

# Nanotechnology

Yung Liou  
P601  
yung@phys.sinica.edu.tw  
Institute of Physics  
Academia Sinica



2nd week



# Background

- Solid state physics
- Quantum physics
- Surface science
- Semiconductor physics
- Thin film
- Analytical chemistry
- Physical chemistry
- Polymer science
- Biology



# Cohesion of solids

- Attractive electrostatic interaction between the negative charges of the electrons and the positive charges of the nuclei.
- The distribution of the outmost electrons and the ion cores.
- Specialized terms: Exchange interaction, van der Waals force and covalent bonds.

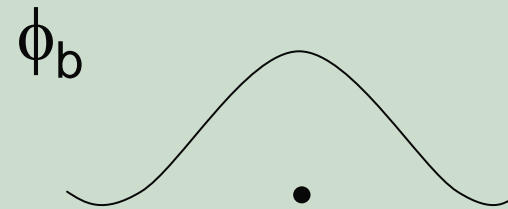
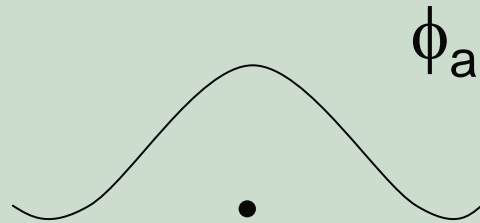


# Van der Waals-London interaction

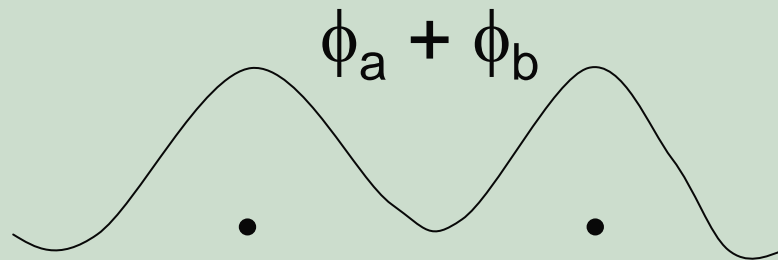
- Dipole moments induce attractive interaction.
- Pauli exclusion principle induce repulsive interaction.
- The cohesive energy of an inert gas crystal is given by summing the Lennard-Jones potential over all pairs of atoms in the crystal.



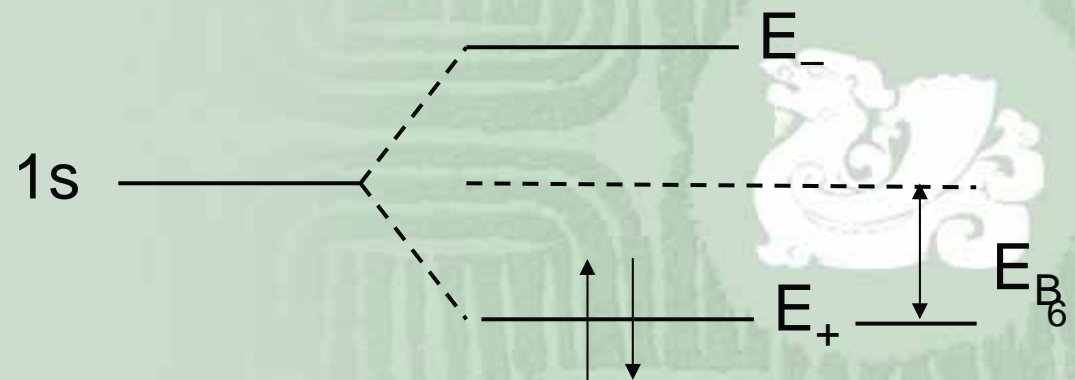
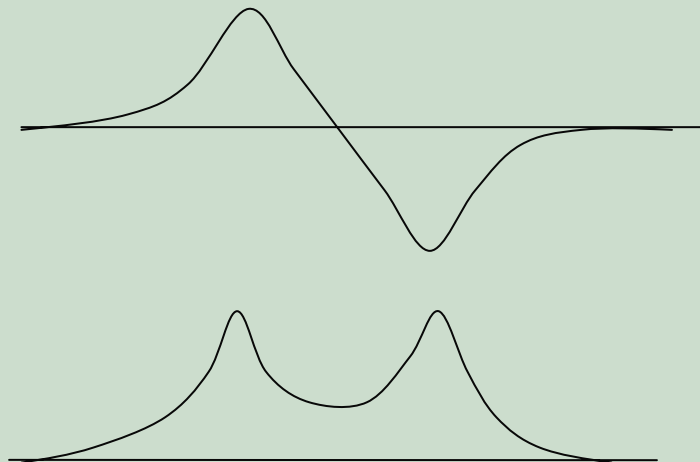
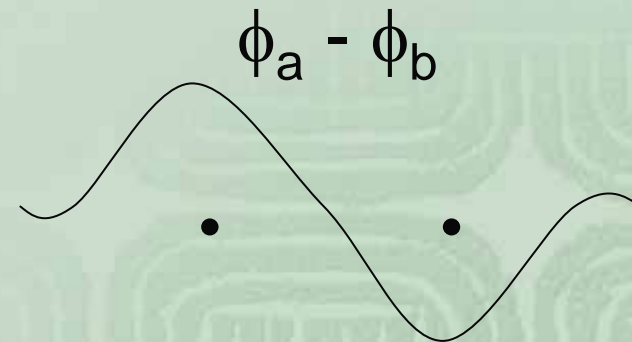
# Pauli exclusion principle



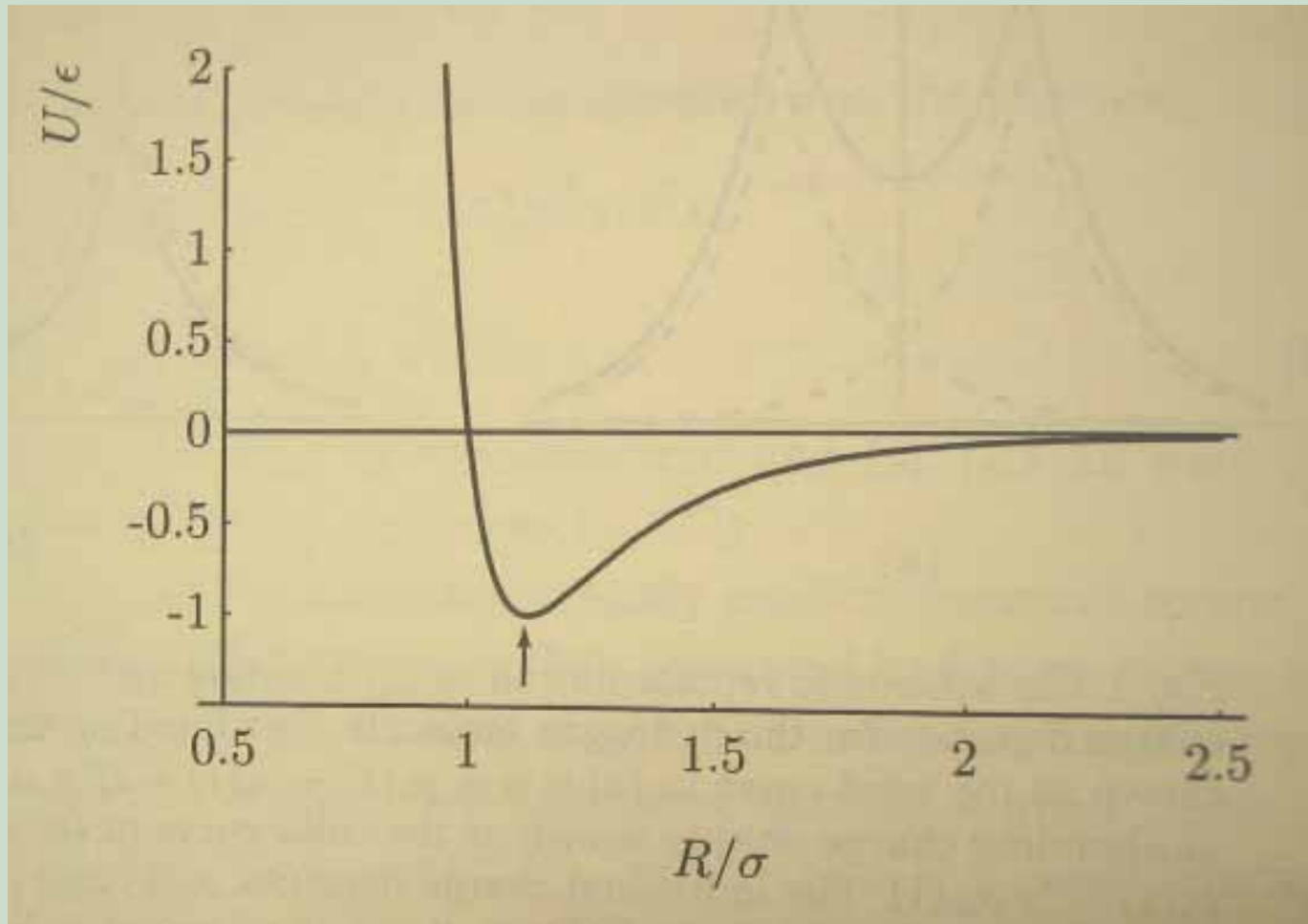
Ground state  
at closer separation



Excited state



# Lennard-Jones potential (interparticle interaction)



$$U = 4\epsilon \left[ \left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^6 \right]$$

Repulsive core :  $R^{-12}$

Attractive tail :  $R^{-6}$

# Crystals of inert gases

- Simplest crystals, transparent insulators, weakly bound, with low melting temperatures.
- The outermost electron shells of the inert gas atoms are completely filled, and the distribution of electron charge in the free atom is spherically symmetric.
- In the crystal the inert gas atoms pack together as closely as possible: the crystal structure are all cubic closed-packed (fcc), except He<sup>3</sup> and He<sup>4</sup>.





# Ionic bonding

- The ionic bond results from the electrostatic interaction of oppositely charged ions.
- The ions arrange themselves in whatever crystal structure gives the strongest attractive interaction compatible with the repulsive interaction at short distance between ion cores.



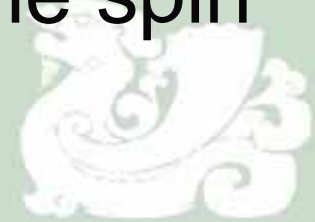
# Covalent bond

- The classical electron pairs or homopolar bond. It is a strong bond, strong direction, with atoms joined to four nearest neighbors at tetrahedral angles, even though this arrangement gives a low filling of space, 0.34 of the available space, compared with 0.74 for a close-packed structure.



# Exchange interaction

- Spin-dependent coulomb interaction.
- The strongest binding occurs when the spins of the two electrons are anti-parallel.
- The binding depends on the relative spin orientation not because there are strong magnetic dipole forces between the spins, but because the Pauli principle modifies the distribution of charge according to the spin orientation.



# Metals

- High electric conductivity, large number of electrons in a metal are free to move about, usually one or two per atom.
- The valence electrons of the atom become the conduction electrons of the metal.
- The bond formed by a conduction electron is not very strong.
- Metals tend to crystallize in relatively close packed structures: fcc, bcc, hcp.
- In transition metals there is additional binding from inner electron shells (d-electron shells).



# Hydrogen bond

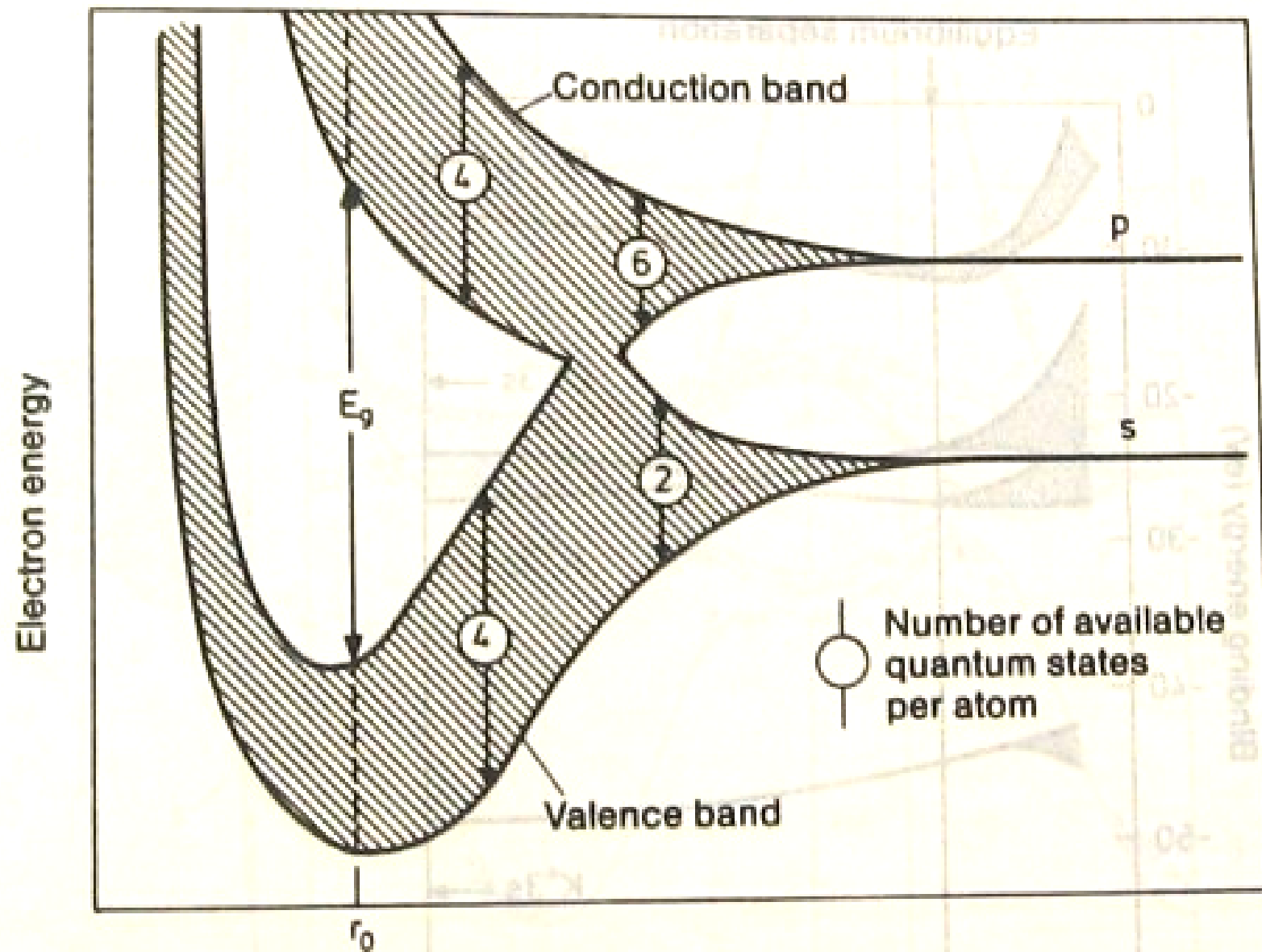
- Ionic in character.
- It is an important part of the interaction between water molecules.
- It is important in certain ferroelectric crystals.



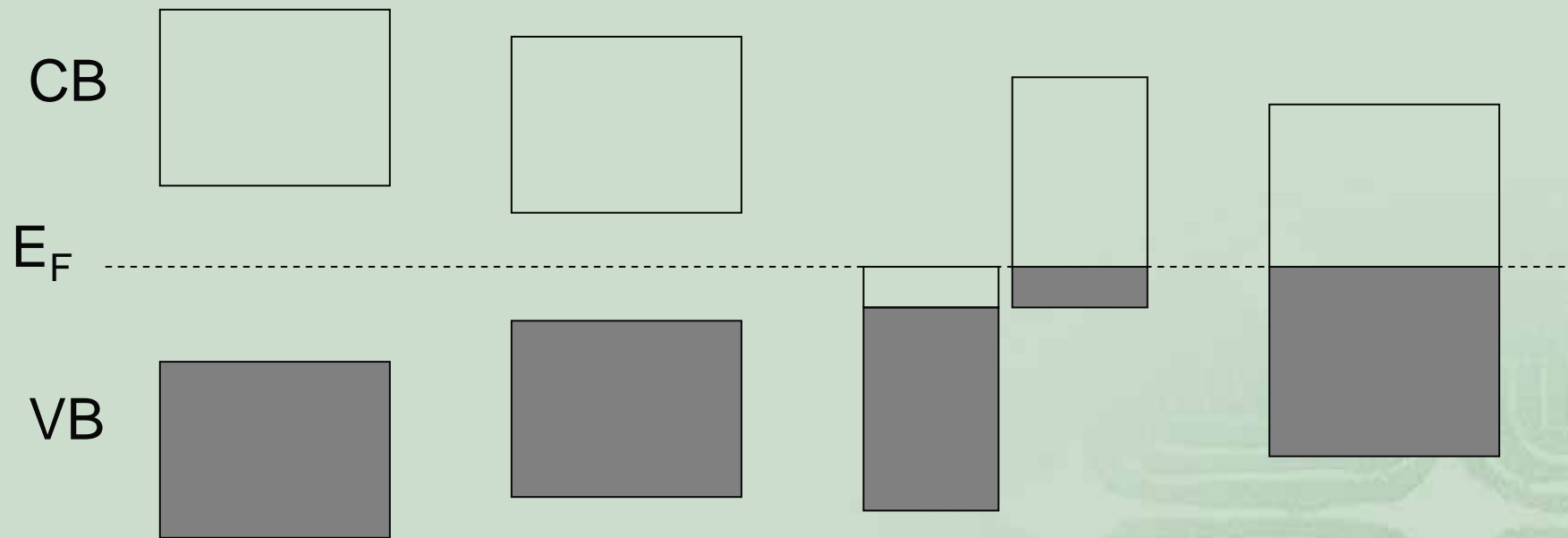
# Energy band

- Electrons in crystals are arranged in energy bands separated by regions in energy for which no wavelike electron orbital exist. Such forbidden regions are called energy gaps or band gaps.
- Large number of atoms are closed to each other and formed a crystal, their interaction with one another lead to a splitting of each of their energy levels and the energy levels will lie on a quasicontinuous scale, energy bands.
- The width of the band depends on the overlap of the wavefunctions (electron) concerned.





