Fabrication and Testing of Advanced Thermoelectric Unicouple for Power Generation Applications

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by

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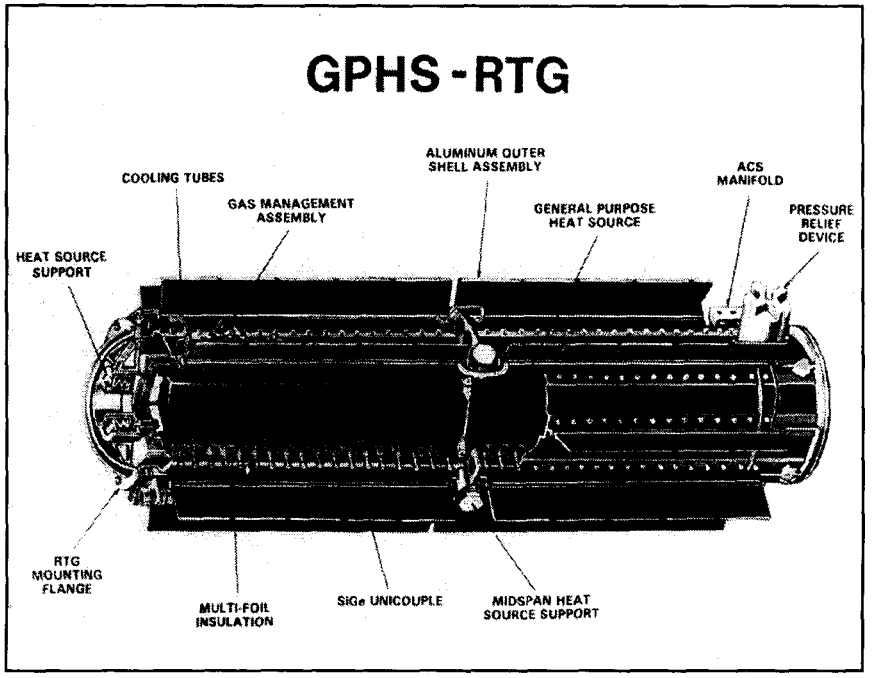
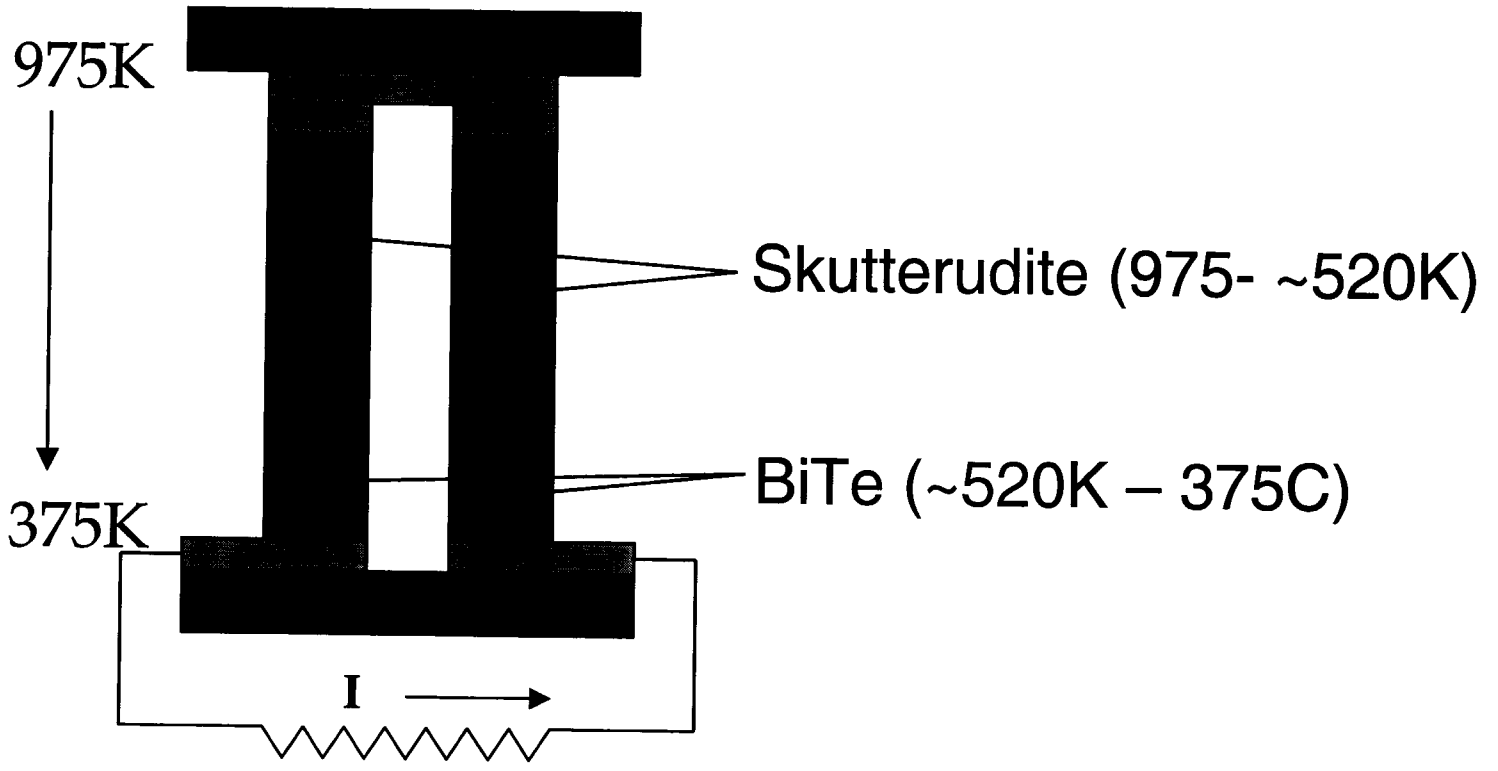
RTG Technology (Key advantage - reliability)



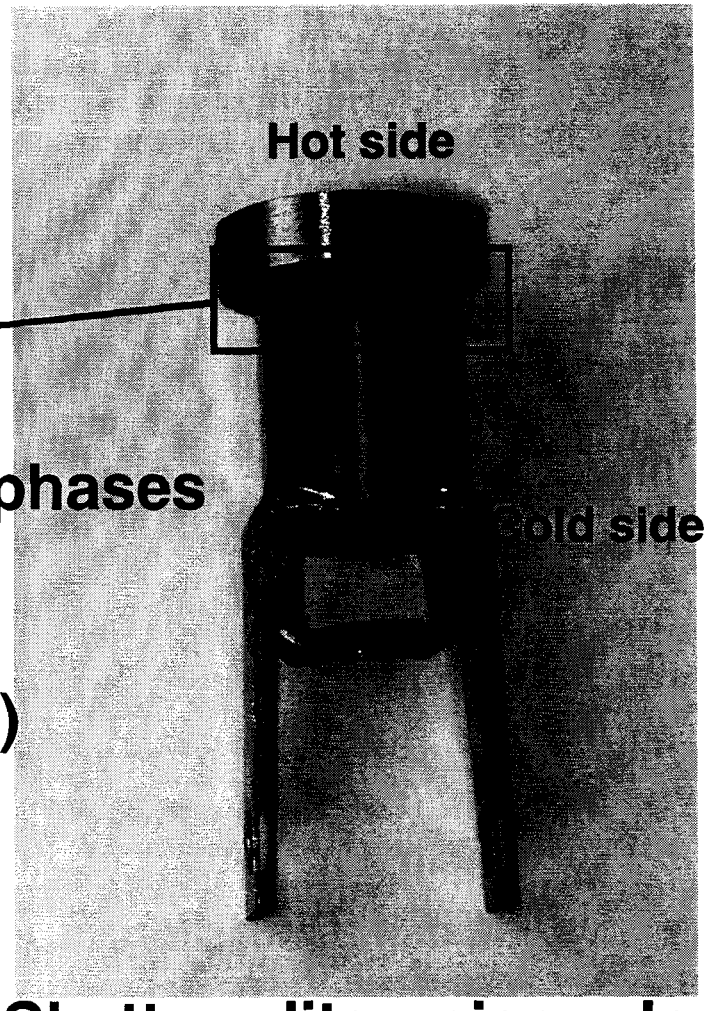
- Radioisotope Thermoelectric Generators (RTGs)
  - Use heat generated by radioactive decay of a radioisotope
  - Used on a number of deep space probe missions
  - Over 20 years of continuous operation for Voyager 1 and 2!
  - Using PbTe and SiGe thermoelectric materials based technology
  - Power output 25 to a few 100 Ws

