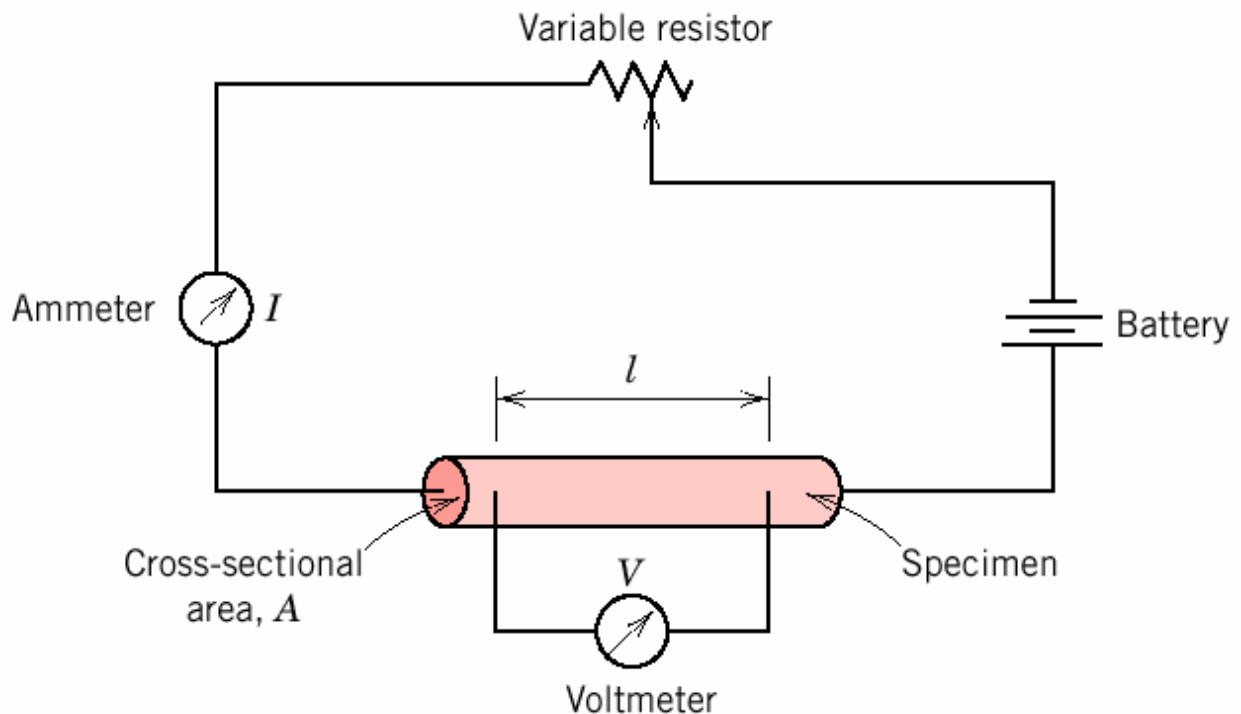


Basic laws and electrical properties of metals (I)

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).

The electrical conductivity (the ability of a substance to conduct an electric current) is the inverse of the resistivity: $\sigma = 1/\rho$

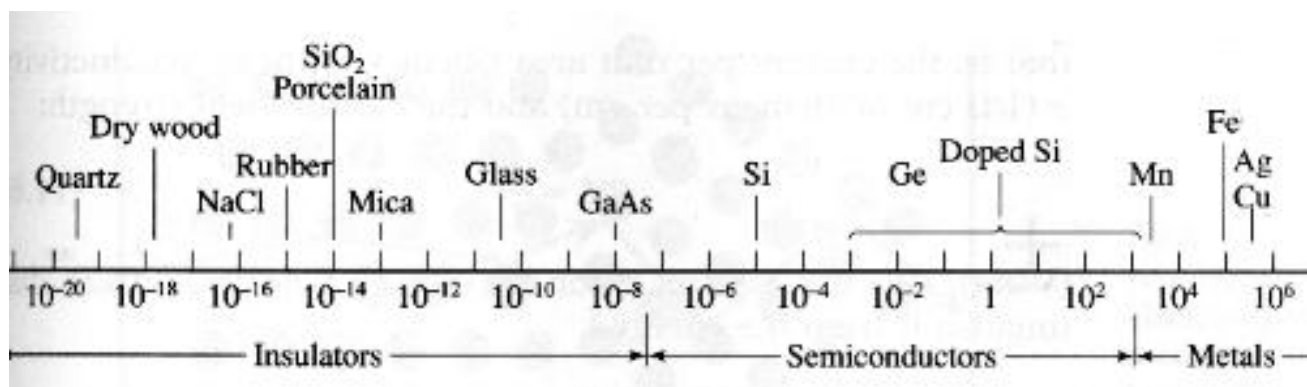
Since the electric field intensity (the voltage difference between two points divided by the distance separating them) in the material is $E = V/l$,

Ohm's law can be rewritten in terms of the current density (the current per unit of specimen area)

$$J = I/A$$

as: $J = \sigma E$

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



one way of classifying solid materials is according to the ease with which they conduct an electric current; within this classification scheme there are three groupings: *conductors*, *semiconductors*, and *insulators*

Metals: $\sigma \sim 10^7 \text{ } (\Omega.\text{m})^{-1}$

Semiconductors: $10^{-6} < \sigma < 10^4 (\Omega.m)^{-1}$

Insulators: σ ($10^{-10} - 10^{-20}$) $(\Omega.m)^{-1}$

Electrical Resistivity (ohm-m)	(log)	Electrical Conductivity (S/m)
	-8	8
intercalated graphite	-7	7 copper, silver iron
graphite (in-plane)	-6	6 stainless steel, metallic glass
graphite (out of plane)	-5	5 $\text{YBa}_2\text{Cu}_3\text{O}_7$ (ab plane)
polyacetylene (doped)	-4	4 $\text{YBa}_2\text{Cu}_3\text{O}_7$ (c-axis)
	-3	3 silicon (doped) ZnO (doped)
TTF-TCNQ	-2	2 seawater
	-1	1 Fe_3O_4
	0	0 germanium
	1	-1
	2	-2
	3	-3 silicon
	4	-4 InSb
	5	-5 water
polyacetylene (undoped)	6	-6 AgCl
	7	-7
	8	-8 ZnO (undoped)
	9	-9
	10	-10
Bakelite	11	-11 NaCl
polypyrrole	12	-12
	13	-13
Lucite (PMMA)	14	-14 Al_2O_3
polyvinyl chloride	15	-15 mica silica
polyethylene, teflon	16	-16 diamond

Example: (a) Compute the electrical conductivity of a 7.0-mm (0.28-in.) diameter cylindrical silicon specimen 57 mm long in which a current of 0.25 A passes in an axial direction. A voltage of 24 V is measured across two probes that are separated by 45 mm. **(b)** Compute the resistance over the entire 57 mm of the specimen.

(a)

$$\sigma = l \rho = l / VA = l / V \pi (d/2)^2$$

And, incorporating values for the several parameters provided in the problem statement, leads to $\sigma = (0.25 \text{ A})(45 \times 10^{-3} \text{ m}) / (24 \text{ V})(\pi)(7.0 \times 10^{-3} \text{ m} / 2)^2 = 12.2 (\Omega \cdot \text{m})^{-1}$

(b)

$$R = l / \sigma A = l / \sigma \pi (d/2)^2 \\ = 57 \times 10^{-3} \text{ m} / [12.2 (\Omega \cdot \text{m})^{-1}] (\pi)(7.0 \times 10^{-3} \text{ m} / 2)^2 = 121.4 \Omega$$

Electronic And Ionic Conduction:

An electric current results from the motion of electrically charged particles in response to forces that act on them from an externally applied electric field. **Positively charged particles** are accelerated in the **field direction**, **negatively charged particles in the direction opposite**. Within most solid materials a current arises from the flow of electrons, which is termed *electronic conduction*. In addition, for ionic materials a net motion of charged ions is possible that produces a current; such is termed **ionic conduction**.

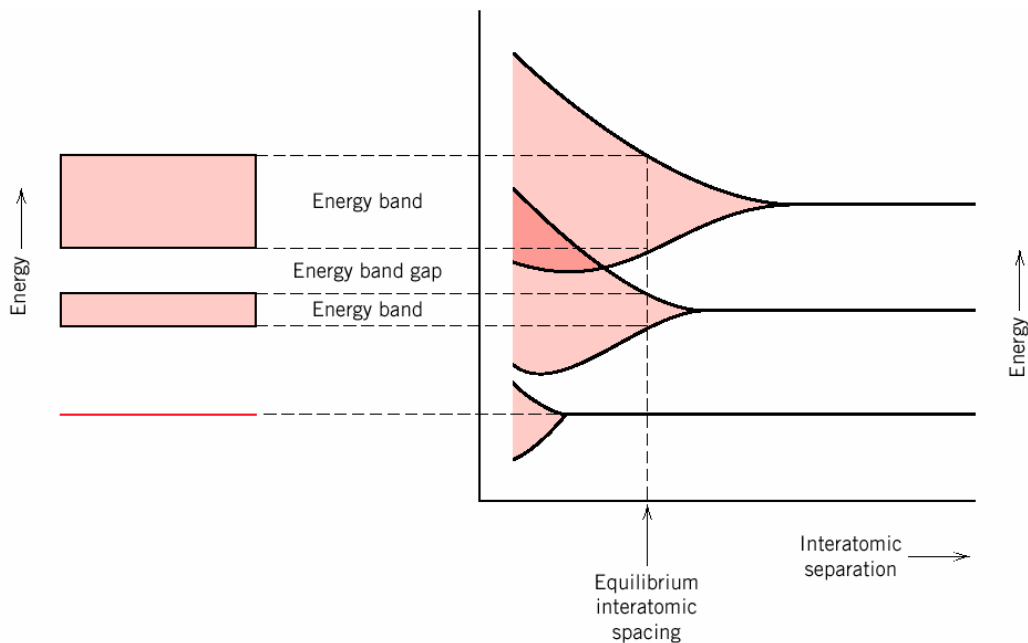
Energy Band Structures in Solids:

In all conductors, semiconductors, and many insulating materials, only electronic conduction exists, and the magnitude of the electrical conductivity is strongly dependent on the number of electrons available to participate in the conduction process.

