



# Update of material R&D activities for $\text{Bi}_2\text{Te}_3$ -based thermoelectric module development

Nancy Yang, 8651, SNL-CA

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# Outline

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- Programmatic goal
- Fundamentals and system concept of TE power generation
- Background & motivation
- Science & Technology progress
- Summary
- Future work

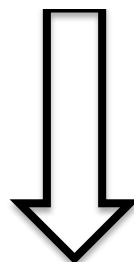




# Programmatic goal

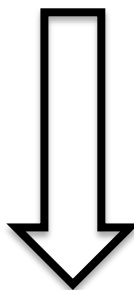
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**Develop materials and capabilities**



Enable design and build

**High performance long-life  $\text{Bi}_2\text{Te}_3$ -based TE device**



Allow

**Mine electrical power from a low level heat source**



## Material factors impact figure of merit (ZT), therefore, power generation efficiency

Figure-of-merit:  $ZT = \frac{S^2}{K_{\text{electronic}} + K_{\text{lattice}}} T$

Seebeck coefficient:  $S = \frac{k_B}{e} [\delta + C - \ln n_c]$

Electrical resistivity:  $\rho = \frac{1}{e\mu n_c}$

Material factors

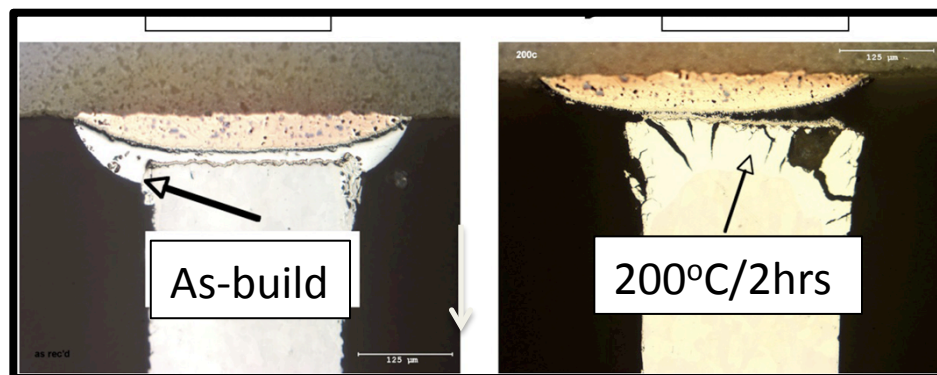
Where  
n = carrier concentration. lattice defects and microstructure dependent.  
K = Thermal conductivity, affected by phonon scattering, grain size dependent  
 $\mu$  = Mobility, grain size, lattice defect and crystal orientation dependent  
 $\sigma$  = Electrical conductivity, inverse of resistivity ( $\rho$ )

### • Maximum Generator Efficiency

$$\eta = \frac{T_h - T_c}{T_h} \frac{\sqrt{1 + ZT_{\text{avg}}} - 1}{\sqrt{1 + ZT_{\text{avg}}} + T_c / T_h}$$



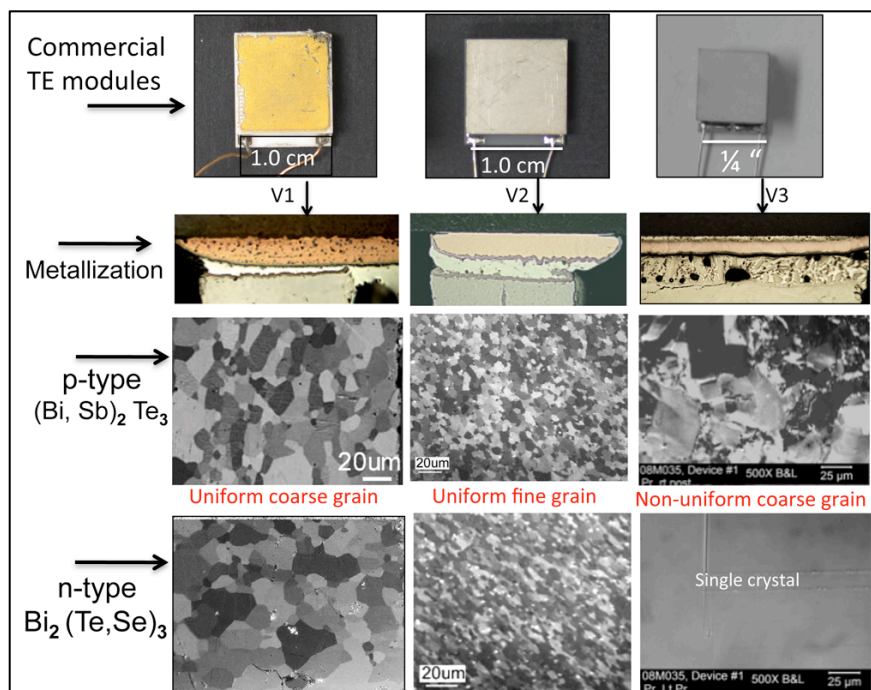
## Background & motivation



Commercial TE module built for cooling application is not a good option

Thermal instability at  $\leq 180^{\circ}\text{C}/2\text{hrs}$ , close to the temperature of interest.

Compromises module integrity ?



Large variation in base alloys metallurgy among the commercial TE modules

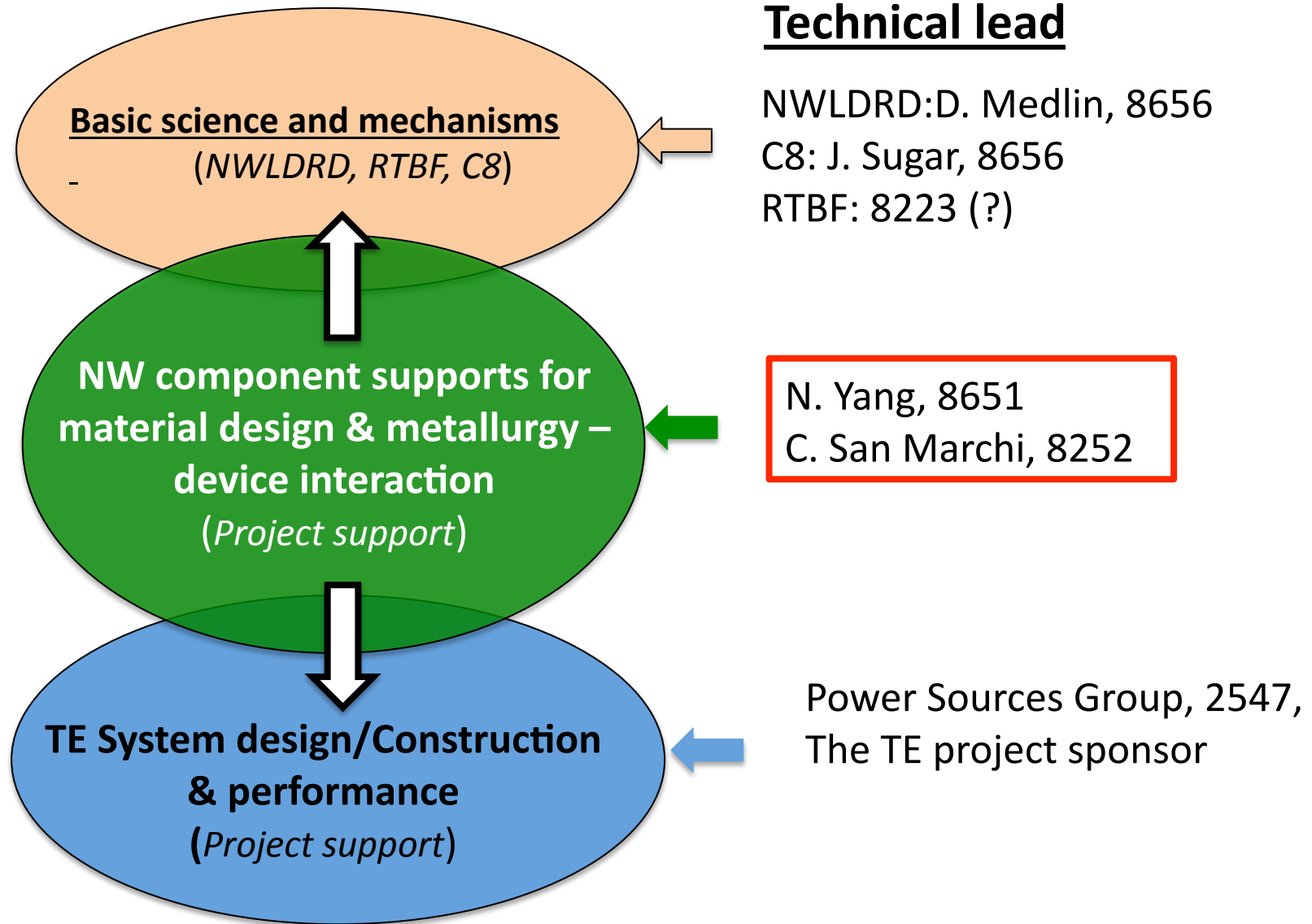
Create challenge for product specification and supply ?

Led to

Current Science & Technology activities



## S&T investments in SNL,CA

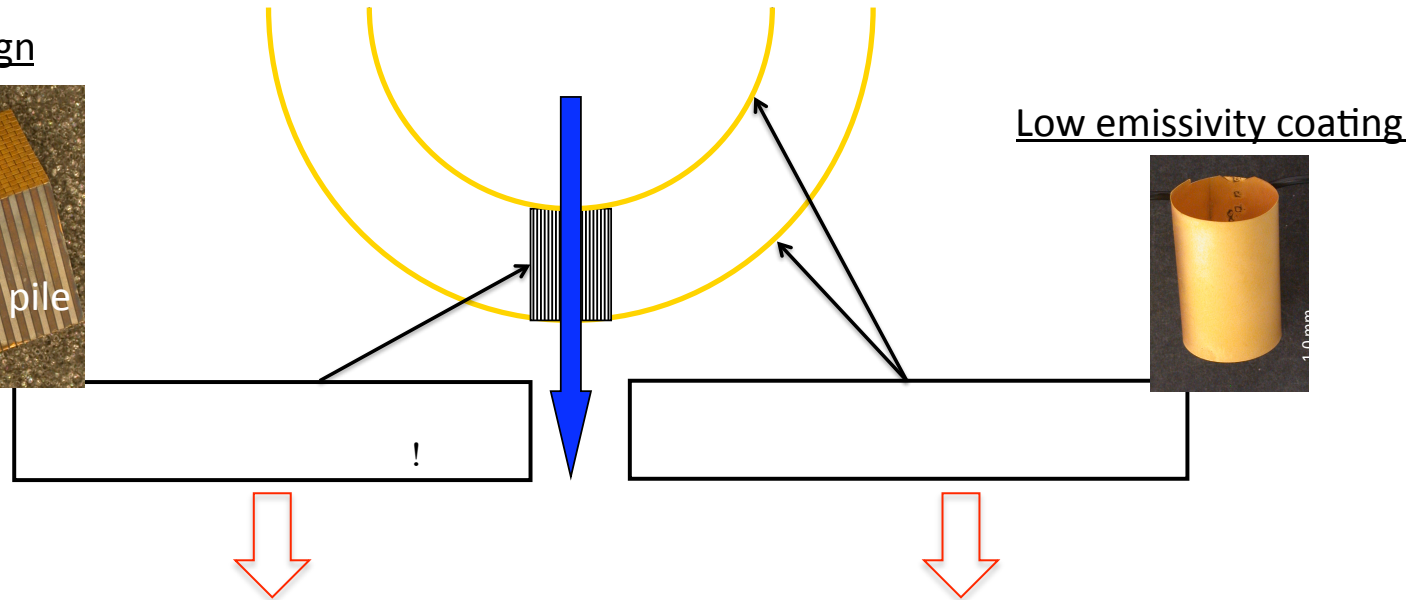
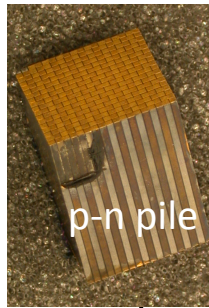
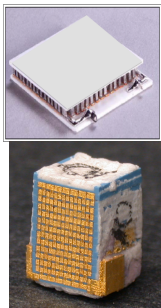




# TE system concept and the associated material science and technology issues

Heat source (100-250°C)

## TE module design



- P-n base alloy metallurgy & material science.
- Interconnect metallization design & processing
  - Material aging /compatibility/ interaction
  - TE transport mechanism
- Thin film processing, metallurgy, thermal aging and coating-substrate interaction

Note: Thin film thermal aging is common to both components



# Current S&T activities and the technical teams

## P and n base alloy

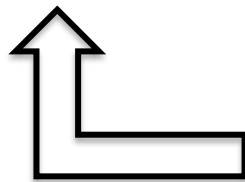
(SNL-CA, 8651)

- **Material synthesis and processing**  
*E. Lavernia/N. Yang/C. San Marchi*
- **Alloy metallurgy & material science**  
*N. Yang /C. San Marchi*
- **Mechanical property**  
*W. Lu*
- **TE transport**  
*K. Reyes/P. Sharma*
- **Predictive model validation**  
*X. Zhou*

## TE module engineering

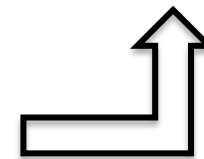
(SNL-NM, 2547)

- **Metallization design & construction**  
*Org. 2547/N. Yang*
- **Thin film processing**
  - Non-electroplating.: *Org. 2547*
  - Metal electroplating: *Banga/Yang*
- **Material-device interaction**
  - Environmental effect: *Yang/Mills/Kruzinga/Karnesky*
  - Thin film metallurgy & reaction:  
*N. Yang/C. San Marchi /X. Zhou*
- **Mechanical behavior**  
*Org. 2547/W. Lu*



## Basic science collaboration

D. Medlin / J. Zimmerman / J. Sugar





# Acknowledgement

Ryan Nishimoto, 8651-----TE measurement, microscopy imaging  
Jeff Chames, 8651-----Thermal aging experiment, microscopy imaging  
Andy Gardea, 8651 -----Optical metallography imaging  
Josh Whaley, 8252 -----TE measurement, hardware design and installation  
Michael Rye, 1822 -----FIB imaging  
Richard Grant, 1822-----Chemical analysis  
April Nissen, 8223----- Emissivity measurement  
Wiley Neel 8226-----TE measurement



