Università di Pisa

LM Materials and Nanotechnology - a.a. 2016/17

Spectroscopy of Nanomaterials II sem – part 4

Quantum confinement (in semiconductors): optical properties of quantum wells, wires, dots

OUTLOOK

There are very many properties depending on size and dimensionality: among them, optical properties (e.g., absorption and emission, but not only, as we will see in the following)

Dealing with nanosized and eventually anisotropically-shaped (2-D, 1-D, 0-D) **semiconductor** particles leads confinement effect to play an important role
→ *optical properties different with respect to bulk counterparts*

Motivations for our interest (here and now):
- quantum confinement is a too relevant topic to be underestimated, which you will eventually corroborate with other consequences (e.g., electrical trasnport) in other courses
- this is an opportunity to revise a few basic quantum mechanics, an always useful task
- a huge variety of devices exists which are based on quantum confinement: they include, e.g., quantum dots sometimes used in labeling samples to be observed by microscopy (already seen something related to that)

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Today's menu:
- Finger food consisting of quantum mechanics basics (cats
  excluded!)
- Main course of confinement effects in slices (quantum
  wells), garnished with a few spaghetti (quantum wires)
  and caviar spheres (quantum dots)
- Colourful balls, coated and uncoated, for dessert
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ULTRA-SHORT PRIMER OF QM

Effects of quantum mechanics (QM) are dominant in many systems (typically, involving small, fast particles): they are essential to understand absorption/emission processes involving electrons

Starting points of QM:
wave-matter complementarity (or dualism), that means, e.g., an e.m. wave can be represented by particles (photons) and particles can be represented by waves

Basic QM tool (consequence of the dualism above):
Wavefunction $\Psi(r,t)$ to describe a quantum particle
→ **probabilistic approach**: $|\Psi(r,t)|^2$ represents the probability to find the particle in *r, r+dr*
→ the concept of trajectory does not apply any more!!

Indeed the **uncertainty principle** (a theorem, truly) states, e.g., in 1-D case:

$$\Delta x \Delta p_x \geq \hbar/2$$

For instance, the more precisely the position of some particle is determined, the less precisely its momentum can be known, and vice versa.[1] The original heuristic argument that such a limit should exist was given by Werner Heisenberg in 1927, after whom it is sometimes named the **Heisenberg principle**.

SCHROEDINGER

> Main problem of the mechanics:
> - To predict *r(t)* e *v(t)* (trajectory) based on knowledge of forces *F*
> - Main tool: equation of motion (Newton) *a = F/m*

Main problem of QM:
- To determine Ψ*(r,t)* starting from the knowledge of local potentials
- Main tool: Schroedinger's equation (non relativistic situations!):

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(\vec{r},t) + V(\vec{r},t) = i\hbar\frac{\partial\Psi(\vec{r},t)}{\partial t}$$

with $\quad \nabla^2\Psi(\vec{r},t) = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\Psi(\vec{r},t)$ (in cartesian coordinates)

V(r,t) is the **potential**, typically depending on *r,t* , ruling the dynamics of the object
Note: classically potential and force are related through *F* = - ∇U

> Schroedinger equation in the 1-D case:
>
> $$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t) + V(x,t) = i\hbar\frac{\partial\Psi(x,t)}{\partial t}$$
>
> (partial derivatives equation)

CONCEPTUAL BASIS OF SCHROEDINGER

1. It must be consistent with the de Broglie-Einstein postulates, (5-8)

$$\lambda = h/p \quad \text{and} \quad v = E/h$$

2. It must be consistent with the equation

$$E = p^2/2m + V \qquad (5\text{-}9)$$

relating the total energy E of a particle of mass m to its kinetic energy $p^2/2m$ and its potential energy V.

3. It must be *linear* in $\Psi(x,t)$. That is, if $\Psi_1(x,t)$ and $\Psi_2(x,t)$ are two different solutions to the equation for a given potential energy V (we shall see that partial differential equations have many solutions), then any arbitrary linear combination of these solutions, $\Psi(x,t) = c_1\Psi_1(x,t) + c_2\Psi_2(x,t)$, is also a solution. This combination is said to be linear since it involves the first (linear) power of $\Psi_1(x,t)$ and $\Psi_2(x,t)$; it is said to be arbitrary since the constants c_1 and c_2 can have any (arbitrary) values. This *linearity* requirement ensures that we shall be able to *add together wave functions* to produce the constructive and destructive interferences that are so characteristic of waves. Interference phenomena are commonplace for electromagnetic waves; all the diffraction patterns of physical optics are understood in terms of the addition of electromagnetic waves. But the Davisson-Germer experiment, and others, show that diffraction patterns are also found in the motion of electrons, and other particles. Therefore, their wave functions also exhibit interferences, and so they should be capable of being added.

4. The potential energy V is generally a function of x, and possibly even t. However, there is an important special case where

$$V(x,t) = V_0 \qquad (5\text{-}10)$$

This is just the case of the free particle since the force acting on the particle is given by

$$F = -\partial V(x,t)/\partial x$$

which yields $F = 0$ if V_0 is a constant. In this case Newton's law of motion tells us that the linear momentum p of the particle will be constant, and we also know that its total energy E will be constant. We have here the situation of a free particle with constant values of $\lambda = h/p$ and $v = E/h$, discussed in Chapter 3. We therefore assume that, in this case, the desired differential equation will have sinusoidal traveling wave solutions of constant wavelength and frequency, similar to the sinusoidal wave function, (5-1), considered in that chapter.

Using the de Broglie-Einstein relations of assumption 1 to write the energy equation of assumption 2 in terms of λ and v, we obtain

$$h^2/2m\lambda^2 + V(x,t) = hv$$

The equation "must be" as it is…

In order to satisfy the linearity assumption 3, it is necessary that every term in the differential equation be linear in $\Psi(x,t)$, i.e., be proportional to the first power of $\Psi(x,t)$. Note that any derivative of $\Psi(x,t)$ has this property. For instance, if we consider the change in the magnitude of $\partial^2\Psi(x,t)/\partial x^2$ that results if we change the magnitude of $\Psi(x,t)$, say by a factor of c, we see that the derivative increases by the same factor and thus is proportional to the first power of the function. This is true since

$$\frac{\partial^2[c\Psi(x,t)]}{\partial x^2} = c\frac{\partial^2\Psi(x,t)}{\partial x^2}$$

where c is any constant. In order that the differential equation itself be linear in $\Psi(x,t)$, it cannot contain any term which is independent of $\Psi(x,t)$, i.e., which is proportional to $[\Psi(x,t)]^0$, or which is proportional to $[\Psi(x,t)]^2$ or any higher power. After obtaining the equation, we shall demonstrate explicitly that it is linear in $\Psi(x,t)$, and in the process the validity of these statements will become apparent.

Now let us use the assumption 4, which concerns the form of the free particle solution. As suggested by that assumption, we shall first try to write an equation containing the sinusoidal wave function, (5-1), and/or derivatives of that wave function. We have already evaluated some of the derivatives in Examples 5-1. Inspecting these, we see that the effect of taking the second space derivative is to introduce a factor of $-k^2$, and the effect of taking the first time derivative is to introduce a factor of $-\omega$. Since the differential equation we seek must be consistent with (5-12), which contains a factor of k^2 in one term and a factor of ω in another, these facts suggest that the differential equation should contain a second space derivative of $\Psi(x,t)$ and a first time derivative of $\Psi(x,t)$. But there must also be a term containing a factor of $V(x,t)$ because it is present in (5-12). In order to ensure linearity, this term must contain a factor of $\Psi(x,t)$. Putting all these ideas together, we try the following form for the differential equation

$$\alpha\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x,t)\Psi(x,t) = \beta\frac{\partial\Psi(x,t)}{\partial t} \qquad (5\text{-}13)$$

The constants α and β have values which remain to be determined. They are used to provide flexibility which, we might guess, will be needed in fitting (5-13) to the various requirements it must satisfy.

EIGENSTATES AND EIGENVALUES

If *V* **does not** depend on time, *V(x)* only, then:

$$\Psi(x,t) = \psi(x)\varphi(t) \quad \text{with} \quad \varphi(t) = e^{-i\frac{E}{\hbar}t}$$

and

$$-\frac{\text{h}^2}{2m}\frac{d^2}{dx^2}\psi(x) + V(x) = E\psi(x)$$

Steady-state Schroedinger equation

The wavefunction for steady state problems can factorized!!

$\psi(x)$: **eigenfunction (eigenstate)**
E : **energy eigenvalue**

5-6 REQUIRED PROPERTIES OF EIGENFUNCTIONS

In the following section we shall consider, in a very general way, the problem of finding solutions to the time-independent Schroedinger equation. These considerations will show that energy quantization appears quite naturally in the Schroedinger theory. We shall see that this extremely significant property results from the fact that *acceptable solutions* to the time-independent Schroedinger equation can be found only for certain values of the total energy E.

To be an acceptable solution, an eigenfunction $\psi(x)$ and its derivative $d\psi(x)/dx$ are required to have the following properties:

$\psi(x)$ must be *finite*.

$\psi(x)$ must be *single valued*.

$\psi(x)$ must be *continuous*.

$d\psi(x)/dx$ must be *finite*.

$d\psi(x)/dx$ must be *single valued*.

$d\psi(x)/dx$ must be *continuous*.

Substituting the assumed form of the solution, $\Psi(x,t) = \psi(x)\varphi(t)$, into the Schroedinger equation, and also restricting ourselves to time-independent potential energies that can be written as $V(x)$, we obtain

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)\varphi(t)}{\partial x^2} + V(x)\psi(x)\varphi(t) = i\hbar\frac{\partial\psi(x)\varphi(t)}{\partial t}$$

Now

$$\frac{\partial^2\psi(x)\varphi(t)}{\partial x^2} = \varphi(t)\frac{\partial^2\psi(x)}{\partial x^2} = \varphi(t)\frac{d^2\psi(x)}{dx^2}$$

the notation $\partial^2\psi(x)/\partial x^2$ being redundant with $d^2\psi(x)/dx^2$ since $\psi(x)$ is a function of x alone. Similarly

$$\frac{\partial\psi(x)\varphi(t)}{\partial t} = \psi(x)\frac{\partial\varphi(t)}{\partial t} = \psi(x)\frac{d\varphi(t)}{dt}$$

Therefore, we have

$$-\frac{\hbar^2}{2m}\varphi(t)\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x)\varphi(t) = i\hbar\psi(x)\frac{d\varphi(t)}{dt}$$

Dividing both sides of this equation by $\psi(x)\varphi(t)$, we obtain

$$\frac{1}{\psi(x)}\left[-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x)\right] = i\hbar\frac{1}{\varphi(t)}\frac{d\varphi(t)}{dt} \tag{5-36}$$

Note that the right side of (5-36) does not depend on x, while the left side does not depend on t. Consequently, their common value cannot depend on either x or t. In other words, the common value must be a constant, which we shall call G. The result of this consideration is that (5-36) leads to two separate equations. One equation is obtained by setting the left side equal to the common value

$$\frac{1}{\psi(x)}\left[-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x)\right] = G \tag{5-37}$$

The other equation is obtained by setting the right side equal to the common value

$$i\hbar\frac{1}{\varphi(t)}\frac{d\varphi(t)}{dt} = G \tag{5-38}$$

The constant G is called the *separation constant*, for the same reason that this technique for solving partial differential equations is called the separation of variables.

$$\frac{d\varphi(t)}{dt} = -\frac{iG}{\hbar}\varphi(t) \tag{5-39}$$

This differential equation tells us that the function $\varphi(t)$, which is its solution, has the property that its first derivative is proportional to the function itself. Anyone with much experience in differentiating would not have difficulty in guessing that $\varphi(t)$ must be an exponential function. Therefore, let us assume that the solution to the differential equation is of the form

$$\varphi(t) = e^{\alpha t}$$

where α is a constant that will be determined shortly. We verify this assumed solution by differentiating it, to obtain

$$\frac{d\varphi(t)}{dt} = \alpha e^{\alpha t} = \alpha\varphi(t)$$

which we then substitute into (5-39). This yields

$$\alpha\varphi(t) = -\frac{iG}{\hbar}\varphi(t)$$

If we set

$$\alpha = -\frac{iG}{\hbar}$$

the assumed solution obviously satisfies the equation. Therefore

$$\varphi(t) = e^{-iGt/\hbar} \tag{5-40}$$

is a solution to (5-38) or (5-39).

