Heterojunctions

Heterostructures

Quantum confined structures

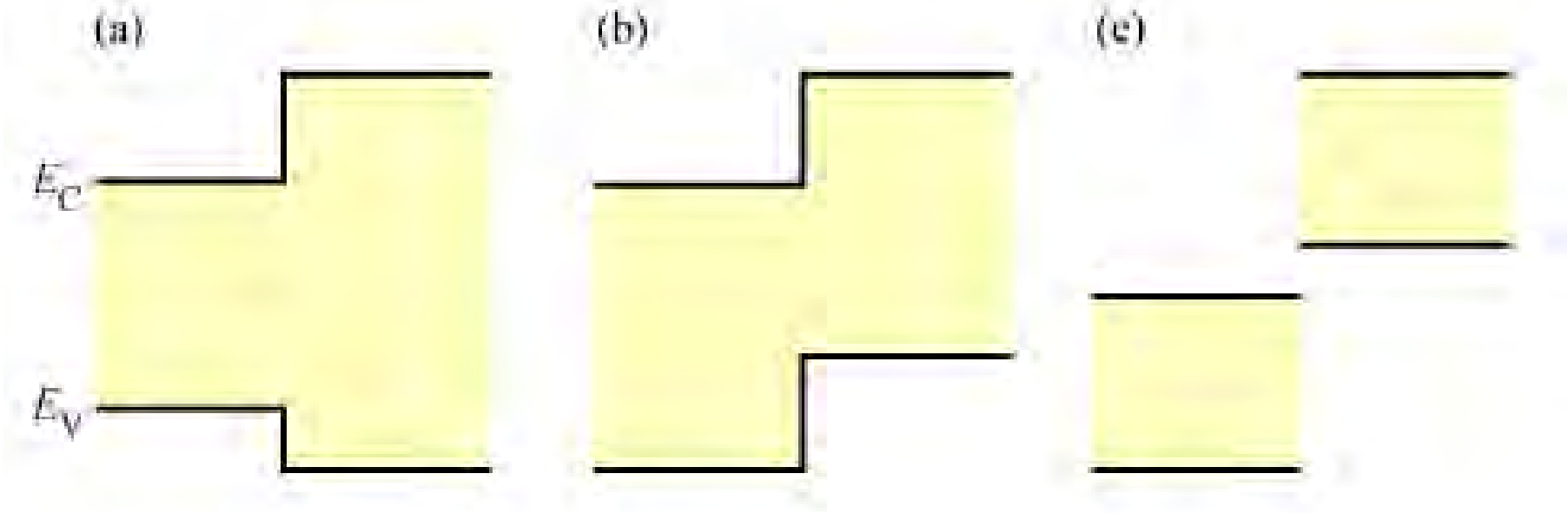
HETEROJUNCTIONS & HETEROSTRUCTURES

HETEROJUNCTION is the interface between two layers or regions of different semiconductors, in other words two semiconductors with different crystal structure or different crystal phase. Semiconductors of different materials or of the same material but different crystal phase have different band gaps as opposed to a homojunction.

HETEROSTRUCTURE is the combination of multiple heterojunctions. The requirement that each material be a semiconductor with unequal band gaps is somewhat loose, especially on small length scales, where electronic properties depend on spatial properties. A more modern definition of heterojunction is the interface between any two solid-state materials, including crystalline and amorphous structures of metallic, insulating, fast ion conductor and semiconducting materials.

Energy Band Alignment

The behaviour of a semiconductor junction depends on the alignment of the bands at the interface. Semiconductor interfaces can be organized into three types of heterojunctions:

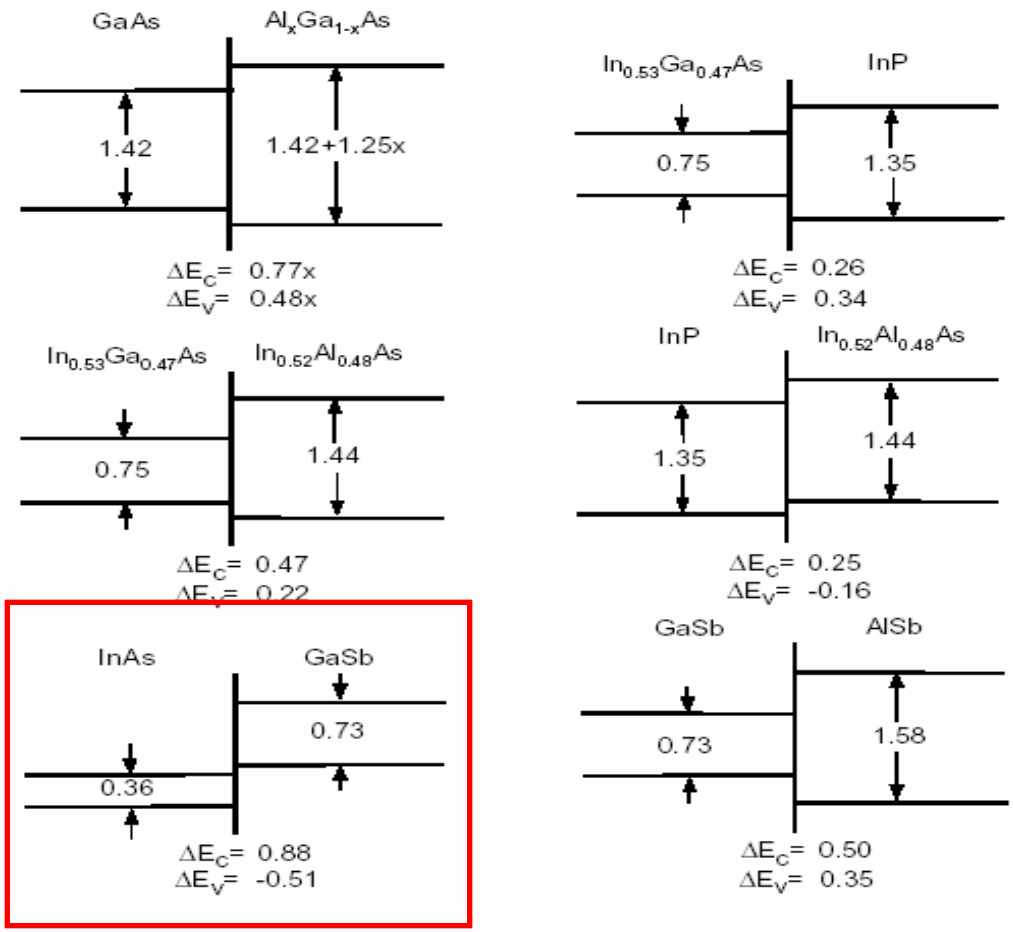


Straddled – Type I Staggered – Type II Broken – Type III

Heterojunction Basics

- Band offsets for common III-V heterojunctions

- Note: broken gap occurs for III-V pairs when both group III and V elements differs
  - Alternate layers will have excess charge carriers in all layers without doping
  - Electrons from GaSb valence band will fill into InAs conduction band…
  - Semimetal



bangap engineering

Optical properties of the materials

Change energy levels and states

Change of density of states

Change of electronic properties

QUANTUM CONFINEMENT & QUANTUM CONFINED STRUCTURES

If one makes a heterostructure with sufficiently thin layers, quantum interference effects begin to appear prominently in the motion of the electrons.

The resulting structure is then called a low-dimensional structure or system: **Nanostructures**

The confinement of particles, usually electrons or holes, to a low- dimensional structure leads to a dramatic change in their behaviour and to the manifestation of size effects that usually fall into the category of quantum-size effects.

Therefore low dimensional structures or materials are also known as Quantum Confined Structures exhibit new physicochemical properties not shown by the corresponding large-scale structures of the same composition. **Suitable control of the properties and responses of nanostructures can lead to new devices and technologies.**

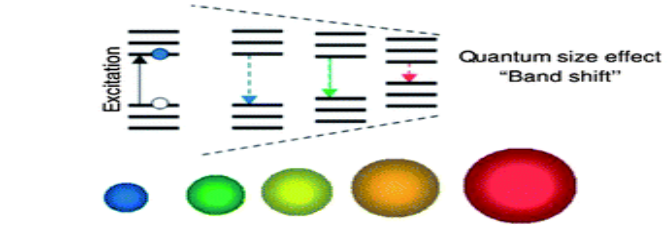
(Recalling Lecture 13)

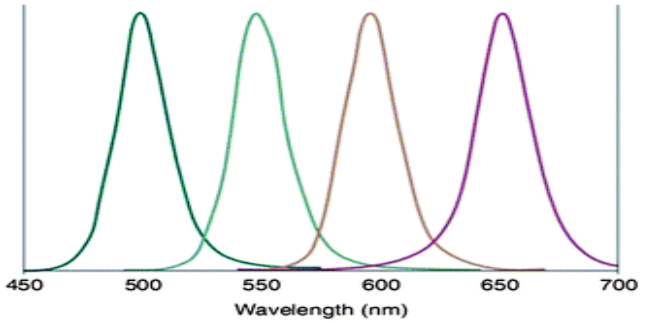
Quantum effects: The quantum confinement is observed when the diameter of the particle is of the same magnitude as the wavelength of the electron (wave function).

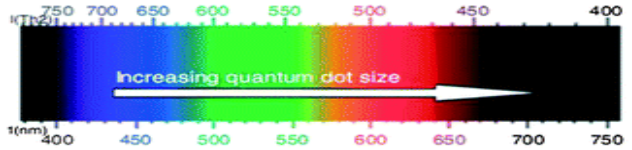
Quantum confinement is responsible for the increase of energy difference between energy states and band gaps, which relates to the optical and electronic properties of the materials. Therefore, when materials are these small, their electronic and optical properties deviate substantially from those of bulk materials (example is gold).

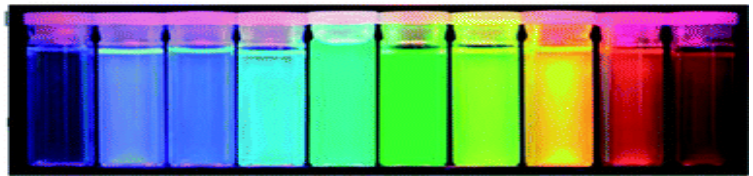
For nanoparticles the size of the particle imposes geometrical constraints on the electrons, which respond by adjusting their energy.

