



# **ELEN E3106/4106 Lecture 3**

## **Bonding Forces and Energy Bands in Solids**

### Outline

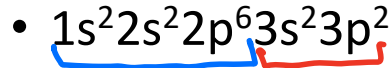
- Bonding forces in solids
- Introduce energy bands and states
- Discuss energy bands in solids and Si
- $E$ - $k$  diagrams
- Direct and indirect  $E_g$  semiconductors
- Effects of alloy composition
- Photoelectric effect

### **Assignments:**

Reading: Streetman and Banerjee §3.1  
Homework 1 due Friday Sept 12<sup>th</sup> by 5pm

# Si Electronic Structure and the Bohr Model

- 14 electrons



- Orbitals:

- 10 core electrons ( $n = 1$  and  $2$ )
  - 4 valence electrons ( $n = 3$ )

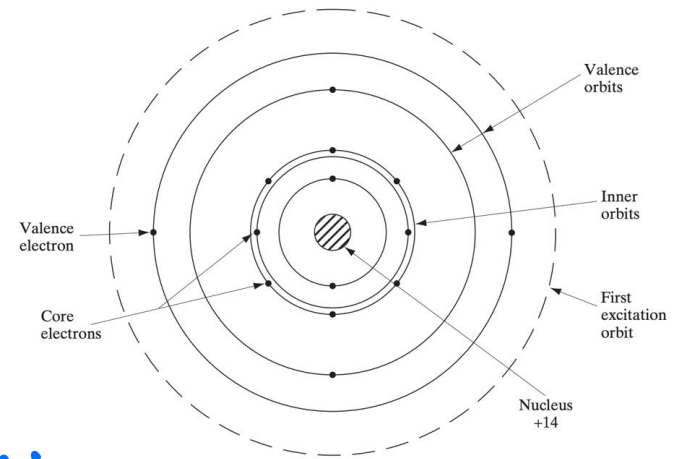
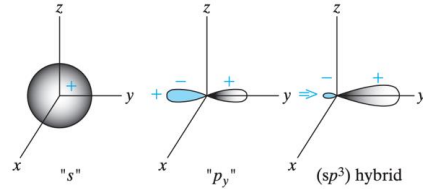
- Attractive force between  $e^-$  and nucleus (+)

- Outer shell  $e^-$  less tightly bound

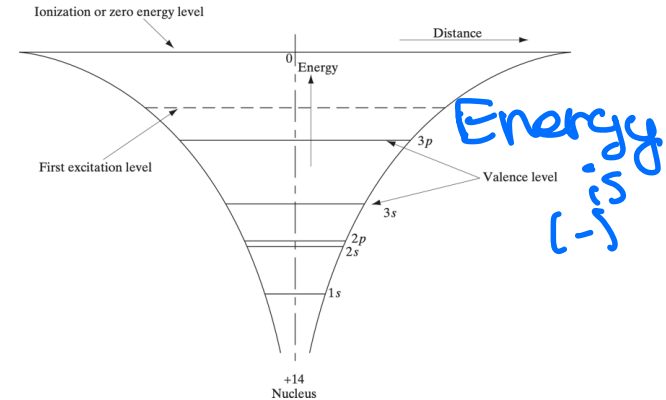
- Bohr model:

$$E_H = -\frac{mq^4}{2(4\pi\epsilon_0 h n)^2} = -\frac{13.6}{n^2} \text{ eV}$$

- (-) indicates that the electron is bound to the nucleus and energy is required to remove it



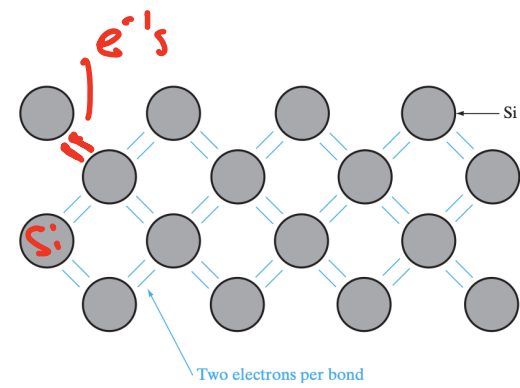
Bohr orbital model of Si atom.



Coulombic potential in Si atom. Source: Textbook

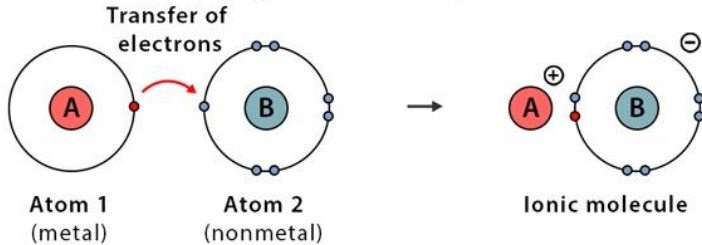
# Bonding in Solids

- Ionic ex:  $\text{Na}^+$  (lost an  $e^-$ ),  $\text{Cl}^-$  (gained an  $e^-$ )
  - All  $e^-$ 's tightly bound, good insulators
- Metallic: outer shell only partially filled  $\rightarrow e^-$  easily given up
  - Ions with closed shells in a sea of  $e^-$ , good conductors
- Covalent ex: diamond lattices, like Si
  - No free electrons at 0K (idealized case) absolute zero
- Some compound semis have mixed bonding ex. GaAs  $\rightarrow$  covalent + ionic



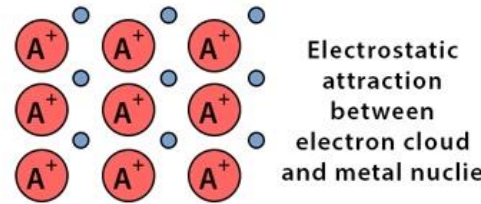
Good insulators  
no free  $e^-$ 's

## Ionic Bond



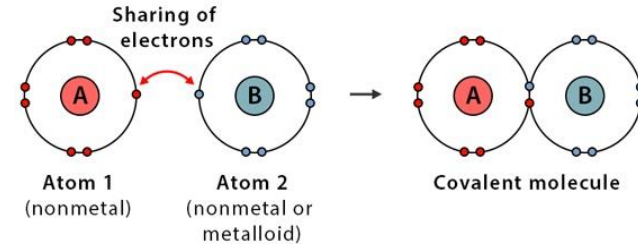
Good conductors  
many free  $e^-$ 's

## Metallic Bond



Shared  $e^-$ 's,  
somewhat conductive

## Covalent Bond



ChemistryLearner.com



## Quick: Quantum Mechanics

- Electrons propagating in crystal can be described by a wave using the “language” of QM
- Schrödinger's Wave Equation  $\Psi(x, y, z, t)$ 
  - Each particle in a physical system is described by a wave function
  - The function (and its space derivative) is continuous, finite, and single-valued
- Takeaway: electrons in an atom are restricted to *discrete* energy levels