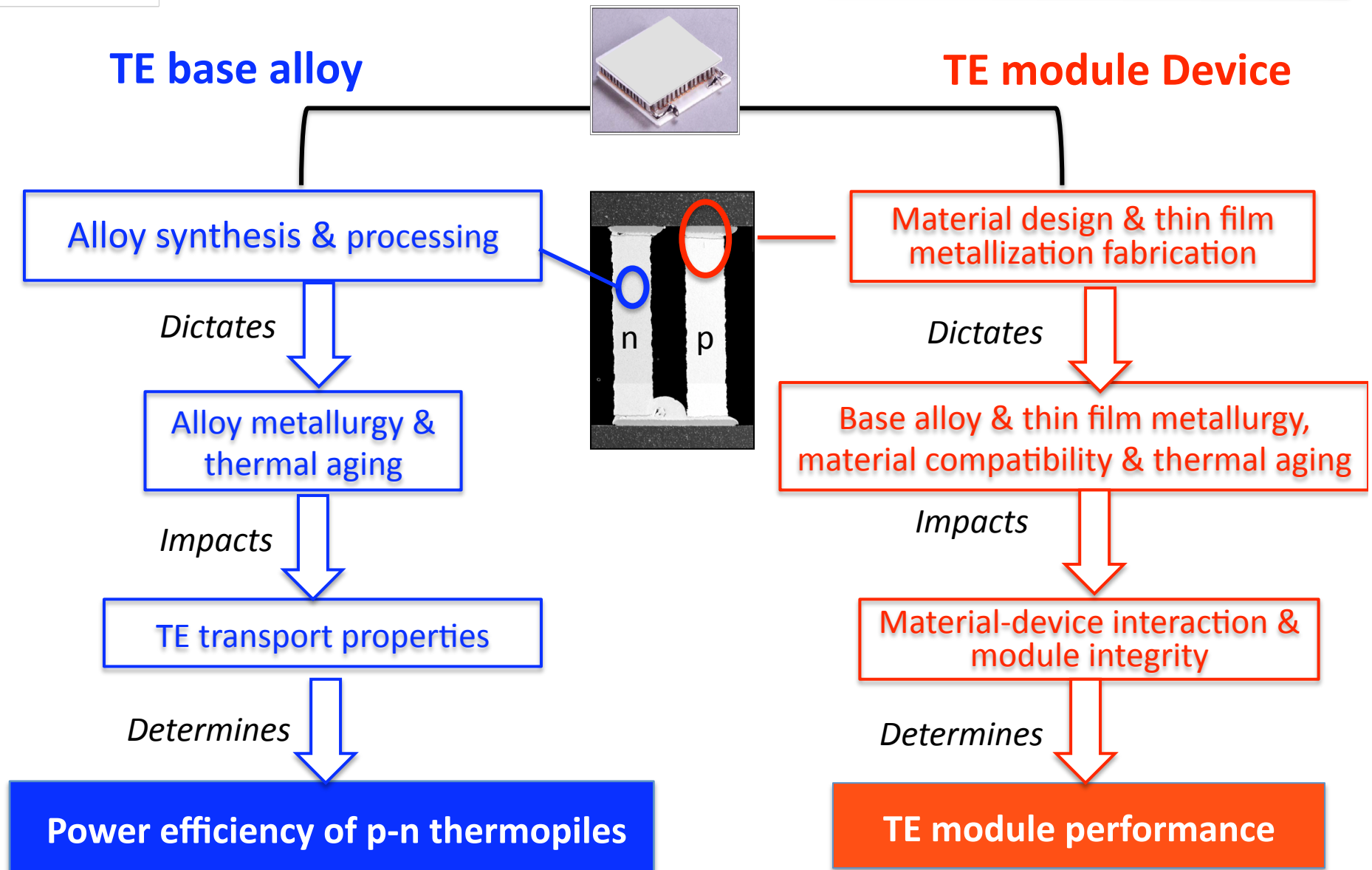
# Summary

- $\text{Bi}_2\text{Te}_3$ -based alloys possess stable metallurgy, therefore, consistent transport property, up to 240°C/year.
- Electroplated thin film Au exhibits strong adhesion and low emissivity to fulfill the function of interconnect metallization and lowering heat emission.
- The  $\text{Bi}_2\text{Te}_3$ -based alloys shows strong texture leading to anisotropic mechanical properties, Au- diffusion and TE transport properties.
- The  $\text{Bi}_2\text{Te}_3$ -based TE system is susceptible to adverse oxygen-induced phase transformation at relatively low oxygen environment.
- Accelerated thermal aging testing at 350°C/1month indicates vulnerability of module integrity of Au/ $\text{Bi}_2\text{Te}_3$  system.





# Material issues to be addressed for TE module





## On going R&D activities and collaborations

### P and type base alloys

- Alloy synthesis & processing

UC Davis

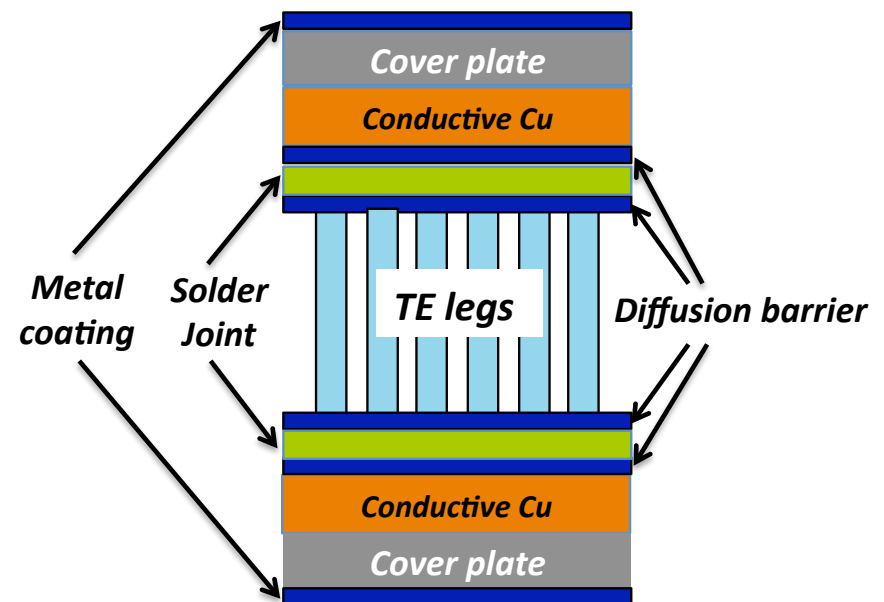
Establish Process-metallurgy-TE  
transport property relationship

SNL, CA

- Alloy metallurgy & thermal aging
  - TE transport properties

### TE module device

- Material design & thin film fabrication



- Alloy metallurgy and material design/  
construction of Interconnect metallization
- Material compatibility & thermal aging for  
the experimental p – n tiles from 2547
- Material-device interaction



# Material Issues to be addressed for the thermal management system

## Low emissivity thin metal coating

## Thin film adhesion & metallurgical stability

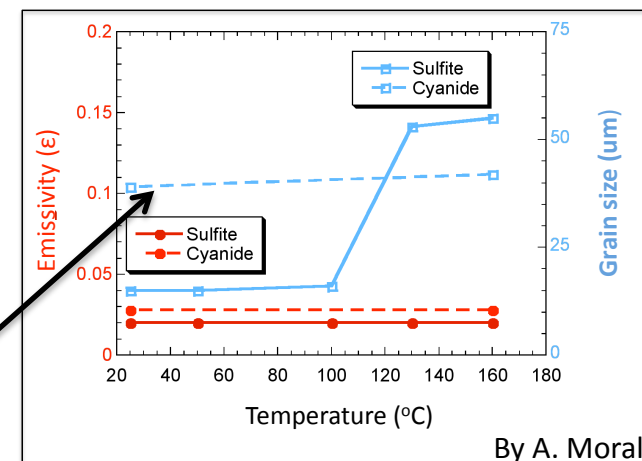
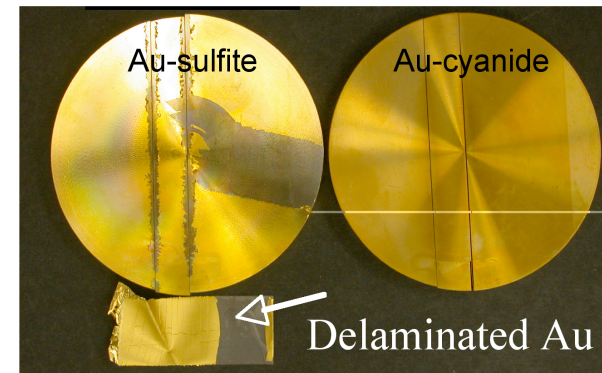


*Applies low emissivity metal coating*

| Metal type | Exp. emissivity $\epsilon$ | Ideal emissivity $\epsilon$ |
|------------|----------------------------|-----------------------------|
| Ni         | 0.04                       | 0.033                       |
| Al         | 0.02                       | 0.019                       |
| Ag         | 0.015                      | 0.016                       |
| Cu         | 0.027                      | 0.015                       |
| Au         | 0.02 (by SNL)              | 0.007                       |
| 304L ss    | 0.12 (by SNL)              | 0.098                       |



*Electroplates gold on 304L stainless steel*



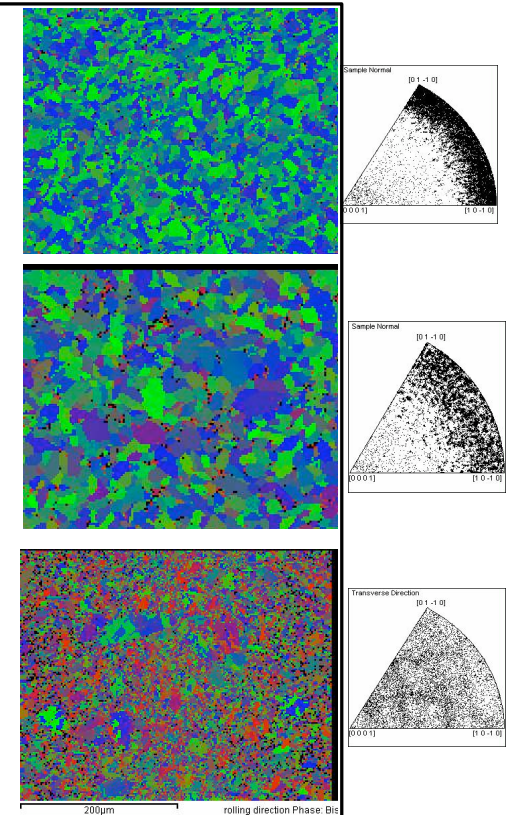
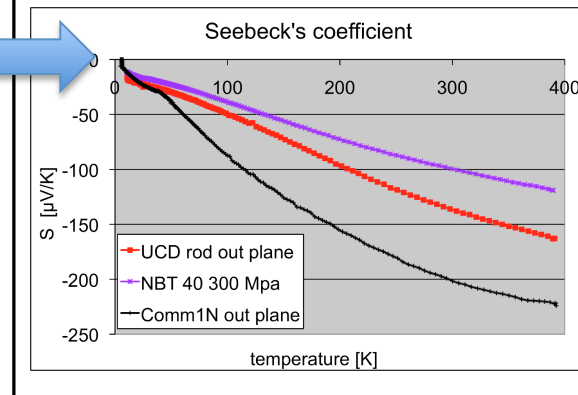
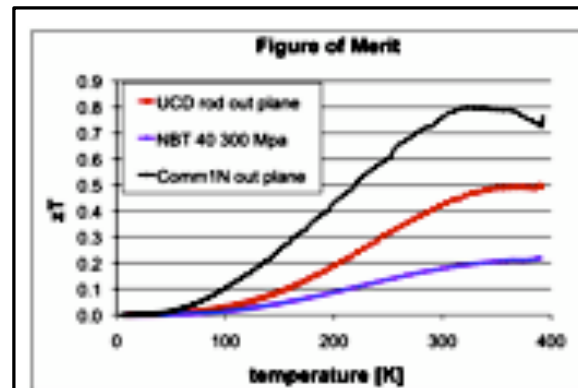
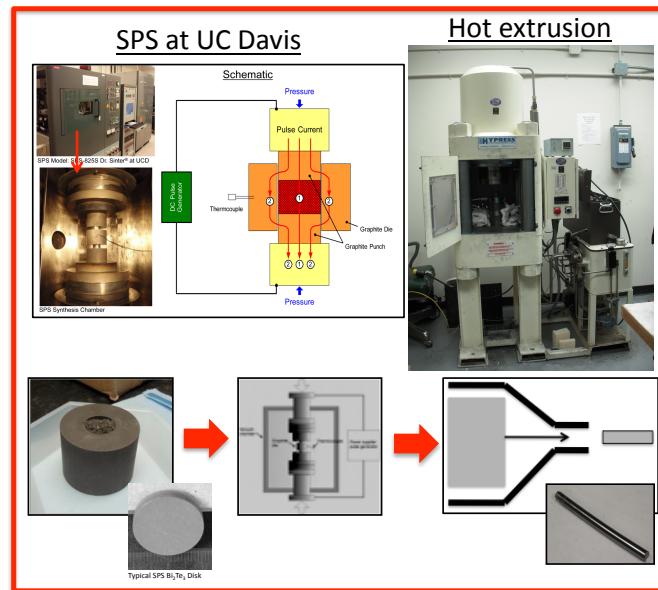
Electroplated Au in cyanide was selected for its strong adhesion, stable microstructure and relatively low heat emissivity



## S&T progress update



# Process development/optimization of spark-plasma-sintering (SPS) & hot extrusion (SNL/UC Davis collaboration)



15

We have gained a better insight into how the SPS/hot extrusion processing controls microstructure/porosity/texture and its subsequent impact on TE transport.

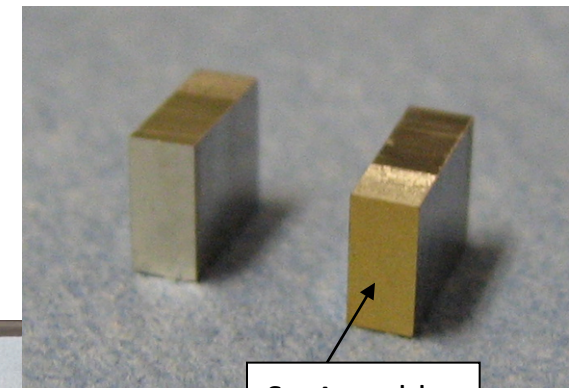




# Thermal aging test matrix for the Au-plated p-n tiles, fabricated by commercial vendor

| <u>Base TE Material</u> | <u>Diffusion Barrier</u> | <u>Solder</u> | <u>Aging Temperature</u> | <u>Aging Period</u> |
|-------------------------|--------------------------|---------------|--------------------------|---------------------|
| p-type Bi-Te            | Electroless Ni           | Sn0.8Au0.2    | 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         |               |                          |                     |

Electroless cobalt diffusion barrier with 80/20 Au/Sn solder on one end



Sn-Au solder

The initial metal selections were based on:

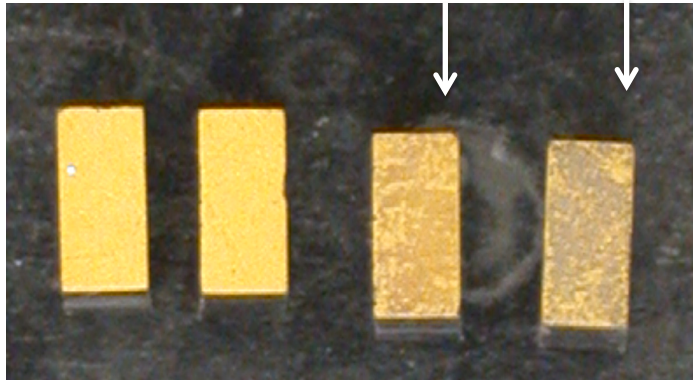
- Compatible thermal expansion coefficient
- Desirable contact resistance
- Stable at temperature of interest.





