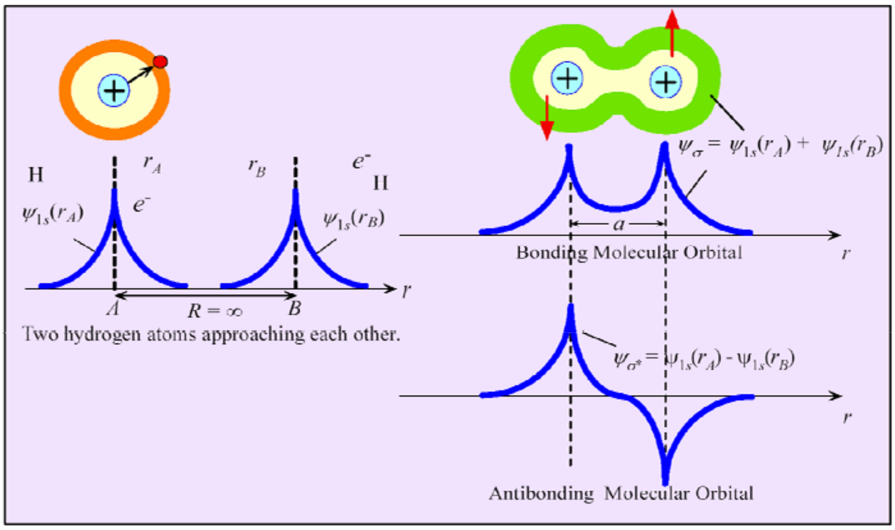
6.Optical and electronic properties of Low dimensional materials

(I). Concept of Energy Band

1. Bonding formation in H_2 Molecules



Formation of molecular orbitals, bonding and antibonding (ψ_σ and $\psi_{\sigma*}$) when two H atoms approach each other. The two electrons pair their spins and occupy the bonding orbital ψ_σ.

Linear combination of atomic orbital (LCAO)

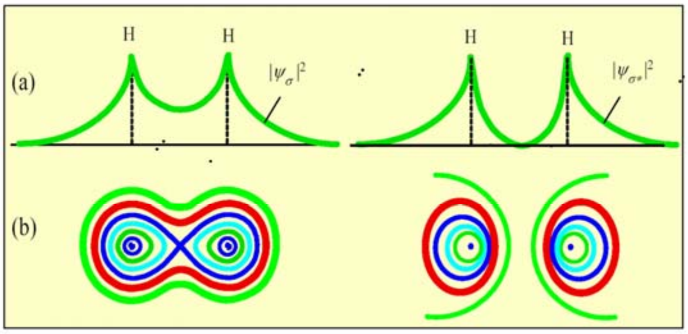
Schrodinger equation: $(-\frac{\hbar^2}{2m}\sum_{i=1,2}\nabla_i^2 + V_{e-ion} + V_{e-e})\psi = E\psi$

$\rightarrow$ find a_1, a_2 s.t. E is min

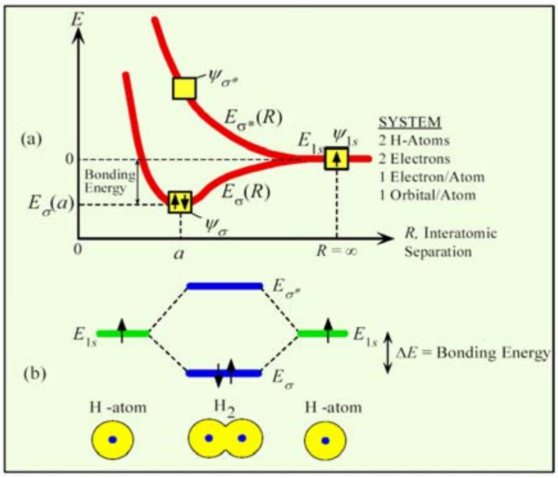
$\psi = a_1\phi_1 + a_2\phi_2$

$[\phi_1(H) + \phi_2(H) \rightarrow \psi(H_2)]$

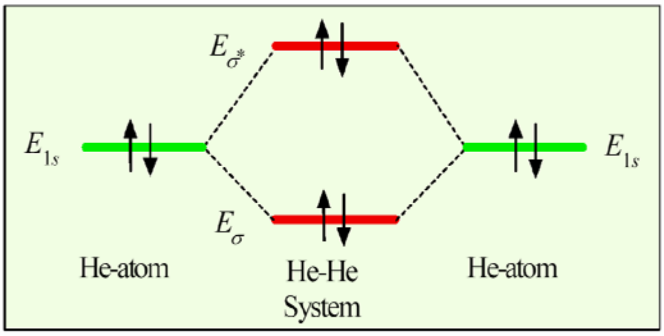
$$\Rightarrow \begin{cases} E = E_b \text{ bonding state } (a_1 = a_2) \Rightarrow \psi_b = A(\phi_1 + \phi_2) \\ E = E_a \text{ antibonding state } (a_1 = -a_2) \Rightarrow \psi_a = A(\phi_1 - \phi_2) \end{cases}$$



(a) Electron probability distributions for bonding and antibonding orbitals, ψ_σ and ψ_{σ^*}. (b) Lines represent contors of constant probability.



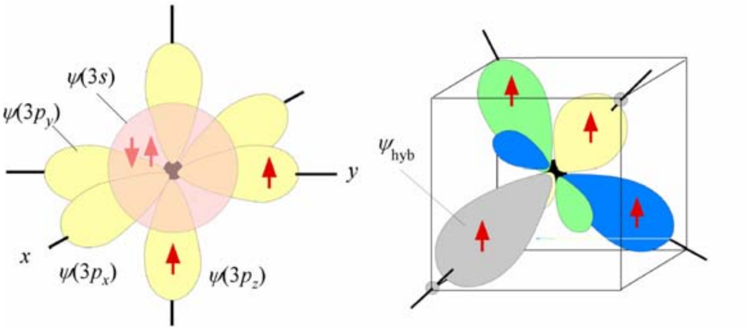
Electron energy in the system comprising two hydrogen atoms. (a) Energy of ψ_σ and $\psi_{\sigma*}$ vs. the interatomic separation, R. (b) Schematic diagram showing the changes in the electron energy as two isolated H atoms, far left and far right, come to form a hydrogen molecule.



Two He atoms have 4 electrons. When He atoms come together 2 of the electrons enter the E_σ and 2 the $E_{\sigma*}$ levels so that the overall energy is greater than two isolated He atoms.