We see that $\varphi(t)$ is an oscillatory function of time of frequency $\nu = G/h$. But, according to the de Broglie-Einstein postulates of (5-8), the frequency must also be given by $\nu = E/h$, where E is the total energy of the particle associated with the wave function corresponding to $\varphi(t)$. The reason is, of course, that $\varphi(t)$ is the function that specifies the time dependence of the wave function. Comparing these expressions, we see that the separation constant must be equal to the total energy of the particle. That is

$$G = E \tag{5-42}$$

Using this value of G in the space equation, (5-37), that we obtained from the separation of variables, we have

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \tag{5-43}$$

After R. Eisberg, R. Resnick, Quantum Physics of Atoms, Molecules, …, Second Edition, Wiley, New York (1985)

EXAMPLE 1: FREE PARTICLE

A free particle (e.g., a photon!) which does not interact at all and moves along the X axis having <u>a well defined</u> impulse p

$V = 0$

A good solution of the Schroedinger equation is:

$$\Psi(x,t) \propto e^{ikx} e^{-i\omega t} = \psi(x)\varphi(t)$$

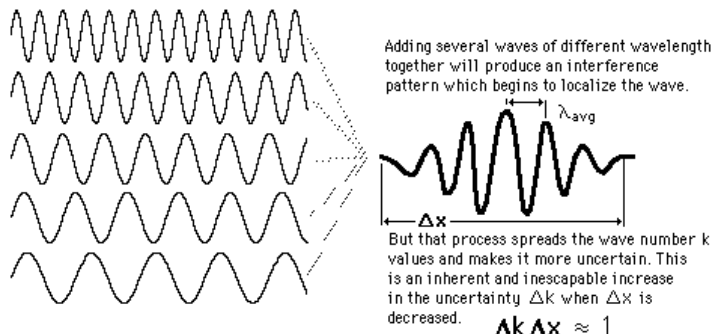$$\psi(x) = e^{ikx}$$

with $p = \hbar k$
(de Broglie wave)

de Broglie wavelength: $\lambda_{dB} = 2\pi/k = h/p$

A "little" problem: it is $|\Psi|^2 = 1$ everywhere
→ the probability of finding the particle is always 1
→ the normalization factor $\int |\psi|^2\,dx$ diverges!

(in agreement with uncertainty: $\Delta p = 0$ → $\Delta x \rightarrow \infty$)

Adding several waves of different wavelength together will produce an interference pattern which begins to localize the wave.

λ_{avg}

Δx

But that process spreads the wave number k values and makes it more uncertain. This is an inherent and inescapable increase in the uncertainty Δk when Δx is decreased. $\Delta k \Delta x \approx 1$

(solution to such "little" problem is in the concept of wavepackets: the wavefunction of the free particle results from superposition of many individual waves with slightly different energy, frequency, wavenumber and localization is achieved)

EXAMPLE 2: POTENTIAL WELL (INFINITE)

A free particle moves along the *X* axis and feels two (infinite) potential barriers at *x* = –*a*/2 and *x* = +*a*/2

The potential reads: $V(x) = \begin{cases} 0 & 0 \le x \le a \\ \infty & x < 0; \; x > a \end{cases}$
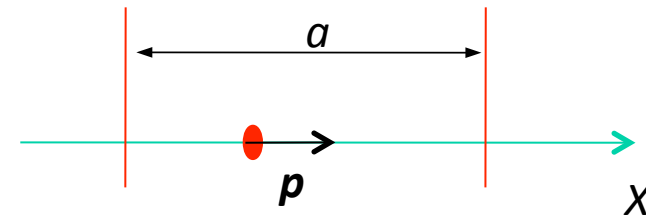
One can easily assume that the particle is **bound** to move within the two potential barriers defining the well

⇩

Ψ(x,t) is given by superposition of a particle moving to the left and one moving to the right

$$\Psi(x,t) = Ae^{i(kx-\omega t)} + Be^{i(-kx-\omega t)} \quad \text{with} \quad \omega = \frac{E}{\hbar}$$

Boundary conditions: *ψ* = 0 at *x* = -*a*/2 and *x* = *a*/2

⇩

A = B or *A = - B*

Note: the derivative of the wavefunction is here non continuous because *V* → ∞

(LONGITUDINAL) CAVITY MODES IN OPTICS

Boundary conditions are identical to those of an "optical cavity" of the simplest configuration:
Two (perfectly reflecting) plane mirrors parallel each other and placed at a relative distance a

$R_1 = \infty$ plane-parallel $R_2 = \infty$

a
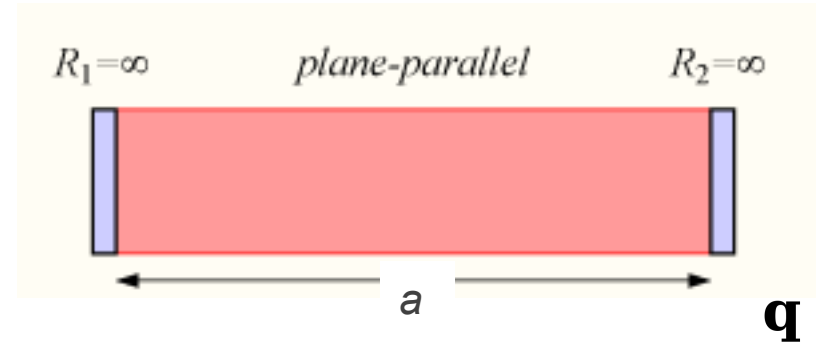
q

✓ **Steady-state** solutions (standing waves) for the e.m. field within the cavity can be found

✓ The boundary conditions impose *E* = 0 at the mirror surface (mirrors are reflective, they do not allow for electric field in the material – e.g., a perfect conductor – they are made of)

✓ Pictorially, the optical cavity allows only standing waves with nodes on the mirror position

① ② ③ ④ ⑤ ⑥
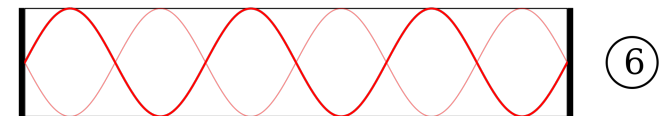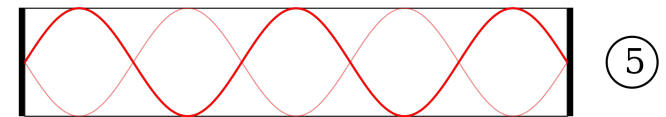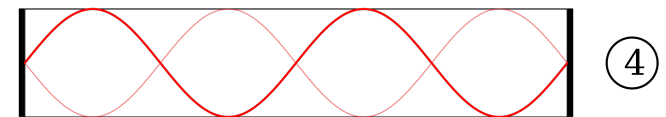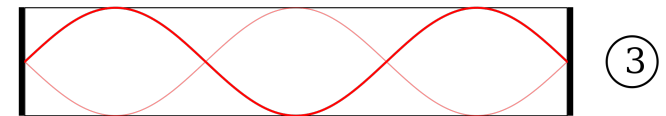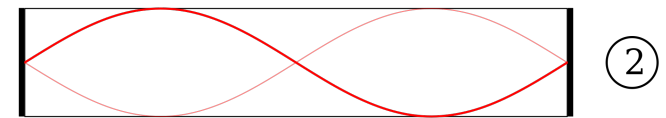
An integer number of **half**-waves is allowed within the cavity

Supported modes:
$$q\frac{\lambda_q}{2} = a \rightarrow q\frac{2\pi/k_q}{2} = a \rightarrow k_q = q\frac{\pi}{a}$$

ENERGY QUANTIZATION

In the potential box: $\psi(x) = A(e^{i(kx)} + e^{i(-kx)}) \propto \cos(kx)$

Boundary conditions: $\psi(x = -\frac{a}{2}) = \psi(x = +\frac{a}{2}) = 0$

$\Longrightarrow$ $\boxed{k_n = n\frac{\pi}{a}}$

Being the particle free within the box, the energy is only kinetic and can be written as:

$$E_n = \frac{p_n^2}{2m} = \frac{\hbar^2 k^2}{2m} = n^2 \frac{\hbar^2 \pi^2}{2ma^2}$$

Spatial confinement → energy quantization
(only discrete levels can exist!)

Note: $n \neq 0$
The energy of the ground state cannot be zero (to not violate uncertainty principle)!

Energy level separation:

$$\Delta E = E_{n+1} - E_n = \left[(n+1)^2 - n^2\right] \frac{\hbar^2 \pi^2}{2ma^2} = \left(n + \frac{1}{2}\right) \frac{\hbar^2 \pi^2}{ma^2}$$
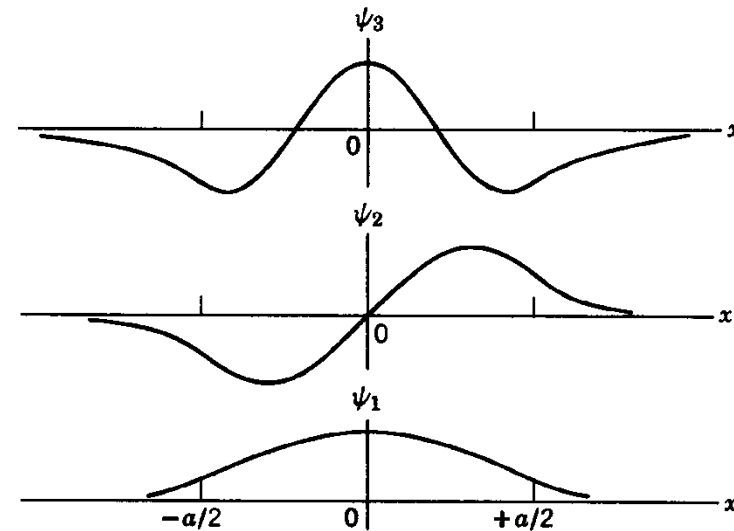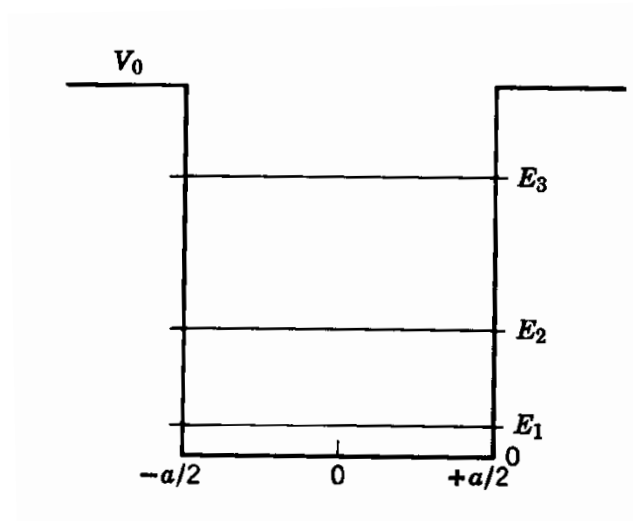
Examples for $n = 1$:
a ball with $m = 0.1$ kg in a box with $a = 10$ cm → $\Delta E \sim 10^{-64}$ J !!
An electron with $m \sim 10^{-30}$ kg in a box with $a = 1$ nm → $\Delta E \sim 1.5 \times 10^{-19}$ J ~ 1 eV !!