High-Efficiency Segmented Unicouples (SKD/BiTe)-975-375°K



Potential Modes of degradation

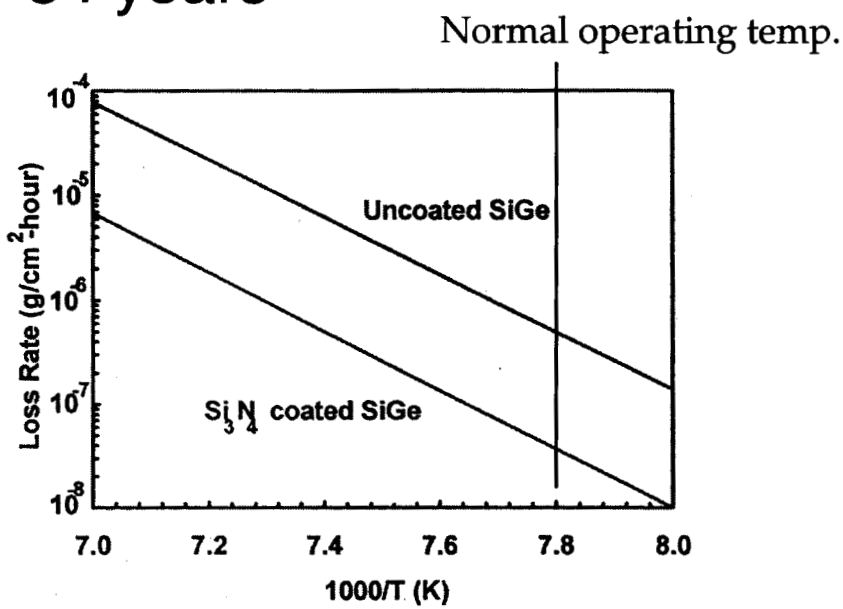
- **Thermal stability**
  - Melting or formation of auxiliary phases
  - Grain growth
  - Dopant re-distribution (migration)
  - ❖Sublimation; loss of mass



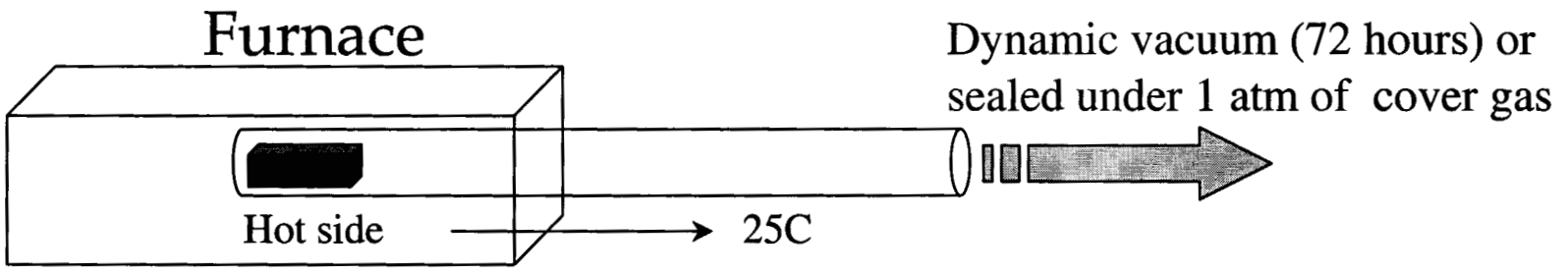
Skutterudite unicouple

Sublimation

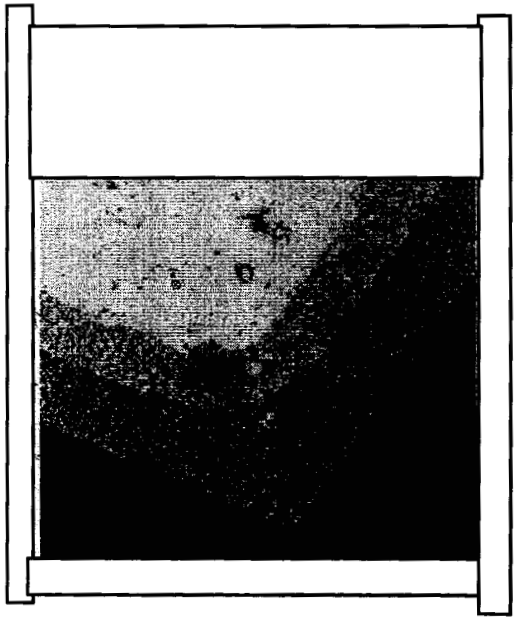
- Loss of mass decreases performance and can cause electrical shorting and cracking
- SiGe- (~10^{-8} g/cm^2-h) at 1273K = 34 years



