Session 3:   Solid State Physics

Chemical Bonds
Energy Bands (E-K diagram)

Outline

- ◉ A
  - • B
  - • C
  - • D
  - • E
- ◉ F
  - • G
- ◉ H
- ◉ I
- ◉ J

Atomic Bonding

Atoms vibrate with small amplitudes about fixed equilibrium positions. We assume that atoms are fixed, unless phonons are considered.
Atoms look like outer valence electrons orbiting around the core. Core consists of nucleus plus inner core electrons.
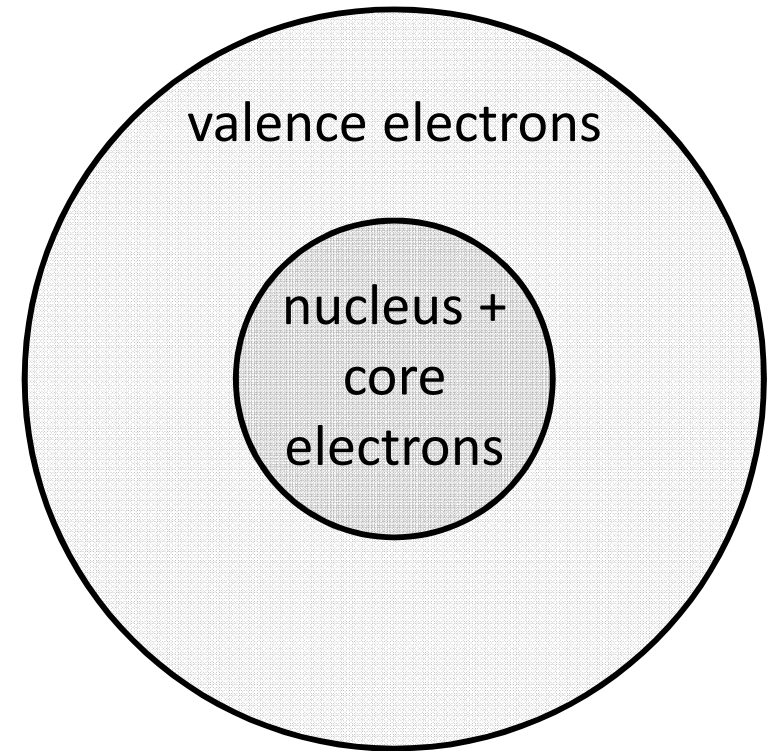
Ionic bond: Na^+Cl^-

Covalent bond: sharing e^- to complete an octet
H need only one atom to complete the octet and therefore we only have H_2. Silicon needs 4 e^- and so can bond to four other Si atoms, forming a crystal.
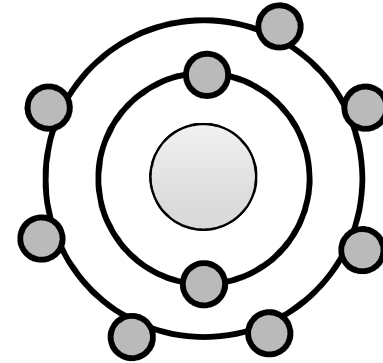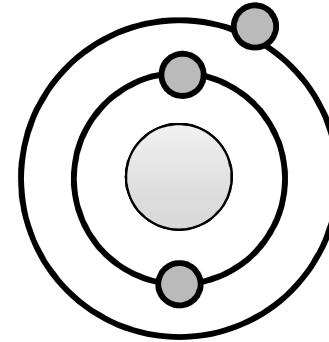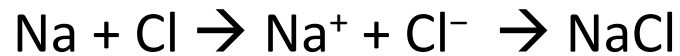
Metallic bond:

Van derWaals:

valence electrons

nucleus + core electrons

Ionic Bonding

Complete transfer of electrons from one atom (usually a metal) to another (non metal ion) (compounds only, not elemental solids). Bond comes from electrostatic attraction between ions.

$$Na + Cl \rightarrow Na^+ + Cl^- \rightarrow NaCl$$

All ionic compounds have a degree of covalent bonding. The larger the difference in electronegativity between two atoms, the more ionic the bond is.
• Bond is strong (high melting point, large elastic modulus)
• Not directional (high density, high coordination number)
• Compounds only
• Good insulators (except near melting point)
• Transparent up to UV (strong bonds →electrons need a lot of energy to become free)
Mathematical form: Energy ~ 1/r , Example: Sodium Chloride

Ionic Bonding

Coulomb force:

$$F = \frac{e^2}{4\pi\epsilon_0 r^2}$$

Energy needed to separate charges e and -e

$$E = \int F.dr = \int_{0.2nm}^{\infty} \frac{-e^2}{4\pi\epsilon_0 r^2} dr = 7eV$$

Polar Bonds

Partly covalent and partly ionic. The more electronegative element will have more negative charge.

Covalent Bonding

Equal sharing of electrons between atoms → both atoms have full shells (Example: Diamond, Silicon)
Note continuum of behavior, ionic → covalent (e.g. III-V compounds GaAs, InSb, are partially covalent and partially ionic.)
• Bond is strong (high melting point, large elastic modulus)
• Directional (from orientation of QM orbitals) → low density
• Saturable (limited number of bonds per atom) ↑
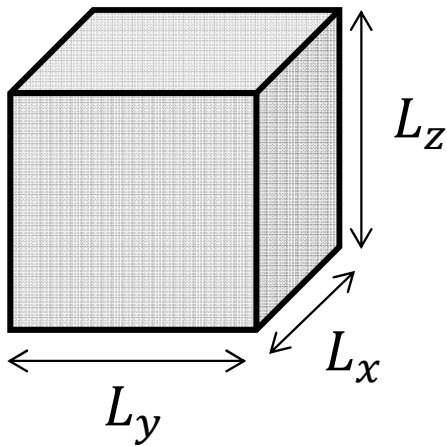• Good insulators

Covalent Bonding: Square well potential

$$V = \begin{cases} 0 & \text{inside cube} \\ \infty & \text{outside cube} \end{cases}$$

$$-\frac{\hbar^2}{2m_0} \nabla^2 \Psi = E\Psi$$

$$\Psi = \frac{2\sqrt{2}}{\sqrt{L_x L_y L_z}} \sin \frac{n_x \pi x}{L_x} \sin \frac{n_y \pi y}{L_y} \sin \frac{n_z \pi z}{L_z}$$

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$
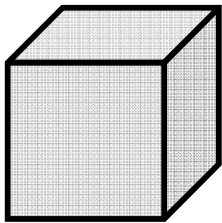
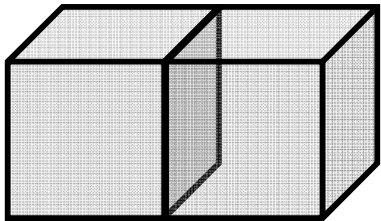# Covalent Bonding: Square well potential

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

Energy of a particle
confined to a cube L×L×L

$$E = \frac{3h^2}{8ml^2}$$

Energy of a particle
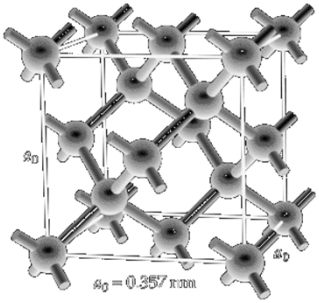confined to a cube L×L×2L

$$E = \frac{9h^2}{32ml^2}$$

Decrease in energy:

$$E = \frac{3h^2}{16ml^2}$$

For L= 0.2 nm: $\Delta E = 14$eV
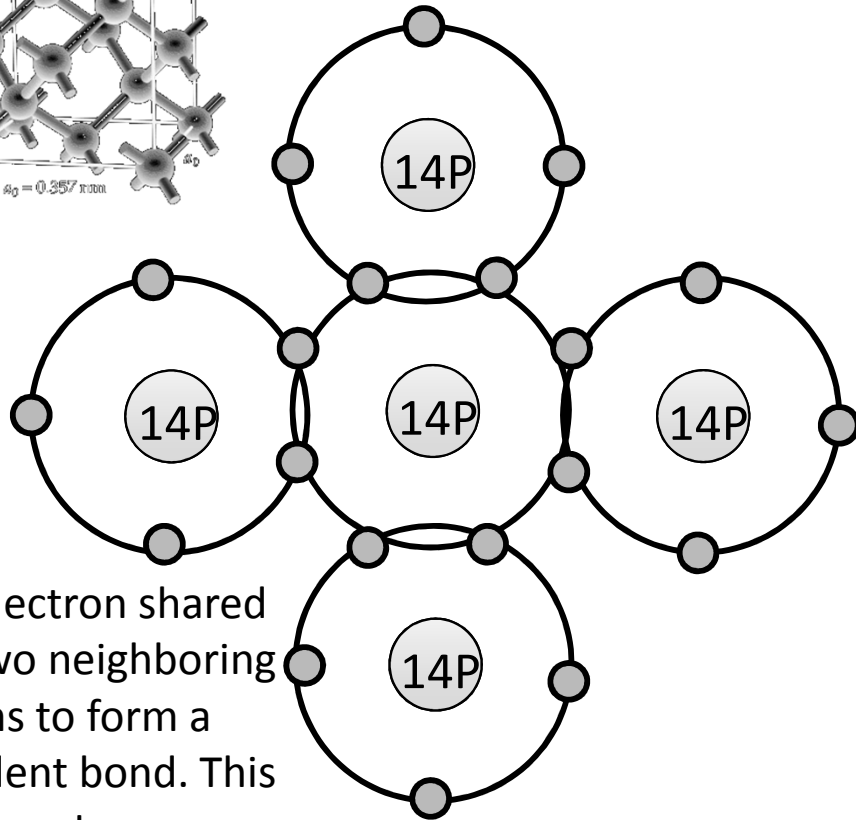
9

Silicon

2D representation

Generation / Recombination
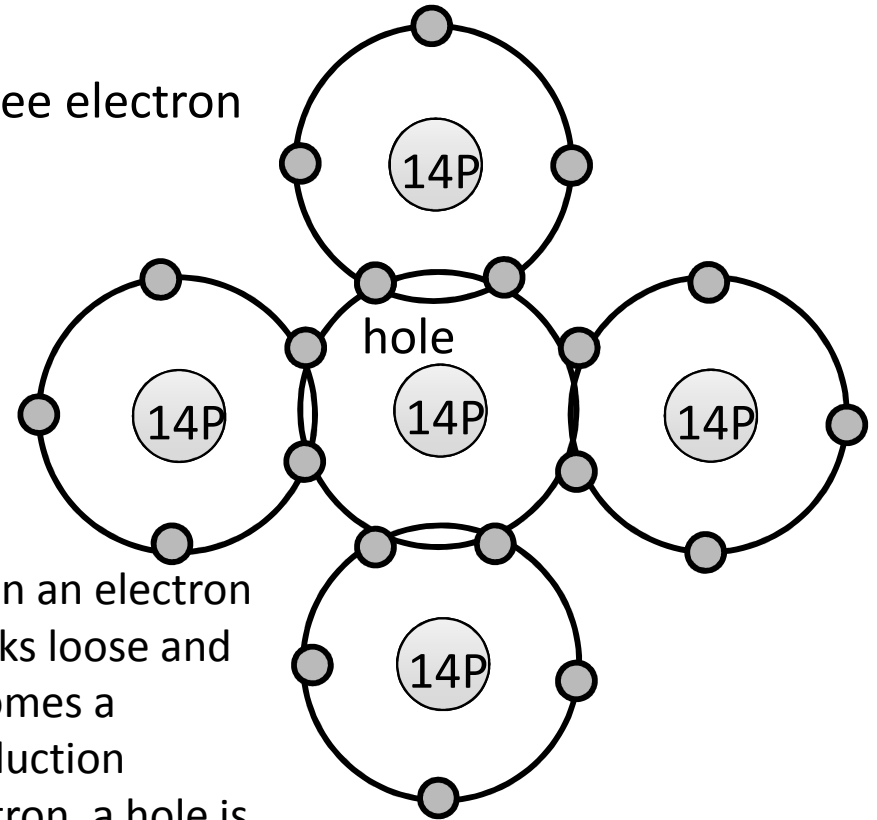
Free electron

hole

An electron shared by two neighboring atoms to form a covalent bond. This way an atom can have a stable structure with eight valence band electrons.
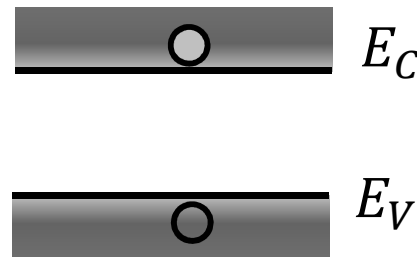
When an electron breaks loose and becomes a conduction electron, a hole is also created.

E_C

E_V

E_C

E_V

10

Metallic Bonding

Positive ions plus gas (sea) of electrons. Think of this as the limiting case of ionic bonding in which the negative ions are electrons. (BUT electrons can't be forced to sit at lattice points from Uncertainty Principle: $\Delta p \Delta x \geq h/2$ as for electrons m is small so the zero point energy $\Delta E = \Delta p^2/2m$ is very large; the electrons would
shake themselves free and are therefore delocalized)
• Bonds are non directional (high coordination number, high density, malleable and ductile)
• Variable strength
• Free electrons → high electrical conductivity, shiny (Electric field associated with incident light makes free electrons at surface move back and forth, re-radiating the light, as a reflected beam)
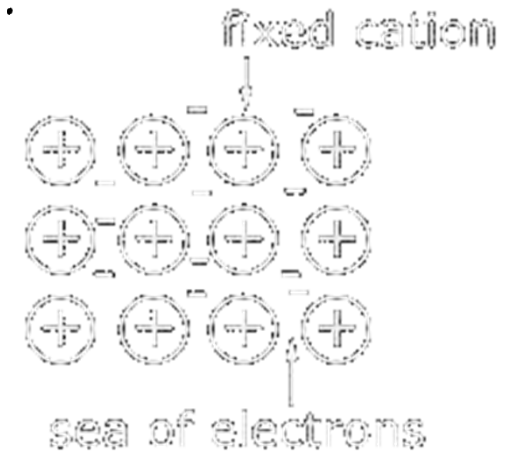
fixed cation

sea of electrons

11
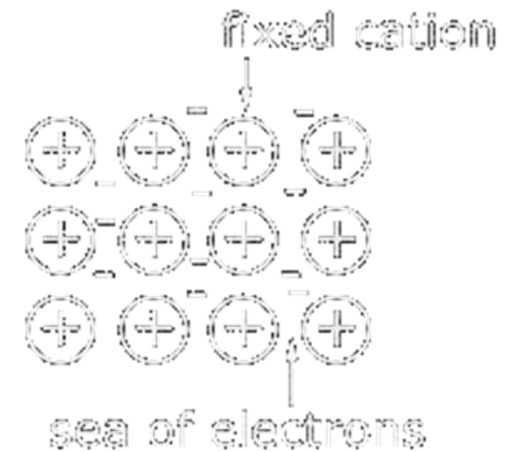
Metallic Bonding

The electron wave functions spread out over the entire crystal.
A three dimensional potential square well is a simple model
for a metal.

