SAND2015-2543C

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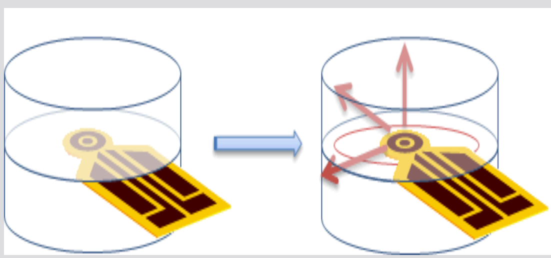
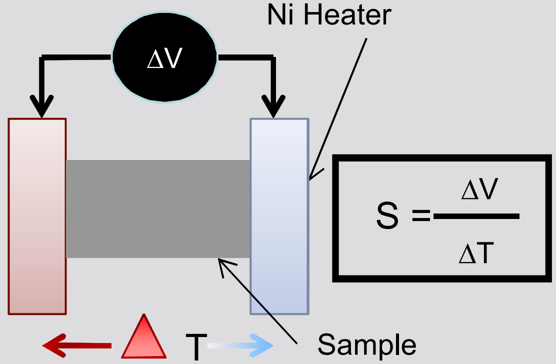
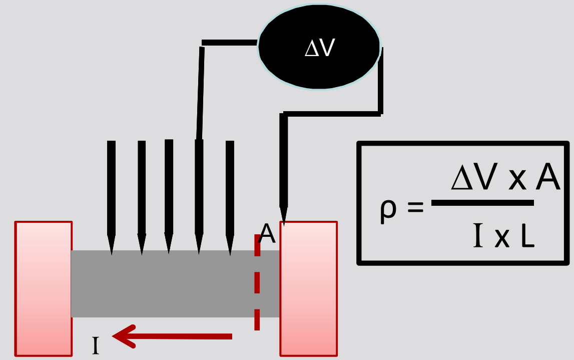
Thermal Conductivity
Thermal Diffusivity
Specific Heat



Seebeck Coefficient



Electrical Resistivity and Contact Resistance



Development of Transport Properties Characterization Capabilities for Thermoelectric Materials and Modules

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U.S. DEPARTMENT OF ENERGY   NNSA National Nuclear Security Administration

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Thermoelectric figure of merit (Z_o and Z_{eff})

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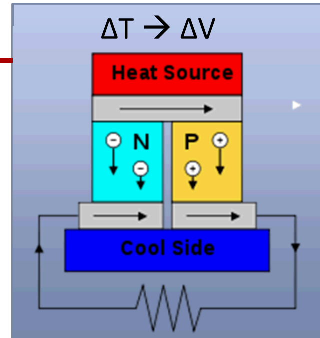
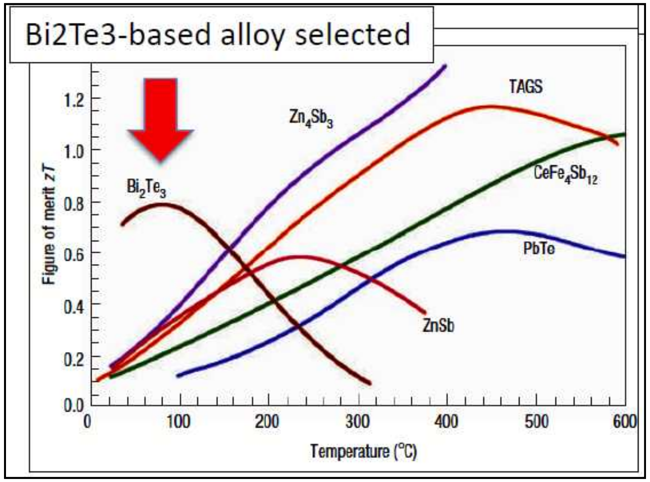
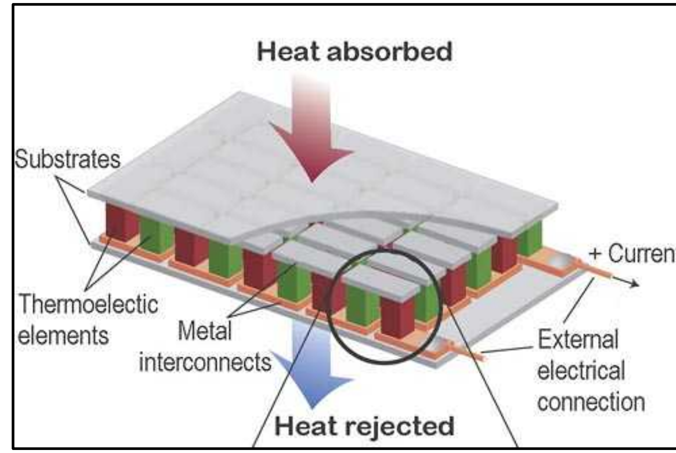
Material



Device





$$Z_o = \frac{S^2}{\rho \kappa}$$

Seebeck Coefficient
- Determined by band structure and carrier density (doping level)
- Semiconductors have higher (useful) S than metals

Thermal Conductivity
- Via phonon and electrical carriers
- Scattering affected by structural features such as grain boundaries and grain size
- Affected by composition

Electrical Resistivity
- Via electrons and holes
- Depends on carrier density and mobility
- Affected by structural features and composition

Thermal efficiency

$$\eta = \frac{T_h - T_c}{T_h} \frac{\sqrt{1 + Z_{eff} T_m} - 1}{\sqrt{1 + Z_{eff} T_m} + T_c / T_h}$$

Materials Term

$$Z_{eff} = Z_o \left(\frac{1}{1 + \frac{2Rc}{R}} \right)$$

Contact Resistance
- Depends on metallization material and process
- Improved by diffusion

Challenges: Significant Measurements Issues

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Home » International Round-Robin on Transport Properties of Bismuth Telluride

INTERNATIONAL ROUND-ROBIN ON TRANSPORT PROPERTIES OF BISMUTH TELLURIDE

- Vehicles Home
- About Vehicle Technologies Office
- Plug-in Electric Vehicles & Batteries

IEA-AMT round-robin testing of n- and p-type bismuth telluride transport properties showed significant measurement issues and highlighted need for standardization of measurements of thermoelectric material properties

wang.pdf

MORE DOCUMENTS & PUBLICATIONS

Reliability of Transport Properties for Bulk Thermoelectrics

Hsin Wang

Oak Ridge National Laboratory
Oak Ridge, TN USA

http://energy.gov/eere/vehicles/downloads/international-round-robin-transport-properties-bismuth-telluride

IEA-AMT Focus: Bulk Thermoelectrics Used for Automotive Waste Heat Recovery

- **Significant gaps exist between literature ZT values and scalable materials**
- **Possible Issues:**
  - **Measurement errors**
  - **No standards for calibration**
  - **Incomplete measurements**
  - **Data extrapolation**
  - **Materials non-uniformity**
  - **Orientation effect**
  - **Measurements on different samples**

