Sublimation Suppression Coatings for Thermoelectric Materials

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Presented By

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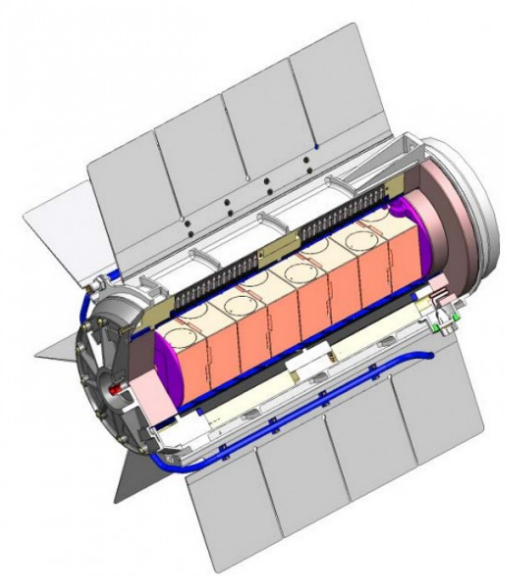
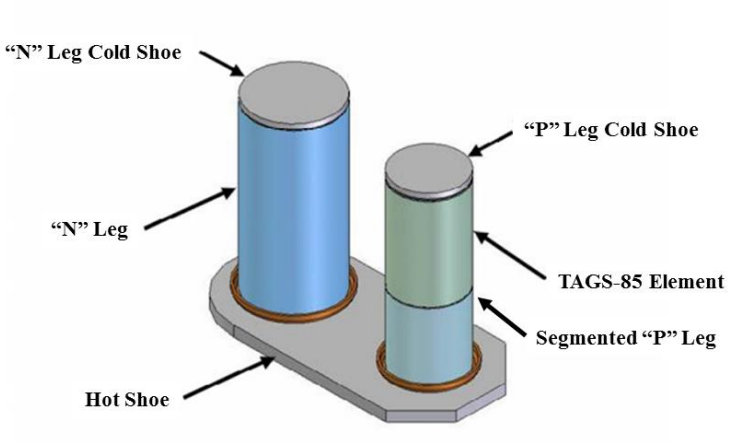
Topics

- **Background**
  - Early studies
  - Sol-Gel coating
  - Atomic Layer Deposition
- **First–Order Experimentation**
- **Results**
  - ALD Coating Thickness
  - ALD Coating Performance
- **Discussion/Summary**
- **Ongoing Investigations**





