



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**



9.1 Conducting Polymers and Organic Metals



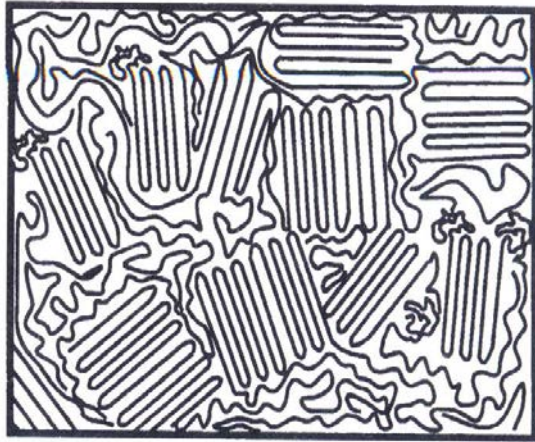
Figure 9.1. (a) Polyethylene. (b) Polyvinylchloride. (The dashed enclosures mark the repeat unit. Polyethylene is frequently depicted as two CH_2 repeat units for historical reasons.



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 Waals type(weak)

Figure 9.2. Simplified representation of a semicrystalline polymer (folded-chain model).

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

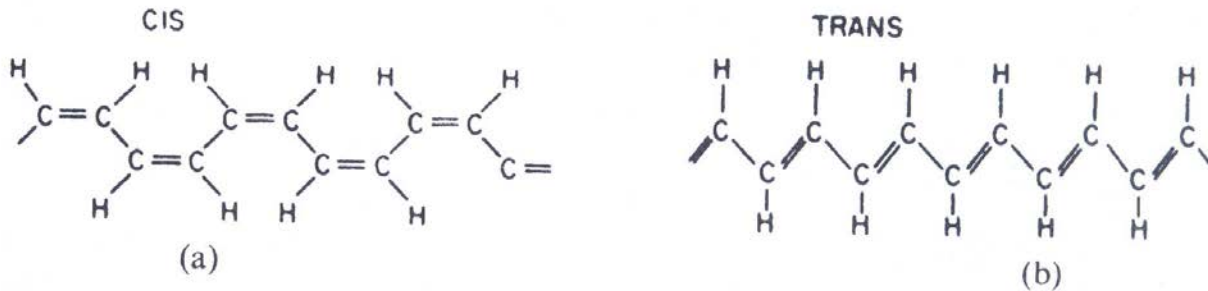


Figure 9.3. Theoretical isomers of polyacetylene (a) *cis-transoidal* isomer, (b) *trans-transoidal* isomer. Polyacetylene is synthesized as *cis*-(CH)_x and is then isomerized into the *trans*-configuration by heating it at 150°C for a few minutes.



Trans-polyacetylene is obtained as silvery flexible film that has a conductivity comparable to that of silicon.

9.1 Conducting Polymers and Organic Metals

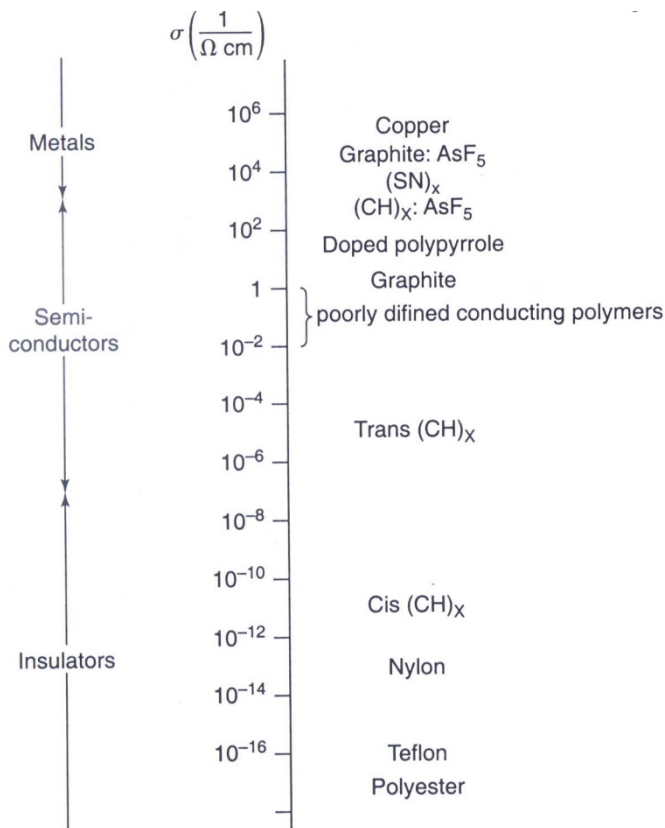


Figure 9.4. Conductivities of polymers in $\Omega^{-1} \text{ cm}^{-1}$. (Compare with Fig. 7.1.)