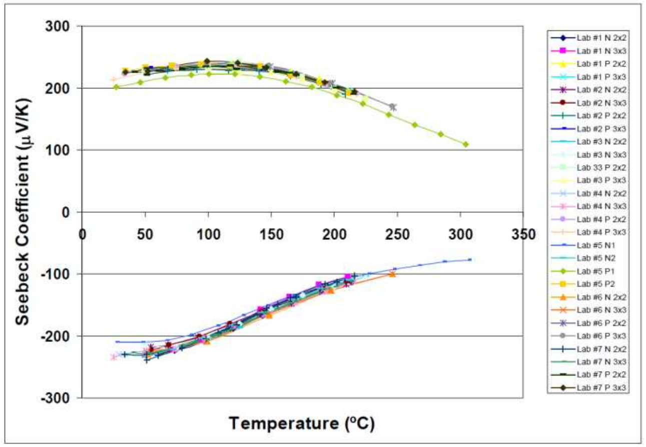
4 Managed by UT-Battelle for the Department of Energy

OAK RIDGE National Laboratory

Findings: Error for ZT from 12 to 21%

Sandia National Laboratories

Round-robin 1: Seebeck Coeffieicnt



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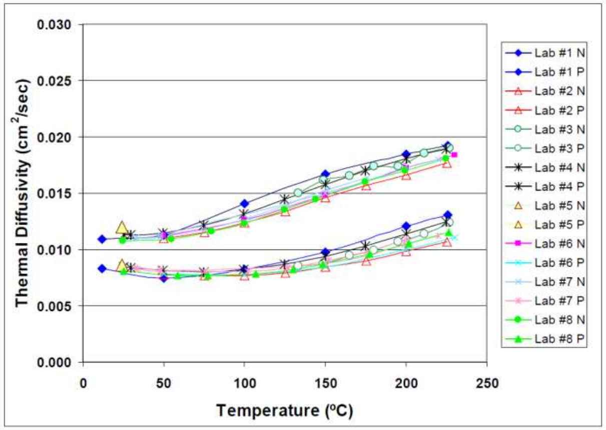
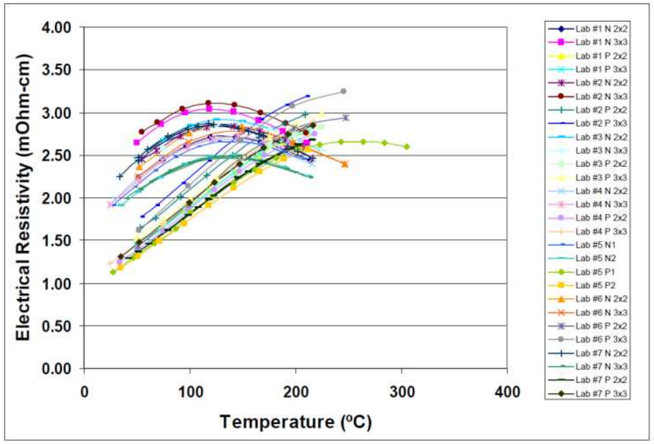
Round-robin 1: Thermal Diffusivity



Results from 8 labs

OAK RIDGE National Laboratory

Round-robin 1: Electrical Resistivity



OAK RIDGE National Laboratory

Summary

- **IEA-AMT is addressing the important issue of measurement standardization of thermoelectrics**
- **Significant measurement issues were observed, especially in specific heat and electrical resistivity.**
- **Good agreements in Seebeck coefficient, electrical resistivity**
- **Thermal diffusivity in good agreement expect for one test (data analysis)**
- **Specific heat remains an issue for reliable ZT**
- **Round-robin 3 underway**
- Overall errors for ZT are from ± 12% to 21%

OAK RIDGE National Laboratory

Development of Thermoelectric Characterization Capabilities at SNL

- <u>Phase I</u>: Instrumental Development and Standardization
  - Figure of merit (Z_o and Z_{eff}) is calculated as function of temperature

$$Z_o = \frac{S^2}{\rho.\kappa}$$

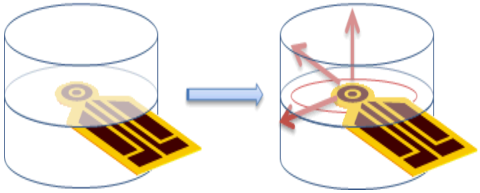
$$Z_{eff} = Z_o\left(\frac{1}{1+\frac{2R_C}{R}}\right)$$

- Seebeck coeffiecient (S)
- Electrical resistivity (ρ)
- Thermal conductivity (κ)
- Contact Resistance (Rc)

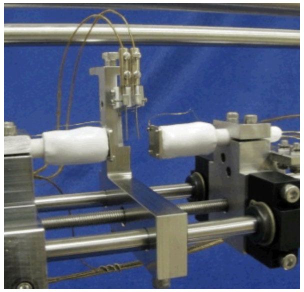
- <u>Phase II</u>: Material thermal aging studies
  - Isothermal aging of Bi2Te3-based Alloys up to 2 year
  - Effect in Zo and Zeff
- <u>Phase III</u>: Advanced Characterization
  - Non-destructive characterization of TE devices
  - Realistic conditions: Temperature gradient and applied current
  - Abnormal environments

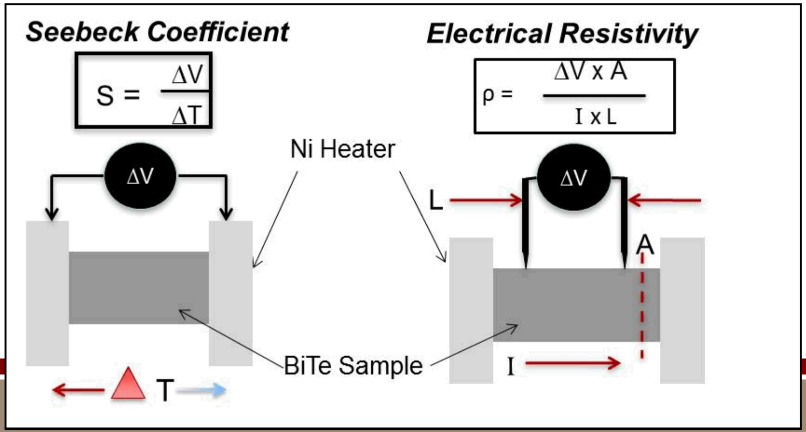
Phase I: Commercial and custom built systems

- **Commercial device:**
  - **TPS 2500S Thermal Property System:** Advanced system for testing the thermal conductivity, thermal diffusivity and specific heat.
  - Hot Disk sensor is used both as a heat source and as a dynamic temperature sensor.
  - The heat generated dissipates through the sample on either side at a rate dependent on the thermal transport characteristics of the material.
  - By recording the temperature versus time response in the sensor, thermal conductivity can accurately be calculated.



