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Extrinsic Semiconductors

Extrinsic semiconductors - electrical properties (conductivity) is dictated by impurity atoms. Example: Si is considered to be extrinsic at room T if impurity concentration is one atom per 10¹²

An extrinsic semiconductor may have different concentrations of holes and electrons.

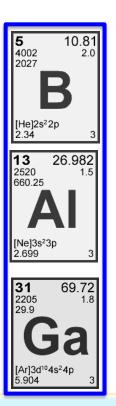
It is called **p-type** if p >> n and **n-type** if n >> p.

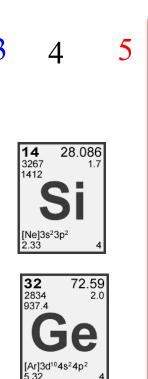
- Two common methods of doping are diffusion and ion implantation.

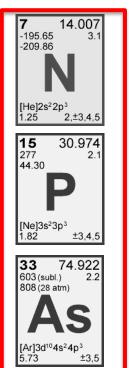
These elements have one less valence erelative to Si



When present as impurities, they will create lots of extra holes called "p-type"







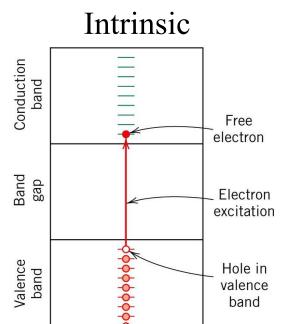
These elements have one more valence erelative to Si



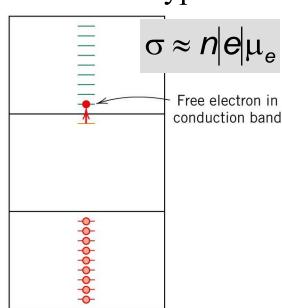
When present as impurities, they will create lots of extra mobile e-called "n-type"



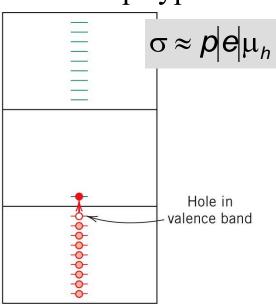
Intrinsic vs. Extrinsic Semiconductors



Extrinsic n-type



Extrinsic p-type



Law of Mass Action: at constant T and equilibrium condition the product of -ve free electron conc. and the +ve hole conc. is a constant

As a doped crystal must remain electrically neutral: Magnitude of total -ve charge density = +ve charge density

At high temperatures when an n-type semiconductor contains only completely ionized donors, the number of electrons is equal to the number of donors (same for holes) is given by the equilibrium equation:

$$n p = n_i^2$$

$$n + N_{\rm a} = p + N_{\rm d}$$

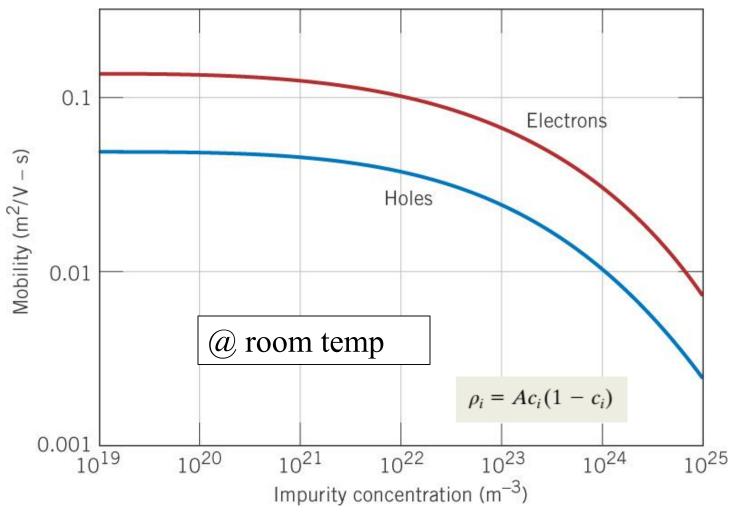
$$n ext{ (n-type)} \sim N_{\mathrm{d}}$$

