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# Interface adhesion and coating integrity effect on the performance of the $Bi_2Te_3$-based thermoelectric module

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# Outline

- Programmatic goal and scientific motivation
- Principle of thermoelectric (TE) power generation and TE module design
- Process development of thin film interconnect metallization
- Experiment and scientific findings
- Summary and conclusions

# Programmatic Goal

**Developing materials and characterization capabilities**

⇓ Enable custom design/build

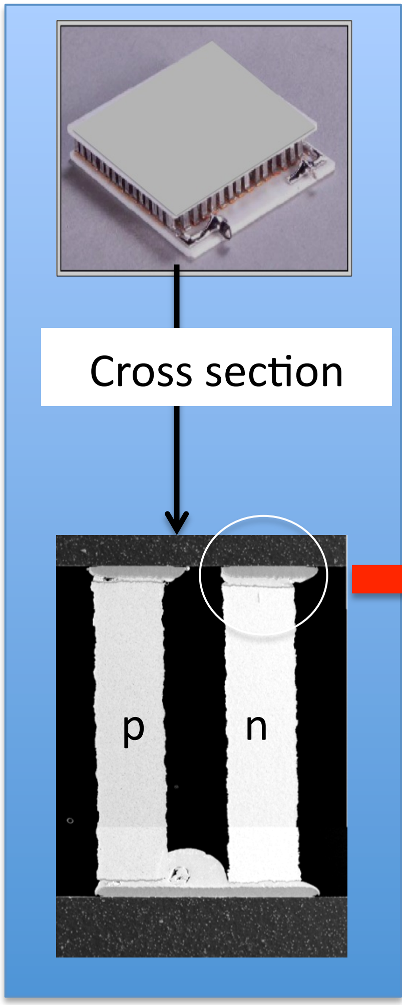
**High performance long-life $Bi_2Te_3$-based TE device**

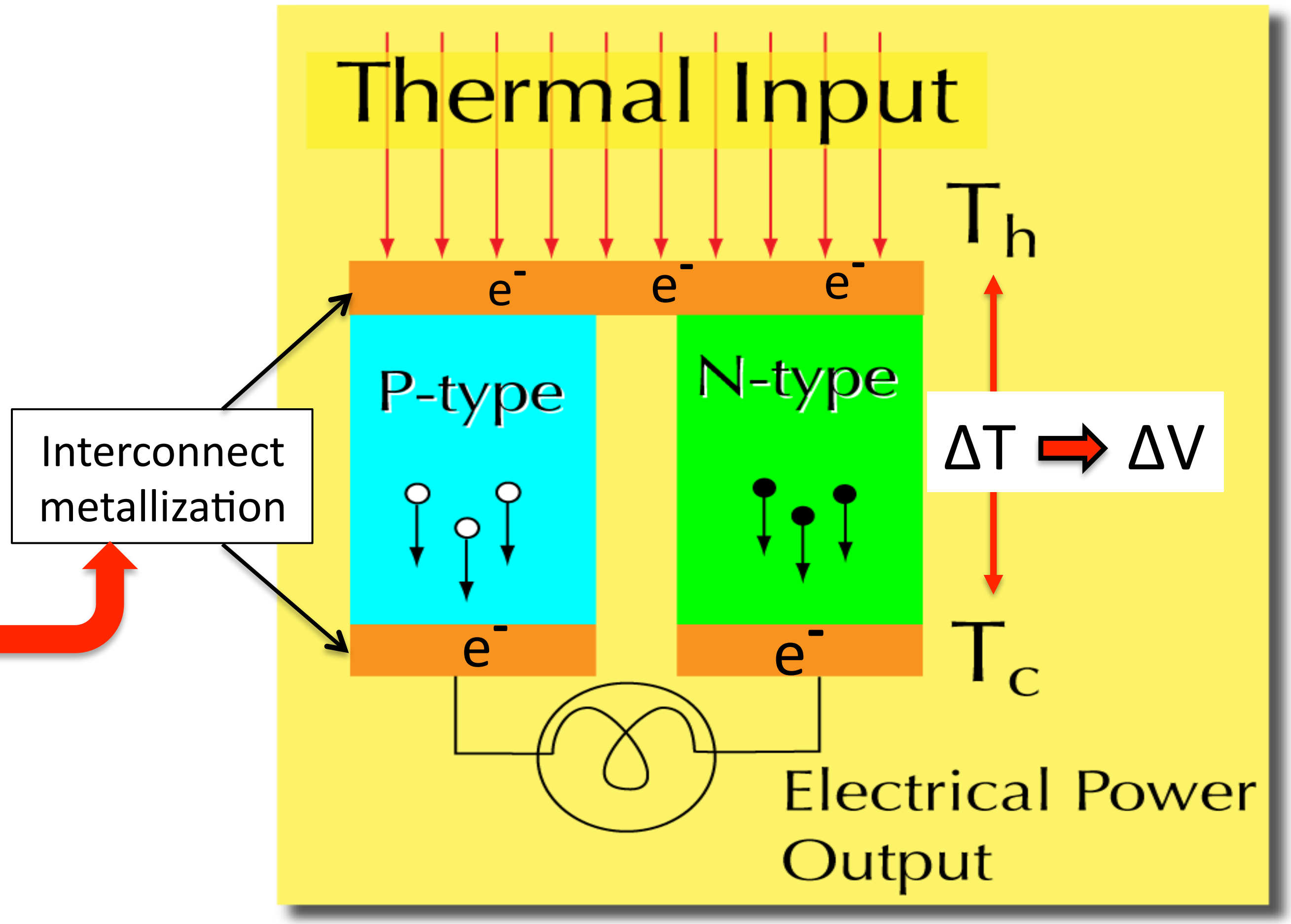
⇓ Allow

Mine electrical power from a low level heat source

# Principle of thermoelectric power generation

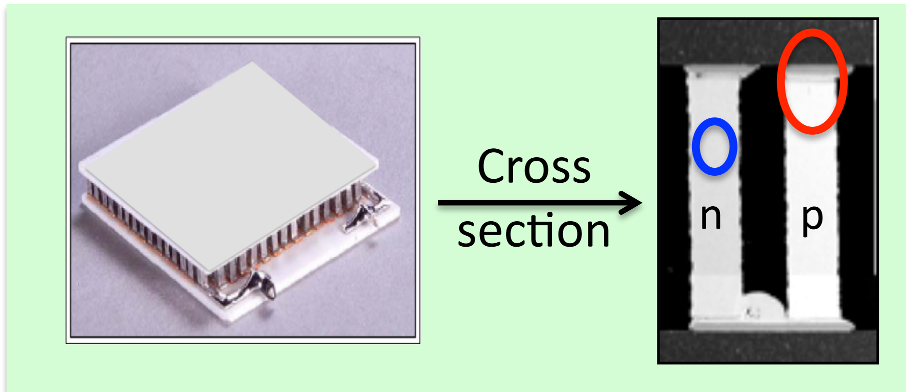
**Typical TE module design & construction**



# Material issues associated with TE module development

**$Bi_2Te_3$-based TE module**




**Today's focus**

**TE Material**

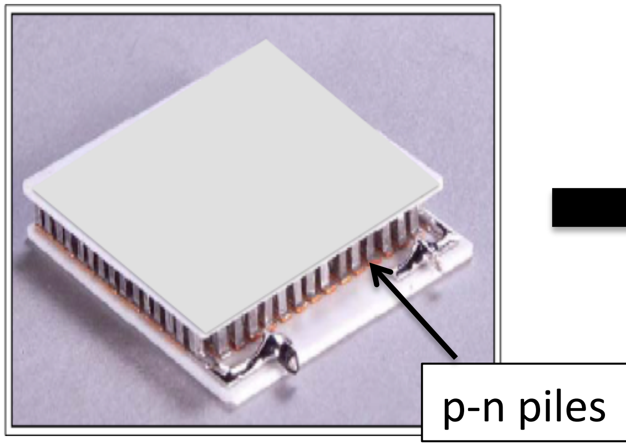
- P- N base alloy synthesis & processing
- Alloy metallurgy & thermal aging
- TE transport property