FINITE POTENTIAL WELL

Boundary conditions do not lead anymore to $\Psi = 0$ outside the well

Major consequences and differences with respect to the infinite case:

➢ there is a finite probability for the particle to tunnel outside the well
➢ there is a "leakage" of the wavefunction outside the well (keeping continuity of wavefunction and of its first derivative)
➢ the number of allowed energy levels is limited

In any case, it is well confirmed that
patial confinement → energy quantization
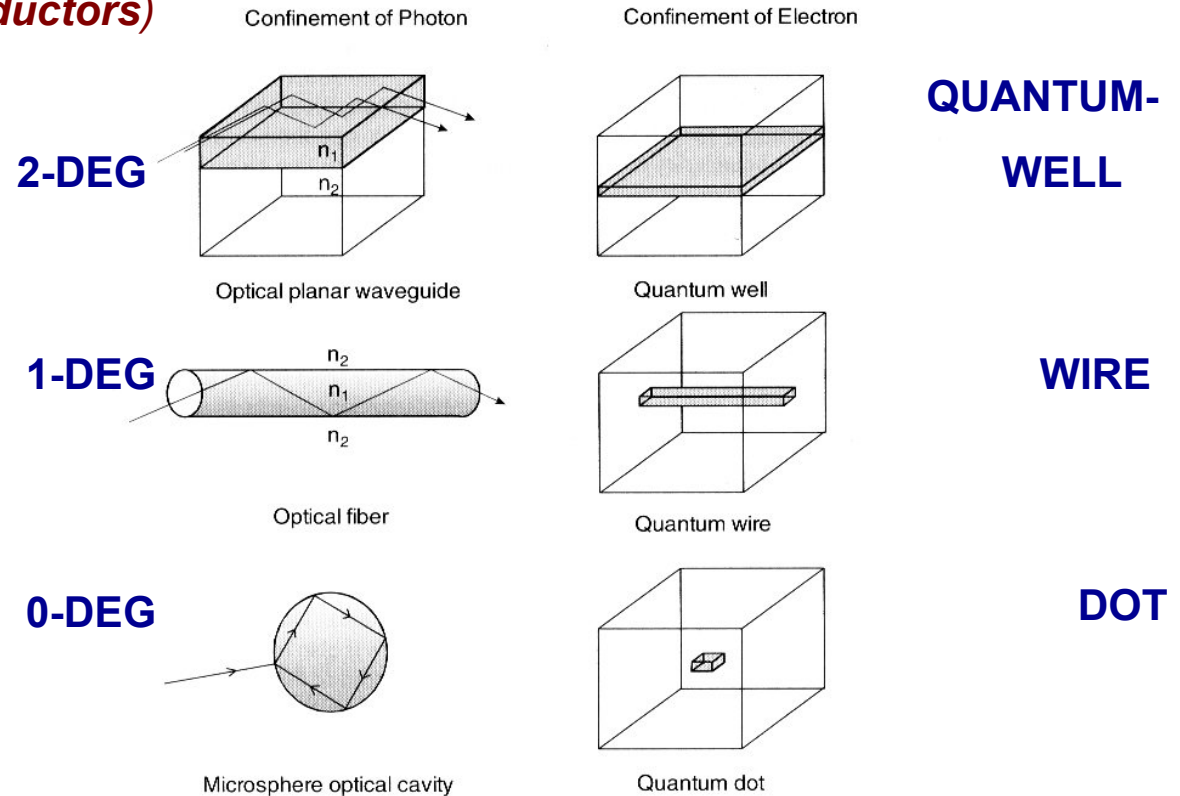
HOW TO REALIZE A POTENTIAL WELL

A potential well for an electron means the electron position is confined, e.g., at the surface of a material

We have seen ΔE can fall within the range of our interest (eV, that is optics!)

We have also seen this usually require nm-sized *a* : at that point, a *cluster* of atoms is obtained, rather than a nanosized object, where individual atom features dominate over confinement
→ *Need to find a "trick" in order to play with slightly larger objects, for instance by replacing m with m* (**effective mass in semiconductors**)*

Moreover, dimensionality (i.e., whether the material can be described as a bulk, or its shape and size makes it similar to a plane, a segment, a point) starts playing a role

(similar to confinement of light in waveguides, but with a much smaller size scale – guiding light with conventional waveguides requires wavelength size scale!)

Confinement of Photon

Confinement of Electron

2-DEG

Optical planar waveguide

Quantum well

QUANTUM-WELL

1-DEG

Optical fiber

Quantum wire

WIRE

0-DEG

Microsphere optical cavity

Quantum dot

DOT

REMINDERS OF SEMICONDUCTORS (Si)

We will restrict to semiconductors, but the most technologically relevant elemental semiconductor, Si (bulk), is not suited for optics, because of energy gap (in the IR) and, mostly, **indirect transitions**
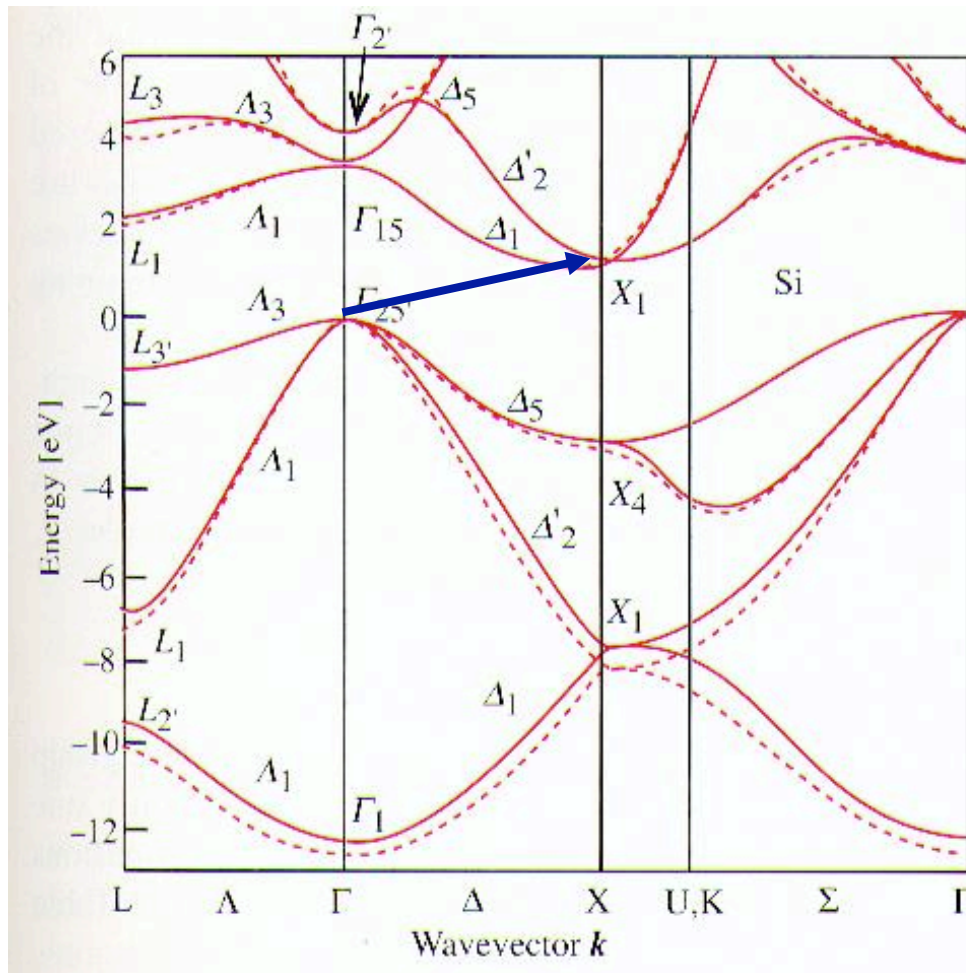
Band structure of Si

The top of valence band and the bottom of the conduction band are displaced each other

⇩

Momentum conservation implies phonons to be involved in the absorption process

⇩

Transition probability is small (10^{-5}-10^{-6} s^{-1}) (and wavelength is in the IR, above 1 μm)

Yu and Cardona
Fundamentals of Semicond.
Springer, Heidelberg (1996)