From bond to band

Hybridization in CH_4 molecule (sp3)

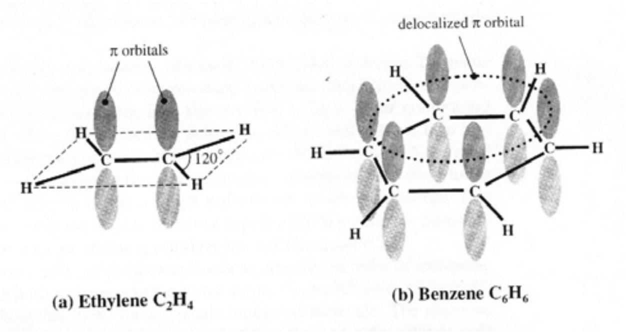


$$\phi_1 = \frac{\varphi_{2s} + \varphi_{2p_x} + \varphi_{2p_y} + \varphi_{2p_z}}{2}, \phi_2 = \frac{\varphi_{2s} + \varphi_{2p_x} + \varphi_{2p_y} - \varphi_{2p_z}}{2}$$

$$\phi_3 = \frac{\varphi_{2s} + \varphi_{2p_x} - \varphi_{2p_y} + \varphi_{2p_z}}{2}, \phi_4 = \frac{\varphi_{2s} - \varphi_{2p_x} + \varphi_{2p_y} + \varphi_{2p_z}}{2}$$

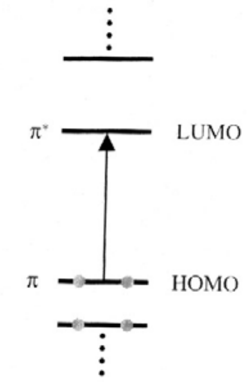
Hybridization in Benzene (sp2)

Planar structure and electron delocalization



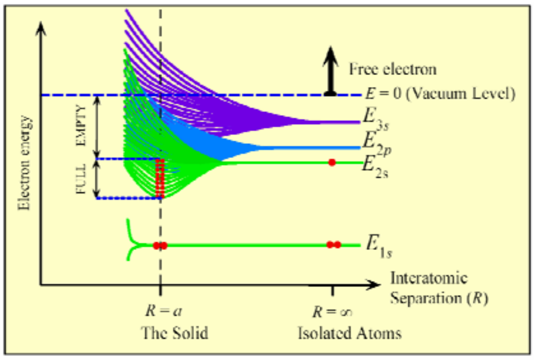
(a) Ethylene C_2H_4

(b) Benzene C_6H_6

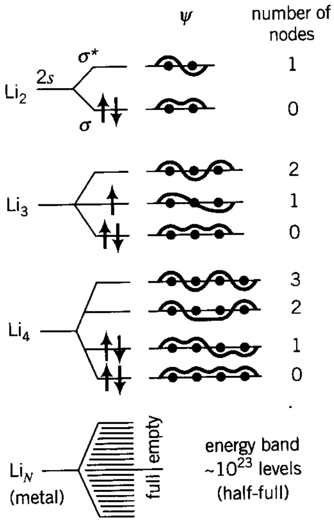


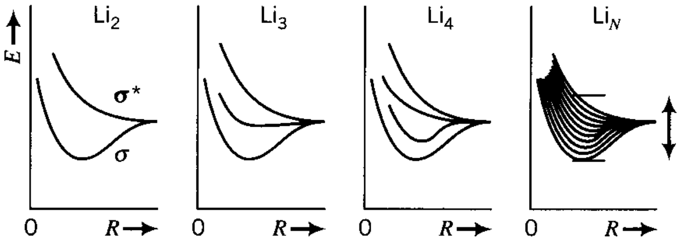
From two to many → Energy bands

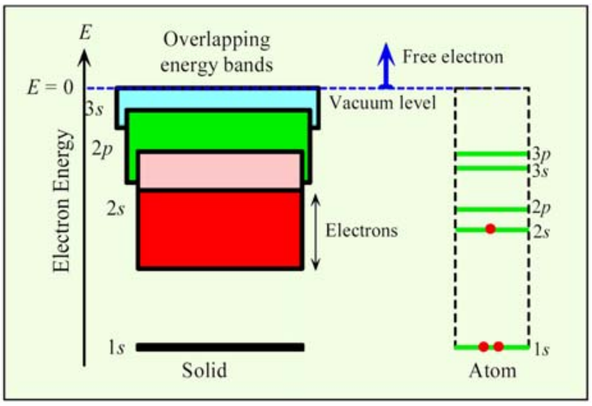
1. **Metal (Li)**



As solid atoms are brought together from infinity, the atomic orbitals overlap and give rise to bands. Outer orbitals overlap first. The 3*s* orbitals give rise to the 3*s* band, 2*p* orbitals to the 2*p* band and so on. The various bands overlap to produce a single band in which the energy is nearly continuous.







In a metal the various energy bands overlap to give a single band of energies that is only partially full of electrons. There are states with energies up to the vacuum level where the electron is free.

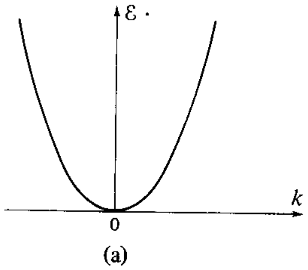
(N atoms interact→N electrons→ N orbitals→ 2N states) 1 electron/state

Free electron model (V=0)

$$E(k)=\frac{\hbar^2}{2m}(k_x{}^2+k_y{}^2+k_z{}^2)$$

$k_x,k_{y,}k_z=0,\pm\frac{2\pi}{L},\pm\frac{4\pi}{L},\cdots,\pm\frac{2n\pi}{L}$ $L:$ lattice constant , $n=$ integer

$$\psi_k=Ae^{i(\vec{k}\cdot\vec{r})}$$

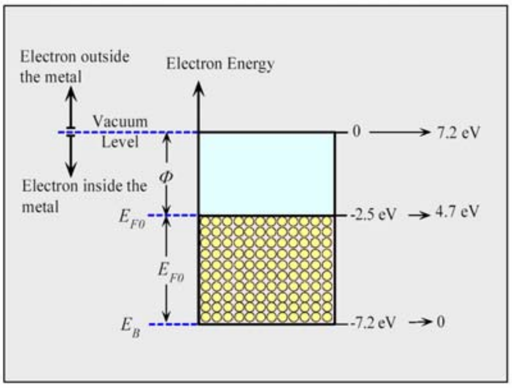


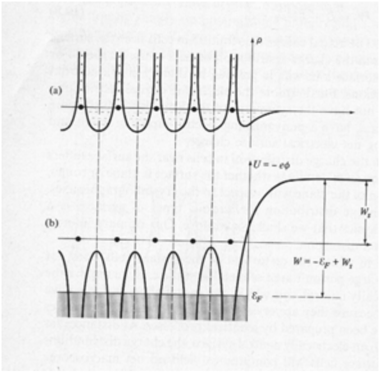
2. Fermi level and workfunction

<u>Fermi level</u> (E_f) for metal : the highest energy level filled by electrons at 0K