Background

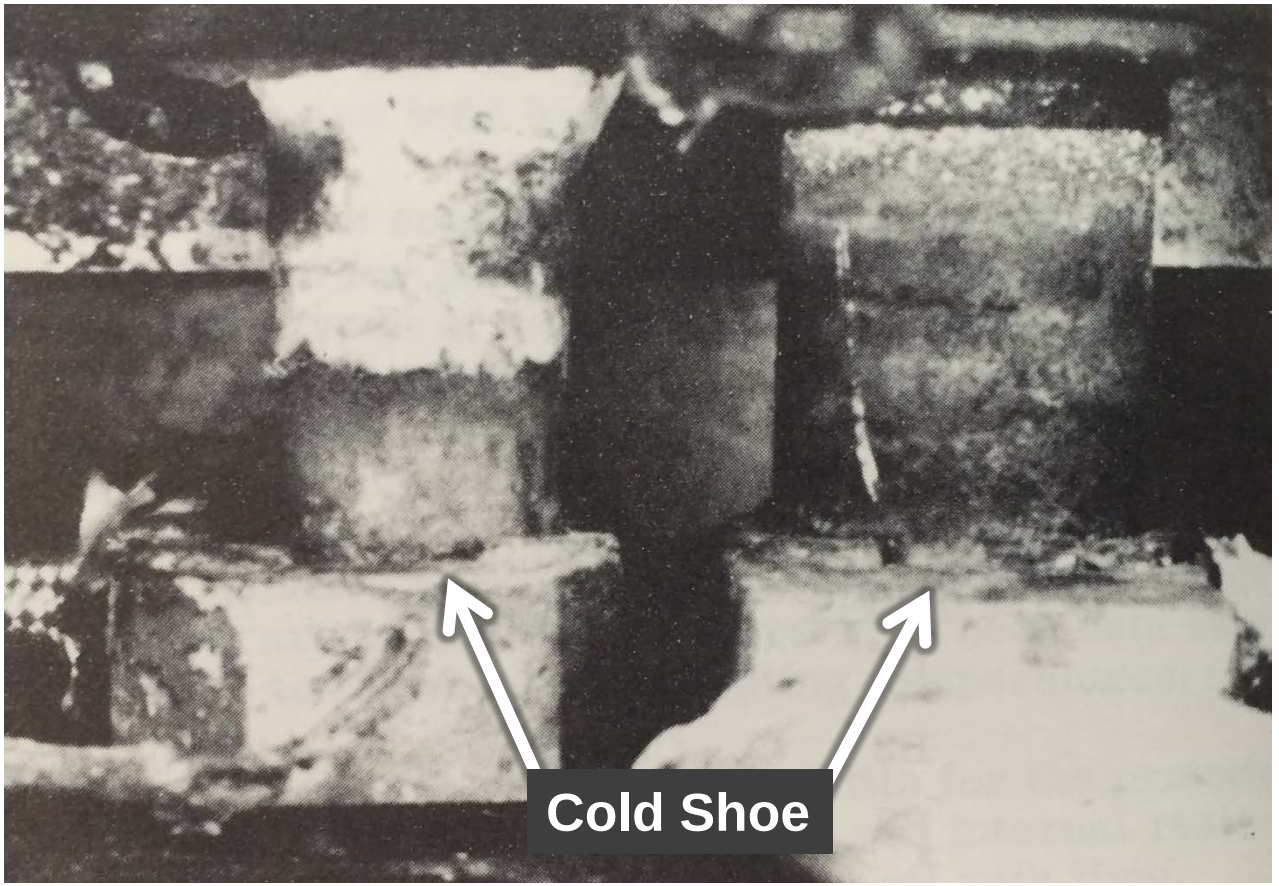
- **5 May 2010 – MMRTG Technical Degradation Interface Meeting, OSC, Germantown, MD.**
  - DOE, NASA, JPL, INL
  - Aerojet, TESI, OSC, UDRI
    - *"No work on sublimation suppression coating for TAGS for over 40 years"*
- **In the early 1970s Emil Skrabek (TESI) conducted studies using**
  - ceramic adhesives
  - phosphate glasses
  - lead oxide based enamels
  - high-temperature engine paints

Background - *Continued*

- **Skrabek's earlier efforts showed:**
  - All the tested coatings failed due to rupture of the coating followed by vaporization of the thermoelectric material
  - The coated TAGS-85 thermoelectric elements exhibit very little performance degradation as long as the coating remained intact
  - Coatings were deemed unreliable as a long-term solution

- **Chosen methodology to minimize the degradation rate of TAGS-85**
  - Pack silica-based insulation in the annulus between the thermoelectric elements and the thermal insulation