# metallurgical instability seen in the Au-coated tiles with Sn-solder and Ni or Co barrier

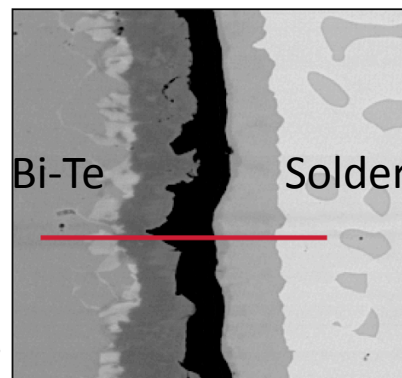
AR    100°C    175°C    250°C



Discoloration on p-tile, with Sn-Au solder and Co barrier, at  $\geq 175^\circ\text{C}/7\text{days}$ .

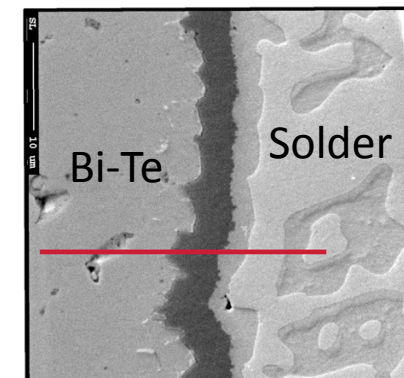
Interfacial reaction in p-tile, with Sn-rich solder and Ni barrier, at  $250^\circ\text{C}/7\text{ days}$ .

With Ni-phosphor barrier

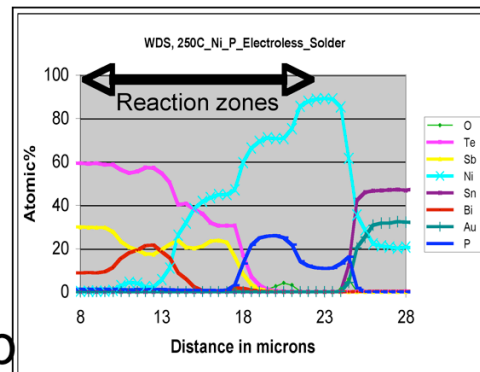


a

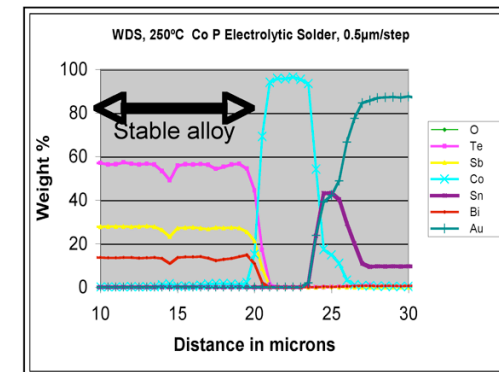
With Co-barrier



c



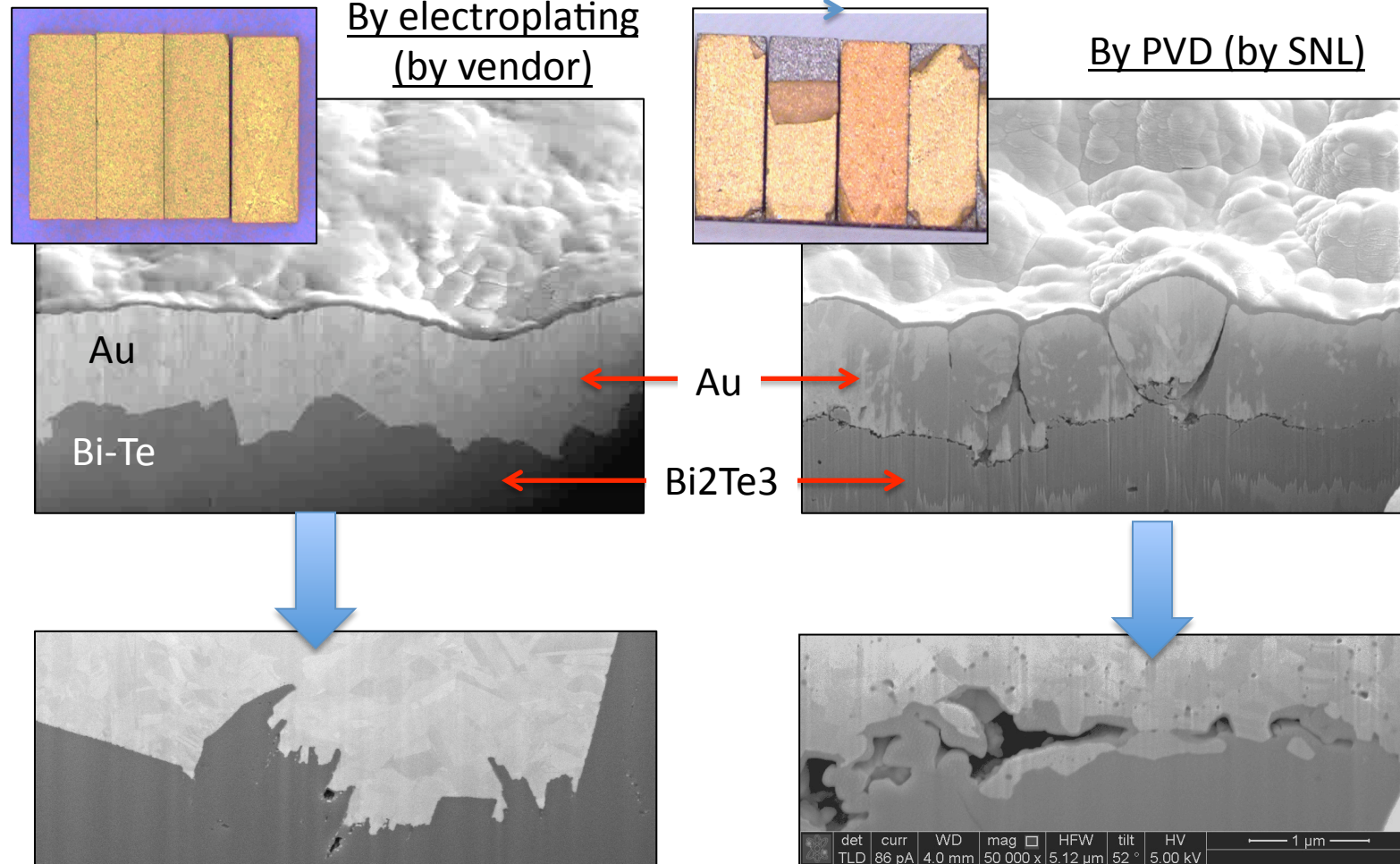
b



d



# Adhesion and coating quality of thin film Au is highly dependent on processing technique



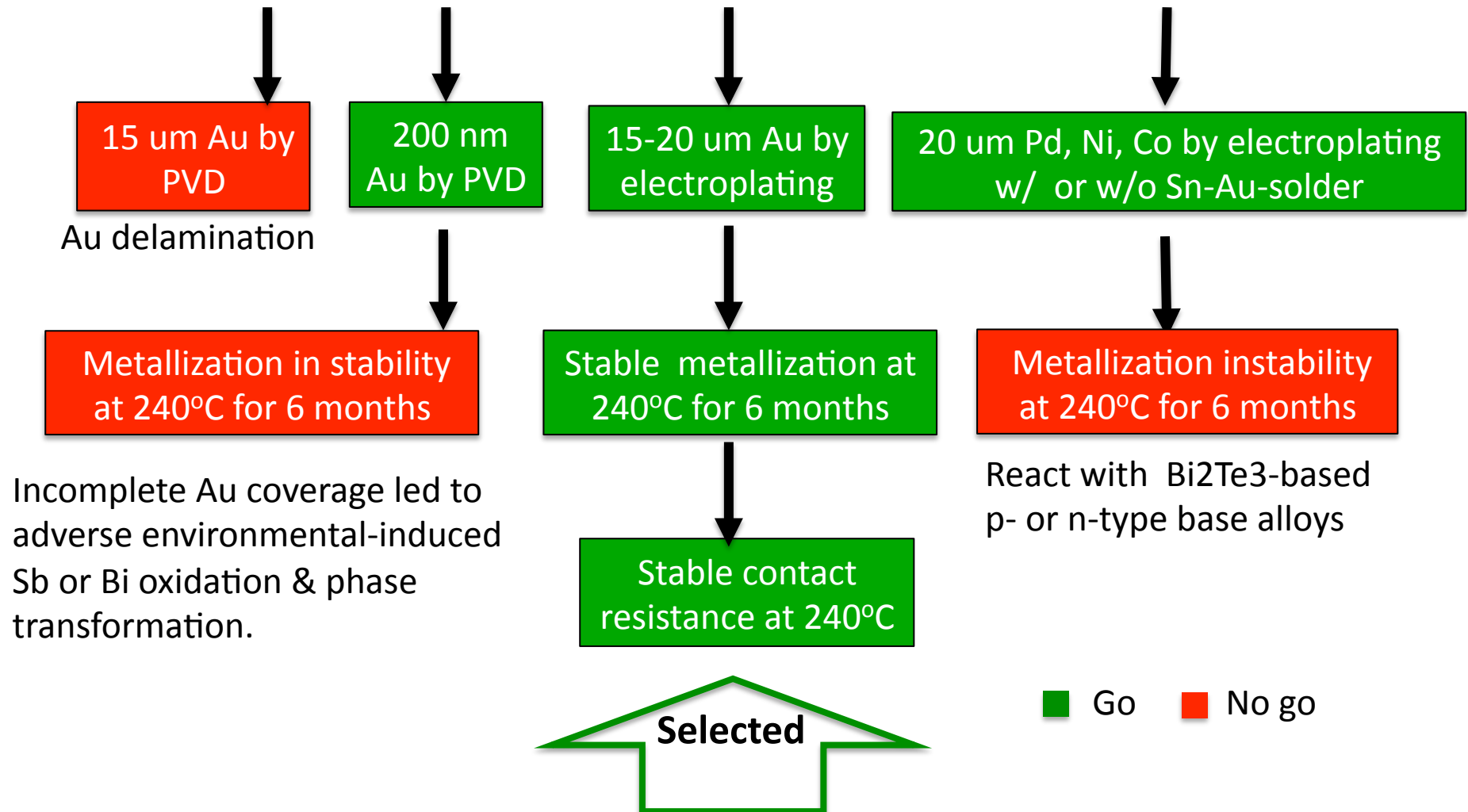
The 3-D SEM image reconstruction from the focus ion beam (FIB) slices verified the presence of thru-thickness pinholes.





## Electroplated Au (10-15 $\mu$ m thick) is the selection for metallization for its strong adhesion and low thin film defect

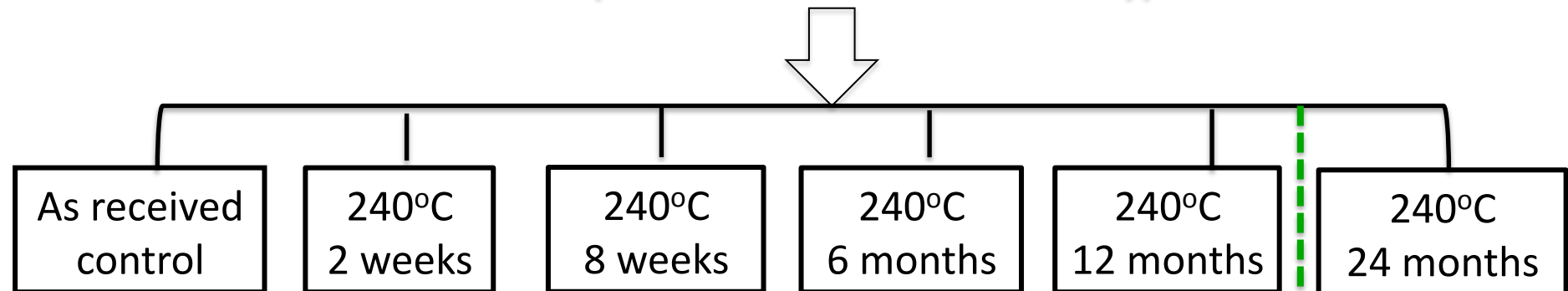
### Process development and optimization for thin film Au metallization





# Thermal aging experiments for p and n tile coated with electroplated Au

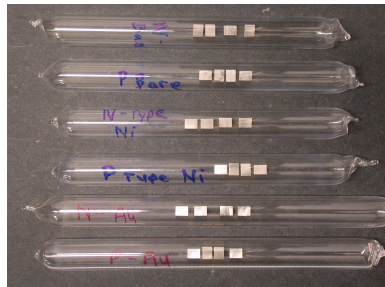
Electroplated Au-metallized P- & N-type tiles



Investigate

- ✓ Thermal conductivity ( $\kappa$ )
- ✓ Seebeck coefficient (S)
- ✓ Electrical resistivity ( $\rho$ )
- ✓ Figure of Merit (ZT)
- ✓ Metallurgical evolution
- ✓ Contact resistance
- ✓ Phase transformation modeling and simulation
- ✓ Mechanical property of base alloys