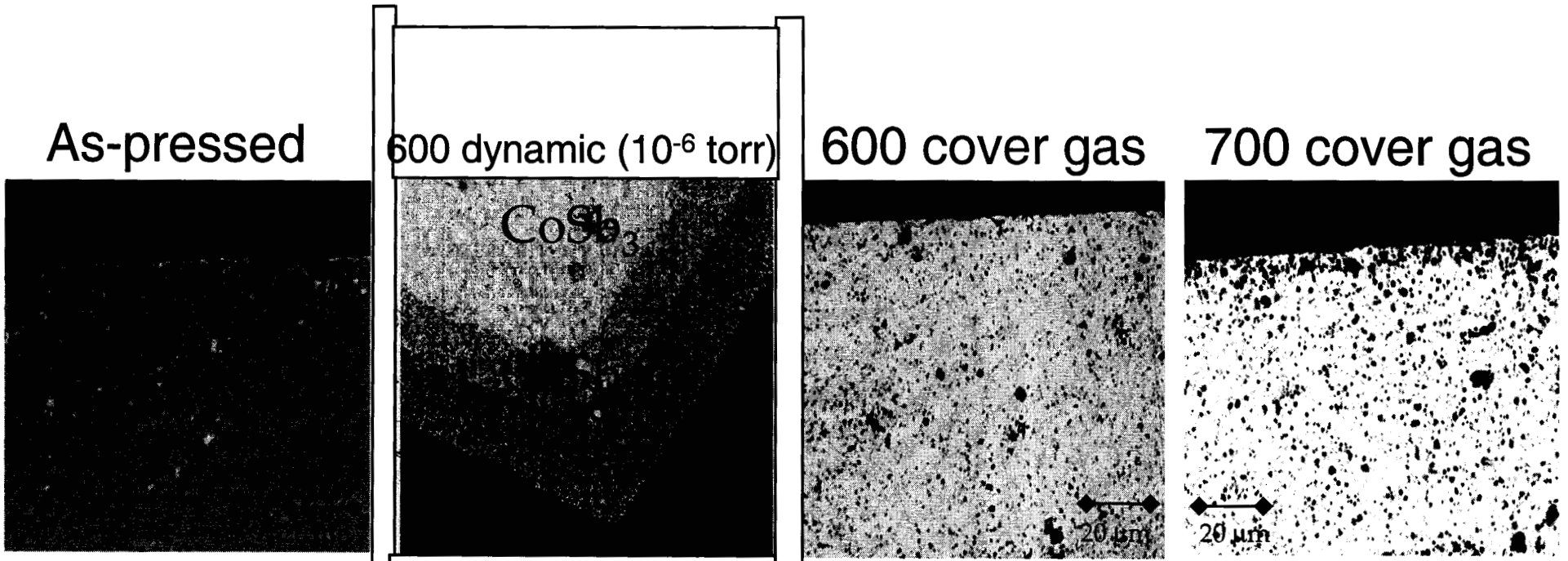
Characterizing Sublimation behavior in SKD antimon



- Cross-section and measure depth of depletion
- Measure weight loss as function of time

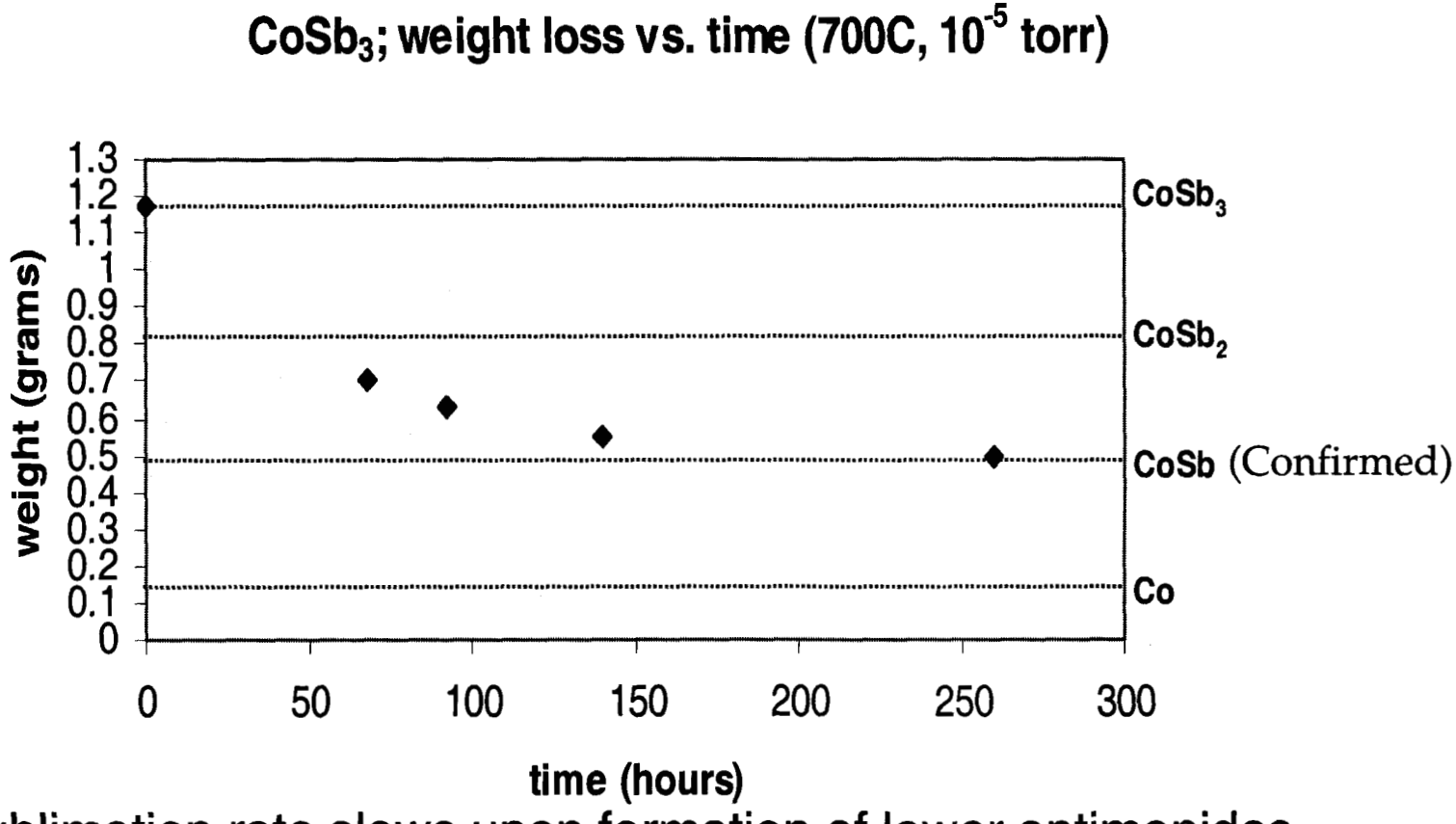


Cross-sectional analysis



- Temperature stability tests have identified Sb sublimation as the predominant material dissociation mechanism in dynamic vacuum
- Sb loss occurs in stages
- Cover gas suppresses Sb sublimation

Weight loss measurements

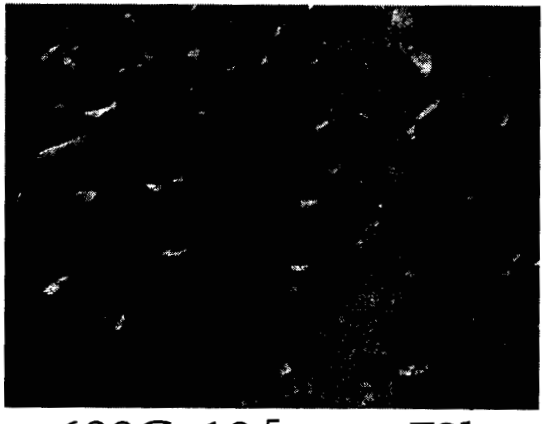


- Sb sublimation rate slows upon formation of lower antimonides
- Mass loss at 8.56×10^{-4} g/cm^{2}h (much higher than uncoated SiGe)
- Future measurements should consider (Surface area/volume)

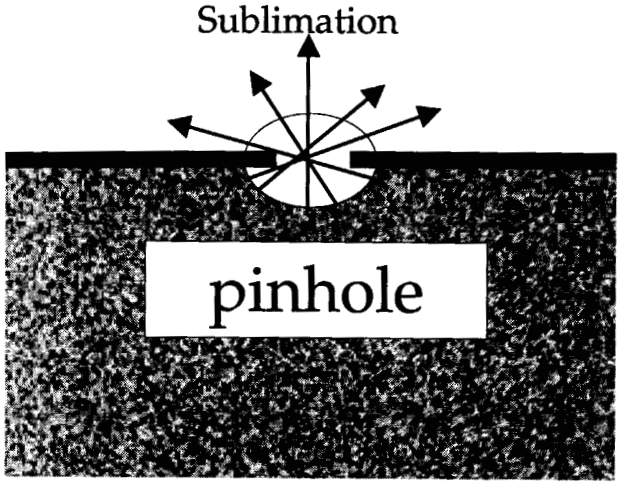
Sputtering thin films

- Sputtered Si_3N_4:

Before heating

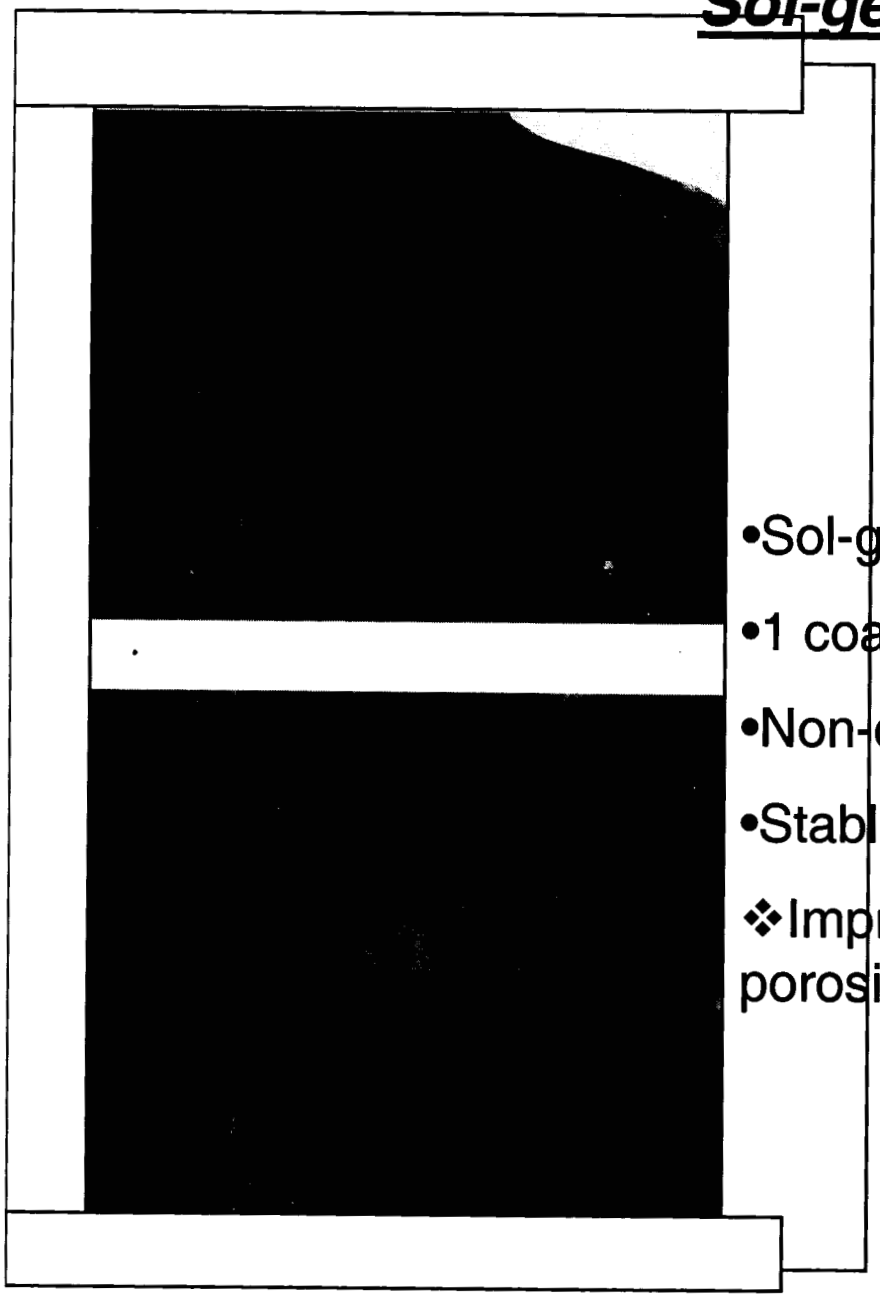


600C, 10^{-5} torr, 72h



- Poor adhesion could result from:
  - CTE mismatch (Si_3N_4= $3x10^{-6}$/K, SKD=6-9 $x10^{-6}$/K)
  - Limited reaction between Si_3N_4 and SKD
  - Pinholes in film allows sublimation → undercutting

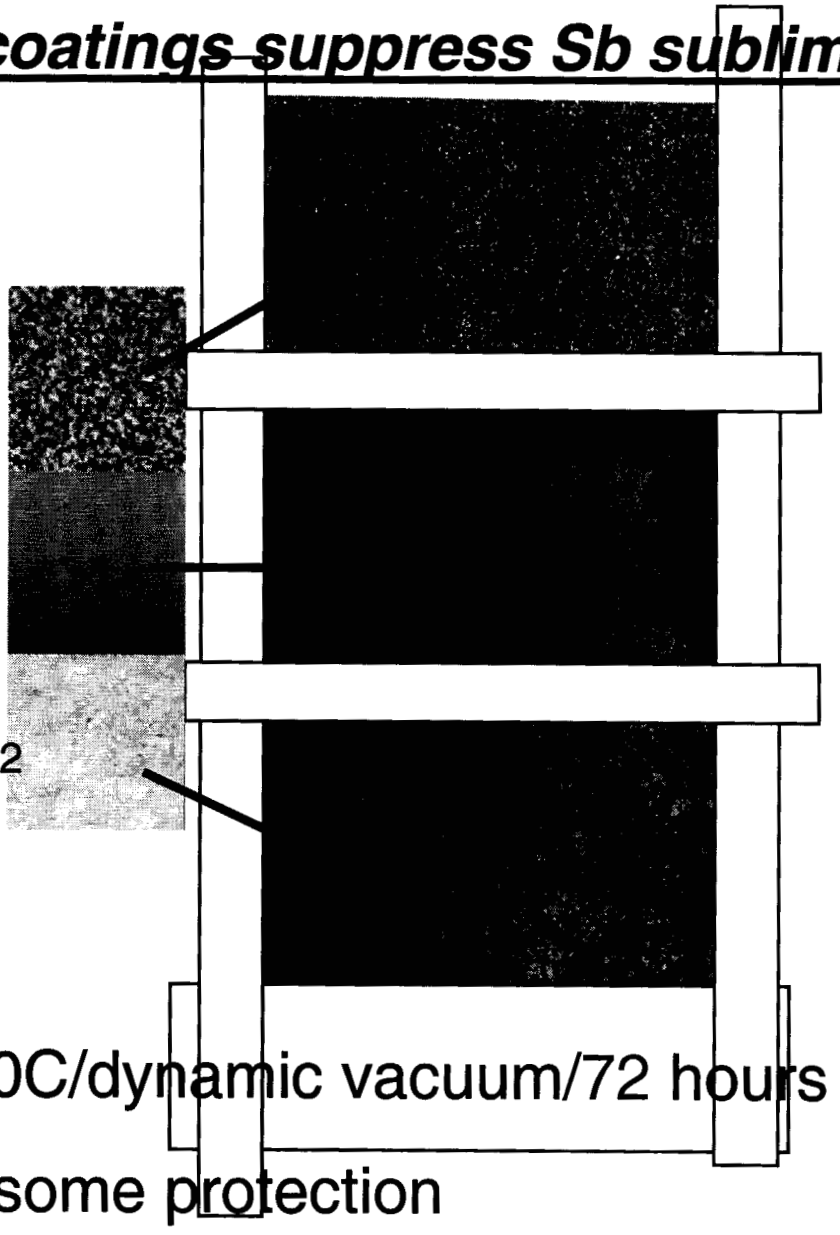
Sol-gel silica coatings



- Sol-gel; dip coating SiO_2 method
- 1 coat: <500 nm
- Non-conductive and thermally insulating
- Stable to 700°C