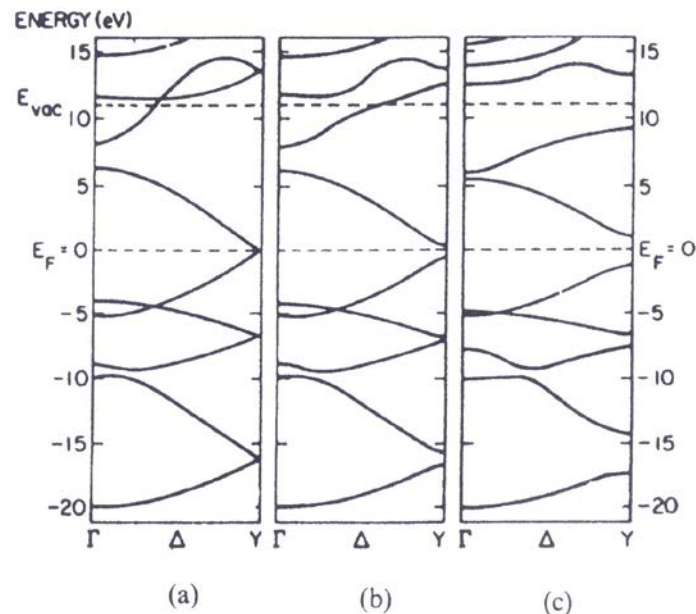
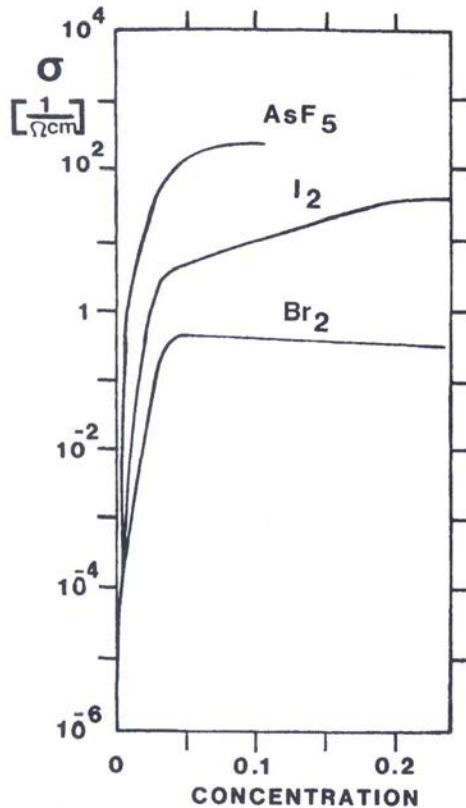


Figure 9.5. Calculated band structure of $\text{trans}-(\text{CH})_x$ for different carbon-carbon bond lengths: (a) uniform (1.39 Å); (b) weakly alternating (C=C, 1.36 Å; C—C, 1.43 Å); and (c) strongly alternating (C=C, 1.34 Å; C—C, 1.54 Å). Note the band gaps at Y as bond alternation occurs. Reprinted 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

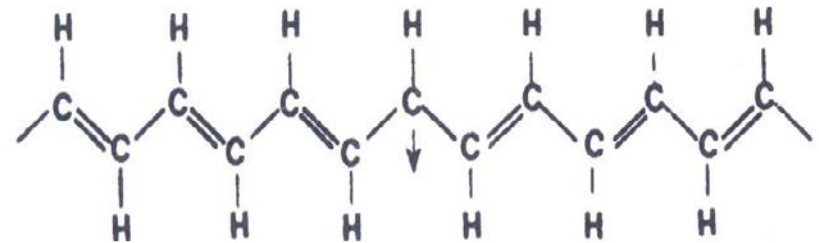


Figure 9.7. A broken symmetry in polyacetylene creates a *soliton*. (An *antisoliton* is the mirror image of a soliton.)