Background - *Continued*

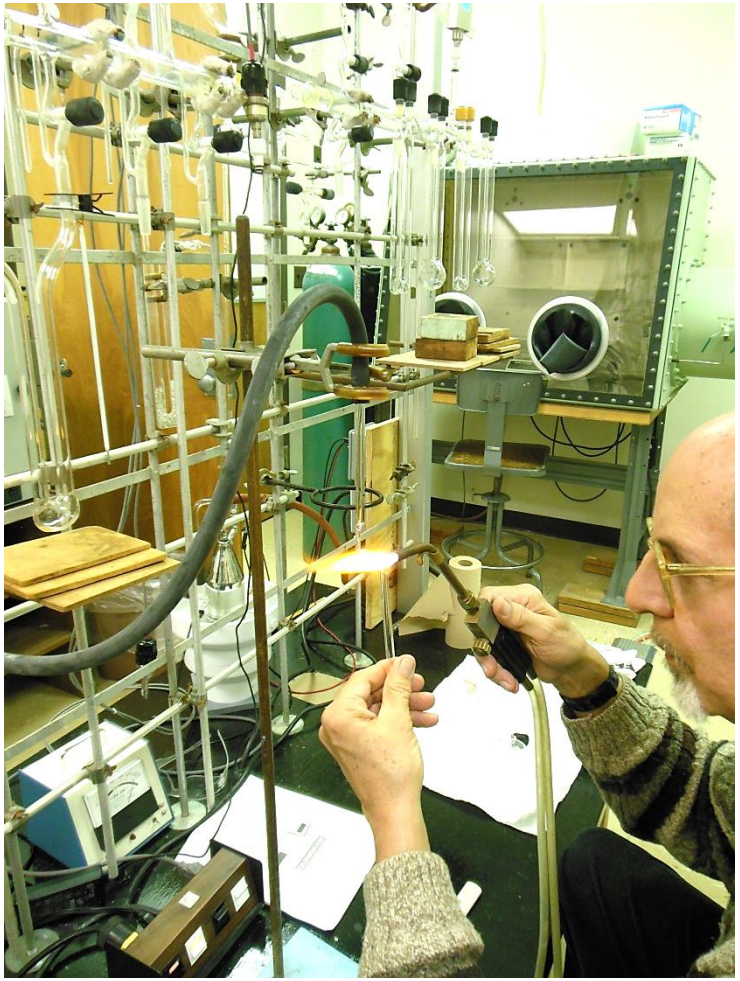


Ceramic Adhesive Coated Element after aging 5370 hours

$T_{hj} = 537°C; T_{cj} = 149°C$

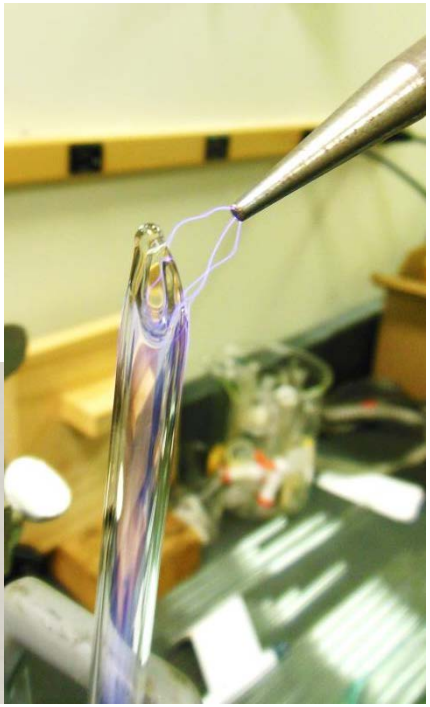
Background - *Continued*

- **Sol-Gel coatings**
  - In 2012-2013 DOE/UDRI sponsored a Grad Student that conducted a Masters Thesis on Sol-Gel coatings for TAGS-85
  - Al_2O_3, TiO_2, and SiO_2 were isothermally aged along with uncoated controls
    - *350°C for 1000, 3000, and 5000 durations*
    - *Auger Electron Spectroscopy (AES) used for depth profiling of coatings*



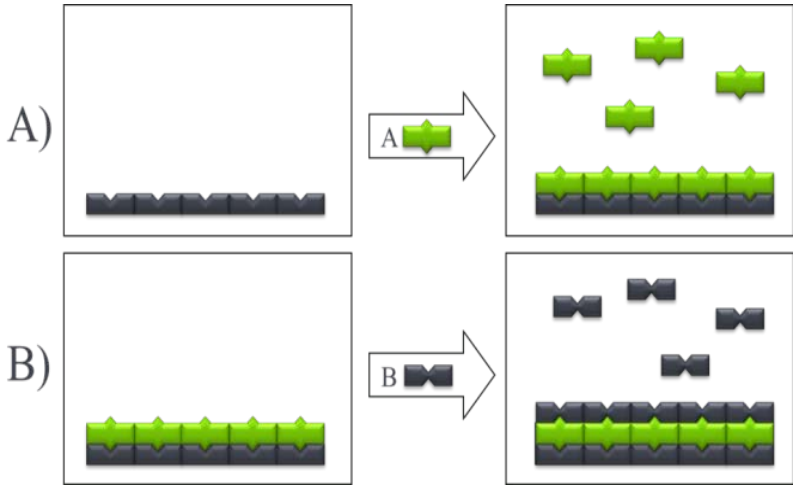
Background - *Continued*

- **Conclusions**
  - AES indicated that Ge was the migrating species
  - Sol-Gel process resulted in a non-uniform coating
  - Sol-Gel may not have been completely densified
  - Al_2O_3 provided the most favorable results



