

Electrical properties



- Electrical conduction
 - How many moveable electrons are there in a material (*carrier density*)?
 - How easily do they move (*mobility*) ?
- Semiconductivity
 - Electrons and holes
 - Intrinsic and extrinsic carriers
 - Semiconductor devices: p-n junctions and transistors
- Conduction in polymers and ionic materials
- Dielectric behavior

Optional reading: 18.14, 18.15, 18.21, 18.23-18.25

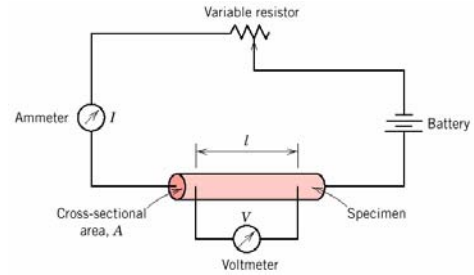
Basic laws and electrical properties of metals (I)

When an electrical potential V [volts, J/C] is applied across a piece of material, a current of magnitude I [amperes, C/s] flows. In most metals, at low values of V , the current is proportional to V , and can be described by **Ohm's law**:

$$I = V/R$$

where R is the electrical resistance [ohms, Ω , V/A].

R depends on the intrinsic resistivity ρ of the material [$\Omega\cdot\text{m}$] and on the geometry (length l and area A through which the current passes): $R = \rho l/A$



In most materials (e.g. metals), the current is carried by electrons (**electronic conduction**). In ionic crystals, the charge carriers are ions (**ionic conduction**).

Basic laws and electrical properties of metals (II)

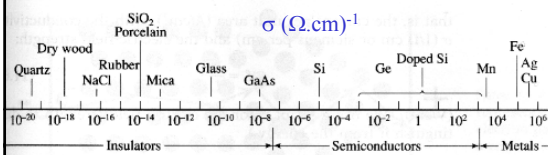
The electrical conductivity (the ability of a substance to conduct an electric current) is the inverse of the resistivity:

$$\sigma = 1/\rho$$

Since the electric field intensity in the material is $E = V/l$, Ohm's law can be rewritten in terms of the current density $J = I/A$ as:

$$J = \sigma E$$

Electrical conductivity varies between different materials by over 27 orders of magnitude, the greatest variation of any physical property



Metals: $\sigma > 10^5 \text{ } (\Omega\cdot\text{m})^{-1}$

Semiconductors: $10^{-6} < \sigma < 10^5 \text{ } (\Omega\cdot\text{m})^{-1}$

Insulators: $\sigma < 10^{-6} \text{ } (\Omega\cdot\text{m})^{-1}$

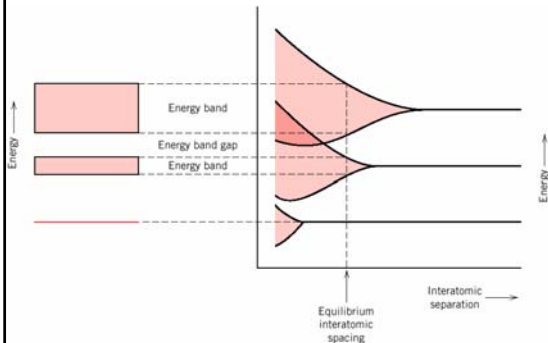
Electrical Resistivity (ohm-m)	(log)	Electrical Conductivity (S/m)
	-8	8
intercalated graphite	-7	7
	-6	6
graphite (in-plane)	-5	5
graphite (out of plane)	-4	4
polyacetylene (doped)	-3	3
	-2	2
TTF-TCNQ	-1	1
	0	0
	1	-1
	2	-2
	3	-3
	4	-4
	5	-5
polyacetylene (undoped)	6	-6
	7	-7
	8	-8
	9	-9
	10	-10
Bakelite	11	-11
polypyrrole	12	-12
	13	-13
Lucite (PMMA)	14	-14
polyvinyl chloride	15	-15
polyethylene, teflon	16	-16
		copper, silver iron
		stainless steel, metallic glass
		YBa ₂ Cu ₃ O ₇ (ab plane)
		YBa ₂ Cu ₃ O ₇ (c-axis)
		silicon (doped)
		ZnO (doped)
		seawater
		Fe ₃ O ₄
		germanium
		silicon
		InSb
		water
		AgCl
		ZnO (undoped)
		NaCl
		Al ₂ O ₃
		mica
		silica
		diamond

Energy Band Structures in Solids (I)

In an isolated atom electrons occupy well defined energy states, as discussed in Chapter 2.