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



9.2 Ionic Conduction

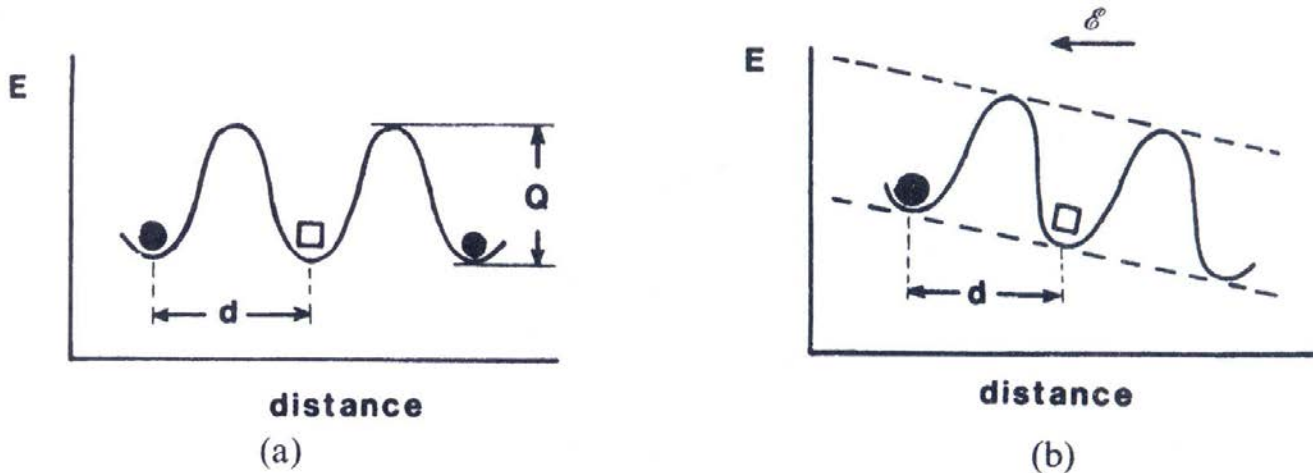


Figure 9.8. Schematic representation of a potential barrier, which an ion (●) has to overcome to exchange its site with a vacancy (□). (a) Without an external electric field; (b) with an external electric field. d = distance between two adjacent, equivalent lattice sites; Q = activation energy.

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_{ion} depends on vacancy concentration in the crystal **➔ Diffusion Theory**

9.2 Ionic Conduction

$$D = D_0 \exp\left[-\left(\frac{Q}{k_B T}\right)\right], \quad \text{Diffusion Theory}$$

$$\mu_{\text{ion}} = \frac{D_e}{k_B T}, \quad \text{Einstein Relation}$$

$$\sigma_{\text{ion}} = \frac{N_{\text{ion}} e^2 D_0}{k_B T} \exp\left[-\left(\frac{Q}{k_B T}\right)\right].$$

$$\sigma_{\text{ion}} = \sigma_0 \exp\left[-\left(\frac{Q}{k_B T}\right)\right].$$

$$\therefore \ln \sigma_{\text{ion}} = \ln \sigma_0 - \left(\frac{Q}{k_B}\right) \frac{1}{T}.$$

