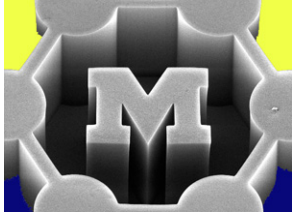
Nanomanufacturing
University of Michigan
ME599-002 |Winter 2010

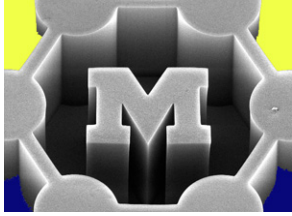


04: **Electronic properties of nanostructures**

January 25, 2010

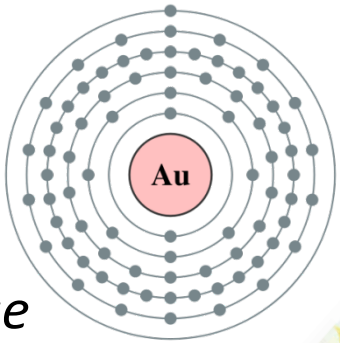
John Hart, Aaron Schmidt
ajohnh@umich.edu
http://www.umich.edu/~ajohnh

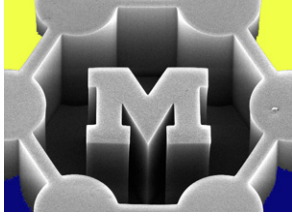
Announcements



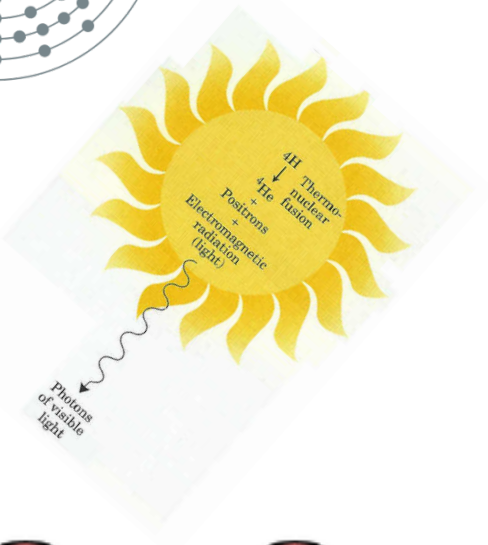
- PS1 due next W Feb/3
  - Some material is yet to be covered in lecture
- Mostafa's office hours Th 4.30-6.30, 1363 GGB

Energy carriers



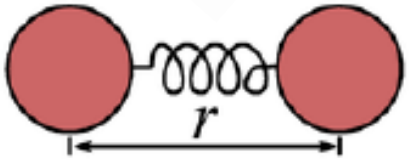


- **Electron -** subatomic particle carrying a negative charge
  → *interaction between electrons is the main cause of chemical bonding*

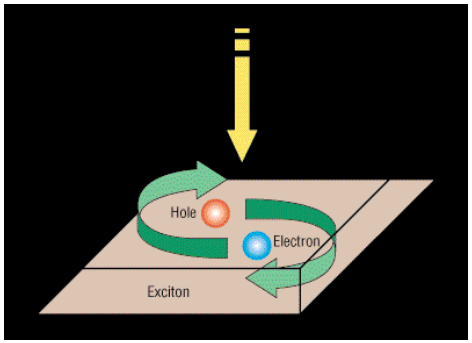


- **Photon** - quantum of electromagnetic field and the basic unit of light

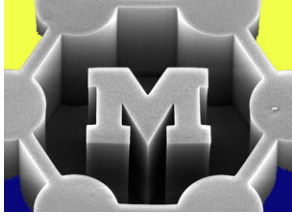
- **Phonon** – a quantized mode of vibration in a lattice



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

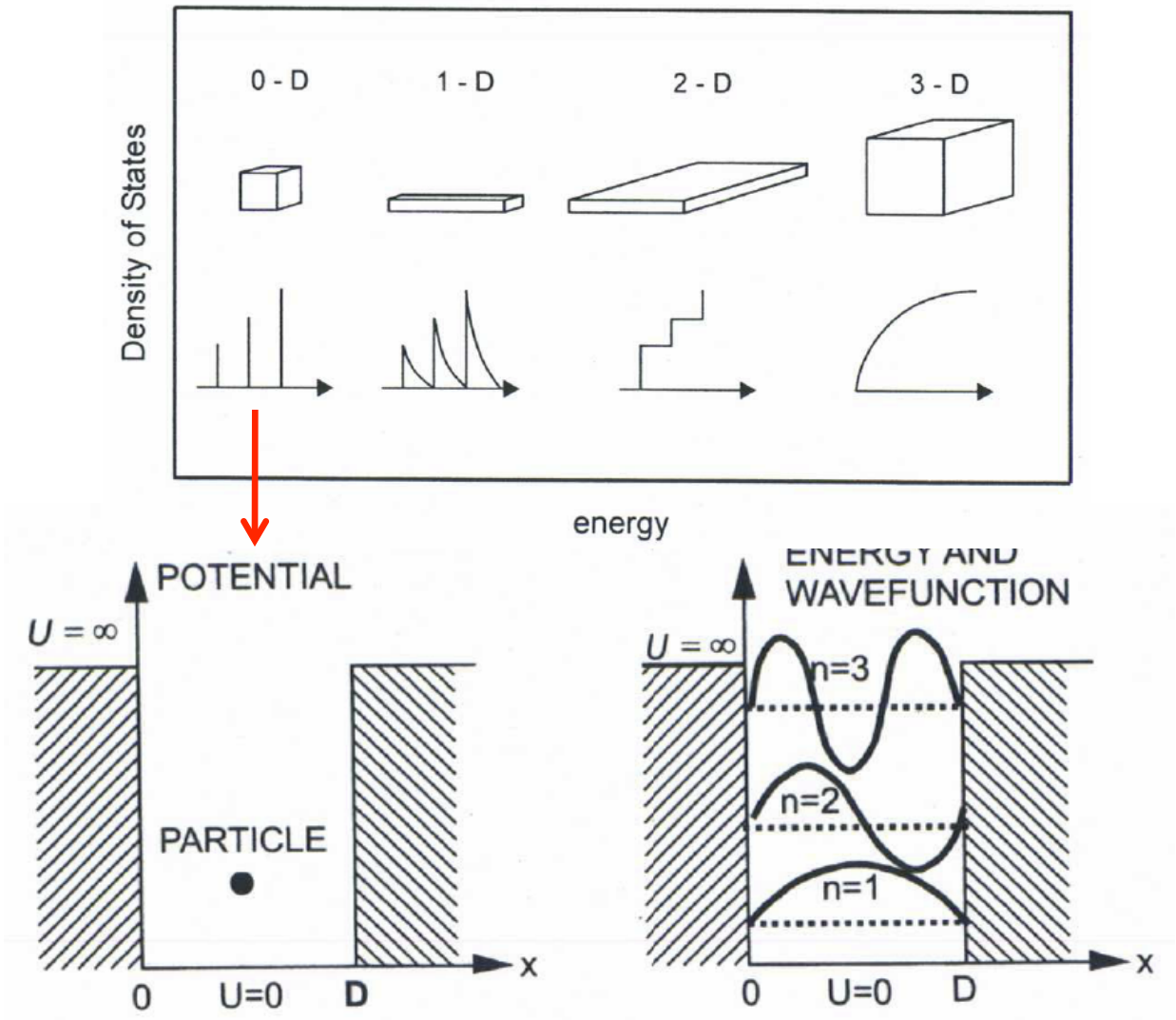


Size effects and confinement



- **Classical size effects:** When the carrier mean free path is comparable to the size of the system → the boundaries become important.

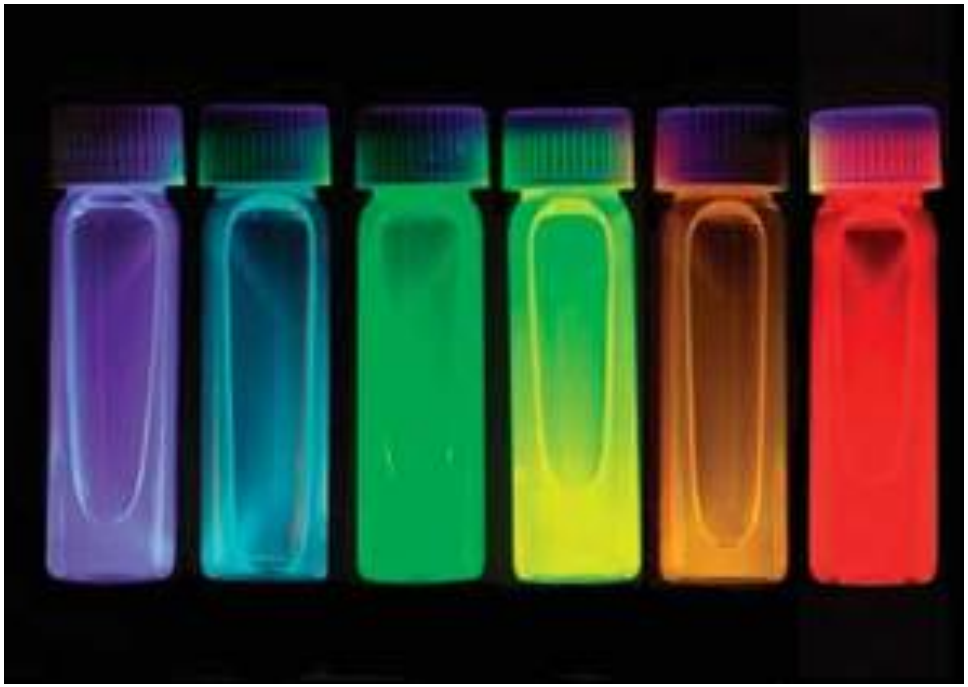
- **Quantum size effects:** When the carrier wavelength is comparable to the size of the system → the waves interfere in a coherent way, causing discretization of allowable energy levels.
  - The density of states is restricted
  - The band structure changes with size of the material
  - Due to aspect ratios, properties of a nanostructure can be highly anisotropic
  - The boundaries are also important in this regime

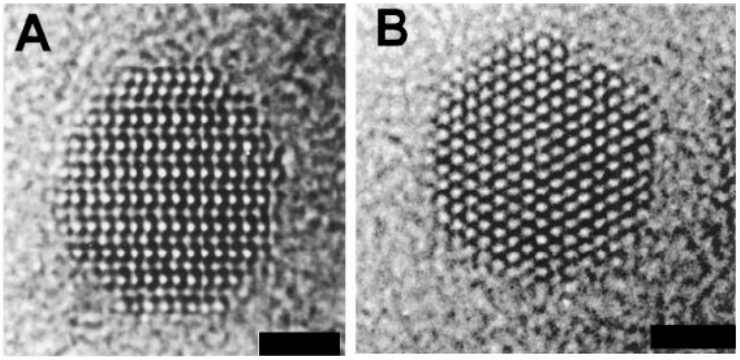


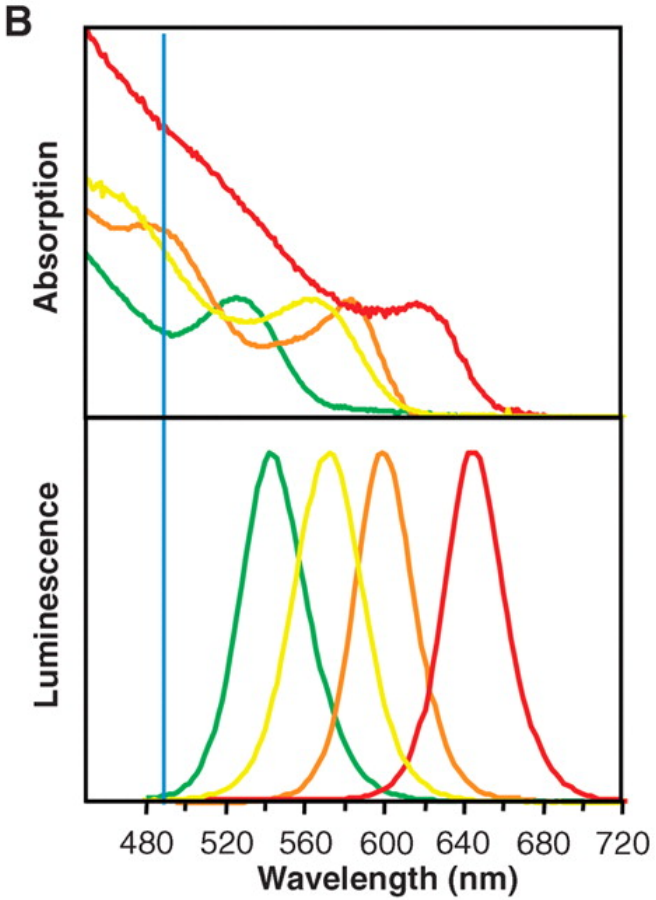
Ψ = *wavefunction (complex function of position and time)*

$|\Psi|^2$ = *probability density*

Size-dependent color of quantum dots

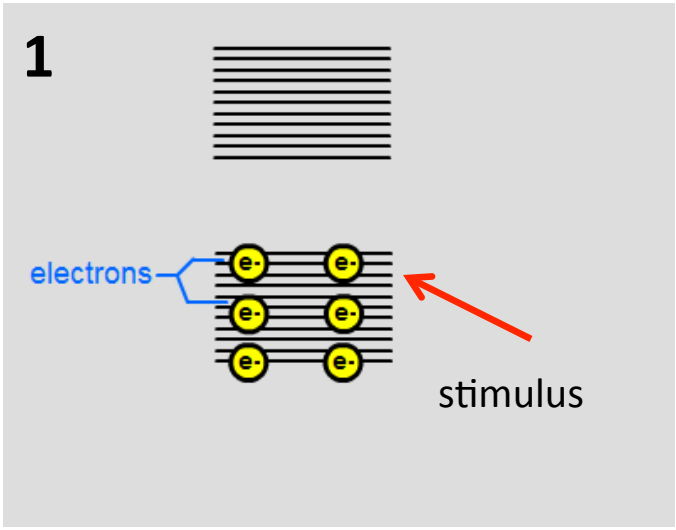


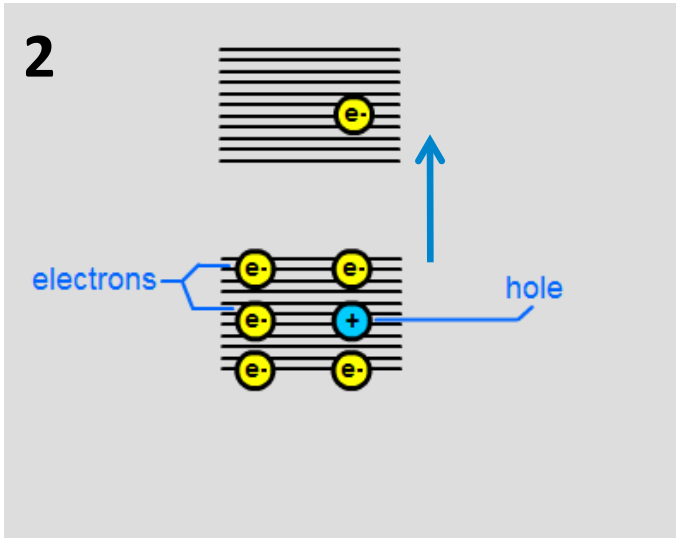


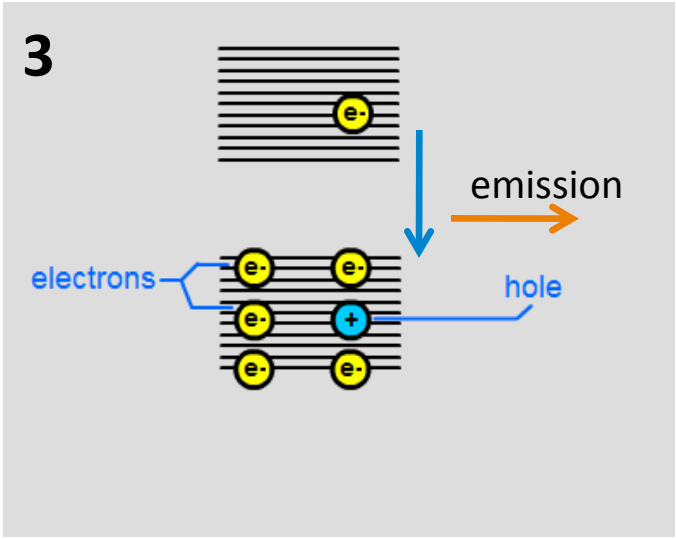


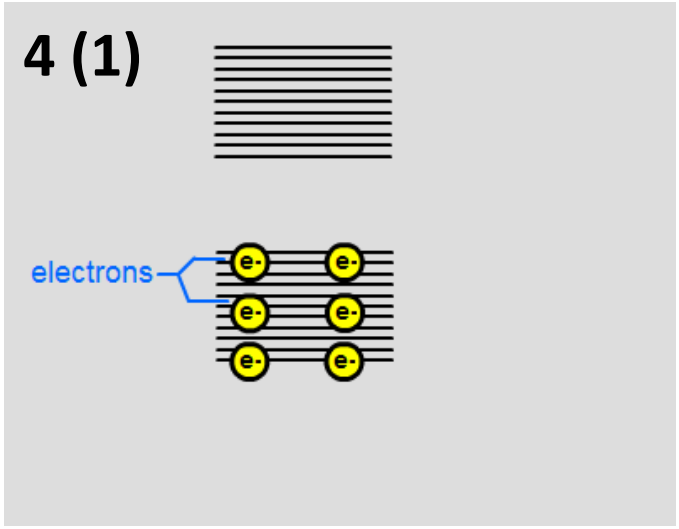
Frankel, Bawendi.