❖ Improve coating quality by minimizing TE porosity

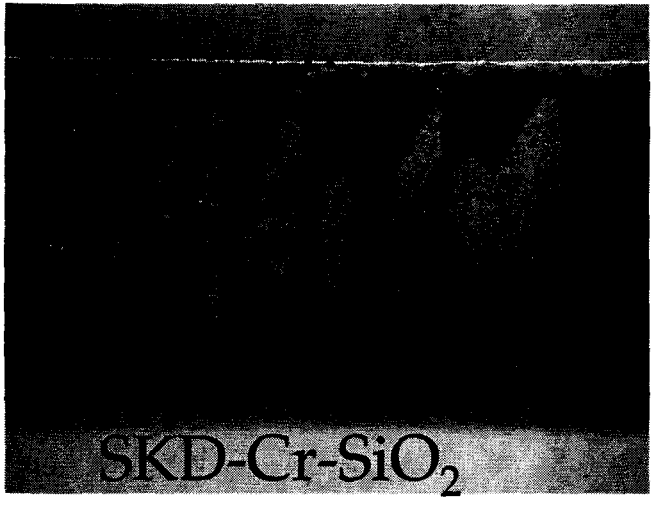
Sol-gel coatings suppress Sb sublimation



- Sample heated to 600C/dynamic vacuum/72 hours
- Single coat provides some protection

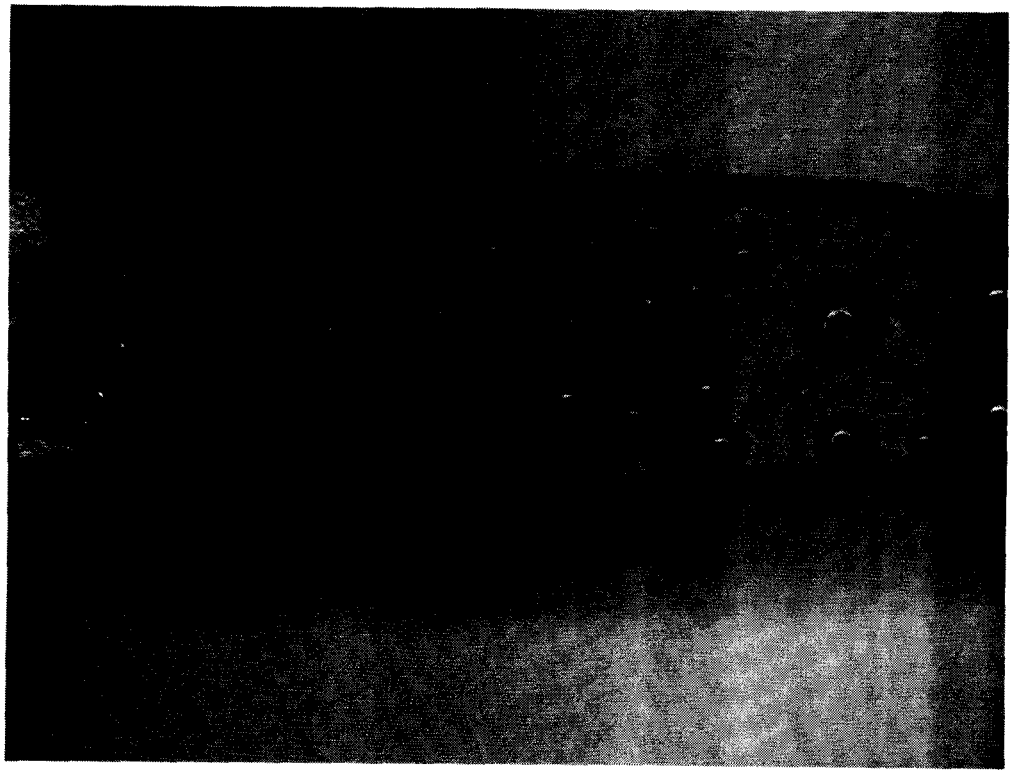
Intermediate, metal-metal oxide reaction layer

- Improve SiO_2 bonding by bonding to a metal oxide surface
- Sputtered 0.5 mm metal, oxidized <400C and coated with sol-gel SiO_2
  - Chrome-Chrome oxide
  - Titanium-Titanium oxide



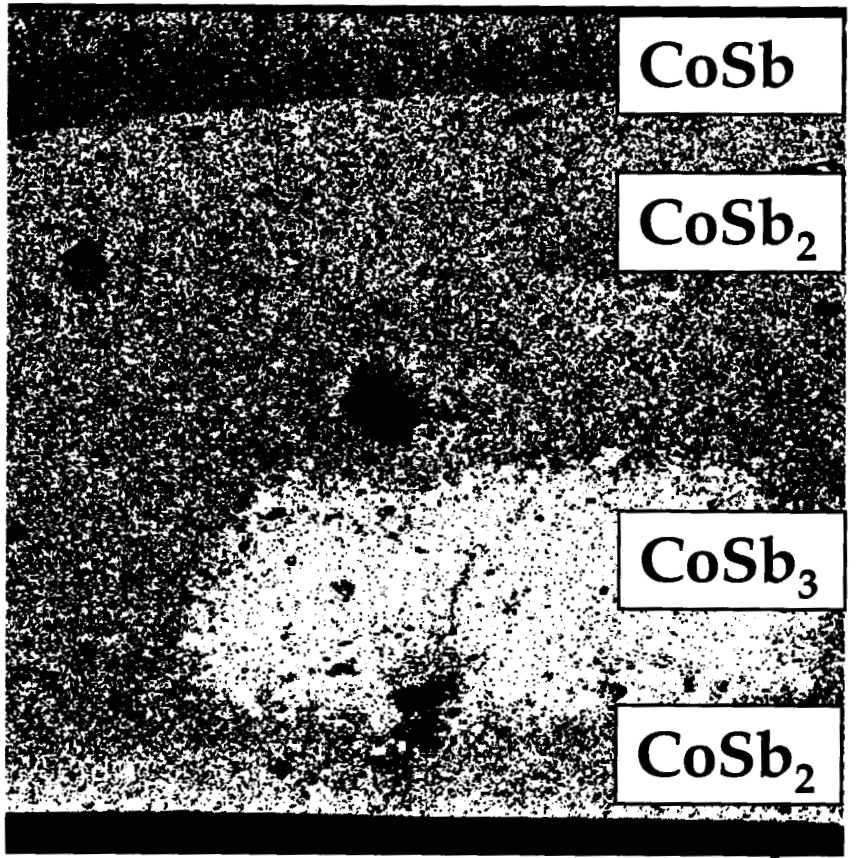
- SiO_2 mismatch is most likely too high