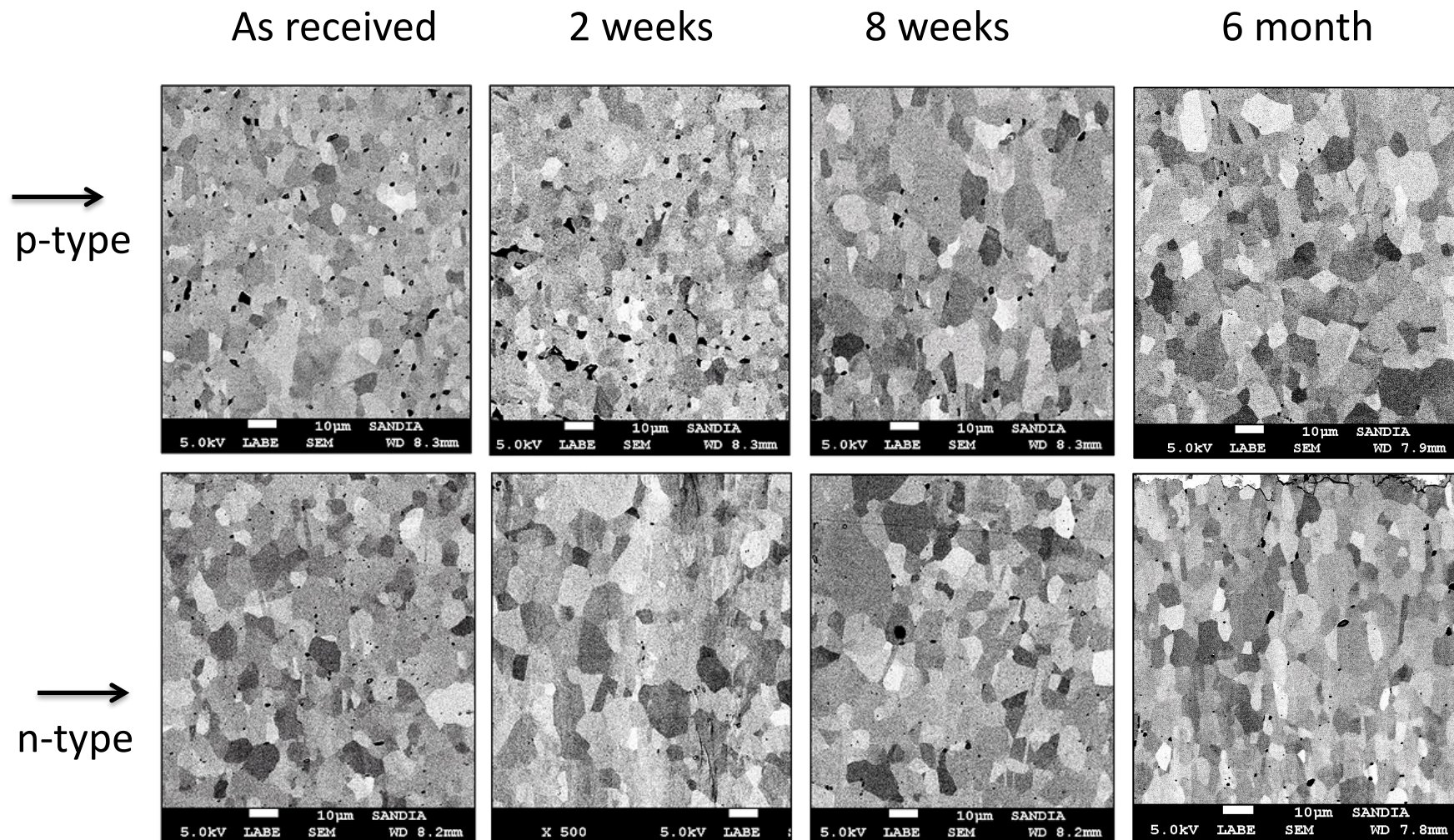
Note: Tiles sealed in argon filled quartz tube



- 240°C/100 days polymer filled module.
- Accelerated aging at 350°C/30 days.



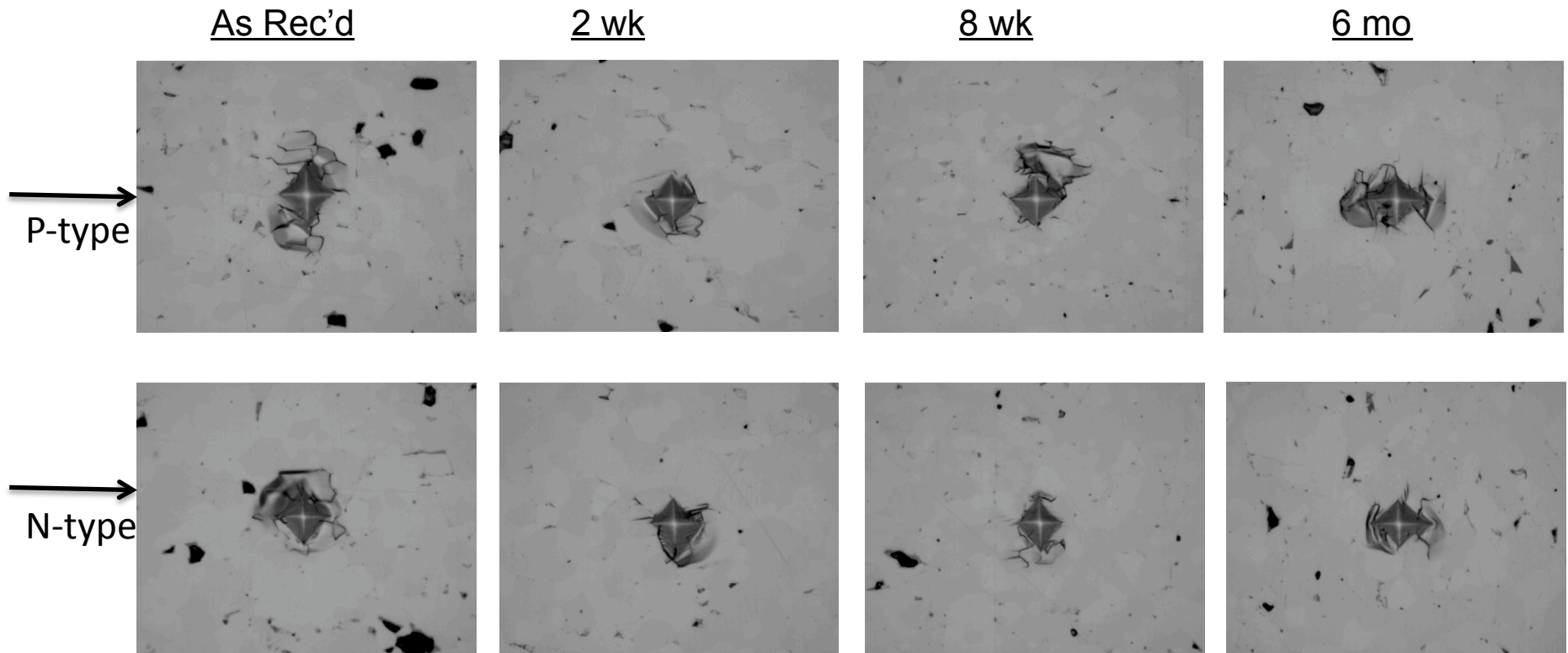
## Stable microstructure of p and n alloys upon aging at 240°C up to 6 months



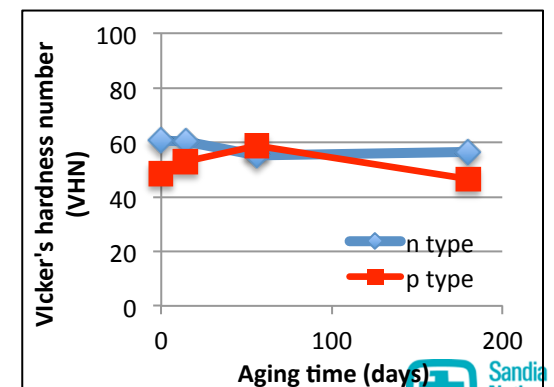
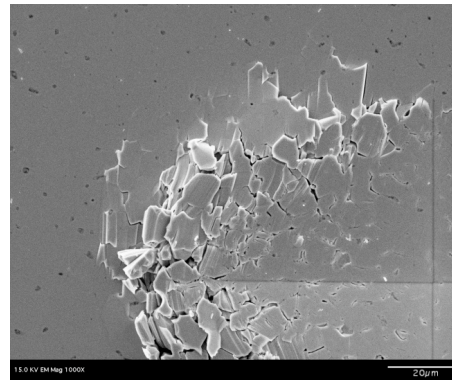




# Stable Vickers hardness upon aging at 240°C up to 6-months



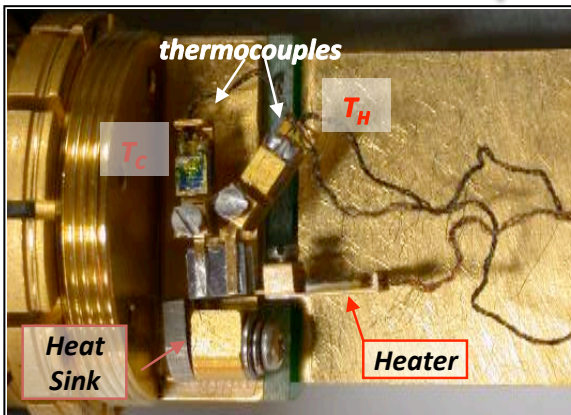
The  $B_{i2} Te_3$ -based alloys in general exhibit brittle fracture, preferentially along the grain boundary and/or basal planes.



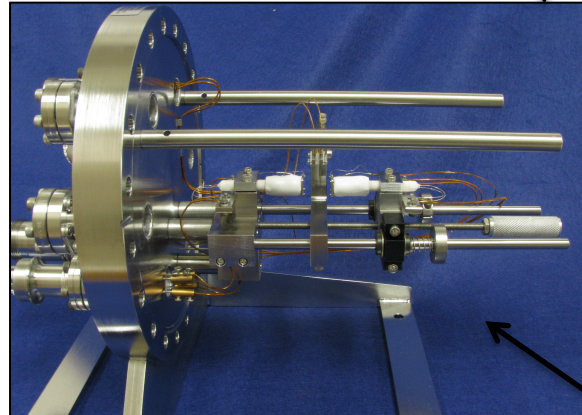


# TE transport properties and contact resistance measurement capabilities developed at SNL-CA.

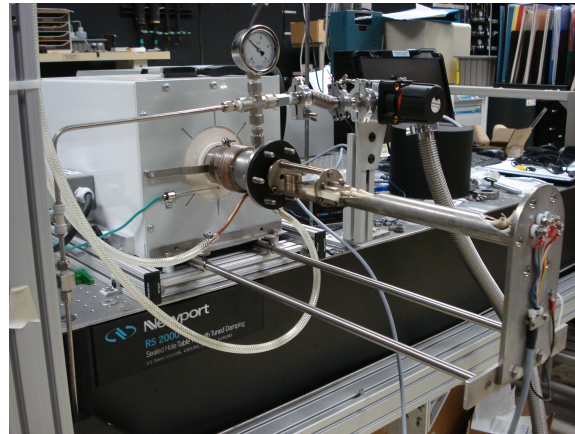
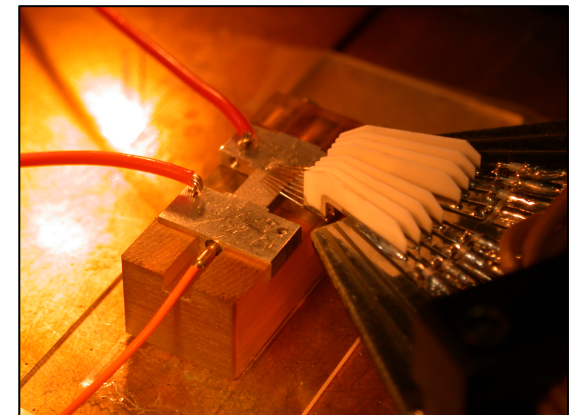
Low temperature systems  
for S and  $\rho$  and  $\kappa$