Background - *Continued*

- **Atomic Layer Deposition (ALD)**
  - ALD is a gas phase coating process. Reactions occur only between the gaseous precursors administered to the reactor, and the functional groups present on the surface of the substrate
  - Allows for coating chemistry and thickness to be precision tailored with angstrom level precision
  - The resulting coatings are chemically-bonded to the surfaces of the substrate, and have been proven to be conformal and pinhole-free, even on high aspect ratio surfaces

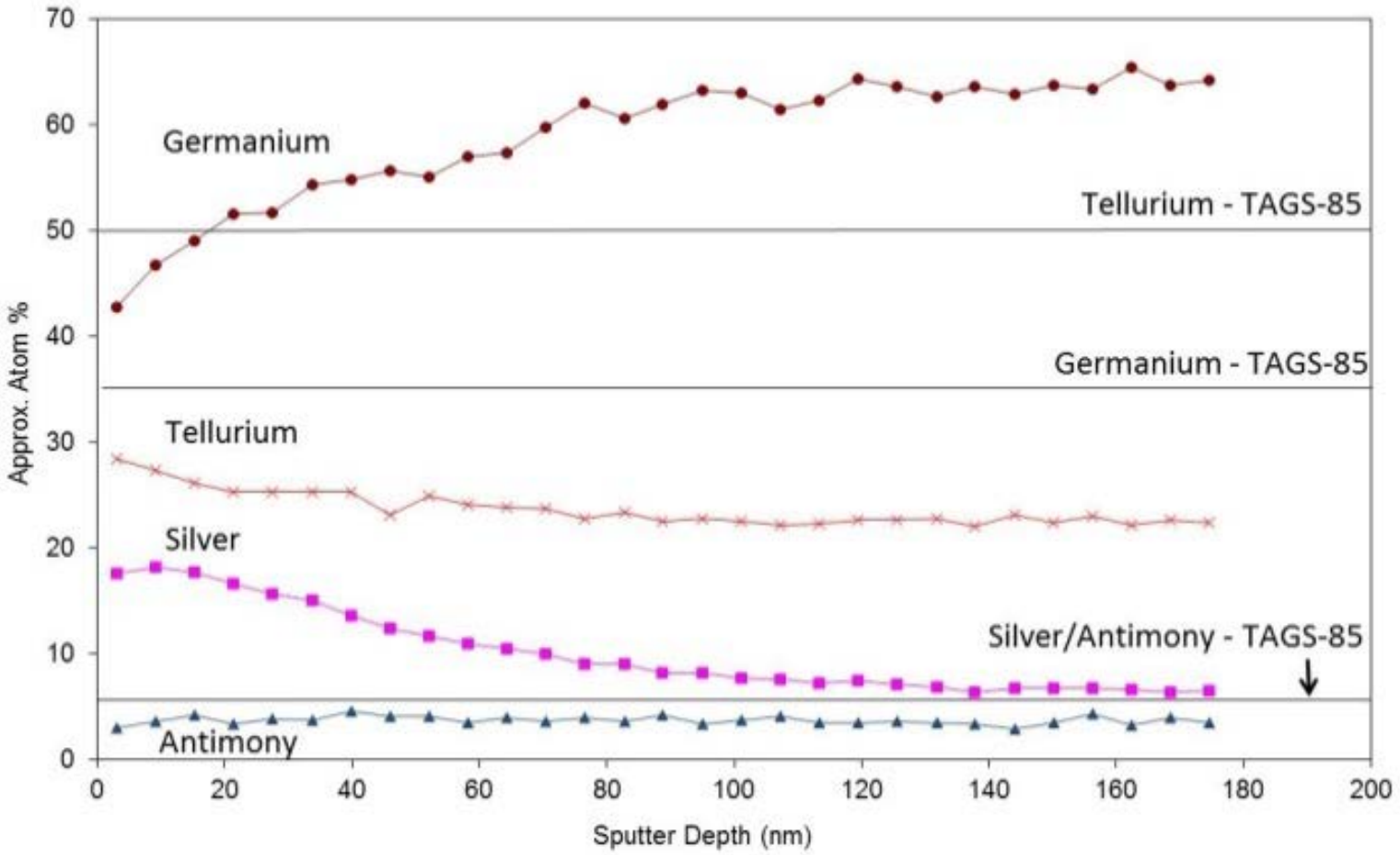


First–Order Experimentation

- **A total of eight (8) TAGS-85 production elements were sequentially coated using either 200 or 400 ALD cycles to produce a 30 or 40 nm thick coating of Al_2O_3, respectively**
  - During the ALD coating process the TAGS-85 substrate temperature was maintained at 150°C.
- **The ALD coated TAGS-85 elements then were individually sealed in low-thermal-expansion borosilicate glass (Pyrex) ampoules using high-vacuum manifold and scientific glass blowing techniques**
- **Isothermally aged at 350°C for 1000, 3000, 5000, and 7000 hours**