- **Custom-built device for Seebeck/Resistivity measurements**
  - To measure resistivity, the sample is located between two heaters with two voltage probes in contact with the top surface. A known current is then sent through the material and a voltage recorded.
  - To measure Seebeck, a temperature gradient is set up across the material and the voltage recorded.





Standardization

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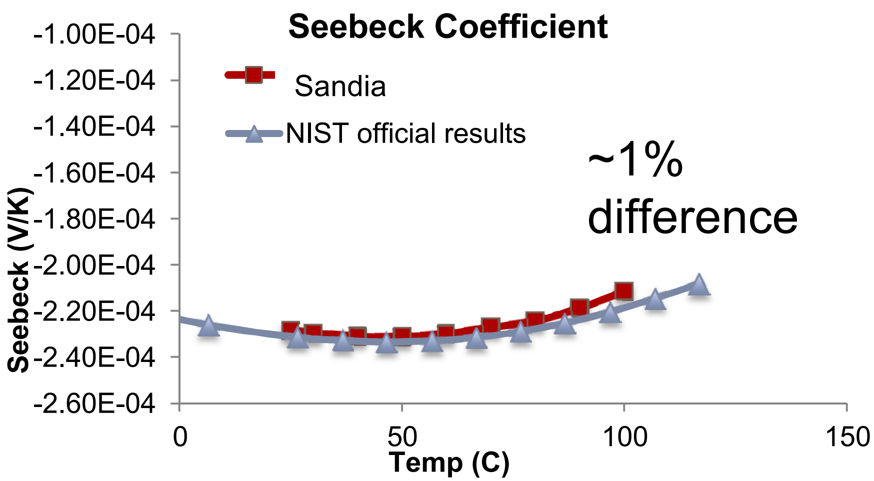
- NIST Standard for Seebeck Coefficient



National Institute of Standards & Technology

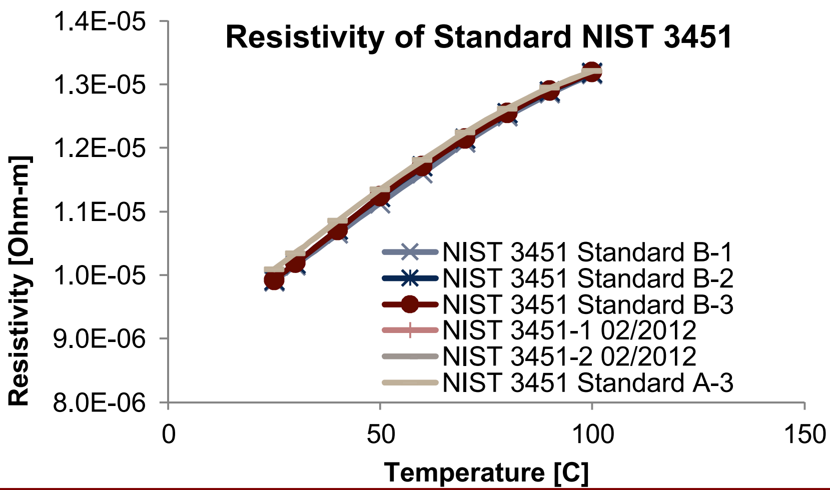
Certificate

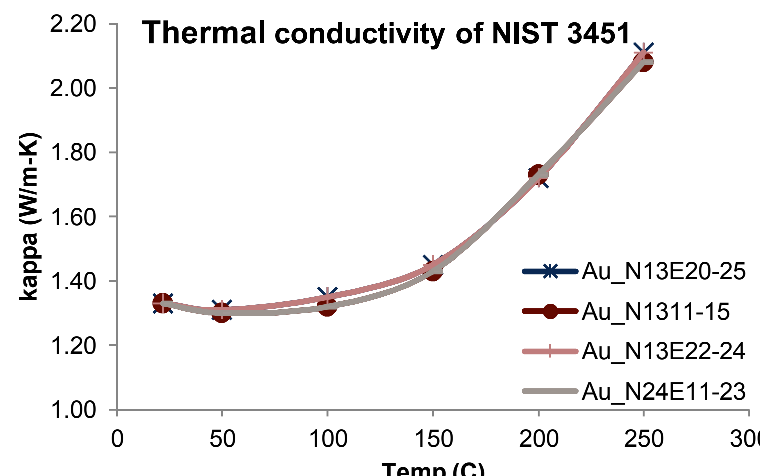
Standard Reference Material® 3451

Low-Temperature Seebeck Coefficient Standard (10 K to 390 K)

- Variation Coefficient is < 1% for all the measurements.
- The data is reproducible over one year.
- NIST standard is used as reference and it is measured periodically.