High temperature systems  
for S,  $\rho$  and  $\kappa$



Contact resistance system

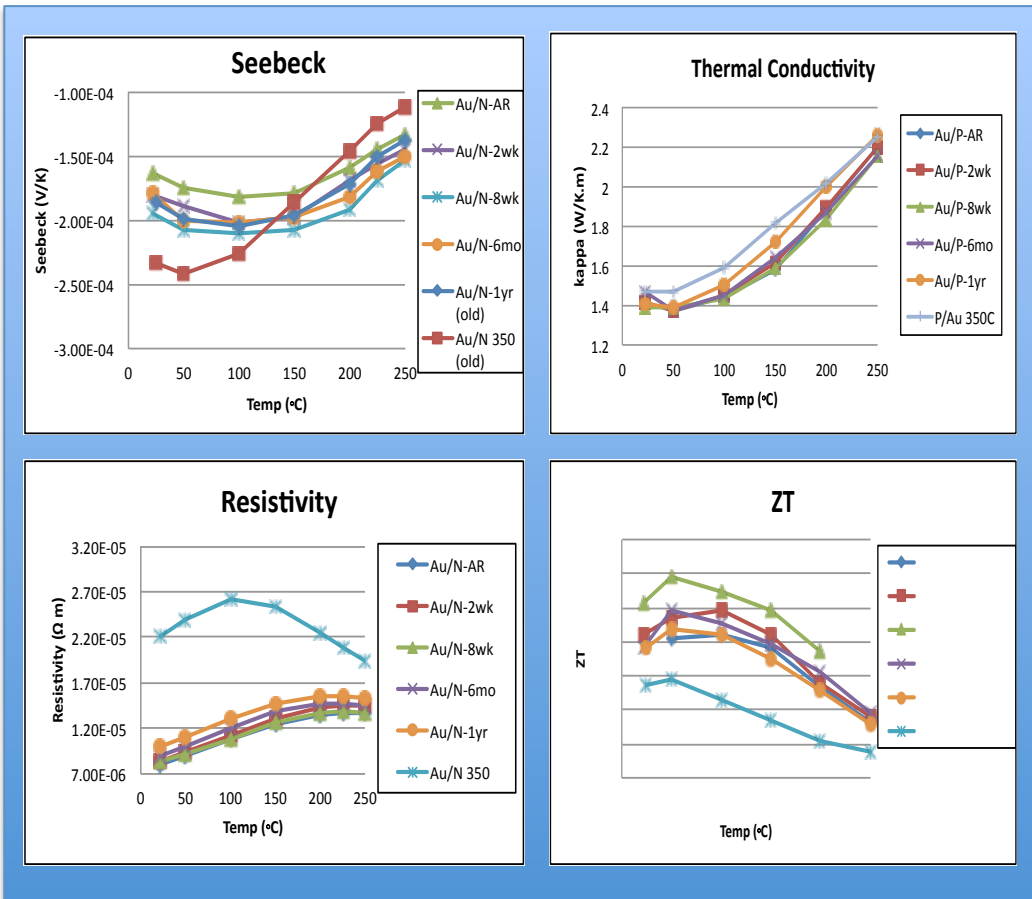


Custom built in SNL

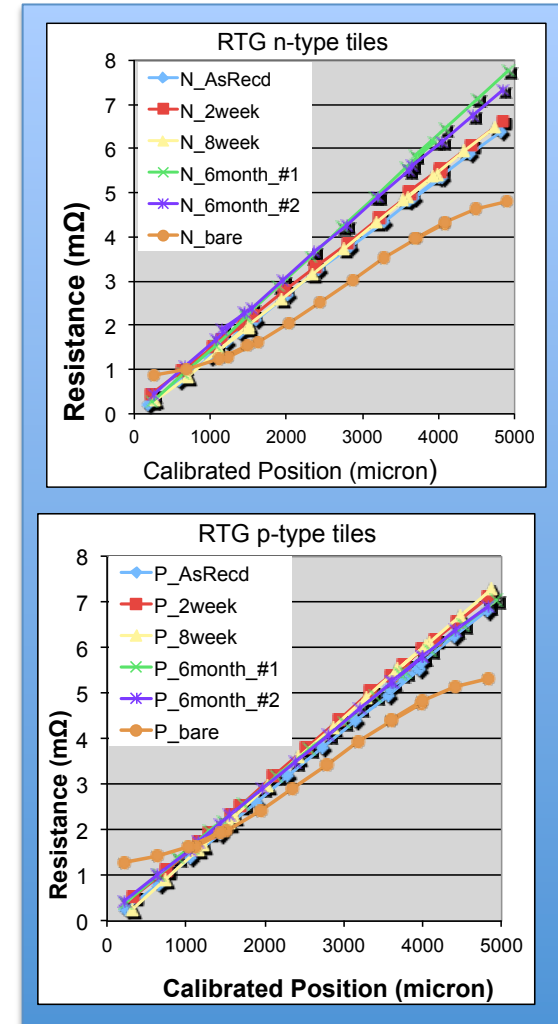


# Stable TE transport property and contact resistance upon aging up to 240°C/6 month, but not to 350°C/30 days

## TE transport properties of n-type



## Contact resistance







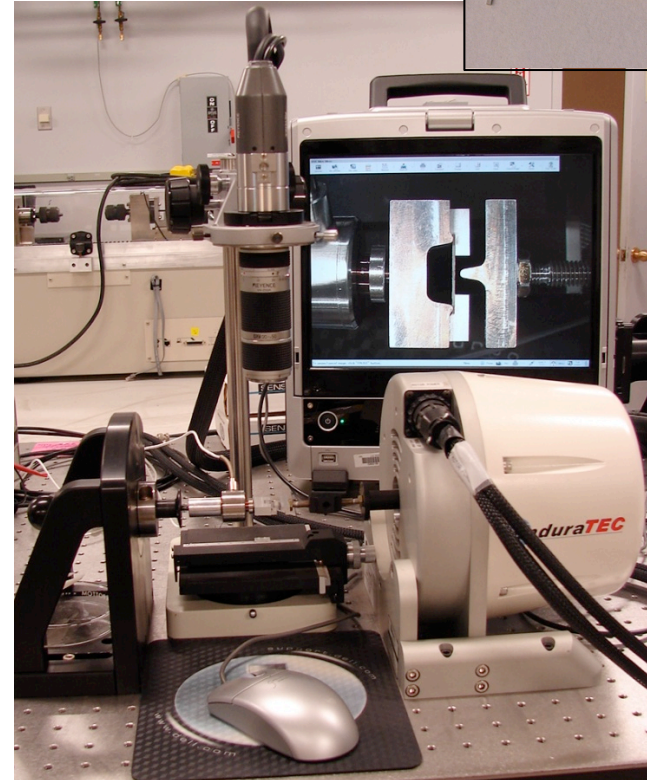
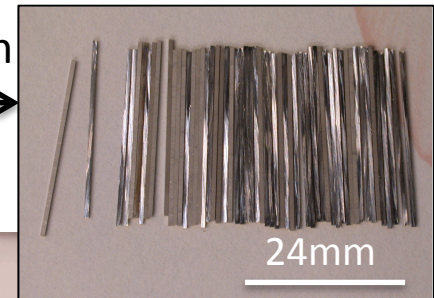
# Mechanical strength by three-Point Bending

- Three-Point-Bending experiment
  - Elastic modulus, strength

$$E = \frac{L^3}{48I} \frac{F}{\delta} \quad \sigma_s = F_{\max} \frac{Lh}{8I}$$

- Nominal specimen dimension  
0.55 x 0.55 x 18(24) mm
- Material anisotropy
  - Preferred and transverse directions
- Properties at various temperatures
  - Ambient condition, 200°C, and low temperature

Sample dimension



By Wei-Yang Lu, 08256



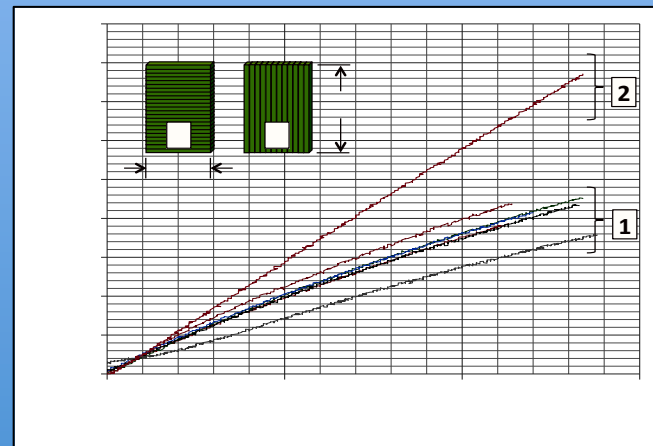
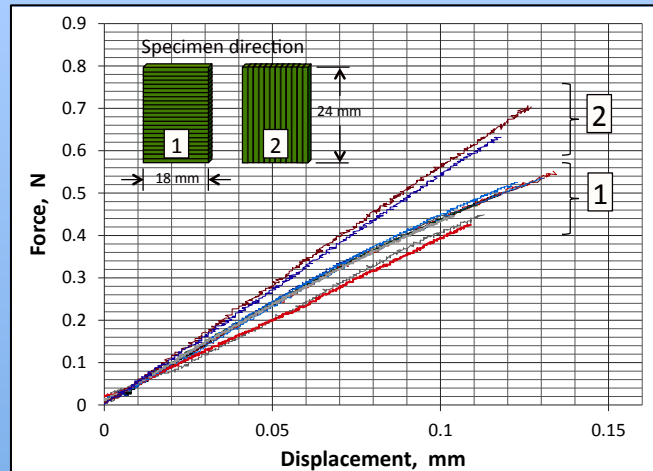
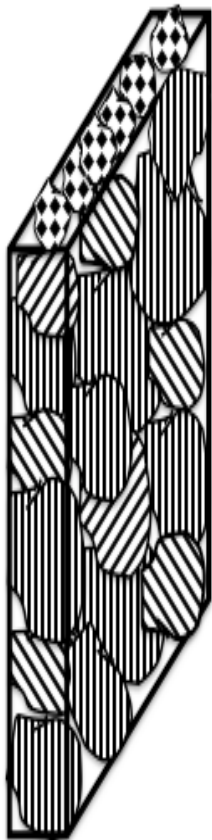


# Anisotropic $\text{Bi}_2\text{Te}_3$ -based alloys impact Mechanical strength and TE transport property

## Mechanical strength

Bend 1: (01-10) out-plane

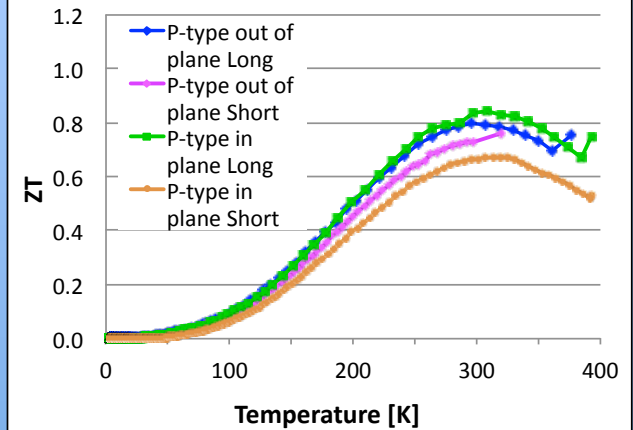
Bend 2: (0001) in-plane



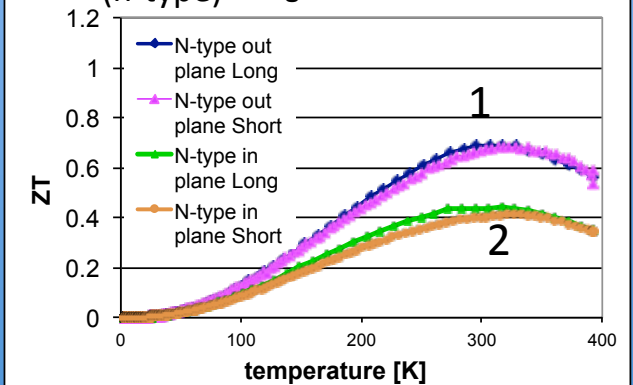
3-point bending by W. Lu

## Figure of Merit

### (p-type) Figure of Merit



### (n-type) Figure of Merit

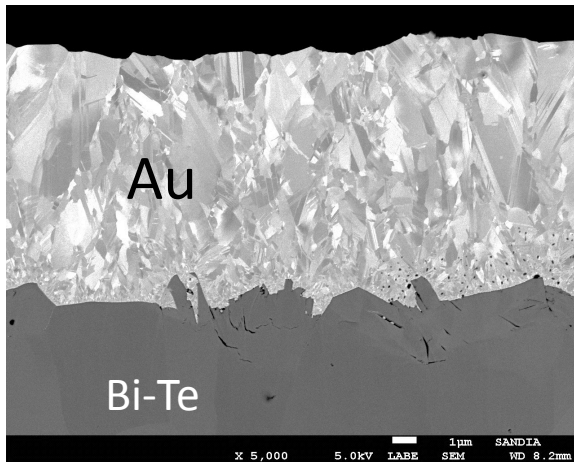


PPMS by N. Nishimoto

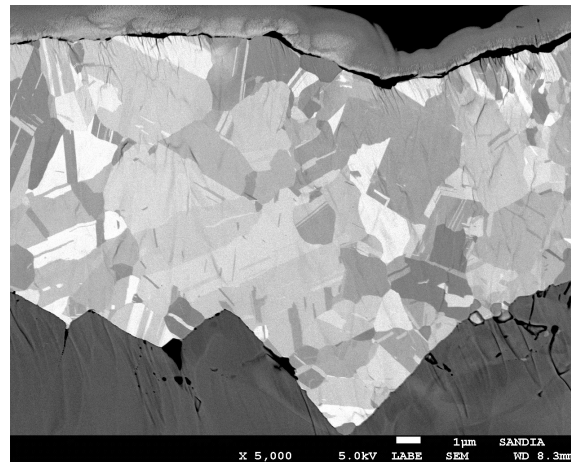


# Grain growth/recrystallization upon aging softens the Au on TE-tile but has little effect on its contact resistance upon aging.

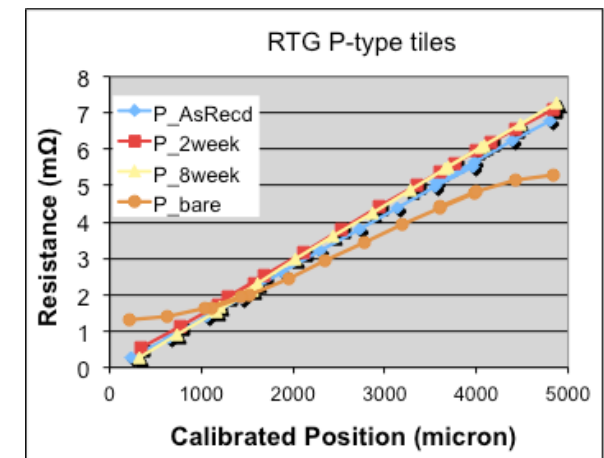
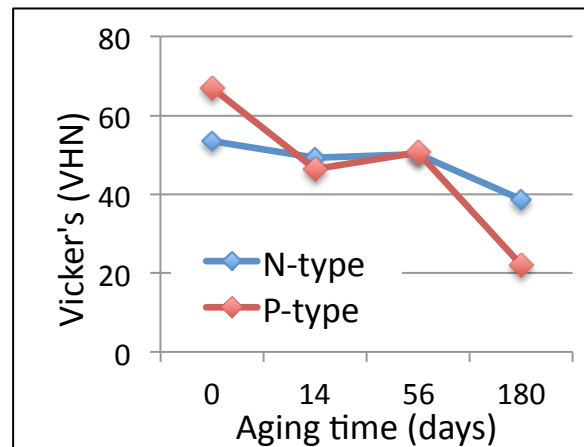
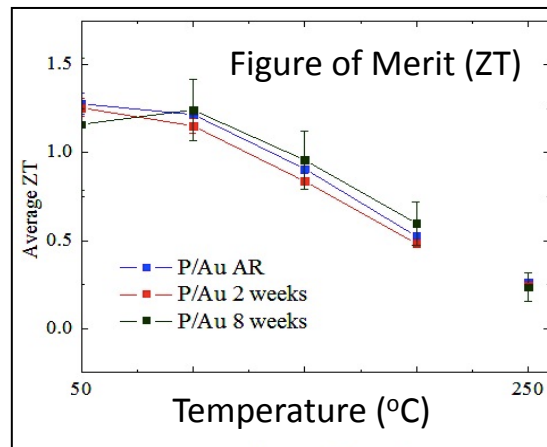
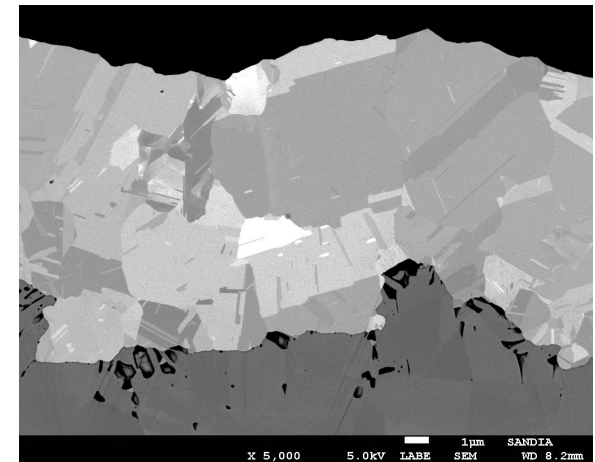
AR



2 weeks.



8 weeks.



Pores at the interface are more visible in the annealed tiles. potentially could weaken the bond strength or structure integrity?



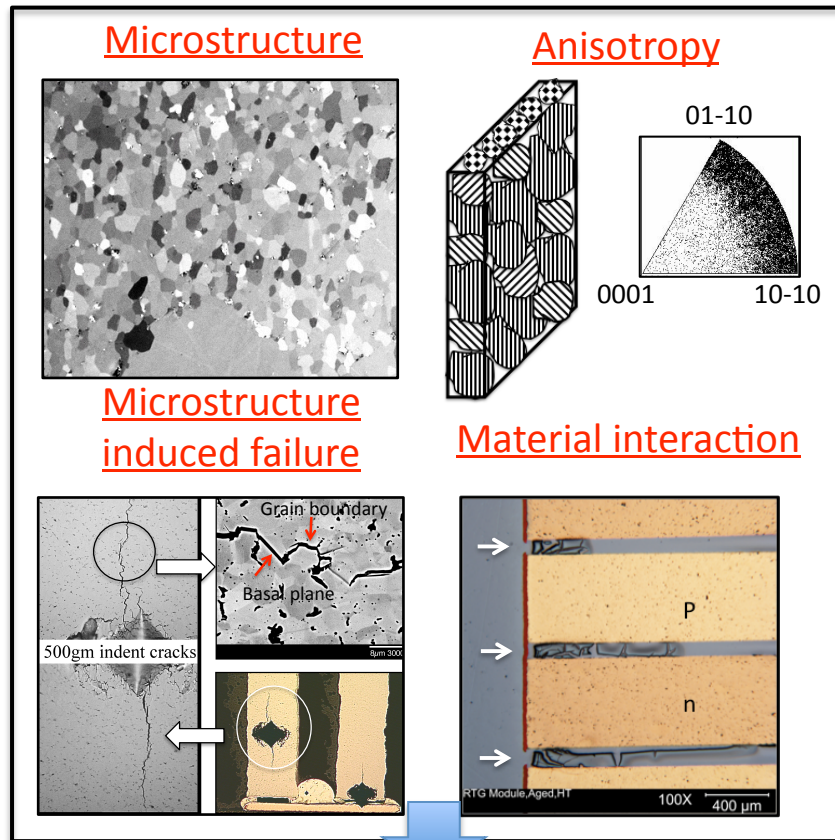
What more needs to be understood ?