$$p ext{ (n-type)} \sim \frac{n_{\mathrm{i}}^2}{N_{\mathrm{d}}}$$





Mobility vs. Impurity concentration

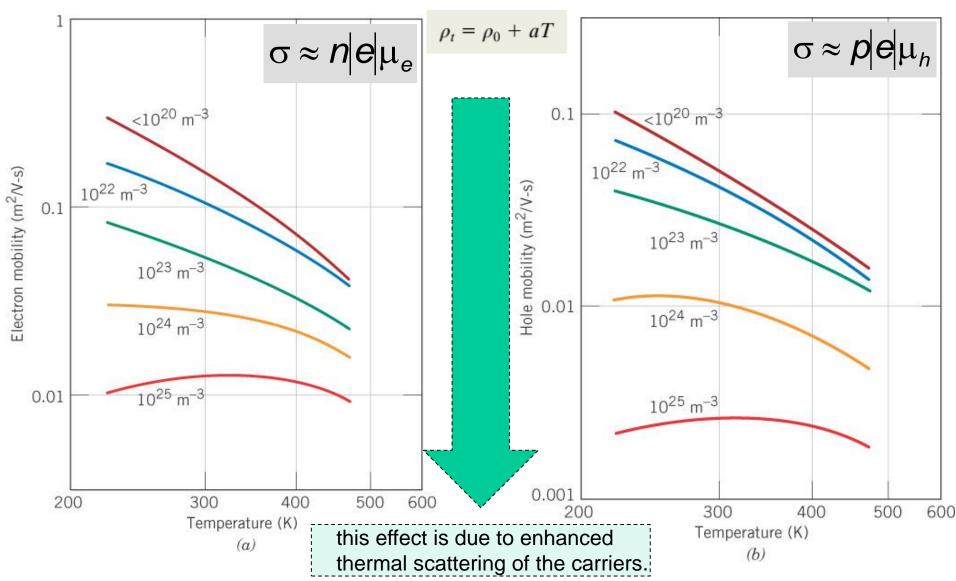


For silicon, dependence of room-temperature electron and hole mobilities (logarithmic scale) on dopant concentration (logarithmic scale).





Mobility vs. Temperature

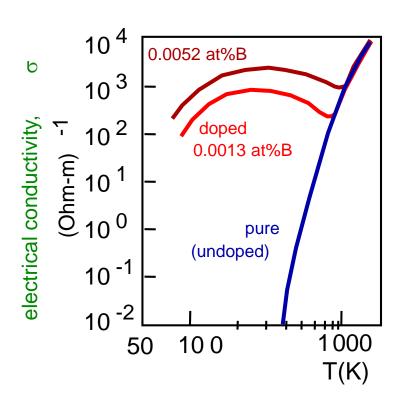


Temperature dependence of (a) electron and (b) hole mobilities for silicon that has been doped with various donor and acceptor concentrations. Both sets of axes are scaled logarithmically.



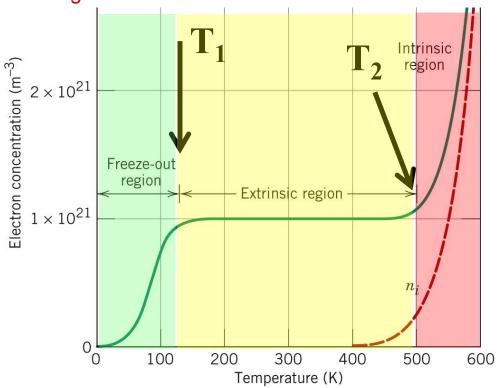
Extrinsic Semiconductors: Doping, Conductivity vs. Temperature

- Data for Doped Silicon:
 - -- σ increases doping
 - -- reason: imperfection sites lower the activation energy to produce mobile electrons.



Extrinsic doping level: 10²¹/m³ of a *n*-type donor impurity (such as P).

- 1) T<T₁: Freeze-out region, thermal energy is not high enough to excite electron from donor state to CB
- 2) T₁<T<T₂: Extrinsic region, thermal energy is high enough to excite electron from donor state to CB
- 3) T>T₂: Intrinsic region, thermal energy is high enough to excite electron from VB to CB