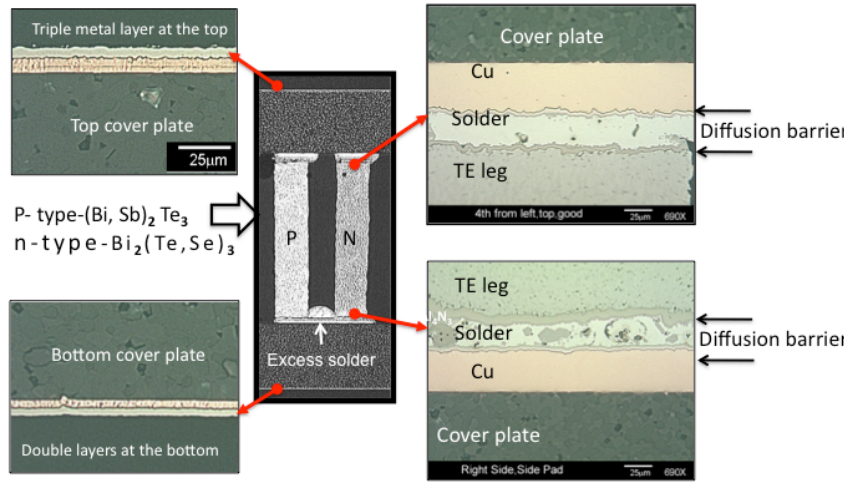
**Module/ Device**

- Contact-metallization design & fabrication
- Material compatibility & thermal aging
- Material-device interaction & structure integrity
- Contact resistance

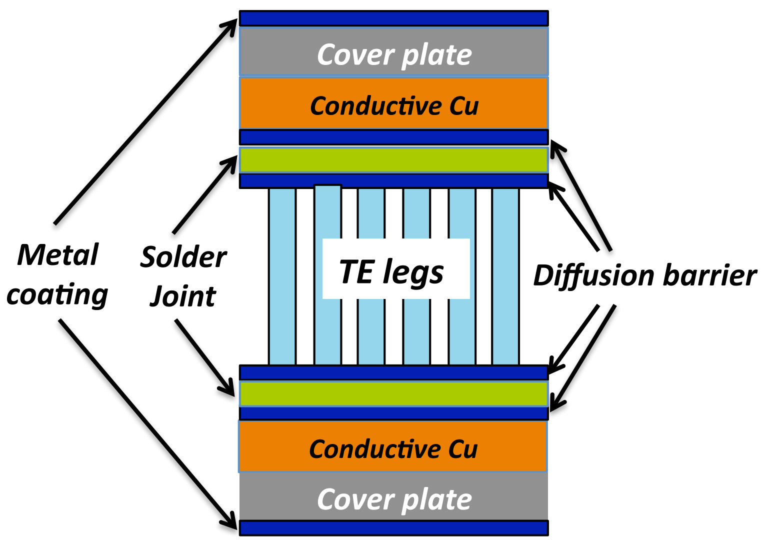
# Feasibility study of commercial $Bi_2Te_3$ TE module option

A general construction of the commercial $Bi_2Te_3$ modules



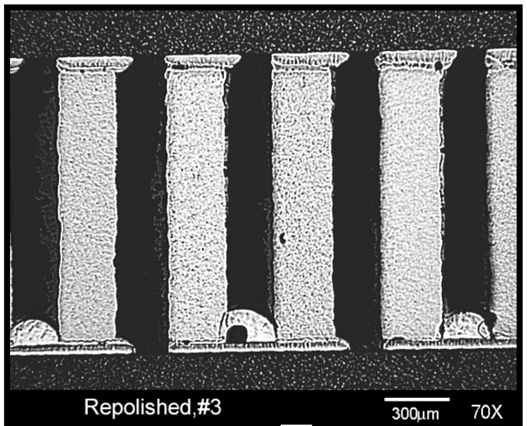

Schematic for module construction and material varieties used for metallization

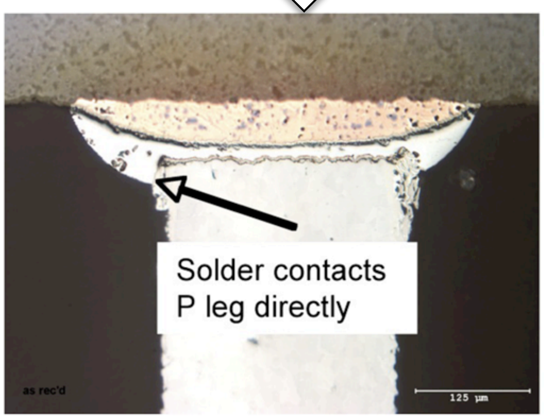



- Top metal coating: Au or Ni/Cu
- Cover plate: AlN or BeO etc..
- Conductive metal layer, Cu, Cu/Ag
- Diffusion barrier (1): Ni, Ni-P, Pd, Co, etc..
- Solder joint: Sn-rich, Bi-rich, In-rich etc..
- Diffusion barrier (2): Ni, Ni-P, Pd, Co, etc..

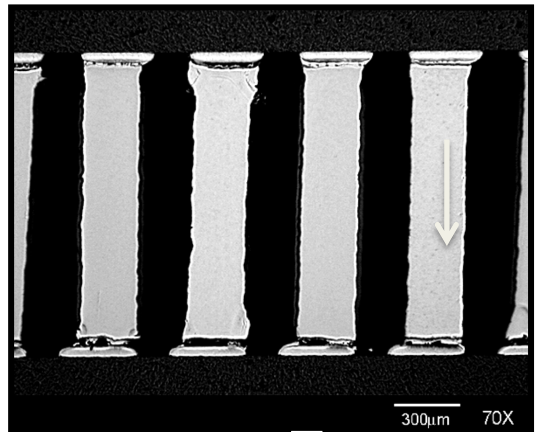
# Material compatibility/thermal aging of the conductive interconnect determines the long-term structure integrity and reliability

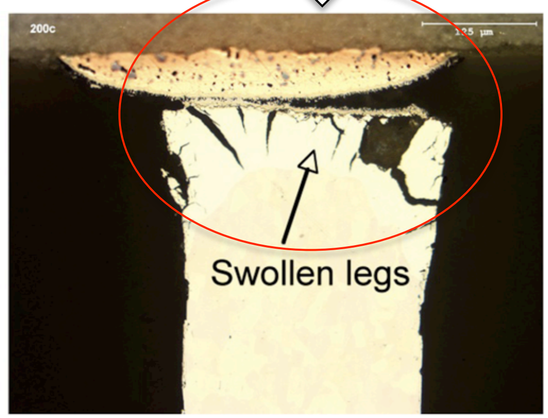
## As-received

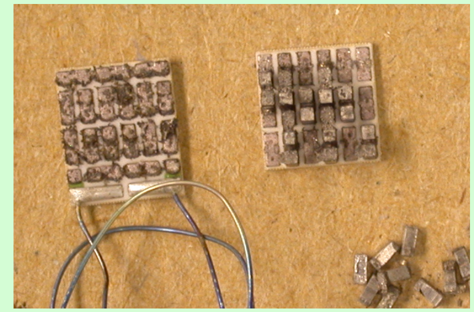



## 200$^o$C/2 hours



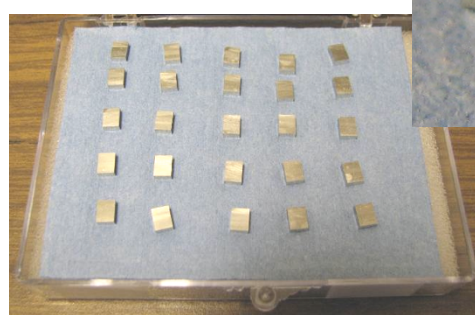



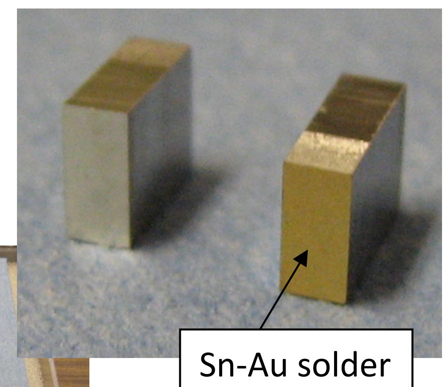
Catastrophic failure of the TE module at 250$^o$C due to solder melting

# Extensive thermal aging study performed on the experimental p-n tiles.

| Base TE Material | Diffusion Barrier | Solder | Aging Temperature | Aging Period |
|---|---|---|---|---|
| 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