Interatomic distance



Insulators

Semiconductors

Metals or  
semimetals

Metals





# Bulk Crystal Structures

- 2-D: 5 types, square, hexagonal, rectangular, centered rectangular (x2).
- 3-D: 14 types, triclinic, monoclinic, orthorhombic, tetragonal, cubic, trigonal, hexagonal.
- Cubic: simple cubic, body-center cubic (bcc), face-center cubic (fcc).



# Surface of Crystals

- Surface: the few (2 - 10) outermost atomic layers (10 – 100 nm) of a solid.
- Surface dangling bonds, surface states, surface energy.
- Surface structure reconstruction, relaxation.
- Steps, defects.



# Material analysis

- Structure, morphology: XRD, SEM, TEM, luminescence (CL, PL), Raman.
- Composition: ICP-MS, Atomic absorption & emission spectrometry, XRF, FTIR, NMR.
- Surface & electronic structures: AES, XPS, RBS, SIMS, STM, AFM.
- Transport (electric conductivity): Hall effect, 4-point measurement.
- Magnetism: VSM, SQUID, EPR, FMR.



# Nanostructures

- When the extent of a solid is reduced in one or more dimensions, the physical, magnetic, electrical and optical properties can be dramatically altered.
- 1 D: carbon nanotubes, quantum wires and conducting polymers.
- 0 D: semiconductor nanocrystals, metal nanoparticles and lithographically patterned quantum dots.



**Table 1** Nanostructures and their assemblies.

Nanostructure	Size	Material
Clusters Nanocrystals Quantum dots	Radius: 1–10 nm	Insulators, semiconductors, metals, magnetic materials
Other nanoparticles	Radius: 1–100 nm	Ceramic oxides
Nanobiomaterials Photosynthetic reaction center	Radius: 5–10 nm	Membrane protein
Nanowires	Diameter: 1–100 nm	Metals, semiconductors, oxides, sulfides, nitrides
Nanotubes	Diameter: 1–100 nm	Carbon, layered chalcogenides
Nanobiorods	Diameter: 5 nm	DNA
2D arrays of nanoparticles	Area: several nm <sup>2</sup> –μm <sup>2</sup>	Metals, semiconductors, magnetic materials
Surfaces and thin films	Thickness: 1–1000 nm	Insulators, semiconductors, metals, DNA
3D superlattices of nanoparticles	Radius: several nm	Metals, semiconductors, magnetic materials

# Definition of Nanoparticles

- A particle with sufficiently small diameter for physical and chemical properties to differ measurably from those of the bulk material.
- Agglomerate: A group of particle held together by relatively weak forces, including Van der Waals forces, electrostatic forces and surface tension.
- Aggregate: A heterogeneous particle in which the various components are not easily broken apart.

# Properties of Nanoparticles

- Electronic structures: Discrete energy levels.
- Size effect: Quantum confinement, blue shift in optical absorption.
- Surface effect: Surface property dominant, surface catalysis.
- Shape effect: Specific stable shapes, structures.



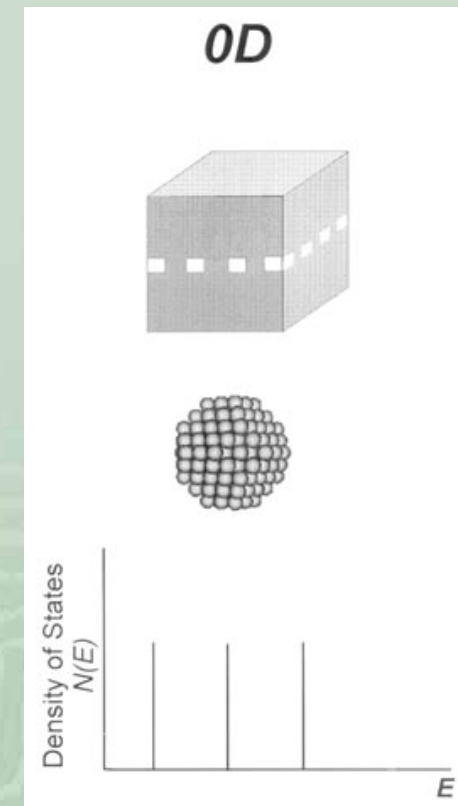
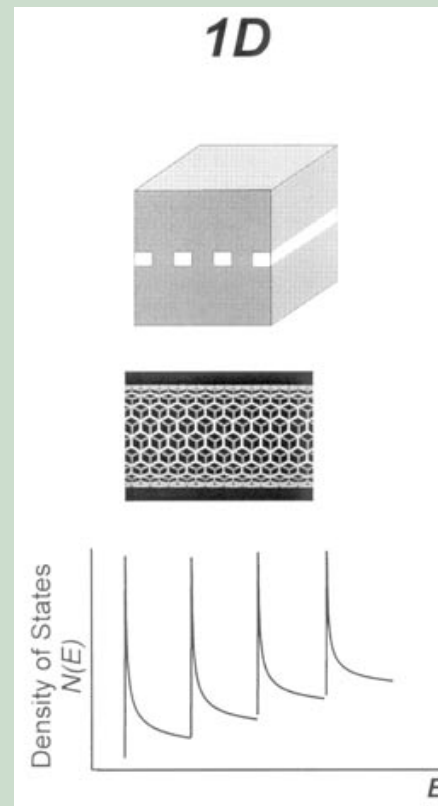
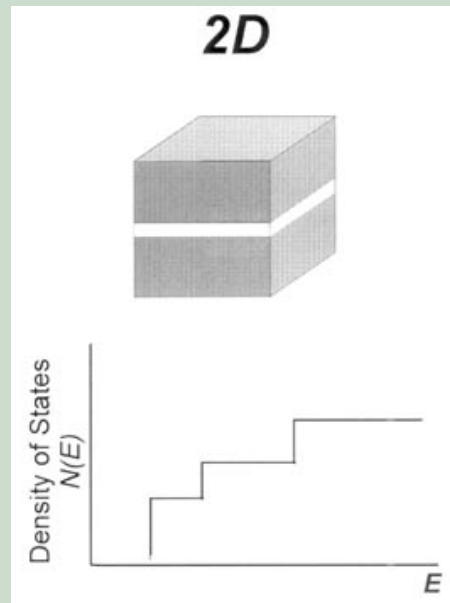
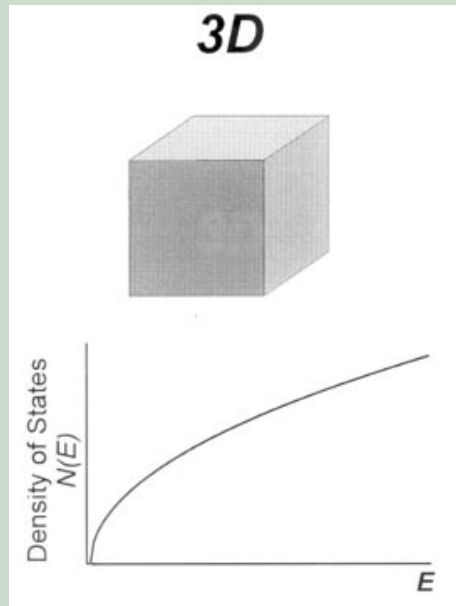
# Electronic structure of 0 D

- Quantized energy levels: A system of electrons fully confined in all three dimensions will have discrete charge and electronic states, as do atoms and molecules.
- Eigenstates and eigenenergies:  $E_{n,l,m} = E_{n,l}$ ;  
 $(r, \theta, \phi) = Y_{l,m}(\theta, \phi) R_{n,l}(r)$ .





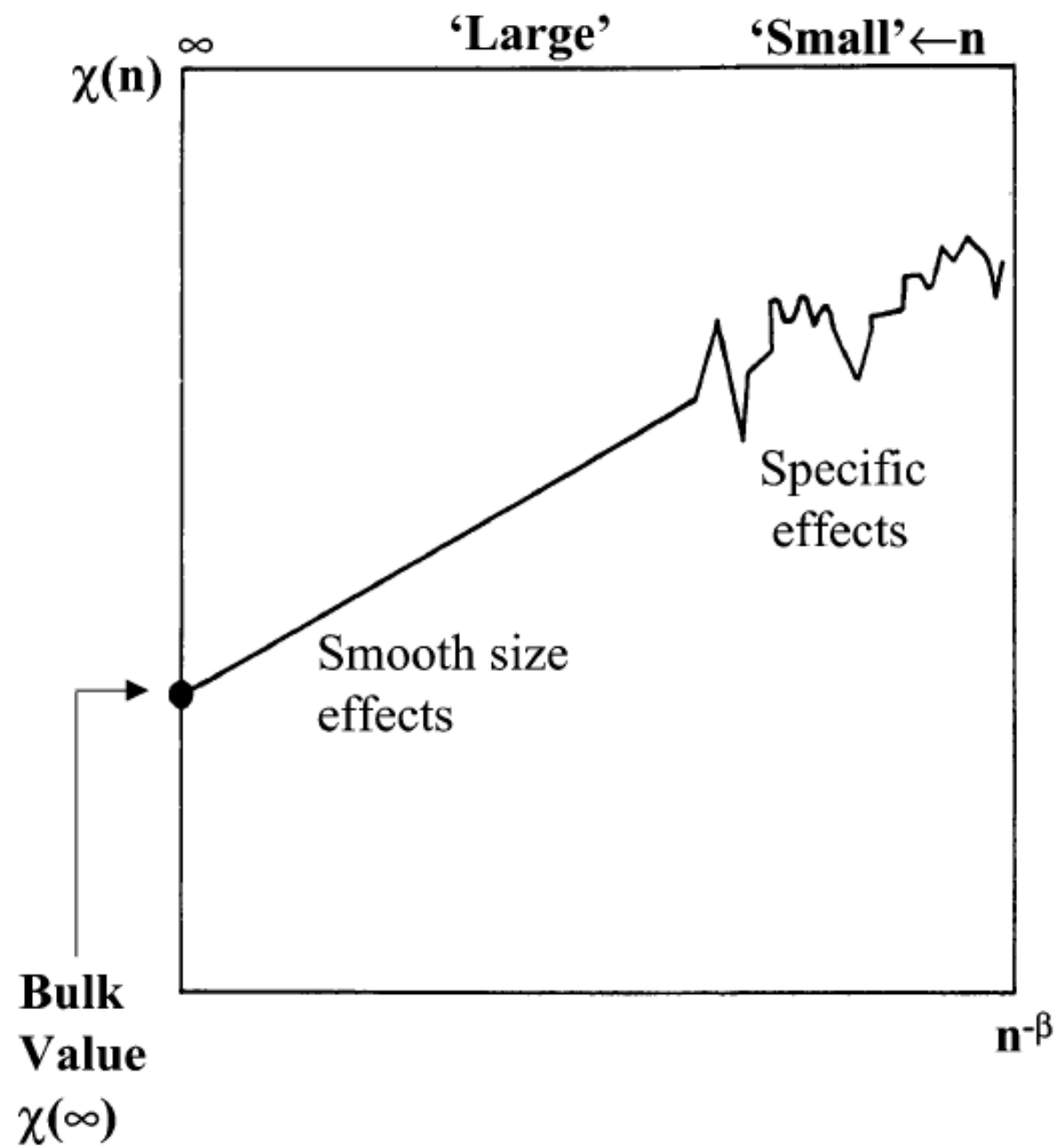
# Changes of electronic density of states



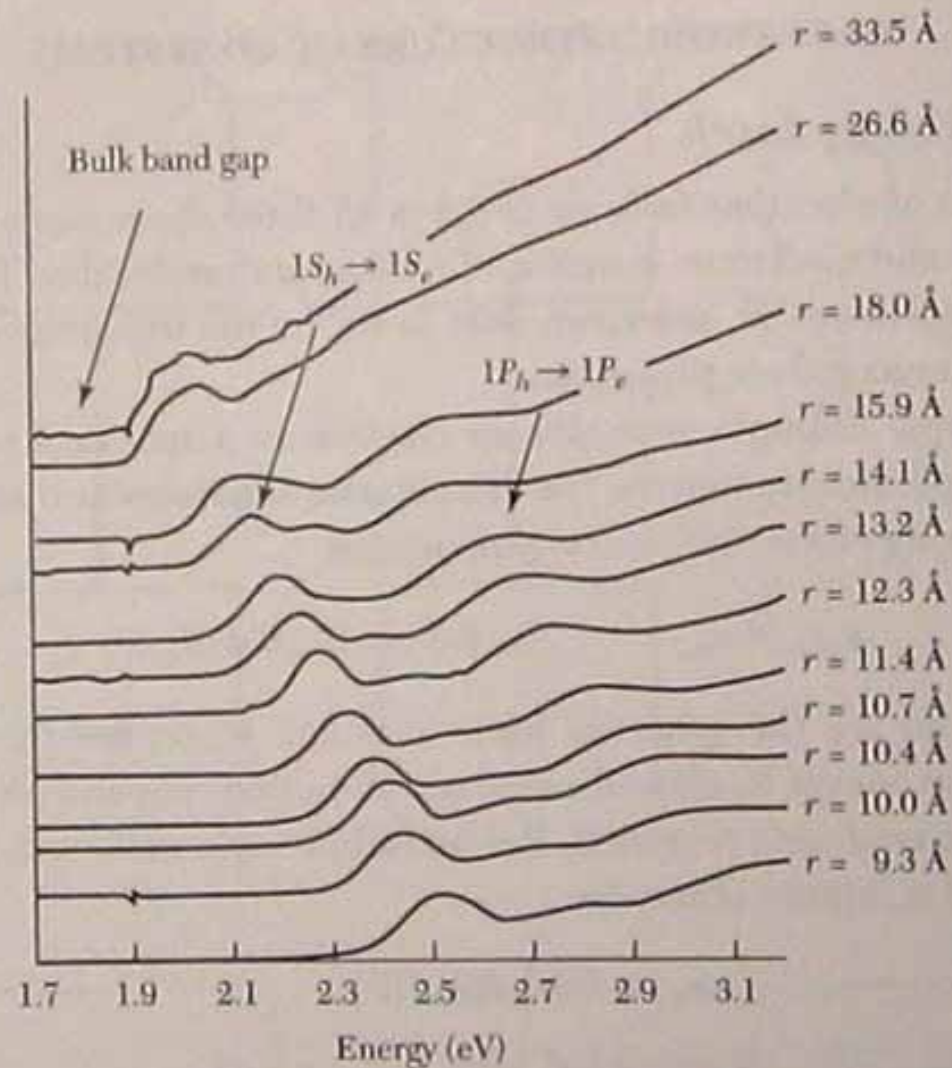
# Size effects

- Specific size effects: These involve self-selection and existence of magic numbers for small and moderately sized clusters and nanostructures.
- Smooth size effects for large nanostructures.
- Coulomb blockade: The staircase for the charging energy indicating the discrete electronic levels.
- Confinement: Boundary effects on electrons or excitons.