For each individual atom there exist discrete energy levels that may be occupied by electrons, arranged into shells and subshells. Shells are designated by integers (1, 2, 3, etc.), and subshells by letters (*s*, *p*, *d*, and *f*). For each of *s*, *p*, *d*, and *f* subshells, there exist, respectively, one, three, five, and seven states.

In an isolated atom electrons occupy well defined energy states. **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)

Fermi level: energy level in solids at which the Fermi-Dirac distribution function is equal to 0.5.

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



Conduction In Terms Of Band And Atomic Bonding Models:

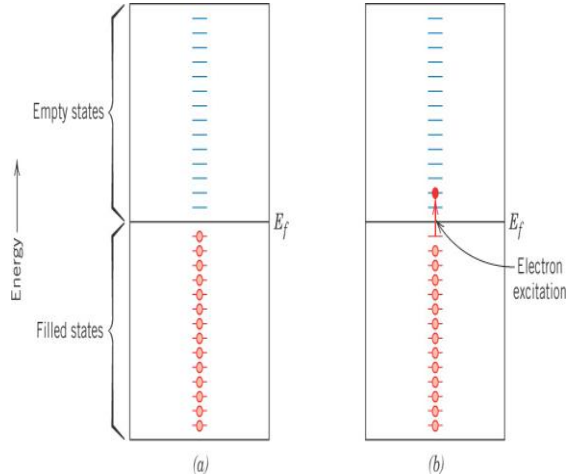
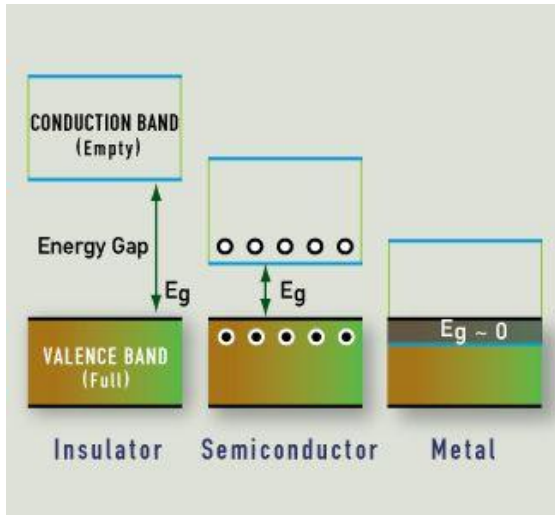
Electrons with energies greater than the Fermi energy (E_f) may be acted on and accelerated in the presence of an electric field. These are the electrons that participate in the conduction process, which are termed **free electrons**. Another charged electronic entity called a **hole** is found in semiconductors and insulators. Holes have energies less than E_f and also participate in electronic conduction.

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.



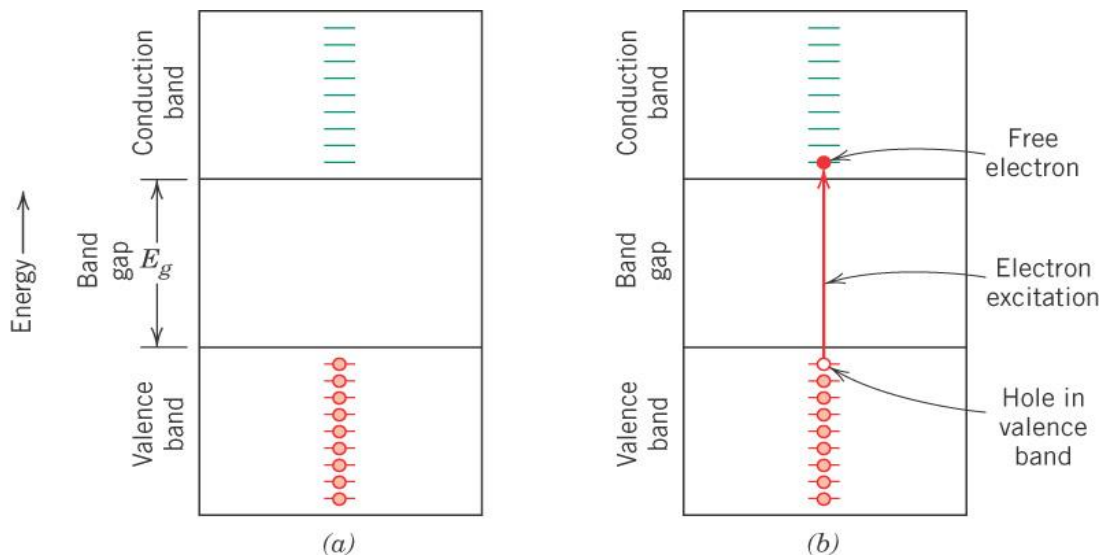
For a metal, occupancy of electron states (a) before and (b) after an electron excitation.

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 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)



For an insulator or semiconductor, occupancy of electron states (a) before and (b) after an electron excitation from the valence band into the conduction band, in which both a free electron and a hole are generated.

- ✓ In semiconductors and insulators, electrons have to jump across the band gap into conduction band to find conducting states above E_f . This is possible only by supplying to an electron the difference in energy between these two states, which is approximately equal to the band gap energy E_g .
- ✓ The energy needed for the jump may come from heat, or from irradiation at sufficiently small wavelength (photoexcitation).
- ✓ The number of electrons excited thermally (by heat energy) into the conduction band depends on the energy band gap width as well as temperature
- ✓ 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.
- ✓

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

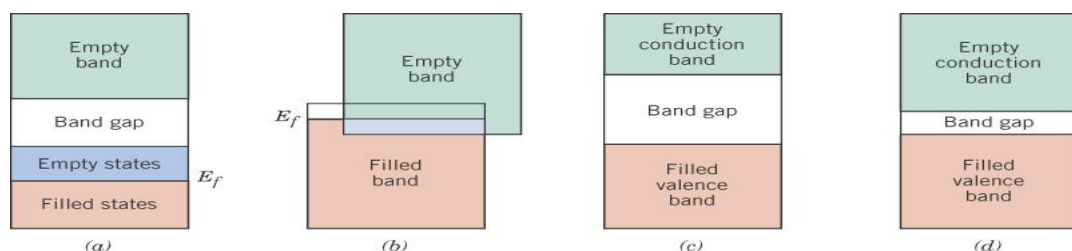
Relation to atomic bonding:

- ✓ **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.

Metals, Semiconductors, and Insulators:

Every solid has its own characteristic energy band structure. In order for a material to be conductive, both free electrons and empty states must be available.

- ✓ *Metals* have free electrons and partially filled valence bands, therefore they are highly conductive (a).
- ✓ *Semimetals* have their highest band filled. This filled band, however, overlaps with the next higher band, therefore they are conductive but with slightly higher resistivity than normal metals (b). Examples: arsenic, bismuth, and antimony.
- ✓ *Insulators* have filled valence bands and empty conduction bands, separated by a large band gap E_g (typically $> 4 \text{ eV}$), they have high resistivity (c).
- ✓ Semiconductors have similar band structure as insulators but with a much smaller band gap. Some electrons can jump to the empty conduction band by thermal or optical excitation (d). $E_g = 1.1 \text{ eV}$ for Si, 0.67 eV for Ge and 1.43 eV for GaAs



The various possible electron band structures in solids at 0 K. (a) The electron band structure found in metals such as copper, in which there are available electron states above and adjacent to filled states, in the same band. (b) The electron band structure of metals such as magnesium, wherein there is an overlap of filled and empty outer bands. (c) The electron band structure characteristic of insulators; the filled valence band is separated from the empty conduction band by a relatively large band gap ($> 2 \text{ eV}$). (d) The electron band structure found in the semiconductors, which is the same as for insulators except that the band gap is relatively narrow ($< 2 \text{ eV}$).

Electron Mobility:

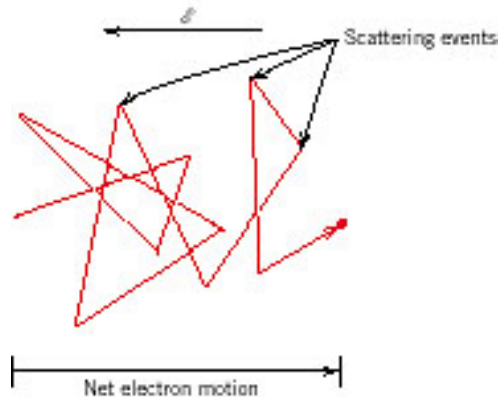
- ✓ The force acting on the electron is $-eE$, where e is the electric charge.
- ✓ This force produces a constant acceleration so that, in the absence of obstacles the electron speeds up continuously in an electric field. This is the case in vacuum (e.g. inside a TV tube) **or in a perfect crystal**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

⇒ “frictional forces” ⇒ resistance ⇒ a net **drift velocity** of electron motion is established:

$$|\mathbf{v}_d| = \mu_e \mathbf{E}$$

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.

