

Charge Transport in Coordination Network Materials: Theoretical Concepts and Experimental Techniques

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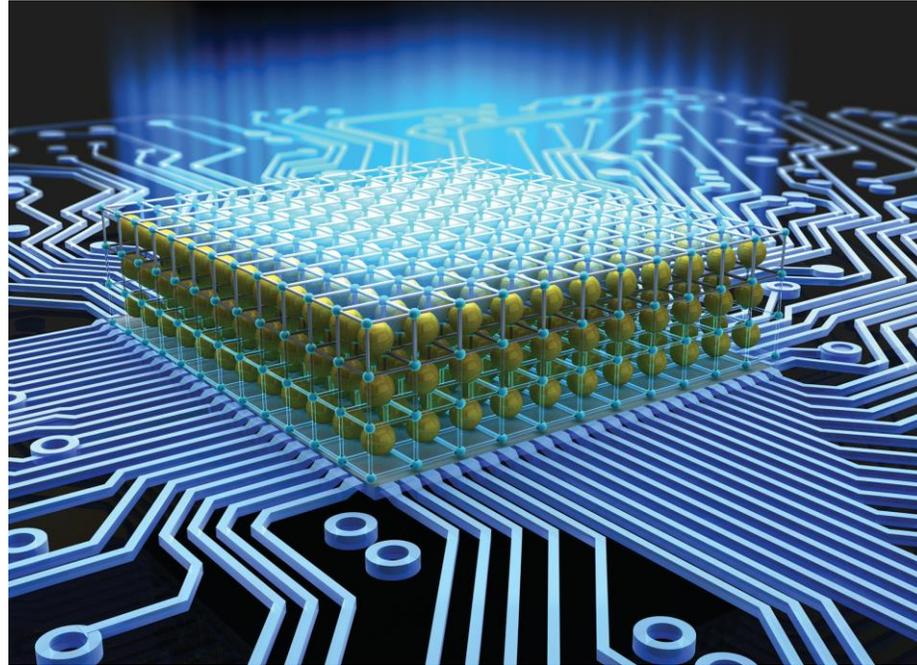
SPP 1928, COORNETs: 1st Workshop “Electrical Conductivity in MOFs”
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Frank Batten College of
Engineering & Technology
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Old Dominion University

Objective: Investigation of MOF Films with potential Microelectronic Applications



Basic premise: A shift away from microcrystalline bulk powder synthesis in chemical labs towards controlled and reliable thin Film Deposition Technologies is required in order to assess and to eventually realize the full application potential of MOF Films in Microelectronic Devices.

Many laboratories achieve now routinely continuous MOF films by various deposition methods to meet more stringent quality and reliability specifications of solid state technology.



For Materials Characterization we distinguish between Physical Characterization and Electrical Characterization

- ❑ During the previous decades a very large amount of Physical Characterization has been performed on Various Coordination Network Materials.
- ❑ However in contrast, very little work has been devoted to electrical characterization. And as a consequence our understanding of electrical phenomena in Coordination Networks is lagging behind.
- ❑ Many Coordination Network Materials can now be synthesized into continuous thin films with a Reasonable quality, which renders them amenable for potential device applications. In order to assess the application potential for devices it is absolutely crucial to perform electrical characterization of these novel materials.

The ability to conduct electrical charge is one of the most important but least understood properties of MOF films and coordination network materials.

What is required is a better understanding of the basic charge transport properties of these materials.

- ❑ The next sections will review basic concepts and background in electrical characterization.



Electrical Properties

ISSUES TO ADDRESS...

- How are electrical conductance and resistance characterized?
- What are the physical phenomena that distinguish conductors, semiconductors, and insulators?
- For metals, how is conductivity affected by imperfections, temperature, and deformation?
- For semiconductors, how is conductivity affected by impurities (doping) and temperature?



Electrical Conduction

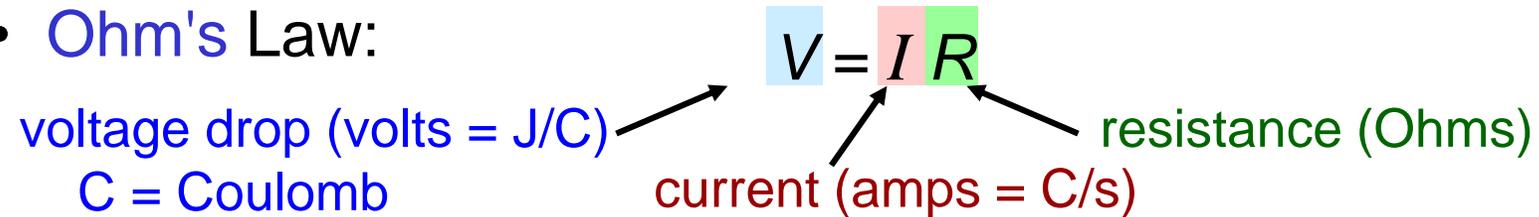
- Ohm's Law:

voltage drop (volts = J/C)
C = Coulomb

$$V = IR$$

current (amps = C/s)

resistance (Ohms)



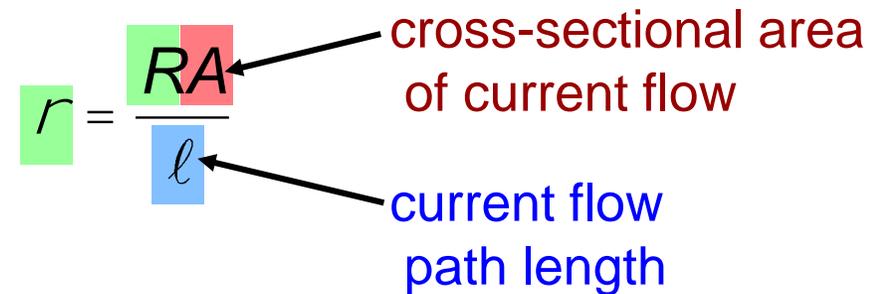
- Resistivity, ρ :

-- a material property that is independent of sample size and geometry

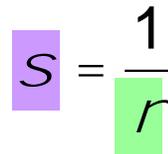
$$r = \frac{RA}{l}$$

cross-sectional area of current flow

current flow path length



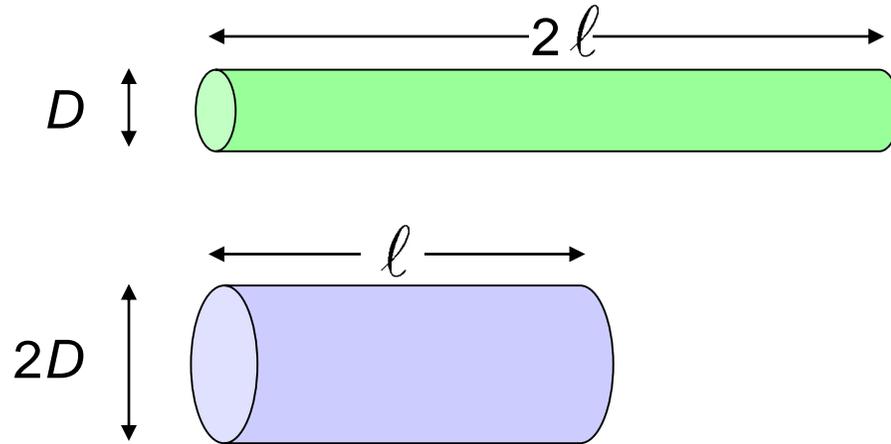
- Conductivity, σ

$$S = \frac{1}{r}$$




Electrical Properties

- Which will have the greater resistance?



$$R_1 = \frac{2rl}{\frac{\rho_C}{e} \frac{D^2}{4}} = \frac{8rl}{\rho_C D^2}$$

$$R_2 = \frac{rl}{\frac{\rho_C}{e} \frac{(2D)^2}{4}} = \frac{rl}{\rho_C D^2} = \frac{R_1}{8}$$

- Analogous to flow of water in a pipe
- Resistance depends on sample geometry and size.



Definitions

Further definitions

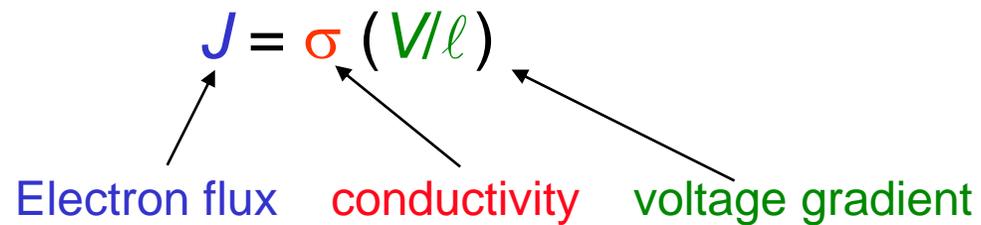
$$\boxed{J = \sigma \varepsilon} \quad \Leftarrow \text{another way to state Ohm's law}$$

$$J \equiv \text{current density} = \frac{\text{current}}{\text{surface area}} = \frac{I}{A} \quad \text{like a flux}$$

$$\varepsilon \equiv \text{electric field potential} = V/\ell$$

$$J = \sigma (V/\ell)$$

Electron flux conductivity voltage gradient





Electrical Conductivity σ : Comparison

- Room temperature values $(\text{Ohm}\cdot\text{m})^{-1} = (\Omega \cdot \text{m})^{-1}$

METALS

Silver

Copper

Iron

conductors

6.8×10^7

6.0×10^7

1.0×10^7

CERAMICS

Soda-lime glass

Concrete

Aluminum oxide

10^{-10} - 10^{-11}

10^{-9}

$<10^{-13}$

SEMICONDUCTORS

Silicon

Germanium

GaAs

4×10^{-4}

2×10^0

10^{-6}

semiconductors

POLYMERS

Polystyrene

Polyethylene

$<10^{-14}$

10^{-15} - 10^{-17}

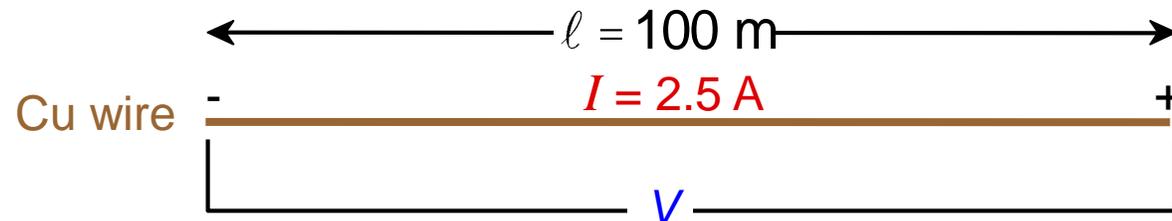
insulators

Selected values from Tables 12.1, 12.3, and 12.4, *Callister & Rethwisch 4e.*



Example: Electrical Conductivity Problem

What is the minimum diameter (D) of the wire so that $V < 1.5$ V?



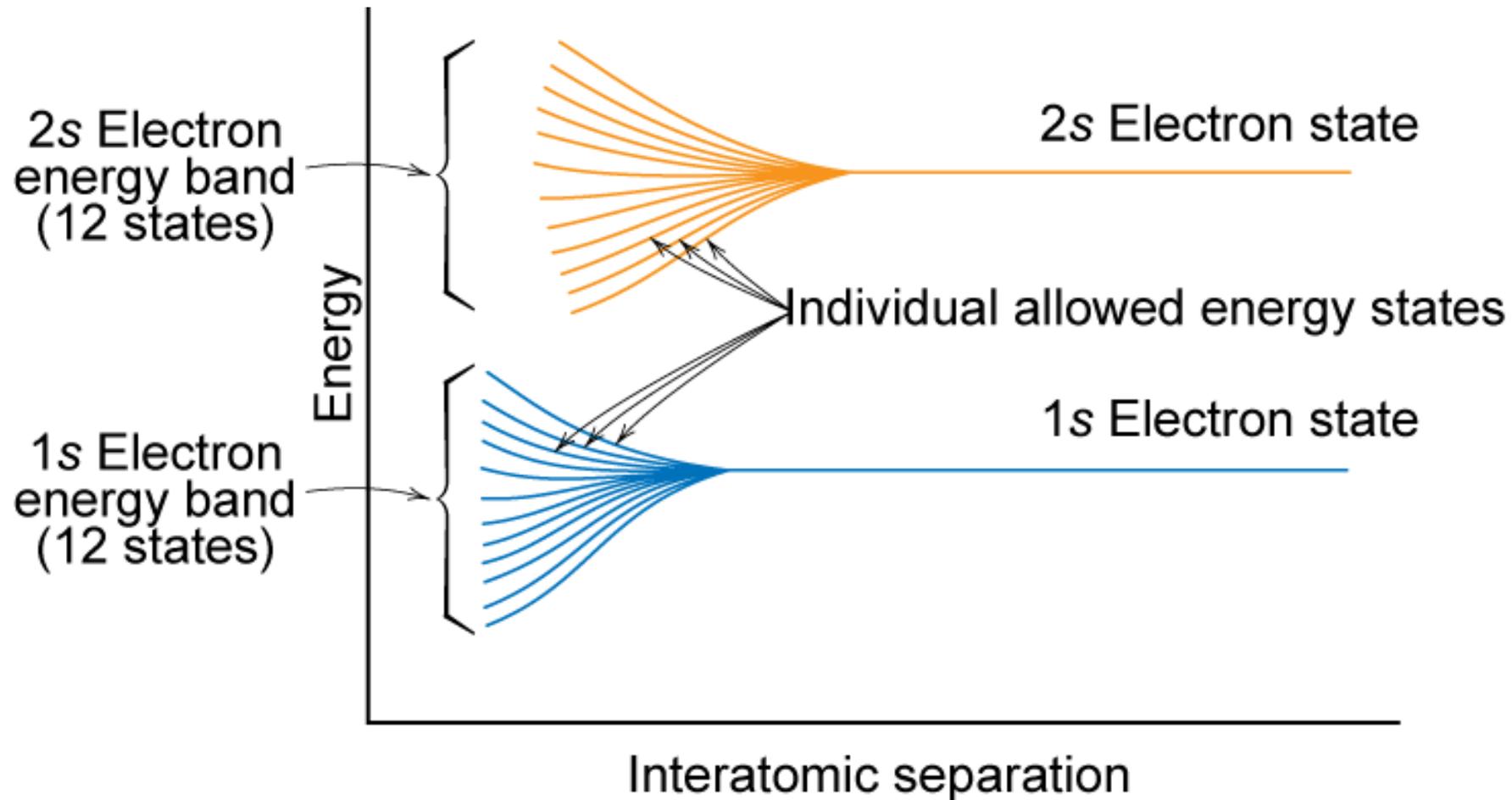
$$R = \frac{l}{A\sigma} = \frac{V}{I}$$

Annotations for the equation above:
- l is labeled "100 m" with an arrow pointing to the numerator.
- A is labeled $\frac{\rho D^2}{4}$ with an arrow pointing to the denominator.
- σ is labeled $6.07 \times 10^7 \text{ (Ohm-m)}^{-1}$ with a green arrow pointing to it.
- V is labeled < 1.5 V with a blue arrow pointing to the numerator of the right-hand side.
- I is labeled 2.5 A with a red arrow pointing to the denominator of the right-hand side.

Solve to get $D > 1.87$ mm



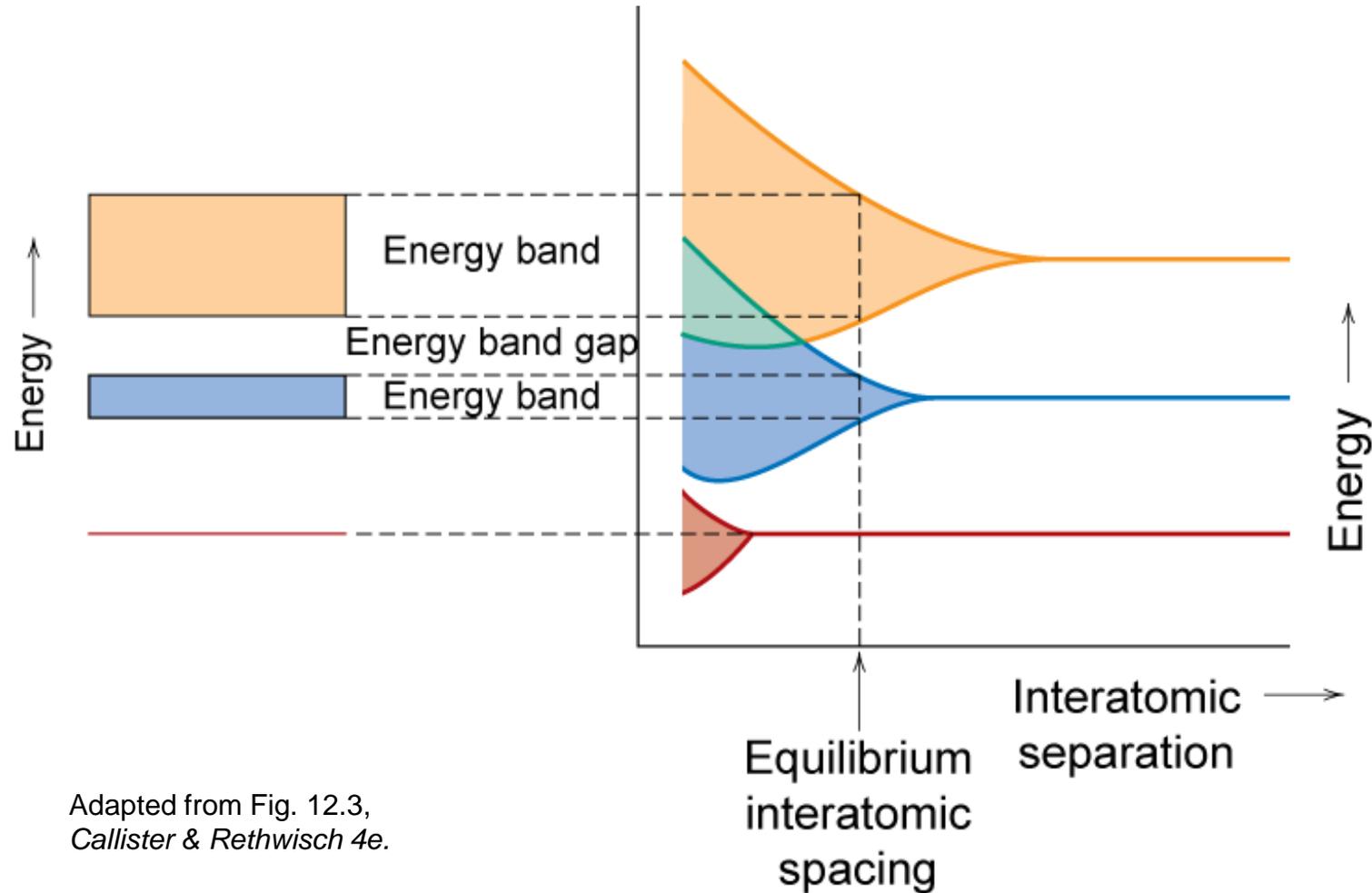
Electron Energy Band Structures



Adapted from Fig. 12.2, *Callister & Rethwisch 4e*.