(Bulk) Si is of bare interest for optics, optoelectronics, photonics
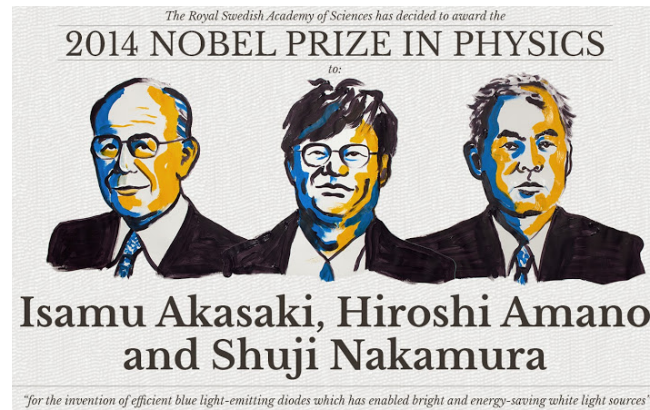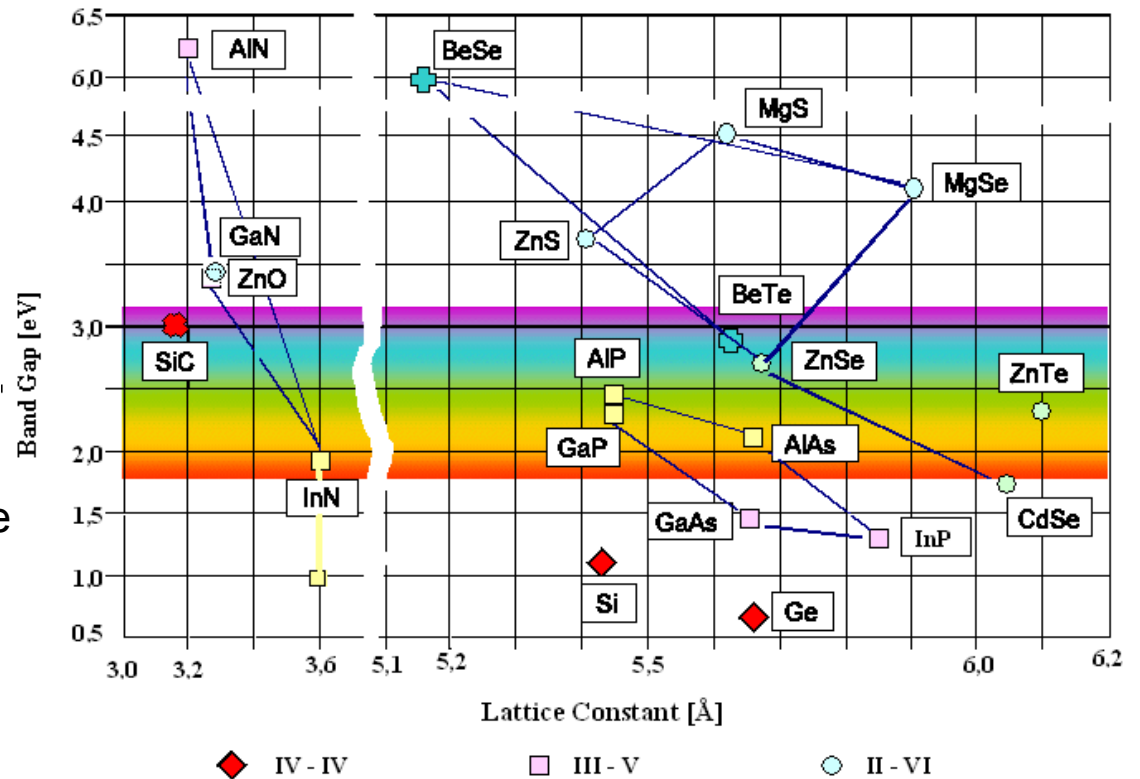
SEMICONDUCTIVE ALLOYS AND SYSTEMS

Luckily, semiconductors can be *artificially* produced in the form of alloys

Lattice constants of the elemental components must be "matched" (a maximum few percent of difference is typically allowed!) in order to have stable, pseudomorphic growth

The simplest combination involves elements belonging to III-V columns of the periodic table, but other combinations are possible (e.g., IV-IV, II-VI)

The so-realized alloys can show a wide range of band-gap energies, usually zincblende or diamond structures, either direct or indirect transitions

A wide choice of semiconductors is available to tune the gap in a broad range (from UV-blue to near-IR) and achieve direct transitions


◆ IV - IV   □ III - V   ◇ II - VI

The Royal Swedish Academy of Sciences has decided to award the
2014 NOBEL PRIZE IN PHYSICS
to
Isamu Akasaki, Hiroshi Amano and Shuji Nakamura
"for the invention of efficient blue light-emitting diodes which has enabled bright and energy-saving white light sources"

Growth of semiconductor alloys is a continued relevant topic, see Nobel Prize in Physics 2014

EPITAXIAL GROWTH I

An additional and historically relevant possibility offered by semiconductor alloys is **epitaxial growth**: e.g., layers (thin films) of one alloy can be grown over a layer made of another alloy

→ Reproduction of crystalline structures requires negligible lattice mismatch
→ Fabrication methods capable of extreme purity are needed

Physical fabrication methods are preferred, such as Molecular Beam Epitaxy (MBE)
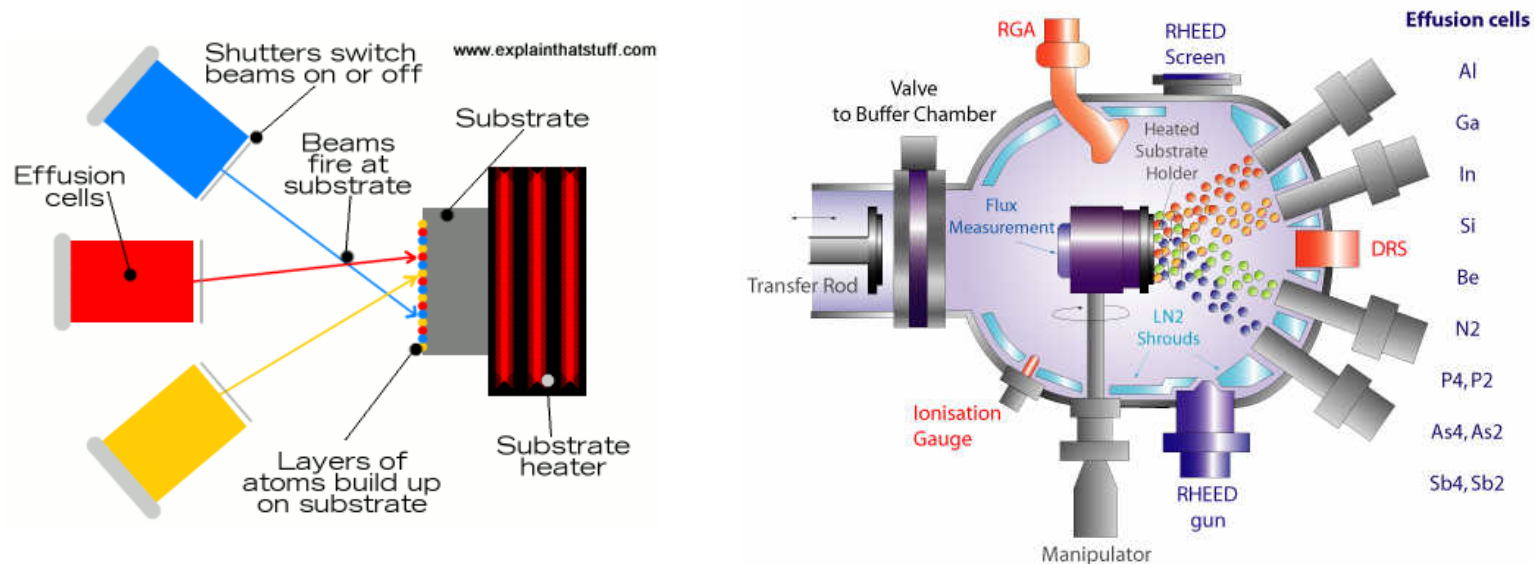

➢ Growth of layers entails deposition of elemental (atomic) components vaporized in a ultra-high vacuum (UHV, residual pressure < 10^{-9} mbar, typ)
➢ Growth rate is intentionally kept very small (e.g., nm per minute) in order to accurately control the layer thickness
➢ Substrate heating promotes formation of the expetced crystal structure in the layers

EPITAXIAL GROWTH II

Other techniques (leading to a larger yield at the expenses of lattice and stoichiometric quality) are, among others:
- Chemical Vapor Deposition (CVD), also in the Plasma-Enhanced version (PE-CVD)
- Liquid Phase Epitaxy (LPE)

CVD **PE-CVD** **LPE**
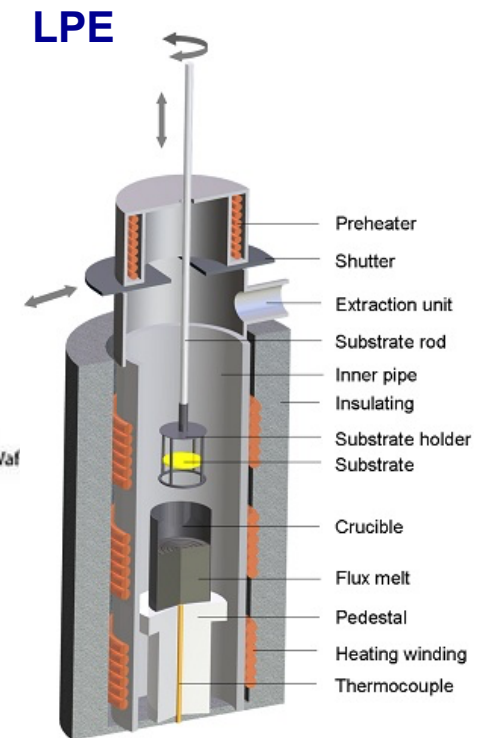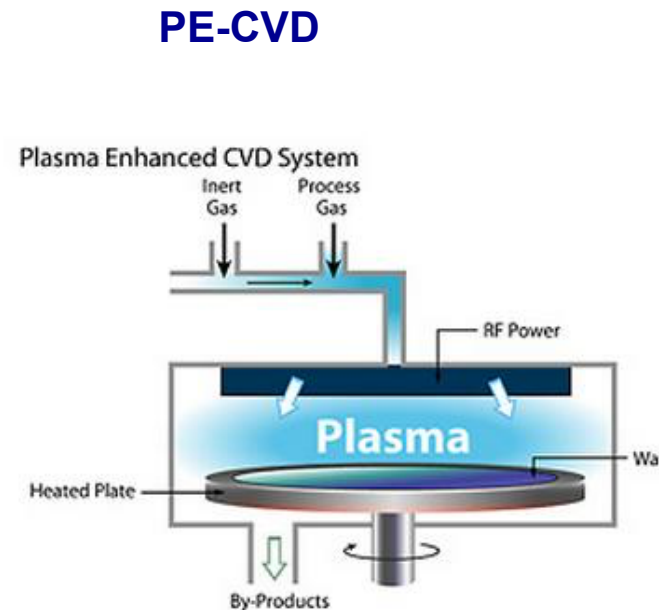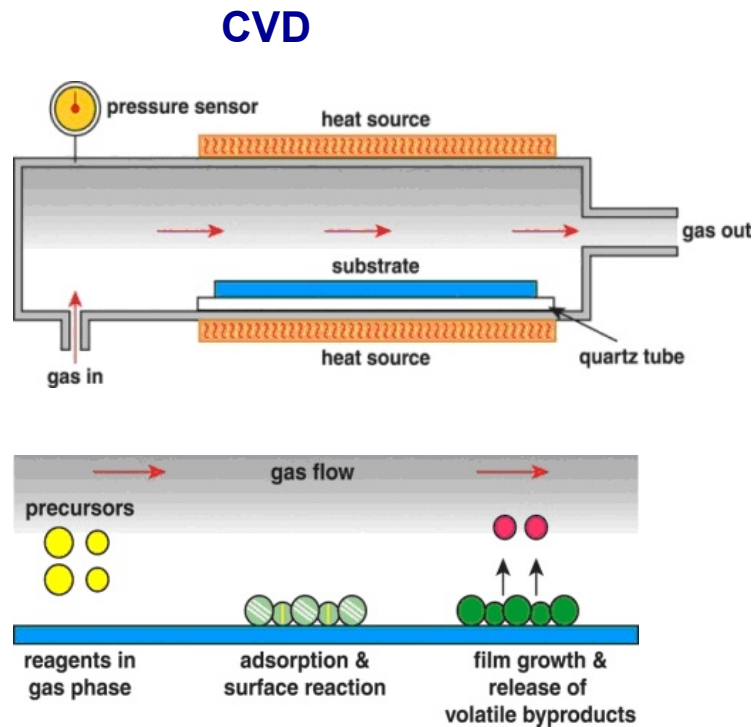
A few issues (they make MBE the technique of choice, unless special materials have to be deposited):
➤ Critical choice of precursor (typically, metal-organic molecules) in CVD
➤ Sometimes poor control of plasma-enhanced decomposition reactions
➤ Liquid phase often associated with the presence of impurities
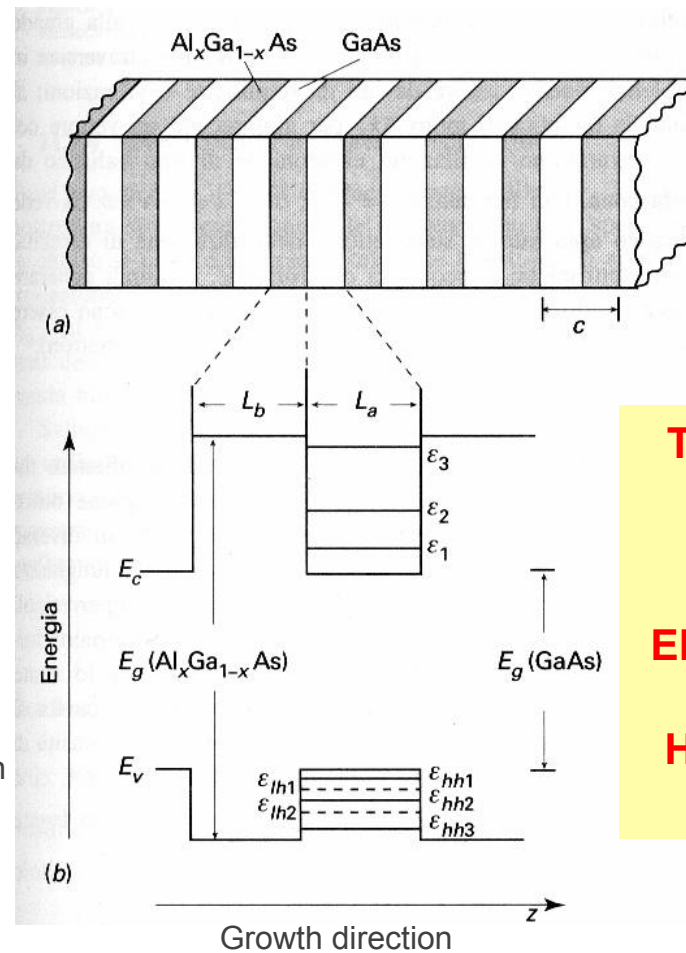
SEMICONDUCTIVE HETEROSTRUCTURES