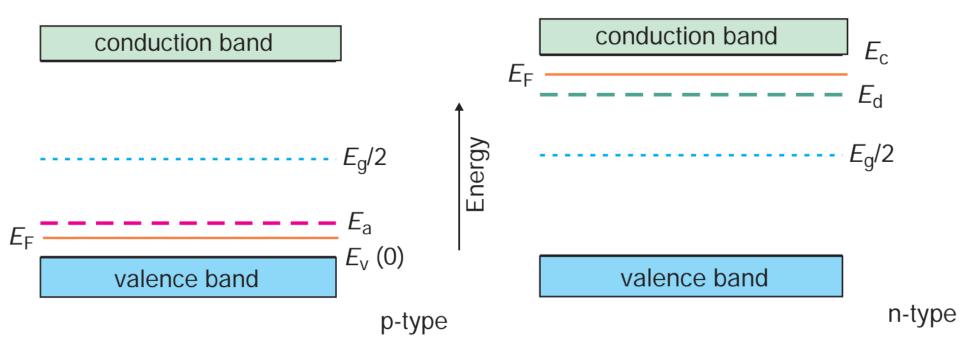






Extrinsic Semiconductor: Fermi Energy (E_f) level

At ordinary temperatures, the Fermi energy moves so as to lie approximately halfway between the bottom of the conduction band and the donor energy levels



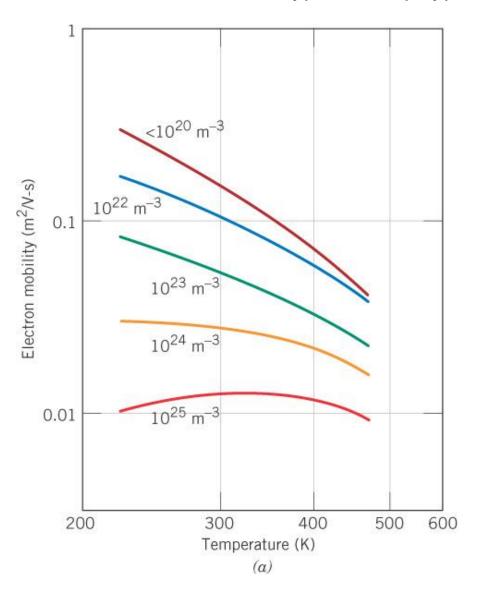
The position of the Fermi energy in (a) a p-type semiconductor, and (b) an n-type semiconductor, at low temperatures