Band Structure Representation



Adapted from Fig. 12.3,
Callister & Rethwisch 4e.



Conduction & Electron Transport

- Metals (**Conductors**):

- for metals empty energy states are adjacent to filled states.

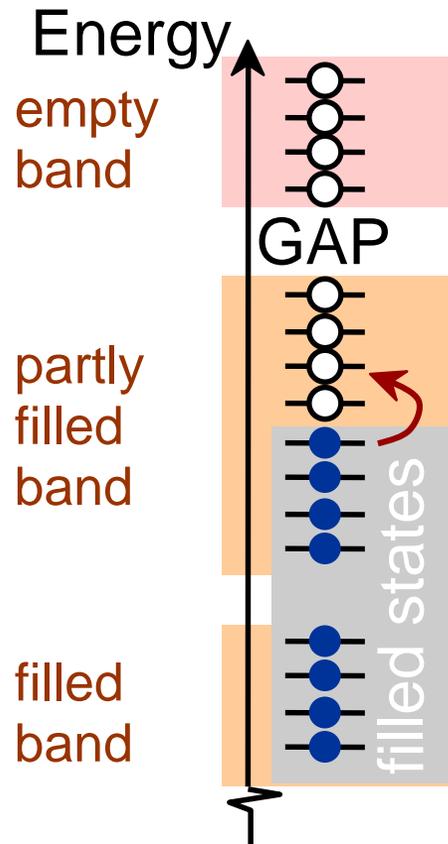
- thermal energy excites electrons into empty higher energy states.

- two types of band structures for metals

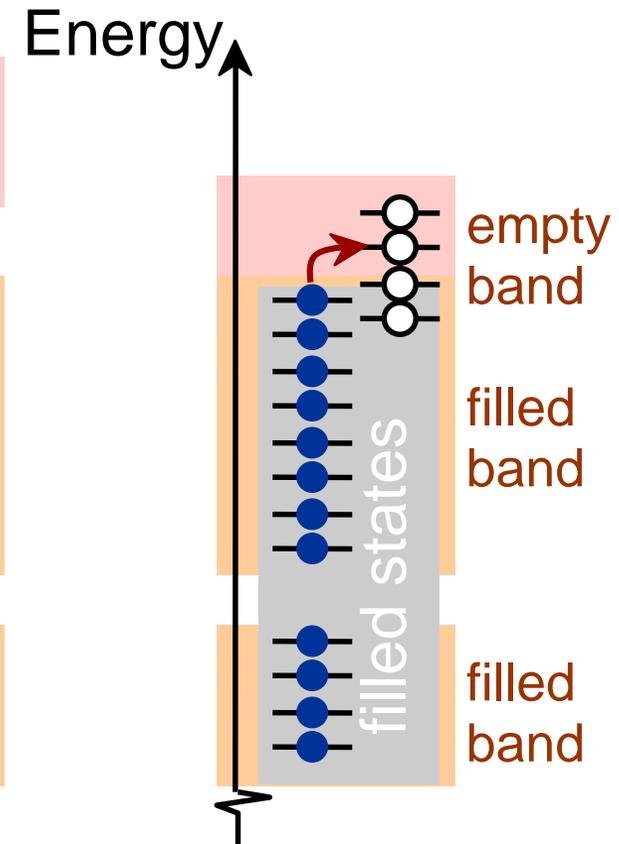
- partially filled band

- empty band that overlaps filled band

Partially filled band

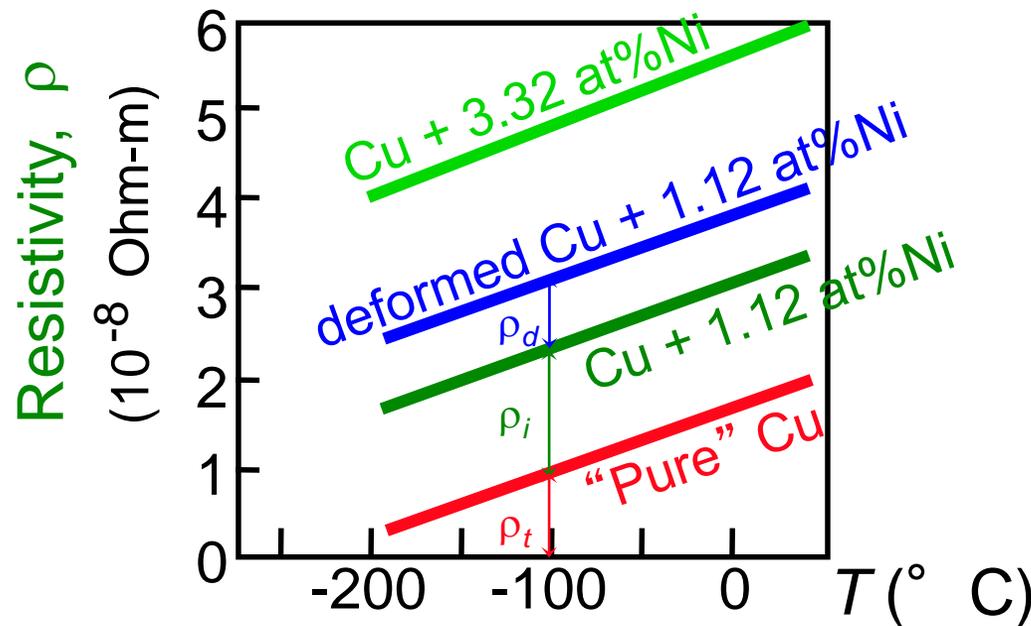


Overlapping bands



Metals: Influence of Temperature and Impurities on Resistivity

- Presence of imperfections increases resistivity
 - grain boundaries
 - dislocations
 - impurity atoms
 - vacancies
- These act to scatter electrons so that they take a less direct path.



- Resistivity increases with:
 - temperature
 - wt% impurity
 - %CW

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

Adapted from Fig. 12.8, Callister & Rethwisch 4e. (Fig. 12.8 adapted from J.O. Linde, *Ann. Physik* 5, p. 219 (1932); and C.A. Wert and R.M. Thomson, *Physics of Solids*, 2nd ed., McGraw-Hill Book Company, New York, 1970.)

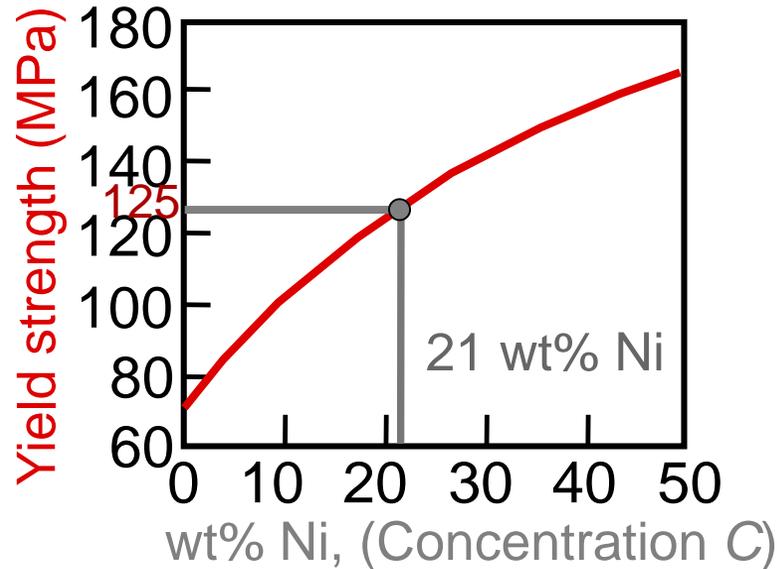


Estimating Electrical Conductivity

- Question:

- Estimate the electrical conductivity σ of a Cu-Ni alloy that has a yield strength of **125 MPa**.

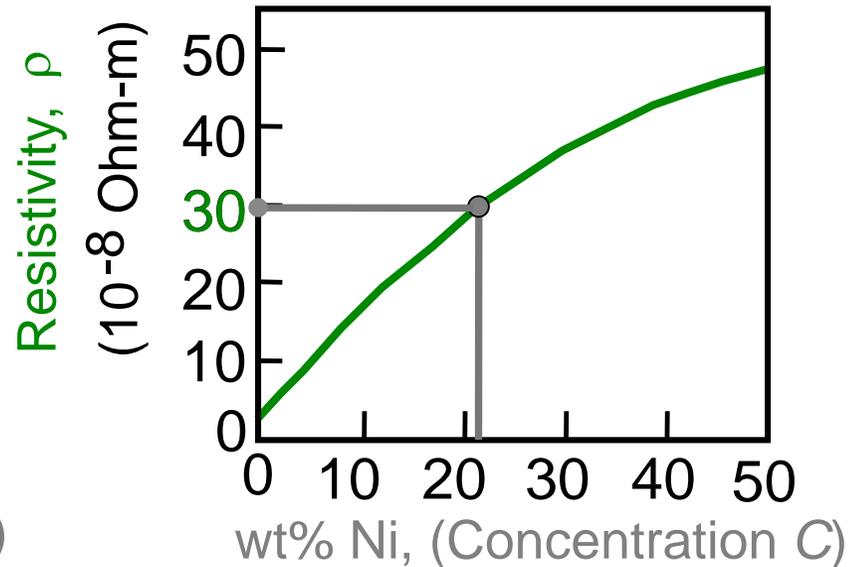
Adapted from Fig. 12.9, Callister & Rethwisch 4e.



Adapted from Fig. 8.16(b), Callister & Rethwisch 4e.

From step 1:

$$C_{\text{Ni}} = 21 \text{ wt\% Ni}$$



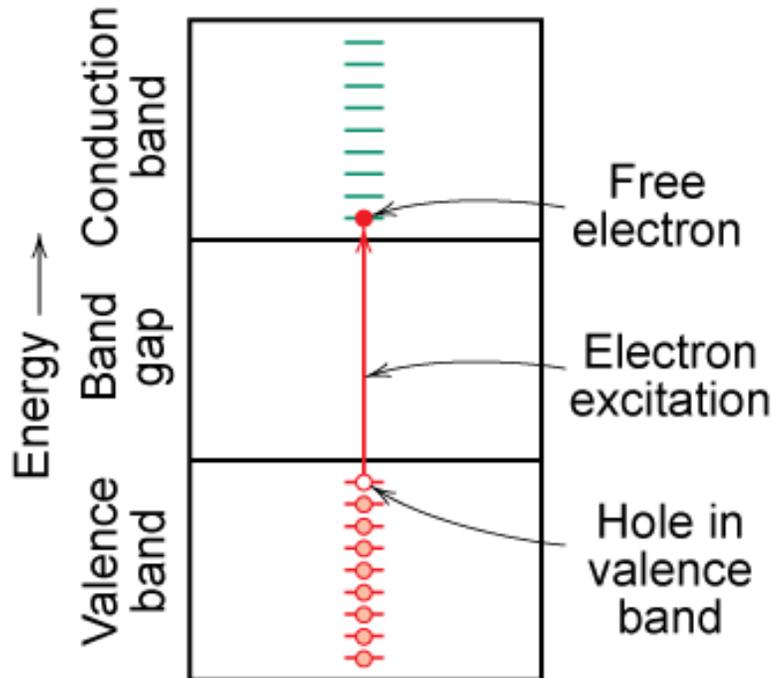
$$r = 30 \times 10^{-8} \text{ Ohm} - \text{m}$$

$$S = \frac{1}{r} = 3.3 \times 10^6 (\text{Ohm} - \text{m})^{-1}$$



Charge Carriers in Insulators and Semiconductors

Adapted from Fig. 12.6 (b),
Callister & Rethwisch 4e.



Two types of electronic charge carriers:

Free Electron

- negative charge
- in conduction band

Hole

- positive charge
- vacant electron state in the valence band

Move at different speeds - **drift velocities**



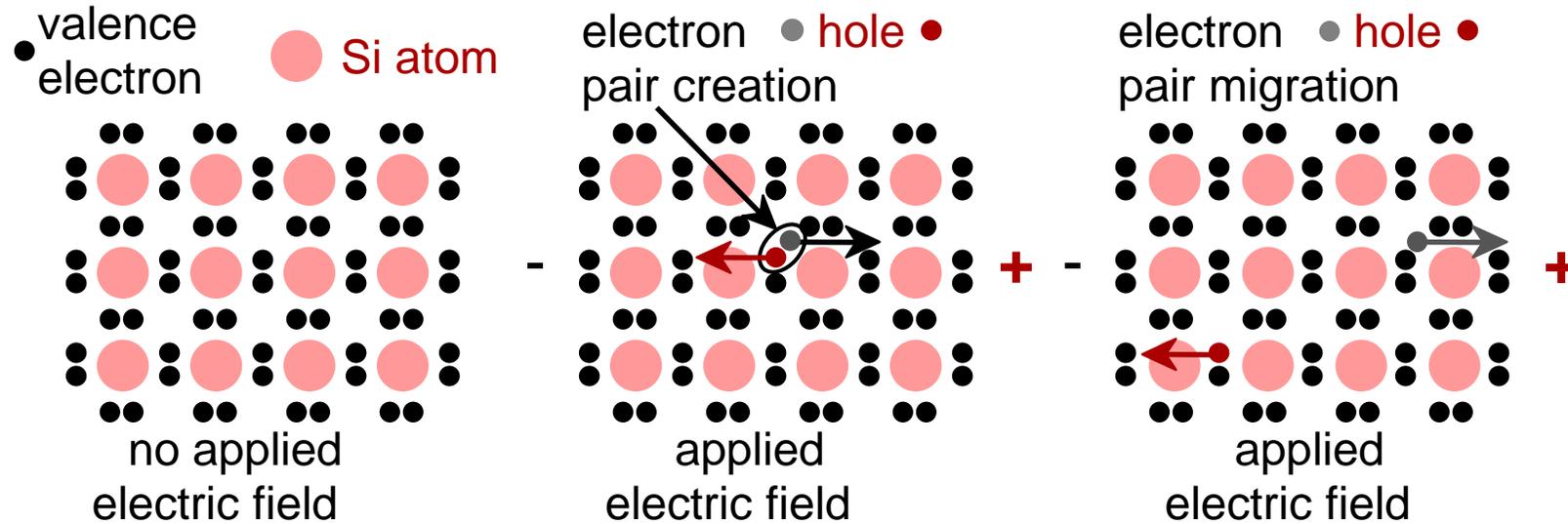
Intrinsic Semiconductors

- Pure material semiconductors: e.g., silicon & germanium
 - Group IVA materials
- Compound semiconductors
 - III-V compounds
 - Ex: GaAs & InSb
 - II-VI compounds
 - Ex: CdS & ZnTe
 - The wider the electronegativity difference between the elements the wider the energy gap.



Intrinsic Semiconduction in Terms of Electron and Hole Migration

- Concept of electrons and holes:



Adapted from Fig. 12.11, Callister & Rethwisch 4e.

- Electrical Conductivity given by:

$$S = n e m_e + p e m_h$$

electrons/m³ → n | e | m_e → electron mobility
 # holes/m³ → p | e | m_h → hole mobility



Number of Charge Carriers n_i

Intrinsic Electrical Conductivity is proportional to the product of mobility and carrier concentration.

The same conductivity could come from a small number of electrons with high mobility for each, or a large number of electrons with a small mobility for each.

$$\sigma = n|e|m_e + p|e|m_h$$

- for intrinsic semiconductor $n = p = n_i$

$$\therefore \sigma = n_i|e|(\mu_e + \mu_h)$$

- Ex: GaAs

$$n_i = \frac{\sigma}{|e|(\mu_e + \mu_h)} = \frac{10^{-6} (\Omega \cdot \text{m})^{-1}}{(1.6 \times 10^{-19} \text{ C})(0.85 + 0.45 \text{ m}^2/\text{V} \cdot \text{s})}$$

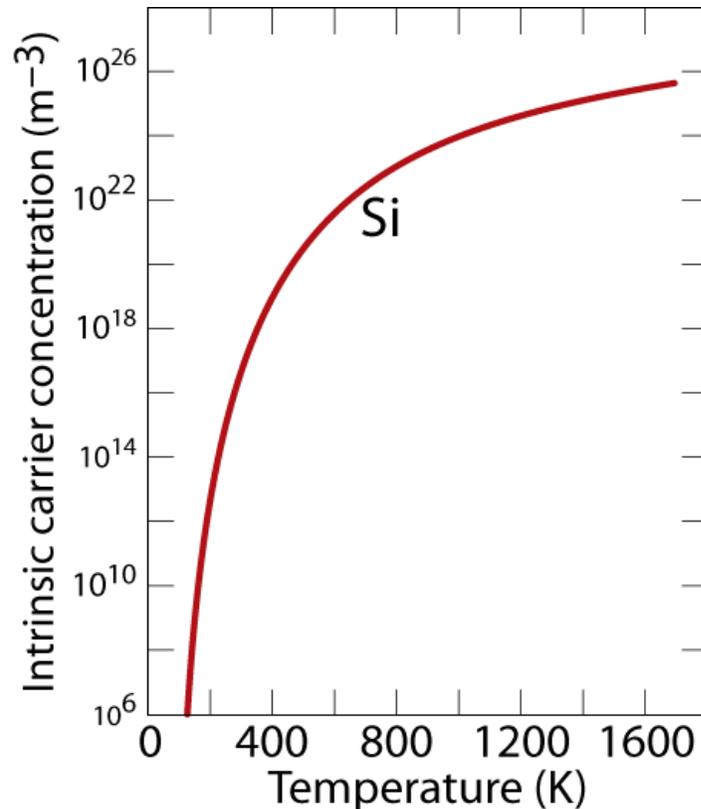
$$\text{For GaAs} \quad n_i = 4.8 \times 10^{24} \text{ m}^{-3}$$

$$\text{For Si} \quad n_i = 1.3 \times 10^{16} \text{ m}^{-3}$$



Intrinsic Semiconductors: Electrical Conductivity versus Temperature

- Data for **Pure Silicon**:
 - σ increases with T
 - opposite to metals



Adapted from Fig. 12.16,
Callister & Rethwisch 4e.

$$\sigma = n_i |e| (m_e + m_h)$$

$$n_i \propto e^{-E_{\text{gap}} / kT}$$

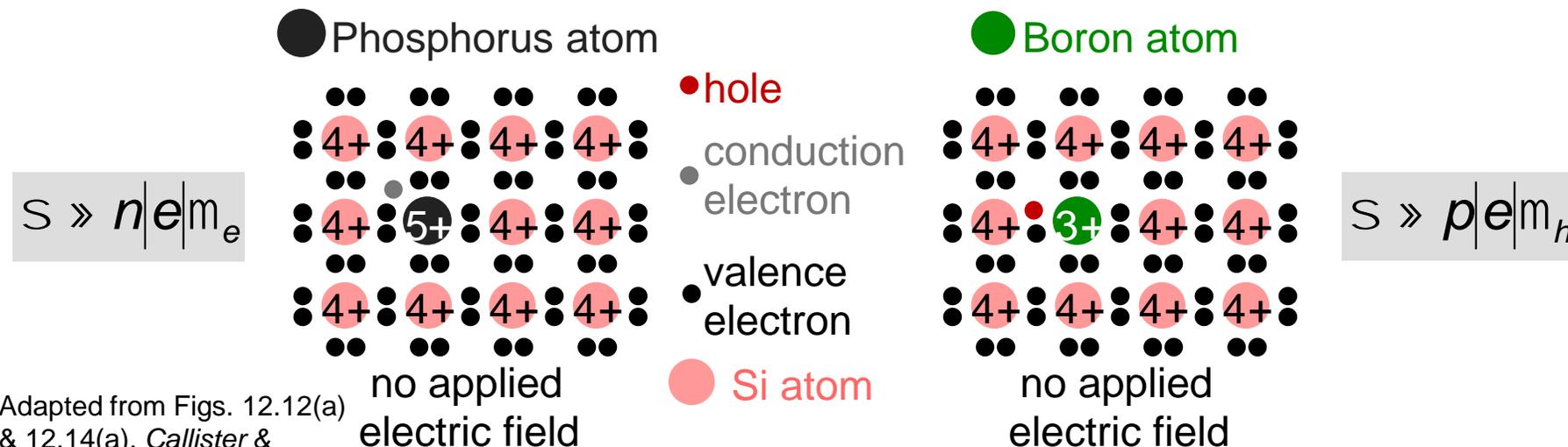
material	band gap (eV)
Si	1.11
Ge	0.67
GaP	2.25
CdS	2.40

Selected values from Table 12.3,
Callister & Rethwisch 4e.