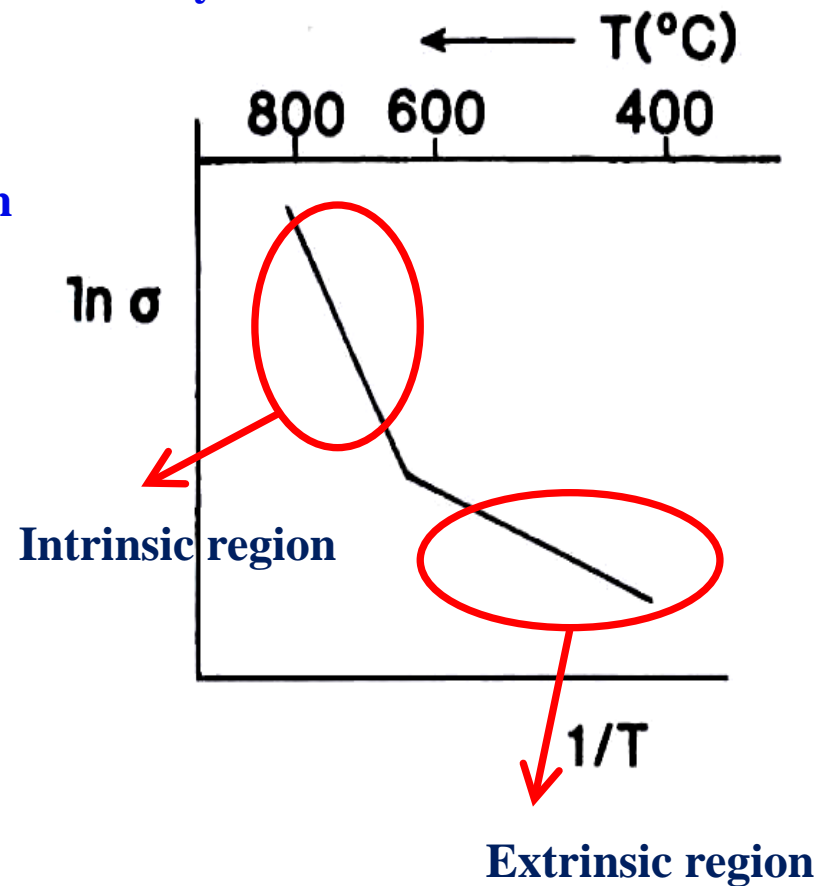
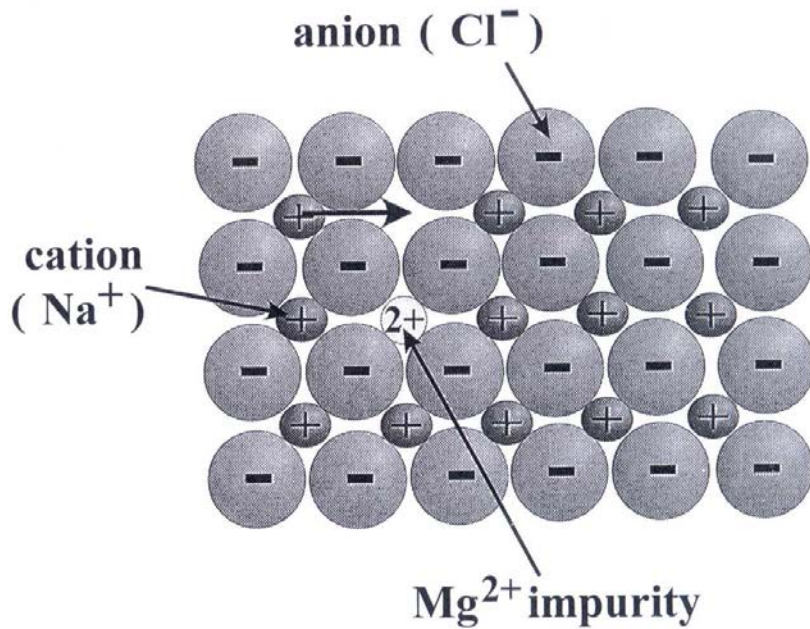


Figure 9.9. Schematic representation of $\ln \sigma$ versus $1/T$ for Na^+ ions in sodium chloride. (Arrhenius plot.)

9.2 Ionic Conduction



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 Mg²⁺ ion.



9.3 Conduction in Metal Oxides



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: $[\text{Ar}]3d^2 4s^2$)

- Noble gas configuration, insulator

- insulator with wide band gap

2. TiO (O : $1s^2 2s^2 2p^4$, Ti: $[\text{Ar}]3d^2 4s^2$) : partially filled $3d^2$

- Metallic

3. ZnO (O : $1s^2 2s^2 2p^4$, Zn: $[\text{Ar}]3d^{10} 4s^2$)

- Insulator for stoichiometric

- *n*-type semiconductor for non-stoichiometric






9.3 Conduction in Metal Oxides



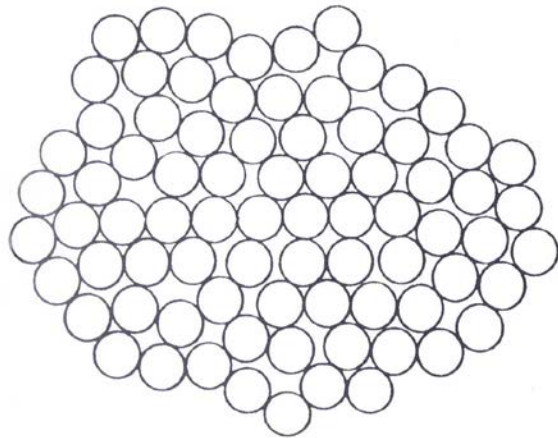
4. SnO₂ (some times doped with In₂O₃)

- **Transparent in the visible region and which is a reasonable conductor in the 1 $\Omega^{-1}\text{cm}^{-1}$ 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: $[\text{Ar}]3p^8 4s^2$)

- **Insulator for stoichiometric**
 - ***p*-type semiconductor for nonstoichiometric**
- 

9.4 Amorphous Materials (Metallic Glasses)

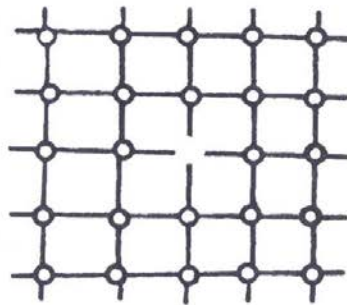


Atomic structure of amorphous metals and alloy

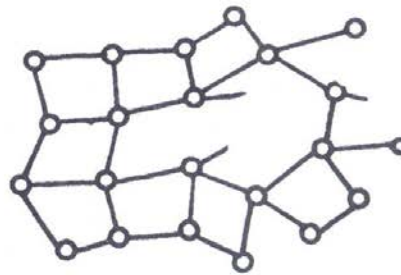
Dense random packing of hard spheres model
(Bernal model)

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**).