This phenomenon is called the **quantum size effect**.









Excitons

- An exciton can form when a material absorbs a photon of higher energy than its bandgap. This excites an electron from the valence band into the conduction band creating and electron-hole pair. The electron in the conduction band is then attracted to the hole by the Coulomb forces generated between the electrons surrounding the hole and the excited electron.

- Excitons, on the other hand, determine the band-to-band transition the optical properties around the band gap,i.e., in the visible including the near UV and IR in the case of semiconductors and in the (V)UV for insulators.

- It is an electrically neutral quasiparticle that exists conceptually in insulators, semiconductors and some liquids.

- The exciton is regarded as an elementary excitation of condensed matter that can travel through a crystal structure and **transport energy without transporting net electric charge.**

Excitons can be treated as "Bohr atoms"

$$r = \frac{4\pi\varepsilon\varepsilon_0\hbar^2}{e^2 m^*}$$

When the size of the nanoparticle approaches that of an exciton, size quantization occurs.

Electronic energy gap:

$$\Delta E = \Delta E^0 + \frac{\hbar^2\pi^2}{2R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - 1.8\frac{e^2}{\varepsilon R}$$

Intrinsic band gap

NP radius

electrostatic correction

Exciton Bohr Diameter

Semiconductor	Exciton Bohr Diameter	Band gap Energy
CuCl	13Å	3.4 eV
ZnSe	84Å	2.58 eV
CdS	56Å	2.53 eV
CdSe	106Å	1.74 eV
CdTe	150Å	1.50 eV
GaAs	280Å	1.43 eV
Si	37Å(longitudinal) 90Å(transverse)	1.11 eV
Ge	50Å(longitudinal) 200Å(transverse)	0.67 eV
PbS	400Å	0.41 eV

The quantum effects of confinement become significant when at least one of the **dimensions of a structure is comparable in length to the** de Broglie wavelength. If at least one dimension of a solid is comparable to the de Broglie wavelength of the particle, a quantum-mechanical treatment of particle motion becomes necessary.

Classification of Low-dimensional Structures/Materials

Low-dimensional structures are usually classified according to the number of reduced dimensions they have. More precisely, the dimensionality refers to the number of degrees of freedom in the particle momentum:

- **Three-dimensional** (3D) structure or bulk structure: No quantization of the particle motion occurs, i.e., the particle is free.

- **Two-dimensional** (2D) structure or quantum well: Quantization of the particle motion occurs in one direction, while the particle is free to move in the other two directions.

- **One-dimensional** (1D) structure or quantum wire: Quantization occurs in two directions, leading to free movement along only one direction.

- **Zero-dimensional** (0D) structure or quantum dot (sometimes called “quantum box”): Quantization occurs in all three directions.

Quantum-Confined Structures…

….When the motion of the electrons (and/or holes) is confined in one or more directions by potential barriers.

The general scheme for classifying quantum-confined structures is given in the following table.

Structure	Confined directions	Free directions (dimensionality)
Quantum well	1(z)	2 (x,y)
Quantum wire	2	1
Quantum dot (or box)	3	none

Quantum size effects become important when the **dimensions of the structure become comparable with the de Broglie wavelength** of the electrons or holes, leading to energy levels called "energy sub-bands", i.e., the carriers can only have discrete energy values. If we consider the free thermal motion of a particle of mass m in the z-direction, the de Broglie wavelength at a temperature T is approximately given by,

$$\lambda_{\mathrm{deB}} \sim \frac{h}{\sqrt{m k_{\mathrm{B}} T}}$$

Some Basic Physics

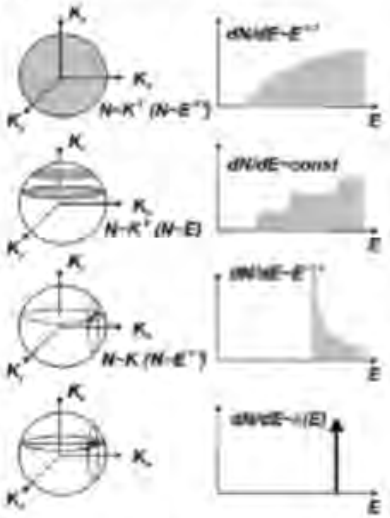
- Density of states (DoS)

$$DoS = \frac{dN}{dE} = \frac{dN}{dk}\frac{dk}{dE}$$

  - *e.g.* in 3D:

$$N(k) = \frac{\text{k space vol}}{\text{vol per state}}$$

$$= \frac{4/3\,\pi k^3}{(2\pi)^3/V}$$



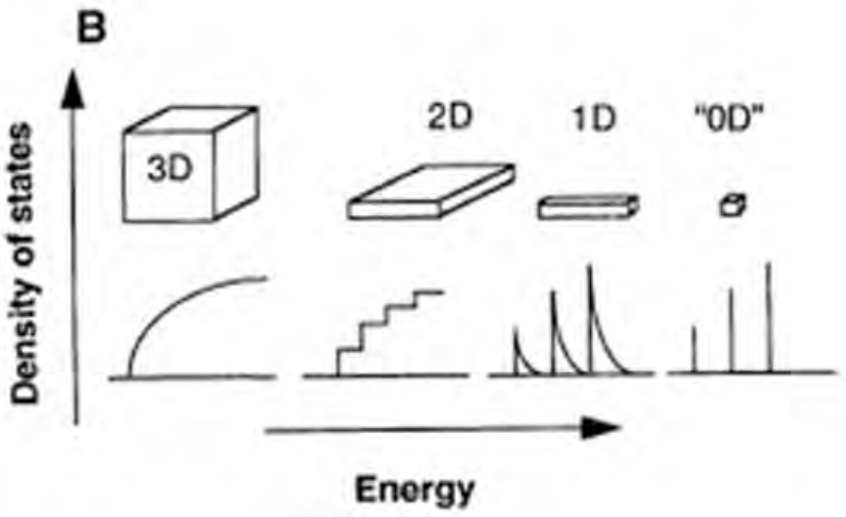
Structure	Degree of Confinement	$\frac{dN}{dE}$
Bulk Material	0D	$\sqrt{E}$
Quantum Well	1D	1
Quantum Wire	2D	$1/\sqrt{E}$
Quantum Dot	3D	$\delta(E)$

The quantization of the motion in the *z*-direction has three main consequences:

1. the quantization energy shifts the effective band edge to higher energy, which provides an extra degree of freedom in the art of bandgap engineering.

2. the confinement keeps the electrons and holes closer together and hence increases the radiative recombination probability.

3. the density of states becomes independent of energy, in contrast to 3-D materials, where the density of states is proportional to $E^{1/2}$.



In zero dimensions the energy states are sharp levels corresponding to the eigenstates of the system.

Many of the useful properties of the QWs follow from these three properties.

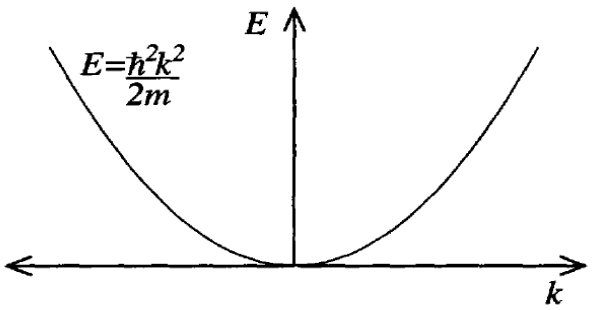
QUANTUM WELLS are potential wells with only discrete energy values.

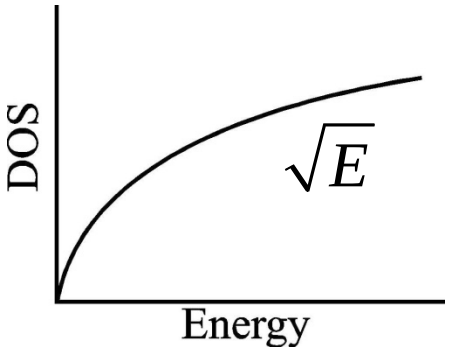
The term “well” refers to a semiconductor region that is grown to possess a lower energy, so that it **acts as a trap for electrons and holes** (electrons and holes gravitate towards their lowest possible energy positions).

Quantum wells are real-world implementation of the “particle in the box” problem; they act as potential wells for charge carriers and are typically experimentally realized by epitaxial growth of a sequence of ultrathin layers consisting of semiconducting materials of varying composition.