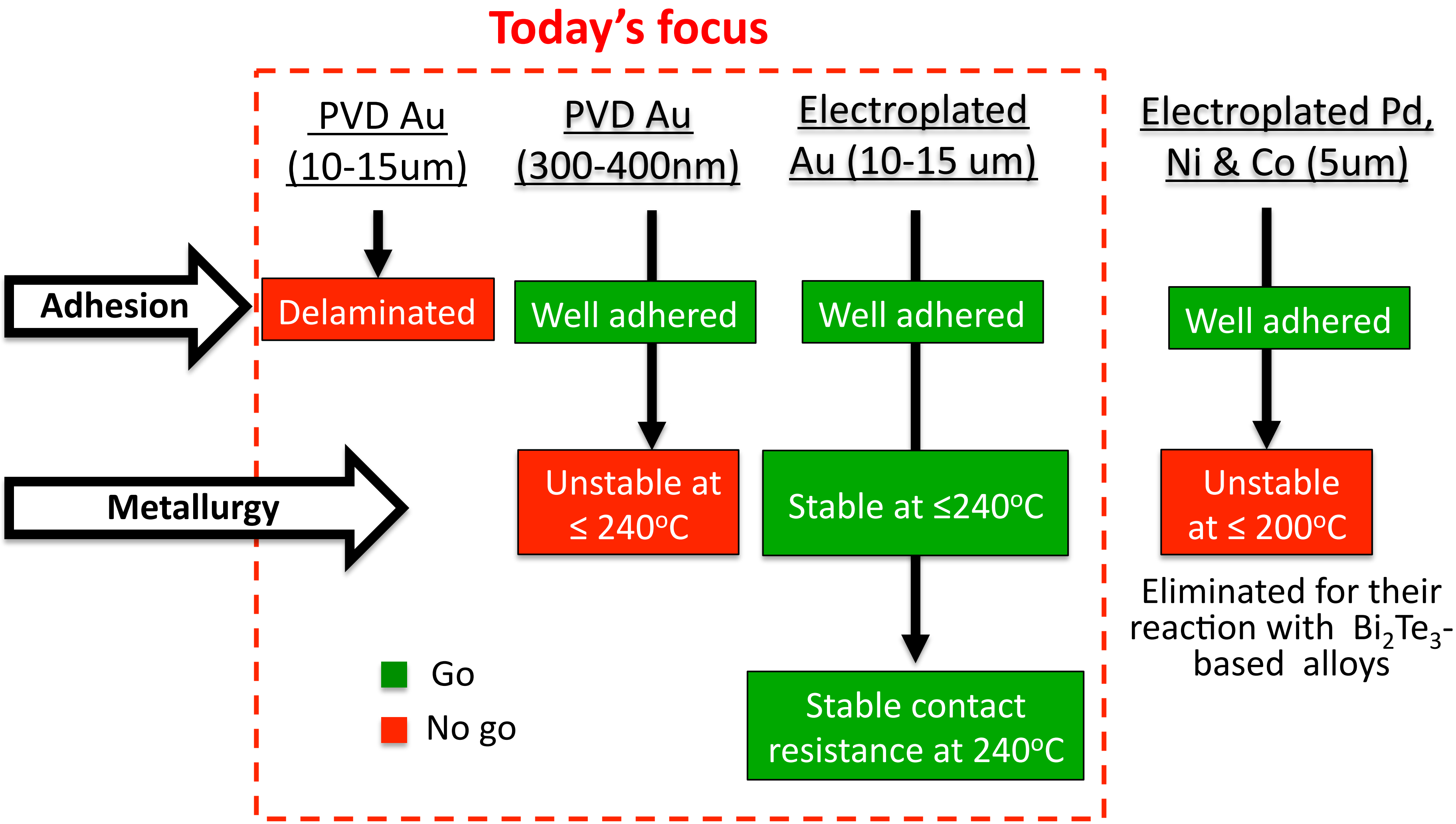





The metal selections were based on:

- Compatible thermal expansion coefficient
- Good contact resistance
- Stable metallurgy

# Process development and optimization for the interconnect metallization

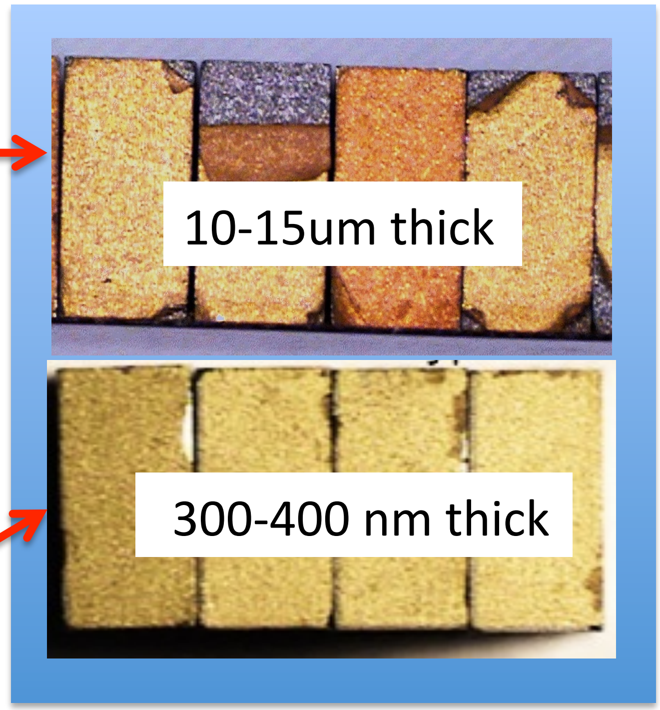



Note: The thin film metallized tiles were prepared by a commercial vendor with the exception of the PVD Au, which were fabricated at SNL, NM

# Contact metallization adhesion to BiTe is one of the key considerations

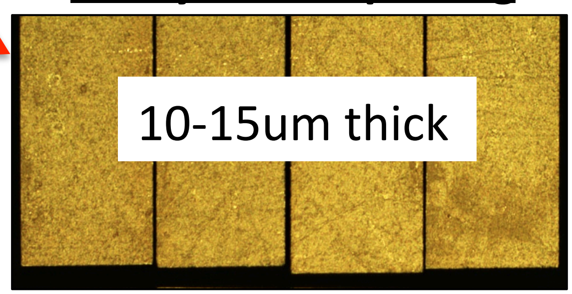
**Au by PVD**

Au film delamination was observed in E-beam and sputter deposited films at 10-15um thickness.