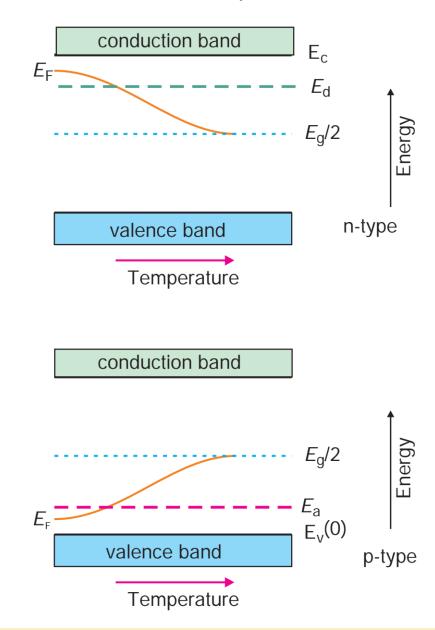




The variation of the position of the Fermi energy

of an n-type and a p-type semiconductor with temperature

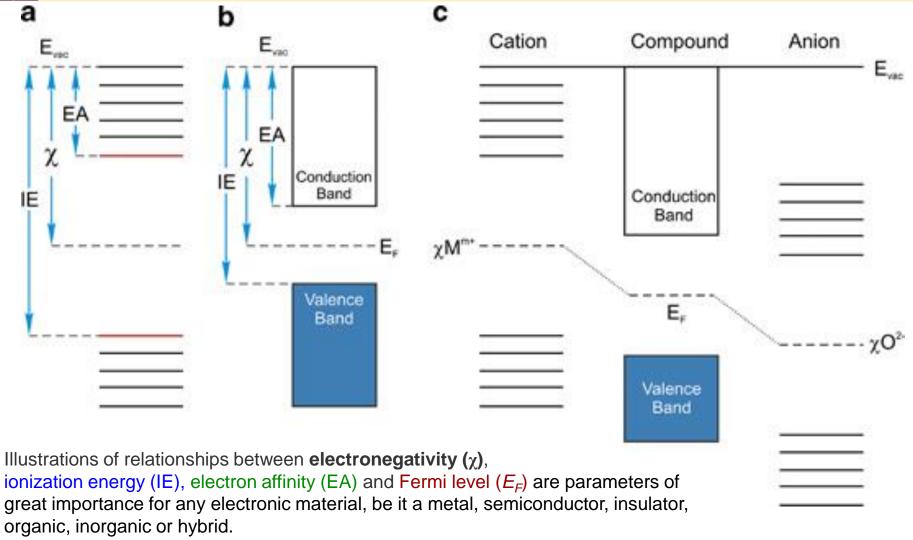








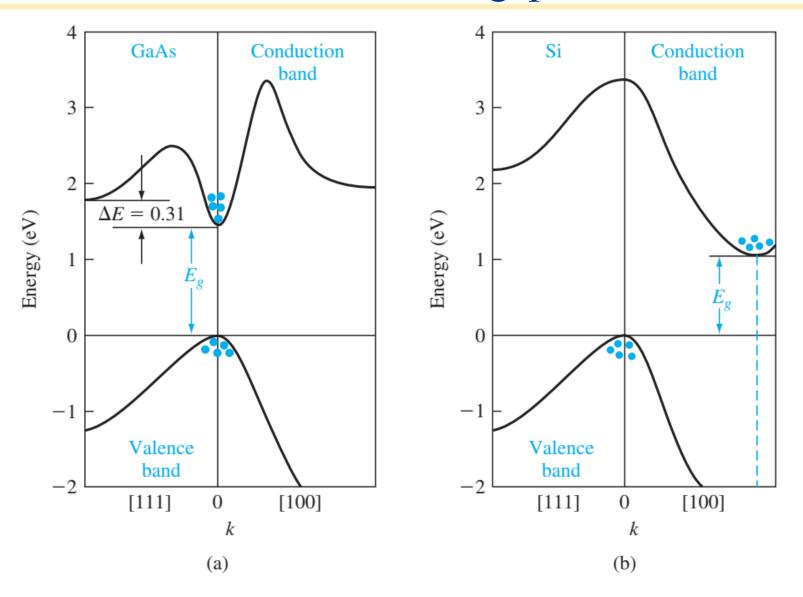
Fermi level, work function and vacuum level w.r.t Band Structure

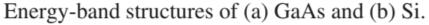


Schematic energy-level diagrams of (a) an isolated atom, (b) a condensed solid semiconductor and (c) a binary oxide. The electronegativity of an isolated metal cation is labeled χM^{m+} , and an isolated oxygen anion is labeled χO^{2-} .



Direct and Indirect Bandgap Semiconductor









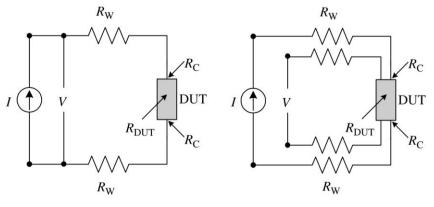
Methods to Determine basic Electrical

properties of materials:

Mobility, types of carriers, and their concentration

- 1. Four Probe Method for resistivity measurement
- 2. Van der Pauw Method

3. Hall Measurement



Two-terminal and four-terminal resistance measurement arrangements.

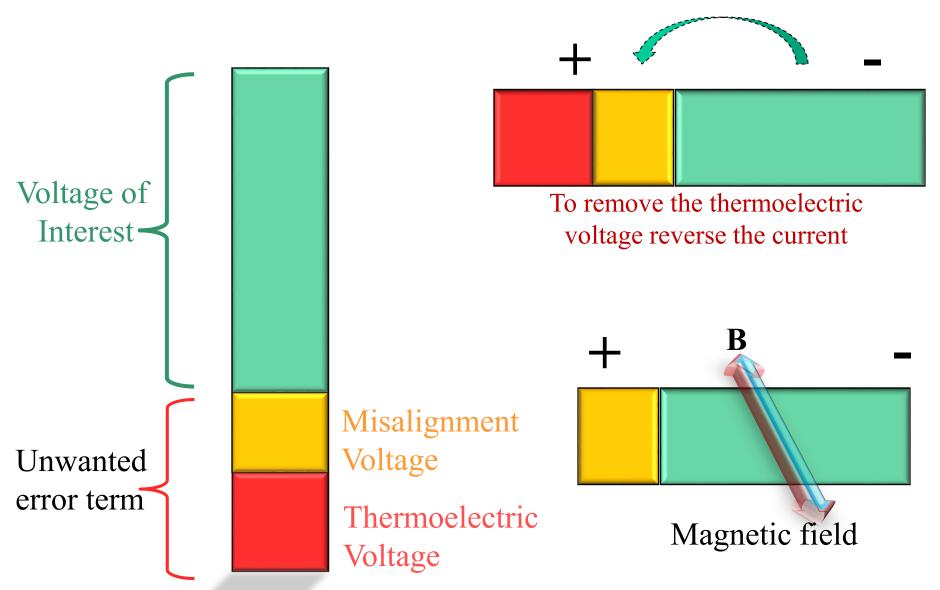
➤ four rather than two probes : eliminate parasitic voltage drops





