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

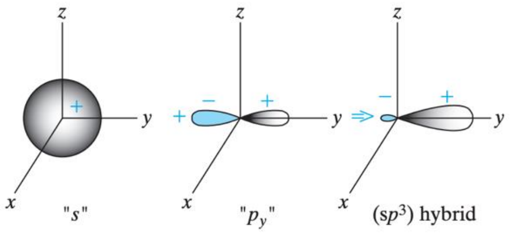
Assignments:

Reading: Streetman and Banerjee §3.1

Homework 1 due Friday Sept 12th by 5pm

Si Electronic Structure and the Bohr Model

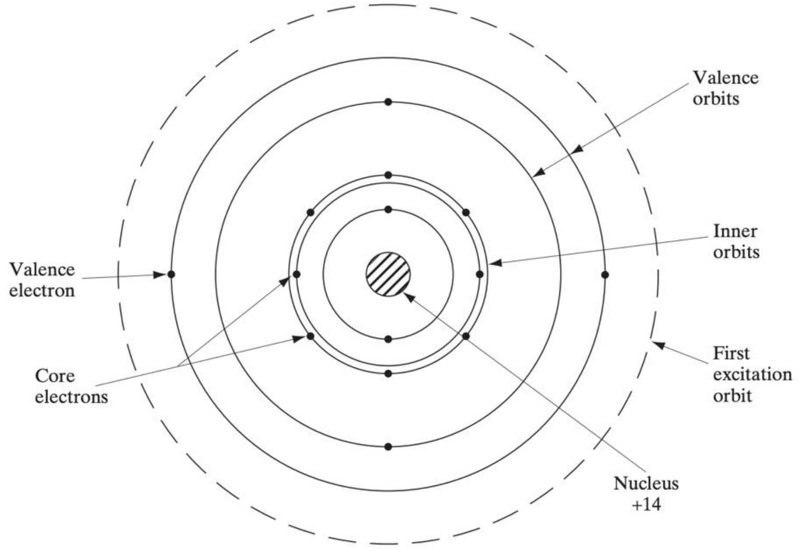
- _____ electrons
  - $1s^2 2s^2 2p^6 3s^2 3p^2$



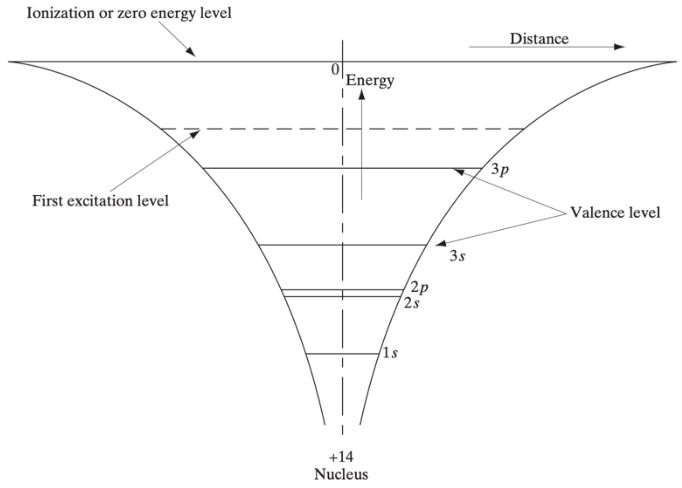
- Orbitals:
  - 10 _______ electrons (**n** = 1 and 2)
  - 4 _________ electrons (**n** = 3)
- Attractive force between ________ and _____
- Outer shell e- less tightly bound
- Bohr model:

$$E_H = -\frac{mq^4}{2\left(4\pi\varepsilon\hbar\mathbf{n}\right)^2} = -\frac{13.6}{\mathbf{n}^2}\ \text{eV}$$

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



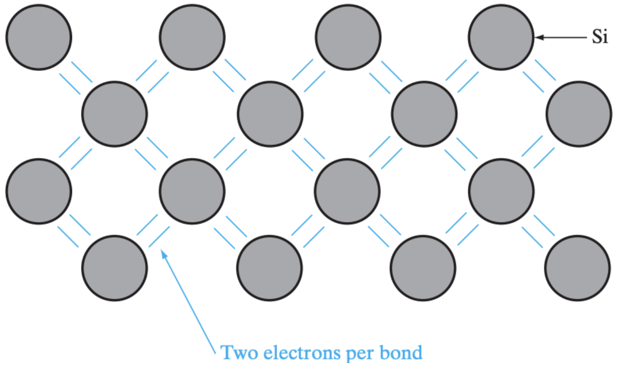
Bohr orbital model of Si atom.

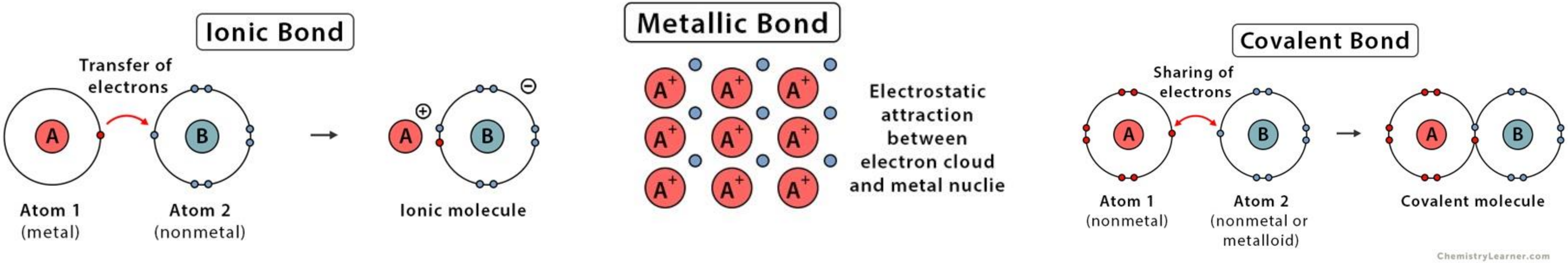


Coulombic potential in Si atom. Source: Textbook

Bonding in Solids

- Ionic ex: Na^+ (lost an e^-), Cl^- (gained an e^-)
  - All e^-'s tightly bound, good ________
- Metallic: _______ shell only partially filled -> e^- easily given up
  - Ions with closed shells in a sea of e^-, good _______
- Covalent ex: diamond lattices, like _____
  - No ______ electrons at 0K (idealized case)
- Some compound semis have _______ bonding