Absorption and emission



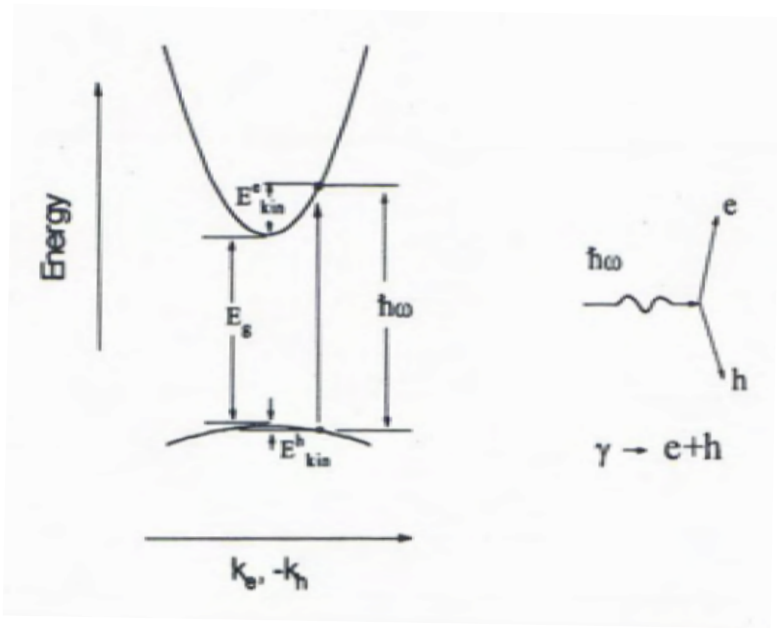


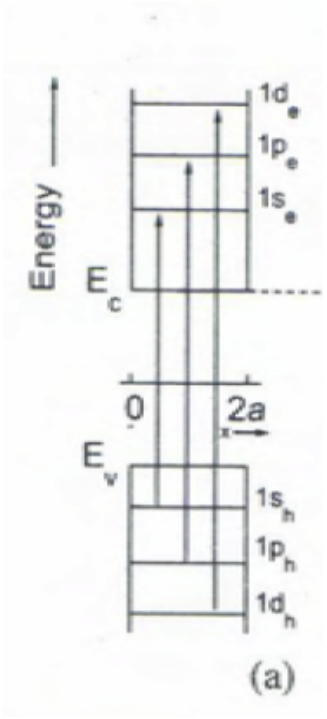




http://www.evidenttech.com/quantum-dots-explained/how-quantum-dots-work.html

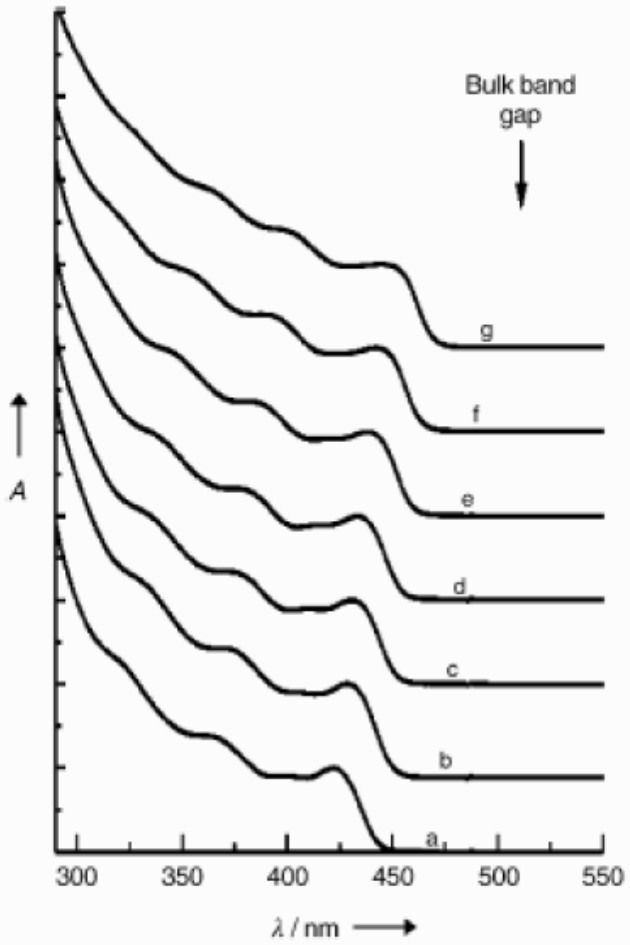
Idealized band model for a quantum dot, assuming strong confinement





$$E_{nl} = E_g + \frac{2\hbar^2}{\mu}\frac{\chi_{nl}^2}{D^2} \qquad \mu^{-1} = m_e^{-1} + m_h^{-1}$$

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



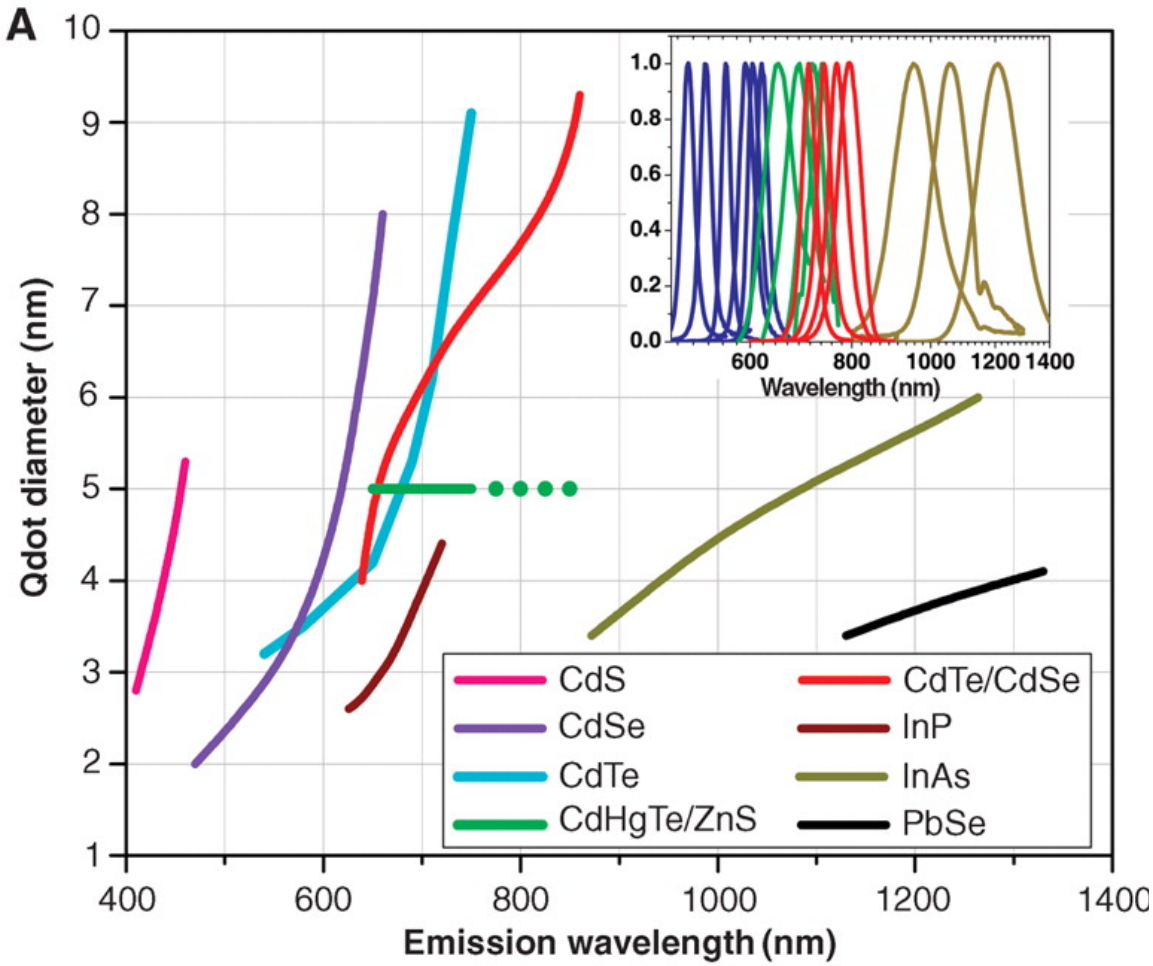
D = 5.2 nm

D = 3.7 nm

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

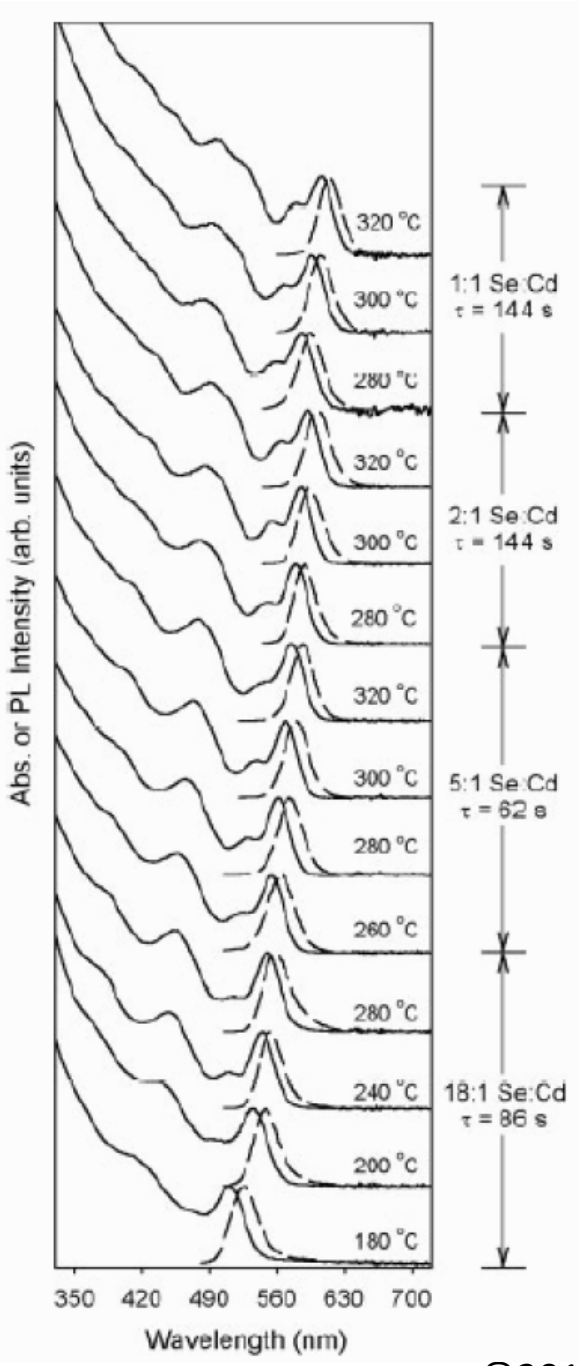
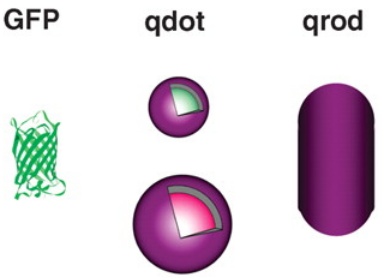


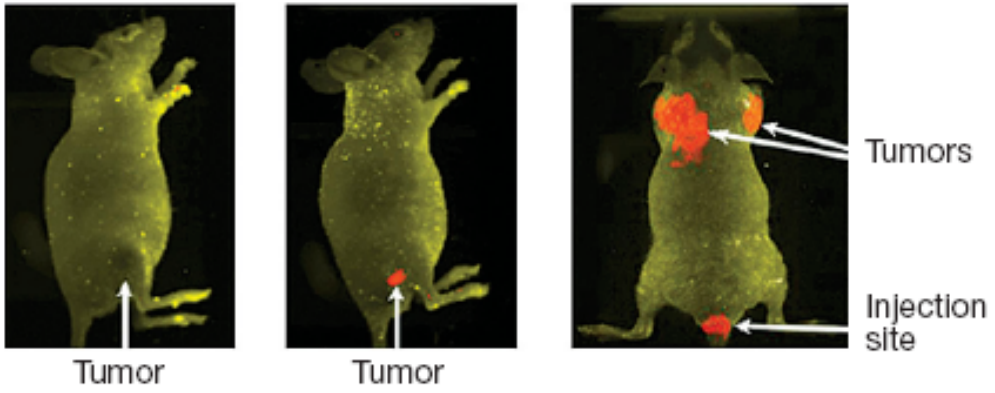
Fig. 4. Size series for samples prepared using four TOPSe concentrations: 1:1 Se/Cd, 2:1 Se/Cd, 5:1 Se/Cd, and 18:1 Se/Cd. For each TOPSe concentration, the average NC size was controlled by varying the temperature at a fixed flow rate. From bottom to top, the positions of the band-edge absorbance peaks 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

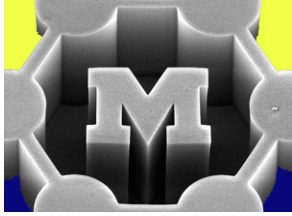
- Previous technology = fluorescent proteins
- New technology = semiconductor nanoparticles
  - Narrow emission peaks
  - Size-dependent emission
  - Long lifetime (resists photobleaching, i.e., photochemical degradation)
  - Diverse chemical linkages to surfaces
- Typical emission lifetimes (at ~10^5 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

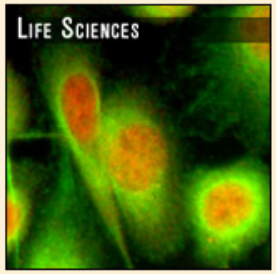
Commercially-available quantum dots



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

Quantum dot products overcome many limits of existing fluorescent labels and probes.

Security & Markings

Better security and brand protection through quantum dots.

LEDs / Displays

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

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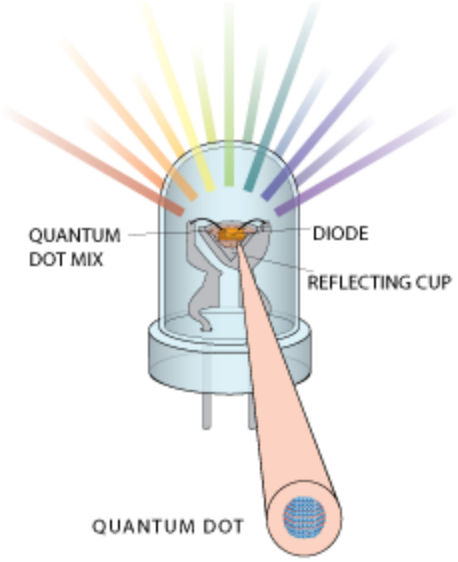
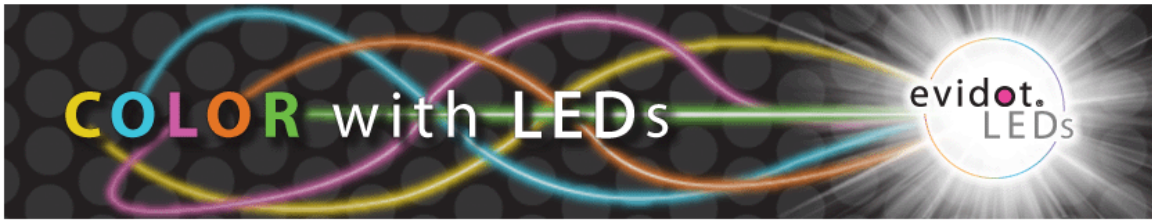
Quantum dot LEDs





Light Emitting Diodes

More Color Possibilities. More White Light Possibilities.

evidot® LEDs provide new colors to solid state lighting, including tunable white LEDs with full spectrum control and high CRI capability.