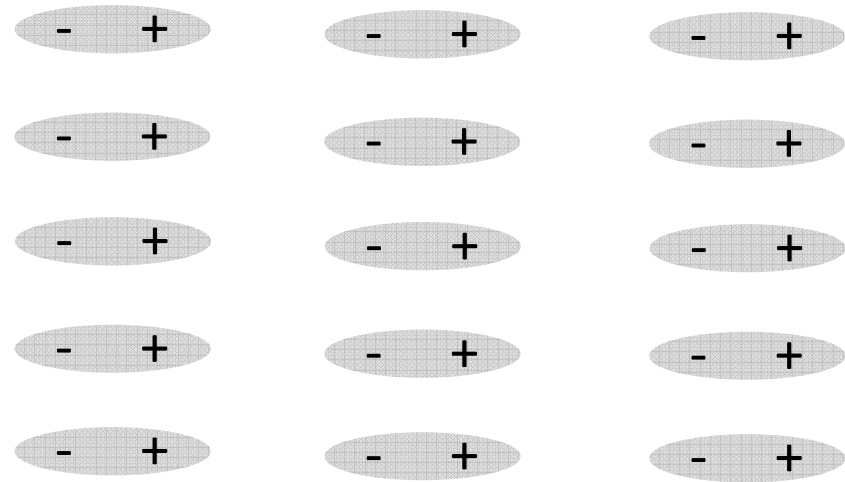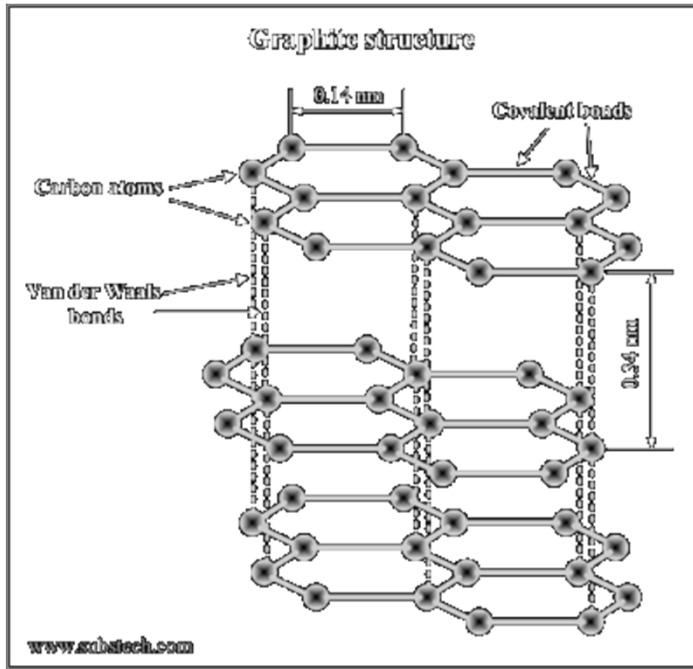$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

fixed cation

sea of electrons

Energy mostly determines by Electrostatic force!

Van der Waals Bond

Even a neutral atom with a full shell, can, at a given instant, have a dipole moment (i.e. one side of the atom more positive than the other) This instantaneous dipole will induce a dipole in a neighboring atom, and the resulting dipole-dipole interaction is the origin of the van der Waals bond. Although the original dipole time-averages to zero, the interaction does not – it is always attractive. Energy $\sim 1/r^6$
• Bond is weak ($\rightarrow$low melting point, large expansion coefficient)
• Non directional so high coordination number BUT
• Long bond lengths ($\rightarrow$low density)
Examples: Solid inert gases (Argon, Neon), molecular solids (solid Oxygen)

13

Hydrogen Bonding

Hydrogen loses its electron and becomes positively charged particularly easily. Therefore the region of a molecule around a hydrogen atom is often quite positive, and this allows an electrostatic bond to form between it and negative parts of neighboring molecules.
Example: ice – the strength of the hydrogen bond explains the anomalously high melting point of ice
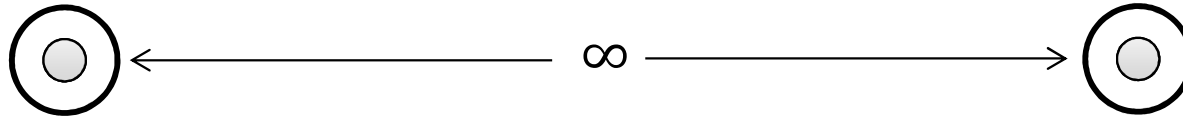
Comparing Bonds

Bond	Energy (GPa)	Example of Bond
Covalent	1,000	Diamond
Ionic	30 – 100	Salt and Ceramics
Metallic	30 – 100	Metals
Hydrogen	8	Ice
Van der Waals	2	Polythene

15

Energy Bands

Always simplify!

Simplest state: Isolated atom
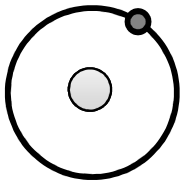
$$\infty$$

Periodic atoms:

d d d d
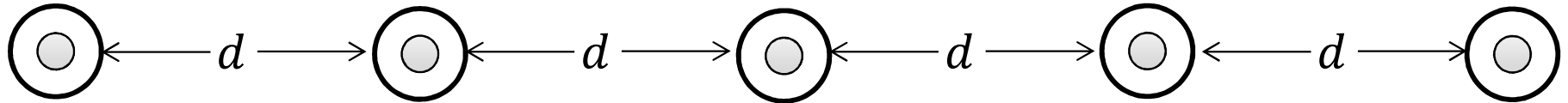
Single isolated atom:
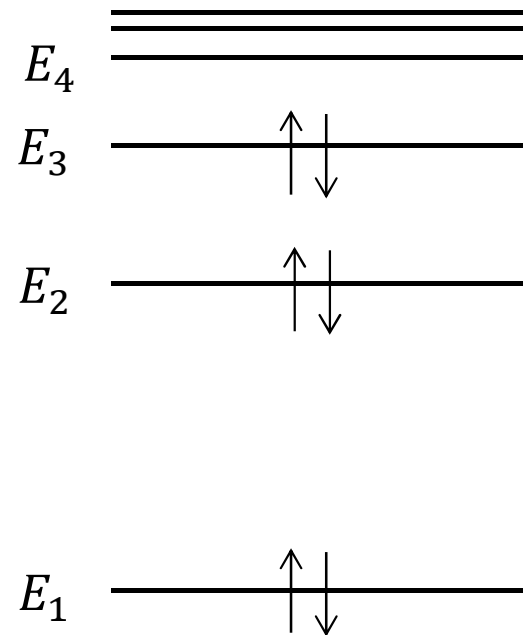
Si:

Z = 14

H:

$1s^2 2s^2 2p^6 3s^2 3p^2$
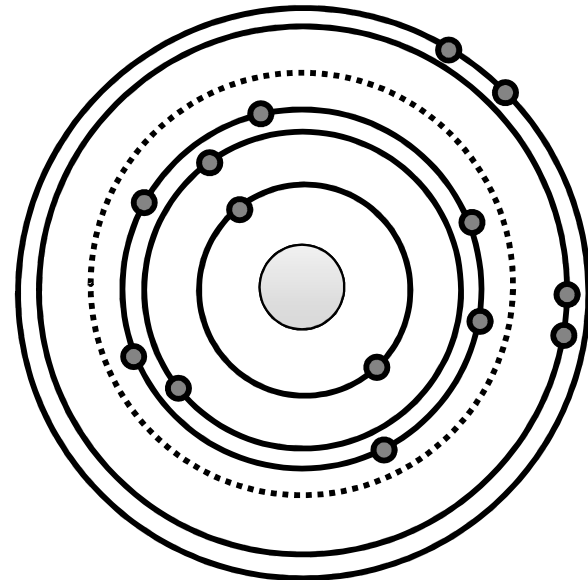
Bohr Atomic Model
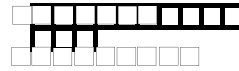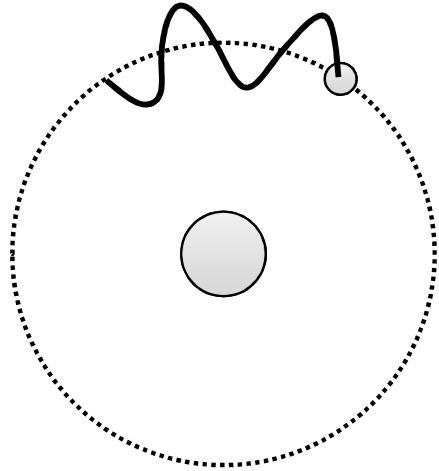
wave-particle duality $\lambda = h/p$

$$mvr = n\hbar$$

de Broglie standing wave

Energy Bands:

E_4

E_3

E_2

E_1
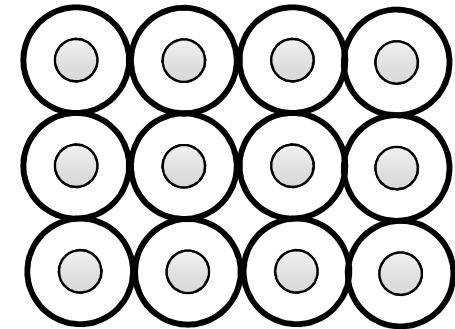
Bohr Atomic Model
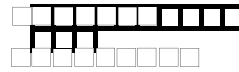
Single atom:

2 atoms:

N atoms:

E_4

E_3

E_2

E_1

E_{32}
E_{31}

E_{22}
E_{21}

E_{12}
E_{11}

2N electrons

E_{2n}
$\vdots$
E_{22}
E_{21}

E_{1n}
$\vdots$
E_{12}
E_{11}

allowed energies
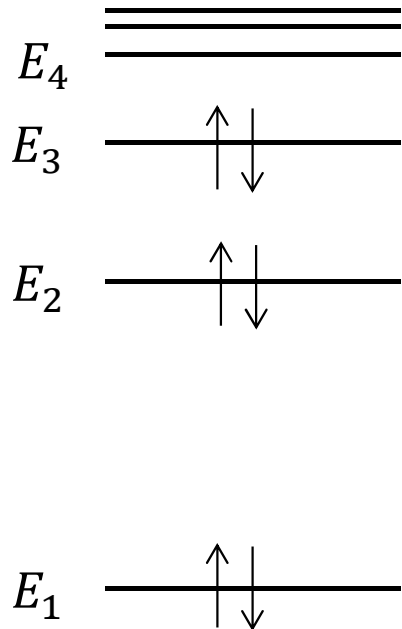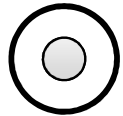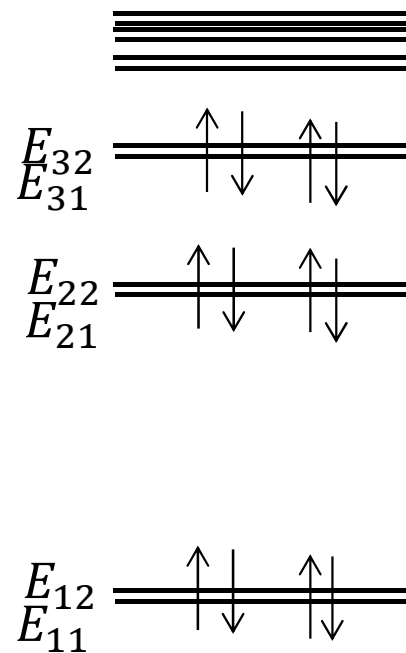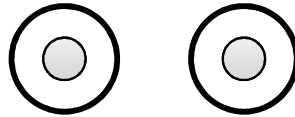
forbidden energies
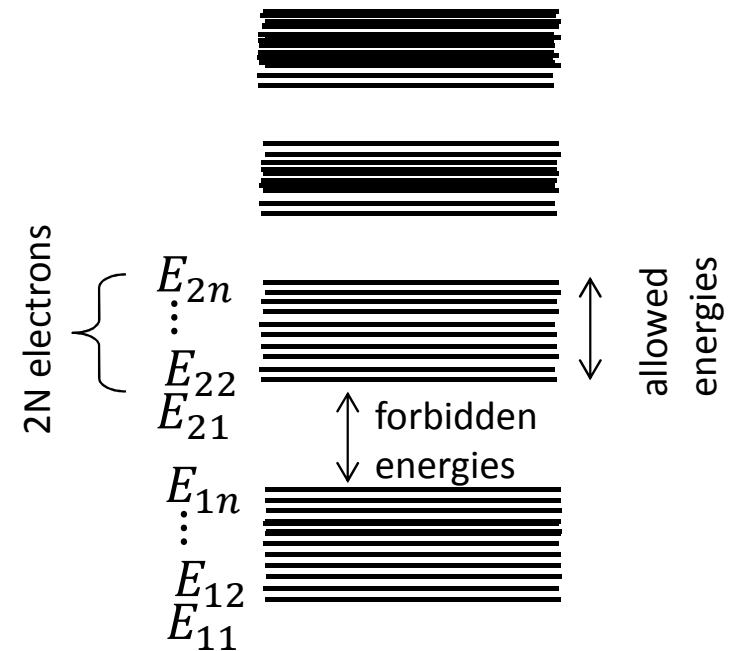
Pauli exclusion principle

18

In a solid, there are so many electrons with energies very near each other that 'bands' of states develop.
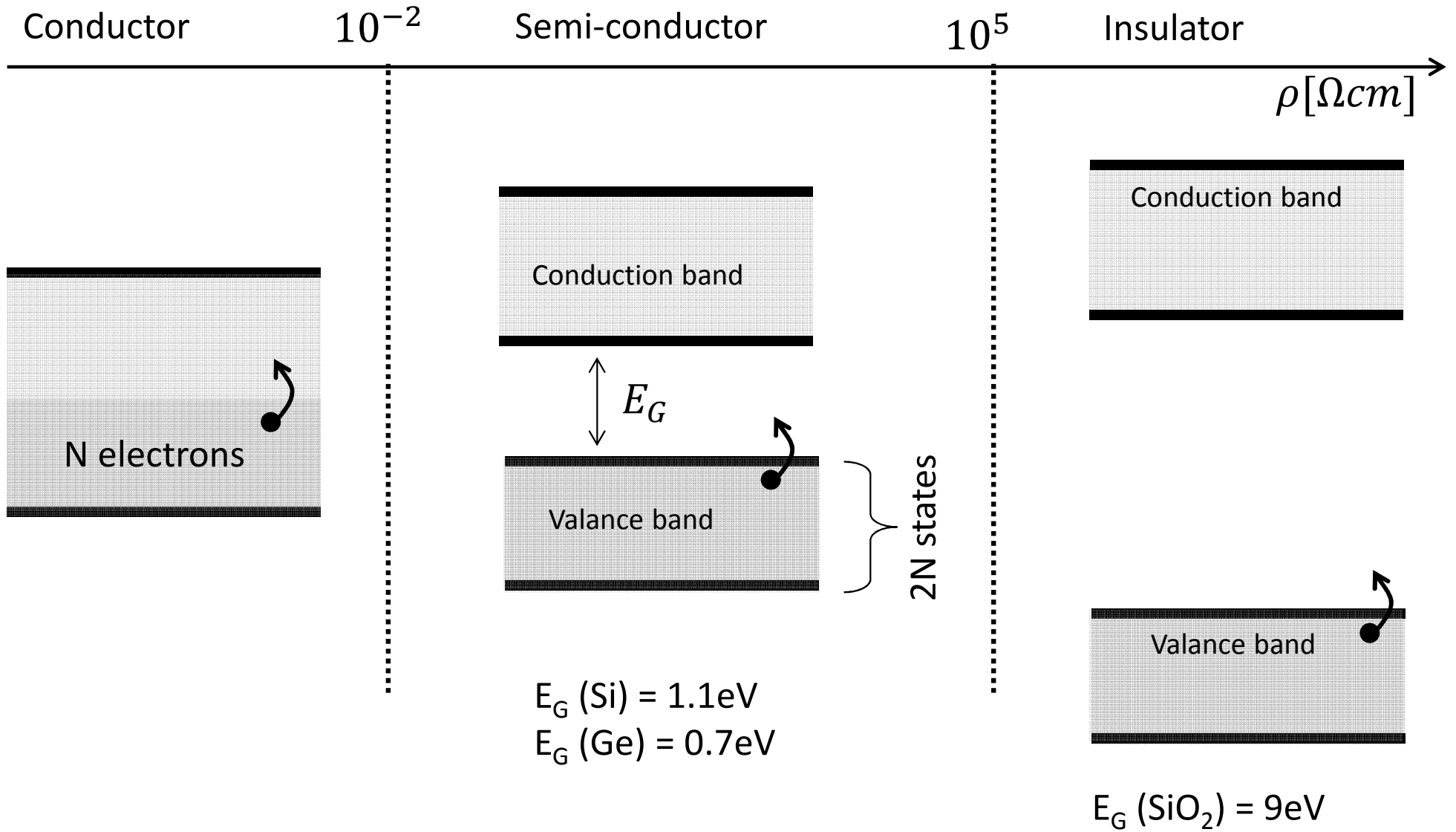
Formation of energy bands as a diamond lattice crystal is formed by bringing isolated silicon atoms together