Methods to eliminate unwanted error term

from the calculation of resistivity





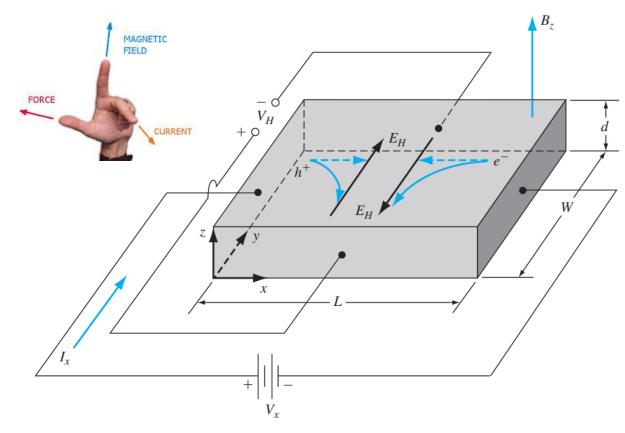


The Hall Effect

How do you determine the majority charge carrier type, concentration, and mobility?

Hall effect is a result of the phenomenon by which a magnetic field applied perpendicular to the direction of motion of a charged particle exerts a force on the particle perpendicular to both the magnetic field and the particle motion directions.

- Apply electrical field to sample (left) so that electrons/hole move along x
- Apply magnetic field (B_z)
 along z. This magnetic
 field induces a voltage
 perpendicular both to the
 magnetic field and the
 current along x
- results in a force on the holes/electrons such that they are deflected along *y* Gives rise to the Hall voltage (*V_H*)

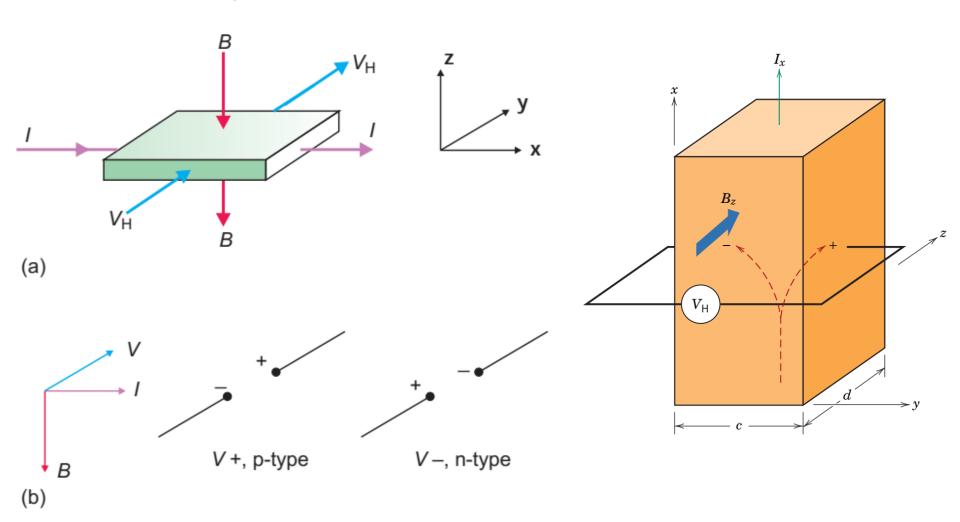






The Hall Effect

Different arrangement







The Hall Effect

The force on a particle having a charge q and moving in a magnetic field is

aiven by $F = qv \times B$ V_H V_H

In steady state, the magnetic field force will be exactly balanced by the induced electric field force. This balance may be written as

$$F = q[E + v \times B] = 0$$

$$qE_y = qv_x B_z$$

The induced electric field in the y direction is called the *Hall field* (E_H). The E_H produces a voltage across the semiconductor- called the *Hall voltage*.