The drift velocity of a free electron is the average electron velocity in the direction of the force imposed by an electric field.



The mobility is the proportionality constant between the drift velocity and the electric field. It is also a measure of the frequency of scattering events (and is inversely proportional to the frequency of scattering).

- ✓ **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

Scattering Events

- ✓ Electric field drifts electrons in the opposite direction to the field
- ✓ The actual speed of electrons is much higher than the drift velocity
- ✓ Scattering is due to the strike with the nuclei
- ✓ When the actual velocity of the electrons is similar to the drift velocity, the system is in the ballistic regime
- ✓ In the ballistic regime there is practically no barrier for the electrons
- ✓ Examples: in vacuum tubes, ~in carbon nanotubes (CNT), superconductors

(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	

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

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

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

Example: (a) Calculate the drift velocity of electrons in silicon at room temperature and when the magnitude of the electric field is 500 V/m. (b) Under these circumstances, how long does it take an electron to traverse a 25-mm length of crystal?

(a) Since the room temperature mobility of electrons is $0.14 \text{ m}^2/\text{V}\cdot\text{s}$

$$v_d = \mu_e E$$

$$= (0.14 \text{ m}^2/\text{V}\cdot\text{s})(500 \text{ V/m}) = 70 \text{ m/s}$$

(b) The time, t , required to traverse a given length, l ($= 25 \text{ mm}$), is just

$$t = l / v_d = 25 \times 10^{-3} \text{ m} / 70 \text{ m/s} = 3.6 \times 10^{-4} \text{ s}$$

Example: At room temperature the electrical conductivity and the electron mobility for aluminum are $3.8 \times 10^7 (\Omega\cdot\text{m})^{-1}$ and $0.0012 \text{ m}^2/\text{V}\cdot\text{s}$ respectively. Compute the number of free electrons per cubic meter for aluminum at room temperature.

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

$$= 3.8 \times 10^7 (\Omega\cdot\text{m})^{-1} / (1.602 \times 10^{-19} \text{ C})(0.0012 \text{ m}^2/\text{V}\cdot\text{s})$$

$$= 1.98 \times 10^{29} \text{ m}^{-3}$$

Example: (a) Calculate the number of free electrons per cubic meter for silver, assuming that there are 1.3 free electrons per silver atom. The electrical conductivity and density for Ag are $6.8 \times 10^7 (\Omega\cdot\text{m})^{-1}$ and 10.5 g/cm^3 , respectively. (b) Now compute the electron mobility for Ag.

Note: for silver, the number of free electrons per cubic meter (n) given that there are 1.3 free electrons per silver atom.

(a)

$$n = 1.3 N_{\text{Ag}} = 1.3 (\rho_{\text{Ag}} N_A / A_{\text{Ag}})$$

$$n = 1.3 [(10.5 \text{ g/cm}^3)(6.023 \times 10^{23} \text{ atoms/mol})] / 107.87 \text{ g/mol}$$

$$n = 7.62 \times 10^{22} \text{ cm}^{-3} = 7.62 \times 10^{28} \text{ m}^{-3}$$

(b)

Now we are asked to compute the electron mobility, μ_e .

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

$$\mu_e = 6.8 \times 10^7 (\Omega\cdot\text{m})^{-1} / (7.62 \times 10^{28} \text{ m}^{-3})(1.602 \times 10^{-19} \text{ C}) = 5.57 \times 10^{-3} \text{ m}^2/\text{V}\cdot\text{s}$$

Conductivity / Resistivity of Metals

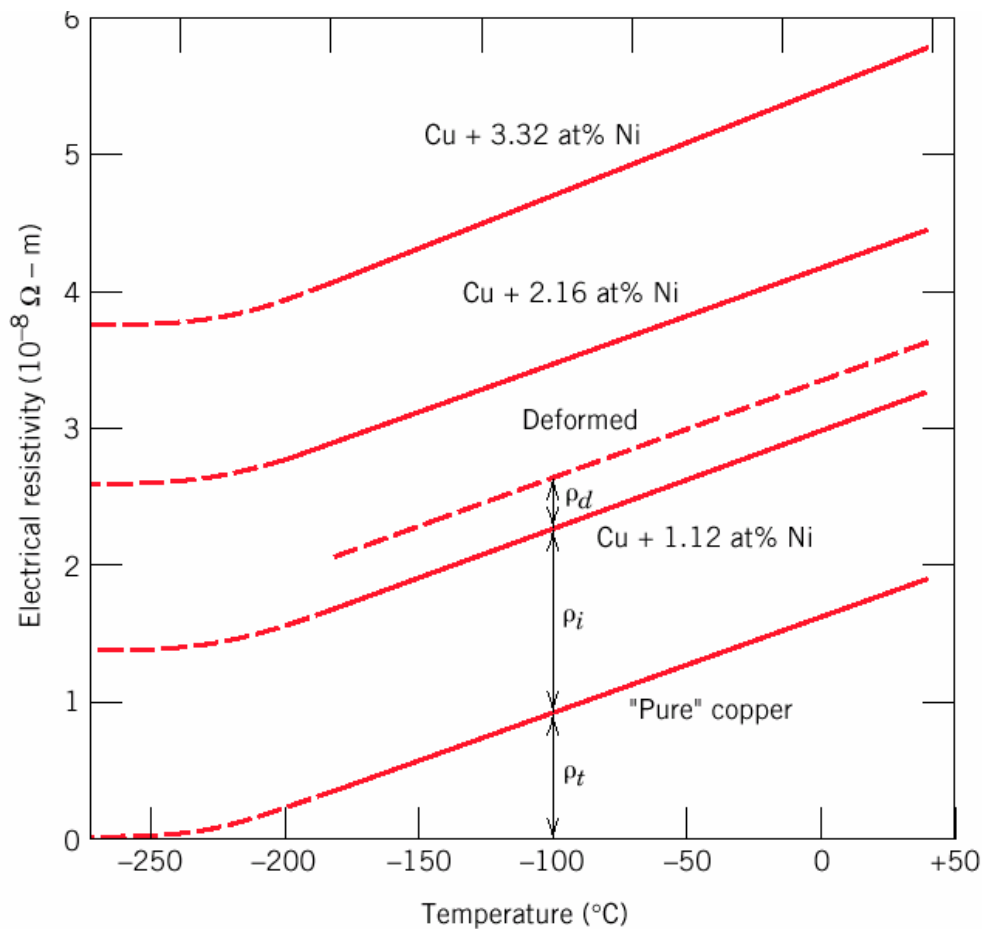
The resistivity ρ is defined by scattering events due to the imperfections, thermal vibrations (phonons) and deformation. Total resistivity ρ_{tot} can be described by the Matthiessen rule:

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

where ρ_{thermal} - from thermal vibrations,

ρ_{impurity} - from impurities,

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



Influence of temperature:

For the pure metal and all the copper–nickel alloys shown in Figure above, the resistivity rises linearly with temperature above about $-200^{\circ}C$ (increasing thermal vibrations and density of vacancies, which serve as electron-scattering centers)

$$\rho_t = \rho_0 + \alpha T$$

where ρ_0 and α are constants for each particular metal.

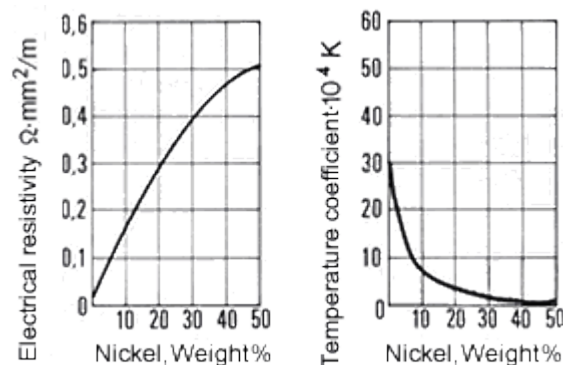
Influence of impurities:

- For additions of a single impurity that forms a solid solution,

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

where c is impurity concentration in terms of the atom fraction (at%_100),

A – composition independent constant that is a function of both the impurity and host metals



Electrical resistivity and temperature coefficient of electrical resistance of Cu-Ni alloys as a function of nickel content

• For two-phase alloy consisting of (α and β phases) – rule-of-mixtures:

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

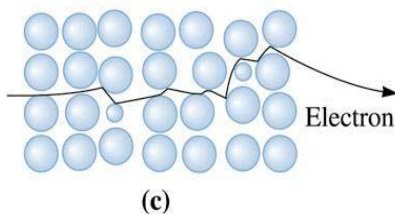
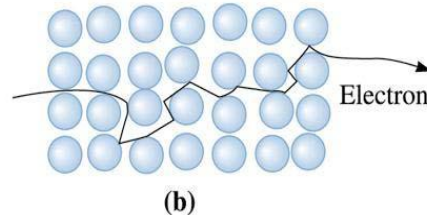
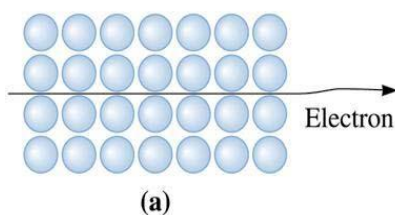
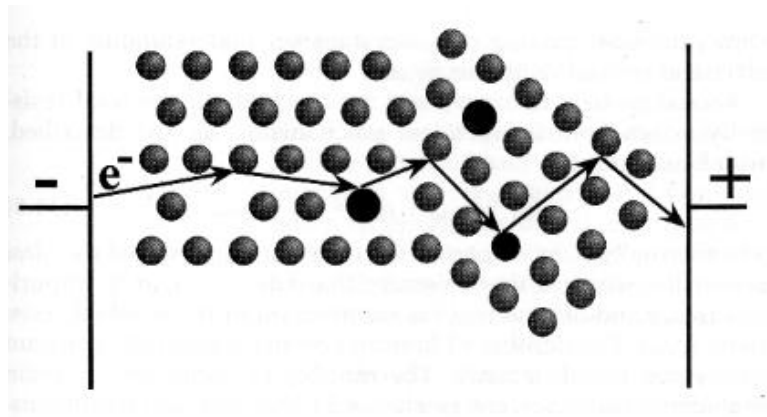
where the V 's and ρ 's represent volume fractions and individual resistivities for the respective phases.

