M.E.T.U.
MIDDLE EAST TECHNICAL UNIVERSITY
GRADUATE SCHOOL OF NATURAL & APPLIED SCIENCES
MICRO & NANO TECHNOLOGY PROGRAM
The Area of Defense Industry, Aeronautics and Astronautics
ANKARA/TURKEY

Correct Measurement of Seebeck Coefficient & Resistivity

Murat Gunes
Advisor Prof. A. Macit Ozenbas
Co-advisor Mehmet Parlak

NIPS Summer School and Workshop, «Energy Harvesting at Micro & Nanoscale"

01.-05.08.2011 Prugia - Italy

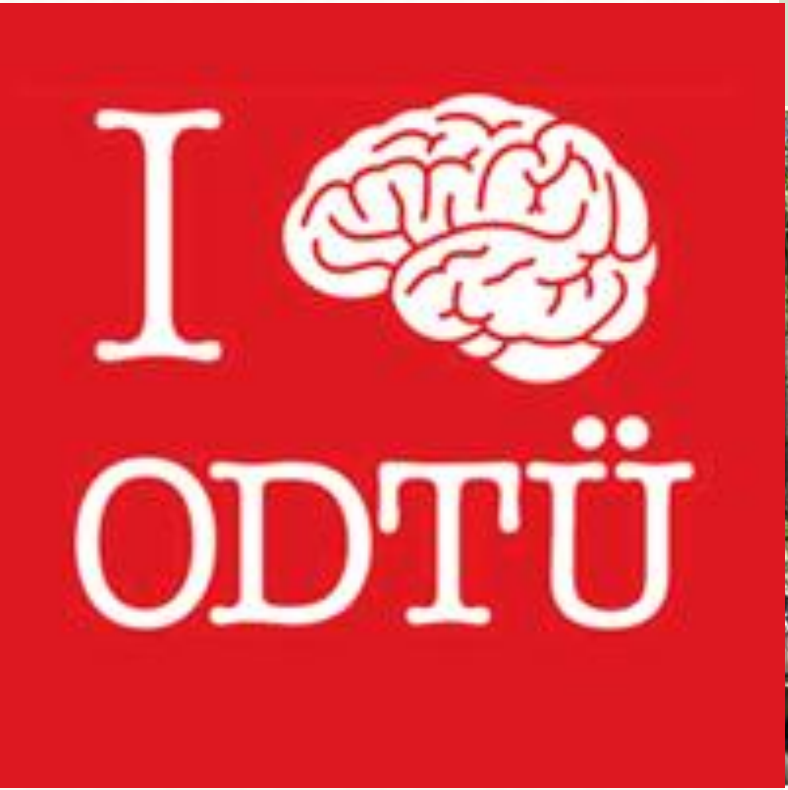
Middle East Technical University: METU

23,000 students of which
4,500 are in masters and
2,700 are in doctorate programs.

METU hosts over **1,500 international students** from nearly **80** different countries

METU actively took part in and managed many Med-Campus, MEDA, COST, Eureka, NASA, NATO, NSF, UN, World Bank, Jean Monnet, INCO, EUMEDIS, 6th and 7th Framework, Erasmus Mundus ECW, Leonardo and Socrates projects.

www.metu.edu.tr
www.mnt.metu.edu.tr

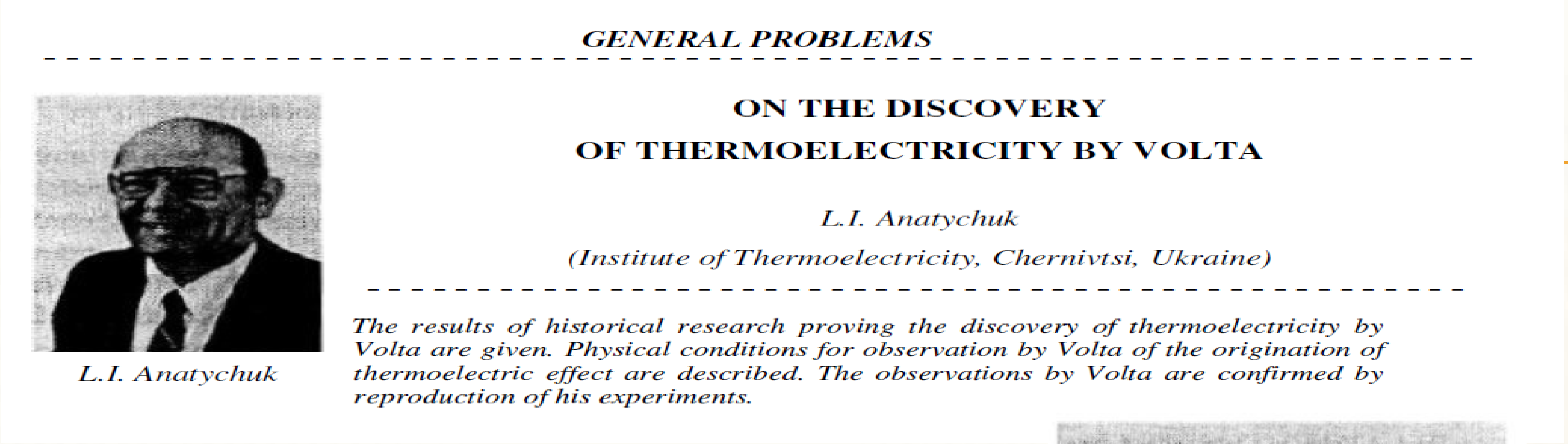


Basic Research Topics in Our Laboratory

Surface Science Research Laboratory (SSRL)

Metallurgical & Material Engineering Department

- Thermoelectrics
  - Synthesis, Structural and Electrical Characterizations
- *Dye-sensitized solar cell* (*DSSC*, DSC or DYSC)
  - Some Synthesis, Characterizations, Moduling
- Piezoelectric –thin film
  - Synthesis, Structural & Ferro-electrical Characterizations,



GENERAL PROBLEMS

L.I. Anatychuk

ON THE DISCOVERY OF THERMOELECTRICITY BY VOLTA

L.I. Anatychuk

(Institute of Thermoelectricity, Chernivtsi, Ukraine)

The results of historical research proving the discovery of thermoelectricity by Volta are given. Physical conditions for observation by Volta of the origination of thermoelectric effect are described. The observations by Volta are confirmed by reproduction of his experiments.

- After studying eath magnetisim he called this invention as thermomagnetism 1825.
- The priority of Volta in the discovery of thermoelectric effect of EMF generation due to temperature difference.
- First, A. Volta carried out purposeful experiments, with a view to discover thermoelectromotive forces arising under the influence of temperature difference
- Volta invented 27 year earlier (Volta wrote to professor of physics in Royal University of Turino abbot Anton Maria Vassali three letters entitled “A new paper on the animal electricity)
- German physicists I. Ritter (1798) and I. Sveiger (1810)

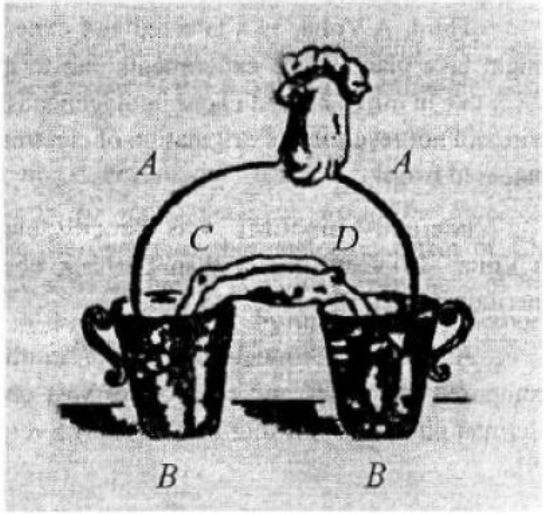


*Fig .2. Scheme of Volta's experiment that resulted in the discovery of thermoelectricity.
A –metal (iron) arc, B –glasses with water,
C and D – frog parts placed in glasses with water.*

- Ref. http://book.boot.users.btopenworld.com/Anat_P2.pdf

Outline

- **Introduction**
  - World Energy Needs
  - Working Principles of Thermoelectric Devices
- **Thermoelectric Effect –Figure of Merit**
- **Thermoelectric Materials**
- **Electrical Characterizations**
  - Resistivity, and Seebeck Coefficient
  - **Conclusion**

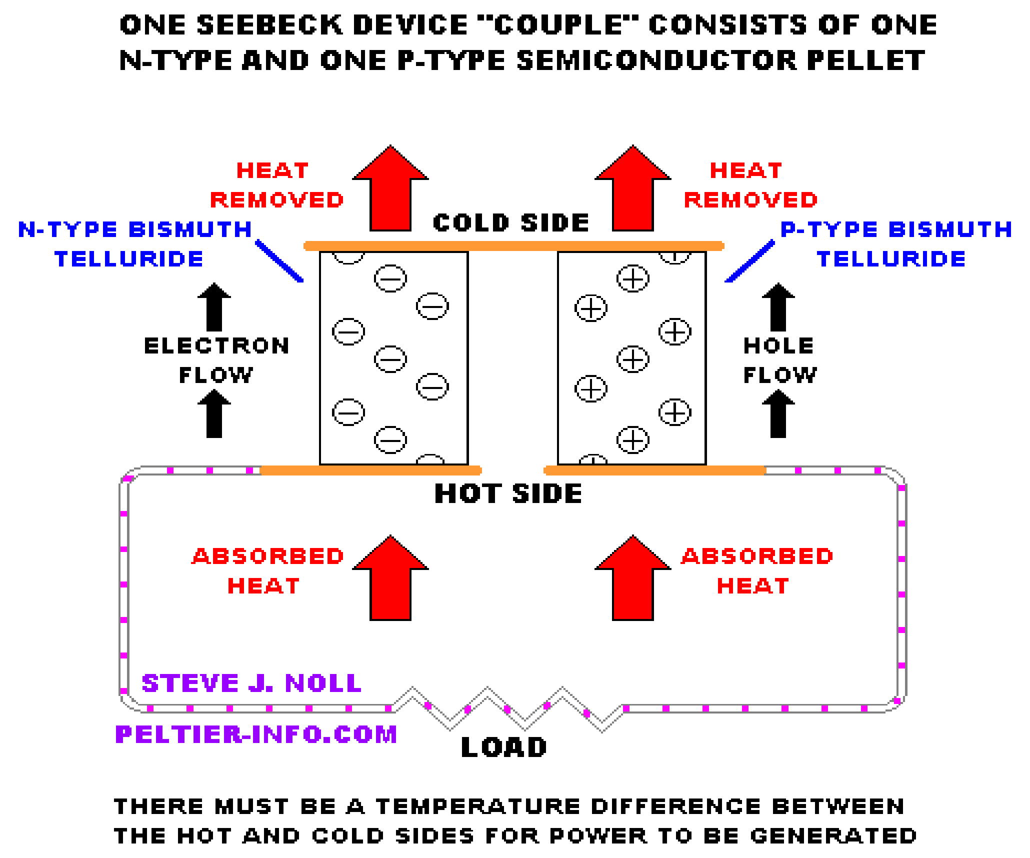
WHAT ARE THERMOELECTRIC MATERIALS?