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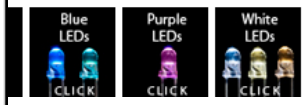
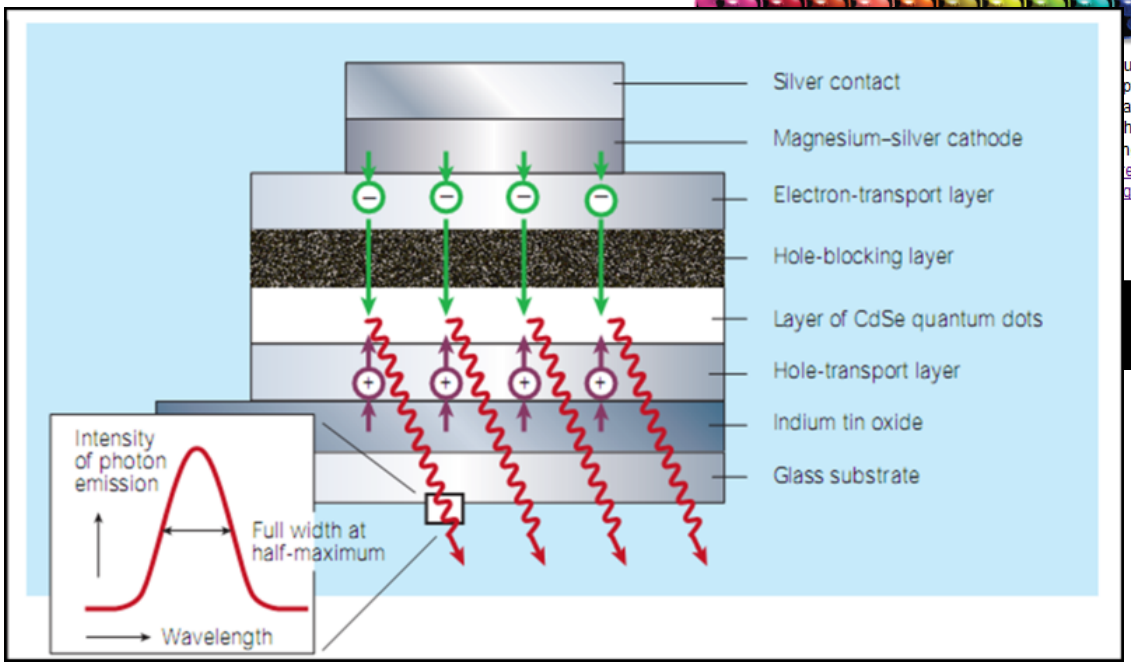
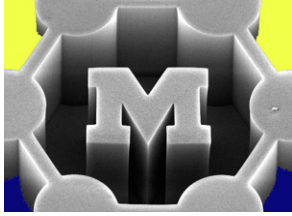




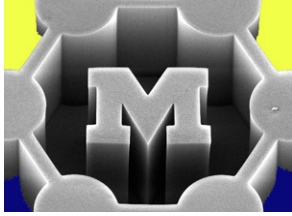
http://www.evidenttech.com

Today's agenda



- Dispersion relations and carrier statistics
- Development of band structure
- Examples:
  - Single electron transistors
  - Electrical properties of CNTs

Today's readings



Nominal: (on ctools)

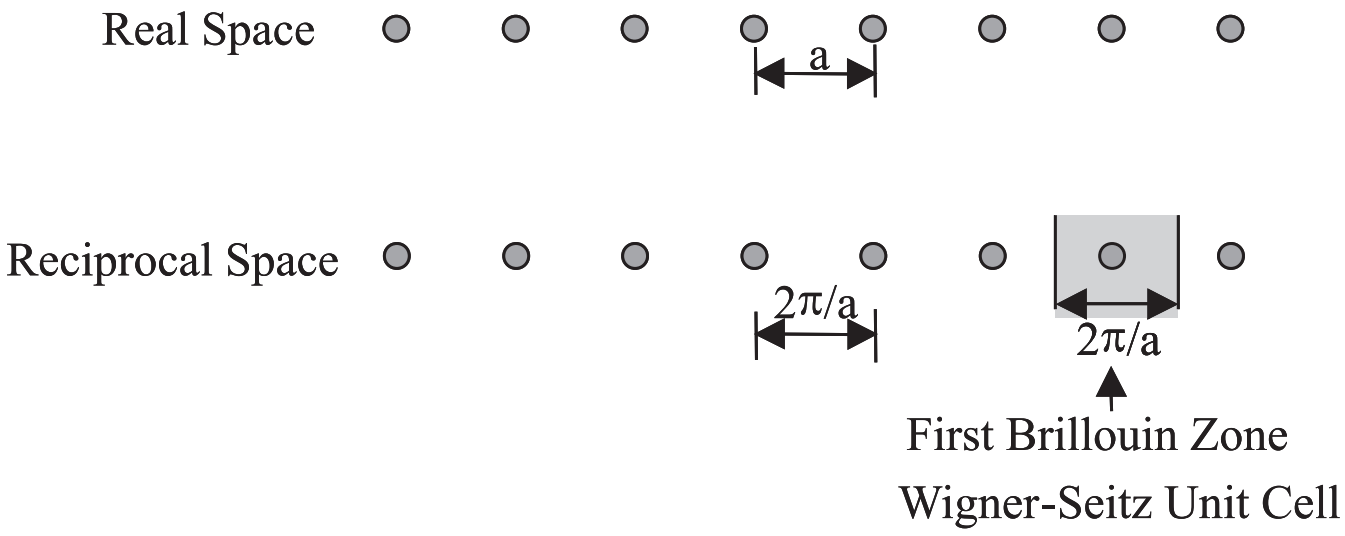
- Chen, Section 3.2
- Rogers, Pennathur, and Adams, excerpt on Nanoelectronics, from Understanding Small Systems
- Avouris, "Carbon-based electronics"

Extras: (on ctools)

- Sheldon et al., "Enhanced semiconductor nanocrystal conductance via solution grown contacts"
- Ho et al., "Scaling properties in transistors that use aligned arrays of single-walled carbon nanotubes"

More on crystals

- Many transport properties are determined by periodicity of the atomic lattice.
- Atomic arrangement determines allowable energy levels (recall from QM: wave modes) of energy carriers.
- In the literature, information is presented in **reciprocal space.**



Chen.

Real space vs. reciprocal space lattices in 3D

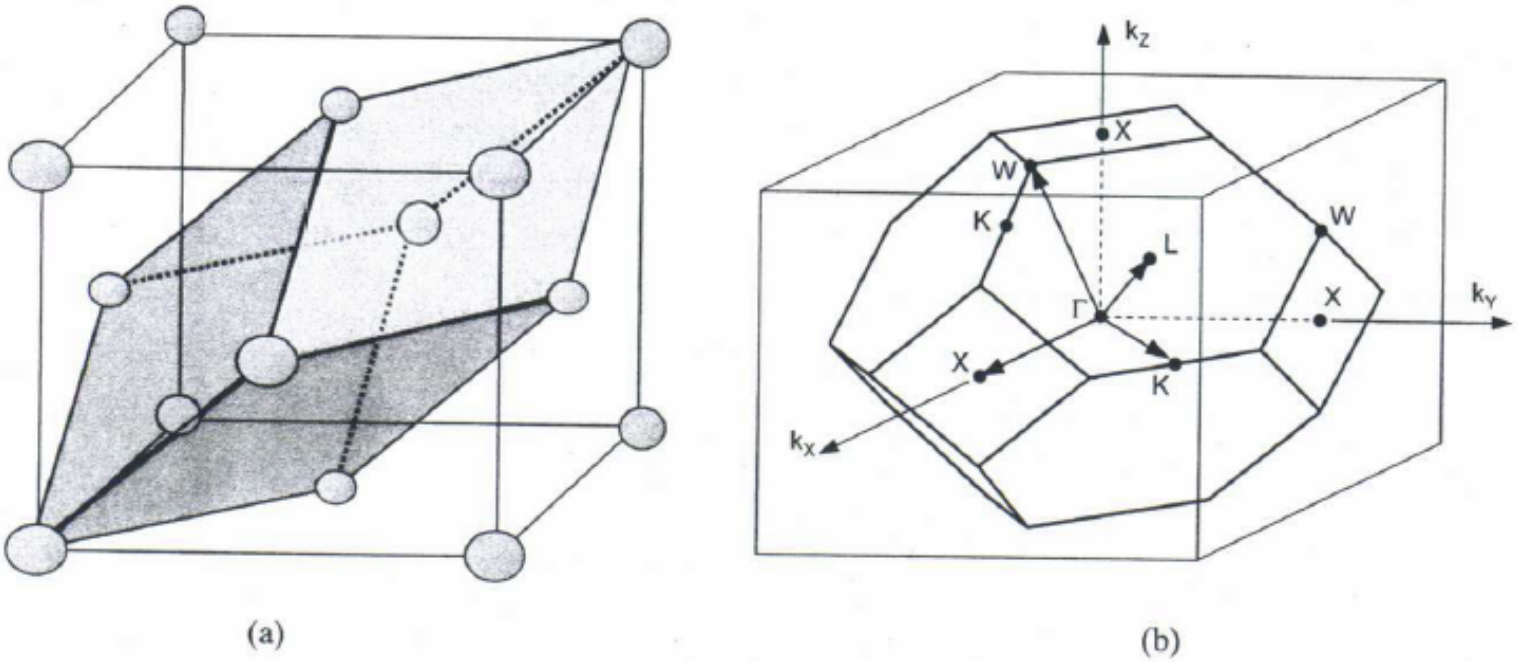
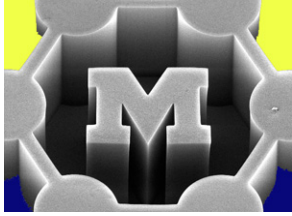


Figure 3.8 Conventional and primitive unit cells in real and reciprocal unit cells of an fcc lattice (a) in real space, (b) in reciprocal space.

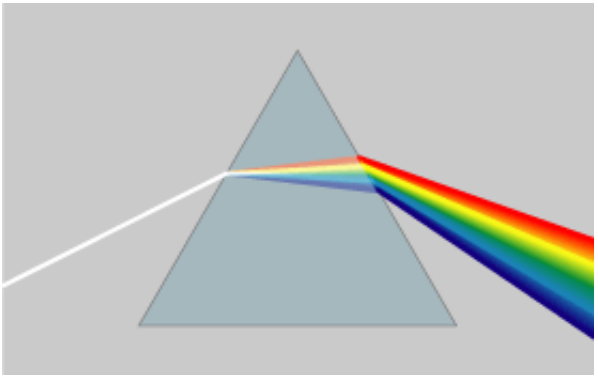
Dispersion relations



- **Dispersion relation**: the relationship between energy and momentum (frequency and wave-vector)

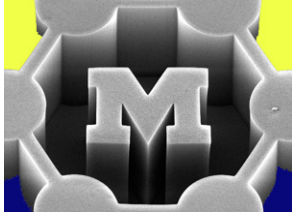
- Light in vacuum: $\omega = ck$

- In real materials, dispersion relations for electrons, phonons, photons, etc. are complicated: frequency a more complex function of wavelength



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

Electrons in a periodic system

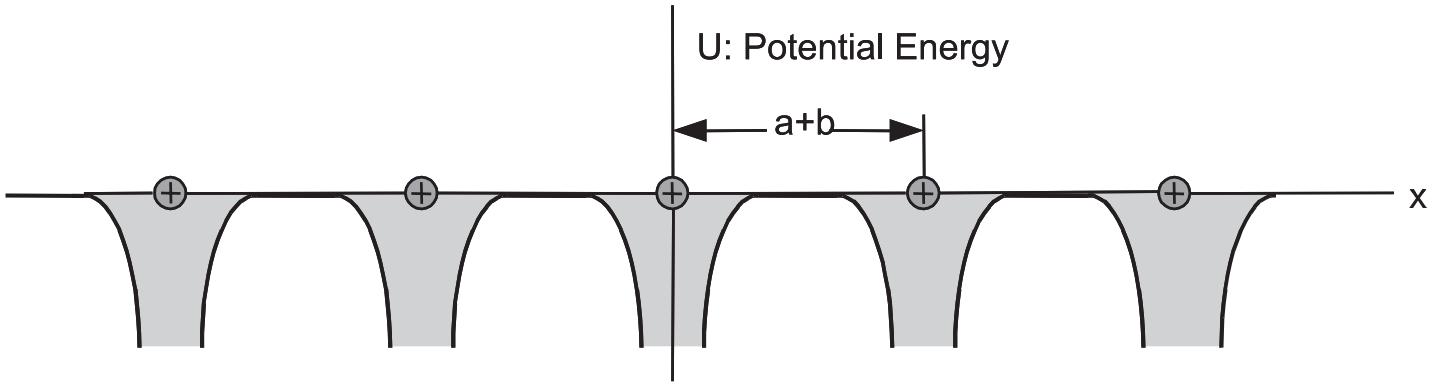


The "free" electron

Schrodinger equation: $-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} - E\Psi = 0$

$\Psi(x) = A \bullet \exp(-ikx) + B \bullet \exp(ikx)$ $\quad E = \frac{\hbar^2 k^2}{2m}$ Parabolic dispersion

A periodic potential



Conductors vs. insulators

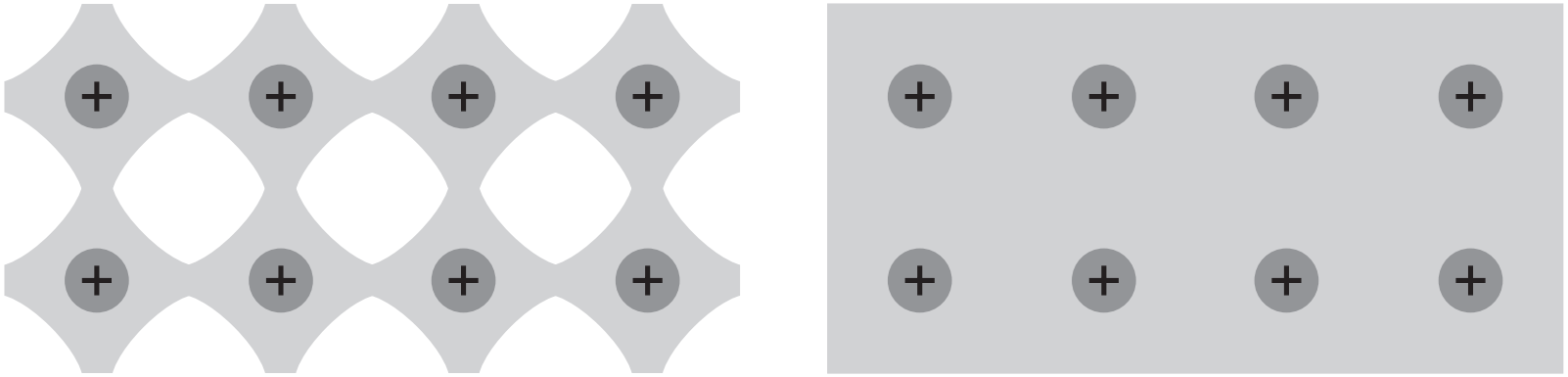


Figure 3.7 Distribution of electrons (gray area) in (a) a covalent bonding crystal and (b) a metallic bonding crystal (after Ashcroft and Mermin, 1970).