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



Movement of an electron through (a) a perfect crystal, (b) a crystal heated to a high temperature, and (c) a crystal containing atomic level defects. Scattering of the electrons reduces the mobility and conductivity.

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 (by about a factor of 5 over high-purity copper). **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: **nickelchromium** alloy

<i>Metal</i>	<i>Electrical Conductivity</i> [$(\Omega\text{-m})^{-1}$]
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

Semiconductivity:

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

Examples: Si, Ge, GaP, GaAs, InSb, CdS, ZnTe
Number of electrons in conduction band increases exponentially with temperature:

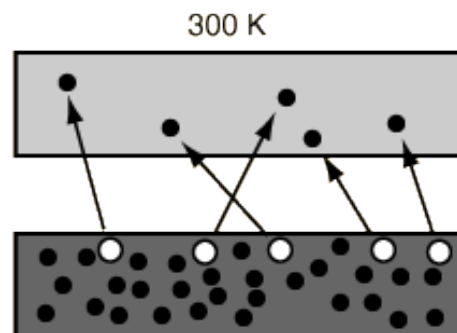
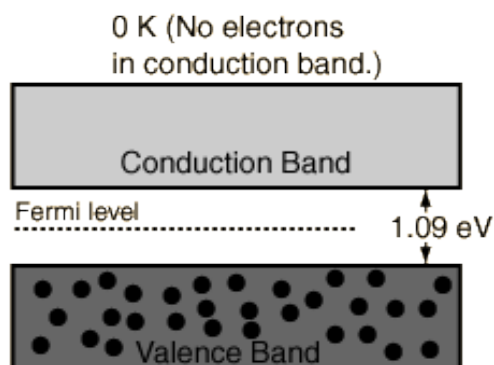
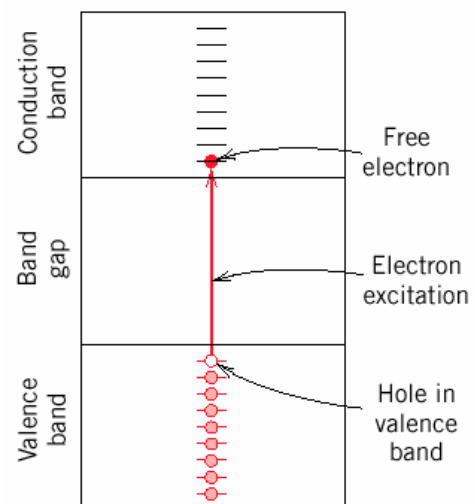
$$n = C T^{3/2} \exp(-E_g/2kT)$$

C is a material constant

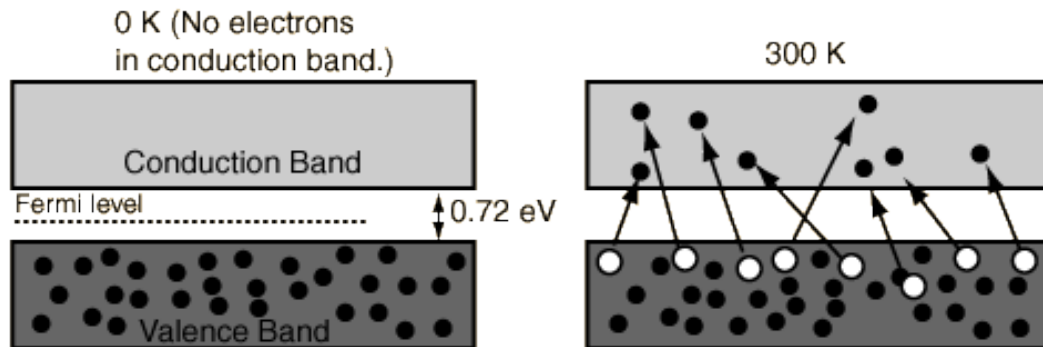
E_g is the bandgap width

Silicon Energy Bands

At finite temperatures, the number of electrons which reach the conduction band and contribute to current can be modeled by the Fermi function. That current is small compared to that in doped semiconductors under the same conditions.



Germanium Energy Bands



- 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.
- Since there are two types of charge carrier (free electrons and holes) in an intrinsic semiconductor, the expression for electrical conduction 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, $\mu_e > \mu_h$
- For intrinsic semiconductors, every electron promoted across the band gap leaves behind a hole in the valence band; thus,
- $n = p = n_i$, where n_i is known as the *intrinsic carrier concentration*
- $\sigma = n|e|(\mu_e + \mu_h) = p|e|(\mu_e + \mu_h) = n_i |e|(\mu_e + \mu_h)$ (only for intrinsic semiconductors)
- n (and p) increase exponentially with temperature, whereas μ_e and μ_h decrease (about linearly) with temperature.
- **The conductivity of intrinsic semiconductors is increasing with temperature (different from metals)**

Example: At room temperature the electrical conductivity of PbS is $25 (\Omega \cdot m)^{-1}$ whereas the electron and hole mobilities are 0.06 and 0.02 $m^2/V \cdot s$, respectively. Compute the intrinsic carrier concentration for PbS at room temperature.

$$\begin{aligned}
 n_i &= \sigma / |e|(\mu_e + \mu_h) \\
 &= 25(\Omega \cdot m)^{-1} / (1.602 \times 10^{-19} C)(0.06 + 0.02) m^2/V \cdot s \\
 &= 1.95 \times 10^{21} m^{-3}
 \end{aligned}$$

Intrinsic and Extrinsic semiconductors:

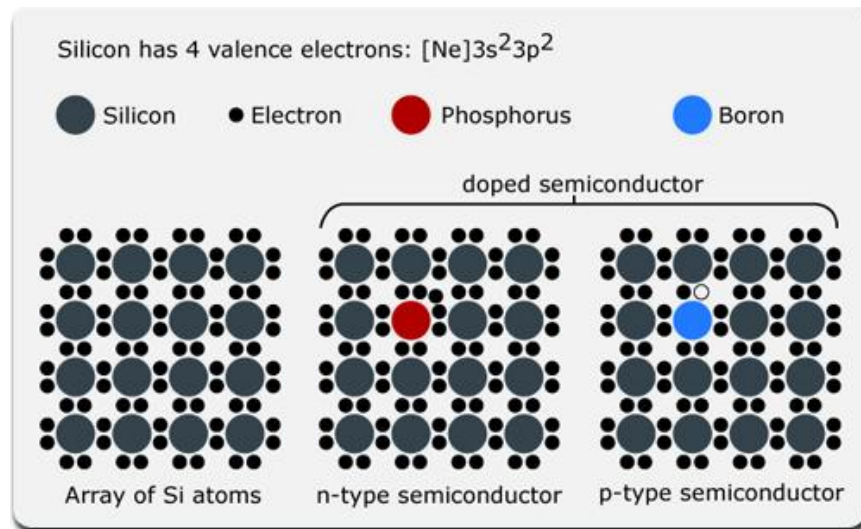


Table 18.3 Band Gap Energies, Electron and Hole Mobilities, and Intrinsic Electrical Conductivities at Room Temperature for Semiconducting Materials

Material	Band Gap (eV)	Electrical Conductivity $[(\Omega \cdot \text{m})^{-1}]$	Electron Mobility $(\text{m}^2/\text{V} \cdot \text{s})$	Hole Mobility $(\text{m}^2/\text{V} \cdot \text{s})$
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

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

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

Molar volume of Si $\approx 12 \text{ cm}^3/\text{mol}$

$$\Omega = V/A, \quad A = C/S$$

$$N_A \approx 6 \times 10^{23} \text{ atoms/mol}$$

$$6 \times 10^{23} / 12 \times 10^{-6} = 5 \times 10^{28} \text{ atoms/m}^3$$

$$\text{fraction of excited electrons per atom} \sim 10^{-3}$$

Example: At room temperature the electrical conductivity of PbS is 25 whereas the electron and hole mobilities are 0.06 and 0.02 m²/V-s, respectively. Compute the intrinsic carrier concentration for PbS at room temperature.

$$\begin{aligned} n_i &= \sigma / |e|(\mu_e + \mu_h) \\ &= 25(\Omega\text{-m})^{-1} / (1.602 \times 10^{-19} \text{C})(0.06 + 0.02) \text{m}^2/\text{V-s} \\ &= 1.95 \times 10^{21} \text{m}^{-3} \end{aligned}$$

Example: Is it possible for compound semiconductors to exhibit intrinsic behavior? Explain your answer.