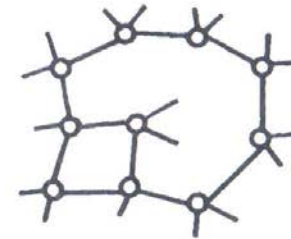
Figure 9.11. Two-dimensional schematic representation of a dense random packing of hard spheres (Bernal model).



(a)



(b)



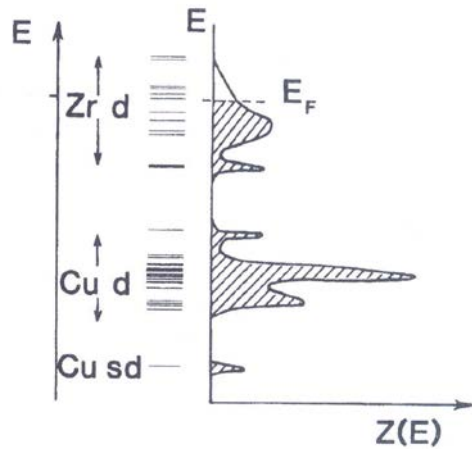
(c)

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

9.4 Amorphous Materials (Metallic Glasses)

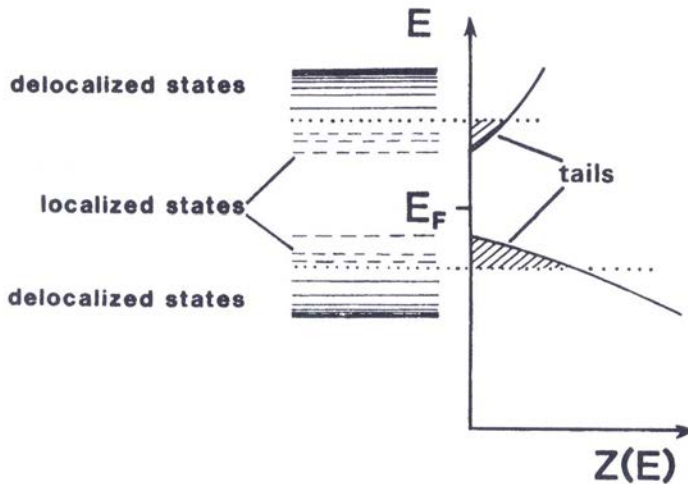


Cluster Model

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

Figure 9.13. Schematic representation of the molecular orbital energy level diagram and the density of states curves for Zr-Cu clusters. The calculated density of states curves agree reasonably well with photoemission experiments.

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

$$\sigma_A = N_A e \mu_A.$$

$$\sigma_A = \sigma_0 \exp \left[- \left(\frac{Q_A(T)}{k_B T} \right) \right].$$

Figure 9.14. Localized and delocalized states and density of states $Z(E)$ for amorphous semiconductors. Note the band tails, which are caused by the localized states.