Classical variable	Quantum operator
$x$	$x$
$f(x)$	$f(x)$
$p(x)$	$\frac{\hbar}{j} \frac{\partial}{\partial x}$
$E$	$-\frac{\hbar}{j} \frac{\partial}{\partial t}$

Kinetic energy + potential energy = total energy

$$\frac{1}{2m} p^2 + V = E$$



$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} + V(x) \Psi(x, t) = -\frac{\hbar}{j} \frac{\partial \Psi(x, t)}{\partial t}$$

Schrödinger's Wave Equation in 3D:

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi + V \Psi = -\frac{\hbar}{j} \frac{\partial \Psi}{\partial t}$$

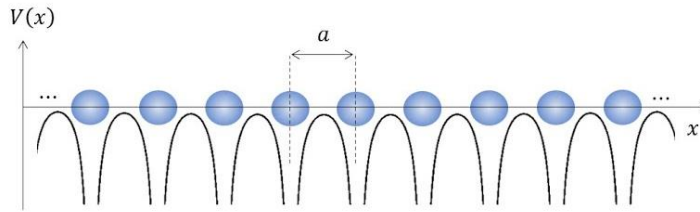
# Bloch's Theorem for Electron Wave Propagation in Crystals



- $e^-$  in a crystal are not completely free, interact with the periodic potential of the lattice
- (F. Bloch, 1928):  $e^-$  wavefunctions are described by plane wave modulated by Bloch Function with same periodicity as the lattice!
  - Wave momentum  $k$  only unique up to  $2\pi/a$
  - Only certain electron energies allowed, but those can propagate unimpeded (theoretically), as long as lattice spacing  $a$  is “perfectly” maintained!
- Implication:  $e^-$  can travel long distances in crystals, much longer than  $a$ , which impacts conduction

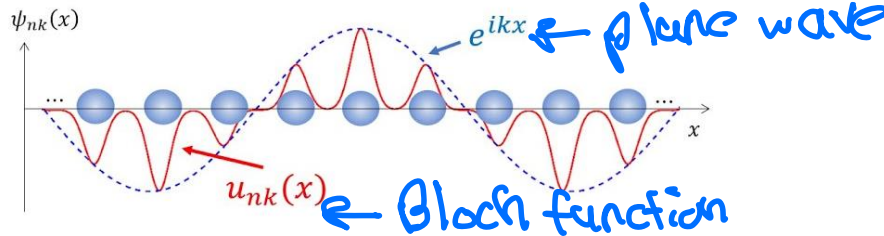
Periodic potential

$$V(x) = V(x + a)$$



Bloch's theorem

$$\psi_{nk}(x) = u_{nk}(x)e^{ikx}$$



# Pauli Exclusion Principle

- No two electrons in an interacting system can have the same quantum numbers **n**, **l**, **m**, and **s**.
- Takeaway: electrons in an atom are restricted to discrete energy levels

$n = 1, 2, 3, \dots$  orbital  
 $l = 0, 1, 2, \dots, (n - 1)$  angular momentum  
 $m = -l, \dots, -2, -1, 0, +1, +2, \dots, +l$  magnetism  
 $s = \pm \frac{\hbar}{2}$  spin

n	l	m	s/ħ	Allowable states in subshell	Allowable states in complete shell
1	0	0	$\pm \frac{1}{2}$	2	2
2	0	0	$\pm \frac{1}{2}$	2	8
	1	-1	$\pm \frac{1}{2}$	6	
		0	$\pm \frac{1}{2}$		
3	1	1	$\pm \frac{1}{2}$	6	18
	2	-2	$\pm \frac{1}{2}$		
		-1	$\pm \frac{1}{2}$		
		0	$\pm \frac{1}{2}$		
		1	$\pm \frac{1}{2}$		
		2	$\pm \frac{1}{2}$		

outer e  
8 allowable  
states b  
3s<sup>2</sup>3

core e<sup>-</sup>s

outer e<sup>-</sup>s  
8 allowable states between  
3s<sup>2</sup> 3p<sup>6</sup>

Quantum numbers and allowable states.

Source: Textbook

# Energy States and Bands

Recall:

Electrons in an atom

Restricted to discrete energy levels (states)



Electrons in a solid

Restricted to a range of energy states, called bands

The energy of a state must always be expressed as an energy difference – the difference between the energy of the state and some known reference.

✓ Vacuum Level

We will use  $E_{vac}$  as the reference.

$E_{vac}$ : energy of a free  $e^-$  outside of the crystal

$$F = - \frac{dE_P}{dr}$$

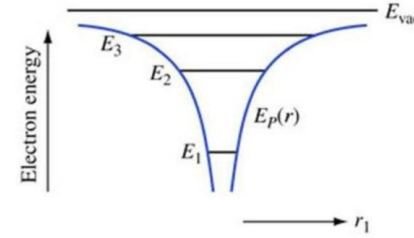
distance

potential energy

$$E_P(r=\infty) = E_{vac}$$

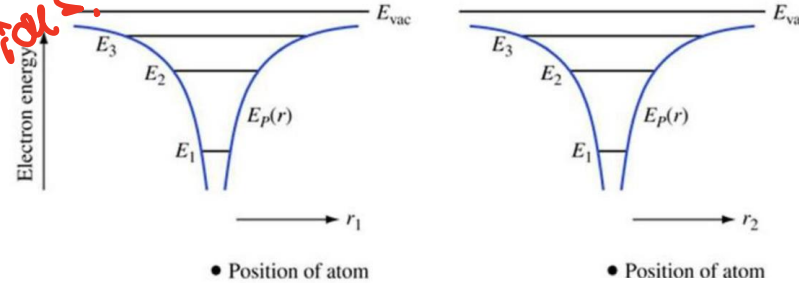
# Energy States and Bands

Energy levels of a single atom



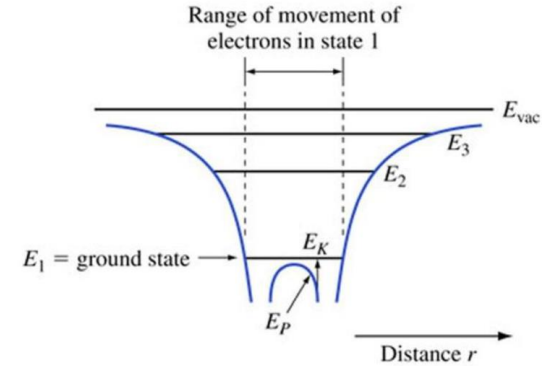
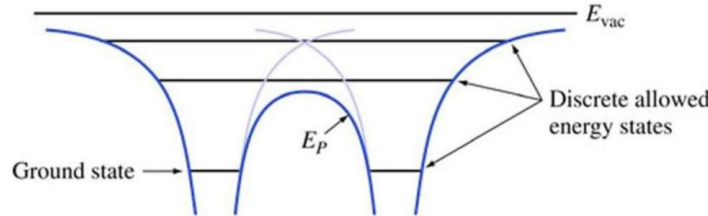
Energy levels of 2 atoms  
far apart

No interactions!



