COMMONWEALTH OF AUSTRALIA

Copyright Regulation

WARNING

This material has been reproduced and communicated to you by or on behalf of the University of Sydney pursuant to Part VB of the *Copyright Act* 1968 (**the Act**).

The material in this communication may be subject to copyright under the Act. Any further reproduction or communication of this material by you may be the subject of copyright protection under the Act.

Do not remove this notice

Electronic Properties of Materials

Lecture 8

Electronic Structure of Materials

Lecture 9

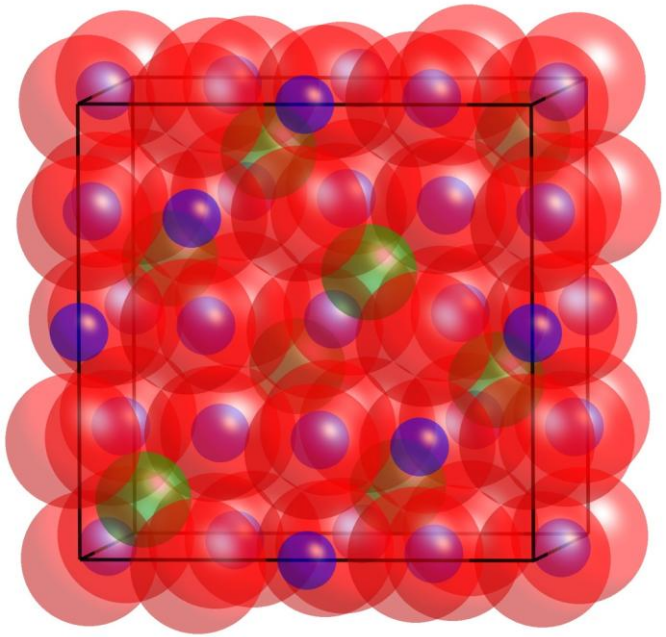
Electronic Properties of Materials

Lecture 10

Dielectric Properties of Materials

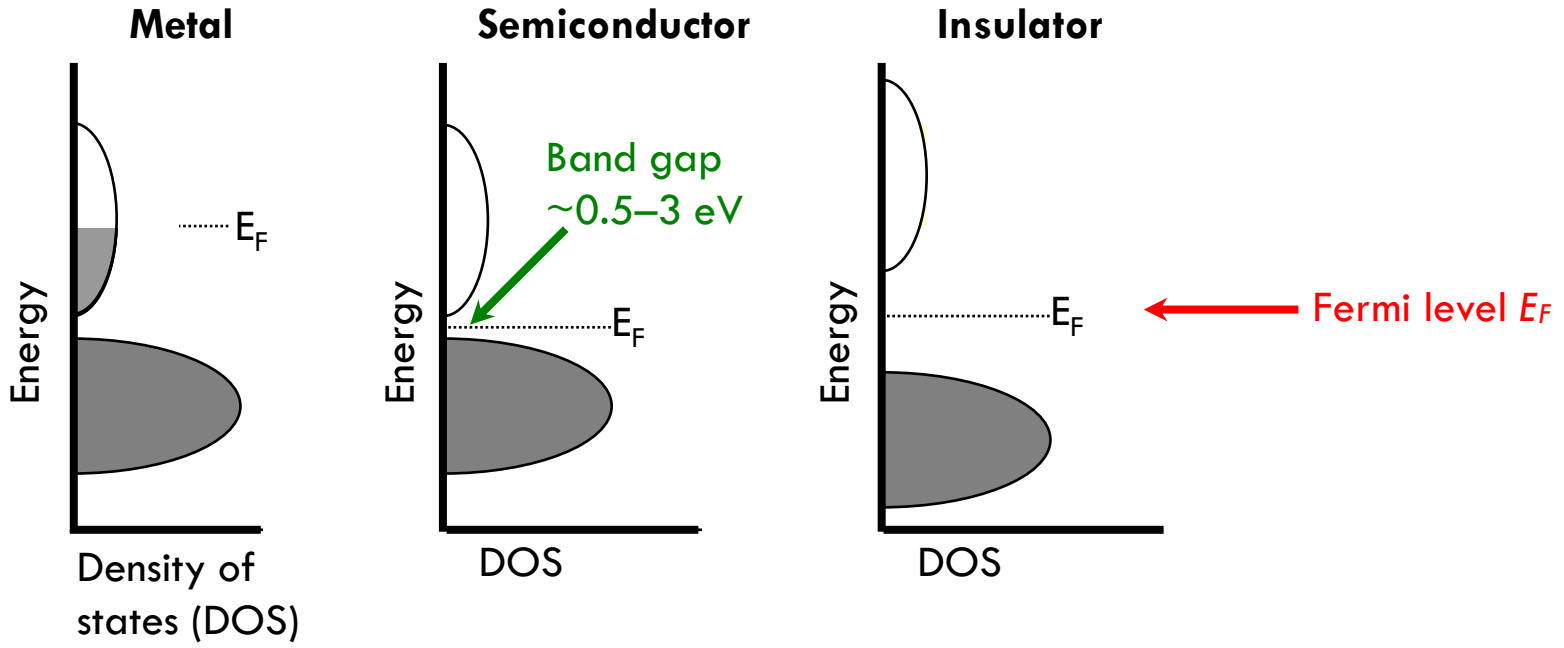
Outline

- Electronic properties
  - From insulating to semiconducting to metallic
  - Electronic transport
- Semiconductors
  - Manipulating band structures and electronic properties
  - Electron/hole doping
  - Intrinsic vs extrinsic semiconductors
  - Applications of semiconductors



Band Structures

We can classify the electronic properties of materials according to their **band structures** and Fermi levels.



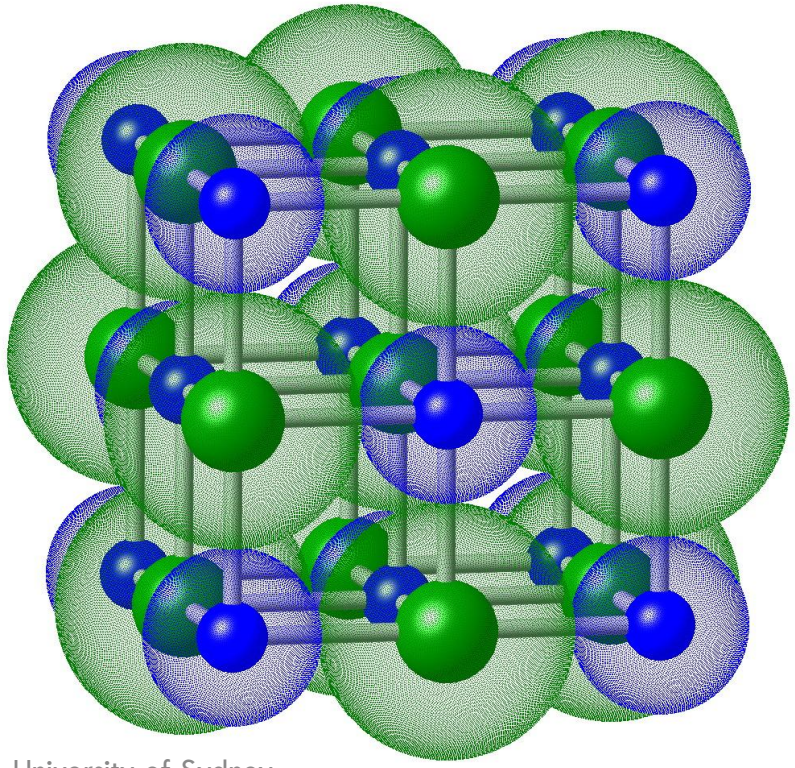
We can **manipulate the electronic properties** of materials by changing their band structures and Fermi levels.

