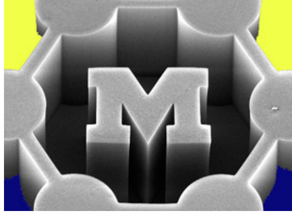

Nanomanufacturing
University of Michigan
ME599-002 |Winter 2010

03: **Energy carriers and size effects**

January 20, 2010

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http://www.umich.edu/~ajohnh

Announcements

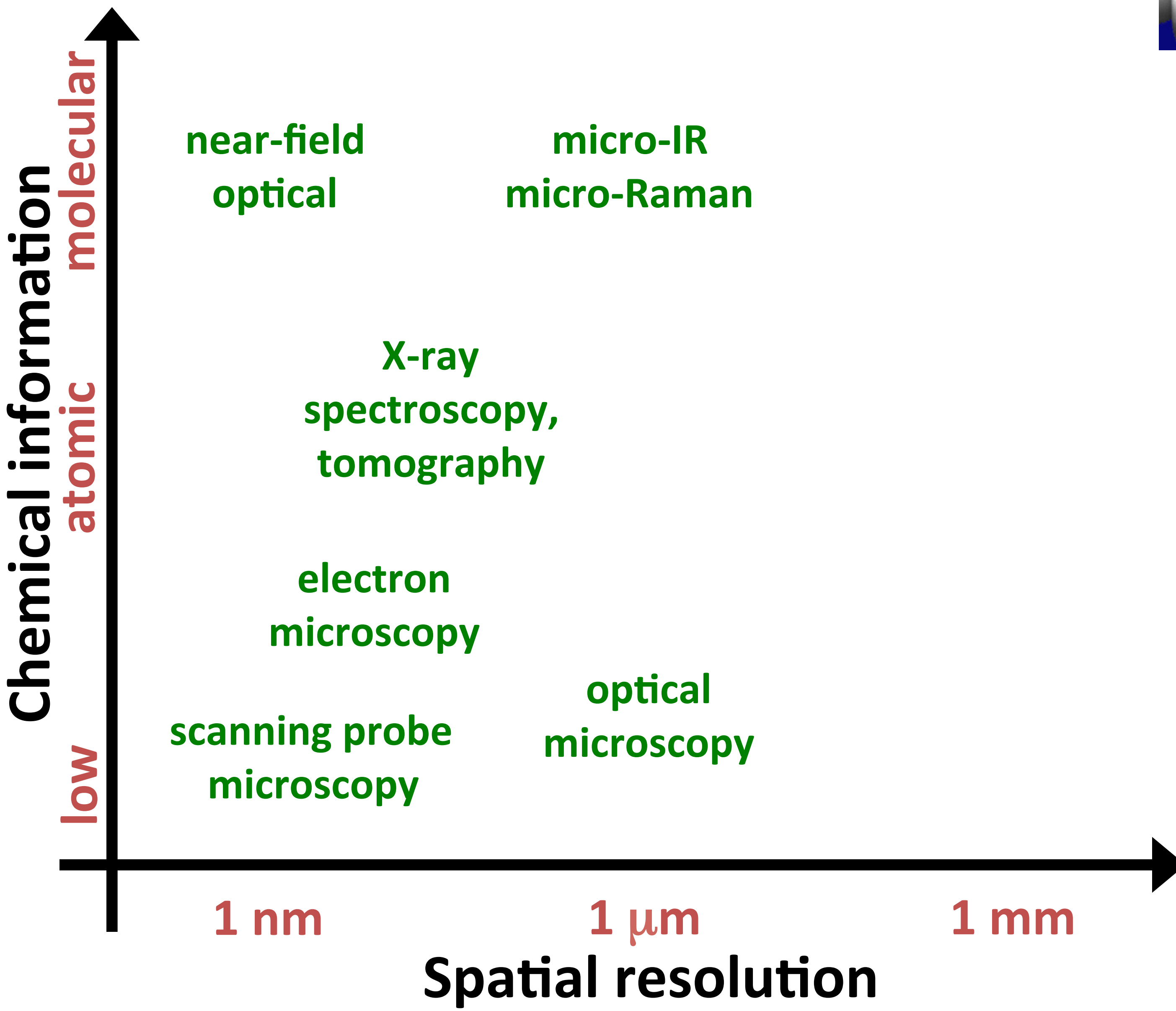
- How many are auditing the course?
- Nanomanufacturing GSI
  - Mr. Mostafa Bedewy
  - mbedewy@umich.edu
  - Office hours: 4.30-6.30 PM Th, location TBA
- PS1 posted, due W Feb/3 –start early!
- Literature searching: see "lab session" video on ctools
- Changes to syllabus
  - Literature review → video assignment (to be posted next week)
  - Attendance/participation grade (5%) → peer review of videos and project reports

Recap: characterization

- Microscopy: techniques and limits
  - Optical
  - Electron
  - Scanning probe (AFM/STM)
- Surface/structural analysis: electron and X-ray techniques
- Optical spectroscopy
  - Raman
  - UV/visible light
  - Infrared

- **This lecture could be an entire course (or more); our goal is to know the very basics of techniques we' ll refer to in later topics.**
- **We' ll overview how to measure properties in the coming lectures (mechanical, electrical, thermal, optical)**

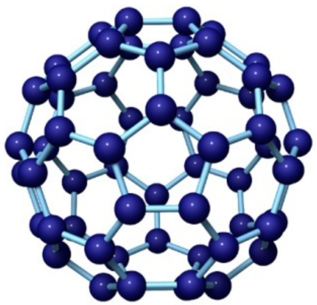
What types of information do we want?

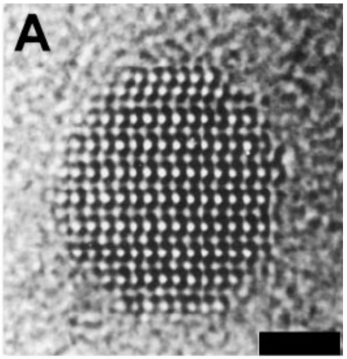


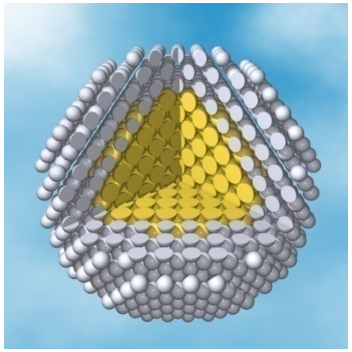
adapted from Park.com, A Practical Guide to Scanning Probe Microscopy

How were these pictures taken?

0-D







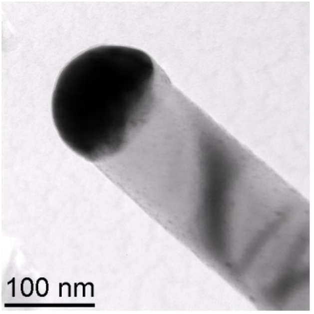
Nanoclusters

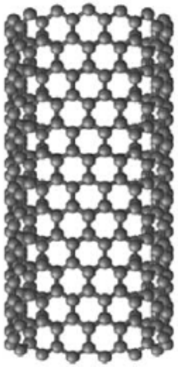
Magic #'s of atoms
≤1 nm size

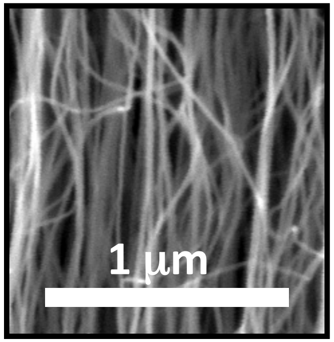
Nanoparticles

100's-1000's of atoms
~1-100 nm diameter

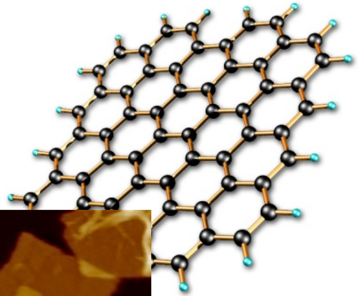
1-D

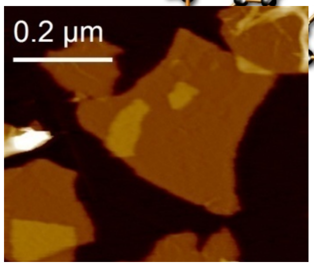






2-D





Nanowires

Filled

Nanotubes

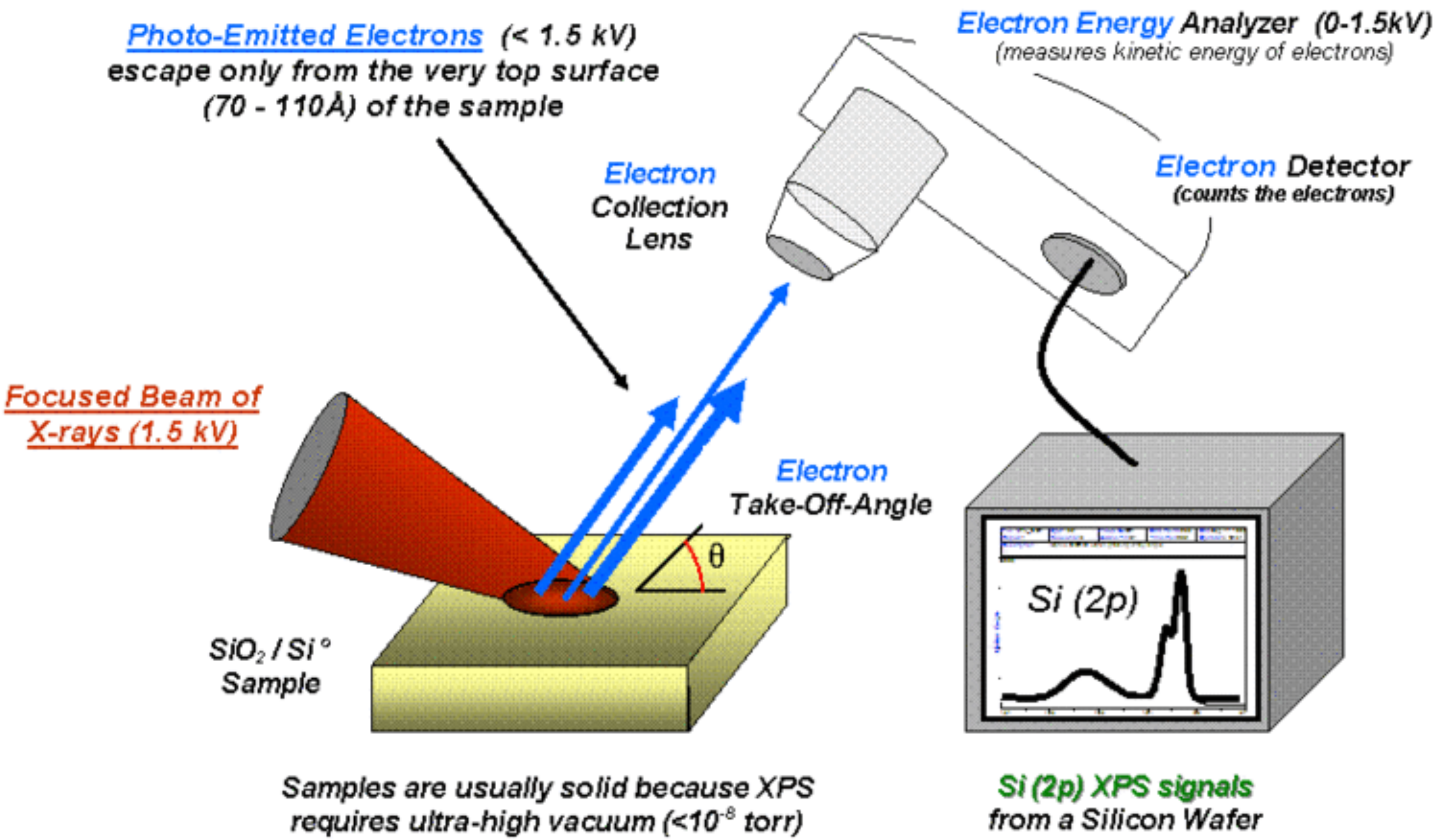
Hollow

~1-100 nm dia, up to mm long and beyond!

Nanosheets

~1 atom thick

X-ray photoelectron spectroscopy (XPS)



X-rays in

Measured

Work function of spectrometer (calibrated)