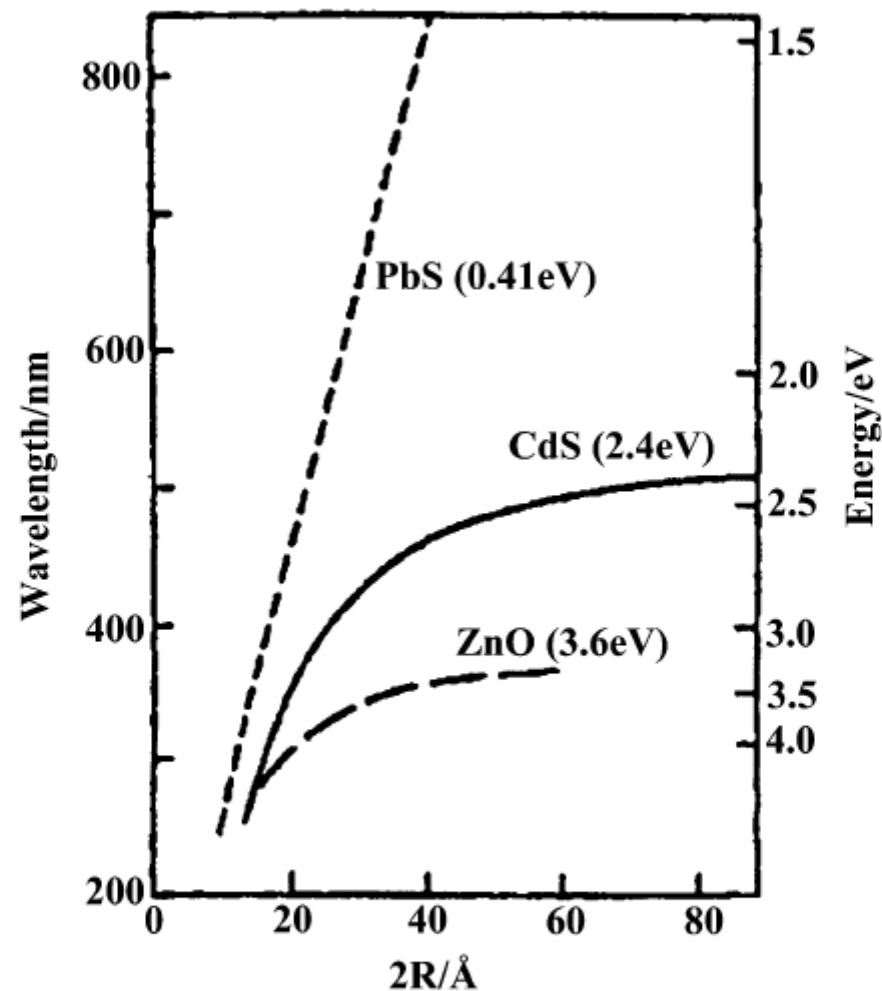


# Optical absorption of CdSe



**Figure 19** Optical absorption spectra for a series of CdSe nanocrystal samples of different average radii. The lowest transition energy in the smallest nanocrystal sample is shifted by nearly 1 eV from the bulk bandgap. Two dominant transitions are labeled. (Courtesy of A. P. Alivisatos.)

# Size-dependent of optical absorption



**Fig. 4** Size dependence of the wavelength of the absorption threshold in semiconductors manifesting exciton confinement. [Reproduced by permission from A. Henglein, *Ber. Bunsen-Ges. Chem.* **99**, 903 (1995). Copyright VCH 1995.]

# Quantum confinement in nanocrystalline Si quantum dots

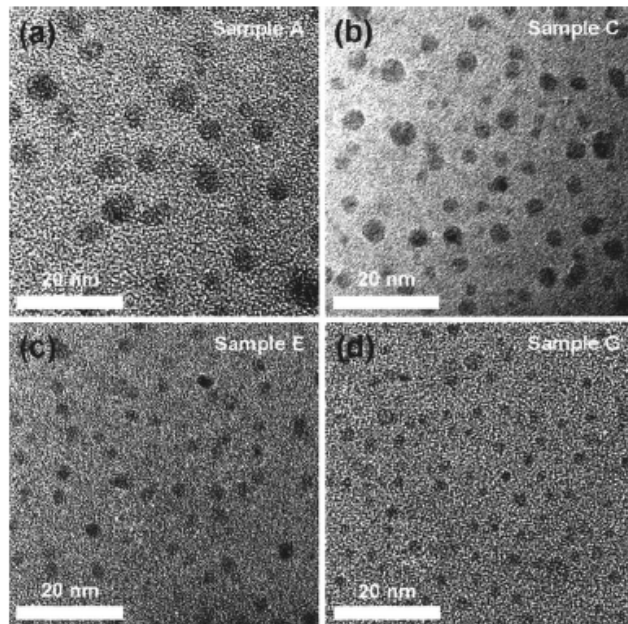


FIG. 2. TEM images of (a) sample A, (b) sample C, (c) sample E, and (d) sample G of the Si QDs embedded in silicon nitride films for measurement of the Si QD size.

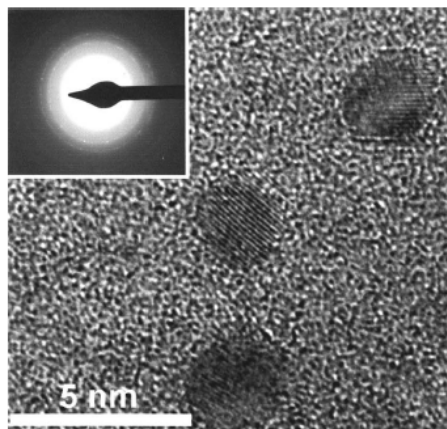


FIG. 3. (a) HRTEM image of crystalline Si QDs. The inset shows the ring patterns for the TED from crystalline Si QDs.

T. -W. Kim,  
APL 88, 123102 (2006).

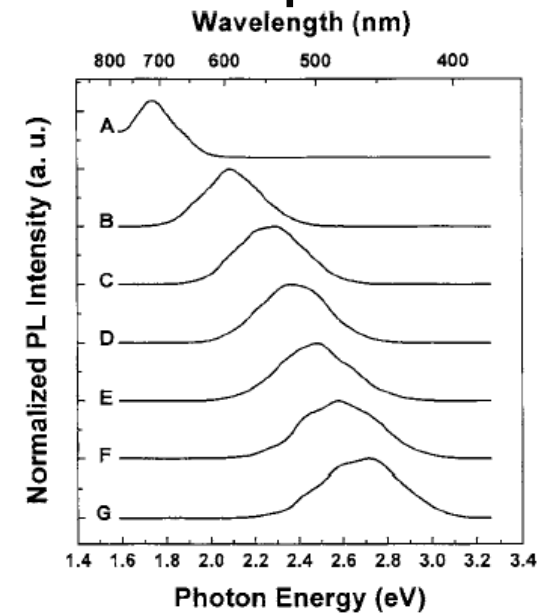


FIG. 1. Room-temperature PL spectra of Si QDs in silicon nitride. The peak energy was controlled by appropriate adjustment of the flow rate of the  $\text{NH}_3$  gas and the chamber pressure.

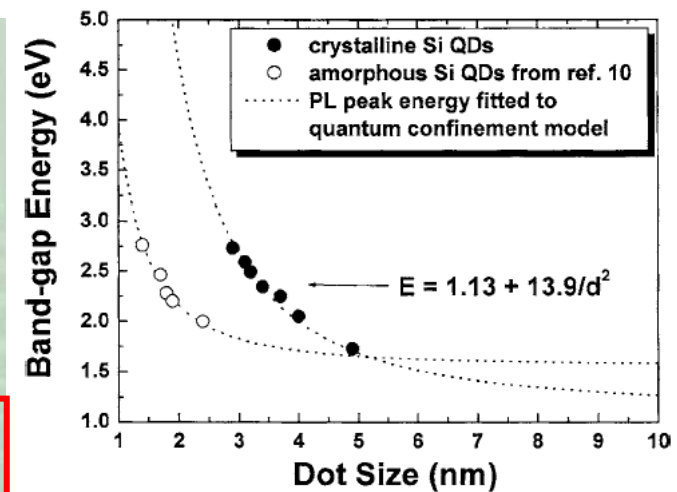
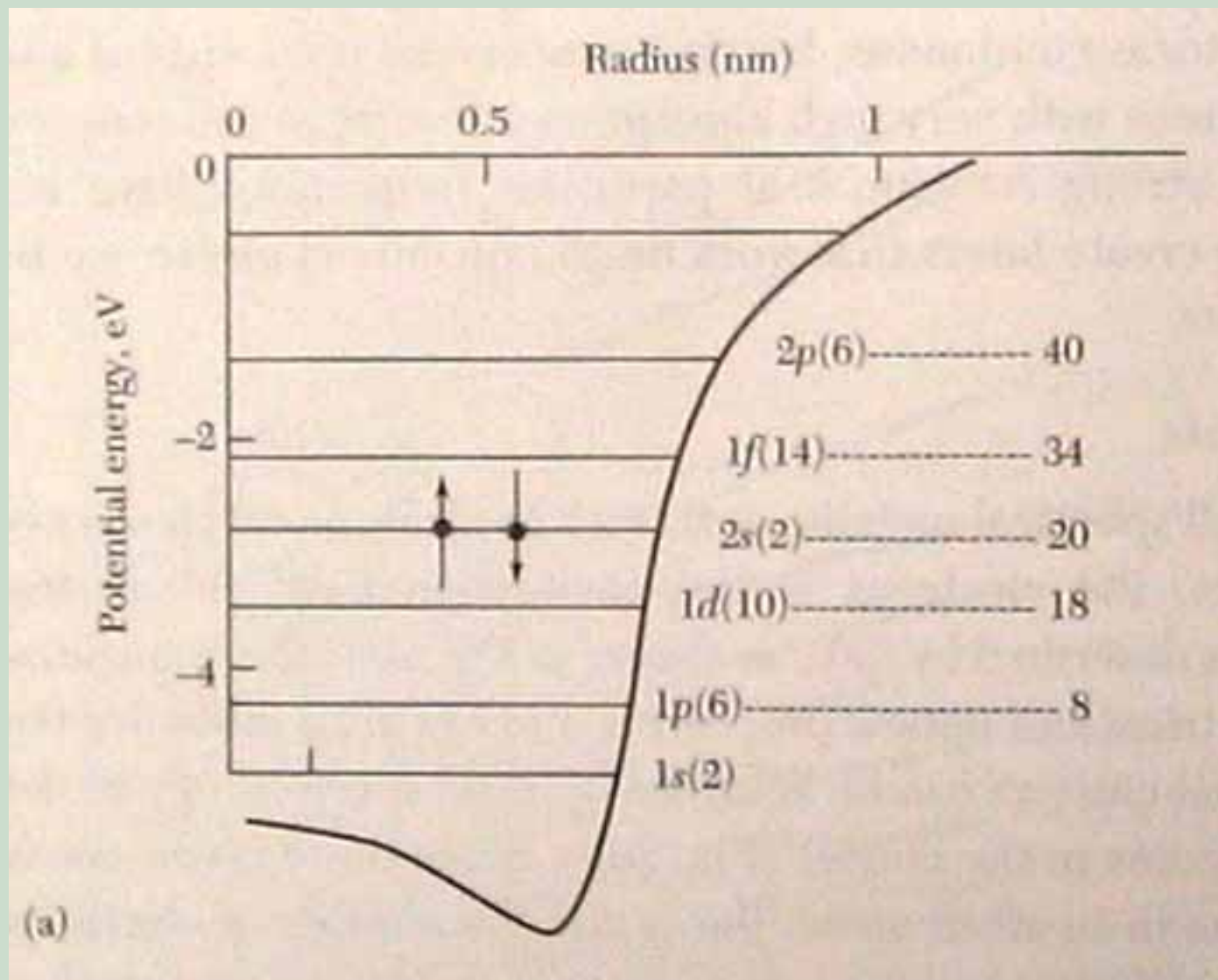


FIG. 4. PL peak energy for crystalline Si QDs as a function of dot size. Dotted lines are fitted curves for amorphous Si QDs and crystalline Si QDs. The filled and open circles are data points obtained for crystalline and amorphous Si QDs, respectively.

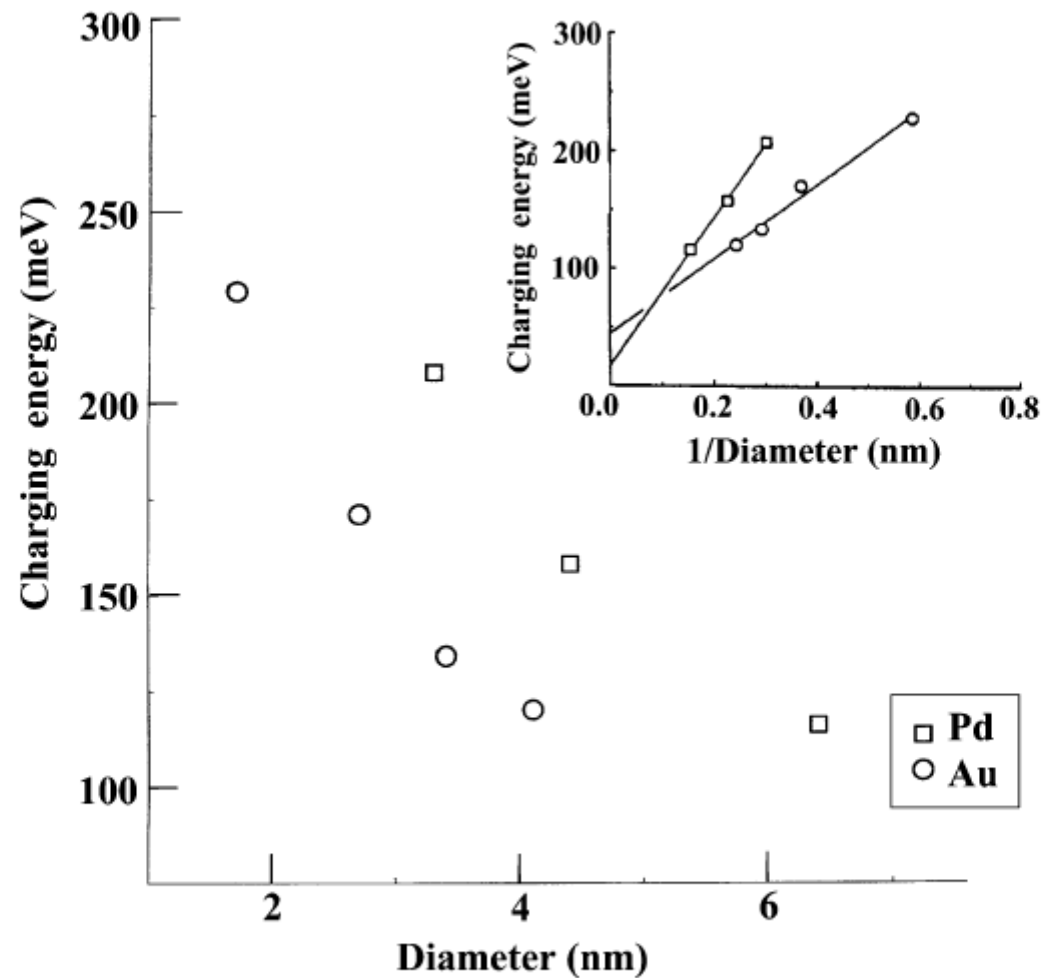


# Metallic dots

Energy levels for small spherical alkali metallic cluster.



# Coulomb-blockade charging energy



**Fig. 3** Size dependence of the nonmetallic gap for Pd nanocrystals. The insert shows the dependence of the charging energy on the reciprocal nanocrystal diameter [57].