Sources: Textbook, Chemistry Learner

Quick: Quantum Mechanics

- Electrons propagating in _______ can be described by a wave using the "language" of QM
- Schrödinger's Wave Equation ______________
  - Each particle in a physical system is described by a ________
  - The function (and its space derivative) is continuous, finite, and ____________
- Takeaway: electrons in an atom are restricted to *discrete* energy levels

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

$$\text{Kinetic energy} + \text{potential energy} = \text{total energy}$$

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

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

Schrödinger's Wave Equation in 3D:

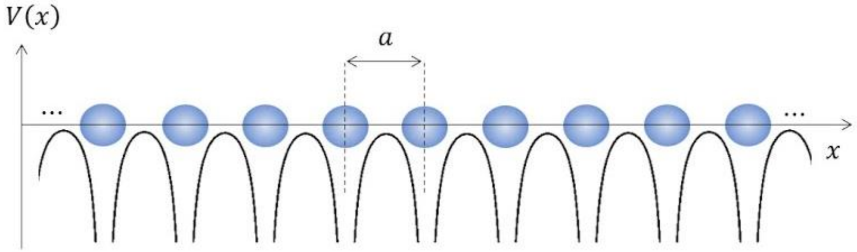
$$-\frac{\hbar^2}{2m}\nabla^2\Psi + \mathrm{V}\Psi = -\frac{\hbar}{j}\frac{\partial\Psi}{\partial t}$$

Bloch's Theorem for Electron Wave Propagation in Crystals

- e^- in a crystal are not completely free, interact with the _____________ of of the lattice
- (F. Bloch, 1928): e^- wavefunctions are described by _____________ modulated by ______________ with same periodicity as the lattice!
    - Wave _________ **k** only unique up to 2π/a
    - Only certain electron energies allowed, but those can propagate unimpeded (theoretically), as long as lattice spacing ____ is "perfectly" maintained!
- Implication: e^- can travel long distances in crystals, much longer than *a*, which impacts conduction

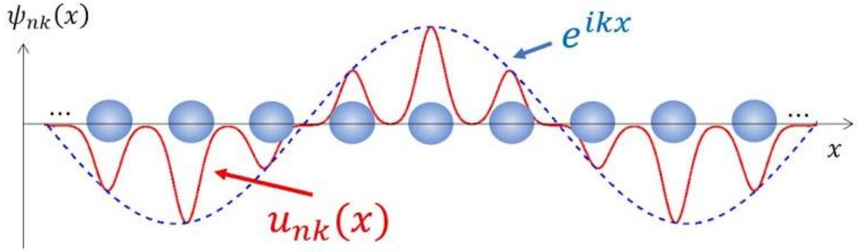
Periodic potential

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



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

$$\mathbf{n} = 1, 2, 3, \ldots$$

$$\boldsymbol{l} = 0, 1, 2, \ldots, (\mathbf{n} - 1)$$

$$\mathbf{m} = -\boldsymbol{l}, \ldots, -2, -1, 0, +1, +2, \ldots, +\boldsymbol{l}$$

$$\mathbf{s} = \pm\frac{\hbar}{2}$$

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	$\pm\frac{1}{2}$		
		1	$\pm\frac{1}{2}$		
3	0	0	$\pm\frac{1}{2}$	2	18
	1	−1	$\pm\frac{1}{2}$	6	
		0	$\pm\frac{1}{2}$		
		1	$\pm\frac{1}{2}$		
	2	−2	$\pm\frac{1}{2}$	10	
		−1	$\pm\frac{1}{2}$		
		0	$\pm\frac{1}{2}$		
		1	$\pm\frac{1}{2}$		
		2	$\pm\frac{1}{2}$		

Quantum numbers and allowable states.
Source: Textbook

Energy States and Bands

Recall:

Electrons in an ________

Restricted to discrete energy ______

→

Electrons in a ________

Restricted to a ______ of energy states, called ______

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

We will use ____ as the reference.

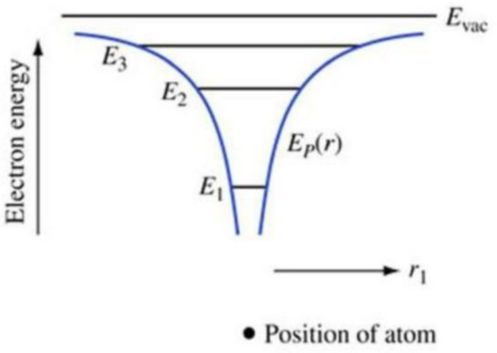
E_{vac} : energy of a ________ outside of the crystal