- *Thermoelectric materials can convert electrical energy into a temperature gradient as well as thermal energy into electrical energy.*
- *Thermoelectric (TE) materials have unique position for dual electrical generation on one side and cooling/ heating on the other side.*
- *Power generation is achieved by applying a temperature difference between two ends of the TE material, while cooling or heating is obtained by applying electrical current*

Working Principle of Thermoelectric Devices

Converting heat energy to the electrical energy directly is called Seebeck Effect or vice versa Peltier Effect.

SEEBECK EFFECT



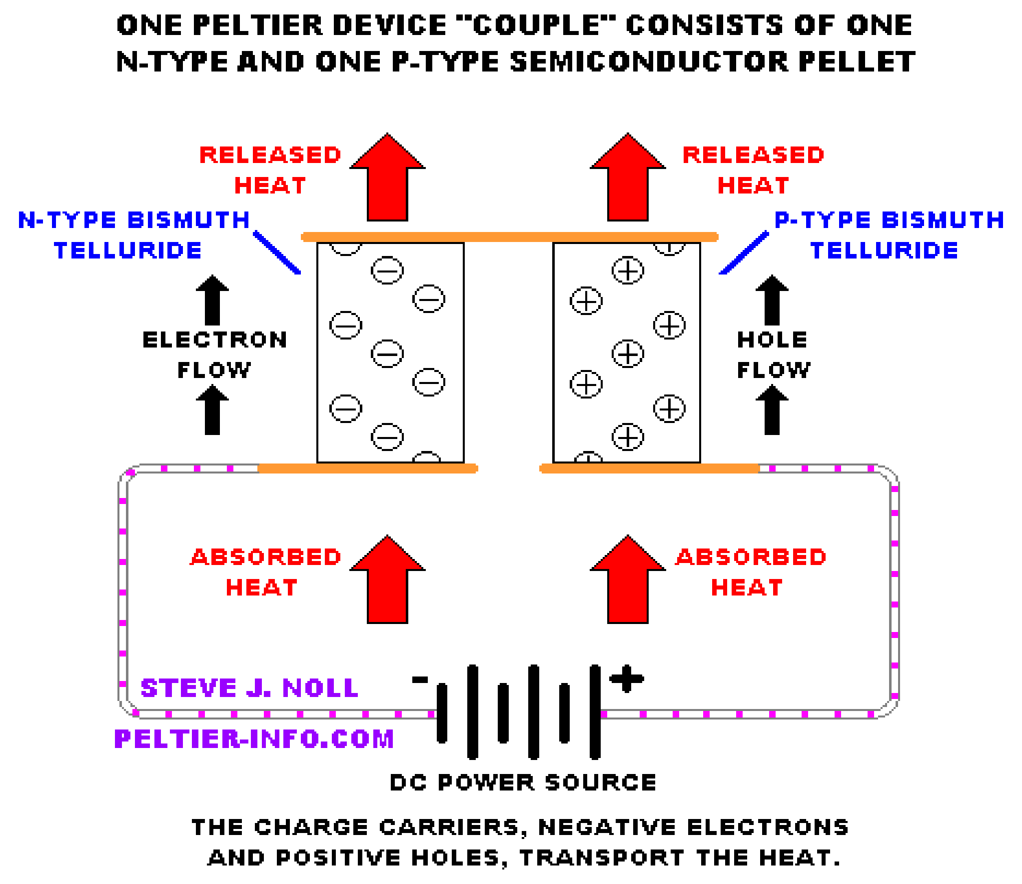
SEEBECK EFFECT

Figure 1. Schematic view of Seebeck Effect

Working Principle of Thermoelectric Devices

Thermoelectricity is the direct conversion of temperature differences to electric voltage and vice versa.

PELTIER EFFECT



ONE PELTIER DEVICE "COUPLE" CONSISTS OF ONE N-TYPE AND ONE P-TYPE SEMICONDUCTOR PELLET

RELEASED HEAT

RELEASED HEAT

N-TYPE BISMUTH TELLURIDE

P-TYPE BISMUTH TELLURIDE

ELECTRON FLOW

HOLE FLOW

ABSORBED HEAT

ABSORBED HEAT

STEVE J. NOLL

PELTIER-INFO.COM

-

\+

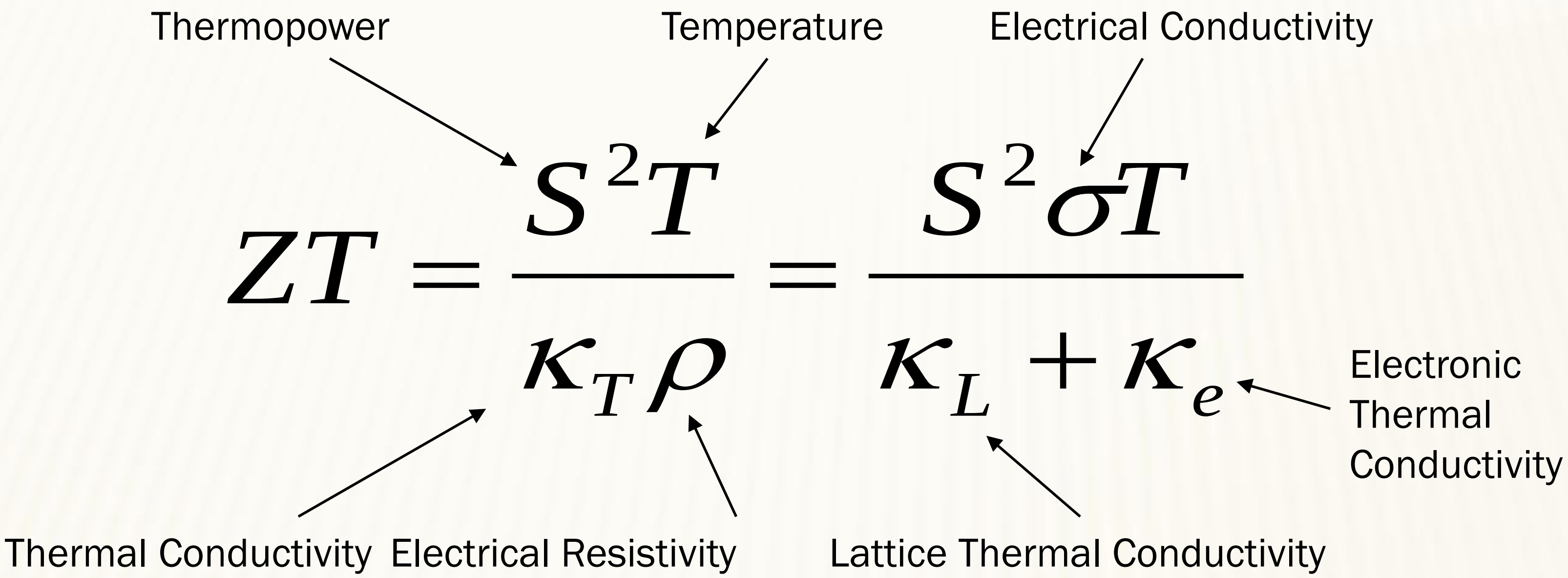
DC POWER SOURCE

THE CHARGE CARRIERS, NEGATIVE ELECTRONS AND POSITIVE HOLES, TRANSPORT THE HEAT.