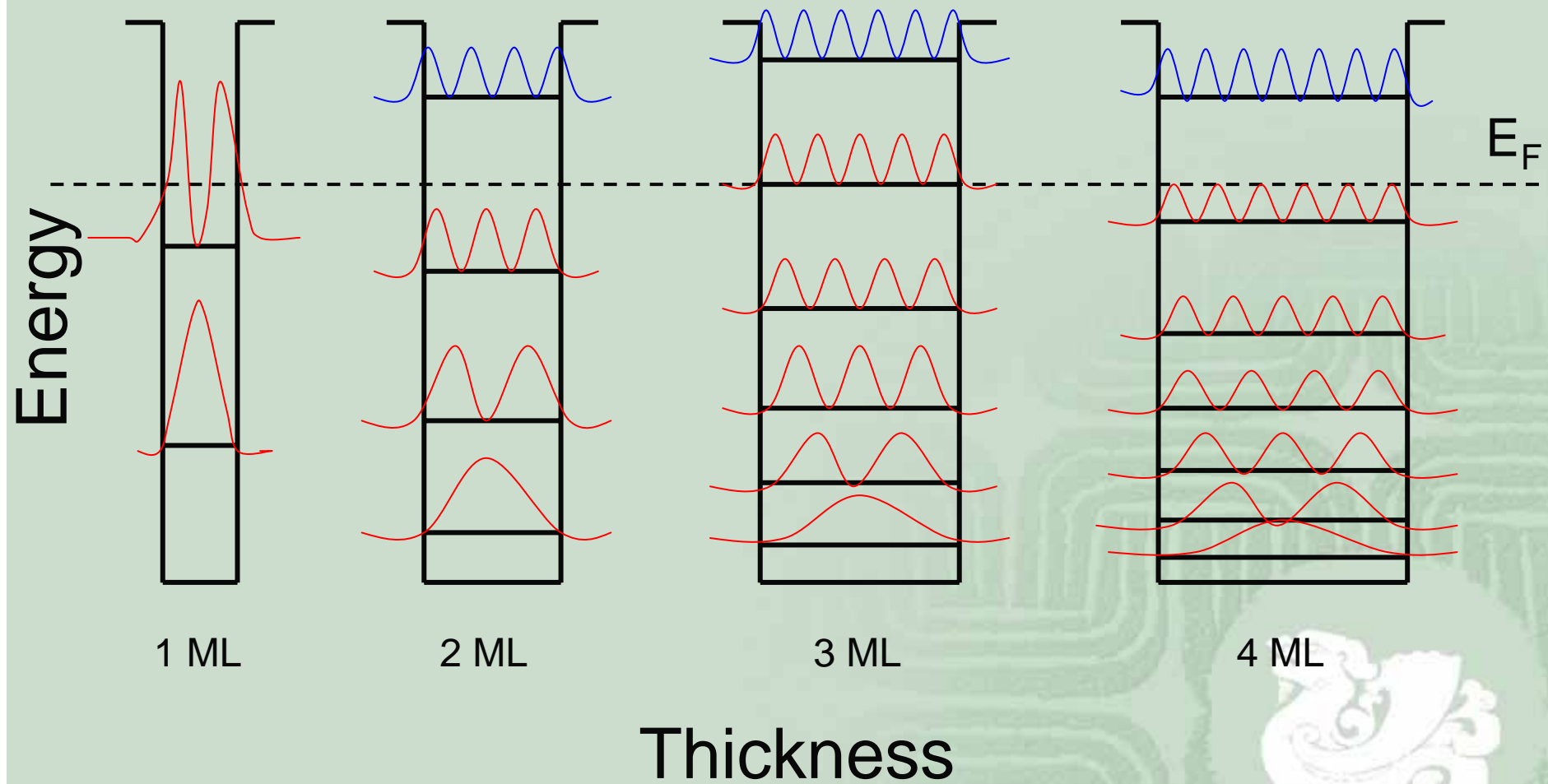


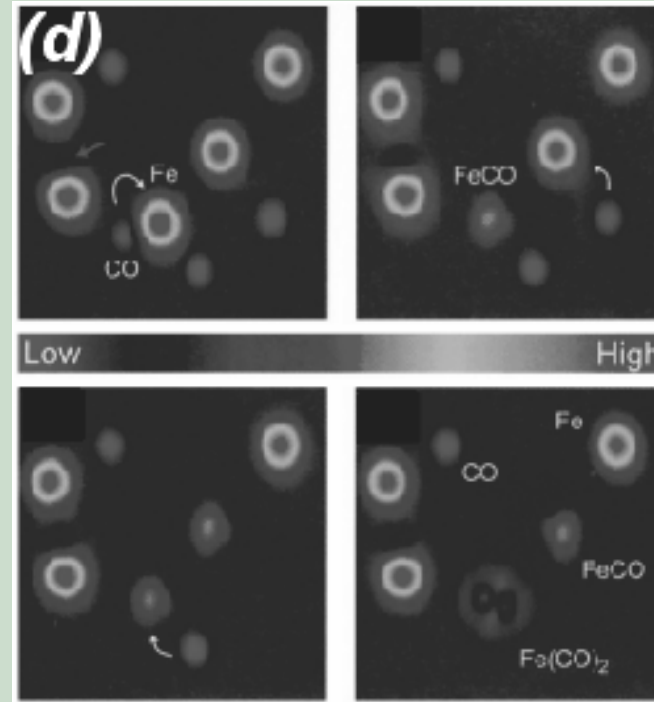
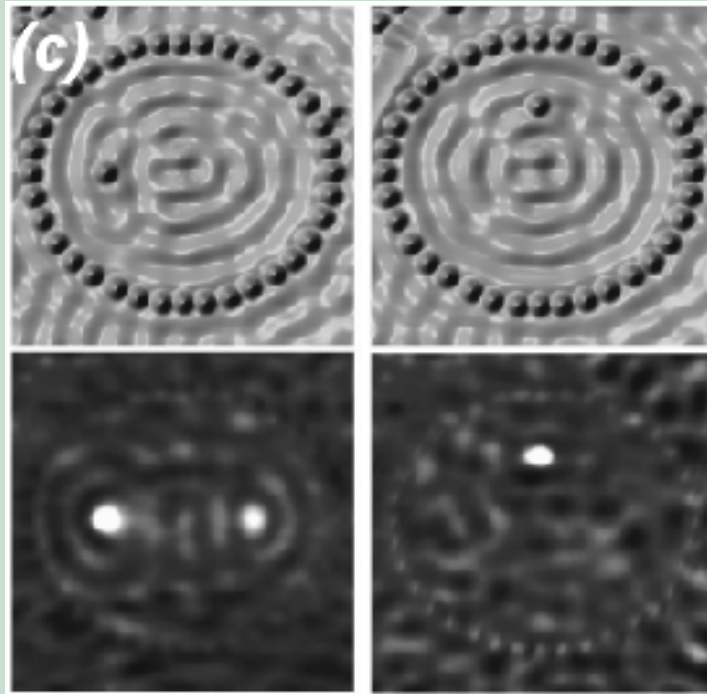
# Quantum Size Effects in Metallic Nanostructures

- Physics Today April 2007, p50.
- In a thin film, the quantization of the wave functions divides the continuous band into discrete subbands.



# Confined electron wavefunctions in thin metal films





(c) quantum mirages—the upper images are conventional topographic STM data whereas the lower images are  $dI/dV$  maps. In the topographic images on the left and right, an individual magnetic impurity (a Co atom) has been positioned within an elliptical corral formed from Co atoms. When the single Co atom is at a focus of the ellipse, the spectroscopic signature associated with the Kondo effect is projected to the other focus (the spectroscopic map on the left). When the Co atom is moved off focus the spectroscopic signature (the ‘quantum mirage’) vanishes the  $dI/dV$  map on the right) (Manoharan *et al* 2000).

(d) Synthesis of individual molecular complexes. Both an FeCO and an Fe(CO)<sub>2</sub> molecule have been synthesized (Lee and Ho 1999).

# Shape effects

- Symmetry-breaking: Structural deformations affect the electronic structure and charge density.
- Collective excitation: Shape deformation induced plasmon-collective vibration excitations.



# Surface effect

- Large ratio of number of surface atoms to bulk atoms in a nanostructure.
- For a spherical nanoparticle of radius  $R$  composed of atoms with an average spacing  $a$ , the ratio is  $N_{\text{surf}}/N = 3a/R$ . For  $R = 6a \sim 1 \text{ nm}$ ,  $N_{\text{surf}}/N \sim 1/2$ , half of the atoms are on the surface.



# Surface effect

Diameter (nm)	Total number of atoms	Atoms on surface	% Surface
50	$3 \times 10^6$	$1 \times 10^5$	3
25	$4 \times 10^5$	$2 \times 10^4$	6
12	$5 \times 10^4$	$6 \times 10^3$	12
7	5000	1200	24
5	3000	900	30
4	1000	360	40
3	500	250	50
2	150	90	60
1	30	25	85



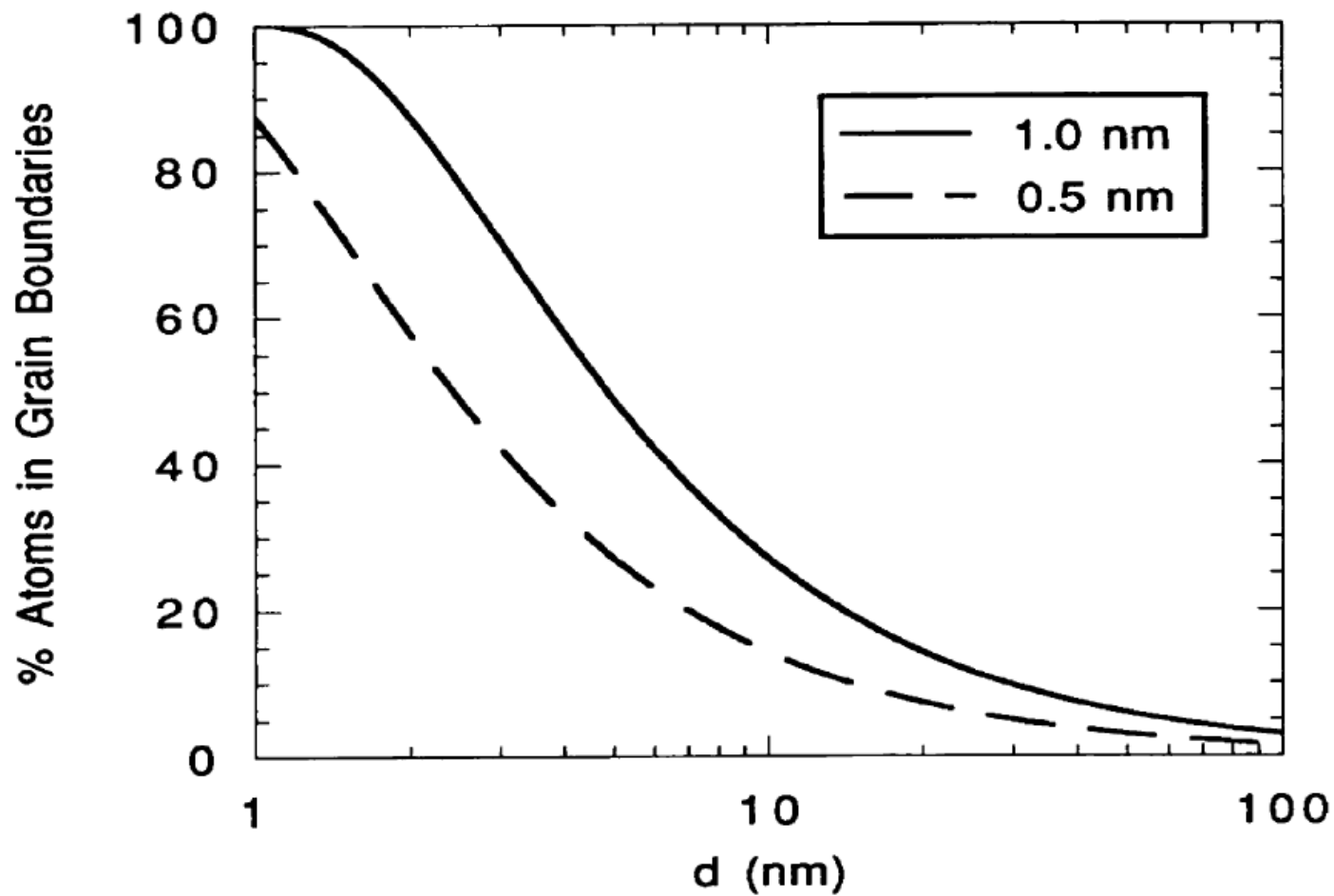




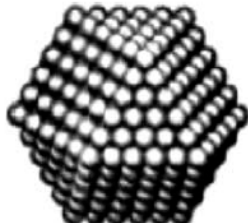



Fig. 5. Range of percentage of atoms in grain boundaries of a nanocrystalline solid as function of grain diameter, assuming that the average grain boundary thickness ranges from 0.5 to 1.0 nm (reprinted from [20] with permission from Annual Review Inc.)

Table 1

The relation between the total number of atoms in full shell clusters and the percentage of surface atoms (reprinted from [5] with permission from John Wiley & Sons)

Full shell clusters	Total number of atoms	Surface atoms (%)
One shell 	13	92
Two shells 	55	76
Three shells 	147	63
Four shells 	309	52
Five shells 	561	45
Seven shells 	1415	35



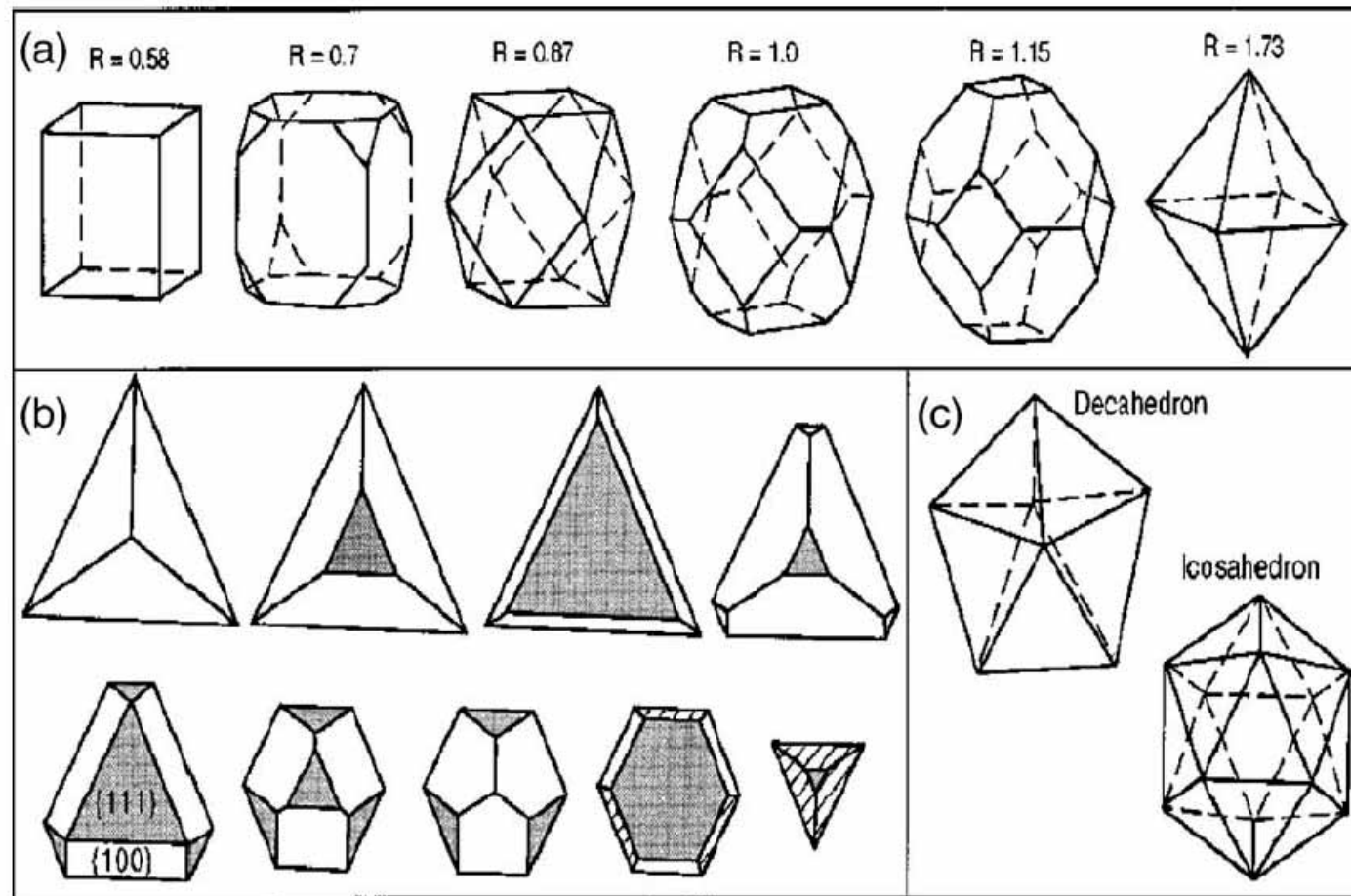
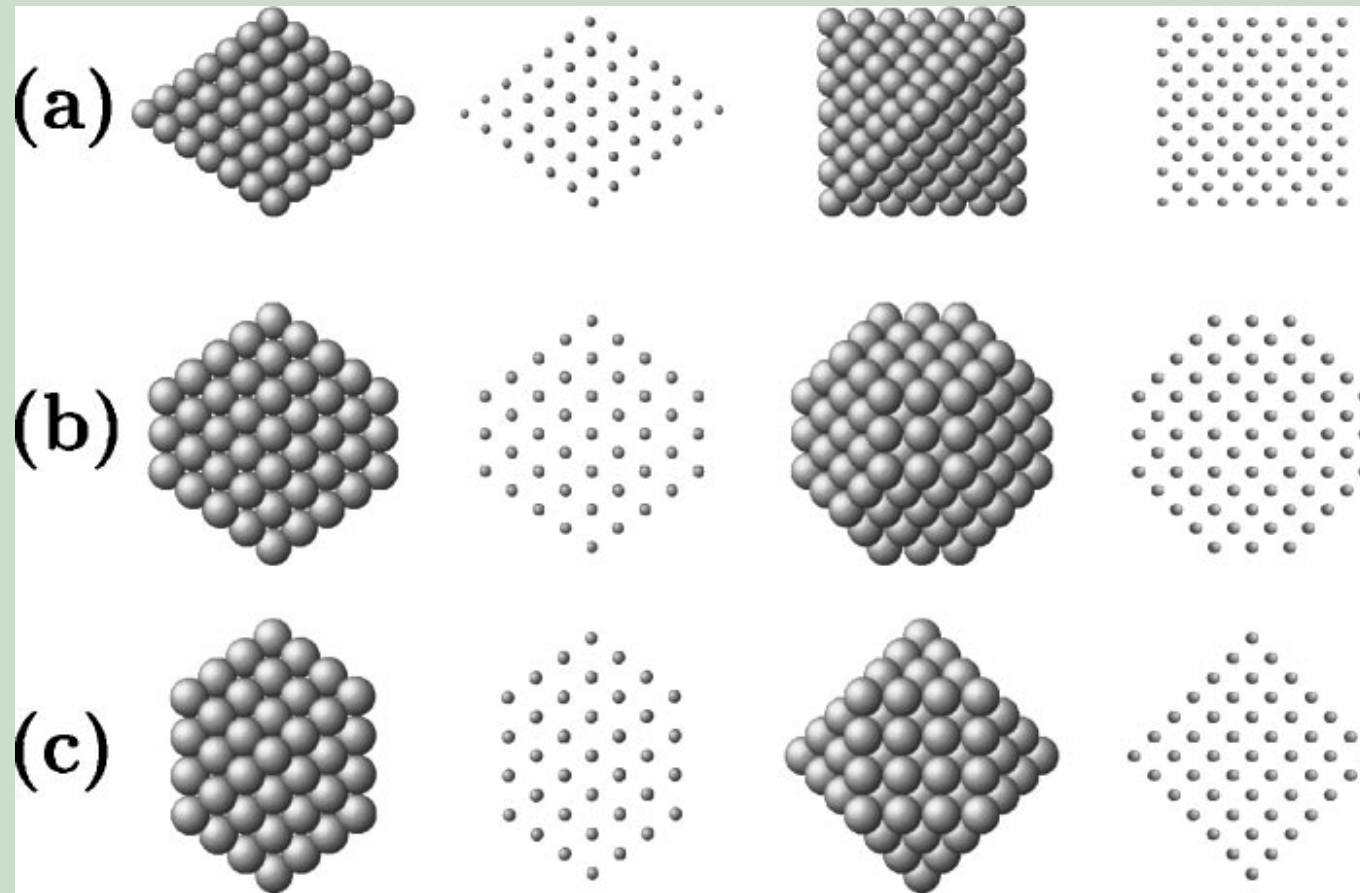


Fig. 2. (a) Geometrical shapes of cubooctahedral nanocrystals as a function of the ratio,  $R$ , of the growth rate along the  $(1\ 0\ 0)$  to that of the  $(1\ 1\ 1)$ . (b) Evolution in shapes of a series of  $(1\ 1\ 1)$  based nanoparticles as the ratio  $\{1\ 1\ 1\}$  to  $\{1\ 0\ 0\}$  increases. The beginning particle is bounded by three  $\{1\ 0\ 0\}$  facets and a  $(1\ 1\ 1)$  base, while the final one is a  $\{1\ 1\ 1\}$  bounded tetrahedron. (c) Geometrical shapes of multiply twinned decahedral and icosahedral particles (reprinted from [10] with permission from American Chemical Society).