$$F = \square E_P = \frac{dE_P}{dr}$$

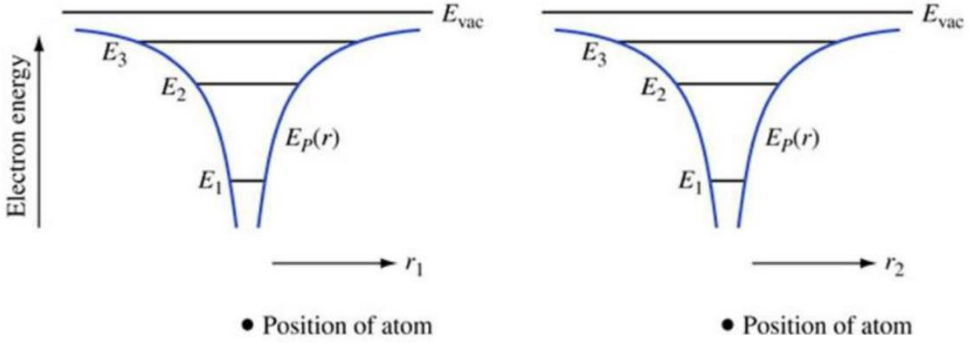
$$E_P(r = \quad) = E_{vac}$$

Energy States and Bands

Energy levels of a single ____

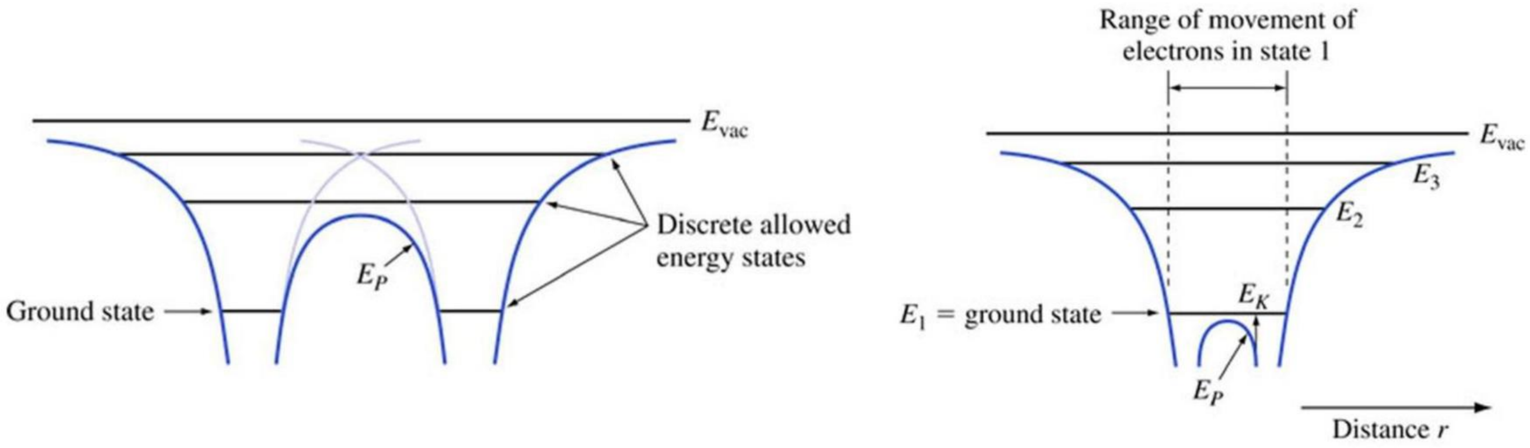


Energy levels of ________
far apart



Energy levels as two atoms moved close together

- _______________ of e^-'s will overlap
- Potential energies will _____
- Molecule may have bound states
- Shared states between atoms help keep molecule together
- There is some stable distance
  - ____!



Source: Anderson & Anderson, *Fundamentals of Semiconductor Devices*

Energy States and Bands

Another way to conceptualize the energy band model:

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

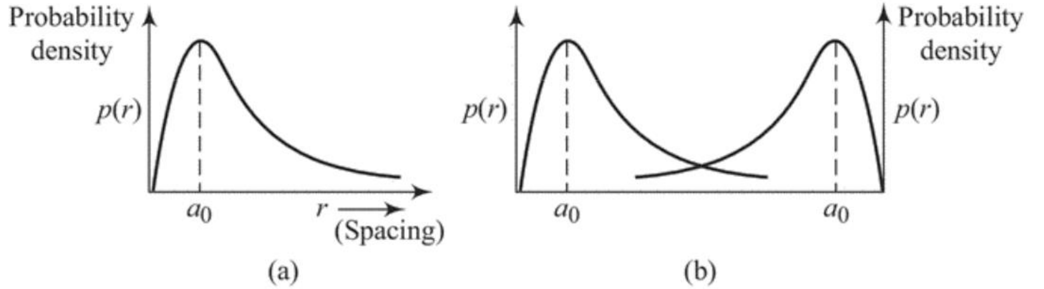


Fig. 3.1 Radial probability density function for (a) one hydrogen atom, (b) two hydrogen atoms in close proximity

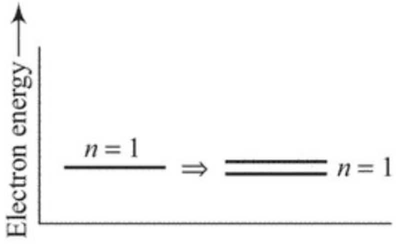


Fig. 3.2 Splitting of discrete quantized energy level

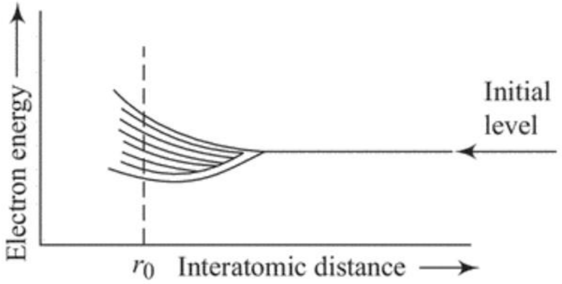


Fig. 3.3 Formation of bands of allowed energy

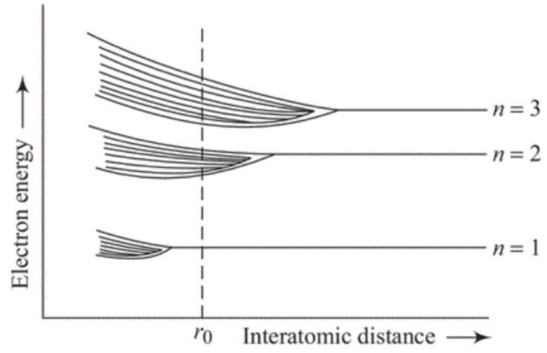
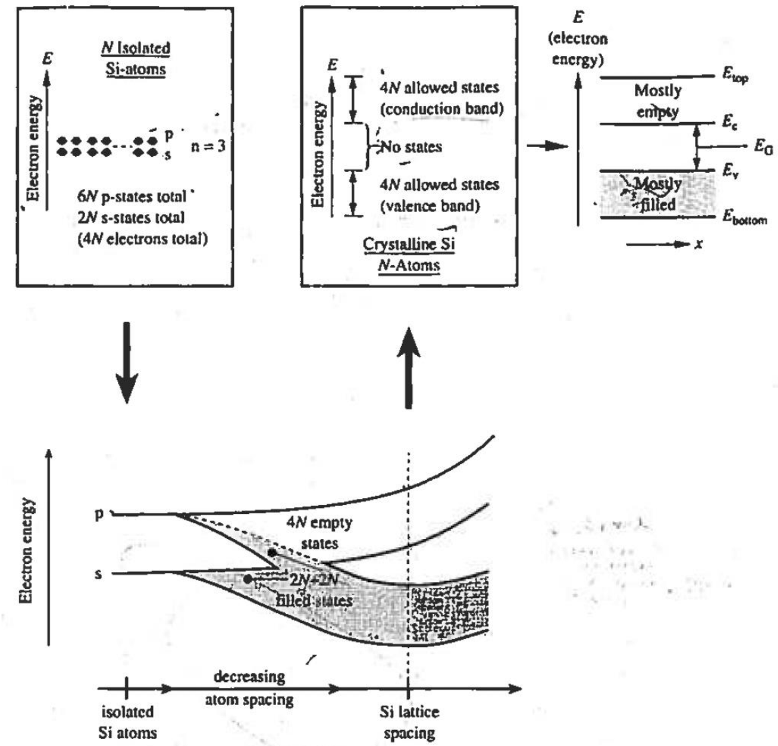