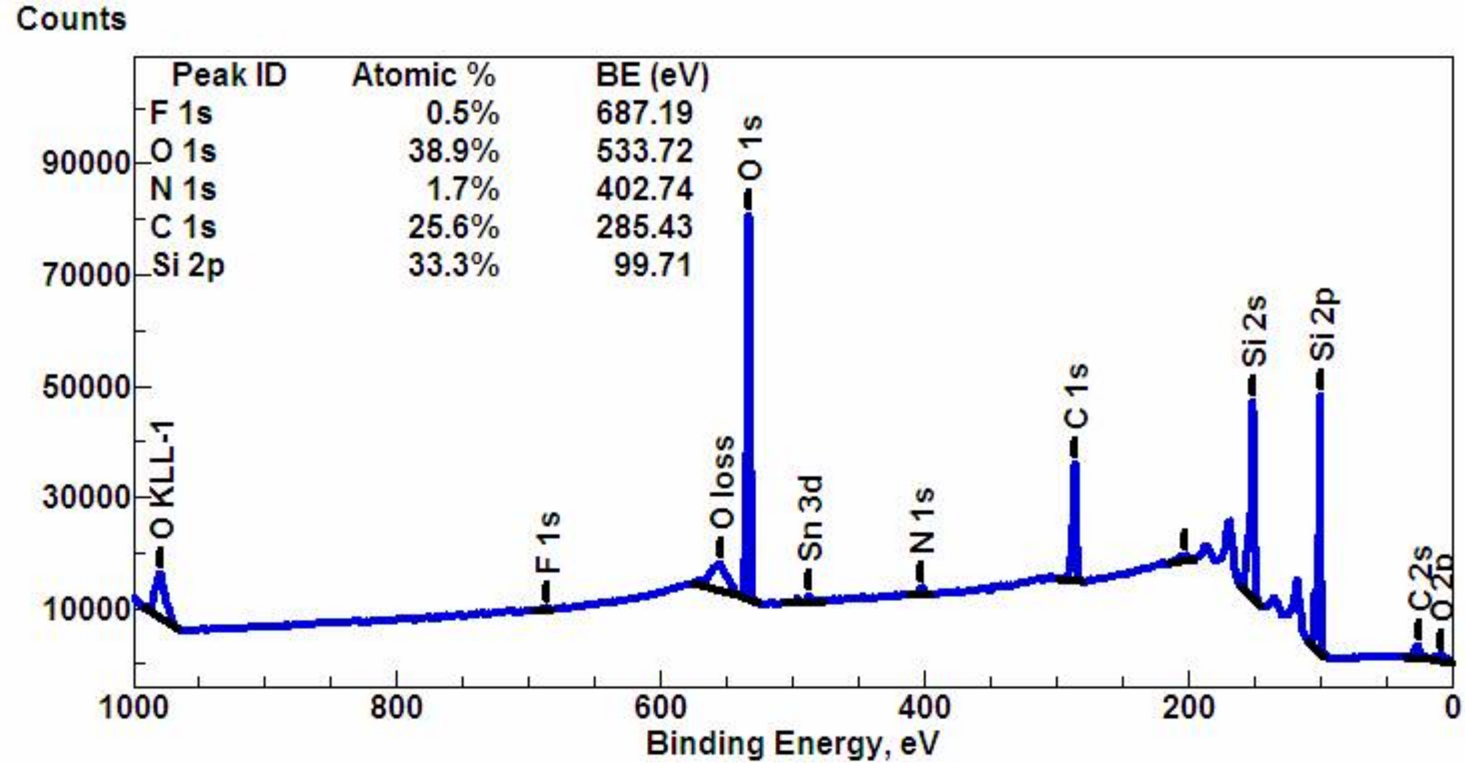
Output used to determine material

$$E_{binding} = E_{photon} - E_{kinetic} - \phi$$

http://en.wikipedia.org/wiki/X-ray_photoelectron_spectroscopy

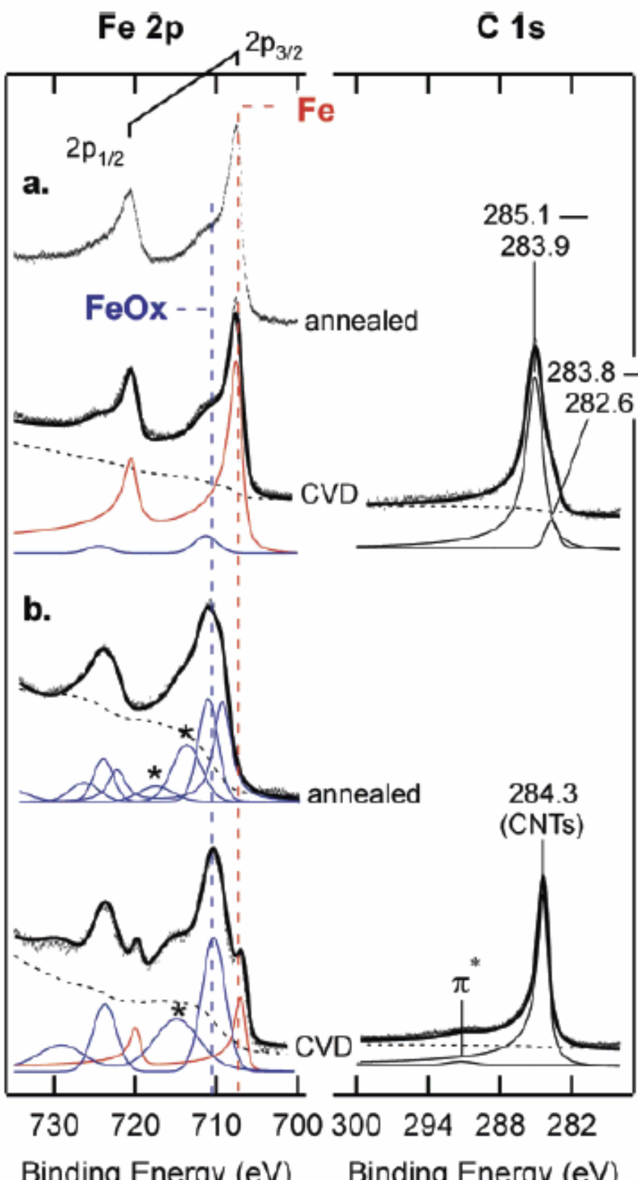
Work function of the spectrometer: http://www.rikenkeiki.com/pages/AC2.htm

XPS



http://en.wikipedia.org/wiki/X-ray_photoelectron_spectroscopy

Is the CNT growth catalyst metal or oxide?



metallic Fe on Al_2O_3

Fe-oxide on Al_2O_3

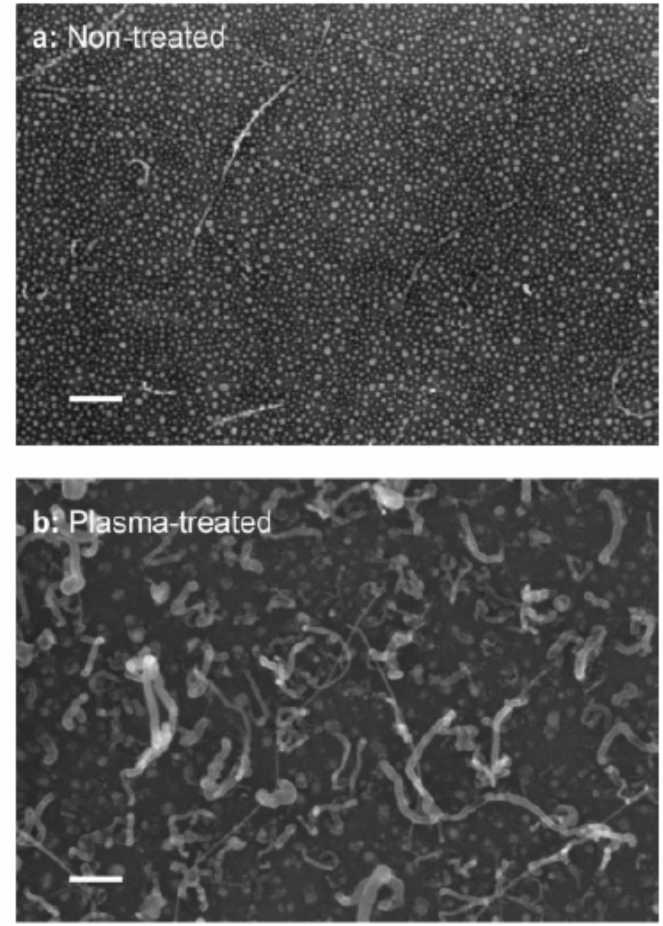
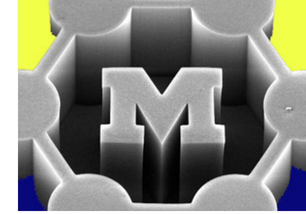


Figure 3. SEM images after CVD onto substrates with Al_2O_3 buffer layers. (a) CVD performed without previous O_2 plasma treatment; (b) CVD performed after O_2 plasma treatment. Scale bars are 100 nm.

Characterization facilities at UM



Electron Microbeam Analysis Laboratory (EMAL)
http://www.emal.engin.umich.edu/
Facilities: Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), X-ray Photo-electron Spectroscopy (XPS), Focused Ion Beam (FIB), and others.

X-Ray MicroAnalysis Laboratory (XMAL)
http://www.mse.engin.umich.edu/research/xmal
Facilities: X-ray Diffraction and X-ray Scattering

Michigan Ion Beam Laboratory (MIBL)
http://www-ners.engin.umich.edu/research/Mibl/index.html
Facilities: Rutherford Backscattering Spectroscopy, Ion Implantation

Today's agenda

- Energy carriers
- Length scales of energy carriers
- Transport regimes; classical size effects
- Wave-particle duality
- Quantum size effects
  - Energy levels
  - Density of States
  - Dispersion relations
- Example: Optical transitions of quantum dots

+ Thanks to Dr. Aaron Schmidt for preparing some of today's slides

Today's readings

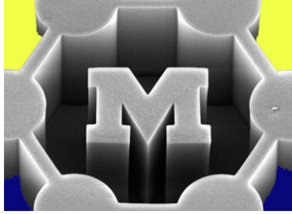
Nominal: (on ctools)

- Rogers, Pennathur, and Adams, excerpt from <u>Nanotechnology: Understanding Small Systems</u> → **a good intro**
- Alivisatos, "Semiconductor Clusters, Nanocrystals, and Quantum Dots"
- Hodes, "When small is different" → **optical and electrical properties**

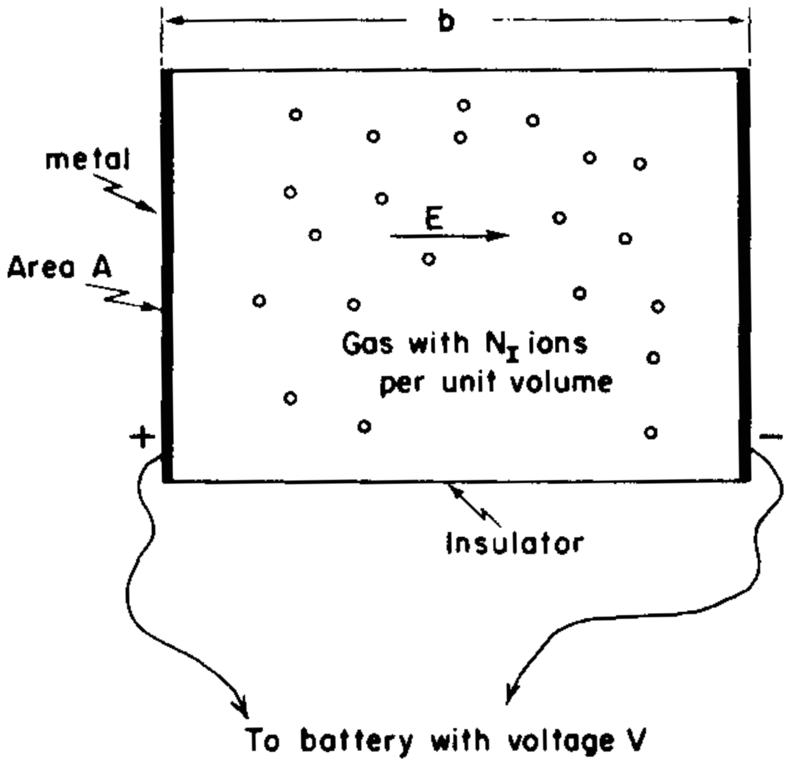
Extras: (on ctools)

- Gaponenko, excerpts from <u>Optical Properties of Semiconductor Nanocrystals</u> → **reference for PS1**
- Chen, excerpts from <u>Nanoscale Energy Transport and Conversion</u> → **read this lightly**

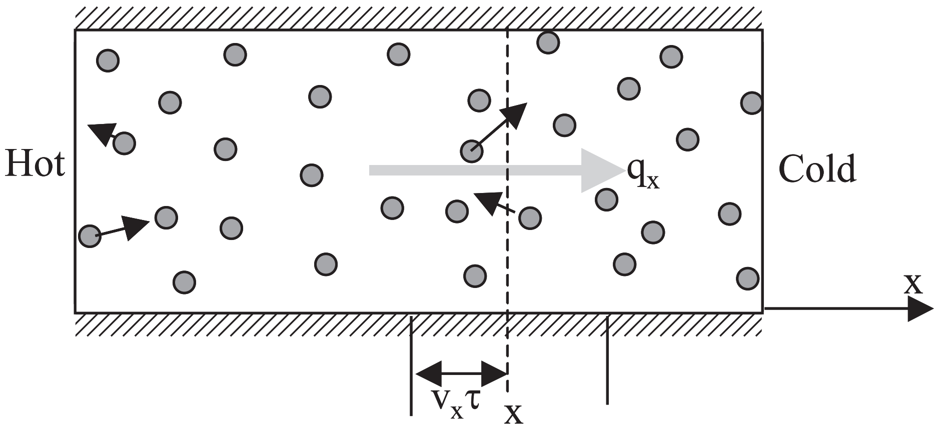
Energy transport: the small-scale picture



Electrical transport

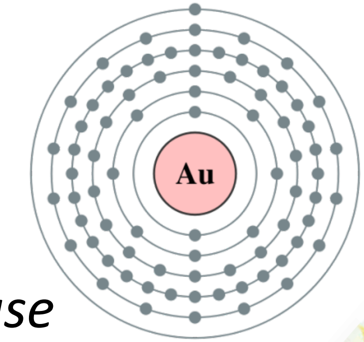


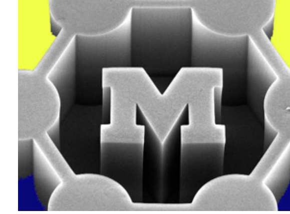
Thermal transport



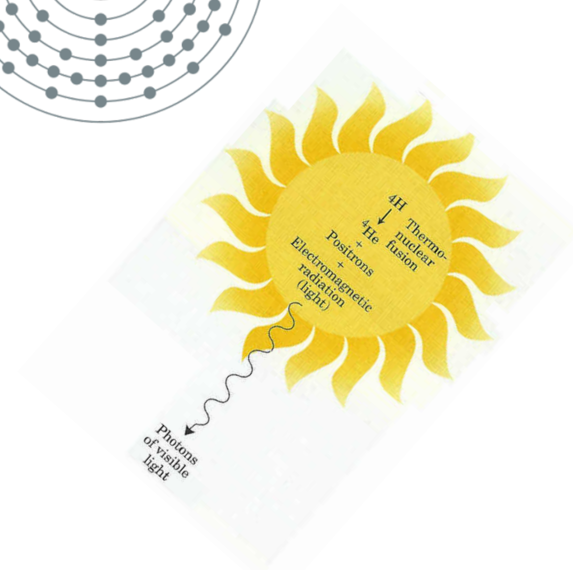
- **All carriers have wavelike (distributed) and particle (discrete) aspects** …more on this later

Energy carriers

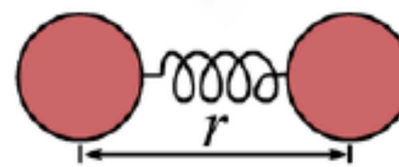




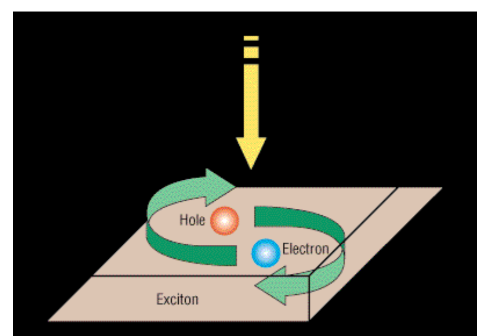
- **Electron -** subatomic particle carrying a negative charge
  → *interaction between electrons is the main cause of chemical bonding*