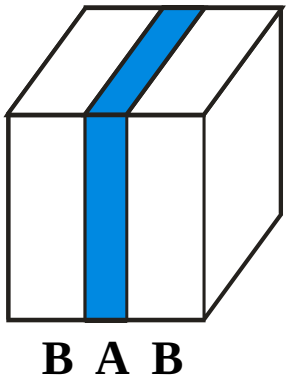
Confinement in 2d nanostructures

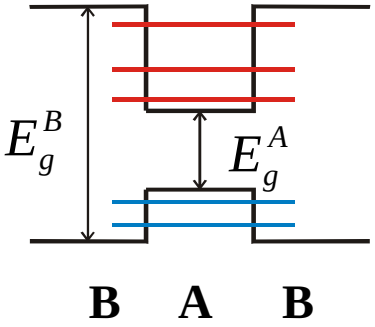
3D systems

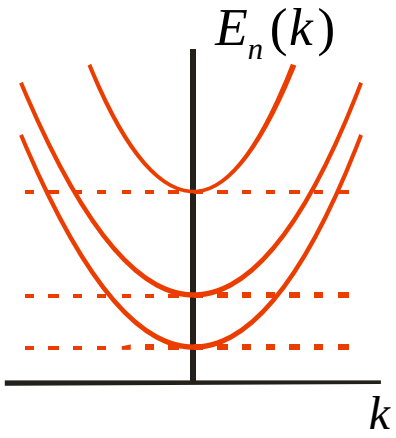


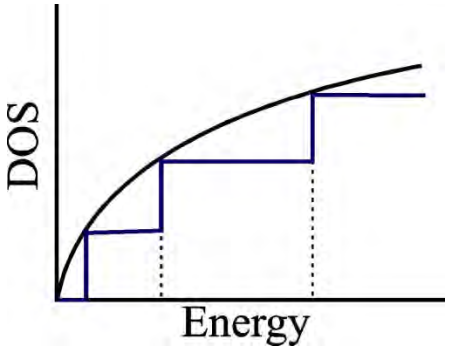


2D systems









$$E_n(k) = \frac{\hbar^2}{2\mu}\left(k_x^2 + k_y^2\right) + E_z^n, \quad n = 1,2,3...$$

Quantum well (QW)

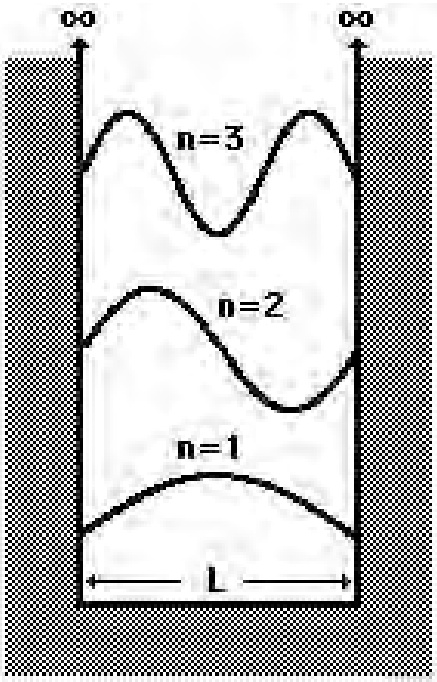
width L, infinite barriers

$$\psi(0) = \psi(L) = 0$$

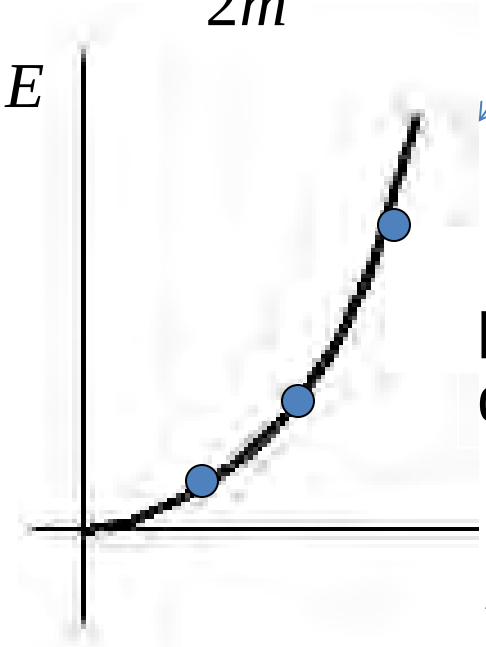
$$\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L} x\right)$$

$$E_n = \frac{h^2}{8mL^2} n^2 = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2$$

$$= \frac{\hbar^2}{2m} k^2$$



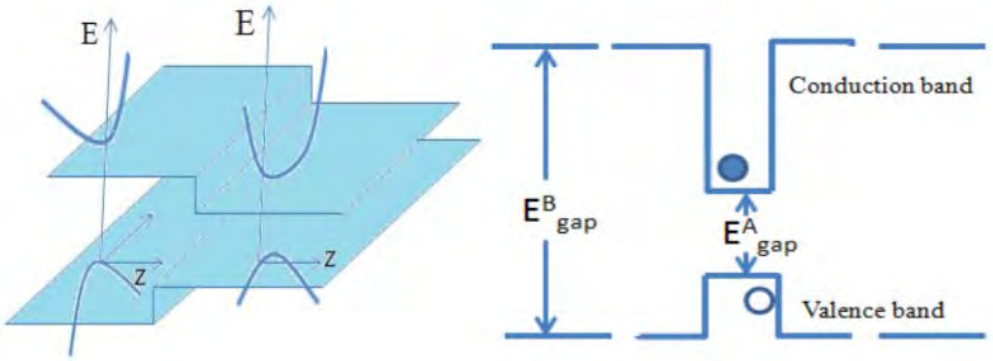
2D: electrons are bound along x, free to move perpendicularly



parabolic dependence

$$k = \frac{n\pi}{L}$$

Two different semiconductors with different band gaps can be joined to form a heterojunction. **The discontinuity in either the conduction or the valence band can be used to form a potential well.** If 1 thin layer of a narrower-band gap material A is sandwiched between 2 layers of a wider-band gap material B, then they form a double heterojunction. If layer 'A' is sufficiently thin for quantum properties to be exhibited, then such a band alignment is called a single quantum well.



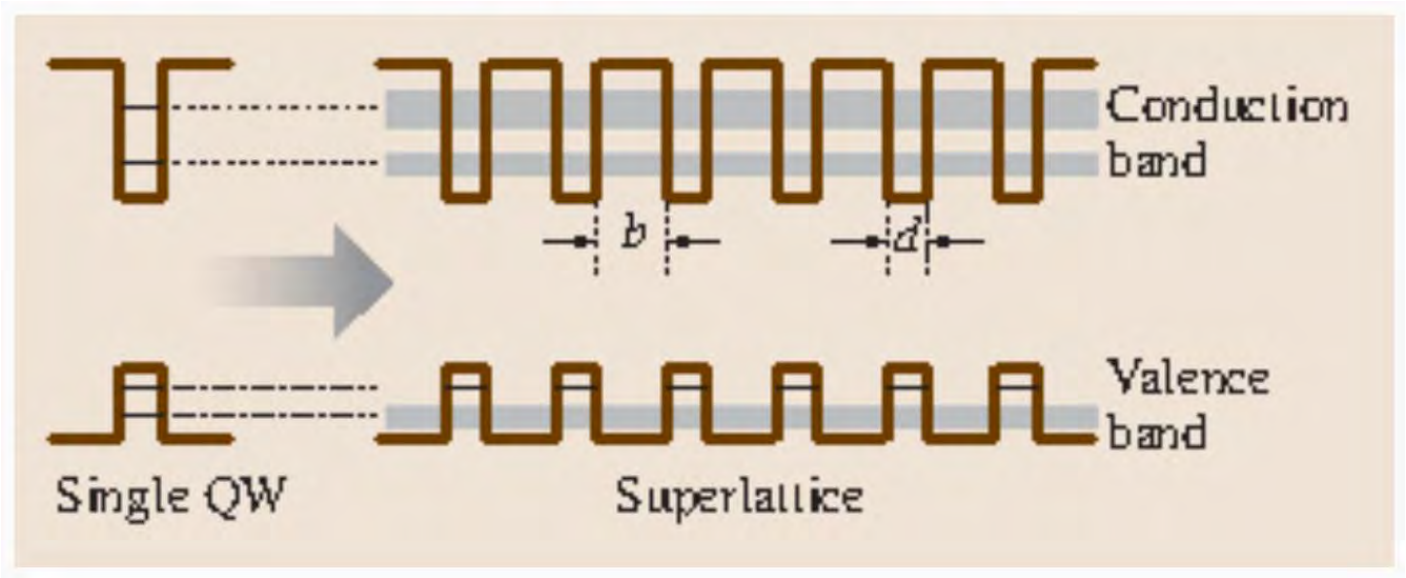
Type of manipulations

- Additional semiconductor layers can be included in the heterostructure, for example a stepped or asymmetric quantum well can be formed by the **inclusion of an alloy between materials A and B.**

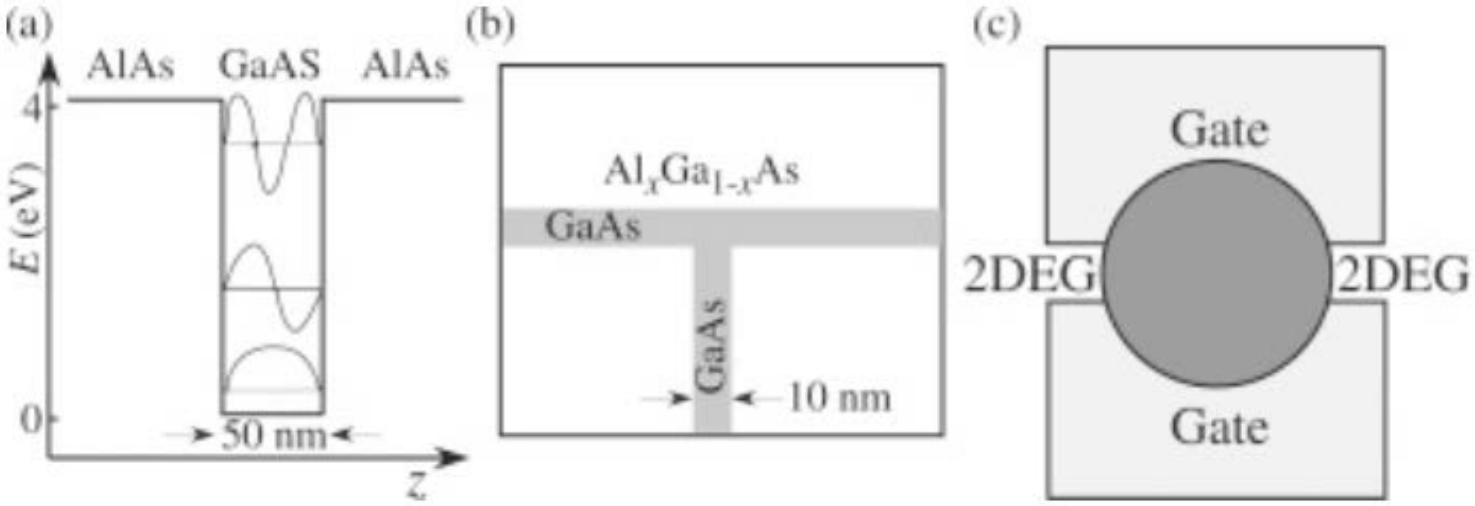
- QWs can be grown as strained layers on top of a lattice with a different unit cell size. (typical example:$In_x Ga_{1-x}N/GaN$). These layers do not satisfy the lattice-matching condition, but as long as the total $In_x Ga_{1-x}N$ thickness is less than the critical value, there is an energy barrier to the formation of dislocations - ***Strained Quantum Wells***.