Energy levels as two atoms moved  
close together

- Wavefunctions of e-'s will overlap
- Potential energies will sum
- Molecule may have bound states
- Shared states between atoms help keep molecule together
- There is some stable distance
  - a !





# Energy States and Bands

Another way to conceptualize the energy band model:

- Probability functions overlap = interaction between  $e^-$
- They are now one system!
- Pauli's exclusion principle: no two  $e^-$ 's can have same energy level
- Discrete quantized energy level of the individual atom therefore splits into 2 states
- At most one  $e^-$  per level after the splitting
- New levels ( bands ) belong to the pair rather than individual atoms
- As many atoms brought into proximity, the quantized levels of individual atoms split into a band

$a_0$

$a_0$ : equilibrium interatomic spacing

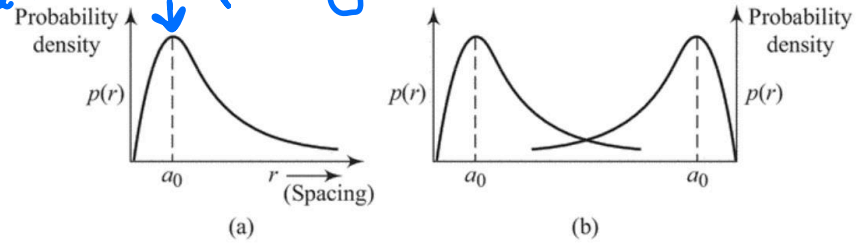


Fig. 3.1 Radial probability density function for (a) one hydrogen atom, (b) two hydrogen atoms in close proximity

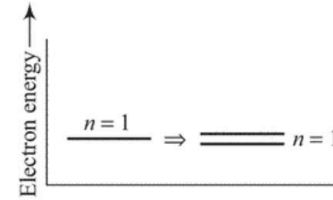


Fig. 3.2 Splitting of discrete quantized energy level

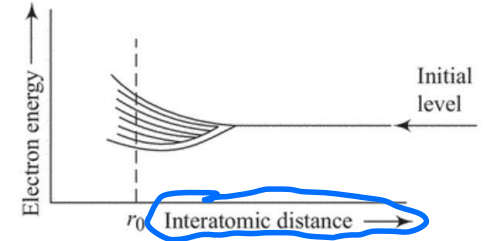


Fig. 3.3 Formation of bands of allowed energy

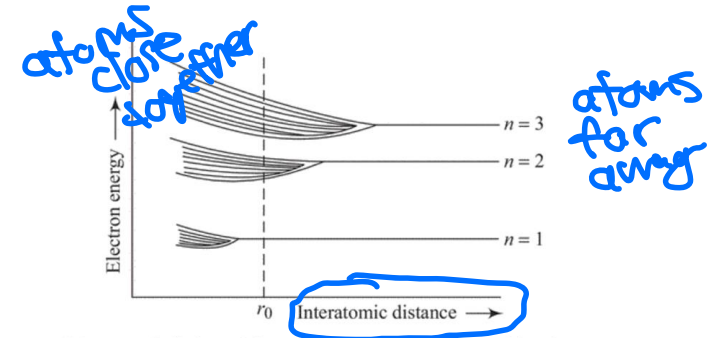
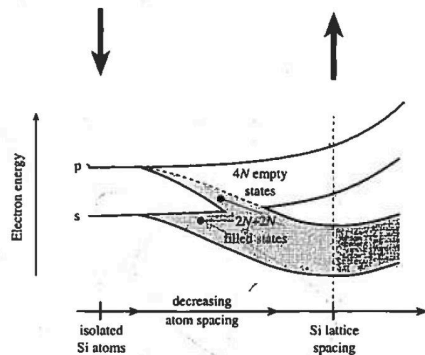
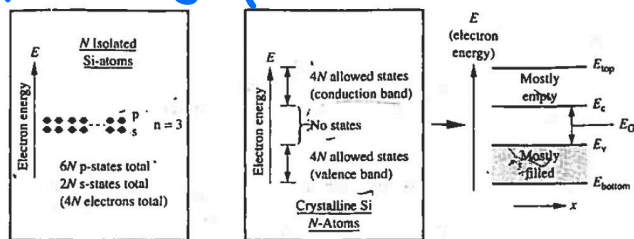


Fig. 3.4 Splitting of three energy states into allowed bands

## Energy Bands in Si

- 3s and 3p states go through a band splitting when  $N$  atoms brought together --  $> 8N$  states total ( $s \rightarrow 2$  states,  $p \rightarrow 6$  states)
- At 0K,  $4N$  lower states are filled with valence  $e^-$ 's --> called valence band
- $4N$  upper states are empty --> called conduction band
- Gap between these bands where there is no allowable energy state is called the  $E_g$ , bandgap (forbidden states)