- **Photon** - quantum of electromagnetic field and the basic unit of light



- **Phonon** – a quantized mode of vibration in a lattice



- **Exciton** - a "quasiparticle", a bound state consisting of an electron and a hole
  → *formalism for transporting energy without transporting net charge*

Wave-particle duality I: The photoelectric effect

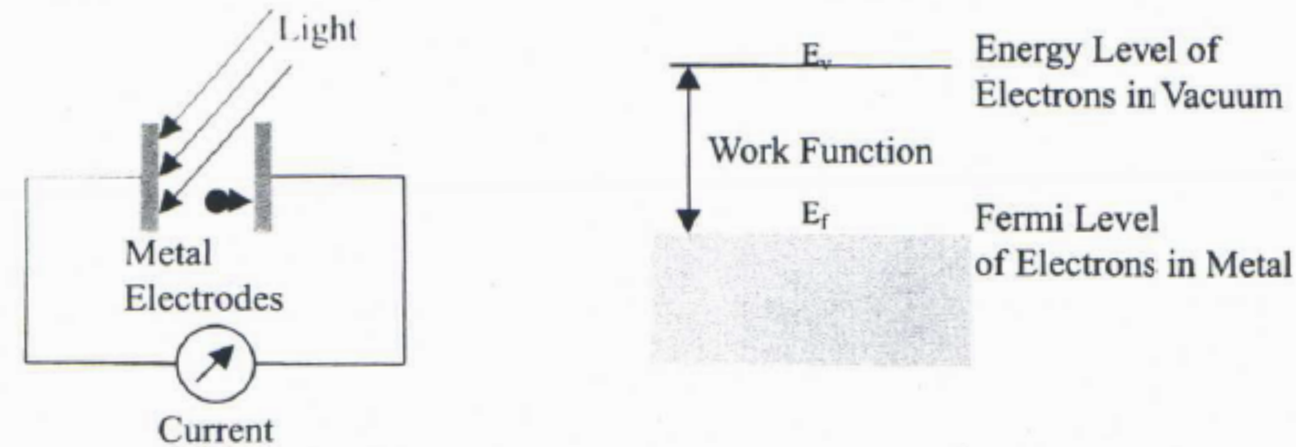
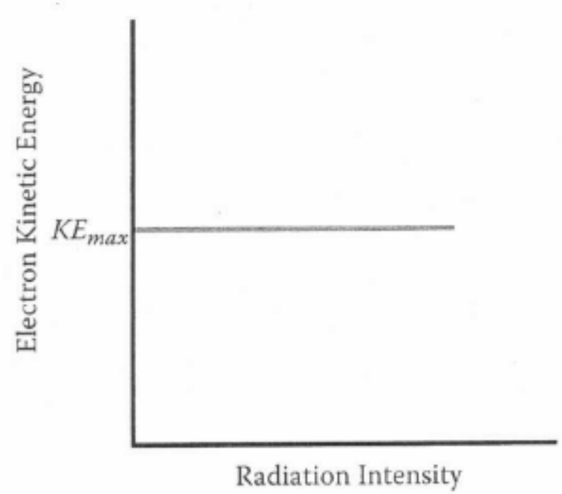
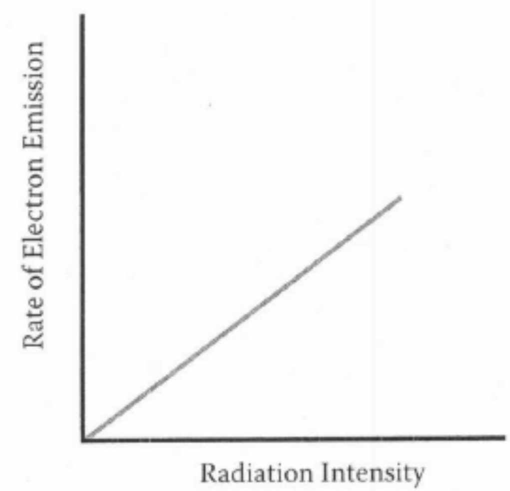


Figure 2.4 (a) Electron emission due to light excitation is called the photoelectric effect. The effect was explained by Einstein through the introduction of corpuscular properties of light. (b) Electrons in a metal have energy close to the Fermi level and their emission out of the metal surface into vacuum is possible only when the photon energy is larger than the work function.





The double slit experiment: particles

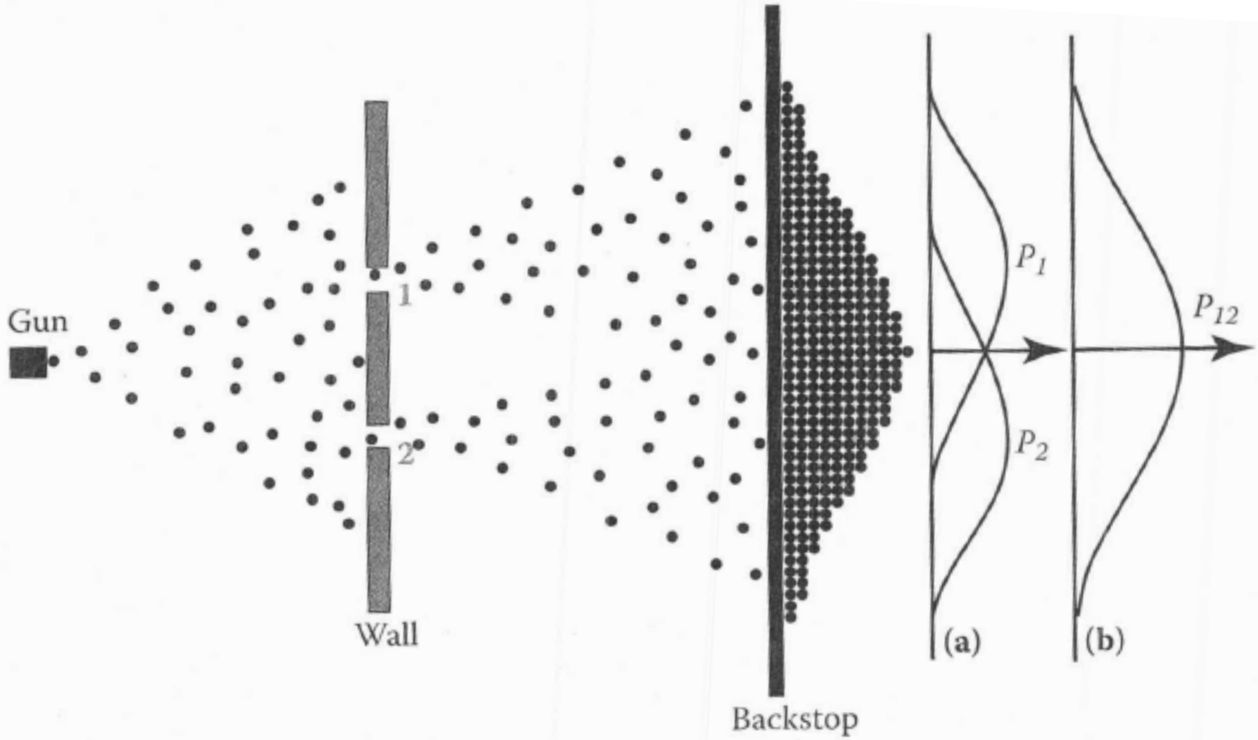


FIGURE 3.12 The double-slit experiment with bullets. A machine gun sprays bullets toward a wall with two slits. Behind the wall is a backstop. The stacks of bullets behind the backstop show how many bullets hit at particular locations during a given time. If we divide by the total number of bullets that hit the backstop during that time, we obtain the probability of a bullet arriving at a particular location. If we do the experiment with slit 2 covered, we obtain the curve P_1 shown in (a). If we cover slit 1, we obtain the curve P_2. With both slits open, we get the sum of these probabilities: $P_1 + P_2 = P_{12}$. This probability distribution is shown in (b).

Rogers, Pennathur, Adams.

The double slit experiment: waves

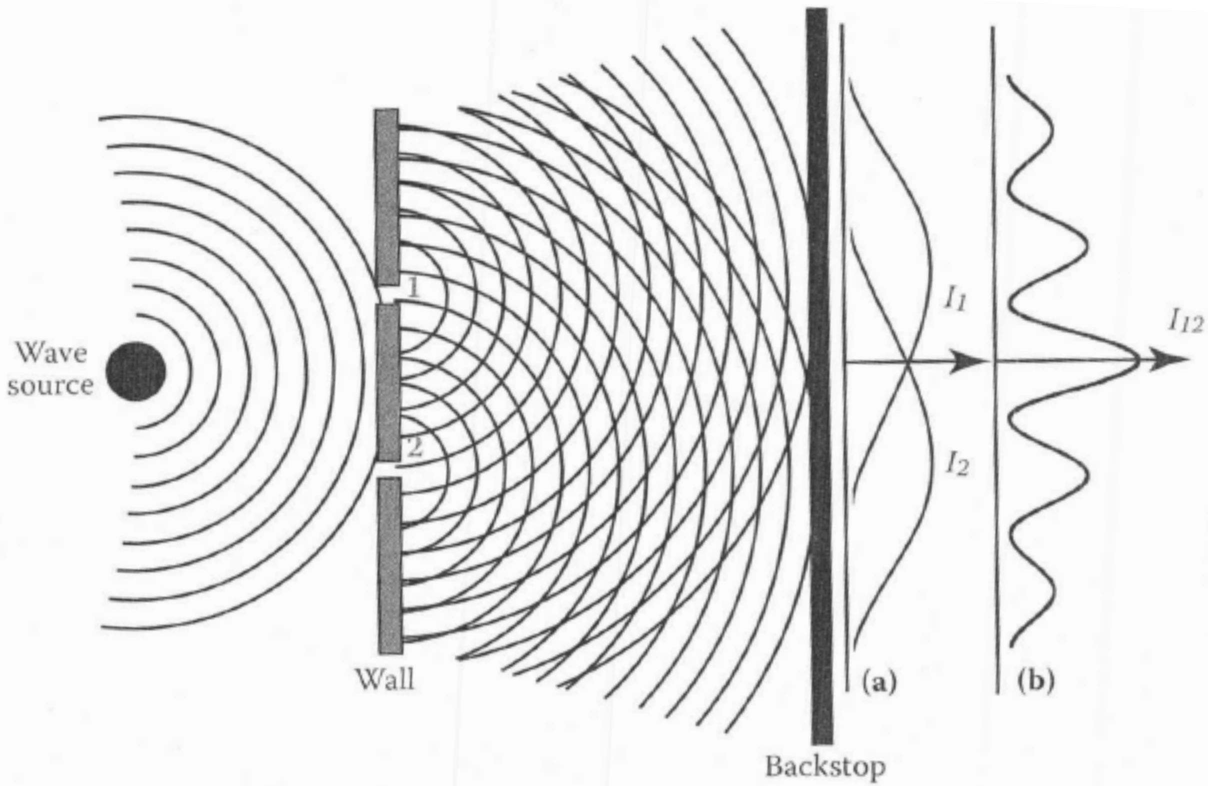


FIGURE 3.13 The double-slit experiment with water waves. A circular wave source creates waves in a shallow pool. The waves pass through slits in a wall and continue on to a backstop that prevents reflection. We measure wave height at various locations along the backstop. The height, or *intensity*, tells us how much energy a given wave has. If we cover slit 2, the intensity at the backstop is the curve I_1 shown in (a). If we cover slit 1, the intensity is the curve I_2. When both slits are open, the waves propagating from slit 1 interfere with those from slit 2. The interference can be constructive or destructive and leads to the shape of the curve we measure when both slits are open (I_{12}).

The slit experiment: electrons → *particles* ***and*** *waves*

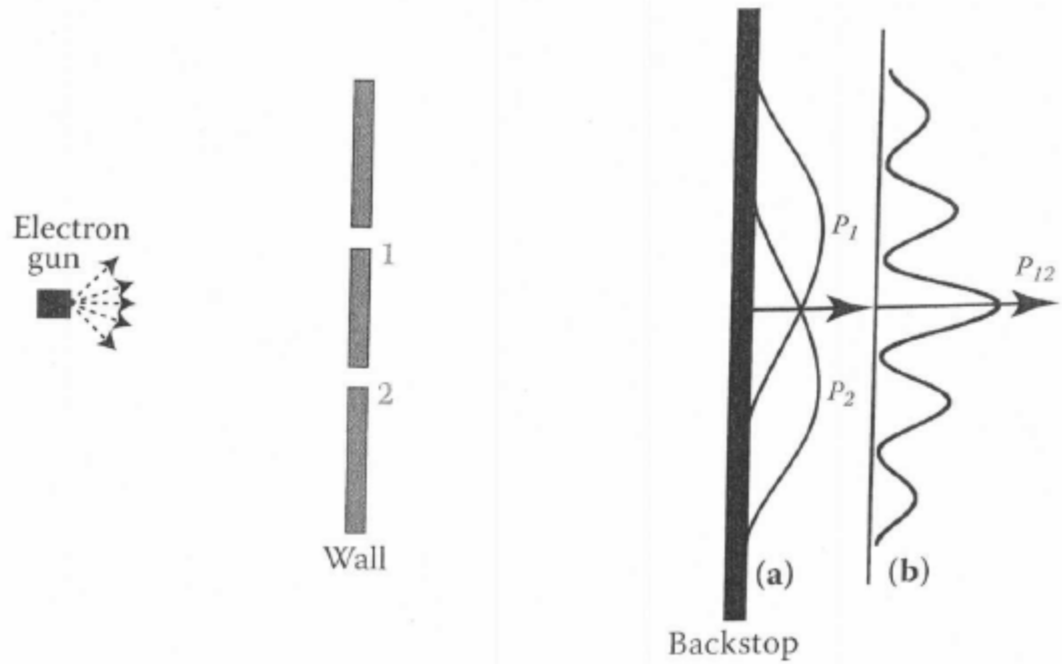


FIGURE 3.14 "The most beautiful experiment in physics." The double-slit experiment was first performed by Thomas Young, using light. Here we use electrons, which are fired from a gun toward the two slits. We count the number and location of electrons hitting the backstop, just like we did with the bullets. If we do the experiment with slit 2 closed, the probability distribution looks like curve P_1 in (a). Covering slit 1, we observe P_2. However, the probability curve when both slits are open does not look like it did with bullets, as we might expect. The curve of P_{12} for electrons is the same as the curve of I_{12} for waves. While electrons arrive one at a time at the backstop, like particles, their probability of arrival is subject to interference, like waves. This is wave–particle duality.