Conduction band

E_C

E_G

E_V

Valance band

x

Electron energy

4N states
0 electrons

4N electrons
4N states

5 A

3p

2N electrons
6N states

3s

2N electrons
2N states

Lattice spacing

solid

Isolated atoms
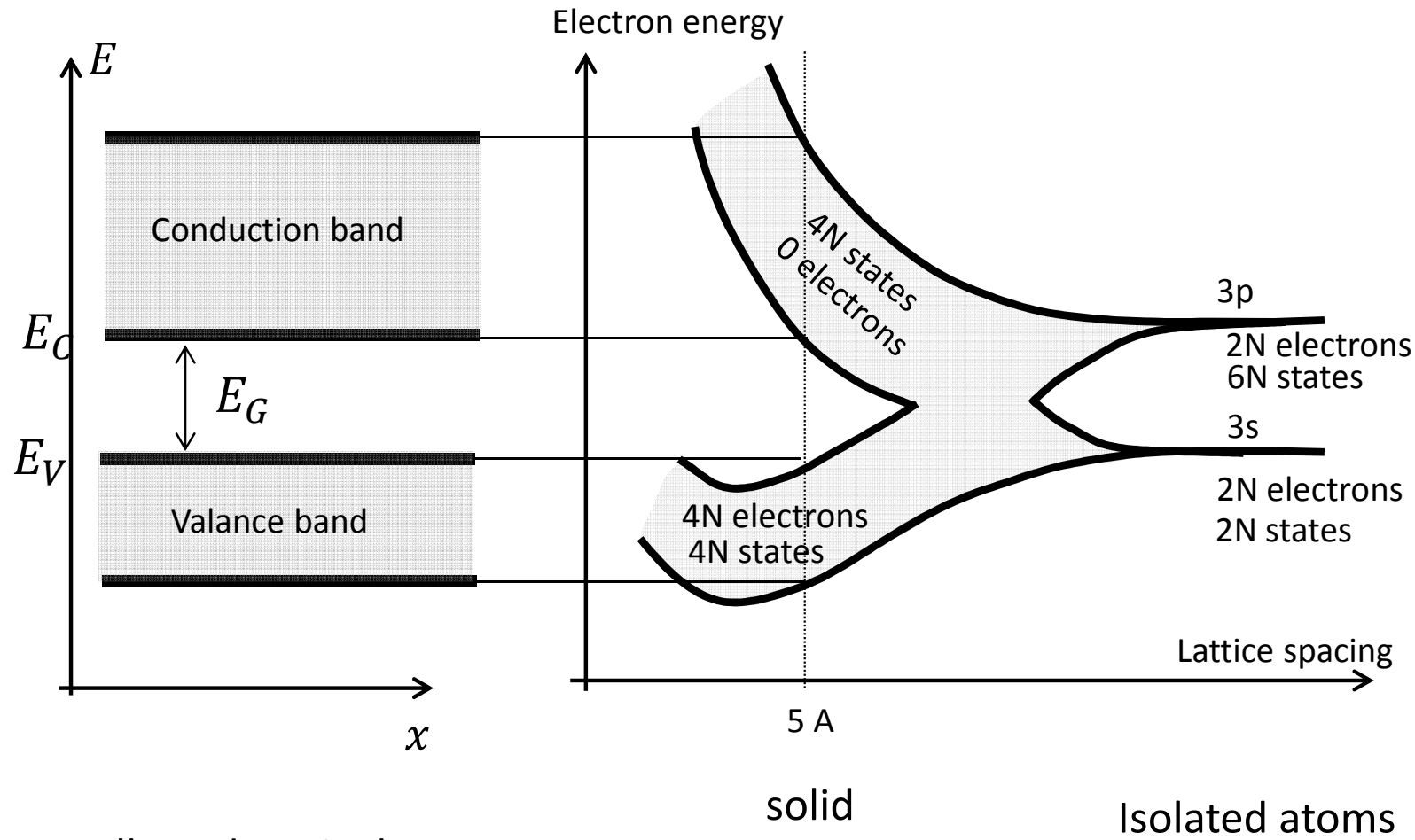
All we draw is the "band diagram"

19

Materials

Conductor $\qquad 10^{-2} \qquad$ Semi-conductor $\qquad 10^{5} \qquad$ Insulator

$$\rho[\Omega cm]$$

N electrons

Conduction band

E_G

Valance band

2N states

Conduction band

Valance band

E_G (Si) = 1.1eV
E_G (Ge) = 0.7eV

E_G (SiO$_2$) = 9eV

empty seat / filled seat
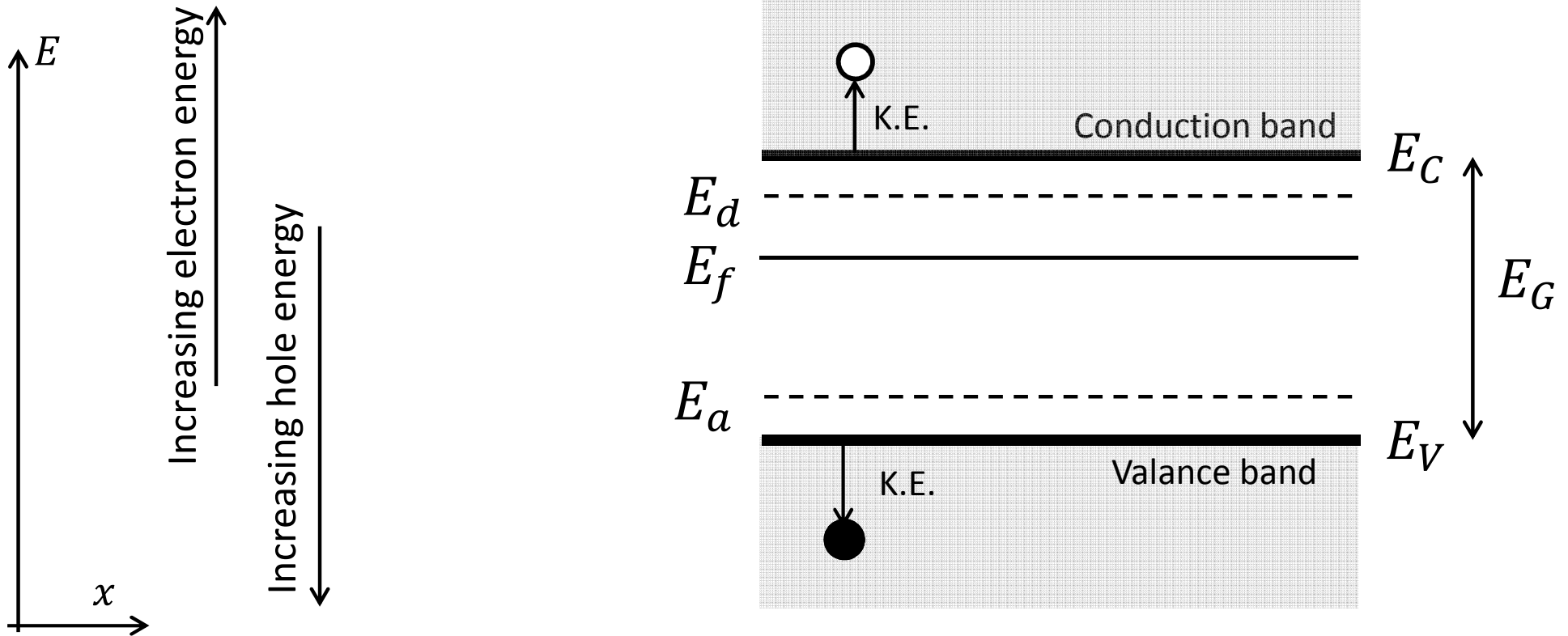
Energy band diagram shows the bottom edge of conduction band, Ec , and top edge of valence band, Ev .

Ec and Ev are separated by the band gap energy, Eg .

Electrons and holes tend to seek their lowest energy positions, electrons tend to fall in energy band diagram, holes float up like bubbles in water.