Ionic or Covalent Bonding?

(Largely) ionic

- Large cations with low valence (groups I, II)
- Small electronegative anions (O^{2-}, F^-)

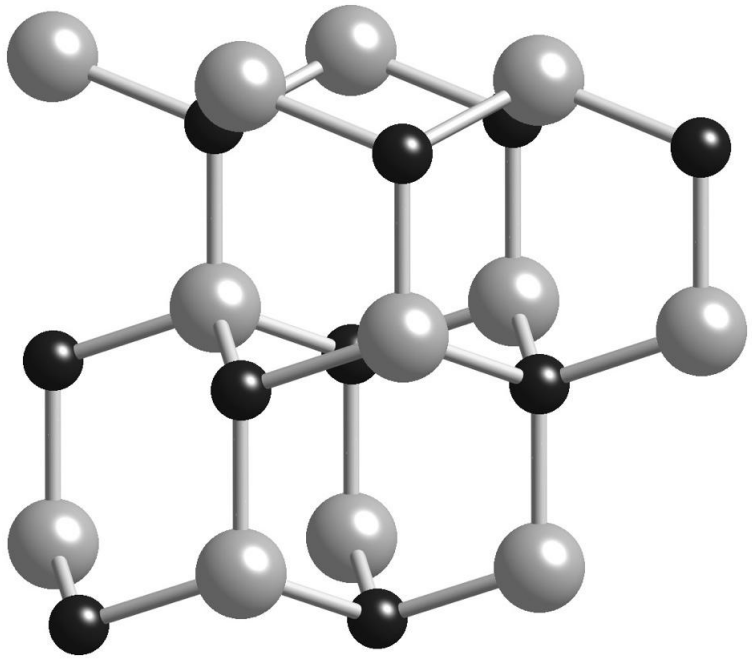
NaCl



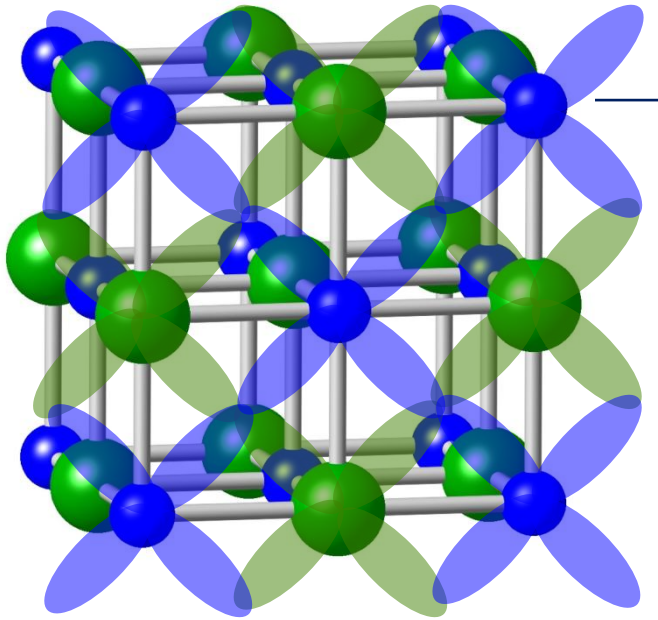
(Largely) covalent

- Small highly polarising cations (B^{3+}, Si^{4+}, P^{5+}, S^{6+})
- Large polarisable anions (I^-, S^{2-})

SiC



Electronic Bonding in Solids



NaCl is largely ionic and the ions have the configurations:

Cl^- : $1s^2 2s^2 2p^6 3s^2 3p^6$

Na^+ : $1s^2 2s^2 2p^6 3s^0 3p^0$

Consider the band structure of NaCl:

- The 3s and 3p orbitals on Cl^- overlap to form a fully-occupied valence band.
- The 3s and 3p orbitals on Na^+ overlap to form an empty conduction band.
- Promoting electrons from the valence to the conduction band is equivalent to moving charge from Cl^- to Na^+.
- This is unlikely due to the electronegativity of the ions and because the band gap is large (~7 eV).
- **The size of the band gap correlates with the difference in electronegativities of the ions.**

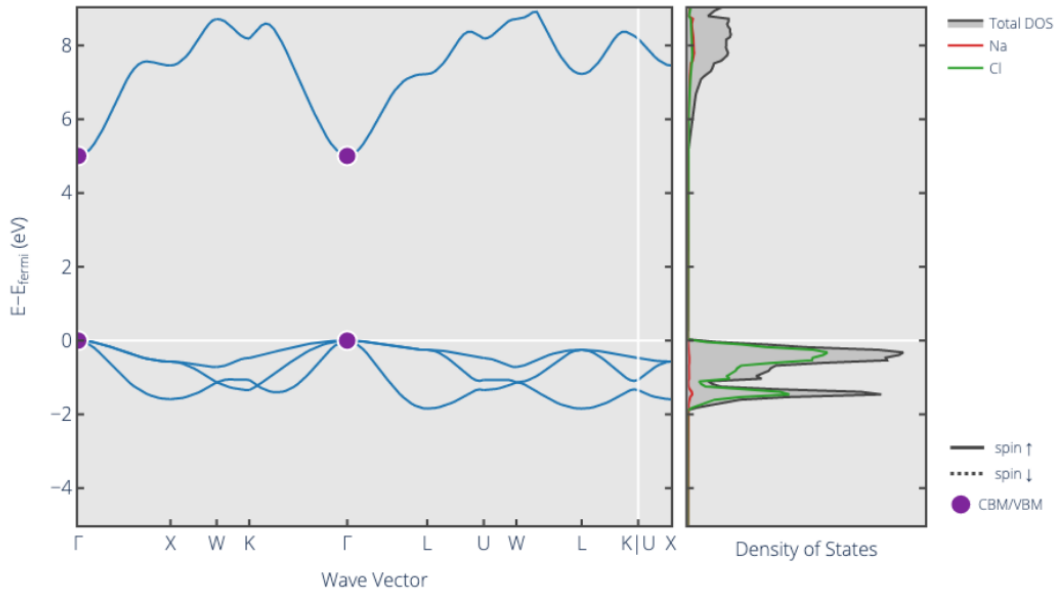
Table 2.17 *Band gaps (eV) of some inorganic solids*

I–VII compounds		II–VI compounds		III–V compounds	
LiF	11	ZnO	3.4	AlP	3.0
LiCl	9.5	ZnS	3.8	AlAs	2.3
NaF	11.5	ZnSe	2.8	AlSb	1.5
NaCl	8.5	ZnTe	2.4	GaP	2.3
NaBr	7.5	CdO	2.3	GaAs	1.4
KF	11	CdS	2.45	GaSb	0.7
KCl	8.5	CdSe	1.8	InP	1.3
KBr	7.5	CdTe	1.45	InAs	0.3
KI	5.8	PbS	0.37	InSb	0.2
		PbSe	0.27	β-SiC	2.2
		PbTe	0.33	α-SiC	3.1

