# AP 5301/8301

## Instrumental Methods of Analysis and Laboratory

## Lecture 6

## Electrical measurements

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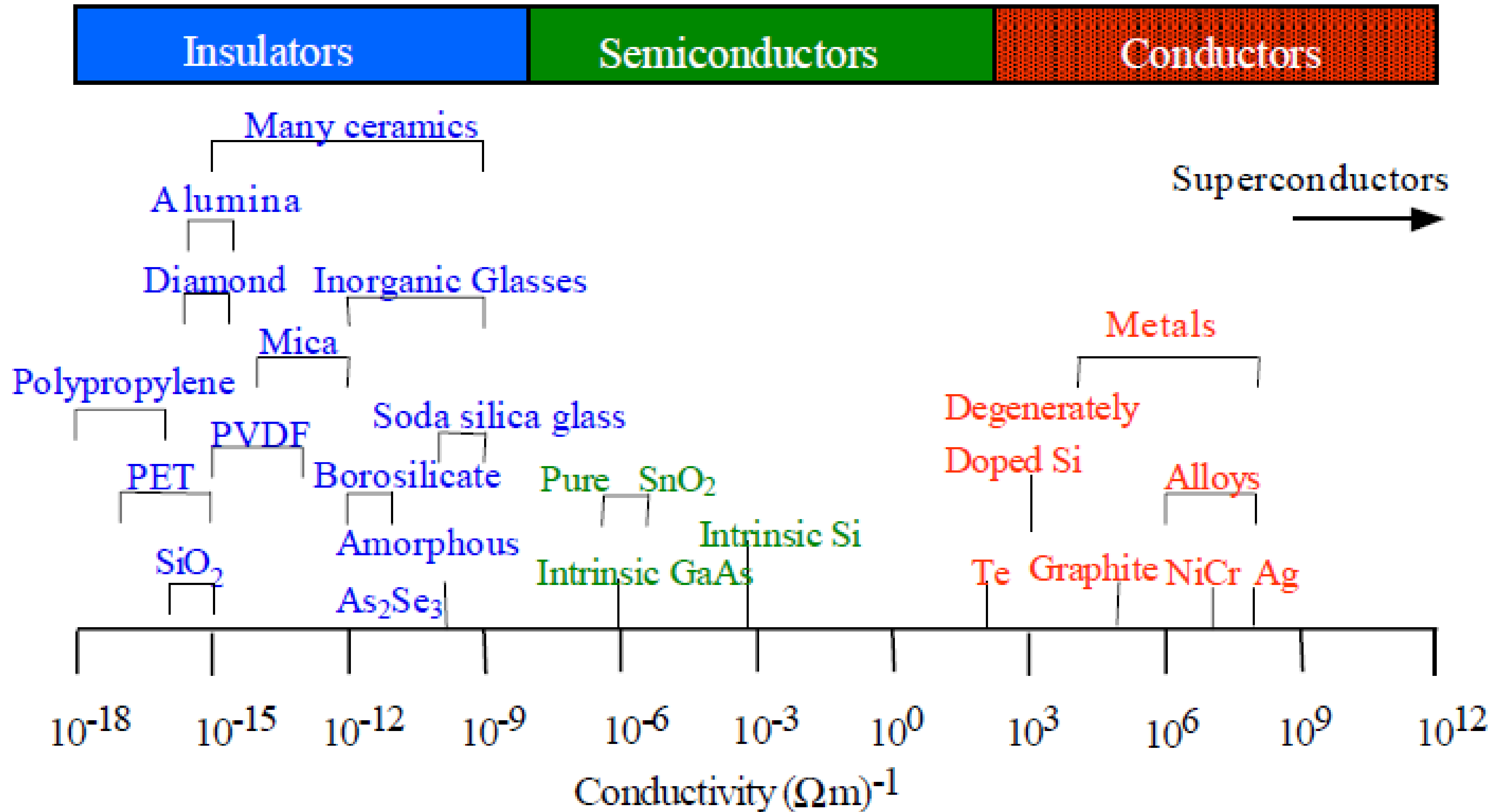
# Lecture 6: outline

- Reviews
  - Classification of solids
  - Semiconductor basics
  - Electrical conduction
- Resistivity measurement: the four point probe
- Spreading resistance profiling
- Hall effect
  - The van der Pauw method
  - Variable temperature Hall
- Capacitance voltage profiling
  - Schottky contact
  - C-V profiling
  - Electrochemical C-V profiling
- Thermoelectric effect
  - Thermoprobe
  - Seebeck coefficient
- Minority carrier lifetime

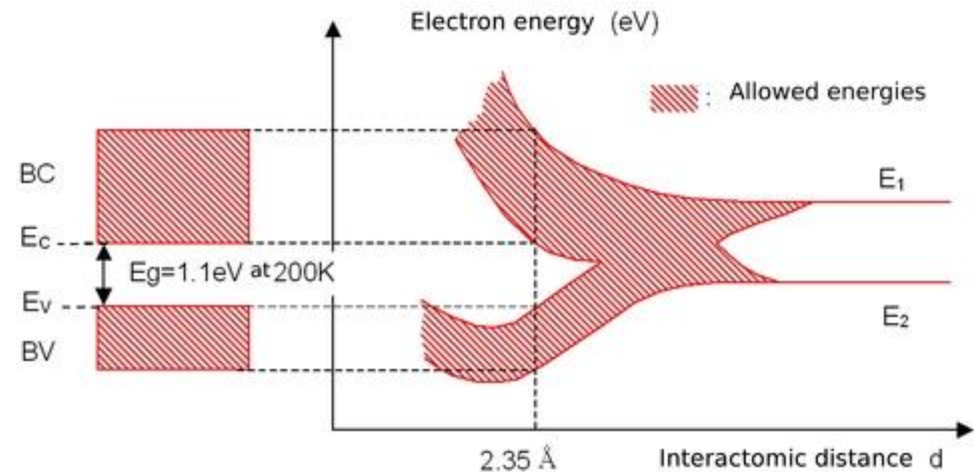
# Conductivity in materials



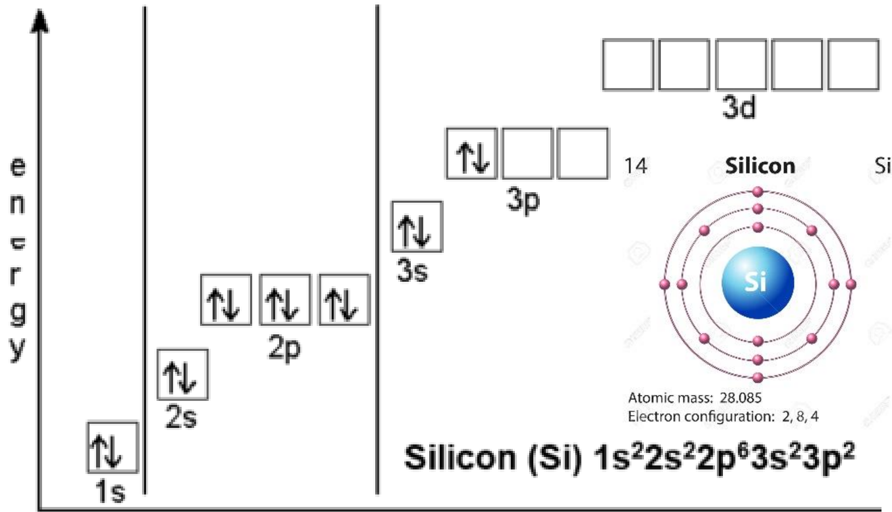

Electrical characterization can be performed on semiconductors and metals to obtain electrical transport properties of the materials

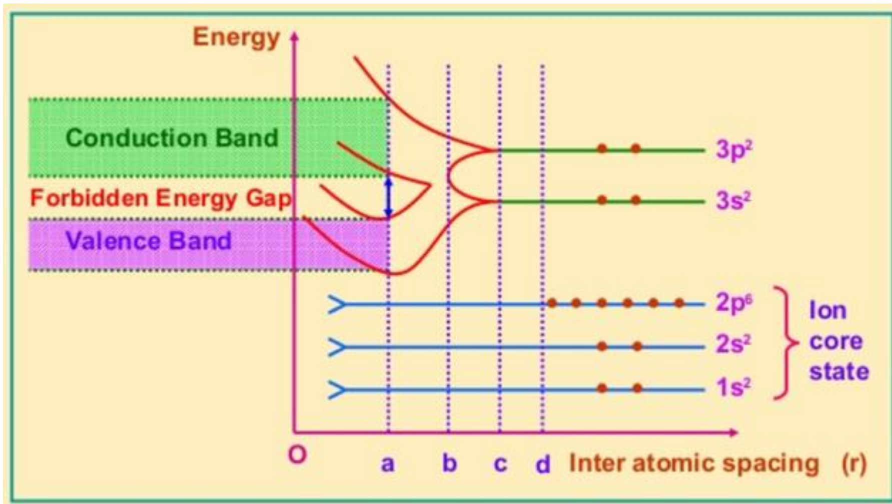
# Energy bands in solids

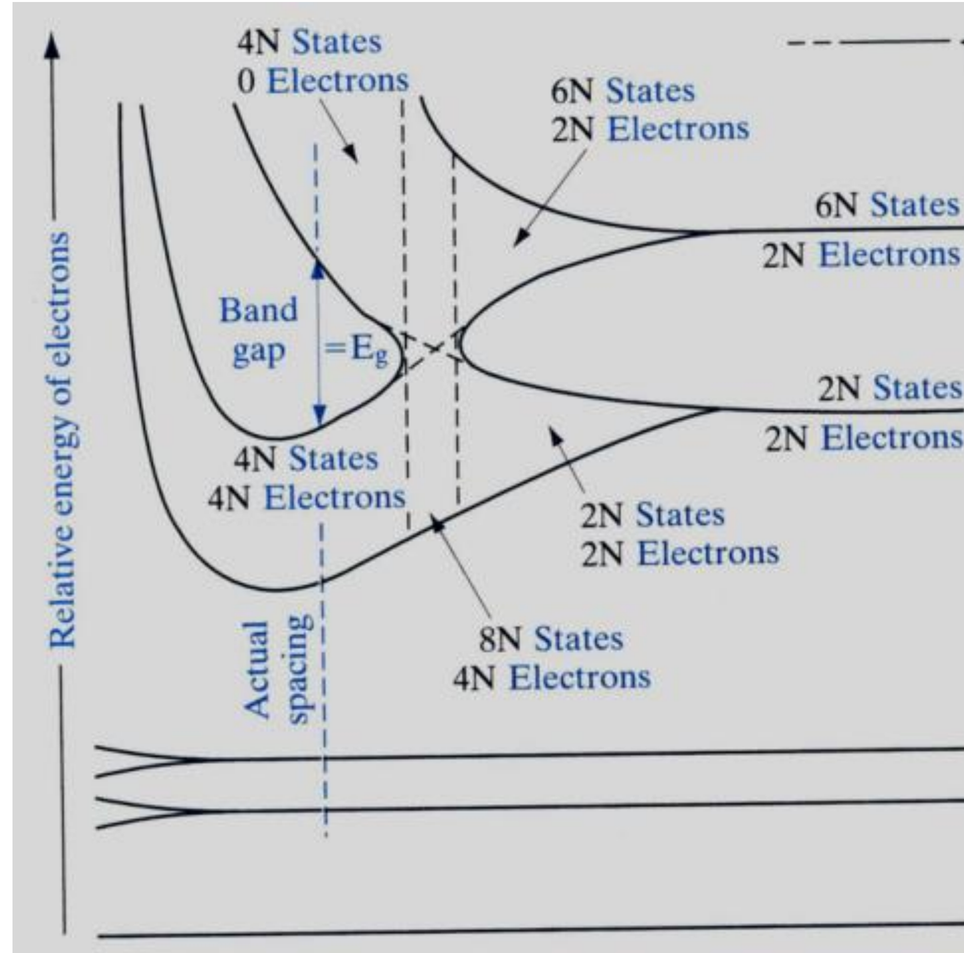
- Consider an isolated silicon atom; its energy levels are quantized
- When two identical atoms are brought closer together, the **quantized** energy levels hybridize and split into **two different levels** because of the mutual interaction of the two atoms.
- When N atoms are moved closer, until they reach the equilibrium inter-atomic distance d, the energy levels split into N levels.
- These N levels are very close to each other if N is large (which is the case in a crystal) so that they eventually form a continuous energy band.
- In a silicon crystal, two **continuous energy bands** exist: a fully occupied **valence band** (VB) and an empty **conduction band** (CB), separated by a forbidden band, which is not accessible for electrons.
- This forbidden region is called the **energy gap** and its width $E_g$ is a characteristic of the material.



# Energy bands in solids

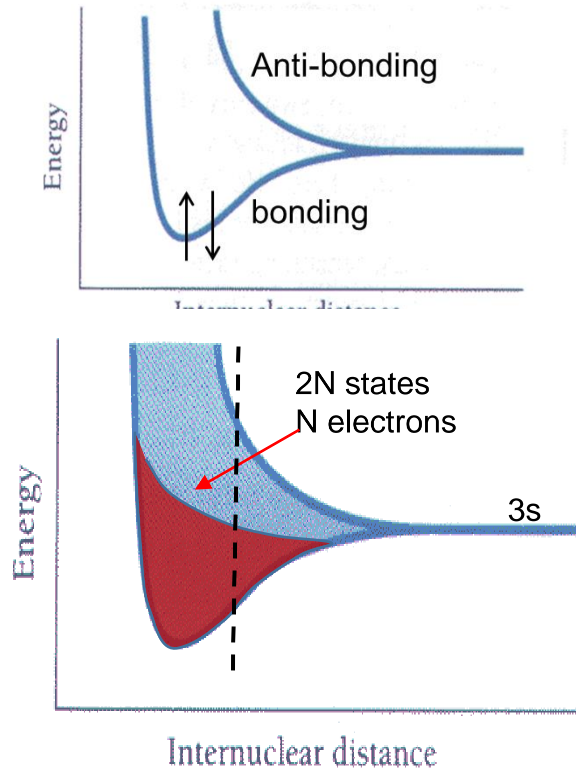


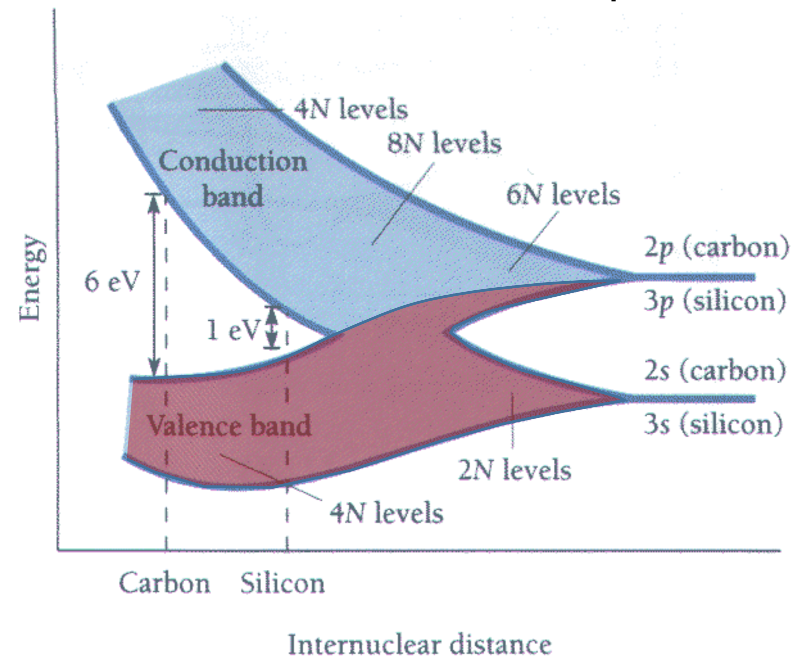



# Energy bands in solids

Na atom: $1s^2\ 2s^2\ 2p^6\ 3s^1$




Energy bands in carbon (and silicon) as a function of interatomic separation.




The shaded area represents N states filled by electrons but there are still N empty states in the band.

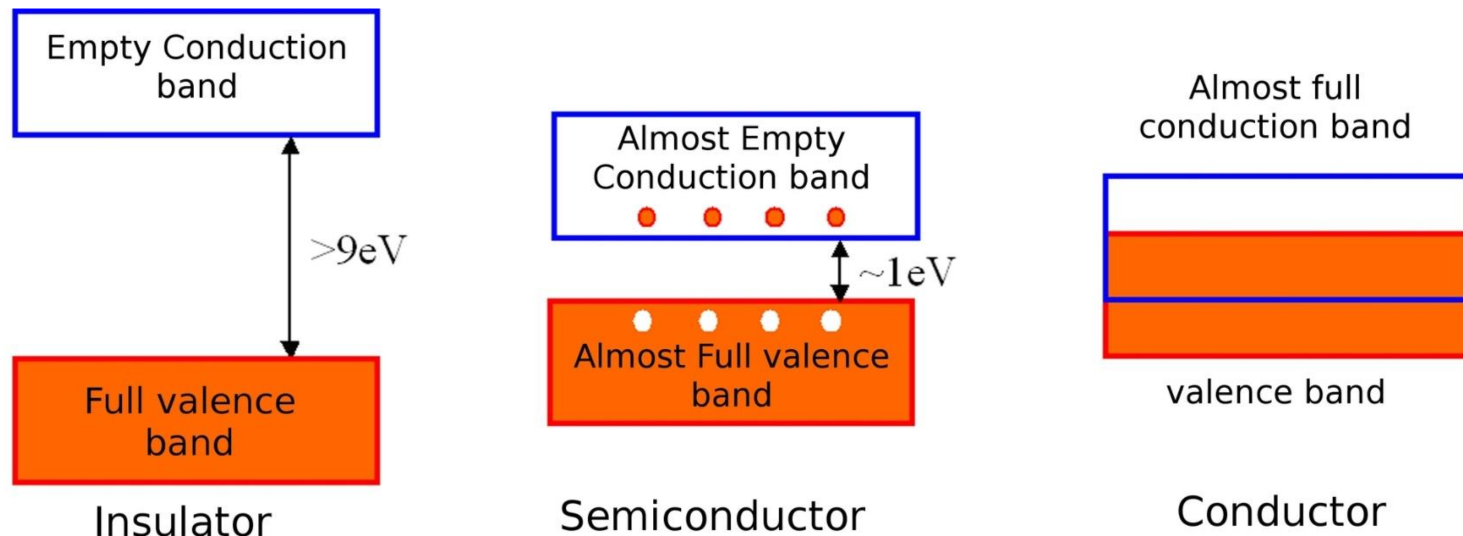
- Electrons can move in the band
- Sodium is a conductor

An empty band with 4N states is separated from a full band by a gap $E_g$

- Electrons in the full valence band cannot move
- Si and diamond are insulators at low temperature

# Conductivity and energy bands

- Electrical conduction is the result of electron motion within each band.
- When an electric field is applied to the material, electrons start to move in the direction opposed to the direction of the electric field.
- An empty energy band or a fully occupied band does not participate in the formation of an electric current — **insulator**
- **Conductors** (metals) have half filled (or overlapped) energy bands so that electrons always have empty state to move
- **Semiconductors** have relatively small gap so that some electrons can be thermally excited to the empty states for conduction.