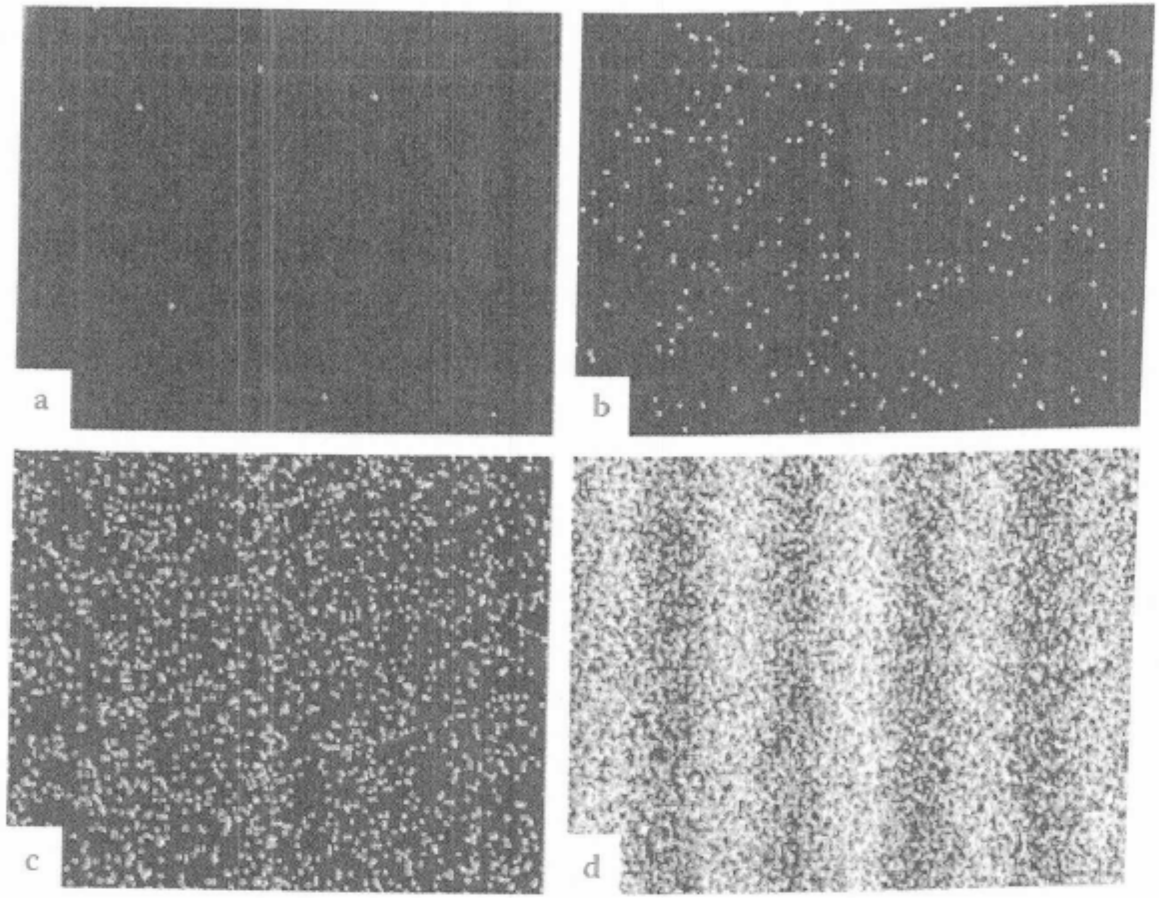


FIGURE 3.15 Experimental data from the electron dual-slit experiment. Each white dot depicts the arrival of a single electron at the backstop detector during an actual dual-slit experiment. Both slits were open. The data shown were captured at four times during the 20-min experiment. The number of electrons in each frame is (a) 8 electrons, (b) 270 electrons, (c) 2000 electrons, and (d) 6000 electrons. We can see the interference pattern in (d), similar to the probability curve P_{12} shown in Figure 3.14. (Data and images courtesy of Hitachi.)

The particle picture

- The **mean free path (MFP)**: the length between collisions ("scattering events")
- Need many collisions to produce the macroscopic laws (i.e. Ohms Law, Fourier's Law, Newtonian Shear Stress, etc.)
- When the MFP is comparable to the size of the system (the "box"), there are not so many collisions. The effects of the boundaries become important. These phenomena are called **"classical size effects"…**

Example of classical size effects: thermal conductivity of thin films

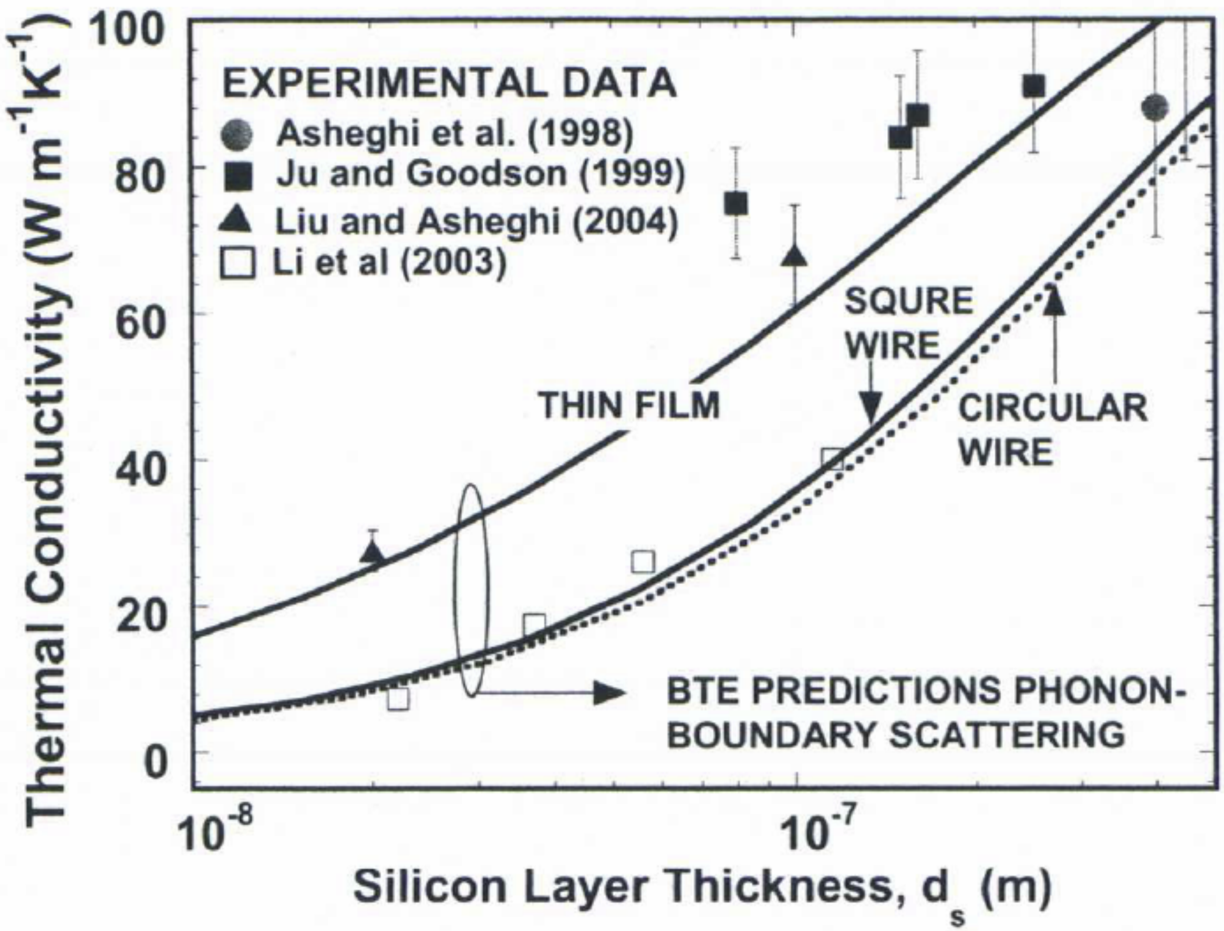
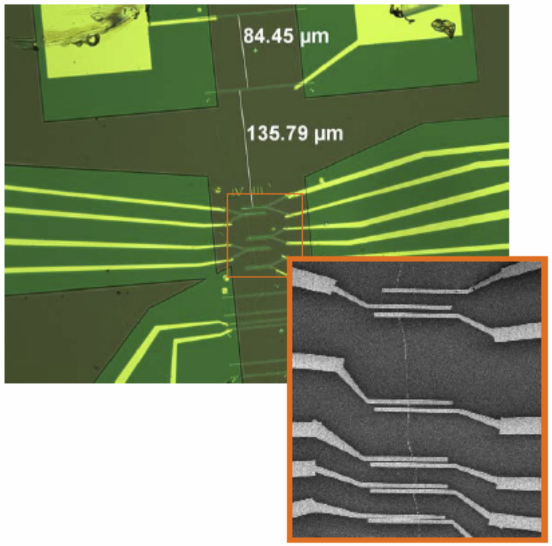
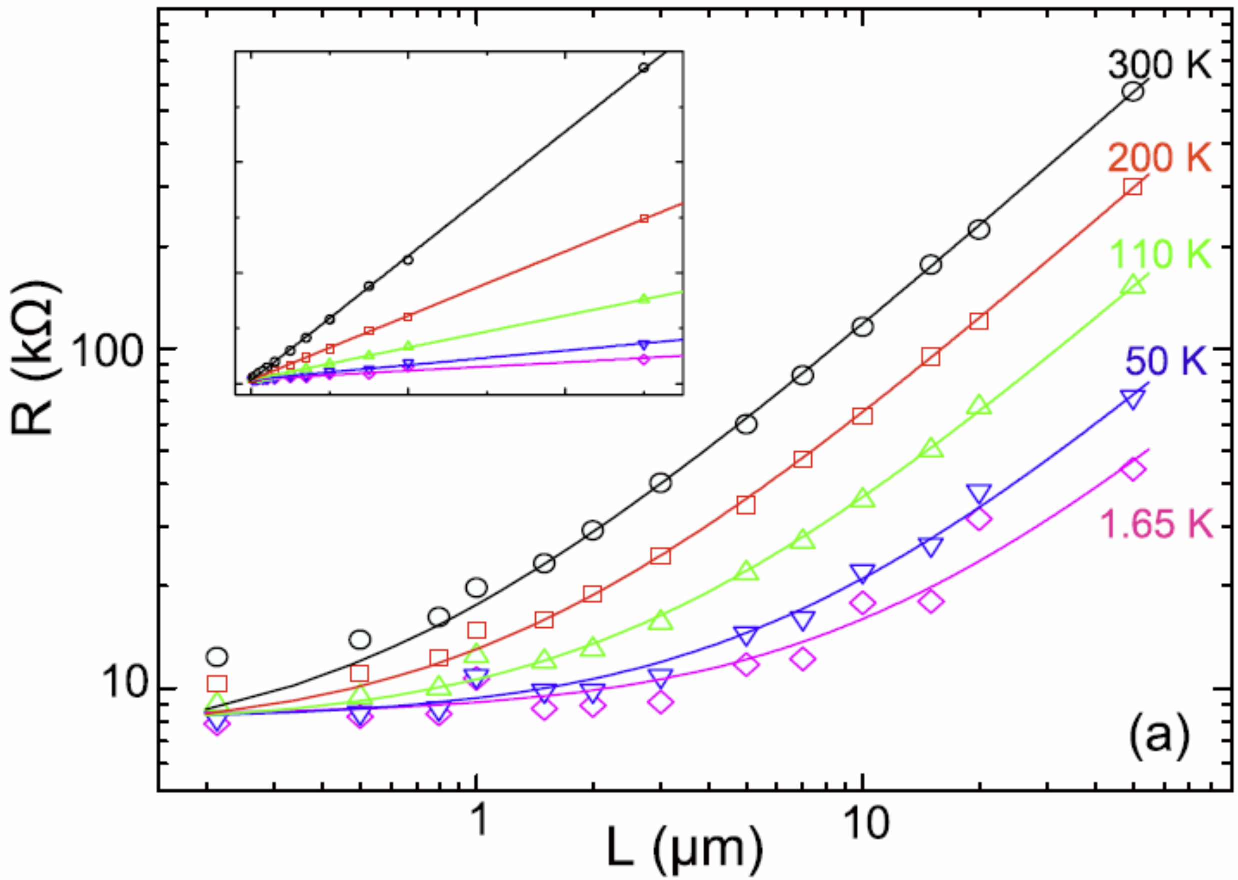


Figure 1.15 Thermal conductivity of silicon films as a function of the film thickness or wire diameter. (Courtesy of M. Ashegli).

Chen.

Example of classical size effects: electrical conductivity of CNTs vs. length





Purewal et al., Phys Rev Lett 98:186808, 2007.

The wave picture

- Important length scale: the **particle wavelength** (the "de Broglie* wavelength"):

$$\lambda = \frac{h}{p}$$

h = 6.626068 × 10^{-34} m^2 kg / s (Planck's constant)

- Quantum mechanics: energy (E) and momentum (p) from the wave

$$E = h\nu$$

$$p = \frac{h}{\lambda} = \frac{h}{2\pi} k = \hbar k$$

k is called the **wave vector**

- When the wavelength is comparable to the size of the system, the waves interfere in a coherent way. This leads to interference effects and discrete energy levels. These phenomena are called "**quantum size effects**".

*de Broglie was awarded the 1924 Nobel Prize in Physics, for his Ph.D. thesis!