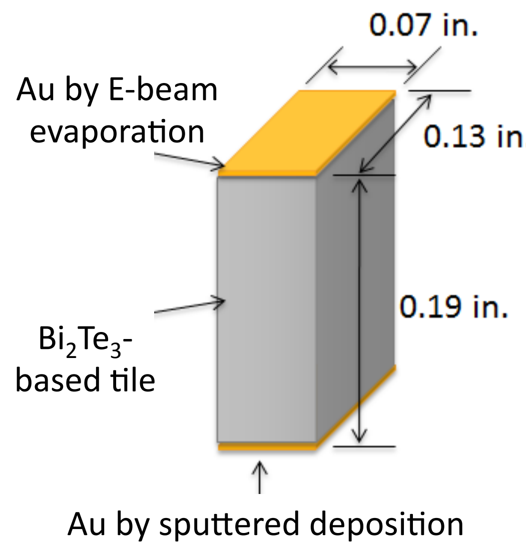



Well adhered Au film

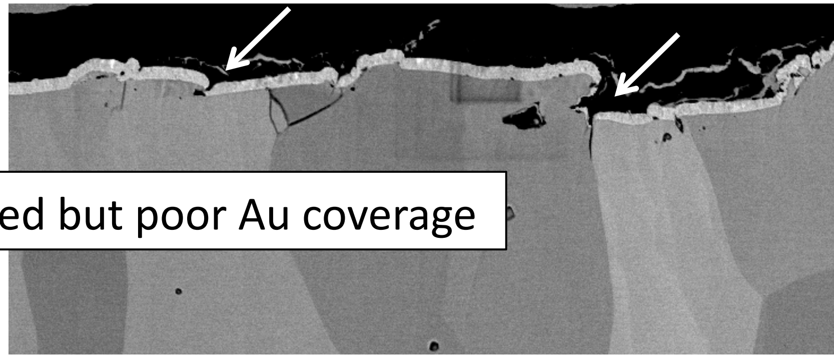
**Au by electroplating**




Specimen dimension

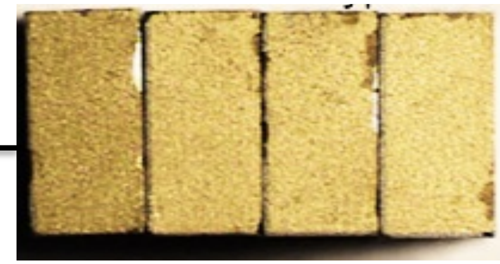


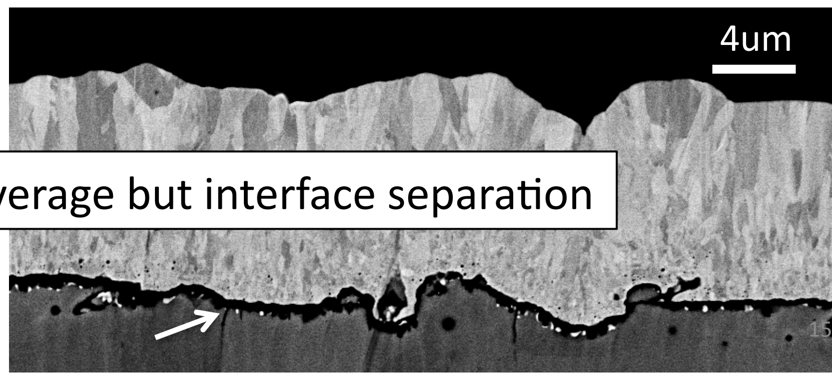
# Microstructure and interface adhesion of Au film are process dependent



Well bonded but poor Au coverage

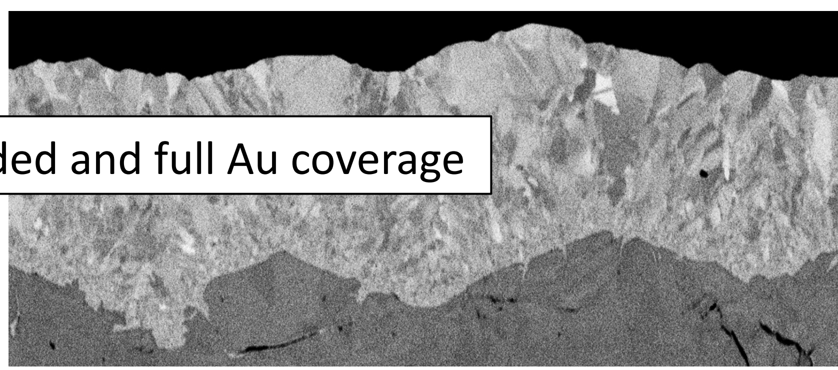
PVD (300-400nm)





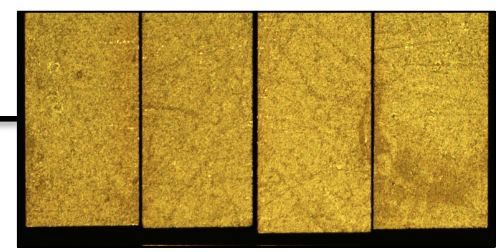

Full Au coverage but interface separation

PVD (10-15um)

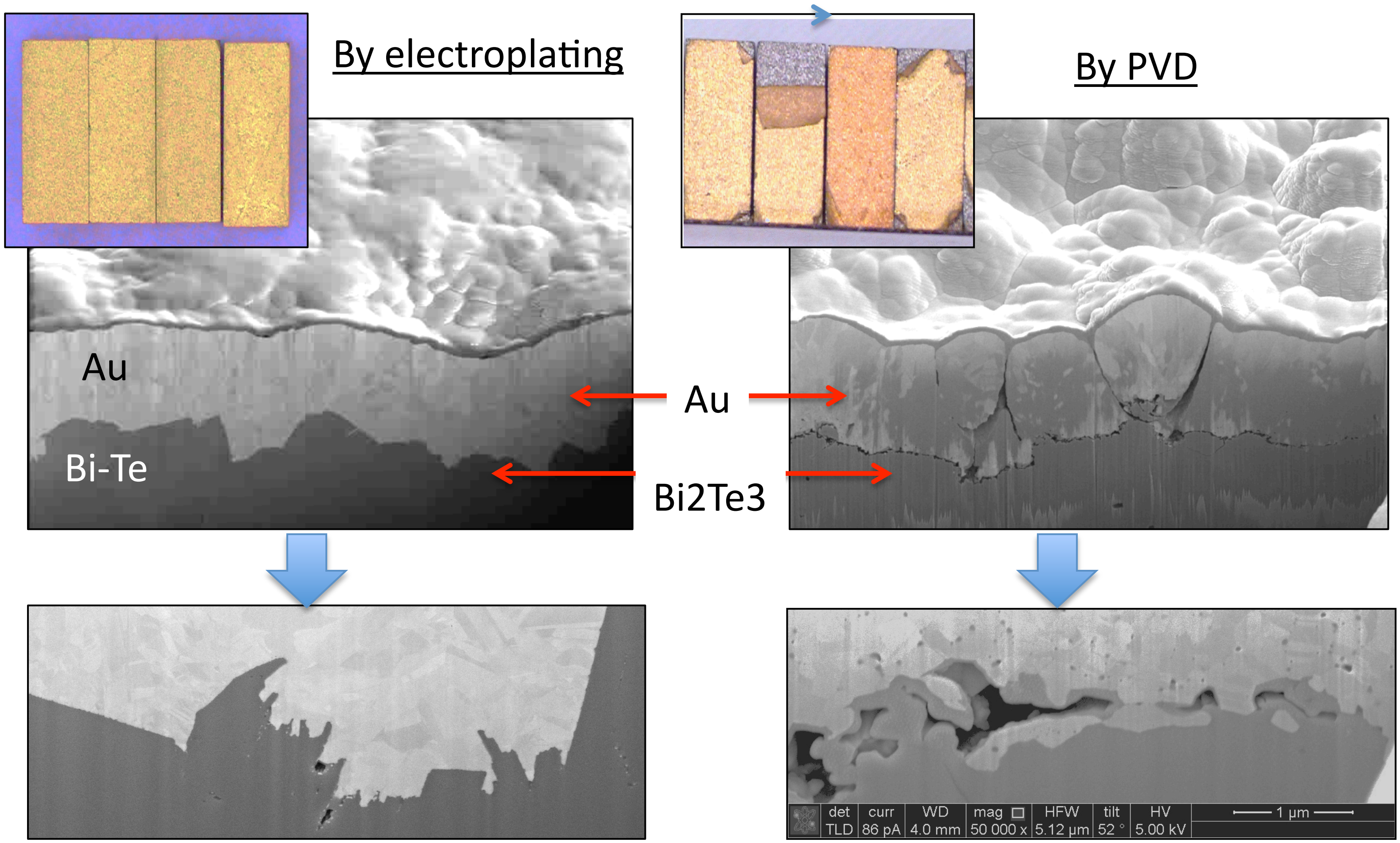


Well bonded and full Au coverage

Electroplated (10-15um)



# 3-D images suggest the thru-thickness pinholes & large interface pores are responsible for the poor adhesion of the 10-15um PVD Au film