Workfunction: $\phi=E_{vac}-E_f$

ϕ results from the formation of *surface dipole*





with electron split off

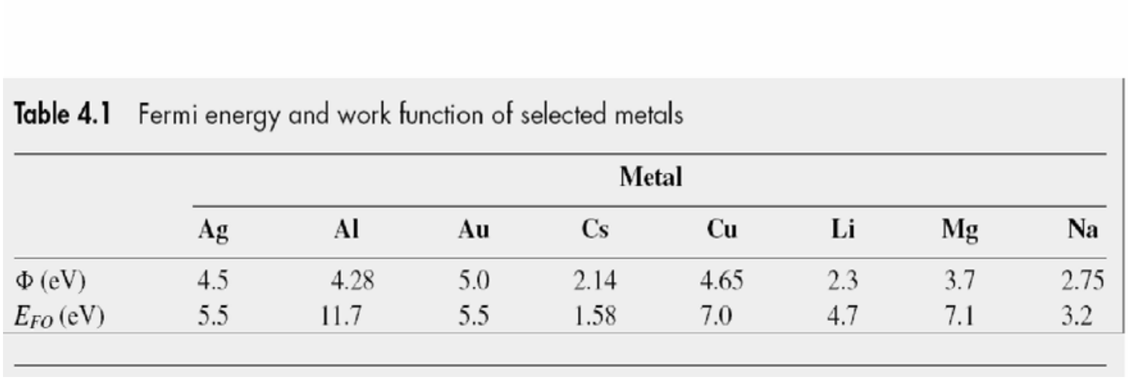
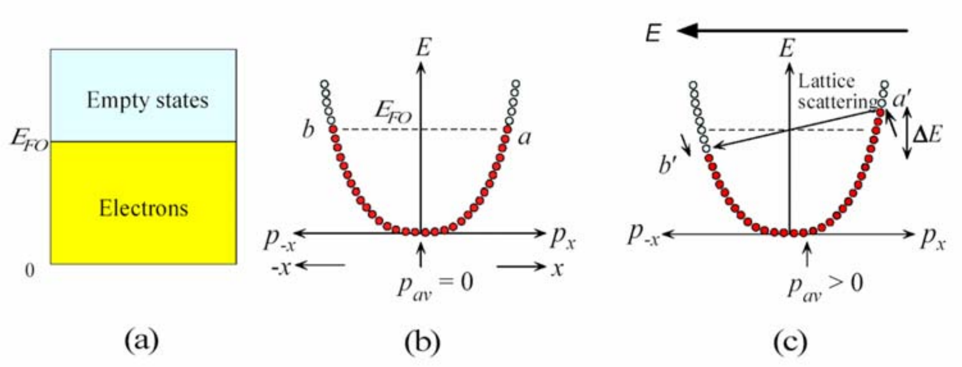


Table 4.1 Fermi energy and work function of selected metals

	Metal							
	Ag	**Al**	**Au**	**Cs**	**Cu**	**Li**	**Mg**	**Na**
Φ (eV)	4.5	4.28	5.0	2.14	4.65	2.3	3.7	2.75
E_{FO} (eV)	5.5	11.7	5.5	1.58	7.0	4.7	7.1	3.2

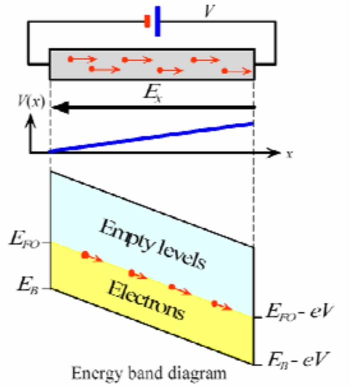
Properties of electrons in a band (under electrical field)

1. For metal:



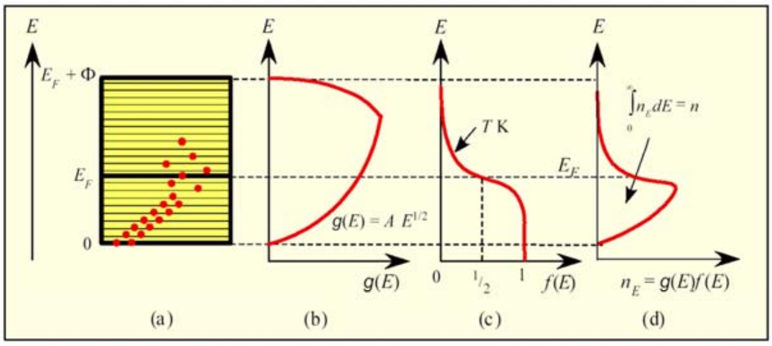
(a) (b) (c)

Free electron model:



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

Quantum theory of metals(V(x)=0)



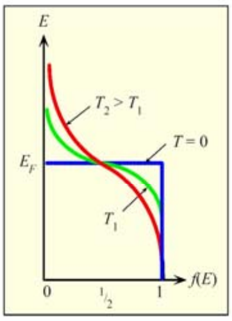
(a) Above 0 K, due to thermal excitation, some of the electrons are at energies above E_F. (b) The density of states, *g(E)* vs E in the band. (c) The probability of occupancy of a state at an energy *E* is *f (E)*. The product *g(E)f (E)* is the number of electrons per unit energy per unit volume or electron concentration per unit energy. The area under the curve with the energy axis is the concentration of electrons in the band.

5. Fermi-Dirac Distribution Function

Determine the # of states that actually contain e^-

Distribution function $f(E) = \dfrac{1}{1 + \exp(\dfrac{E - E_f}{kT})}$

$$n = \frac{\text{total number of } e^-}{volume} = \int f(E)g(E)dE$$



The Fermi-Dirac function, *f*(*E*), describes the statistics of electrons in a solid. The electrons interact with each other and the environment so that they obey the Pauili Exclusion Principle.

◎ Nearly free electron model (NFE) $V(X) \neq 0$

A simple model

1. e^- : a traveling wave in a solid with a weak potential disturbance
2. periodic by ionic core

Bragg's diffraction

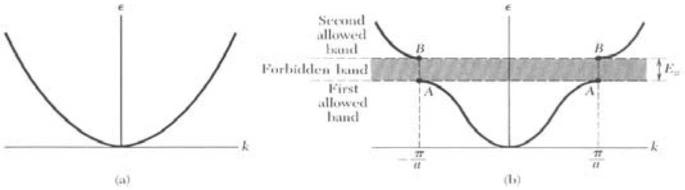
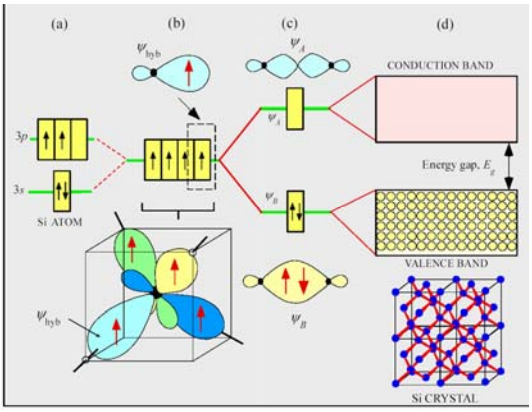
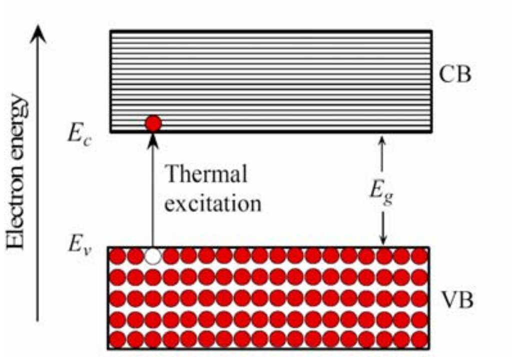


Figure 2 (a) Plot of energy ϵ versus wavevector k for a free electron. (b) Plot of energy versus wavevector for an electron in a monatomic linear lattice of lattice constant a. The energy gap E_g shown is associated with the first Bragg reflection at $k = \pm \pi/a$; other gaps are found at $\pm n\pi/a$, for integral values of n.

Semiconductor (Si) :Formation of band gap.