9.4 Amorphous Materials (Metallic Glasses)

9.4.1 Xerography

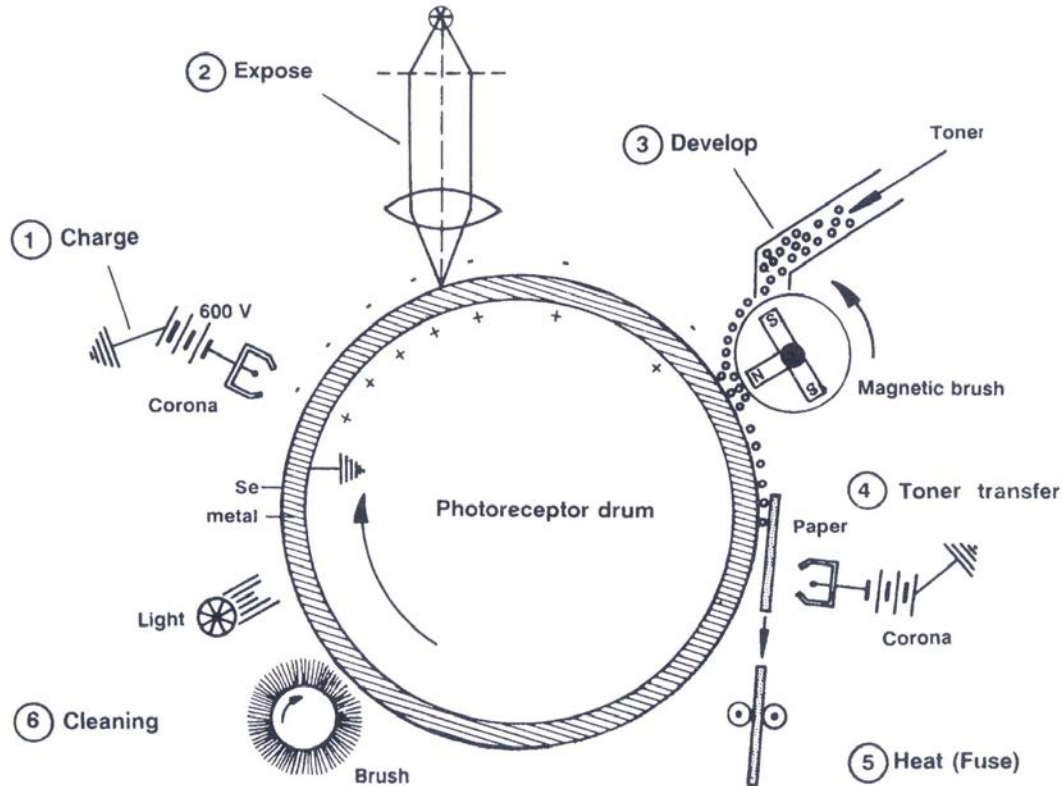
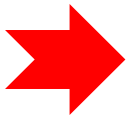


Figure 9.15. Schematic representation of the electrophotography process. The individual steps are explained in the text.



When deposited on a cylindrically shaped metallic substrate, constitutes the photoreceptor drum

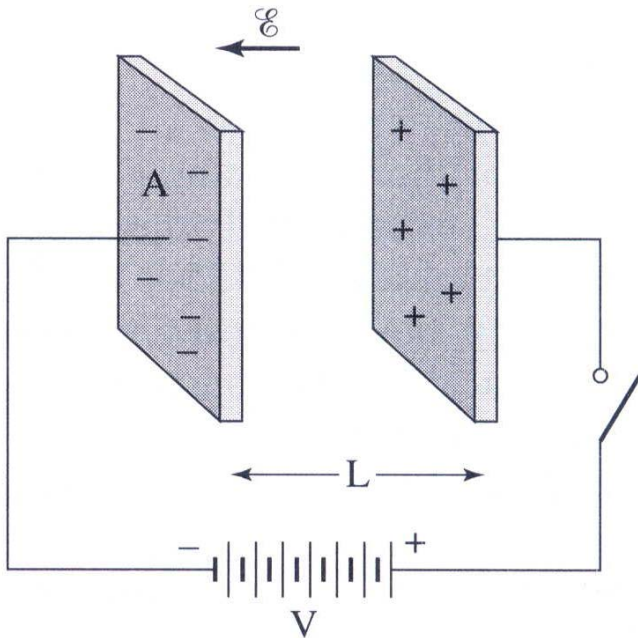
9.5 Dielectric Properties



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

Capacitance, C

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



$$C = \epsilon_r \epsilon_0 \frac{A}{L}$$

$$\epsilon_r = \frac{C}{C_{\text{vac}}}$$

ϵ_r : dielectric constant (unitless), or *relative permittivity*,

ϵ_0 : permittivity of empty space , 8.85×10^{-12} 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

Potassium tantalate niobate	6000	
Barium titanate (BaTiO_3)	4000	Ferroelectric
Potassium Niobate (KNbO_3)	700	
Rochelle salt ($\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$)	170	
<hr/>		
Water	81.1	
Acetone	20	
Silicon	11.8	
GaAs	10.9	
Marble	8.5	
Soda-lime-glass	6.9	
Porcelain	6.0	
Epoxy	4.0	
Fused silica	4.0	Dielectric
Nylon 6,6	4.0	
PVC	3.5	
Ice	3.0	
Amber	2.8	
Polyethylene	2.3	
Paraffin	2.0	
Air	1.000576	