When atoms come together to form a solid, their valence electrons interact with each other and with nuclei due to Coulomb forces. In addition, two specific quantum mechanical effects happen. First, by Heisenberg's uncertainty principle, constraining the electrons to a small volume raises their energy, this is called *promotion*. The second effect, due to the Pauli exclusion principle, limits the number of electrons that can have the same energy.

As a result of these effects, the valence electrons of atoms form wide **electron energy bands** when they form a solid. The bands are separated by **gaps**, where electrons cannot exist.

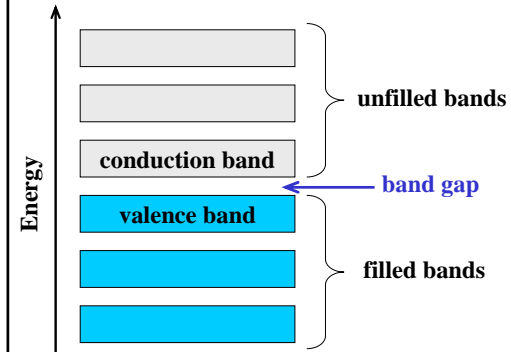


Energy Band Structures and Conductivity

The highest filled state at 0 K **Fermi Energy** (E_F)

The two highest energy bands are:

- **Valence band** – the highest band where the electrons are present at 0 K
- **Conduction band** - a partially filled or empty energy band where the electrons can increase their energies by going to higher energy levels within the band when an electric field is applied



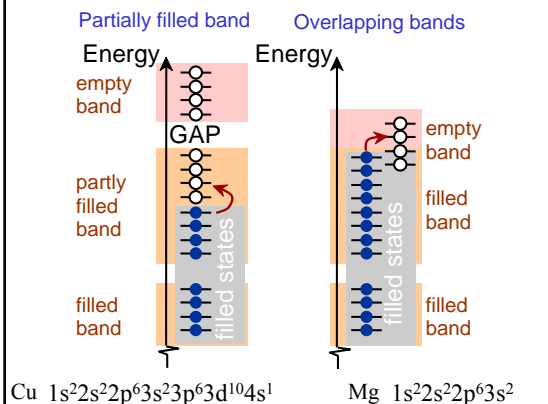
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Energy Band Structures and Conductivity (metals)

In **metals (conductors)**, highest occupied band is partially filled or bands overlap.

Conduction occurs by promoting electrons into conducting states, that starts right above the Fermi level. The conducting states are separated from the valence band by an infinitesimal amount.

Energy provided by an electric field is sufficient to excite many electrons into conducting states.



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Energy Band Structures and Conductivity (semiconductors and insulators)

In **semiconductors and insulators**, the valence band is filled, no more electrons can be added (Pauli's principle).

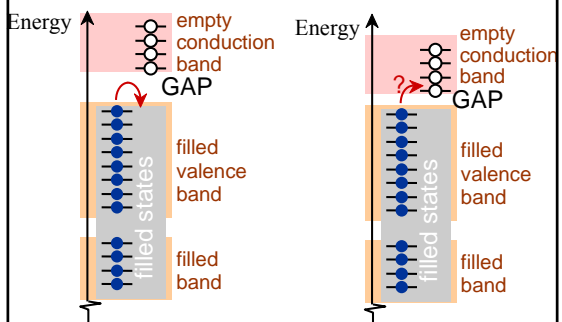
Electrical conduction requires that electrons be able to gain energy in an electric field. To become free, electrons must be promoted (excited) across the band gap. The excitation energy can be provided by heat or light.