x-axis flipped

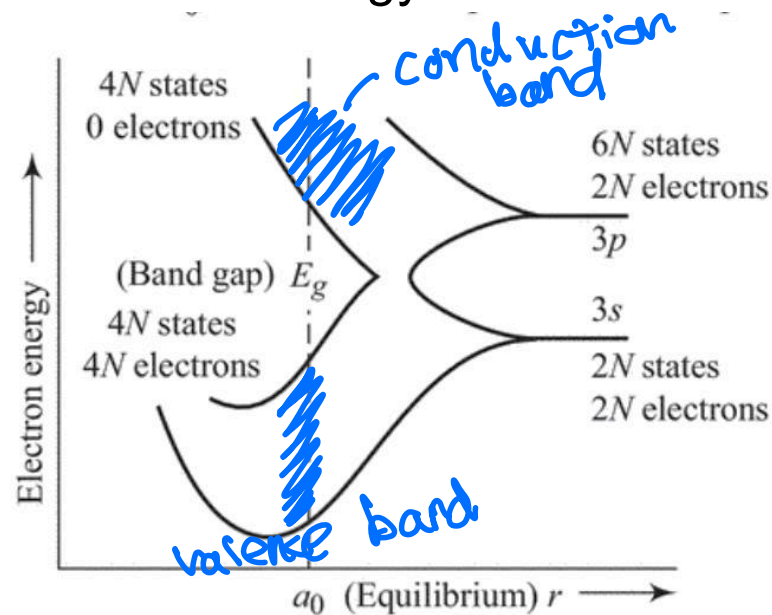
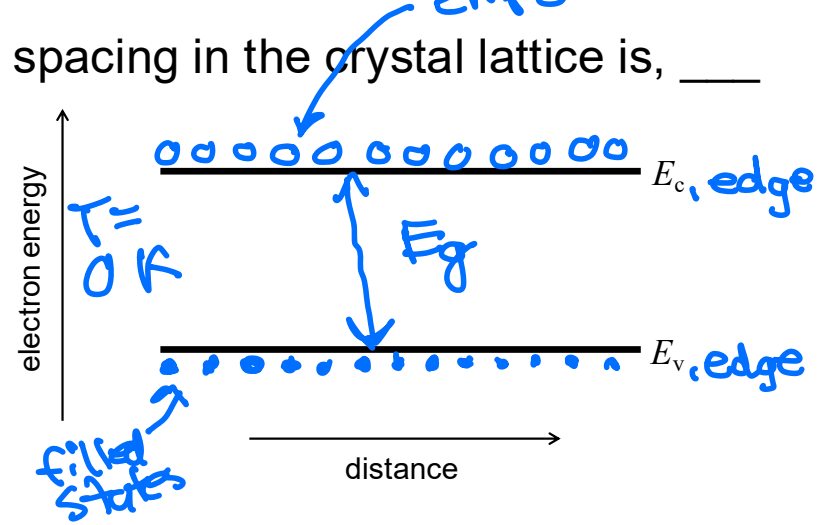
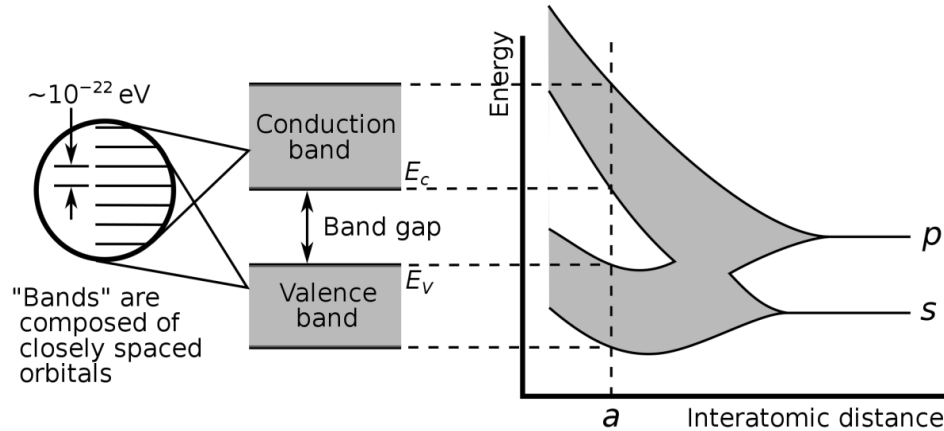


Fig. 3.6 Splitting of 3s and 3p states of silicon

# Simplified Energy Band Diagram

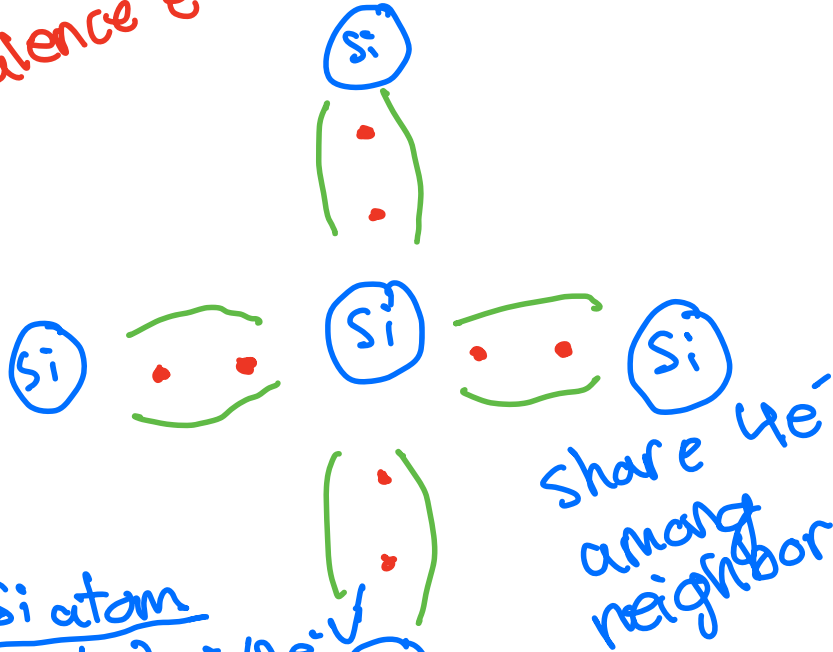
- Energy band diagrams are frequently simplified when analyzing semiconductor devices
- Electronic properties are dominated by the highest partially empty band and the lowest partially full band. Often sufficient to only consider those bands *\* At room temp.*
- Band edges are drawn as horizontal lines
- Bandgap is taken from where the natural interatomic spacing in the crystal lattice is, \_\_\_\_\_