A. Intrinsic semiconductor

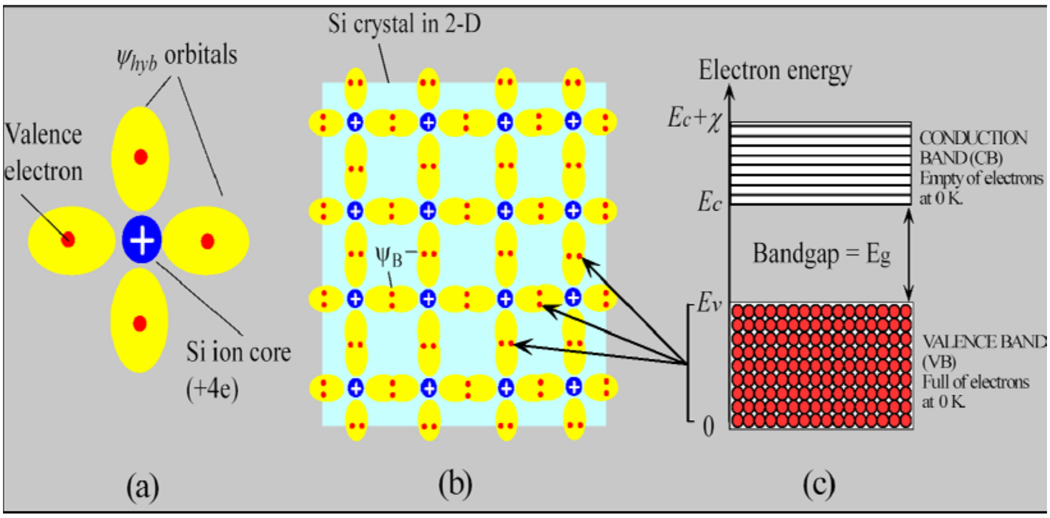
＊ Basic concepts:

1. Band Gap
2. Electron affinity χ
3. electron (e^-), and hole (h^+)

4. Thermal and photon generation

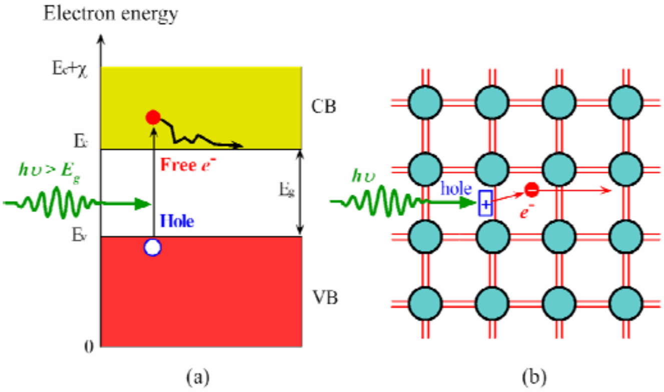
5. Recombination

1. Silicon crystal and energy band diagram:



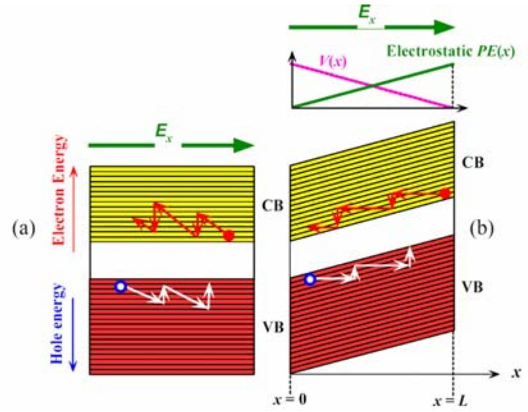
electron affinity χ v.s. workfunction ??

2. Electrons and holes



(a) A photon with an energy greater than Eg can excite an electron from the VB to the CB. (b) When a photon breaks a Si-Si bond, a free electron and a hole in the Si-Si bond is created.

Conduction in Semiconductor



When an electric field is applied, electrons in the CB and holes in the VB can drift and contribute to the conductivity. (a) A simplified illustration of drift in E_x. (b) Applied field bends the energy bands since the electrostatic *PE* of the electron is $-eV(x)$ and $V(x)$ decreases in the direction of E_x whereas *PE* increases.

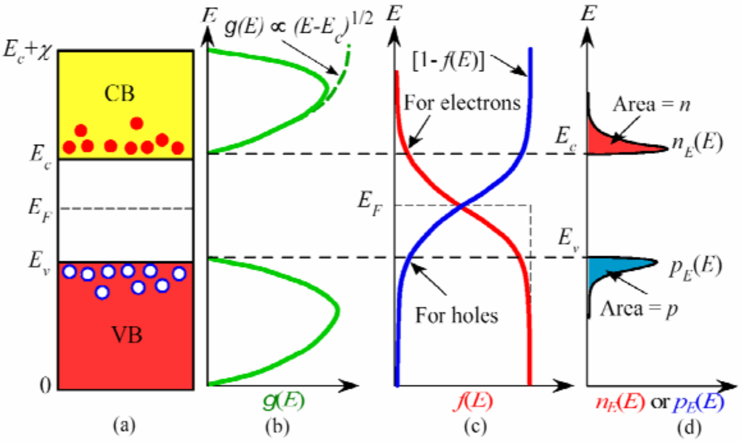
$$J = nev_{de} + pev_{dh}$$

$$v_{de} = \mu_e E_x,\; v_{dh} = \mu_h E_x$$

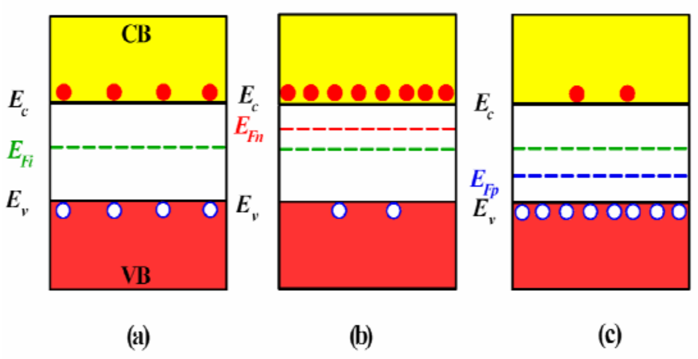
$$\mu_e = \frac{e\tau_e}{m_e^*},\quad \mu_h = \frac{e\tau_h}{m_h^*}$$

$$\Rightarrow \sigma = en\mu_e + ep\mu_h$$

Electron and Hole concentration



(a) Energy band diagram. (b) Density of states (number of states per unit energy per unit volume). (c) Fermi-Dirac probability function (probability of occupancy of a state). (d) The product of $g(E)$ and $f(E)$ is the energy density of electrons in the CB (number of electrons per unit energy per unit volume). The area under $n_E(E)$ vs. E is the electron concentration in the conduction band.



Energy band diagrams for (a) intrinsic (b) *n*-type and (c) p-type semiconductors. In all cases, $np = n_i^2$

(1) Intrinsic semiconductor → Fermi level is in the middle of V.B and C.B

(2) n type semiconductor → Fermi level is near to C.B → n ↑

(3) p type semiconductor → Fermi level is near to V.B → p ↑

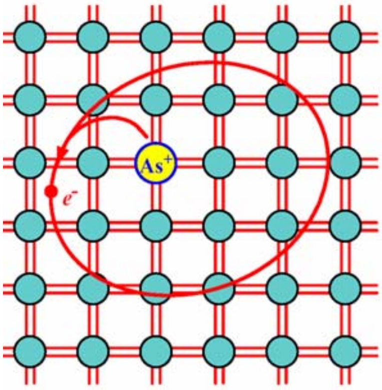
※By adding impurity (doping)

1. n-type → n>p → $(E_c-E_f) < (E_f-E_v)$
2. p-pype → p>n →$(E_c-E_f) > (E_f-E_v)$

But $np=n_i^2$ (n_i depends on T, by mass law)

B. Extrinsic Semiconductor

N-type doping



Arsenic doped Si crystal. The four valence electrons of As allow it to bond just like Si but the fifth electron is left orbiting the As site. The energy required to release to free fifth-electron into the CB is very small.

described by H-atom model.