Intrinsic vs Extrinsic Electrical Conduction

- **Intrinsic:**
 - case for pure Si
 - # electrons = # holes ($n = p$)
- **Extrinsic:**
 - electrical behavior is determined by presence of impurities or dopants that introduce excess electrons or holes
 - $n \neq p$
- **n -type Extrinsic:** ($n \gg p$)
- **p -type Extrinsic:** ($p \gg n$)

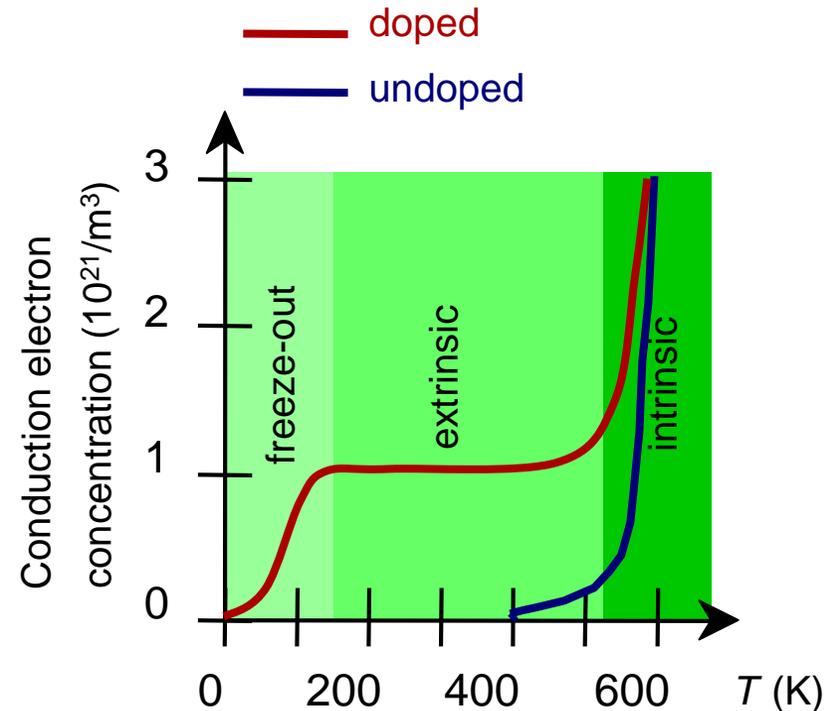


Adapted from Figs. 12.12(a) & 12.14(a), Callister & Rethwisch 4e.



Extrinsic Semiconductors: Electrical Conductivity vs. Temperature

- Data for **Doped Silicon**:
 - doping increases σ
 - reason: imperfection sites lower the activation energy to produce mobile electrons.
- Comparison: **intrinsic** vs **extrinsic** conduction...
 - extrinsic doping level: $10^{21}/\text{m}^3$ of a *n*-type donor impurity (such as P).
 - for $T < 100$ K: "freeze-out", thermal energy insufficient to excite electrons.
 - for $150 \text{ K} < T < 450 \text{ K}$: "extrinsic"
 - for $T \gg 450 \text{ K}$: "intrinsic"



Adapted from Fig. 12.17, *Callister & Rethwisch 4e*. (Fig. 12.17 from S.M. Sze, *Semiconductor Devices, Physics, and Technology*, Bell Telephone Laboratories, Inc., 1985.)



Summary

- **Electrical *conductivity* and *resistivity* are:**
 - material parameters
 - geometry independent
- **Conductors, semiconductors, and insulators...**
 - differ in range of conductivity values
 - differ in availability of electron excitation states
- **For metals, *resistivity* is increased by**
 - increasing temperature
 - addition of imperfections
 - plastic deformation
- **For pure semiconductors, *conductivity* is increased by**
 - increasing temperature
 - doping [e.g., adding B to Si (*p*-type) or P to Si (*n*-type)]
- **Other electrical characteristics**
 - ferroelectricity
 - piezoelectricity



Resistivity, Sheet Resistance, Hall Effect, Seebeck Effect

**Four-point Probe
Semiconductor Resistivity
van der Pauw Measurements
Conductivity Type
Mobility
Hall Effect
Seebeck Effect**



2-Terminal or 4-Terminal Measurements?

- Two terminal

- Voltage and current measured at *same* contact points

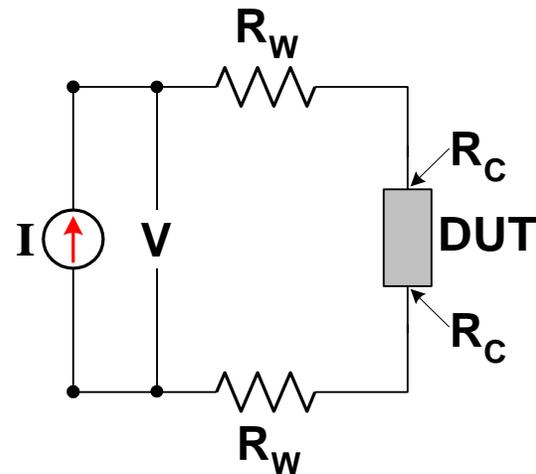
$$V = (2R_W + 2R_C + R_{DUT})I \Rightarrow R_{equ} = 2R_W + 2R_C + R_{DUT}$$

- Four terminal

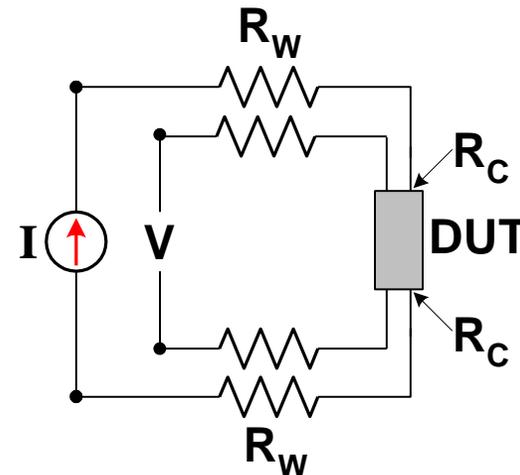
- Voltage and current measured at *different* contact points

$$V = R_{DUT}I \Rightarrow R_{equ} = R_{DUT}$$

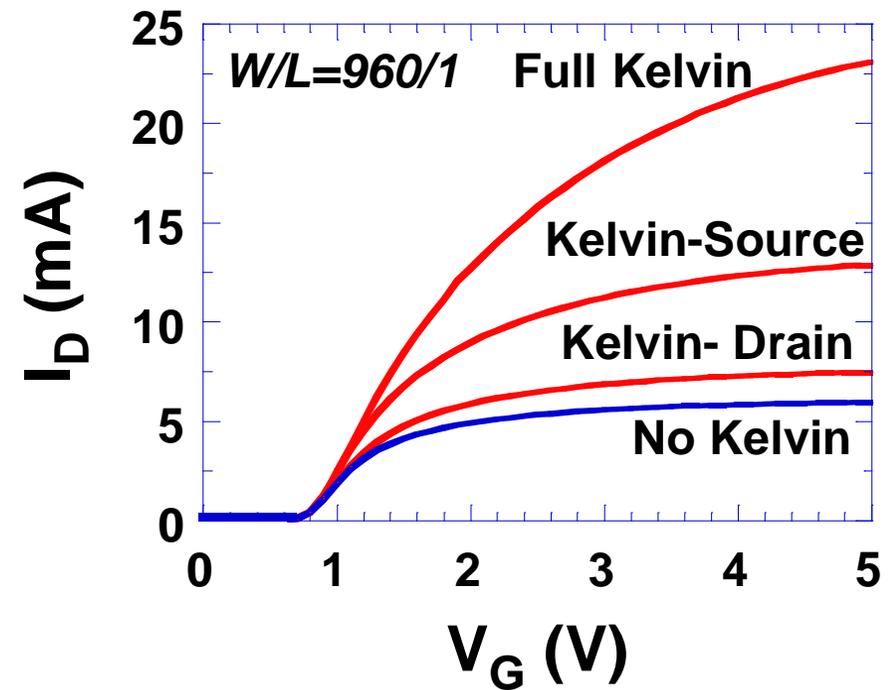
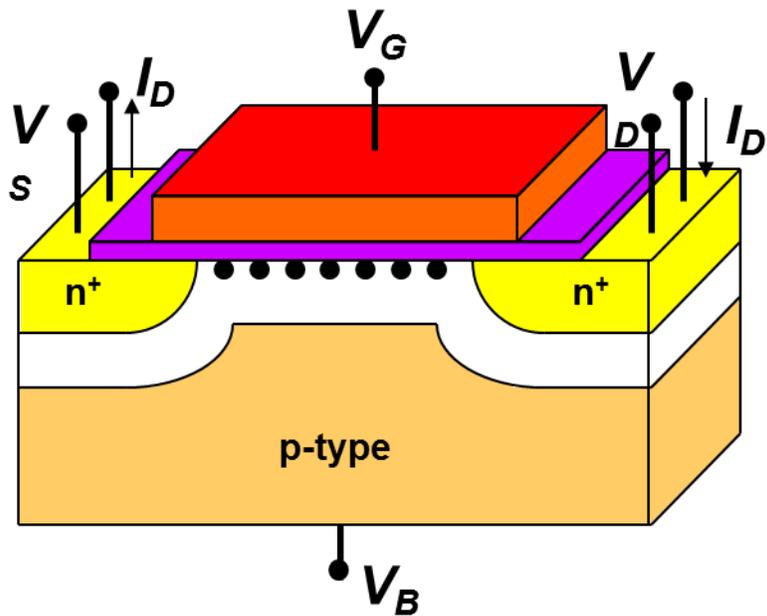
2-Terminal



4-Terminal



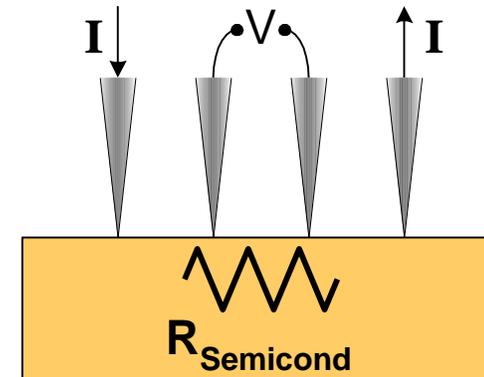
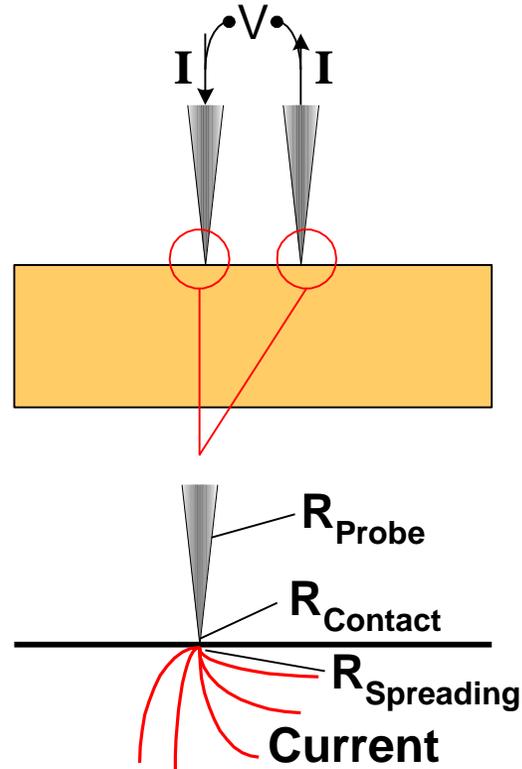
Four-Terminal/Kelvin Measurements



Courtesy of J. Wang, ASU

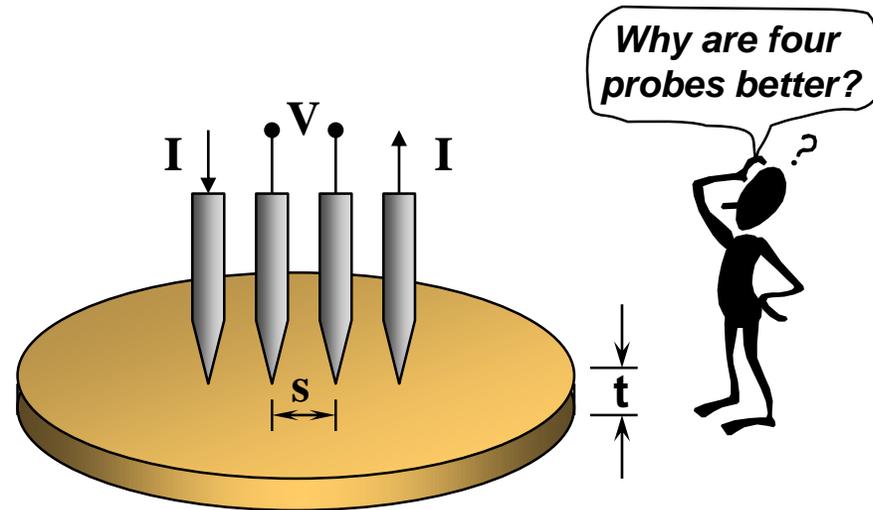
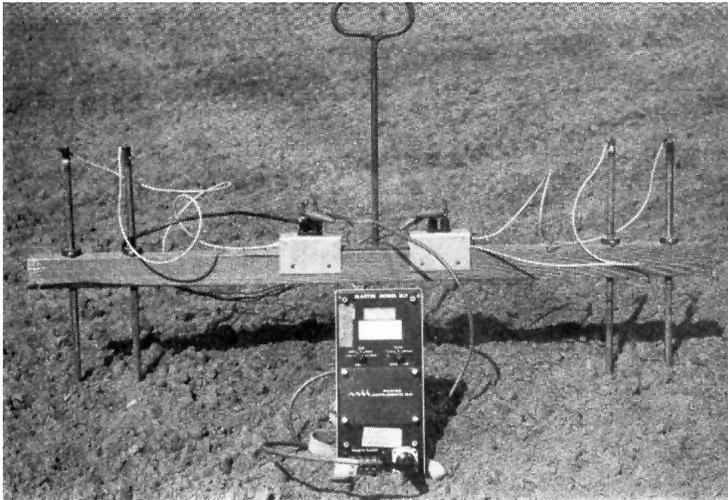
Kelvin Measurements

- Kelvin measurements refer to 4-probe measurements
- Two probes:
 - $2R_{\text{Probe}} + 2R_{\text{Contact}} + 2R_{\text{Spreading}}$
- Four probes:
 - R_{Semicond}



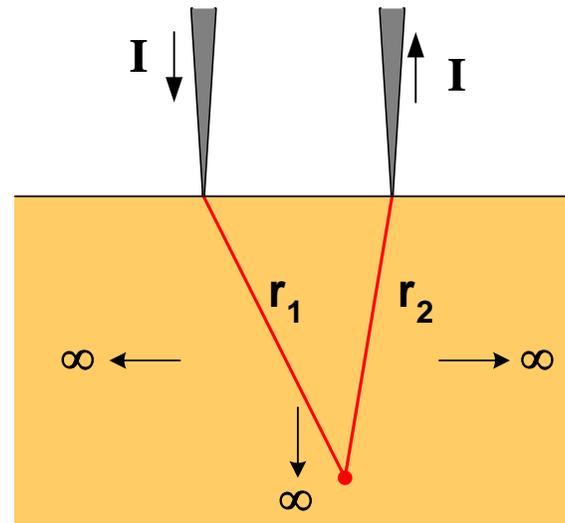
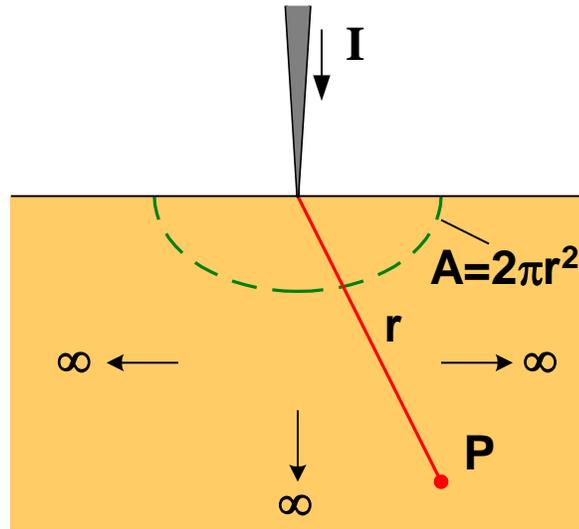
Four Point Probe

- The four point probe is used to determine the *resistivity* and *sheet resistance*



Four Point Probe

- Derivation of the basic four point probe equation



$$V = IR; \quad \varepsilon = J\rho = -\frac{dV}{dr}; \quad J = \frac{I}{A} = \frac{I}{2\pi r^2}$$