Electromagnetic spectrum

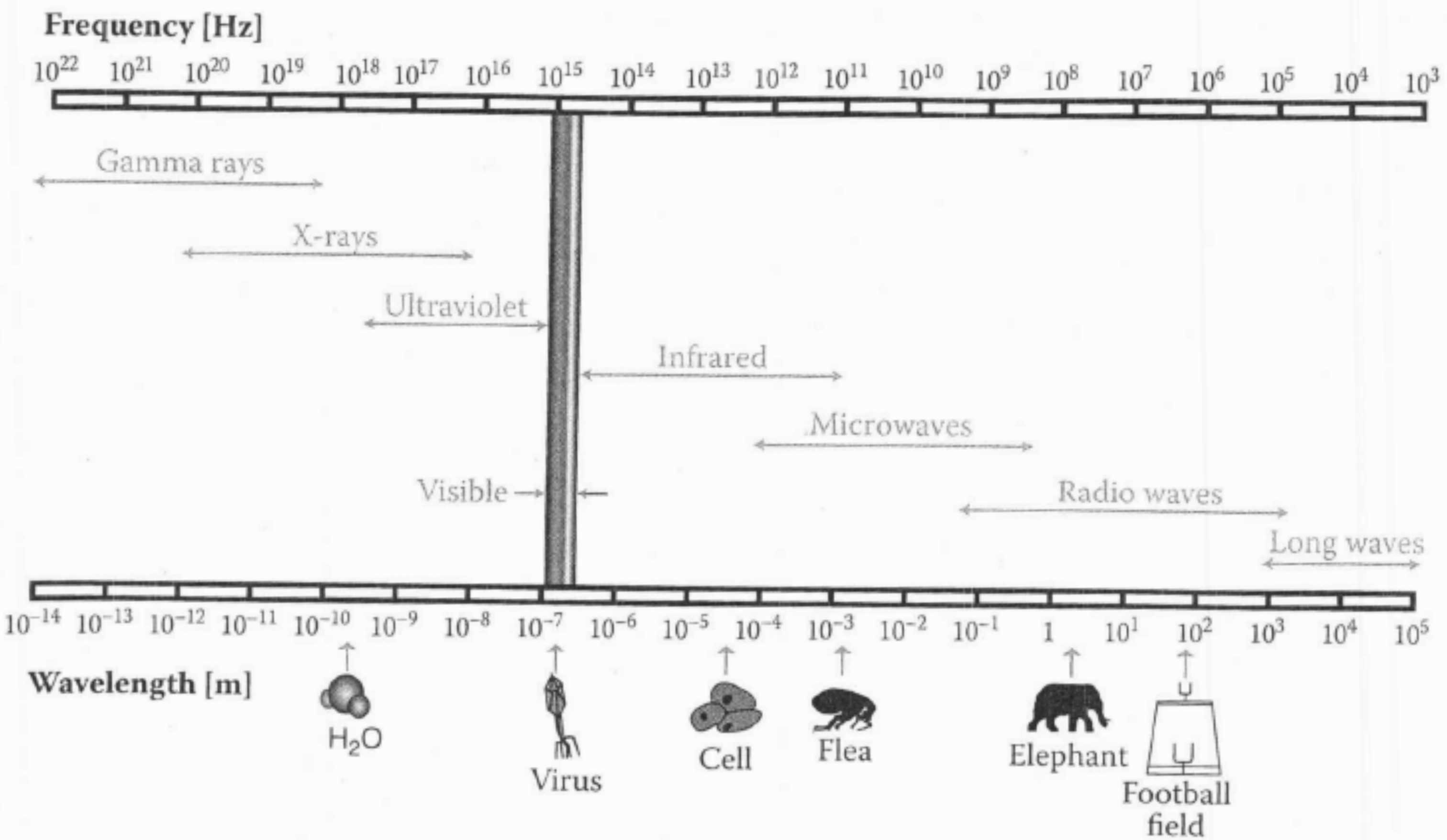


FIGURE 3.5 The electromagnetic spectrum. Everyday things of varying size aid in visualizing the size of wavelengths in different parts of the spectrum.

Transport regimes

Table 1.4 Transport regimes of energy carriers; O represents order of magnitude

Important Length Scales	Regimes	Photon	Electron	Phonon	Fluids
Coherence length, ℓ_c Phase-breaking length, ℓ_p ℓ_c: for photon: µm–km for phonon: 10 Å for electron: 100 Å $\ell_p \gtrsim$ Mean free path	$D < O(\ell_p)$ $D < O(\ell_c)$ Wave regime	Maxwell EM theory	Quantum mechanics	Quantum mechanics	Super fluidity
	$D \sim O(\ell_p)$ $D \sim O(\ell_c)$ wave–particle transition	coherence theory	Quantum Boltzmann equation		
Mean free path, Λ Photon: 100 Å–1 km Electron: 100–1000 Å Photon: 100–1000 Å	Particle regime $D > O(\ell_c)$, $D > (\ell_p)$: $D < O(\Lambda)$ ballistic	ray tracing	Ballistic transport	Ray tracing	Free molecular flow
	$D \sim O(\Lambda)$ quasi-diffusive	radiative transfer equation	Boltzmann transport equation	Boltzmann transport equation	Boltzmann transport equation
	$D > O(\Lambda)$ diffusive	diffusion approximation	Ohm's law	Fourier's law	Newton's shear stress

Chen.

Wave effects: traveling and standing waves

Traveling waves

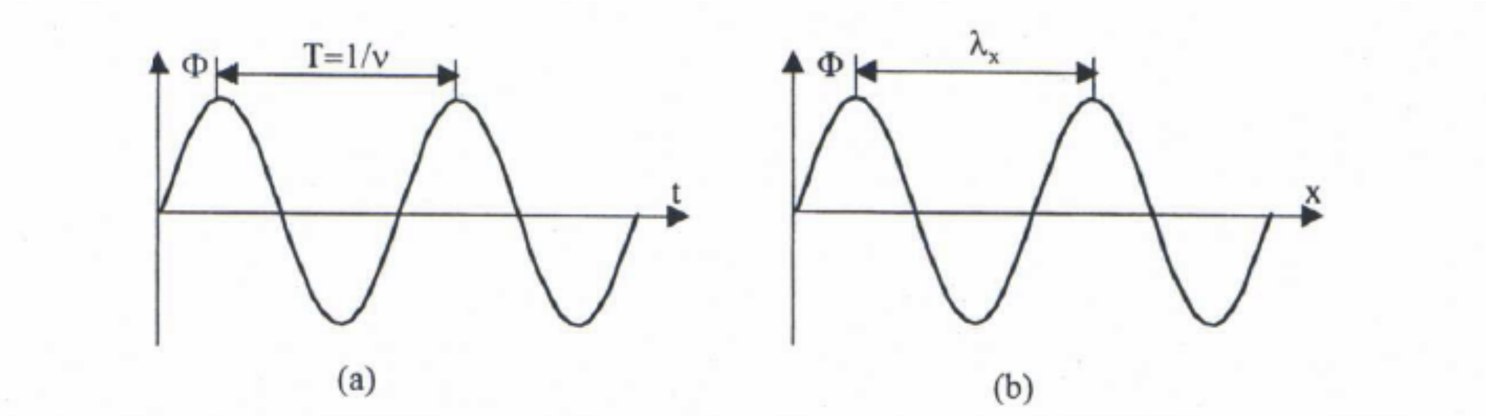
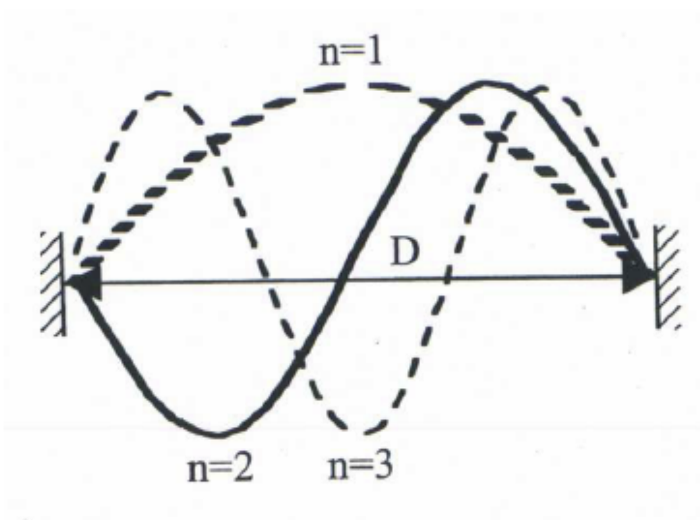


Figure 2.1 Traveling wave: (a) temporal variation at a fixed point; and (b) spatial variation at a fixed time.

Standing waves



1D potential well: "particle in a box"

- Standing wave modes = discrete energy levels

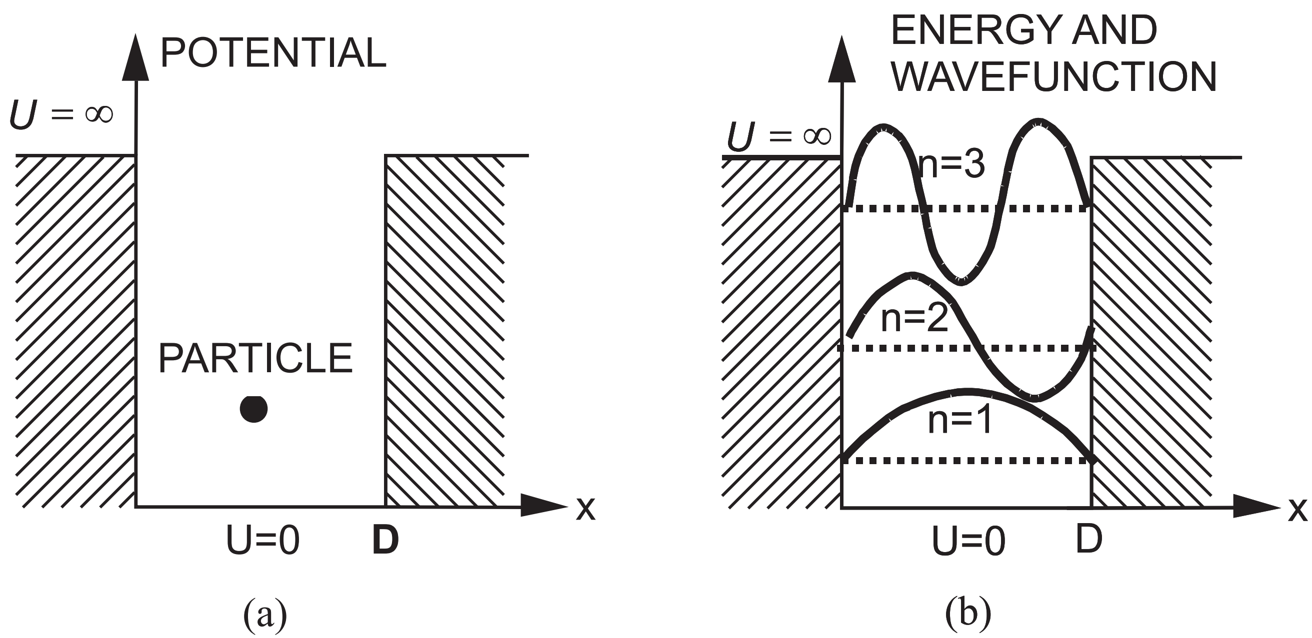
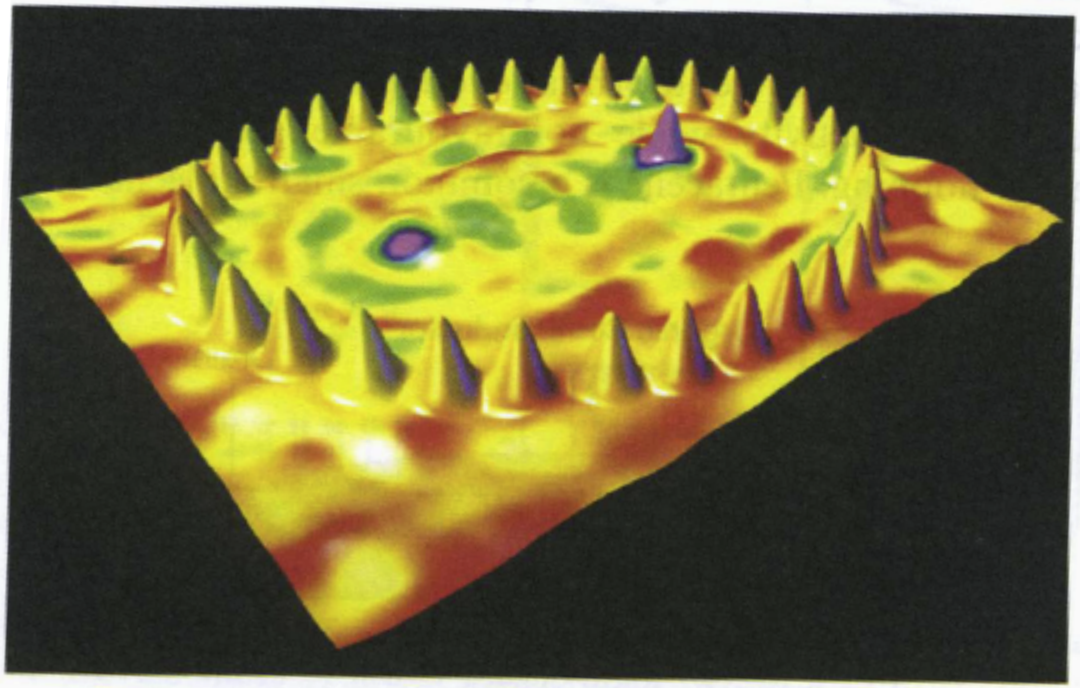
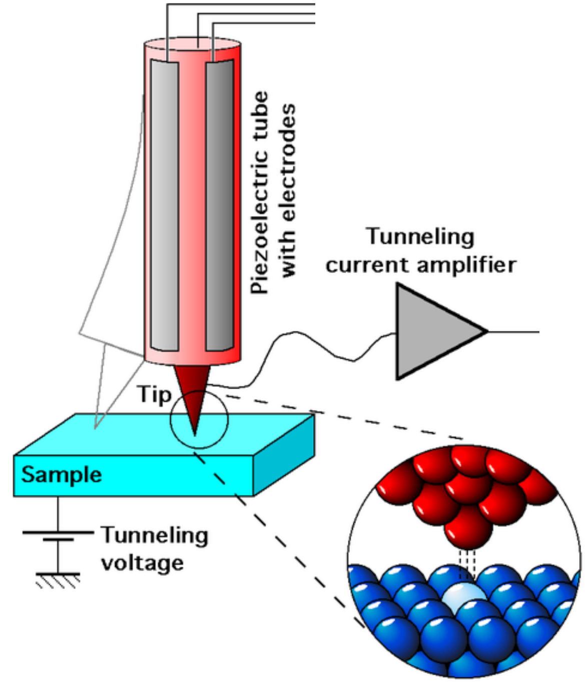


Figure 2.5 (a) One-dimensional potential well with infinite potential heights on both sides and zero potential inside the box. (b) Particle energy quantization in the box and wavefunction for the first three levels.