Figure 2. Schematic view of Peltier Effect

PELTIER EFFECT

Figure of Merit (ZT)



Thermopower

Temperature

Electrical Conductivity

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

Electronic
Thermal
Conductivity

Thermal Conductivity

Electrical Resistivity

Lattice Thermal Conductivity

Waste Energy Recovery

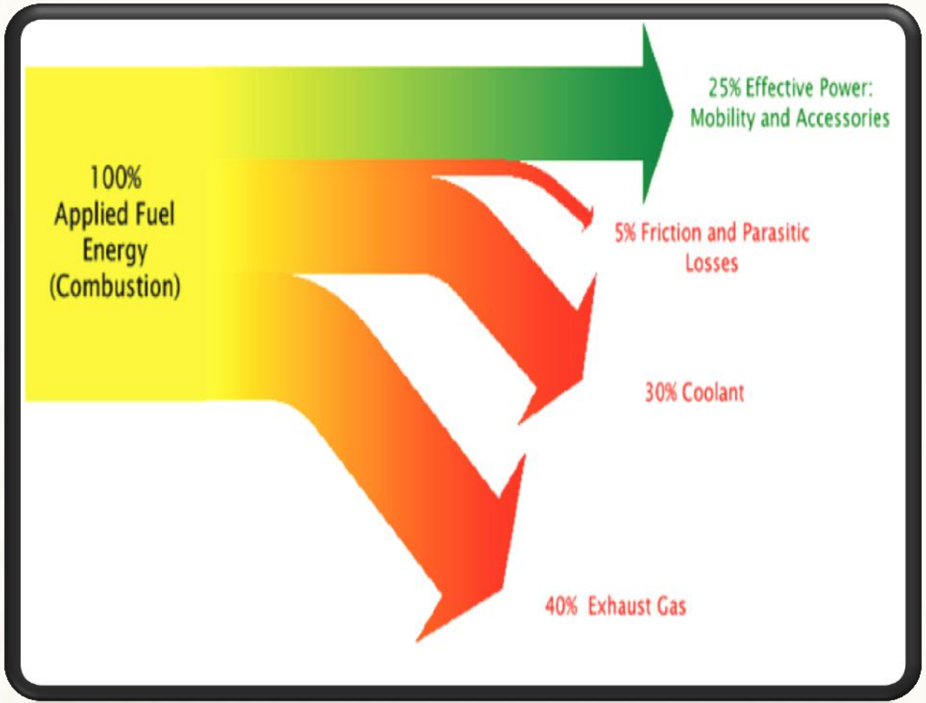
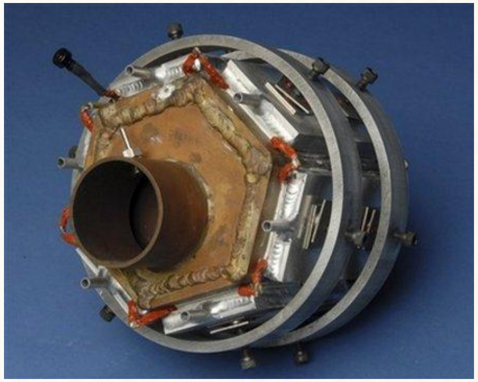


Figure 3. Typical energy split in gasoline internal combustion engines.



http://green.autoblog.com/

BMW has won an ÖkoGlobe award.

BMW Group Wins Award For Thermoelectric Generator

CO_2 emissions of 140 g CO_2/km or lower

Transform huge amounts of waste energy to electrical energy
(Recover and effectively utilize the waste energy)

Comparison of TE Materials

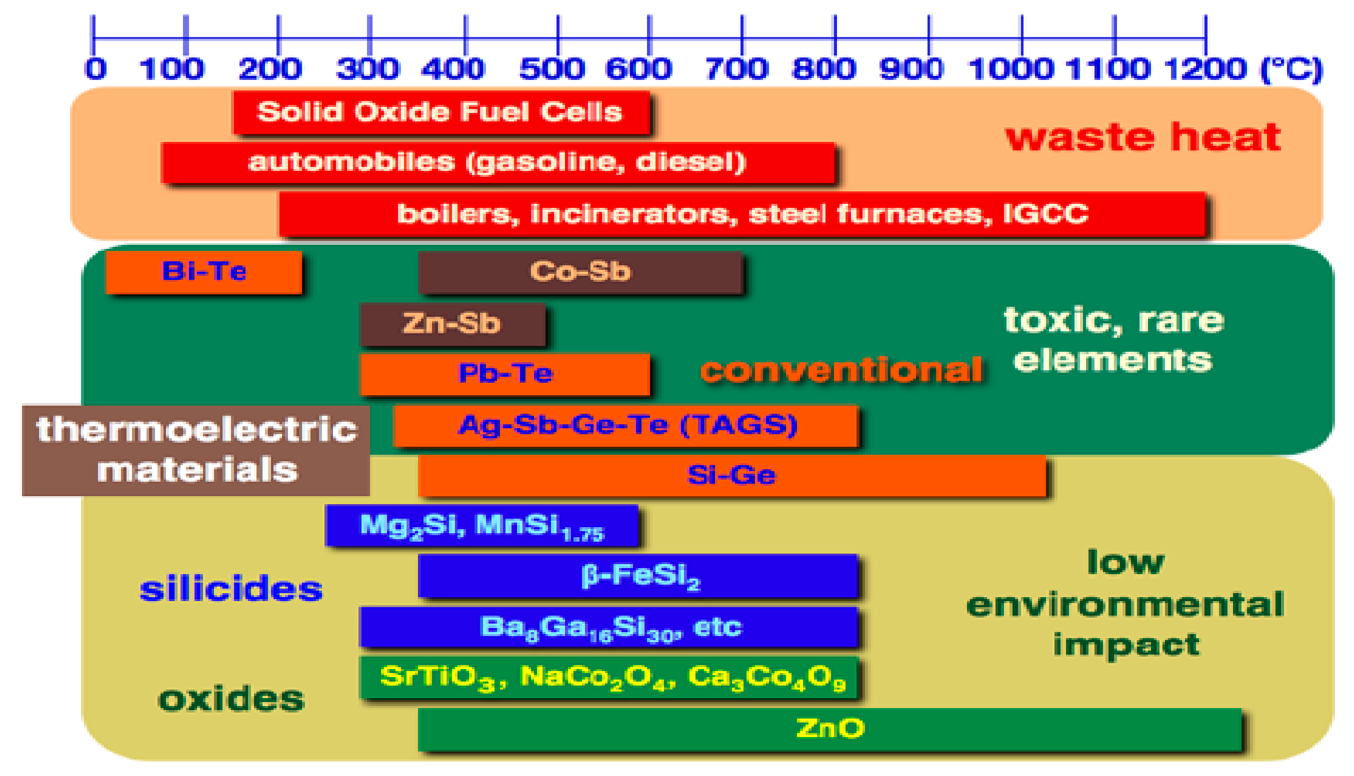


Figure 4. *Thermoelectric Materials for Heat-to-Electricity Direct Energy Conversion*

Ref. Michitaka Ohtaki, Micro Review, Faculty of Engineering Sciences, Kyushu University

Temperature Measurement

Thermocouples

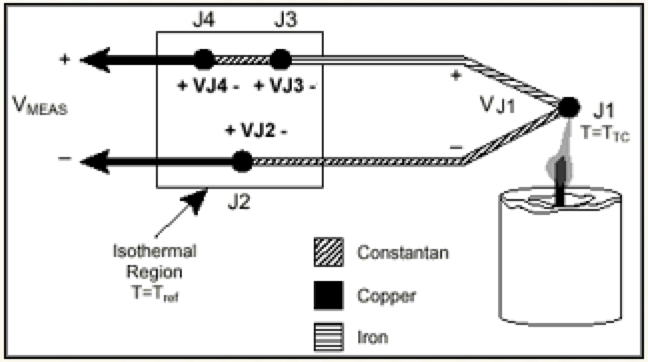
- By using the Thermocouple Law of Intermediate Metals and making some simple assumptions, you will find that

the measured voltage depends on the thermocouple type, thermocouple voltage, and the cold-junction temperature.

The measured voltage is independent of the composition of the measurement leads and the cold junctions, J2 and J3.

- According to the Thermocouple Law of Intermediate Metals inserting any type of wire into a thermocouple circuit has no influence on the output as long as both ends of that wire are the same temperature, or isothermal.

junctions J2 and J4 are the same type (copper-constantan). Because both are in the isothermal region, J2 and J4 are also the same temperature.



Ref. National Insturments:Thermocouples

Temperature Measurement

Thermocouple reference tables are generated with the reference junction held at 0 °C, therefore, to determine the temperature at the thermocouple junction we can start with Equation 2 shown below, where V_{MEAS} is the voltage measured by the data acquisition device, and $V_{TC}\,(T_{TC} - T_{ref})$ is the Seebeck voltage created by the difference between T_{TC} (the temperature at the thermocouple junction) and T_{ref} (the temperature at the reference junction):

Equation 2: $V_{MEAS} = V_{TC}\,(T_{TC} - T_{ref})$

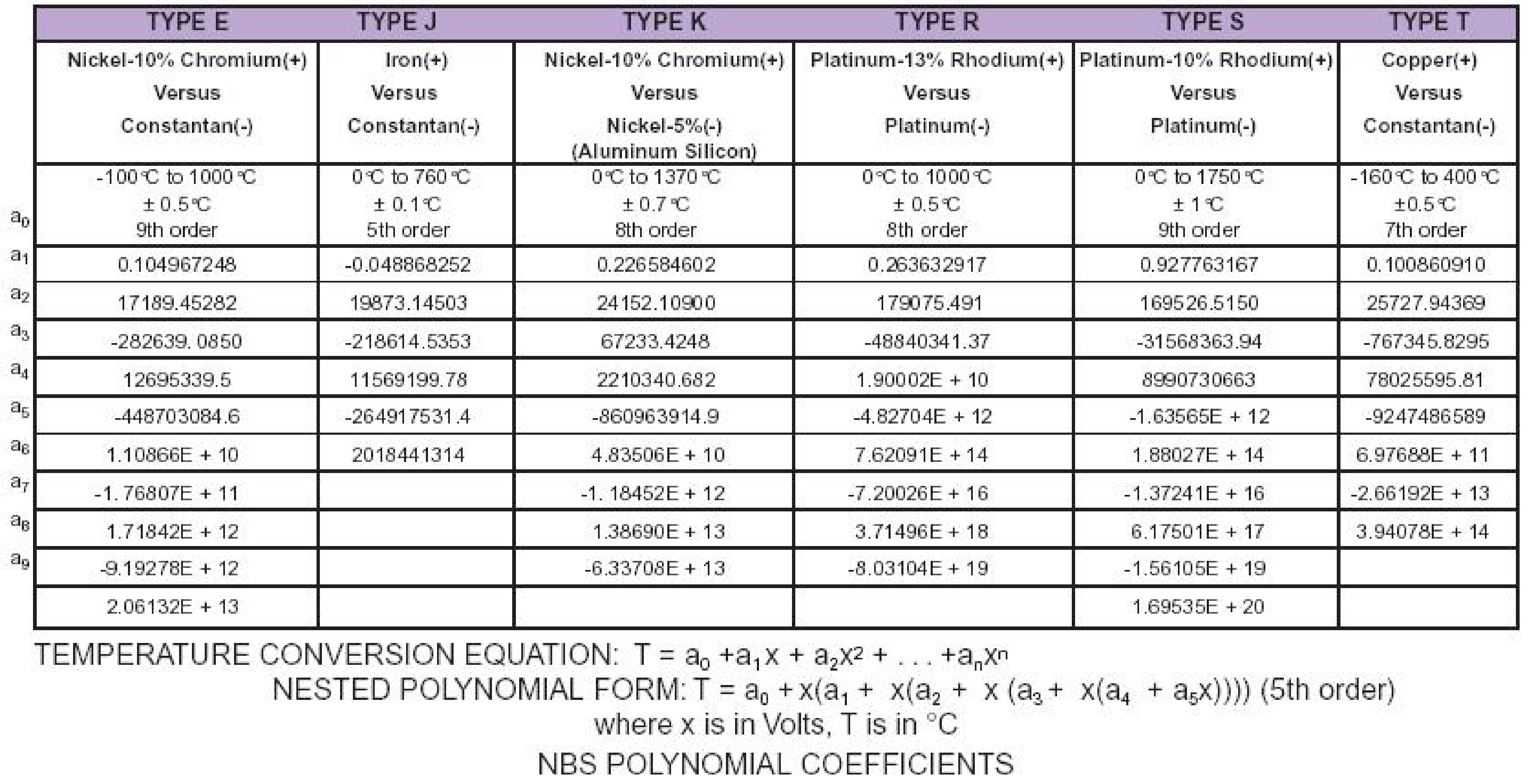
We can rewrite Equation 2 as shown in Equation 3 where $V_{TC}\,(T_{TC})$ is the voltage measured by the thermocouple assuming a reference junction temperature of 0 °C, and $V_{TC}\,(T_{ref})$ is the voltage that would be generated by the same thermocouple at the current reference temperature assuming a reference junction of 0 °C:

Equation 3: $V_{MEAS} = V_{TC}\,(T_{TC}) - V_{TC}\,(T_{ref})$
Equation 4: $V_{TC}\,(T_{TC}) = V_{MEAS} + V_{TC}\,(T_{ref})$

In Equation 4, the computed voltage of the thermocouple assumes a reference junction of 0 °C. Therefore, by measuring V_{MEAS} and T_{ref} , and knowing the voltage-to-temperature relationship of the thermocouple, we can determine the temperature at the primary junction of the thermocouple.

Ref. National Insturments:Thermocouples

Temperature Measurement



	TYPE E	TYPE J	TYPE K	TYPE R	TYPE S	TYPE T
	Nickel-10% Chromium(+) **Versus** **Constantan(-)**	**Iron(+)** **Versus** **Constantan(-)**	**Nickel-10% Chromium(+)** **Versus** **Nickel-5%(-)** **(Aluminum Silicon)**	**Platinum-13% Rhodium(+)** **Versus** **Platinum(-)**	**Platinum-10% Rhodium(+)** **Versus** **Platinum(-)**	**Copper(+)** **Versus** **Constantan(-)**
a_0	-100 °C to 1000 °C ± 0.5 °C 9th order	0 °C to 760 °C ± 0.1 °C 5th order	0 °C to 1370 °C ± 0.7 °C 8th order	0 °C to 1000 °C ± 0.5 °C 8th order	0 °C to 1750 °C ± 1 °C 9th order	-160 °C to 400 °C ±0.5 °C 7th order
a_1	0.104967248	-0.048868252	0.226584602	0.263632917	0.927763167	0.100860910
a_2	17189.45282	19873.14503	24152.10900	179075.491	169526.5150	25727.94369
a_3	-282639. 0850	-218614.5353	67233.4248	-48840341.37	-31568363.94	-767345.8295
a_4	12695339.5	11569199.78	2210340.682	1.90002E + 10	8990730663	78025595.81
a_5	-448703084.6	-264917531.4	-860963914.9	-4.82704E + 12	-1.63565E + 12	-9247486589
a_6	1.10866E + 10	2018441314	4.83506E + 10	7.62091E + 14	1.88027E + 14	6.97688E + 11
a_7	-1. 76807E + 11		-1. 18452E + 12	-7.20026E + 16	-1.37241E + 16	-2.66192E + 13
a_8	1.71842E + 12		1.38690E + 13	3.71496E + 18	6.17501E + 17	3.94078E + 14
a_9	-9.19278E + 12		-6.33708E + 13	-8.03104E + 19	-1.56105E + 19	
	2.06132E + 13				1.69535E + 20	

TEMPERATURE CONVERSION EQUATION: $T = a_0 + a_1x + a_2x^2 + \dots + a_nx^n$

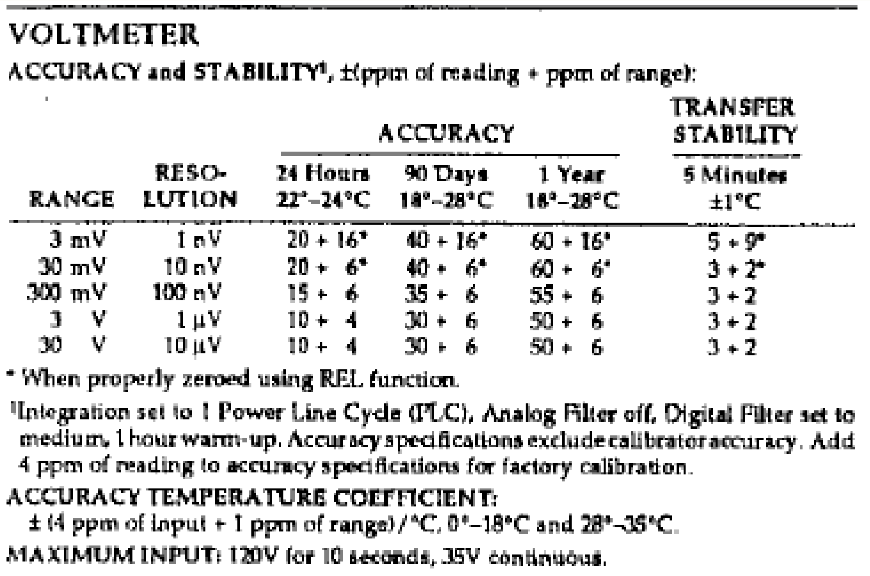
NESTED POLYNOMIAL FORM: $T = a_0 + x(a_1 + x(a_2 + x(a_3 + x(a_4 + a_5x))))$ (5th order)

where x is in Volts, T is in °C

NBS POLYNOMIAL COEFFICIENTS

"Technical Notes: Thermocouple Accuracy". *IEC 584-2(1982)+A1(1989)*. Retrieved 2010-04-28

Voltage Measurement



VOLTMETER

ACCURACY and STABILITY[1], ±(ppm of reading + ppm of range):

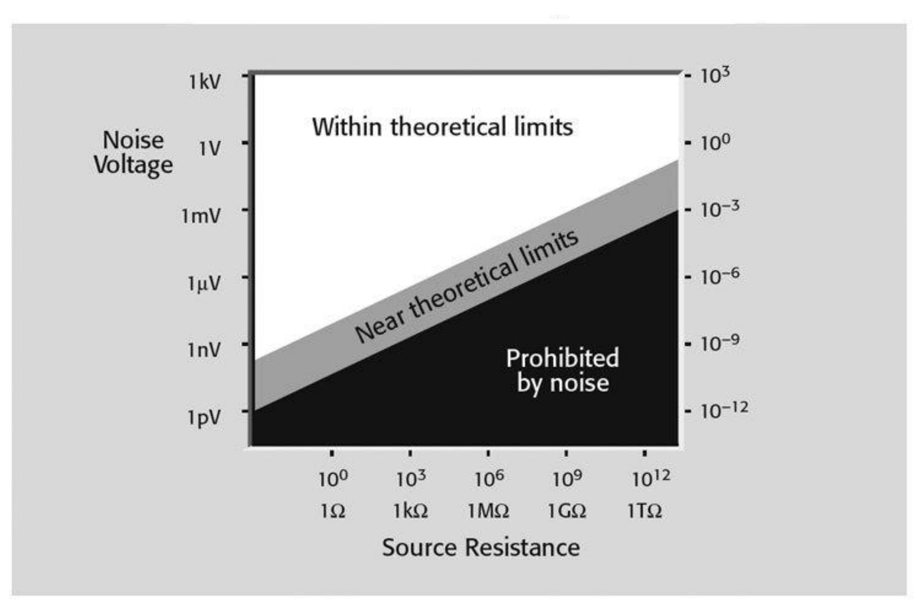
		ACCURACY			TRANSFER STABILITY
RANGE	RESO-LUTION	24 Hours 22°–24°C	90 Days 18°–28°C	1 Year 18°–28°C	5 Minutes ±1°C
3 mV	1 nV	20 + 16*	40 + 16*	60 + 16*	5 + 9*
30 mV	10 nV	20 + 6*	40 + 6*	60 + 6*	3 + 2*
300 mV	100 nV	15 + 6	35 + 6	55 + 6	3 + 2
3 V	1 µV	10 + 4	30 + 6	50 + 6	3 + 2
30 V	10 µV	10 + 4	30 + 6	50 + 6	3 + 2

* When properly zeroed using REL function.

[1] Integration set to 1 Power Line Cycle (PLC), Analog Filter off, Digital Filter set to medium, 1 hour warm-up. Accuracy specifications exclude calibrator accuracy. Add 4 ppm of reading to accuracy specifications for factory calibration.

ACCURACY TEMPERATURE COEFFICIENT:
± (4 ppm of input + 1 ppm of range) / °C, 0°–18°C and 28°–35°C.

MAXIMUM INPUT: 120V for 10 seconds, 35V continuous.