21

Measuring E$_G$ by Light Absorption

E$_G$ can be determined from the minimum energy (hv) of photons that are absorbed by the semiconductor.

photon

photon energy:
$hv > E_G$

Conduction band

E_C

E_G

E_V

Valance band
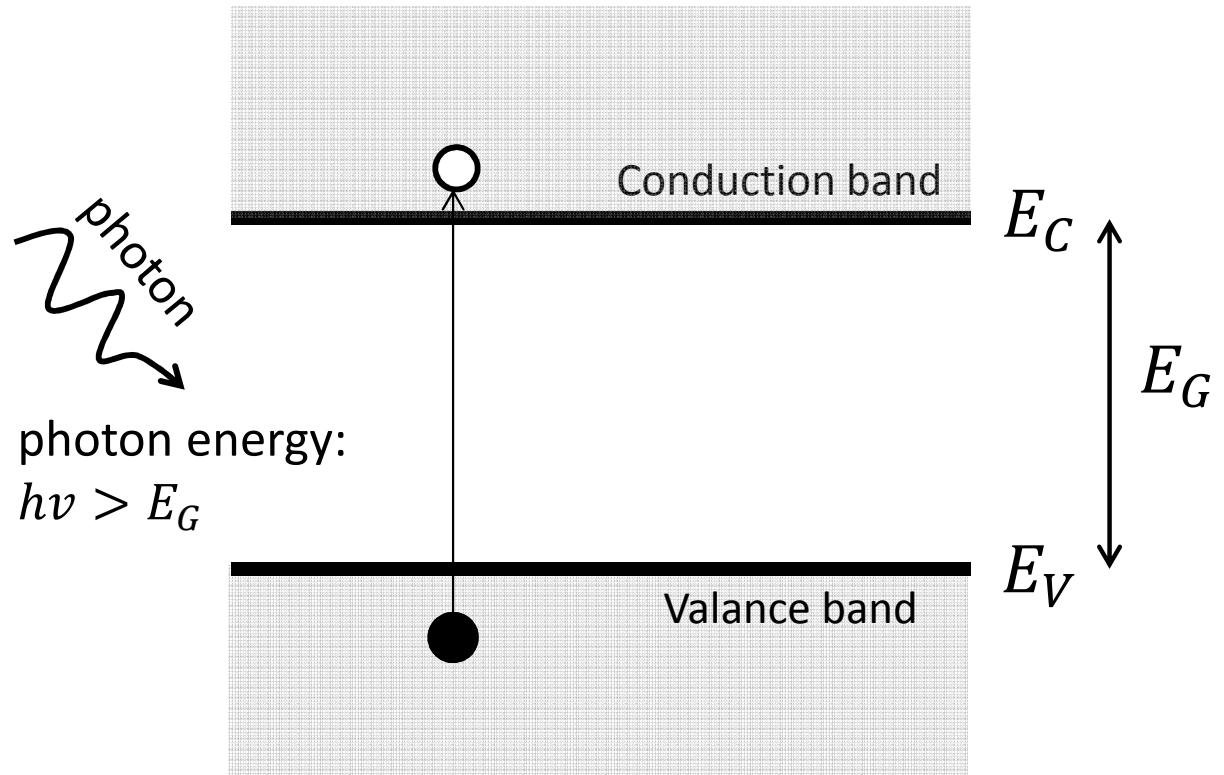
Bandgap energies of selected semiconductors

Semi conductor	InSb	Ge	Si	GaAs	GaP	ZnSe	Diamond
EG(eV)	0.18	0.67	1.12	1.42	2.25	2.7	6

22

Electron / Hole Current
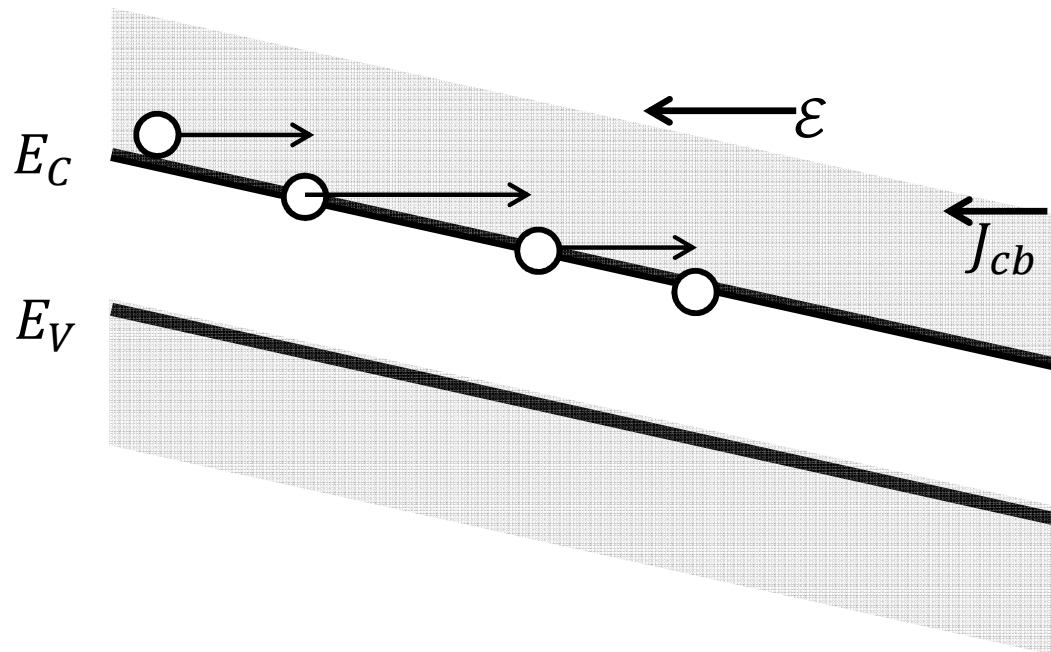
$\mathcal{E}$

v_i J_{cb}

E_C

E_V

In semiconductor, electrons that are in the conduction band move by applying the electric field

$$J_{cb} = \sum_{cb}(-q)v_i$$

As number or electrons in conduction band is much less than that in conductors hence $\rho_{SemiCond} > \rho_{Cond}$
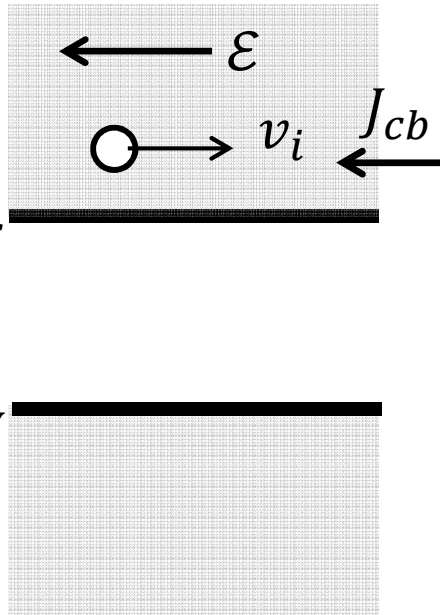
More realistic picture could be:
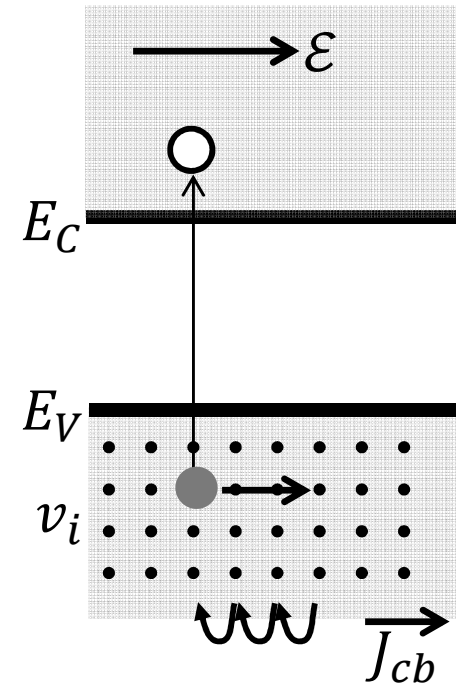
E_C

E_V

$\mathcal{E}$

J_{cb}

Electron / Hole Current

For each electron in CB there is a hole in VB (thermal excitation), Now applying an electric field will for electrons in VB to fill the empty location, hence "hole" is moving in direction of electric field!
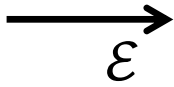
$$J_{cb} = \sum_{vb}(-q)v_i = \sum_{filled}(-q)v_i - \sum_{empty}(-q)v_i = \sum_{empty}qv_i$$

Therefore "hole" can be considered as a positively charged particle (or an electron with negative mass!)