9.5 Dielectric Properties

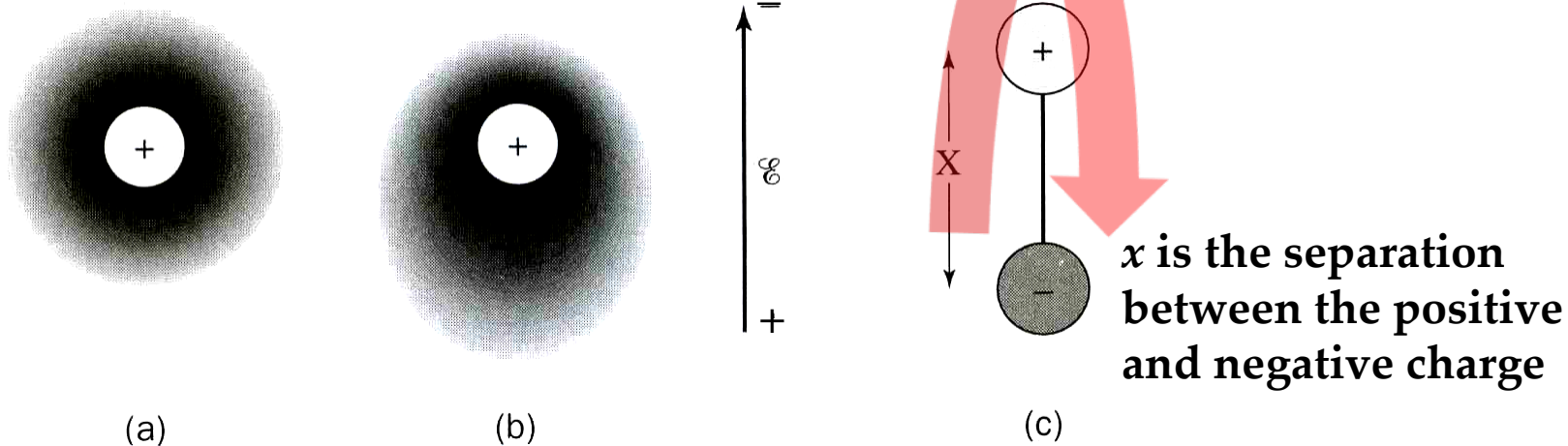


Figure 9.17. An atom is represented by a positively charged core and a surrounding, negatively charged, electron cloud (a) in equilibrium and (b) in an external electric field. (c) Schematic representation of an electric dipole as, for example, created by separation of the negative and positive charges by an electric field, as seen in (b).

$$p = q \cdot x, \quad \text{Electric dipole moment}$$

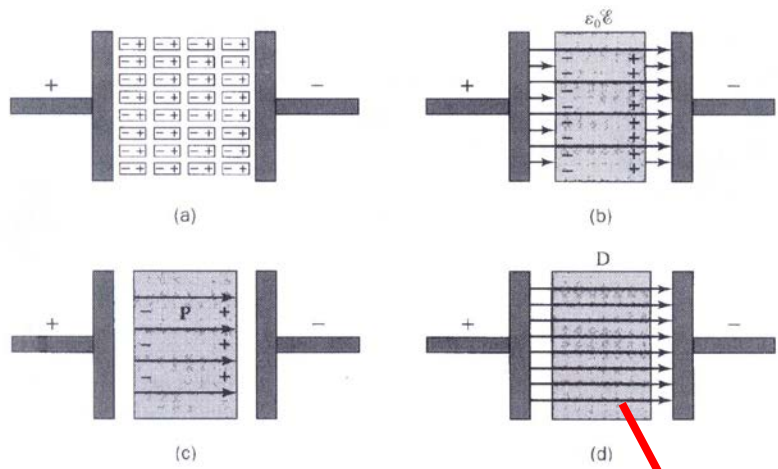
$$E = \frac{E_{\text{vac}}}{\epsilon_r} \qquad D = \epsilon_r \epsilon_0 E = \frac{q}{A}$$

$$D = \epsilon_0 E + P$$



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

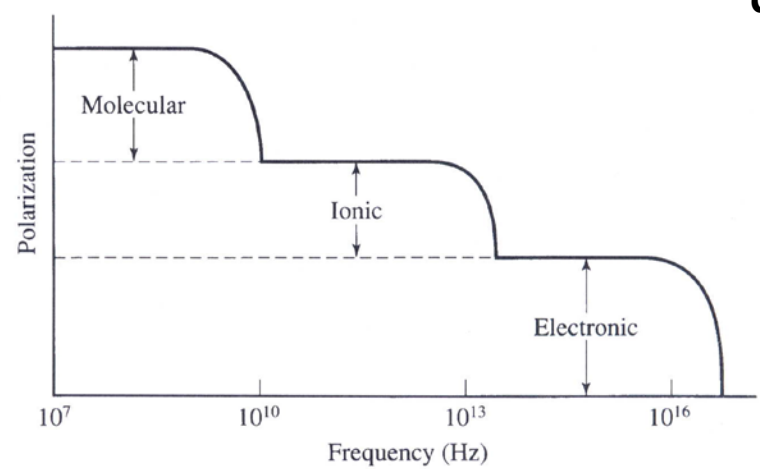
9.5 Dielectric Properties



- 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)