The real 2D potential well



Quantum mirage inside an elliptical ring of 36 Co atoms on a Cu(111) surface. A further Co atom placed at one of the two focus points inside the ellipse (purple peak) gives rise to a similar effect in the second focus point (purple spot) where no adatom exists
(Reprinted from Ref. 11, cover picture of the issue, with permission from the publisher)



Density of States (DoS) and confinement

- **Density of states**: the number of allowed states (modes) in a system per unit volume and unit energy interval

$$D(E) = \frac{\#\ \text{states between } E \text{ and } E + dE}{V \bullet dE}$$

- **Quantum confinement restricts the density of states of a material (nanostructure)**

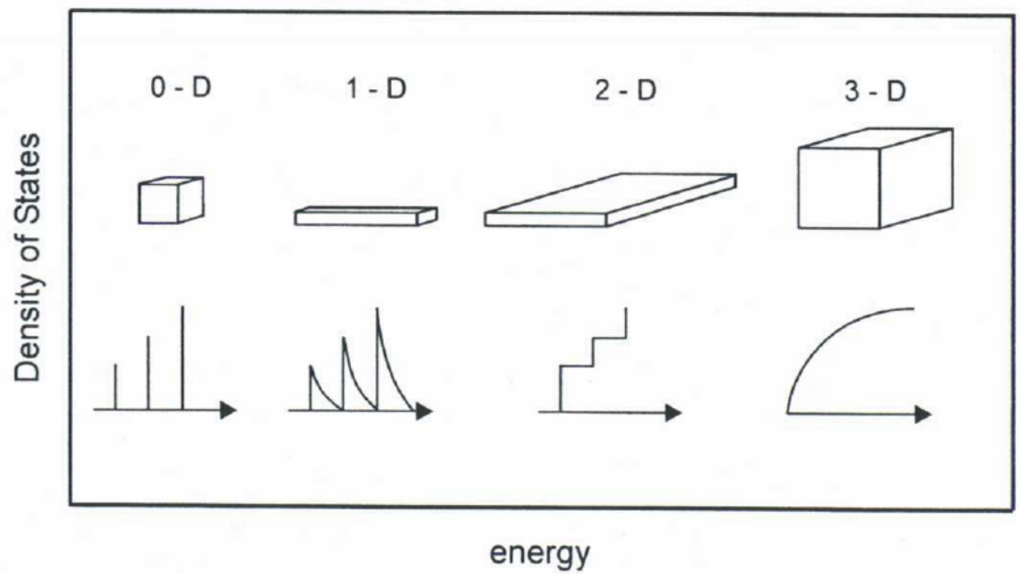
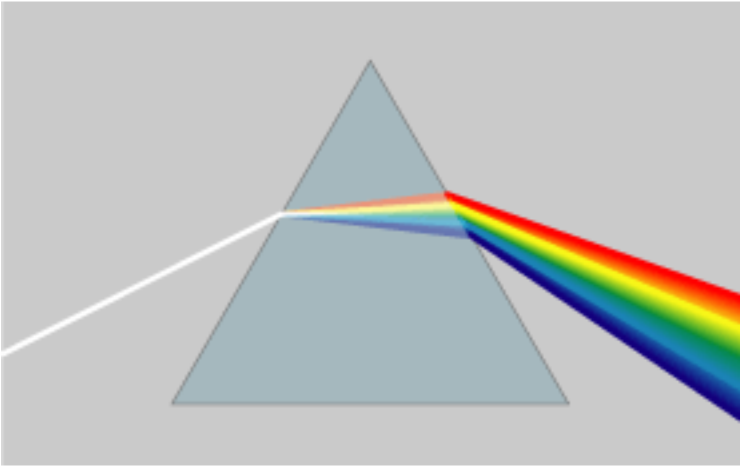


Figure 2 *Schematic representation of the effect of system dimensionality (a) Quantum dots, small clusters, colloids or nanocrystallites (0-D), ideally with discrete energy spectrum. (b) Quantum wire, chain (1-D) with non-negligible extension in the second and third dimension. (c) Quantum well, thin film or layer (2-D) with non-negligible thickness. (d) Bulk material (3-D)*
(Redrawn with permission from Ref. 3. Copyright (1996) AAAS)

Dispersion relations

- **Dispersion relation**: the relationship between energy and momentum (frequency and wave-vector)
- In real materials, dispersion relations for electrons, phonons, photons, etc. are complicated

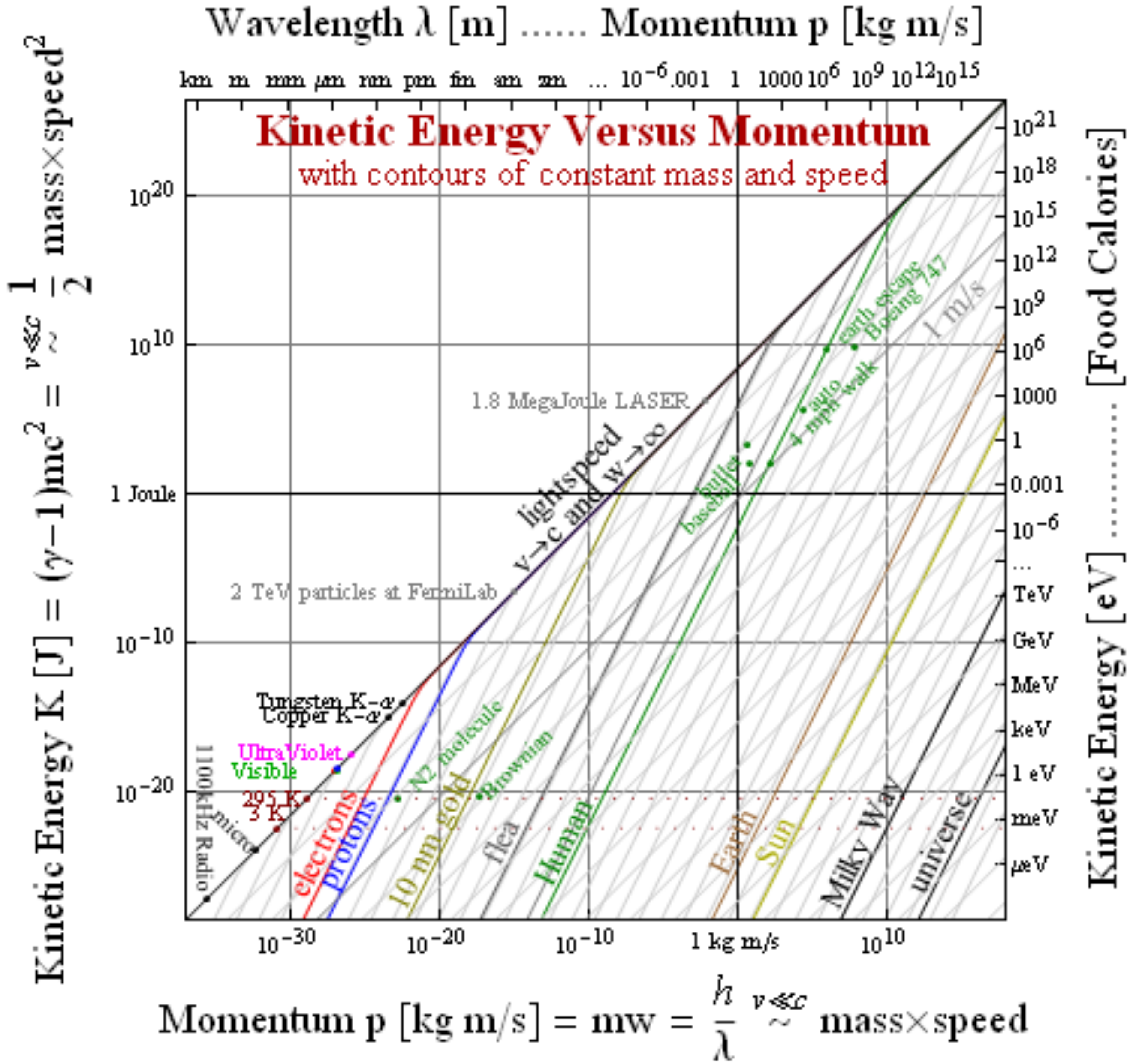
In matter, c depends on frequency



Light in vacuum: $f = c/\lambda$

http://en.wikipedia.org/wiki/Dispersion_relation

KE vs. p (momentum) in free space



http://en.wikipedia.org/wiki/Dispersion_relation

Band gaps

- Certain energies cannot be reached, creating “gaps” in the dispersion relation. These are called “band gaps”.
- Electrons, phonons and photons can have band gaps.

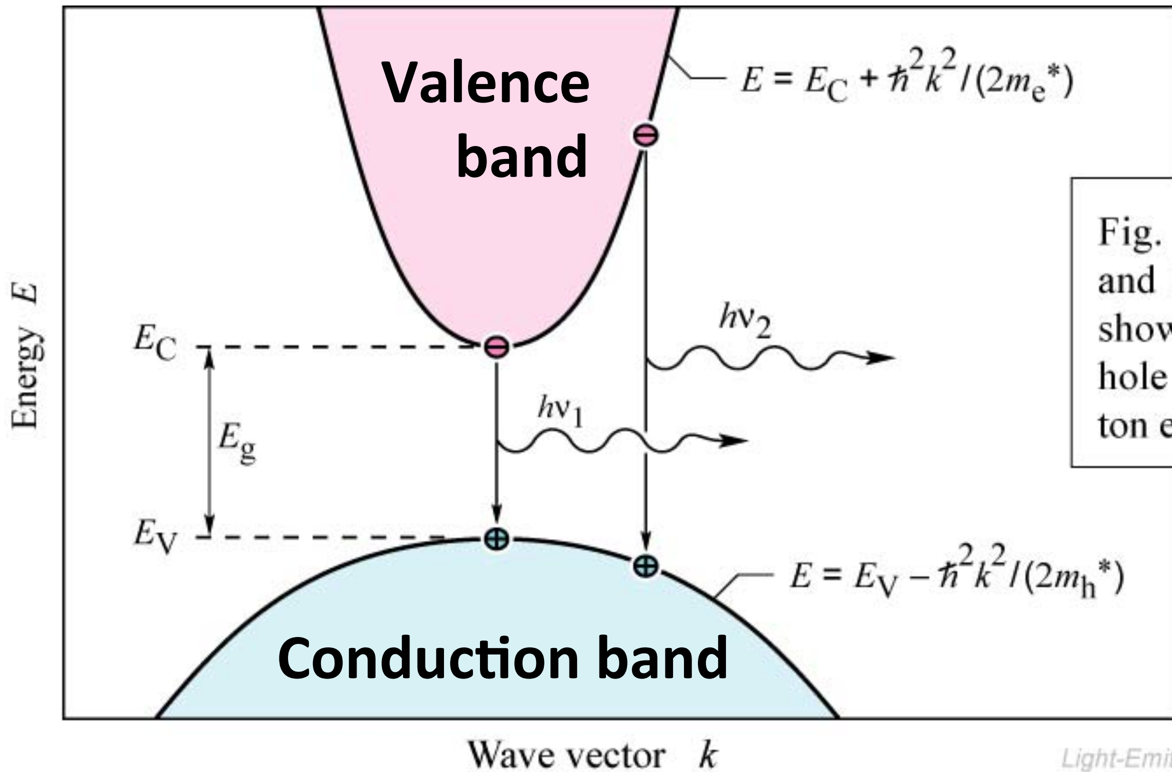


Fig. 5.1. Parabolic electron and hole dispersion relations showing “vertical” electron-hole recombination and photon emission.

E. F. Schubert
Light-Emitting Diodes (Cambridge Univ. Press)
www.LightEmittingDiodes.org

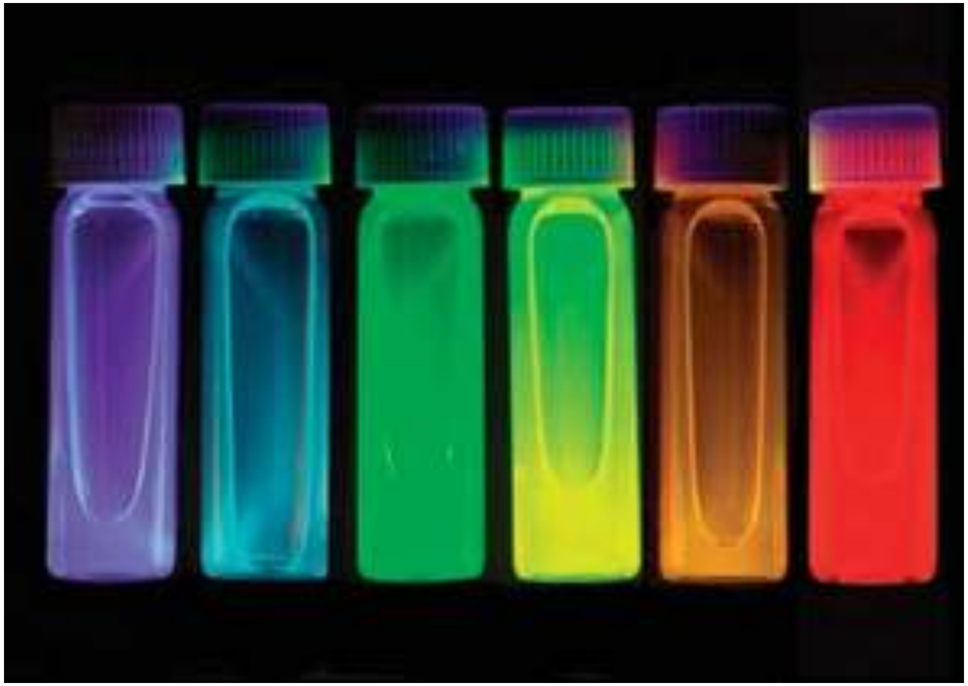
Band gap parameters of common semiconductors

	Band gap energy Eg (eV)	Exciton Rydberg Ry^* (meV)	Electron effective mass m_e/m_0	Hole effective mass m_h/m_0[a]	Exciton Bohr radius a_B (nm)
Ge	0.744[b]		⊥ 0.19 ‖ 0.92	0.54 (hh) 0.15 (lh)	
Si	1.17[b]	15	⊥ 0.081 ‖ 1.6	0.3 (hh) 0.043 (lh)	4.3
GaAs	1.518	5	0.066	0.47 (hh) 0.07 (lh)	12.5
CdTe	1.60		0.1	0.4	
CdSe	1.84	16	0.13	⊥ 0.45 ‖ 1.1	4.9
CdS	2.583	29		⊥ 0.7 ‖ 2.5	2.8
ZnSe	2.820	19	0.15	0.8 (hh) 0.145 (lh)	3.8
AgBr	2.684[b]	16			4.2
CuBr	3.077	108	0.25	1.4 (hh)	1.2
CuCl	3.395	190	0.4	2.4 (hh)	0.7

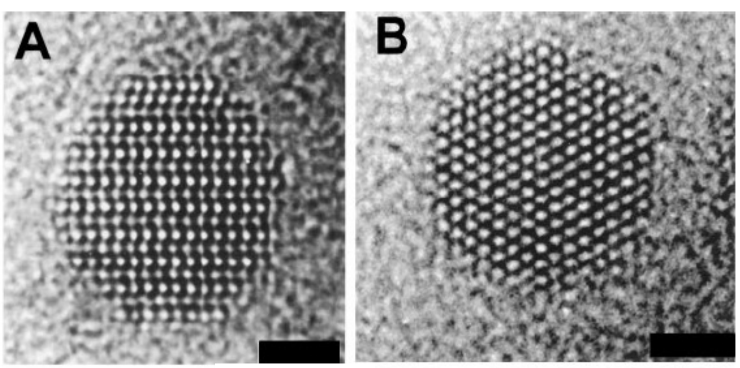
[a] hh – heavy hole, lh – light hole
[b] Indirect band gap
Source: After Landholt-Boernstein 1982.