# Characteristics of semiconductors

- Semiconductors can be composed of a single element such as Si and Ge or it can consist of two or more elements for compound semiconductors.
- A binary III-V (or II-V) semiconductor such as GaAs (ZnSe) is one comprising one element from Column III (II) and one from Column V (VI).

| | II | III | IV | V | VI | |
|---|---|---|---|---|---|---|
| | | B | C | N | O | F |
| | | Al | Si | P | S | Cl |
| Cu | Zn | Ga | Ge | As | Se | Br |
| Ag | Cd | In | Sn | Sb | Te | I |
| Au | Hg | Tl | Pb | Bi | Po | At |

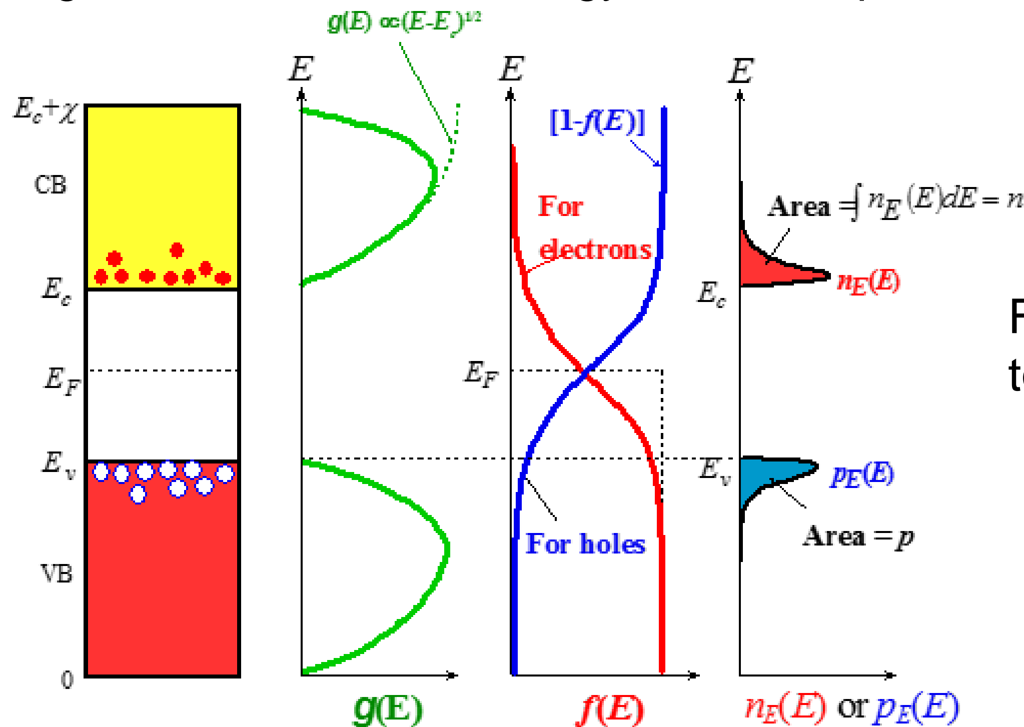
- The electrical **conductivity** of a semiconductor material **increases with increasing temperature**, opposite to that of a metal.
- the electrical properties of a semiconductor can be modified by controlled addition of **impurities**, or by the application of electrical fields or light.
- Current conduction in a semiconductor occurs through the movement of **free electrons** (n-type) and **"holes"** (p-type).
- When semiconductors are joined to metals, to different semiconductors, and to the same semiconductor with different doping, the resulting junction often strips the electron excess or deficiency (holes) out from the semiconductor near the junction -- **depletion region.**

# Fermi-Dirac distribution

- At a finite temperature $T$ the probability of occupation of an electron state of energy $E$ at thermal equilibrium is given by the **Fermi-Dirac distribution** function

$$f(E,T) = \frac{1}{e^{(E-E_F)/k_B T} + 1}$$

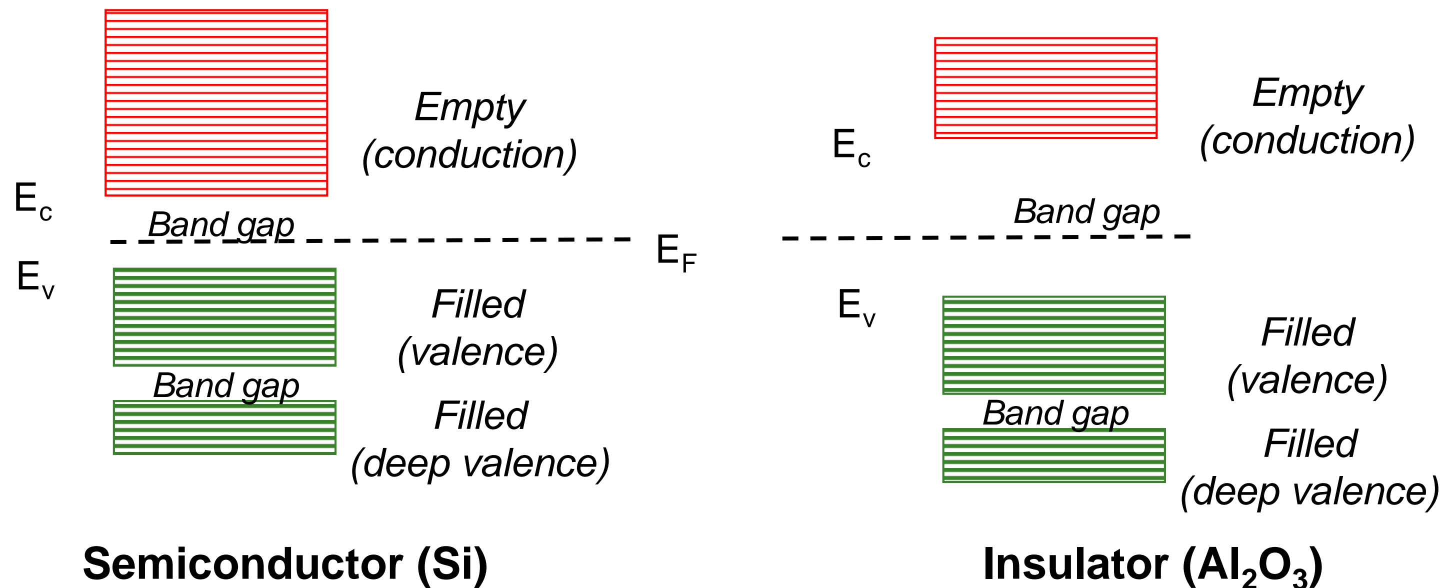
- The Fermi-Dirac distribution function $f(E,T)$ determines the probability of finding an electron at the energy $E$ and temperature $T$.




Fermi level $E_F$ corresponds to the energy at which $f=1/2$

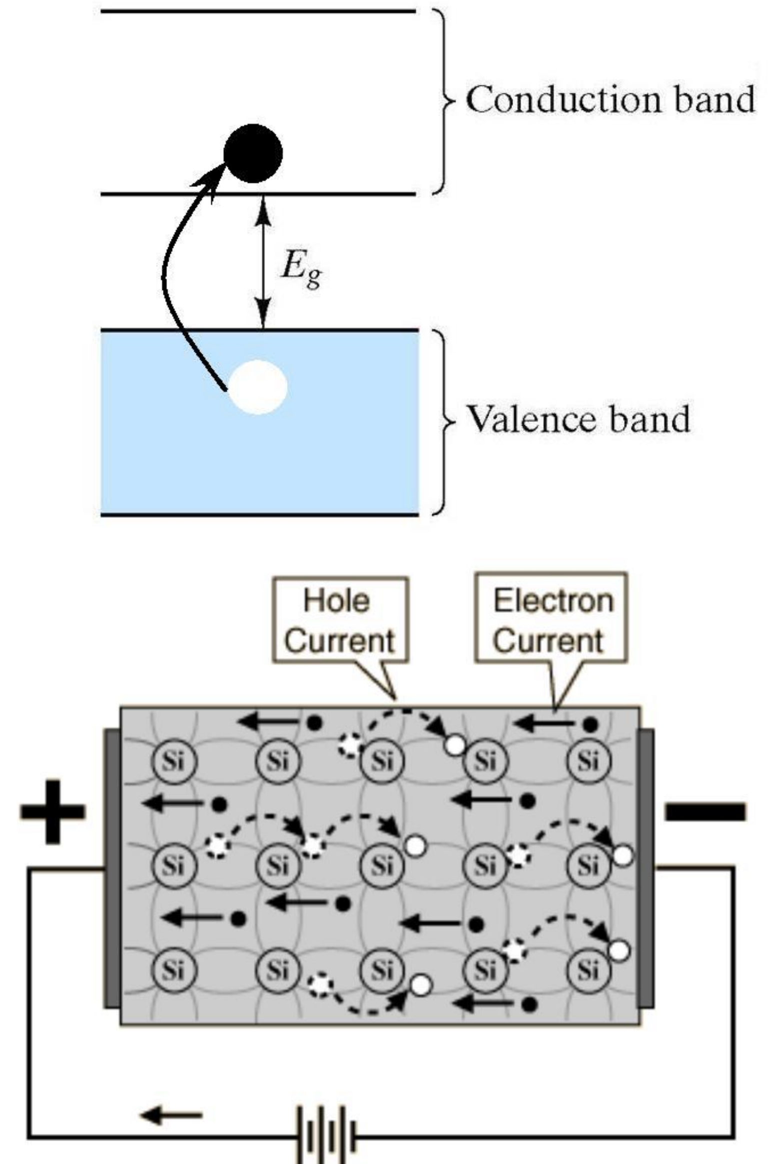
# Valence and conduction bands

- Semiconductors and insulators have **totally full valence bands** and **empty conduction bands** with a bandgap between them.
- Energy levels $E_c$ (conduction band minimum) is at the base of the conduction band and $E_v$ (valence band maximum) is at the top of the valence band
- The Fermi energy level $E_F$ is in the bandgap for insulators.
- $E_F$ is close to $E_c$ for n-type (conduction by electrons in the CB), and close to $E_v$ for p-type (conduction by holes-missing electrons in the VB) materials.



# Electrons and holes

- As the temperature of a semiconductor is raised from 0 K, some electrons in the valence band receive enough thermal energy to be excited across the band gap to the conduction band.
- The result is a material with some electrons in an otherwise empty conduction band and some unoccupied states in an otherwise filled valence band.
- An empty state in the valence band is referred to as a hole.
- Electron ($e^-$) in the CB and holes ($h^+$) in the VB respond to an external field and move in opposite directions
- Movement of hole is actually the hopping of electrons in the valence band into the vacant bond
- *Current* due to electrons and holes is in the same direction, i.e. $I_{total} = I_e + I_h$



# Equilibrium carrier density

- Electron concentration in the conduction band

$$n(T) = 2(\frac{m_e k_B T}{2\pi\hbar^2})^{3/2} e^{(E_F - E_g)/k_B T} = N_C e^{(E_F - E_g)/k_B T}$$

where $N_C = 2(\frac{m_e k_B T}{2\pi\hbar^2})^{3/2}$ is the **effective density of states** for the CB

- Hole concentration in the valence band

$$p(T) = 2(\frac{m_h k_B T}{2\pi\hbar^2})^{3/2} e^{-E_F/k_B T} = N_V e^{-E_F/k_B T}$$

where $N_V = 2(\frac{m_h k_B T}{2\pi\hbar^2})^{3/2}$ is the effective density of states for the VB

$$np = n_i^2 = N_C N_V e^{-E_g/k_B T}$$

- The $np$ product of a semiconductor is a constant at a given temperature under thermal equilibrium (**law of mass action**)

- For an intrinsic semiconductor:

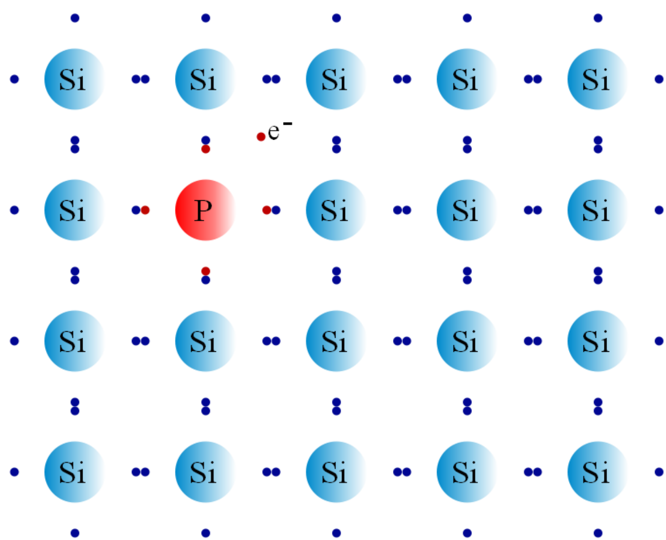
$$n_i = \sqrt{N_C N_V} e^{-E_g/2k_B T}$$

$$E_{Fi} = \frac{E_g}{2} + \frac{3}{4} k_B T \ln\frac{m_h}{m_e} = \frac{E_g}{2} + \frac{1}{2} k_B T \ln\frac{N_V}{N_C}$$

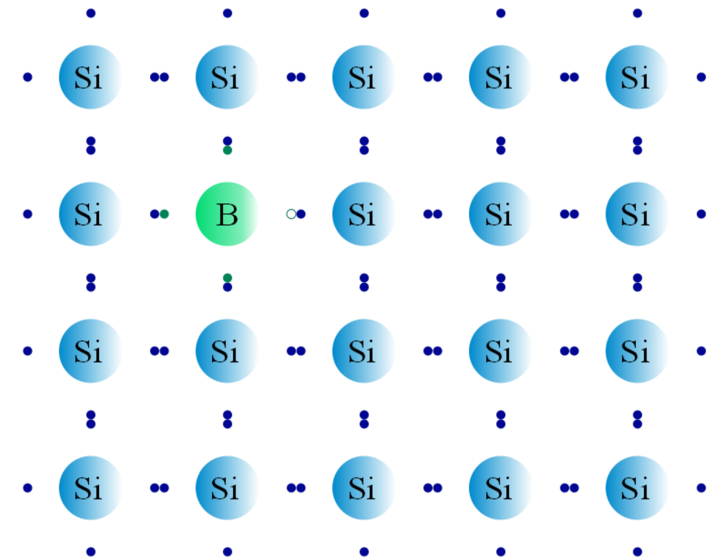
# Extrinsic (Doped) semiconductors

- The effect of **doping** with impurities is to alter the carrier densities and thus shift the Fermi Energy level toward $E_c$ (n-type with more electrons) or $E_v$ (p-type with more holes).
- Intrinsic semiconductors have equal numbers of both types of carriers. In most applications, however, one needs to have one types of carriers only and none of the other. This can be achieved by doping.
- **Extrinsic semiconductors** are formed by introducing impurities, or doping agents, into an intrinsic semiconductor in order to change its electrical properties.
- A **donor** impurity has **one extra electron** that it can "donate" to the semiconductor to make it n-type (electron conducting).
  - They typically have energy levels just below the conduction band and can be thermally activated to the conduction band
- An **acceptor** impurity has **one less electron** so that it can "accept" an electron from the semiconductor making it p-type (hole conducting)
  - Acceptors typically have energy levels just above the valence band so that holes can be thermally activated to the valence band

# Semiconductor doping




| boron 5 B 10.811 | carbon 6 C 12.011 | nitrogen 7 N 14.007 |
|---|---|---|
| aluminium 13 Al 26.982 | silicon 14 Si 28.086 | phosphorus 15 P 30.974 |
| gallium 31 Ga 69.723 | germanium 32 Ge 72.61 | arsenic 33 As 74.922 |
| indium 49 In 114.82 | tin 50 Sn 118.71 | antimony 51 Sb 121.76 |




Doping by an element with an extra valence electron to add electrons is called “n-type” (negative) doping. The added electrons will be in the conduction band.

Doping by an element with one less valence electron to remove electrons from the valence band is called “p-type” (positive) doping.

# Donors and Acceptors

## Group IV

II III IV V VI

| | | | | | | |
|---|---|---|---|---|---|---|
| | | B | C | N | O | F |
| | | Al | Si | P | S | Cl |
| Cu | Zn | Ga | Ge | As | Se | Br |
| Ag | Cd | In | Sn | Sb | Te | I |
| Au | Hg | Tl | Pb | Bi | Po | At |

acceptors donors

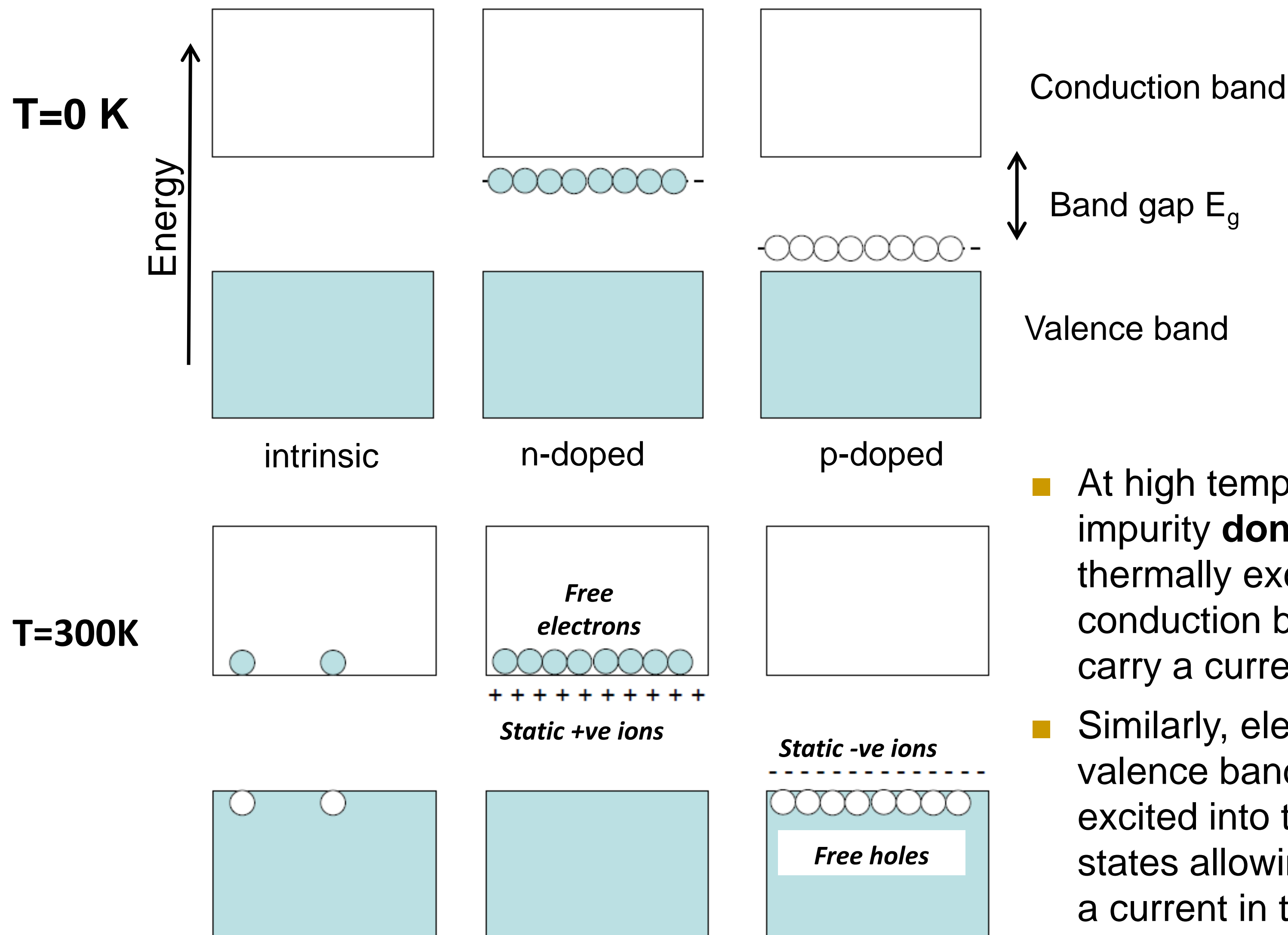
## Group III-V

II III IV V VI

| | | | | | | |
|---|---|---|---|---|---|---|
| | | B | C | N | O | F |
| | | Al | Si | P | S | Cl |
| Cu | Zn | Ga | Ge | As | Se | Br |
| Ag | Cd | In | Sn | Sb | Te | I |
| Au | Hg | Tl | Pb | Bi | Po | At |

acceptors amphoteric donors

# N- and p-type doping




- At high temperatures, impurity **donor** electrons are thermally excited into the conduction band and can carry a current.
- Similarly, electrons in the valence band are thermally excited into the **acceptor** states allowing holes to carry a current in the valence band.

# Conduction electrons

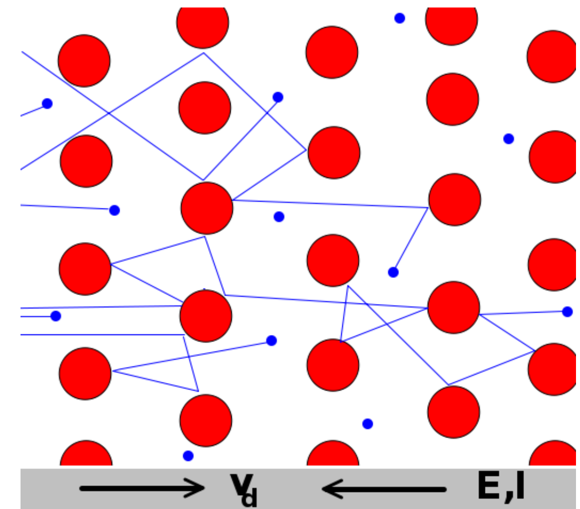
- In order to understand electrical behaviors of solids (metals or semiconductors), their electrons have to be considered.
- Electrons in a metal can be described **classically** by the **Drude model** and with quantum mechanical supplement by the **free electron model**
- Both models are simplifications but are able to describe many properties of metals
- The Drude model (1900) used the **kinetic theory**, assuming that the microscopic behavior of electrons in a solid may be treated classically

Assumptions:

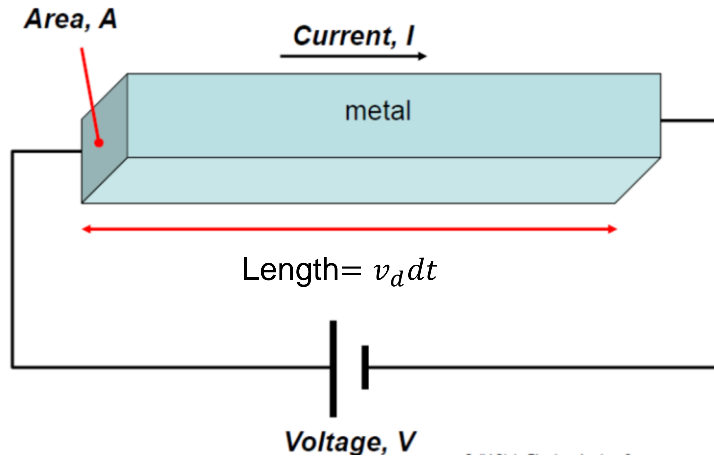
— matter consists of light negatively charged electrons which are mobile, & heavy, static, positively charged ions,

— neglecting electron-electron interactions and electron-ion interactions (**free electrons**)

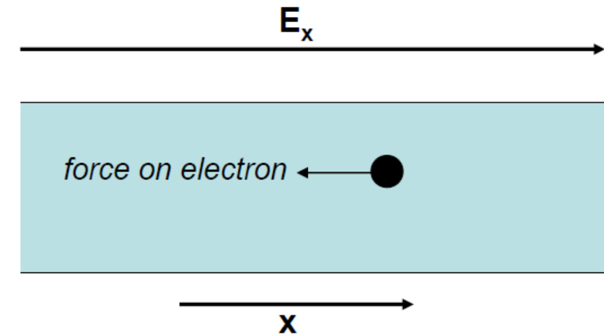
— The probability of an electron suffering a collision in a short time $dt$ is $dt/\tau$, where $\tau$ is the **mean free time** between collision and $\frac{1}{\tau}$ is the electron scattering rate.