Table from West "Basic Solid State Chemistry"

Electronic Bonding in Solids

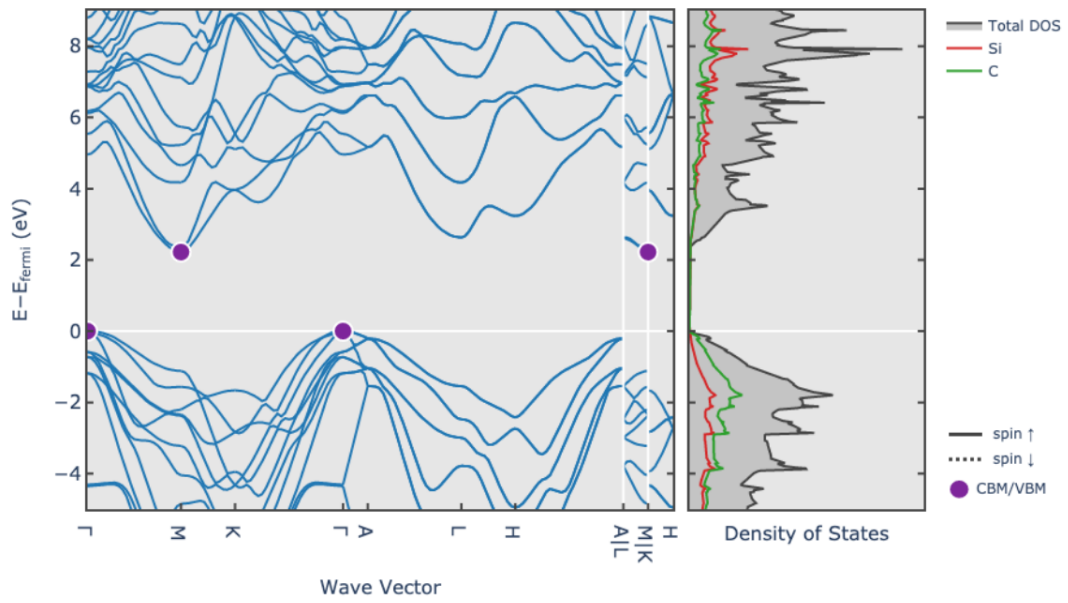
NaCl band structure



Warning! Semi-local DFT tends to severely underestimate bandgaps. Please see the wiki for more info.

https://materialsproject.org/materials/mp-22862/

SiC band structure



Warning! Semi-local DFT tends to severely underestimate bandgaps. Please see the wiki for more info.

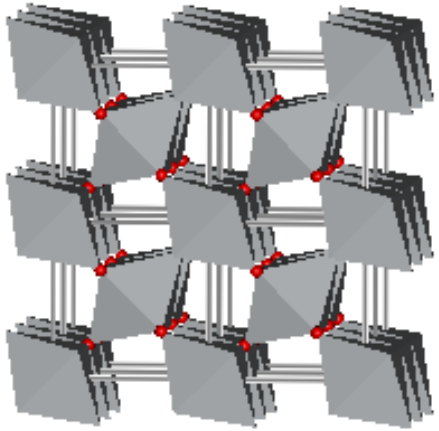
https://materialsproject.org/materials/mp-11714/

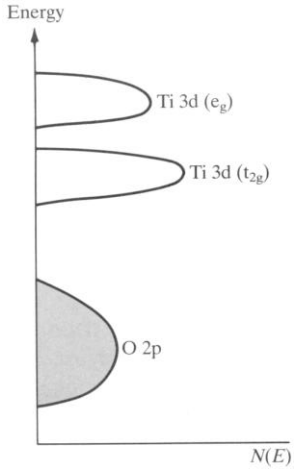
Trends in Electronic Conductivity

Titanium Chalcogens (Group 16): Oxide vs. Sulfide

TiO_2 (rutile)

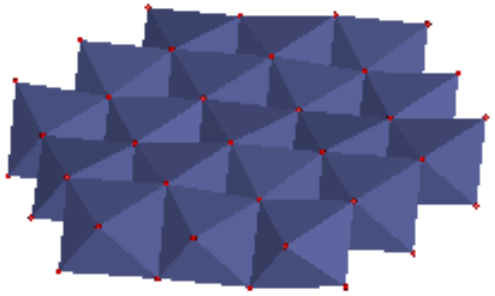
- Insulator
- $\sigma \sim 10^{-10}$ S cm^{-1}

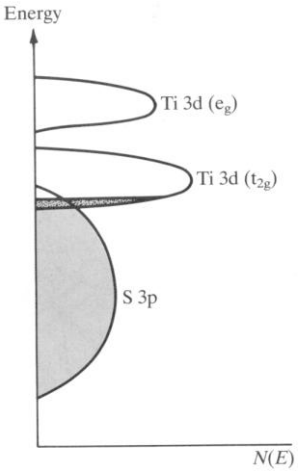




TiS_2

- Metallic due to band overlap
- $\sigma \sim 10^{6}$ S cm^{-1}





Trends in Electronic Conductivity

Transition Metal Oxides: Rhenium vs. Tungsten

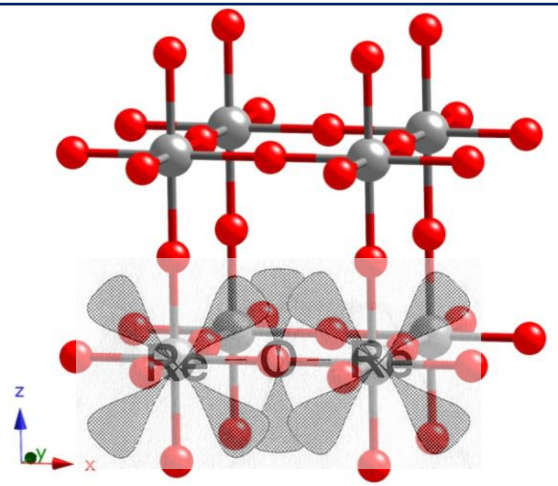
ReO_3 and WO_3 have the *same* crystal structure but *different* electronic structure.

ReO_3 is metallic

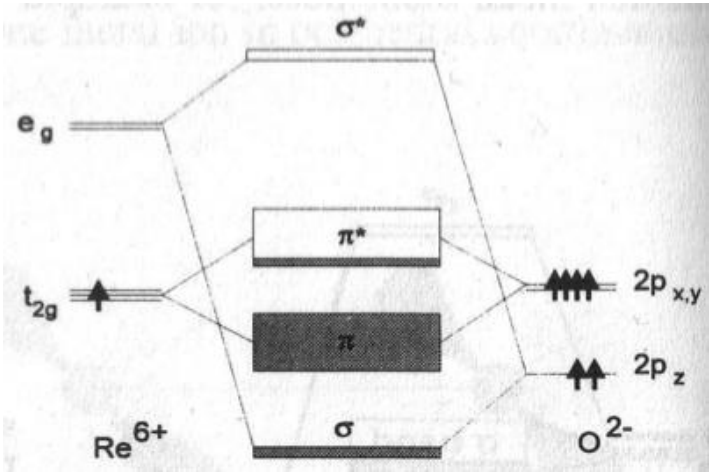
- Re^{6+} has one *5d*-electron that can delocalise throughout the band formed by the π-type overlap of t_{2g} orbitals on the transition metal cation and *p* orbitals on the O anion.