Electrons in a periodic system

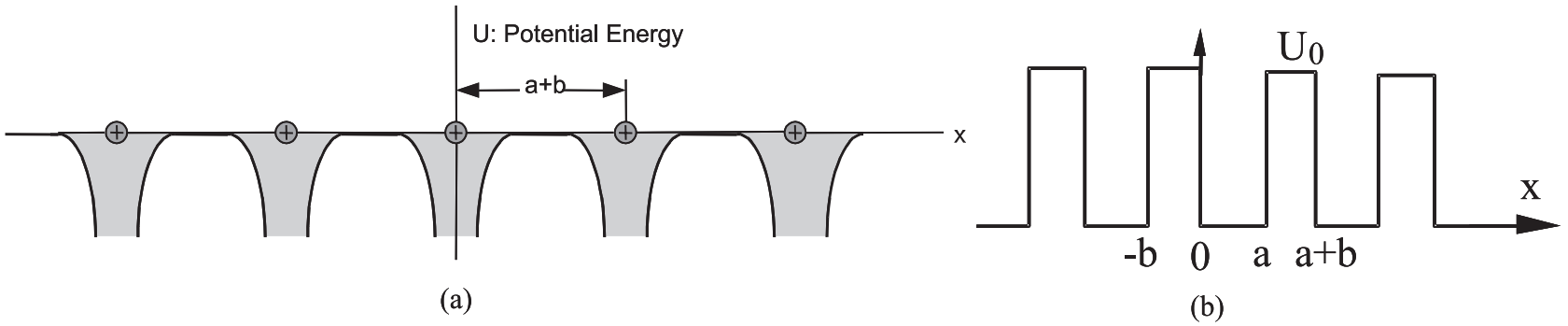


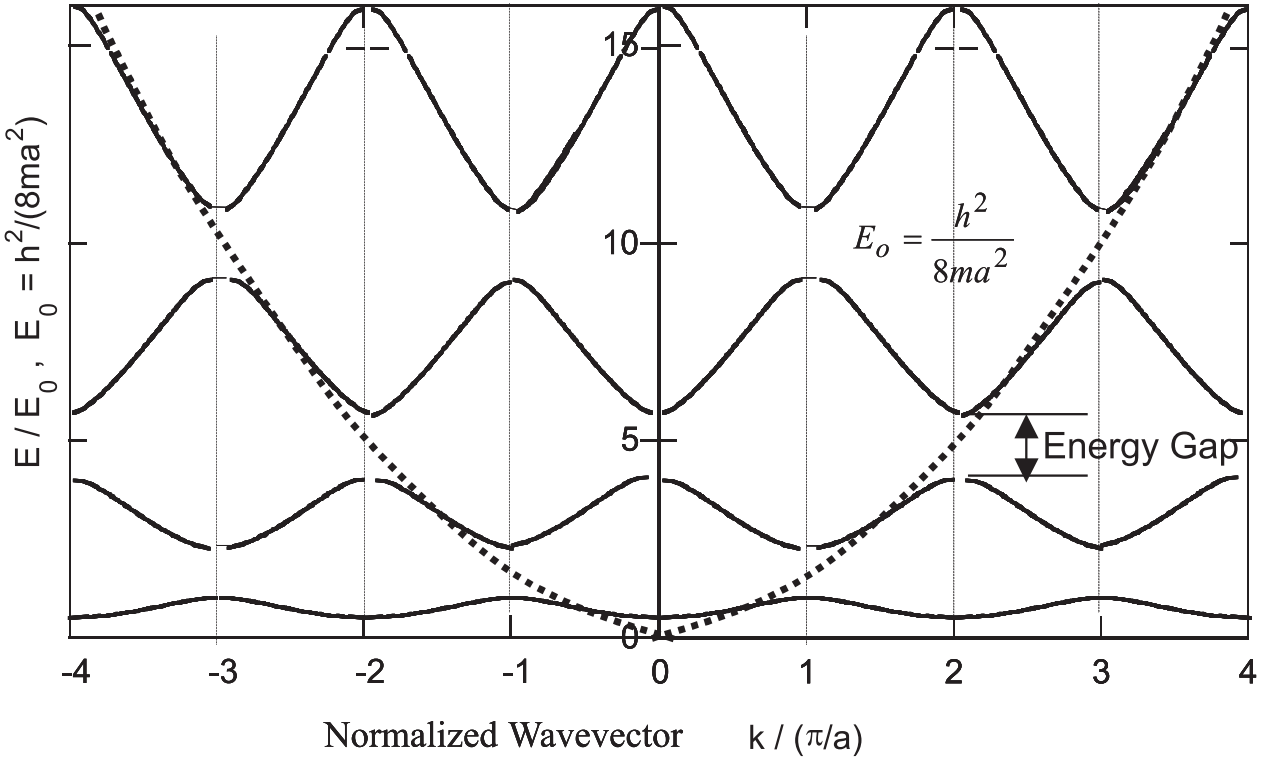
Figure 3.11 One-dimensional periodic potential model: (a) sketch of atomic potential; (b) Kronig-Penney model.

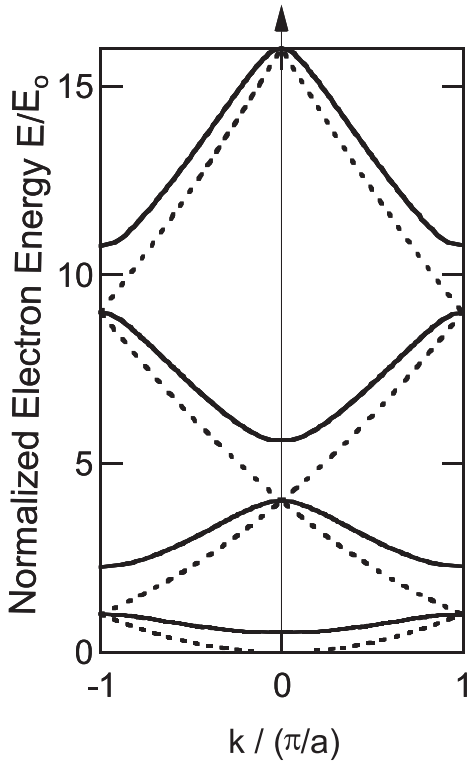
$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + (U - E)\Psi = 0 \qquad U(x) = \begin{cases} 0 & 0 < x \le a \\ U_0 & -b < x \le 0 \end{cases}$$

Bloch theorem: $\Psi[x + (a + b)] = \Psi(x)\exp[ik(a + b)]$

Dispersion relation -> energy gaps

- Wave effects leads to certain energies (frequencies) that are forbidden: **band gaps**

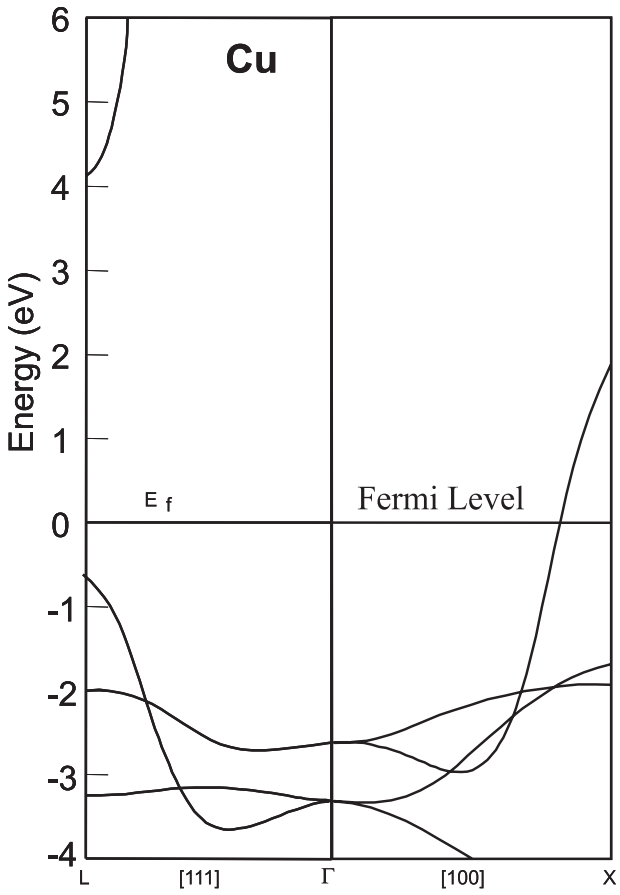


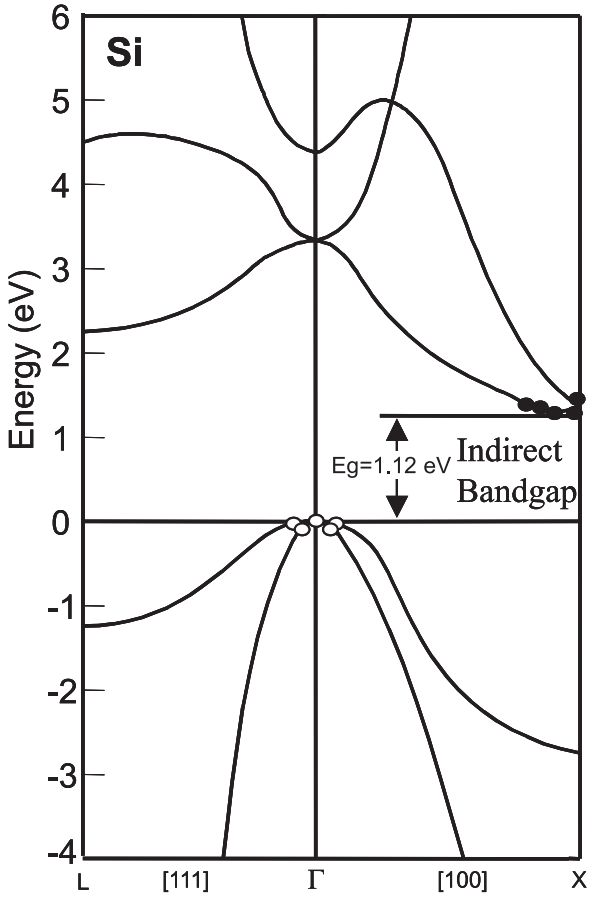


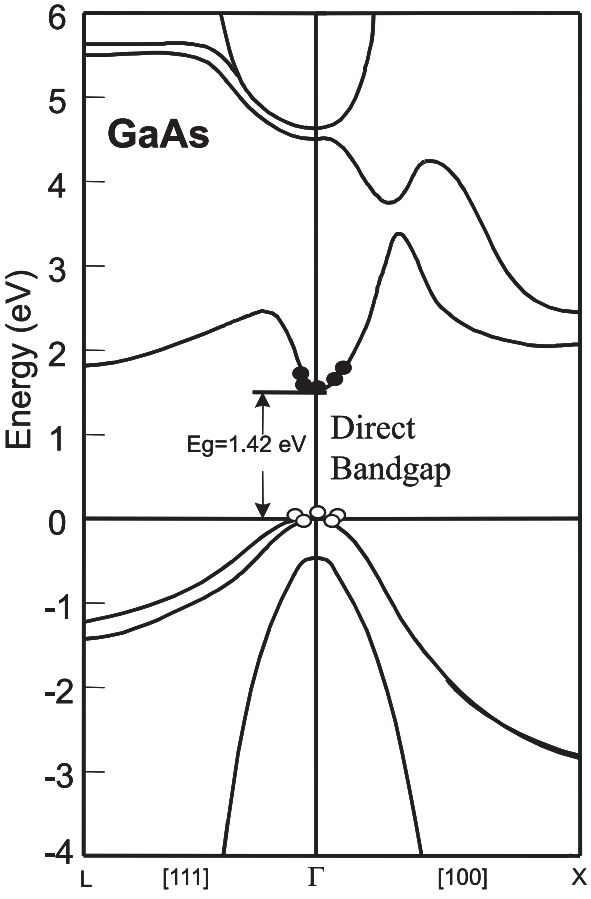
Chen, chapter 3.

Some band diagrams of real materials

Plotted along directions of high symmetry

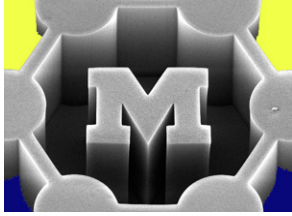






Chen, chapter 3.

Carrier statistics



- The **occupation function, f(E):** Expected number of carriers with a given energy
- This is determined by statistical physics and carrier interactions, i.e. Pauli exclusion

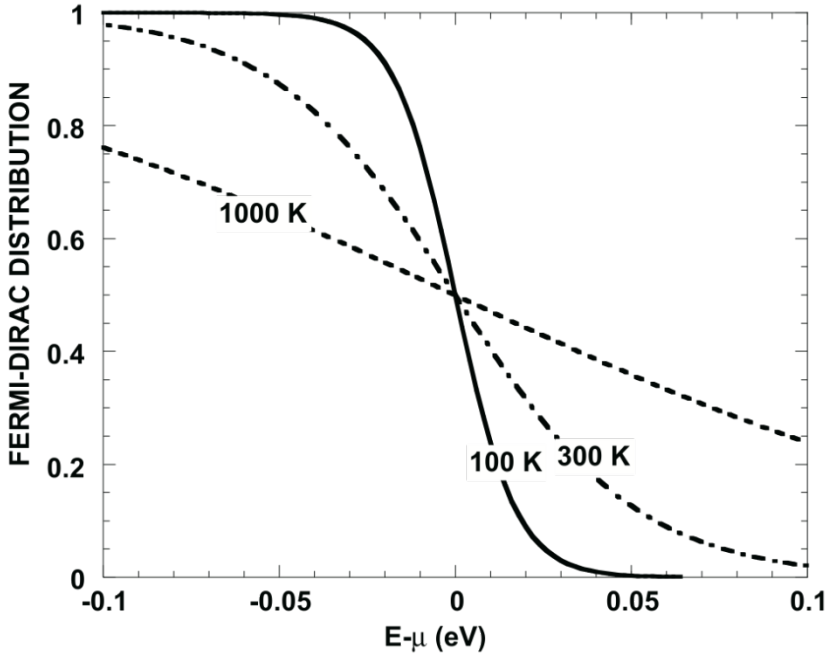
- Bosons (Photons, phonons): $$f(E) = \frac{1}{\exp\left(\frac{E}{k_{\mathrm{B}}T}\right) - 1}$$

- Fermions (Electrons, holes): $$f(E) = \frac{1}{\exp\left(\frac{E-\mu}{k_{\mathrm{B}}T}\right) + 1}$$

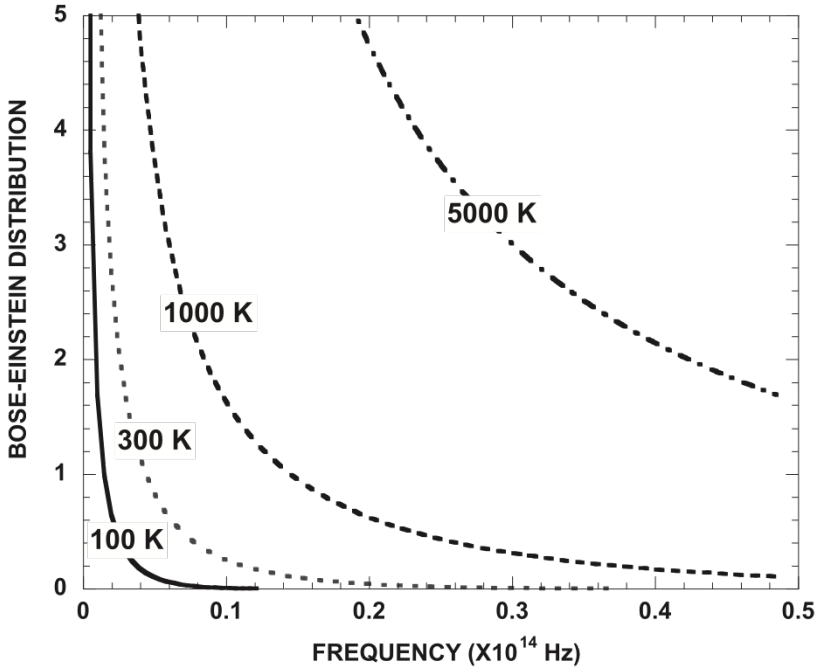
- μ is called the **chemical potential**. It's where occupancy is ½. At T = 0 K, μ is called the **Fermi Energy** and is the highest filled energy state

Carrier statistics

$$f(E) = \frac{1}{\exp\left(\frac{E-\mu}{k_B T}\right) + 1}$$

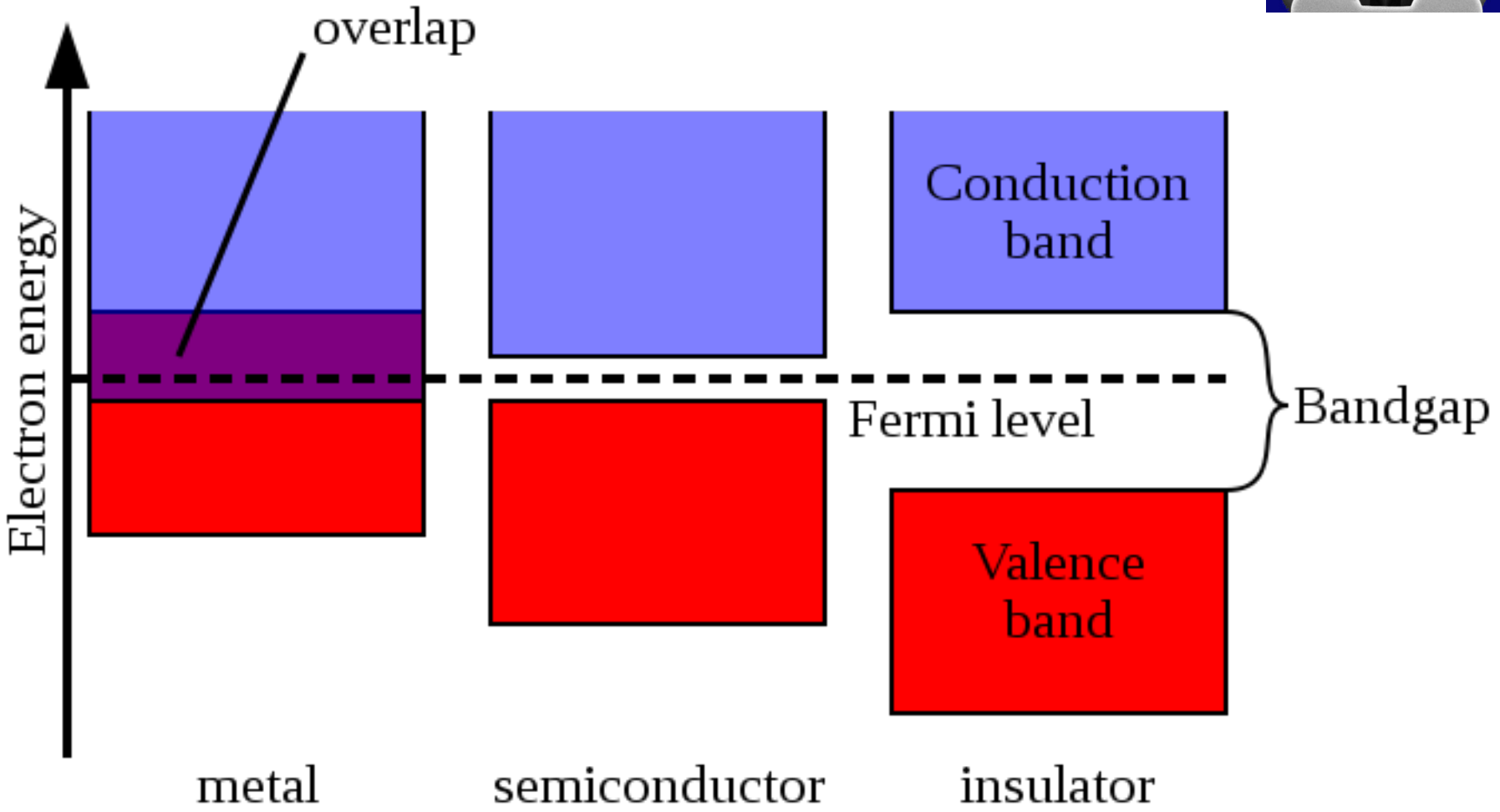


$$f(E) = \frac{1}{\exp\left(\frac{E}{k_B T}\right) - 1}$$



The actual number of carriers in a state, per unit volume and energy: $n(E) = f(E) \times \mathrm{DOS}$