# Electrical conductivity




Consider an electric field in the x-direction, $E_x$




The current flowing through the cross-sectional area A, $I = \frac{Q}{dt}$,

where $Q = (ne)(Av_d dt)$ is the total charge flowing through *A*, *n* is the free carrier concentration, $v_d$ is the drift velocity and *e* is the electron charge.

So, $I = -nAv_d e$

And the current density: $J = \frac{I}{A} = -nv_d e$

Ohm's Law: $V = IR \text{ or } I = V/R$, or

$$J = \frac{1}{\rho} E \text{ or } J = \sigma E$$

where $\rho$ is the resistivity and $\sigma$ is the conductivity

Force on an electron is $F = -eE_x$

Newton's 2nd Law: $-eE = m\frac{d^2x}{dt^2}$

Acceleration: a $= \frac{d^2x}{dt^2} = -\frac{eE}{m}$

**Drift velocity** due to the electric field:

$$v_d = -\frac{eE\tau}{m} = -\mu E$$

where $\tau$ is the average time for collision

$\mu = \frac{e\tau}{m}$ is the mobility

$$J = \sigma E = -nv_d e = -ne\mu E$$

So the conductivity $\sigma = ne\mu$ and resistivity $\rho = 1/ne\mu$

# Drude conductivity

- Electrons move with a **drift velocity** $v_d$ under an electric field $\mathbf{E}$)

$$v_d = -\frac{e\mathbf{E}\tau}{m} = -\mu\boldsymbol{E}$$

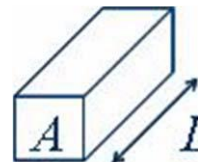
- The **scatterings** of electrons by ions give rise to **resistance**
- The current density **J** under an electric field $\mathbf{E}$ can then be expressed as

$$\mathrm{J} = -env_d$$

$$\mathbf{J} = \left(\frac{ne^2\tau}{m}\right)\mathbf{E} = \sigma\mathbf{E}$$

where $\sigma = \left(\frac{ne^2\tau}{m}\right)$ is the DC conductivity

or $\sigma = ne\mu$ and $\mu = \frac{e\tau}{m}$ is the mobility



- Resistivity $\rho = \frac{1}{\sigma}$; resistance $R = \frac{\rho L}{A} = \frac{\rho L}{Wt}$

Note that $\rho$ has the unit $\Omega$-cm and is **thickness independent**

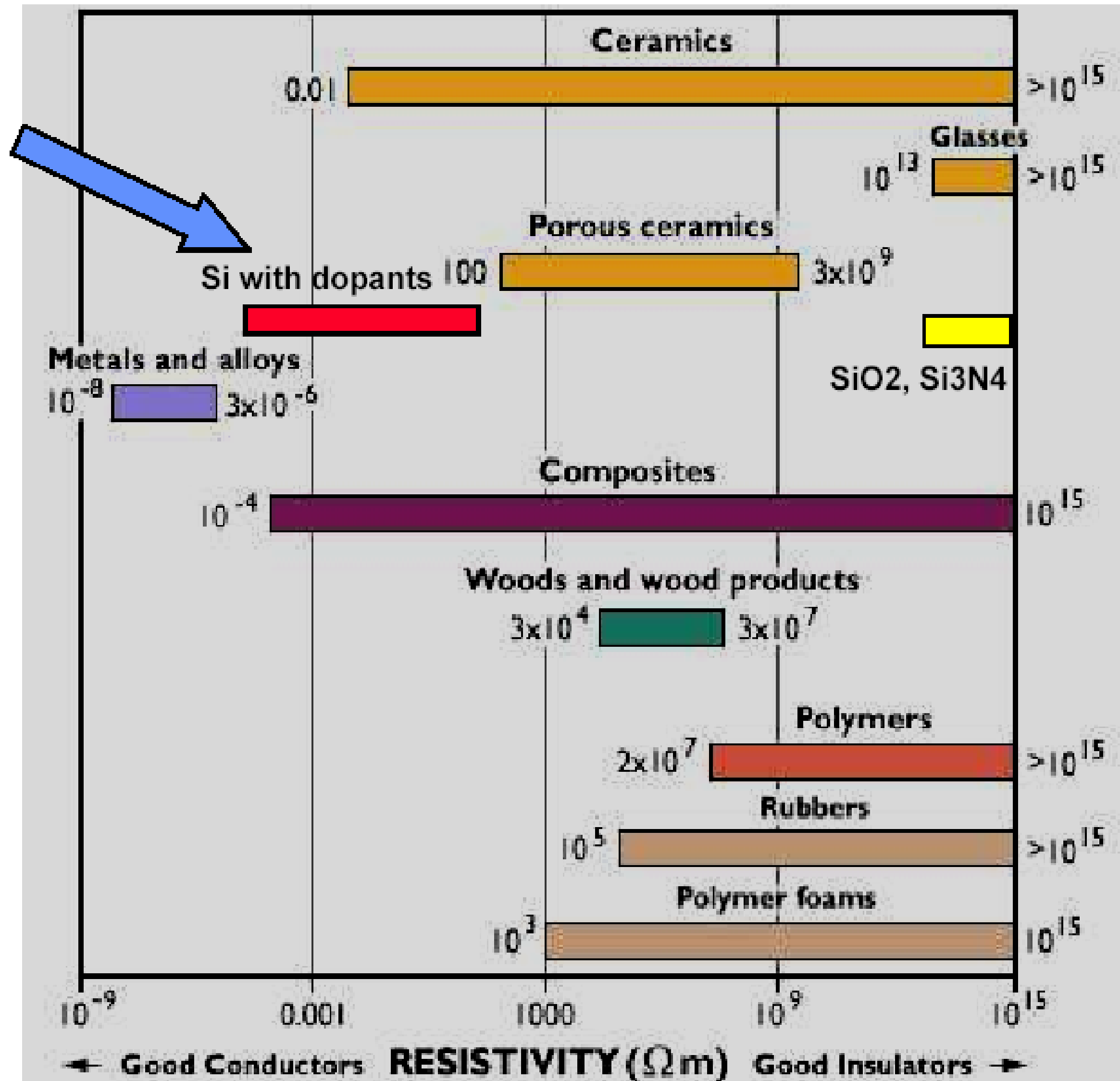
- Resistance of thin films is sometimes express as sheet resistance $R_s$

$$R_s = \frac{\rho}{t} \; and \; R = R_s\frac{L}{W}$$

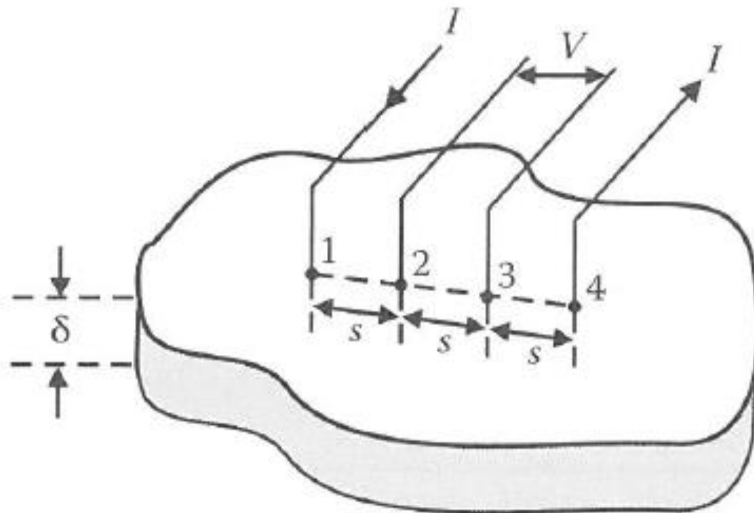
$R_s$ is given in $\Omega/\square$; so a square sheet with $R_s = 100\Omega/\square$ has a resistance of 100 $\Omega$ regardless of the size of the square

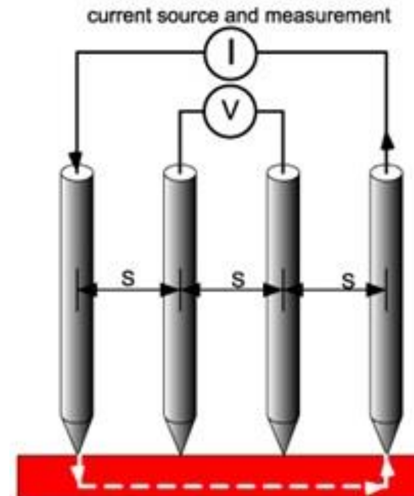
# Resistivity for different materials

Adding parts/billion to parts/thousand of "dopants" to pure Si can change resistivity by 8 orders of magnitude !

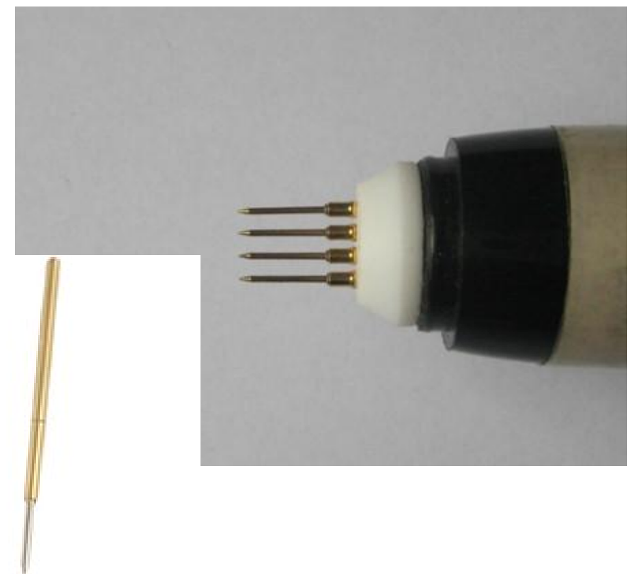


# Resistivity: the four point probe

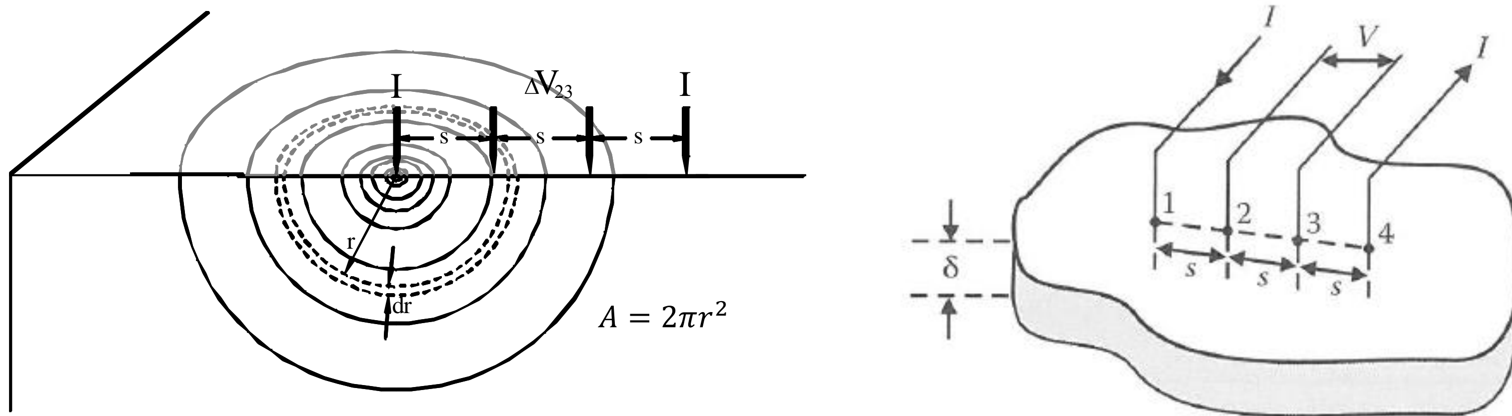


- The **four point probe** is commonly used to determine the **resistivity** of semiconductor samples (wafers)
- The outer 2 probes are connected to a current source
- The two inner probes are high impedance voltage sensors
- The sample thickness $\delta$ is assumed to be constant



# Four point probe: thick sample $\delta \gg s$

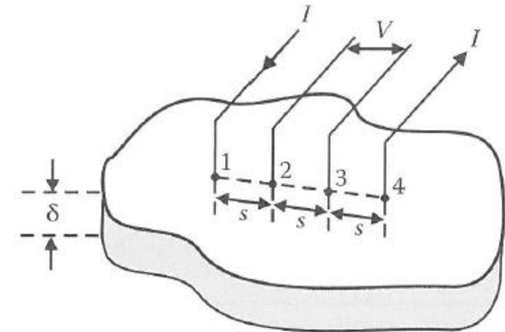



- Current flows out **radially** from the tip as **hemispheres**.
- The voltage drop $dV$ across a hemispherical shell of radius r and thickness $dr$ is $dV = IdR = I\rho \frac{dr}{2\pi r^2}$; R is the resistance and $\rho$ is the resistivity
- The voltage drop on the surface between points 2 and 3 is

$$\int_{s}^{2s} dV = -I\rho \frac{1}{2\pi r}\Big|_{2}^{2s} = I\rho \frac{1}{4\pi s}$$

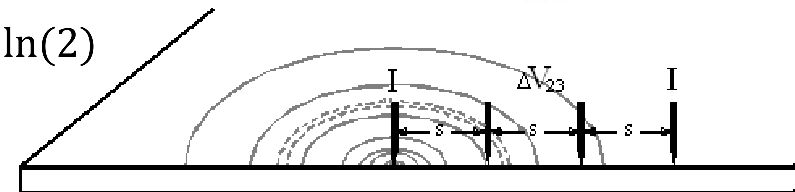
- Considering also the current probe at point 4, the total voltage drop between 2 and 3 is $V_{23} = I\rho \frac{1}{2\pi s}$
- Resistivity can be measured: $\rho = 2\pi s \frac{V_{23}}{I}$

# Four point probe: thin sample $s \gg \delta$




- For thin film sample where $\delta$ is on the order of nm (thin film), the current entering at point 1 becomes **circular equipotential** lines.
- The voltage drop between 2 and 3 is given by

$$\int_s^{2s} dV = \int_s^{2s} I\rho \frac{dr}{2\pi r\delta} = \frac{I\rho}{2\pi\delta}[\ln(2s) - \ln(s)] = \frac{I\rho}{2\pi\delta}\ln(2)$$




- Considering also current from point 4:

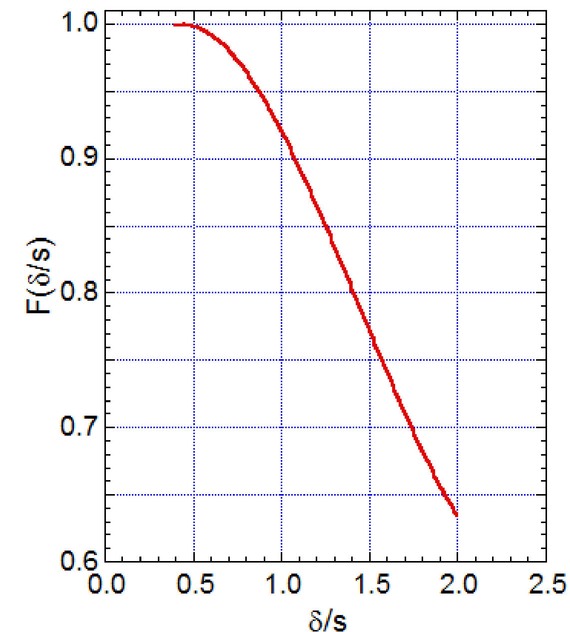
$$V_{23} = \frac{I\rho}{\pi\delta}\ln(2)$$

$$\rho = \frac{V_{23}}{I}\frac{\pi\delta}{\ln(2)} \quad or\ R_s = \frac{\rho}{\delta} = \frac{V_{23}}{I}\frac{\pi}{\ln(2)}$$

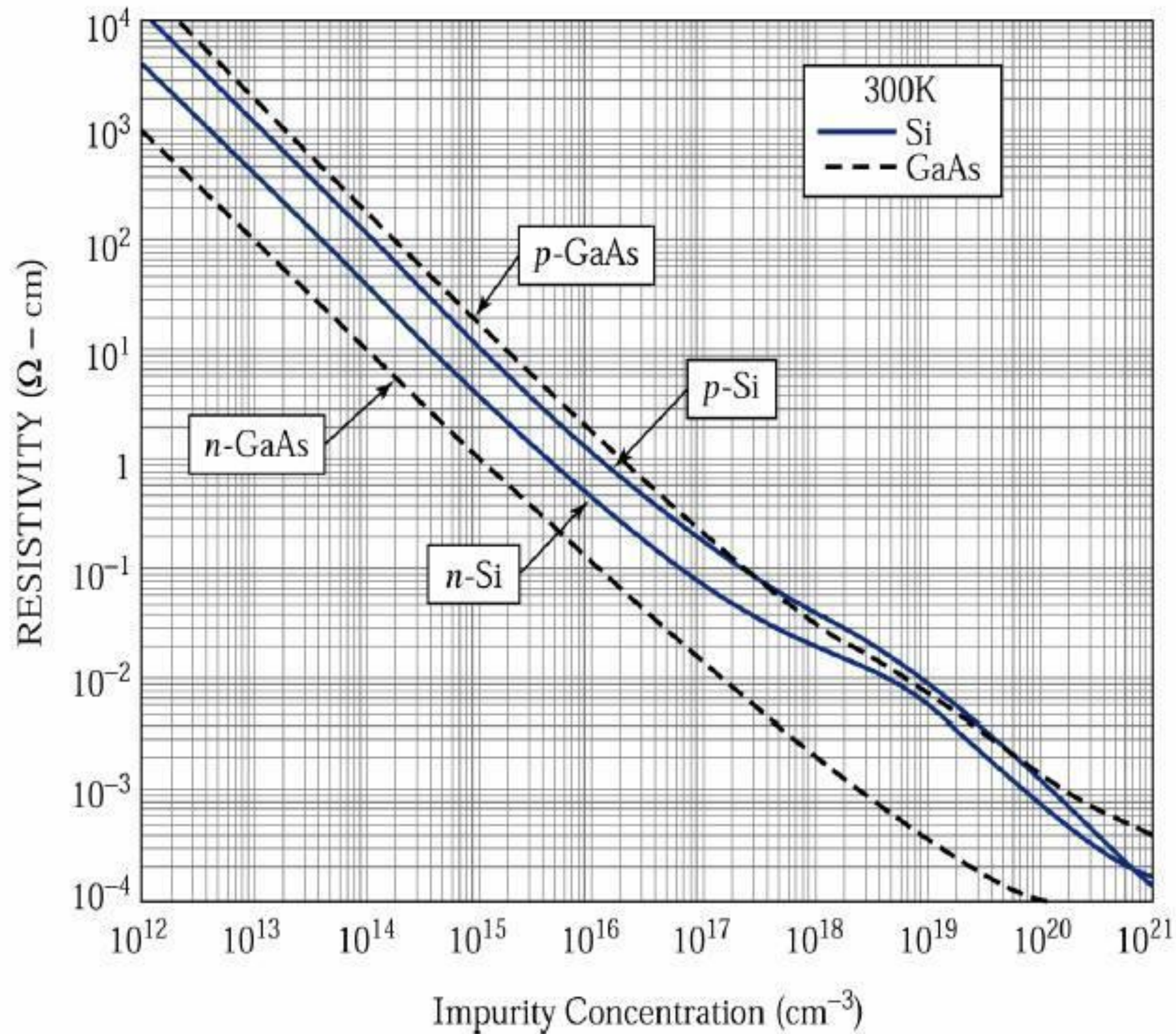
- For samples with $\delta \sim s$ a correction factor is introduced

$$\rho = \frac{V_{23}}{I}\frac{\pi\delta}{\ln(2)}F(\delta/s)$$

  - Thin film regime when $\delta/s = 0.4, F(\delta/s) \approx 1$
  - Thick film regime when $\delta/s > 2, F(\delta/s) < 0.6336$