- No NIST standard for resistivity or thermal conductivity

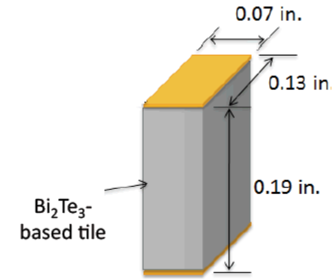


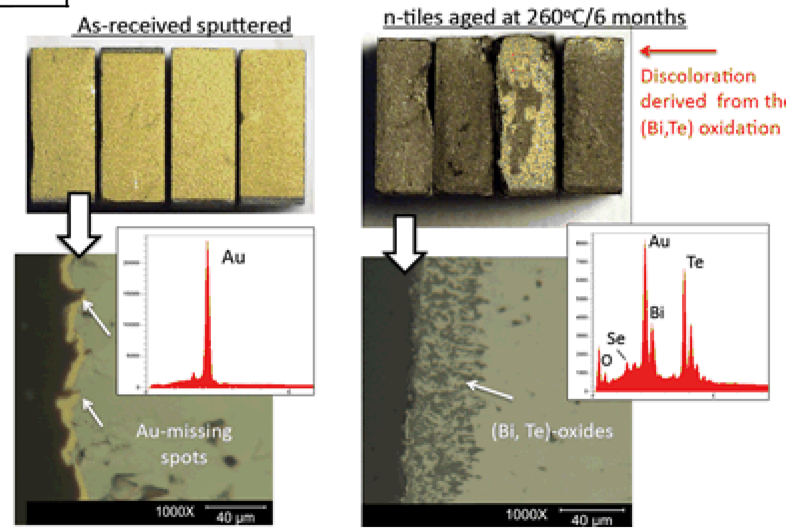


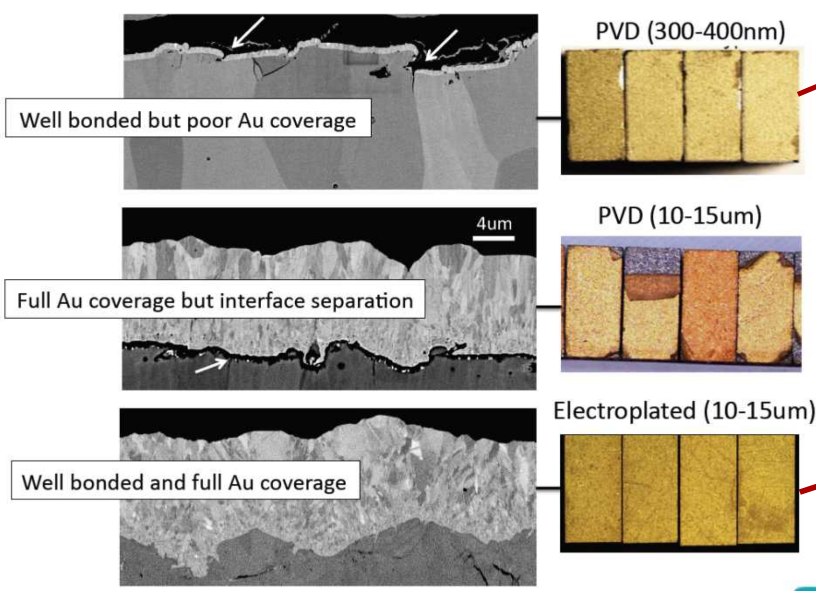
Phase II: Thermal Aging Studies

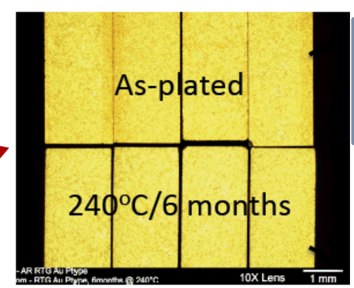
Base TE Material	Diffusion Barrier	Aging Temperature	Aging Period
p-type Bi-Te	Electroless Ni	100 ° C	2 weeks
n-type Bi-Te	Electroless Co	175 ° C	8 weeks
	Electrolytic Co	240 ° C	Six months
	Electroless Pd	350 °C	1 year
	Electrolytic Pd		2 years