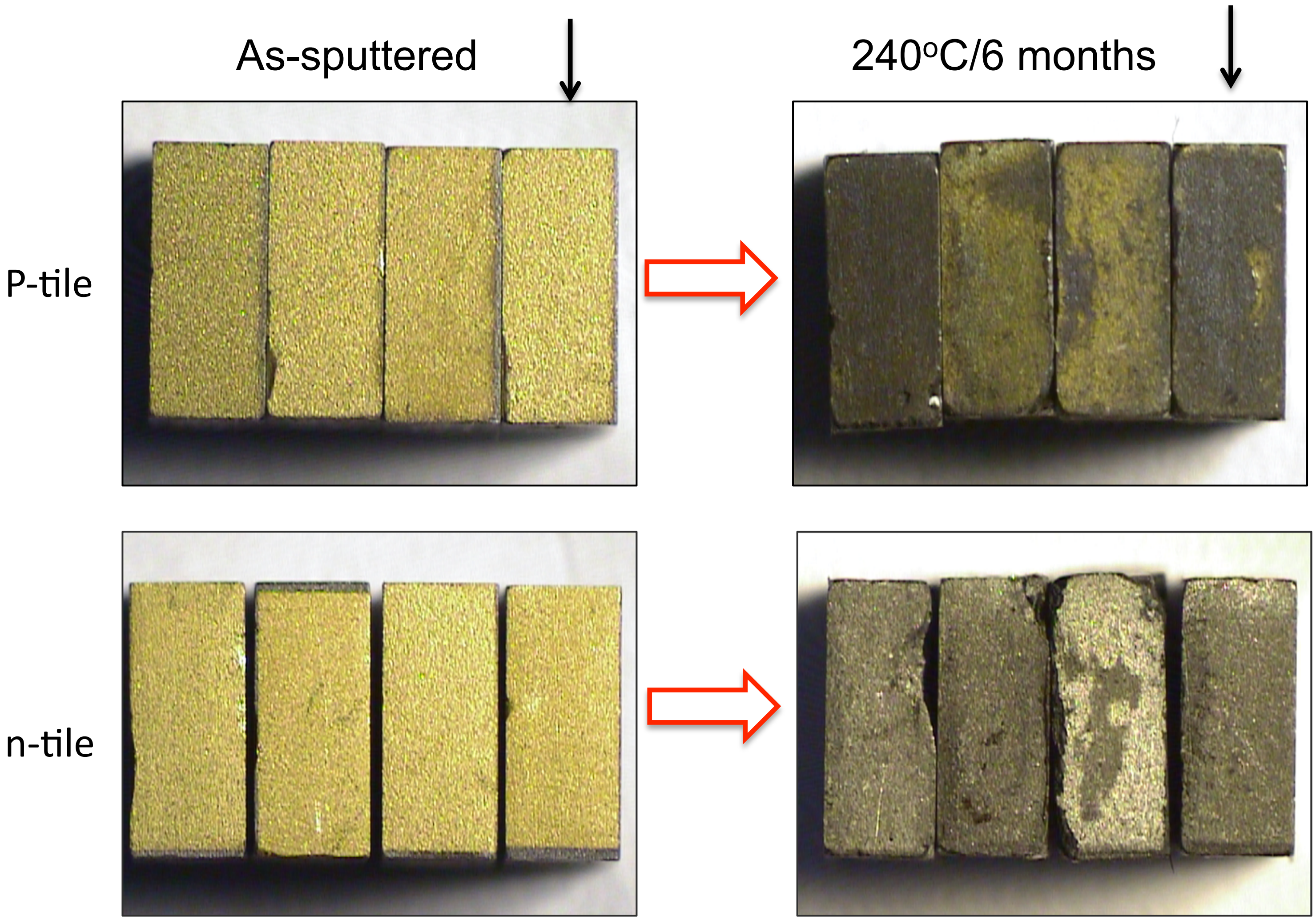



The plated-in Au provides good mechanical locking for adhesion

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

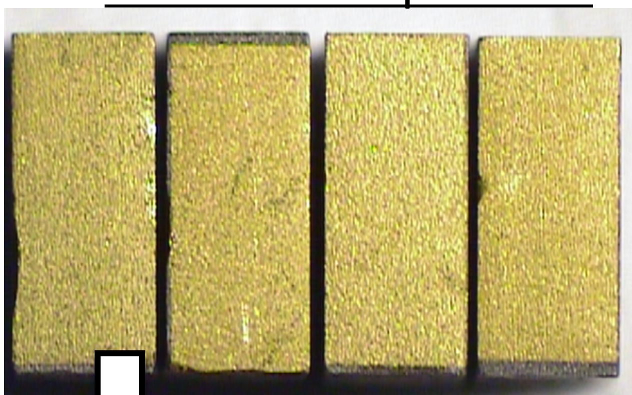
# Thermal stability of the Au films and its effect on the contact resistance

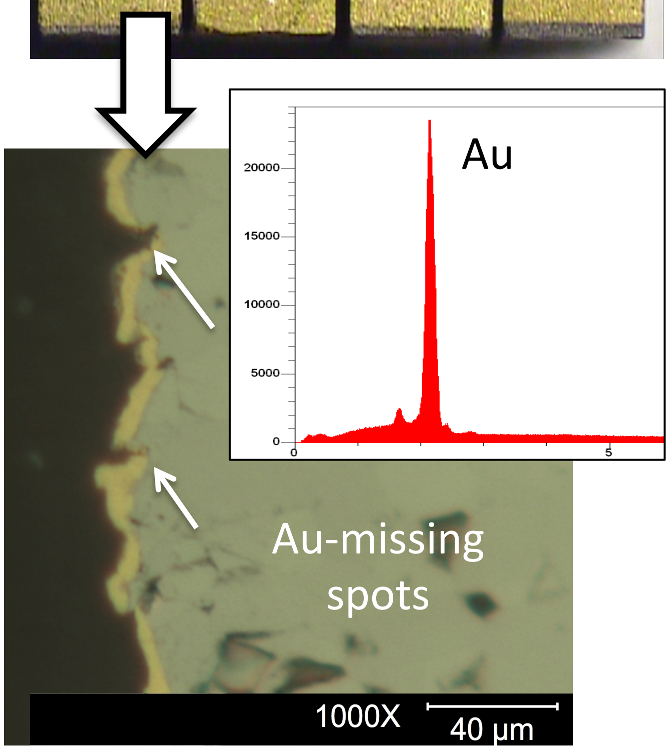
# The ≤400nm PVD Au discolored upon aging at 240ºC/6 months.



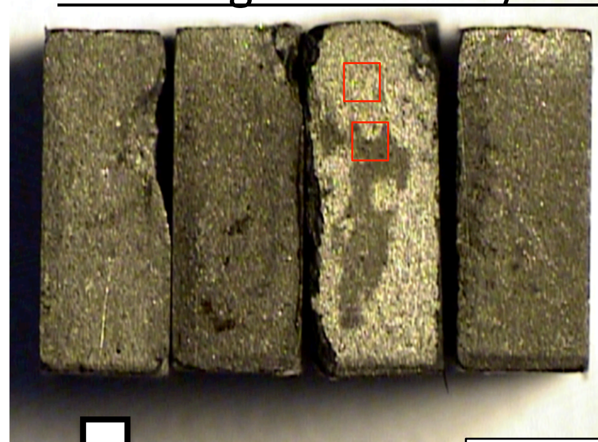
# The porous PVD Au (≤400nm) on the rough p & n tiles is susceptible to (Bi,Sb or Te)-oxidation upon oxygen exposure