Insulators:

wide band gap (> 2 eV)

Semiconductors:

narrow band gap (< 2 eV)



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Energy Band Structures and Conductivity (semiconductors and insulators)

- In semiconductors and insulators, electrons have to jump across the band gap into conduction band to find conducting states above E_f
- The energy needed for the jump may come from heat, or from irradiation at sufficiently small wavelength (photoexcitation).
- The difference between semiconductors and insulators is that in semiconductors electrons can reach the conduction band at ordinary temperatures, where in insulators they cannot.
- The probability that an electron reaches the conduction band is about $\exp(-E_g/2kT)$ where E_g is the band gap. If this probability is $< 10^{-24}$ one would not find a single electron in the conduction band in a solid of 1 cm^3 . This requires $E_g/2kT > 55$. At room temperature, $2kT = 0.05 \text{ eV} \Rightarrow E_g > 2.8 \text{ eV}$ corresponds to an insulator.
- An electron promoted into the conduction band leaves a **hole** (positive charge) in the valence band, that can also participate in conduction. Holes exist in metals as well, but are more important in semiconductors and insulators.

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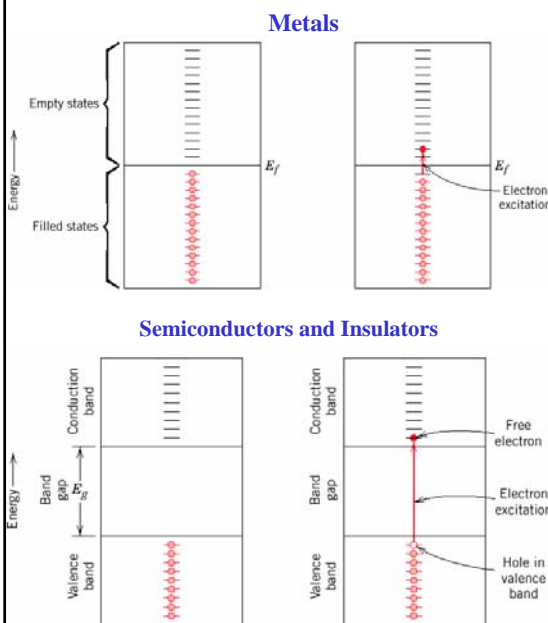
Energy Band Structures and Bonding (metals, semiconductors, insulators)

Relation to atomic bonding:

- **Insulators** – valence electrons are tightly bound to (or shared with) the individual atoms – strongest ionic (partially covalent) bonding.
- **Semiconductors** - mostly covalent bonding somewhat weaker bonding.
- **Metals** – valence electrons form an “electron gas” that are not bound to any particular ion.

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Energy Band Structures and Conductivity (metals, semiconductors, insulators)



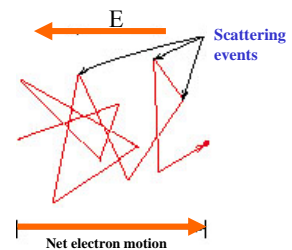
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Electron Mobility

- The force acting on the electron is $-eE$, where e is the electric charge.
- This force produces a constant acceleration so that, in the absence of obstacles the electron speeds up continuously in an electric field. This is the case in vacuum (e.g. inside a TV tube) **or in a perfect crystal** (this is a conclusion from quantum mechanics).
- In a real solid, the electrons **scatter** by collisions with imperfections and due to atomic thermal vibrations. \Rightarrow “frictional forces” \Rightarrow resistance \Rightarrow a net **drift velocity** of electron motion is established:

$$|v_d| = \mu_e E$$

where μ_e – **electron mobility** [$\text{m}^2/\text{V}\cdot\text{s}$]. The “friction” transfers part of the energy supplied by the electric field into the lattice as heat. That is how electric heaters work.



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Electron Mobility

➤ **Electrical conductivity** is proportional to number of free electrons and electron mobility:

$$\sigma = n|e| \mu_e$$

n - number of "free" or conduction electrons per unit volume

(m) = Metal (s) = Semicon	Mobility (RT) μ ($\text{m}^2\text{V}^{-1}\text{s}^{-1}$)	Carrier Density N_e (m^{-3})
Na (m)	0.0053	2.6×10^{28}
Ag (m)	0.0057	5.9×10^{28}
Al (m)	0.0013	1.8×10^{29}
Si (s)	0.15	1.5×10^{10}
GaAs (s)	0.85	1.8×10^6
InSb (s)	8.00	