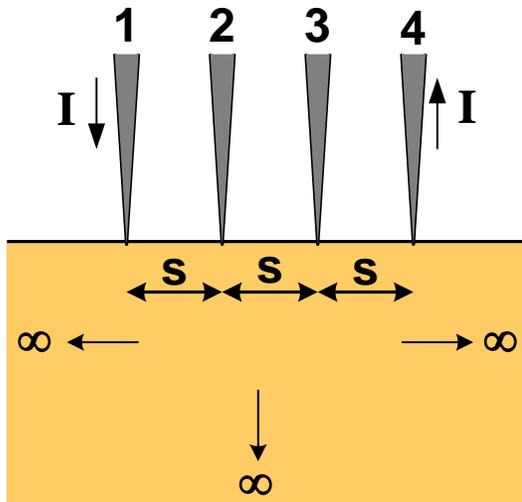
$$\int_0^V dV = -\frac{I\rho}{2\pi} \int_{\infty}^r \frac{dr}{r^2} \Rightarrow V = \frac{I\rho}{2\pi}$$

$$V = \frac{I\rho}{2\pi r_1} - \frac{I\rho}{2\pi r_2}$$

$$V = \frac{I\rho}{2\pi} \left(\frac{1}{r_1} - \frac{1}{r_2} \right)$$

Four Point Probe

- For four *in-line* probes



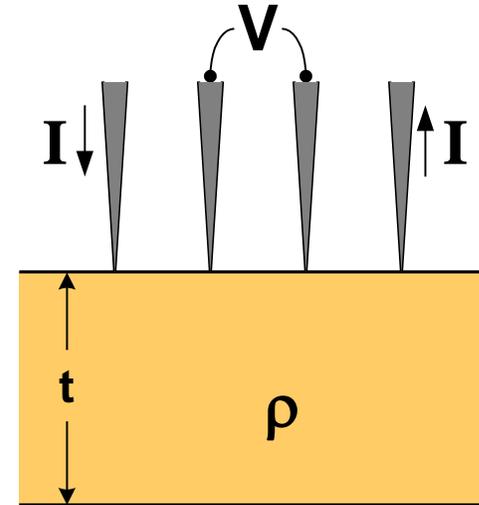
$$V_2 = \frac{I\rho}{2\pi} \left(\frac{1}{s} - \frac{1}{2s} \right); \quad V_3 = \frac{I\rho}{2\pi} \left(\frac{1}{2s} - \frac{1}{s} \right)$$

$$V = V_{23} = V_2 - V_3 = \frac{I\rho}{2\pi} \left(\frac{1}{s} - \frac{1}{2s} - \frac{1}{2s} + \frac{1}{s} \right) = \frac{I\rho}{2\pi s}$$

$$\rho = 2\pi s \frac{V}{I} \quad \Omega\text{-cm}$$

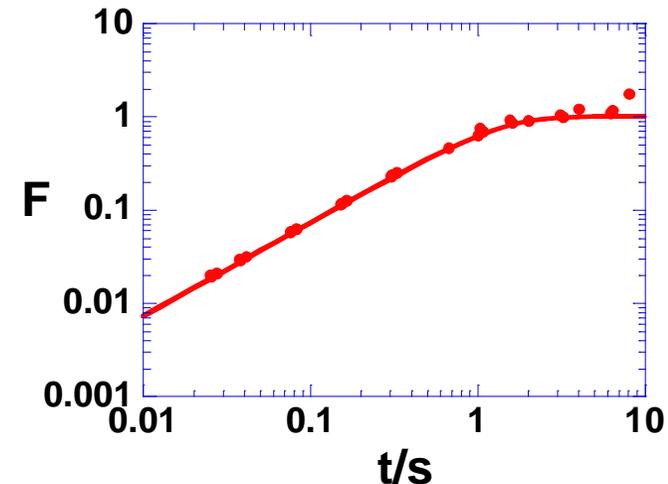
Four Point Probe

- Since wafers are not infinite in extent, need to correct for
 - Conducting/non-conducting bottom boundary
 - Wafer thickness
 - Nearness to wafer edge
 - Wafer size
- For *non-conducting* bottom surface boundary

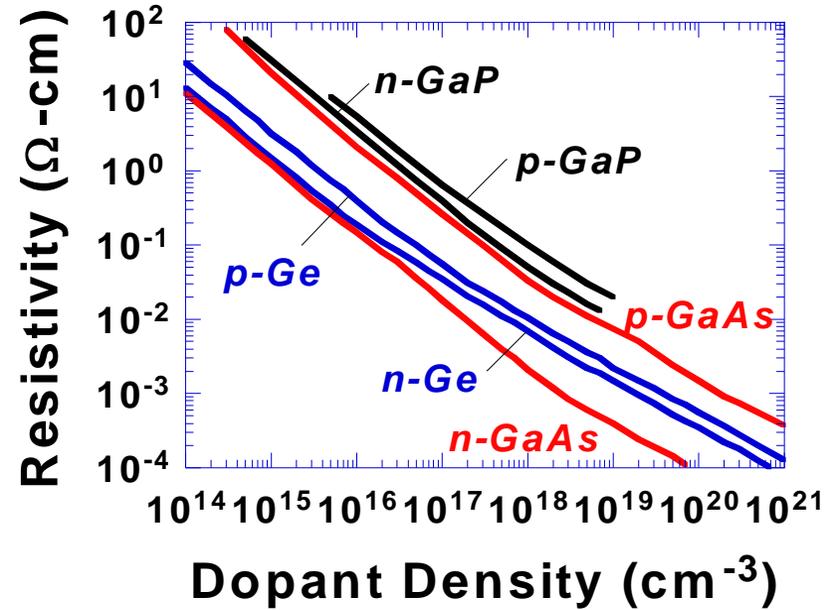
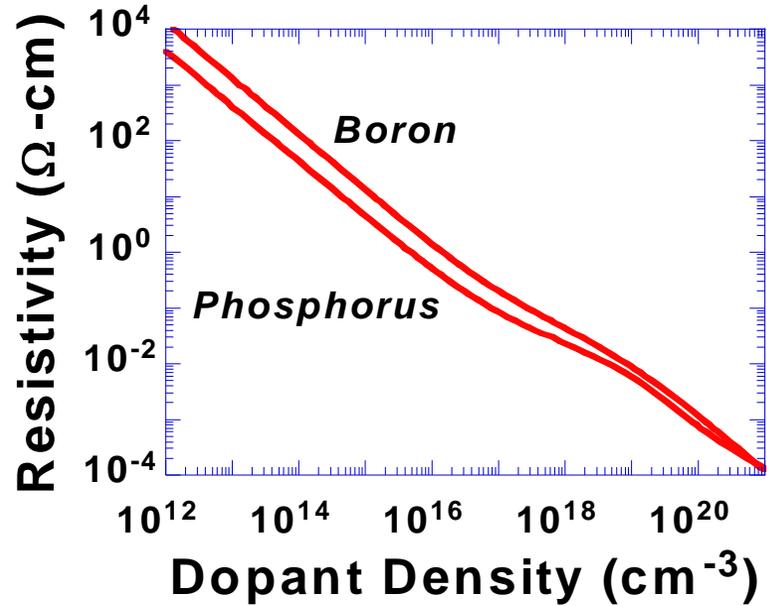


$$\rho = 2\pi s F \frac{V}{I} (\Omega \cdot \text{cm})$$

$$F = \frac{t/s}{2 \ln[\sinh(t/s)/\sinh(t/2s)]}$$



Resistivity



Thin Layers

- Consider a thin film on an insulator
 - Metal layer on insulator
 - Poly-Si layer on insulator
 - n on p or p on n

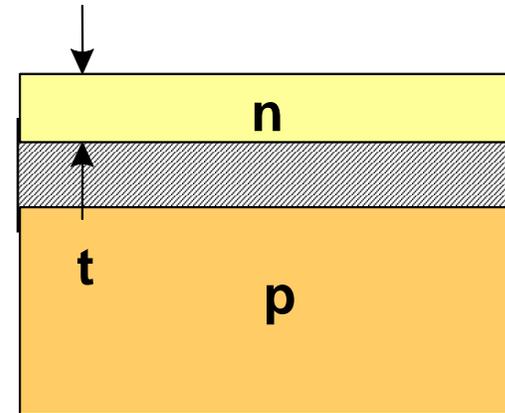
$$F = \frac{t/s}{2\ln[\sinh(t/s)/\sinh(t/2s)]}$$

Usually $t \ll s$

Recall $\sinh x \cong x$ for $x \ll 1$

$$\therefore F \approx \frac{t/s}{2\ln(2)}$$

$$\rho = 2\pi s \frac{t/s}{2\ln 2} \frac{V}{l} = \frac{\pi}{\ln 2} t \frac{V}{l} = 4.532t \frac{V}{l}$$



What Is Sheet Resistance?

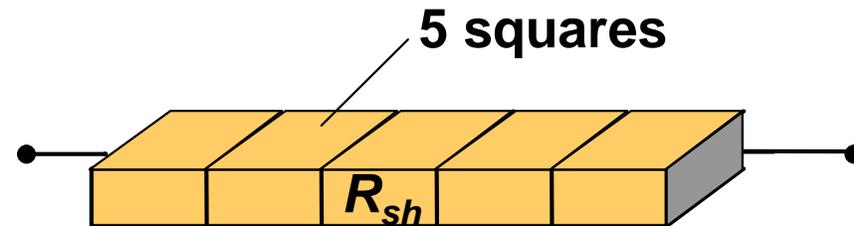
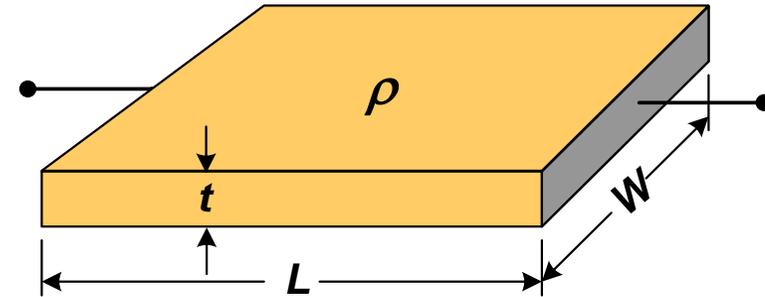
- The resistance between the contacts is

$$R = \frac{\rho L}{A} = \frac{\rho}{t} \frac{L}{W} \text{ ohms}$$

- L/W has no units
- ρ/t should have units of ohms
- But . . . $R \neq \rho/t$!
- Sheet resistance $R_{sh} = \rho/t$ (ohms/square)

$$R = R_{sh} \times \text{number of squares (ohms)}$$

- Resistance independent of the size of the square



Sheet Resistance

$$\rho = \frac{\pi}{\ln 2} t \frac{V}{I}$$

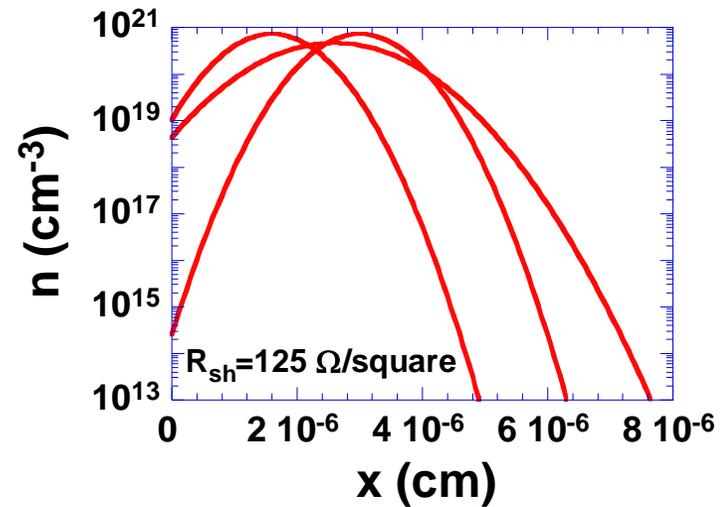
- Frequently do not know t
 - Ion implanted layer
 - Diffused layer
 - Metal film
 - Poly-Si layers
- Define *sheet resistance* R_{sh}
- For uniformly-doped layer

$$R_{sh} = \frac{\rho}{t} = \frac{1}{\sigma t} = \frac{\pi}{\ln 2} \frac{V}{I}$$

Sheet Resistance

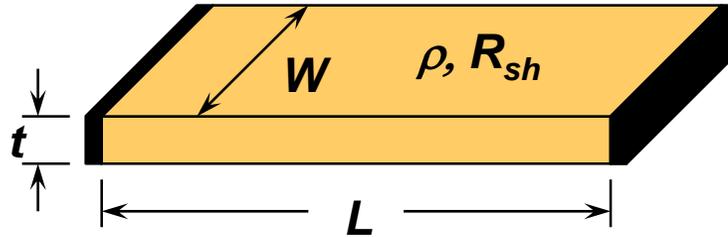
- For *non-uniformly* doped layers

$$R_{sh} = \frac{1}{\int_0^t \sigma dx} = \frac{1}{q \int_0^t n \mu_n dx}$$



Sheet Resistance

- ◆ Sheet resistance ρ_s depends on the total number of implanted or diffused impurities and on the layer thickness



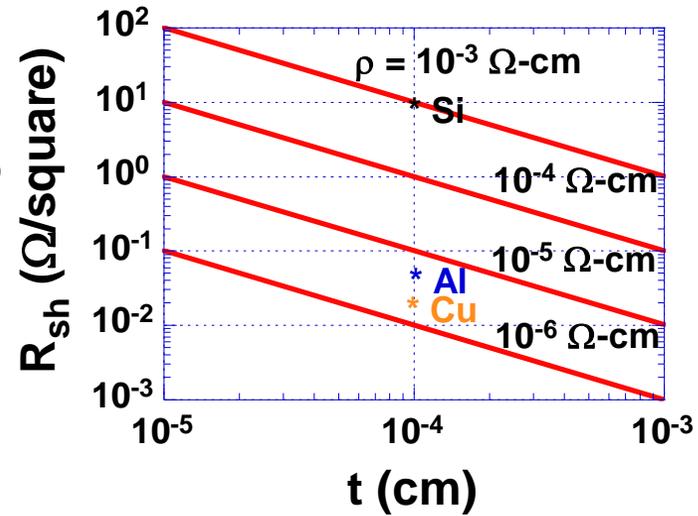
Uniformly doped:

$$R_{sh} = \frac{\rho}{t} = \frac{1}{\sigma t} = \frac{1}{qn\mu_n t} \text{ Ohms / square}$$

Non-uniformly doped:

$$R_{sh} = \frac{1}{q \int_0^t n\mu_n dx} \text{ Ohms / square}$$

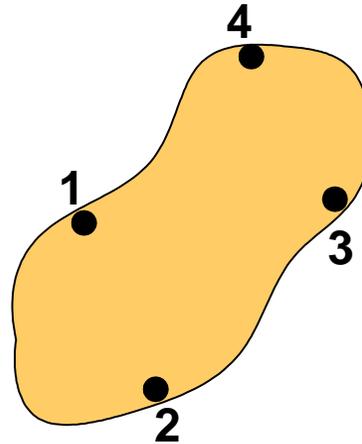
$$R = \frac{R_{sh} L}{W} \text{ Ohms}$$



van der Pauw Measurements

- Instead of a four-point probe, one can use an arbitrarily shaped sample
 - Current flows through two adjacent contacts
 - Voltage is measured across the other two contacts

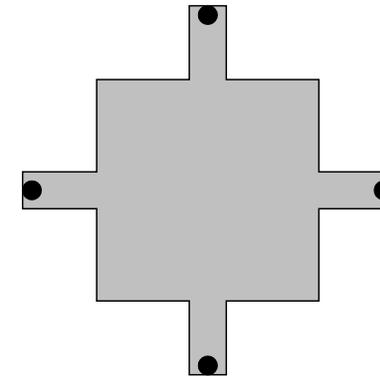
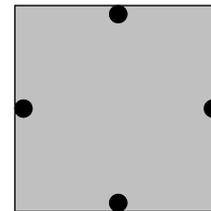
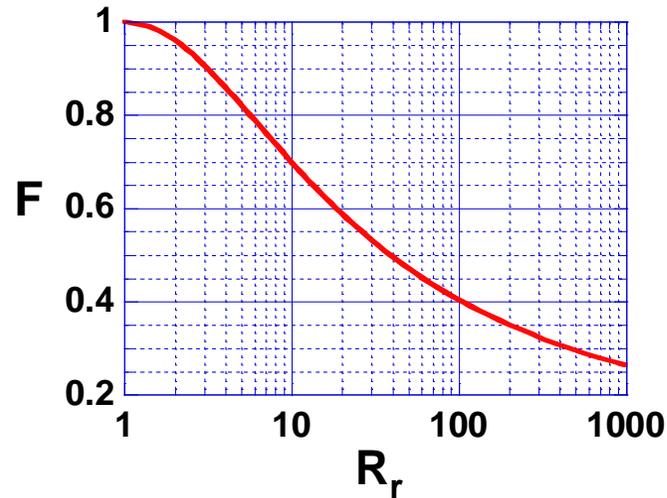
$$\rho = \frac{\pi t}{\ln 2} F\left(\frac{R_{12,34} + R_{23,41}}{2}\right); \quad R_{12,34} = \frac{V_{34}}{I_{12}}; \quad R_{23,41} = \frac{V_{41}}{I_{23}}$$



van der Pauw Measurements

- F function is determined from

$$\frac{R_r - 1}{R_r + 1} = \frac{F}{\ln 2} \cosh^{-1} \left(\frac{\exp(\ln 2 / F)}{2} \right) \quad R_r = \frac{R_{12,34}}{R_{23,41}}$$

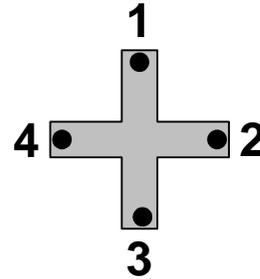


For symmetrical samples, e.g., circles or squares, $F = 1$

$$\rho = \frac{\pi t}{\ln 2} R_{12,34}; R_{sh} = \frac{\pi}{\ln 2} R_{12,34}$$

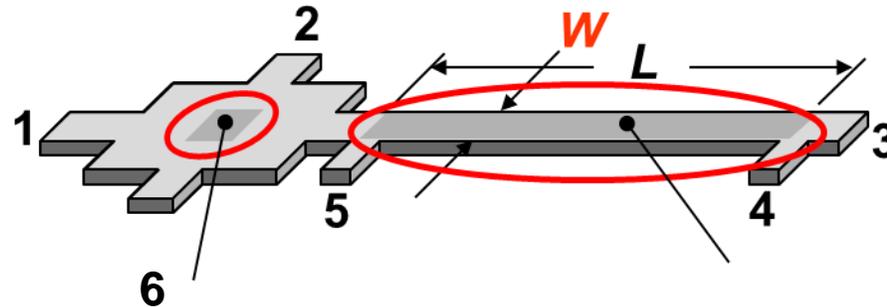
Line Width

□ Greek Cross



$$R_{sh} = \frac{\pi}{\ln 2} \frac{V_{34}}{I_{12}}$$

□ Cross bridge test structure



$$R_{sh} = \frac{\pi}{\ln(2)} \frac{V_{12}}{I_{65}}; R_{line} = \frac{V_{54}}{I_{13}} = R_{sh} \frac{L}{W} \Rightarrow \boxed{W = R_{sh} \frac{L}{R_{line}}}$$

Used to determine line width W

Mobilities

- **Conductivity Mobility:** $\mu_p = 1/q\rho\rho$
 - Majority carrier mobility; need carrier concentration and resistivity
- **Drift Mobility:** $\mu_p = v_d/\epsilon$
 - Minority carrier mobility
 - Need drift velocity and electric field (Haynes-Shockley experiment)
- **Hall Mobility:** $\mu_H = R_H/\rho$
 - Need Hall measurement
- **MOSFET Mobility:**
 - MOSFET mobility lowest, carriers are scattered at the Si-SiO₂ interface
 - Interface is microscopically rough

The Electron Mobility characterizes how quickly an electron can move through a solid Material when pulled by an applied Electric Field

□ Electron/hole mobility is a measure of carrier scattering in semiconductor materials