Yes, compound semiconductors can exhibit intrinsic behavior. They will be intrinsic even though they are composed of two different elements as long as the electrical behavior is not influenced by the presence of other elements.

Example: For each of the following pairs of semiconductors, decide which will have the smaller band gap energy, E_g , and then cite the reason for your choice. (a) C (diamond) and Ge, (b) AlP and InSb, (c) GaAs and ZnSe, (d) ZnSe and CdTe, and (e) CdS and NaCl.

(a) Germanium will have a smaller band gap energy than C (diamond) since Ge is lower in row IVA of the periodic table (Figure 2.6) than is C. In moving from top to bottom of the periodic table, E_g decreases.

(b) Indium antimonide will have a smaller band gap energy than aluminum phosphide. Both of these semiconductors are III-V compounds, and the positions of both In and Sb are lower vertically in the periodic table (Figure 2.6) than Al and P.

(c) Gallium arsenide will have a smaller band gap energy than zinc selenide. All four of these elements are in the same row of the periodic table, but Zn and Se are more widely separated horizontally than Ga and As; as the distance of separation increases, so does the band gap.

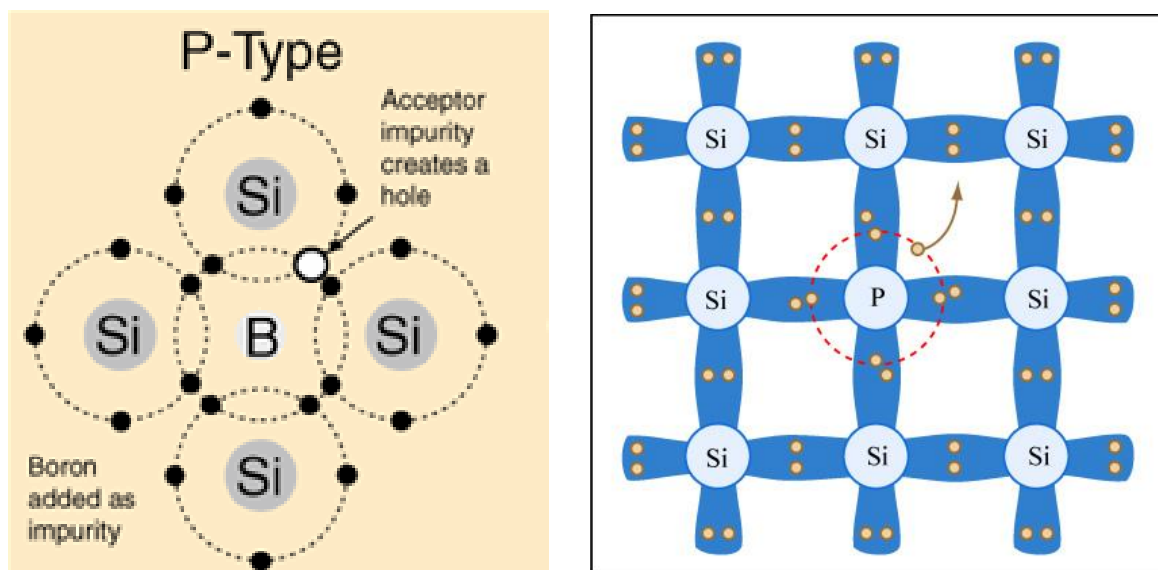
(d) Cadmium telluride will have a smaller band gap energy than zinc selenide. Both are II-VI compounds, and Cd and Te are both lower vertically in the periodic table than Zn and Se.

(e) Cadmium sulfide will have a smaller band gap energy than sodium chloride since Na and Cl are much more widely separated horizontally in the periodic table than are Cd and S.

Extrinsic semiconductors:

The pure semiconductor mentioned earlier is basically neutral. It contains no free electrons in its conduction bands. Even with the application of thermal energy, only a few covalent bonds are broken, yielding a relatively small current flow. A much more efficient method of increasing current flow in semiconductors is by adding very small amounts of selected additives to them, generally no more than a few parts per million. These additives are called impurities and the process of adding them to crystals is referred to as **doping**. The purpose of semiconductor doping is to increase the number of free charges that can be moved by an external applied voltage. When an impurity increases the number of free electrons, the doped semiconductor is negative or *n*-type, and the impurity that is added is known as an *n*-type impurity. However, an impurity that reduces the number of free electrons, causing more holes, creates a positive or *p*-type semiconductor, and the impurity that was added to it is known as a *p*-type impurity. Semiconductors which are doped in this manner - either with *n*- or *p*-type impurities - are referred to as **extrinsic** semiconductors.

n-Type Semiconductor



The *n*-type impurity loses its extra valence electron easily when added to a semiconductor material, and in so doing, increases the conductivity of the material by contributing a free electron. This type of impurity has 5 valence electrons and is called a **pentavalent** impurity. Arsenic, antimony, bismuth, and phosphorous are pentavalent impurities. Because these materials give or donate one electron to the doped material, they are also called **donor** impurities.

When a pentavalent (donor) impurity, like phosphorous, is added to silicon, it will form covalent bonds with the silicon atoms. Figure above illustrates this by showing a phosphorous atom (P) in a silicon (Si) lattice structure ($N_D = N$ Phosphorus $\sim n$). Notice the phosphorous atom in the center of the lattice. It has 5 valence electrons in its outer shell but uses only 4 of them to form covalent bonds with the silicon atoms, leaving 1 electron relatively free in the crystal structure. Pure silicon may be converted into an *n*-type semiconductor by „doping” it with any donor impurity having 5 valence electrons in its outer shell. Since this type of semiconductor (*n*-type) has a surplus of electrons, the electrons are considered **majority** carriers, while the holes, being few in number, are the **minority** carriers. Conduction occurs mainly by the free electrons (thus *n*-type) $\sigma \sim n|e|\mu_e \sim N_D |e|\mu_e$.

Conduction in the *n*-type semiconductor, or crystal, is similar to conduction in a copper wire. That is, with voltage applied across the material, electrons will move through the crystal just as current would flow in a copper wire. The positive potential of a battery will attract the free electrons in the crystal. These electrons will leave the crystal and flow into the positive terminal of the battery. As an electron leaves the crystal, an electron from the negative terminal of the battery will enter the crystal, thus completing the current path. Therefore, the majority current carriers in the *n*-type material (electrons) are repelled by the negative side of the battery and move through the crystal toward the positive side of the battery.

p-Type Semiconductor

The second type of impurity, when added to a semiconductor material, tends to compensate for its deficiency of 1 valence electron by acquiring an electron from its neighbor. Impurities of this type have only 3 valence electrons and are called **trivalent** impurities. Aluminum, indium, gallium, and

boron are trivalent impurities. Because these materials accept 1 electron from the doped material, they are also called **acceptor** impurities.

A trivalent (acceptor) impurity element can also be used to dope silicon. In this case, the impurity is 1 electron short of the required amount of electrons needed to establish covalent bonds with 4 neighboring atoms. Thus, in a single covalent bond, there will be only 1 electron instead of 2. This arrangement leaves a hole in that covalent bond. Figure above illustrates this theory by showing what happens when silicon is doped with an boron (B) atom. Notice, the boron atom in the figure is 1 electron short of the required amount of electrons needed to form covalent bonds with 4 neighboring atoms and, therefore, creates a hole in the structure ($N_A = N_{\text{Boron}} \sim p$). Gallium and Indium, which are also trivalent impurities, exhibit these same characteristics when added to silicon. The holes can only be present in this type semiconductor when a trivalent impurity is used. Note that a hole carrier is not created by the removal of an electron from a neutral atom, but is created when a trivalent impurity enters into covalent bonds with a tetravalent (4 valence electrons) crystal structure. The holes in this type of semiconductor (*p*-type) are considered the **majority** carriers since they are present in the material in the greatest quantity. The electrons, on the other hand, are the **minority** carriers.

Current Flow in the *p*-type Material is by positive holes, instead of negative electrons. A hole moves from the positive terminal of the *p*-material to the negative terminal. Electrons from the external circuit enter the negative terminal of the material and fill holes in the vicinity of this terminal. At the positive terminal, electrons are removed from the covalent bonds, thus creating new holes. This process continues as the steady stream of holes (hole current) moves toward the negative terminal.

Conduction occurs mainly by the holes (thus *p*-type).

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

Notice in both *n*-type and *p*-type materials, current flow in the external circuit consists of electrons moving out of the negative terminal of the battery and into the positive terminal of the battery. Hole flow, on the other hand, only exists within the material itself.