# Nanocrystals

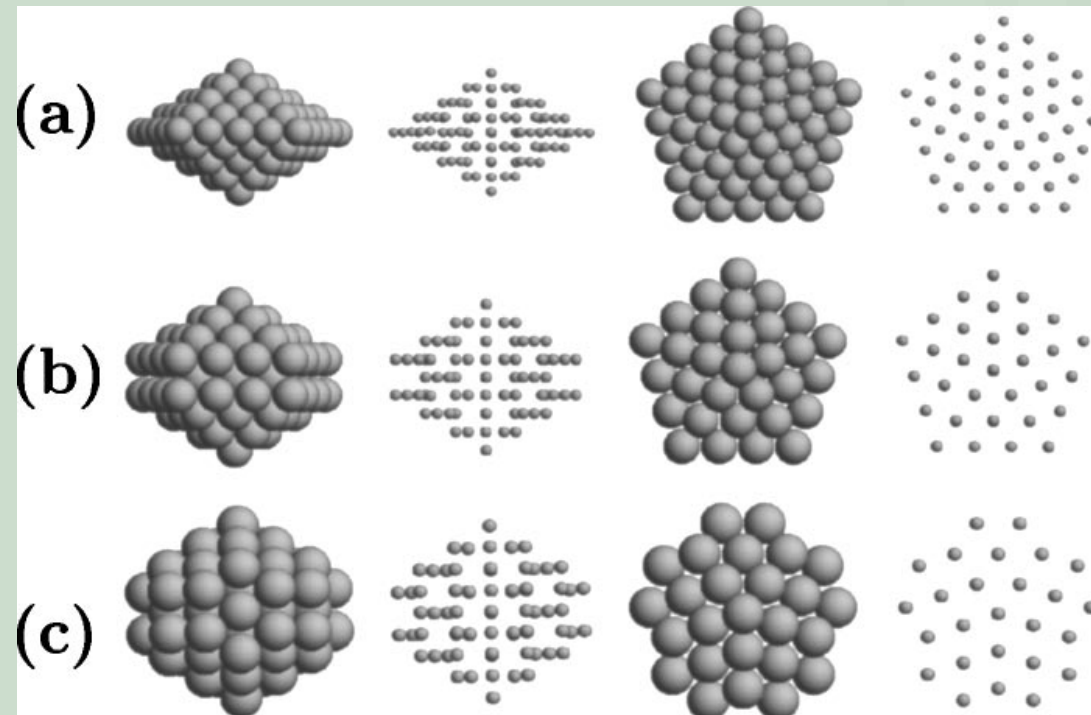
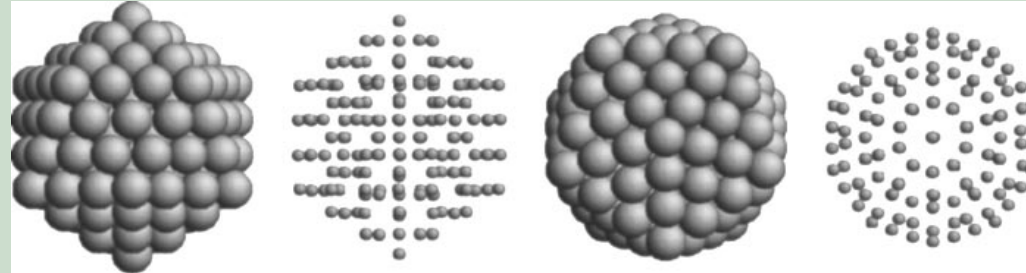


Face-centered-cubic clusters: (a) octahedron; (b) truncated octahedron; (c) cuboctahedron.



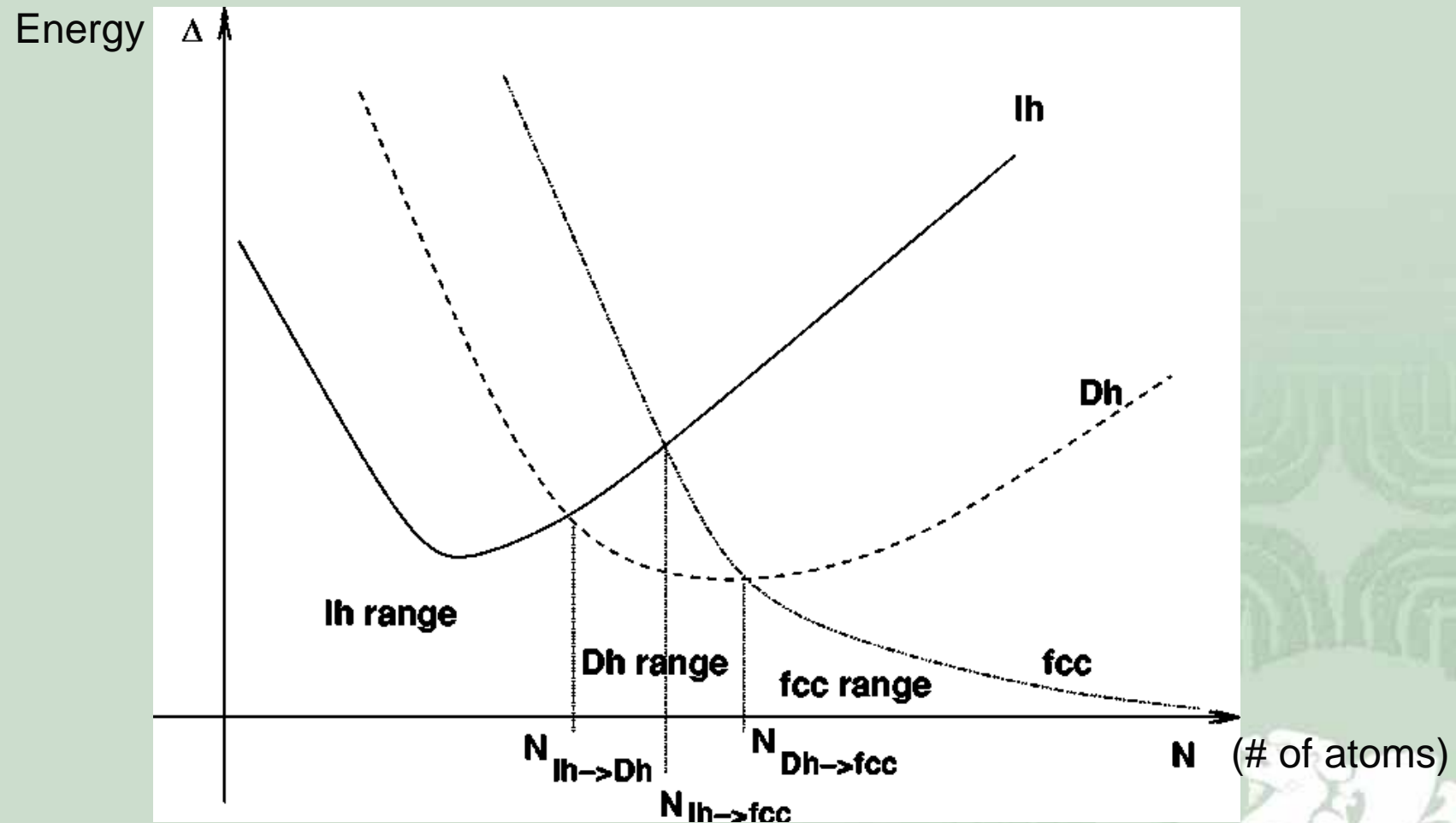
# Clusters

Icosahedral clusters.



Decahedral clusters: (a) regular decahedra; (b) Inotruncated decahedra (Ino, 1969); (c) Marks truncated decahedra.

# Stability of clusters



Qualitative behavior of  $\Delta$  for crystalline, icosahedron, and decahedron clusters.

# Electronic structure of 1 D

- The quantized electronic states of nanostructures determine their electrical and optical properties, and they also influence the physical and chemical properties.
- The coulomb interactions between electrons cannot be ignored in nanostructures.



# Nanowire

The energies and eigenstates in a wire, with  $x$  and  $y$  dimensions in nanoscale but continuous in  $z$  are given by:

$$E = E_{i,j} + \hbar^2 k^2 / 2m, \quad \psi(x, y, z) = \psi_{i,j}(x, y) e^{ikz}$$

$i, j$  are the quantum numbers labeling the eigenstates in the  $x, y$  plane and  $k$  is the wavevector in the  $z$  direction.





The total density of states is:

$$D(E) = \sum_{i,j} D_{i,j}(E)$$

Density of states of each subband is given by:

$$D_{i,j}(E) = dN_{i,j}/dE = (dN_{i,j}/dk)(dk/dE) \\ = (2)(2)(L/2\pi)[m/2\hbar^2(E-E_{i,j})]^{1/2}$$

Spin  
degeneracy

$\pm k$

$$= 4L/h \quad i,j$$

$$= 0$$

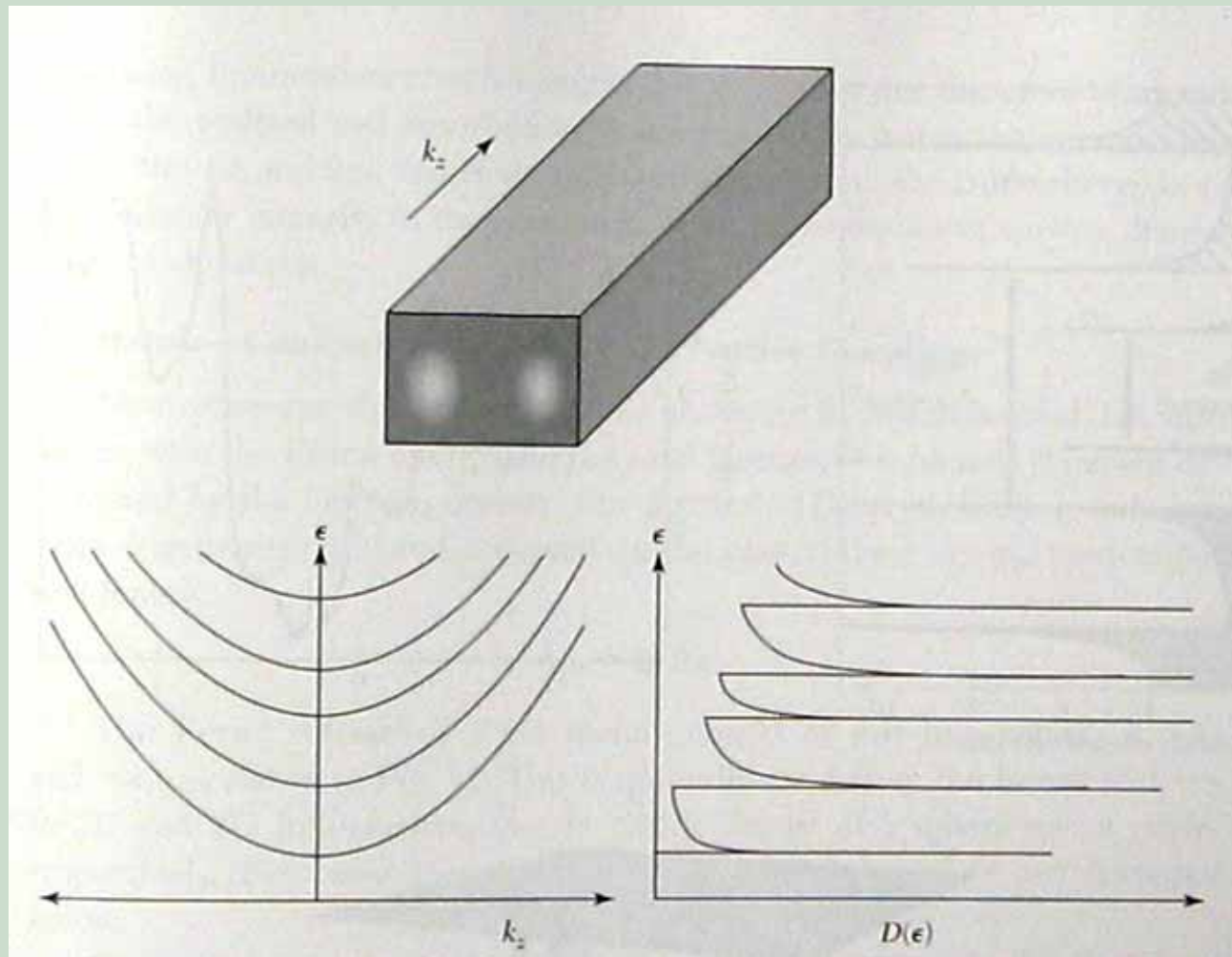
$$\text{For } E > E_{i,j}$$

$$\text{For } E < E_{i,j}$$

$v_{i,j}$ : Velocity of  
the electron in the  
i, j subband with  
Kinetic energy  
 $E - E_{i,j}$ .

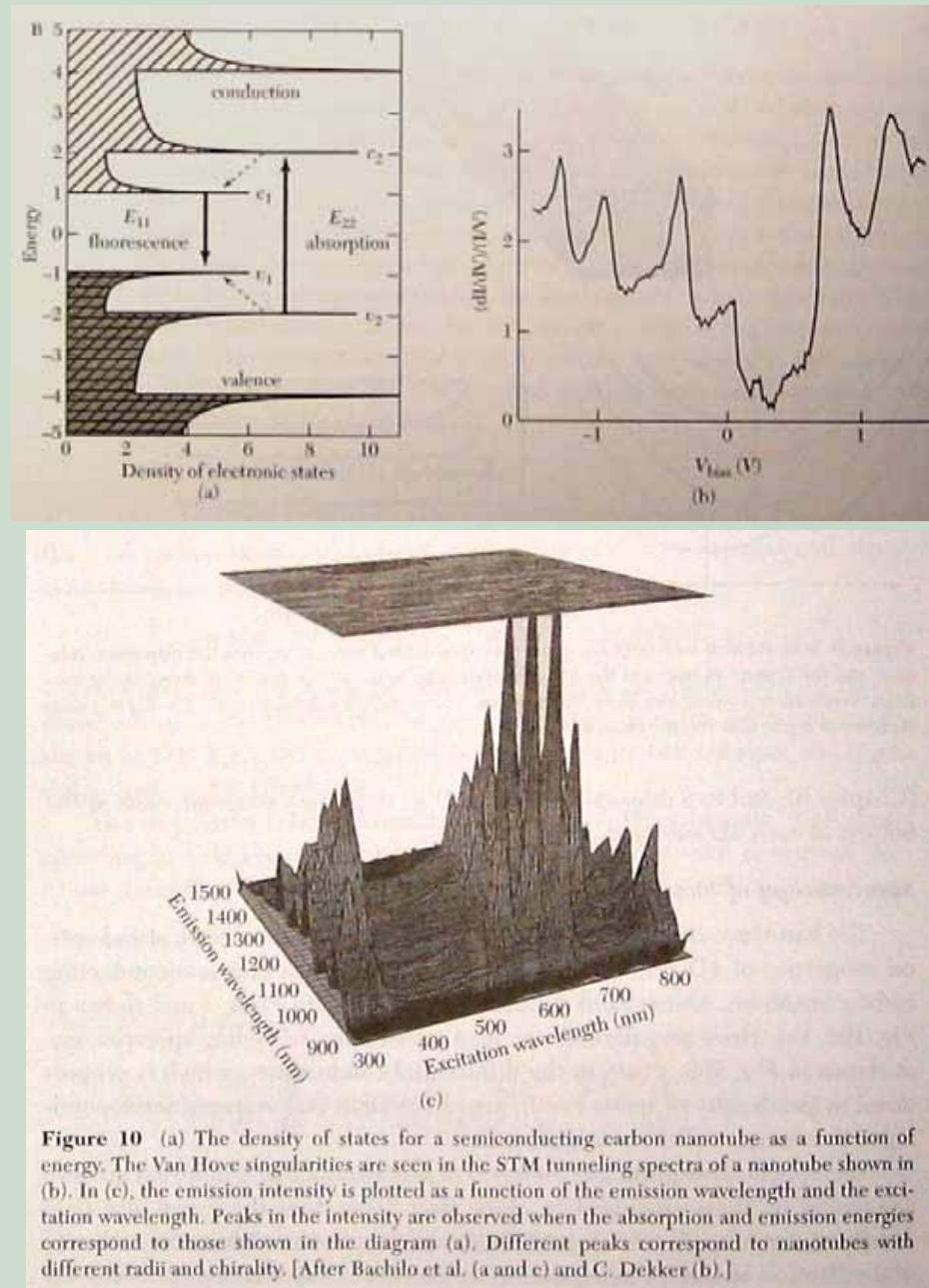
# Van Hove singularities

The density of states diverges as  $(E - E_{i,j})^{-1/2}$  at each subband threshold.