$\mathcal{E}$

E_C

E_V

v_i

J_{cb}

Analogy

Electric field $\rightarrow$ gravitational field

$$\mathcal{E}$$

E_C ——————

E_V ——————

$$J = 0$$

electron $\rightarrow$ droplet
hole $\rightarrow$ bubble

$$\mathcal{E}$$

E_C

E_V

$$J = \sigma\mathcal{E}$$

25
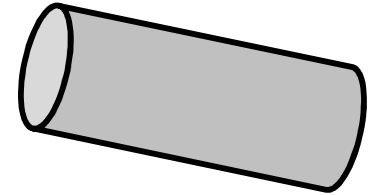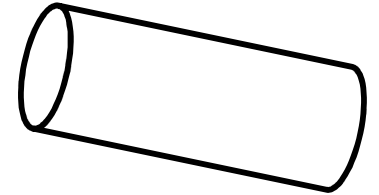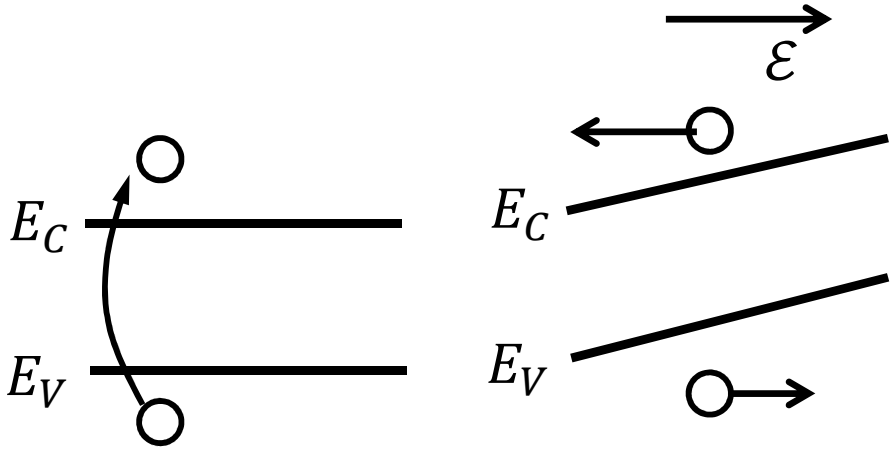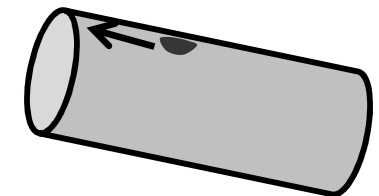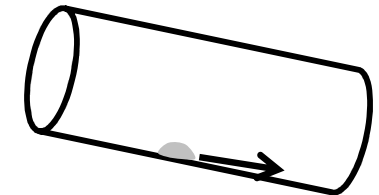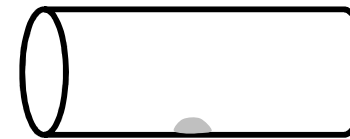
Consider a free electron with mass m,

Wave-particle duality:

$$\lambda = h/p \quad \rightarrow \quad p = \hbar k \qquad E = h\upsilon$$

$$E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \quad \rightarrow \quad E \propto k^2$$
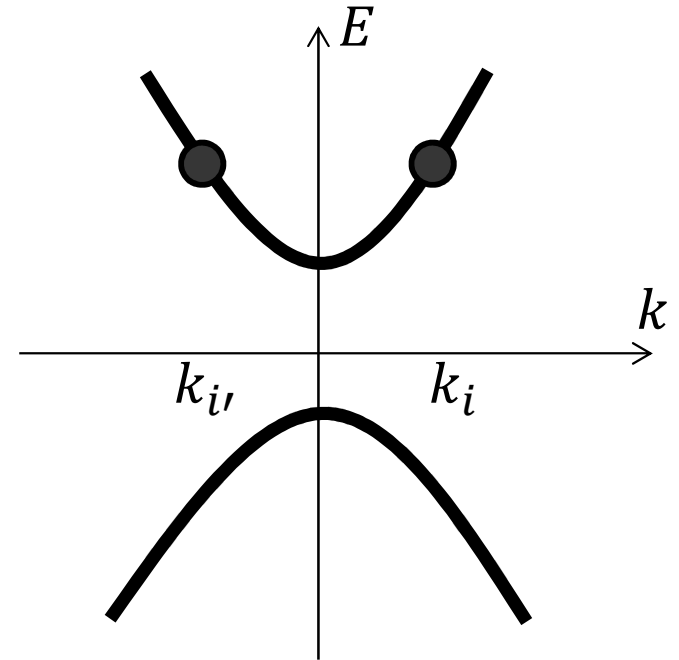
Available states: 10^{22}/cm^3

Number of e$^-$ & h$^+$ s: 10^{10}/cm^3

→ Freely moving electrons

26

Effective Mass

The electron wave function is the solution of the three dimensional Schrodinger wave equation
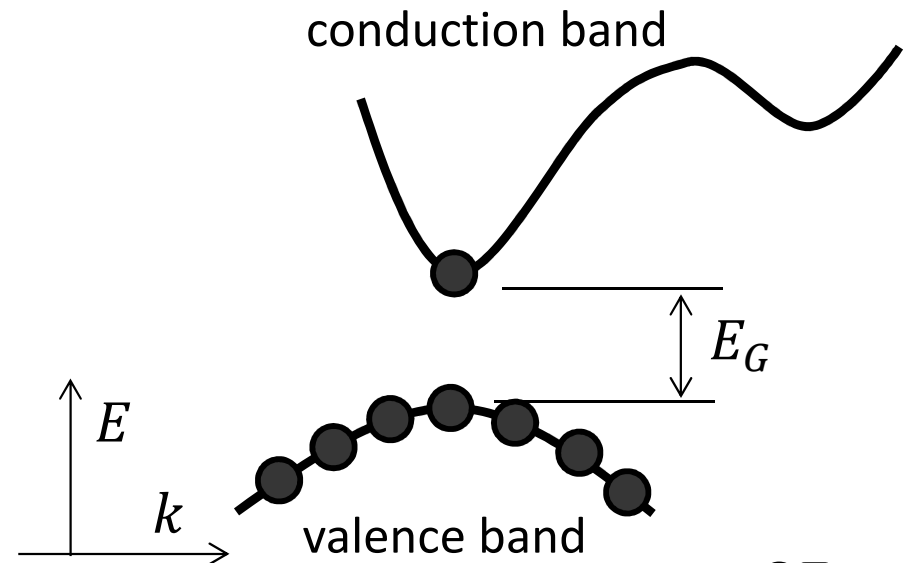
$$\frac{-\hbar^2}{2m}\nabla^2\psi + V(r)\psi = E\psi$$

The solution is of the form $e^{\pm i\,\boldsymbol{k}\cdot\boldsymbol{r}}$

Where k = wave vector = 2π/electron wavelength

For each k, there is a corresponding E.

acceleration = $\dfrac{-q\mathcal{E}}{\hbar^2}\dfrac{d^2E}{dk^2} = \dfrac{F}{m}$

effective mass = $\dfrac{\hbar^2}{d^2E/dk^2}$

conduction band

E_G

E

k

valence band

27

Effective Mass

In 3-D crystals the electron acceleration will not be colinear. Thus, in general we have an effective mass tensor as

$$\frac{1}{m^*_{ij}} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k_i \partial k_j}$$

In an electric field, $\mathcal{E}$, an electron or a hole accelerates.

electrons $\quad a = \dfrac{-q\mathcal{E}}{m_n}$

holes $\quad a = \dfrac{q\mathcal{E}}{m_p}$

electron and hole effective masses at 300K

for density of states calculations

	Si	Ge	GaAs
m_n / m_0	0.26	0.12	0.067
m_p / m_0	0.34	0.21	0.34

for conductivity calculations

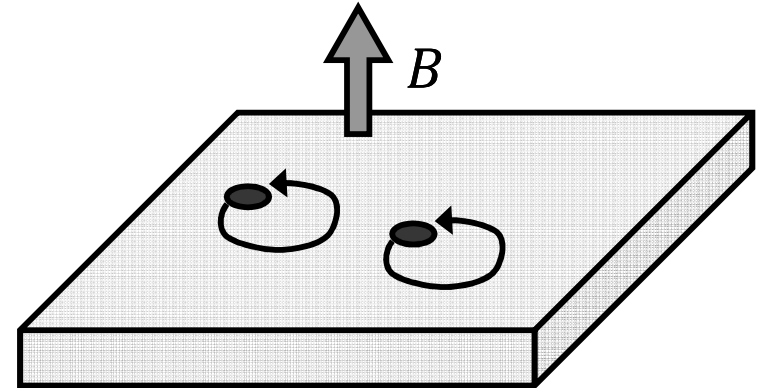|	Si	Ge	GaAs
m_n / m_0	1.1	0.55	0.067
m_p / m_0	0.81	.37	0.45