As-received sputtered

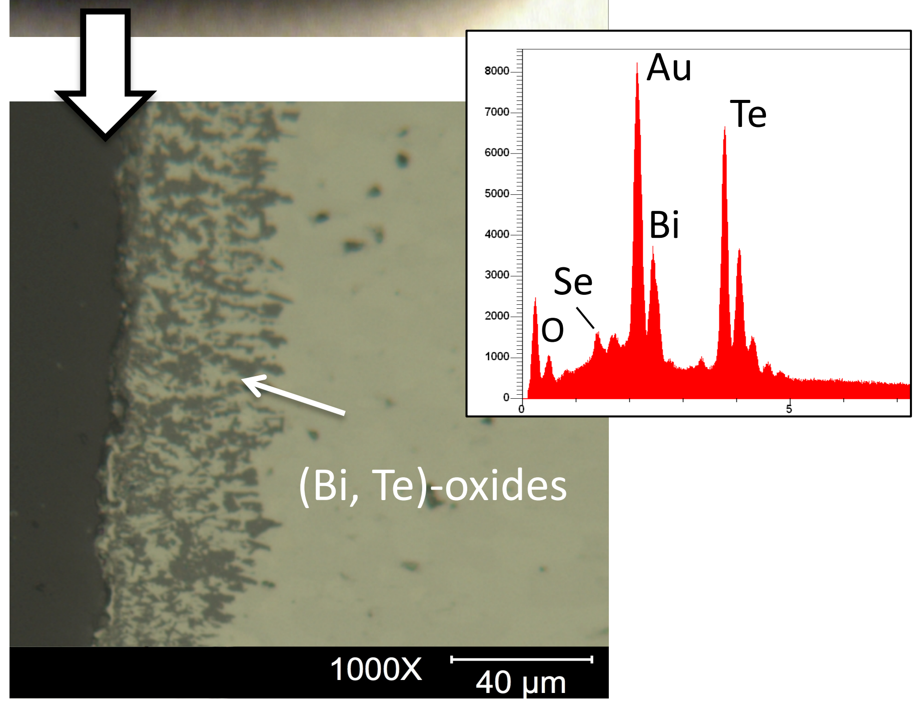





n-tiles aged at 260°C/6 months

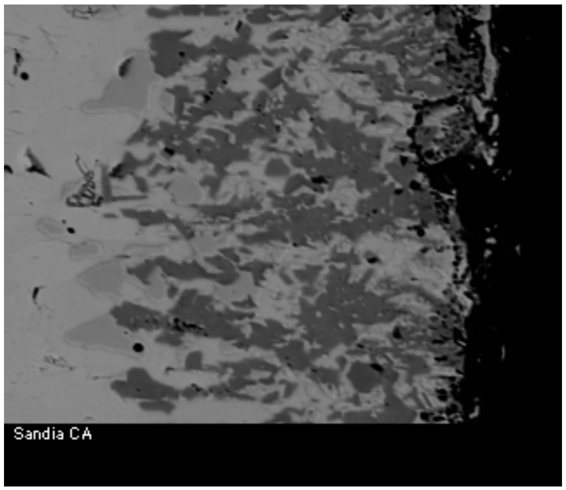


Discoloration derived from the (Bi,Te) oxidation

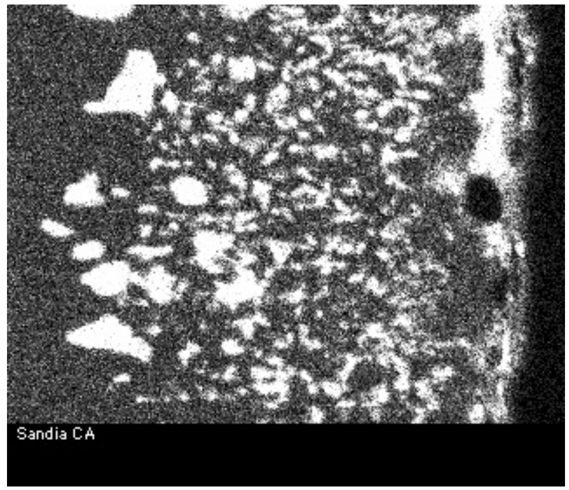


# X-ray maps show absence of Au film, $AuTe_2$ and (Bi,Te) oxides on the n- tile, coated with ≤400nm PVD Au aged at $260^oC$/6 months

