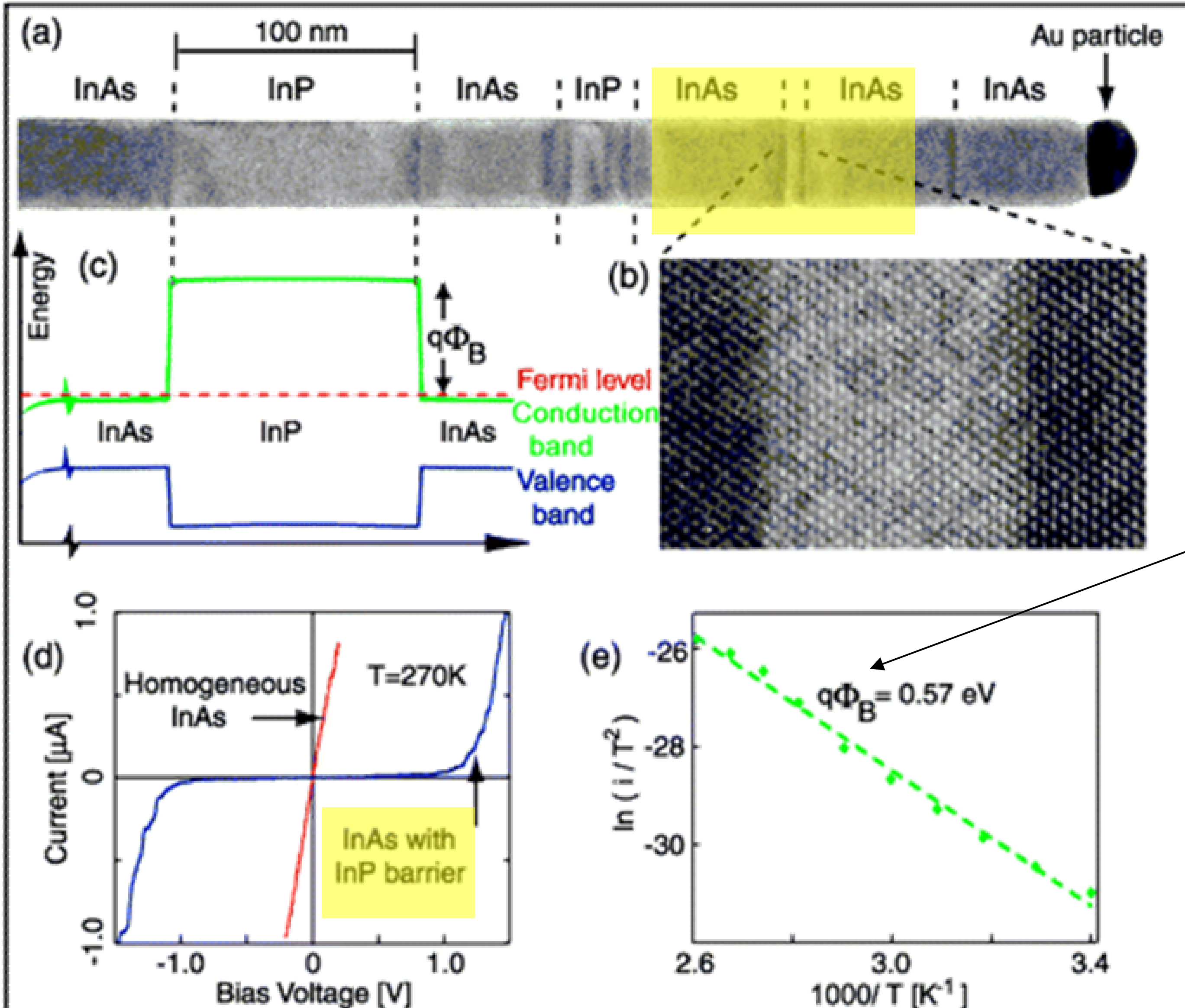
radial heterostructure growth

InAs/InP segmented nano-whiskers

TEM **TED** **Inverse FT** **Superimposed, colour-coded