➢ In practice, this allows considerable extra flexibility in the bandgap engineering that can be achieved.

Still more complex structures can be formed, such as symmetric or asymmetric double quantum well and **multiple quantum wells** or **superlattices**.



The difference between the latter is the extent of the interaction between the quantum wells; a multiple quantum well exhibits the properties of a collection of isolated single quantum wells, whereas **in a superlattice the quantum wells do interact**.



quantum well quantum wire quantum dot

(a) Schematic diagram of an AlAs/GaAs quantum well. The electrons are confined along *z* (showing the three lowest energy confined eigenstates) and free to move in the *x*-*y* plane. (b) A quantum wire is formed at the intersection of the T-shaped (shaded) region formed by two 10 nm GaAs type I quantum wells, confined by $Al_x\ Ga_{1-x}\ As$ barriers. (c) Application of gates on a 2D electron gas (2DEG) to confine electrons into a lateral quantum dot, typically of size of a few tens of nanometer.

Ref.: https://www.sciencedirect.com/topics/physics-and-astronomy/quantum-wells

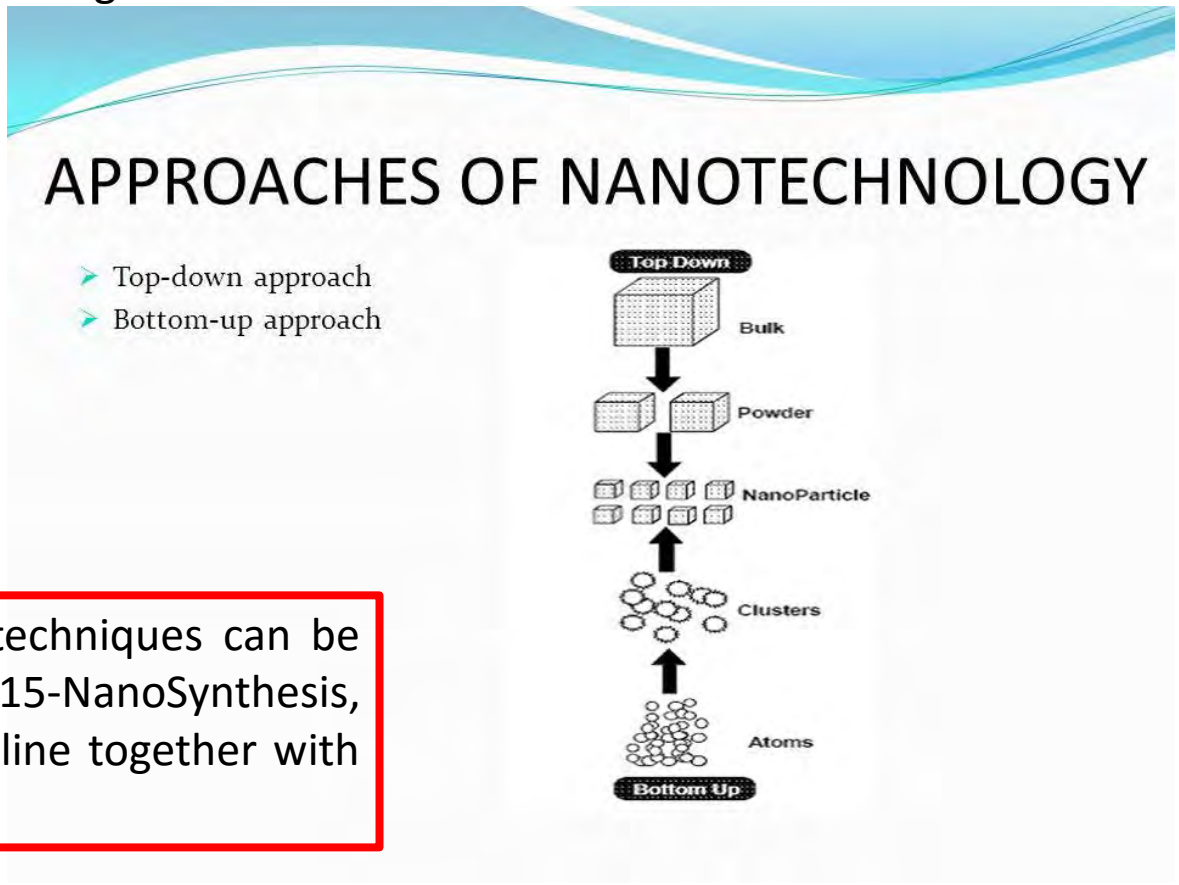
Building things at the Nanoscale

Top-down approach

Process that starts by a bulk amount of the material we plan to use for nanowires and carve it away down to the right size.

Bottom-up approach

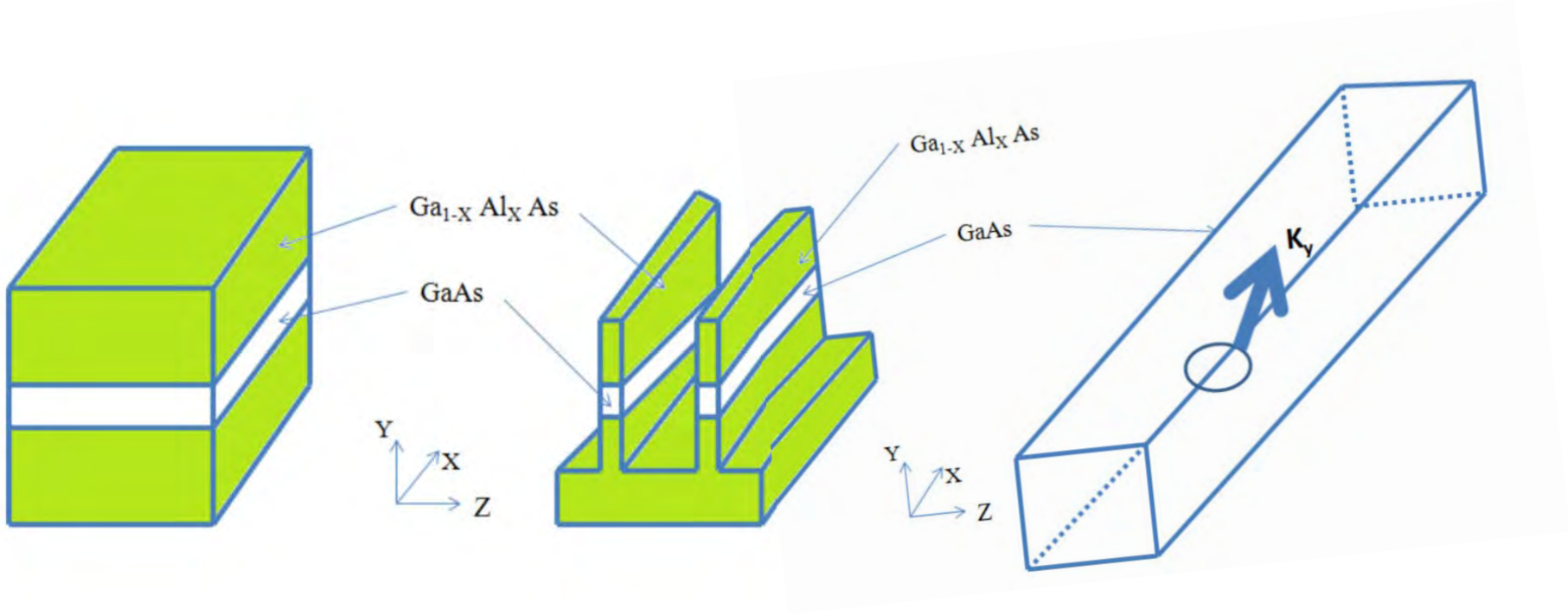
Assembly process where smaller particles join to make a larger structure.



More details on the techniques can be found in powerpoint L15-NanoSynthesis, that will be placed online together with this lectures.

QUANTUM WIRE

A quantum well layer can be patterned* to leave a free standing strip of quantum well material; the electron (or hole) is now free to move in only one direction. Any charge carriers are still confined along the heterostructure growth (z-) axis, as they were in the quantum well, but in addition (provided the strip is narrow enough) they are now confined along an additional direction, either the x- or the y-axis, depending on the lithography.

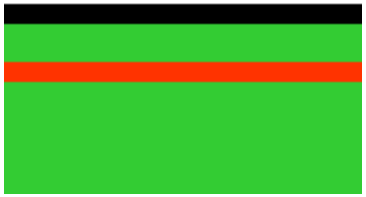


*By Photolithography or electron-beam lithography, and etched.