□ Lattice scattering

- Silicon atoms

□ Ionized impurity scattering

- Dopant atoms

□ Interface scattering

- Surface roughness at SiO₂/Si interface

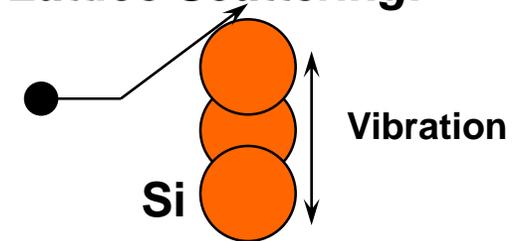
□ Silicon bulk

- $\mu_n \approx 3 \mu_p$

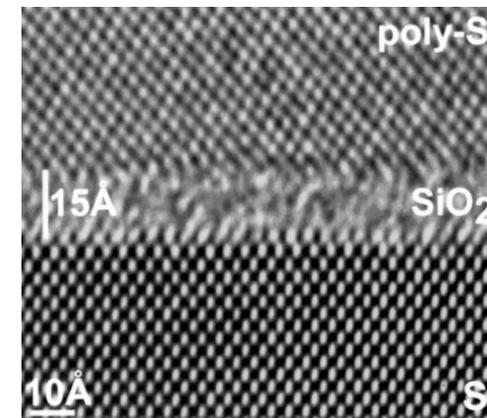
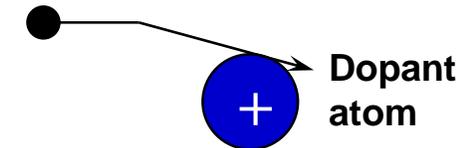
- MOSFET mobility (effective mobility) ≈ 0.3 bulk mobility

$$\frac{1}{\mu} = \frac{1}{\mu_l} + \frac{1}{\mu_i} + \frac{1}{\mu_s}$$

Lattice Scattering:



Ionized Impurity Scattering:

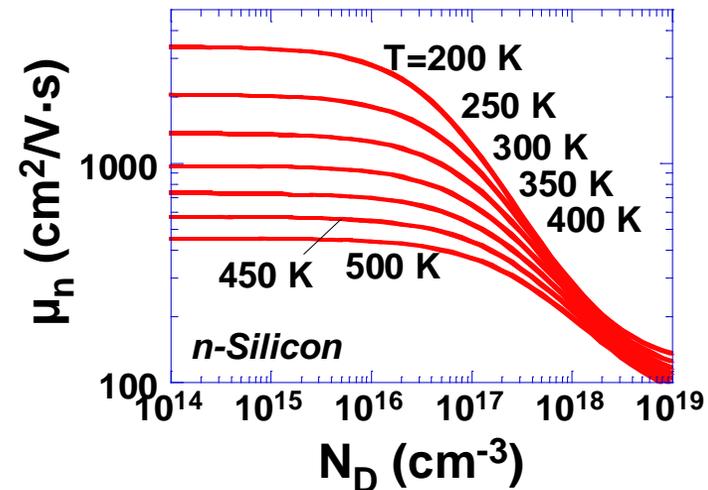
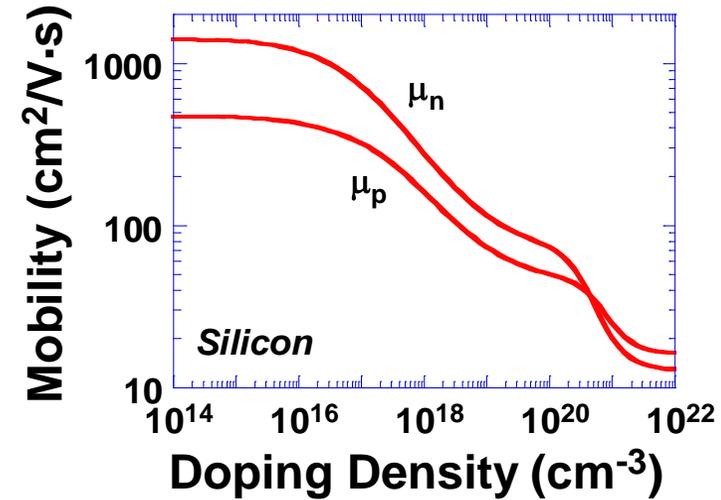
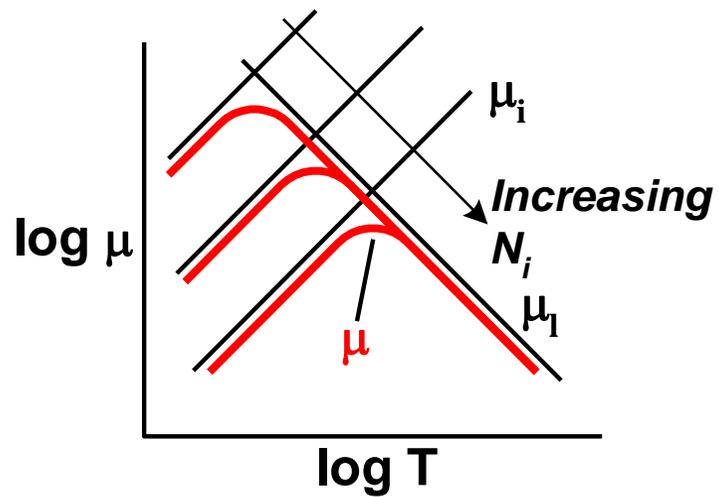


Courtesy of M.A. Gribelyuk, IBM.

Mobilities

- For bulk semiconductors, lattice and ionized impurity scattering dominate the mobility

$$\mu_l = T^{-1.5}; \mu_i = \frac{T^{1.5}}{N_i}$$



Why are Hall Effect Measurements important for Electrical Characterization?

A Hall effect measurement System using van der Pauw sample configuration can actually be used to determine quite a few material parameters

Hall Effect Measurements allow determination of:

- Hall voltage (V_H)
- Hall coefficient (R_H)
- Conductivity type (**n or p type**)
- Charge carrier density n_i ($\#/cm^3$)
- Carrier mobility μ ($cm^2/V\cdot s$)
- Resistivity
- Magnetoresistance

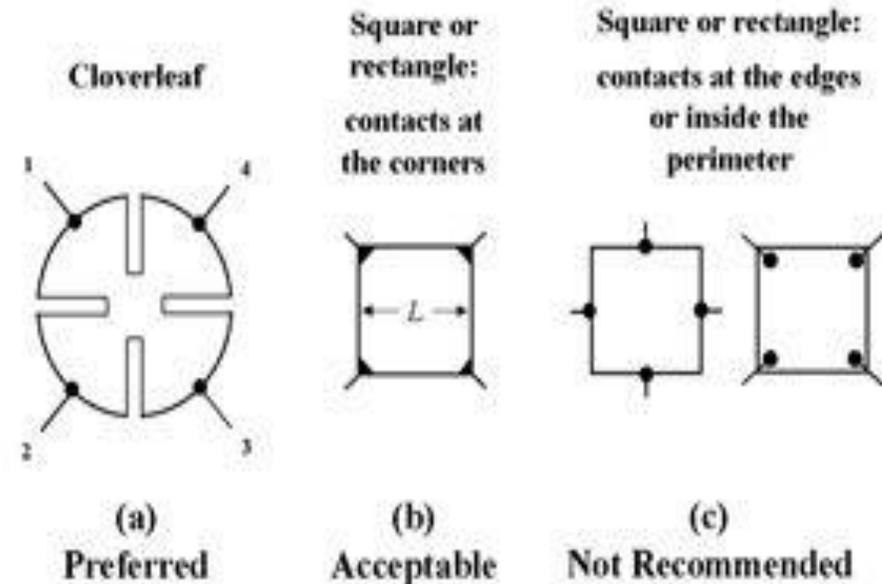


Figure 4

Recommended van der Pauw Sample Geometry according to National Institute of Standards & Technology (NIST)



Physical Property Measurement System -PPMS From Quantum Design for Hall Effect Measurement of MOF films

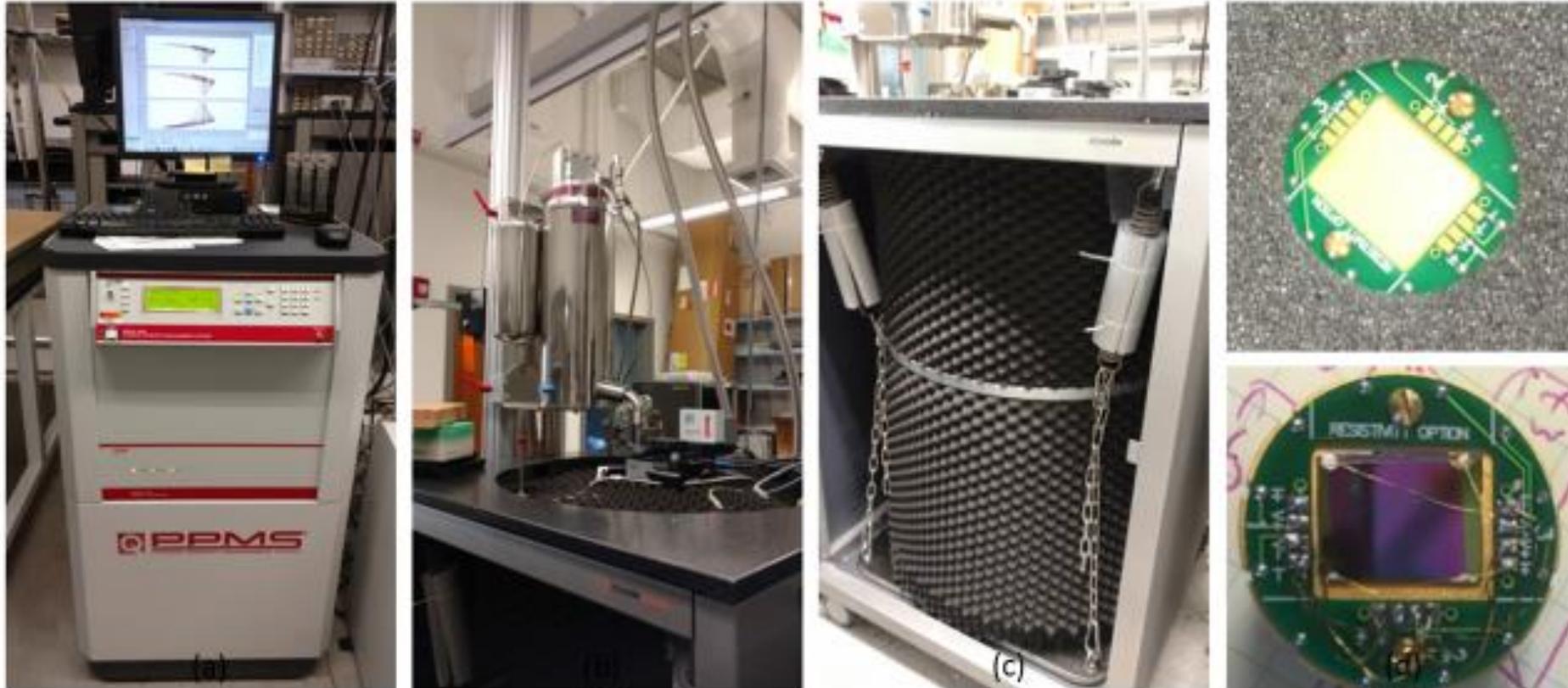
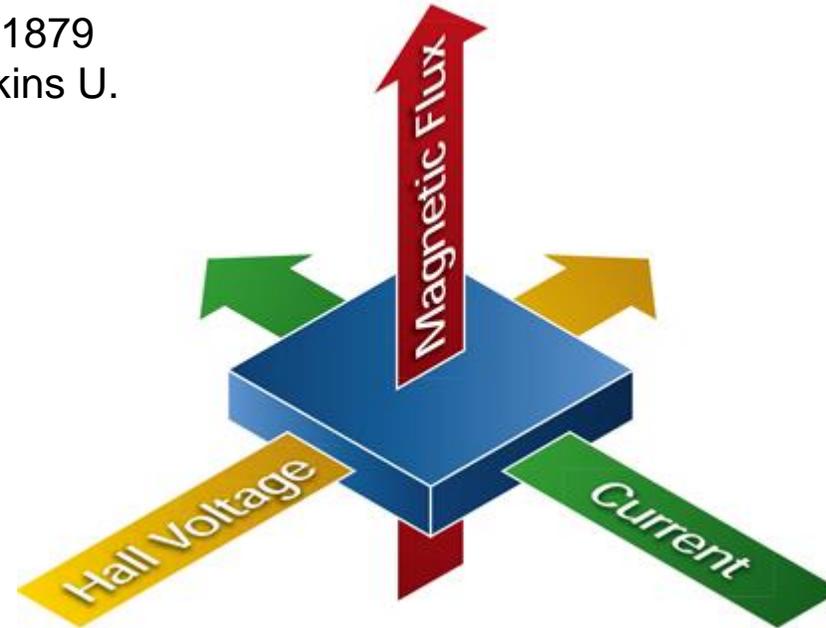


Figure. (a-c) Photographs of PPMS equipment with magnetic fields up to 9 tesla and temperature range of 1.9 K ~ 400 K. (d) Photographs of Resistivity measurement pucks.



Principle of Hall Effect Measurement

Hall Effect discovered by Edwin Hall in 1879
During his PhD research at Johns Hopkins U.

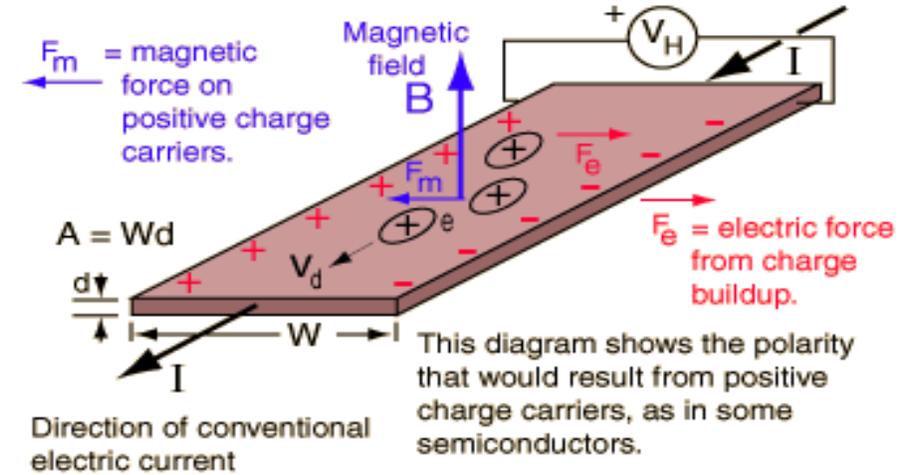
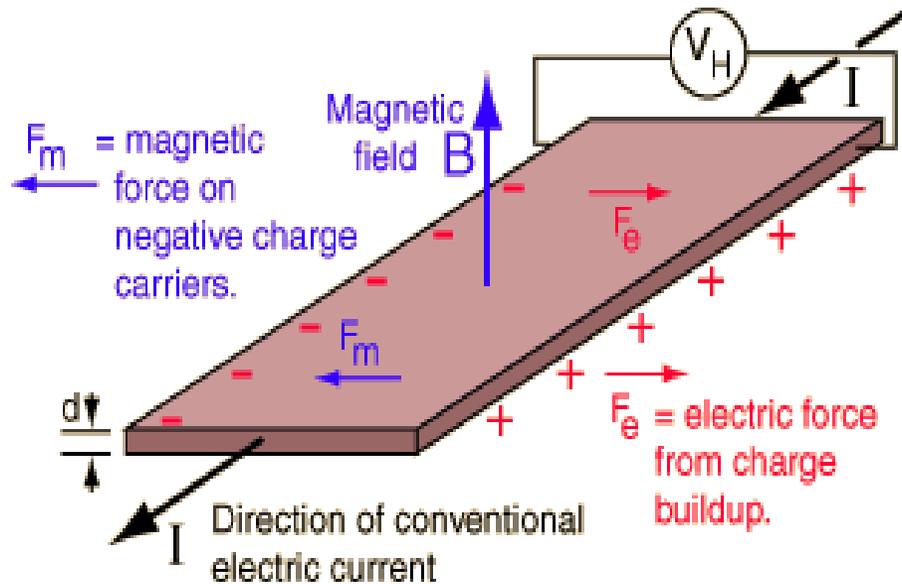


The underlying physics is the Lorentz force, that is, the force on a point charge due to electromagnetic fields.

A magnetic field through a sample and a current along the length of the sample creates an electrical current perpendicular to both the magnetic field and the current, which in turn creates a transverse voltage that is perpendicular to both the magnetic field and the current.



Basic Physics of Hall Effect



Hall Voltage for Negative Charge Carriers

Transverse Hall Voltage for Positive Charge Carriers

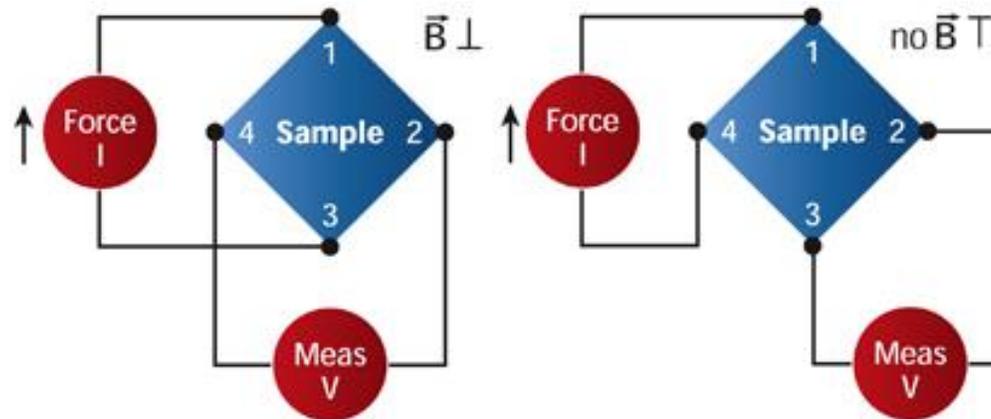
- **The Hall effect is an extension of the Lorentz force**, which describes the force exerted on a charged particle—such as an electron—moving through a magnetic field. If the magnetic field is oriented perpendicular to the direction of the electron's motion, the electron experiences a force that is perpendicular to both the direction of motion and the orientation of the magnetic field.
- The direction of the Lorentz force is governed by a **right-hand rule** that takes into account the direction in which the electron is traveling relative to the magnetic field.
- If an electric current flows through a conductor in a magnetic field, the magnetic field exerts a transverse force on the moving charge carriers which tends to push them to one side of the conductor. This is most evident in a thin flat conductor as illustrated. A buildup of charge at the sides of the conductors will balance this magnetic influence, producing a measurable voltage between the two sides of the conductor.