- ***Figure 5.*** *Theoretical limits of voltage measurements*

Based on Keithley-182. Ref.Keithley-182 Digital Nanovoltmeter Manuel.

2 & 4 Probe Techniques

- The axial-flow technique (two-probe), the temperature difference and the electric potential are measured on the probes which are in direct contact with the ends of the specimen(Goldsmid and Tritt).
- The potentiometric arrangement (or four-probe),), the temperature difference and the voltage difference are measured at two points *on the sample* (or inserted within the sample) equidistant from the hot and cold sinks and on the axis parallel to the thermal gradient.
- To maintain accuracy, the diameter of each temperature/voltage probe must be much smaller than the effective distance between them. There is some debate as to which method provides the most accurate determination of temperature and voltage difference at the same points.
- Wood (Rev. Sci. Instrum., 1985, 56, 719) compared the results of thermocouples pressed on the ends of a sample with those obtained by inserting them in holes drilled in the sample. For the temperature and the material evaluated, the results were consistent within the measurement uncertainty.

Electrical Characterization

- Contact issue

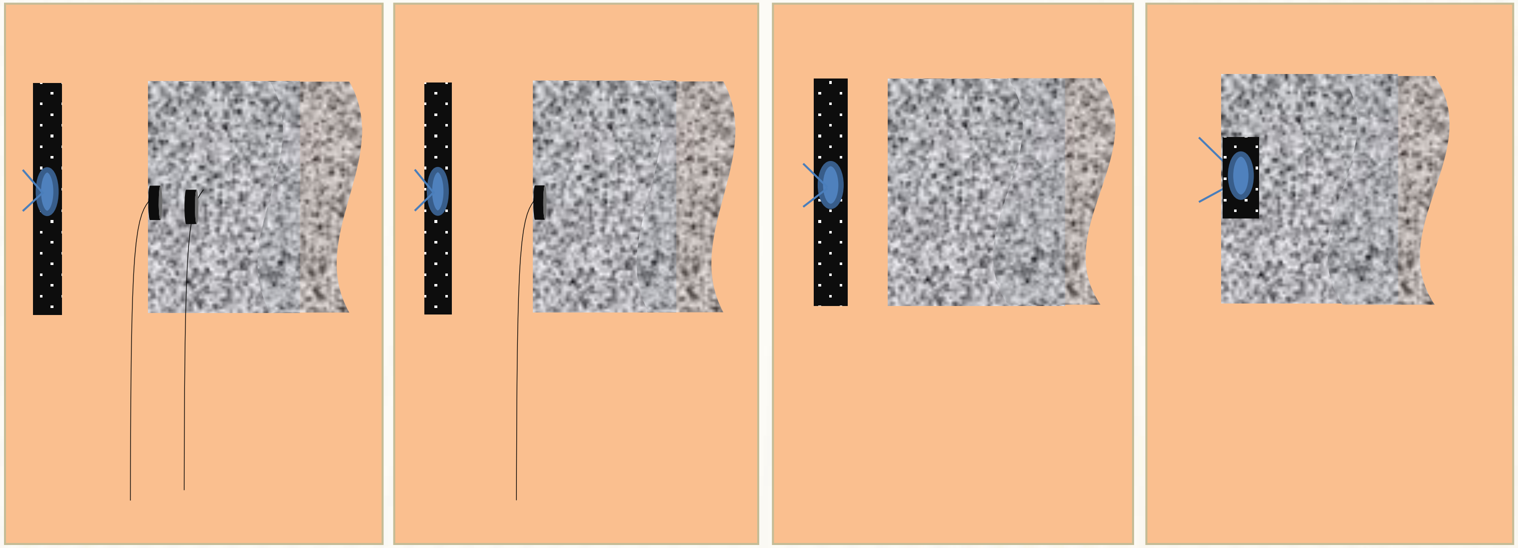


Figure 6. Detailed types of contacts

«accurate» Measurement

- Considering the diversity of research materials in both geometry and contact resistance, the potentiometric arrangement may benefit longer, lower cross-sectional area specimens, while the axial-flow arrangement may benefit shorter or disk-shaped specimens, provided the thermal resistance of the sample is larger than the thermal resistance of the contact interface. Thus, a versatile and flexible apparatus would not only enable comparative measurements on materials with different contact resistances, thermal conductivities, and heat capacities, but also expand the practical range of sample geometries.

- The primary requirements for "good" Seebeck coefficient measurements are:
  - the spatially synchronous measurement of voltage and temperature, that is, the voltage and temperature must be measured at the same location and at the same time;
  - probes in very good thermal and electrical contact with the specimen; and
  - the acquisition of low voltages (microvoltages) with minimal extraneous contributions.

Martin, Tritt, and Uher J. Appl. Phys. **108**, 121101 2010

Methods of TE Voltage Measurement

- Measurement of the Seebeck voltage requires the open circuit condition $J=0$(where J is the electrical current density), such that the junctions are isothermal and the electrochemical potential is continuous.
- In the Harman method (or Z meter), the ohmic voltage is measured under both isothermal and adiabatic conditions, such that $J\neq0$ and the temperature difference forms due to the induced Peltier effect at the contacts.

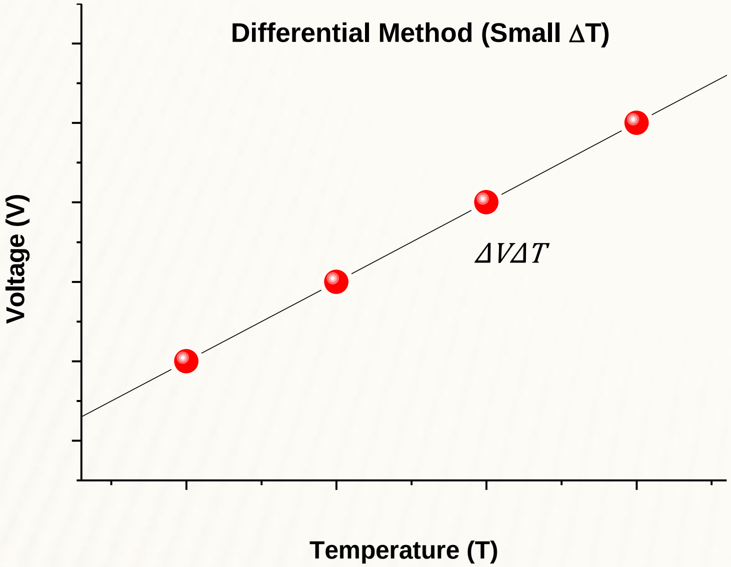
- Differential Method –DC Method
  - The steady-state condition
  - The quasi-steady-state condition

- Integral Method –DC Method

- 3 ω -AC Method

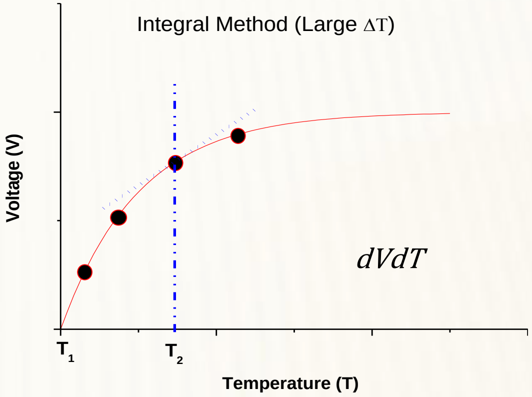
C. A. Domenicali, Rev. Mod. Phys., 1954, 26, 237

Methods of TE Voltage Measurement



$$\frac{\Delta V_{ab}}{\Delta T} = S_{ab}(T_o) + \Delta S_{ab}(T_o)$$

Direct Measurement



$$S_{ab}(T_2) = S_b(T_2) - S_a(T_2) = \frac{dV_{ab}(T_1,T_2)}{dT_2}$$

Curve fitting is necessary

- Walking polynomial
- Spline fit
- Global least-squares fits of varying order
- Orthogonal coefficient decrease
- F-test

Methods of TE Voltage Measurement

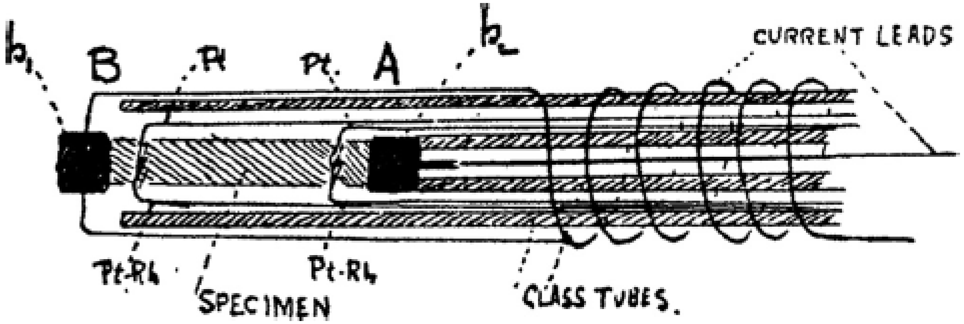


FIG. 6. Early Seebeck coefficient apparatus described by Bidwell (Ref. 72).Reprinted with permission from C. C. Bidwell, Phys. Rev. **19**, 447 (1922). Copyright 1922 by the American Physical Society.