“Pseudowires”

Lithography and etching

Formation of 2d quantum well



Coating with resist

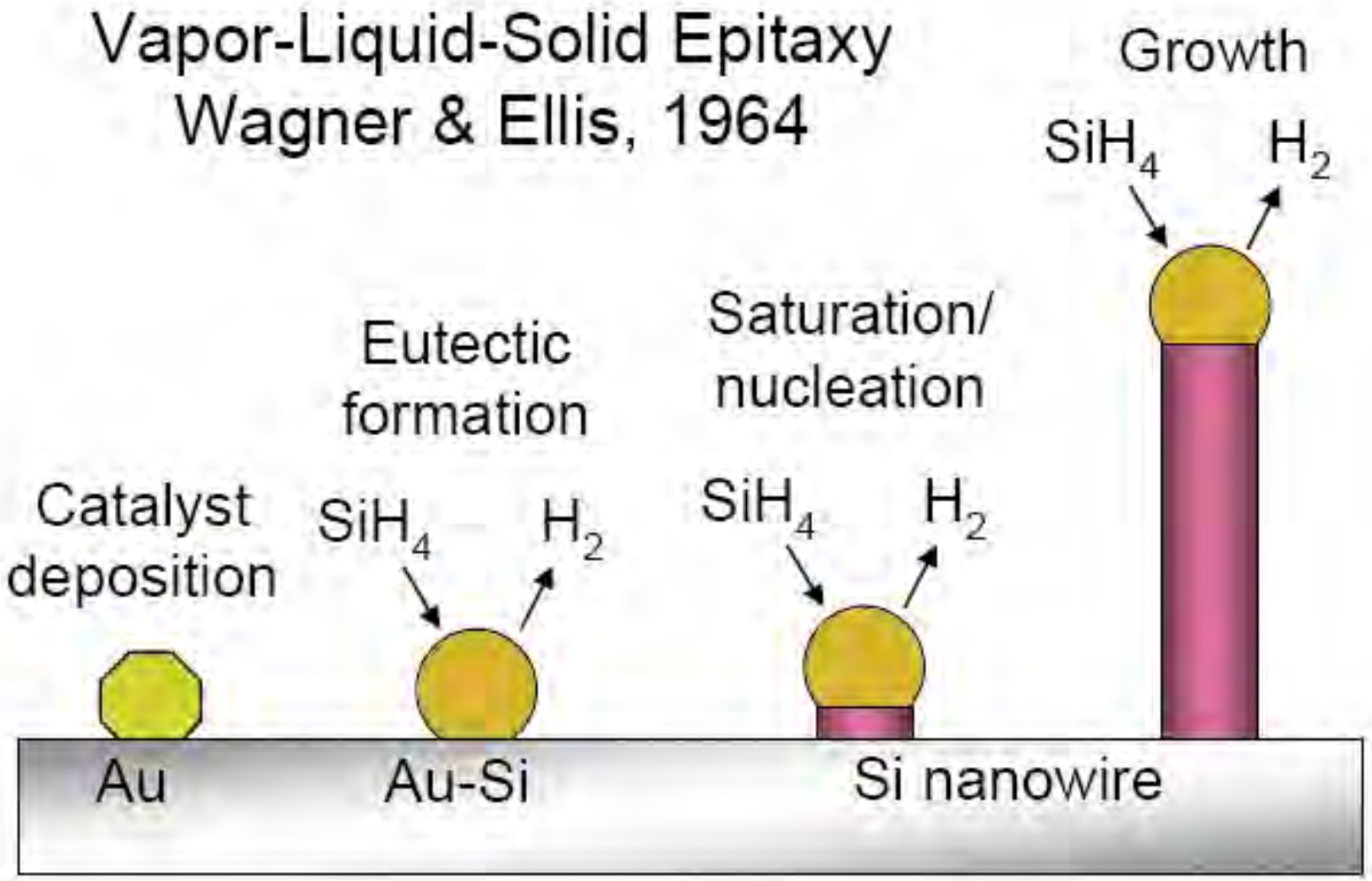
Create pattern

Etch, until wire remains

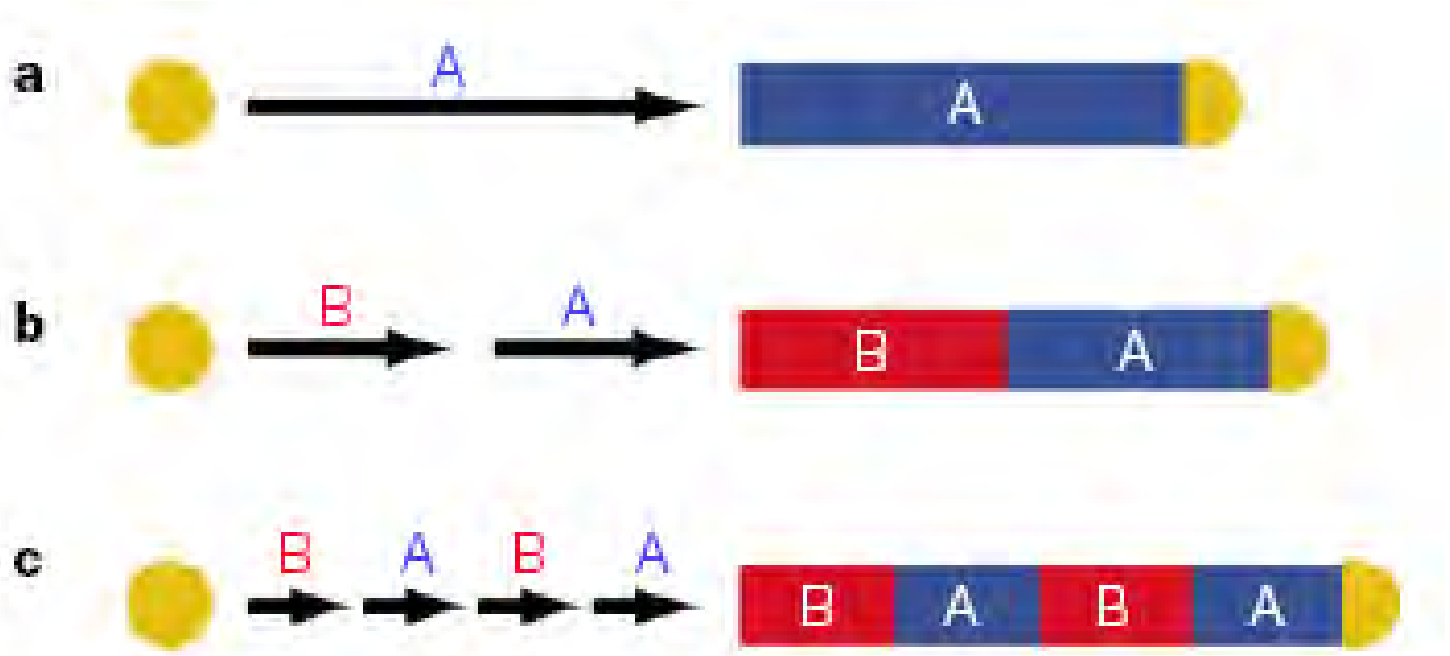
Sometimes overgrown again to shield wire!

Disadvantages: optical and electrical dead layer because of defects due to etching

Growing Nanowires



Nanowire superlattice

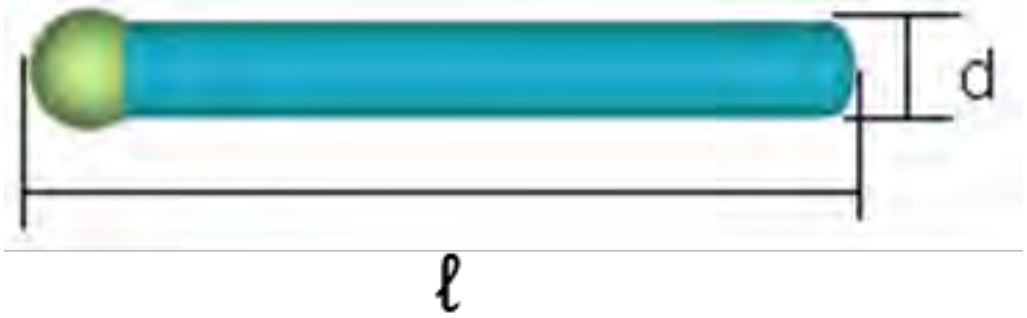


Upon completion of the first growth step, a different material (red) can be grown from the end of the nanowire. Repetition of steps leads to a compositional superlattice within a single nanowire.

Diameter (d) of NWs range from 1 nm – 100 nm.

Length (ℓ) varies from 10 nm – 1 μm

- Nanowires: wires with large aspect ratios (ℓ/d > 20)
- Nanorods: wires with small aspect ratios (ℓ/d)
- Nanotubes: hollow wires



Summary of single crystal nanowires synthesized

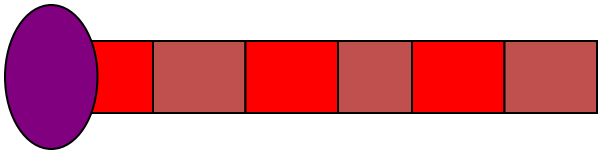
Material	Growth Temperature [°C]	Minimum Diameter [nm]	Average Diameter [nm]	Structure	Growth Direction	Ratio of Components
GaAs	800–1030	3	19	ZB	<111>	1.00 : 0.97
GaP	870–900	3–5	26	ZB	<111>	1.00 : 0.98
$GaAs_{0.6}P_{0.4}$	800–900	4	18	ZB	<111>	1.00 : 0.58 : 0.41
InP	790–830	3–5	25	ZB	<111>	1.00 : 0.98
InAs	700–800	3–5	11	ZB	<111>	1.00 : 1.19
$InAs_{0.5}P_{0.5}$	780–900	3–5	20	ZB	<111>	1.00 : 0.51 : 0.51
ZnS	990–1050	4–6	30	ZB	<111>	1.00 : 1.08
ZnSe	900–950	3–5	19	ZB	<111>	1.00 : 1.01
CdS	790–870	3–5	20	W	<100>, <002>	1.00 : 1.04
CdSe	680–1000	3–5	16	W	<110>	1.00 : 0.99
$Si_{1-x}Ge_x$	820–1150	3–5	18	D	<111>	$Si_{1-x}Ge_x$

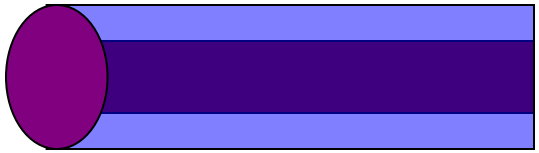
- Nanowire heterostructures

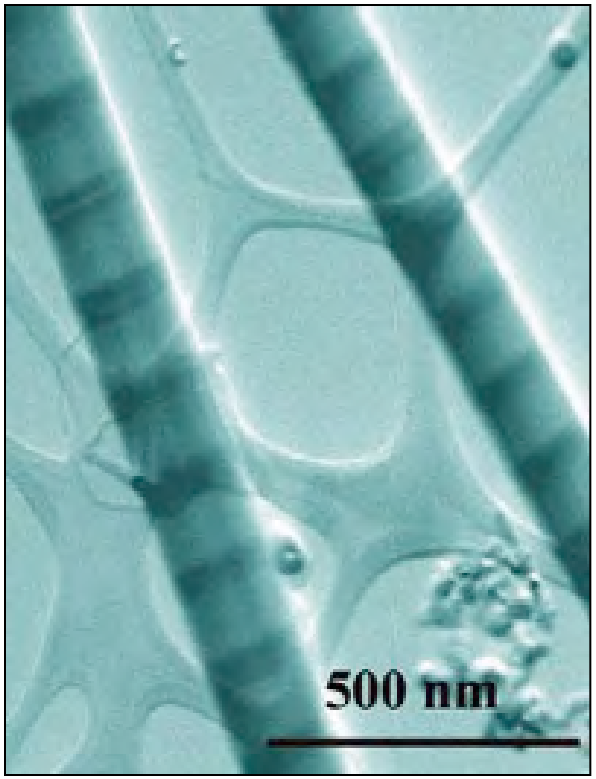
  + axial heterostructures, *e.g.* GaP-GaAs heterojunction