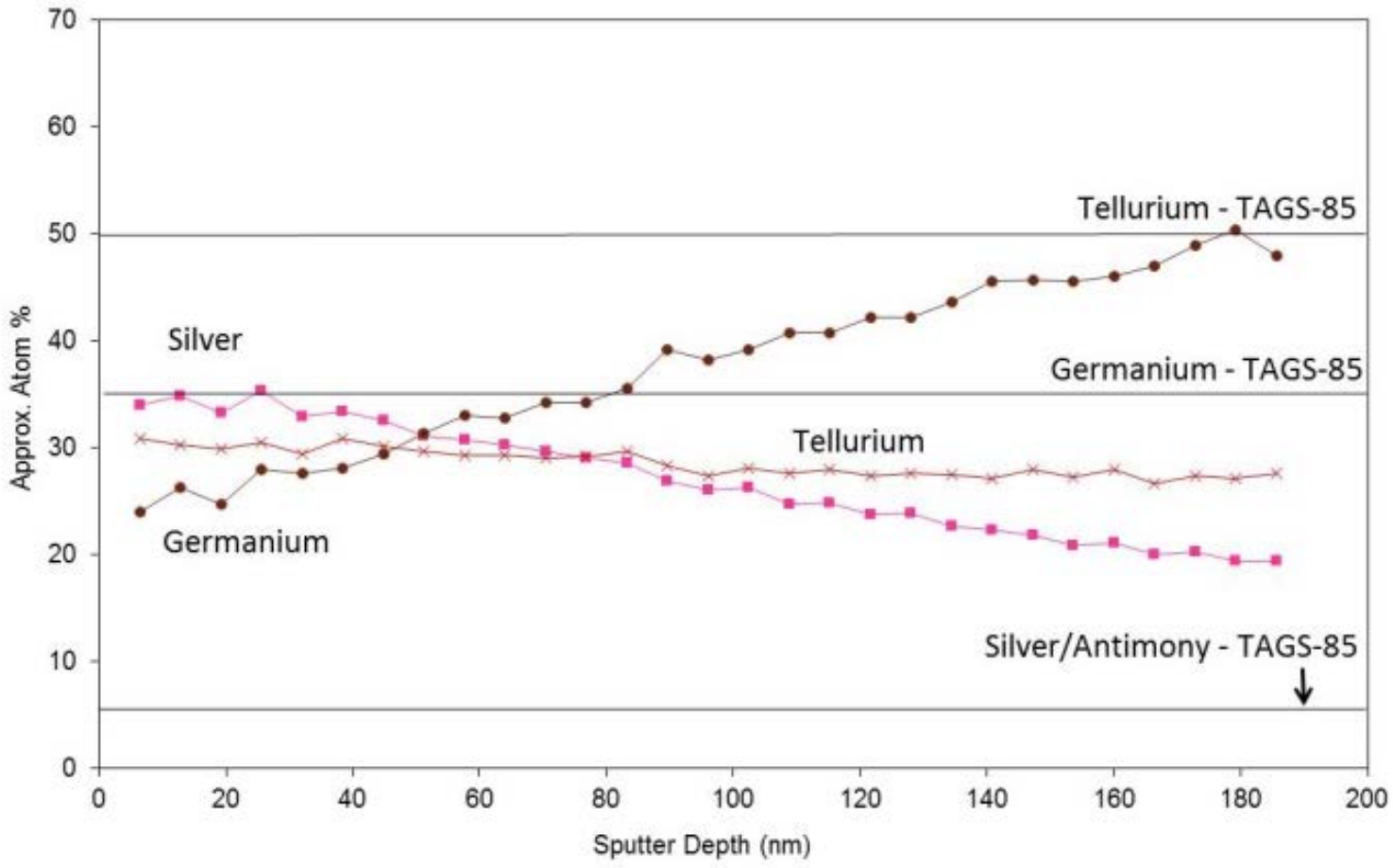
Results – Uncoated Tags-85

AES depth profile for an uncoated, unaged TAGS-85 element