28

Measuring Effective Mass

Cyclotron Resonance Technique

Centripetal force = Lorentzian force

$$\frac{m_n v^2}{r} = qvB$$

$$v = \frac{qBr}{m_n}$$

$$f_{cr} = \frac{v}{2\pi r} = \frac{qB}{2\pi m_n}$$

- f_{cr} is the Cyclotron resonance frequency.
- It is independent of v and r.
- Electrons strongly absorb microwaves of that frequency.
- By measuring f_{cr}, m_n can be found.
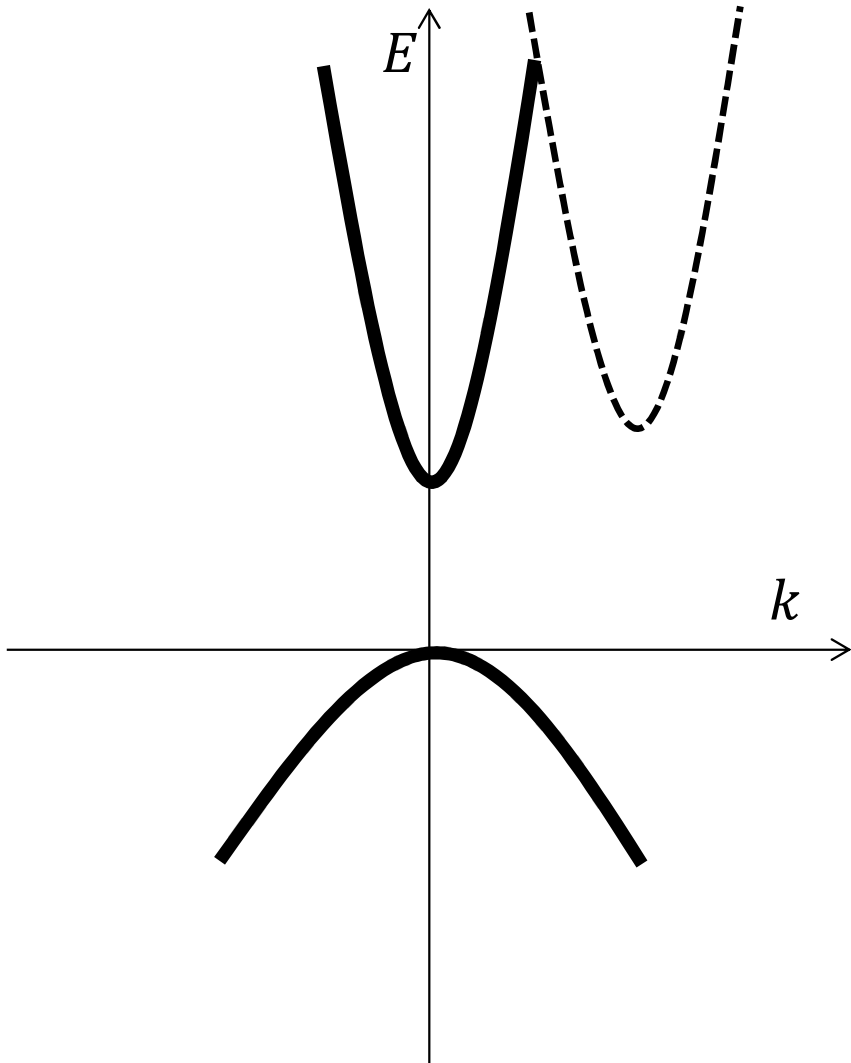
Example: Effective Mass
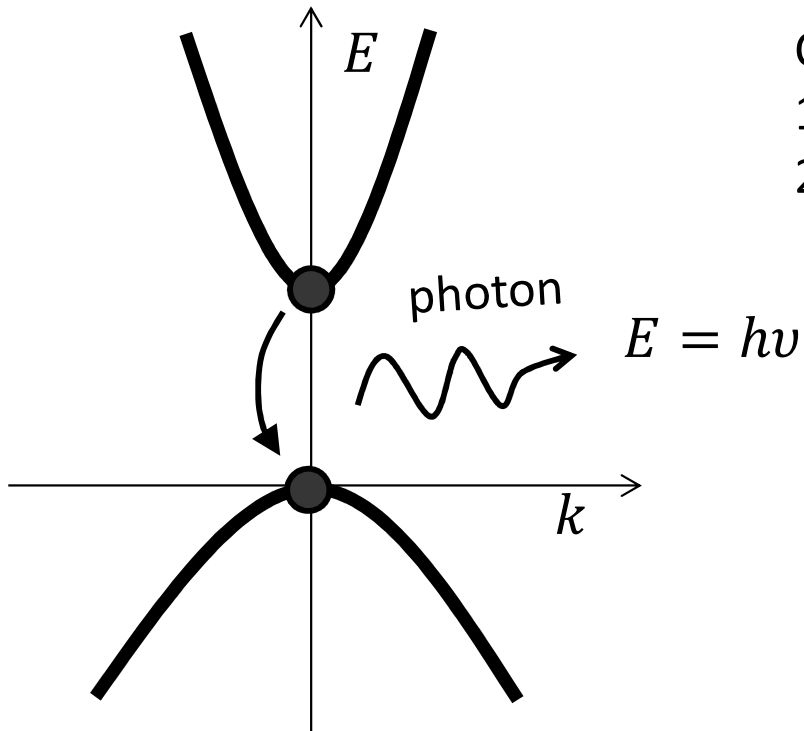
A schematic energy-momentum diagram for a special semiconductor with $m_n = 0.25\ m_0$ and $m_p = m_0$.

Direct / Indirect

Direct Materials

GaAs

Indirect Materials

Si , Ge
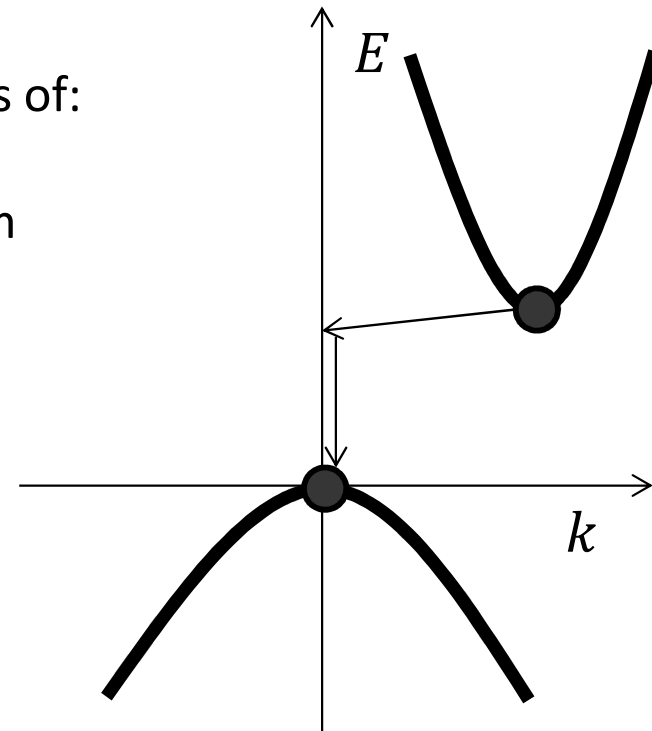
Conservations of:
1. Energy
2. Momentum

photon

$E = hv$

Applications: LEDs, Lasers

31

Direct / Indirect

Si

GaAs

300 K E_g : 1.12 eV
E_L : 2.0 eV
E_X : 1.2 eV
E_{so} : 0.044 eV
E_{c1} : 3.4 eV
E_{c2} : 4.2 eV

300 K E_g : 1.42 eV
E_L : 1.71 eV
E_X : 1.90 eV
E_{so} : 0.34 eV

<111>
Wave vector
heavy holes
light holes

valley
<111>
Wave vector
heavy holes
band

32