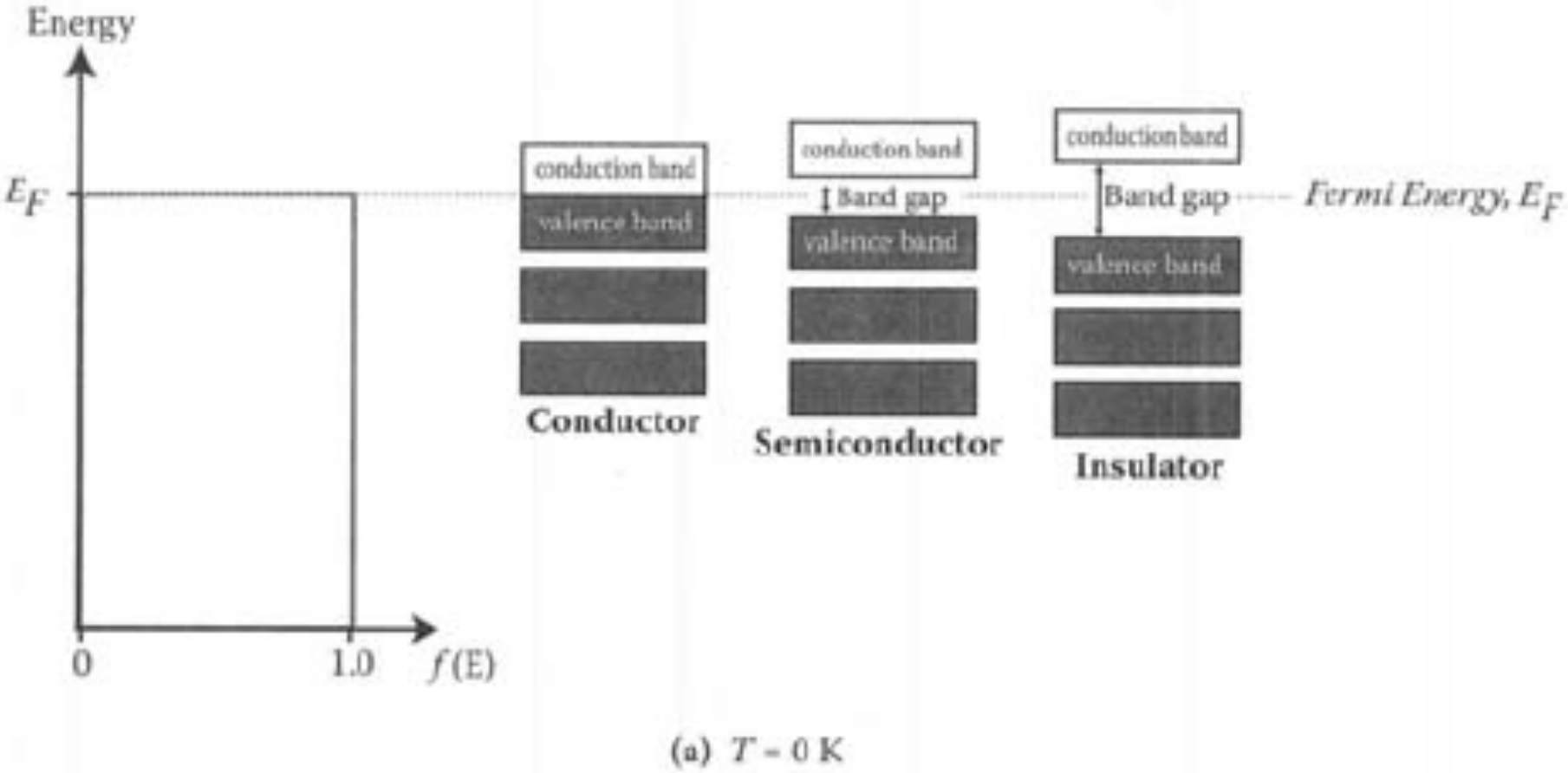
Metal, semiconductor, insulator



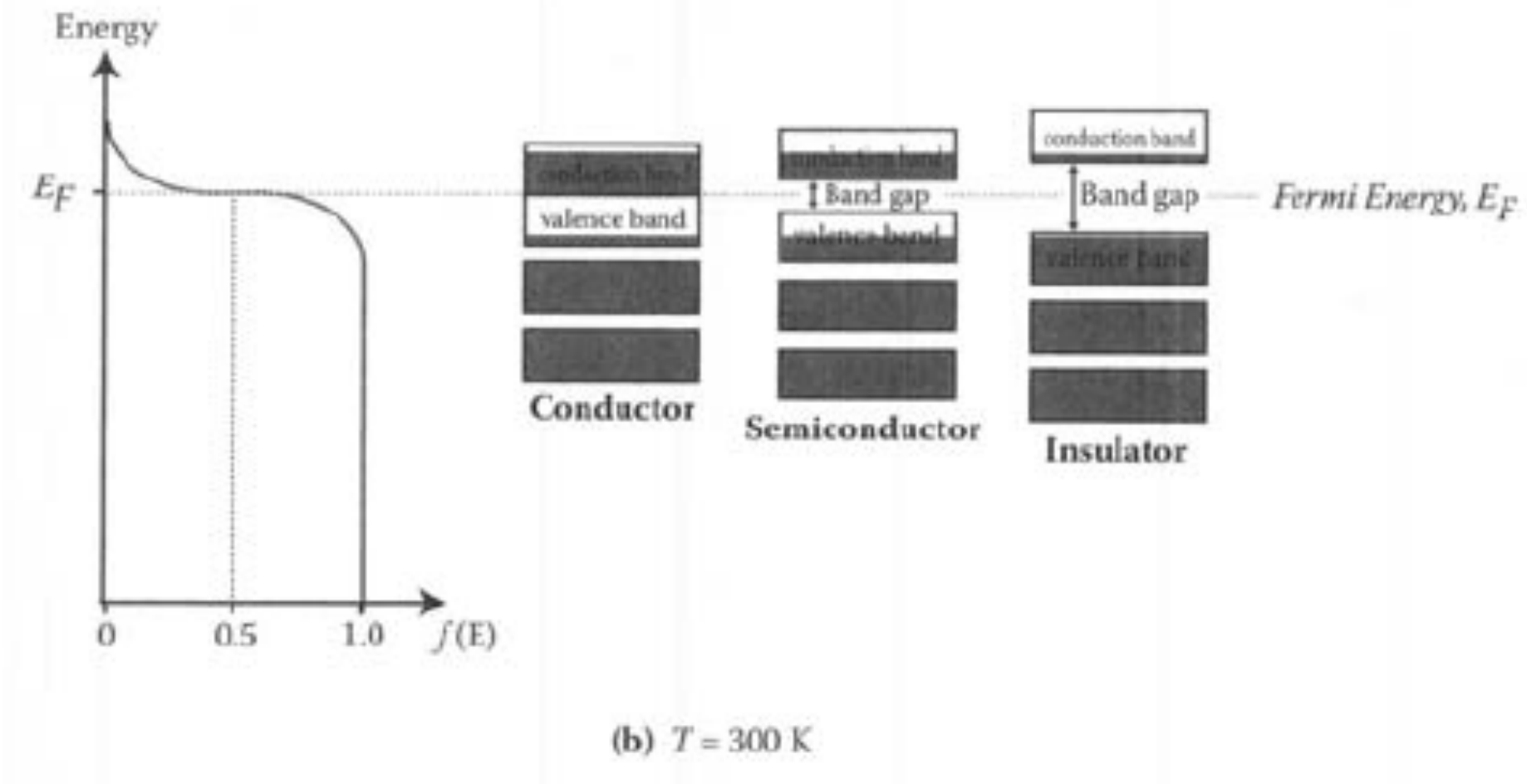
a practical semiconductor has ≈3 eV band gap

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

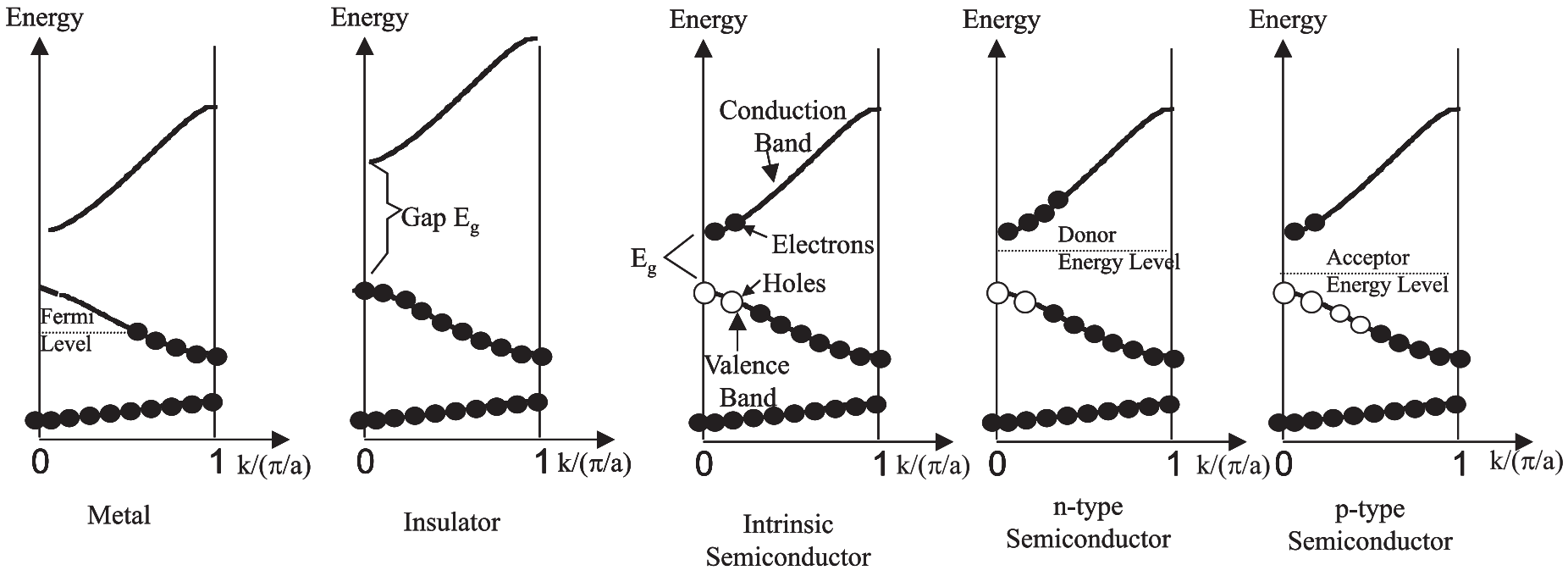
Fermi energy



Fermi energy



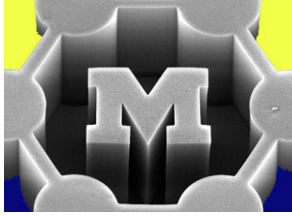
Metal, semiconductor, insulator



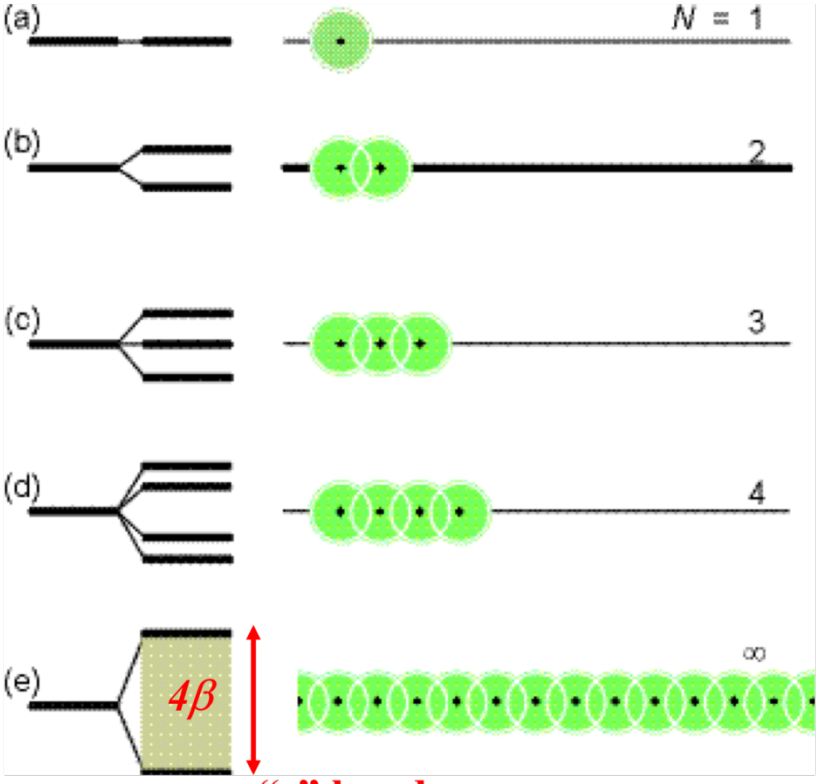
a practical semiconductor has ≈3 eV band gap

Chen, chapter 3.

Band formation from atoms



◆ Simple model for a solid: the one-dimensional solid, which consists of a single, infinitely long line of atoms, each one having one s orbital available for forming molecular orbitals (MOs).



When the chain is extended:

➔ The ***range of energies*** covered by the MOs is ***spread***

➔ This range of energies is filled in with ***more and more orbitals***

➔ The ***width of the*** range of energies of the MOs is ***finite***, while the number of molecular orbitals is ***infinite***: This is called a ***band*** .