# Resistivity of semiconductors

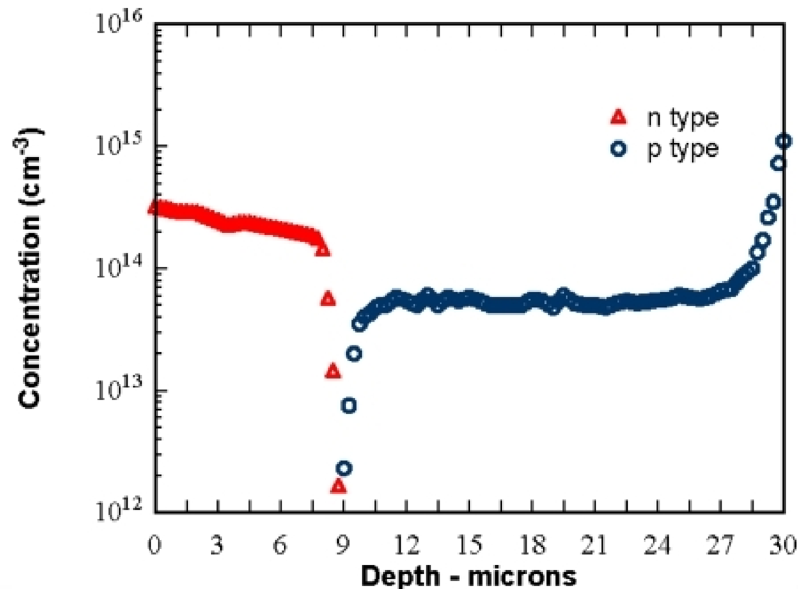


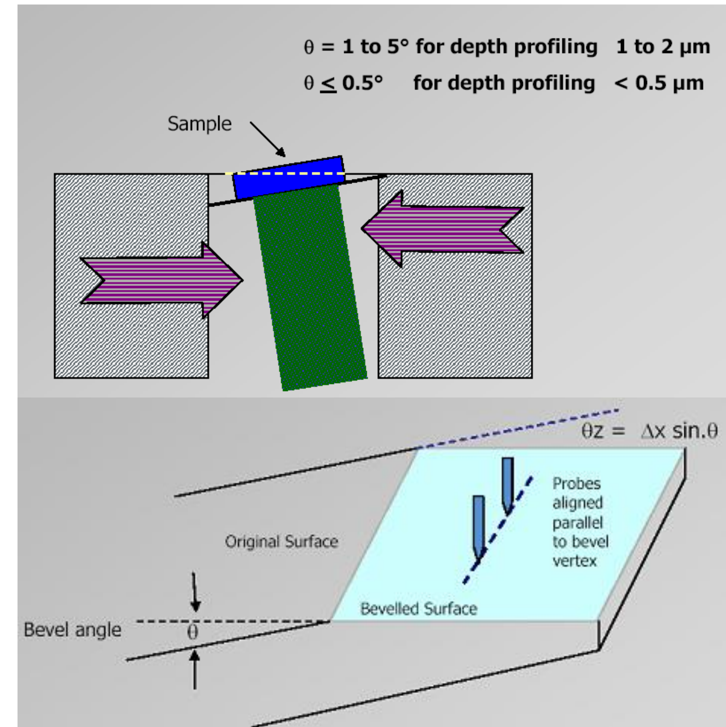

Resistivity versus impurity concentration for Si and GaAs.

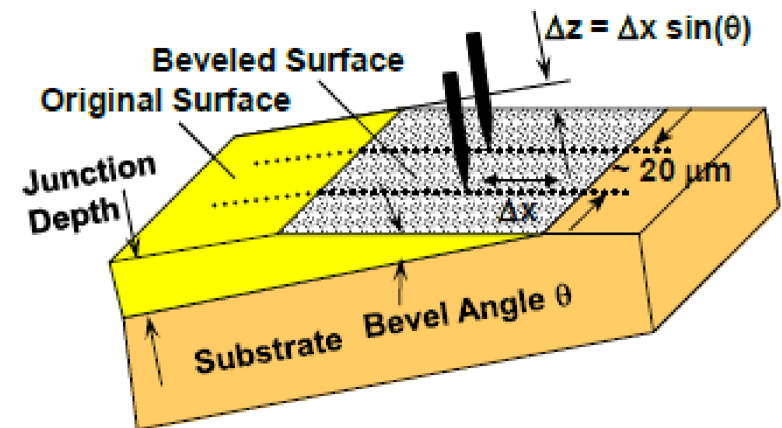
# Spreading resistance profiling

Spreading resistance profiling (SRP) is a technique used to analyze **resistivity versus depth** in semiconductors. The carrier concentration can be inferred from the resistivity profile provided by SRP.

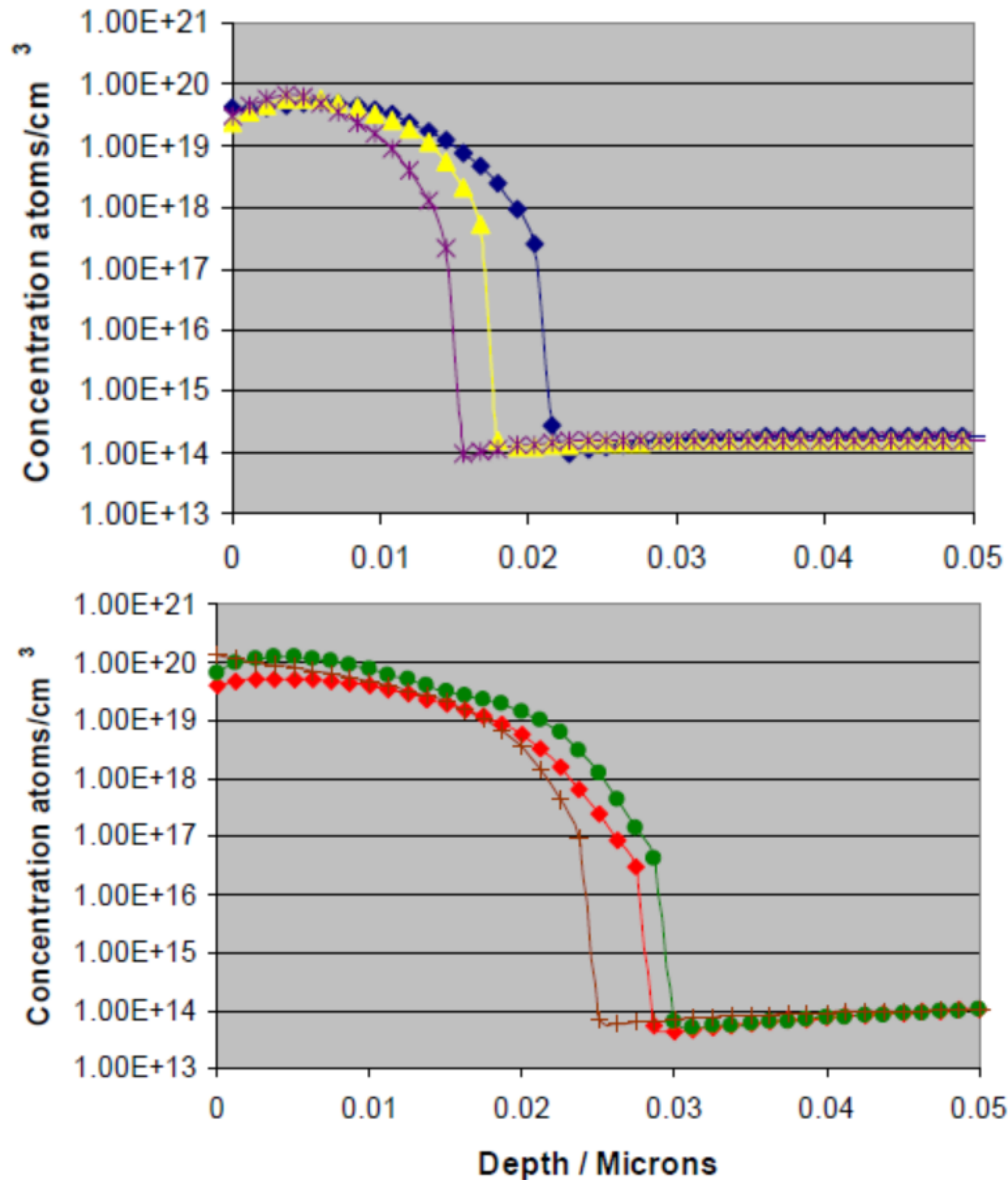
- The wafer is **beveled** extending the layer thickness, bevel angle (1-5°)
- Measurements made with 2 probes on the beveled surface at 2-10 μm increments ~30-200 nm in depth



# SRP: example




**Ultra shallow Boron Implants 5e14, 200eV –Various Anneals**

SRP measurements showing the variations in the junction depths close to the desired $x_j$ values of 200Å and 300Å respectively

# Spreading resistance profiling

- Fine Tungsten Alloy tip used as probe
- ~80% of the total potential drop to occur within a distance of about 5r
- The spreading resistance of ideal metal-semiconductor contacts can be calculated
  - For flat-bottom probe of diameter *d*

$$R_{sp} = \frac{\rho}{2d}$$

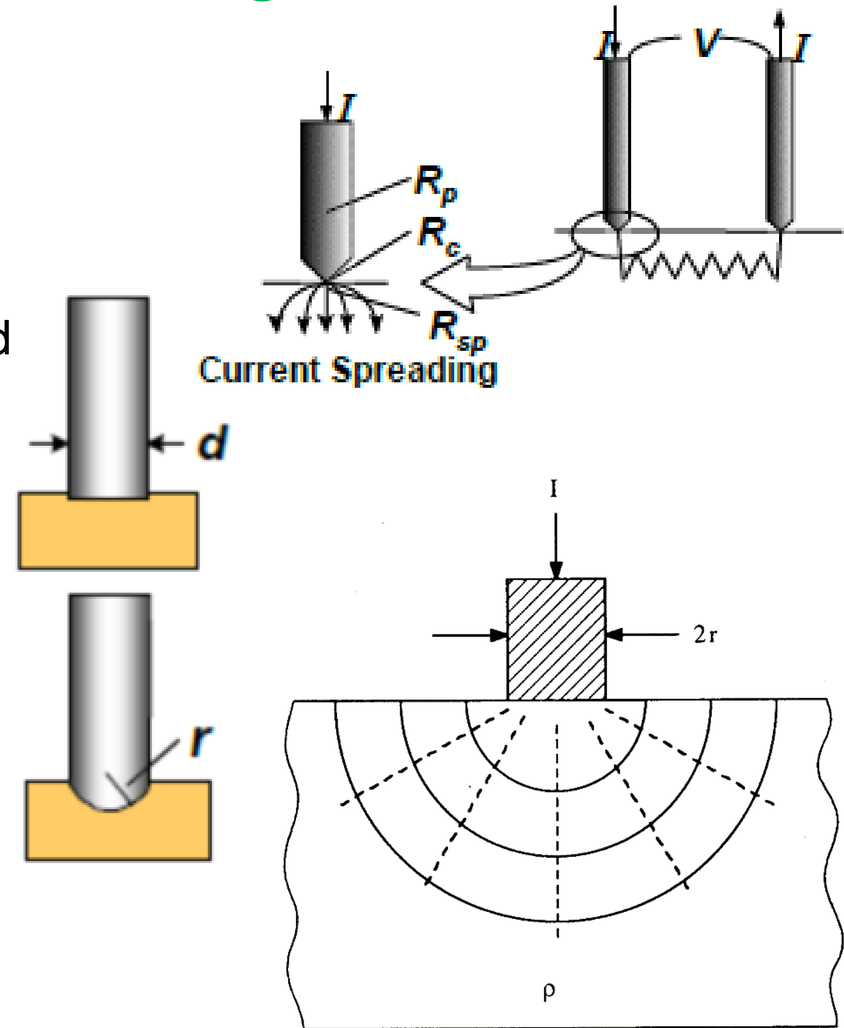
  - For hemispherical probe of radius *r*

$$R_{sp} = \frac{\rho}{2\pi r}$$

  - For a “real” probe

$$R_{sp} = k\frac{\rho}{2\pi r}$$

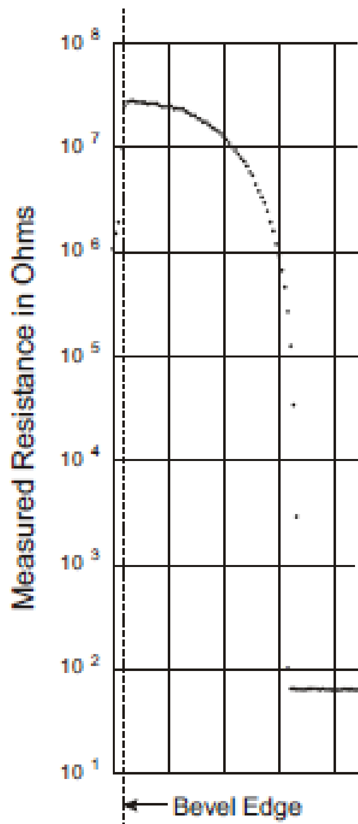
  k must be experimentally determined
- These measurements are **invasive** and may leave metal contamination on the surface




$$R = \frac{V}{I} = 2R_p + 2R_c + 2R_{sp} \approx 2R_{sp}$$

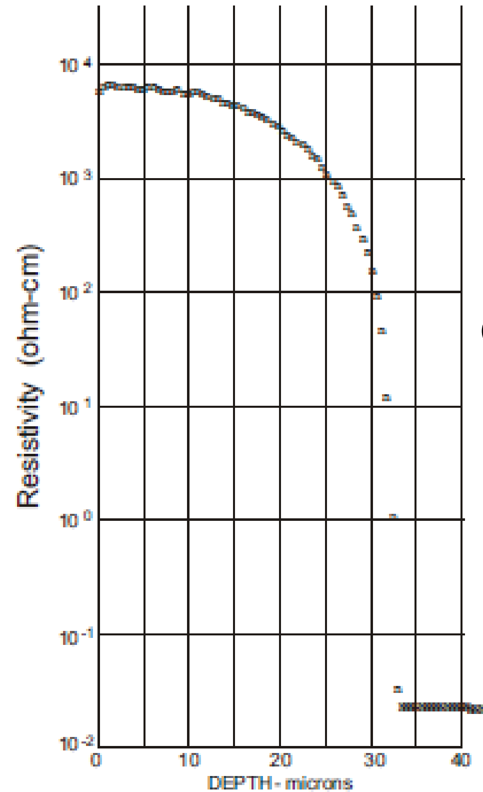
# Spreading resistance profiling

Example: high resistivity epilayer



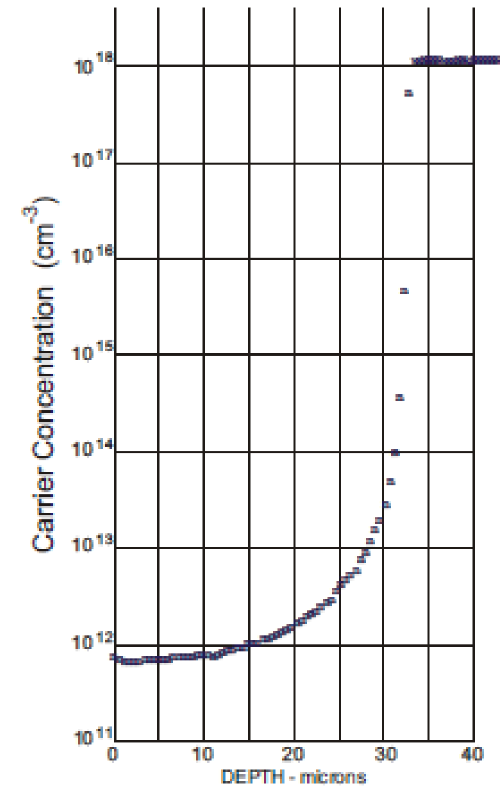

Raw data

Data reduction




Resistivity

Calculate using published carrier-mobility values




Carrier concentration

*SOLECON LABS, Reno, Nevada*

# SRP: Strengths and weaknesses

Birds Eye View of SRA Sample and Probes

- Automatic probe lowering mechanism which places the probe tips without any lateral motion and with a well-calibrated force on the surface.
- The tips consist of very hard tungsten-osmium alloys.
- Applied contact pressure exceeding 1000 $kgf/mm^2$.

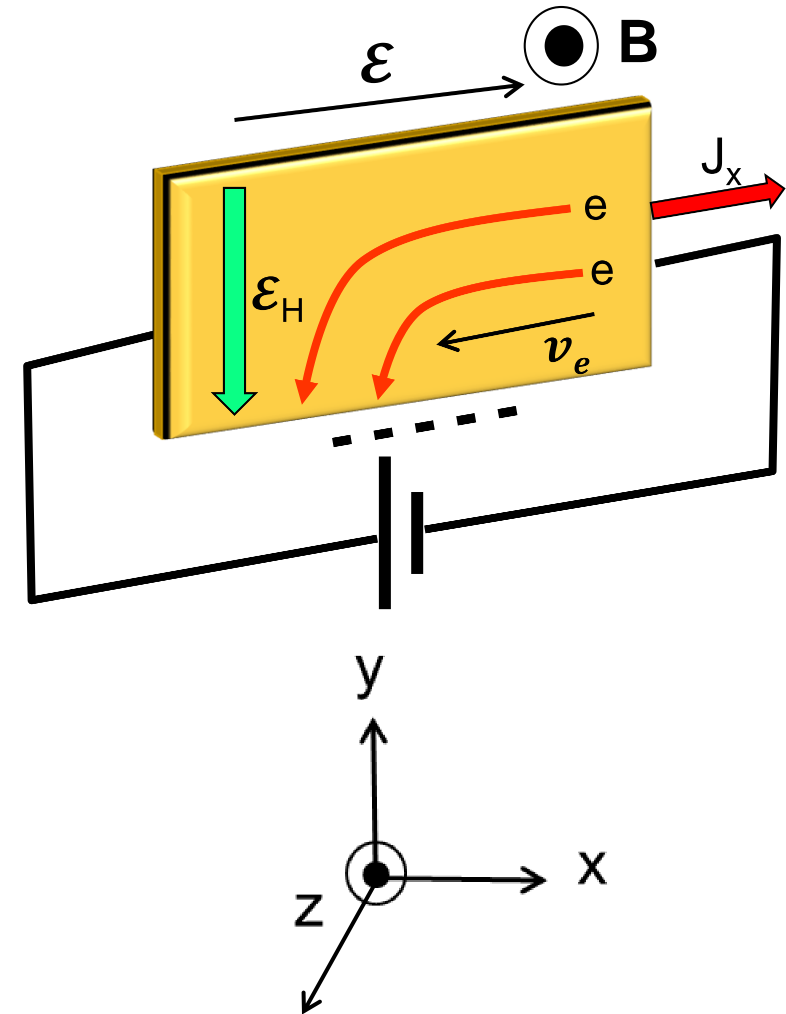
- High sensitivity
- Large dynamic range
- Good depth resolution (nm)
- SRP measures resistivity, to obtain carrier concentration profile, requires
  - detailed knowledge of the mobility as a function of dopant concentration
  - calibration measurements of known resistivity profiles and significant modeling efforts
- Required skilled sample preparation and sophisticated equipment
- Direct measurement of carrier concentration: Hall effect and Capacitance – Voltage measurements

# Hall Effect

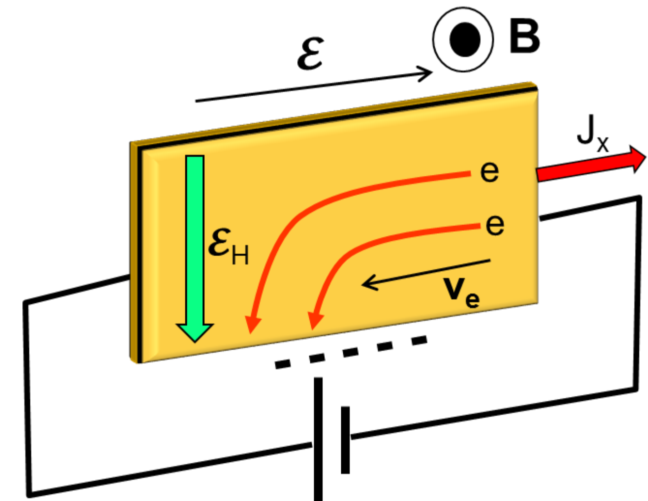
- The Hall effect describes the behavior of **free carriers** in a semiconductor when an **electric** and a **magnetic field** are applied.
- Consider an n-type semiconductor with an applied electric field $\mathcal{E}$ and a ⊥ magnetic field **B**
  - electrons drift along the sample
  - Total force acting on electrons

    $\mathbf{F}=q(\mathcal{E}+\mathbf{v}\times\boldsymbol{B})$ → Lorentz force
  - and the y component of the force is

    $\mathbf{F}_L = -e(\mathbf{v}\times\mathbf{B}) = ev_x B \quad v_x < 0$
  - The electrons will drift toward the bottom edge of the sample thus creating an electric field, **Hall field** $\mathcal{E}_\mathrm{H}$, in the negative y-direction.