WO_3 is an insulator

- W^{6+} has no *5d*-electrons, so this band is empty.



Crystal structure of ReO_3 and WO_3



Band structure of ReO_3

Figures from Weller "Inorganic Materials Chemistry"

Trends in Electronic Conductivity

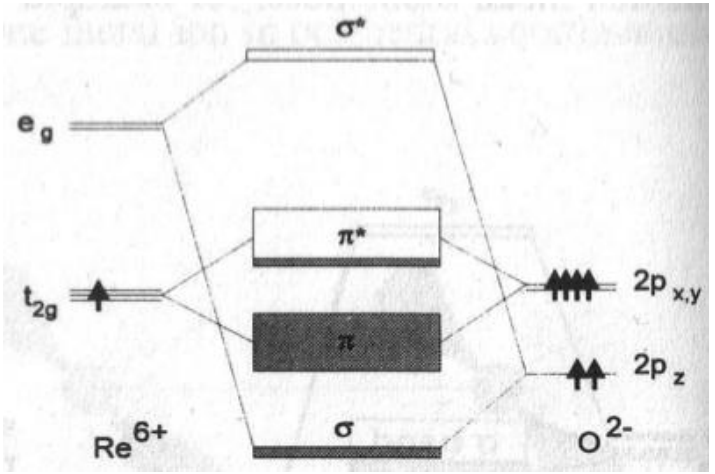
Transition Metal Oxides: Rhenium vs. Tungsten

Modifying WO_3 can make it metallic.

- E.g., doping with Na^+
- Tungsten bronze – $Na^+_x[W^{(6-x)+}O^{2-}_3]$ – has *x* 5*d*-electrons per W cation in the conduction band.



Na-doped WO_3

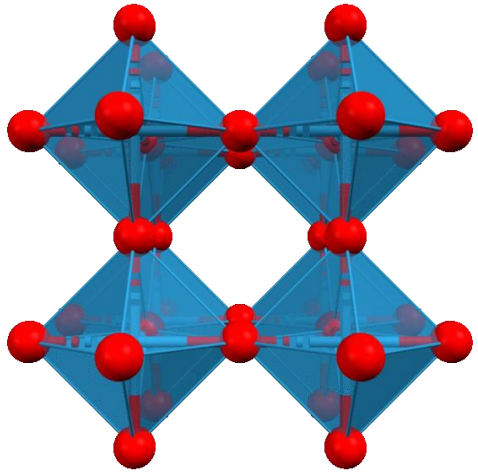


Band structure of ReO_3

Figures from Weller "Inorganic Materials Chemistry"

Trends in Electronic Conductivity

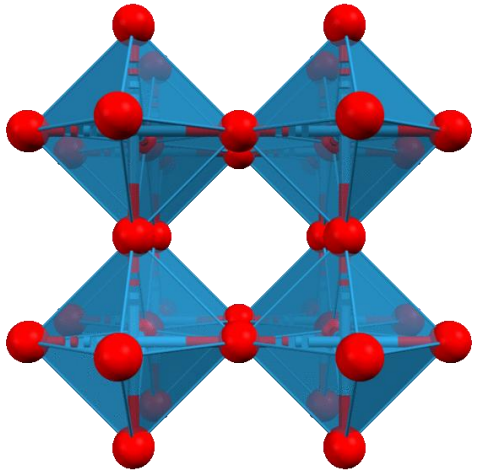
Transition Metal Oxides: Rhenium vs. Tungsten