images**



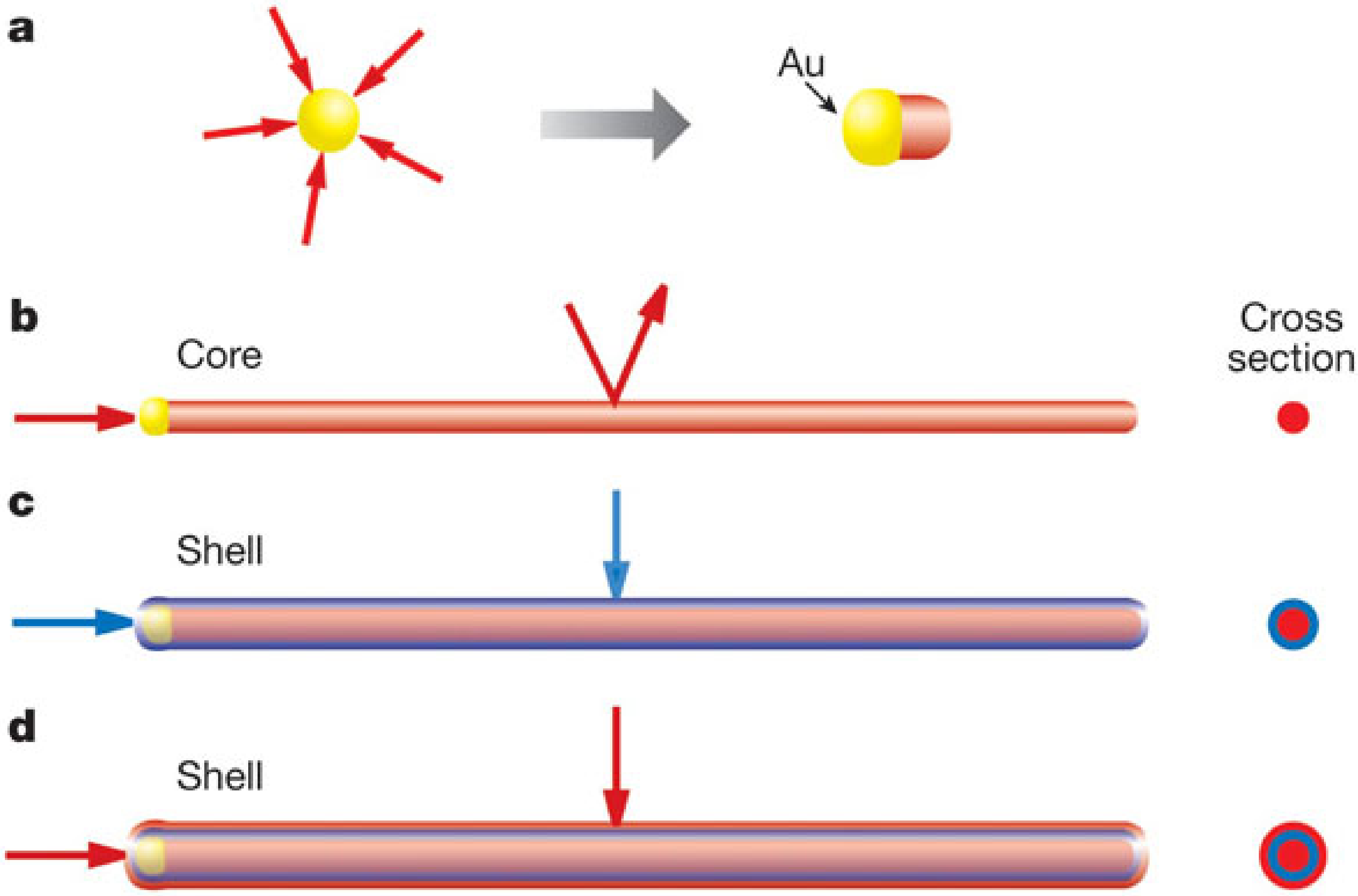
Charge transport over InP barrier



effective barrier height (thermionic excitation)

