Part II Electrical Properties of Materials

Chap. 7 Electrical Conduction in Metals and Alloys
Chap. 8 Semiconductors
Chap. 9 Electrical Properties of Polymers, Ceramics, Dielectrics, and Amorphous Materials
Polymers consist of (macro)molecules which are long and chainlike. Several atoms combine and form a specific building block, called a monomer, and thousands of monomer combine to a polymer.
9.1 Conducting Polymers and Organic Metals

The binding force between individual atoms within a chain

*covalent (mostly) + ionic in nature*

The binding force between macromolecules:

*Van der Walls type (weak)*

Polyacetylene: the simplest conjugated organic polymer; the prototype of a conducting polymer

Trans-polyacetylene is obtained as silvery flexible film that has a conductivity comparable to that of silicon.
9.1 Conducting Polymers and Organic Metals

Figure 9.4. Conductivities of polymers in $\Omega^{-1} \text{ cm}^{-1}$. (Compare with Fig. 7.1.)

Figure 9.5. Calculated band structure of $\text{trans-}(CH)_x$ for different carbon-carbon bond lengths: (a) uniform (1.39 Å); (b) weakly alternating ($C=C$, 1.36 Å; $C-C$, 1.43 Å); and (c) strongly alternating ($C=C$, 1.34 Å; $C-C$, 1.54 Å). Note the band gaps at $Y$ as bond alternation occurs. Reprinted with permission from P.M. Grant and I.P. Batra, *Solid State Comm.* 29, 225 (1979).
9.1 Conducting Polymers and Organic Metals

Conductivity increases by doping in polymer-based semiconductor

![Graph showing conductivity change of polyacetylene as a result of doping.](image)

Figure 9.6. Conductivity change of polyacetylene as a result of doping.

“Soliton” is a structural distortion in a conjugated polymer and is generated when a single bond meets another single bond.

![Diagram of a soliton in polyacetylene.](image)

Figure 9.7. A broken symmetry in polyacetylene creates a soliton. (An antisoliton is the mirror image of a soliton.)
9.2 Ionic Conduction

The ionic conduction is caused by the movement of some charged ions which hop from lattice site to lattice site under the influence of electric field.

\[ \sigma_{\text{ion}} = N_{\text{ion}} e \mu_{\text{ion}} \]

\( N_{\text{ion}} \) depends on vacancy concentration in the crystal

\[ \Rightarrow \text{Diffusion Theory} \]
9.2 Ionic Conduction

\[ D = D_0 \exp\left[-\left(\frac{Q}{k_B T}\right)\right] \]  
\[ \mu_{\text{ion}} = \frac{D_e}{k_B T}. \]  
\[ \sigma_{\text{ion}} = \frac{N_{\text{ion}} e^2 D_0}{k_B T} \exp\left[-\left(\frac{Q}{k_B T}\right)\right]. \]  
\[ \sigma_{\text{ion}} = \sigma_0 \exp\left[-\left(\frac{Q}{k_B T}\right)\right]. \]  
\[ \therefore \ln \sigma_{\text{ion}} = \ln \sigma_0 - \left(\frac{Q}{k_B T}\right)\frac{1}{T}. \]

Figure 9.9. Schematic representation of \( \ln \sigma \) versus \( 1/T \) for \( \text{Na}^+ \) ions in sodium chloride. (Arrhenius plot.)
Whenever vacant lattice site is created, an overall charge neutrality needs to be maintained.

Both a cation and anion are removed from a lattice (Shottky defect).

Formation of vacancy-interstitial pair (Frenkel defect)

Figure 9.10. Schematic representation of a \{100\} plane of an ionic crystal having the NaCl structure. The diffusion of a cation into a cation vacancy is shown. Also depicted is the creation of a cation vacancy when replacing a Na\(^+\) ion with a Mg\(^{2+}\) ion.
Metal oxide can be insulating, have metallic conduction properties, or be semiconducting: For understanding the mechanisms involved in metal oxides, their electronic configuration in the orbital (or band structure) should be considered. (Appendix 3. p.409)

1. TiO$_2$ (O: $1s^2\ 2s^2\ 2p^4$, Ti: $[Ar]3d^24s^2$)
   - Noble gas configuration, insulator
   - Insulator with wide band gap

2. TiO (O: $1s^2\ 2s^2\ 2p^4$, Ti: $[Ar]3d^24s^2$) : partially filled $3d^2$
   - Metallic

3. ZnO (O: $1s^2\ 2s^2\ 2p^4$, Zn: $[Ar]3d^{10}4s^2$)
   - Insulator for stoichiometric
   - $n$-type semiconductor for non-stoichiometric
4. SnO$_2$ (some times doped with In$_2$O$_3$)
   - Transparent in the visible region and which is a reasonable conductor in
     the 1 $\Omega^{-1}$cm$^{-1}$ range
   - Used in optoelectronics to provide electrical contacts without blocking
     the light from reaching a device: indium-tin-oxide (ITO)

5. NiO (O :1s$^2$ 2s$^2$2p$^4$, Ni: [Ar]3p$^8$4s$^2$)
   - Insulator for stoichiometric
   - $p$-type semiconductor for nonstoichiometric
Atomic structure of amorphous metals and alloy
Dense random packing of hard spheres model (Bernal model)
In transition metal-metalloid compounds (such as Ni-P), small metalloid atoms are thought to occupy the holes which occur as a consequence of this packing (Bernal-Polk model).

Figure 9.11. Two-dimensional schematic representation of a dense random packing of hard spheres (Bernal model).

Figure 9.12. Defects in crystalline and amorphous silicon. (a) Monovacancy in a crystalline semiconductor; (b) one and (c) two dangling bonds in a continuous random network of an amorphous semiconductor. (Note the deviations in the interatomic distances and bond angles.)