Single electron transistor (SET)

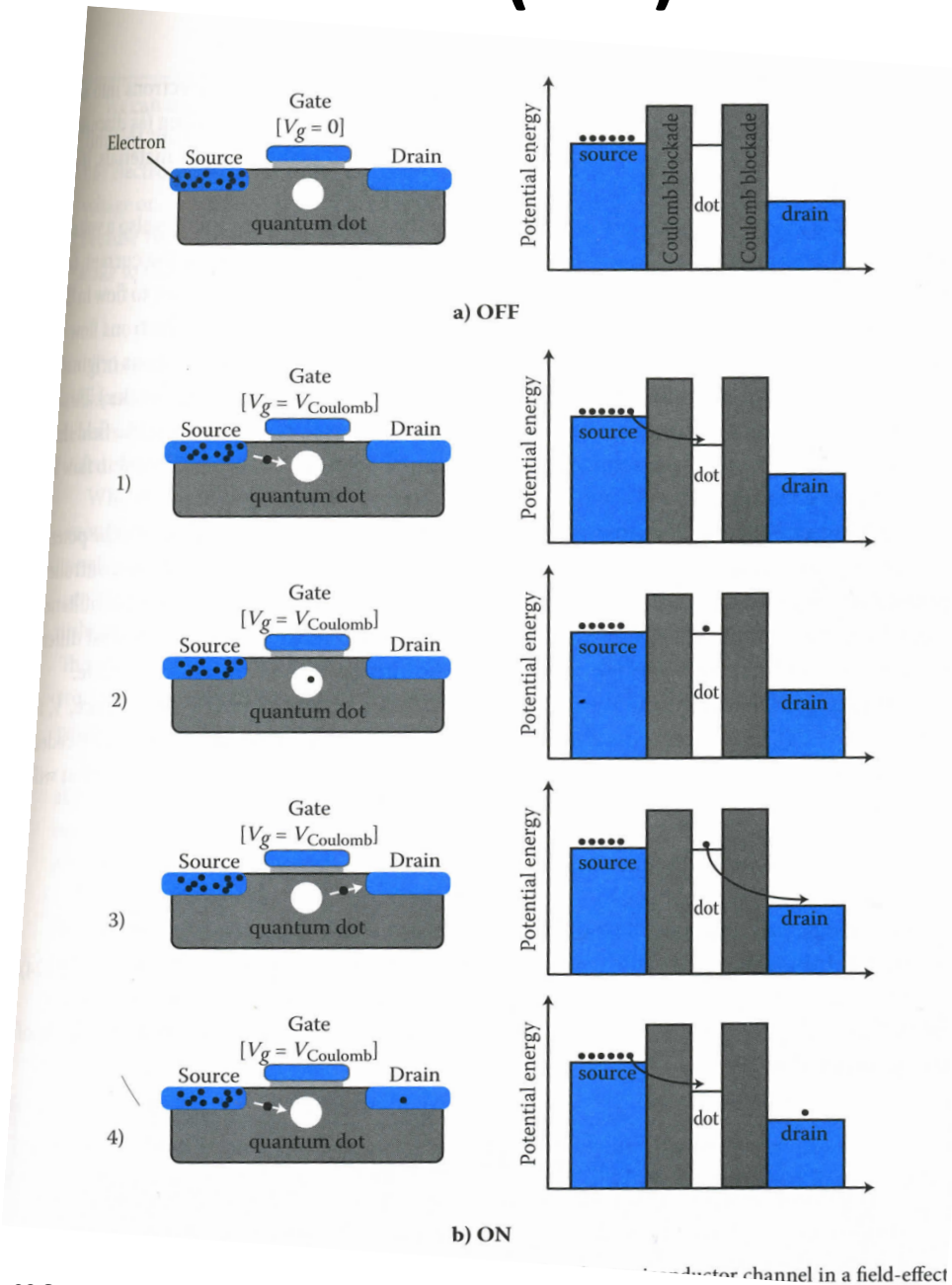


FIGURE 6.18 A single-electron transistor (SET). As opposed to the semiconductor channel in a field-effect transistor, the SET has an electrically isolated quantum dot located between the source and drain. (a) The SET in "off" mode. The corresponding potential energy diagram shows that it is not energetically favorable for electrons in the source to tunnel to the dot. (b) The SET in "on" mode. At the lowest setting, electrons tunnel one at a time, via the dot, from source to drain. This is made possible by first applying the proper gate voltage, $V_{gate} = e/2C_{dot}$, so that the potential energy of the dot is made low enough to encourage an electron to tunnel through the Coulomb blockade energy barrier to the quantum dot. Once the electron is on it, the dot's potential energy rises. The electron then tunnels through the Coulomb blockade on the other side to reach the lower potential energy at the drain. With the dot empty and the potential lower again, the process repeats.

Single electron transistor

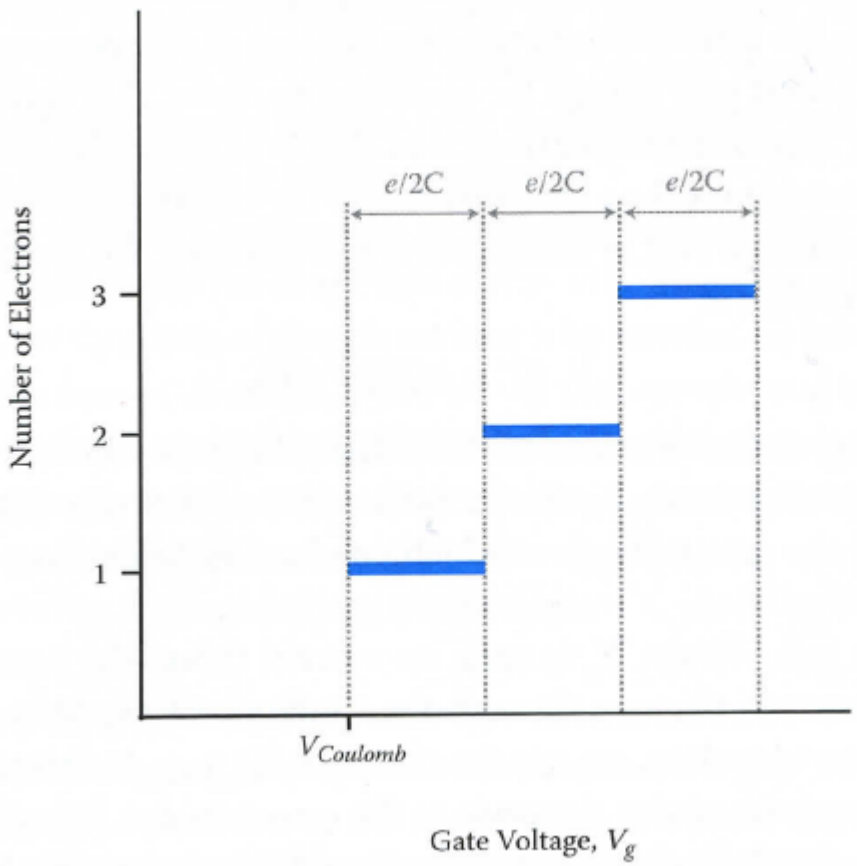
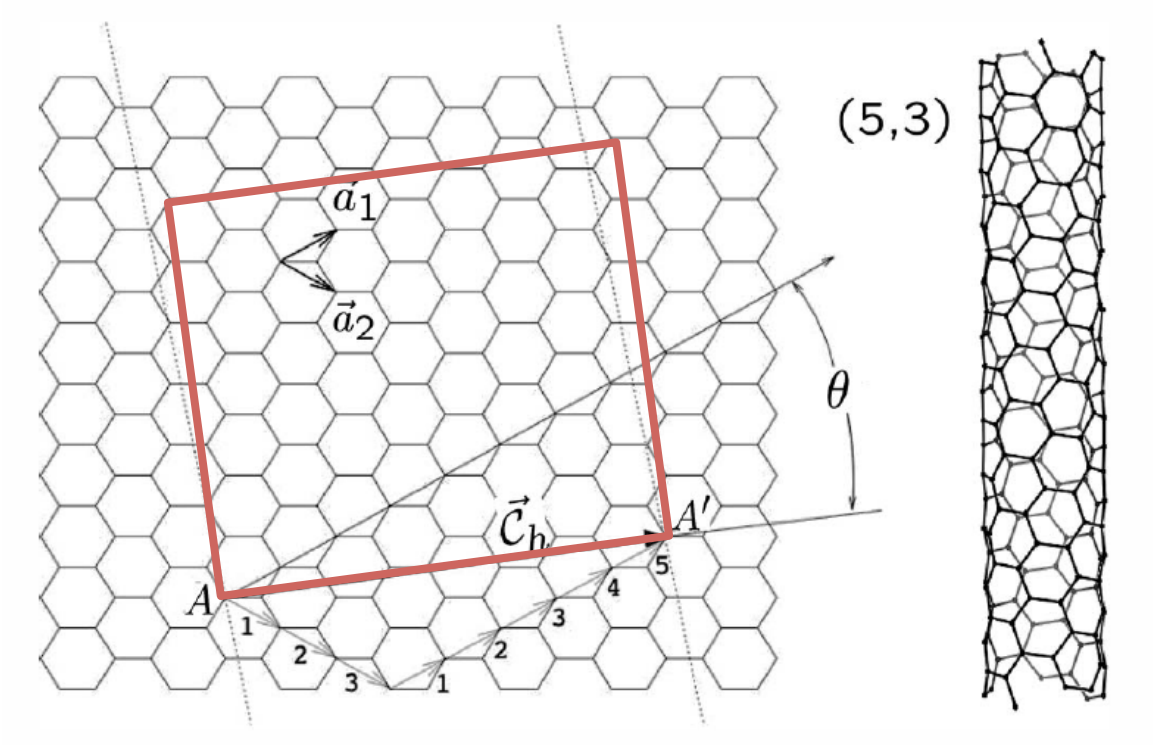


FIGURE 6.19 The electrical behavior of an ideal SET as a function of gate voltage. The number of electrons on the quantum dot is zero until the Coulomb blockade is overcome at $V_{Coulomb}$, at which point electrons tunnel one at a time from the source to the drain via the quantum dot. Because the energy on the dot is quantized, only discrete gate voltages enable the tunneling of electrons and consequent increases in the number of electrons in the dot. The separation between these gate voltages is $e/2C$. This is the voltage necessary to increase the number of electrons on the dot by one. The current-versus-voltage chart at the bottom shows the corresponding spikes in the source-to-drain current through the transistor at discrete gate voltages. Between the spikes, the number of electrons on the dot remains fixed. Typical gate voltages for such a device are a few millivolts; typical source-to-drain currents are in the picoampere range.

Rogers, Pennathur, Adams.

CNT lattice and unit cell



Charlier et al., Review of Modern Physics 79(2), 2007.

"Closing" a CNT: forced periodicity

- Like the 0D quantum well, the geometric constraint of a seamless CNT forces periodicity on the wavefunction in the circumferential direction.

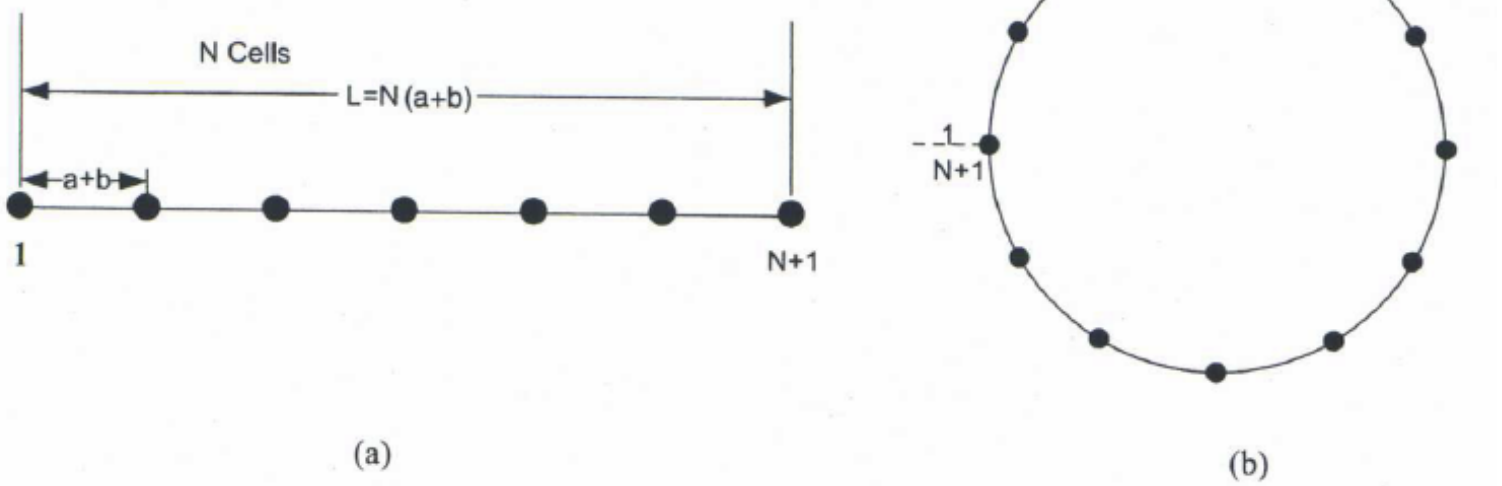
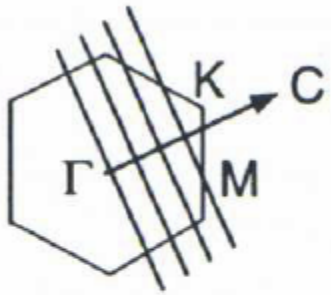


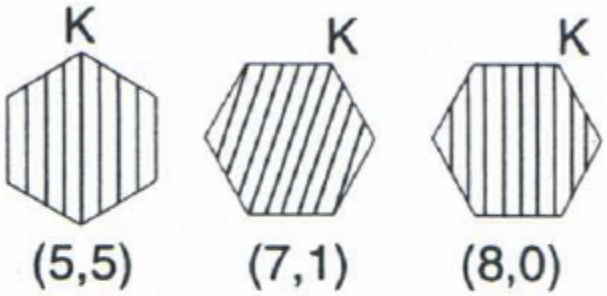
Figure 3.15 The von Karman boundary condition joins the two boundary points in (a) into a periodic loop in (b).

Boundary condition in reciprocal space

$$k \cdot C = 2\pi p$$

p = integer
k = parallel to C



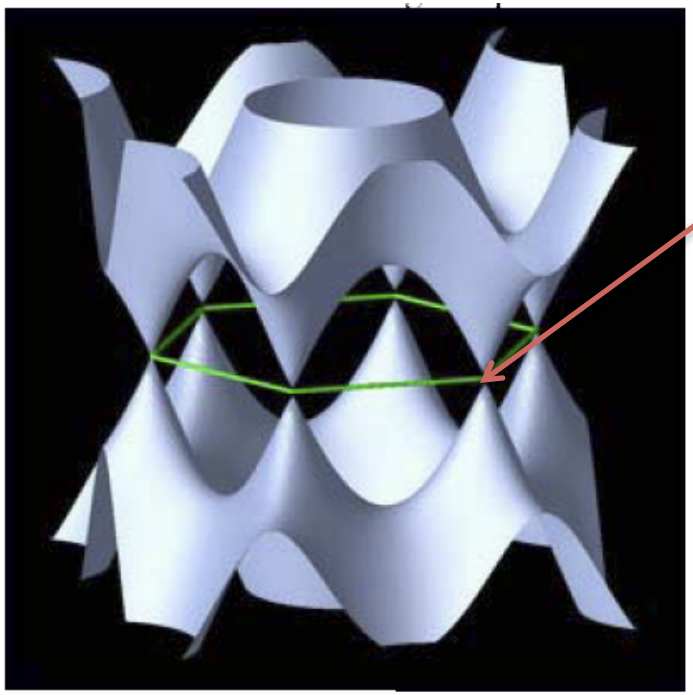


n-m = 3p : metal
n-m ≠ 3p : semiconductor

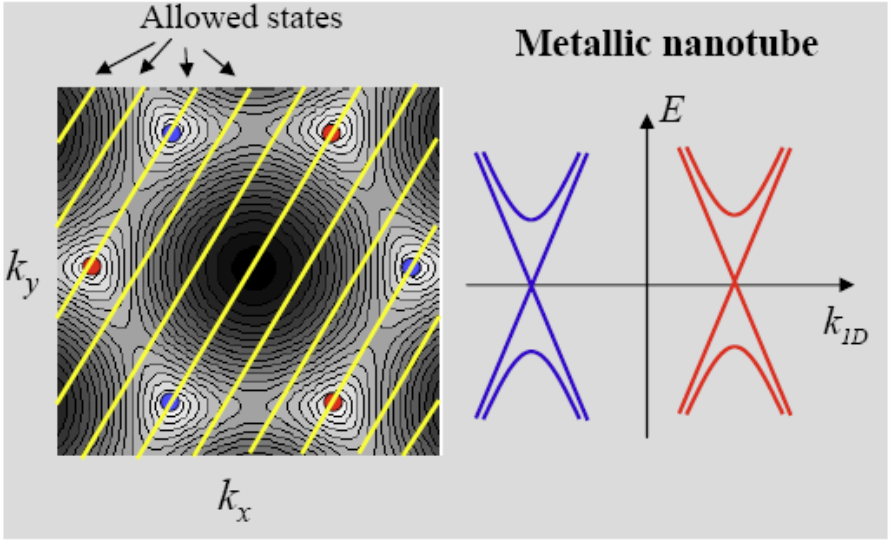
Fig. 4.14. Allowed k-vectors of the (5,5), (7,1) and (8,0) tubes mapped onto the graphene Brillouin zone

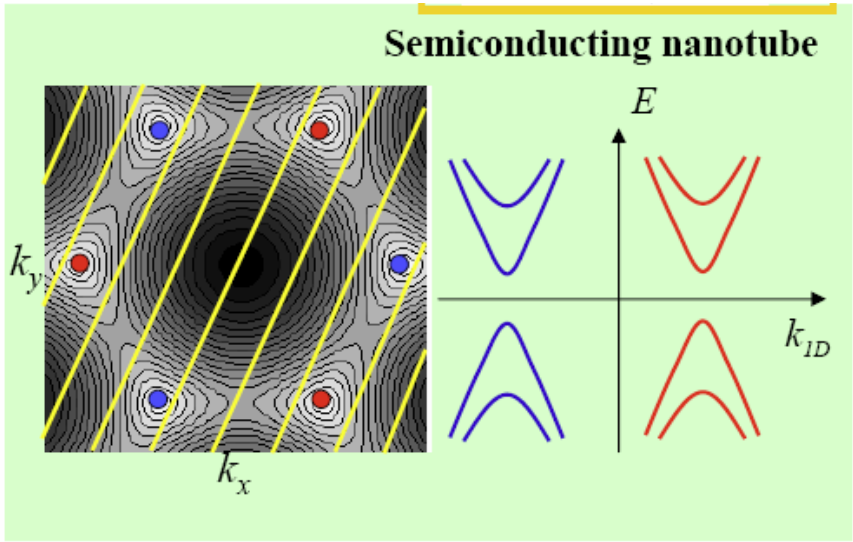
- A CNT is metallic if the "stripes" perpendicular to the circumferential direction intersect the K-points in reciprocal space
- This is geometrically satisfied by the n-m = 3p condition and means that the bands intersect to permit conduction, as in graphite
- Band gap is inversely proportional to diameter, so practically CNTs with >3 nm diameter exhibit metallic behavior at room temperature

Ducastelle, Saito.