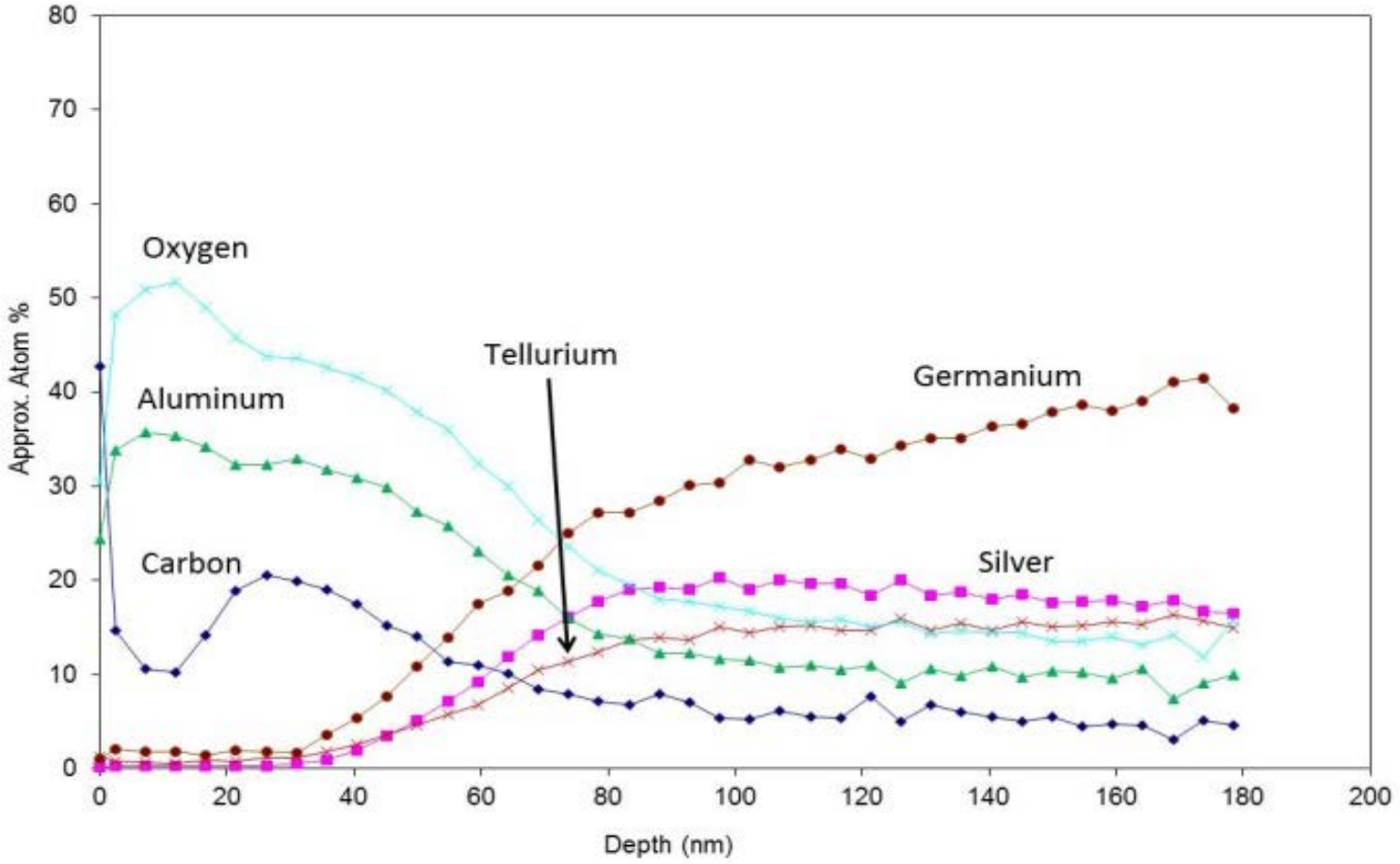
Results – Uncoated Tags-85

AES depth profile for TAGS-85 aged for 3000 hrs at 350°C



Results – ALD Al_2O_3 Coated Tags-85