$$n_{\text{metal}} \gg n_{\text{semi}}$$

$$\mu_{\text{metal}} < \mu_{\text{semi}}$$



$$\sigma_{\text{metal}} \gg \sigma_{\text{semi}}$$

Conductivity / Resistivity of Metals

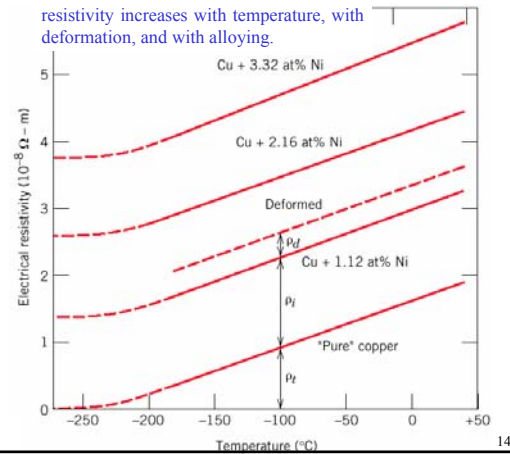
The resistivity ρ is defined by scattering events due to the imperfections and thermal vibrations. Total resistivity ρ_{tot} can be described by the Matthiessen rule:

$$\rho_{\text{total}} = \rho_{\text{thermal}} + \rho_{\text{impurity}} + \rho_{\text{deformation}}$$

where ρ_{thermal} - from thermal vibrations,

ρ_{impurity} - from impurities,

$\rho_{\text{deformation}}$ - from deformation-induced defects



Conductivity / Resistivity of Metals

Influence of temperature:

Resistivity rises linearly with temperature (increasing thermal vibrations and density of vacancies)

$$\rho_T = \rho_0 + aT$$

Influence of impurities:

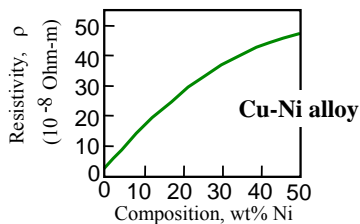
- Impurities that form solid solution

$$\rho_i = A c_i (1 - c_i)$$

where c_i is impurity concentration, A – composition independent constant

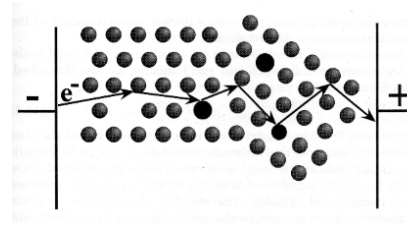
- Two-phase alloy (α and β phases) – rule-of-mixtures:

$$\rho_i = \rho_\alpha V_\alpha + \rho_\beta V_\beta$$



Conductivity / Resistivity of Metals

Influence of plastic deformation:



Normally, the influence of plastic deformation on electrical resistivity is weaker than the influence of temperature and impurities

In general, presence of any imperfections (crystal defects) increases resistivity

- grain boundaries
- dislocations
- impurity atoms
- vacancies

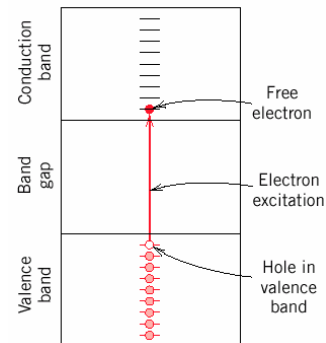
Materials of Choice for Metal Conductors

- One of the best material for electrical conduction (low resistivity) is **silver**, but its use is restricted due to the high cost
- Most widely used conductor is **copper**: inexpensive, abundant, high σ , but rather soft – cannot be used in applications where mechanical strength is important.
- Solid solution alloying and cold working improve strength but decrease conductivity. **Precipitation hardening** is preferred, e.g. Cu-Be alloy
- When weight is important one uses **aluminum**, which is half as good as Cu and more resistant to corrosion.
- **Heating elements** require low σ (high R), and resistance to high temperature oxidation: **nickel-chromium** alloy

Metal	Electrical Conductivity [($\Omega\cdot m$) ⁻¹]
Silver	6.8×10^7
Copper	6.0×10^7
Gold	4.3×10^7
Aluminum	3.8×10^7
Iron	1.0×10^7
Brass (70 Cu–30 Zn)	1.6×10^7
Platinum	0.94×10^7
Plain carbon steel	0.6×10^7

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Semiconductivity



Intrinsic semiconductors - electrical conductivity is defined by the electronic structure of pure material.

Extrinsic semiconductors - electrical conductivity is defined by impurity atoms.