Gaponenko.

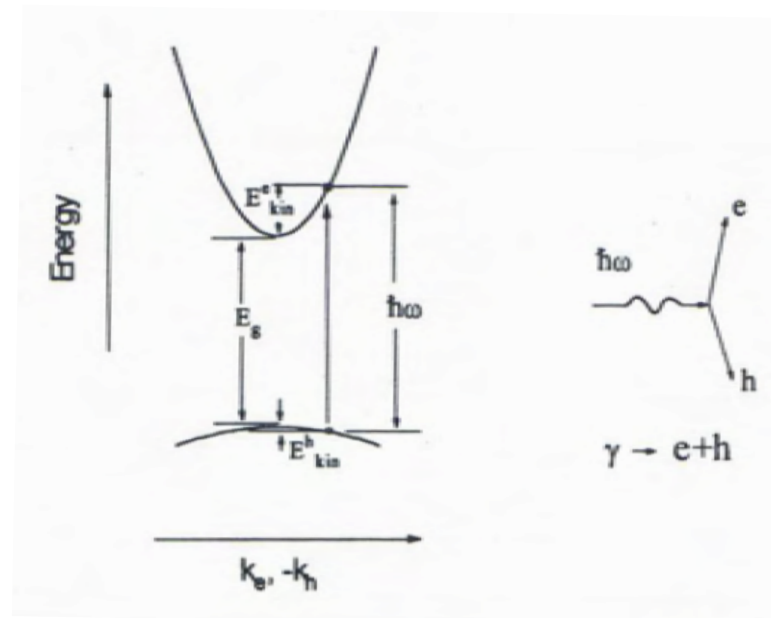
Size-dependent color of quantum dots



<100> CdSe <001> CdSe

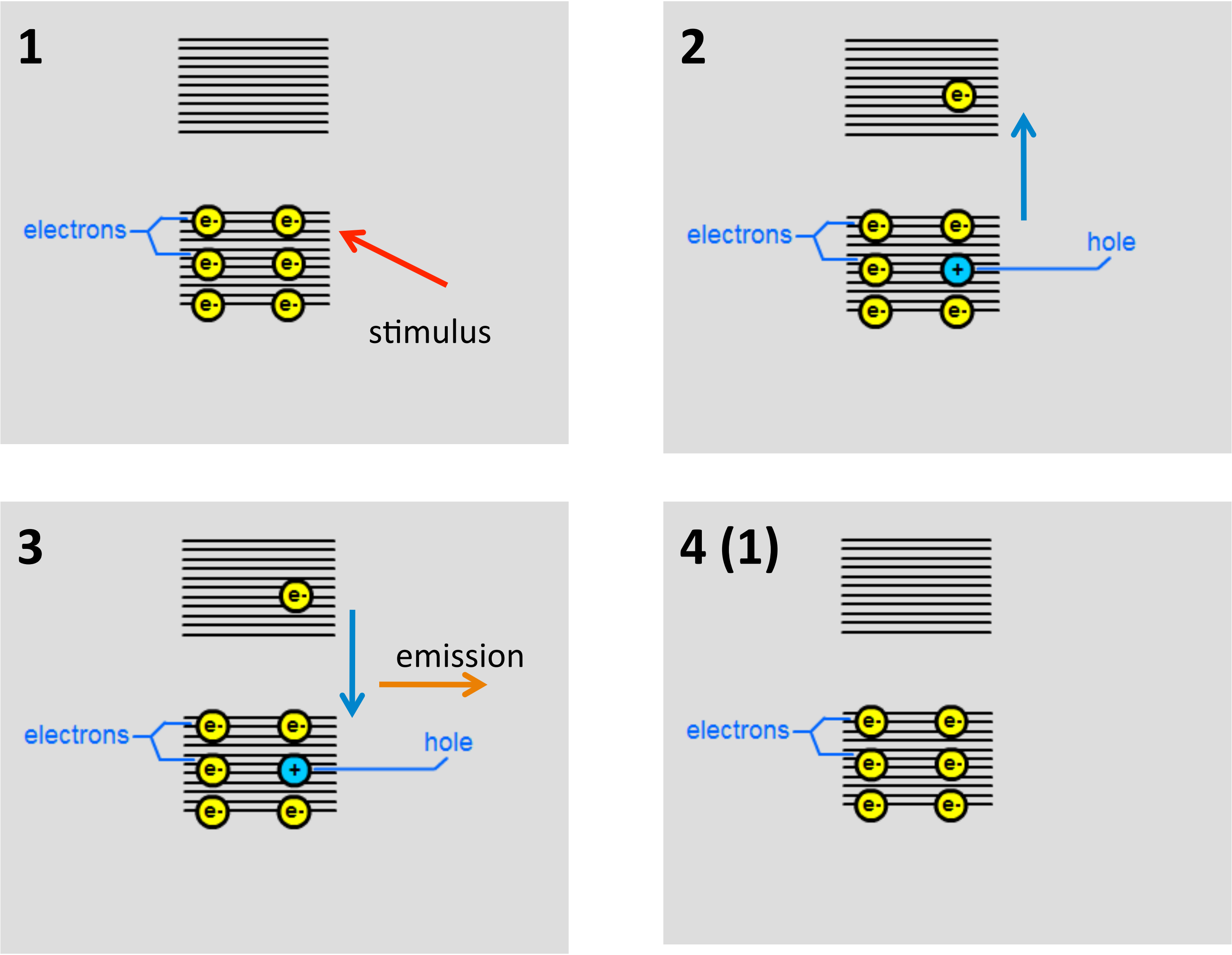


1.5 nm



Frankel, Bawendi.

Absorption and emission



http://www.eviddenttech.com/quantum-dots-explained/how-quantum-dots-work.html

Idealized band model for a quantum dot, assuming strong confinement

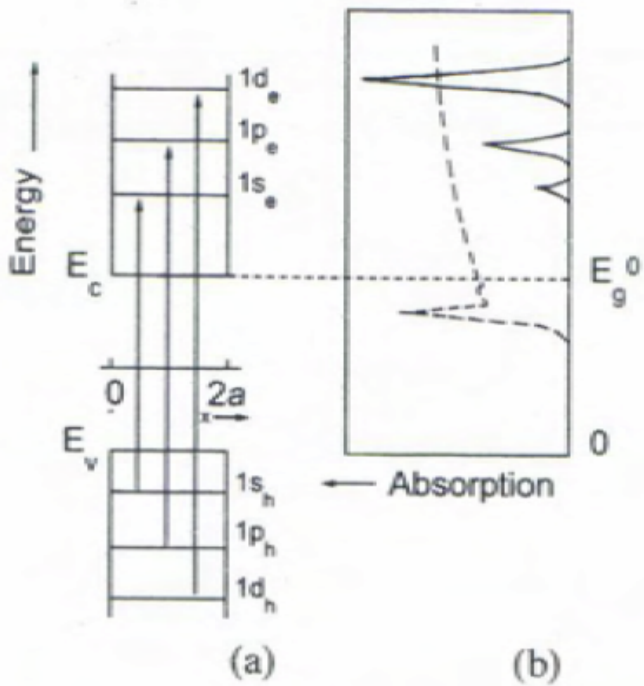


Fig. 2.1. A sketch of optical properties of an ideal spherical quantum dot with isotropic scalar effective masses of noninteracting electron and hole. Electron and hole energy levels (a) obey a series of states inherent for a particle in a spherical box with an infinite barrier. Selection rules allow optical transitions coupling the hole and the electron states with the same quantum numbers. Therefore, the optical absorption spectrum of the parent bulk crystal reduces to a number of discrete bands (b).

Gaponenko.

As size increases (confinement decreases), absorption approaches bulk character

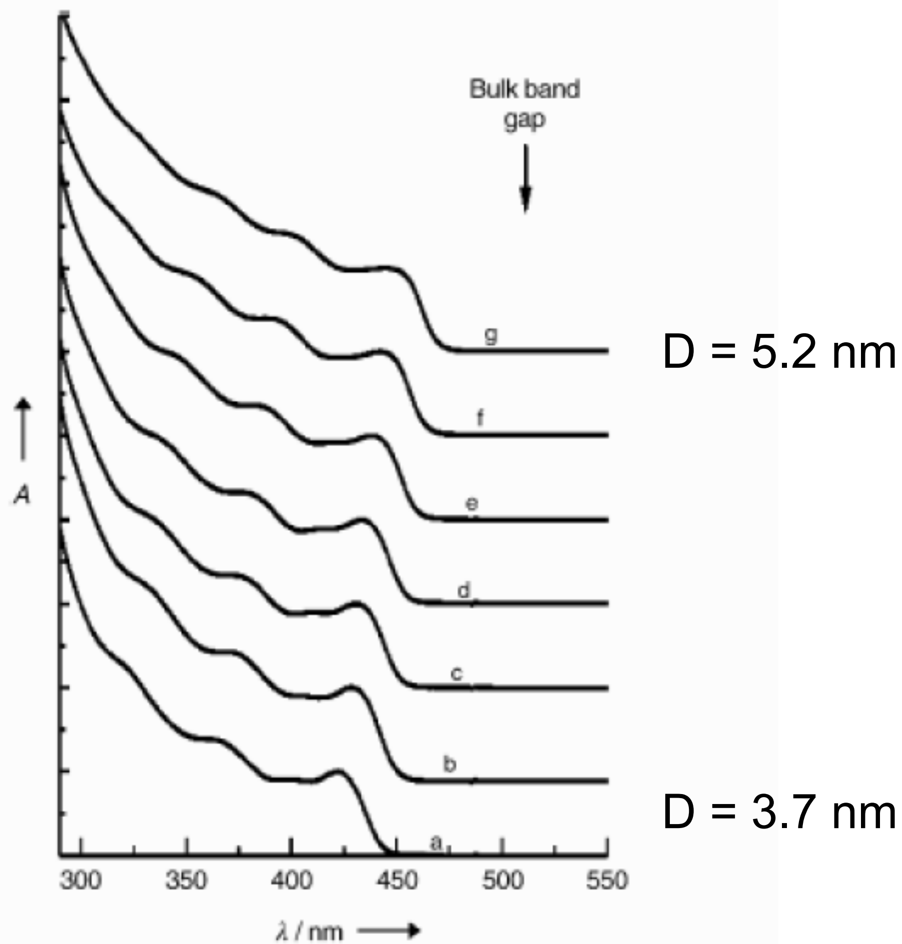
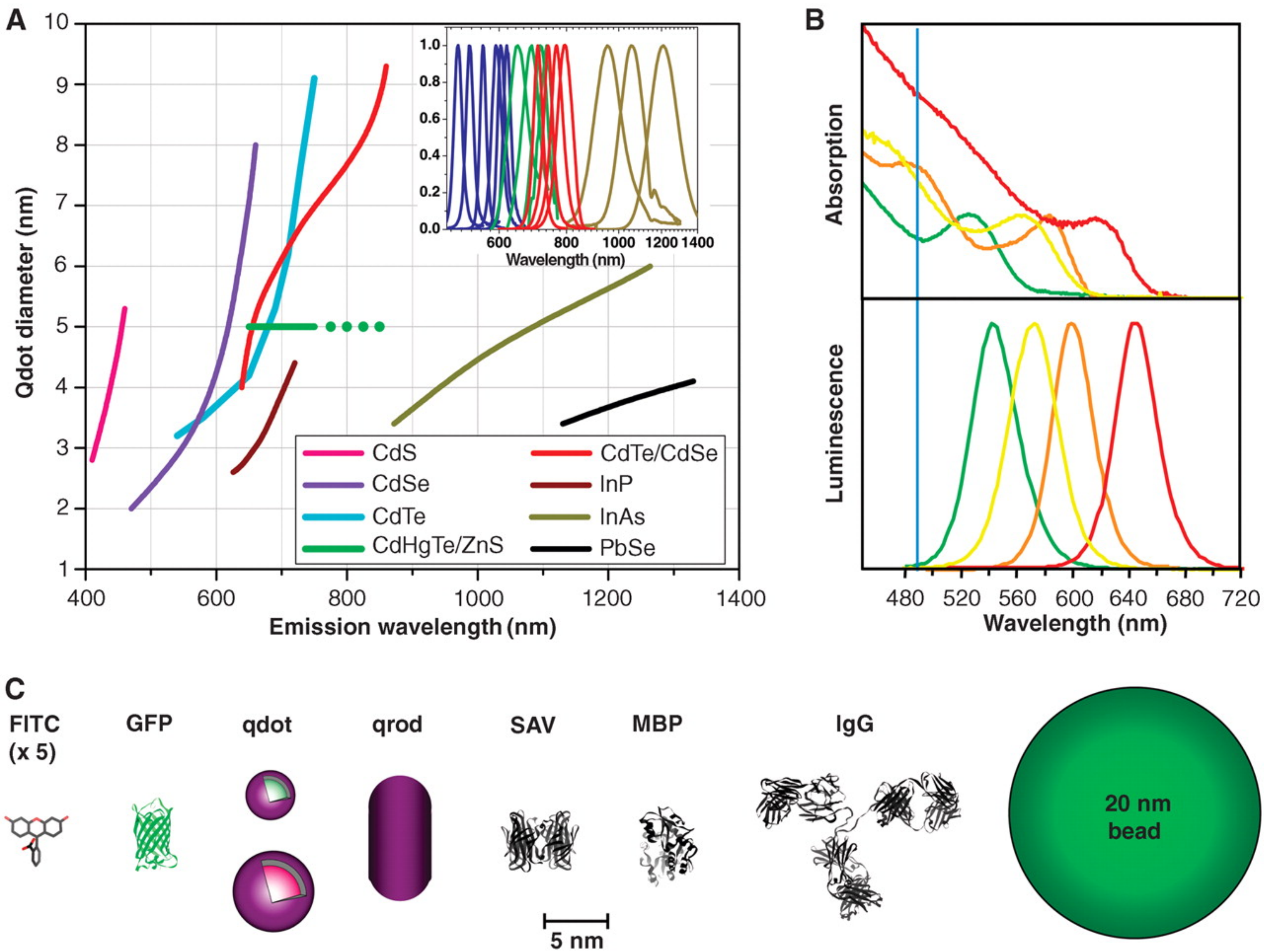


Figure 1. Absorption spectra of a size-series of large CdS nanocrystals ranging from 3.7±0.4 nm to 5.2±0.4 nm in diameter. The longest wavelength absorption feature occurs at a) $\lambda = 422$, b) 427, c) 432, d) 435, e) 439, f) 444, and g) 448 nm.