◦ Binding energy: $\left(E_H = -\frac{e^4 m_0}{2(4\pi\varepsilon_0\hbar)^2 n^2} = -13.6\,eV\right)$

If for Si: $\varepsilon_0 \to \varepsilon_r\varepsilon_0 = \varepsilon =$ dielectric constant for Si

$n = 1,$

$$\Rightarrow E_{doping} = -\frac{e^4 m_e^*}{2(4\pi\varepsilon_0\varepsilon_r\hbar)^2} = -\frac{13.6}{\varepsilon_r^{\ 2}}\frac{m_e^*}{m_0}$$

for Si: $m_e^* \approx 0.2m_0,\ \varepsilon_{\mathrm{r}} = 11.9 \Rightarrow E_d \approx 20meV$

Ge: $m_e^* \approx 0.1m_0,\ \varepsilon_{\mathrm{r}} = \qquad \Rightarrow E_d \approx 5meV$

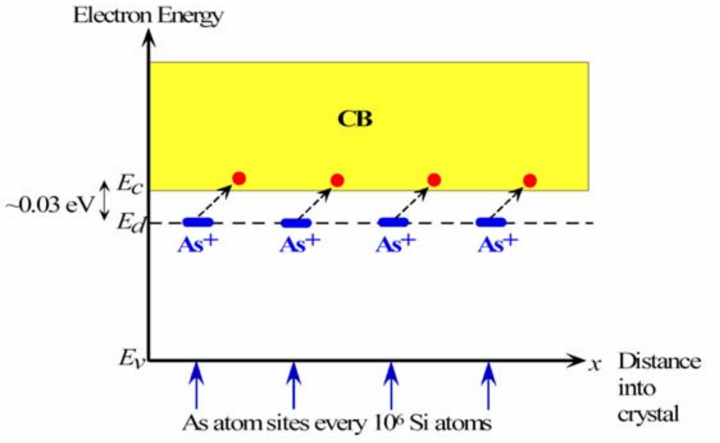
◦ Bohr radius

$$a_H = \frac{4\pi\varepsilon_0\hbar^2}{m_0 e^2} = 0.53\ \text{Å}$$

dopent Bohr radius: $a_d = \dfrac{4\pi\varepsilon_0\varepsilon_r\hbar^2}{m_e^* e^2} = 0.53 \times \dfrac{\varepsilon_r}{m_e^*/m_0}\ \text{Å}$

For Si→ $a_d = 30$ Å, Ge→ $a_d = 80$ Å

1. Doping and impurity



Energy band diagram for an n-type Si doped with 1 ppm As. There are donor energy levels just below E_c around As^+ sites.

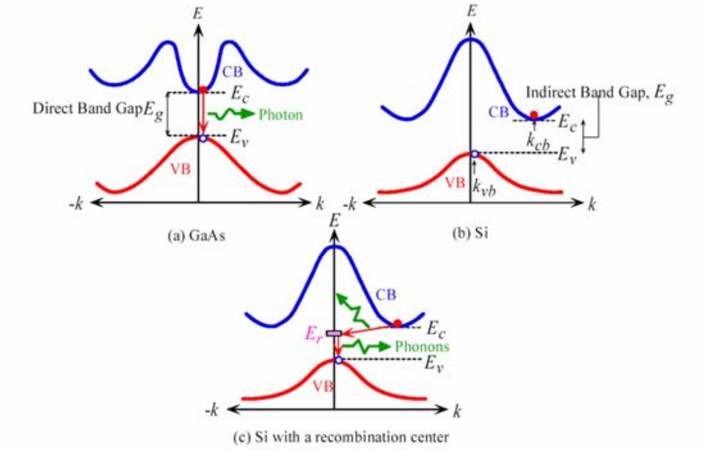
◦ Shallow donor and acceptor:

※Shallow donor/ acceptor: the energy level of donor/acceptor is near to C.B/V.B

→ easy to totally ionized

$$\left.\begin{array}{l}\text{shallow donor: } N_d \rightarrow N_d^+ + e^-,\ N_d \approx N_d^+ \\ \text{shallow acceptor: } N_a + e^- \rightarrow N_a^-,\ N_a^- \approx N_a\end{array}\right\}\text{totally ionized}$$

1. Direct v.s. indirect band gap



(a) In GaAs the minimum of the CB is directly above the maximum of the VB. GaAs is therefore a direct band gap semiconductor. (b) In Si, the minimum of the CB is displaced from the maximum of the VB and Si is an indirect band gap semiconductor. (c) Recombination of an electron and a hole in Si involves a recombination center.

direct bandgap: $E_f = E_i + \hbar\omega$ (consevation of energy)

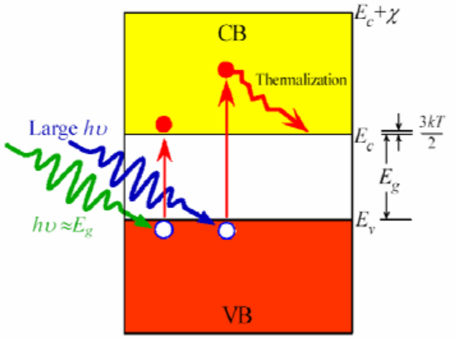
$$\hbar k_f = \hbar k_i \text{ (conservation of p)}$$

indirect bandgap: $E_f = E_i + \hbar\omega \pm \hbar\Omega$

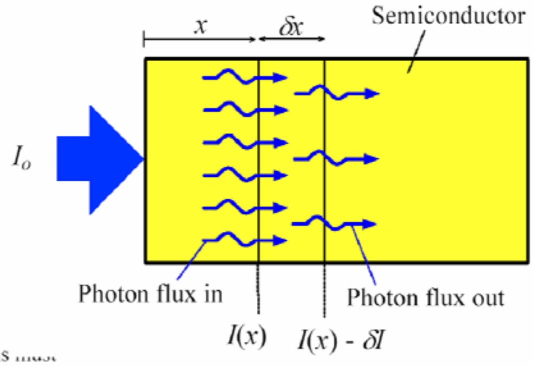
$$\hbar k_f = \hbar k_i \pm \hbar q$$

$(\hbar\Omega, \hbar q \rightarrow phonon)$

Optical absorption:



Optical absorption generates electron hole pairs. Energetic electrons must loose their excess energy to lattice vibrations until their average energy is (3/2)kT in the conduction band.