Fig. 3.4 Splitting of three energy states into allowed bands

Source: Bhattachara, *Solid State Electronic Devices*

Energy Bands in Si

- ____ and ____ states go through a band splitting when *N* atoms brought together --> 8*N* states total
- At 0K, 4*N* lower states are filled with valence e^-'s --> called ___________
- 4*N* upper states are empty --> called ____________
- Gap between these bands where there is no allowable energy state is called the ____________



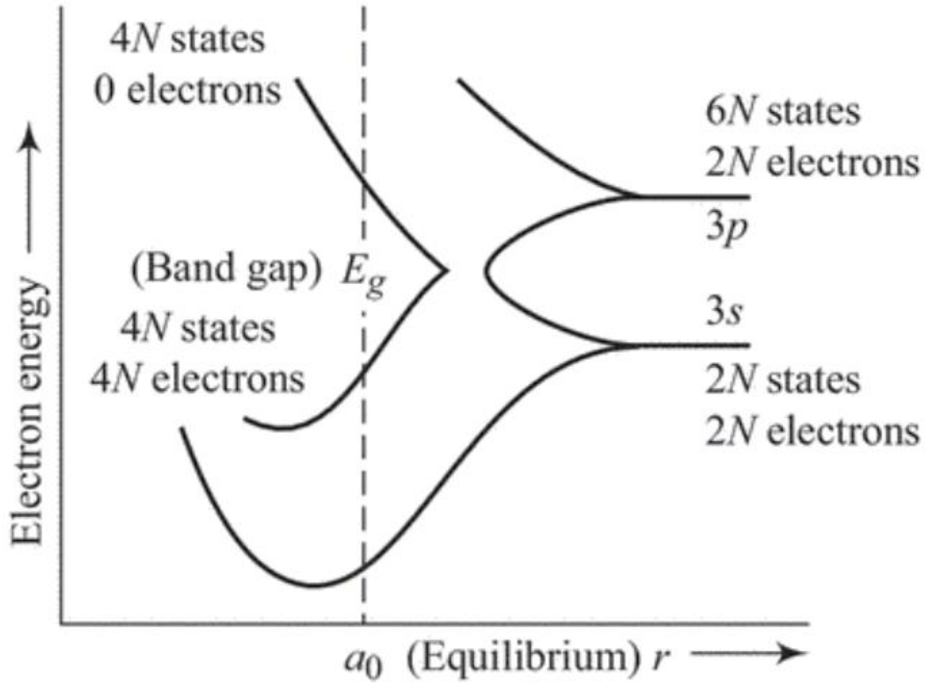
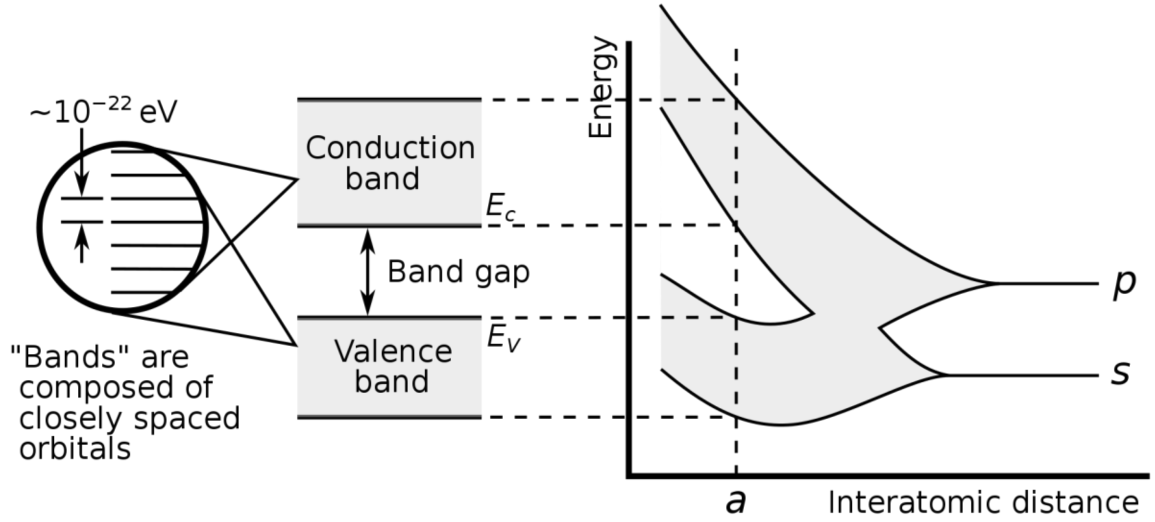


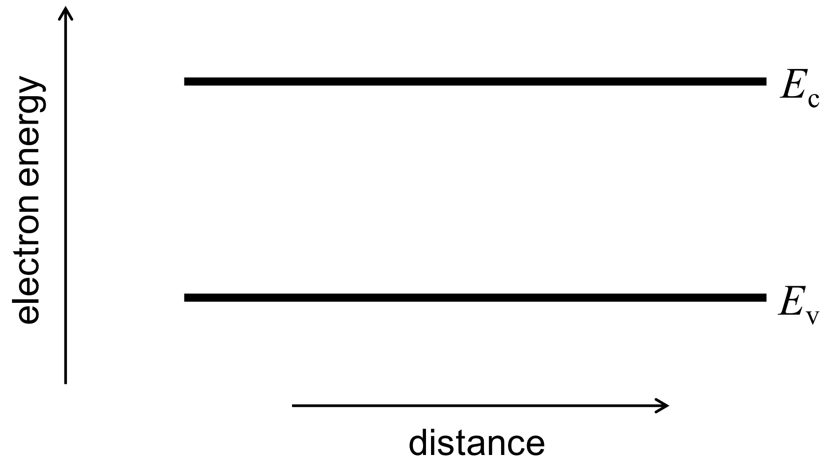
Fig. 3.6 Splitting of 3s and 3p states of silicon