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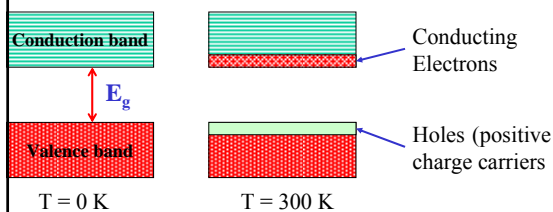
Intrinsic semiconductors (I)

Examples: Si, Ge, GaP, GaAs, InSb, CdS, ZnTe

Number of electrons in conduction band increases exponentially with temperature:

$$n = C T^{3/2} \exp(-E_g/2kT)$$

C is a material constant
 E_g is the bandgap width



An electron promoted into the conduction band leaves a **hole** (positive charge) in the valence band. In an electric field, electrons and holes move in opposite direction and participate in conduction.

In Si ($E_g = 1.1$ eV) one out of every 10^{13} atoms contributes an electron to the conduction band at room temperature.

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Intrinsic semiconductors (II)

Since both electrons and holes are charge carriers in an intrinsic semiconductor, the conductivity is

$$\sigma = n|e|\mu_e + p|e|\mu_h$$

where p is the hole concentration and μ_h the hole mobility.

Electrons are more mobile than holes, $\mu_e > \mu_h$

In an intrinsic semiconductor, a hole is produced by the promotion of each electron to the conduction band. Therefore, $n = p$ and

$$\sigma = n|e|(\mu_e + \mu_h) = p|e|(\mu_e + \mu_h)$$

(only for intrinsic semiconductors)

n (and p) increase exponentially with temperature, whereas μ_e and μ_h decrease (about linearly) with temperature. \Rightarrow **The conductivity of intrinsic semiconductors is increasing with temperature (different from metals!)**

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Intrinsic semiconductors (III)

← Field

Free electron

Hole

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Intrinsic semiconductors (IV)

Table 18.3 Band Gap Energies, Electron and Hole Mobilities, and Intrinsic Electrical Conductivities at Room Temperature for Semiconducting Materials

Material	Band Gap (eV)	Electrical Conductivity [$(\Omega \cdot m)^{-1}$]	Electron Mobility ($m^2/V \cdot s$)	Hole Mobility ($m^2/V \cdot s$)
Elemental				
Si	1.11	4×10^{-4}	0.14	0.05
Ge	0.67	2.2	0.38	0.18
III-V Compounds				
GaP	2.25	—	0.03	0.015
GaAs	1.42	10^{-6}	0.85	0.04
InSb	0.17	2×10^4	7.7	0.07
II-VI Compounds				
CdS	2.40	—	0.03	—
ZnTe	2.26	—	0.03	0.01

Let's calculate carrier concentration for Si at 300 K

$$\sigma = n|e|(\mu_e + \mu_h) \implies n = \frac{\sigma}{|e|(\mu_e + \mu_h)}$$

$$n = \frac{4 \times 10^{-4} \Omega^{-1} m^{-1}}{1.6 \times 10^{-19} C \times (0.14 + 0.05) m^2 V^{-1} s^{-1}} = 1.3 \times 10^{16} m^{-3}$$

molar volume of Si $\approx 12 \text{ cm}^3/\text{mol}$ $\Omega = \frac{V}{A}$ $A = \frac{C}{s}$
 $N_A \approx 6 \times 10^{23} \text{ atoms/mol}$
 $6 \times 10^{23} / 12 \times 10^{-6} = 5 \times 10^{28} \text{ atoms/m}^3$
fraction of excited electrons per atom $\sim 10^{-13}$

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Extrinsic semiconductors

Extrinsic semiconductors - electrical conductivity is defined by impurity atoms.

Example: Si is considered to be extrinsic at room T if impurity concentration is one impurity per 10^{12} lattice sites (remember our estimation of the number of electrons promoted to the conduction band by thermal fluctuations at 300 K)

Unlike intrinsic semiconductors, an extrinsic semiconductor may have different concentrations of holes and electrons.

It is called **p-type** if $p > n$ and **n-type** if $n > p$.

One can engineer conductivity of extrinsic semiconductors by controlled addition of impurity atoms - **doping** (addition of a very small concentration of impurity atoms). Two common methods of doping are **diffusion** and **ion implantation**.

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n-type extrinsic semiconductors (I)

Excess electron carriers are produced by substitutional impurities that have more valence electron per atom than the semiconductor matrix.