Hall Effect Measurement Protocol

- To determine carrier mobility measure the Hall voltage (V_H) by forcing both a magnetic field perpendicular to the sample and a current through the sample.
- The combination of the current flow (I) and the magnetic field (B) causes a transverse current. The resulting potential (V_H) is measured across the device – the transverse Hall Voltage.
- Accurate measurements of both the sample thickness (t) and its resistivity (ρ) are also required.
- With these five parameters (B , I , V_H , t , and resistivity (ρ), the Hall mobility can be calculated.

$$\mu H = \frac{|V_H t|}{BI\rho}$$

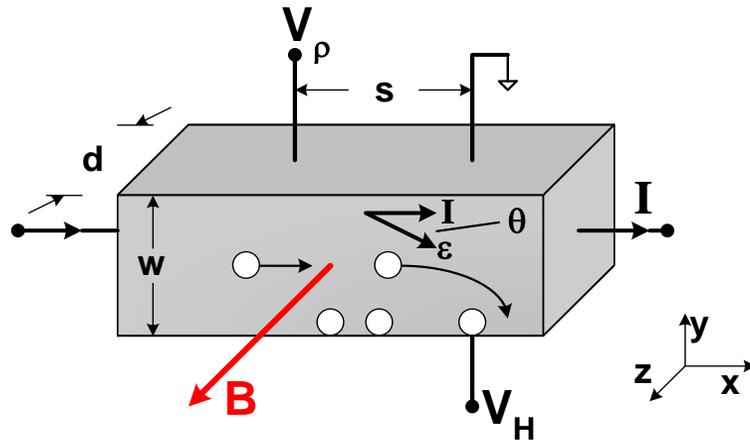


Hall effect voltage vs. van der Pauw resistance measurement configurations

in Hall effect measurement, the current is forced on opposite nodes of the sample and then the voltage is measured on the other opposite nodes so the force and the measure contact points are interlaced

Hall Effect

- Hall effect is commonly used during the development of new semiconductor material



$$\vec{F} = q(\vec{\varepsilon} + \vec{v} \times \vec{B}) \quad \text{Lorentz Force}$$

$$I = qA p v_x = q w d p v_x$$

$$\varepsilon_y = B v_x = \frac{B I}{q w d p}$$

$$\int_0^{V_H} dV = V_H = -\int_w^0 \varepsilon_y dy = -\int_w^0 \frac{B I}{q w d p} dy = \frac{B I}{q d p}$$

$$R_H = \frac{dV_H}{B I} \quad \text{Hall coefficient}$$

Hall Effect

□ Resistivity

$$\rho = \frac{dw}{s} \frac{V_p}{l}$$

□ Carrier density

$$p = \frac{r}{qR_H}; n = -\frac{r}{qR_H}$$

($r \sim 1 - 2$, Hall scattering factor)

□ Mobility

$$p = \frac{r}{qR_H} \Rightarrow q\mu_p p = \sigma = \frac{r\mu_p}{R_H} = \frac{\mu_H}{R_H} \Rightarrow \mu_H = |\sigma R_H| = r\mu_p$$

MOSFET *Effective* Mobility

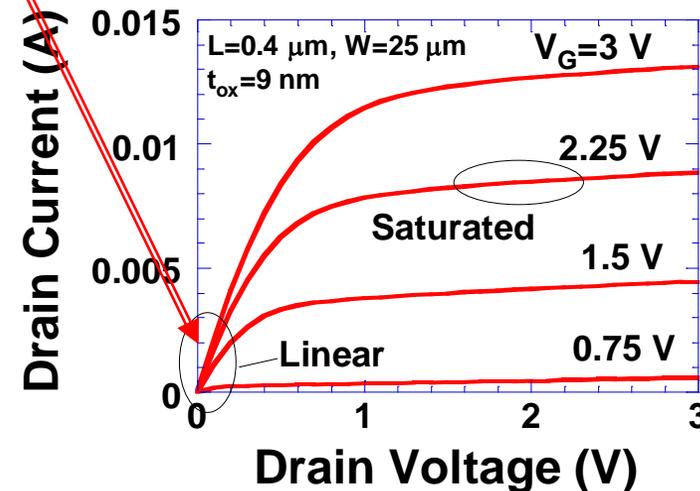
- **Effective mobility** determined from drain current – drain voltage characteristics
- The MOSFET drain current for small V_D (50 - 100 mV) is

$$I_D = (W/L)\mu_{eff}Q_N V_D \approx (W/L)\mu_{eff}C_{ox}(V_G - V_T)V_D$$

- Determine $g_d = \Delta I_D / \Delta V_D$ for low V_D
- Solve for μ_{eff}

$$\mu_{eff} = \frac{Lg_d}{WQ_N} \approx \frac{Lg_d}{WC_{ox}(V_G - V_T)}$$

- Need g_d , Q_N , V_T



Motivation: It has been established that MOF Films exhibit fairly large Seebeck Coefficient Values

- Introduction
- Principle of Seebeck Coefficient Measurements
 - Differential method
 - Integral method
- Seebeck Coefficient Measurements in Bulk and Thin Films
 - In-plane direction measurement
 - Vertical direction measurement
- Applications
- Conclusions

■ Thermoelectric Effect

1. Seebeck Effect

A electrical potential (voltage) within a p-n junction is generated due to a temperature gradient.

$$V = \int_{T_1}^{T_2} S_{AB} dT$$

2. Peltier Effect

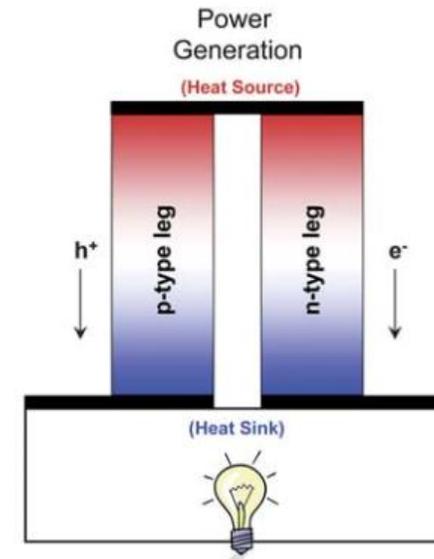
Heat is absorbed or released at the interface of p-n junction when a current flows across the interface.

$$\pi = I/q$$

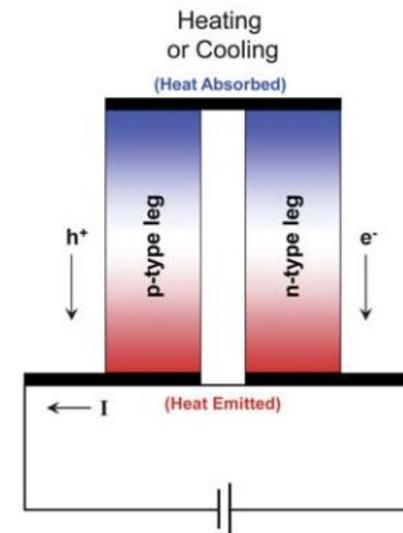
3. Thompson Effect

Heat is absorbed or released in a single homogeneous conductor when a current passes through it in a temperature gradient.

$$q = \beta I \Delta T$$



Schematic of TE power generator



Schematic of TE refrigerator

Motivation

- ❑ The challenge for green renewable energy technologies is to increase conversion efficiency. This is true for Photovoltaics and Thermoelectrics.
- ❑ MOF Films may have the potential to constitute a new class of hybrid thermoelectric materials.
 - **Efficiency of Thermoelectric (TE) Materials**

The efficiency of TE power generator and TE refrigerator is expressed by ε and η :

$$\varepsilon = \frac{T_H - T_C}{T_H} \left[\frac{(1 + ZT)^{1/2} - 1}{(1 + ZT)^{1/2} + (T_C/T_H)} \right] \text{ (TE power generator)}$$

$$\eta = \frac{T_C [(1 + ZT)^{1/2} - T_C/T_H]}{(T_H - T_C) [(1 + ZT)^{1/2} + 1]} \text{ (TE refrigerator)}$$

Where T_C , T_H are hot-side, cold-side temperature, respectively. ZT is figure of merit.

▪ Efficiency of Thermoelectric (TE) Material

- The conversion efficiency of TE materials is related to a quantity, figure of merit ZT, which is defined as:

$$ZT = \frac{S^2 \sigma T}{\kappa_e + \kappa_L}$$

Where S: Seebeck coefficient

σ : Electrical conductivity

T: Temperature

κ_e : Thermal conductivity due to electrons

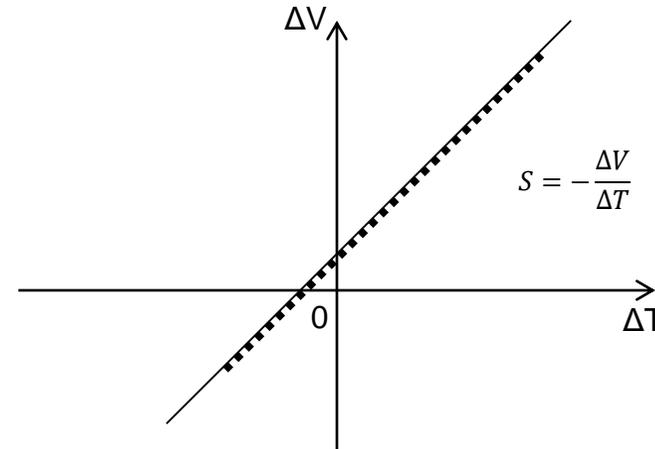
κ_L : Thermal conductivity due to phonons or lattice vibrations

Principle of Seebeck Coefficient Measurements

- **Differential method**

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

ΔT is kept small, usually 4~20 K.

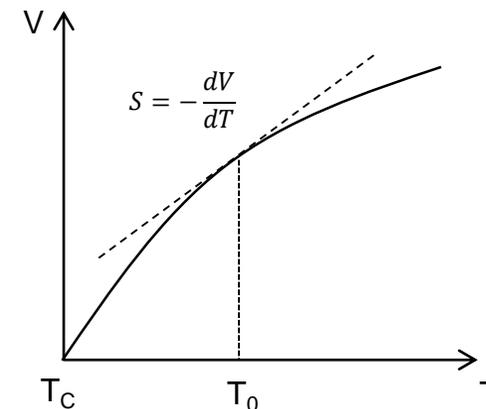


- **Integral method**

$$S = -\frac{dV}{dT}$$

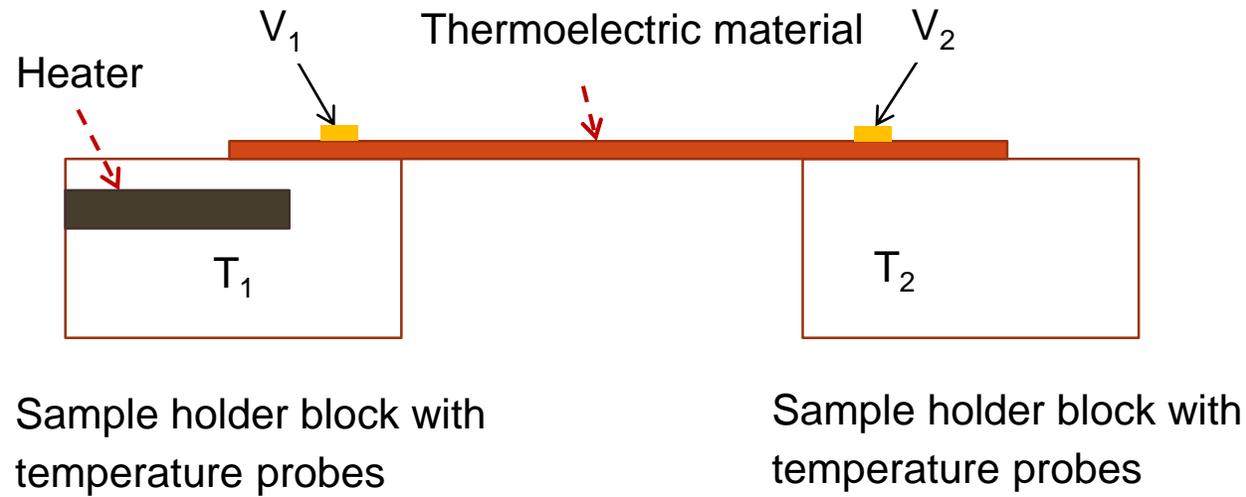
ΔT is varied slowly.

All voltage and temperature difference measurement should be measured simultaneously.



Seebeck coefficient measurement

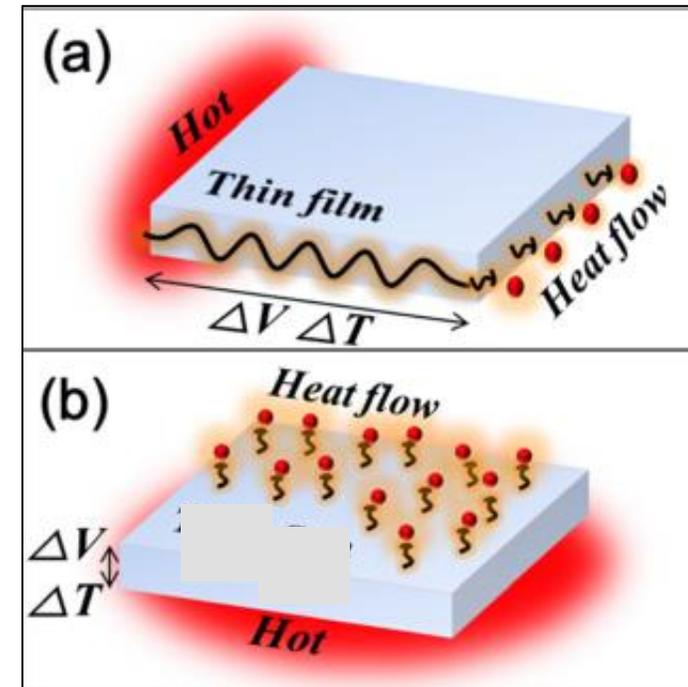
- **Typical Schematic Diagram of Seebeck Coefficient Measurements**



Schematic diagram of commercially available Seebeck Coefficient Measurement system.

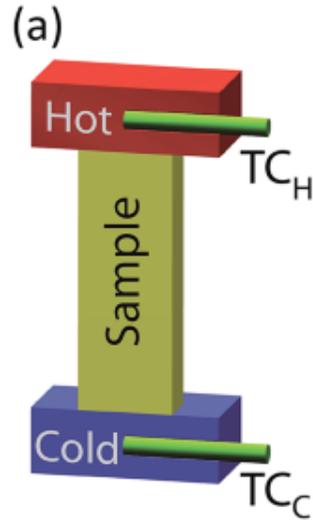
Seebeck Coefficient Measurements in Bulk Material and Thin Films

- **In-plane direction (horizontal) measurement**
For homogeneous thin film
- **Vertical direction measurement**
For heterogeneous film, bulk, superlattice structure

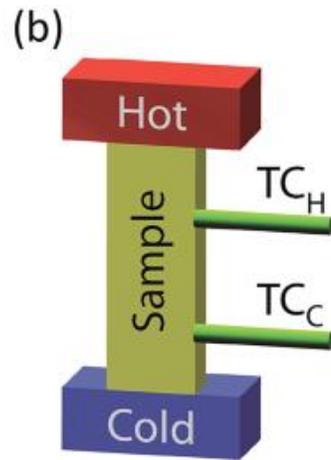


Seebeck coefficient measurement in different directions. (a) horizontal and (b) vertical heat flow of thermoelectric material.

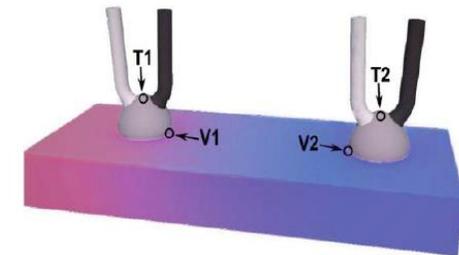
Seebeck Coefficient Measurements in Bulk Materials



- ✓ No reaction between thermocouple and sample
- ✓ Thermal and electrical contact resistance between thermocouple and sample results in error.
- ✓ Can be applied in scanning system.



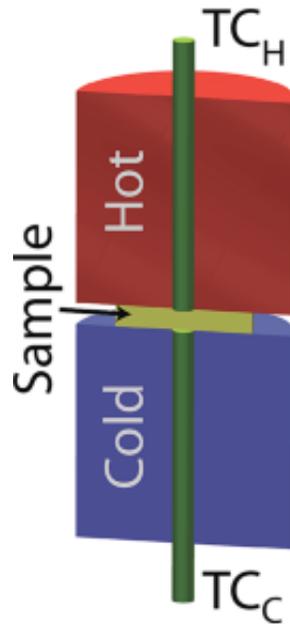
- ✓ Eliminates thermal contact resistance between thermocouple and sample.
- ✓ Cold finger effect
- ✓ Deformation, sample fracture or breakage may occur.
- ✓ Spatial variation issue



The thermocouple made with beads

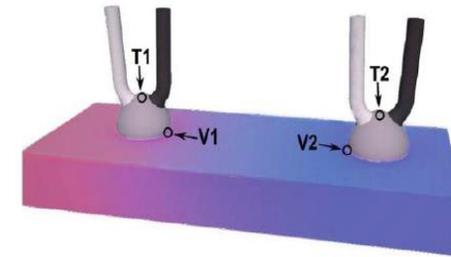
Different design for Seebeck coefficient measurement,
(a) 2-point geometry; (b) off-axis lateral design;

Seebeck Coefficient Measurements in Bulk Materials



Uniaxial design for Seebeck coefficient measurement

- ✓ Exclude cold finger effect
- ✓ Eliminate sample degradation
- ✓ Achieve isothermal contact between thermocouple and sample
- ✓ No spatial issue by using cross-wire thermocouple



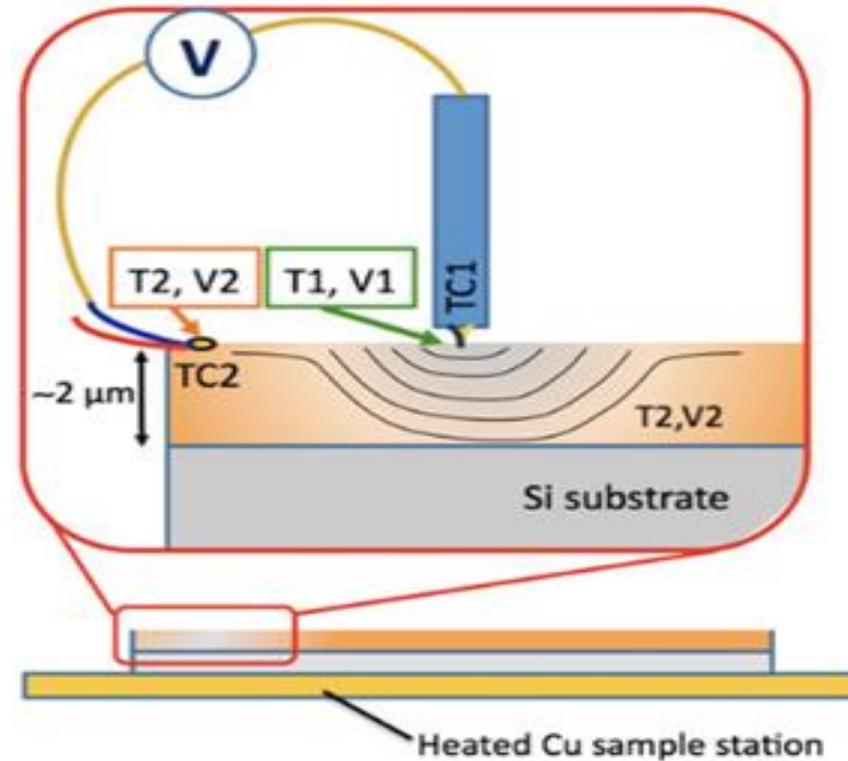
Thermocouple made with beads



Thermocouple with cross-wire geometry

The diameter of wire: 125 μm

- Seebeck Coefficient Measurements in Films



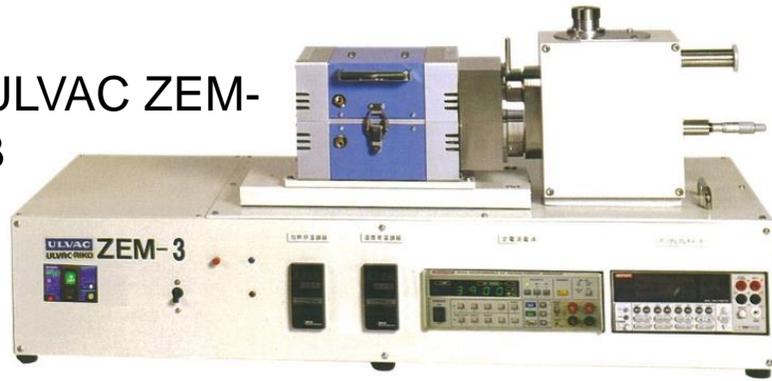
Schematic diagram of Seebeck coefficient measurement in thin film