ReO_3

$5d^1$

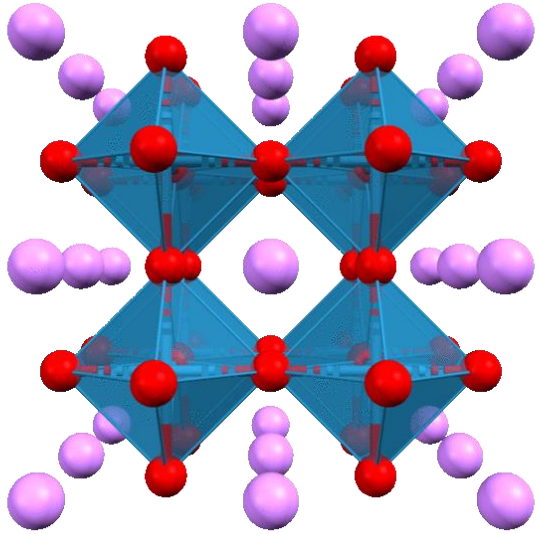
metallic



WO_3

$5d^0$

insulating



$NaWO_3$

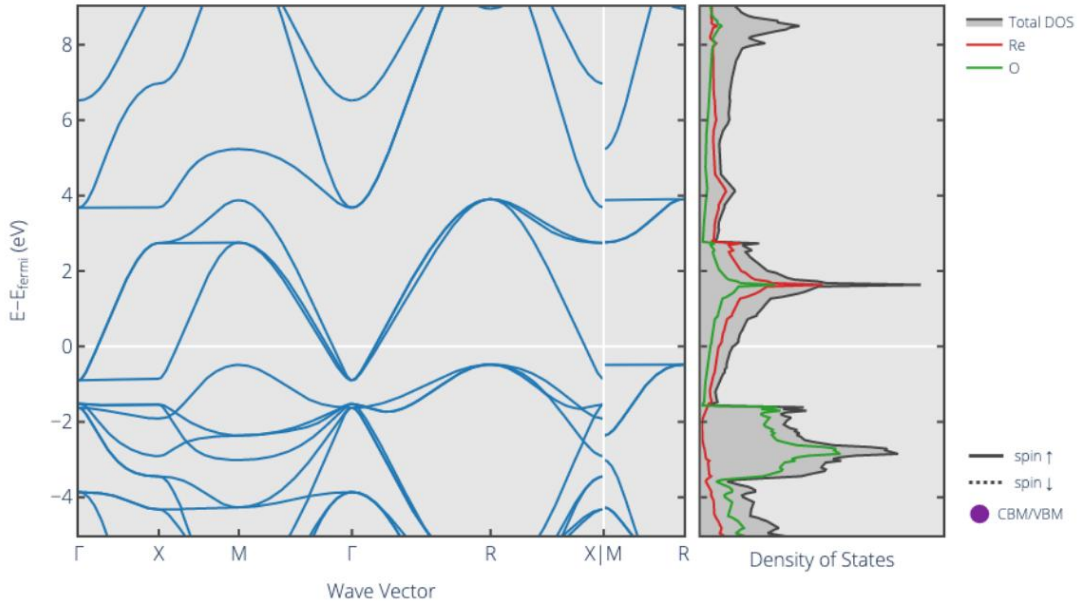
$5d^1$

metallic

Trends in Electronic Conductivity

Transition Metal Oxides: Rhenium vs. Tungsten

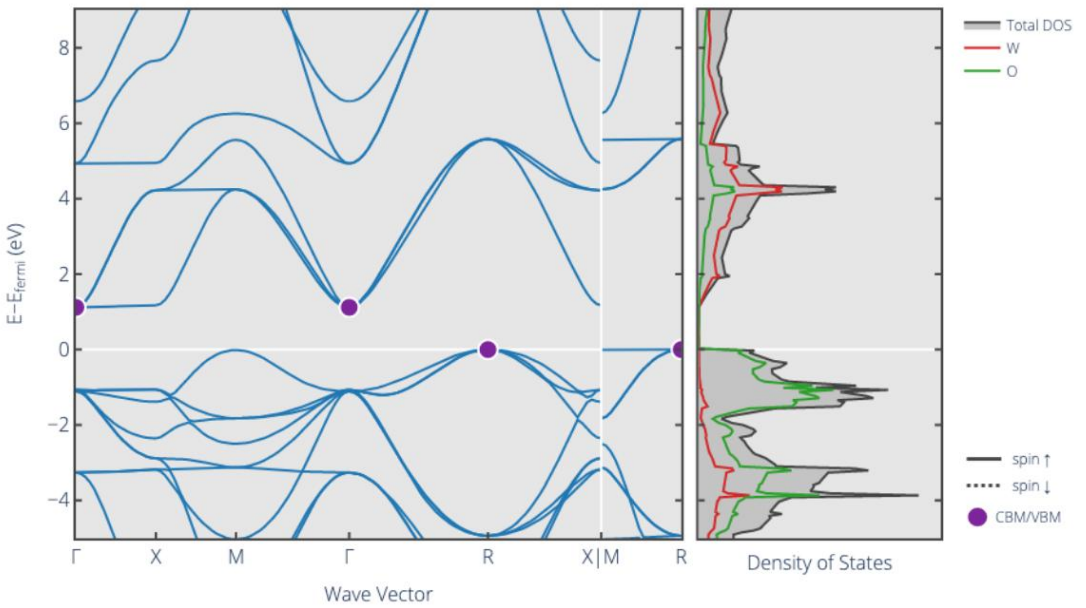
ReO_3 band structure



Warning! Semi-local DFT tends to severely underestimate bandgaps. Please see the wiki for more info.

https://materialsproject.org/materials/mp-190/

WO_3 band structure



Warning! Semi-local DFT tends to severely underestimate bandgaps. Please see the wiki for more info.

https://materialsproject.org/materials/mp-19390/

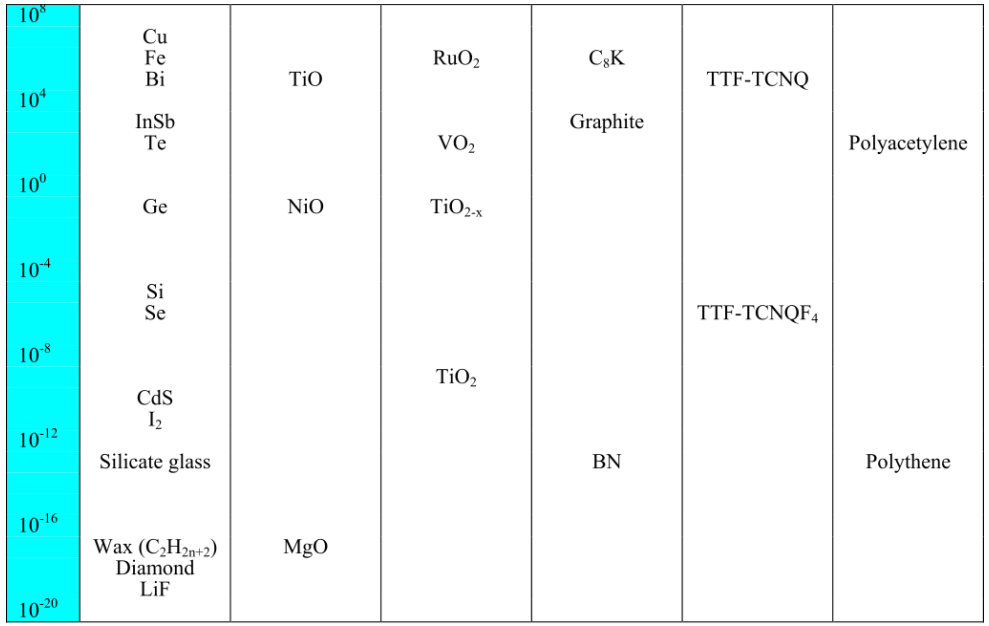
Conductivity and Resistivity

Conductivity, σ (S cm^{-1}), is inversely proportional to **resistivity,** ρ.

$$\sigma = 1/\rho$$

Small changes in structure or composition can drastically affect the band structure and hence the conductivity.

The conductivities of materials span >25 orders of magnitude.



Resistivity and Carrier Concentration

Resistivity is affected by differences in **carrier concentration, *n***, and **mobility, μ.**

$$\sigma = ne\mu$$

Carrier concentration, *n*

- The carrier concentration only includes electrons that can easily be excited from occupied states into empty states, thus propagating through the crystal.
- In the absence of external excitations (light, voltage, etc.) the excitation must be thermal, which is on the order of kT (~0.03 eV at room temperature).
- Only electrons whose energies are within a few kT of the Fermi level, E_F, can contribute to the electrical conductivity.
- Generally, this means that E_F should cut a band to achieve appreciable carrier concentration.

Resistivity and Carrier Mobility

Carrier mobility, μ

$$\mu = e\tau/m^*$$

Where e = electronic charge

m^* = effective mass, which depends upon the band width, which in turn depends upon orbital overlap

τ = relaxation time between scattering events

Entities that scatter the carriers and reduce mobility include:

- A defect or impurity: τ is inversely proportional to the amount of impurities
- Lattice vibrations (phonons): τ is inversely proportional to T

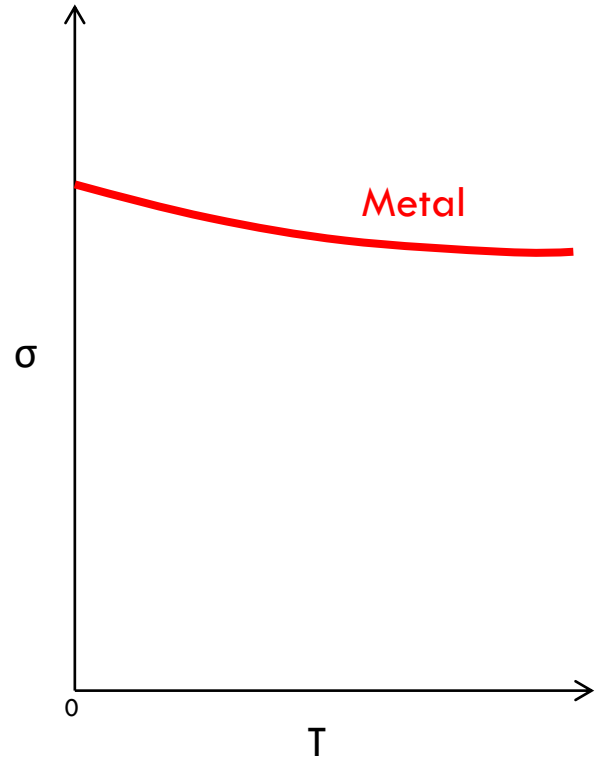
Temperature Dependence – Metals

$$\sigma = 1/\rho$$

$$\sigma = ne^2\tau/m^* \qquad \text{(Drude model)}$$

In metals:

- Carrier concentration, *n*, changes very slowly with temperature *T*.
- τ is inversely proportional to *T* (i.e., τ decreases as T increases).
- **Conductivity decreases as temperature increases.**
- A plot of σ vs. $1/T$ (or ρ vs. *T*) is essentially linear.