K-point
(reciprocal lattice point)





Kim.

Periodic Table of Carbon Nanotubes

zigzag ($m = 0$)

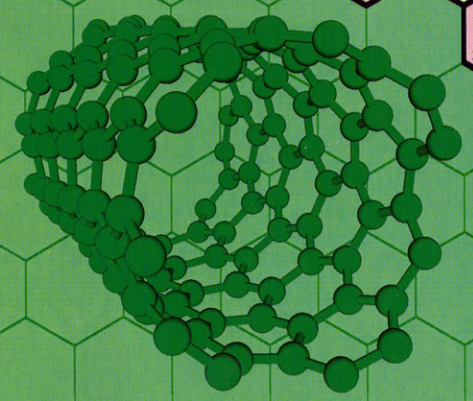
armchair ($n = m$)

(n,m)	(1,0)	(2,0)	(3,0)	(4,0)	(5,0)	(6,0)	(7,0)	(8,0)	(9,0)	(10,0)	(11,0)	(12,0)	(13,0)	(14,0)	(15,0)	(16,0)	(17,0)
d_t (Å) $d{:}d_R$	0.78 1:1	1.57 2:2	2.35 3:3	3.13 4:4	3.92 5:5	4.70 6:6	5.48 7:7	6.27 8:8	7.05 9:9	7.83 10:10	8.62 11:11	9.40 12:12	10.18 13:13	10.97 14:14	11.75 15:15	12.54 16:16	13.32 17:17
E_g (eV)	5.484	1.078	0.740	1.494	1.348	0.185	1.087	0.986	0.082	0.827	0.764	0.046	0.663	0.622	0.030	0.552	0.523
T (Å) θ	4.26 0°	4.26 0°	4.26 0°	4.26 0°	4.26 0°	4.26 0°	4.26 0°	4.26 0°	4.26 0°	4.26 0°	4.26 0°	4.26 0°	4.26 0°	4.26 0°	4.26 0°	4.26 0°	4.26 0°
N	4	8	12	16	20	24	28	32	36	40	44	48	52	56	60	64	68
(1,1)	1.36 1:3	2.07 1:1	2.82 1:1	3.59 1:3	4.36 1:1	5.14 1:1	5.91 1:3	6.69 1:1	7.47 1:1	8.25 1:3	9.04 1:1	9.82 1:1	10.60 1:3	11.38 1:1	12.16 1:1	12.94 1:3	13.73 1:1
	0.0	4.880	1.839	0.267	2.199	1.166	0.110	1.346	0.865	0.058	0.961	0.686	0.036	0.746	0.568	0.024	0.608
	2.46 30°	11.28 19.1°	15.37 13.9°	6.51 10.9°	23.74 8.9°	27.95 7.6°	10.73 6.6°	36.42 5.8°	40.67 5.2°	14.97 4.7°	49.16 4.3°	53.42 4.0°	19.22 3.7°	61.92 3.4°	66.18 3.2°	23.48 3.0°	74.69 2.8°
	4	28	52	28	124	172	76	292	364	148	532	628	244	844	964	364	1228
(2,2)	2.71 2:6	3.41 1:1	4.15 2:2	4.89 1:3	5.65 2:2	6.41 1:1	7.18 2:6	7.95 1:1	8.72 2:2	9.50 1:3	10.27 2:2	11.05 1:1	11.83 2:6	12.61 1:1	13.39 2:2		
	0.0	1.975	2.146	0.114	1.139	1.380	0.067	0.836	0.990	0.041	0.665	0.766	0.027	0.553	0.623		
	2.46 30°	18.58 23.4°	11.28 19.1°	8.87 16.1°	15.37 13.9°	34.89 12.2°	6.51 10.9°	43.26 9.8°	23.74 8.9°	17.23 8.2°	27.95 7.6°	60.14 7.1°	10.73 6.6°	68.61 6.2°	36.42 5.8°		
	8	76	56	52	104	268	56	412	248	196	344	796	152	1036	584		
(3,3)	4.07 3:9	4.77 1:1	5.48 1:1	6.22 3:3	6.96 1:1	7.72 1:1	8.47 3:3	9.24 1:1	10.00 1:1	10.77 3:9	11.54 1:1	12.31 1:1	13.09 3:3	13.86 1:1			
	0.0	1.509	1.269	0.057	0.980	0.885	0.043	0.744	0.691	0.030	0.604	0.569	0.021	0.510			
	2.46 30°	25.93 25.3°	29.84 21.8°	11.28 19.1°	37.89 17.0°	41.99 15.3°	15.37 13.9°	50.26 12.7°	54.43 11.7°	6.51 10.9°	62.80 10.2°	67.00 9.5°	23.74 8.9°	75.42 8.4°			
	12	148	196	84	316	388	156	556	652	84	868	988	372	1252			
(4,4)	5.43 4:12	6.12 1:1	6.83 2:2	7.56 1:3	8.29 4:4	9.04 1:1	9.79 2:6	10.54 1:1	11.30 4:4	12.06 1:3	12.83 2:2	13.59 1:1					
	0.0	1.302	1.056	0.032	0.999	0.779	0.028	0.788	0.624	0.022	0.644	0.523					
	2.46 30°	33.30 26.3°	18.58 23.4°	13.70 21.1°	11.28 19.1°	49.16 17.5°	8.87 16.1°	57.35 14.9°	15.37 13.9°	21.88 13.0°	34.89 12.2°	73.96 11.5°					
	16	244	152	124	112	532	104	724	208	316	536	1204					
(5,5)	6.78 5:15	7.47 1:1	8.18 1:1	8.90 1:3	9.63 1:1	10.36 5:5	11.11 1:3	11.86 1:1	12.61 1:1	13.36 1:3	14.12 5:5						
	0.0	1.000	0.978	0.020	0.749	0.788	0.020	0.604	0.649	0.016	0.521						
	2.46 30°	40.67 27.0°	44.51 24.5°	16.14 22.4°	52.38 20.6°	11.28 19.1°	20.15 17.8°	64.51 16.6°	68.61 15.6°	24.24 14.7°	15.37 13.9°						
	20	364	436	172	604	140	268	916	1036	388	260						
(6,6)	8.14 6:18	8.83 1:1	9.53 2:2	10.24 3:3	10.97 2:2	11.70 1:1	12.44 6:6	13.18 1:1	13.93 2:2								
	0.0	0.853	0.780	0.013	0.667	0.623	0.014	0.550	0.521								
	2.46 30°	48.04 27.5°	25.93 25.3°	18.58 23.4°	29.84 21.8°	63.66 20.4°	11.28 19.1°	71.71 18.0°	37.89 17.0°								
	24	508	296	228	392	892	168	1132	632								
(7,7)	9.50 7:21	10.18 1:1	10.88 1:1	11.59 1:3	12.31 1:1	13.04 1:1	13.77 1:3	14.51 7:7									
	0.0	0.764	0.688	0.009	0.646	0.564	0.011	0.553									
	2.46 30°	55.42 27.8°	59.22 25.9°	21.03 24.2°	67.00 22.7°	70.95 21.4°	24.98 20.2°	11.28 19.1°									
	28	676	772	292	988	1108	412	196									
(8,8)	10.86 8:24	11.54 1:1	12.24 2:2	12.94 1:3	13.66 4:4	14.38 1:1											
	0.0	0.658	0.639	0.007	0.545	0.552											
	2.46 30°	62.80 28.1°	33.30 26.3°	23.48 24.8°	18.58 23.4°	78.26 22.2°											
	32	868	488	364	304	1348											
(9,9)	12.21 9:27	12.90 1:1	13.59 1:1	14.30 3:3	15.01 1:1												
	0.0	0.590	0.556	0.005	0.498												
	2.46 30°	70.18 28.3°	73.96 26.7°	25.93 25.3°	81.67 24.0°												
	36	1084	1204	444	1468												
(10,10)	13.57 10:30	14.25 1:1	14.95 2:2														
	0.0	0.542	0.507														
	2.46 30°	77.56 28.4°	40.67 27.0°														
	40	1324	728														
(11,11)	14.93 11:33	15.61 1:1															
	0.0	0.489															
	2.46 30°	84.94 28.6°															
	44	1588															

metallic tubes | semimetallic tubes | semiconducting tubes

The semi-empirical bandgap E_g is calculated according to H. Yorikawa and S. Muramatsu, Phys. Rev. B **52**, 2723 (1995) for the semiconducting tubes (no curvature effects) and A. Kleiner and S. Eggert, Phys. Rev. B **63**, 073408 (2001) for the metallic and semi-metallic tubes (includes curvature). All other values are evaluated from the expressions below.

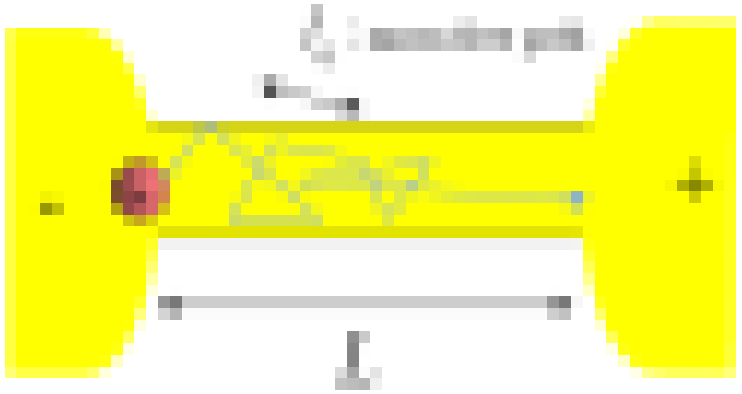
$a_{C\text{–}C}$	carbon–carbon distance		1.421 Å (graphite)
a	length of unit vector	$\sqrt{3}\, a_{C\text{–}C}$	2.461 Å
$\mathbf{a}_1,\ \mathbf{a}_2$	unit vectors	$\frac{a}{2}(\sqrt{3}, 1),\ \frac{a}{2}(\sqrt{3}, -1)$	in (x, y) coordinates
$\mathbf{b}_1,\ \mathbf{b}_2$	reciprocal unit vectors	$\frac{2\pi}{a}(\frac{1}{\sqrt{3}}, 1),\ \frac{2\pi}{a}(\frac{1}{\sqrt{3}}, -1)$	in (x, y) coordinates
$\mathbf{C}_h$	chiral vector	$n\mathbf{a}_1 + m\mathbf{a}_2$	n, m integer
L	circumference of tube	$L = \lvert\mathbf{C}_h\rvert = a\sqrt{n^2 + m^2 + nm}$	$0 \le m \le n$
d_t	diameter of tube	$d_t = L/\pi$	
θ	chiral angle	$\tan\theta = \frac{\sqrt{3}m}{2n+m}$	$0° \le \theta \le 30°$
d	highest common divisor of (n, m)		
d_R	highest common divisor of $(2n + m, 2m + n)$	$d_R = \begin{cases} d & \text{if } n - m \text{ is not a multiple of } 3d \\ 3d & \text{if } n - m \text{ is a multiple of } 3d \end{cases}$	
$\mathbf{T}$	translational vector of 1D unit cell	$\mathbf{T} = t_1\mathbf{a}_1 + t_2\mathbf{a}_2$ $t_1 = (2m + n)/d_R$ $t_2 = -(2n + m)/d_R$	t_1, t_2 integer
T	length of $\mathbf{T}$	$T = \sqrt{3}L/d_R$	
N	number of atoms per 1D unit cell	$N = 4(n^2 + m^2 + nm)/d_R$	$N/2$ = hexagons/unit cell



atomistix
www.atomistix.com

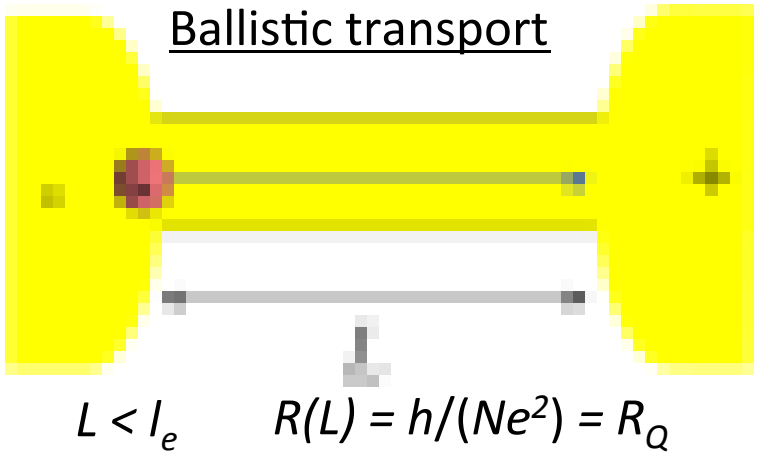
Diffusive vs. ballistic transport

Diffusive transport



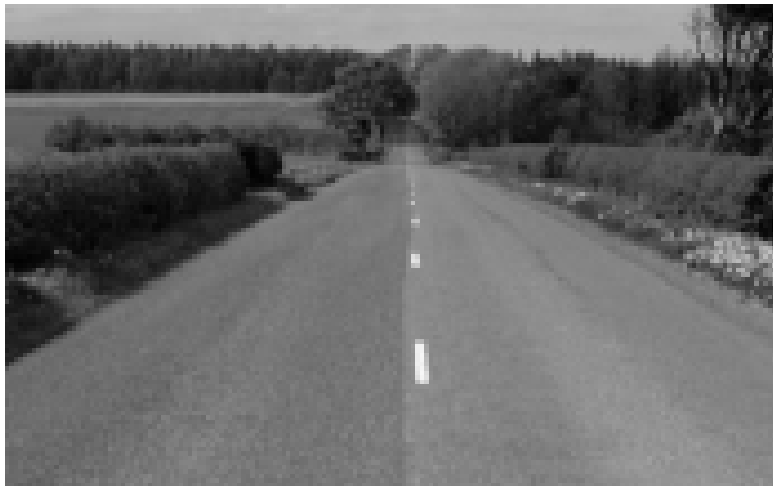
$l_e << L$ $\quad R(L) = rL$

Ballistic transport



$L < l_e$ $\quad R(L) = h/(Ne^2) = R_Q$

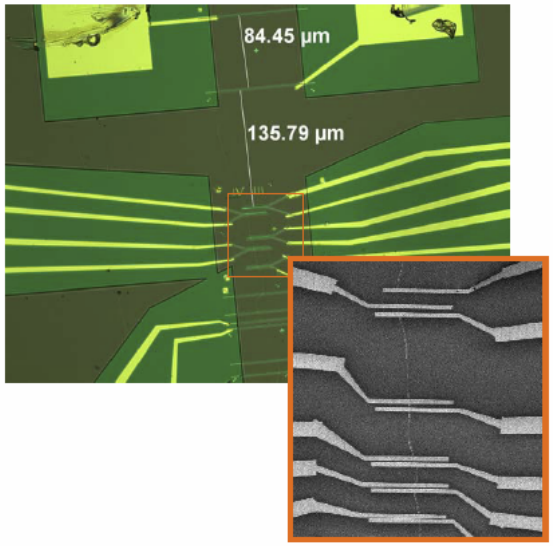
(P. Kim, @NT' 06)

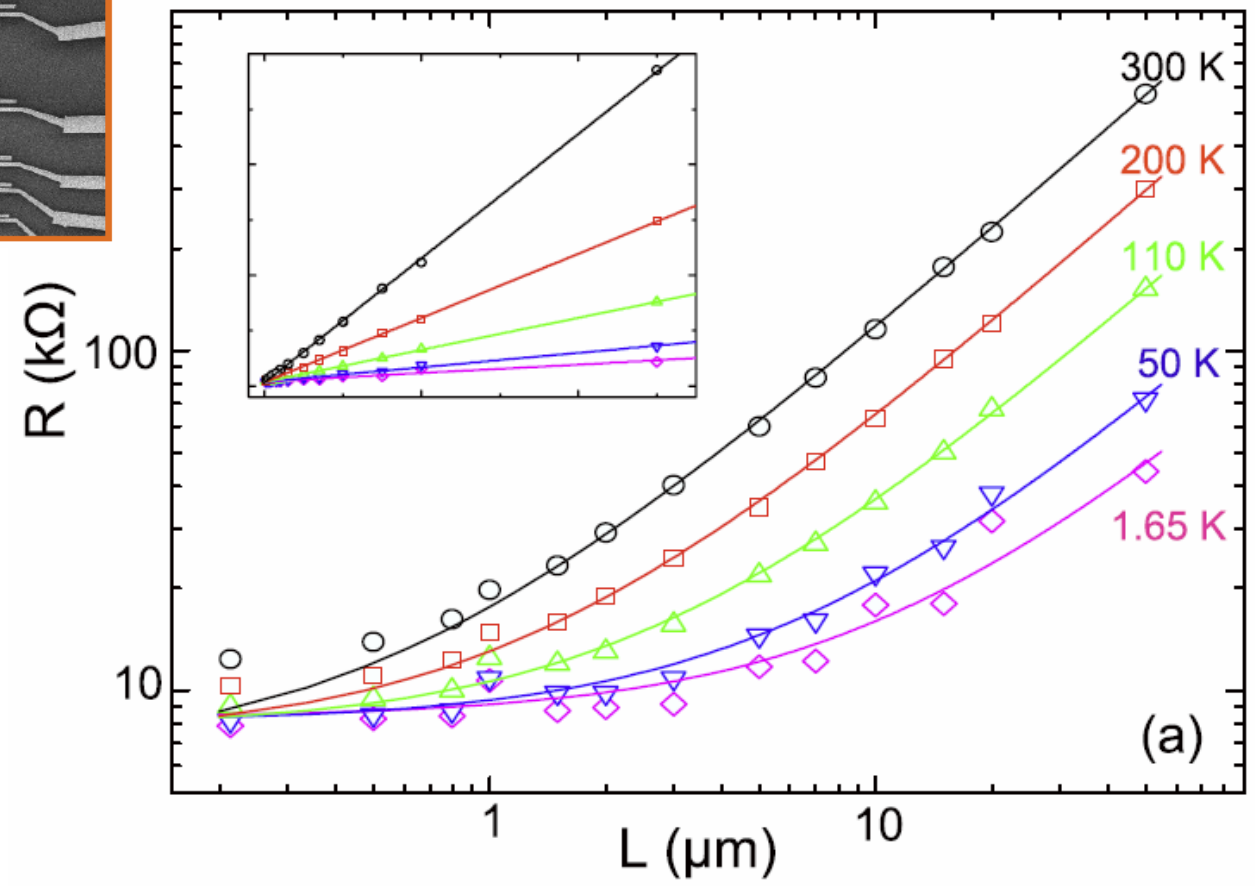


(J. Chen, IBM)

Ballistic SWNT-FETs: Javey et al, Nature 424:654-7, 2003.
MWNT ballistic transport: Li et al, Physical Review Letters 95:086601, 2005.