Figure 9.18. Schematic representation of two capacitor plates between which a dielectric material is inserted. (a) Induction of electric dipoles of opposite charge. (b) Weakening of the electric field *within* the dielectric material [Eq. (9.13)]. (c) The direction of the polarization vector is from the negative induced charge to the positive induced charge see Fig. 9.17(b). (d) The dielectric displacement, D , within the dielectric material is the sum of $\epsilon_0 \mathcal{E}$ and P [Eq. (9.15)].

due to polarization



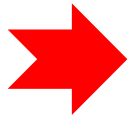
How quickly do the dipoles to reorient or to align under a rapidly changing electric filed (in alternating circuit)

Polarization mechanisms which can respond equally quick to an alternating electric field

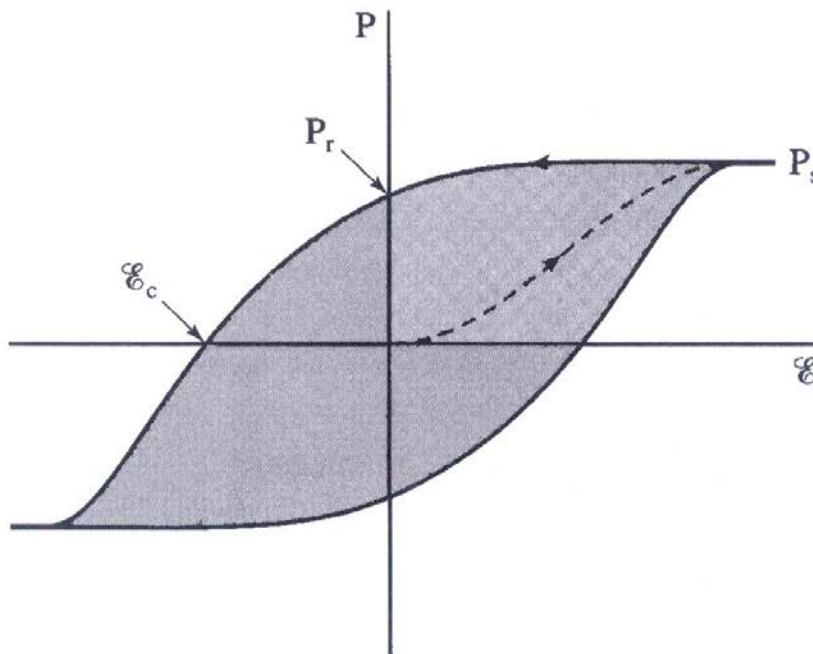
Figure 9.19. Schematic representation of the polarization as a function of excitation frequency for different polarization mechanisms.

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

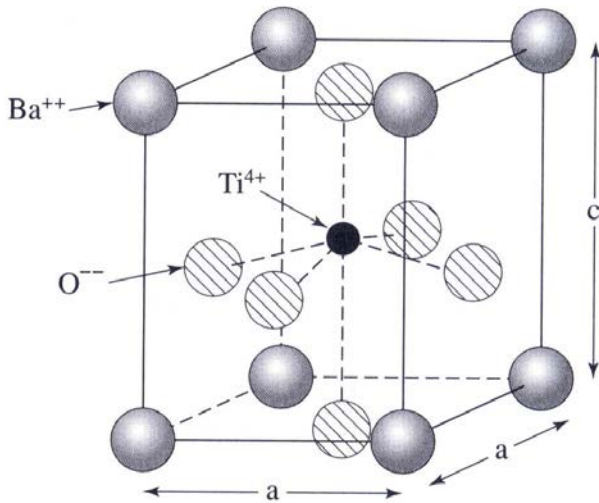
E_C : coercive field

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

9.6 Ferroelectricity, Piezoelectricity, and Electrostriction



Mechanism for spontaneous polarization

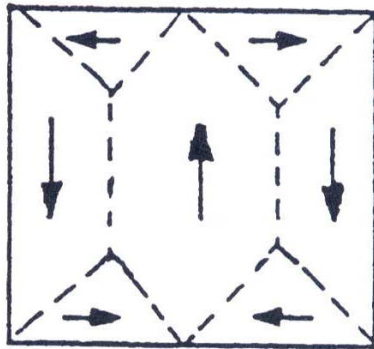


Tetragonal BaTiO₃ :

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

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.



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

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.