Source: Pierret, *Semiconductor Device Fundamentals,* Bhattachara, *Solid State Electronic Devices*

Simplified Energy Band Diagram

- Energy band ________ are frequently simplified when analyzing semiconductor devices
- Electronic properties are dominated by the __________________________ and the __________________________.Often sufficient to only consider those bands
- Band edges are drawn as _______________
- Bandgap is taken from where the natural interatomic spacing in the crystal lattice is, ___





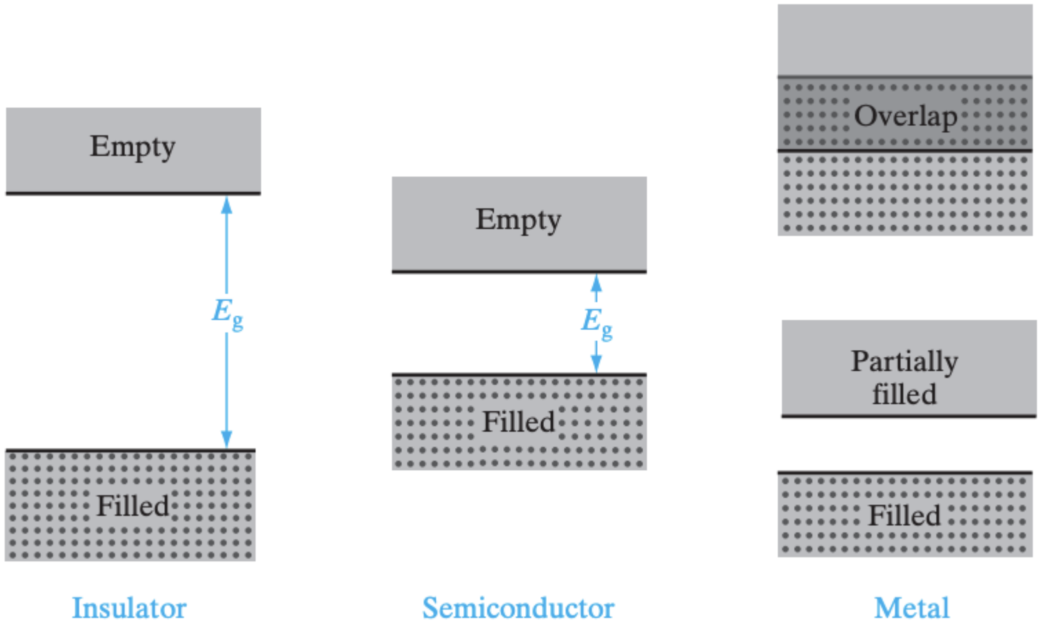
Semiconductor	InSb	Ge	Si	GaAs	GaP	ZnSe	Diamond
E_g (eV)	0.18	0.67	1.12	1.42	2.25	2.7	6.0

Sources: Wikipedia, C. Hu, *Modern Semiconductor Devices for Integrated Circuits*

Bond and Band Model of Si

Energy Band Structures in Solids

- Energy bands can be used to conceptualize the three types of ______
- For e⁻'s to experience acceleration in E-field (and contribute to ________________), they must be able to move into ______________
- Key takeaway: ______ is essentially a measure of how difficult it is to remove an electron from its bound state in a material
- A _________ band gap means it takes more energy to remove an electron!



Band structures shown at 0K.

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_2 (silica glass)	~9
LiF (lithium fluoride)	13.6

Bandgaps of common solar cell materials

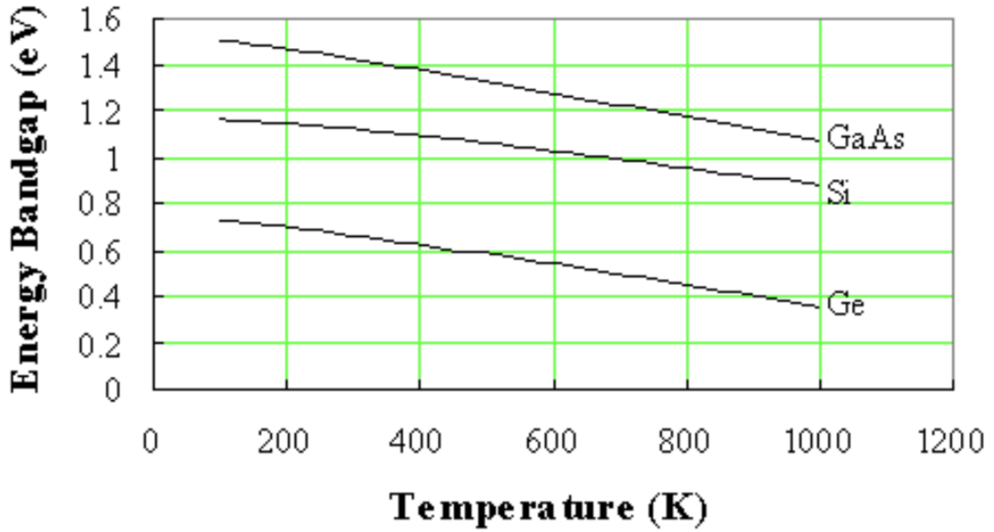
Sources: Textbook, doi: 10.1039/C4EE04073B

Temperature Dependency of the Bandgap

- E_g tends to __________ as the temperature is increased
- Thermal energy --> amplitude of the atomic vibrations ___________ --> Interatomic spacing increases
- Increased interatomic spacing decreases the average ________ seen by e$^-$, which in turn reduces E_g
- This effect is quantified by the ________________ of a material

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

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



Sources: Van Zeghbroeck, *Principles of Semiconductor Devices*

E-k diagrams

- For a single free electron, relationship between kinetic *E* and **k**:

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

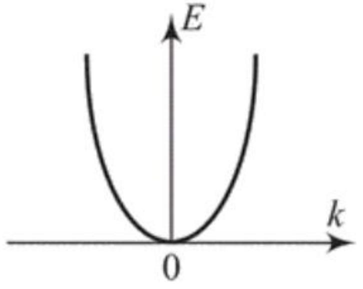


Fig. 3.8 *E*-**k** diagram for a single free electron

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

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

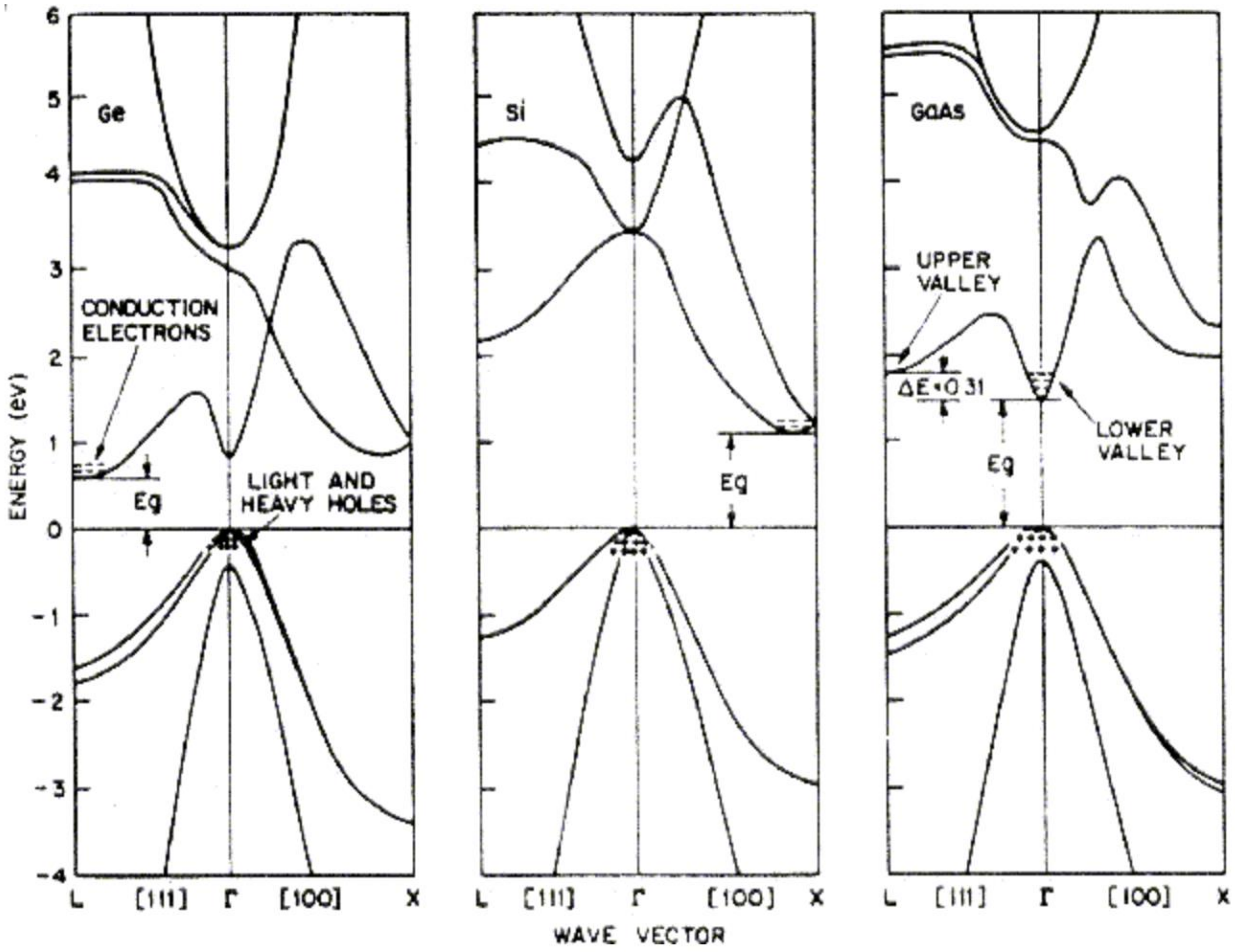
Implications:

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

Sources: Bhattachara, *Solid State Electronic Devices*

E-k diagrams in Semiconductors

- Energy band diagrams of semiconductors are complex!
- We plot energy as a function of **k** along major ___________in the crystal, since the band diagram depends on the direction in the crystal.
- Some bands completely _____, some completely _________, and some ________________

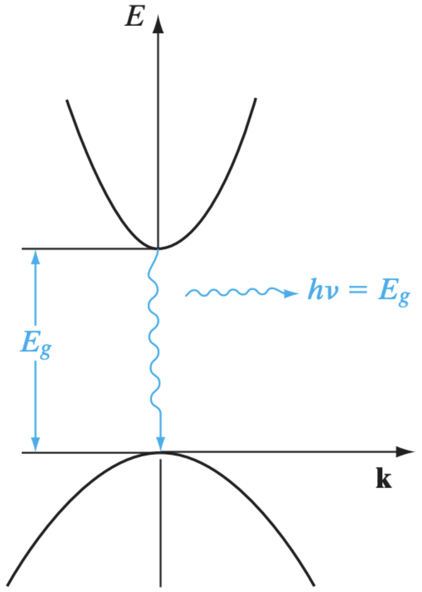


Energy band diagrams. Left to right: Ge, Si, GaAs

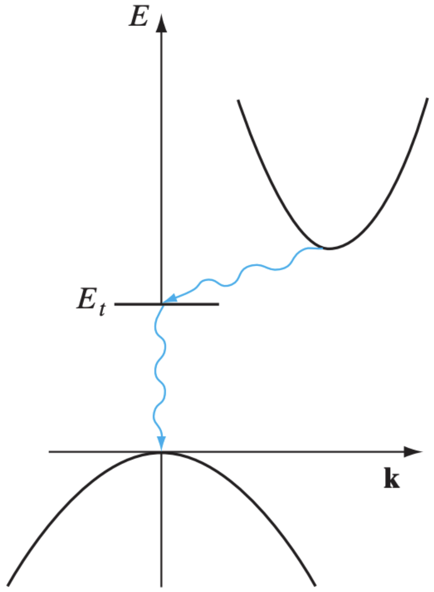
Sources: Bhattachara, *Solid State Electronic Devices*

Direct and Indirect Semiconductors

- $E_{c,min}$ and $E_{v,max}$ do not occur at same **k** --> ________
- Indirect transition, involving a change in ____, requires a change of momentum for the e$^-$
- Implications for _____electronics!