Enamel coatings



- Enamel powder (various silica and metal oxides) sintered at low temperatures (700C)
- Antimony vapor forms low temperature phase that does not wet the surface (Sb_2O_3 melts at 520C)

Key Observation:



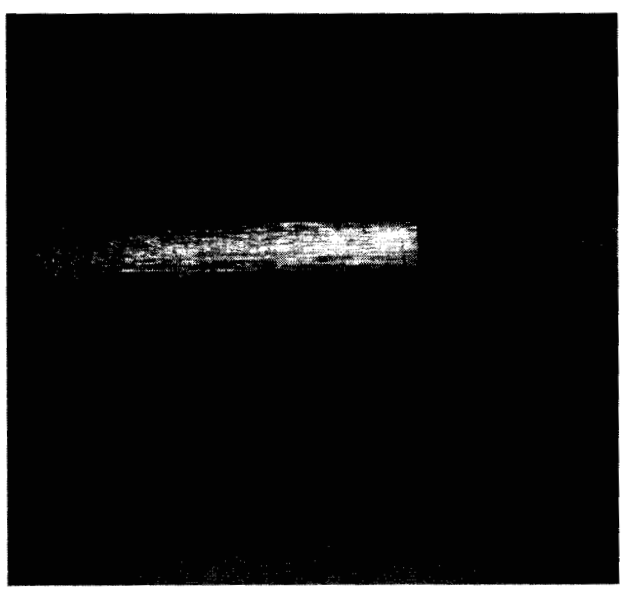
Sample heated to 800C in argon 3 days

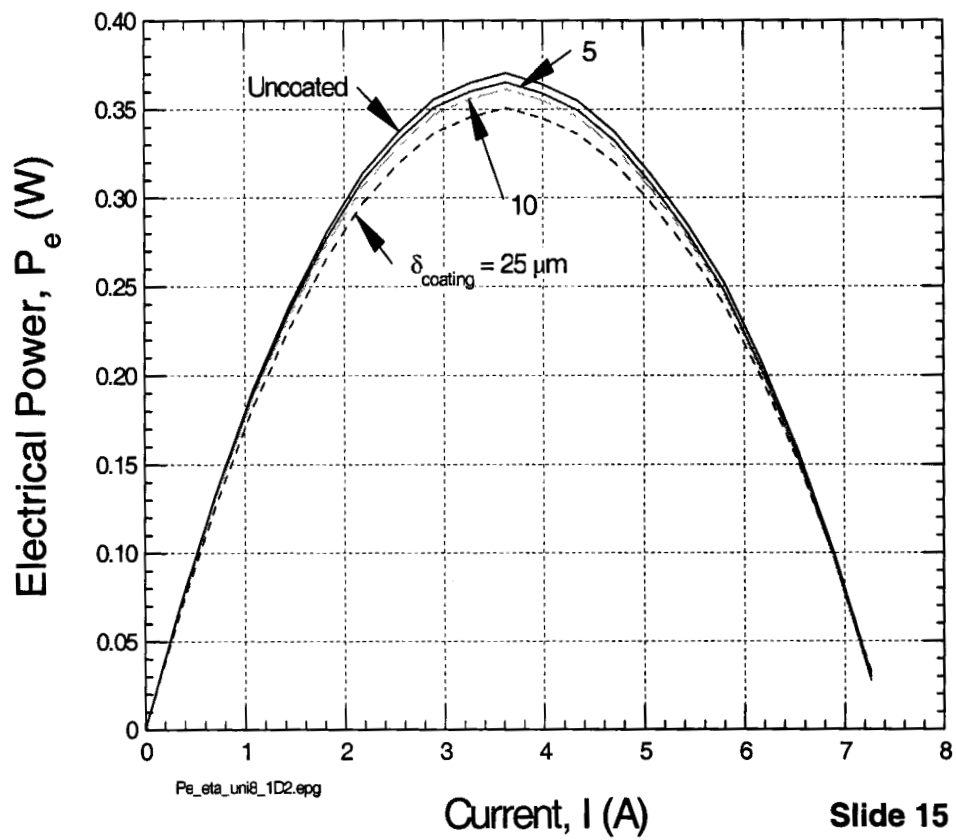
- Side facing quartz ampoule decomposed to $CoSb_2$
- Other sides decomposed to CoSb
- ❖Inner wall of ampoule clearly impedes Sb vapor transport

Side facing inner wall of quartz ampoule

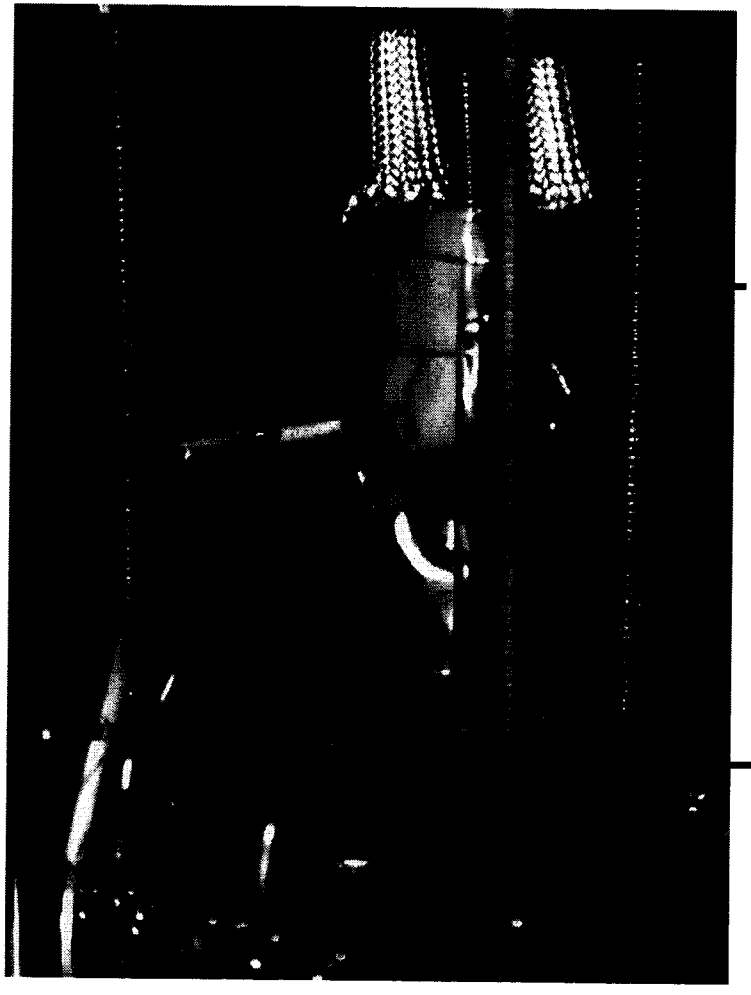
Fabricating SKD legs with foil coatings

- Coatings are bound to the legs during hot-pressing
- Continuous, crack and pinhole-free
- Thin (~10 mm) has minimal impact on TE properties