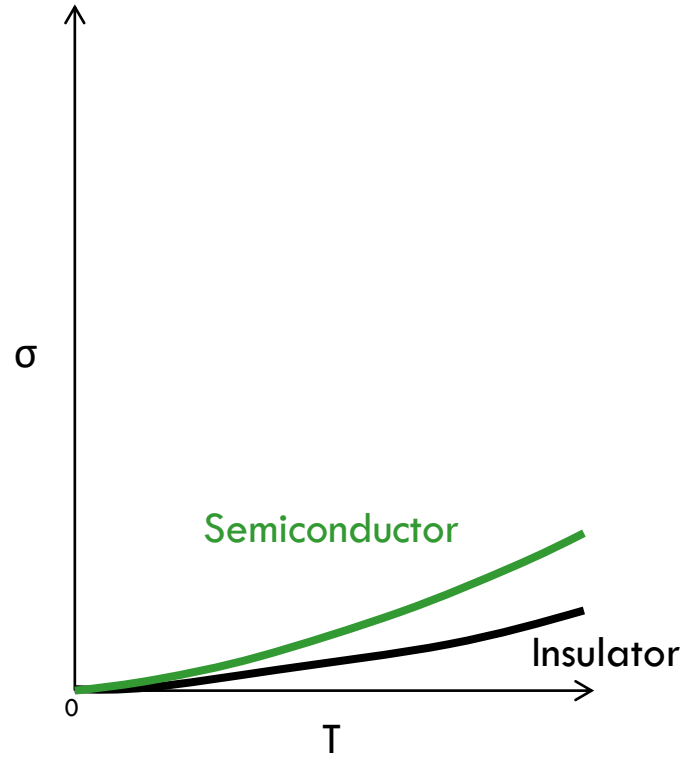
Temperature Dependence – Semiconductors

$$\sigma = 1/\rho$$

$$\sigma = ne^2\tau/m^*$$

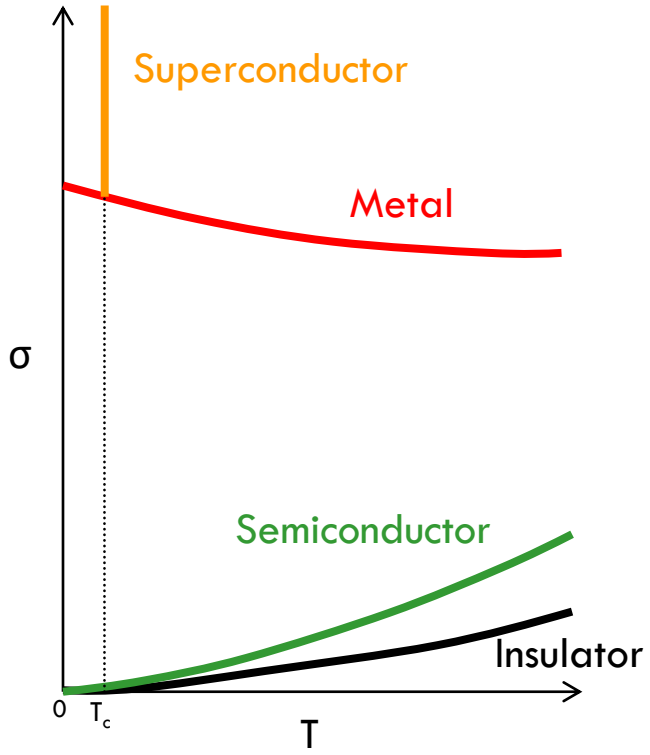
In semiconductors:

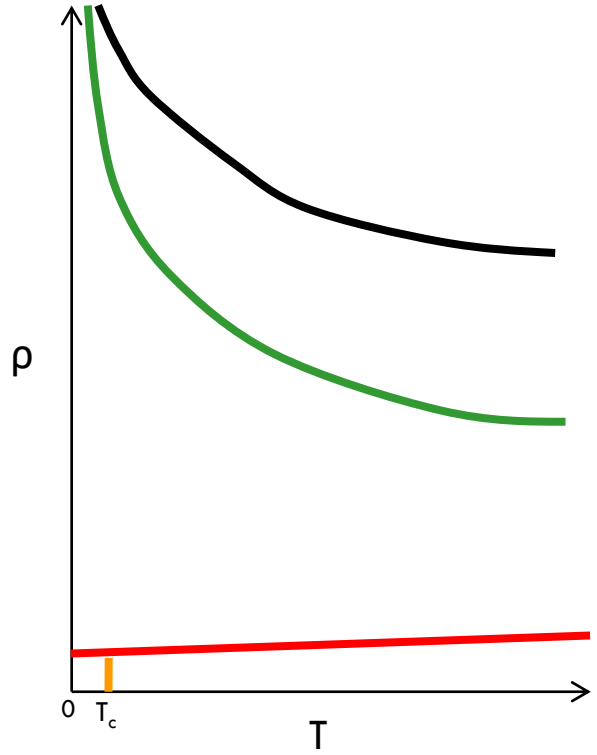
- The carrier concentration, n, increases as T increases, due to excitations across the band gap, E_g.
- n is proportional to $\exp\{-E_g/2kT\}$.
- τ is inversely proportional to T.
- The exponential dependence of n dominates, so **conductivity increases as temperature increases.**
- A plot of $\ln \sigma$ vs. $1/T$ is essentially linear.



Temperature dependence – Classifying Materials

Rather than characterising a material as metallic, semiconducting or insulating solely according to the magnitude of the conductivity, we consider its temperature dependence:





Intrinsic semiconductors

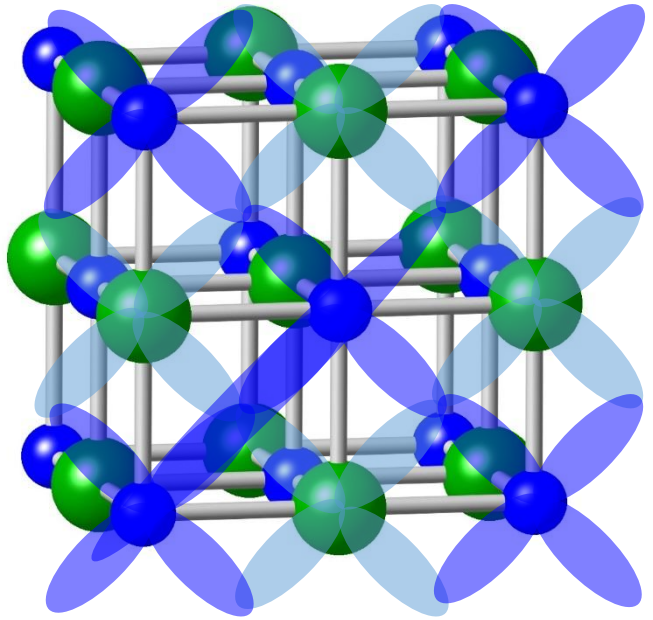
An intrinsic semiconductor is a pure, undoped, semiconducting material. E.g., rock-salt type binary compounds not involving *d* electrons.