	PVD/sputter Au		
	Electroplated Au		

Today's Focus (PVD/sputter Au, Electroplated Au)









No Surface oxidation or interfacial reaction

Transport properties changes????

TE transport properties for the n-type aged up to 2 yr @ 240°C

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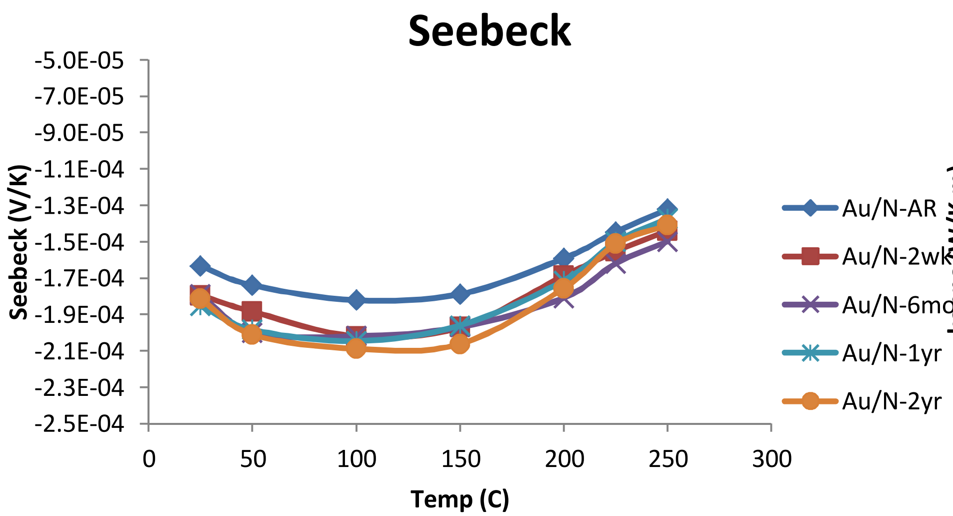
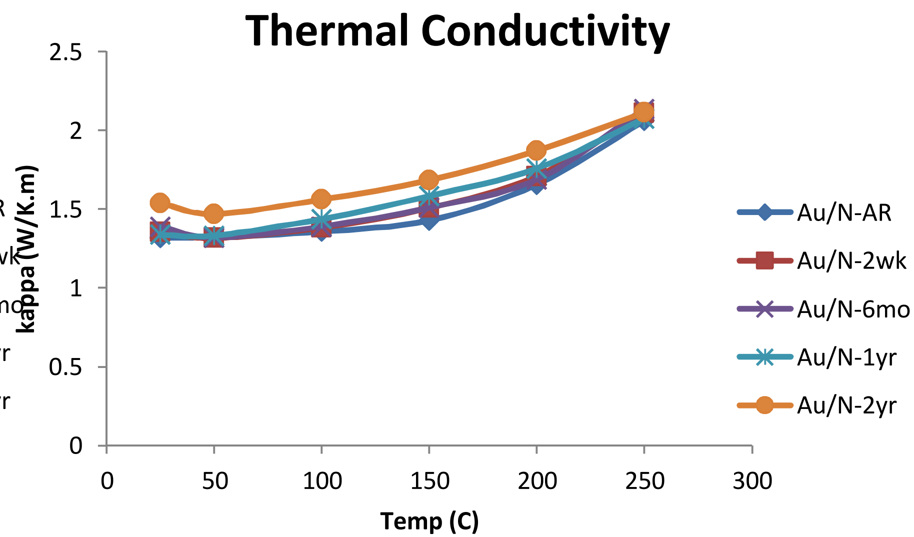
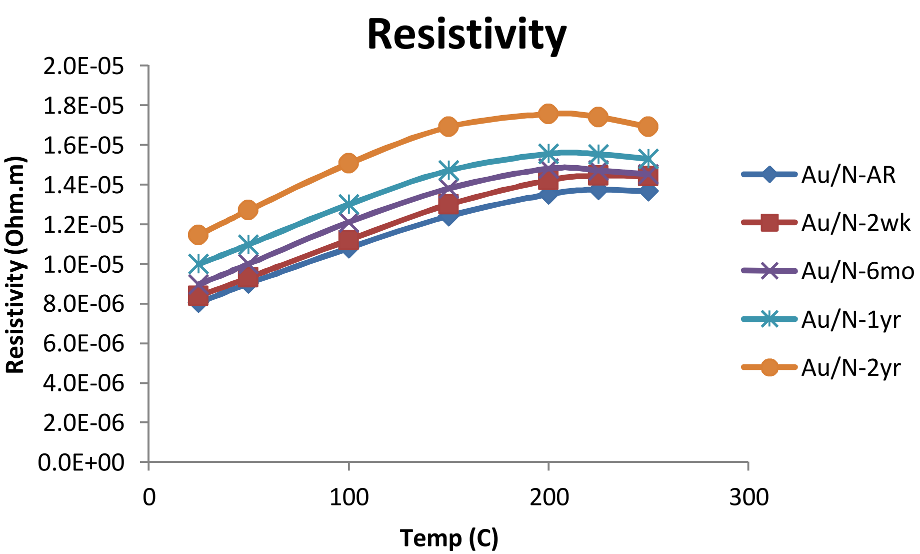
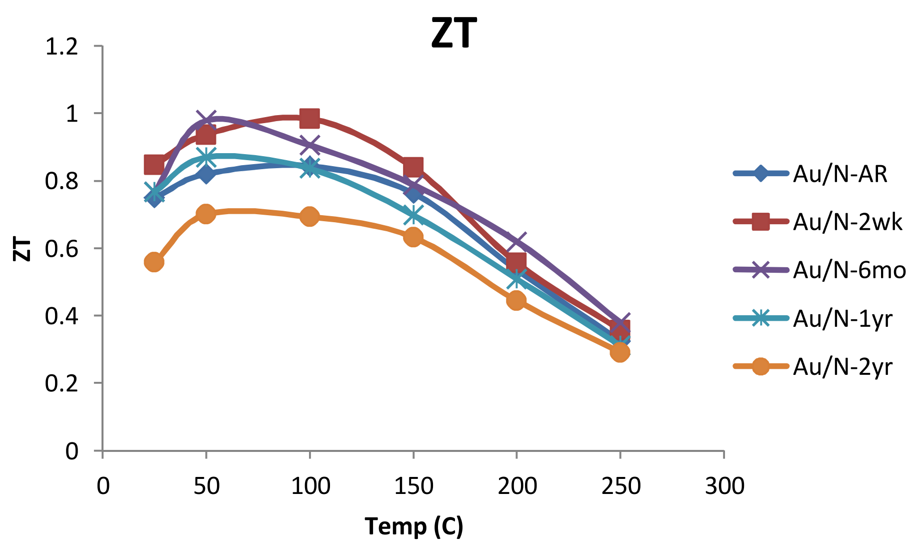
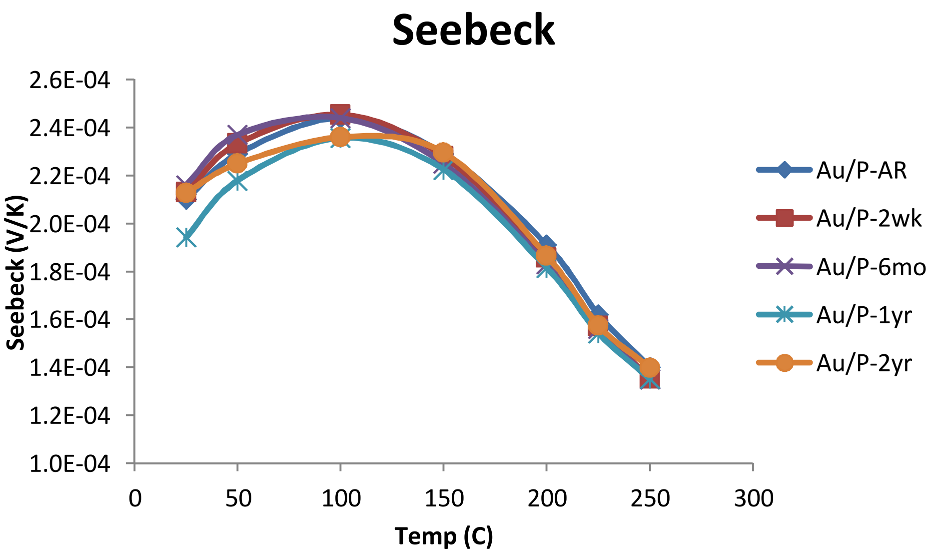