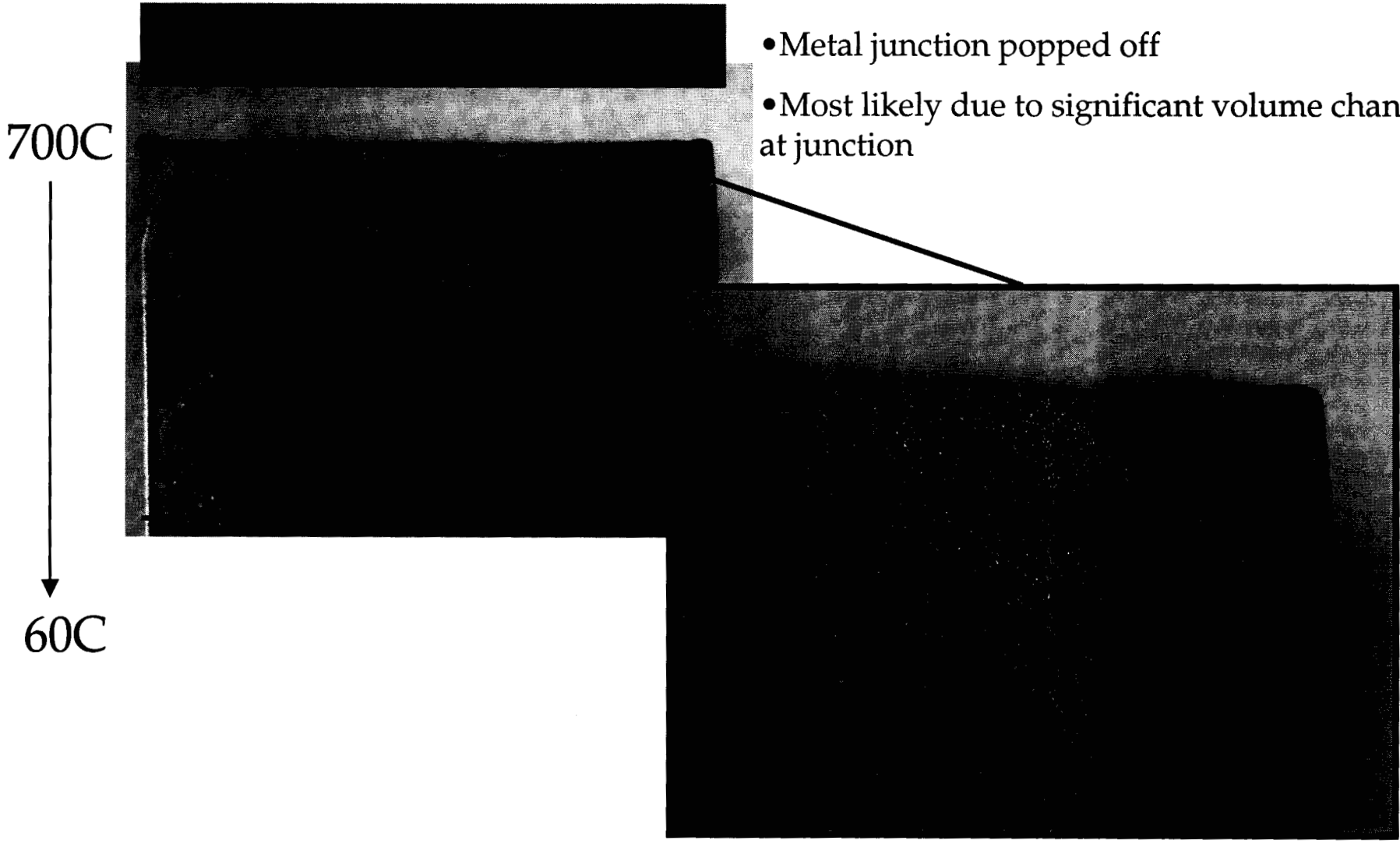
Life-test testing



Heater

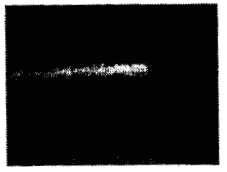
Cold sink

Uncoated, tested in-gradient for 20 days

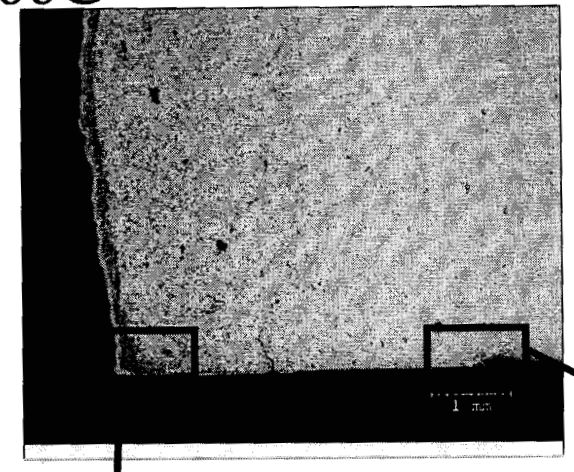


- Metal junction popped off
- Most likely due to significant volume change at junction