※Beer's law

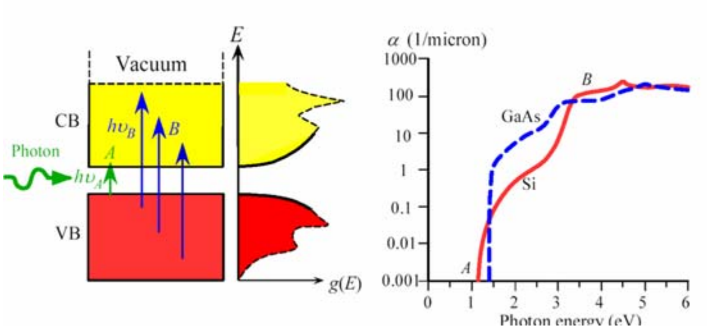
$$\delta I = -\alpha I \delta x \Rightarrow \alpha = \frac{-\delta I}{I \delta x} \Rightarrow I(x) = I_0 \exp(-\alpha x)$$

α : absorption ocefficient

x: distance

when δ=1/α: penetration depth

Absorption coefficient depends on density of states $g(E)$



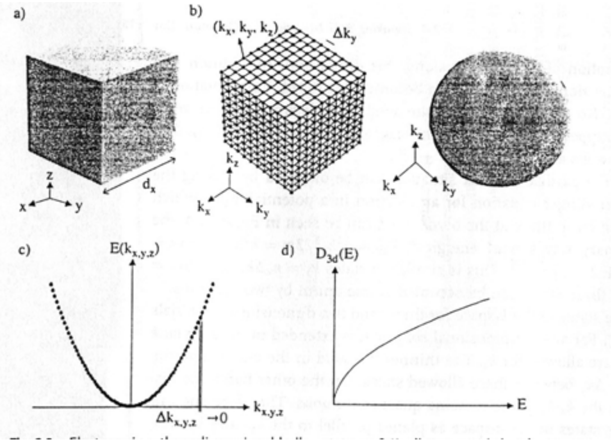
Optical properties of low dimensional materials

Quantum confinement effect

Bulk: no quantum effect

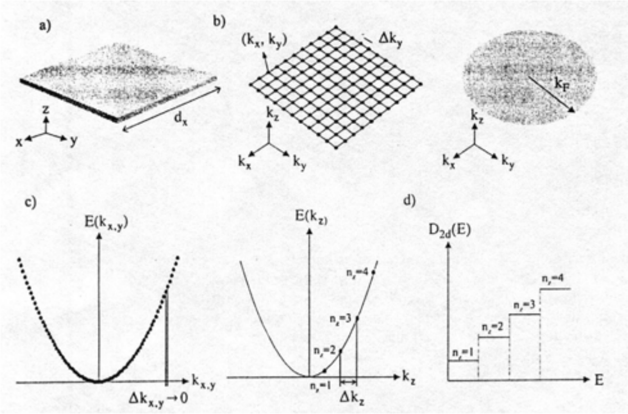
Quantum well: 1-D quantum confinement, 2 free domensions
Quantum wire: 2-D quantum confinement, 1 free domensions
Quantum dot: 3-D quantum confinement, 0 free domensions

Bulk $\Rightarrow$ concept of band $\Rightarrow$ 3D band structure



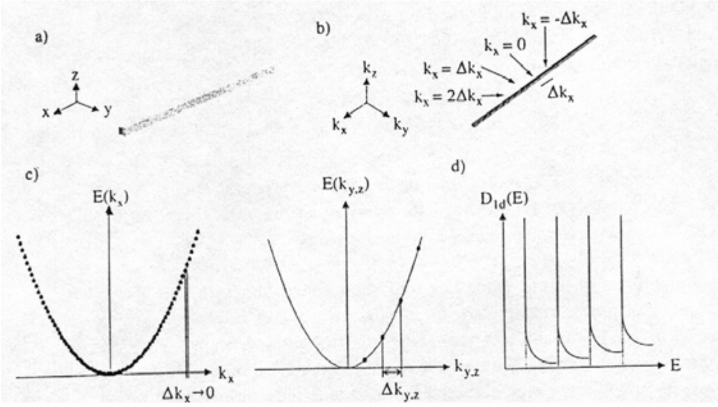
3D crystal

Well $\Rightarrow$ 2D band structure (1-D confinement, 2-D free electron)



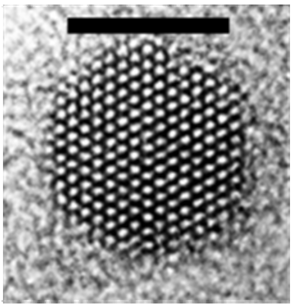
2D Quantum Well

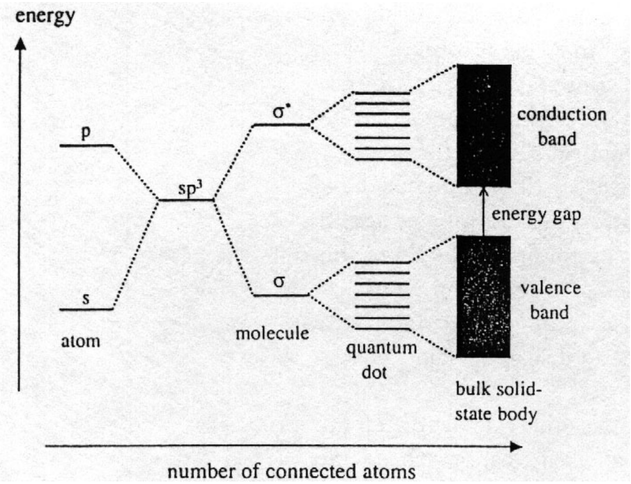
Wire $\Rightarrow$ 1D band structure (2-D confined, 1-D free electron)



1-D quantum wire

Dot $\Rightarrow$ 3-D confined





Q: when should we consider "quantum confinement effects? "

Ans: Uncertainty Principles, $\Delta x \cdot \Delta p \geq \hbar$

$$\Rightarrow \quad \Delta p_x \sim \frac{\hbar}{\Delta x} \quad \Rightarrow \quad E_{confinement} \sim \frac{(\Delta p_x)^2}{2m} = \frac{\hbar^2}{2m(\Delta x)^2}$$

Classical physics: $E_{classical} = \frac{1}{2}kT$ for 1D direction

$\Rightarrow$ if $E_{confinement} > E_{classical}$, $\Delta x \sim \sqrt{\frac{\hbar^2}{mk_0T}}$ (roughly)

At room temperature, $m = 0.1\, m_0 \Rightarrow \Delta x = 5$ nm

Use the concepts of infinite Quantum well

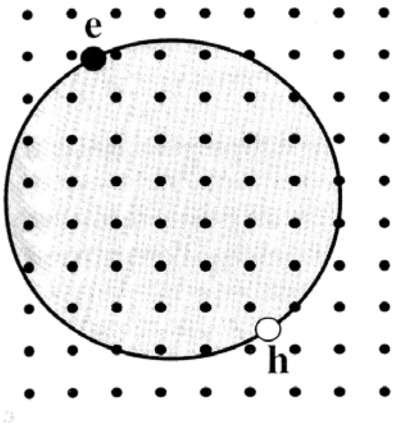
$E_n = \frac{\hbar^2 k^2}{2m} = \frac{n^2\pi^2\hbar^2}{2md^2}$ where d is the thickness of the well