Defect in crystalline | Defect in amorphous
A series of clusters were assumed which exhibit the symmetry of closed-packed lattice fcc (as Cu) and hcp (as for Zr).

Stronger binding forces between the atoms in covalently bound materials, the valence electrons are tightly bound, or localized → the density of state for localized state extends into the ”band gap”

Electrical conductivity for amorphous semiconductors

$$\sigma_A = N_A e\mu_A \cdot$$

$$\sigma_A = \sigma_0 \exp \left[ -\left( \frac{Q_A(T)}{k_BT} \right) \right].$$
When deposited on a cylindrically shaped metallic substrate, constitutes the photoreceptor drum.
9.5 Dielectric Properties

Capacitance, $C$

$$C = \frac{q}{V}$$

the ability to store an electric charge, $q$ per unit applied voltage, $V$.

$$C = \varepsilon_r \varepsilon_0 \frac{A}{L} \quad \varepsilon_r = \frac{C}{C_{\text{vac}}}$$

$\varepsilon_r$ : dielectric constant (unitless), or relative permittivity,

$\varepsilon_0$ : permittivity of empty space, $8.85 \times 10^{-12} \text{ F/m}$

Figure 9.16. Two metal plates, separated by a distance, $L$, can store electric energy after having been charged momentarily by a battery.
### 9.5 Dielectric Properties

Table 9.1. DC dielectric constants of some materials

<table>
<thead>
<tr>
<th>Material</th>
<th>DC Dielectric Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium tantalate niobate</td>
<td>6000</td>
</tr>
<tr>
<td>Barium titanate (BaTiO₃)</td>
<td>4000</td>
</tr>
<tr>
<td>Potassium Niobate (KNbO₃)</td>
<td>700</td>
</tr>
<tr>
<td>Rochelle salt (NaKC₄H₄O₆·4H₂O)</td>
<td>170</td>
</tr>
<tr>
<td>Water</td>
<td>81.1</td>
</tr>
<tr>
<td>Acetone</td>
<td>20</td>
</tr>
<tr>
<td>Silicon</td>
<td>11.8</td>
</tr>
<tr>
<td>GaAs</td>
<td>10.9</td>
</tr>
<tr>
<td>Marble</td>
<td>8.5</td>
</tr>
<tr>
<td>Soda-lime-glass</td>
<td>6.9</td>
</tr>
<tr>
<td>Porcelain</td>
<td>6.0</td>
</tr>
<tr>
<td>Epoxy</td>
<td>4.0</td>
</tr>
<tr>
<td>Fused silica</td>
<td>4.0</td>
</tr>
<tr>
<td>Nylon 6,6</td>
<td>4.0</td>
</tr>
<tr>
<td>PVC</td>
<td>3.5</td>
</tr>
<tr>
<td>Ice</td>
<td>3.0</td>
</tr>
<tr>
<td>Amber</td>
<td>2.8</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>2.3</td>
</tr>
<tr>
<td>Paraffin</td>
<td>2.0</td>
</tr>
<tr>
<td>Air</td>
<td>1.000576</td>
</tr>
</tbody>
</table>

Ferroelectric

Dielectric
9.5 Dielectric Properties

Electric dipole moment

\[ p = q \cdot x, \]

\[ E = \frac{E_{\text{vac}}}{\varepsilon_r} \]

\[ D = \varepsilon_r \varepsilon_0 E = \frac{q}{A} \]

\[ D = \varepsilon_0 E + P \]

Polarization: the process of dipole formation (or alignment of already existing dipoles) under the influence of an external electric field that has an electric field strength, \( E \)

Figure 9.17. An atom is represented by a positively charged core and a surrounding, negatively charged, electron cloud (a) in equilibrium and (b) in an external electric field. (c) Schematic representation of an electric dipole as, for example, created by separation of the negative and positive charges by an electric field, as seen in (b).
Dipole formation of all involved atoms within a dielectric material cause a charge redistribution so that the surface nearest to the positive capacitor plate is negatively charge (and vice versa).

Due to polarization

How quickly do the dipoles to reorient or to align under a rapidly changing electric field (in alternating circuit)

Polarization mechanisms which can respond equally quick to an alternating electric field
9.6 Ferroelectricity, Piezoelectricity, and Electrostriction

Ferroelectric materials

A spontaneous polarization without the presence of an external electric field: suitable for the manufacturing of small sized, highly efficient capacitors.

Hysteresis loop

- $P_S$: saturation polarization
- $P_r$: remanent polarization
- $E_C$: coercive field

Figure 9.20. Schematic representation of a hysteresis loop for a ferroelectric material in an electric field. Compare to Figure 15.6.
Mechanism for spontaneous polarization

Tetragonal BaTiO₃:

A large number of such dipole moment line up in a clusters (also called *domains*) In the virgin state, the polarization directions of the individual domains are randomly oriented: no net polarization

An external field orients the dipoles of favorably oriented domains parallel to \( E \): those domains in which the dipoles are already nearly parallel to \( E \) at the expense of unfavorably oriented domains

Spontaneous alignments of electric dipoles within a domain and random alignment of the dipole moments of several domains in a ferroelectric material

Figure 9.21. Tetragonal crystal structure of barium titanate at room temperature. Note the upward displacement of the Ti⁴⁺ ion in the center compared to the downward displacement of all surrounding O²⁻ ions. \( a = 0.398 \) nm; \( c = 0.403 \) nm.

Figure 9.22. Schematic representation of spontaneous alignments of electric dipoles within a domain and random alignment of the dipole moments of several domains in a ferroelectric material such as BaTiO₃. Compare to Figure 15.9.