# Carbon nanotube (semiconducting)



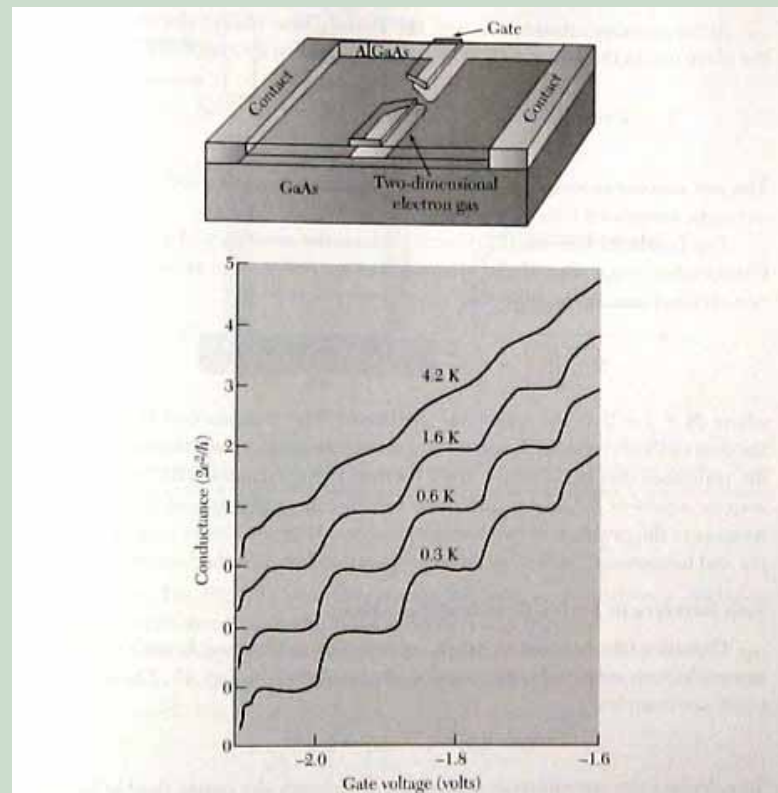
# Coulomb interaction

- Coulomb interactions cause scattering among electrons near the Fermi energy.
- For 3D metals, scattering is strongly suppressed near  $E_F$  by the restrictions of energy/momentum conservation combined with the Pauli exclusion principle.
- The ground state of the interacting 1D electron gas is believed not to be a Fermi liquid, but rather a Luttinger liquid whose low energy excitations are collective in nature (phonons or plasmons).



# Electrical transport in 1 D

- Conductance quantization:  $G_q = 2e^2/h$ .



**Figure 14** Conductance quantization in a short channel electrostatically defined in a GaAs/AlGaAs heterostructure at different temperatures. A negative gate voltage  $V_g$  applied to the metallic gates on the surface of the sample depletes the carriers in the underlying two-dimensional electron gas, creating a narrow channel. The channel is fully depleted of carriers at  $V_g = -2.1$  V. Individual 1D subbands become occupied with increasing  $V_g$ , with each new subband adding a conductance of  $2e^2/h$ . (Courtesy of H. Van Houten and C. Beenakker.)



# Imaging techniques for nanostructures

- Electron: Transmission electron microscopy (TEM), scanning electron microscopy (SEM), scanning tunneling microscopy (STM).
- Force: Atomic force microscopy (AFM), magnetic force microscopy (MFM).
- Photon: Near field optical microscopy.

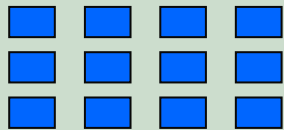
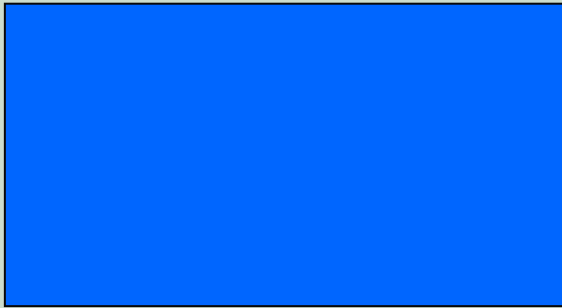


# Nanostructure fabrications

- Bottom-up approach: Growth and self-assembly to build nanostructures from atomic or molecular precursors. (There is plenty of room at the bottom).
- Top-down approach: Lithographic patterning to structure macroscopic materials at the nanoscale. (“There is plenty of room at the top”, Jean-Marie Lehn).

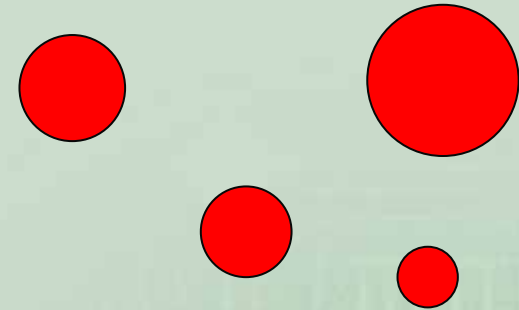


Top-down

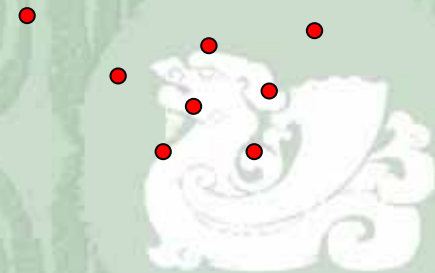


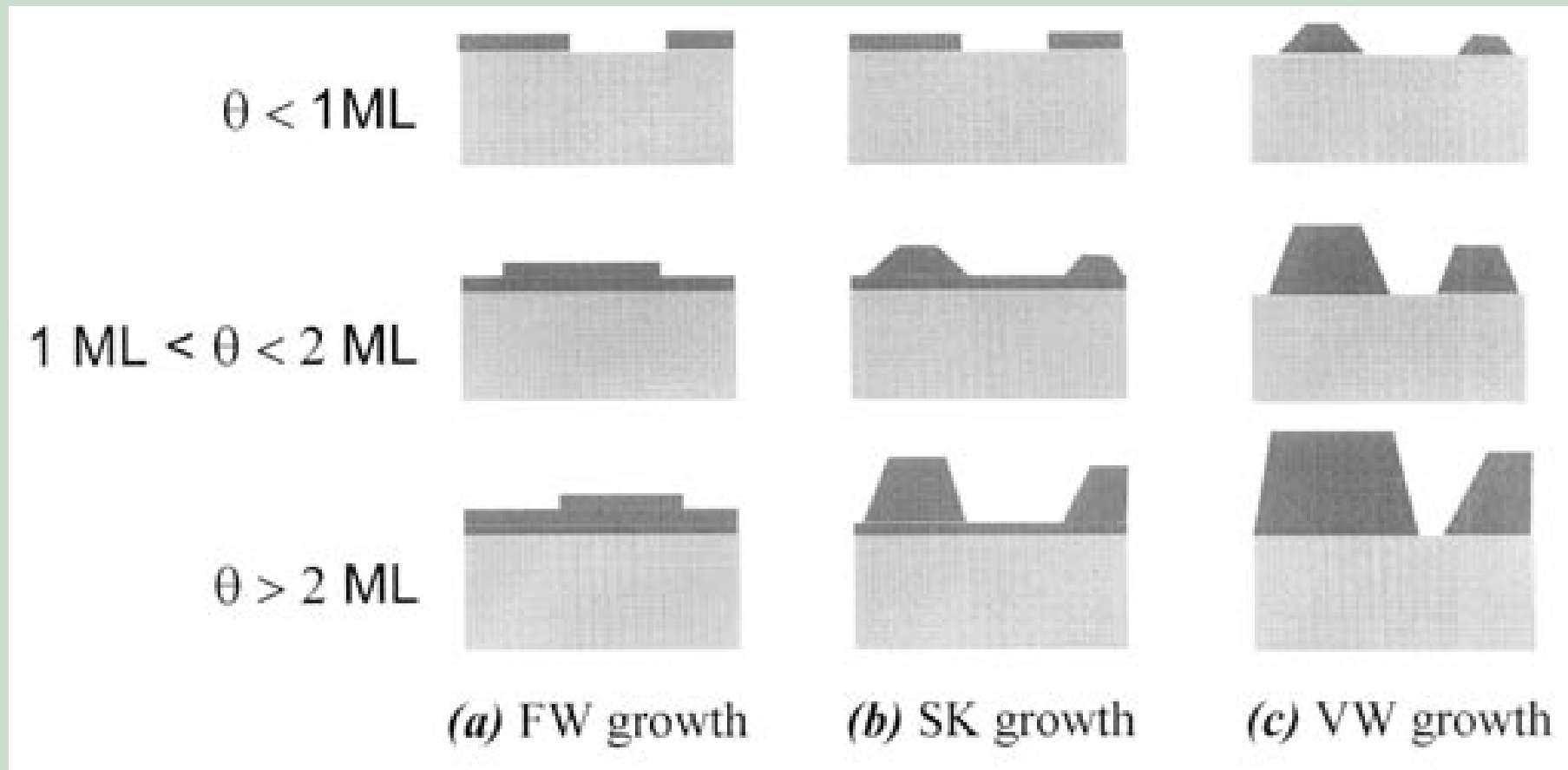
Bottom-up

Big



Small



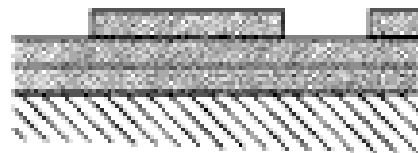


A schematic illustration of various thin-film growth modes ( represents the total adsorbate coverage).

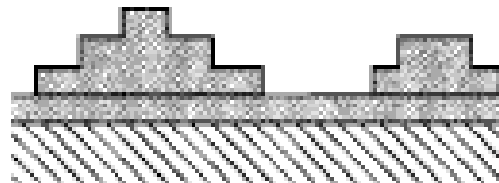
- (a) Frank–van der Merwe (FM) growth—strict layer-by-layer epitaxial growth;
- (b) Stranski–Krastanov (SK) growth—growth occurs in a layer-by-layer (i.e. 2D) fashion up to a certain critical thickness (which is generally related to the lattice mismatch between the adsorbate and substrate materials) and then switches to a 3D, i.e. islanding growth mode;
- (c) Vollmer–Weber (VW) growth—this occurs when the adsorbate and substrate surface (and interface) free energies are such that it is thermodynamically favourable for the overlayer to form islands from the onset of growth.



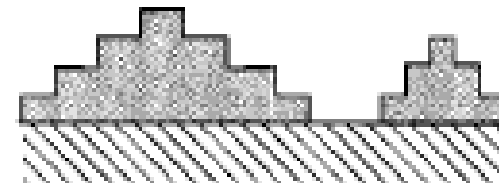
### a) Equilibrium Growth



Layer-by-Layer



Stranski-Krastanov

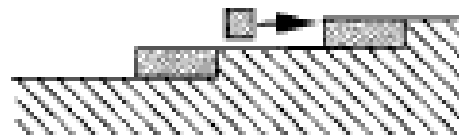


Island Growth

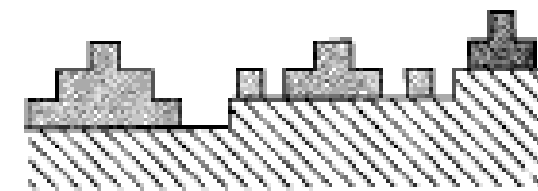
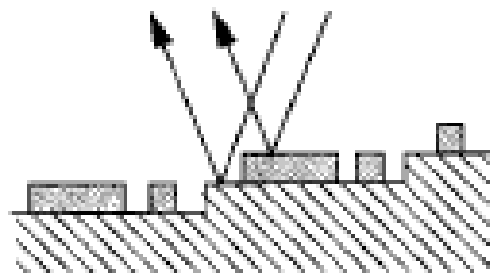
$$\gamma_{\text{substrate}} > \gamma_{\text{overlayer}} + \gamma_{\text{interface}}$$

$$\gamma_{\text{substrate}} < \gamma_{\text{overlayer}} + \gamma_{\text{interface}}$$

### b) Non-Equilibrium Growth



High Temperature  
Low Deposition Rate  
High Step Density

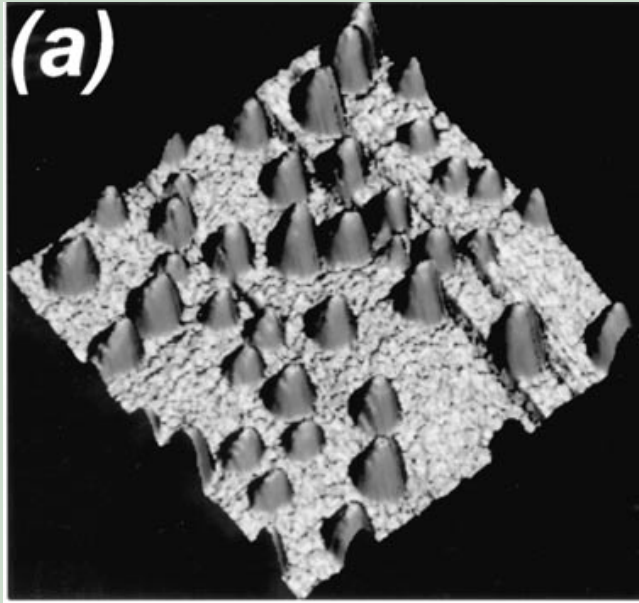


Low Temperature  
High Deposition Rate  
Low Step Density

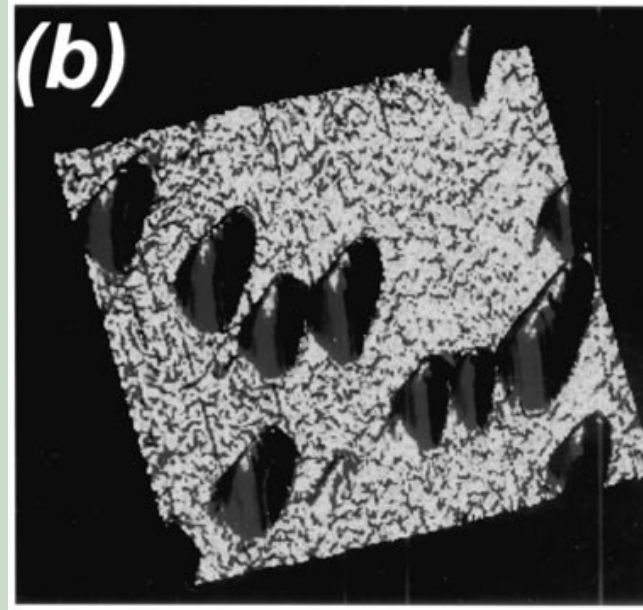


# Controlling the shape of SK-grown nanocrystals

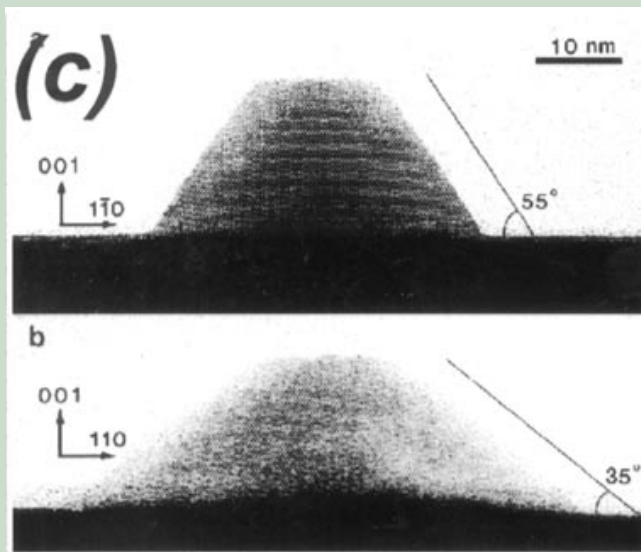
InAs clusters  
on GaAs(100)



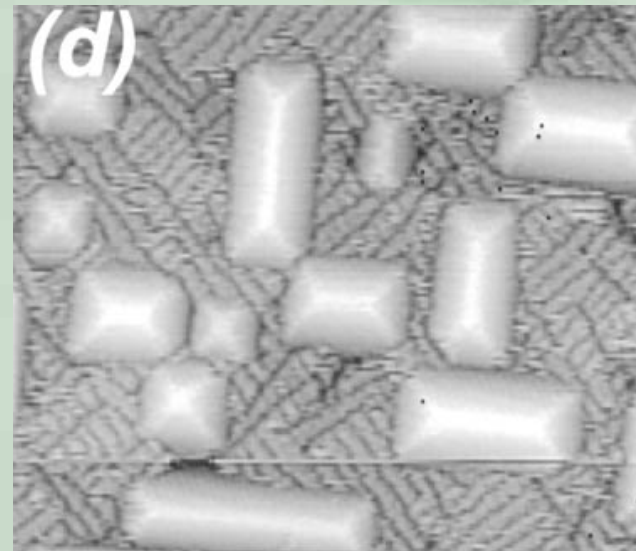
InAs clusters  
on GaAs(311)