  + radial heterostructures, *e.g.* Si-Ge

  + Nanowire superlattices







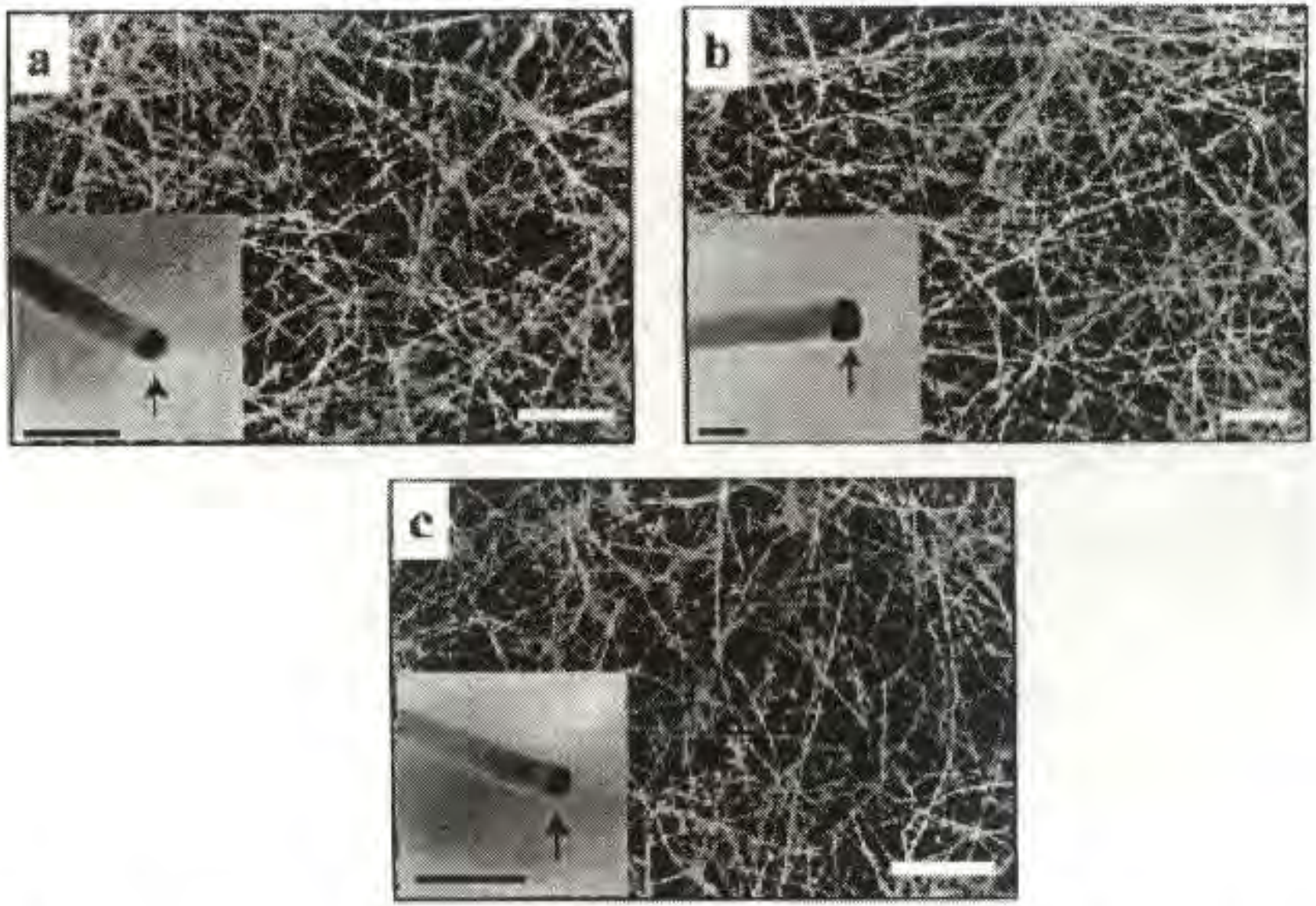
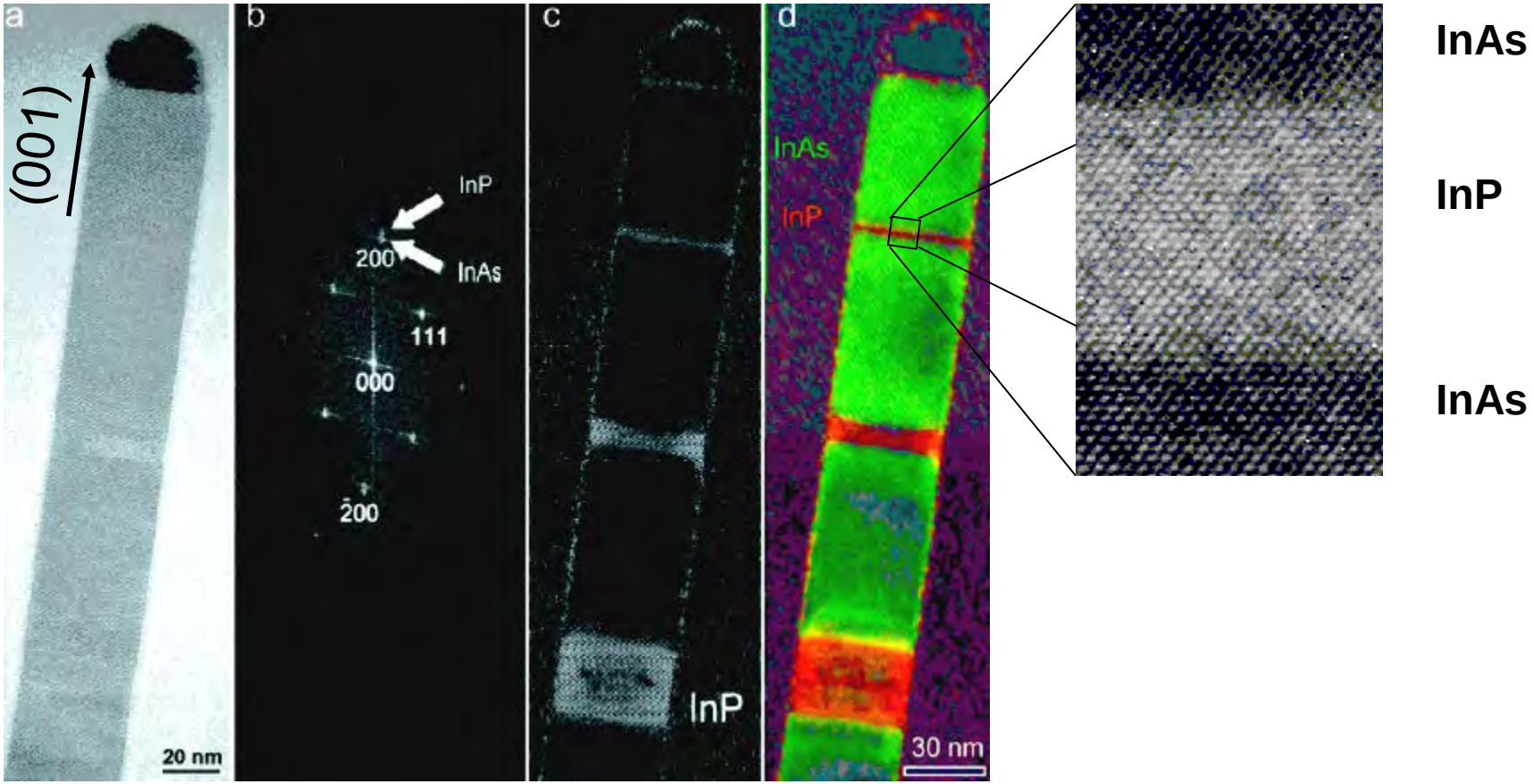


Fig. 4.15. Field-emission SEM images of compound semiconductor nanowires grown by VLS method: (a) GaAs, (b) GaP, and (c) $GaAs_{0.6}P_{0.4}$. The scale bars are 2 μm. [X. Duan and C.M. Lieber, *Adv. Mater.* **12**, 298 (2000).]