Example: phosphorus (or As, Sb...) with 5 valence electrons, is an **electron donor** in Si since only 4 electrons are used to bond to the Si lattice when it substitutes for a Si atom. Fifth outer electron of P atom is weakly bound in a **donor state** ($\sim 0.01 \text{ eV}$) and can be easily promoted to the conduction band.

Impurities which produce extra conduction electrons are called **donors**, $N_D = N_{\text{Phosphorus}} \sim n$

Elements in columns V and VI of the periodic table are donors for semiconductors in the IV column, Si and Ge.

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n-type extrinsic semiconductors (II)

The hole created in donor state is far from the valence band and is immobile. Conduction occurs mainly by the donated electrons (thus n-type).

$$\sigma \sim n|e|\mu_e \sim N_D |e|\mu_e$$

(for extrinsic n-type semiconductors)

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p-type extrinsic semiconductors (I)

Excess holes are produced by substitutional impurities that have fewer valence electrons per atom than the matrix.

A bond with the neighbors is incomplete and can be viewed as a **hole** weakly bound to the impurity atom.

Elements in columns III of the periodic table (B, Al, Ga) are donors for semiconductors in the IV column, Si and Ge. Impurities of this type are called **acceptors**, $N_A = N_{\text{Boron}} \sim p$

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p-type extrinsic semiconductors (II)

The energy state that corresponds to the hole (**acceptor state**) is close to the top of the valence band. An electron may easily hop from the valence band to complete the bond leaving a hole behind. Conduction occurs mainly by the holes (thus p-type).

$$\sigma \sim p|e|\mu_p \sim N_A |e|\mu_p$$

(for extrinsic p-type semiconductors)

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Temperature variation of conductivity

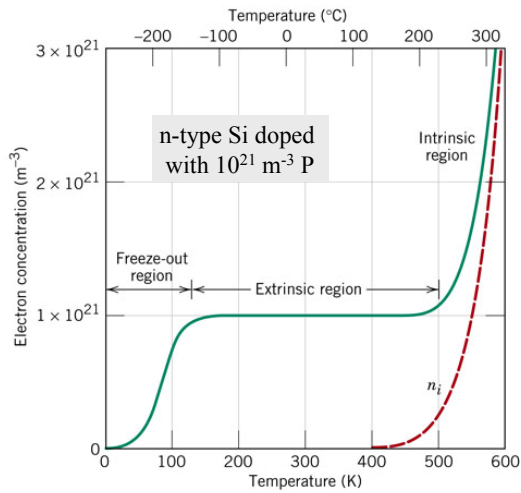
Basic equation for conductivity: $\sigma = n|e|\mu_e + p|e|\mu_h$

Therefore, the temperature dependence of thermal conductivity is defined by the temperature dependences of **carrier concentration** and **mobility**

Carrier concentration vs T: Intrinsic semiconductors

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Carrier concentration vs T: Extrinsic semiconductors



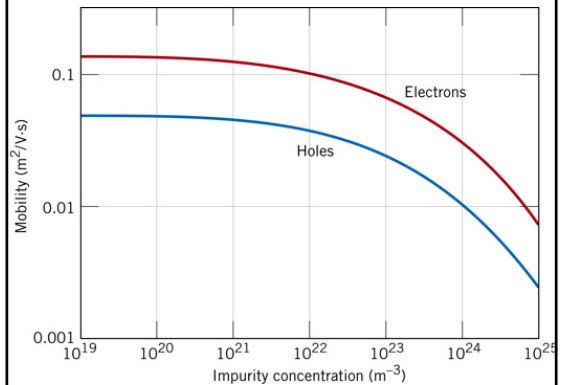
- Extrinsic region:** All P donor state electrons are excited
- Freeze-out region:** Thermal energy is too low for exciting the electrons from P donor states to the conduction band
- Intrinsic region:** Excitations across the band gap dominate

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Carrier mobility

Dopants are impurities and, like in metals, the mobility of carriers decreases with impurity concentration