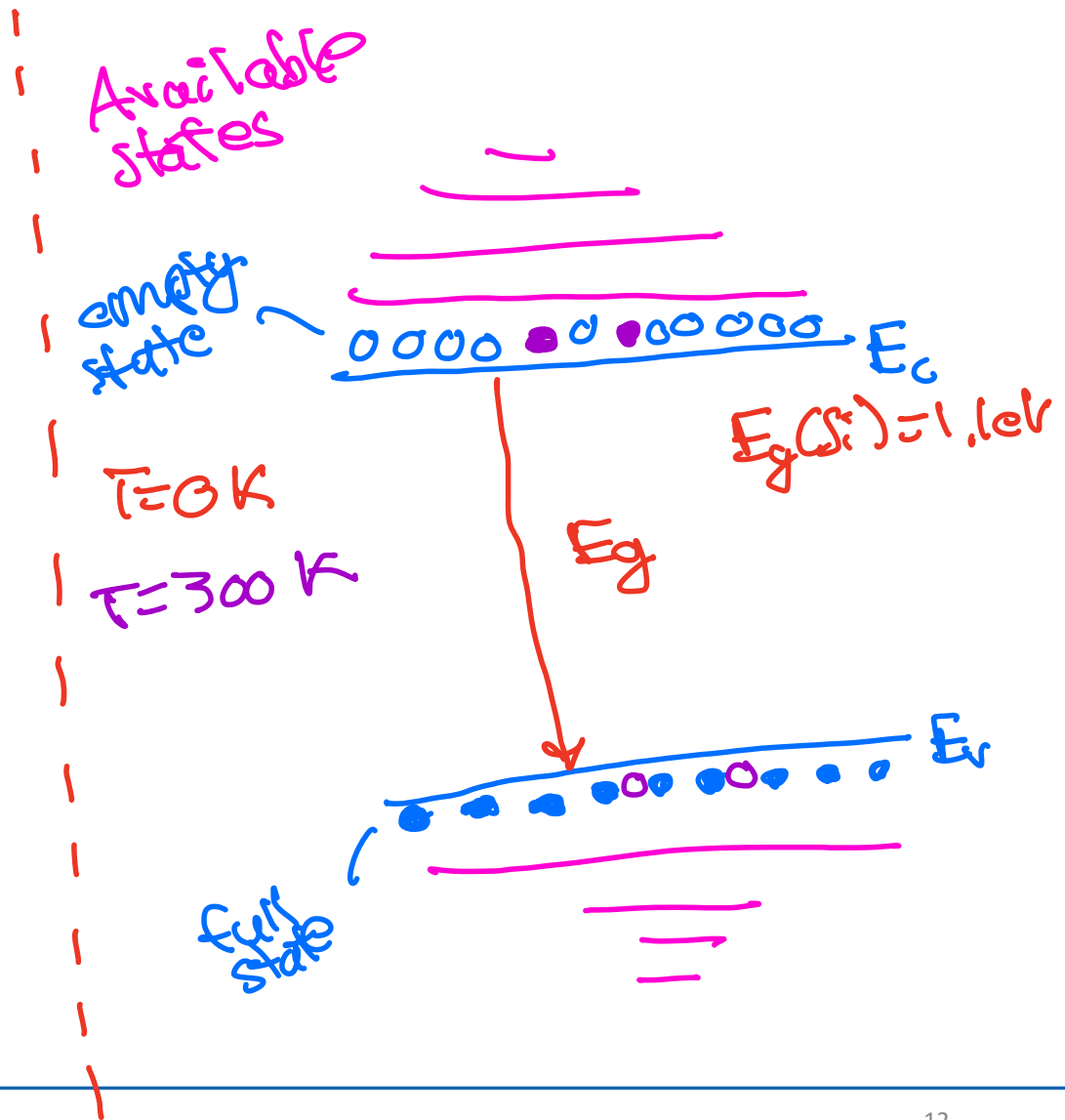
Semiconductor	InSb	Ge	Si	GaAs	GaP	ZnSe	Diamond
$E_g$ (eV)	0.18	0.67	1.12	1.42	2.25	2.7	6.0

# Bond and Band Model of Si

Covalent bond  
Valence  $e^-$ 's

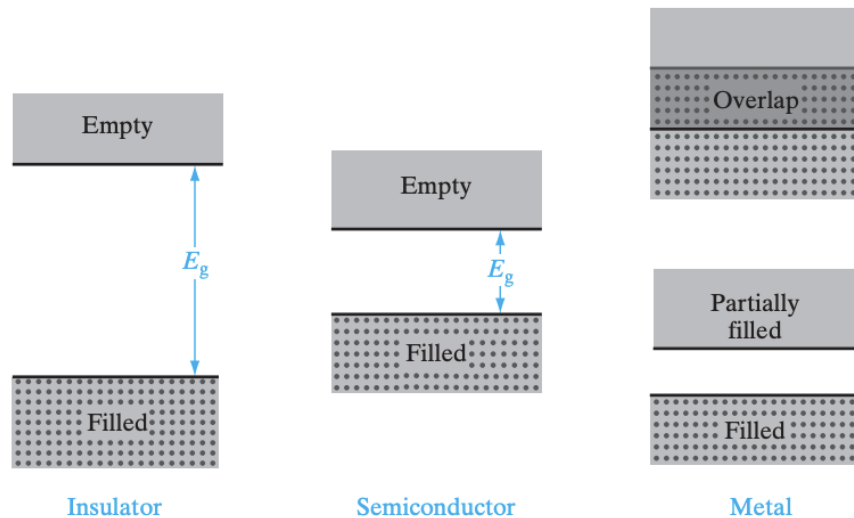


1 Si atom  
 1st  $\rightarrow 1s^2$  2/2  $e^-$  ✓  
 2nd  $\rightarrow 2s^2 2p^6$  8/8  $e^-$  ✓  
 3rd  $\rightarrow 3s^2 3p^6$  4/8  $e^-$  x



## Energy Band Structures in Solids

- Energy bands can be used to conceptualize the three types of solids
- For e<sup>-</sup>'s to experience acceleration in E-field (and contribute to current flow), they must be able to move into new energy state
- Key takeaway:  $E_g$  is essentially a measure of how difficult it is to remove an electron from its bound state in a material
- A wider band gap means it takes more energy to remove an electron!



Band structures shown at 0K.

Handwritten labels for the band structures:

- conductor (pointing to Metal)
- semis (pointing to Semiconductor)
- insulator (pointing to Insulator)

Material	Bandgap [eV]
Metals	0
PbS (lead sulfide)	0.4
Si (silicon)	1.1
CdTe (cadmium telluride)	1.4
CIGS (copper indium gallium diselenide)	1.0–1.7
C (diamond)	5.5
SiO <sub>2</sub> (silica glass)	~9
LiF (lithium fluoride)	13.6