AES depth profile for unaged ALD Al_2O_3 coated TAGS-85



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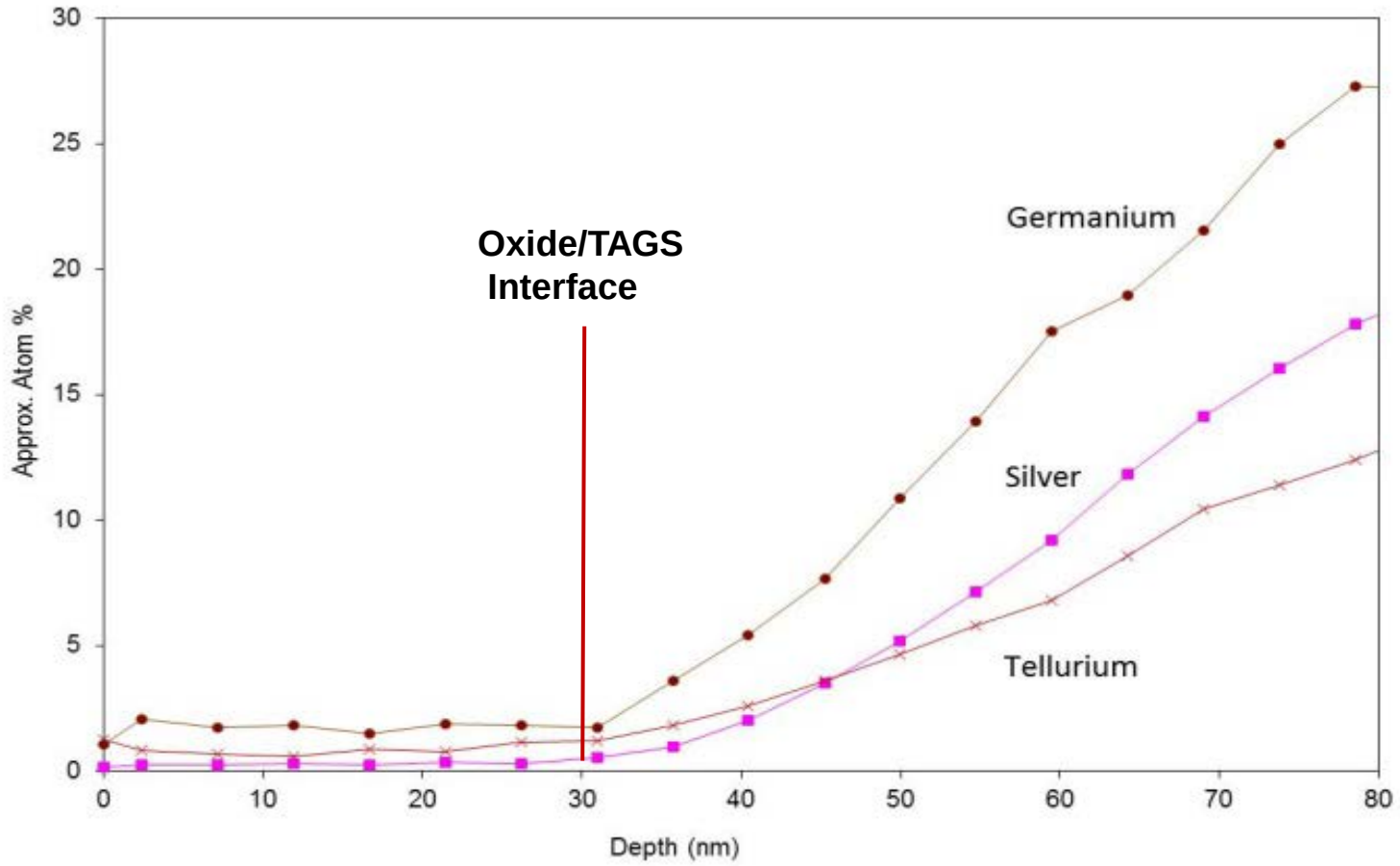