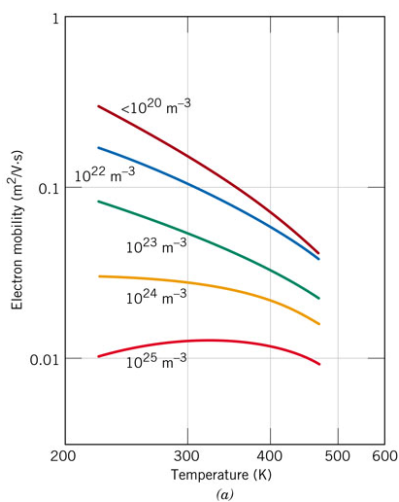
At dopant levels less than $10^{20} m^{-3}$ the effect of dopants on mobility is negligible



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Carrier mobility

For dopant concentrations below $10^{24} m^{-3}$, mobility of both electrons and holes decreases with increasing temperature due to the enhanced thermal scattering.

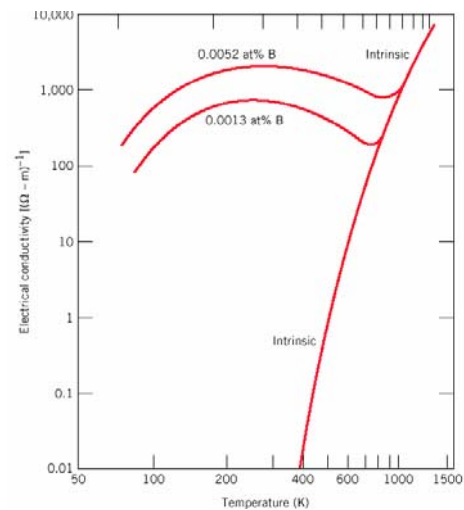


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Temperature variation of conductivity

Basic equation for conductivity: $\sigma = n|e|\mu_e + p|e|\mu_h$

In **intrinsic semiconductors**, the temperature dependence of mobilities, μ_e and μ_h is weak as compared to the strong exponential dependence of carrier concentration



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Conduction in Polymers and Ionic Materials

Ionic Materials

- In ionic materials, the band gap is large and only very few electrons can be promoted to the valence band by thermal fluctuations.
- Cation and anion diffusion can be directed by the electric field and can contribute to the total conductivity: $\sigma_{\text{total}} = \sigma_{\text{electronic}} + \sigma_{\text{ionic}}$
- High temperatures produce more Frenkel and Schottky defects which result in higher ionic conductivity.

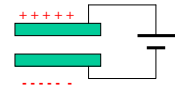
Polymers

- Polymers are typically good insulators but can be made to conduct by doping.
- A few polymers have very high electrical conductivity - about one quarter that of copper, or about twice that of copper per unit weight.

Capacitance

When a voltage V is applied to two parallel conducting plates, the plates are charged by $+Q$, $-Q$, and an electric field E develops between the plates.

The charge remains on the plates even after the voltage has been removed.



The ability to store charge is called **capacitance** and is defined as a charge Q per applied voltage V :

$$C = Q / V \text{ [Farads]}$$

For a parallel-plate capacitor, C depends on **geometry of plates and material between plates**

$$C = \epsilon_r \epsilon_0 A / L = \epsilon A / L$$

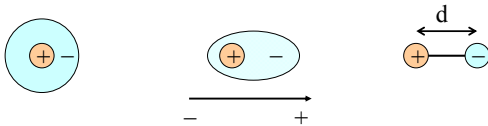
where A is the area of the plates, L is the distance between plates, ϵ is the **permittivity** of the dielectric medium, ϵ_0 is the permittivity of a vacuum ($8.85 \times 10^{-12} \text{ F/m}^2$), and ϵ_r is **relative permittivity (or dielectric constant) of the material**, $\epsilon_r = \epsilon / \epsilon_0 = C / C_{\text{vac}}$

Dielectric Materials

The dielectric constant of vacuum is 1 and is close to 1 for air and many other gases. But when a piece of a dielectric material is placed between the two plates in capacitor the capacitance can increase significantly.

$$C = \epsilon_r \epsilon_0 A / L \quad \text{with } \epsilon_r = 81 \text{ for water, } 20 \text{ for acetone, } 12 \text{ for silicon, } 3 \text{ for ice, etc.}$$

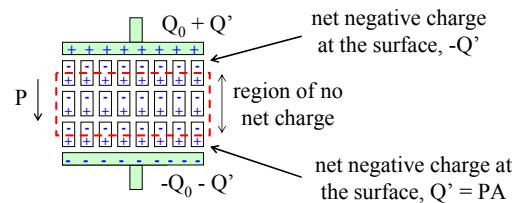
A **dielectric material** is an **insulator** in which **electric dipoles** can be induced by the electric field (or permanent dipoles can exist even without electric field), that is where positive and negative charge are separated on an atomic or molecular level



Magnitude of electric dipole moment is $p = q d$

Dielectric Materials

Dipole formation and/or orientation along the external electric field in the capacitor causes a charge redistribution so that the surface nearest to the positive capacitor plate is negatively charged and vice versa.