$\Rightarrow D(E) \propto \sqrt{E}$ → 3D

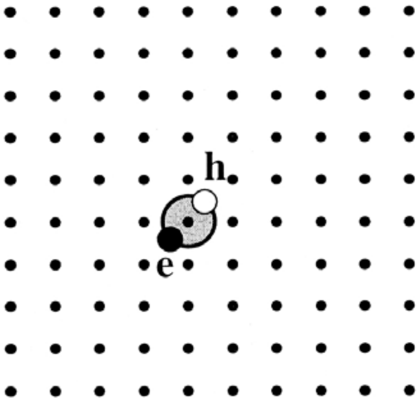
$\propto$ constant → 2D

$\propto (E)^{-\frac{1}{2}}$ → 1D

Exciton



(a) Free exciton



(b) Tightly bound exciton

Binding energy and Bohr’s radius

$e^- + h^+ \rightarrow$ exciton

◦ free exciton $E_b \approx 0.01\ eV$

◦ tightly bound exciton $E_b > 0.1\ eV$

Free exciton

$$\frac{1}{\mu} = \frac{1}{m_e^{\ *}} + \frac{1}{m_h^{\ *}}$$

$$E(n) = -\frac{\mu}{m_0}\frac{1}{\varepsilon_r^{\ 2}}\frac{13.6}{n^2} = -\frac{\mu}{m_0}\frac{1}{\varepsilon_r^{\ 2}}\frac{R_H}{n^2} = -\frac{R_x}{n^2}$$

$$where\ R_x = \left(\frac{\mu}{m_0 \varepsilon_r^{\ 2}}\right) R_H$$

$$r_n = \frac{m_0}{\mu}\varepsilon_r n^2 a_H = n^2 a_x$$

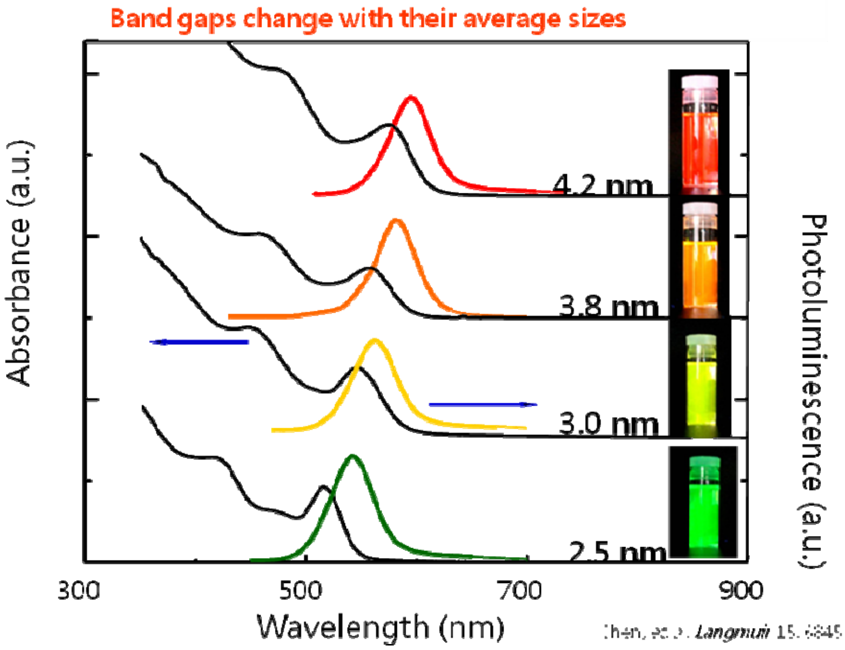
$$a_x = \left(\frac{m_0 \varepsilon_r}{\mu}\right) a_H$$

GsAs

$$m_e^* = 0.067m_0 \ , \ m_h^* = 0.2m_0 \ , \ \varepsilon_r = 12.8$$

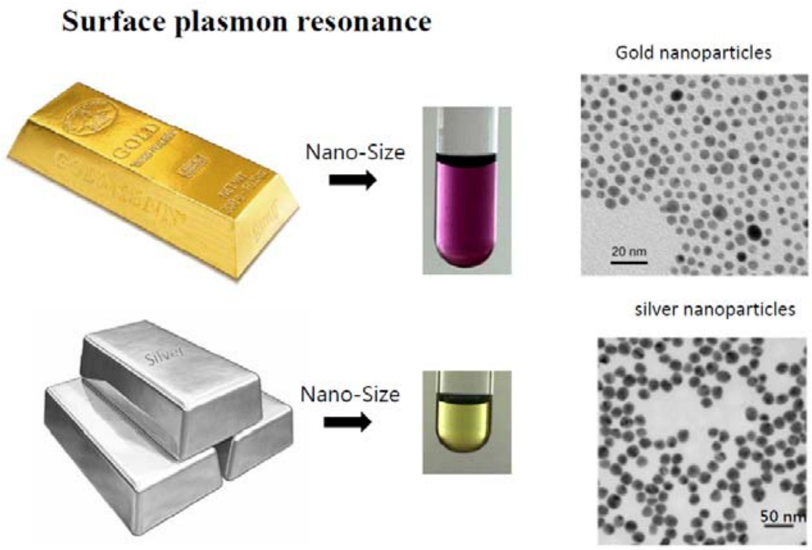
$$\because \mu = \left(\frac{1}{0.067m_0} + \frac{1}{0.2m_0} \right)^{-1} = 0.05m_0$$

$$R_x = \frac{0.05}{12.8^2} \times 13.6 = 4.2meV \approx kT$$

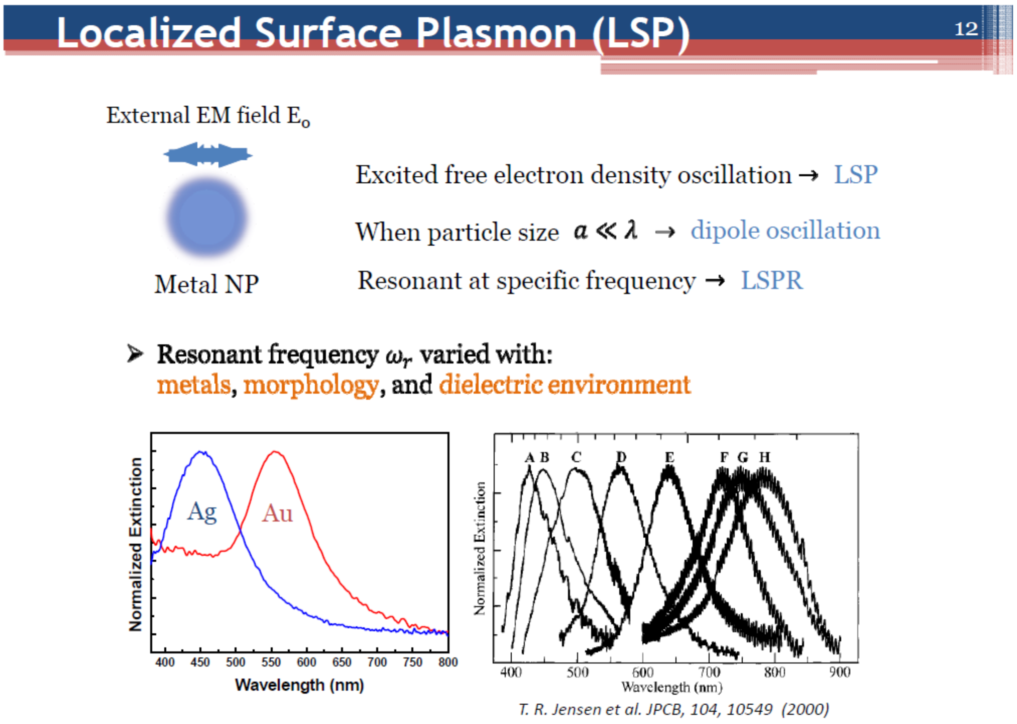


Chen, et al. *Langmuir* 15, 6845 (1999)

Plasmonic Nanoparticles



Plasmons are the oscillations of free electrons which are the consequence of the formation of a dipole in the material due to electromagnetic waves. The electrons migrate in the material to restore its initial state; however, the light waves are constantly oscillating leading to a constant shift in the dipole, so the electrons are forced to oscillate at the same frequency as the light. This coupling only occurs when the frequency of the light is equal to or less than the plasma frequency and is greatest at the plasma frequency and is therefore called the resonant frequency.