Example: An *n*-type semiconductor is known to have an electron concentration of $5 \times 10^{17} \text{ m}^{-3}$. If the electron drift velocity is 350 m/s in an electric field of 1000 V/m, calculate the conductivity of this material.

$$\begin{aligned} \mu_e &= v_d / E \\ &= 350 \text{ m/s} / 1000 \text{ V/m} = 0.35 \text{ m}^2/\text{V.s} \\ \sigma &= n|e|\mu_e \\ &= (5 \times 10^{17} \text{ m}^{-3})(1.602 \times 10^{-19} \text{ C})(0.35 \text{ m}^2/\text{V.s}) \\ &= 0.028 (\Omega.\text{m})^{-1} \end{aligned}$$

Example: (a) The room-temperature electrical conductivity of a silicon specimen is $500 (\Omega.\text{m})^{-1}$. The hole concentration is known to be $2 \times 10^{22} \text{ m}^{-3}$. Using the electron and hole mobilities for silicon (0.05 and $0.14 \text{ m}^2/\text{V.s}$, respectively), compute the electron concentration. **(b)** On the basis of the result in part (a), is the specimen intrinsic, *n*-type extrinsic, or *p*-type extrinsic? Why?

$$\begin{aligned} n &= \sigma - p|e|\mu_h / |e|\mu_e \\ &= 500 (\Omega.\text{m})^{-1} - (2.0 \times 10^{22} \text{ m}^{-3})(1.602 \times 10^{-19} \text{ C})(0.05 \text{ m}^2/\text{V.s}) / (1.602 \times 10^{-19} \text{ C})(0.14 \text{ m}^2/\text{V.s}) \\ &= 2.97 \times 10^{20} \text{ m}^{-3} \end{aligned}$$

(b) This material is *p*-type extrinsic since p ($2.0 \times 10^{22} \text{ m}^{-3}$) is greater than n ($2.97 \times 10^{20} \text{ m}^{-3}$).

Temperature variation of conductivity:

A couple of features of this plot are worth noting.

- ✓ First, the concentrations of electrons and holes increase with temperature because, with rising temperature, more thermal energy is available to excite electrons from the valence to the conduction band .
- ✓ In addition, at all temperatures, carrier concentration in Ge is greater than for Si. This effect is due to germanium's smaller band gap (0.67 versus 1.11 eV).
- ✓ Thus, for Ge, at any given temperature more electrons will be excited across its band gap.

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

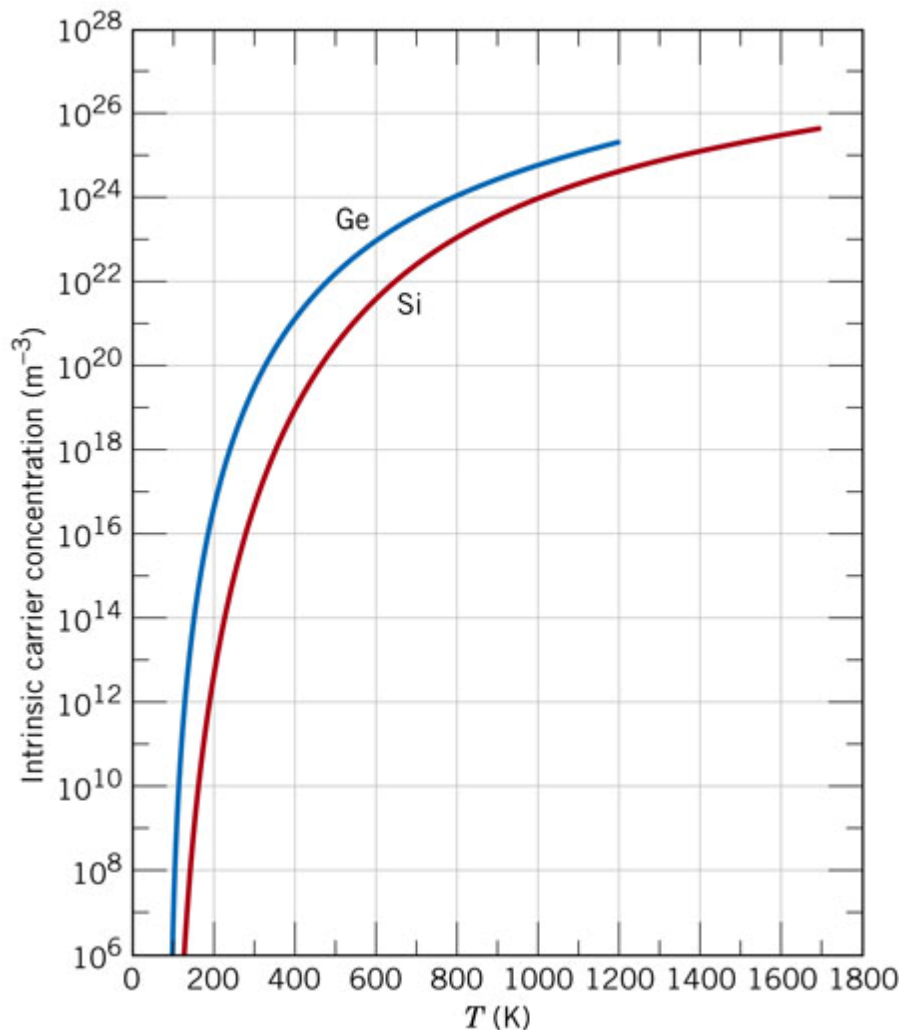


Figure: Intrinsic carrier concentration (logarithmic scale) as a function of temperature for germanium and silicon.

For intrinsic semiconductors $n = p \sim \exp(-E_g/2kT)$

$E_g = 0.57$ eV for Ge

$E_g = 1.11$ eV for Si

Carrier concentration vs T: Extrinsic semiconductors:

The carrier concentration–temperature behavior for an *extrinsic* semiconductor is much different. For example, electron concentration versus temperature for silicon that has been doped with phosphorus atoms is plotted in Figure below. [For comparison, the dashed curve shown is for intrinsic Si].

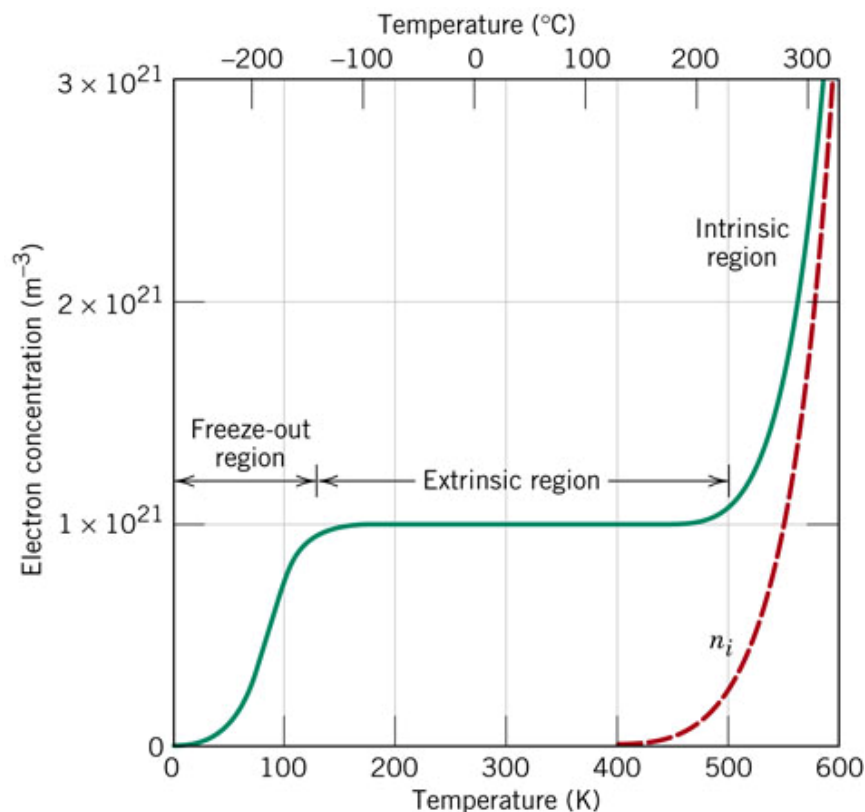
Noted on the extrinsic curve are three regions. At intermediate temperatures (between approximately 150 K and 450 K) the material is *n*-type (inasmuch as P is a donor impurity), and electron concentration is constant; this is termed the “**extrinsic-temperature region**”.

n-type Si doped with 10^{21} m^{-3} P

The range of temperatures over which this extrinsic region exists will depend on impurity concentration; furthermore, most solid-state devices are designed to operate within this temperature range.

At low temperatures, below about 100 K, electron concentration drops dramatically with decreasing temperature, and approaches zero at 0 K. Over these temperatures, the thermal energy is insufficient to excite electrons from the P donor level into the conduction band. This is termed the “**freeze-out temperature region**”.