$$V_H = \pm E_H W \qquad \qquad V_H \stackrel{\checkmark}{=} v_x W B_z$$

where E_H is assumed positive in the +y direction

For a p-type semiconductor, the drift velocity of holes can be written as

$$J_{\mathsf{x}} = \mathsf{v}_{\mathsf{dx}} \, \mathsf{e} \, \rho \, \Longrightarrow \, v_{\mathsf{dx}} = \frac{J_{\mathsf{x}}}{ep} = \frac{I_{\mathsf{x}}}{(ep)(Wd)} \, \Longrightarrow \, V_{\mathsf{H}} = \frac{I_{\mathsf{x}} \, B_{\mathsf{z}}}{epd} \, \Longrightarrow \, V_{\mathsf{H}} = \frac{R_{\mathsf{H}} I_{\mathsf{x}} B_{\mathsf{z}}}{d}$$

Hole concentration

$$p = \frac{I_x B_z}{edV_H}$$

 R_H is the Hall coefficient, which is constant for a given material =

$$R_{H} = \frac{1}{|e|p}$$





The Hall Effect: n-type

For an n-type semiconductor, the Hall voltage is given by

$$V_H = -\frac{I_x B_z}{ned}$$



$$V_H = \frac{R_H I_x B_z}{d}$$

• R_H is the Hall coefficient, which is constant for a given material =

$$\mathsf{R}_\mathsf{H} = \frac{1}{|e|n}$$

Electron concentration=

$$n = -\frac{I_x B_z}{edV_H}$$

Hall voltage is negative for the n-type semiconductor; therefore, the electron concentration is actually a positive quantity.

How to calculate the low-field majority carrier mobility?

For a p-type semiconductor, we can write

$$J_x = ep\mu_p E_x$$

Remember $(J_x = \sigma E)$

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

The current density and electric field can be converted to current and voltage

$$\frac{I_x}{Wd} = \frac{ep\mu_p V_x}{L}$$

The hole mobility is

$$\mu_p = \frac{I_x L}{epV_x Wd}$$

The electron mobility is -

$$\mu_e = \frac{I_{\chi}L}{enV_{\chi}Wd}$$

$$\mu_e = |R_{\rm H}|\sigma$$





Important Equations

Type of semiconductor

P-type

N-type

Majority Carrier Concentration

$$p = \frac{I_x B_z}{edV_H}$$

$$n = -\frac{I_x B_z}{edV_H}$$

Hall voltage

$$V_H = \frac{R_H I_x B_z}{d}$$

$$V_H = \frac{R_H I_x B_z}{d}$$

Hall Coefficient (R_H)

$$R_H = \frac{1}{|e|p}$$

$$R_{H} = \frac{1}{|e|n}$$

Majority carrier Mobility (μ)

$$\mu_p = \frac{V_H d}{I_x B_z \rho}$$

$$\mu_e = \frac{V_H d}{I_{\chi} B_Z \rho}$$

HOME WORK: Derive these equation in terms of resistance?





Schematic of Hall Effect experiment

The blade of the probe should be slipped between the magnet **VOLTAGE MEASUREMENT** pole pieces so that the sensing element is centered. **WHITE KIETHLEY 2010** HALL PROBE VOLTS (**MULTIMETER GREEN** сом () 0 0 0 0 0 0 0 0 AMPS (**BETWEEN MAGNET POLES RED CURRENT MEASUREMENT BLACK KIETHLEY 2000** volts() **MULTIMETER** 0-12V + PWR SUPPLY COM (00000000 AMPS (**Constant Current Supply**