Alternating layers of different crystalline semiconductors produces an **heterostructure**

Using semiconductors with different band gap energies leads to a (**multiple**) **quantum well (MQW)**
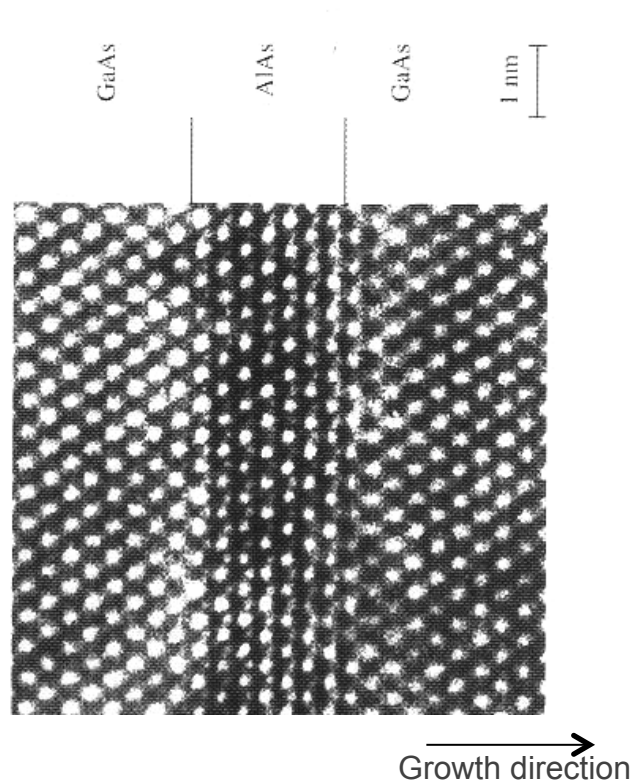
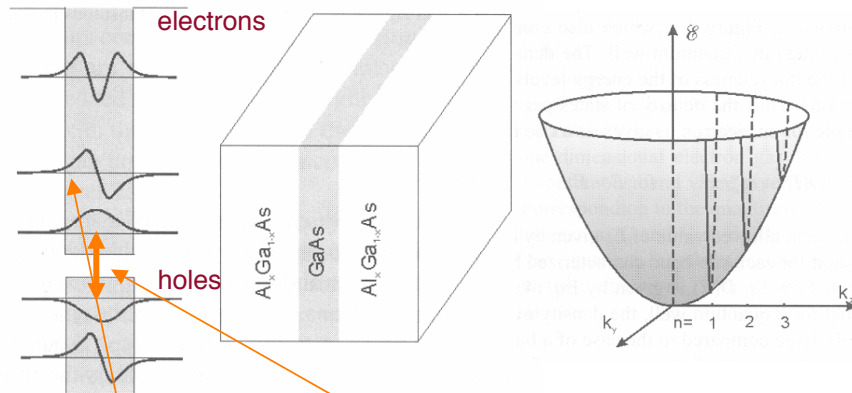

HR-TEM image
(dots correspond to atoms)

$E_{gGaAs} \sim 1.4$ eV

$E_{gAlAs} \sim 2.2$ eV

The lower band-gap layer acts as a potential well for the electron

Electron wavefunction confined in the lower band-gap layer Hole wavefunction confined in the higher band-gap layer

QUANTUM WELLS I

electrons

holes

$Al_xGa_{1-x}As$ GaAs $Al_xGa_{1-x}As$

- For energies $E < V$, the energy levels of the electron are quantized for the direction z of the confinement; hence they are given by the model of particle in a one-dimensional box. The electronic energies in the other two dimensions (x and y) are not discrete and are given by the effective mass approximation discussed in Chapter 2. Therefore, for $E < V$, the energy of an electron in the conduction band is given as

$$E_{n,k_x,k_y} = E_C + \frac{n^2 h^2}{8 m_e^* l^2} + \frac{\hbar^2 (k_x^2 + k_y^2)}{2 m_e^*} \qquad (4.1)$$

where $n = 1, 2, 3$ are the quantaum numbers. The second term on the right-hand side represents the quantized energy; the third term gives the kinetic energy of the electron in the x–y plane in which it is relatively free to move. The symbols used are as follows: m_e^* is the effective mass of electron, and E_C is the energy corresponding to the bottom of the conduction band.

Equation (4.1) shows that for each quantum number n, the values of wavevector components k_x and k_y form a two-dimensional band structure. However, the wavevector k_z along the confinement direction z takes on only discrete values, $k_z = n\pi/l$. Each of the bands for a specific value of n is called a sub-band. Thus n becomes a sub-band index. Figure 4.2 shows a two-dimensional plot of these sub-bands.

- For $E > V$, the energy levels of the electron are not quantized even along the z direction. Figure 4.1 shows that for the AlGaAs/GaAs quantum well, the quantized levels $n = 1$–3 exist, beyond which the electronic energy level is a continuum. The total number of discrete levels is determined by the width l of the well and the barrier height V.

- The holes behave in analogous way, except their quantized energy is inverted and the effective mass of a hole is different. Figure 4.1 also shows that for the holes, two quantized states with quantum numbers $n = 1$ and 2 exist for this particular quantum well (determined by the composition of AlGaAs and the width of the well). In the case of the GaAs system, two types of holes exist, determined by the curvature (second derivative) of the band structure. The one with a smaller effective mass is called a *light hole* (lh), and the other with a heavier effective mass is called a *heavy hole* (hh). Thus the $n = 1$ and $n = 2$ quantum states actually are each split in two, one corresponding to lh and the other to hh.

- Because of the finite value of the potential barrier ($V \neq \infty$), the wavefunctions, as shown for levels $n = 1, 2$, and 3 in the case of electrons and levels $n = 1$ and 2 in the case of holes, do not go to zero at the boundaries. They extend into the region of the wider bandgap semiconductor, decaying exponentially into this region. This electron leakage behavior has already been discussed in Section 2.1.3 of Chapter 2.

- The lowest-energy band-to-band optical transition (called the interband transition) is no longer at E_g, the energy gap of the smaller bandgap semiconductor, GaAs in this case. It is at a higher energy corresponding to the difference between the lowest energy state ($n = 1$) of the electrons in the conduction band and the corresponding state of the holes in the valence band. The effective bandgap for a quantum well is defined as

$$E_g^{\text{eff}} = (E_C - E_V) + \frac{h^2}{8 l^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) \qquad (4.2)$$

In addition, there is an excitonic transition below the band-to-band transition. These transitions are modifications of the corresponding transitions found for a bulk semiconductor. In addition to the interband transitions, new transitions between the different sub-bands (corresponding to different n values) within the conduction band can occur. These new transitions, called intraband or inter-sub-band transitions, find important technologic applications such as in quantum cascade lasers. The optical transitions in quantum-confined structures are further discussed in the next section.

QUANTUM WELLS II

Different kinds of MQW exist, where confinement is realized for electron and hole wavefunctions in the same or in different layers

Most relevant configuration: electrons and holes are confined in the same layer
Most favoured for exciton formation
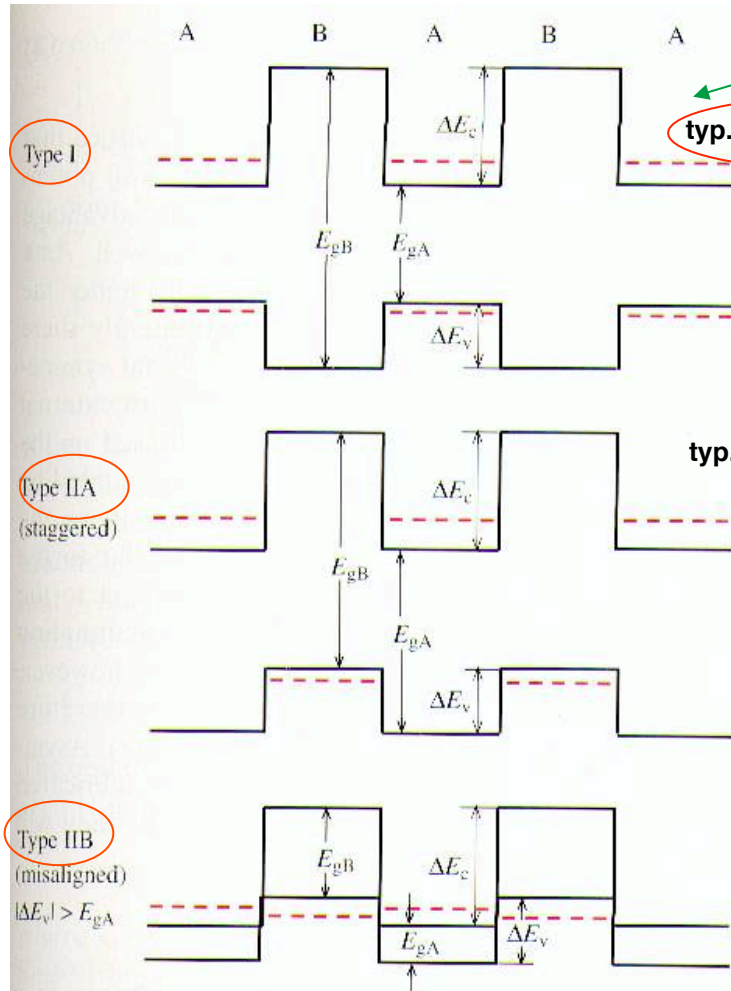
typ. thickness > 2 nm

typ. thickness < 2 nm

e.g.: A=GaAs (E_{gA} ~ 1.4 eV, lattice 5.653 Å)
   B=AlAs (E_{gB} ~ 2.2 eV, lattice 5.62 Å)
or B=$Ga_{1-x}Al_xAs$ (x typ. ≤ 0.3)