Bandgaps of common solar cell materials

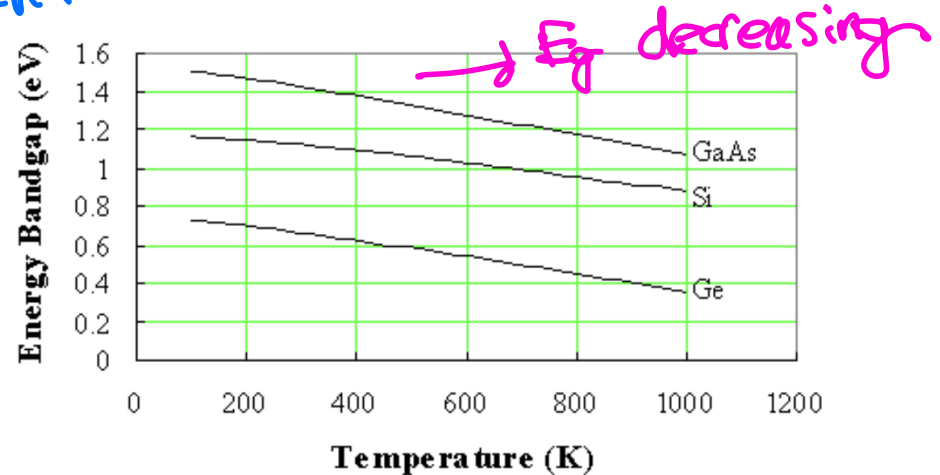
# Temperature Dependency of the Bandgap

- $E_g$  tends to decrease as the temperature is increased
- Thermal energy --> amplitude of the atomic vibrations increase --> Interatomic spacing increases
- Increased interatomic spacing decreases the average potential seen by  $e^-$ , which in turn reduces  $E_g$
- This effect is quantified by the linear expansion coefficient of a material

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{T + \beta}$$

*linear expansion coefficient*  
*fitting params*

	Germanium	Silicon	GaAs
$E_g(0)$ (eV)	0.7437	1.166	1.519
$\alpha$ (meV/K)	0.477	0.473	0.541
$\beta$ (K)	235	636	204



## E-k diagrams

- For a single free electron, relationship between kinetic  $E$  and  $\mathbf{k}$ :

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

↑  
wave  
vector

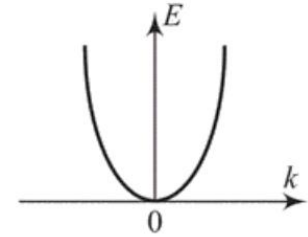


Fig. 3.8  $E$ - $\mathbf{k}$  diagram for a single free electron

- Assume a single  $e^-$  is traveling through perfectly periodic lattice
- Recall: periodicity can be different in various crystal direction
- Bloch function:  $U(\mathbf{k}_x, x) \rightarrow$  modulates space-dependent wavefunction according to periodicity of the lattice

Implications:

$$x = x + a$$

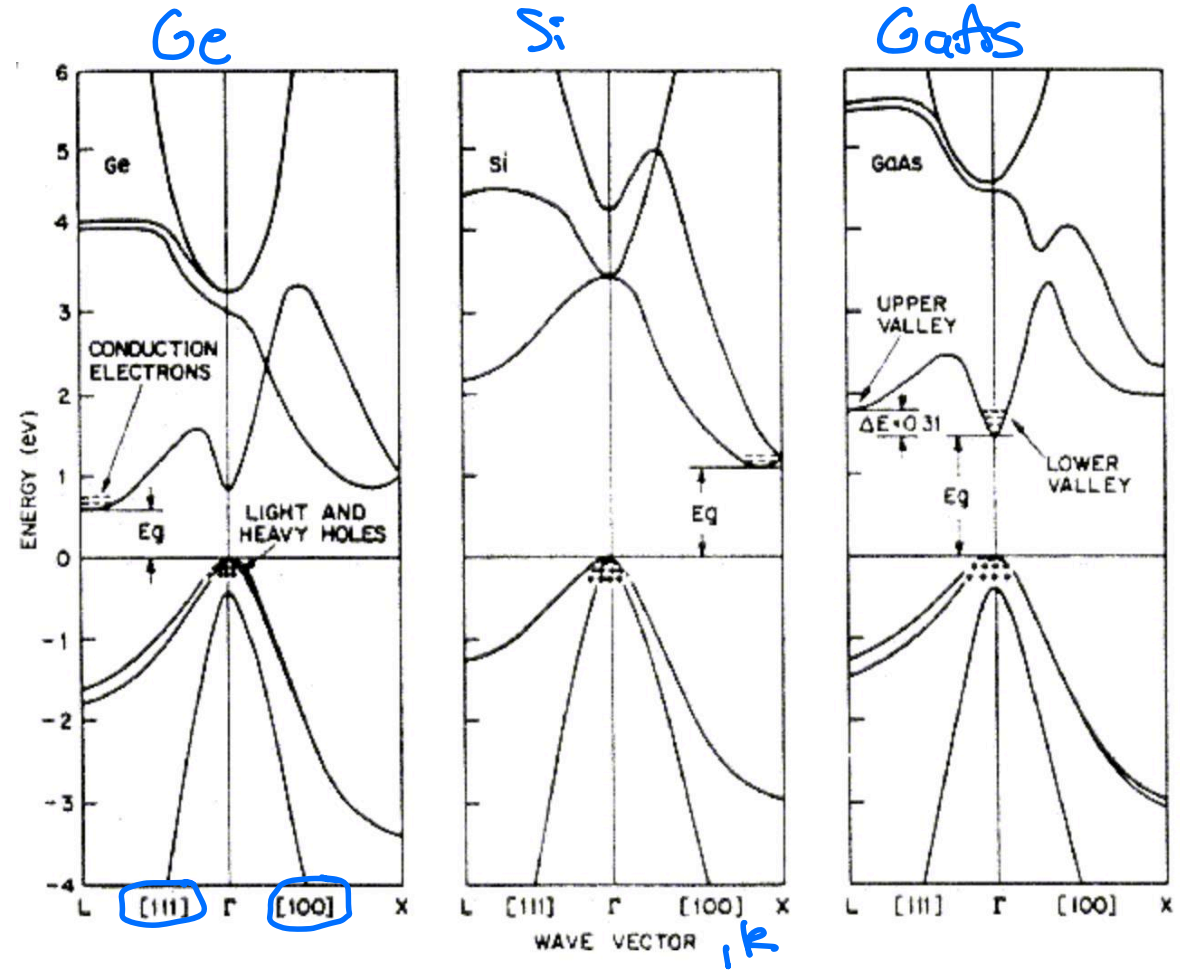
$$\psi_{\mathbf{k}}(x) = U(\mathbf{k}_x, x)e^{j\mathbf{k}_x x}$$

- Probability of detecting  $e^-$  at a specified point in crystal is a periodic function of  $x$ , since positions displaced from one another by lattice constant ( $a$ ), are equally probable
- Positions of an  $e^-$  inside a period ( $a$ ) are all different
- For a given  $k$  (which corresponds to motion in a certain direction in the crystal), only certain energy levels  $E$  are accessible to an  $e^-$