Dipole formation induces additional charge Q' on plates: total plate charge $Q_t = |Q + Q'|$.

Therefore, $C = Q_t / V$ has increased and dielectric constant of the material $\epsilon_r = C / C_{\text{vac}} > 1$

The process of dipole formation/alignment in electric field is called **polarization** and is described by $P = Q' / A$

Dielectric Materials

In the capacitor **surface charge density** (also called **dielectric displacement**) is

$$D = Q/A = \epsilon_r \epsilon_0 E = \epsilon_0 E + P$$

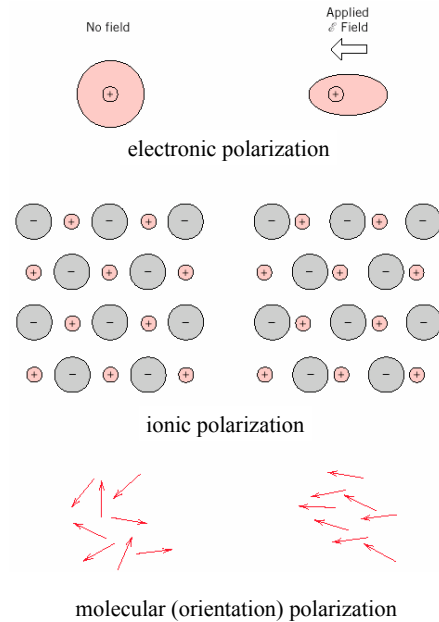
Polarization is responsible for the increase in charge density above that for vacuum

Mechanisms of polarization (dipole formation/orientation)

- **electronic** (induced) polarization: Applied electric field displaces negative electron “clouds” with respect to positive nucleus. Occurs in all materials.
- **ionic** (induced) polarization: In ionic materials, applied electric field displaces cations and anions in opposite directions
- **molecular** (orientation) polarization: Some materials possess **permanent electric dipoles** (e.g. H₂O). In absence of electric field, dipoles are randomly oriented. Applying electric field aligns these dipoles, causing net (large) dipole moment.

$$P_{\text{total}} = P_e + P_i + P_o$$

Mechanisms of polarization

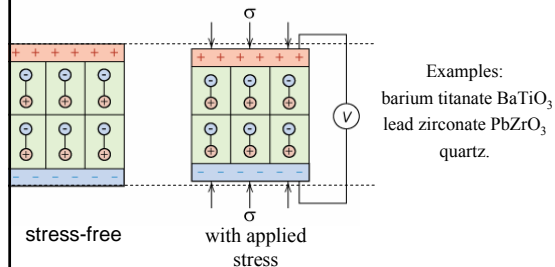


Dielectric strength

Very high electric fields (>10⁸ V/m) can excite electrons to the conduction band and accelerate them to such high energies that they can, in turn, free other electrons, in an avalanche process (or electrical discharge). The field necessary to start the avalanche process is called **dielectric strength** or breakdown strength.

Piezoelectricity

In some ceramic materials, application of external forces produces an electric (polarization) field and vice-versa. Applications of **piezoelectric** materials is based on conversion of mechanical strain into electricity (microphones, strain gauges, sonar detectors)



Summary

Make sure you understand language and concepts:

- Acceptor state
- Capacitance
- Conduction band
- Conductivity, electrical
- Dielectric constant
- Dielectric strength
- Donor state
- Doping
- Electrical resistance
- Electron energy band
- Energy band gap
- Extrinsic semiconductor
- Free electron
- Hole
- Insulator
- Intrinsic semiconductor
- Matthiessen's rule
- Metal
- Charge carrier mobility
- Ohm's law
- Permittivity
- Piezoelectric
- Polarization
- Resistivity, electrical
- Semiconductor
- Valence band