# Hall Effect




- At steady-state, the induced Hall field applies a force $F_H$ on the electrons such that it has the same magnitude as $F_L$, the y component of $F_H$

$$F_H = -e\mathcal{E}_H$$

- To maintain the steady flow of current in the x-direction, the y component of the total force acting on the electrons must vanish

$$F_L + F_H = -e\mathcal{E}_H + ev_x B = 0$$

- Expressing the Hall field in terms of current, we have

$$J_x = n(-e)v_x \longrightarrow \mathcal{E}_H = -\frac{1}{ne}J_x B$$

- The Hall field is proportional to the current and the magnetic field. The ***Hall coefficient*** is defined as

$$R_H = \frac{\mathcal{E}_{H,e}}{J_x B} = -\frac{1}{ne}$$

Hall coefficient **negative**

- Note that for the hole carriers, $J_x = pev_x$

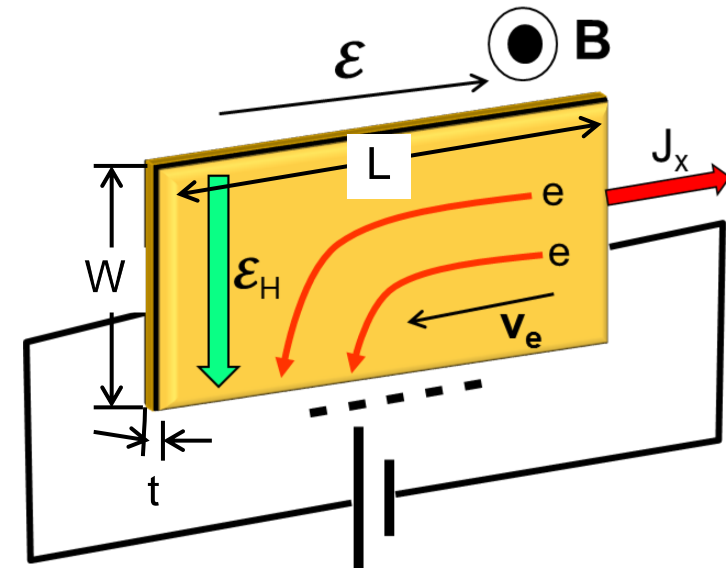
$$R_H = \frac{\mathcal{E}_{H,h}}{J_x B} = \frac{1}{pe}$$

Hall coefficient **positive**

# Hall effect and mobility

- Alternatively, one can calculate the Hall coefficient from the measured current, $I_x$, and measured voltage, $V_H$ :

$$R_H = \frac{\mathcal{E}_H}{J_x B} = \frac{(V_H/W)}{(I_x/tW)B} = \frac{V_H t}{I_x B}$$




- A measurement of the Hall voltage is often used to determine the **type** of semiconductor (*n*-type or *p*-type), the free carrier **density** and the carrier **mobility**.

$$\rho = \frac{1}{ne\mu} \longrightarrow \mu_e = -\frac{\rho}{R_{H,e}} \ and \ \mu_p = \frac{\rho}{R_{H,p}}$$

- Carrier density can be found:

$$n = -\frac{1}{eR_{H,e}} \ and \ p = \frac{1}{eR_{H,p}}$$

- For samples with both electron and holes: $R_H = \frac{1}{e}\frac{p-n^2 n}{(p+bn)^2}$, where $b = \left| {}^{\mu_n}/_{\mu_p} \right|$

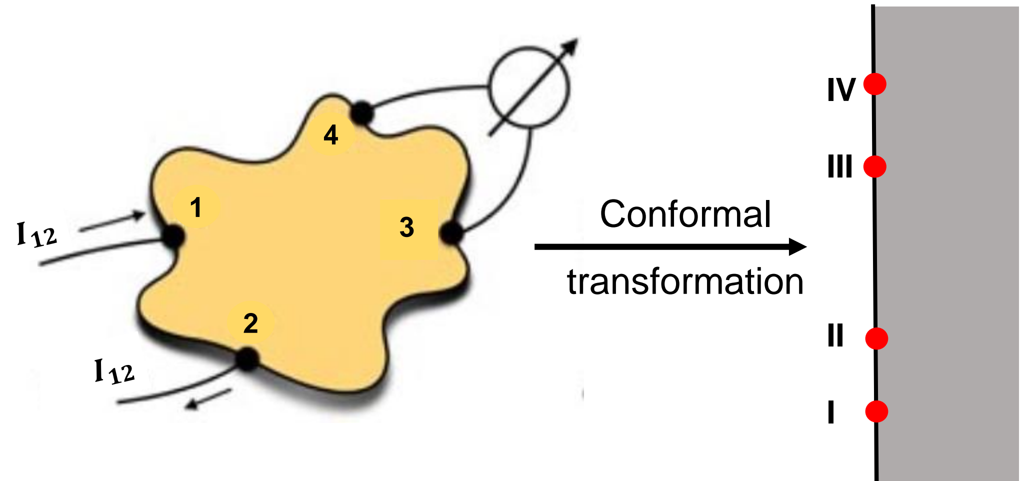
- The Hall effect is the only method that yields **free carrier type, concentration and mobility** directly and independently of other material properties.

# The van der Pauw geometry

The **van der Pauw** method is a technique commonly used to measure the resistivity and the Hall coefficient of a sample. Its power lies in its ability to accurately measure the properties of a sample of any **arbitrary shape**, so long as the sample

- — is approximately two-dimensional (i.e. it is much thinner than it is wide),
- — must not have any isolated holes,
- — must be homogeneous and isotropic,
- — all four contacts must be located at the edges of the sample, and
- — has contacts with the area at least an order of magnitude smaller than the area of the entire sample.

Van der Pauw applied a **conformal transformation** of an arbitrary shaped sample of constant thickness $\delta$ onto a semi-infinite half plane.

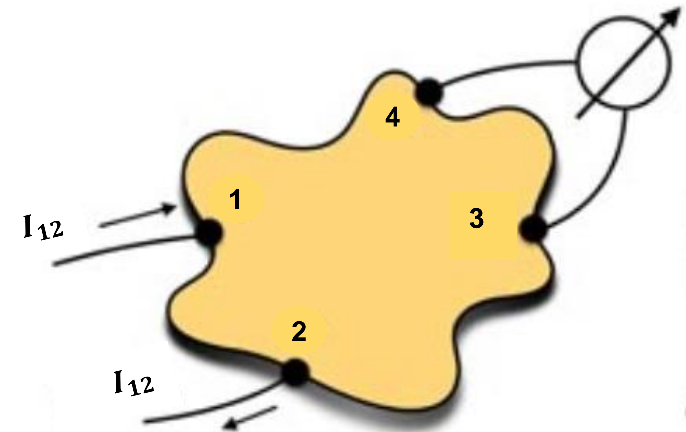


# Resistivity: van der Pauw method

Using the van der Pauw method, the resistivity can be expressed as

$$\rho = \frac{\pi\delta}{\ln(2)} \frac{R_{12,34} + R_{23,41}}{2} f(R_{12,34}/R_{23,41})$$

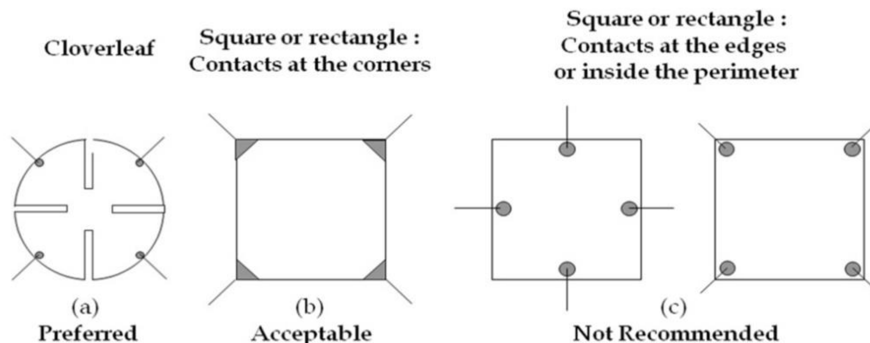
where $R_{12,34}(R_{23,41})$ is the resistance obtained from the ratio of the voltage across contacts 3 and 4 (4 and 1) to the current through contacts 1 and 2 (2 and 3). The factor $f$ depends on the ratio of the resistance values.

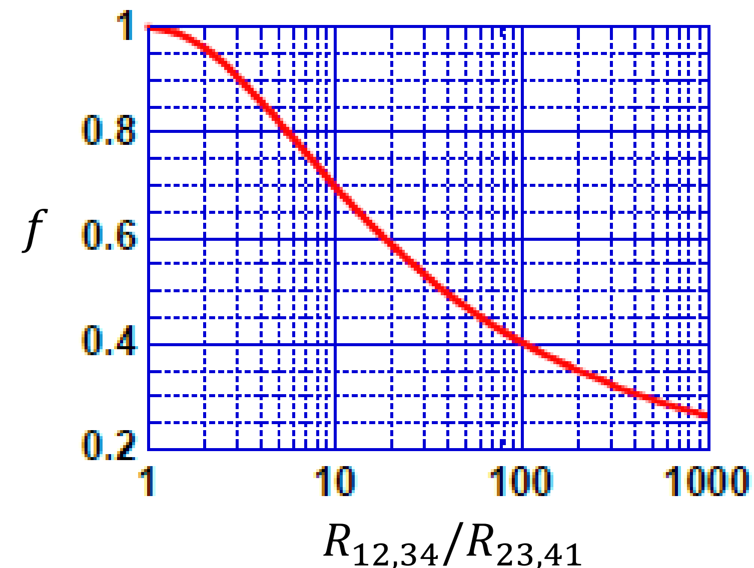



$$R_{12,34} = \frac{V_{34}}{I_{12}}; R_{23,41} = \frac{V_{41}}{I_{23}}$$

In most common cases, the samples are nearly circular or square shaped, and $f \approx 1$.

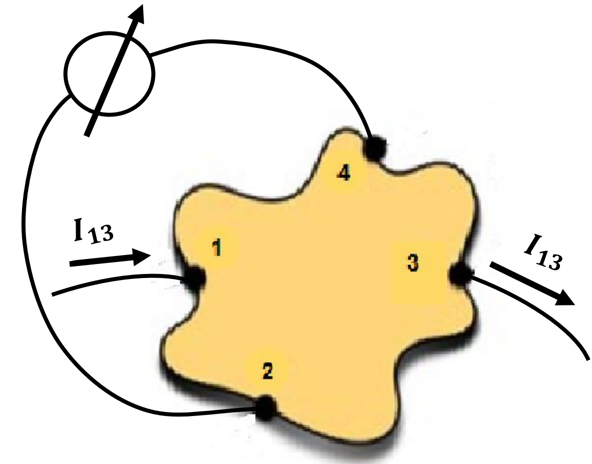
Sample configurations:



# Hall effect: van der Pauw method

- Hall effect measurements can be performed by passing the current from 1 to 3 and measuring the voltage between 2 and 4, or by sending the current from 2 to 4 and determining the voltage between 3 and 1, with an applied magnetic field perpendicular to the sample surface.




- We know $R_H = \frac{\mathcal{E}_H}{J_x B} = \frac{(V_H/W)}{(I_x/tW)B} = \frac{V_H t}{I_x B}$,

$$R_H = \delta \frac{\Delta R_{24,13}}{B},$$

where $\Delta R_{24,13}$ is the change in resistance due to the B field.

- The free carrier concentration $n = \frac{1}{eR_H}$ is given by:

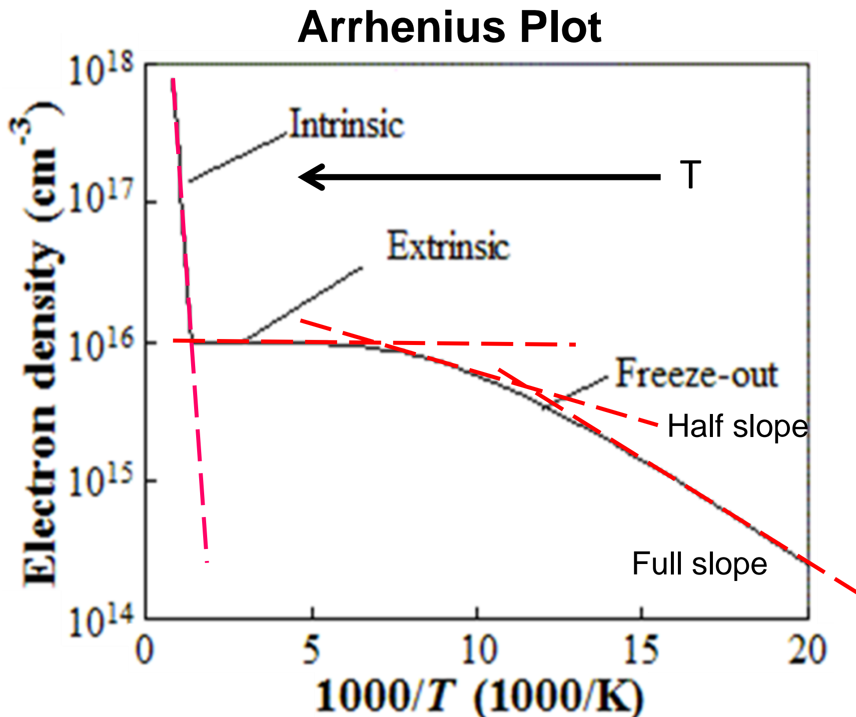
$$n = \frac{1}{\delta} \frac{B}{e\Delta R_{24,13}}$$

- With known resistivity and carrier concentration, the mobility is given by:

$$\mu = \frac{1}{ne\rho} = \frac{2\ln(2)}{\pi B} \frac{\Delta R_{24,13}}{R_{12,34} + R_{23,41}} \frac{1}{f}$$

# Variable Temperature Hall Effect

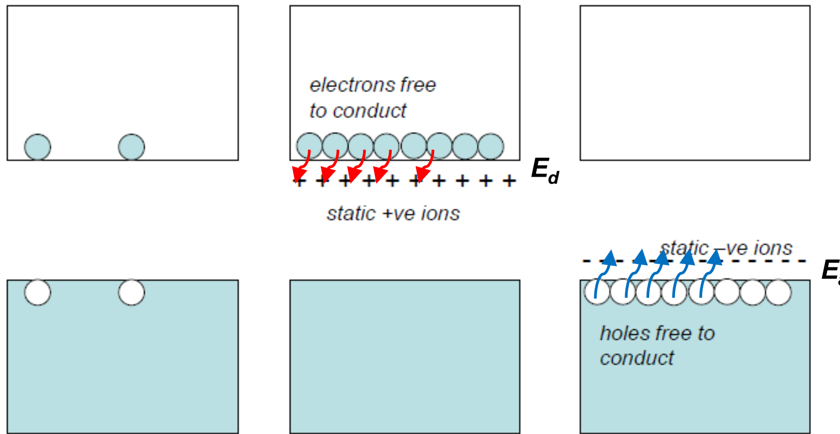
For a semiconductor sample with both donors and acceptors $N_d$ and $N_a$. A variable temperature Hall effect measurement plotted as $\ln(n)$ vs. $\frac{1}{T}$ —**Arrhenius plot** can tell us a lot of information




- At high temperature: Intrinsic
  - $n_i \propto e^{-E_g/2k_BT}$
  - slope= $\frac{-E_g}{2k_BT}$
- Medium Temperature: $k_BT \gg E_d$
  - Extrinsic or saturation regime
  - $n = N_d - N_a$
- Low temperature: freeze out region
  - $n \propto e^{-E_d/2k_BT}$
  - slope= $\frac{-E_d}{2k_BT}$ (half slope)
  - At even lower temperature
    $n \propto e^{-E_d/k_BT}$ (full slope)
  - The concentration at which the half slope turns into full slop corresponds to $N_a$

Variable temperature Hall effect measurements provide a convenient way to obtain donor or acceptor binding energies.

# VT Hall Effect: freeze out curve




For a n-type semiconductor with $N_d$ donors and $N_a$ acceptors with $N_d > N_a$, the number of neutral (occupied) donor states,

$$N_d^{(o)} = \frac{N_d}{1 + e^{-E_d/k_BT}\left({}^{N_C}/_{n}\right)} = N_d - N_a - n$$

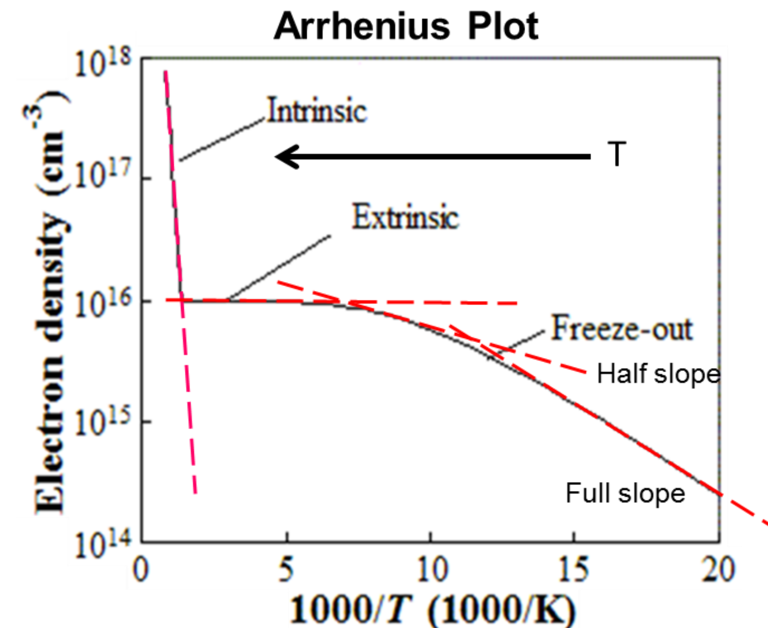
$$\frac{(N_a + n)n}{(N_d - N_a - n\ )} = N_C e^{-E_d/k_BT}$$

As temperature decreases, the electron (hole) in the CB (VB) start to relax back into the donor (acceptor) levels:

- For $N_d \gg n \gg N_a$: $n \approx \sqrt{N_C N_d} e^{-E_d/2k_BT}$
  - Slope of the Arrhenius plot is $-E_d/2k_B$
- As temperature decreases further, *n* becomes small such that $n \ll N_d, N_a$:

$$n \approx \left(\frac{N_d - N_a}{N_a}\right) N_C e^{-E_d/k_BT}$$

  - This is the “full slope regime”



# VT Hall Effect: carrier mobility

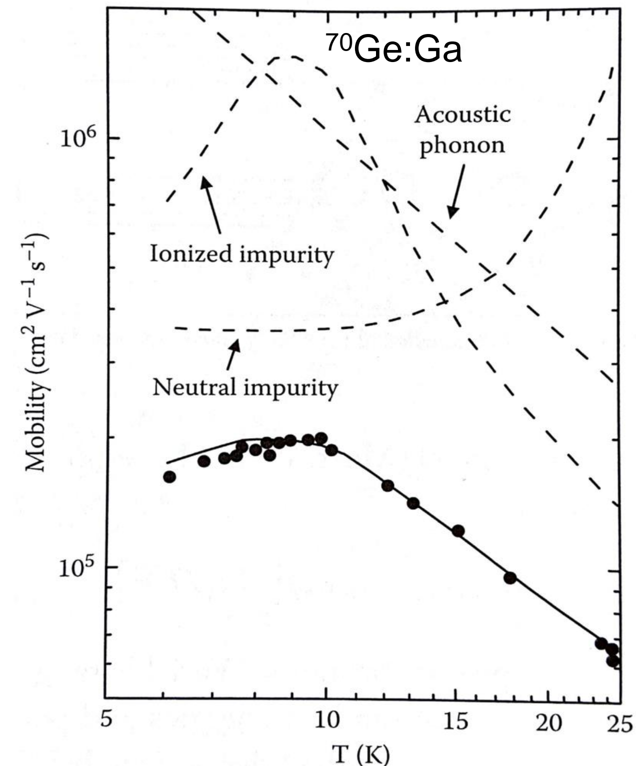
In a semiconductor, the scattering rates $\sim\frac{1}{\tau}$ are additive and $\mu = \frac{e\tau}{m}$ so that the total mobility $\mu$ follows **Matthiessen's rule**:

$$\frac{1}{\mu} = \frac{1}{\mu_{ph}(T)} + \frac{1}{\mu_o} + \frac{1}{\mu_{ii}}$$

phonons ($\mu_{ph}(T)$) defects ($\mu_o$) Ionized impurity ($\mu_{ii}$)