Bidwell then measured the Seebeck coefficient and resistivity of germanium rods

2.4 cm long between 191 and 675 °C

Martin, Tritt, and Uher J. Appl. Phys. **108**, 121101 2010

Methods of TE Voltage Measurement

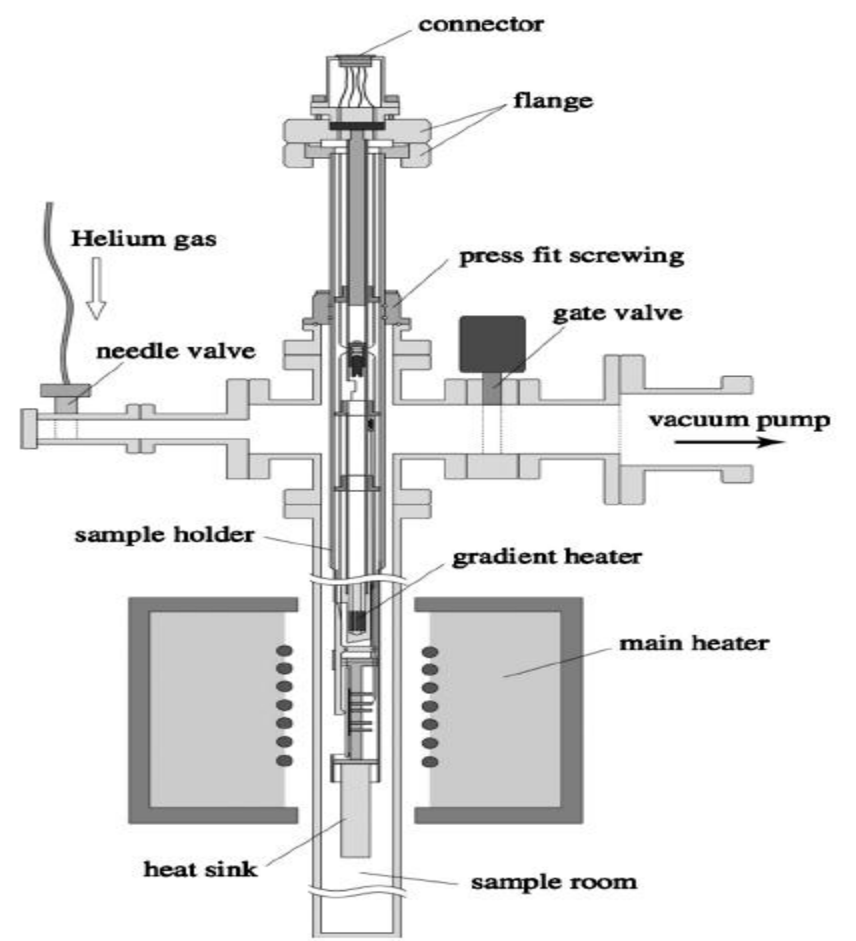
by Burkov

and the other

by Zhou and Uher

provide detailed descriptions of the apparatus and instrumentation ssuggested for high temperature implementation of the differential

steady-state method.



G. 7. Seebeck coefficient apparatus described by Burkov (Ref. 77).Re-
nted with permission from A. T. Burkov, A. Heinrich, P. P. Konstantinov,
Nakama, and K. Yagasaki, Meas. Sci. Technol. 12, 264 (2001). Copyright
01 by the Institute of Physics.

Martin, Tritt, and Uher J. Appl. Phys. **108**, 121101 2010

Methods of TE Voltage Measurement

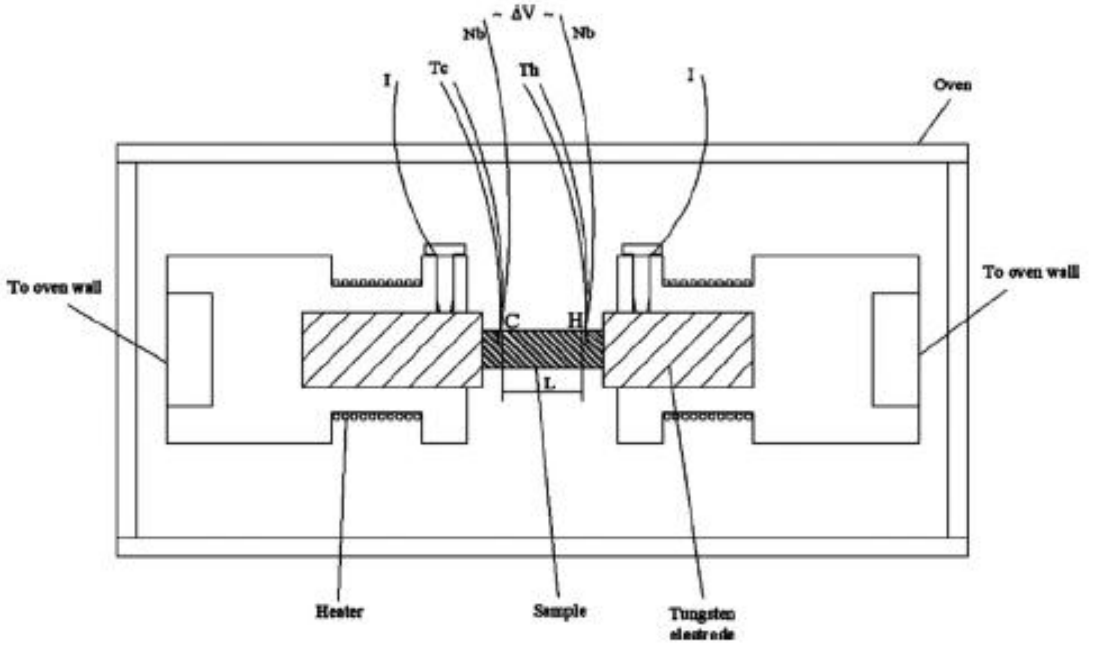


FIG. 8. Seebeck coefficient apparatus described by Zhou and Uher (Ref. 78).Reprinted with permission from Z. Zhou and C. Uher, Rev. Sci. Instrum. 76, 023901 (2005). Copyright 2005, American Institute of Physics.

Martin, Tritt, and Uher J. Appl. Phys. **108**, 121101
2010

Methods of TE Voltage Measurement

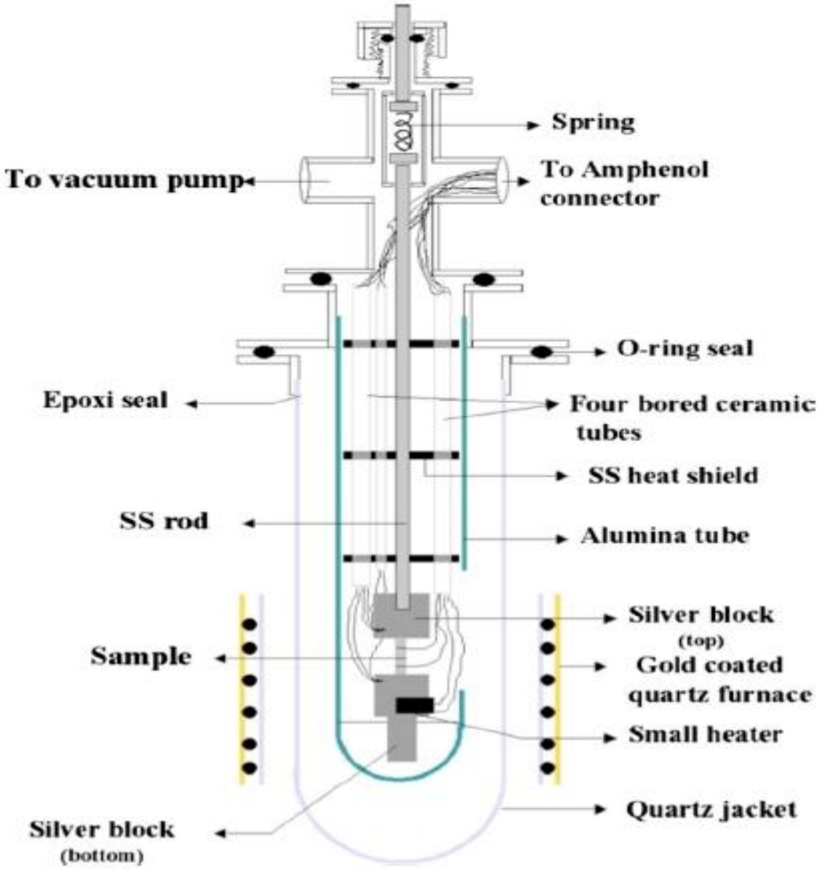
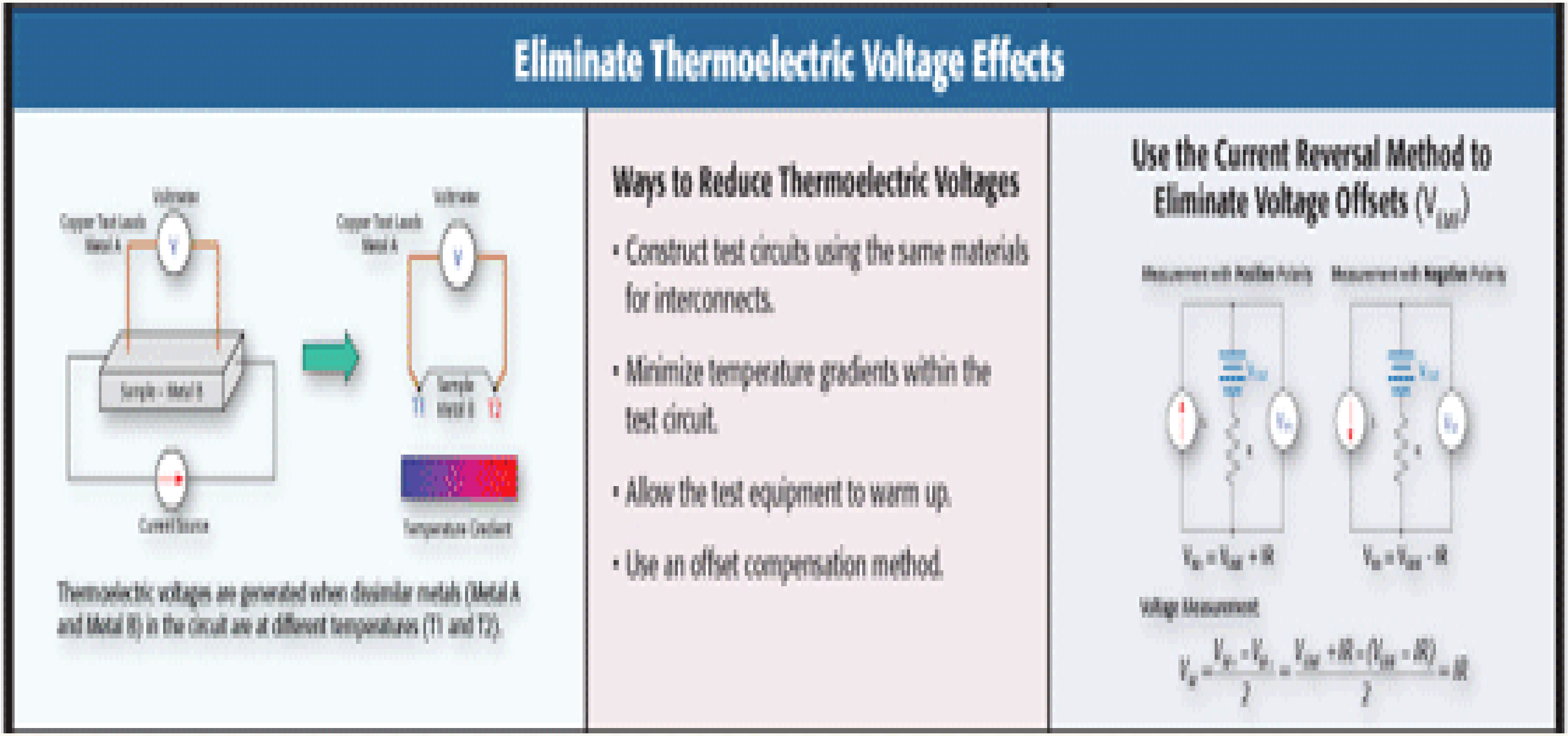