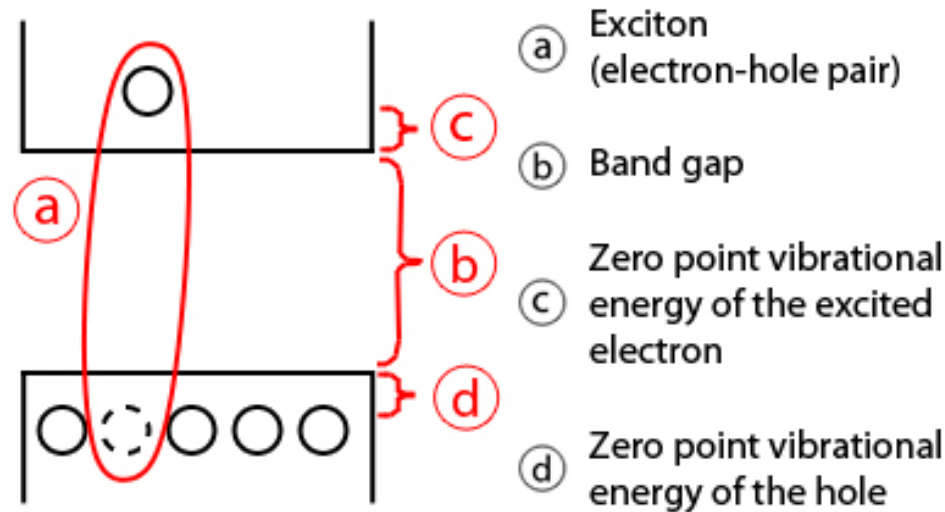**Table 4.1.** Semiconductor Material Parameters

Material	Periodic Table Classification	Bandgap Energy (eV)	Bandgap Wavelength (μm)	Exciton Bohr Radius (nm)	Exciton Binding Energy (meV)
CuCl	I–VII	3.395	0.36	0.7	190
CdS	II–VI	2.583	0.48	2.8	29
CdSe	II–VI	1.89	0.67	4.9	16
GaN	III–V	3.42	0.36	2.8	
GaP	III–V	2.26	0.55	10–6.5	13–20
InP	III–V	1.35	0.92	11.3	5.1
GaAs	III–V	1.42	0.87	12.5	5
AlAs	III–V	2.16	0.57	4.2	17
Si	IV	1.11	1.15	4.3	15
Ge	IV	0.66	1.88	25	3.6
$Si_{1-x}Ge_x$	IV	$1.15-0.874x$ $+0.376x^2$	$1.08-1.42x$ $+3.3x^2$	$0.85-0.54x$ $+0.6x^2$	$14.5-22x$ $+20x^2$
PbS	IV–VI	0.41	3	18	4.7
AlN	III–V	6.026	0.2	1.96	80

Yu and Cardona
Fundamentals of Semicond.
Springer, Heidelberg (1996)

EXCITONS I

As you know, excitons are quasi-bound states consisting of an electron and a hole in a semiconductor (stemming from some pair generation mechanism):

o In the bulk the binding energy is typically very low (Wannier-Mott type, binding energy typ < tens of meV)

o The confinement, especially in Type I quantum wells, enhance probability of superposition between electron and hole wavefunctions → increased probability of exciton formation (and apparent increase of the binding energy)

Exciton energy levels are similar to hydrogen-like atoms
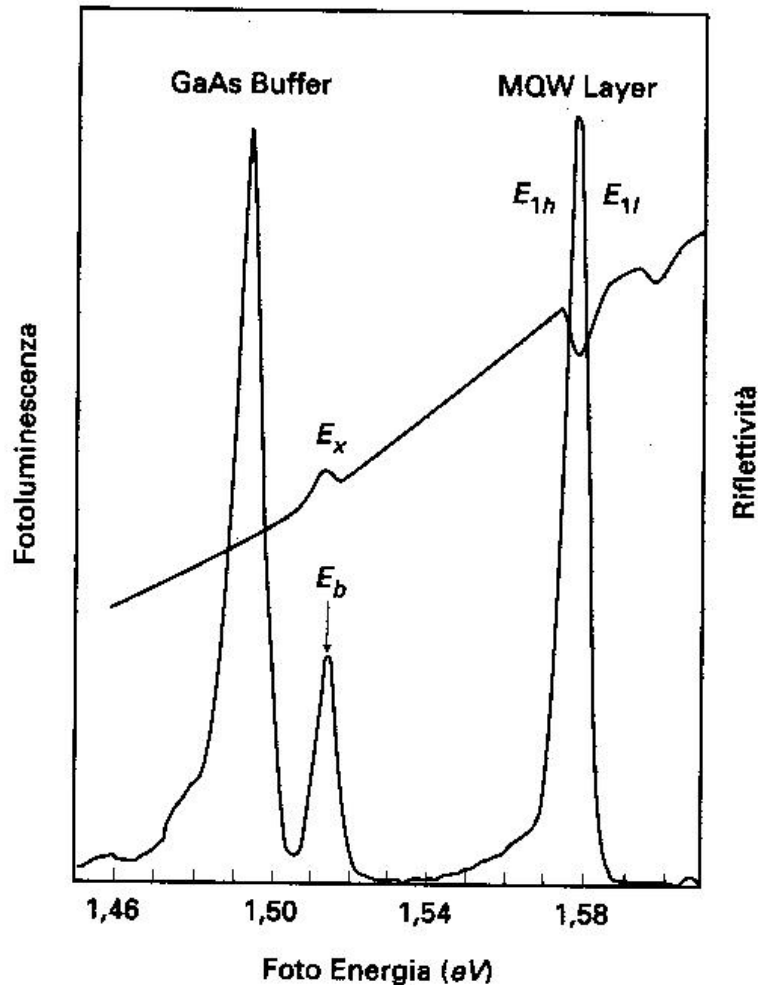
$$E_n = -\frac{Ry}{n^2}\frac{\mu}{m_e^*\varepsilon}$$

with Ry = 13.6 eV Rydberg constant, $\mu = (1/m_e^* + 1/m_{hole})^{-1}$ reduced mass, m_e^* effective mass of the electron, ε relative dielectric constant

**Depending on material parameters, a new, potentially engineered, discrete energy spectrum can occur**

"Artificial atoms" are created!

Note that, exciton formation can take place also in many other systems including, e.g., organic crystals, conjugated polymers, dielectric with localized defects, etc.

EXCITONS II

Since in zincblende structures there are typically two bands crossing at the top of the valence bands, excitons of two classes, named *heavy* and *light hole* excitons, can exist (remember that effective masses of the quasi-particles in solid state physics are given by the curvature of the dispersion relation, and the mentioned bands have different curvatures)


Heavy and light hole exciton absorption in GaAs/GaAsAl MQW @ 4K
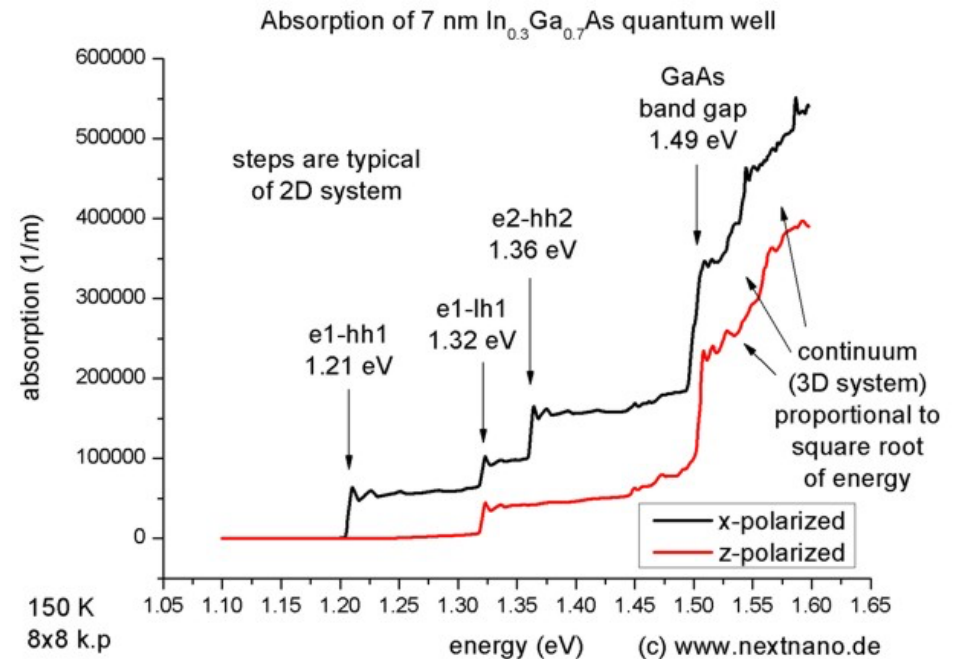
Numerical simulation of heavy and light hole exciton absorption in InGaAs Q-wire @ 150K

OPTICAL PROPERTIES AND QUANTUM CONFINEMENT

Summarizing:

The optical properties of semiconductors (e.g., absorption at photon energy above the band-gap) are modified because of the combined effects of:

1. **Interband and intraband** transitions involving quasi-discrete levels arising from confinement
2. Transitions between **exciton** quasi-discrete levels
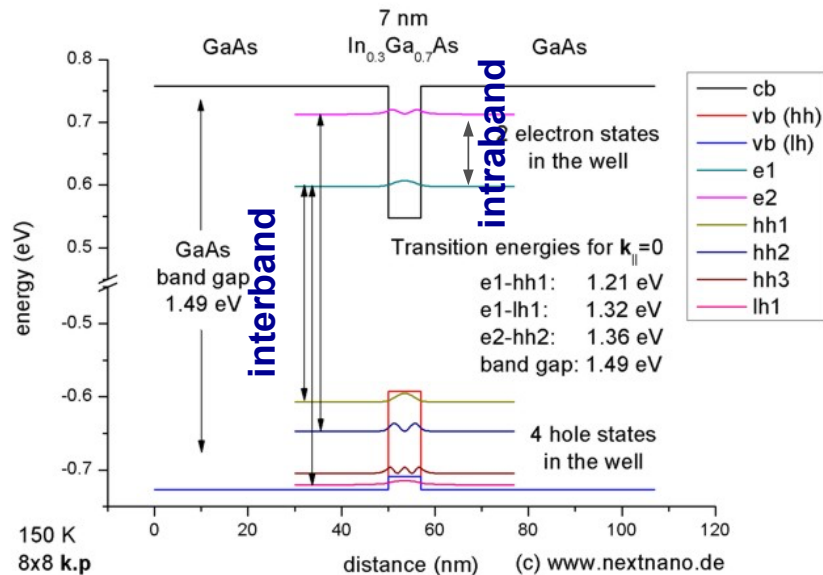
$$E_{\text{confinement}} = \frac{\hbar^2 \pi^2}{2a^2} \left(\frac{1}{m_e} + \frac{1}{m_h} \right) = \frac{\hbar^2 \pi^2}{2\mu a^2}$$

$$E_{\text{exciton}} = -\frac{1}{\epsilon_r^2} \frac{\mu}{m_e} R_y = -R_y^*$$

$$E = E_{\text{bandgap}} + E_{\text{confinement}} + E_{\text{exciton}}$$

$$= E_{\text{bandgap}} + \frac{\hbar^2 \pi^2}{2\mu a^2} - R_y^*$$

In a Q-dot

Quantum confinement in semiconductors is hugely exploited in devices, e.g.:
✓ most diode lasers and LEDs use MQWs of various material alloys
✓ many very-high frequency electronic devices use MQW (transport properties are peculiar, as well)