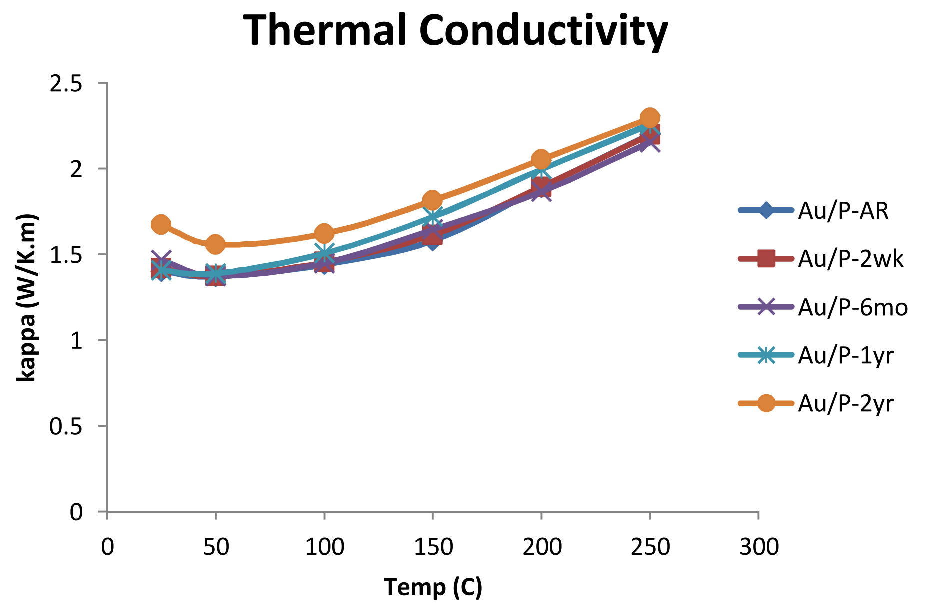


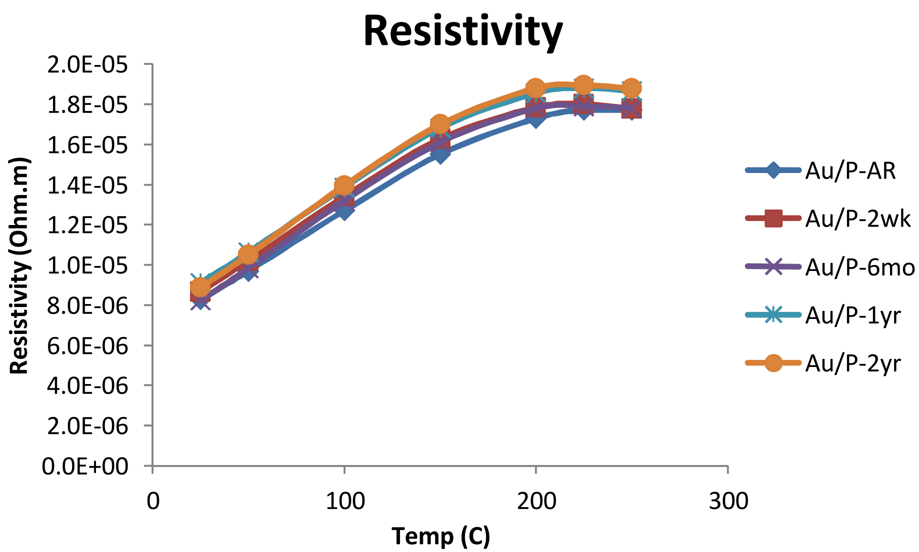


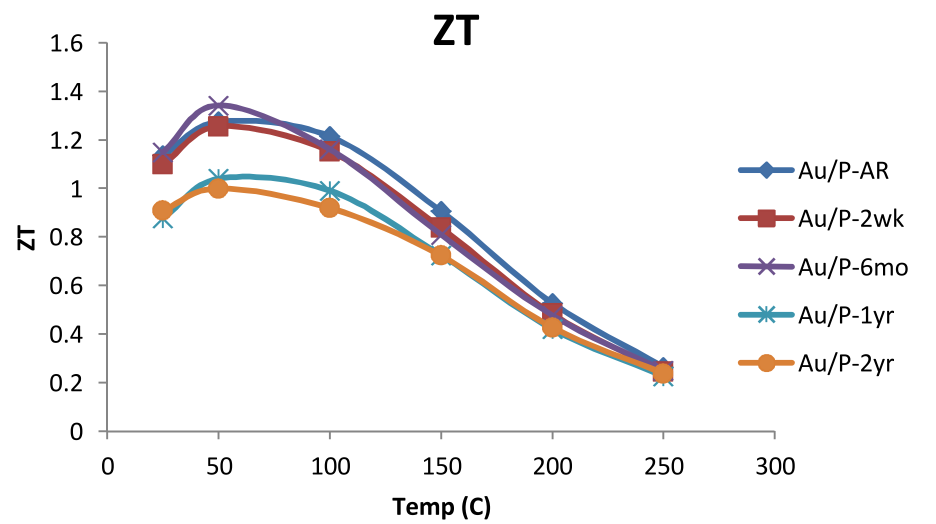


TE transport properties for the p-type aged up to 2 yr @ 240°C





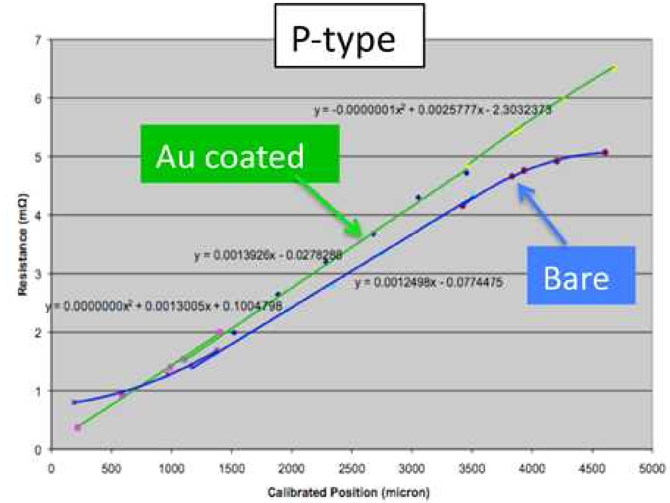


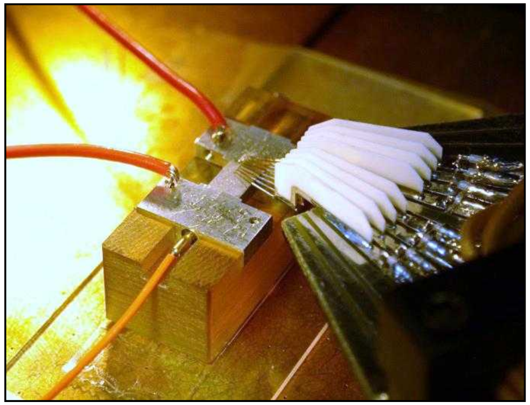


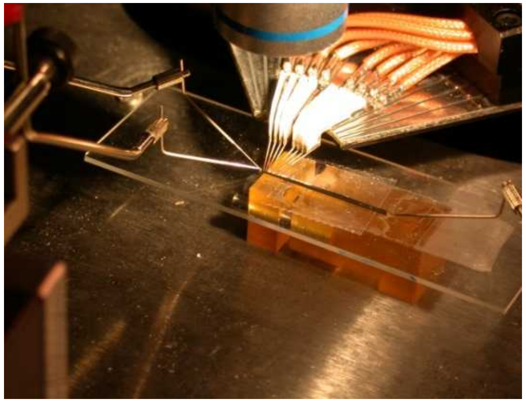
Phase III: Advanced Characterization

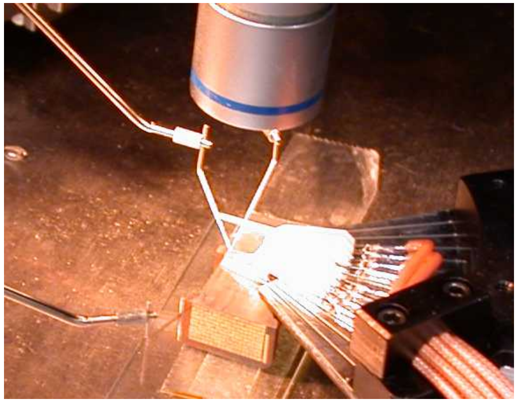
- Contact resistance and bulk resistivity measurements by 4-point probe method using custom built in-house device
- current is injected across two faces of the sample while voltage measurements are taken at equal distances (400µm) on the top face.

slope → resistivity | y-intercept → contact resistance









Original setup to measure tiles → New setup to measure thin elements → Modified setup to measure TE Modules