FIG. 10. (Color online) Seebeck coefficient apparatus described by Ponnambalam and Tritt (Ref. 84).Reprinted with permission from V. Ponnambalam, S. Lindsey, N. S. Hickman, and T. M. Tritt, Rev. of Sci. Instrum. 77, 073904 (2006). Copyright 2006, American Institute of Physics.

Martin, Tritt, and Uher J. Appl. Phys. **108**, 121101 2010

Resistance Measurements

- Wire – for example mercury probe, MEMS
- Film – for example mercury probe, MEMS
- Bulk – four probe method is adviced



Eliminate Thermoelectric Voltage Effects

Thermoelectric voltages are generated when dissimilar metals (Metal A and Metal B) in the circuit are at different temperatures (T1 and T2).

Ways to Reduce Thermoelectric Voltages

- Construct test circuits using the same materials for interconnects.
- Minimize temperature gradients within the test circuit.
- Allow the test equipment to warm up.
- Use an offset compensation method.

Use the Current Reversal Method to Eliminate Voltage Offsets (V_{EMF})

$V_{M+} = V_{EMF} + IR$

$V_{M-} = V_{EMF} - IR$

Voltage Measurement

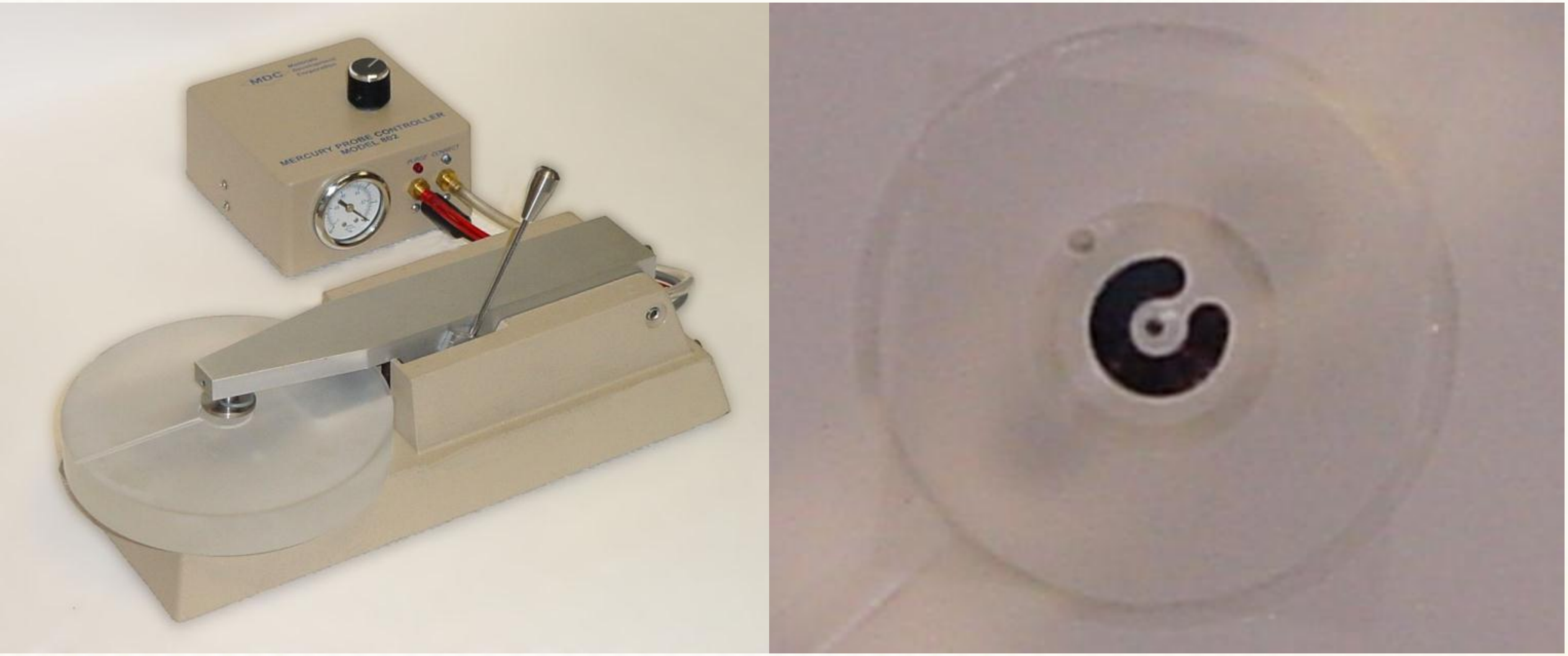
$$V_M = \frac{V_{M+} - V_{M-}}{2} = \frac{V_{EMF} + IR - (V_{EMF} - IR)}{2} = IR$$

Ref. Keithley.com

Film Resistance

- 3-point spreading resistance measurements

Mercury Probe Resistance Measurement



2 Probe Resistance Measurement

http://www.mdc4cv.com/mercuryprobe.htm

Resistivity Measurement of a Single Wire

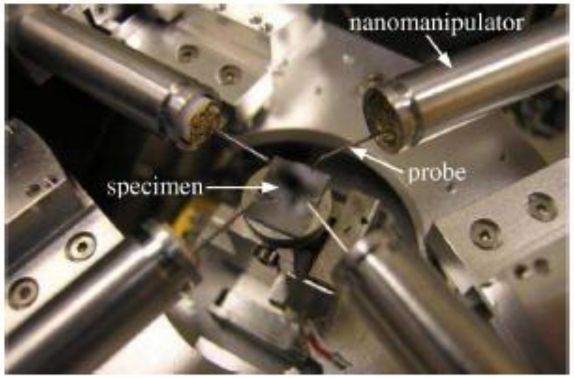


Fig. 1. Four nanomanipulators with probes installed for manipulation inside an SEM.

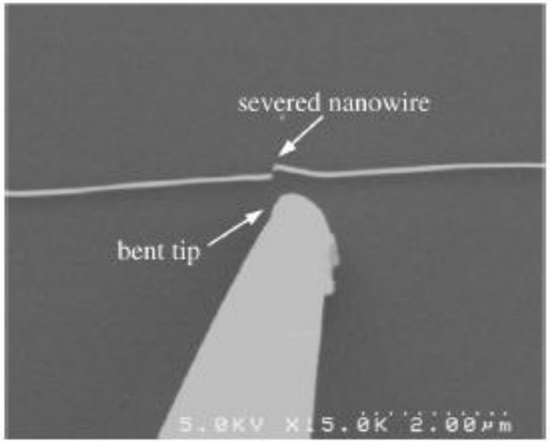


Fig. 7. Manual operation often causes probe tip damage and sometimes inadvertently severs a nanowire.

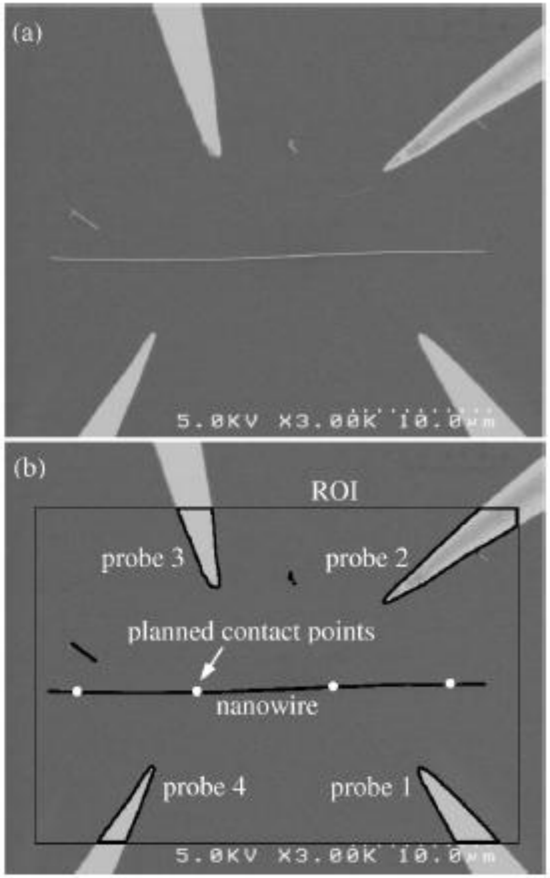


Fig. 2. Visual recognition of probes and nanowires from SEM visual feedback. (a) Four probes and nanowires. (b) Probes and nanowires are recognized from image processing.