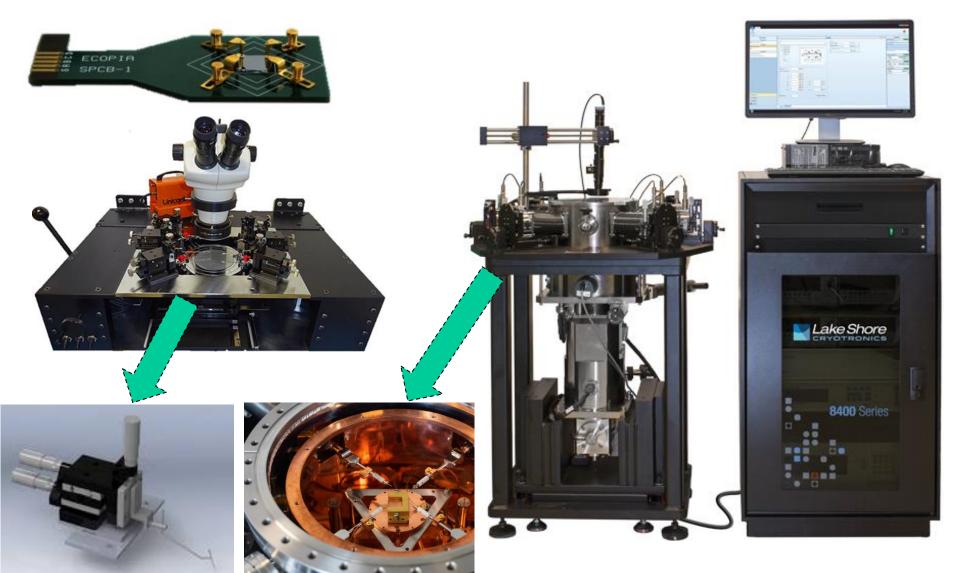
Schematic of Hall Effect experiment.







Probe station







Electrical Conduction in Ionic Ceramics and in Polymers

Most polymers and ionic ceramics are insulating materials at room temperature. With rising temperature, insulating materials experience an increase in electrical conductivity.

Material	Electrical Conductivity $[(\Omega \cdot m)^{-1}]$
Graphite	$3 \times 10^4 - 2 \times 10^5$
Ceramics	y .
Concrete (dry)	10^{-9}
Soda-lime glass	$10^{-10} - 10^{-11}$
Porcelain	$10^{-10} - 10^{-12}$
Borosilicate glass	~10 ⁻¹³
Aluminum oxide	<10 ⁻¹³
Fused silica	<10 ⁻¹⁸
Polymers	Y
Phenol-formaldehyde	$10^{-9} - 10^{-10}$
Poly(methyl methacrylate)	<10 ⁻¹²
Nylon 6,6	$10^{-12} - 10^{-13}$
Polystyrene	<10 ⁻¹⁴
Polyethylene	$10^{-15} - 10^{-17}$
Polytetrafluoroethylene	<10 ⁻¹⁷





Conduction in Ionic Materials

Both **cations** and **anions** in ionic materials possess an electric charge, and are capable of migration or diffusion when an electric field is present.

 $\sigma_{\text{total}} = \sigma_{\text{electronic}} + \sigma_{\text{ionic}}$

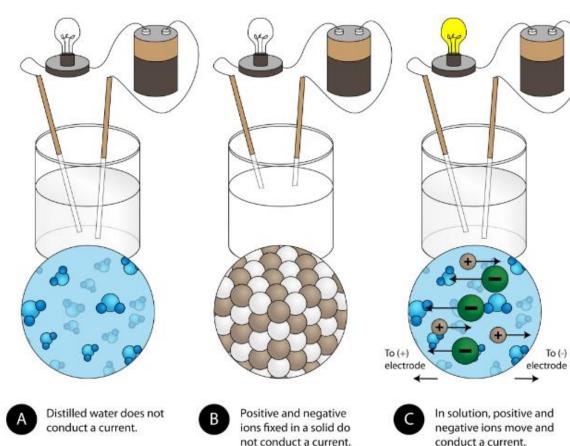
Thus an electric current results from the **net movement of these charged ions + current due to any electron motion**.

Anion and cation migrations are in opposite directions.

The mobility associated with ionic species

$$\mu_I = \frac{n_I e D_I}{kT} \qquad \sigma = nZq\mu$$

n and *D* represent, respectively, the valence and diffusion coefficient of a particular ion;



Ionic compound Sodium chloride Electrical conductivity Water





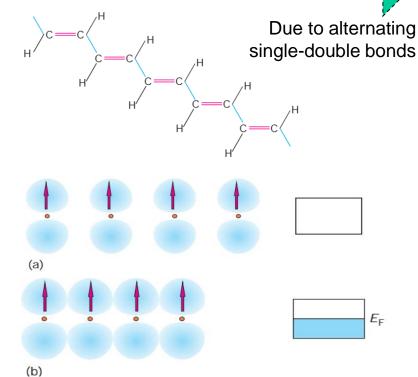
Electrical Conduction in Polymers

(c)

Usually Polymers are poor conductors of electricity

1 sp-hybrid σ bond and two Π bonds

Polymerisation



Conjugated polymers: (a) a chain of isolated half-occupied p orbitals would lead to an insulator; (b) a chain of overlapping half-occupied p orbitals would lead to a half-filled conduction band and metallic conductivity.