Localized Surface Plasmon (LSP)

12

External EM field E_o

Metal NP

Excited free electron density oscillation → LSP

When particle size $a \ll \lambda$ → dipole oscillation

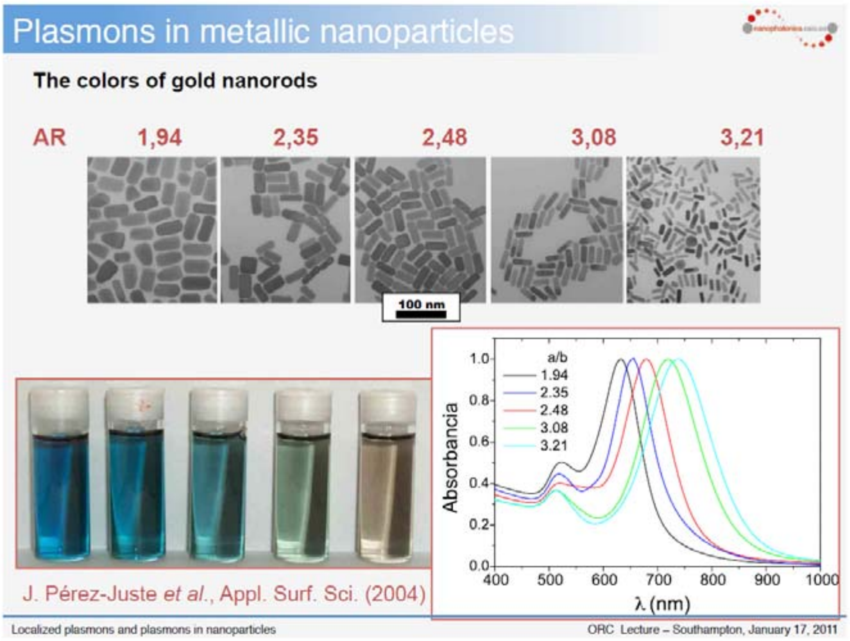
Resonant at specific frequency → LSPR

- **Resonant frequency ω_r varied with:**
  metals, morphology, and dielectric environment

T. R. Jensen et al. JPCB, 104, 10549 (2000)

Nanoparticle plasmons have the additional property of being dependent on their geometry and size, the scattering and absorbance cross-sections describe the intensity of a given frequency to be scattered or absorbed

Different Geometries (Gold nanorods)



Plasmons in metallic nanoparticles

The colors of gold nanorods

AR 1,94 2,35 2,48 3,08 3,21

J. Pérez-Juste *et al.*, Appl. Surf. Sci. (2004)

Localized plasmons and plasmons in nanoparticles

ORC Lecture – Southampton, January 17, 2011

Applications:

1. **Surface-enhanced Raman scattering (SERS)** is a phenomenon strongly dependent on the surface Plasmon excitations of metal nanostructures. Raman scattering from vibrational bands of a molecule at or near a nanostrucutred surface is greatly enhanced due to extremely high local electromagnetic fields associated with localized surface Plasmon resonances. E-beam lithography can be used to fabricate nanostructures with controllable size and period.

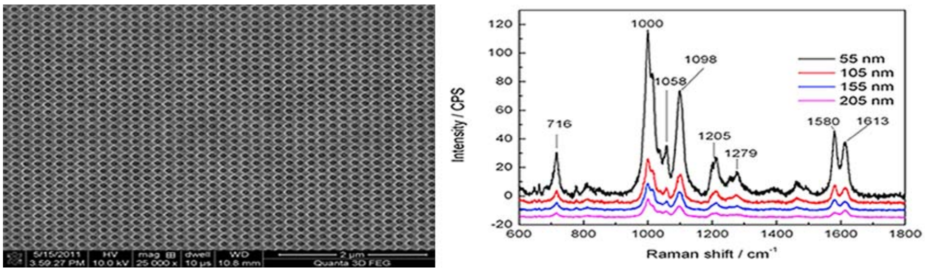
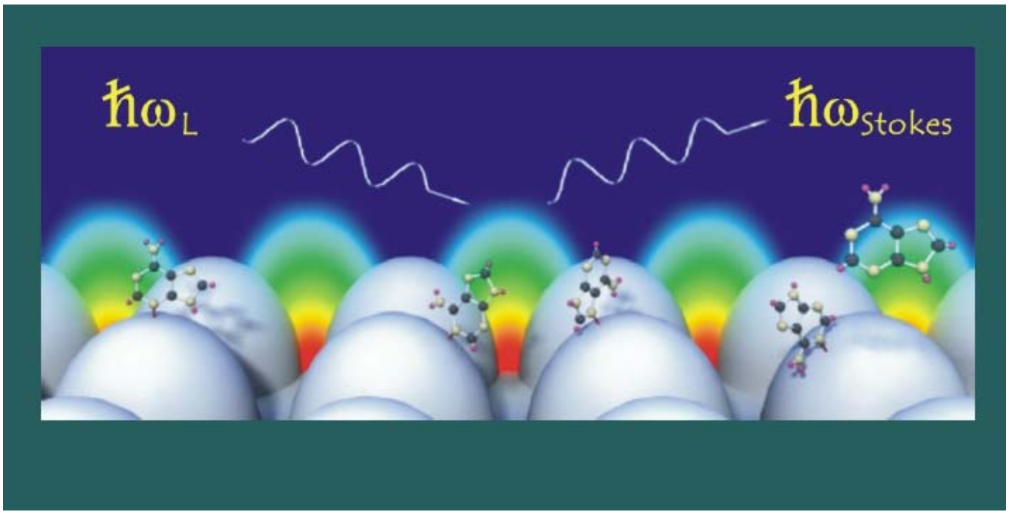


Figure 1 shows gold nanohole array fabricated with e-beam lithography (left) and SERS spectra from nanohole-arrays of the same hole-size but different hole-spacing with detection of 4 mM 4-mercaptopyridine molecules.



SERS by Dr. Yuh-Lin Wang, IAMS, Academic Sinica

2. **Plasmonic solar cells:** (Metal Nanoparticle Plasmonic Solar Cell)

A common design is to deposit metal nanoparticles on the top surface of the thin film SC. When light hits these metal nanoparticles at their surface plasmon resonance, the light is scattered in many different directions. This allows light to travel along the SC and bounce between the substrate and the nanoparticles enabling the SC to absorb more light.