Heterostructures nanowires

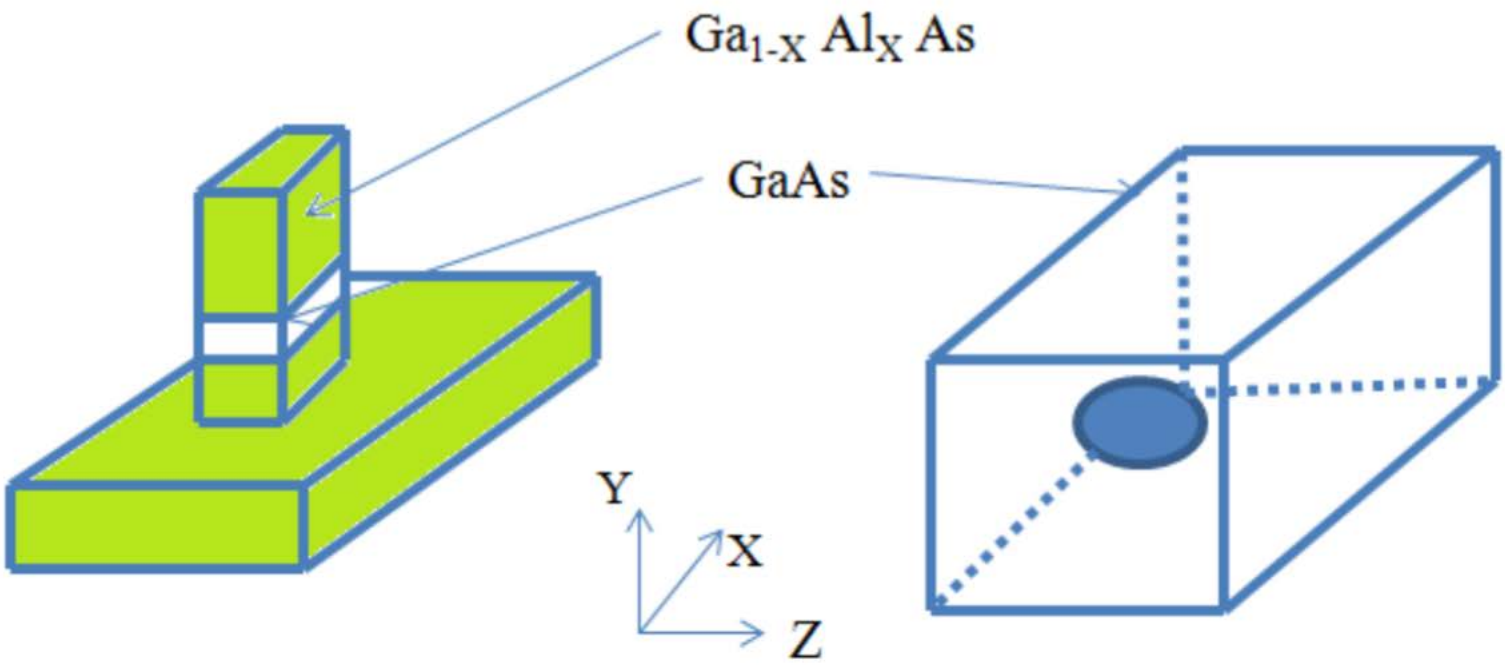


- Almost atomically sharp interfaces
- No strain-induced dislocations (stress can relax at the surface)

Björk *et al*., NanoLetters **2**, 87 (2002)

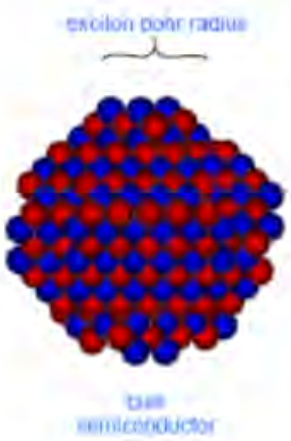
QUANTUM DOTS

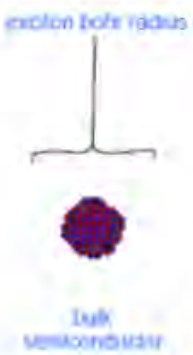
Quantum dots can again be formed by further patterning (lithography and etching) to leave pillars rather than wires, then a charge carrier can become confined in all three dimensions.

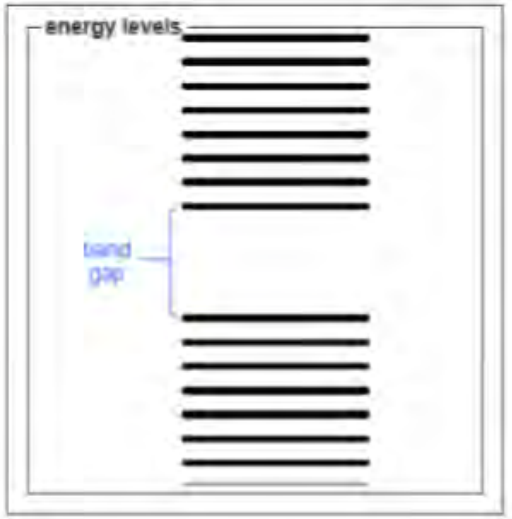


Discrete Energy Levels

- The energy levels depend on the size, and also the shape of the quantum dot.
- Smaller quantum dot:
  - Higher energy required to confine excitons to a smaller volume.
    - Energy levels increase in energy and spread out more.
    - Higher band gap energy.







Figures are from "Quantum Dots Explained." Evident Technologies. 2008.

Fabrication Methods

- Goal: to engineer potential energy barriers to confine electrons in 3 dimensions

- 3 primary methods
  - Lithography
  - Colloidal chemistry
  - Epitaxy

Colloidal Particles

- Engineer reactions to precipitate quantum dots from solutions or a host material (*e.g.* polymer)
- In some cases, need to "cap" the surface so the dot remains chemically stable (*i.e.* bond other molecules on the surface)
- Can form "core-shell" structures
- Typically group II-VI materials (*e.g.* CdS, CdSe)
- Size variations ("size dispersion")

CdSe core with ZnS shell QDs

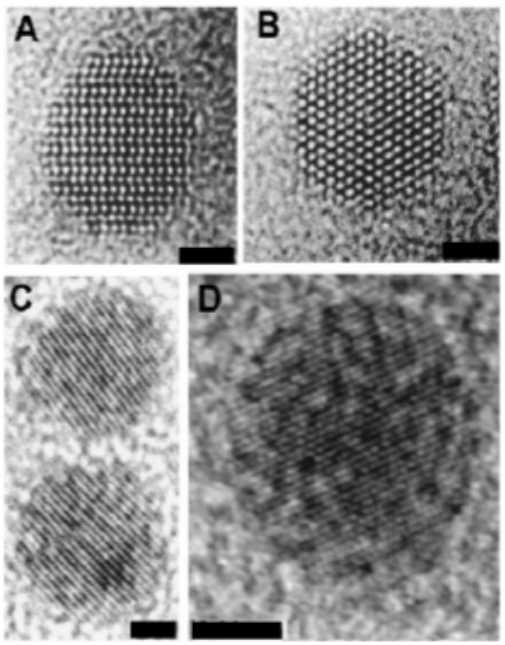
Red: bigger dots!

Blue: smaller dots!

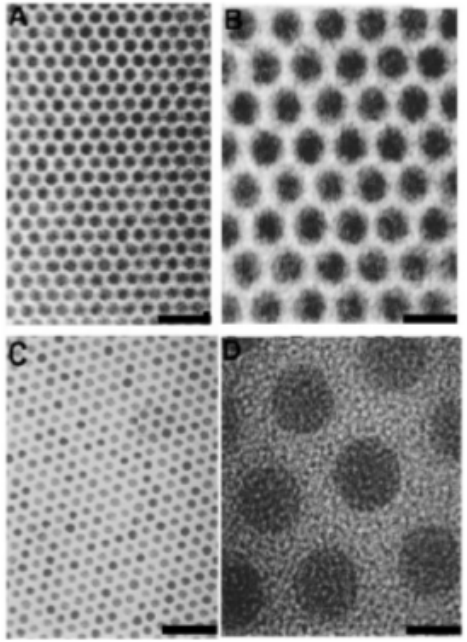
Evident Technologies: http://www.evidenttech.com/products/core_shell_evidots/overview.php

Sample papers: Steigerwald et al. Surface derivation and isolation of semiconductor cluster molecules. J. Am. Chem. Soc., 1988.

Quantum Dots by Chemical Synthesis



(a)

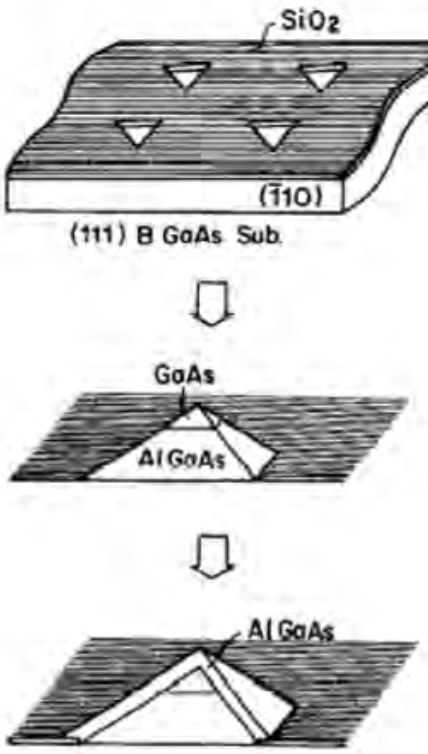


(b)

TEM images of (a) chemically synthesised nanoparticles and (b) their superlattice

Epitaxy: Patterned Growth

- Growth on patterned substrates
  - Grow QDs in pyramid-shaped recesses
  - Recesses formed by selective ion etching
  - Disadvantage: density of QDs limited by mask pattern



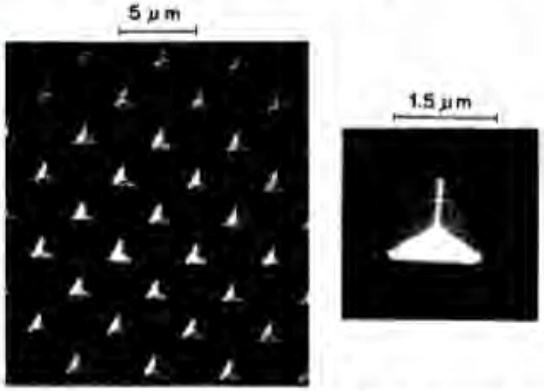
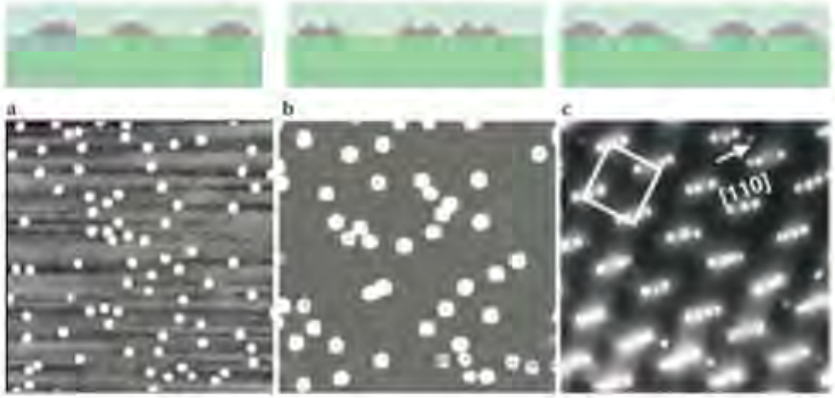


FIG. 3. Schematic view and SEM image of GaAs tetrahedral structure.