We will restrict hereafter to Q-dots absorption/emission properties

DIMENSIONALITY AND DENSITY OF STATES

Density of states (DOS) represents the number of states available for a certain energy

Clearly, DOS enters in defining the transition probability (aka "oscilator strength"): the larger the DOS, the stronger the transition

Quantum mechanics says that, in the so-called momentum space a unit of momentum occupies a h^3 volume (in 3-D, otherwise h^2 and h in 2-D and 1-D, respectively) and the density of states $g(p)dp$ is:

In 3-D, a certain momentum p (i.e., in between p and $p+dp$) of a quantum particle defines a spherical shell having a volume
$$4\pi p^2 dp \qquad g(p)dp = \frac{V}{h^3}4\pi p^2 dp$$

In 2-D, a certain momentum p (i.e., in between p and $p+dp$) of a quantum particle defines a circular corona having a surface
$$2\pi p dp \qquad g(p)dp = \frac{S}{h^2}2\pi p dp$$

In 1-D, a certain momentum p (i.e., in between p and $p+dp$) of a quantum particle defines a segment having a length
$$dp \qquad g(p)dp = \frac{L}{h}dp$$

with V, S, L physical volume, surface, length allowed to the quantum particle

Assuming a free quantum particle:
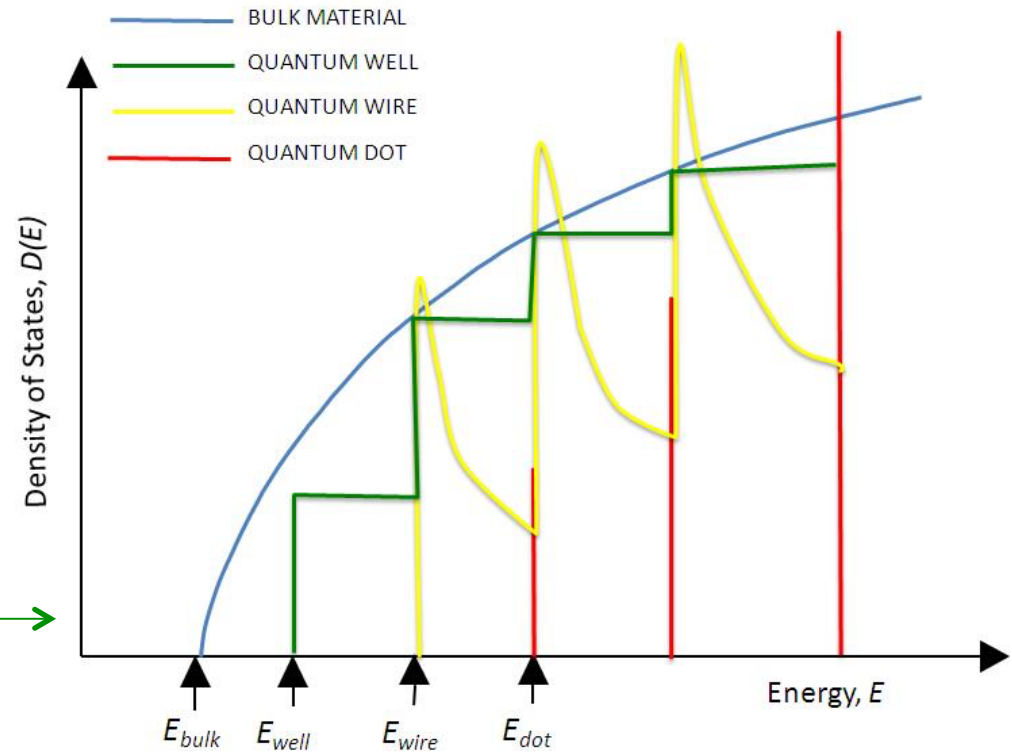$$E = \frac{p^2}{2m}$$
$$p = \sqrt{2m}\sqrt{E}$$
$$dp = \sqrt{\frac{m}{2}}\frac{dE}{\sqrt{E}}$$

Mathematical expressions of $g(p)dp$ depends on dimensionality

DOS IN 3-D, 2-D, 1-D, 0-D

3-D: $\quad g(E) \propto \sqrt{E}$

2-D: $\quad g(E) \propto \text{constant}$

1-D: $\quad g(E) \propto \dfrac{1}{\sqrt{E}}$

0-D: $\quad g(E) \propto \delta\text{-functions}$

Obviously, the actual DOS must take into account the presence of the band-gap (3-D case) or the occurrence of discrete energy levels (due to quantum confinement)

While in the bulk DOS tends to zero at the minimum required energy for a transition (the band-edge), for lower dimensionality DOS is not zero at the minimum required energy for a transition (corresponding to quasi-discrete levels) and ideally diverges for quantum-dots

Lowering the dimnesionality leads to an inherent enhancement of the transition probability

In Q-dots, very "strong" transitions are allowed corresponding to quasi-discrete levels
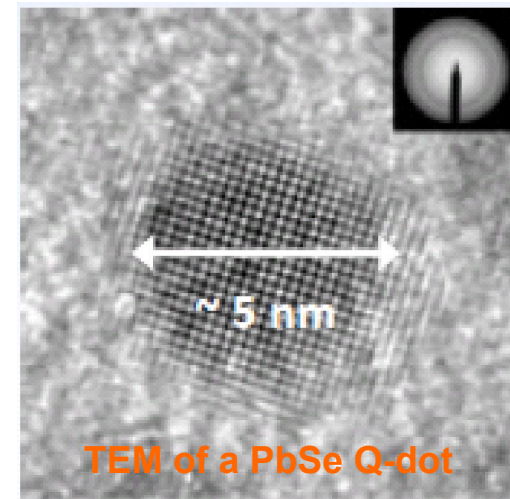
QUANTUM DOTS I

Quantum dots find a number of applications taking advantage of the possibility to tailor their energy levels ("artificial atoms")
For our specific interests, we restrict hereafter to their role as chromophores, i.e., nanoparticles showing specific and engineered absorption/emission properties
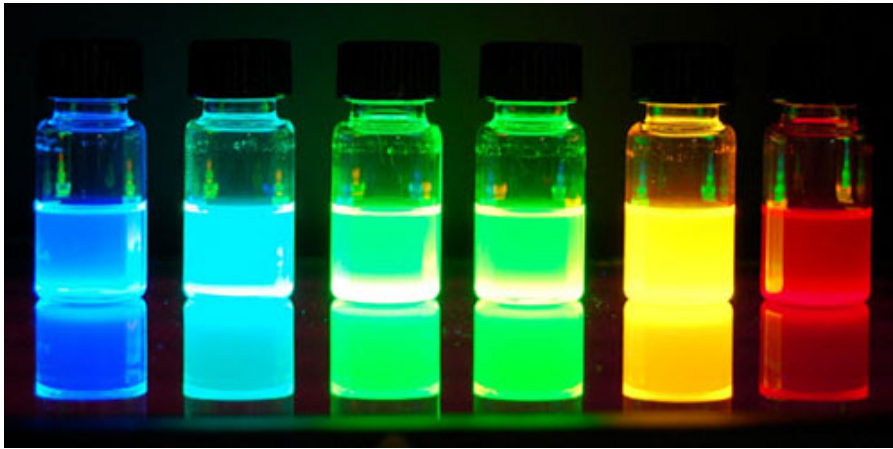
Photoluminescnece (i.e., fluorescence emission) from commercial (Sigma-Aldrich) of CdS_xSe_{1-x}/ZnS (6 nm average diameter) in the colloidal phase: illumination is accomplished in the blue-UV region and different colors reflect the different energy levels involved in the transitions

Quantum dots are often prepared in the colloidal suspension phase, i.e., non-precipitating nanoparticles, ready, e.g., to be functionalized and attached to organic or inorganic systems in order to have a fluorescent marker, or label


~ 5 nm

TEM of a PbSe Q-dot

QUANTUM DOTS II

Periodic Table of the Elements

Most frequent element combination of the semiconductor alloy

Quantum Dot Size and Color

Tailoring of the optical properties is based on size (red-shifted as diameter *a* increases, obviously), but also on composition (elemental choice and stoichiometry), affecting band-gap energy

CORE/SHELL

An important issue in applications of Q-dots is their quantum yield, that is the "efficiency" of their fluorescence emission (i.e., the probability that an incident excitation photon produces a spontaneously emitted photon)

Despite the presence of quasi-discrete levels and the related DOS made of δ-functions, **non radiative** processes are a concurrent path for de-excitation