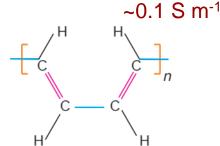
Ex: polyacetylene, polyparaphenylene, polypyrrole, and polyaniline

Polymers to become electronically conducting is due to the presence of conjugated single and double bonds and/or aromatic units in the polymer chain

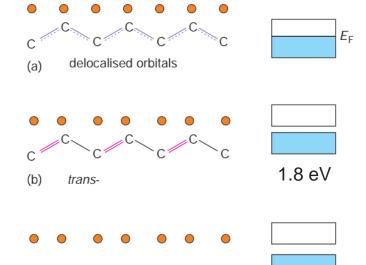
trans-polyacetylene

etylene *cis*-polyacetylene

$$c = c$$
 -10^{-3} S m
 $c = c$
 h



Distortion of a polymer chain:



- (a) delocalized orbitals along a polymer chain lead to equally spaced atoms and a half-filled energy band;
- (b) Peierls distortion in trans-polyacetylene;
- (a) Peierls distortion in cis-polyacetylene; both leading to alternating short and long bonds and a band structure similar to that of an intrinsic semiconductor.

Conduction in polymers of high purity is electronic

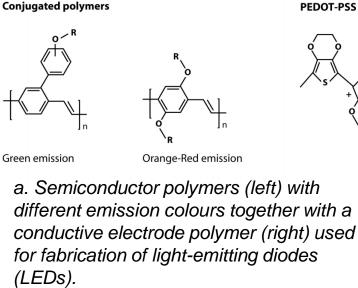
2 eV



Electrical Conduction in Polymers: Doping

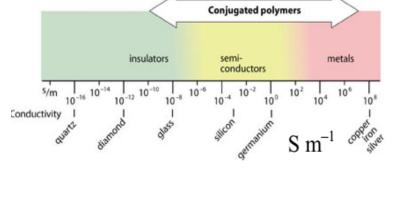
Doping with electron acceptors such as halogens (chlorine, iodine, etc.) oxidise the polymer, in this process, electrons are taken from the filled lower band and used to form halide ions, leaving holes, which result in a **p-type** material.

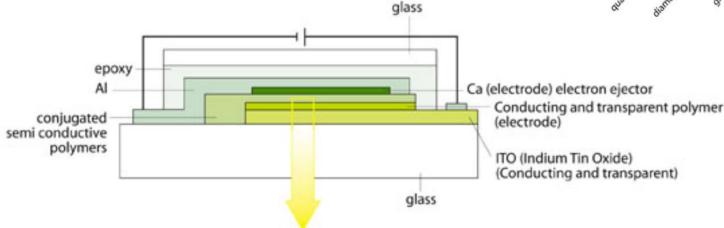
The Nobel Prize in Chemistry, 2000: Conductive polymers



with a ht) used

Doping with alkali metals, (lithium, sodium, etc), reduces the polymer. In this process, the alkali metal donates electrons to the empty band, forming an alkali metal ion and transforming the polymer into an **n-type** material.





Cross-section of a OLED



Summary

- Electrical conductivity and resistivity are:
 - -- material parameters.
 - -- geometry independent.
- Electrical resistance is:
 - -- a geometry and material dependent parameter.
- Conductors, semiconductors, and insulators...
 - -- differ in accessibility of energy states for conductance electrons.
- · For metals, conductivity is increased by
 - -- reducing deformation
 - -- reducing imperfections
 - -- decreasing temperature.
- For pure semiconductors, conductivity is increased by
 - -- increasing temperature
 - -- doping (e.g., adding B to Si (*p*-type) or P to Si (*n*-type).





Summary

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. Remember electro-negativity.
 - Semiconductors mostly covalent bonding somewhat weaker bonding. Sharing of electrons.
 - Metals valence electrons form an "electron gas" that are not bound to any particular ion.