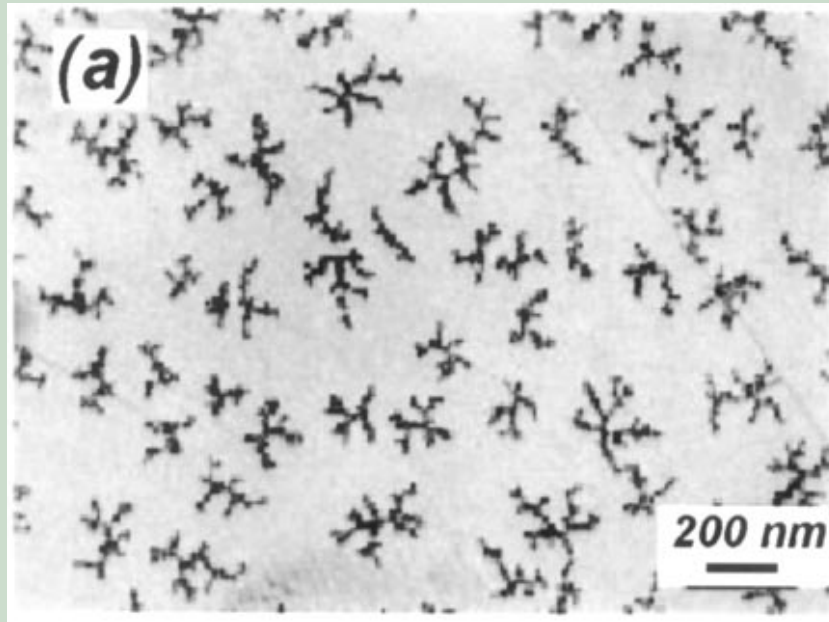
InP clusters  
on GaAs



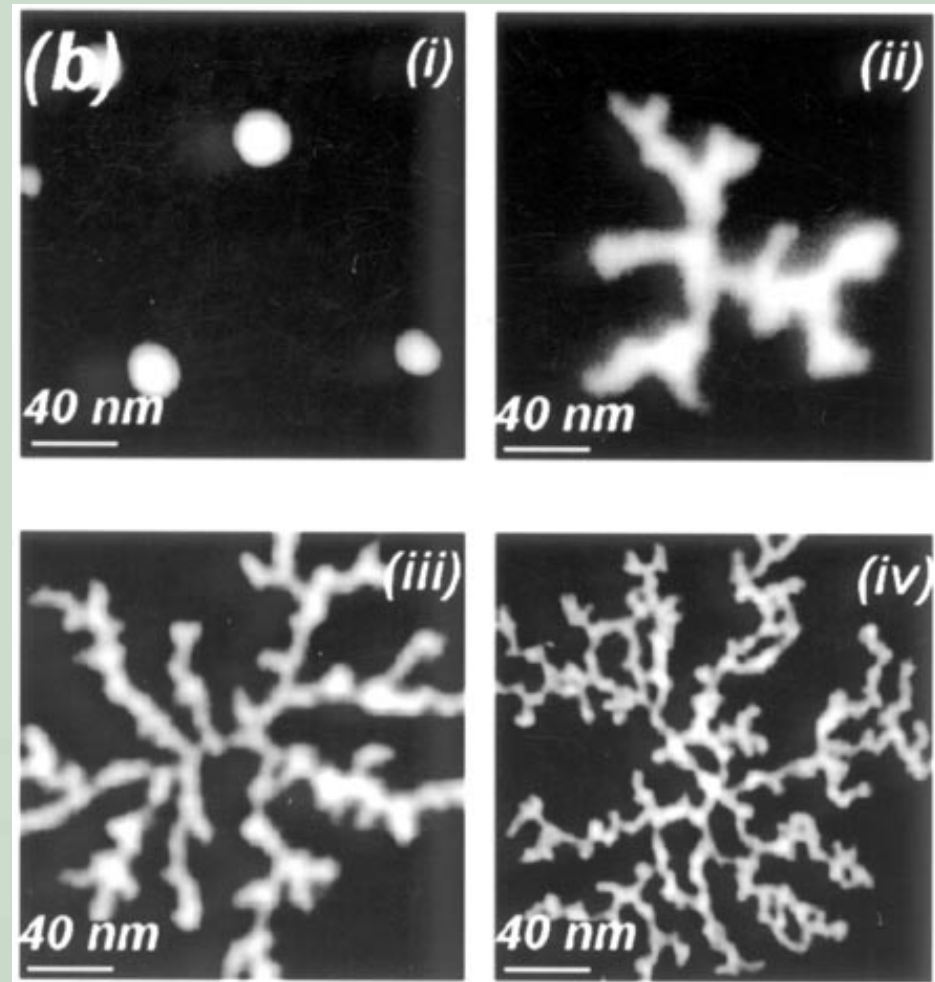
Ge clusters  
on Si



# Sb on graphite



- (a) Fractal islands formed following the deposition of Sb clusters on graphite (Bardotti *et al* 1995).
- (b) Scanning transmission electron microscope (STEM) images of the islands formed from Sb clusters of various sizes deposited onto graphite. The average number of atoms per deposited cluster,  $n$ , in each case is: (i) 4, (ii) 90, (iii) 150, (iv) 500 (Yoon *et al* 1999).



# Lithography

- Parallel: Optical, x-ray, ion-beam, extreme ultraviolet, imprint.
- Serial: E-beam, laser, focus ion beam.
- Other lithography: Microcontact printing, nanosphere lithography, scanning probe lithographies, dip-pen nanolithography, field induced oxidation, feedback controlled lithography.



# Particle wavelength (A) at various energies

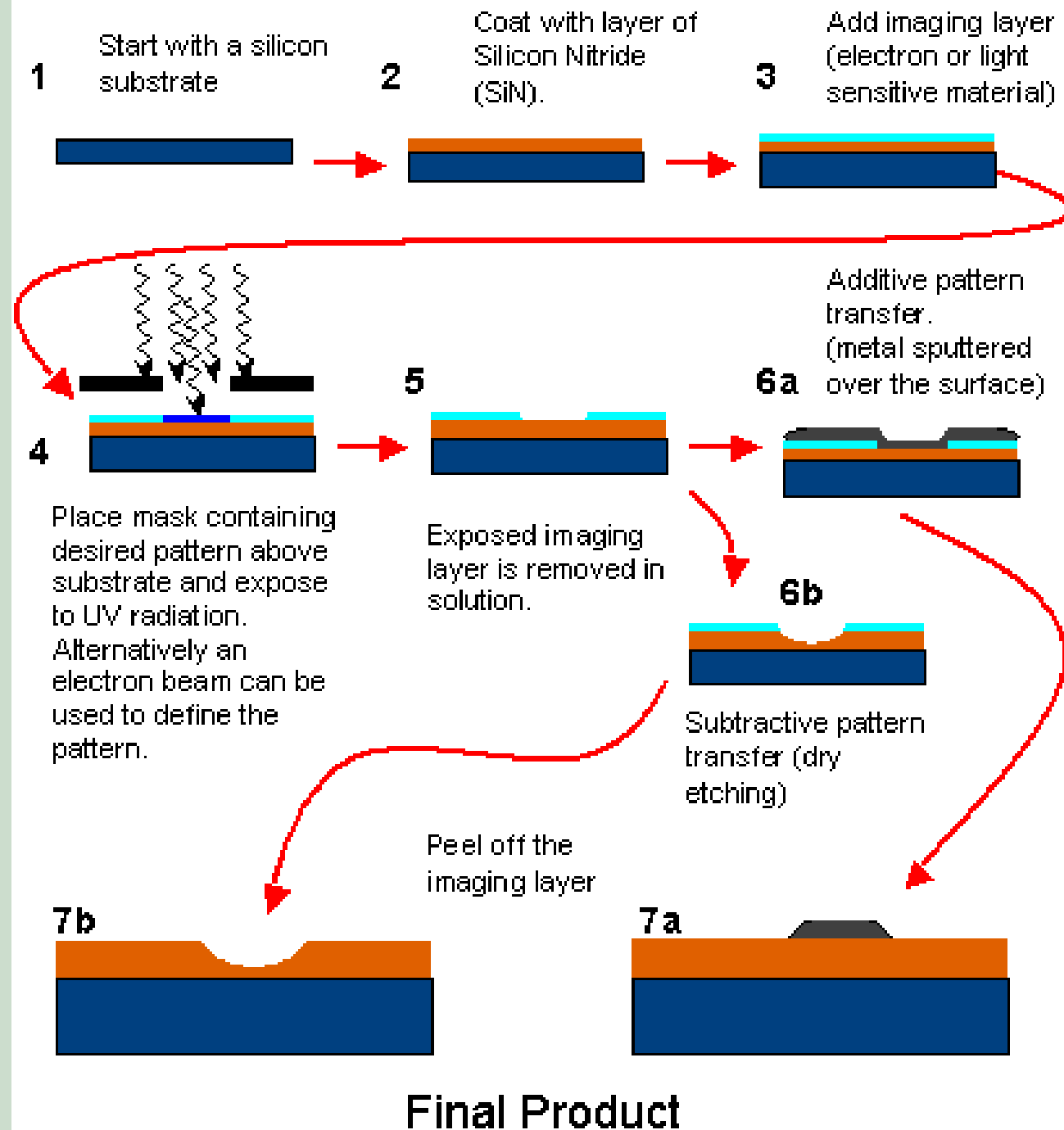
Particles	1 eV	10 eV	100 eV	1 KeV	10 KeV	100 KeV	1 MeV
Photon	12400	1240	124	12.4	1.24	0.124	0.012
Electron	12.3	3.89	1.23	0.39	0.12	0.037	0.0087
Proton	0.29	0.091	0.029	0.0091	0.0029	0.00091	0.00028

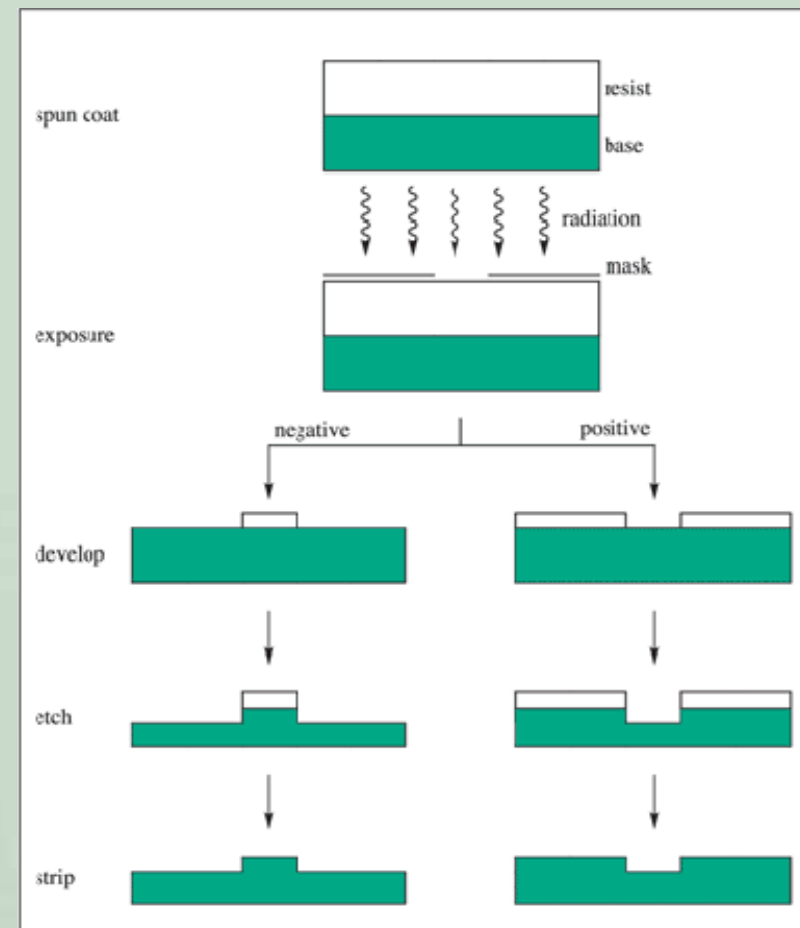
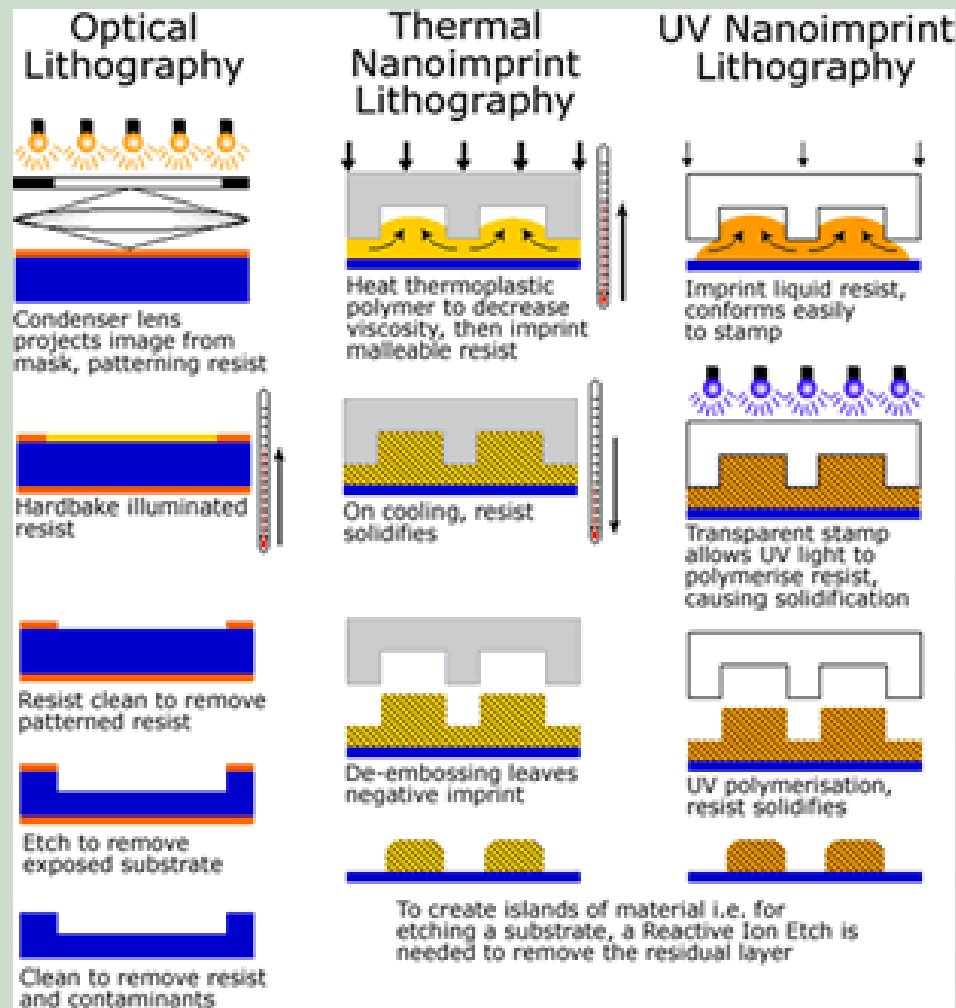
Photon:  $\lambda \text{ (A)} = 12400/E$  ,  $E \text{ (eV)}$ .