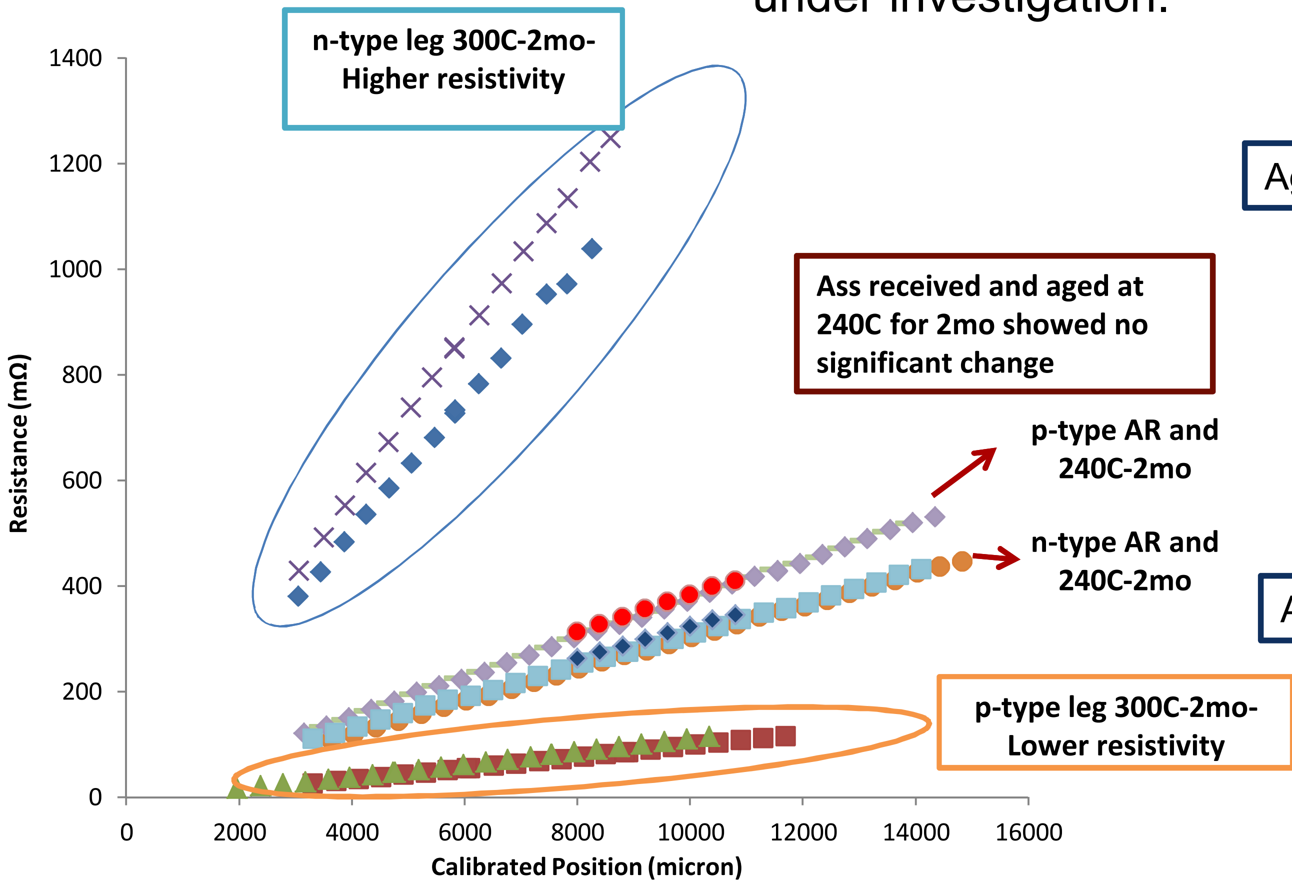
Original setup to measure tiles
- Sample size limitation
- Fixed setup

New setup to measure thin elements
- Sample size flexibility
- 2D adjustable probes
- Samples: thin elements (cross section = 0.25 mm^2) with any lengths.

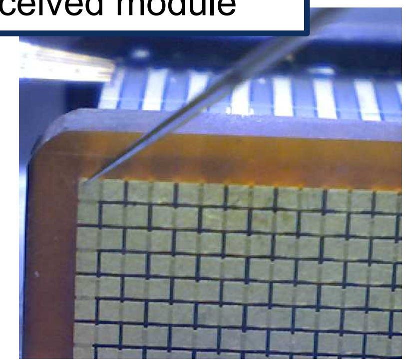
Modified setup to measure TE Modules
- Front/rear cameras for 3D adjustments
- Samples: TE modules
- Contact resistance of metallization on the hot and the cold end.

Resistivity changes of modules at abnormal temperature

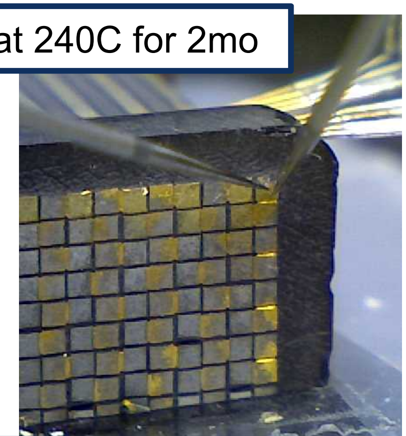
The resistivity changes at abnormal temperatures are under investigation.



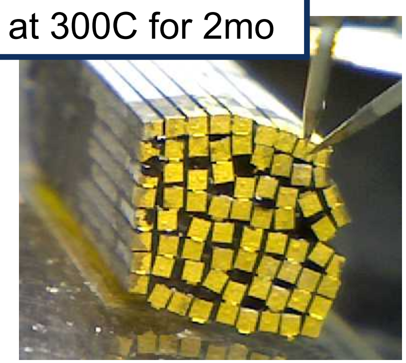
As received module



Aged at 240C for 2mo



Aged at 300C for 2mo



Summary

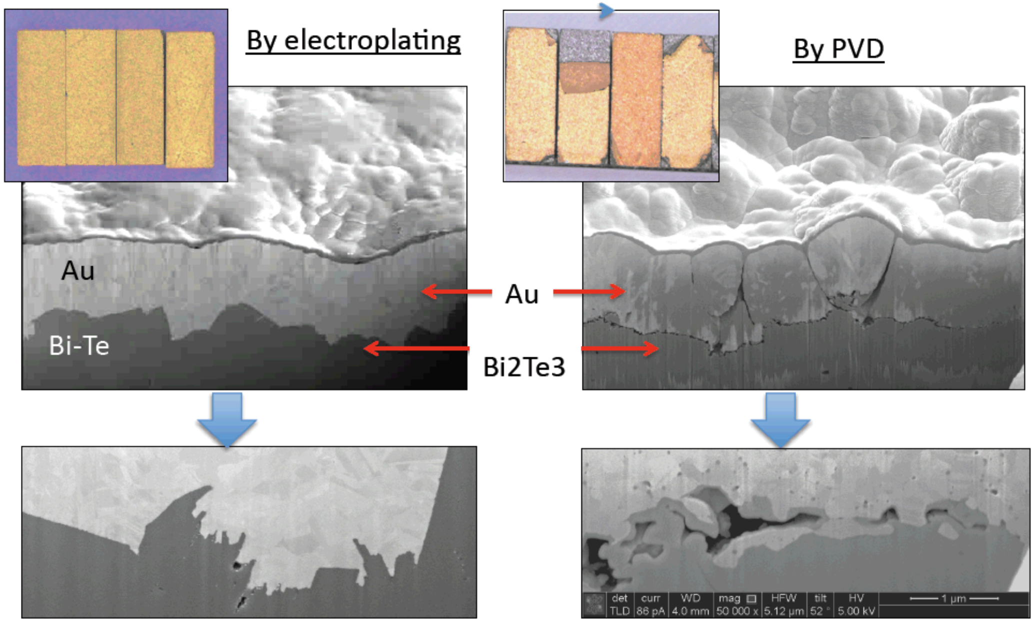
- International Round-Robin study found that significant measurements issues and 12-21% differences on ZT values.
- Sandia has dedicated several years on the development of reliable and reproducible in-house thermoelectric characterization capabilities.
- Sandia has conducted thermal aging studies up to 2yr to determine how the performance of the bulk material and metallization changes with aging time and temperature.
  - Electroplated Au metallization is thermal stable
  - Bulk Bi_2Te_3-based alloys showed a change in transport properties (in particular in resistivity) after 2 yr aging.
- Advanced instrumentation makes possible the non-destructive analysis of thermoelectric modules.
- Based on the resistivity changes, we are conducting further studies to determine the root causes of these changes.