(a) Direct



(b) Indirect

Source: Textbook

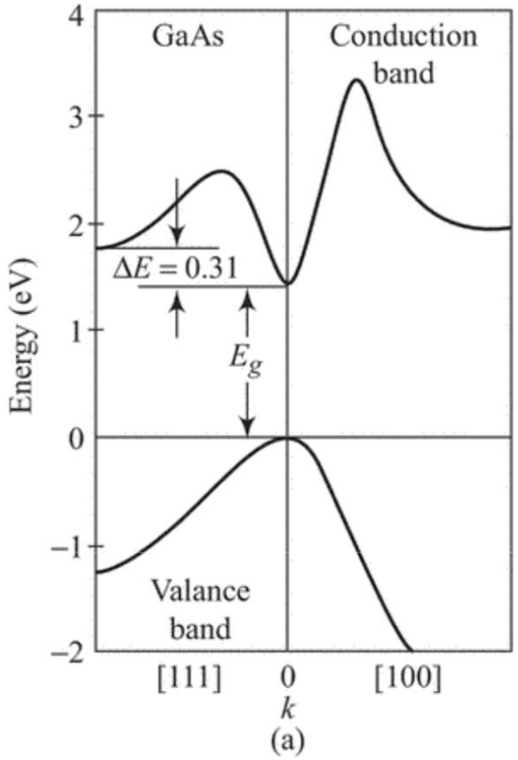


Fig. 3.10 *E*-**k** diagram for GaAs

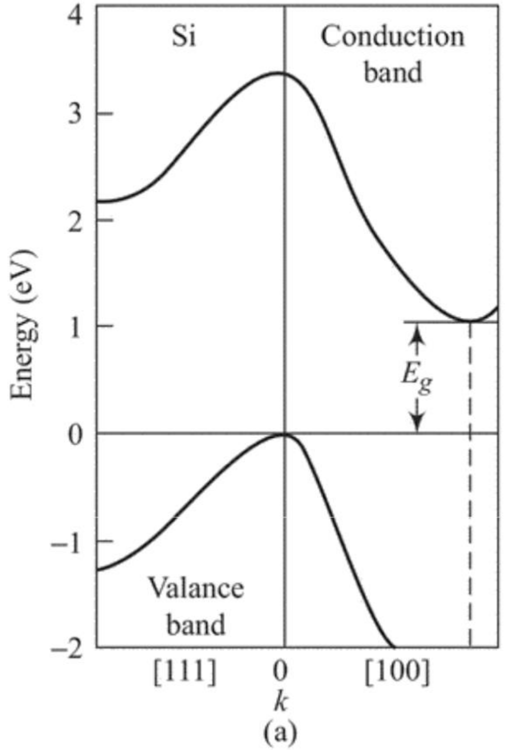
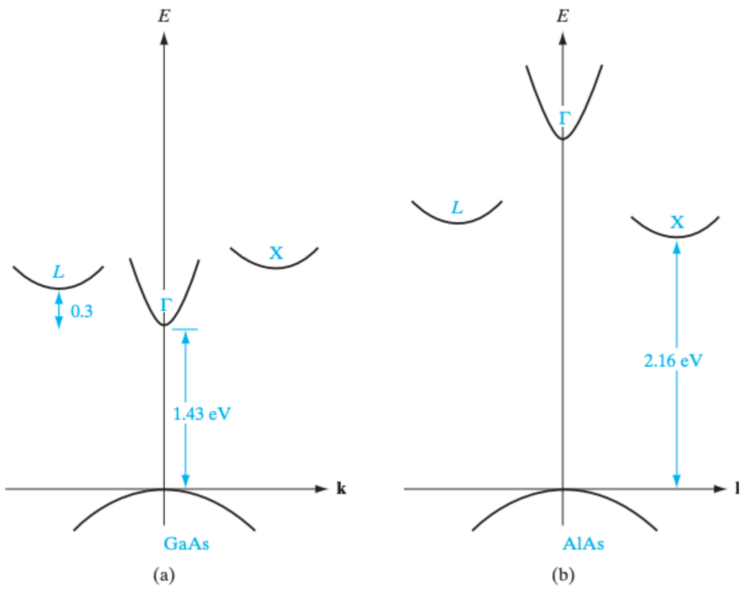