4/9/13

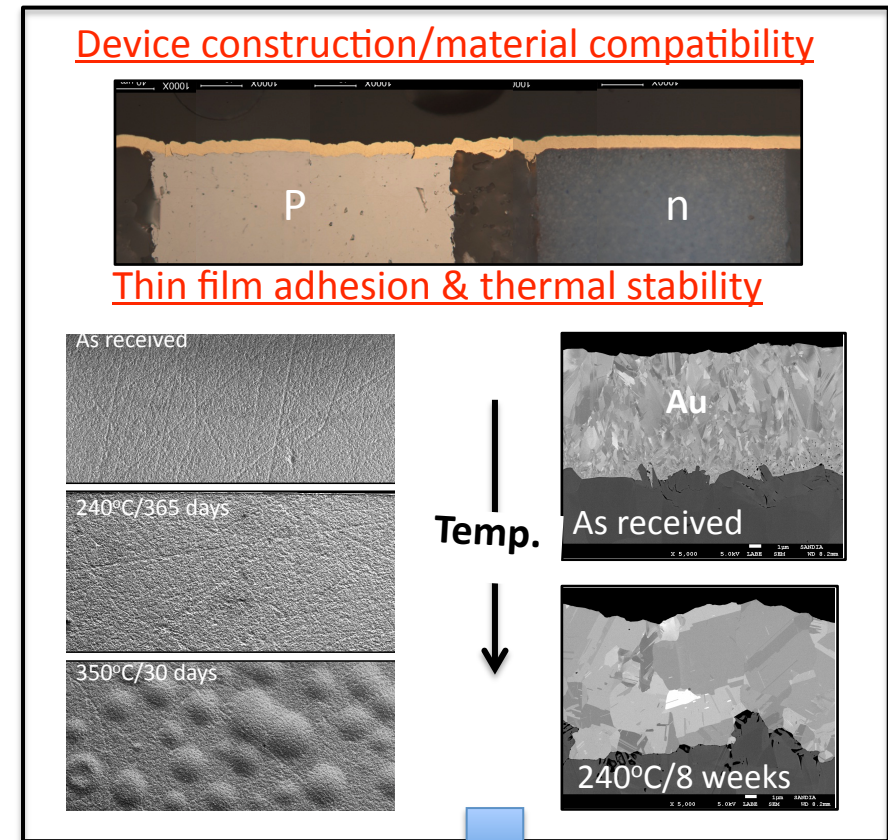


# Understanding of the material impact at the TE system level?

## p-n base alloy & polymer support

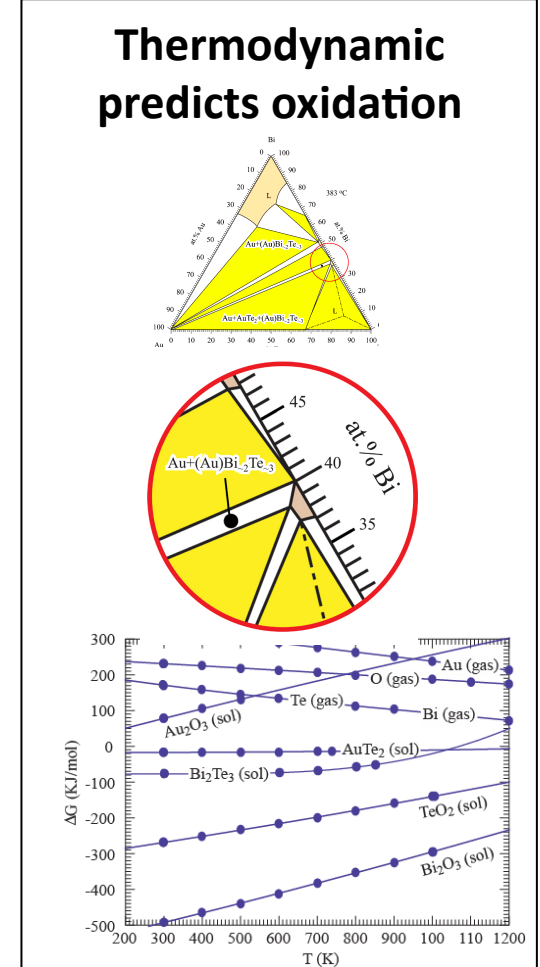
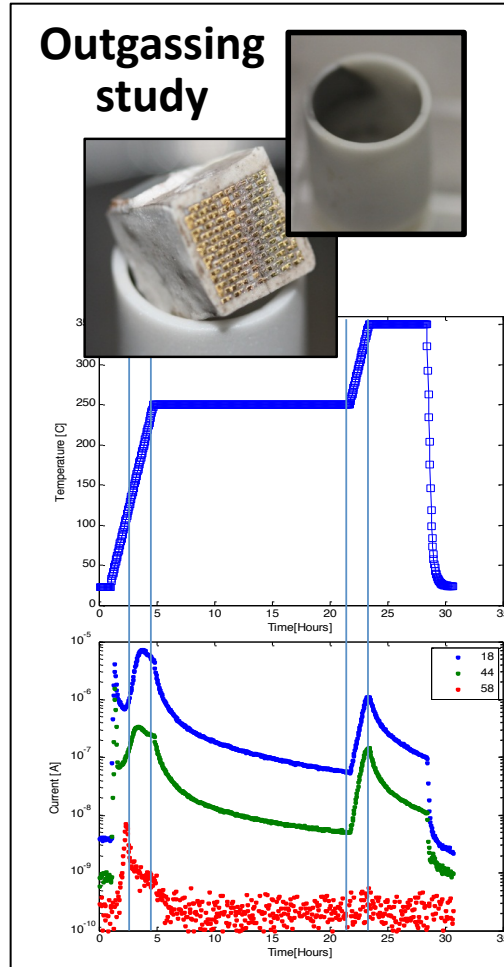
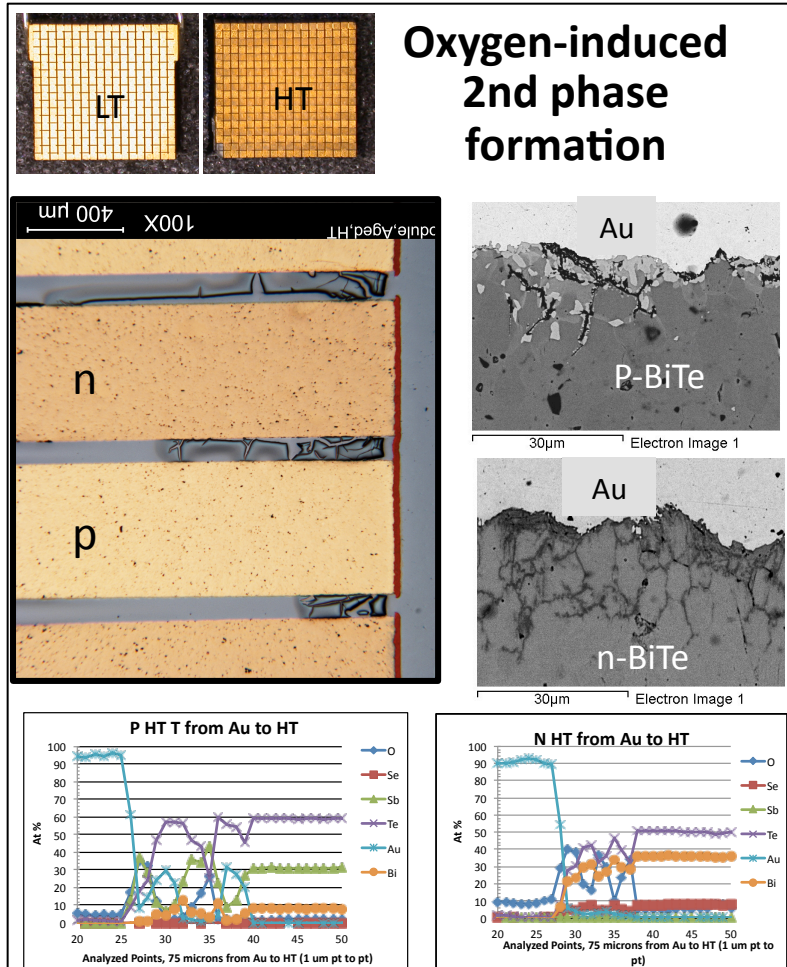


## Thin film metallization





# Need metallurgy, outgassing characterization and thermodynamic modeling together to determine and predict environmental effect.



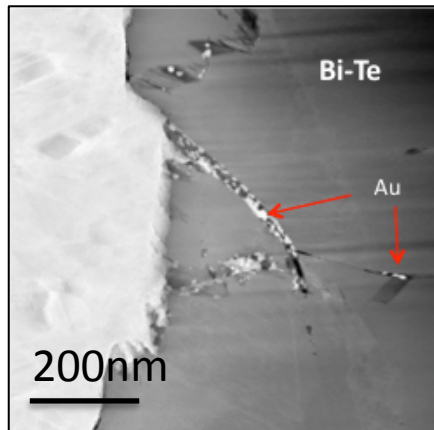
Interface oxidation and phase transformation of Au-Bi<sub>2</sub>Te<sub>3</sub> system observed at relatively low oxygen partial pressure.



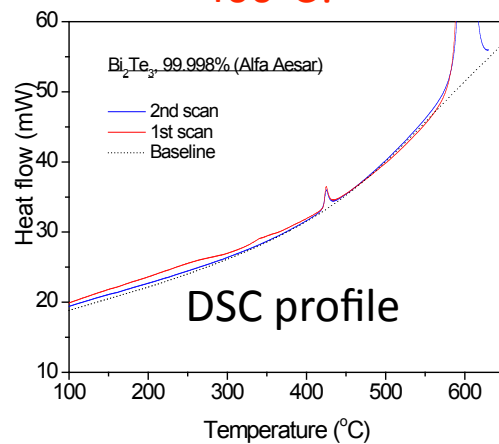


# Validation between experiment and predictive modeling for understanding of the ultimate TE system stability

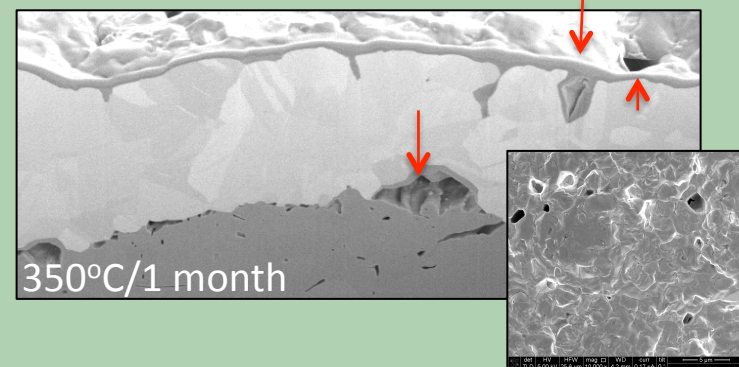
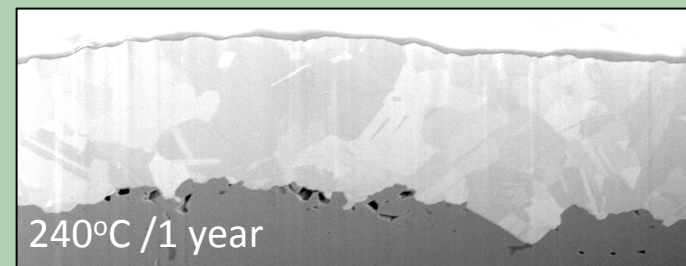
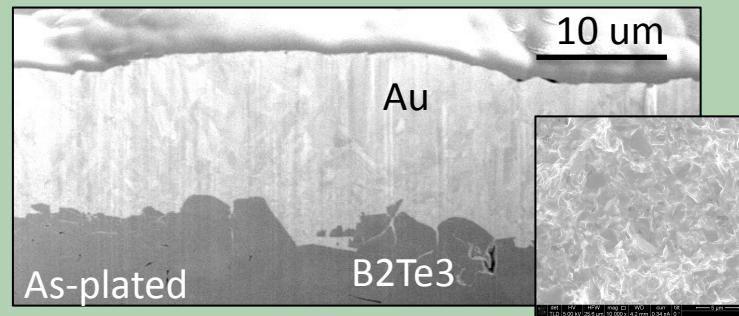
## Au plated into cracks



## Te evaporation at ~400°C?

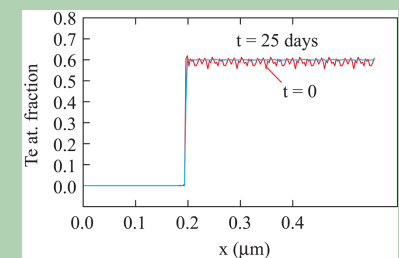
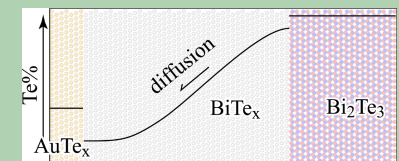
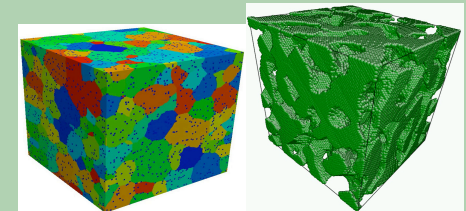
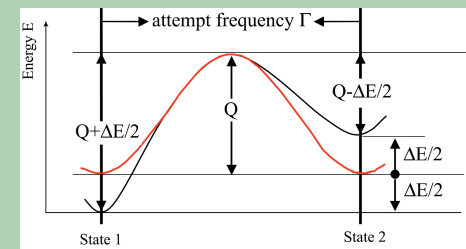