Acknowledgements

- Coauthors: Nancy Yang, Jeff Chames, Ryan Nishimoto and Josh Whaley
- Peter Sharma and Alf Morales
- Sandia CA and NM
- Dale Hume, president of Thermtest, Inc.

Questions?

Extras

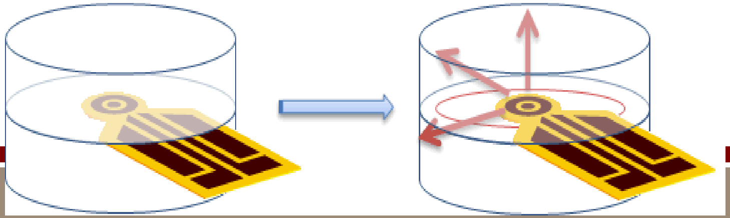


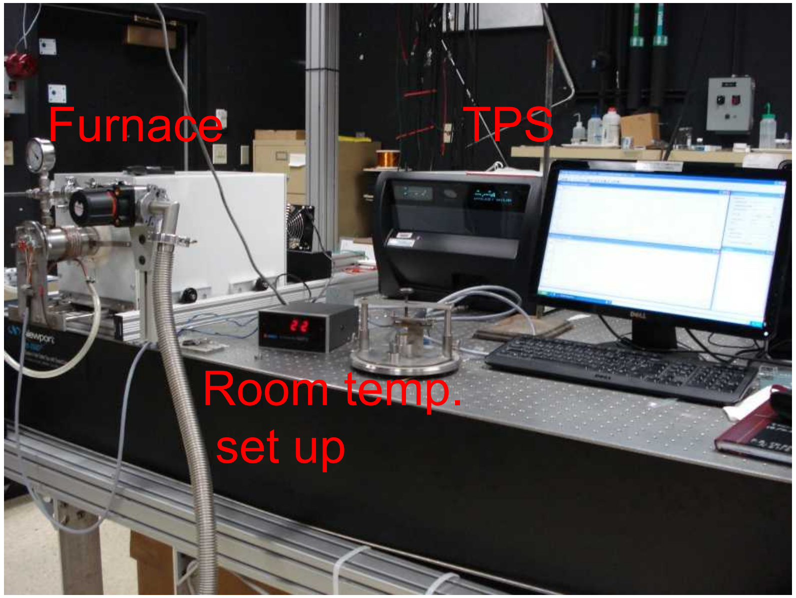
The plated-in Au provides good mechanical locking for adhesion

The PVD Au is unable to fill the surface defect to provide mechanical locking.

Thermal Conductivity measurement procedure

- Hot Disk Sensor- consists of an electrically conducting pattern of a thin sheet of Nickel.
- Hot Disk sensor is fitted between two pieces of the sample each one with a plane surface facing the sensor.
- Hot Disk sensor is used both as a heat source and as a dynamic temperature sensor.
  - Apply an electrical current, high enough to increase the temperature of the sensor between a fraction of a degree up to several degrees.
  - At the same time recording the resistance (temperature) increase as a function of time.
- The heat generated dissipates through the sample on either side at a rate dependent on the thermal transport characteristics of the material.
- By recording the temperature versus time response in the sensor, thermal conductivity can accurately be calculated.



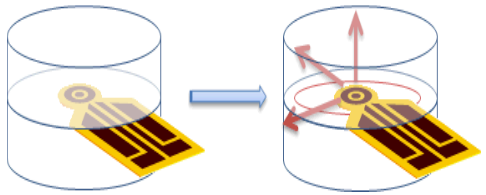


TPS 2500S Thermal Property System

- Advanced system for testing the thermal conductivity, thermal diffusivity and specific heat of solids, liquids, pastes & powders.
- Accuracy: Better than 5%
- Repeatability: Typically better than 1%
- Thermal Conductivity : 0.005 to 500 W/mK
- ***New system***- low temperature test cell and bath (s) for -40 to 200 / 300C.

TPS 2500S Thermal Property System

- Hot Disk Sensor- consists of an electrically conducting pattern of a thin sheet of Nickel.
- Hot Disk sensor is fitted between two pieces of the sample each one with a plane surface facing the sensor.
- Hot Disk sensor is used both as a heat source and as a dynamic temperature sensor.
  - Apply an electrical current, high enough to increase the temperature of the sensor between a fraction of a degree up to several degrees.
  - At the same time recording the resistance (temperature) increase as a function of time.
- The heat generated dissipates through the sample on either side at a rate dependent on the thermal transport characteristics of the material.
- By recording the temperature versus time response in the sensor, thermal conductivity can accurately be calculated.
- The Thin Film Module allows for thermal conductivity measurements on single layer thin films and coatings.



Specifications

TC: 0.005 - 10 W/(mK)
Temp: -160 to 300 °C
Repeatability: Typically better than 3%
Sample thickness: 0.01 - 2 mm

ThermTest Inc
ThermoPhysical Measurements & Instrumentation

Sandia National Laboratories

Seebeck Coefficient and Resistivity Measurement

The custom built in-house device has been used to measure the Seebeck coefficient and electrical resistivity of thermoelectric materials within the temperature range of 22 ° C to 350 ° C.

- To measure resistivity, the sample is located between two heaters with two voltage probes in contact with the top surface. A known current is then sent through the material and a voltage recorded.
- To measure Seebeck, a temperature gradient is set up across the material and the voltage recorded.