# E-k diagrams in Semiconductors

- Energy band diagrams of semiconductors are complex!
- We plot energy as a function of **k** along major directions in the crystal, since the band diagram depends on the direction in the crystal.
- Some bands completely filled, some completely empty, and some partially filled w/ e<sup>-</sup>

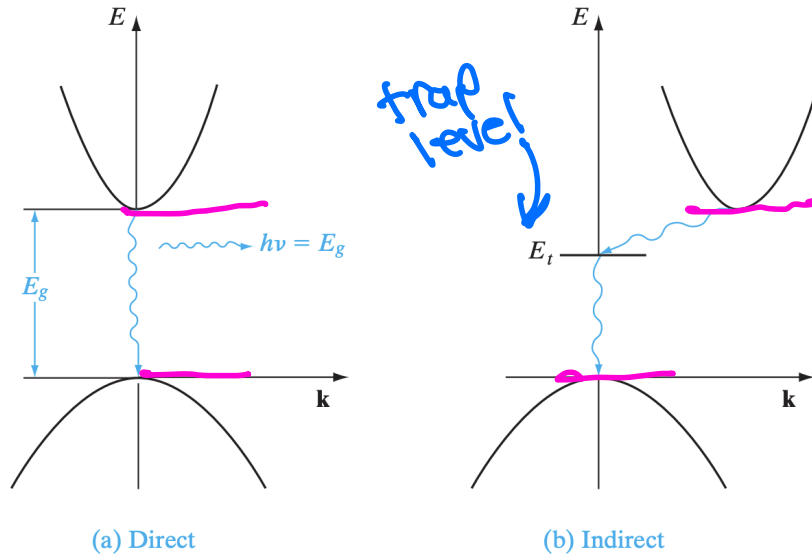


Energy band diagrams. Left to right: Ge, Si, GaAs



# Direct and Indirect Semiconductors

- $E_{c,min}^{E_{c,edge}}$  and  $E_{v,max}^{E_{v,edge}}$  do not occur at same  $k \rightarrow$  indirect bandgap
- Indirect transition, involving a change in  $k$ , requires a change of momentum for the  $e^-$
- Implications for opto electronics!



Source: Textbook

Sources: Textbook, Bhattachara, *Solid State Electronic Devices*

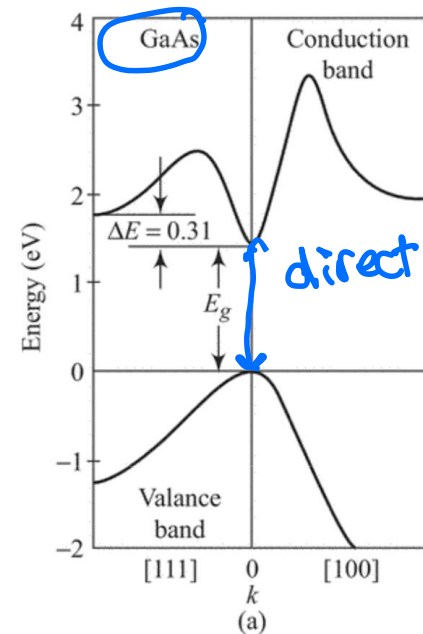


Fig. 3.10 E-k diagram for GaAs

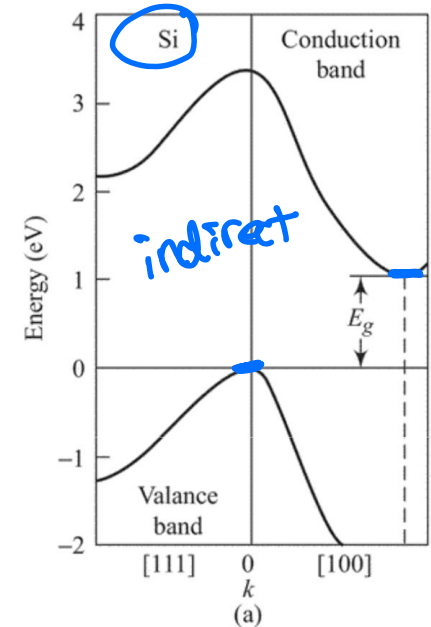
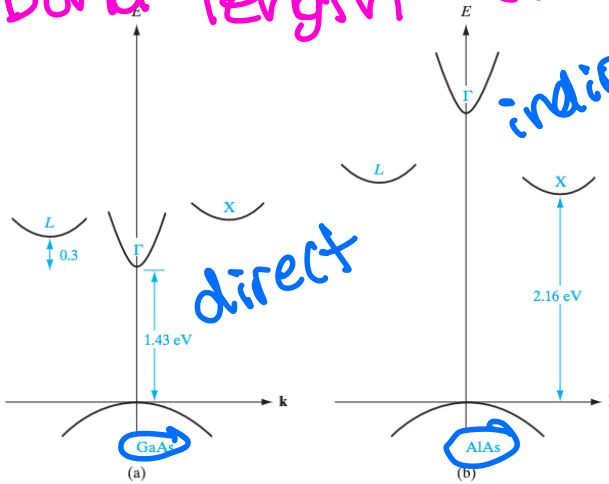


Fig. 3.11 E-k diagram for Si

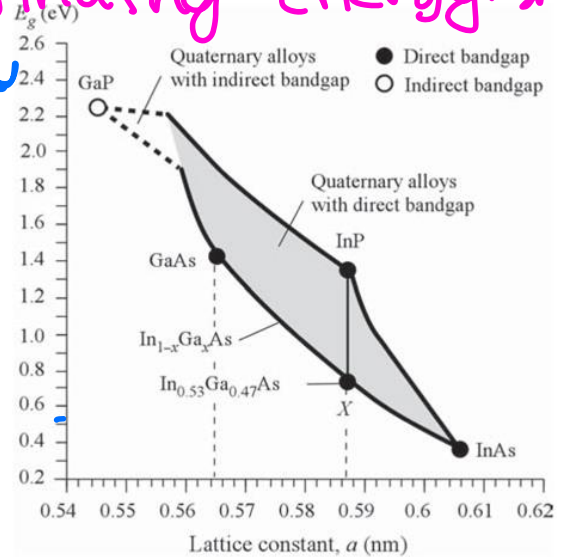
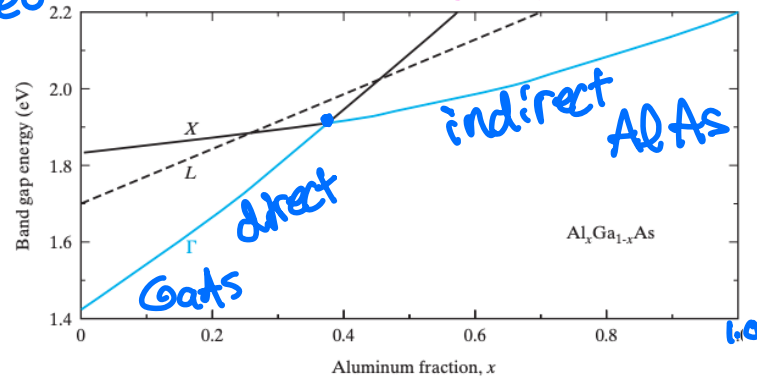
# Alloy Composition