SWNT resistance vs. length

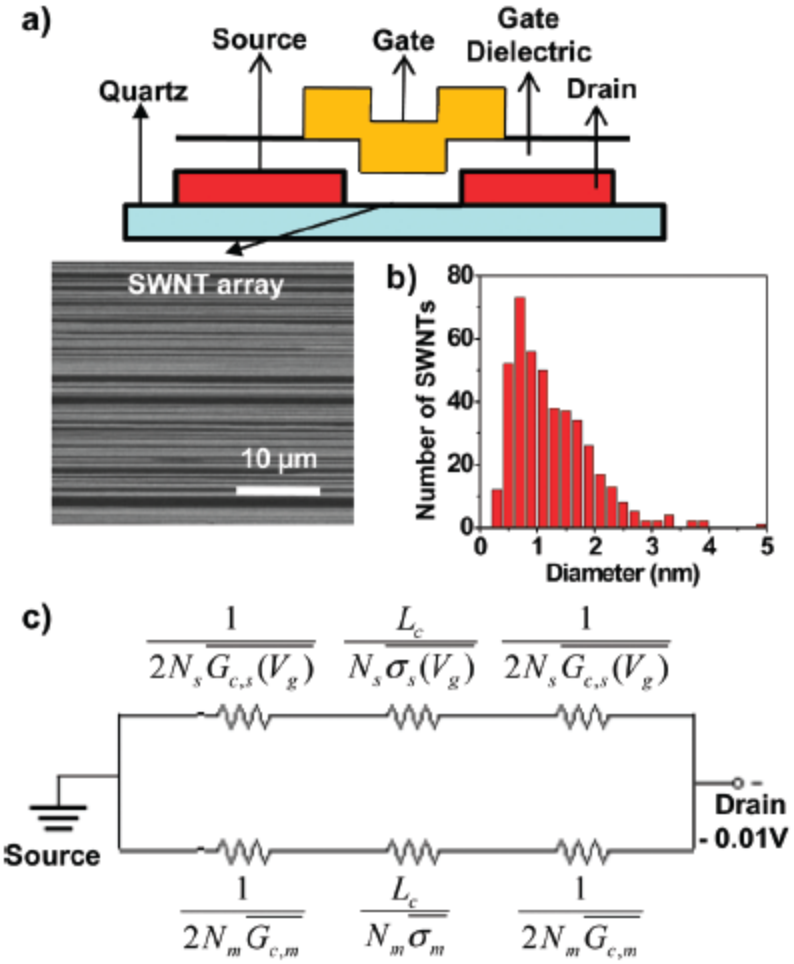




Purewal et al., Phys Rev Lett 98:186808, 2007.

SWNT array transistors

- Mixture of metallic and semiconducting SWNTs; contact effects.



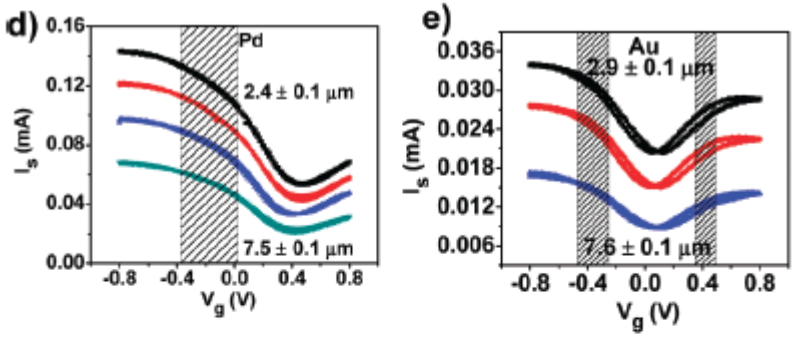
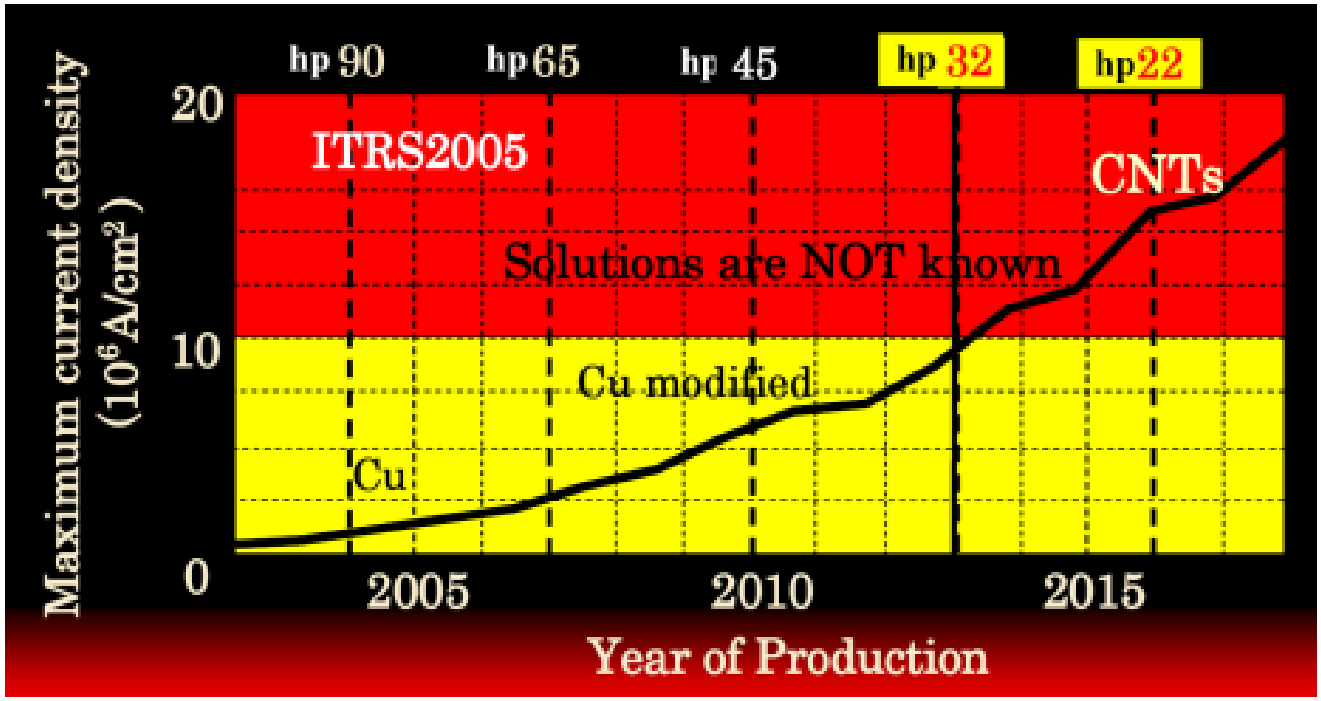
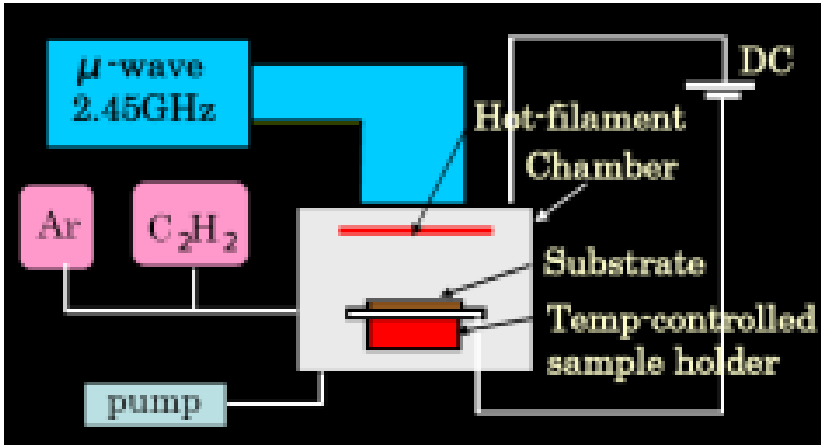


FIGURE 1. (a) Schematic illustration of a single-walled carbon nanotube (SWNT) array transistor with an SEM image of a representative array in the frame below. (b) Typical diameter distribution of SWNTs measured by AFM. (c) Equivalent circuit model for a device with channel length L_c, showing the resistances contributed by the inverse of the average conductances of the contacts to the semiconducting and metallic SWNTs (i.e., $1/\bar{G}_{c,s}$ and $1/\bar{G}_{c,m}$), respectively) and the role of the SWNTs in transport through the channel (i.e., $L_c/\bar{\sigma}_s$ and $L_c/\bar{\sigma}_m$). The numbers of s-SWNT and m-SWNT are N_s and N_m, respectively. Representative transfer curves of (d) Pd and (e) Au electrode devices with channel width (W) = 400 μm at $V_d = -0.01$ V. The channel lengths of the Pd devices are 2.4 ± 0.1 μm (black symbols), 3.7 ± 0.3 μm (red symbols), 4.4 ± 0.1 μm (blue symbols), and 7.5 ± 0.1 μm (green symbols) from top to bottom. The channel lengths of the Au devices are 2.9 ± 0.1 μm (black symbols), 3.7 ± 0.1 μm (red symbols), and 7.6 ± 0.1 μm (blue symbols) from top to bottom. The highlighted regions show the range of V_g values that were analyzed. The bottom frames show combinations of L_c and gate voltages at minimum current ($V_{g(min)}$), for (f) Pd and (g) Au devices. The devices that form the focus of the analysis are shown in red. Two other clusters of devices, indicated in blue and green, were also analyzed.

Ho et al., Nano Letters (ASAP), 2010.

CNT interconnects (Fujitsu)

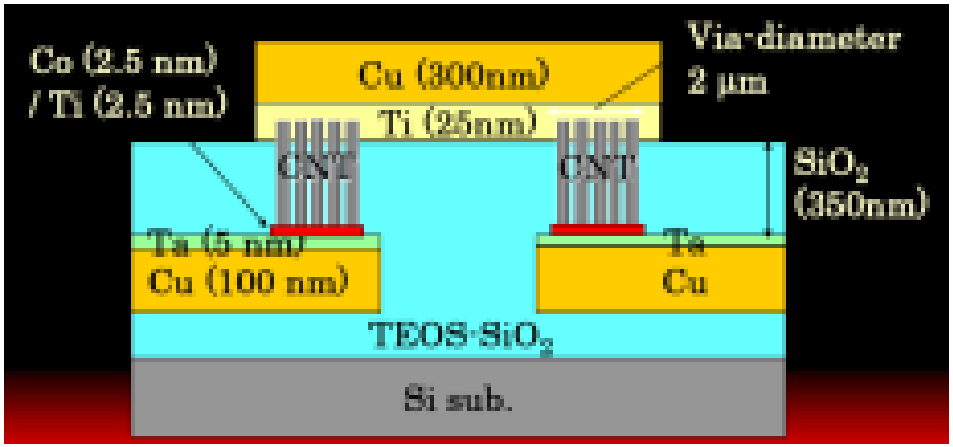


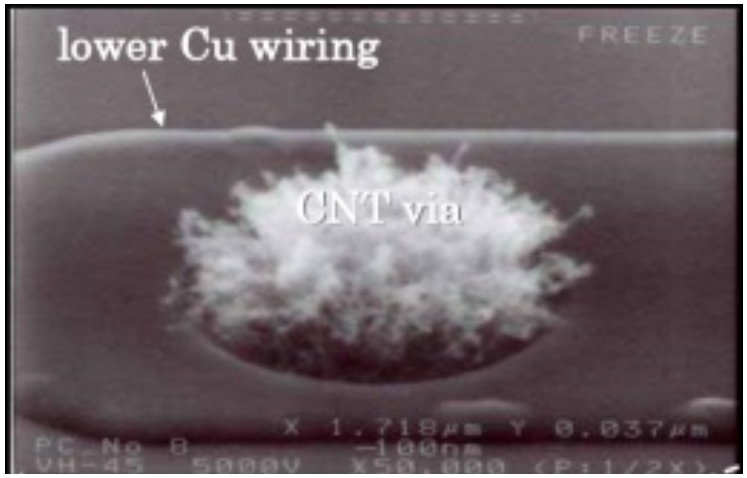


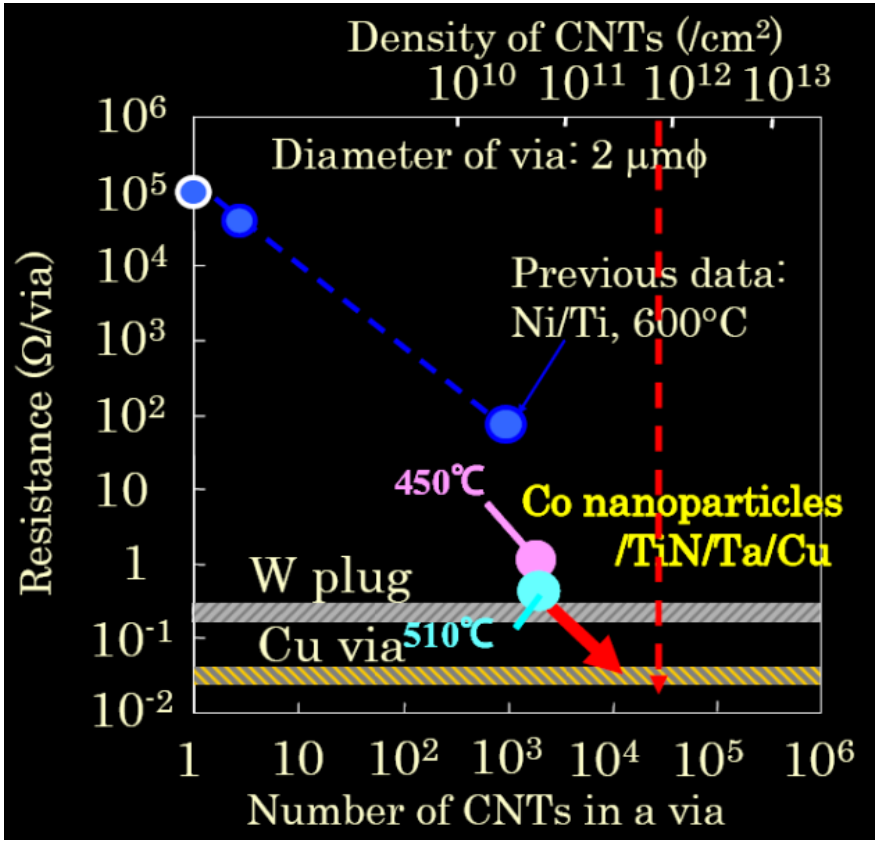
CNTs on 300mm wafer

Y. Awano, Fujitsu / many publications

CNT interconnects (Fujitsu)







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