RU *et al.* IEEE TRANSACTIONS ON NANOTECHNOLOGY, VOL. 10, NO. 4, JULY 2011

Correction tests

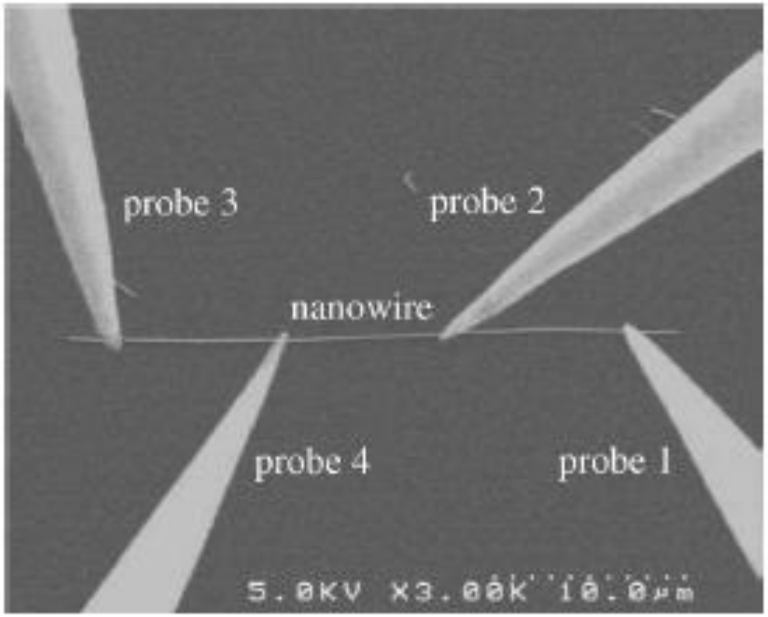


Fig. 10. Four probes landing on target positions for four-point probe measurement.

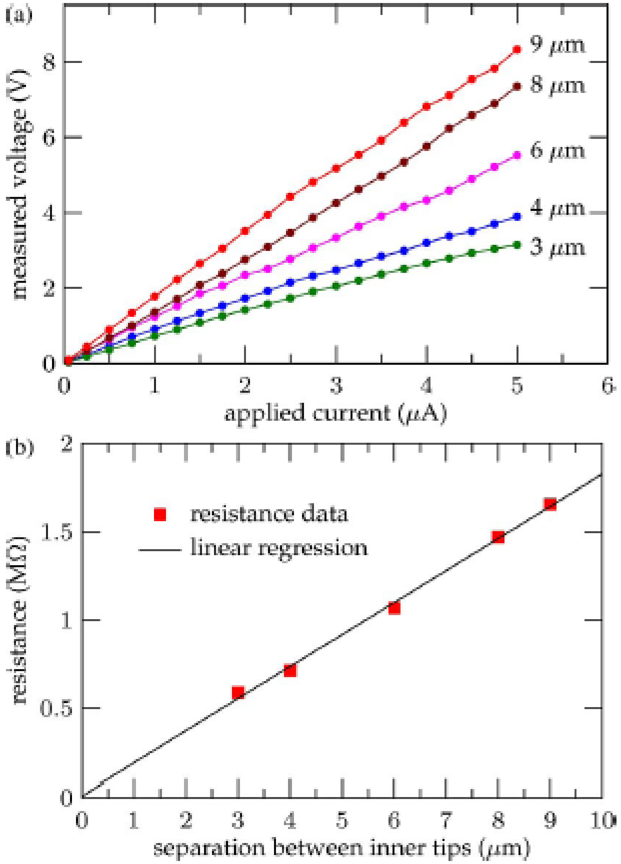
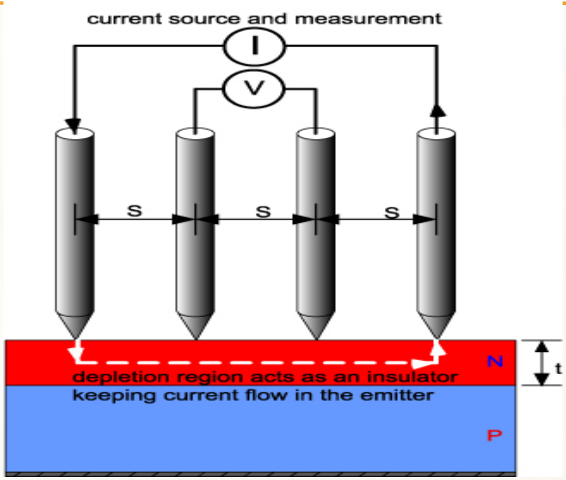


Fig. 11. Four-probe measurement results of a nanowire. (a) I–V data of a nanowire with regard to different separations between the two inner probes. (b) Separation-resistance relationship.

The Measurement of Bulk Resistivity



The measurement of bulk resistivity is similar to that of sheet resistivity except that a resistivity in cm^{-3} is reported using the wafer thickness, t:

$$\rho = \frac{\pi}{ln\,(2)}t\left(\frac{V}{I}\right) = 4.523t\left(\frac{V}{I}\right)$$

Where t is the layer/wafer thickness in cm.

The simple formula above works for when the wafer thickness less than half the probe spacing (t < s/2) (Schroder). For thicker samples the formula becomes:

$$\rho = \frac{V}{I}\frac{\pi t}{ln\left(\frac{sinh\left(\frac{t}{s}\right)}{sinh\left(\frac{t}{2s}\right)}\right)}$$

Where s is the probe spacing.

Cartridge with 4 Pin Connector

Ref. Jandel.com

4 probe contact with silver paint –at low temp

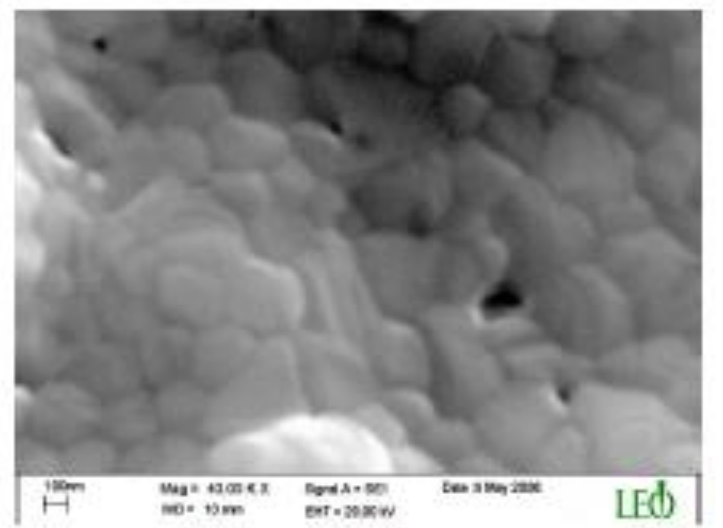


Fig. 2. SEM photographs of the $La_{0.67}Ca_{0.33}MnO_3$ film.

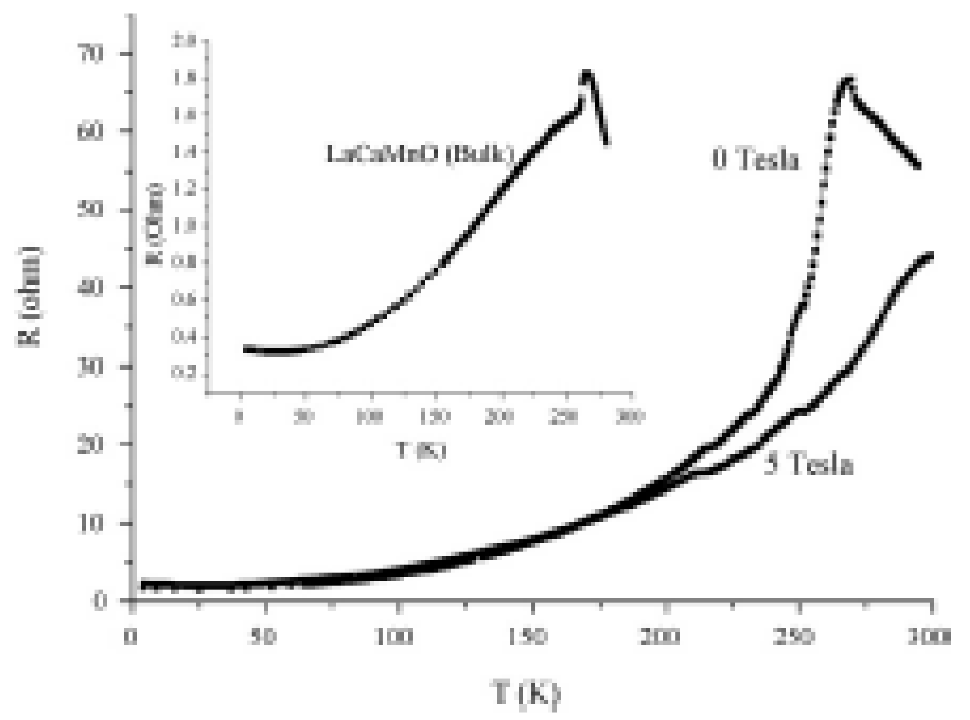


Fig. 4. Resistance variation of the $La_{0.67}Ca_{0.33}MnO_3$ film as a function of temperature at 0 and 5 T magnetic field. Inset shows resistance variation of the bulk $La_{0.67}Ca_{0.33}MnO_3$.

M. Gunes et al. / Materials Science and Engineering B 136 (2007) 41–45

Conclusion

- The importance of thermal and voltage contacts
- Very carefull desing and implementation
- Wireing
- The measurement capability of devices
- Different measurement atmoshphere for different materials
- Simultaneous measurement of TE voltage and temperature

Thank you for kind attention