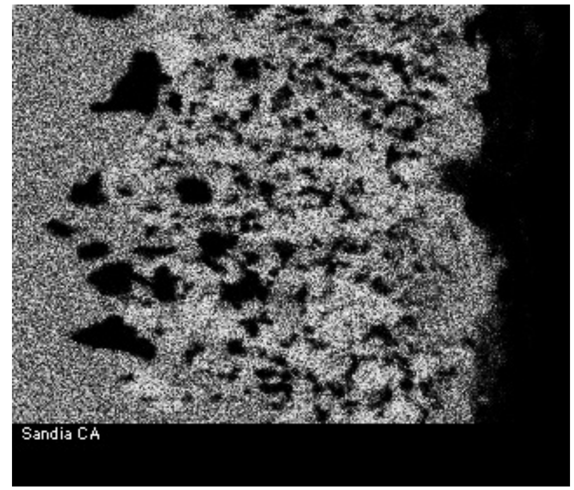
BEI



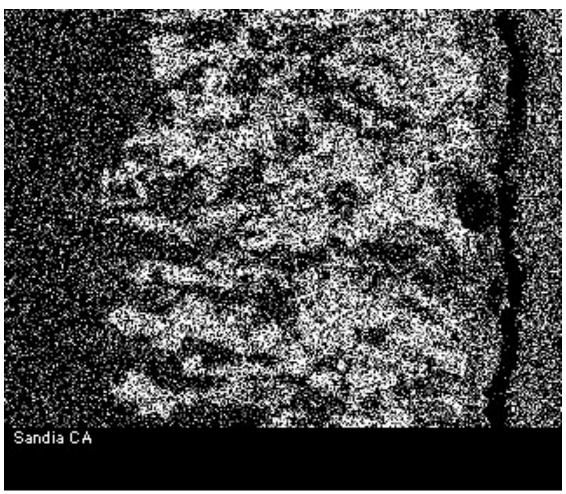

Au



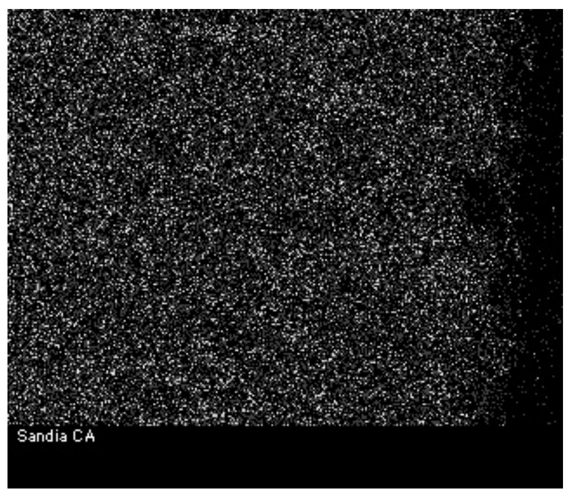

Bi



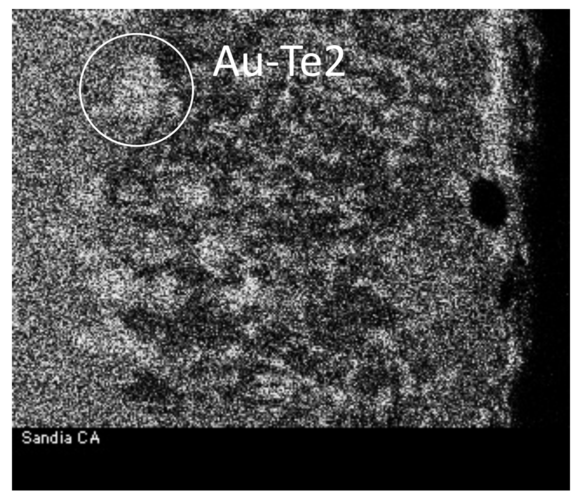

O




Se

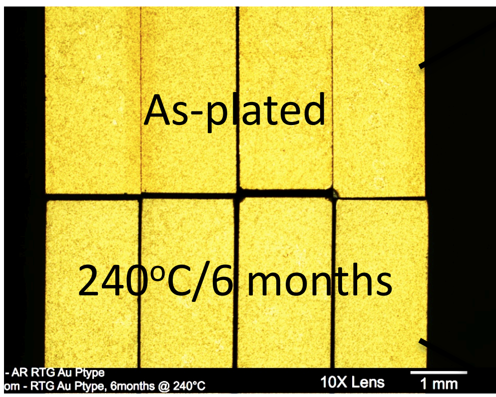


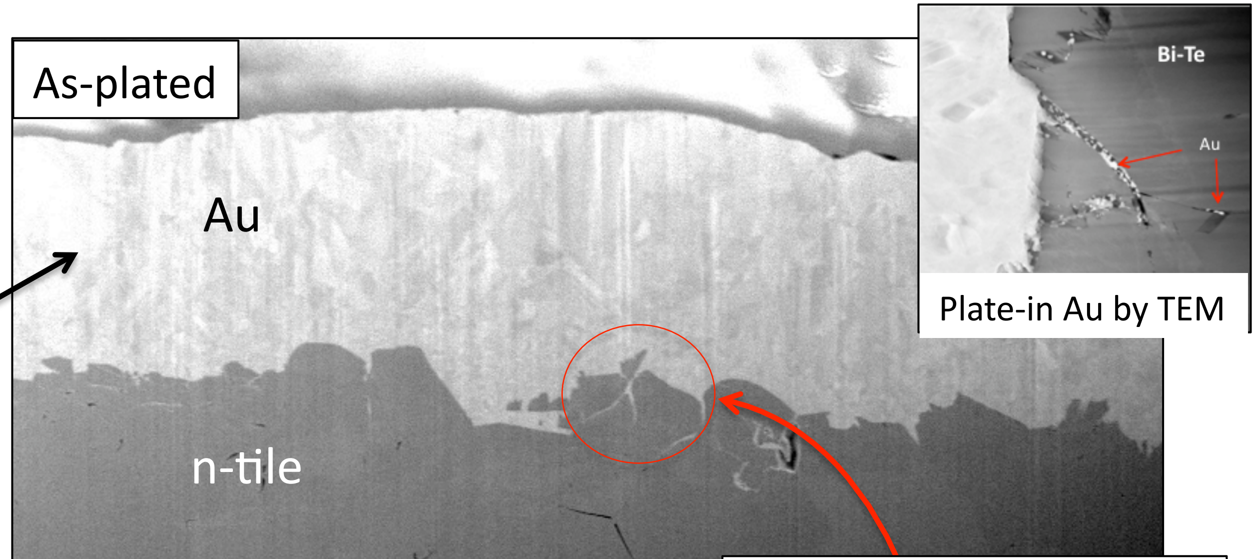

Te



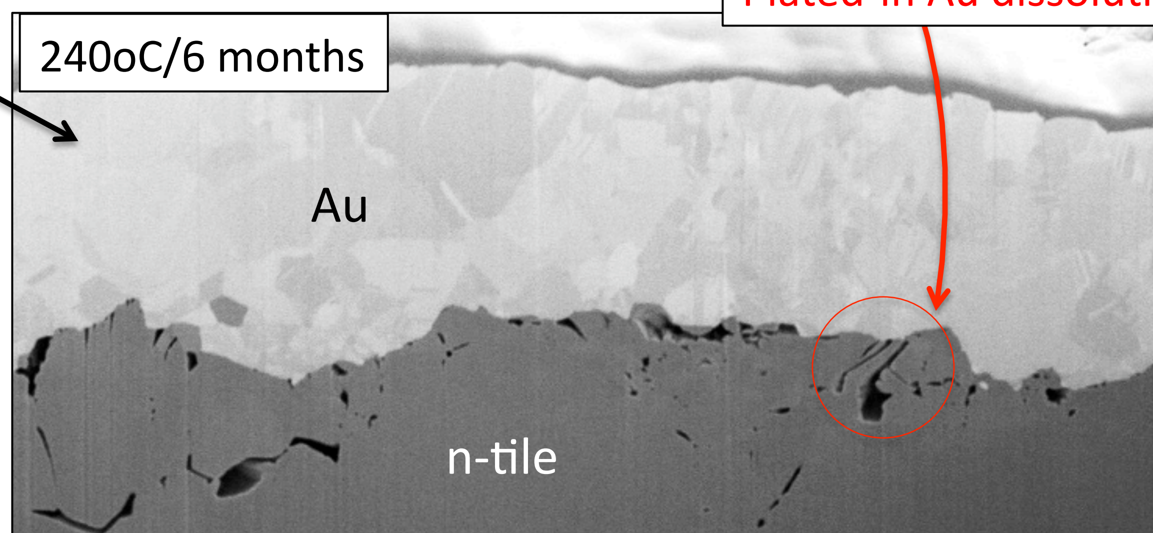
# No surface oxidation or interfacial reaction seen in the p-n tiles with the 10 um electroplated Au, aged at 240ºC/6 months

Plate-in Au



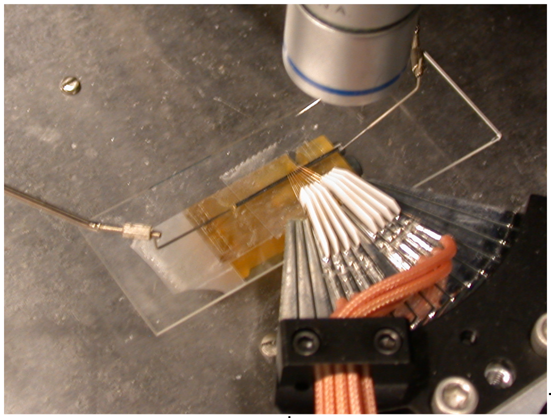

Plated-in Au dissolution




Upon thermal aging, recrystallization/ grain growth and dissolution of the plate-in Au were evident .

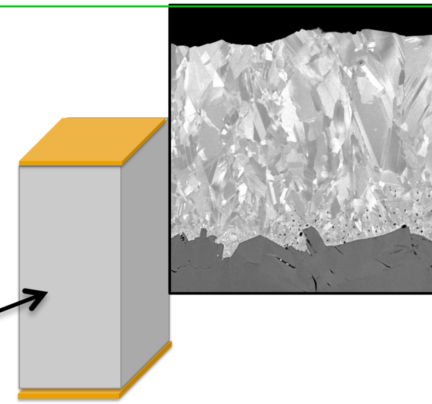
# Contact resistance was measured by 4-point probe method. For a ideal metal coating, contact resistance goes to zero.

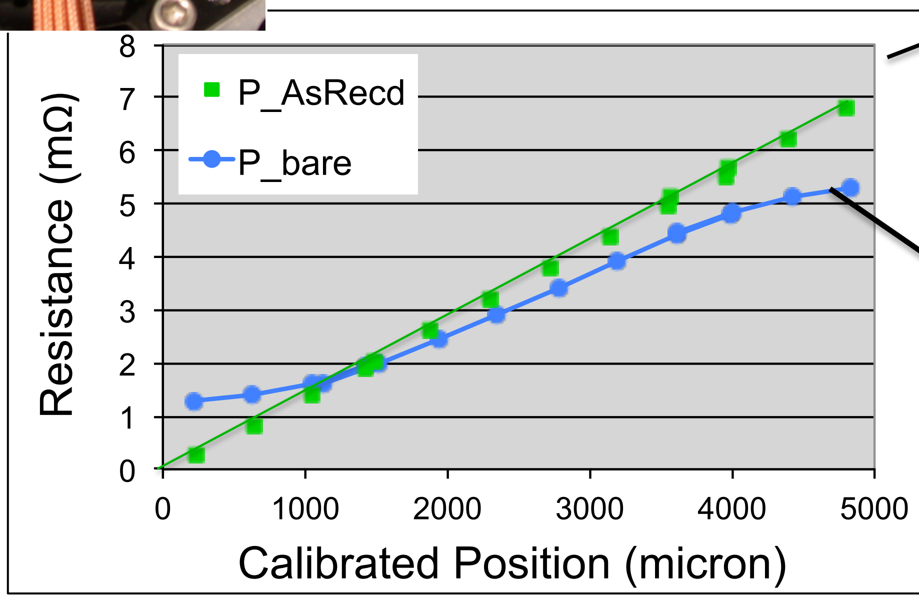
**Procedure for 4-point probe technique**



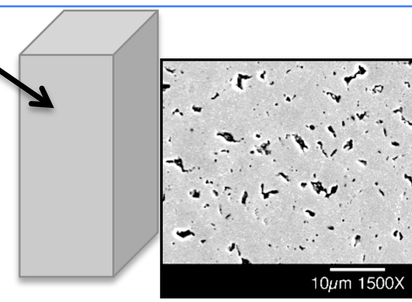
- Current injects across two end faces. Voltage is measured at several points on the top face.
- Correcting by the geometry of the sample, the slope yields the bulk resistivity and the intercept yields the specific contact resistance.

A well adhered dense electroplated Au (10-15um)