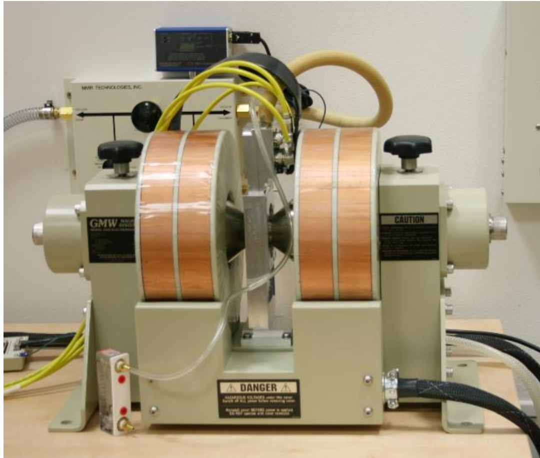
$\mu$ decreases as dopant and defect concentration increase

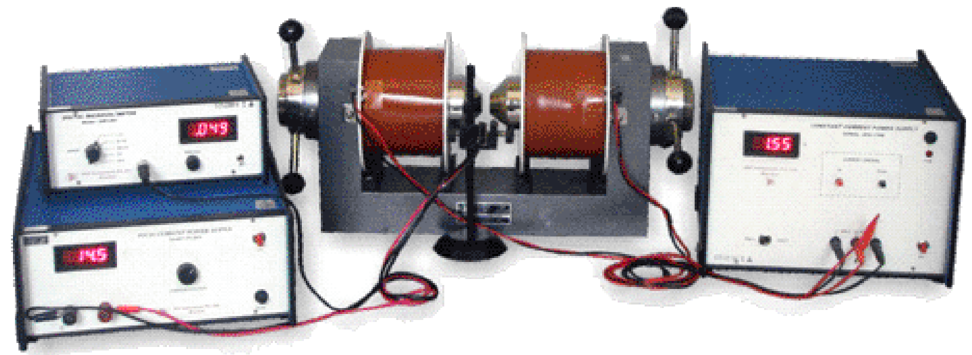
- At **high temperatures,**
  - **phonon scattering** dominates and mobility decreases with increasing temperature.
  - More ionized impurity scattering, reducing mobility
- At **lower temperatures**,
  - neutral impurity scattering dominates
  - Ionized impurity scattering also plays a role because the cross section increases as carrier kinetic energy decreases



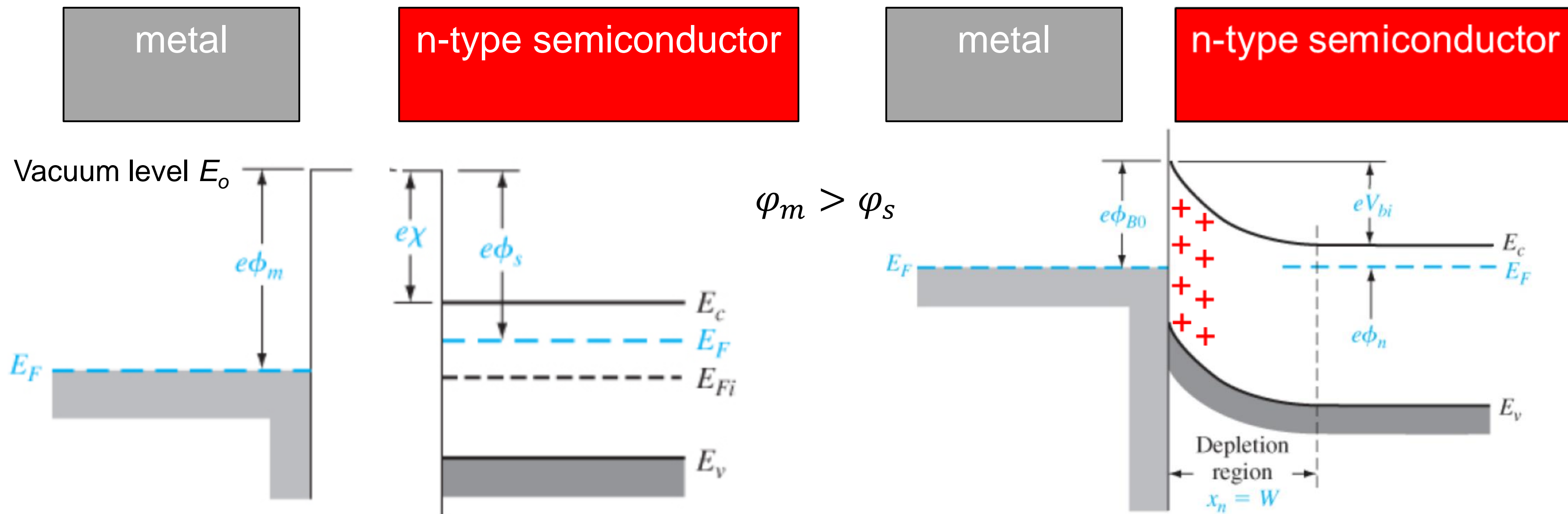

*Itoh et al., Phys. Pev. B, 50, 16995 (1994).*

# Hall effect equipment



# Metal-semiconductor junctions-Schottky




- $\varphi_m$ -metal **work function** is the minimum energy required to free up electrons from metal
- $\chi = (E_o - E_C)$ is the **electron affinity**, a fundamental semiconductor property
- $\varphi_s$ is the semiconductor work function,

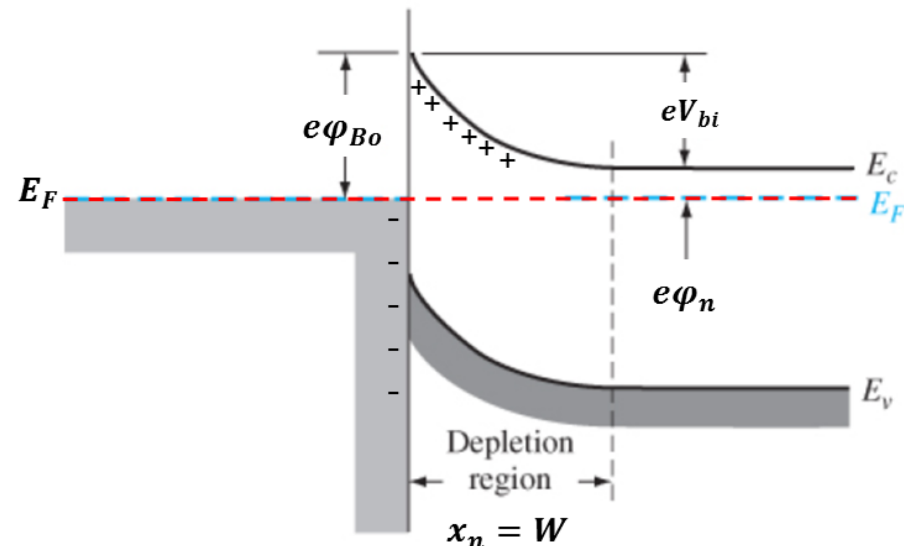
  $\varphi_s = E_o - E_F$, depends on doping

- In order for the Fermi level to become a constant throughout the system in **thermal equilibrium**, electrons from the semiconductor flow into the lower energy states in the metal.
- The barrier is known as the **Schottky barrier** $\varphi_{Bo} = \varphi_m - \chi$

# Schottky contact

Consider a metal-n-type semiconductor

- The work function difference and surface pinning lead to a **potential barrier** which forms a depletion region W in the semiconductor.
- The net ionized donor concentration in this depletion region constitutes a positive space charge.




- **Poisson equation** relates the potential $\varphi$ and the space charge concentration

$$\frac{d^2\varphi}{dx^2} = -\frac{|e|N}{\varepsilon\varepsilon_o}, \text{ where } N = N_d^+ - N_a^-$$

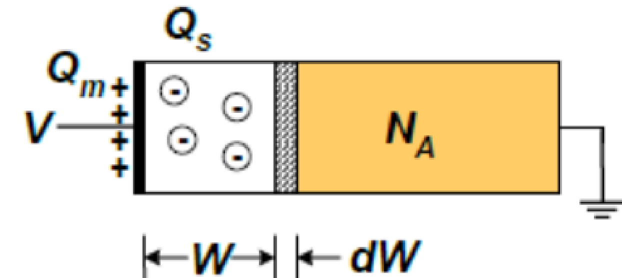
$$\varphi(x) = -(x - W)^2 \frac{|e|N}{\varepsilon\varepsilon_o} \quad (0 < x < W)$$

- In an extrinsic semiconductor the free carrier concentration can be assumed to equal to the net dopant concentration

$$n = N_d^+ - N_a^- \quad \text{(n-type)}$$

$$p = N_a^- - N_d^+ \quad \text{(p-type)}$$

# Capacitance-voltage profiling




Capacitance–voltage profiling is a technique for characterizing semiconductor materials and devices.

- The technique typically uses a metal–semiconductor junction (Schottky barrier).

- By varying the voltage applied to the junction it is possible to vary the depletion width giving rise to the **profiling** capability.
- The capacitance of the depletion region

$$C = \frac{dQ}{dV} = \varepsilon\varepsilon_o \frac{A}{W}, \qquad A \text{ is the area defined by the metal contact}$$

- When the depletion region is increased by $dW$

$$dQ = |e|N(x)dW \text{ and } C = |e|N(x)\frac{dW}{dV}$$

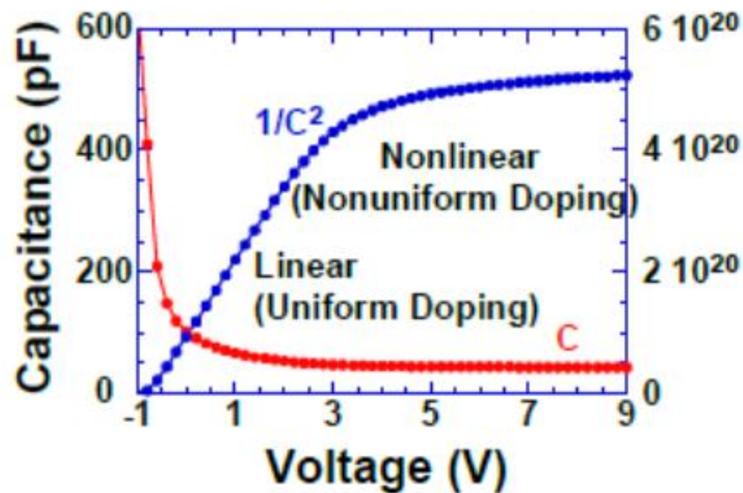
$$\frac{dC}{dV} = -\frac{C^3}{\varepsilon\varepsilon_o A|e|N(x)}$$

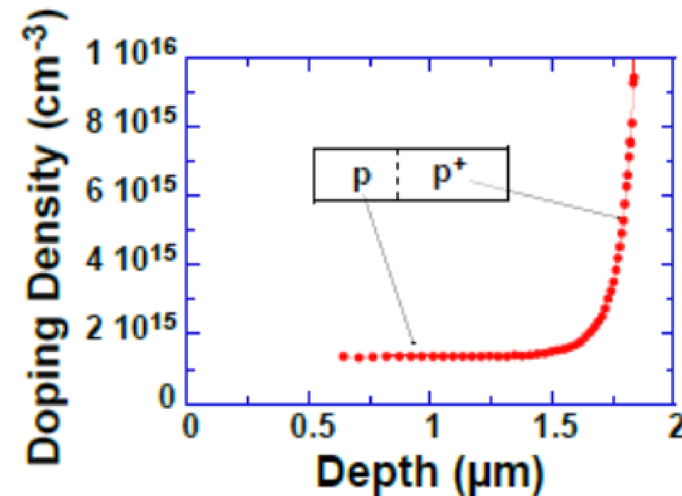
Using the identity: $\frac{d(1/C^2)}{dV} = -\frac{2}{C^3}\frac{dC}{dV}$, $\boxed{\frac{d(1/C^2)}{dV} = \frac{2}{\varepsilon\varepsilon_o A|e|N(x)}}$

- The slope of a $1/C^2$ vs, V plot is inversely proportional to the **net ionized dopant concentration**

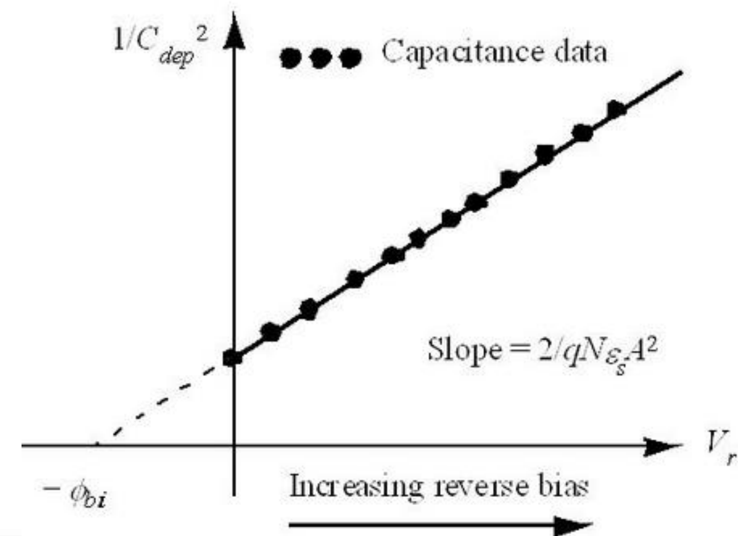
# C-V profiling

- C - V curves are always nonlinear
- $1/C^2 - V$ curves clearly show carrier or doping density non-uniformities




- The intercept of the C-V curve can determine the $V_{bi}$
- In practice, care should be exercised as the ohmic- contacts (particularly the “back contact”) can lead to errors in the determination of *N(x)*.



# C-V: Strengths and Limitations

- Simple and convenient measurements
- Easy with a modern capacitance bridge to measure accurately very low capacitances down to the femto Farad ($10^{-15}$ F) range
- Directly measure the **net-dopant concentration**
- **Non-destructive** method
- Effects of stray capacitances, temporal drifts in the capacitance because of surface states and/or deep levels in the bulk of the semiconductor
- Limited depth resolution ~ $3L_D$

  $L_D$ Debye length

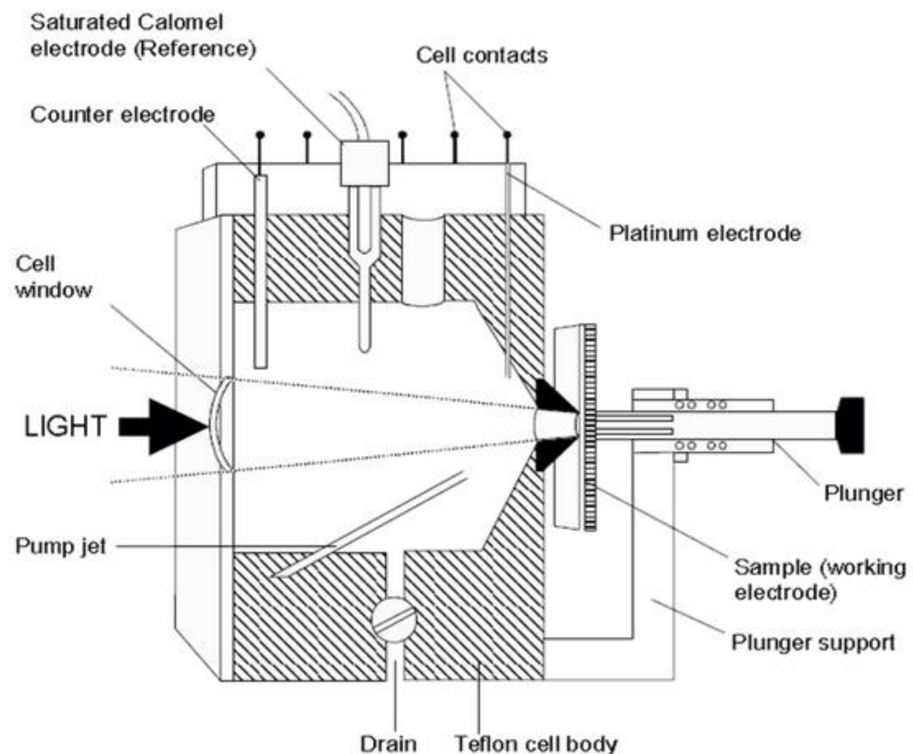
  $$L_D = \left( \frac{\varepsilon \varepsilon_o kT}{e^2 N_d} \right)^{\frac{1}{2}}$$

  For $N_d = 10^{18}/cm^3$ at RT, $L_D = 3.9$ nm

  For $N_d = 10^{20}/cm^3$ at RT, $L_D = 0.39$ nm
- Limited range of profile depth: junction breakdown

# Electrochemical C-V profiling

- The Electrochemical Capacitance-Voltage (**ECV**) profiling technique uses an **electrolyte-semiconductor** Schottky contact to create a depletion region.
- Depth profiling is achieved by electrolytically etching the semiconductor between the capacitance measurements with no depth limitation.
- The sample is pressed against a sealing ring in the **electrochemical cell** containing an **electrolyte**. The ring opening defines the contact area.
- The depletion region is created by applying a potential between the semiconductor and the platinum (counter) electrode measured with respect to the reference saturated calomel electrode.
- The etching conditions are controlled by the current circuit between the semiconductor and the counter electrode, usually assisted by illumination.