T. Fukui et al. GaAs tetrahedral quantum dot structures fabricated using selective area metal organic chemical vapor deposition. Appl. Phys. Lett. May, 1991

Epitaxy: Self-Organized Growth

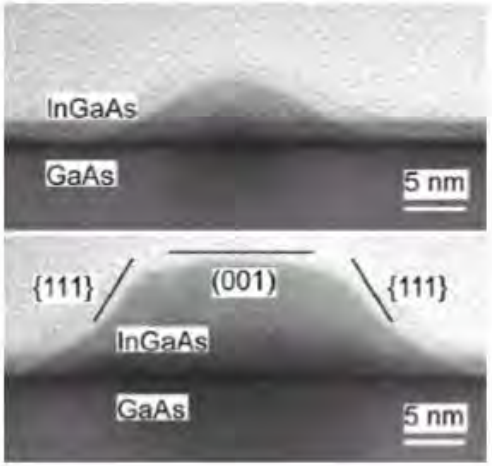
- Self-organized QDs through epitaxial growth and strain
  - Stranski-Krastanov growth mode (use MBE, MOCVD)
    - Islands formed on wetting layer due to lattice mismatch (size ~10s nm)
  - Disadvantage: size and shape fluctuations, ordering
  - Control island initiation
    - Induce local strain, grow on dislocation, vary growth conditions, combine with patterning



AFM images of islands epitaxiall grown on GaAs substrate.
(a) InAs islands randomly nucleate.
(b) Random distribution of InxGa1-xAs ring-shaped islands.
(c) A 2D lattice of InAs islands on a GaAs substrate.

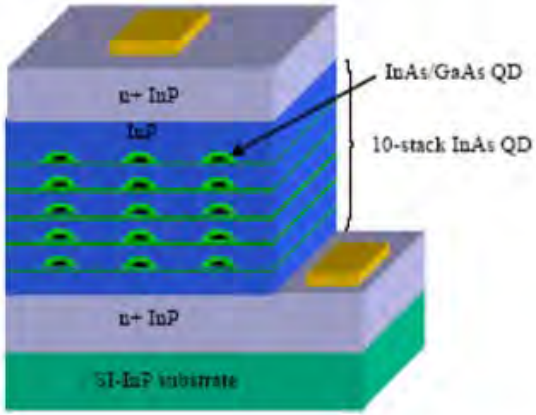
P. Petroff, A. Lorke, and A. Imamoglu. Epitaxially self-assembled quantum dots. Physics Today, May 2001.

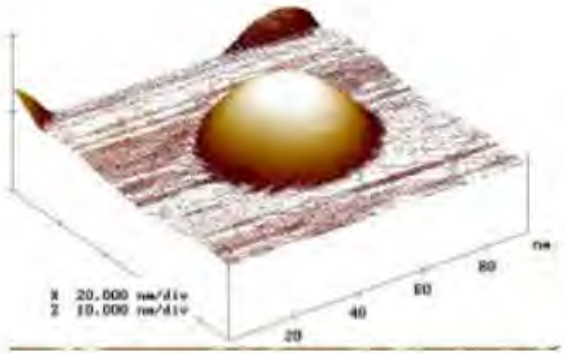
Quantum Dots
(Structure and Formation)



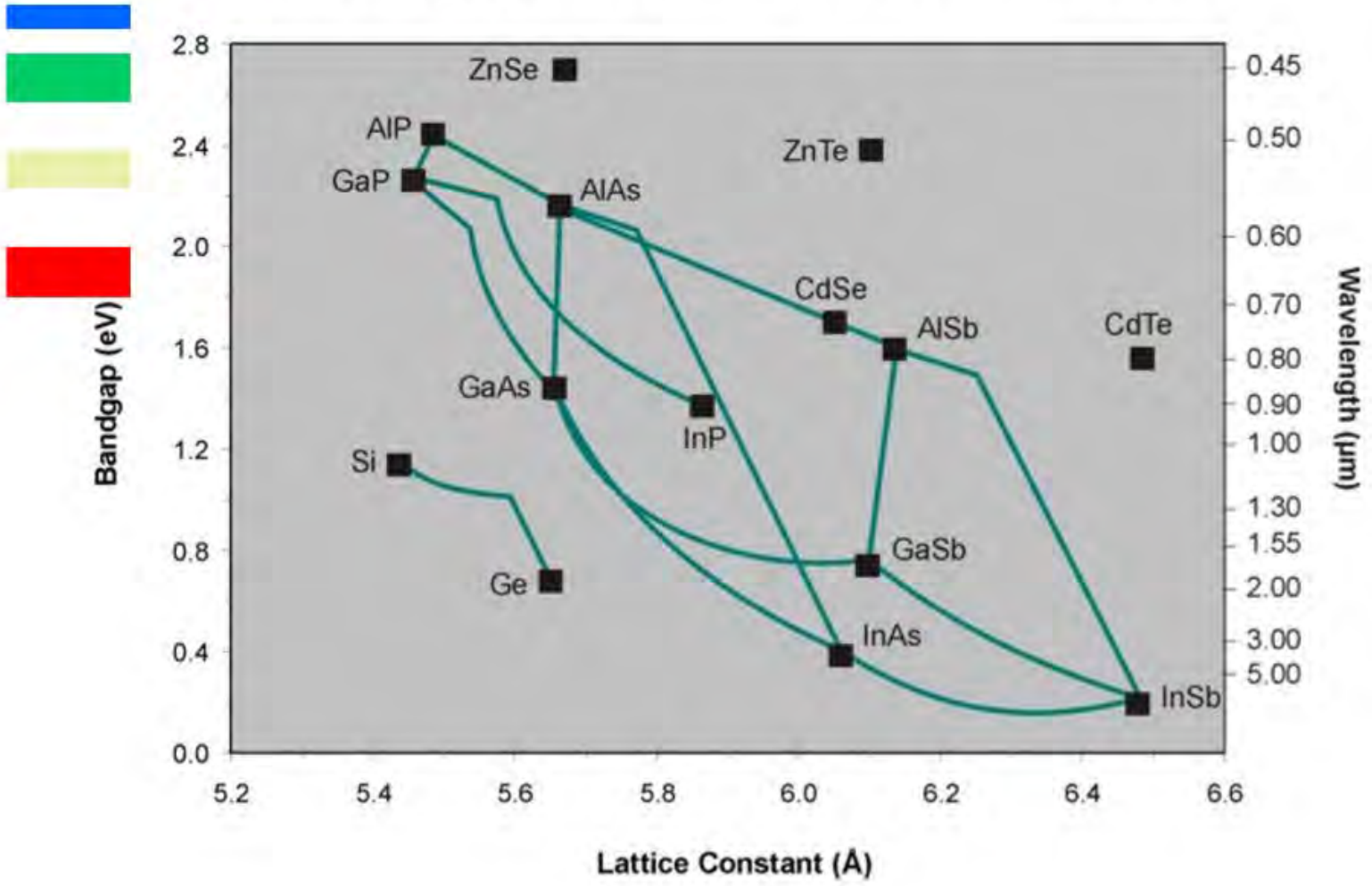
Self-Assembly (a.k.a. Stranski-Krastanov Method): Mismatched lattice constants cause surface tension which results in QD formation with surprisingly uniform characteristics.

GaAs → 5.6533 Å InAs → 6.0584 Å





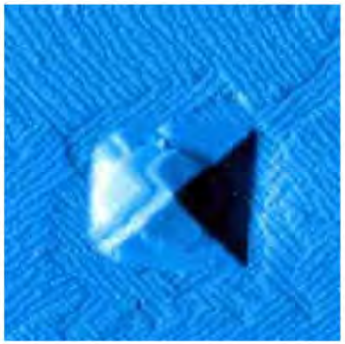
Bandgap vs. Lattice Constant



Some examples of QD Heterostructures

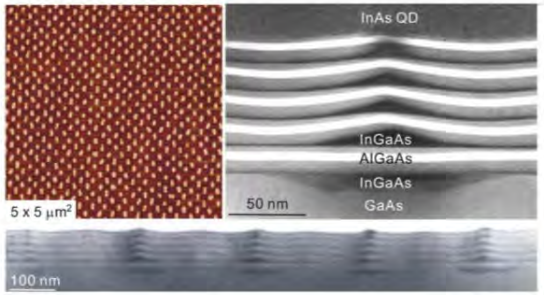
SiGe Heterostructures

Typical sizes: wetting layer 2 nm,
dot height 5-10 nm, dot width 100-160 nm



InAs/InGaAs/GaAs Heterostructures

Typical sizes: dot height 10 nm,
dot width 30-40 nm



We can make use of these dots, wires and wells to fabricate a device: a transistor or a gate or a memory device and they can work with voltage levels less than **0.2 V** and **current in the nano to pico Amps**.

Most of the **nanoelectronic devices** are based on the semiconductor nanostructures fabricated by **tailoring the band gaps** of desired level.

The major focus of the band gap engineering is to design non- traditional devices with unusual electron transport and optical effects.

Nanostructures	Typical nanoscale dimension
Thin films and quantum wells (two-dimensional structures)	1–1000 nm (thickness)
Quantum wires, nanowires, nanorods and nanopillars (one-dimensional structures)	1–100 nm (radius)
Nanotubes	1–100 nm (radius)
Quantum dots, nanodots (zero-dimensional structures)	1–10 nm (radius)
Porous nanomaterials, aerogels	1–50 nm (particle size, pore size)
Sculptured thin films	10–500 nm

Next Lecture

Quantum confinement in more detail

Understanding the QC effects with exercises