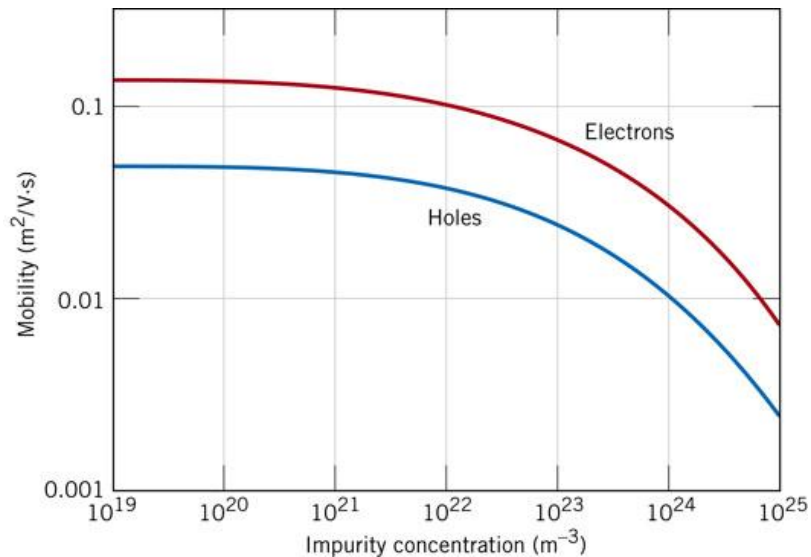
at the high end of the temperature scale of figure below, electron concentration increases above the P content, and asymptotically approaches the intrinsic curve as temperature increases. This is termed the “**intrinsic temperature region**”



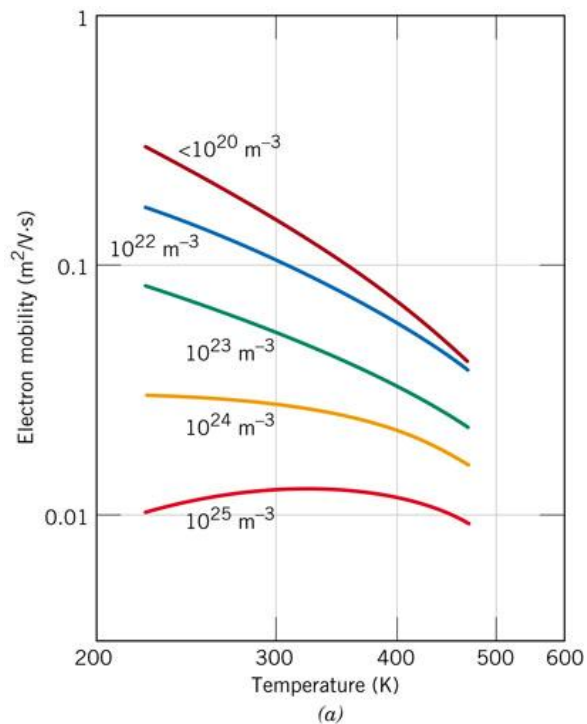
Carrier mobility:

Dopants are impurities and, like in metals, the mobility of electrons and holes decreases with impurity concentration. Also worth noting is that the mobility of electrons is always larger than the mobility of holes.

At dopant levels less than 10^{20} m^{-3} both carrier mobilities are at their maximum levels and the effect of dopants on mobility is negligible.



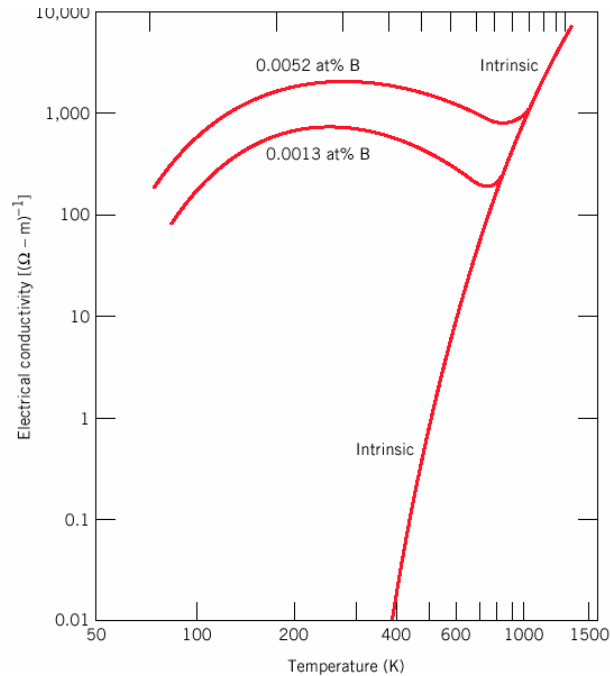
For dopant concentrations below 10^{24} m^{-3} , mobility of both electrons and holes decreases with increasing temperature due to the enhanced thermal scattering of the carriers.



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.



Example: calculate the intrinsic electrical conductivity of germanium at 175 °C , where the Ge Conductivity at room temperature (298 K) is $[2.2 (\Omega \cdot m)^{-1}]$ and E_g is (0.67 eV) . If the conductivity for intrinsic germanium near room temperature is found equal to $\sigma = CT^{3/2} \exp (E_g / 2kT)$

$$\begin{aligned} \ln \sigma &= \ln C - (3/2) \ln T - E_g / 2kT \\ \ln C &= \ln \sigma + (3/2) \ln T + E_g / 2kT \\ &= \ln(2.2) + (3/2) \ln(298) + 0.67 \text{ eV} / (2)(8.62 \times 10^{-5} \text{ eV/K})(298 \text{ K}) \\ &= 22.38 \end{aligned}$$

Now, again using first Equation, we are able to compute the conductivity at 448 K (175°C)

$$\begin{aligned} \ln \sigma &= \ln C - (3/2) \ln T - E_g / 2kT \\ &= 22.38 - (3/2) \ln(448 \text{ K}) - 0.67 \text{ eV} / (2)(8.62 \times 10^{-5} \text{ eV/K})(448 \text{ K}) \\ &= 4.548 \end{aligned}$$

which leads to $\sigma = e^{4.548} = 94.4 (\Omega \cdot m)^{-1}$.

Example: Calculate the room-temperature electrical conductivity of silicon that has been doped with 10^{23} m^{-3} of arsenic atoms. If the electron mobility, at an impurity concentration of 10^{23} m^{-3} , is $0.065 \text{ m}^2/\text{V.s}$.

$$\sigma = n|e|\mu_e = (10^{23} \text{ m}^{-3})(1.602 \times 10^{-19} \text{ C})(0.065 \text{ m}^2/\text{V.s}) = 1040 (\Omega \cdot m)^{-1}$$

Example: Estimate the electrical conductivity, at 135 °C, of silicon that has been doped with 10^{24} m^{-3} of aluminum atoms. If the hole mobility, at an impurity concentration of 10^{24} m^{-3} and at 135 °C , is $0.007 \text{ m}^2/\text{V.s}$.

$$\sigma = p|e|\mu_h = (10^{24} \text{ m}^{-3})(1.602 \times 10^{-19} \text{ C})(0.007 \text{ m}^2/\text{V.s}) = 1120 (\Omega \cdot m)^{-1}$$

Conduction in Polymers and Ionic Materials:

- Most polymers and ionic ceramics are insulating materials at room temperature and, a filled valence band is separated from an empty conduction band by a relatively large band gap, usually greater than 2 eV. Thus, at normal temperatures only very few electrons may be excited across the band gap by the available thermal energy, which accounts for the very small values of conductivity.
- 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: $\sigma_{\text{total}} = \sigma_{\text{electronic}} + \sigma_{\text{ionic}}$
- Either contribution may predominate depending on the material, its purity, and, of course, temperature.
- A mobility may be associated with each of the ionic species as follows
$$\mu_I = \frac{n_I e D_I}{kT}$$
where n_I and D_I represent, respectively, the valence and diffusion coefficient of a particular ion
- High temperatures produce more Frenkel and Schottky defects which result in higher ionic conductivity.
- in spite of the two conductivity contributions, most ionic materials remain insulative, even at elevated temperatures

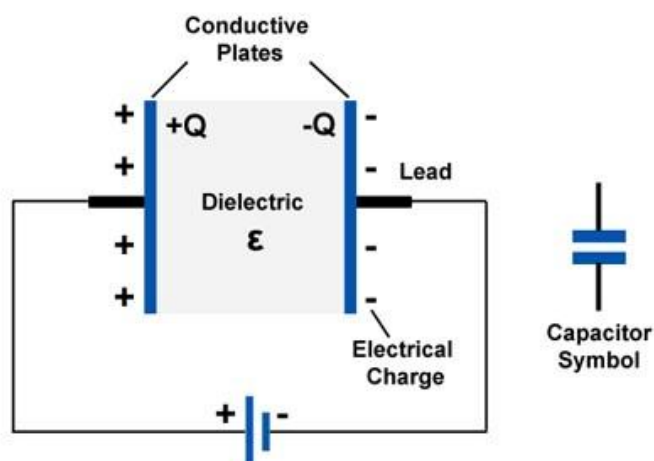
Polymers:

- 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 :
 $C = Q / V$ [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**, $\epsilon_r = \epsilon / \epsilon_0 = C / C_{\text{vac}}$

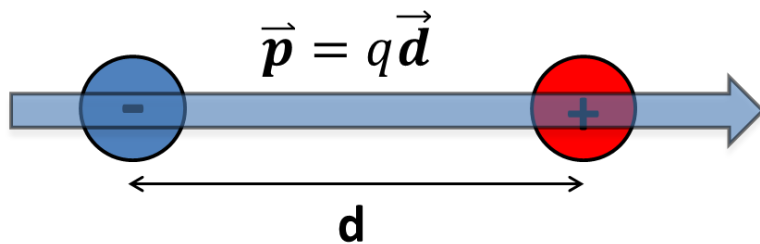
Dielectric Materials:

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.

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

with $\epsilon_r = 81$ for water, 20 for acetone, 12 for silicon, 3 for ice, etc.

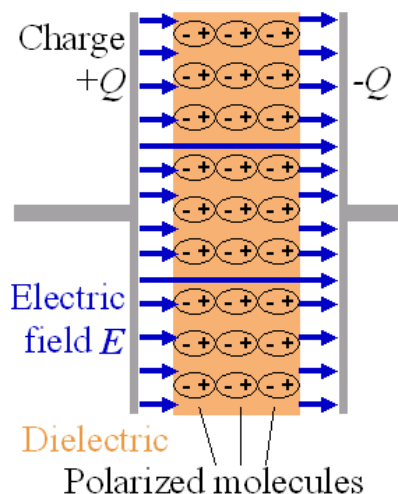
A **dielectric material** is an insulator in which **electric dipoles** can be induced by the electric field (or permanent dipoles can exist even without electric field), that is where positive and negative charge are separated on an atomic or molecular level.