Iwanaga, Shiho, and G. Jeffrey Snyder. "Scanning Seebeck Coefficient Measurement System for Homogeneity Characterization of Bulk and Thin-Film Thermoelectric Materials." *Journal of electronic materials* 41.6 (2012): 1667-1674

Applications

- Examples of Commercial Equipment for Seebeck Coefficient Measurements

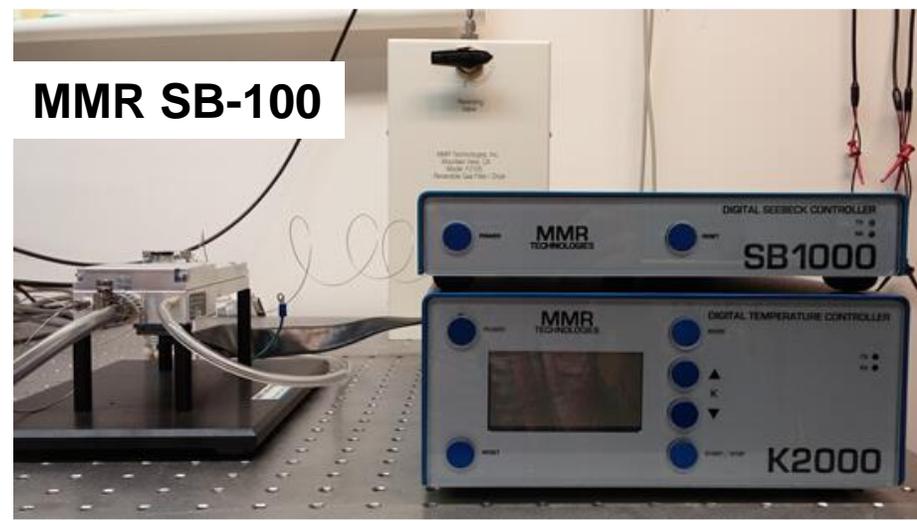
ULVAC ZEM-3



Linseis LSR-3

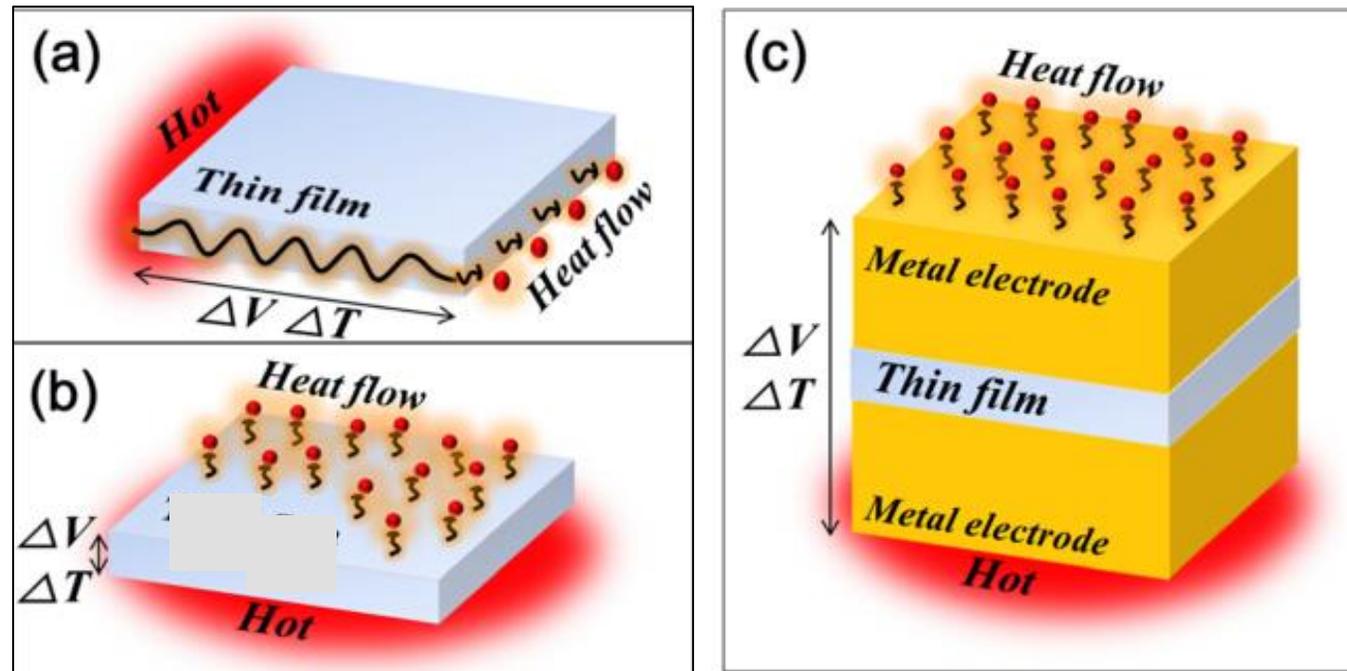


MMR SB-100

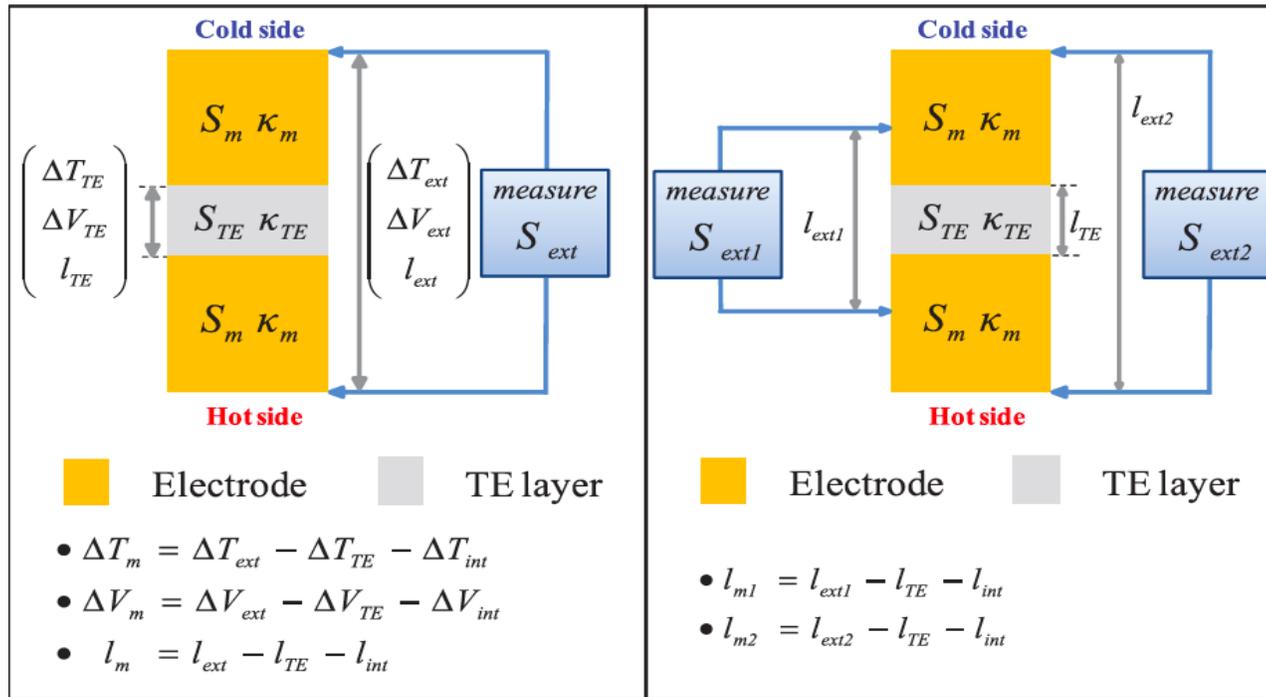


Applications

- Home-designed Devices for Seebeck Coefficient Measurement



Schematic illustration of the Seebeck voltage and temperature difference for (a) horizontal and (b) vertical heat flow of thermoelectric material. (c) Vertical heat flow across a film with metal electrodes. This structure causes a large temperature difference at both sides of the electrode when the electrode is thick enough



$$Q = -\kappa A \frac{\Delta T}{\Delta x}$$

$$\Delta T_{TE} : \Delta T_m : \Delta T_{int} = \frac{l_{TE}}{\kappa_{TE}} : \frac{l_m}{\kappa_m} : \frac{l_{int}}{\kappa_{int}}$$

$$S_{TE} = \frac{\Delta V_{TE}}{\Delta T_{TE}} = \frac{\Delta V_{ext} - \Delta V_m - \Delta V_{int}}{\Delta T_{TE}}$$

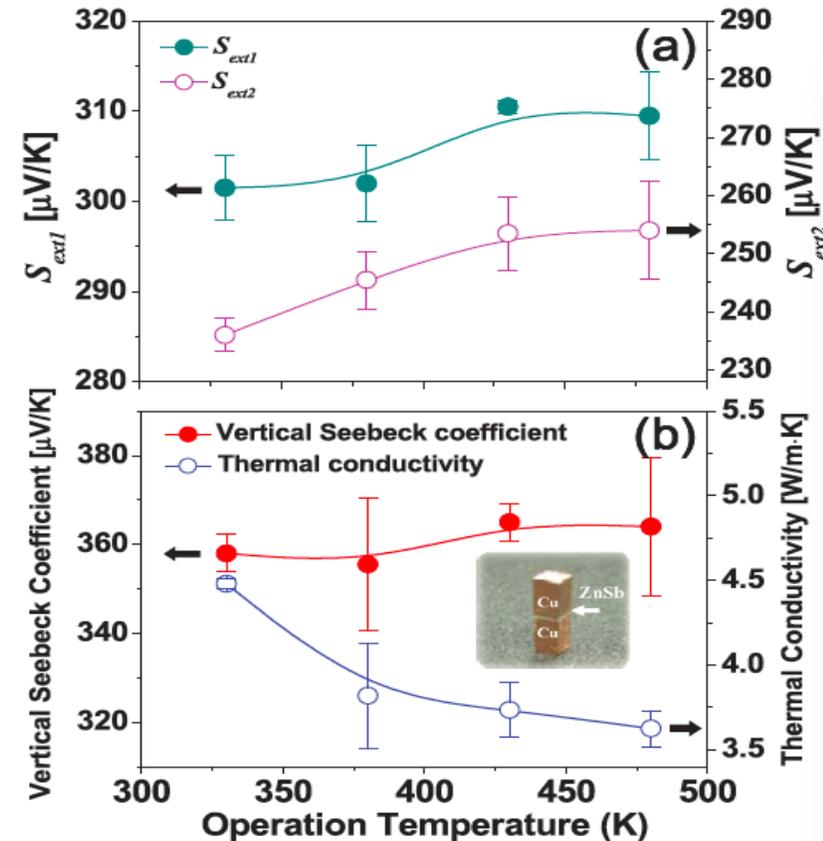
$$S_{TE} = \frac{S_{ext} \Delta T_{ext} - S_m \Delta T_m - S_{int} \Delta T_{int}}{\Delta T_{TE}}$$

$$S_{TE} = \frac{l_m}{l_{TE} \kappa_m} (S_{ext} - S_m) \kappa_{TE} + S_{ext}$$

Table. The meaning of each symbol

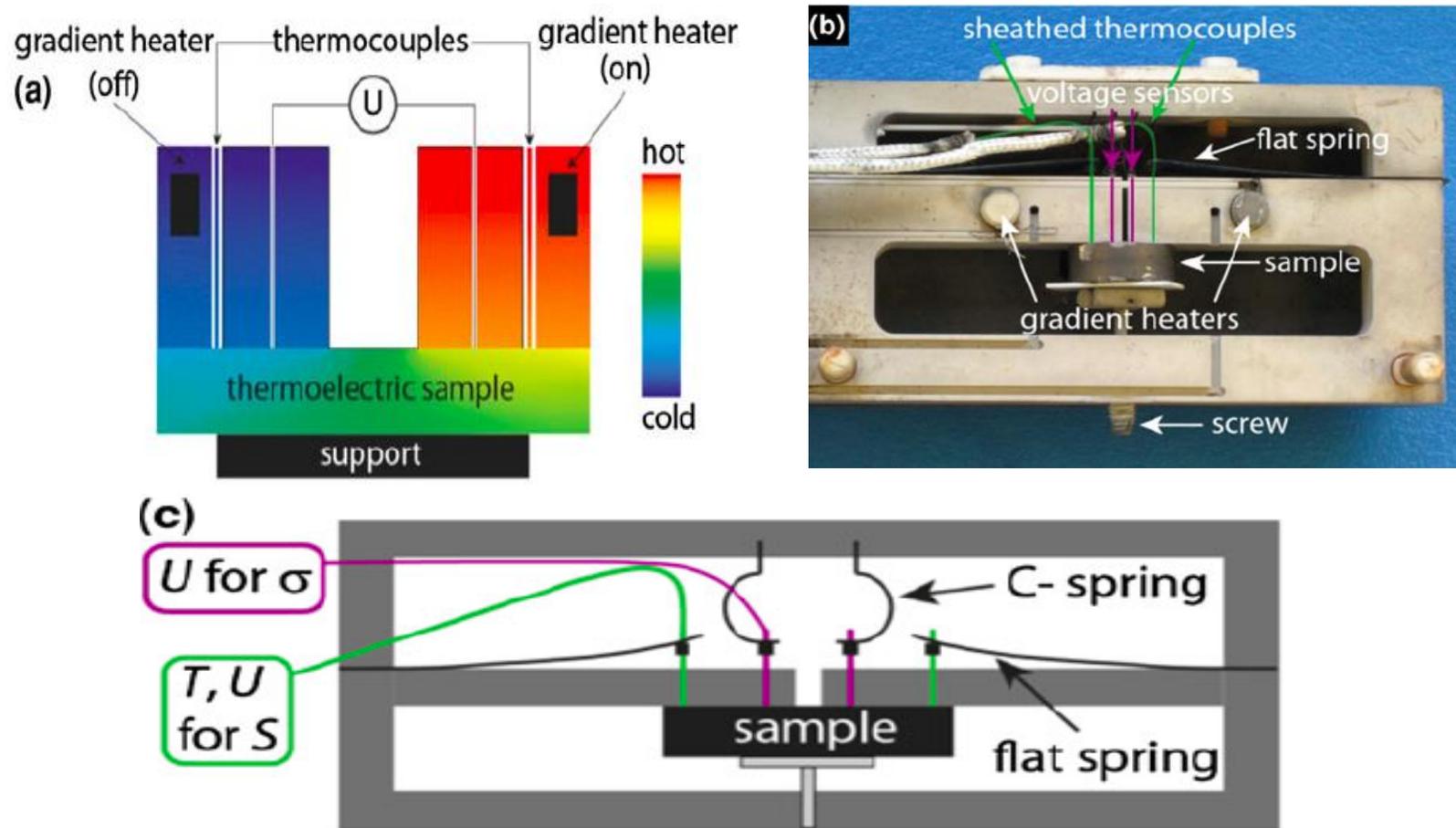
	Metal	TE sample	Interfacial layer	External structure
Temperature difference ΔT	ΔT_m	ΔT_{TE}	ΔT_{in}	ΔT_{ext}
Voltage difference ΔV	ΔV_m	ΔV_{TE}	ΔV_{in}	ΔV_{ext}
Thickness l	l_m	l_{TE}	l_{int}	l_{ext}
Seebeck coefficient S	S_m	S_{TE}	S_{int}	S_{ext}
Thermal conductivity κ	κ_m	κ_{TE}	κ_{int}	κS_{ext}

Experimental Results of Seebeck Coefficient in Sandwich Structures

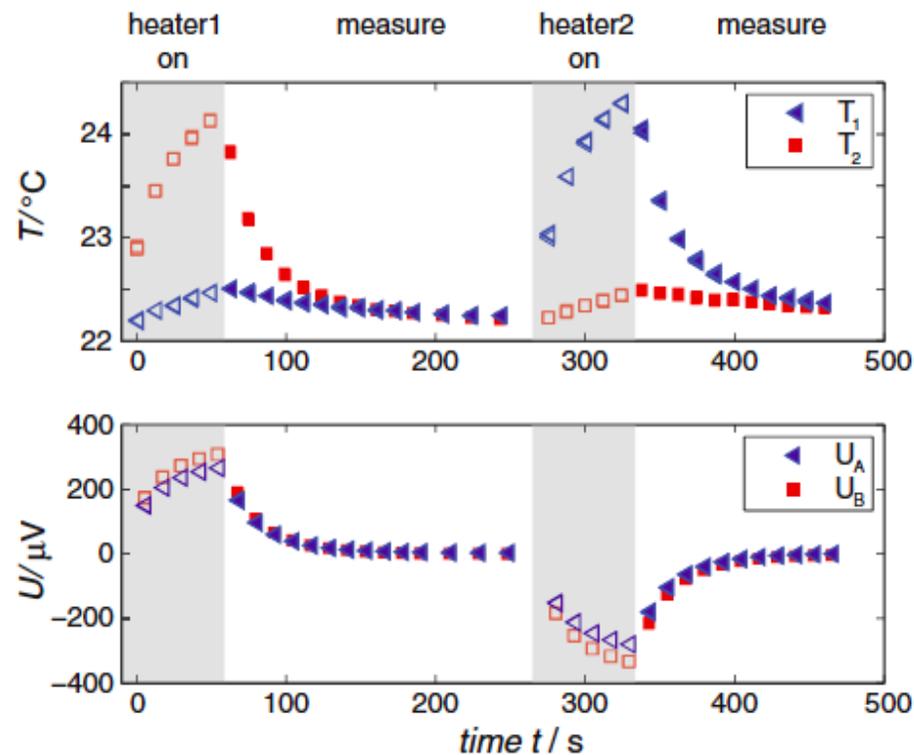


(a) The measured S_{ext1} and S_{ext2} values of the sandwich structure as a function of operation temperature, (b) the calculated vertical Seebeck coefficient and thermal conductivity of ZnSb film