Dangling bonds at the Q-dot surface are known to provide excitation effective non-radiative paths
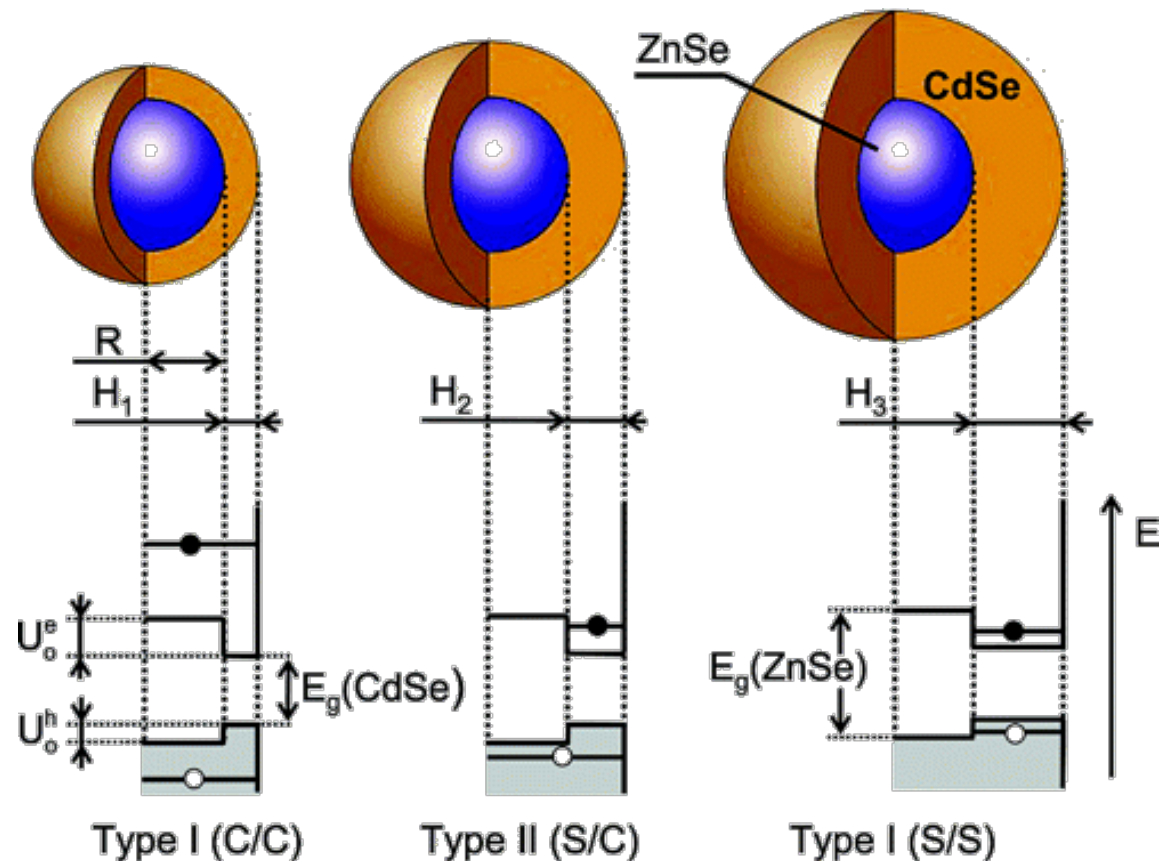
Core-shell Q-dot structures have been implemented in order to prevent non-radiative de-excitation at the surface owing to confinement of electron and hole wavefunctions in the ("isolated") inner shell

Different types of core-shell Q-dots developed, similar to quantum wells, all leading to enhance the quantum yield

FABRICATION

From Wikipedia: Colloidal semiconductor nanocrystals are synthesized from solutions, much like traditional chemical processes. The main difference is the product neither precipitates as a bulk solid nor remains dissolved.[3] Heating the solution at high temperature, the precursors decompose forming monomers which then nucleate and generate nanocrystals. Temperature is a critical factor in determining optimal conditions for the nanocrystal growth. It must be high enough to allow for rearrangement and annealing of atoms during the synthesis process while being low enough to promote crystal growth. The concentration of monomers is another critical factor that has to be stringently controlled during nanocrystal growth. The growth process of nanocrystals can occur in two different regimes, "focusing" and "defocusing". At high monomer concentrations, the critical size (the size where nanocrystals neither grow nor shrink) is relatively small, resulting in growth of nearly all particles. In this regime, smaller particles grow faster than large ones (since larger crystals need more atoms to grow than small crystals) resulting in "focusing" of the size distribution to yield nearly monodisperse particles. The size focusing is optimal when the monomer concentration is kept such that the average nanocrystal size present is always slightly larger than the critical size. Over time, the monomer concentration diminishes, the critical size becomes larger than the average size present, and the distribution "defocuses".
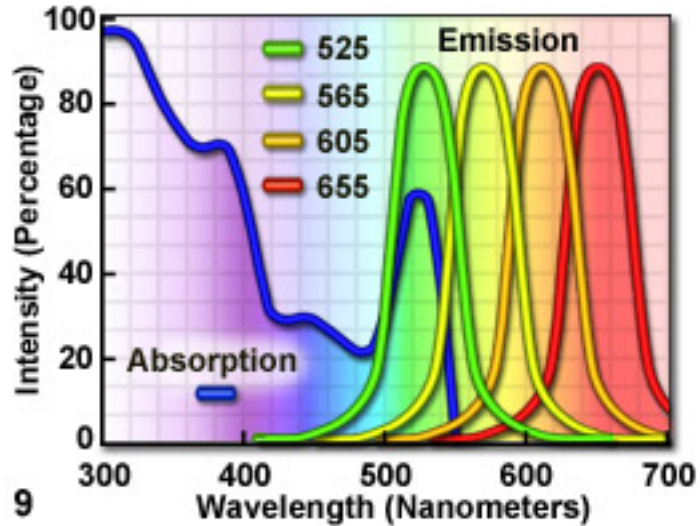
Many variants of liquid phase (chemical) fabrication process have been developed capable of batch production of Q-dots with small size dispersion

Note: other fabrication methods (mostly physical) are in use for Q-dots grown on solid substrates, not considered here!
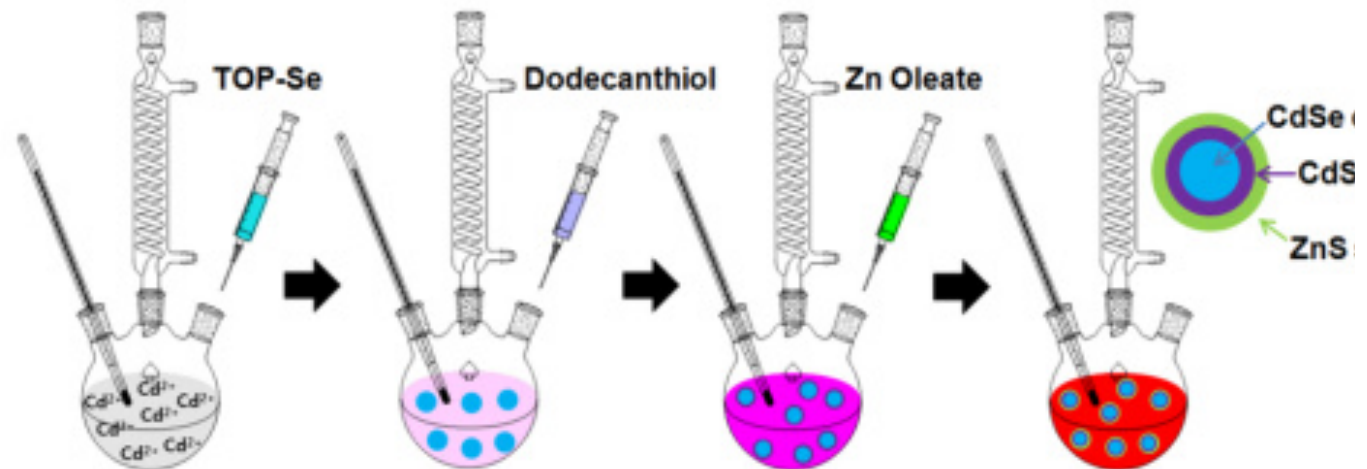
# SUMMARY OF PROPERTIES


Quantum Dot Spectral Profiles

Broad coverage of visible-NIR spectrum available

Quantum yield above 50% frequently reported (note that the exciton binding energy for a small-sized Q-dot can exceed hundreds of meV, being stable at room temperature)

Acceptable resistance to photobleaching (**but blinking phenomena** frequently occurs!)

Ease of surface fucntionalization for applications as label/marker/tag in organic and inorganic imaging
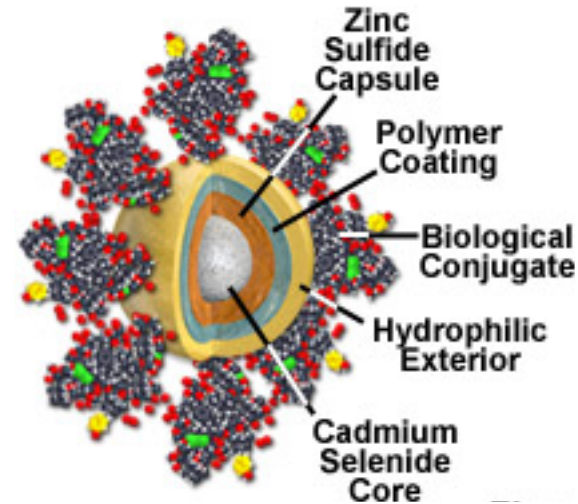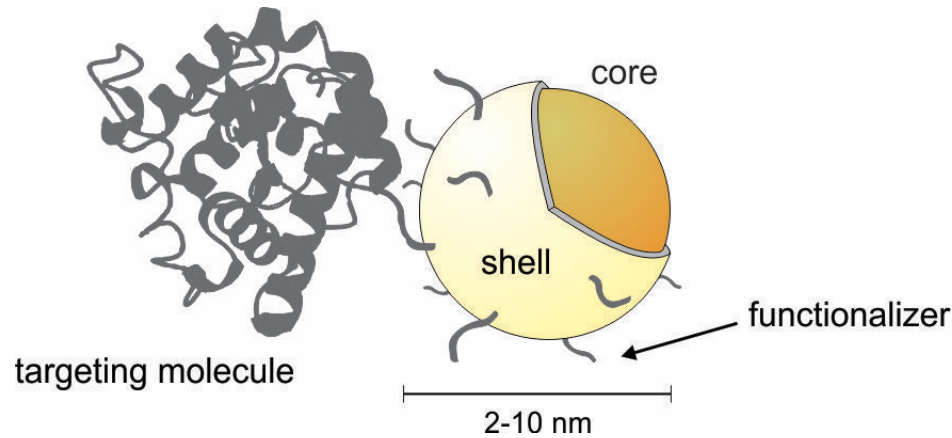
CONCLUSIONS

✓ Quantum confinement effects are among the most striking phenomena ruling the different behavior of nanoparticles compared to bulk counterparts

✓ Roughly speaking,
  (i) discrete energy level
  (ii) exciton ("artificial atoms")
  (iii) DOS
contribute to realize systems whose optical properties can be effectively tailored by engineering composition, size, dimensionality

✓ Very very many applications are found: here we focused onto Q-dots as fluorescent markers/ labels/tags: they can even exceed performance of conventional (organic) dyes and are thus an extremely powerful method for spectroscopy/microscopy at the nanoscale

We will see in the next lecture how emission spectroscopy can be exploited for pushing resolving power beyond the diffraction limit

FURTHER READING

For a very well done overview of quantum physics phenomena:

R. Eisberg, R. Resnick, Quantum Physics of Atoms, Molecules, …, Second Edition, Wiley, New York (1985). [In particular, the chapter regarding tunneling and confinement]

As an advanced reference for solid state physics:

P. Yu, M. Cardona, Fundamentals of Semiconductors, Springer-Verlag, Berlin (2010).

For generalities on quantum confinement and nanophotonics:

P.N. Prasad, Nanophotonics, Wiley, New York (2004). [In particular, chapter 4]

For a (old, but still valid) review on quantum dots as fluorescent markers:

W.C.W. Chan, et al., Luminescent quantum dots for multiplexed biological detection and imaging, Current Opinion in Biotechnology 13, 40–46 (2002). [Open access]

For a more recent one:

D. Bera, et al., Quantum dots and their multimodal applications: a review, Materials 3, 22660-2345 (2010). [Open access]

For a review more specifically addressing fabrication and synthesis:

M.Z. Hu and T. Hzu, Semiconductor Nanocrystal Quantum Dot Synthesis Approaches Towards Large-Scale Industrial Production for Energy Applications, Nanoscale Research Letters 10, 469 (2015). [Open access]