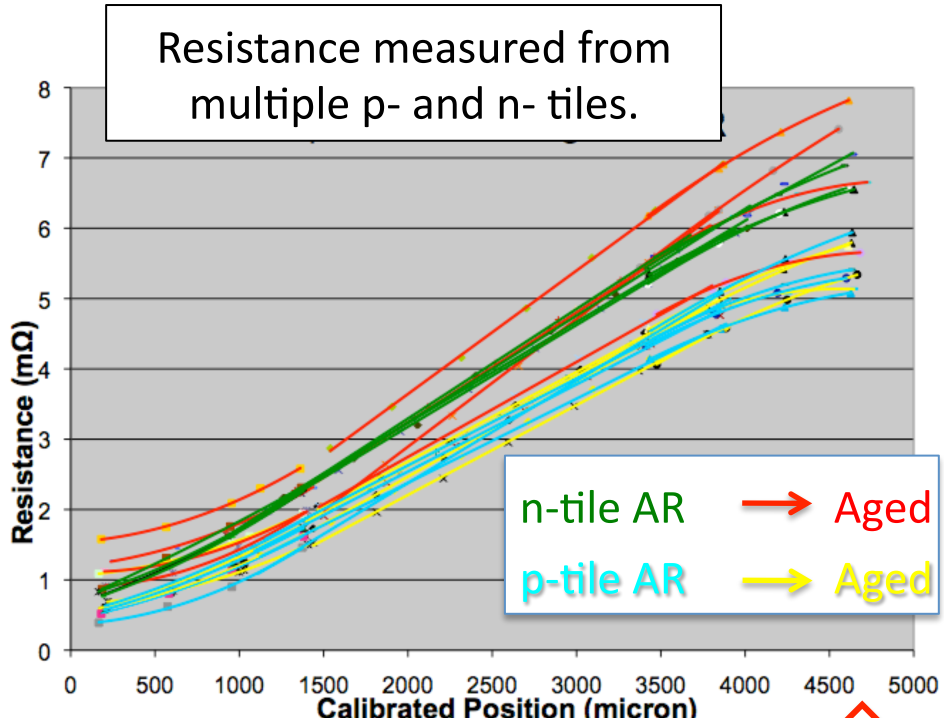



A bare TE tile with process-induce pores

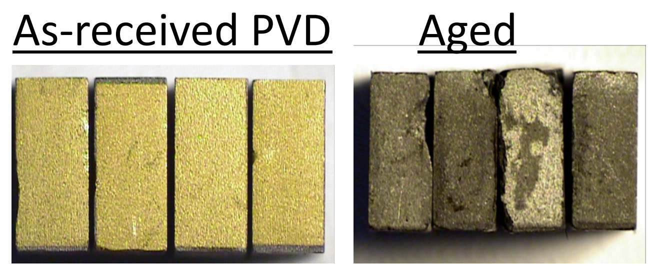


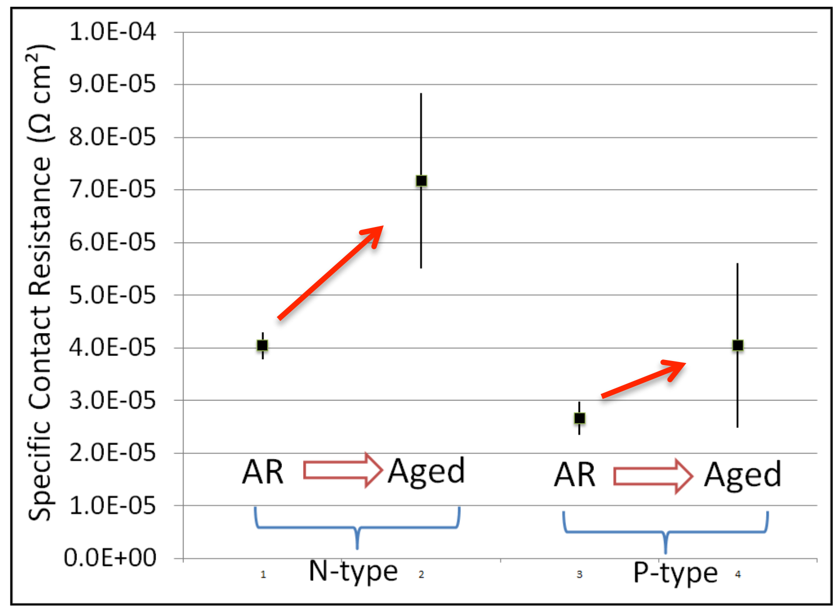

For the porous bare p-tile without Au , the resistance is >zero and nonlinear.

# The ≤400nm PVD Au film may not be a effective conductive interconnect due to its elevated contact resistance.




The non-zero contact resistance of the ≤400nm PVD Au film is attributed to the presence of bare spots and/or aging-induced (Bi,Sb Te)-oxides (?).

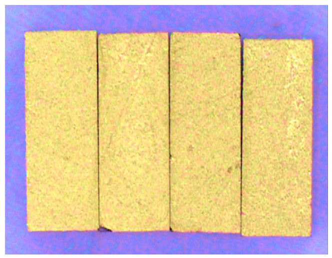


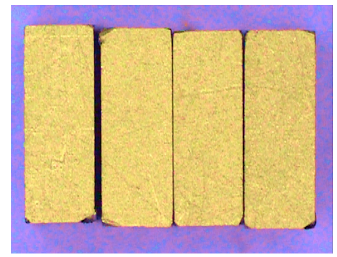




The specific contact resistance increases slightly upon aging at 240°C/6 months.

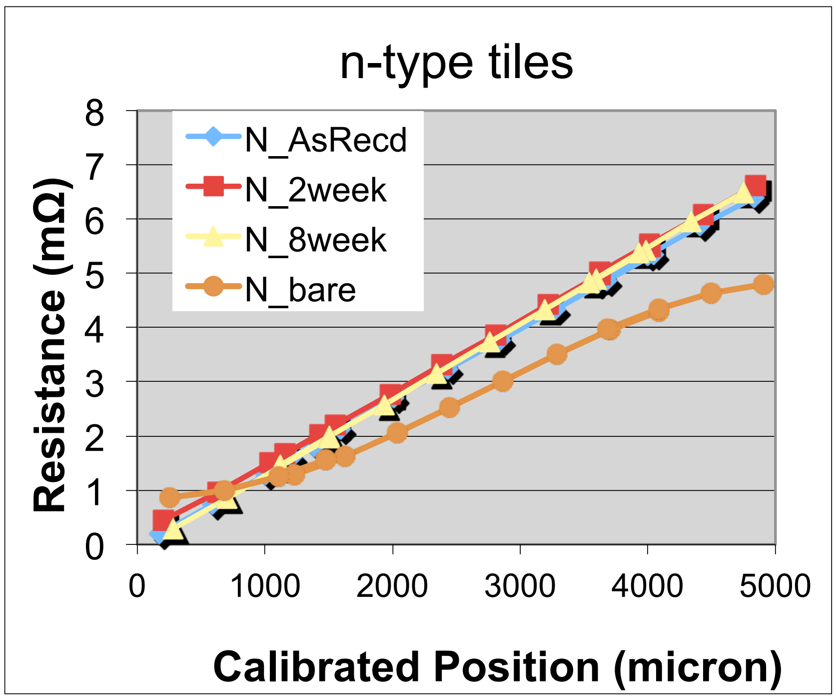
# The thermally stable thick ( ≥10um ) electroplated Au film with zero consistent resistance is an effective conductive interconnect.

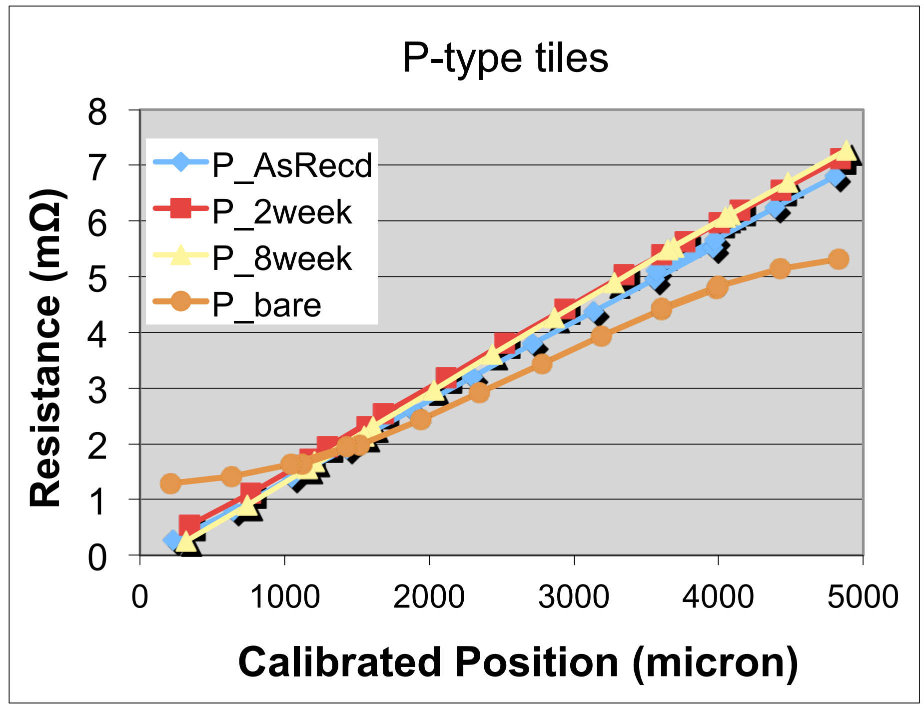
<u>n-tile</u>
as-received





<u>n-tile</u>
240°C/8 weeks aged



# Summary and conclusions

- The metallurgy and interface adhesion of the conductive thin film interconnect used in TE modules is process dependent which in turn impact the contact resistance.
- The discontinuous ≤400nm PVD Au on the mechanically machined $Bi_2Te_3$ surface, is susceptible to surface oxidation that raises the contact resistance.
- The ≥10um PVD Au exhibits poor interface adhesion, caused film stress and/or poor mechanical locking? therefore, was eliminated for the current module application.
- The 10-15um electroplated Au film exhibits near-zero contact resistance, attributed to the strong adhesion & defect free, desirable for the current TE module design.