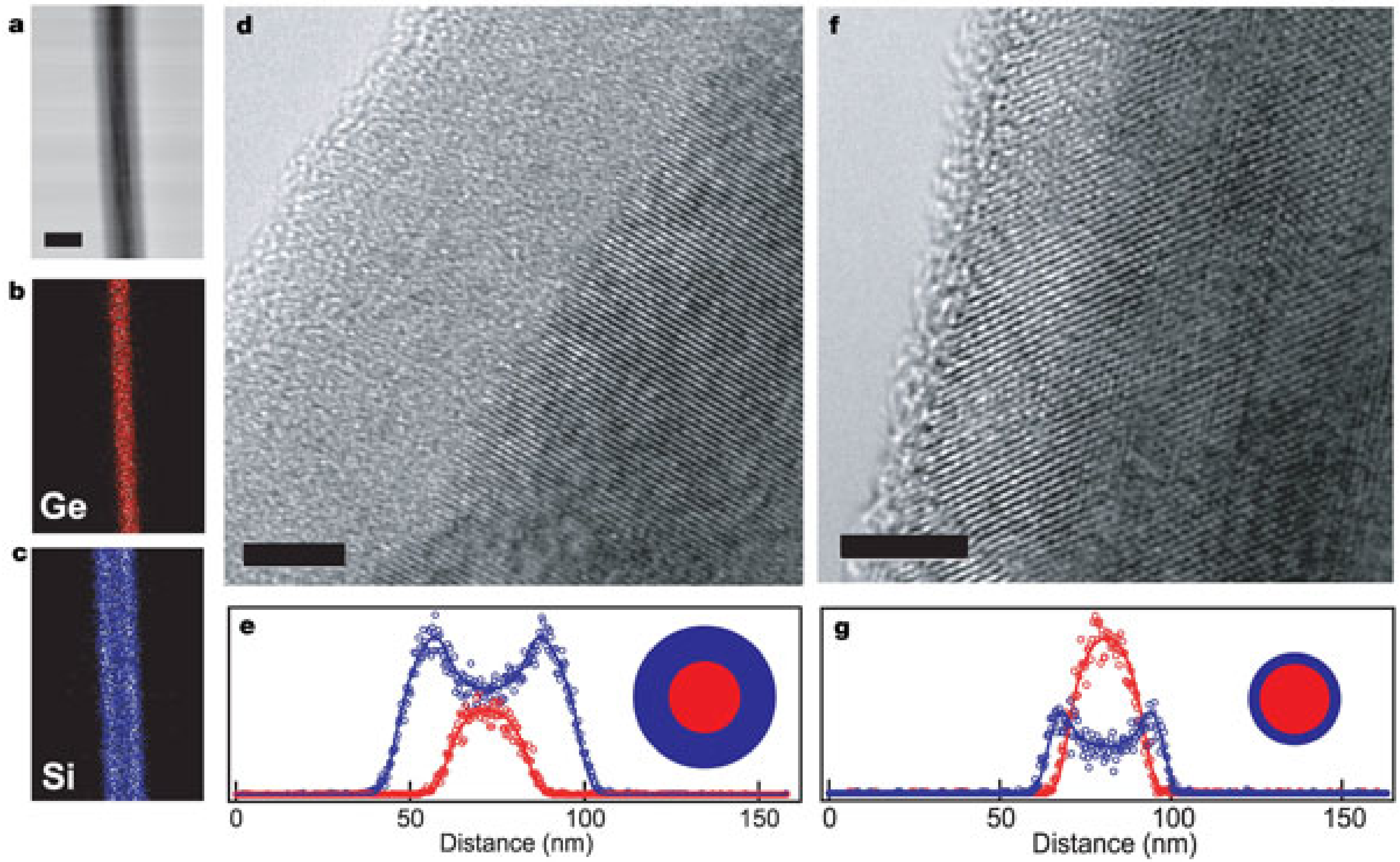
Core-shell semiconductor nanowires

synthesis by chemical vapour deposition:



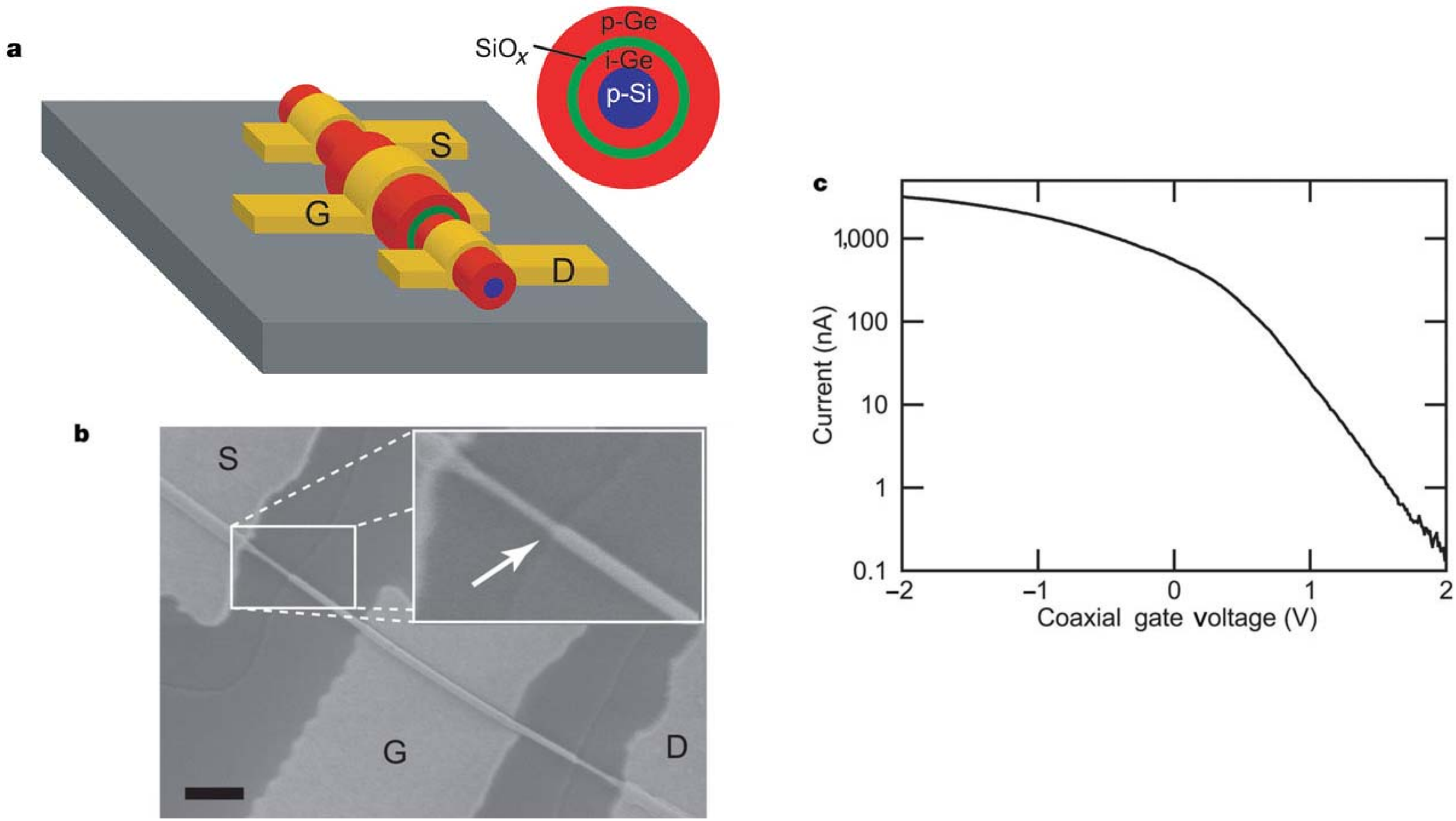
Core-shell semiconductor nanowires

TEM/EDX analysis of Ge-Si core-shell nanowires:



Core-shell semiconductor nanowires

coaxially gated nanowire field-effect transistor from Ge-Si core-shell nanowires :



Electrons confined to nm dimensions

- can the electrons still be considered to be independent ?
- can the electrons still move in all three dimensions ?