- Energy bands vary with composition in ternary and quaternary compositions
  - Ex.  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  where  $x$  varies from 0 to 1
- Bandgap magnitude, direct or indirect, and lattice constant can be tailored
- Relationship between lattice constant and bandgap?

As  $a \downarrow$ ,  $E_g \uparrow$  (atoms packed more tightly together  $\rightarrow$  shorter bond length  $\rightarrow$  stronger bonds  $\rightarrow$  higher e<sup>-</sup> binding energy  $\rightarrow$  larger bandgap!)



Source: Textbook



Source: III-V Compound Semiconductors In Optoelectronics

# Photoelectric effect

- Einstein's external photoelectric effect:
  - Under certain conditions, light striking a metal surface can cause electrons to be ejected
  - Conditions: photon(s) must have a minimum energy (material dependent) required to eject an  $e^-$  (this is called the work function),  $\Phi$

1)  $E < \Phi$ : no emission

2)  $E = \Phi$ : emission,  $e^-$  have no kinetic energy

$$E = h\nu = \Phi$$

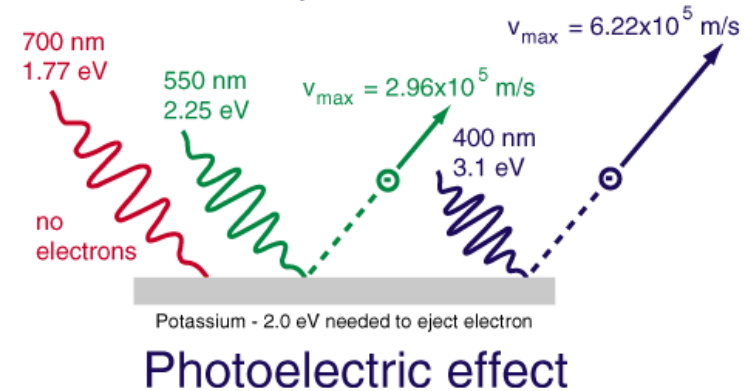
3)  $E > \Phi$ : emission,  $e^-$  have kinetic energy such that:

$$E = h\nu = \Phi + KE = \Phi + \frac{1}{2}mv_{max}^2$$

$E$  = energy of photon;  $h$  = Planck's constant

$\nu$  = frequency;  $\Phi$  = work function

$\uparrow$   $h\nu$



# Internal Photoelectric effect

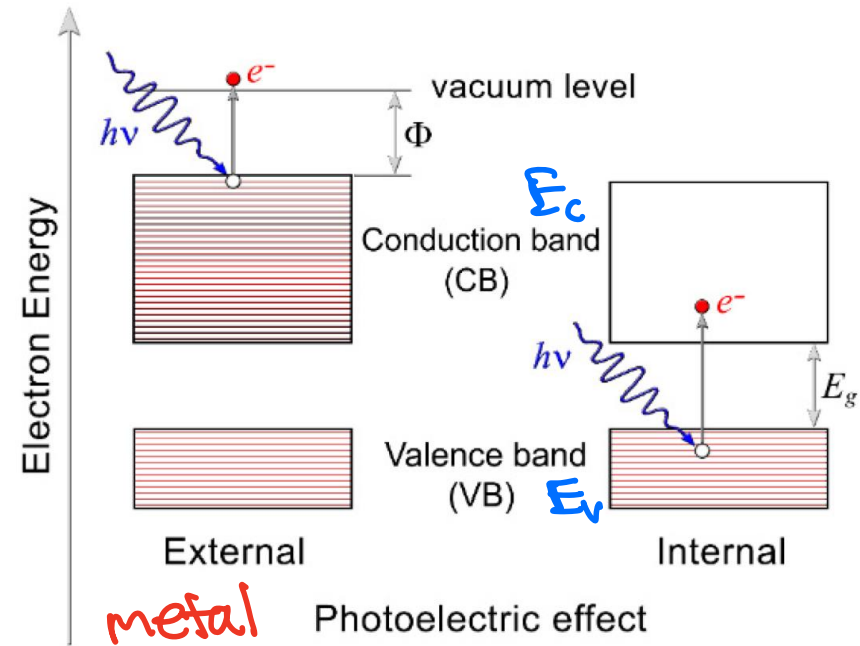
- Planck's equation for the energy of a photon:

$$E = h\nu = \frac{hc}{\lambda}$$

$h$  = Planck's constant;  $\nu$  = frequency;  
 $c$  = speed of light;  $\lambda$  = wavelength

- When light is absorbed by a semiconductor, electron-hole pairs (EHPs) are created in proportion to the light intensity (# of photons)
- Photon(s) must have sufficient energy to excite the  $e^-$  across the bandgap
- Therefore,  $E_g$  can be determined from the minimum energy ( $h\nu$ ) of photons that are absorbed!
- What if  $E_{\text{photon}} < E_g$ ?

Material will behave as if transparent



## Example: Measuring the Band-Gap Energy

- If a semiconductor is transparent to light with a wavelength longer than  $0.87 \mu\text{m}$ , what is its band-gap energy?

$$\begin{aligned} E_g &= h\nu = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3 \times 10^8 \text{ m/s})}{0.87 \mu\text{m}} \\ &= \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3 \times 10^8 \text{ m/s})(10^6 \mu\text{m/m})}{0.87 \mu\text{m}} \\ &= \frac{1.24 \text{ eV}\cdot\mu\text{m}}{0.87 \mu\text{m}} \end{aligned}$$

$$\boxed{E_g = 1.42 \text{ eV}} \rightarrow \text{check Appendix III: Probably GaAs}$$

\* 1 eV = measure of the K.E. that a single electron will gain accelerating through electric potential difference of 1 V in vacuum

$$1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$$