## Grain growth/void formation upon accelerated aging at 350°C



## Model validation

### Kinetic Monte Carlo modeling

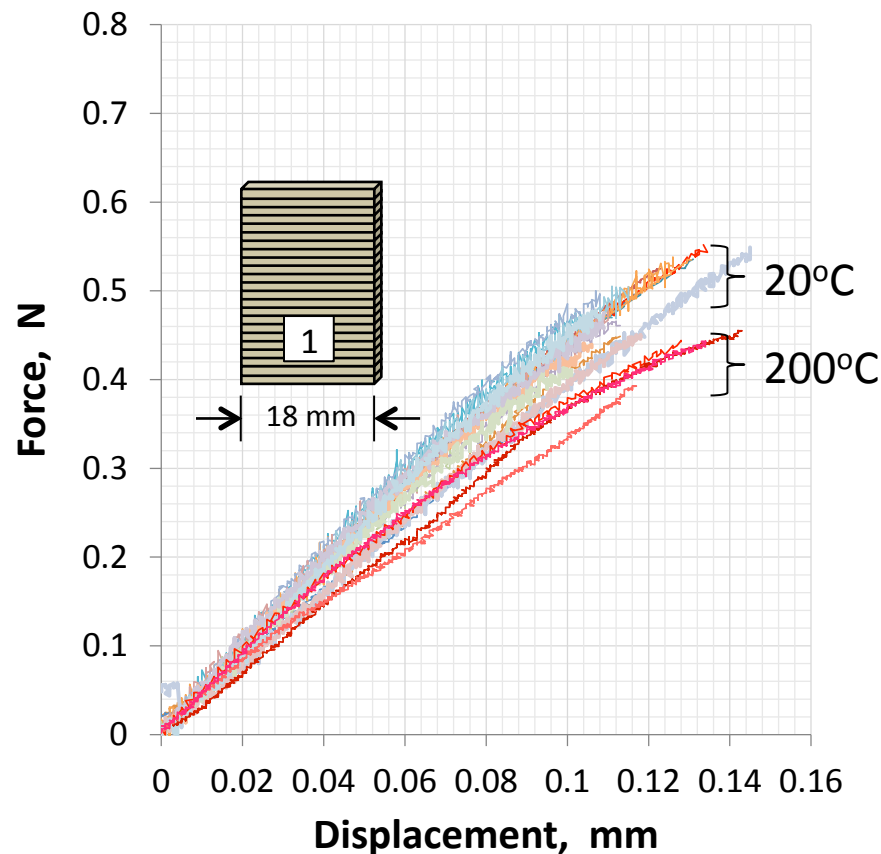


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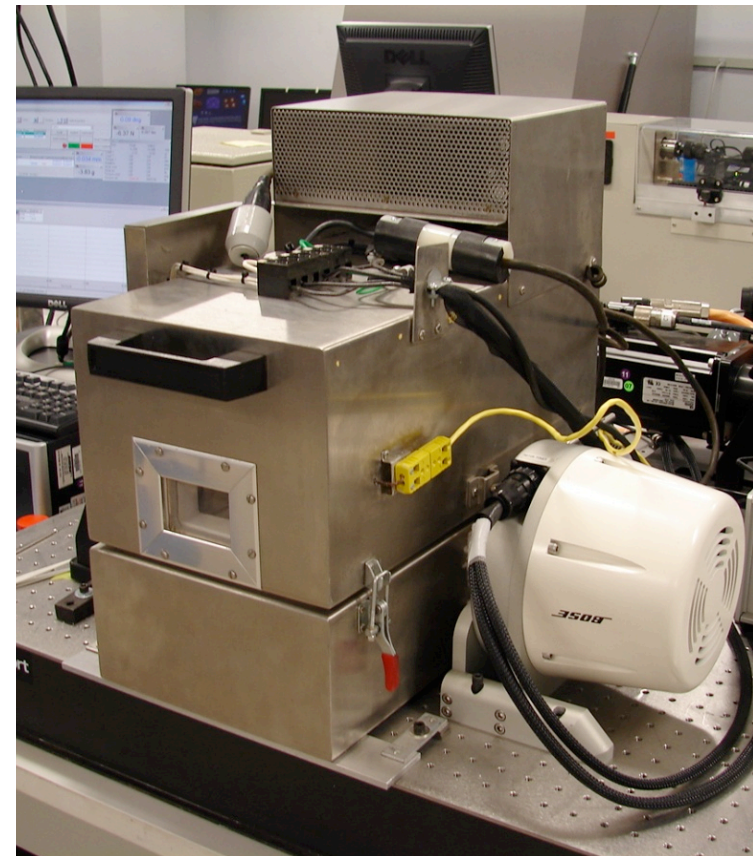


# On-going technique development for investigating temperature effect on mechanical properties

## Bending of N-type Specimens



## High temperature 3-point bend tester

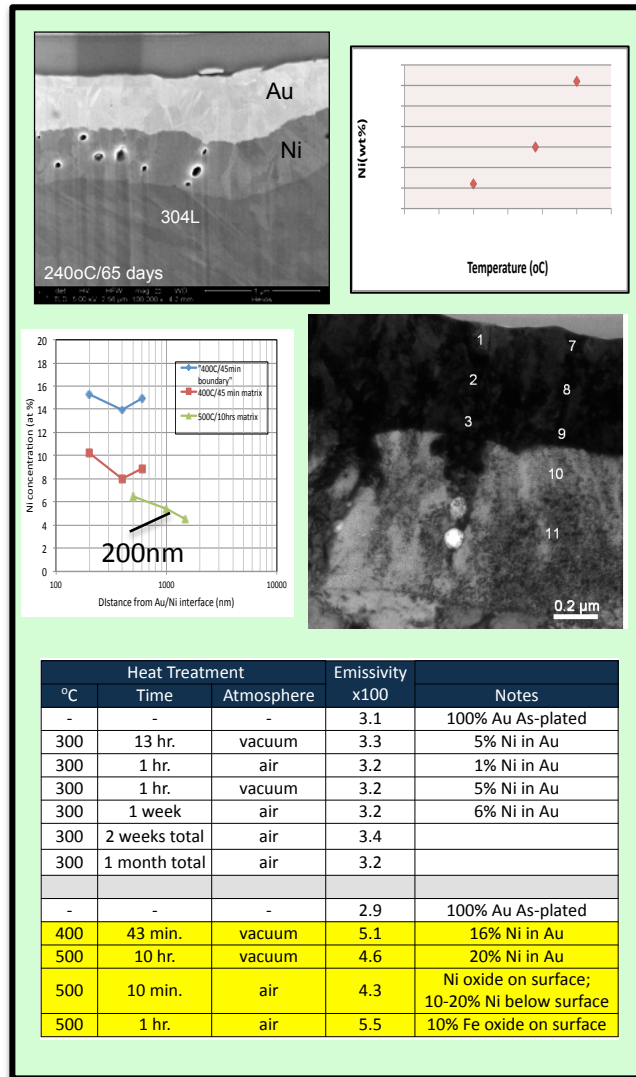


By Wei-Yang Lu, 08256

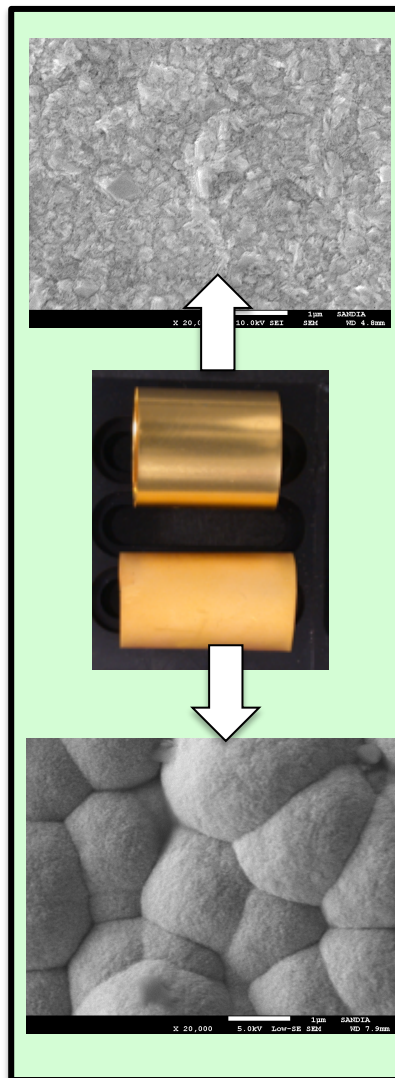


# Electroplating development/optimization to achieve ultimate thin film adhesion, thermal stability and emissivity.

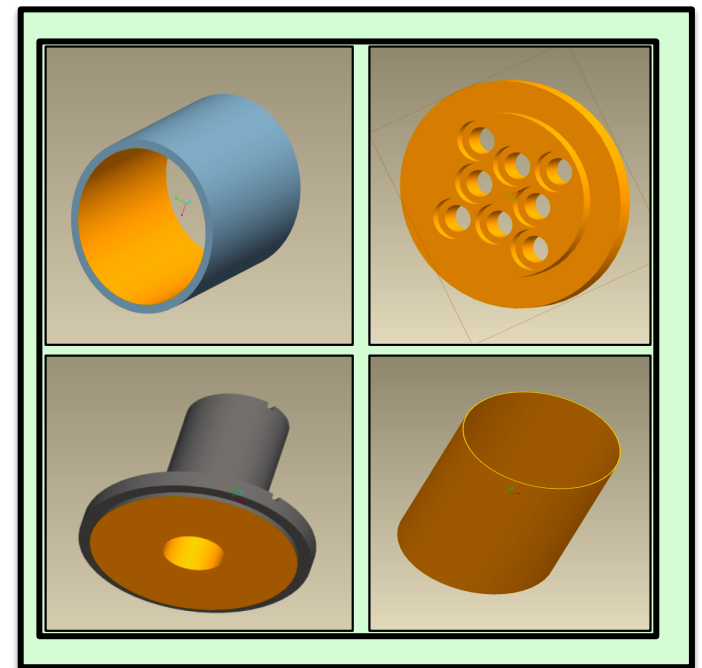
## Adhesion/Au-Ni diffusion/emissivity



## Surface topography



## Complex designs to be plated

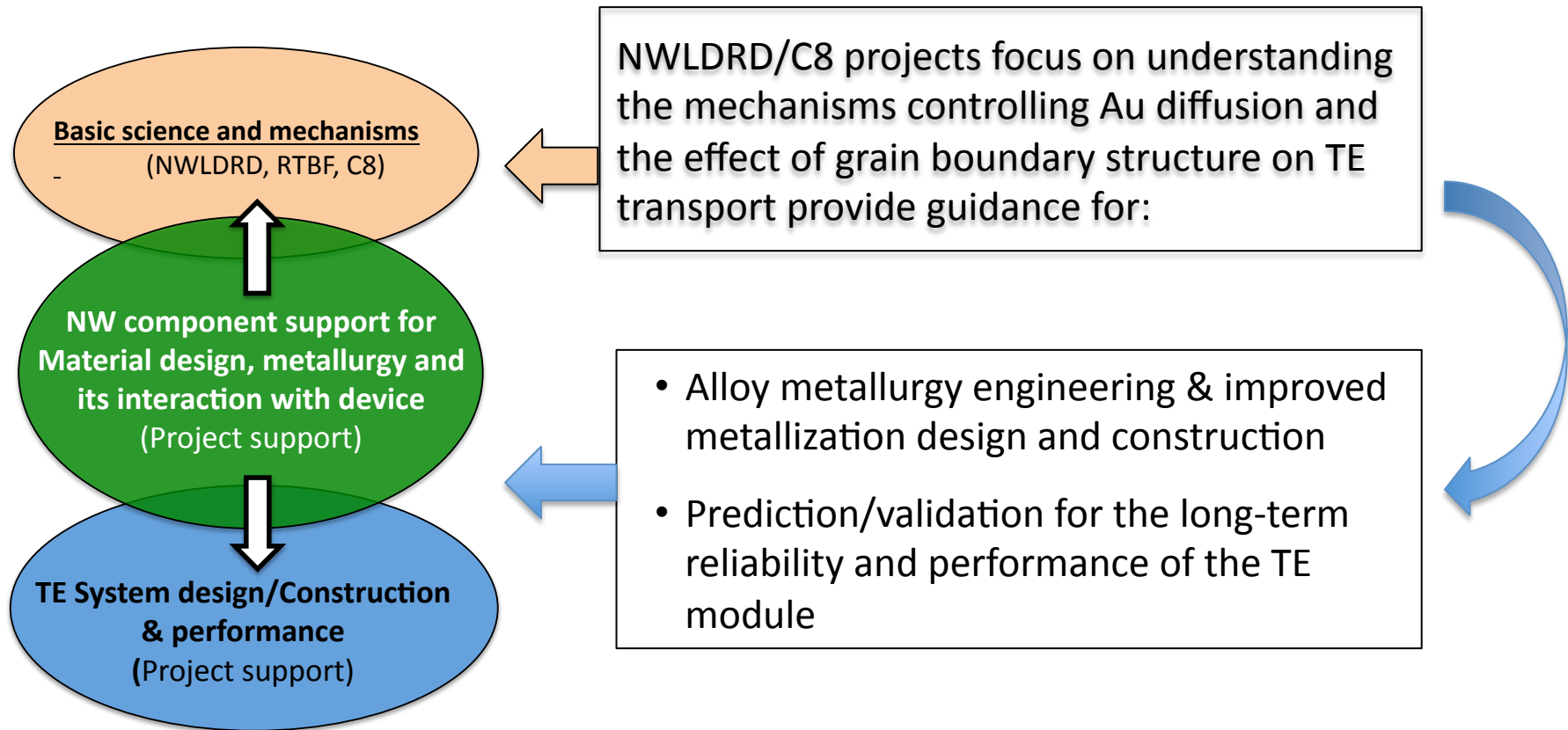


- Plating parameter controls surface topography that affect heat emissivity
- Ni diffusion to Au surface at  $\geq 300^\circ\text{C}$  promotes surface oxidation that raises emissivity





## Collaboration with basic science activities is needed to enable the design of a next generation TE system with improved performance





# Fundamental research provides an understanding on how microstructure impacts TE transport in $\text{Bi}_2\text{Te}_3$



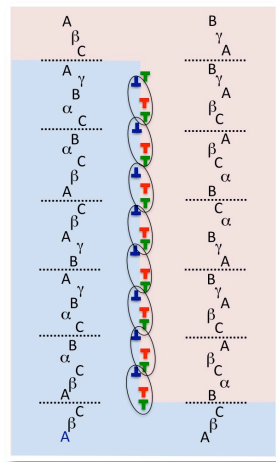
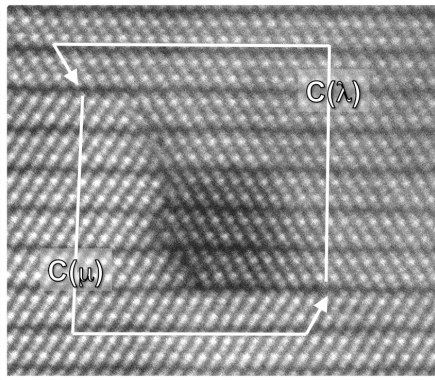
**Why? Sandia's TE devices employ strongly textured polycrystalline  $\text{Bi}_2\text{Te}_3$ -based materials.**