- Anion s and p orbitals form a fully-occupied valence band.
- Cation s and p orbitals form an empty conduction band.
- The band gap is small enough for intrinsic semiconduction in some cases, especially III-V compounds.

Table 2.17 *Band gaps (eV) of some inorganic solids*

I–VII compounds		II–VI compounds		III–V compounds	
LiF	11	ZnO	3.4	AlP	3.0
LiCl	9.5	ZnS	3.8	AlAs	2.3
NaF	11.5	ZnSe	2.8	AlSb	1.5
NaCl	8.5	ZnTe	2.4	GaP	2.3
NaBr	7.5	CdO	2.3	GaAs	1.4
KF	11	CdS	2.45	GaSb	0.7
KCl	8.5	CdSe	1.8	InP	1.3
KBr	7.5	CdTe	1.45	InAs	0.3
KI	5.8	PbS	0.37	InSb	0.2
		PbSe	0.27	β-SiC	2.2
		PbTe	0.33	α-SiC	3.1

Table from West "Basic Solid State Chemistry"



Cl^-, S^{2-}, P^{3-} : $1s^2 2s^2 2p^6 3s^2 3p^6$

Na^+, Mg^{2+}, Al^{3+} : $1s^2 2s^2 2p^6 3s^0 3p^0$

Extrinsic Semiconductors

Intrinsic semiconductors with band gaps ~kT are very rare. Most semiconductors used in electronics are extrinsic, i.e., they are doped with an impurity atom.

- **n-type semiconductors** (in which the charge carriers are negative electrons) contain dopants with occupied energy levels close to an empty conduction band.

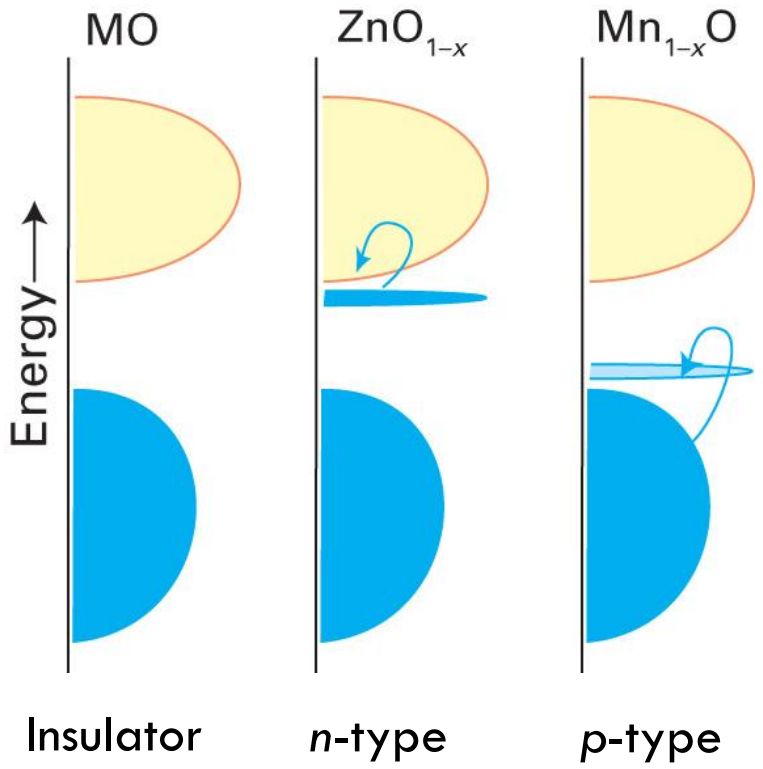
  E.g., As ([Ar]$4s^2 4p^3$) doped into Si ([Ne]$3s^2 3p^2$)

- **p-type semiconductors** (in which the charge carriers are positive holes) contain dopants with unoccupied energy levels close to a filled valence band.

  E.g., Ga ([Ar]$4s^2 4p^1$) doped into Si ([Ne]$3s^2 3p^2$)

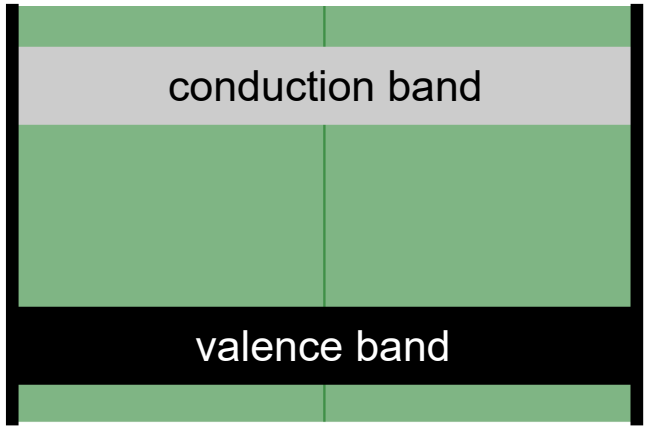
- Doping can also be achieved by site vacancies

  E.g., oxygen vacancy in ZnO_{1-x}



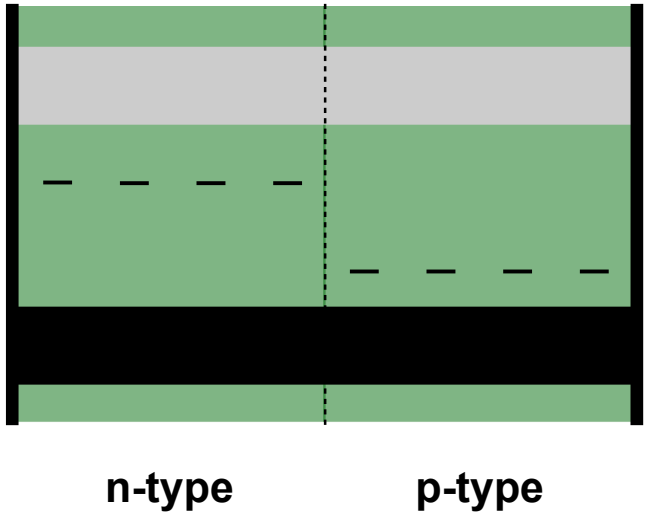
p–n Semiconductor Junctions

- Join an n-type semiconductor to a p-type semiconductor
- Electrons will be thermally promoted into the conduction band
- Electrons diffuse from the n- to the p-type region
- This leaves the n-type region with a net positive charge and the p-type region with a net negative charge, establishing an electric field