■ Home-designed Devices for Seebeck Coefficient Measurements



(a) Schematic diagram of Seebeck coefficient measurement, (b) sample holder, (c) illustrates the mechanical and electrical connections



Measurement routine for determination of Seebeck coefficient

$$U_A = -(S - S_A)\Delta T$$

$$U_B = -(S - S_B)\Delta T$$

$$\frac{\partial U_A}{\partial \Delta T} = -(S - S_A),$$

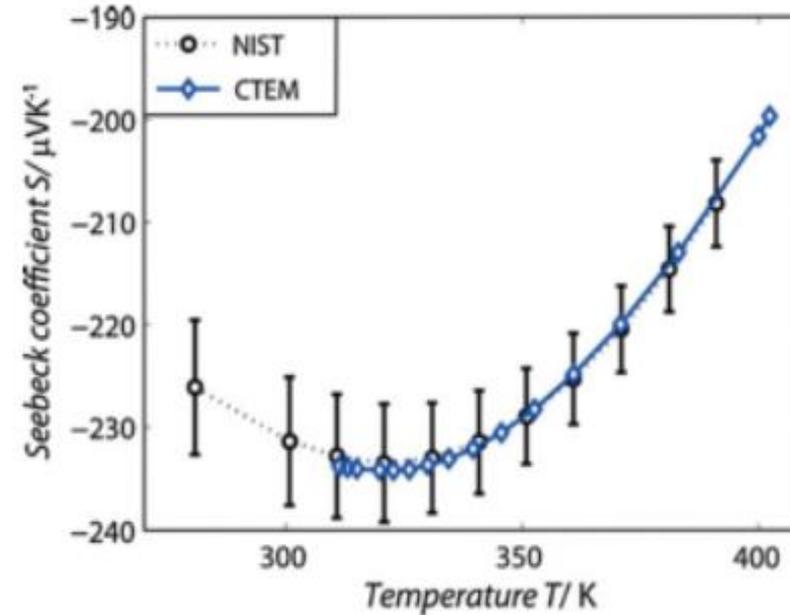
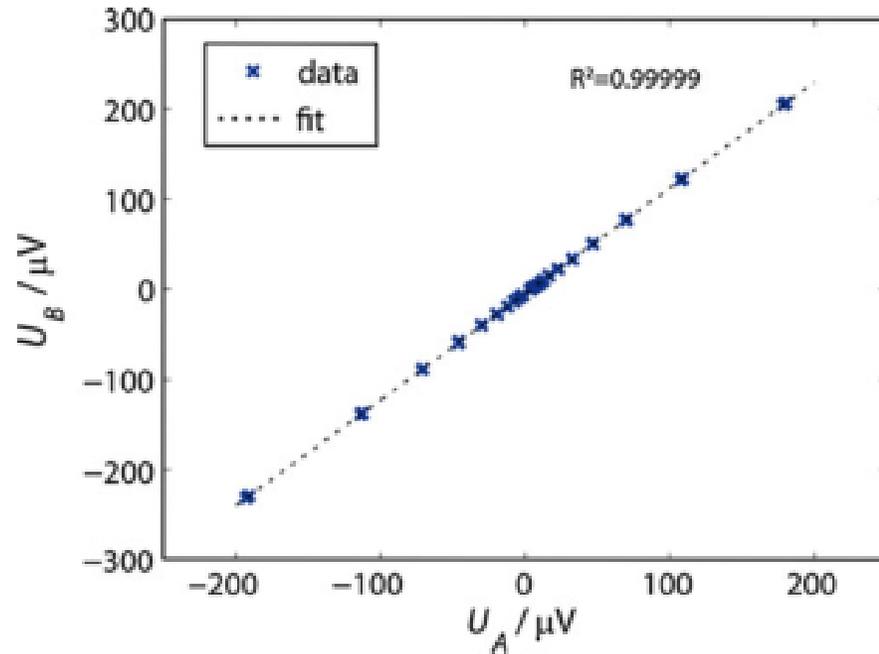
$$\frac{\partial U_B}{\partial \Delta T} = -(S - S_B)$$

$$S(\bar{T}) = \frac{S_{TC}(\bar{T})}{1 - \frac{\partial U_B}{\partial U_A}} + S_A(\bar{T})$$

Where

- ✓ $S_{TC} = S_B - S_A$,
- ✓ S_{TC} : Seebeck coefficient of the thermocouple as tabulated.
- ✓ S_A : the Seebeck coefficient of wire with more negative

Experimental Results of Seebeck Coefficient Measurements

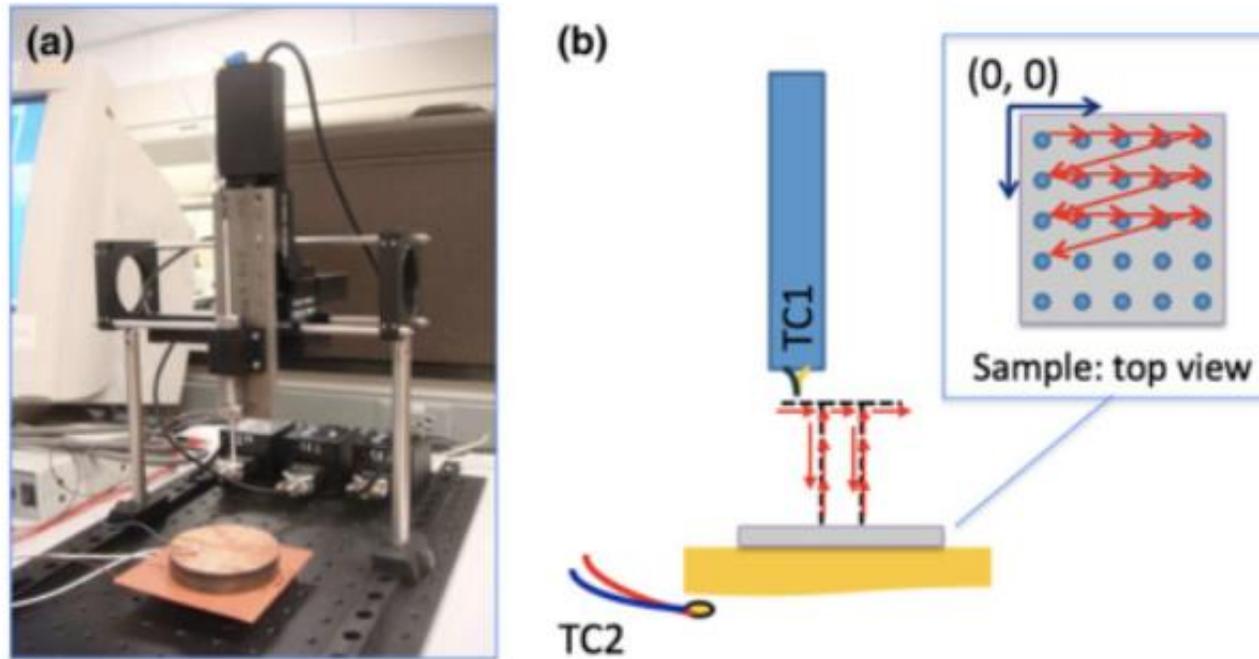


Plot of U_B versus U_A . Comparison of Seebeck coefficient measured from NIST SRM 3451 (Bi_2Te_{3+x}) using Custom-Designed system mentioned above

De Boer, J., et al. "High-temperature measurement of Seebeck coefficient and electrical conductivity." *Journal of electronic materials* 42.7 (2013): 1711-1718

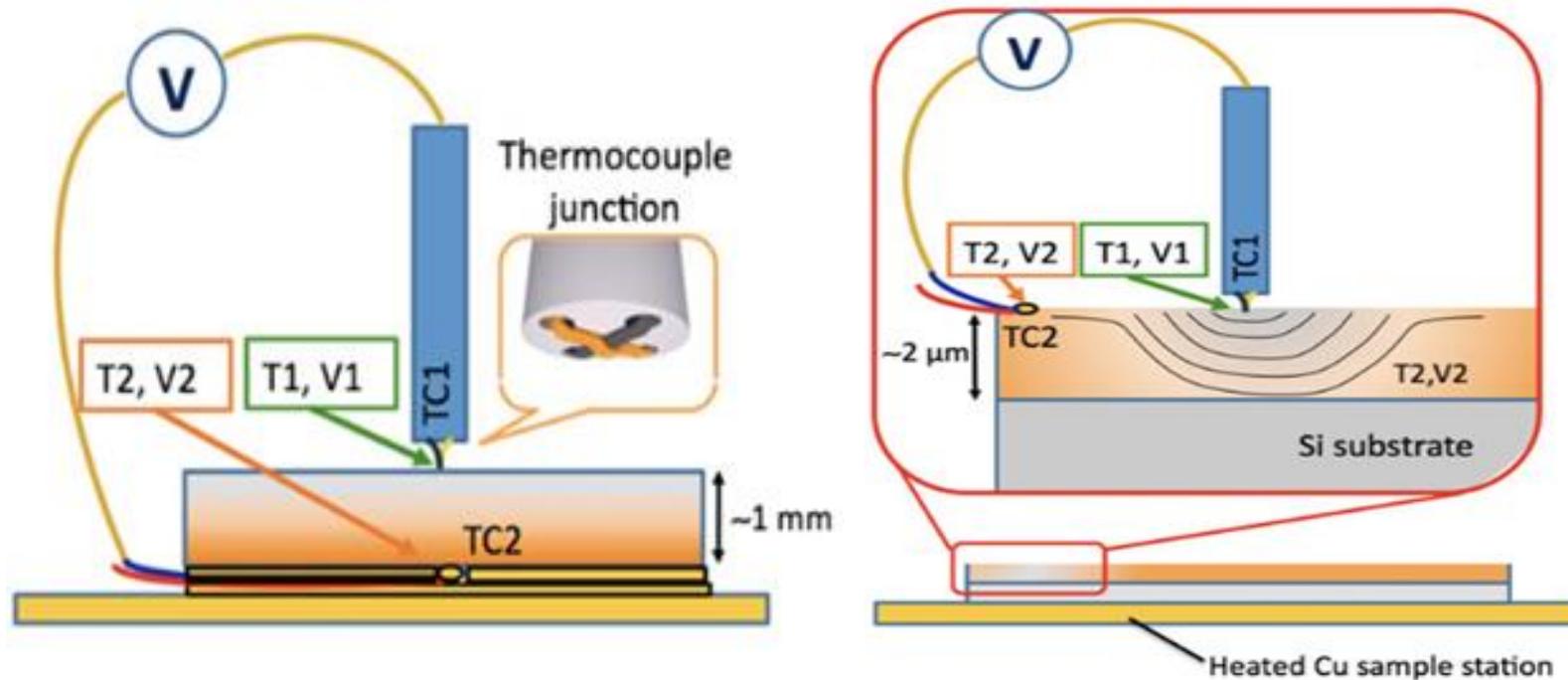
- **Home-designed Devices for Seebeck Coefficient Measurements**

- ✓ **Scanning Seebeck Coefficient Measurement System**



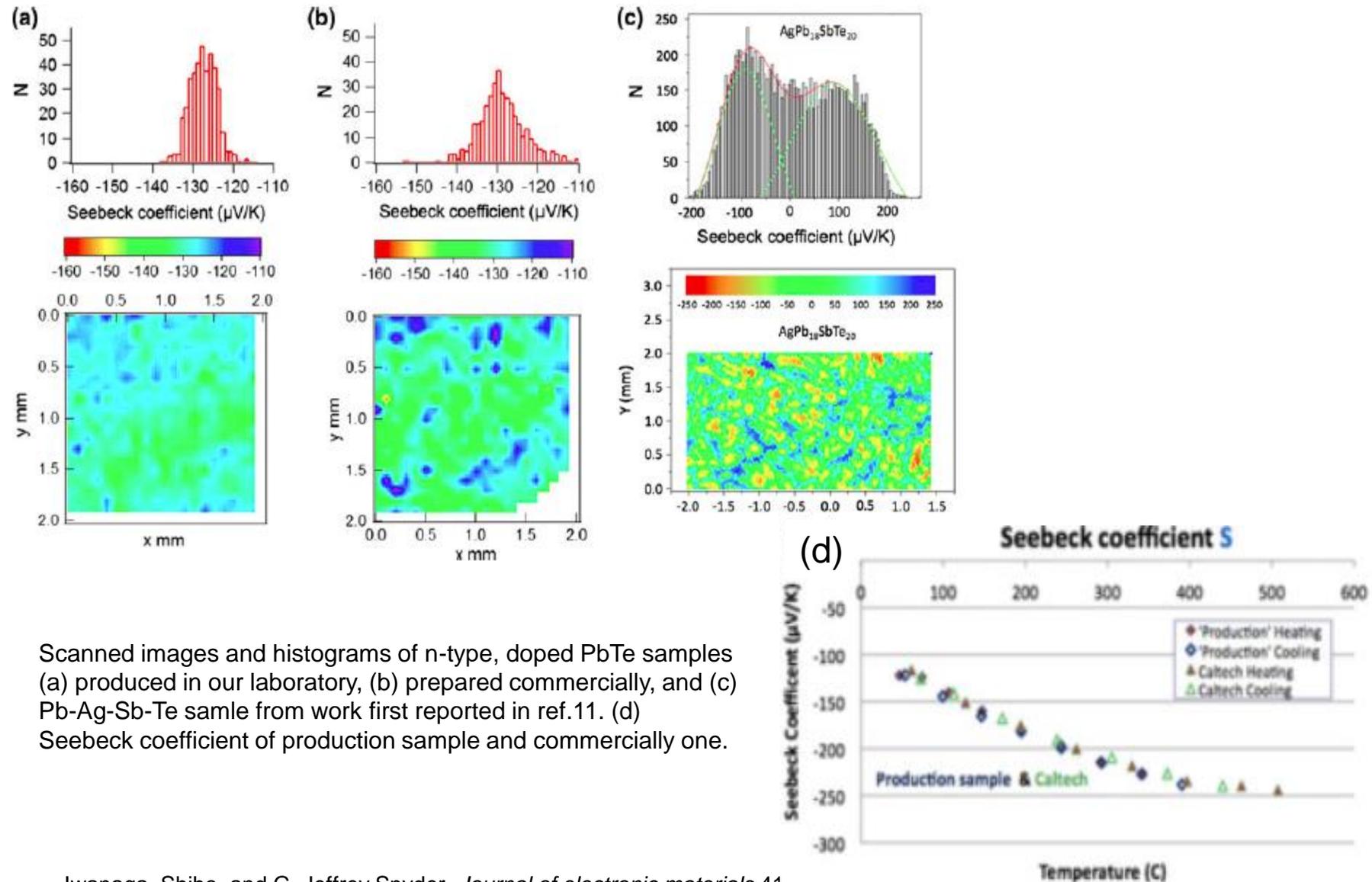
(a) Set-up for scanning Seebeck coefficient measurement system, (b) scanning map

✓ Scanning Seebeck Coefficient Measurements in bulk Material and thin Films



Schematic of the set-up for S measurement in bulk samples and thin films

Experimental Results of Seebeck Coefficient in Scanning System



Scanned images and histograms of n-type, doped PbTe samples (a) produced in our laboratory, (b) prepared commercially, and (c) Pb-Ag-Sb-Te sample from work first reported in ref.11. (d) Seebeck coefficient of production sample and commercially one.

Conclusions

- In order to optimize TE materials and to increase efficiency of TE generators, we need to measure Seebeck coefficient accurately.
- There are two main commonly used methods for Seebeck coefficient measurement: integral method and differential method.
- The thermoelectric properties of TE materials in in-plane and vertical direction are different. For bulk materials and heterogeneous films, the Seebeck coefficient in vertical direction is usually measured. For homogeneous thin films, the Seebeck coefficient in in-plane direction is usually measured.
- The challenge with Seebeck coefficient measurements of MOF Films lies in achieving proper electrical Ohmic contacts and increase electrical conductivity σ .

CALL FOR PAPERS

1st International Symposium on Electronic, Thermal and Electrochemical Properties of Metal Organic Frameworks (MOFs): Technology, Applications and Emerging Devices

228th Electrochemical Society Fall Meeting, October , 2018
Moon Palace Resort, Cancun, Mexico

During recent years research on electronic and electrochemical properties of Metal Organic Framework (MOF) based thin film materials and applications has created a new research field for specific functionalization of interfaces and surfaces. The work of various international research groups has contributed to discoveries of new physicochemical properties of MOFs with high application potentials. MOF synthesis and characterization have been supported by recent advances in theoretical models leading to better understanding of the fundamental materials science of MOFs. Today, highly porous and layered MOF materials have been successfully integrated into new technological applications ranging from microelectronics to sensors, batteries and photovoltaic devices as well as to functional thin film materials in the field of electrochemistry, optoelectronics, thermoelectrics, magnetism, data storage as well as to photo/electrocatalysis chemical reactors and gas storage.

The 1st International Symposium sponsored by the Electronics and Photonics Division of the Electrochemical Society brings together researchers in chemistry, materials science, physics, devices and process engineers and related interdisciplinary areas, to seek and capture the state-of-the art in MOF based fundamental aspects and latest technological applications. This symposium offers a new interdisciplinary and international platform, and aims to contribute towards advancing the fundamental understanding of the layered MOF thin films and aiming to improve technological applications thereof.

Original contributions are solicited that cover all fundamental and applied aspects including electronic, thermal and electrochemical transport properties and phenomena, device/ system fabrication and integration of MOF thin films into emerging technological device applications.

All oral presentations will be grouped into topical sessions. Invited Keynote speakers will present critical reviews covering recent advances and future directions in the diverse field of fundamental and applied MOF properties. Authors who wish to present a paper in the Symposium must submit an electronic abstract in English to the Electrochemical Society Headquarters. The authors are also required to send an electronic copy of the abstract to the Symposium Organizers with their indication of preference for verbal or poster presentation, and advice if the submission is a student presentation.



- Abstracts are due by March 28, 2018.
- Authors who wish to present a paper in the Symposium must submit electronically a 500- word abstract in English to The Electrochemical Society Headquarters. The template can be found here:
- http://www.electrochem.org/meetings/guidelines/abst_temp_info.htm
- Abstracts are to be submitted through this link:
- <http://www.electrochem.org/meetings/>
- Conference proceedings paper submission May 30, 2018 to June 27, 2018
- An ECS Transactions is planned to be available at the meeting. All authors accepted for presentation are obligated to submit their proceedings manuscript for the issue no later than June 27, 2014. All manuscripts will be submitted online, and must be in either MS Word or PDF format. The ECST Submission Site will be open beginning May 30, 2014, therefore limited time is available for submission of papers. Detailed instructions for full manuscript preparation are available at the Electrochemical Society website:
- http://www.electrochem.org/dl/ecst/ecst_a_inst.htm
- The manuscript preparation instructions must be followed to avoid delays and additional editing.
- Student Travel Grants
- There are travel grants available to graduate students and we urge them to apply early. To apply on-line please go to the following website:
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