# ECV-Biorad system

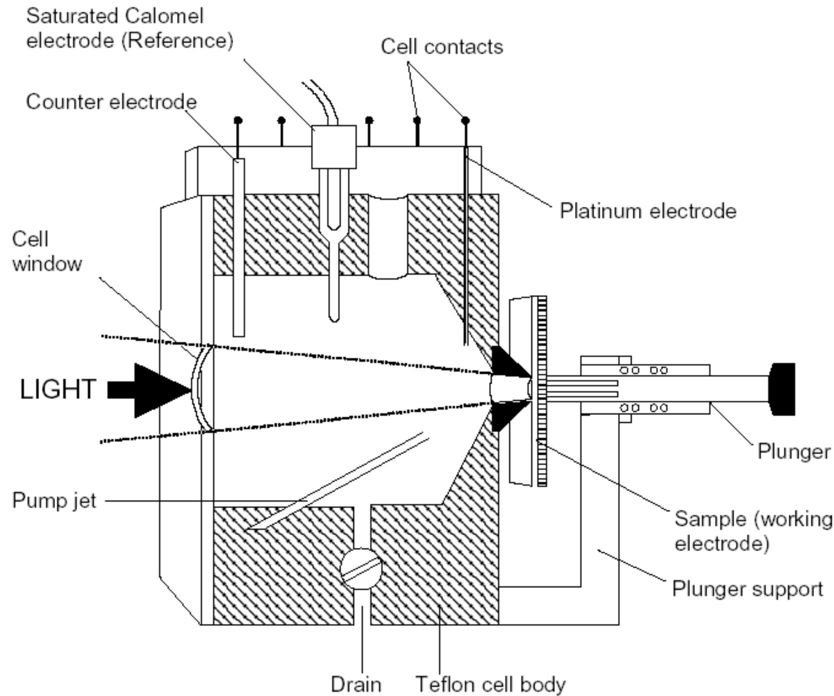



Figure 7-1 The electrochemical cell

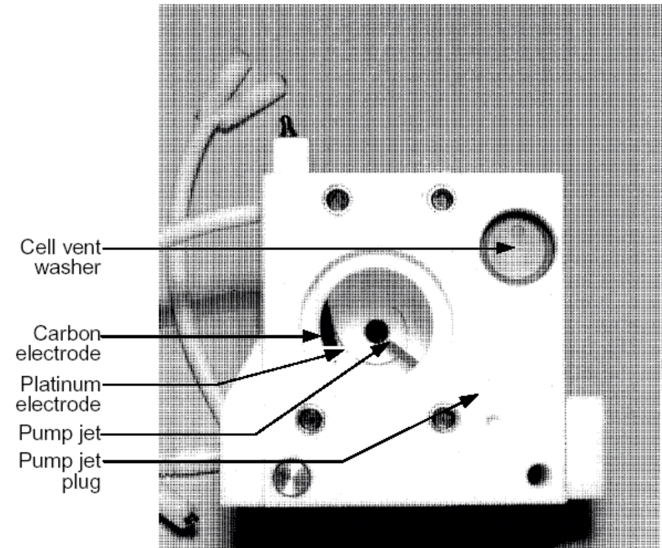
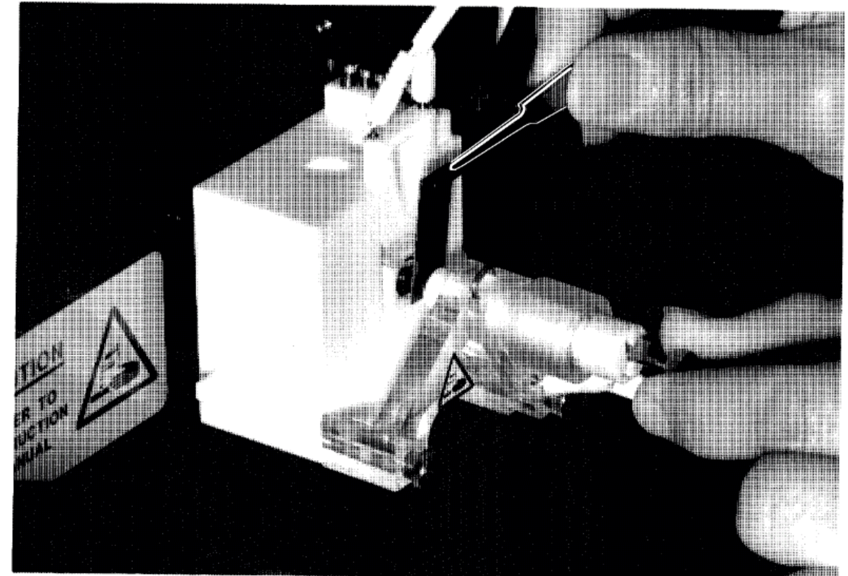



Figure 7-5 Pump tube adjustment



# Electrochemical C-V

$$C = \frac{\varepsilon\varepsilon_o}{x_d}$$

$$\frac{d(1/C^2)}{dV} = \frac{2}{\varepsilon\varepsilon_o eN}$$

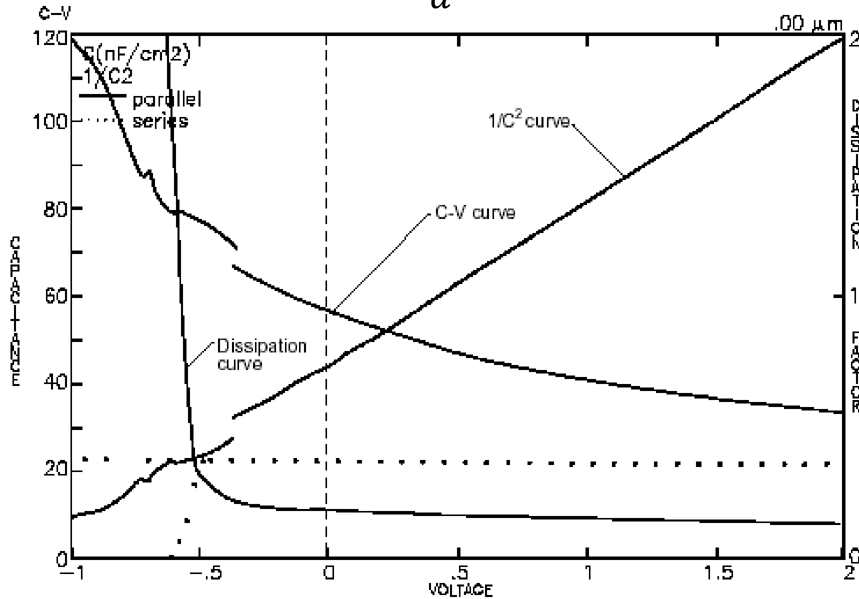



Figure 3-7 CV plot of n-type GaAs with Tiron

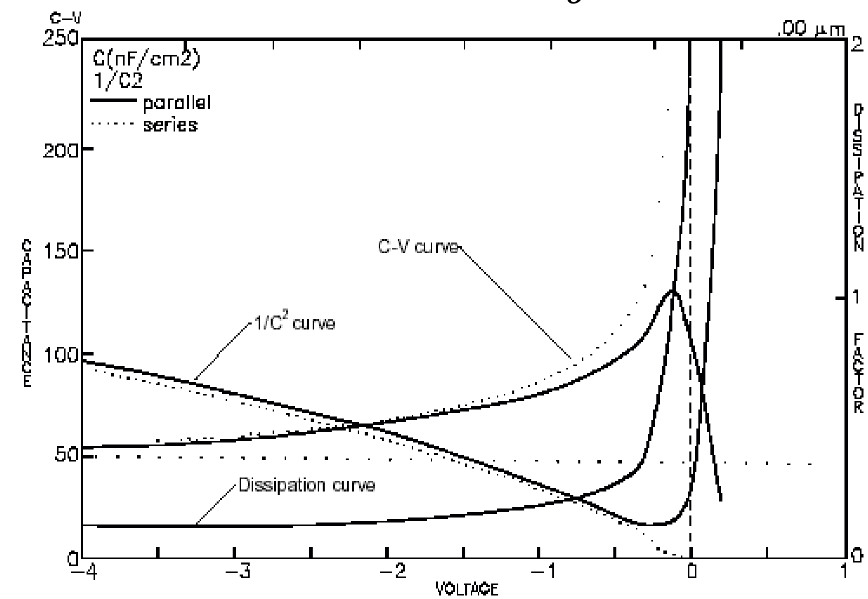


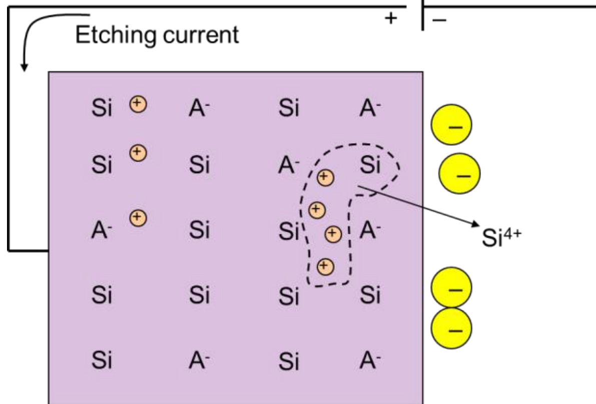

Figure 3-6 CV plot of p-type GaAs with Tiron

For **n-type** semiconductors the **capacitance** of the depletion layer will **decrease** as the semiconductor is made **more positive** than its rest potential. Consequently *dC/dV* and hence *N* will be negative.

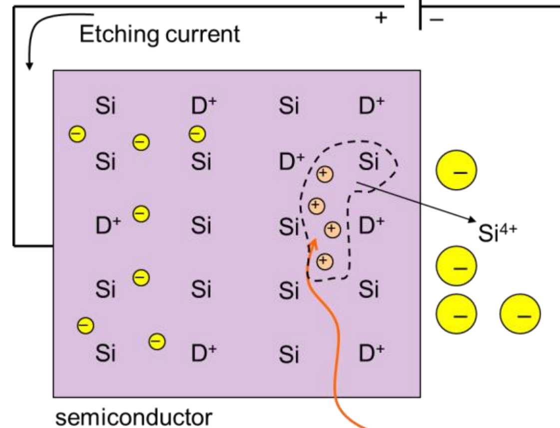
For **p-type** semiconductors the **capacitance** of the depletion layer will **decrease** as the semiconductor is made **more negative** than its rest potential, hence *dC/dV* and *N* will be positive.

# ECV-etching

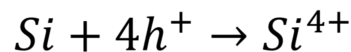
Dissolution of semiconductor materials depends on the presence of holes.




p-type Si under forward bias




n-type Si under reverse bias



$$Si + 4h^{+} \rightarrow Si^{4+}$$

For p-type materials holes are plentiful and dissolution is readily achieved by forward biasing the semiconductor /electrolyte junction.

For n-type materials, holes have to be created by illuminating the semiconductor/electrolyte junction with light with energy >$E_g$

- The etching process depends on the flow of charge
- The etching rate is proportional to the current flowing between the working and counter electrodes.
- The amount of material removed and consequently the etched depth $W_r$ is given by Faraday's law of electrolysis

$$W_r = \frac{M}{zF\rho a}\int_0^t I dt$$

# ECV: limitations

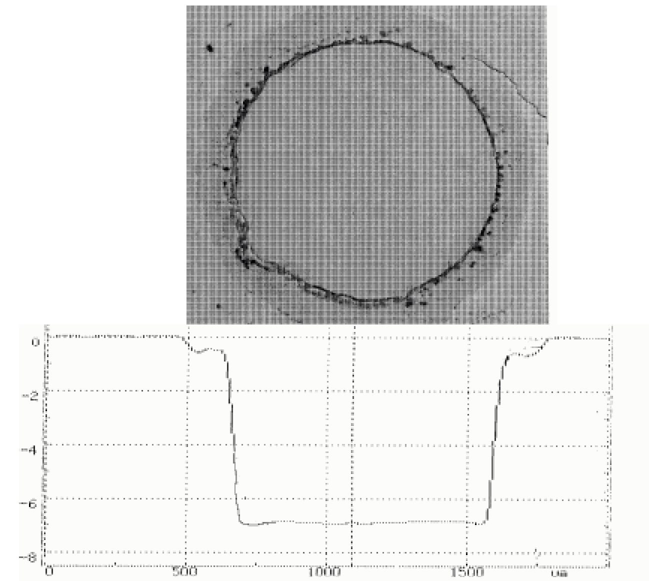
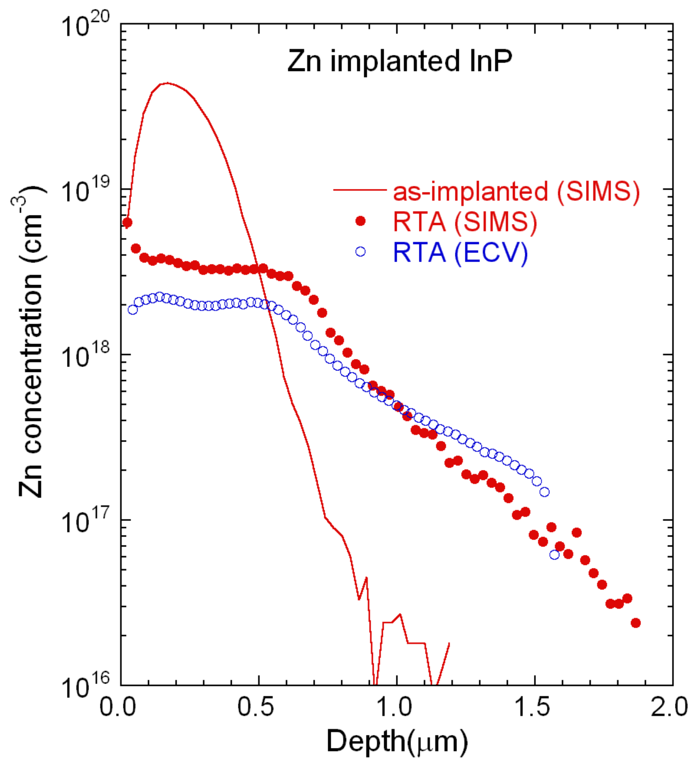
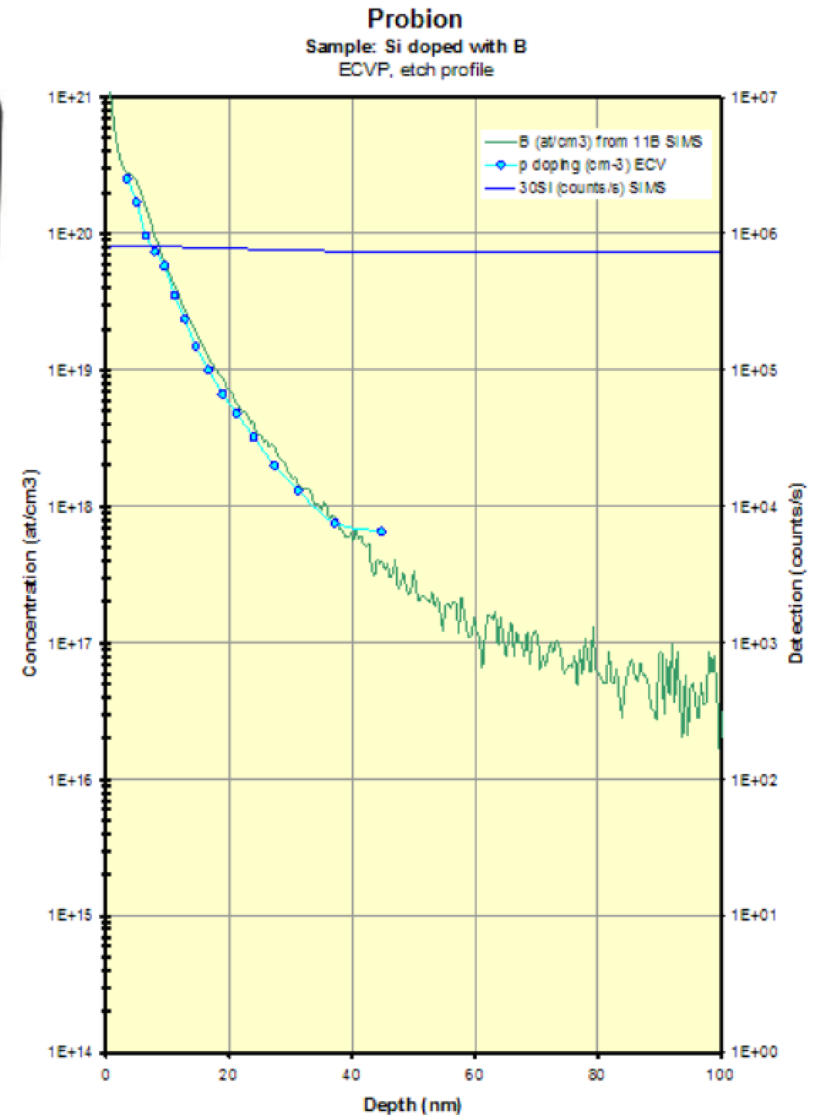



Figure 8-1 Photo of a good etch hole profiled using Tiron in 35% Al, AlGaAs, and corresponding stylus depth profile

- Large dynamic range in doping concentration ($10^{15}$-$10^{21}$cm$^{-3}$)
- Essentially no limit in probe depth (> several microns)
- Destructive in nature
- May be complicated by deep traps
- Different electrolyte must be used for different semiconductor so that etching can be achieved
- Depth resolution limited by Debye length ($3L_D$)
- Absolute accuracy of the carrier concentration and etch depth depends on a precise measurement of the **contact area**.
  - bubbles in the O-ring or O-ring distortion and wear
  - The O-ring must be soft enough to form a seal with variable semiconductor surfaces, but sufficiently rigid to precisely define the Schottky contact area.
- The ECV profile measures the "**net ionized dopants**" not the carrier concentration

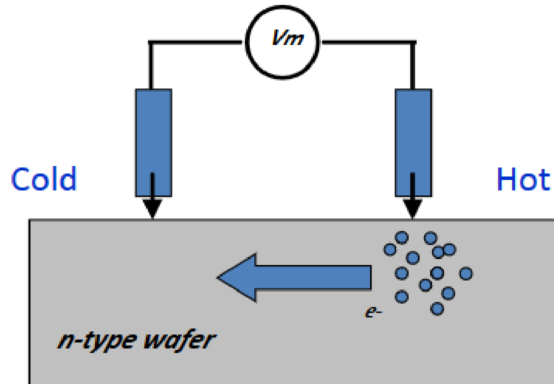
# ECV: examples

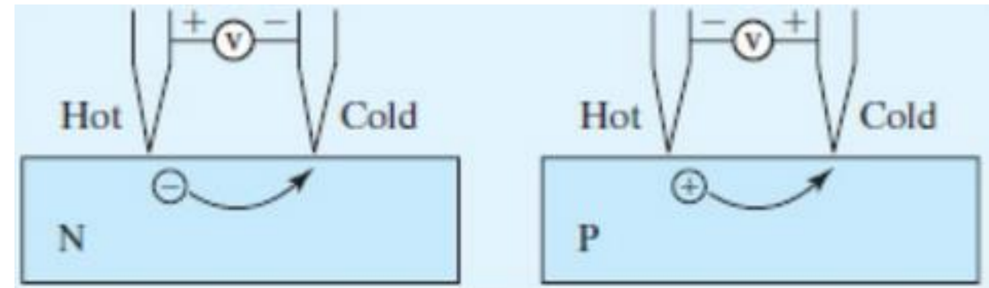


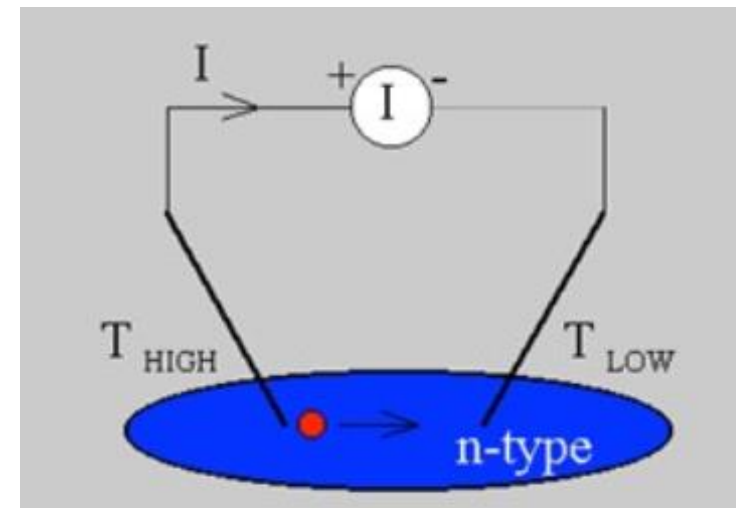

*Yu and Ridgway, Nucl. Instrum. Meth. B168, 65 (2000).*

# Thermoprobe (hot probe)

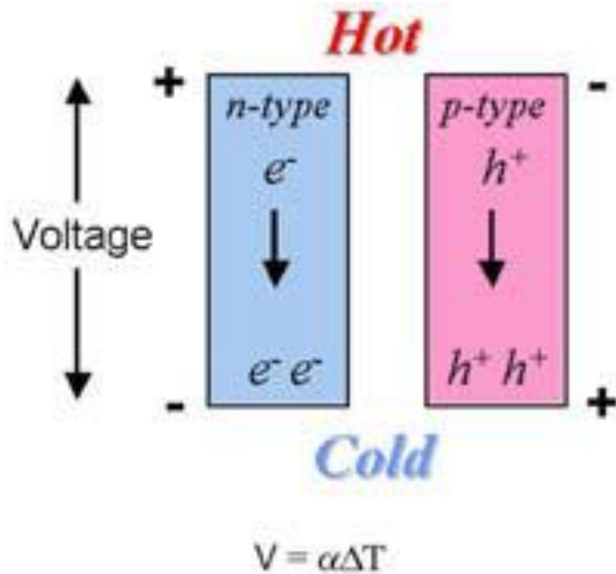


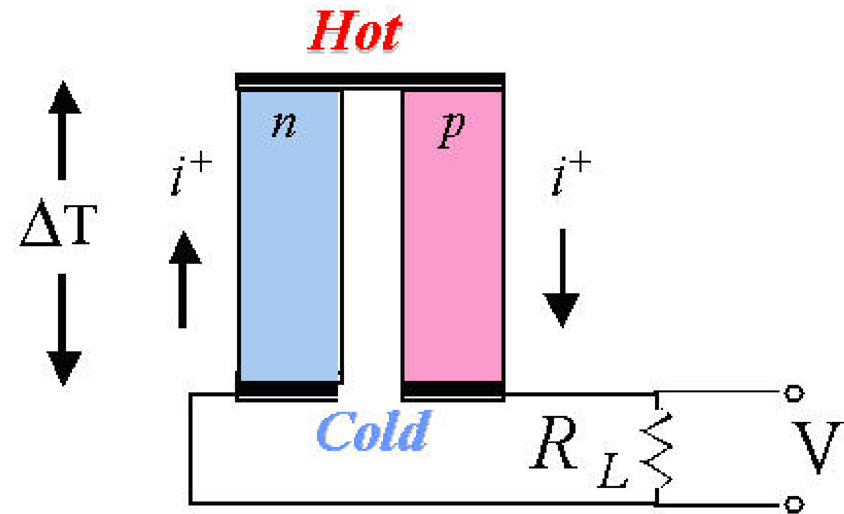




- The application of a temperature gradient induces a small voltage in a semiconductor— **thermoelectric effect.**
- The **thermoprobe** or **hot probe** is a simple tool that uses the thermoelectric effect to determine the type of conduction.
- One can measure the open circuit voltage (**Seebeck voltage**) and the **sign** of the voltage tells the type of the sample.
- Alternatively the direction of the **current** (short-circuit current) can be used to tell the type since electron and hole currents are of opposite sign.