Coated n-type tested in-gradient for 20 days



700C →

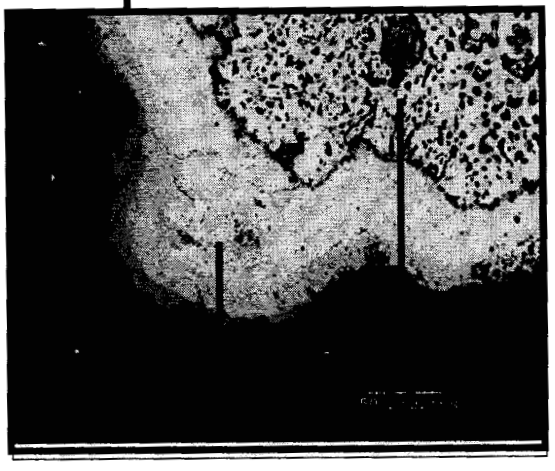


$CoSb_3$

$CoSb_2$

$CoSb$

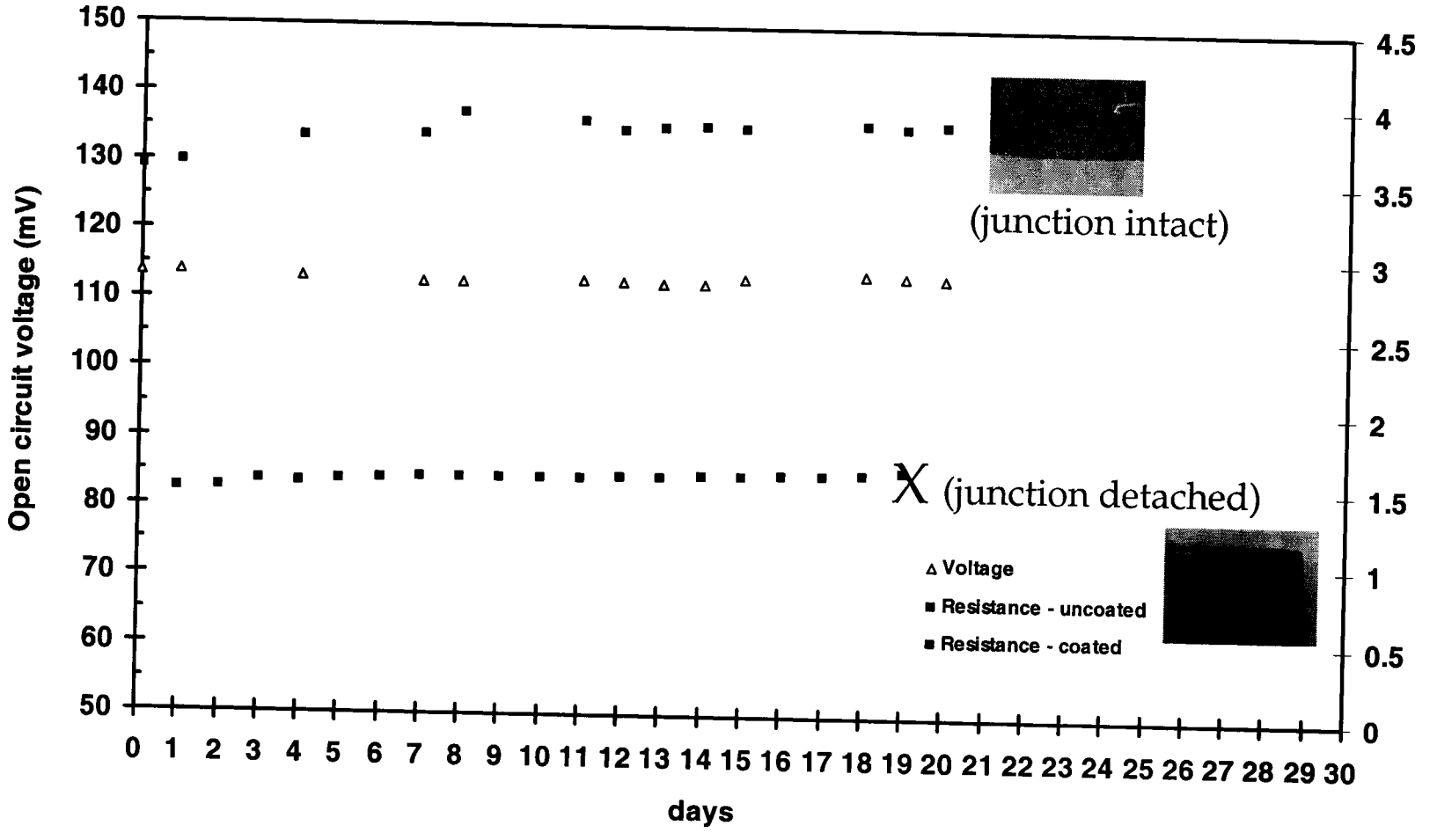
Coating stops



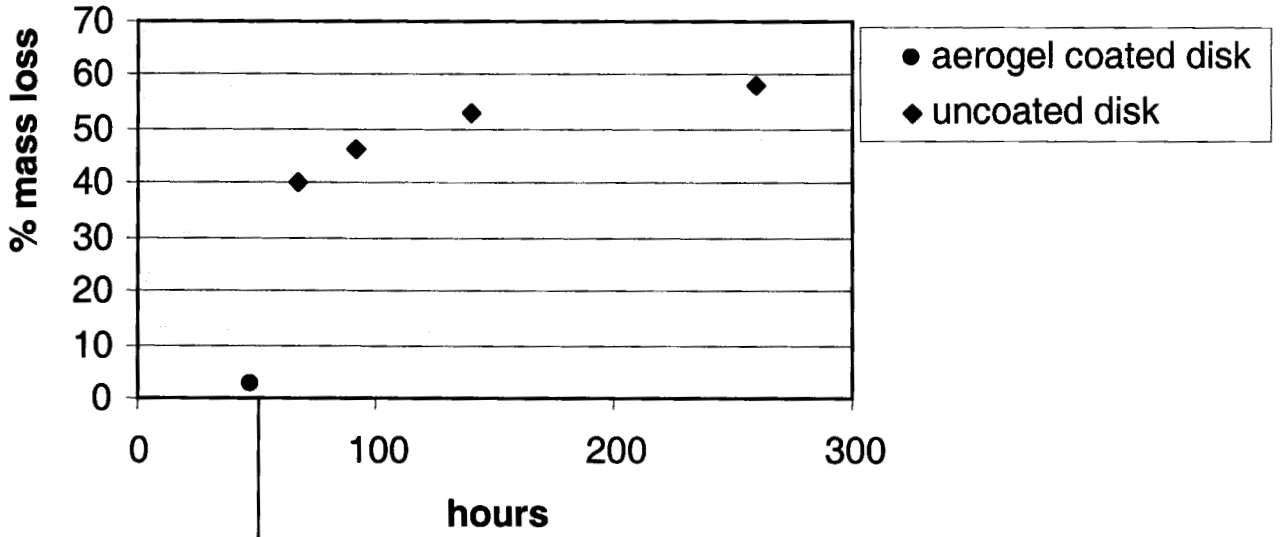
- No apparent degradation after 20 days
- Metal junction still intact
- Significant improvement!

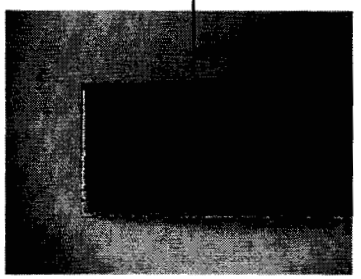
Coating provides baffle-safety valve effect-confinement to a microannular environment, helping to maintain "equilibrium"

Life test data for coated vs. uncoated n-type

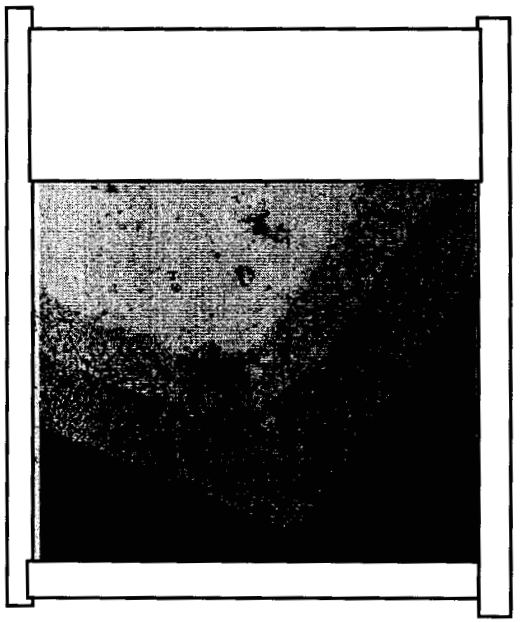


Sublimation suppression with aerogel

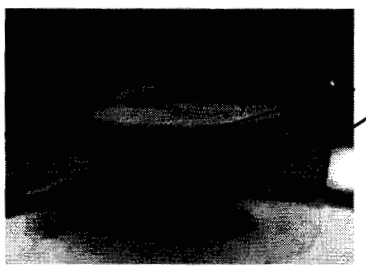




Aerogel coated $CoSb_3$: despite some cracks in aerogel, no depletion layer after 48h at 700C



before heating



after 48h at 700C

Cracks most likely result from aerogel shrinkage around disk: need to improve thermal stability and/or strength of aerogel

Summary

- Sublimation of Antimony has been determined as the primary mode of thermal degradation in Skutterudite Antimonides

- Methods for suppressing Antimony Sublimation have been established
  - Operating in 1 Atm. of cover gas suppressed Antimony sublimation
  - Fabricating SKD legs with robust, continuous coatings suppresses Antimony sublimation in high vacuum
    - These coatings do not interfere with thermoelectric properties
    - Currently running life tests on coated p-type
    - Considering alternative coatings

Acknowledgements

- NASA, DARPA and ONR