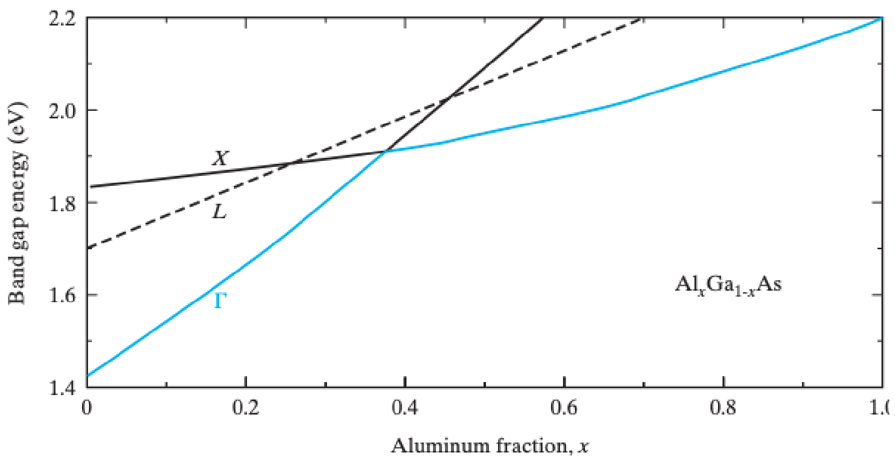
Fig. 3.11 *E*-**k** diagram for Si

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

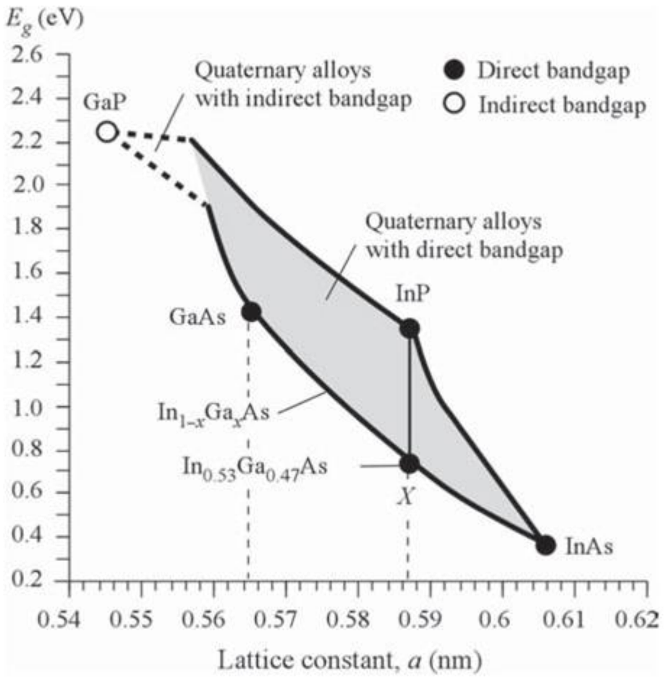
Alloy Composition

- Energy bands vary with composition in ________ and quaternary compositions
  - Ex. $Al_xGa_{1-x}As$ where x varies from 0 to 1
- Bandgap magnitude, direct or indirect, and ___________ can be tailored
- Relationship between lattice constant and bandgap?





Source: Textbook



Source: III-V Compound Semiconductors In Optoelectronics

Photoelectric effect

- Einstein's ____________ photoelectric effect:
  - Under certain conditions, light striking a ______ 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 ___________)

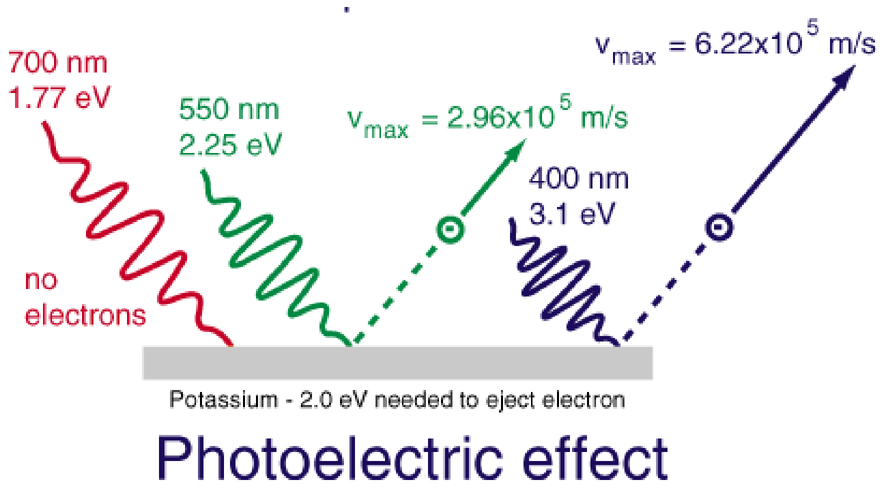
1) $E < \Phi$: no emission
2) $E = \Phi$: emisson, e^- have no kinetic energy

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

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 = ______________;
ν = frequency; Φ = work function



Source: fscj.edu

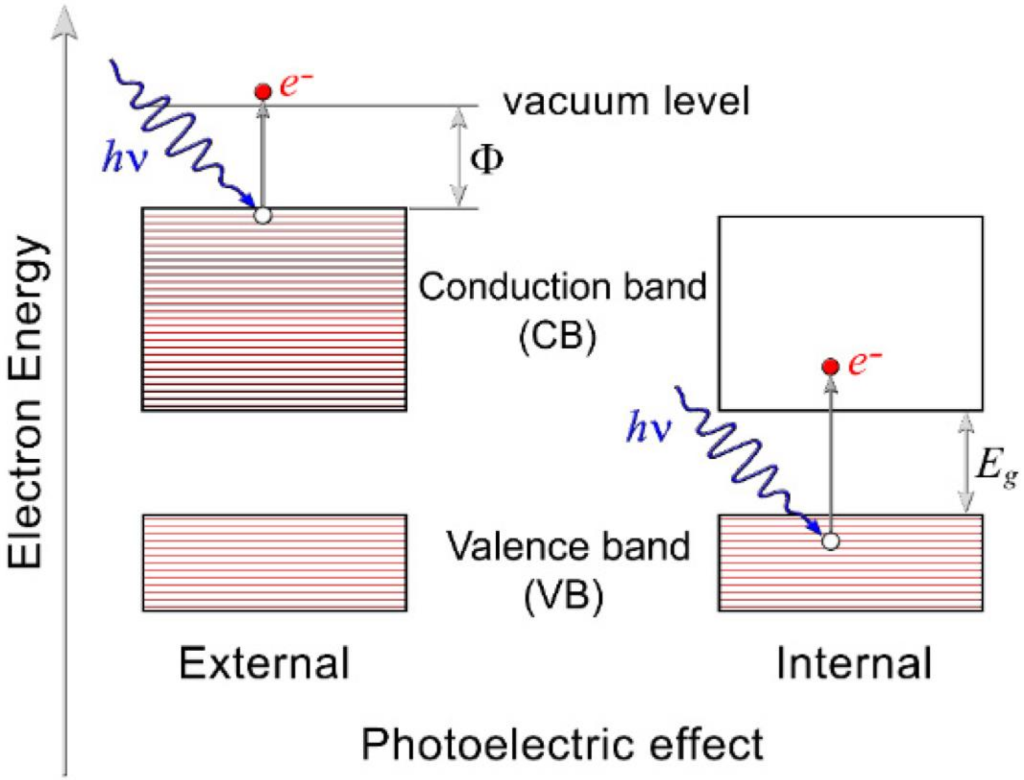
Internal Photoelectric effect

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

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

h = Planck's constant; ν = frequency;
c = speed of light; λ = wavelength

- When light is __________ by a semiconductor, electron-hole pairs (________) 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 $E_{photon} < E_g$?



Source: doi: 10.3390/cryst9100531

Example: Measuring the Band-Gap Energy

- If a semiconductor is transparent to light with a wavelength longer than 0.87 μm, what is its band-gap energy?

Source: C. Hu, *Modern Semiconductor Devices for Integrated Circuits*