**Texture and grain size strongly influence TE transport and diffusional properties.**

**However, we do not yet understand how these transport processes depend on specifics of GB structure.**

**We are generalizing our understanding to more complex grain boundaries:**

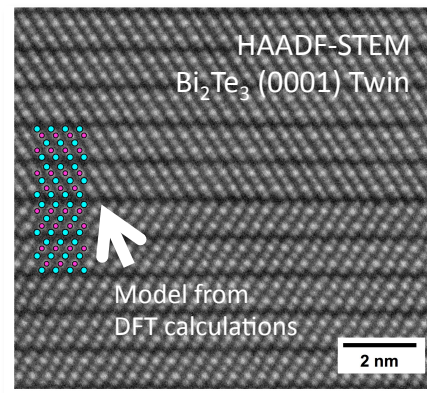
**Example: HRSTEM and defect model of stepped  $\text{Bi}_2\text{Te}_3$  grain boundary**



Medlin and Yang, Journal of Electronic Materials, (2012)

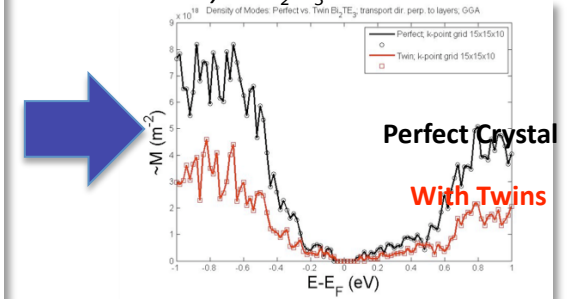
4-15-2013-TE update-NY

**Our approach: Use experimentally determined interface structure as input for *ab initio* electronic structure calculations**



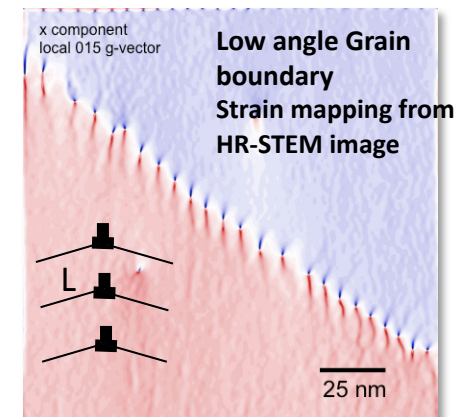
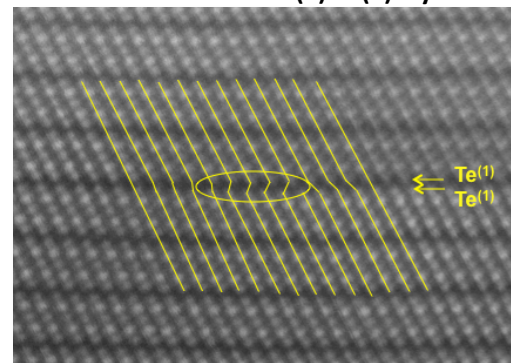
Medlin, Ramasse, Spataru, Yang  
J.Appl. Phys (2010)

*Lower density of modes from band structure calculations suggests reduced electronic conductivity at  $\text{Bi}_2\text{Te}_3$  twin*



(Spataru, Shaughnessy)

**Dislocation Core structure in  $\text{Bi}_2\text{Te}_3$   
Dissociation on Te(1)-Te(1) layer**



**Interfacial defects (e.g. dislocations and steps) provide “building blocks” for developing generalized models of interfacial structure.**







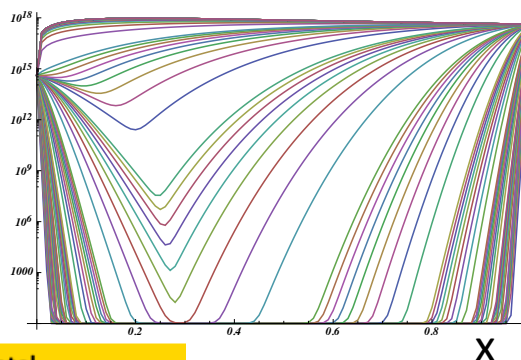
# Modeling and simulation enables gaining insight on how diffusional processes underpin aging behavior

Au is used as contact material in Sandia's  $\text{Bi}_2\text{Te}_3$  Based TE-Power systems

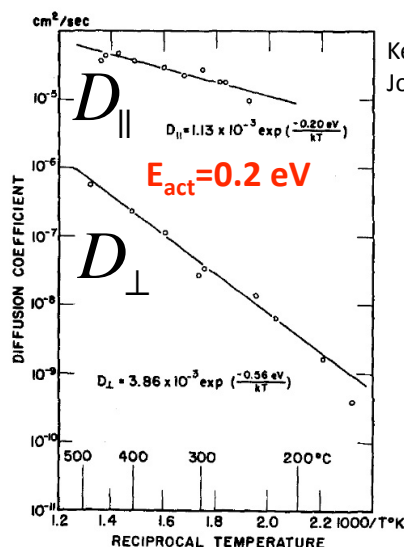
→ diffusion is fast and anisotropic

*We are developing models and methods, including specialized routines for use within Sandia's Sierra-Aria finite element analysis framework, to study diffusive aging in single and polycrystals.*

$c(x,t)$  (J. Zimmerman, N. Bartelt, L. Erickson, C. Battaile, J. Foulk)



*Simulations predict the time evolution of concentration and diffusive flux and their dependency on the heat of transport, as well as the anisotropic nature of diffusion.*



Keys and Dutton,  
Journal of Applied Physics (1963)

*Our ab initio, density functional theory (DFT) calculations predict a ~0.2 eV barrier for migration by Au intercalated at Te double-layer, consistent with experiment.*

*Ongoing work is focused on understanding Au substitutional mechanisms responsible for other diffusion paths.*

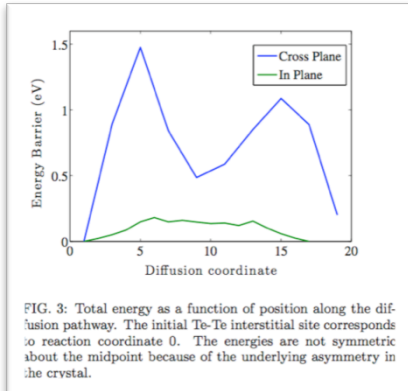
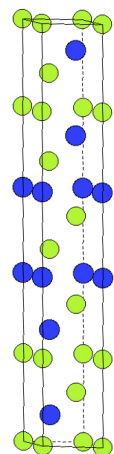
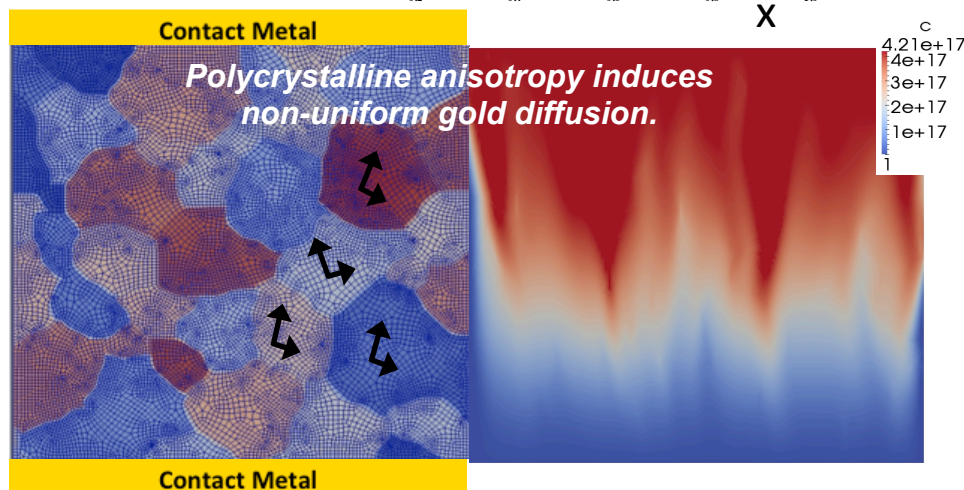


FIG. 3: Total energy as a function of position along the diffusion pathway. The initial Te-Te interstitial site corresponds to reaction coordinate 0. The energies are not symmetric about the midpoint because of the underlying asymmetry in the crystal.

(M. Shaughnessy, N. Bartelt)



Contact Metal

*Polycrystalline anisotropy induces non-uniform gold diffusion.*

Contact Metal

*Ongoing work is aimed at extending to 3D geometries and including grain boundary diffusion.*



# Summary

- $\text{Bi}_2\text{Te}_3$ -based alloys possess stable metallurgy, therefore, consistent transport property, up to 240°C/year.
- Electroplated thin film Au exhibits strong adhesion and low emissivity to fulfill the function of interconnect metallization and lowering heat emission.
- The  $\text{Bi}_2\text{Te}_3$ -based alloys shows strong texture leading to anisotropic mechanical properties, Au- diffusion and TE transport properties.
- The  $\text{Bi}_2\text{Te}_3$ -based TE system is susceptible to adverse oxygen-induced phase transformation at relatively low oxygen environment.
- Accelerated thermal aging testing at 350°C/1month indicates vulnerability of module integrity of Au/ $\text{Bi}_2\text{Te}_3$  system.



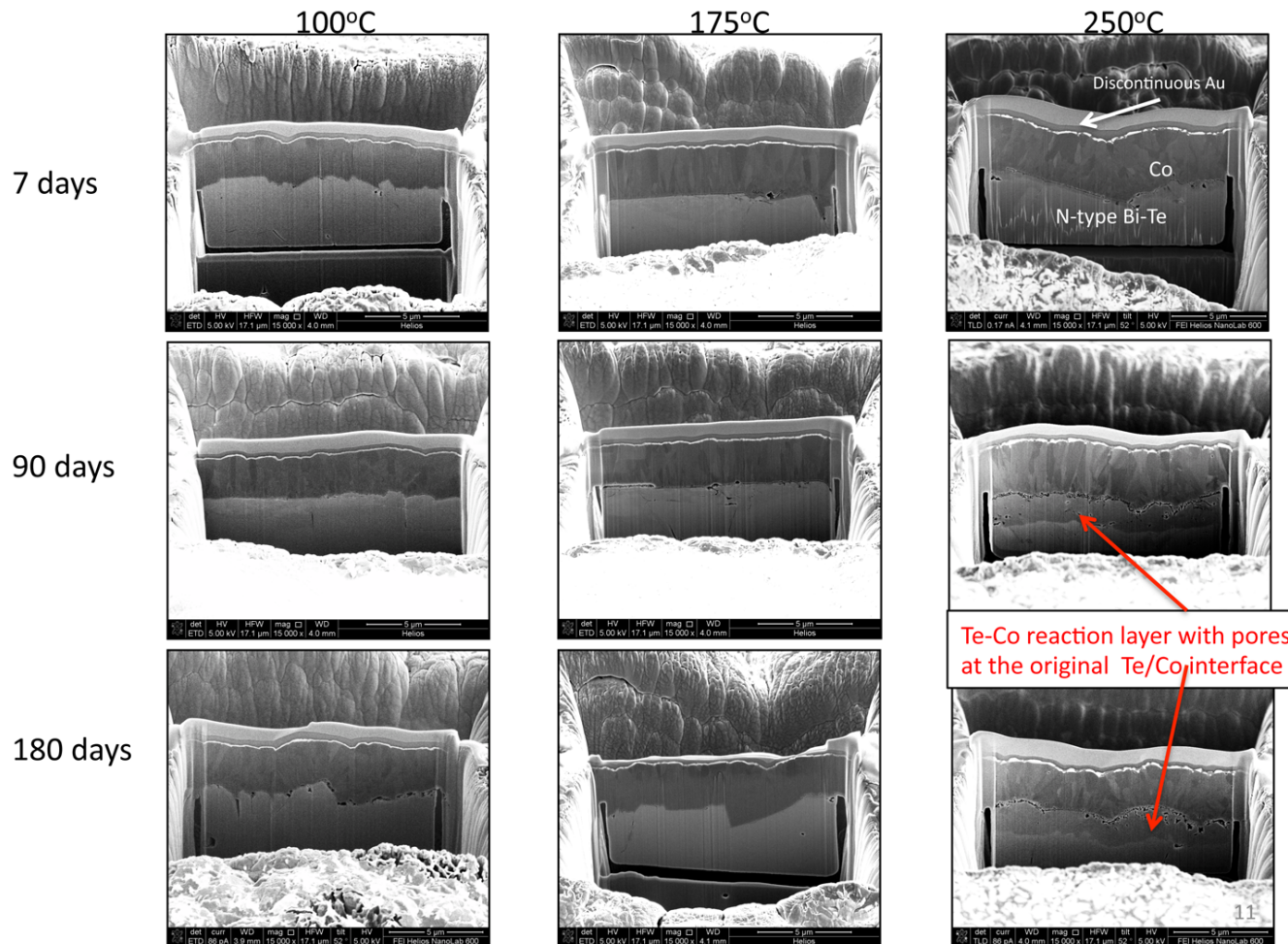
# Future effort

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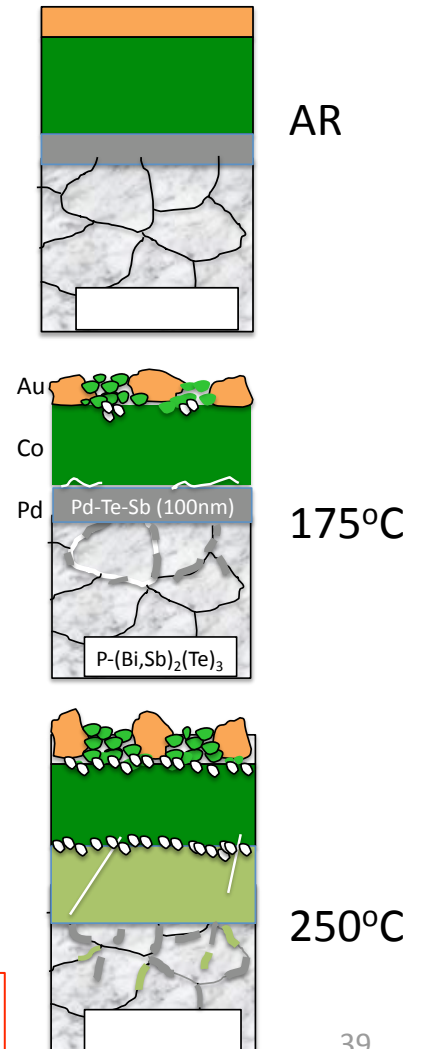
- Continue the thermal aging experiment up to 2-years
- Effect of thermal aging on contact resistance subjects to the similar aging testing conditions, at 240°C/30days to 1 year.
- Develop thermodynamic /kinetic predictive modeling to validated the instability observed in the accelerated test at 350°C/30 days
- Alloy/processing development/optimization, e.g., additive, for improved ZT?



# Thermal instability of Co barrier in the n- tiles was verified by FIB/SEM imaging



## Schematic



Thin film Au, without diffusion barrier, found to be a effective interconnect metallization.