Electron:  $\lambda \text{ (A)} = 12.3/E^{1/2}$

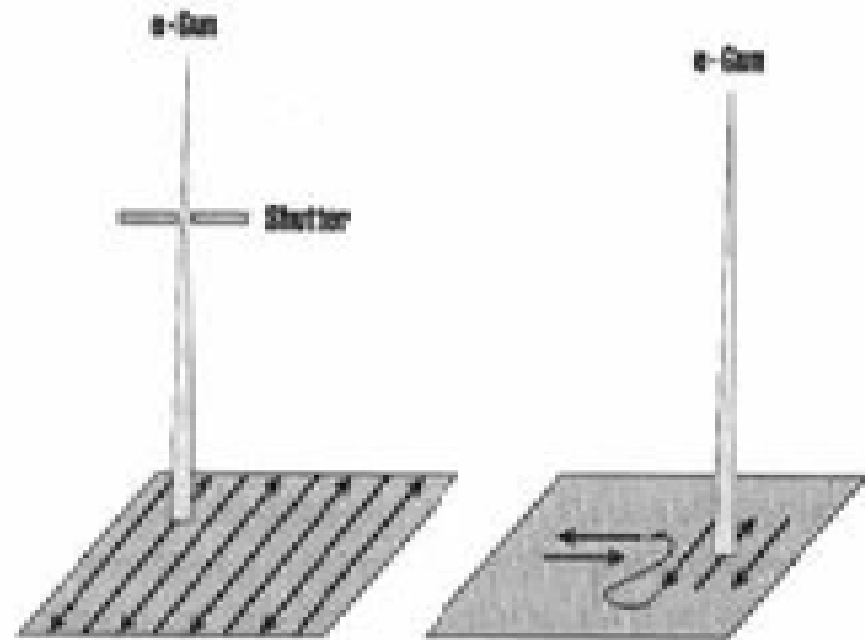
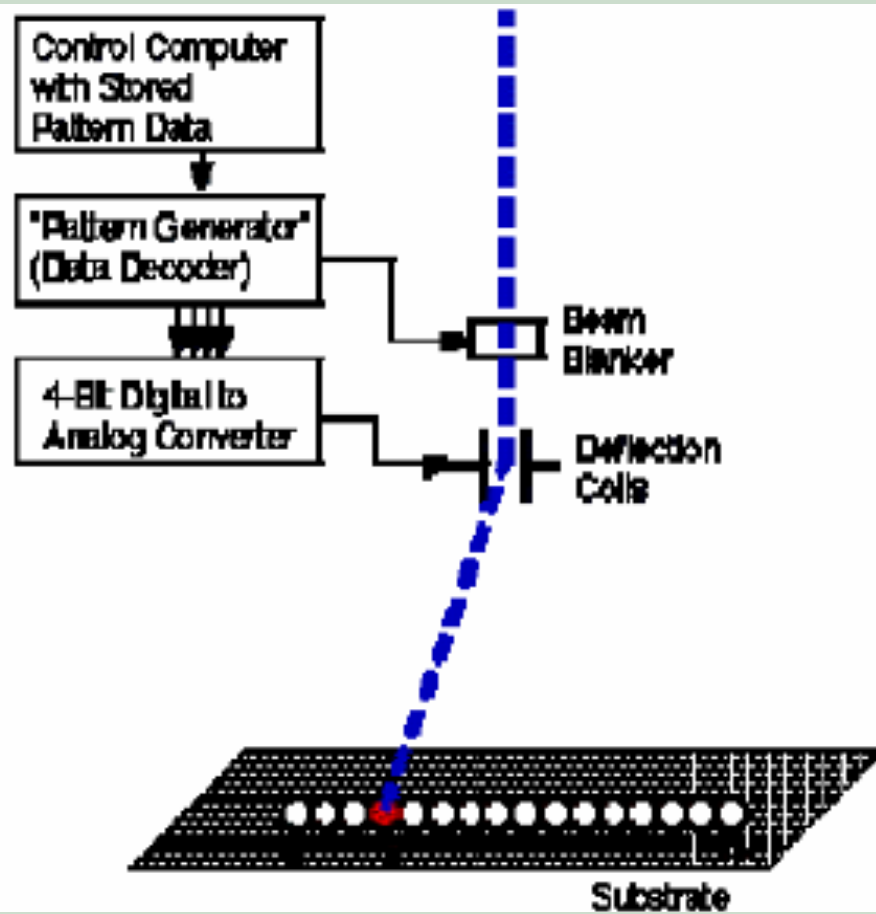
Proton:  $\lambda \text{ (A)} = 0.29/E^{1/2}$







# E-beam lithography





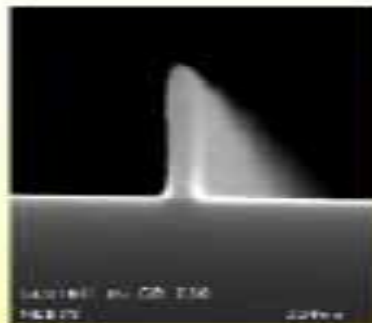
# Organic E-beam Resist

Polymer <sup>a</sup>	Tone	Sensitivity (C/cm <sup>2</sup> )	Resolution (μm)
PMMA	Positive	$4 \times 10^{-5} - 8 \times 10^{-5}$	0.1
P(GMA-co-EA)	Negative	$3 \times 10^{-7}$ (10 keV)	1.0
PBS	Positive	$8 \times 10^{-7}$ (10 keV)	0.5
COP	Negative	$4 \times 10^{-7}$	1.0
P(GMA-co-EA)	Negative	$3 \times 10^{-7}$ (10 keV)	1.0
PGMA	Negative	$5 \times 10^{-7}$ (20 keV)	1.0
PCA	Positive	$5 \times 10^{-7}$ (20 keV)	0.5

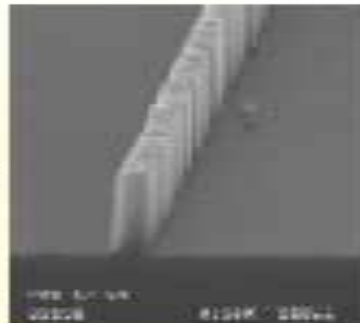
PMMA: polymethyl methacrylate;  
 P(GMA-co-EA): poly(glycidyl methacrylate-  
 co-ethyl acrylate;  
 PBS: poly(butene-1-sulfone);  
 COP: copolymer methyl methacrylate;  
 PGMA: poly(glycidyl methacrylate;  
 PCA: copolymer of -cyano ethyl acrylate  
 and -amine ethyl acrylate





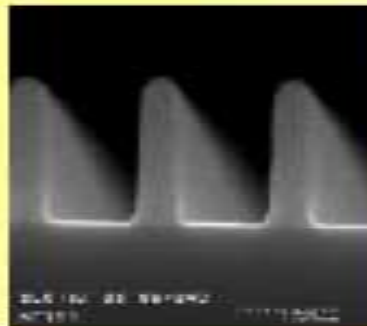


$L=60\text{ nm}$



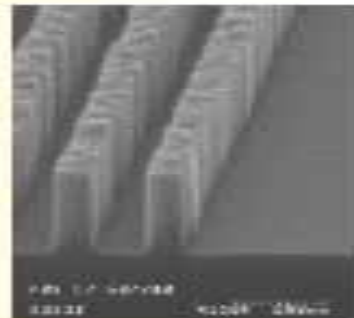
**Litho (Sumitomo NEB33)**

**Etched (200 nm poly)**



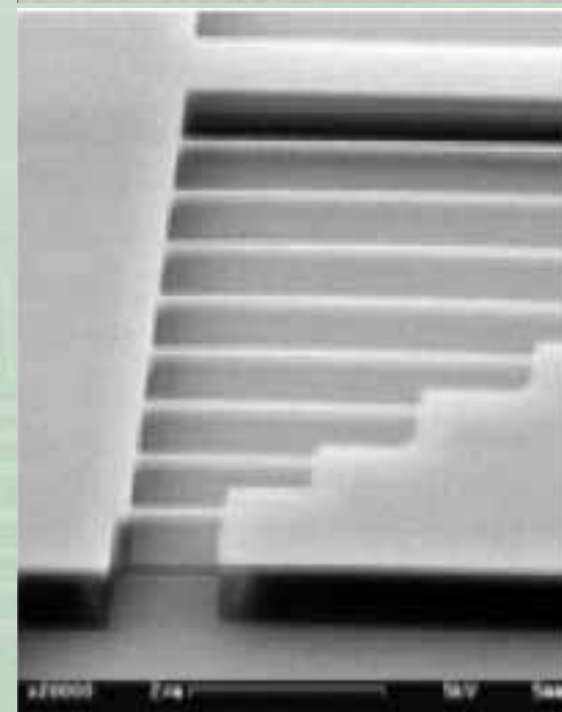
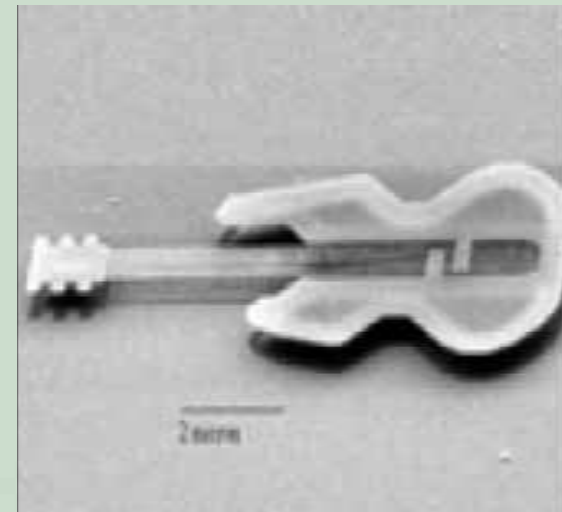
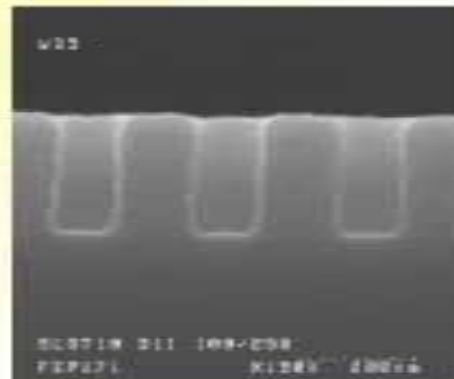
$L=60\text{ nm}$

$S=180\text{ nm}$



**Contact level**

**100 nm pitch 250 nm**



## Nanostructured silicon for studying fundamental aspects of nanomechanics

R. H. Blick<sup>1</sup>, A. Erbe, I. Proch, A. Kraus, D. V. Scheible, F. W. Bell, E. Hoehberger, A. Hoerner, J. Kirschbaum, H. Lorenz and J. P. Kotthaus

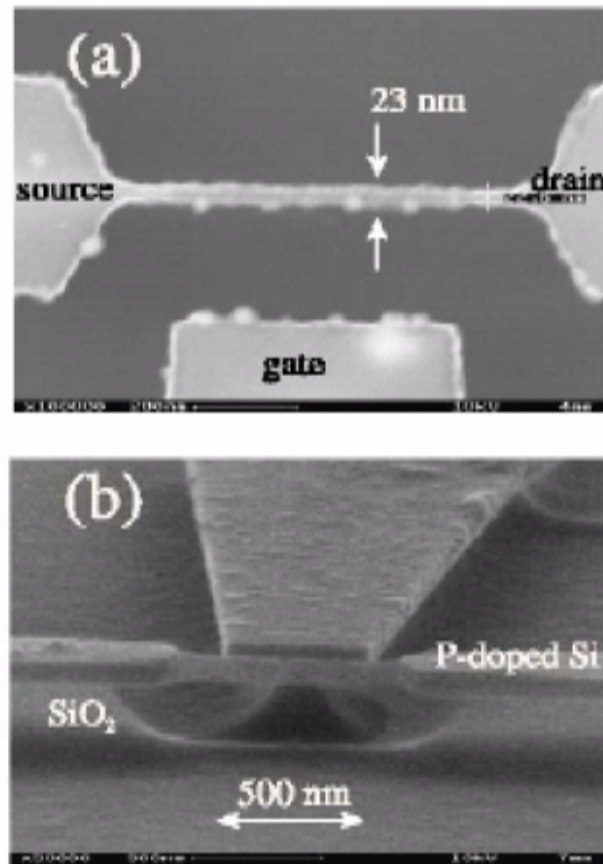
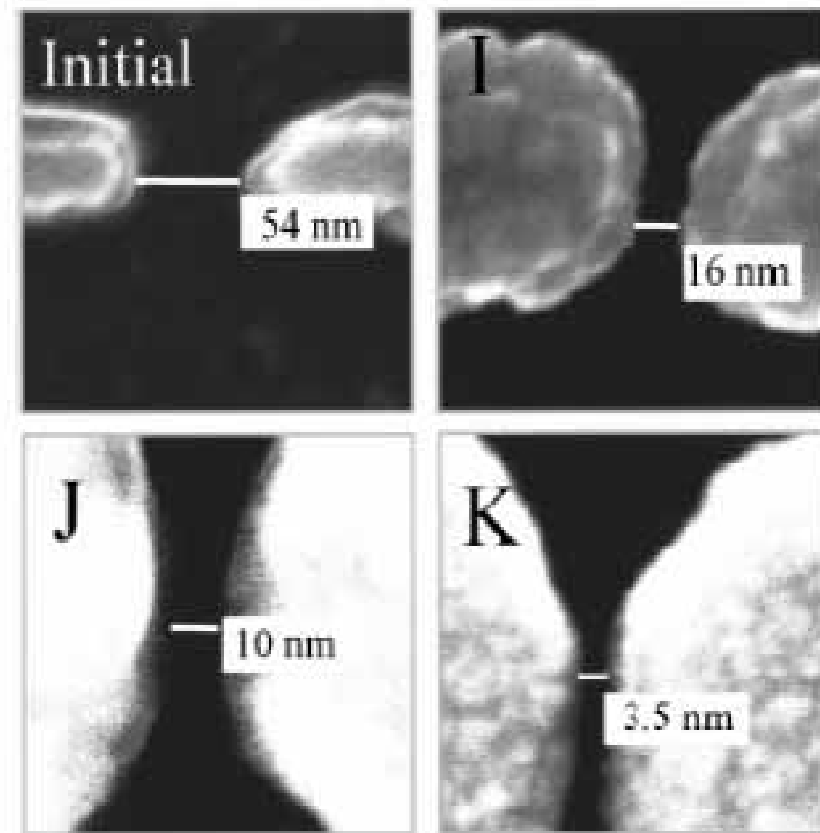


Figure 24. (a) Top view and (b) side view of the smallest suspended silicon nanowire fabricated with a width of 23 nm. The highly doped wire is clearly underetched; the gate allows tuning of the carrier density in the wire.

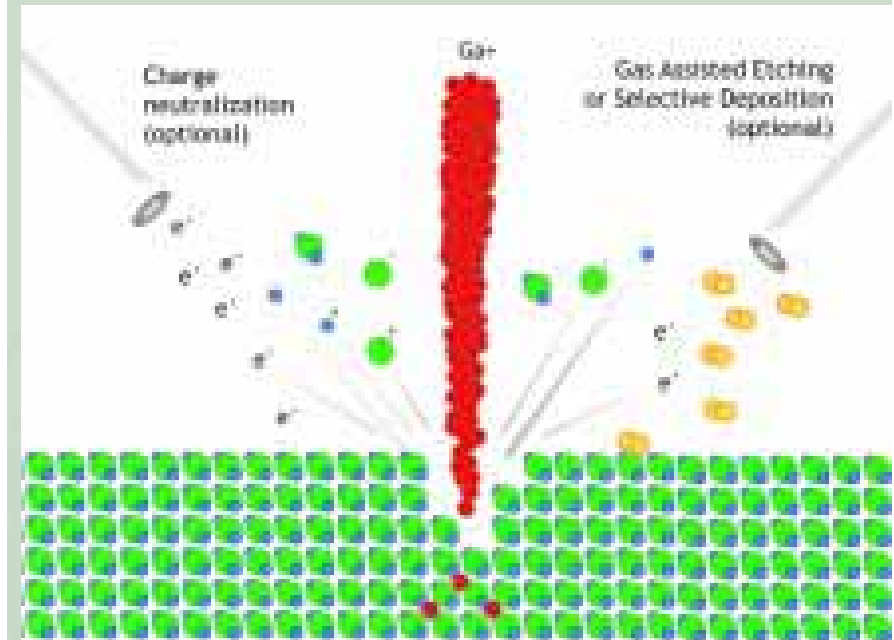
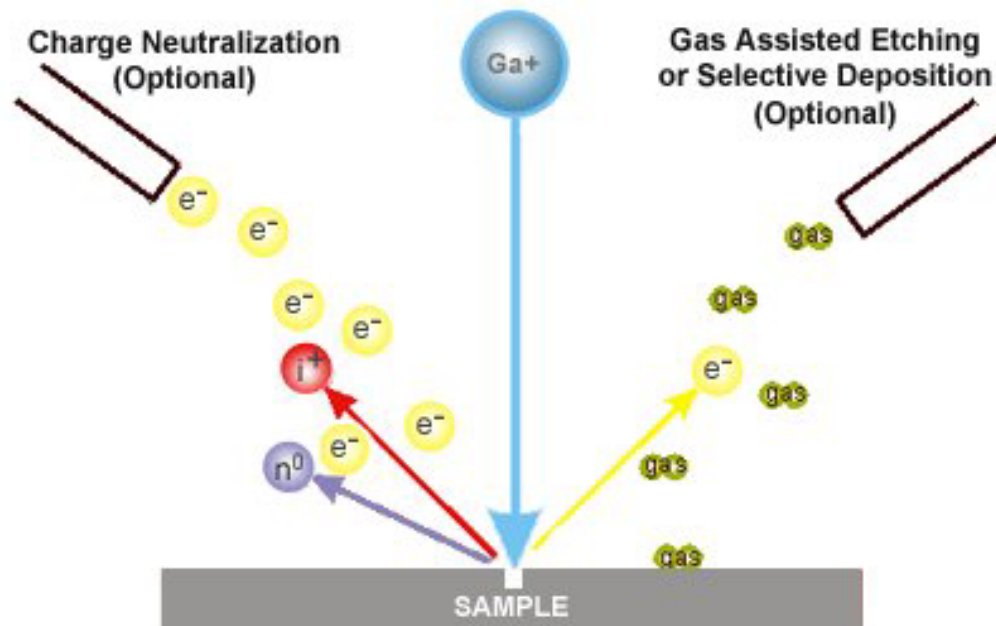
## Nanometer-spaced electrodes with calibrated separation

Y. V. Kanyenic,<sup>1</sup> H. S. J. Van der Zant, A. F. Morpurgo, L. Gurevich, and L. P. Kouamshouan

Department of Applied Sciences and DPMES, Delft University of Technology Lorentzweg 1, 2628 CJ Delft, The Netherlands



# Focus Ion Beam (FIB)



# Nanostructuring with focus ion beam (FIB)

Material processing with focused ion and electron beams is done in a direct writing mode and enables fast and flexible fabrication of nanostructures with well defined geometry.