Alivisatos.

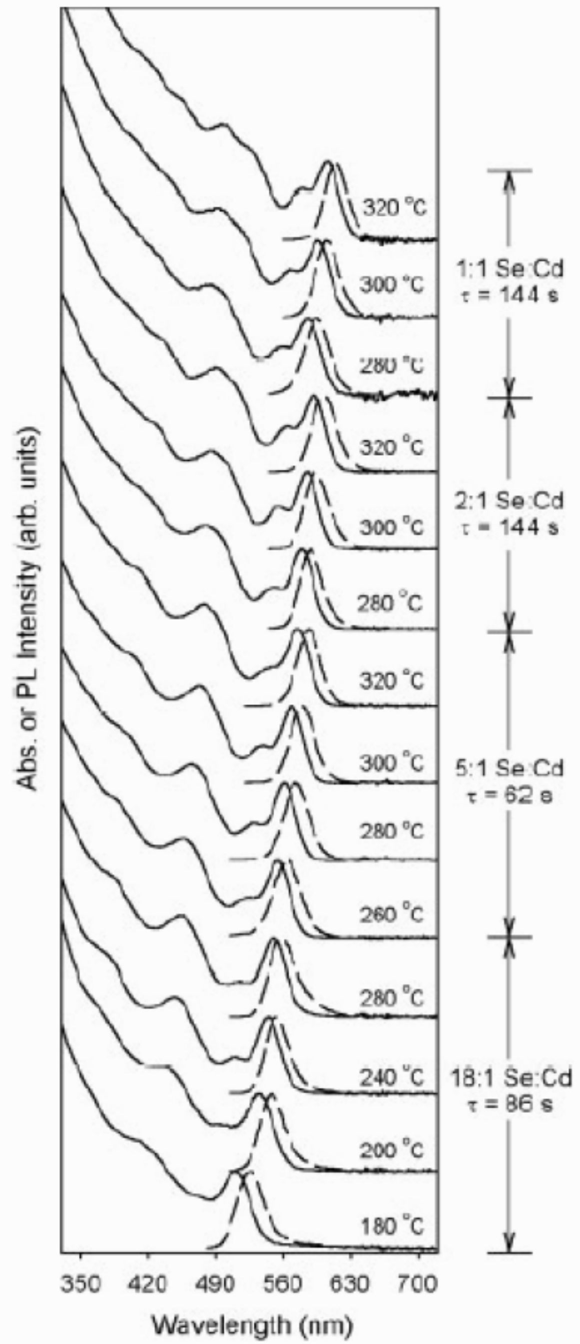
Examples: different semiconductor crystals



Michalak et al., Science 307:538-544, 2005.

Manufacturing: tuning optical properties by synthesis conditions

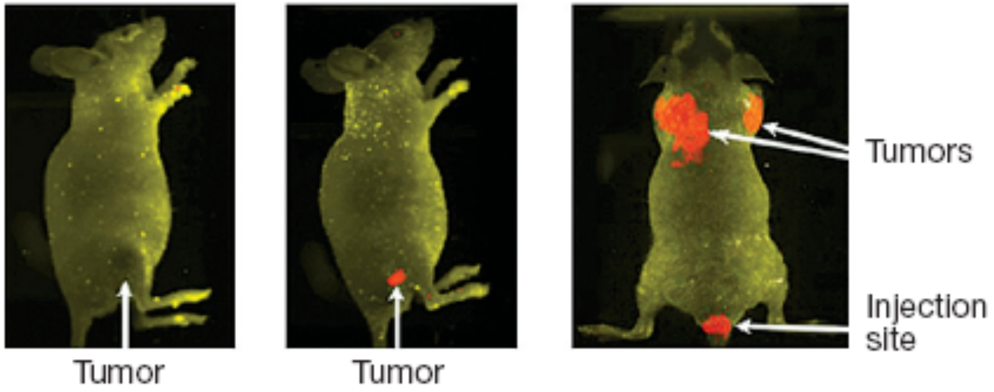
Fig. 4. Size series for samples prepared using four TOPSe concentrations: 1:1 Se/Cd, 2:1 Se/Cd, 5:1 Se/Cd, and 18:1 Se/Cd. For each TOPSe concentration, the average NC size was controlled by varying the temperature at a fixed flow rate. From bottom to top, the positions of the band-edge absorbance peaks in nm (and average NC radii in nm) are as follows: 510 (1.52), 535 (1.78), 545 (1.90), 551 (1.98), 555 (2.03), 561 (2.10), 569 (2.20), 575 (2.27), 579 (2.32), 585 (2.39), 592 (2.48), 586 (2.40), 597 (2.55), 606 (2.70).



Alivisatos.

Imaging with quantum dots

- Previous technology = fluorescent proteins
- New technology = semiconductor nanoparticles
  - Narrow emission peaks
  - Size-dependent emission
  - Long lifetime (resists photobleaching, i.e., photochemical degradation)
  - Diverse chemical linkages to surfaces
- Typical emission lifetimes (at ~10^5 photons/s)
  - Green fluorescent protein = 0.1-1 s
  - Organic dye = 1-10 s
  - CdSe/ZnS quantum dot = 10^5 s



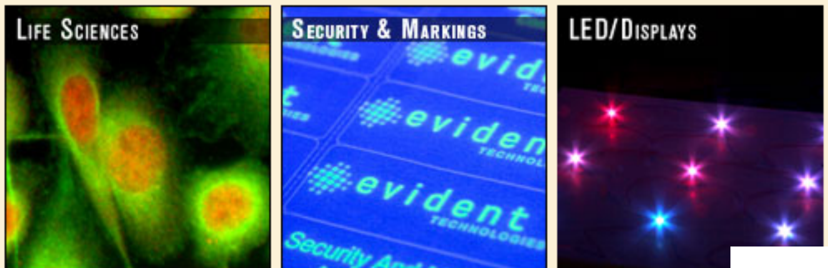
Gao et al., Nature Biotechnology 22(8):969-976, 2004.
http://en.wikipedia.org/wiki/Photobleaching

Commercially-available quantum dots

Product Development & Business Units

We team with top companies to develop products based on our proprietary quantum dot technology. Our teaming formula can save time and money getting to market, accelerate market penetration, and drive product revenue.

Fast-tracking Quantum Dot Products to Market
Quantum Dots for Product Development



Life Sciences	Security & Markings	LEDs / Displays
Quantum dot products overcome many limits of existing fluorescent labels and probes.	Better security and brand protection through quantum dots.	New LED colo application fle with quantum technologies.

CdSe/ZnS Core-Shell Product Availability

Wavelength	Peak Tolerance	System	Type	Part Number	Price
490mn	+/- 10nm	CdSe/ZnS	Core-Shell	ED-C11-TOL-0490	50 mg - $399 200 mg - $649 500 mg - $1099 1000 mg - $1499
520nm				ED-C11-TOL-0520	
540nm				ED-C11-TOL-0540	
560nm				ED-C11-TOL-0560	
580nm				ED-C11-TOL-0580	
600nm				ED-C11-TOL-0600	
620nm				ED-C11-TOL-0620	

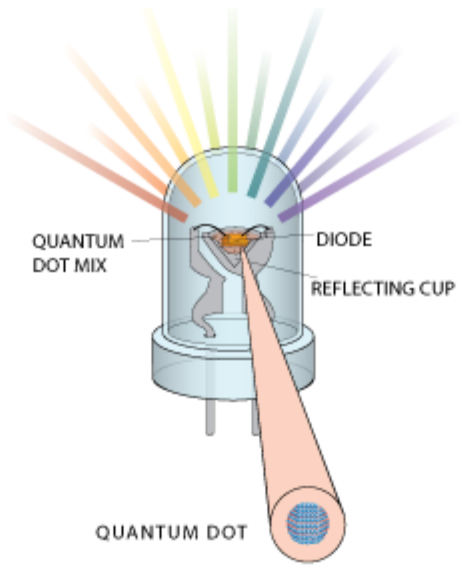
490 520 540 560 580 600 620

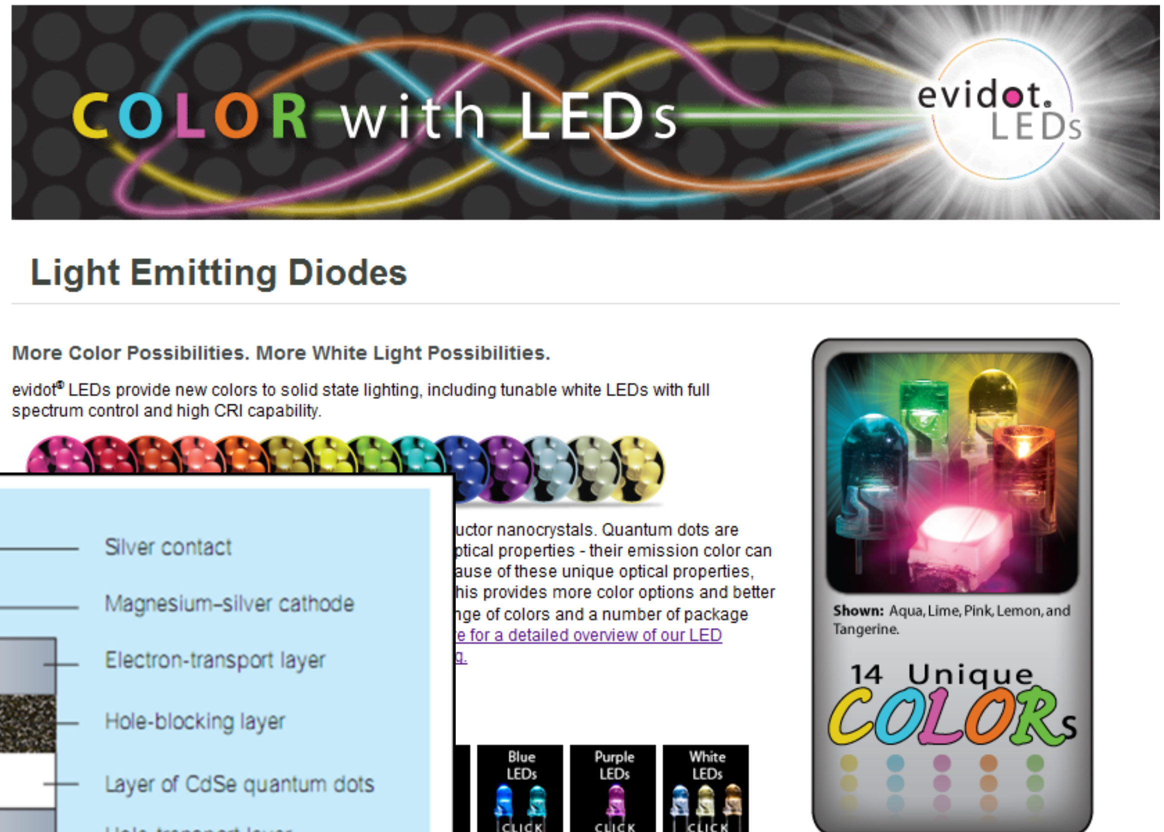
Add to cart:

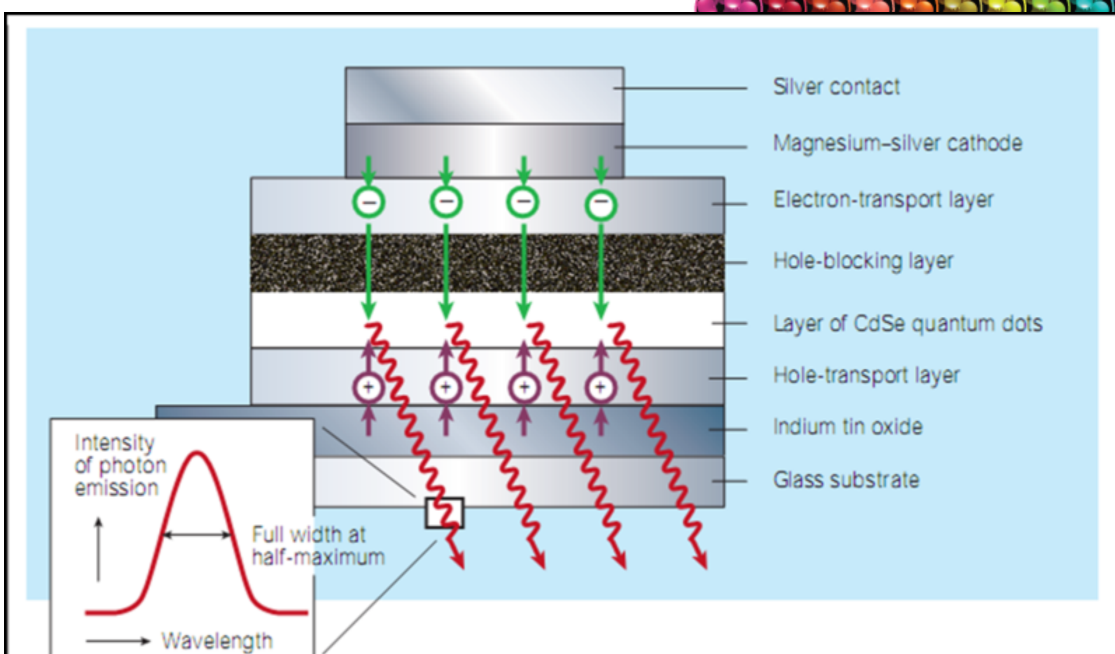
490nm | 50 mg | Add to Cart

http://www.evidenttech.com

Quantum dot LEDs







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