# Seebeck effect




http://mmr-tech.com/PDFs/seebeckPPT.pdf

Charge Carrier Diffusion:

- Charge carriers diffuse when one end of a conductor is at a different temperature than the other
  - Hot carriers diffuse from the hot end to the cold end
  - Cold carriers diffuse from the cold end to the hot end
- Motion of charge carriers results in an electrical current

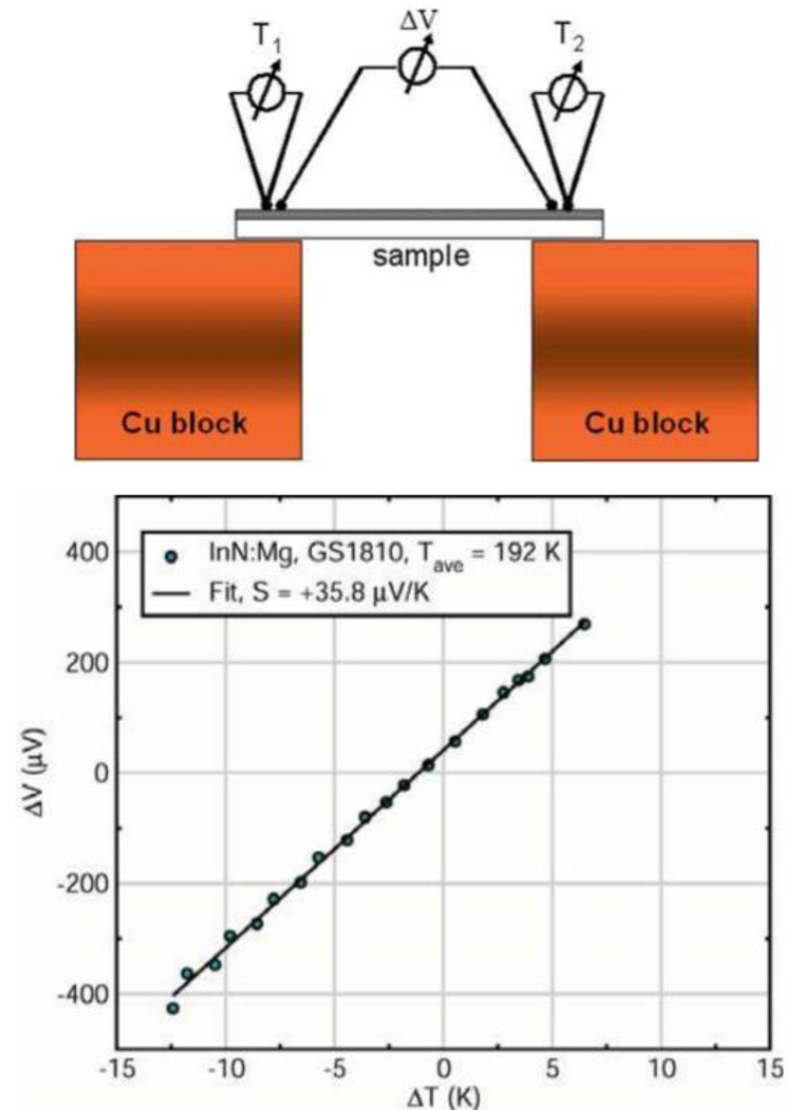
# Seebeck coefficient

Quantitative information on the thermoelectric effect can also be obtained:

- A sample is suspended between two copper blocks, which are held at different temperatures
- The **open-circuit voltage** between the two contacts $\Delta V$ is measured by a high impedance meter.
- The temperature at each contact is measured by a thermocouple.
- The temperature difference is varied while keeping the average temperature constant.
- The **Seebeck coefficient** of the thermoelectric effect is defined as

$$S = \frac{\Delta V}{\Delta T}$$

- Holes give rise to a positive $S$ and electron result in a negative $S$.




*Ager et al., Phys. Stat. Sol. B* ***245****, 873 (2008).*

# Seebeck coefficient measurement

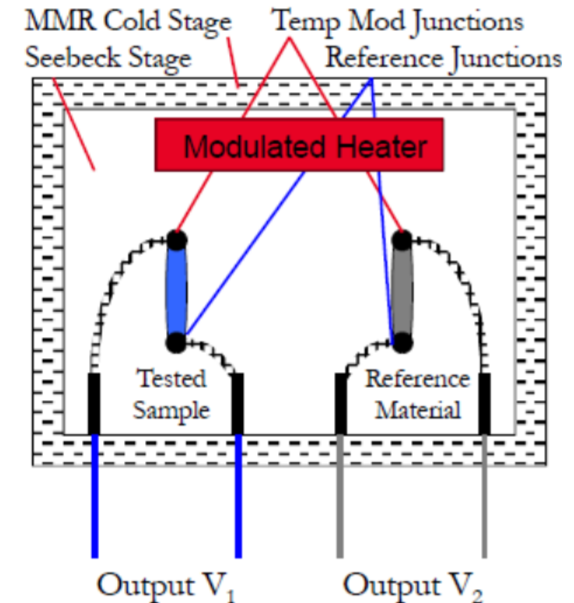
- Two pairs of thermocouples:
  - One based on junctions of Cu-Metal with known properties
  - One based on Cu-Metal of unknown properties
- Computer controlled heater, located close to working junctions, far from reference

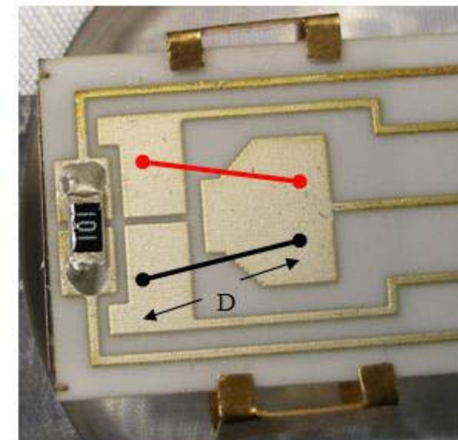
Principle of operation:

- Assume all four thermocouples have same temperature

$$V_1 \ and \ V_2 = zero$$

- Apply power to heater to create temperature difference between working and reference junctions
  - Get some non-zero values for $V_1$ and $V_2$
  - Assume the temperature difference is the same for both pairs
  - Obtain the ratio of the specific thermovoltages equal to the differences in the voltages $V_1$ and $V_2$

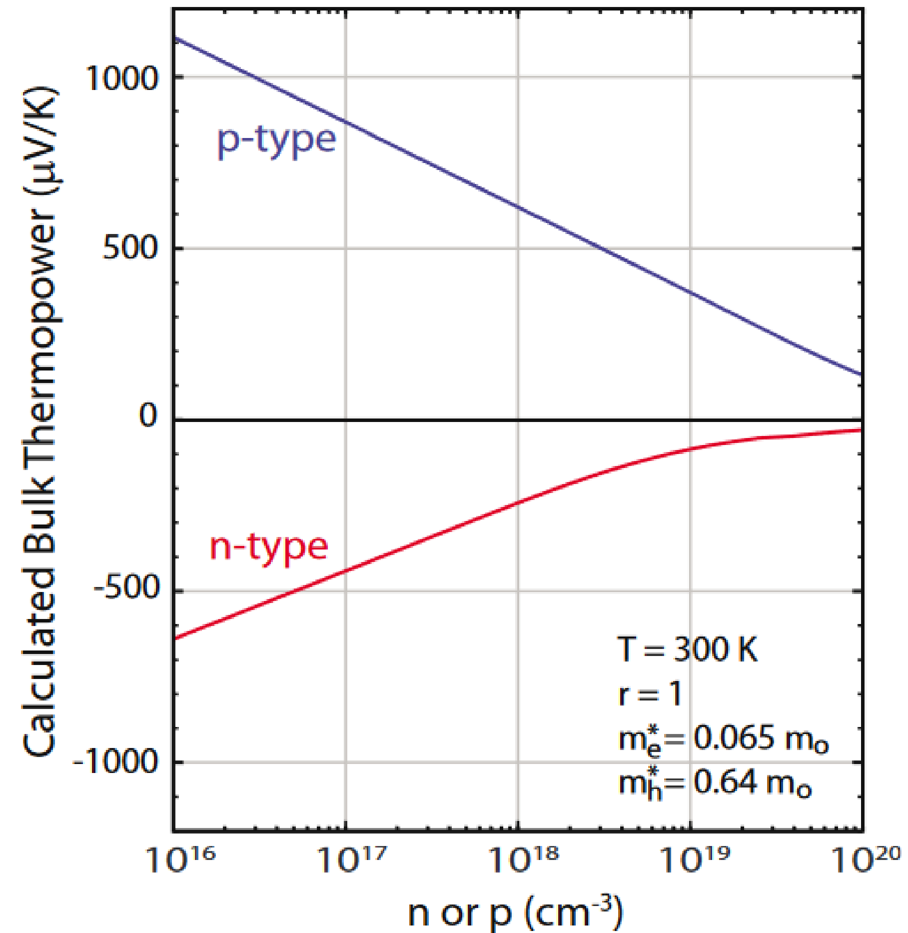



http://mmr-tech.com/PDFs/seebeckPPT.pdf

# Seebeck coefficient

- The Seebeck coefficient or thermopower $S = \frac{\Delta V}{\Delta T}$ is a property dependent on the electronic structure near the fermi-level and is sensitive to effective mass, carrier concentration, and band shape
- Through modeling , these parameters can be estimated from the value of $S$.




Calculated carrier concentration dependence of the thermopower at 300 K of n- and p-type InN.

*Miller et al., J. Appl. Phys.* ***107****, 113712 (2010).*

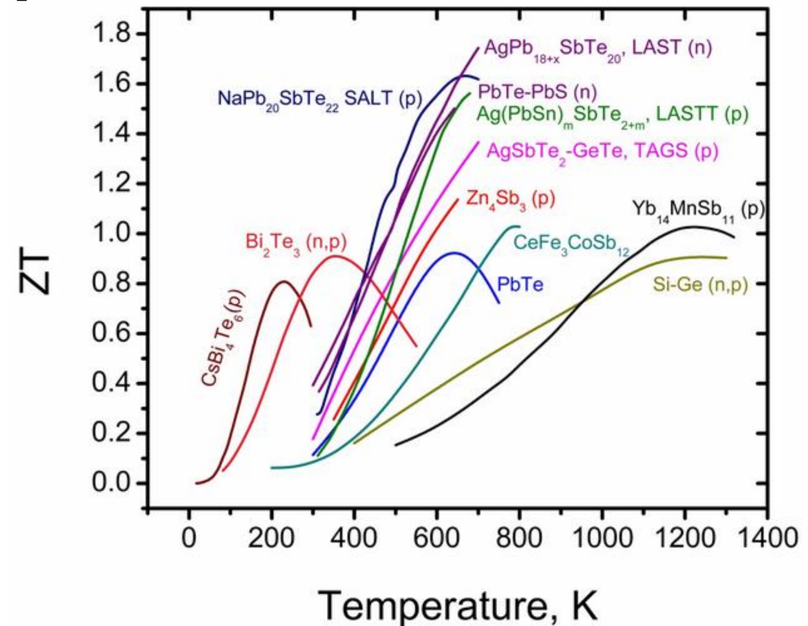
# Thermoelectric materials

- Thermoelectric materials are used in thermoelectric systems for cooling or heating in niche applications, and are being studied as a way to **regenerate electricity from waste heat**.
- The ability of a given material to efficiently produce thermoelectric power is related to its dimensionless **figure of merit** given by:

$$ZT = \frac{\sigma S^2 T}{\lambda}$$

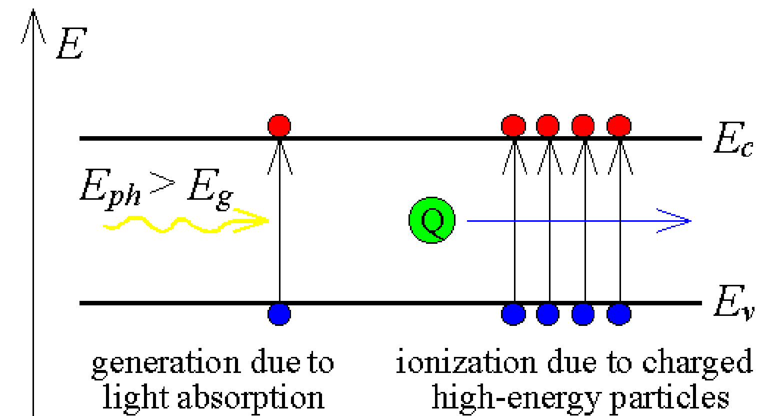
which depends on the Seebeck coefficient $S$, thermal conductivity $\lambda$, electrical conductivity $\sigma$, and temperature $T$

- The usefulness of a material in a thermoelectric generator or a thermoelectric cooler depends on its **power factor**$= \sigma S^2$
  - Materials with a high power factor are able to 'generate' more energy
  - For good efficiency, materials with high electrical conductivity, low thermal conductivity and high Seebeck coefficient are needed.

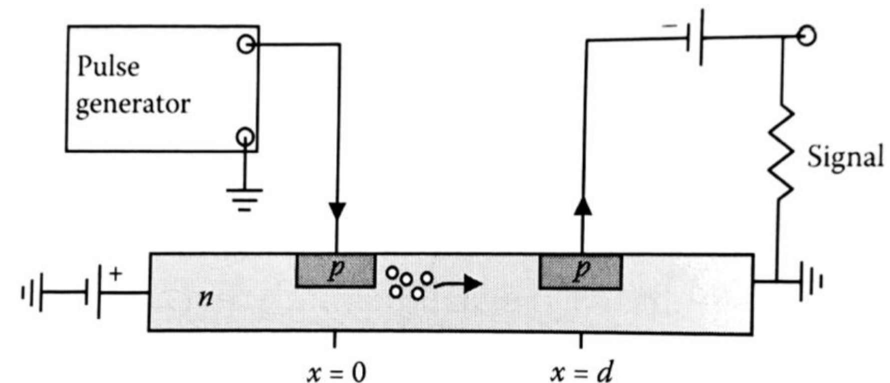


# Minority carrier lifetime

- Free carriers can be generated by exposing a semiconductor to an external excitation, e.g. light or electric field.
- After a semiconductor is exposed to an external excitation, it will return to its equilibrium condition.
- The dominant physical parameter describing the return of a semiconductor to its equilibrium condition is **the minority lifetime $\tau$**.
- Short $\tau$ is important for **fast switches** while long $\tau$ leads to efficient $p-n$ junction **rectifiers and solar cells**.
- The **Haynes-Shockley experiment** measures the transport of minority carriers




**Haynes-Shockley experiment**

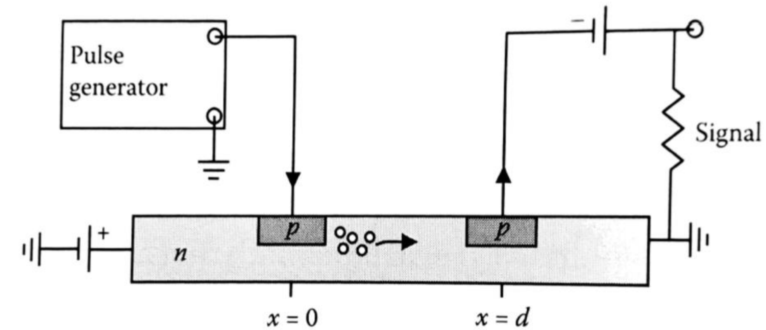


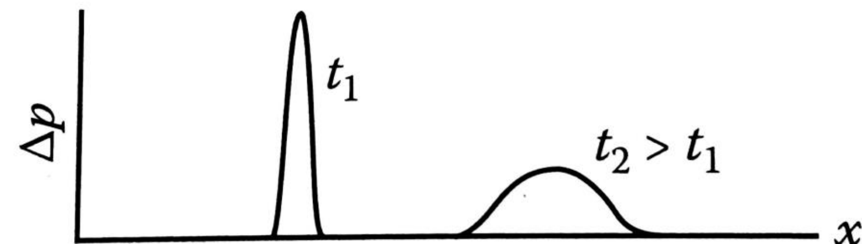

A constant electric field ($E$) along a long semiconductor bar is set up by applying a relatively small bias. The two contacts are on p-type layers unders reversed bias

# Minority carrier lifetime: Haynes-Shockley

- When a forward bias pulse is applied, holes are injected into the n-type semiconductor
- The holes drift ($v_d$) in the field towards the right and are collected at $x = d$.
- The collected holes produce a voltage drop across the load resistor and displayed on a scope.
- The drift mobility $\mu$ is obtained from the drift time $t_o, v_d = \frac{d}{t_o} = \mu E$

The **Haynes-Shockley experiment** :




- The hole packet drifts and broadens with time:

$$\Delta p(x,t) = \frac{\Delta p_o}{\sqrt{4\pi D t}} e^{-t/\tau_p} e^{-(x - v_d t)^2/4Dt}$$

where $\Delta p_o \propto \mathrm{injet\ hole\ at\ t} = 0,$

- $D$ is the hole diffusion coefficient and can be obtained from the width of the pulse
- $\tau_p$ is the minority hole lifetime and is determined by measuring the peak of $\Delta p$ as the distance $d$ is changed

# Minority carrier lifetime: photoconductivity

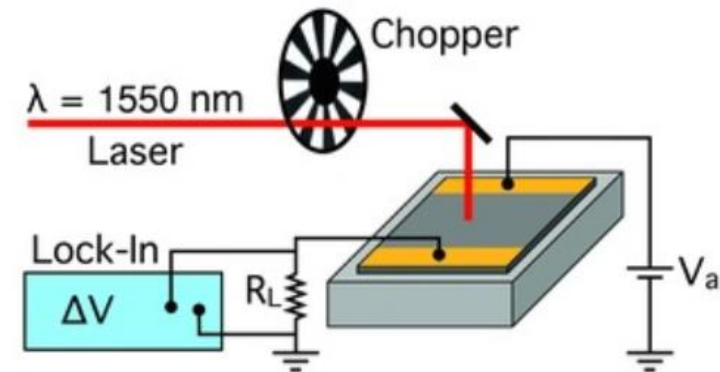
The minority lifetime of a semiconductor can also be obtained from a **photoconductivity decay** measurement:

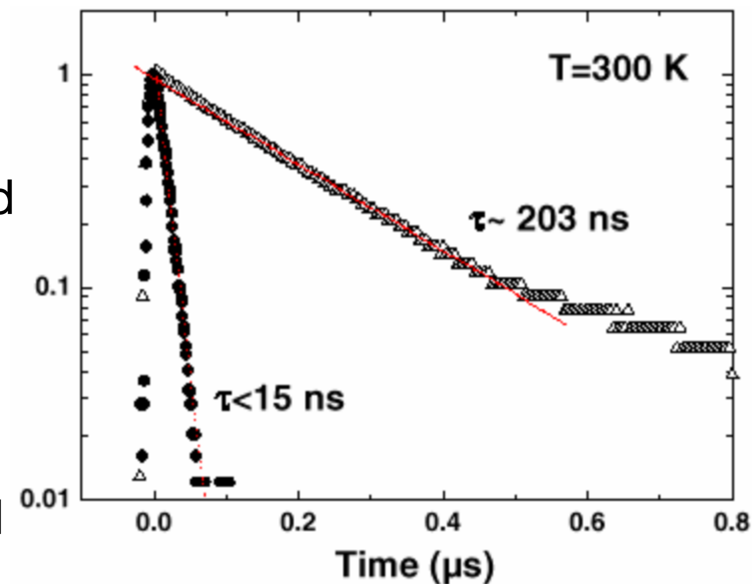
- A semiconductor bar is illuminated by a mechanically chopped short optical pulses ($h\nu > E_g$)
- The increase in conductivity is measured by applying a constant current source across the semiconductor bar
- The change in the bias voltage $\Delta V$ across the bar **decreases exponentially** as the excess carriers disappear through recombination

$$\Delta V = \Delta V_o e^{-t/\tau}$$

  where $\Delta V_o$ is the change in bias at $t = 0$ and $\tau$ is the carrier lifetime.

- Optical excitation has the advantages of covering a wide range of time and intensity scales
- Minority lifetime of a semiconductor is a good measure of its quality



# Electrical measurements: a comparison

| | 4 point probe | Hall effect | CV | ECV | thermopower |
|---|---|---|---|---|---|
| Information obtained | Resistivity | Free carrier concentration, mobility | Net ionized dopant concentration | Net ionized dopant concentration | Seebeck coefficient |
| Conduction type (n or p) | No | Yes | Yes | Yes | Yes |
| Sample size | From mm to wafer | 0.5 to 2 cm square | 0.5 to 2 cm square | >0.5 cm | >0.5 cm |
| Depth profiling | No | No | Yes | Yes | Mo |
| Destructive | Somewhat | No | Need to form a Schottky contact | Yes | No |
| Equipment cost | Low | Low to high (from <20kUSD to >200k USD) | Low | High (>150k USD) | Low to medium |