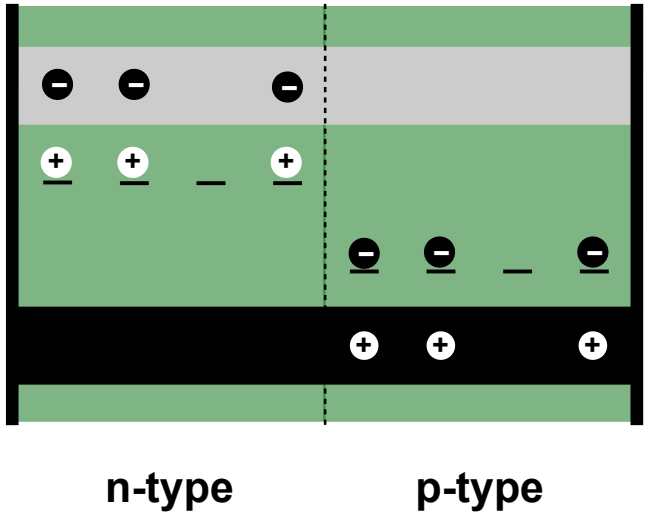
p–n Semiconductor Junctions

- Join an n-type semiconductor to a p-type semiconductor
- Electrons will be thermally promoted into the conduction band
- Electrons diffuse from the n- to the p-type region
- This leaves the n-type region with a net positive charge and the p-type region with a net negative charge, establishing an electric field



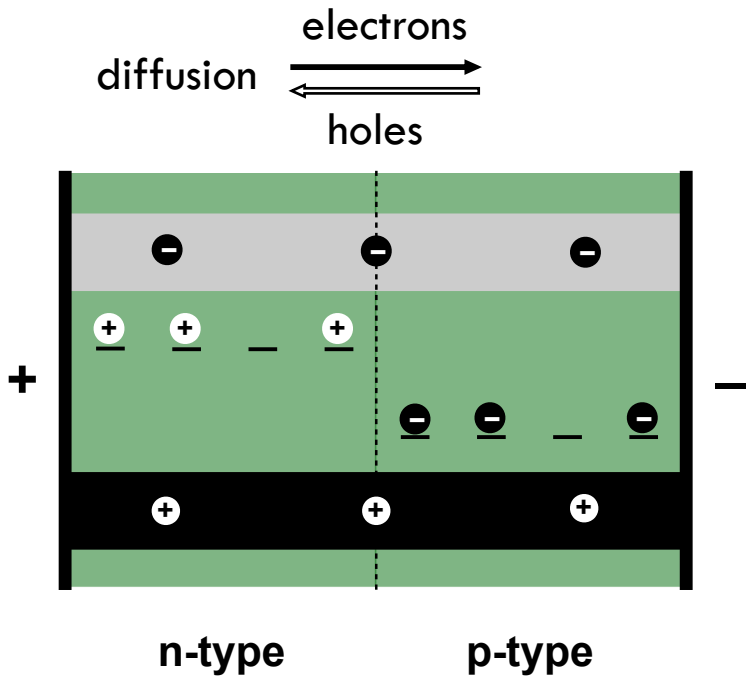
p–n Semiconductor Junctions

- Join an n-type semiconductor to a p-type semiconductor
- Electrons will be thermally promoted into the conduction band
- Electrons diffuse from the n- to the p-type region
- This leaves the n-type region with a net positive charge and the p-type region with a net negative charge, establishing an electric field



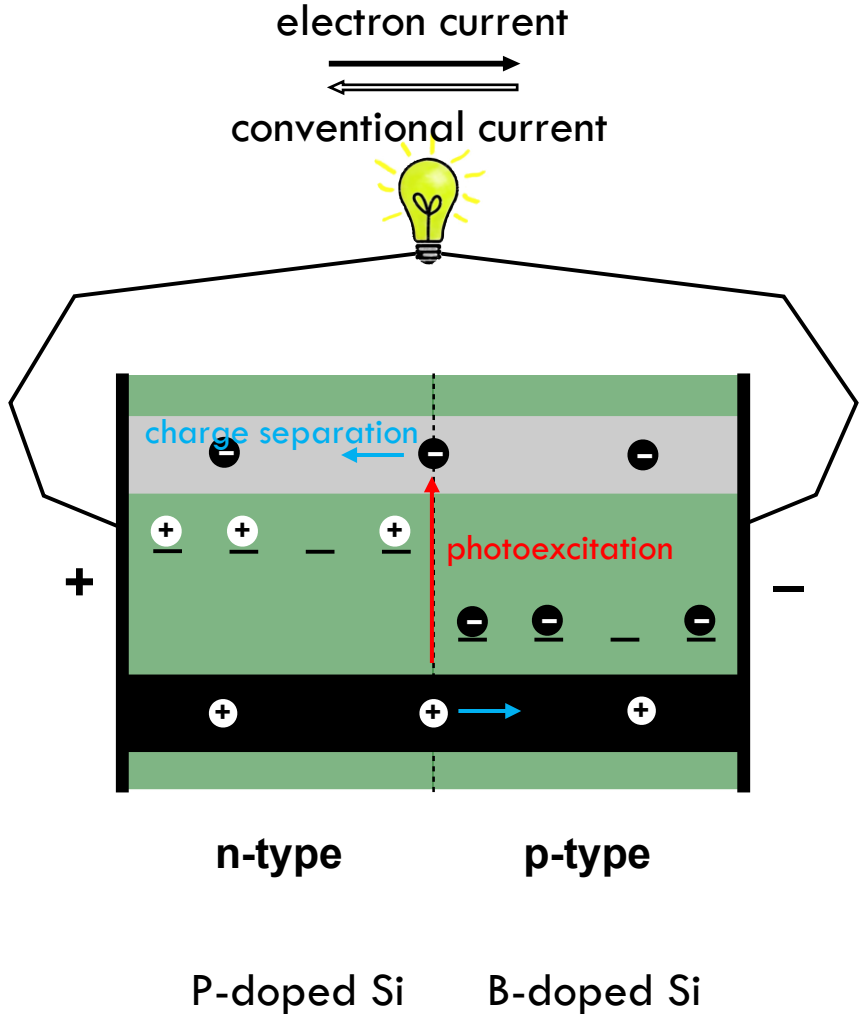
p–n Semiconductor Junctions

- Join an n-type semiconductor to a p-type semiconductor
- Electrons will be thermally promoted into the conduction band
- Electrons diffuse from the n- to the p-type region
- This leaves the n-type region with a net positive charge and the p-type region with a net negative charge, establishing an electric field



Photovoltaics

- If the p- and n-type regions have a constant supply of new carriers (electrons or holes) from incoming photons, a current will flow
- An applied current can normally only flow in one direction – the junction acts as a rectifier
- With the right resistance in the circuit, the current and voltage can be optimsed
- This is the basis of a photovoltaic (PV) diode – a solar cell
- The solar spectrum ranges from IR (1.1 eV) to UV (3.5 eV)
- The band gap for Si is 1.1 eV, and for GaAs is 1.4 eV



Learning Outcomes

After this lecture you should be able to

- Distinguish metals/semiconductors/insulators based on band structures/DOS and on the temperature dependence of conductivity/resistivity.
- Differentiate between intrinsic, p- and n-doped semiconductors.
- Explain how a p-n junction works in applications such as photovoltaics.
- Complete the lecture worksheet and start preparing for the in-semester test to be held in week 5 (covering content from lectures 2 to 11).

Further reading: Weller, Overton, Rourke & Armstrong, Inorganic Chemistry 6th Ed. OUP, 2014, Chapter 3.1–3.5; Weller, Inorganic Materials Chemistry, OUP, 1994, Chapter 5; West, Basic Solid State Chemistry, Wiley, 1999, Chapter 2.