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.



In capacitor, the surface charge density D , or quantity of charge per unit area of capacitor plate (C/m^2), is proportional to the electric field.

When a vacuum is present, then $D_0 = \epsilon_0 E$

The constant of proportionality being ϵ_0 . Furthermore, an analogous expression exists for the dielectric case; that is, $D = \epsilon E$

Sometimes, D is also called the **dielectric displacement**

Schematic representations of (a) the charge stored on capacitor plates for a vacuum, (b) the dipole arrangement in an unpolarized dielectric, and (c) the increased charge storing capacity resulting from the polarization of a dielectric material.

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

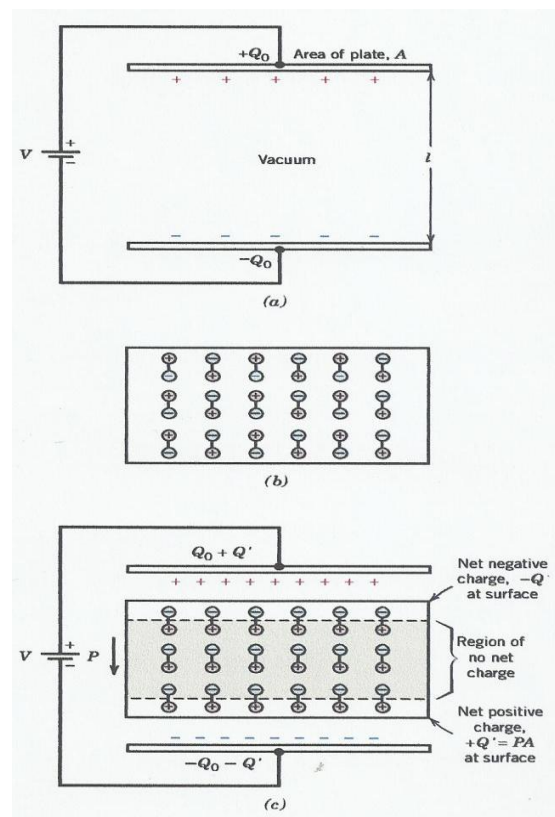
$$\epsilon_r = C / C_{vac} > 1$$

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

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

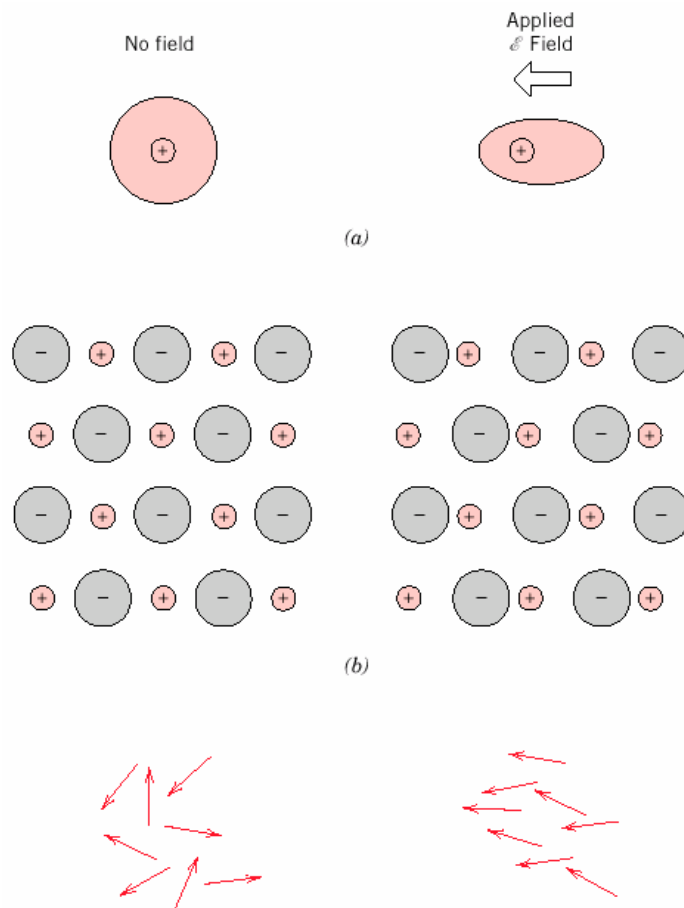
$$D = Q/A = \epsilon_r \epsilon_0 E = \epsilon_0 E + P$$

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. H_2O). In absence of electric field, dipoles are randomly oriented. Applying electric field aligns these dipoles, causing net (large) dipole moment.
- $P_{total} = P_e + P_i + P_o$



molecular (orientation) polarization

Dielectric strength:

Very high electric fields ($>10^8$ 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.

Example: A parallel-plate capacitor using a dielectric material having an ϵ_r of 2.2 has a plate spacing of 2 mm (0.08 in.). If another material having a dielectric constant of 3.7 is used and the capacitance is to be unchanged, what must be the new spacing between the plates?

$$C = \epsilon_r \epsilon_0 A / l$$

Now, let us use the subscripts 1 and 2 to denote the initial and final states, respectively. Since $C_1 = C_2$, then $\epsilon_{r1} \epsilon_0 A / l_1 = \epsilon_{r2} \epsilon_0 A / l_2$

And, solving for l_2 , then: $l_2 = \epsilon_{r2} l_1 / \epsilon_{r1} = (3.7)(2\text{mm}) / 2.2 = 3.36 \text{ mm}$

Example: Consider a parallel-plate capacitor having an area of 3225 mm², a plate separation of 1 mm, and with a material having a dielectric constant of 3.5 positioned between the plates. **(a)** What is the capacitance of this capacitor? **(b)** Compute the electric field that must be applied for 2×10^{-8} C to be stored on each plate.

$$C = \epsilon_r \epsilon_0 A / l$$

$$= (3.5)(8.85 \times 10^{-12} \text{ F/m})(3225 \text{ mm}^2)(1 \text{ m}^2 / 106 \text{ mm}^2) / 10^{-3} \text{ m} = 10^{-10} \text{ F} = 100 \text{ pF}$$

(b) Now we are asked to compute the electric field that must be applied in order that 2×10^{-8} C be stored on each plate. First we need to solve for V

$$V = Q/C = 2 \times 10^{-8} \text{ C} / 10^{-10} \text{ F} = 200 \text{ V}$$

The electric field E may now be determined using

$$E = V / l = 200 \text{ V} / 10^{-3} \text{ m} = 2.0 \times 10^5 \text{ V/m}$$

Example: For CaO, the ionic radii for Ca^{+2} and O^{2-} ions are 0.100 and 0.140 nm, respectively. If an externally applied electric field produces a 5% expansion of the lattice, compute the dipole moment for each $\text{Ca}^{+2} - \text{O}^{2-}$ pair. Assume that this material is completely unpolarized in the absence of an electric field.

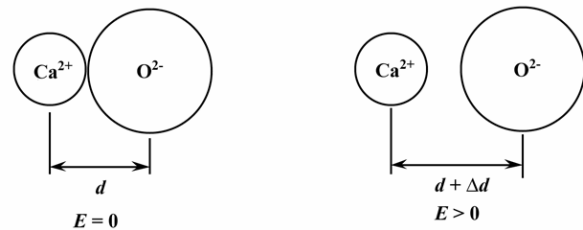
$$d = r_{\text{Ca}^{2+}} + r_{\text{O}^{2-}} = 0.100 \text{ nm} + 0.140 \text{ nm} = 0.240 \text{ nm}$$

$$\text{and } \Delta d = 0.05 d = (0.05)(0.240 \text{ nm}) = 0.0120 \text{ nm} = 1.20 \times 10^{-11} \text{ m}$$

the dipole moment, p , is just $p = q \Delta d$

$$= (1.602 \times 10^{-19} \text{ C})(1.20 \times 10^{-11} \text{ m})$$

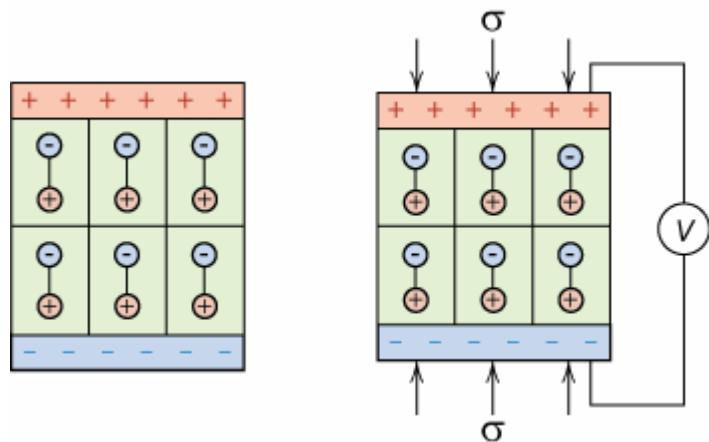
$$= 1.92 \times 10^{-30} \text{ C.m}$$



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)

Examples:
barium titanate BaTiO_3
lead zirconate PbZrO_3
quartz.



Without stress

with applied stress