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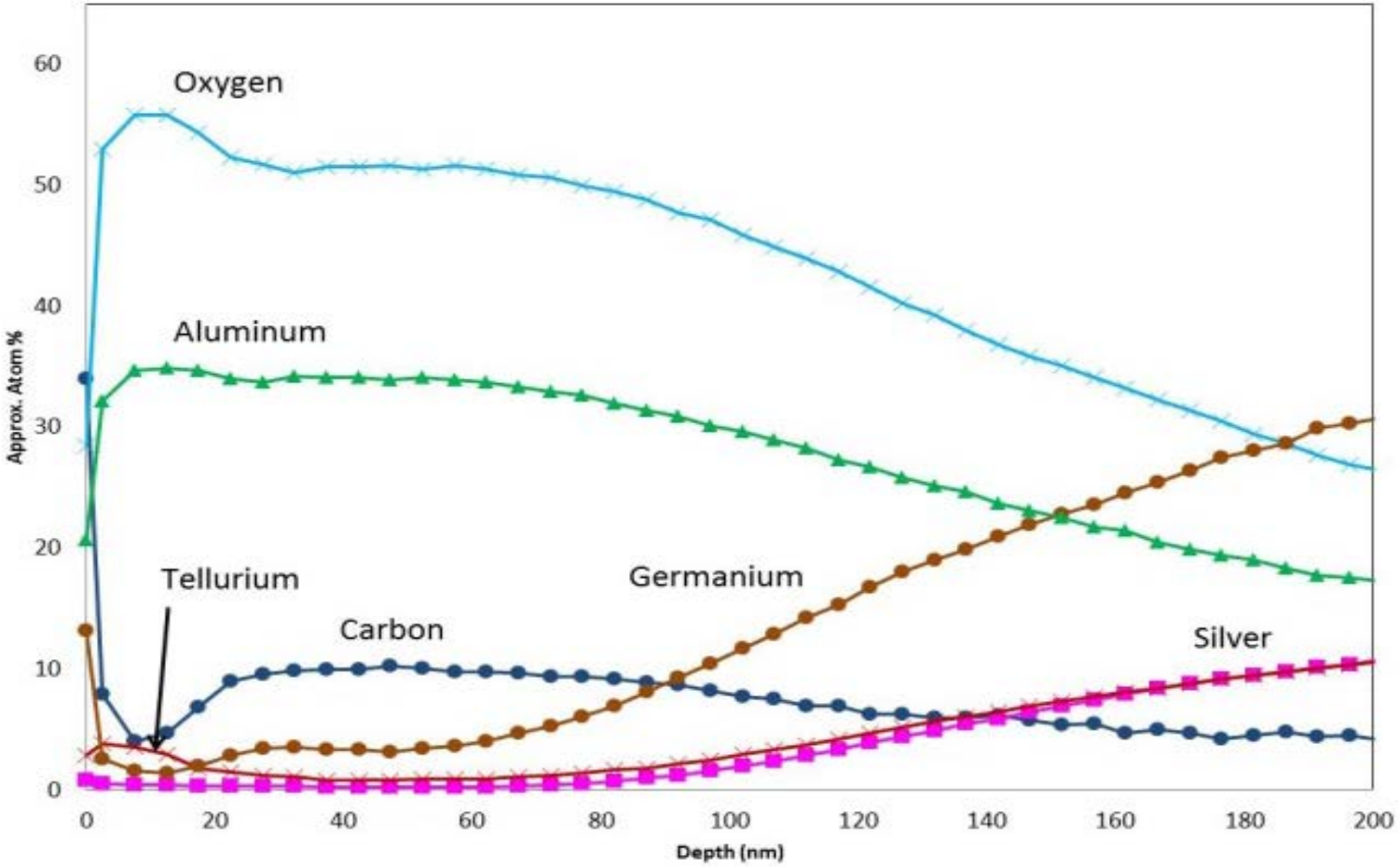
AES depth profile for coated TAGS-85 aged at 350°C for 3000 hrs



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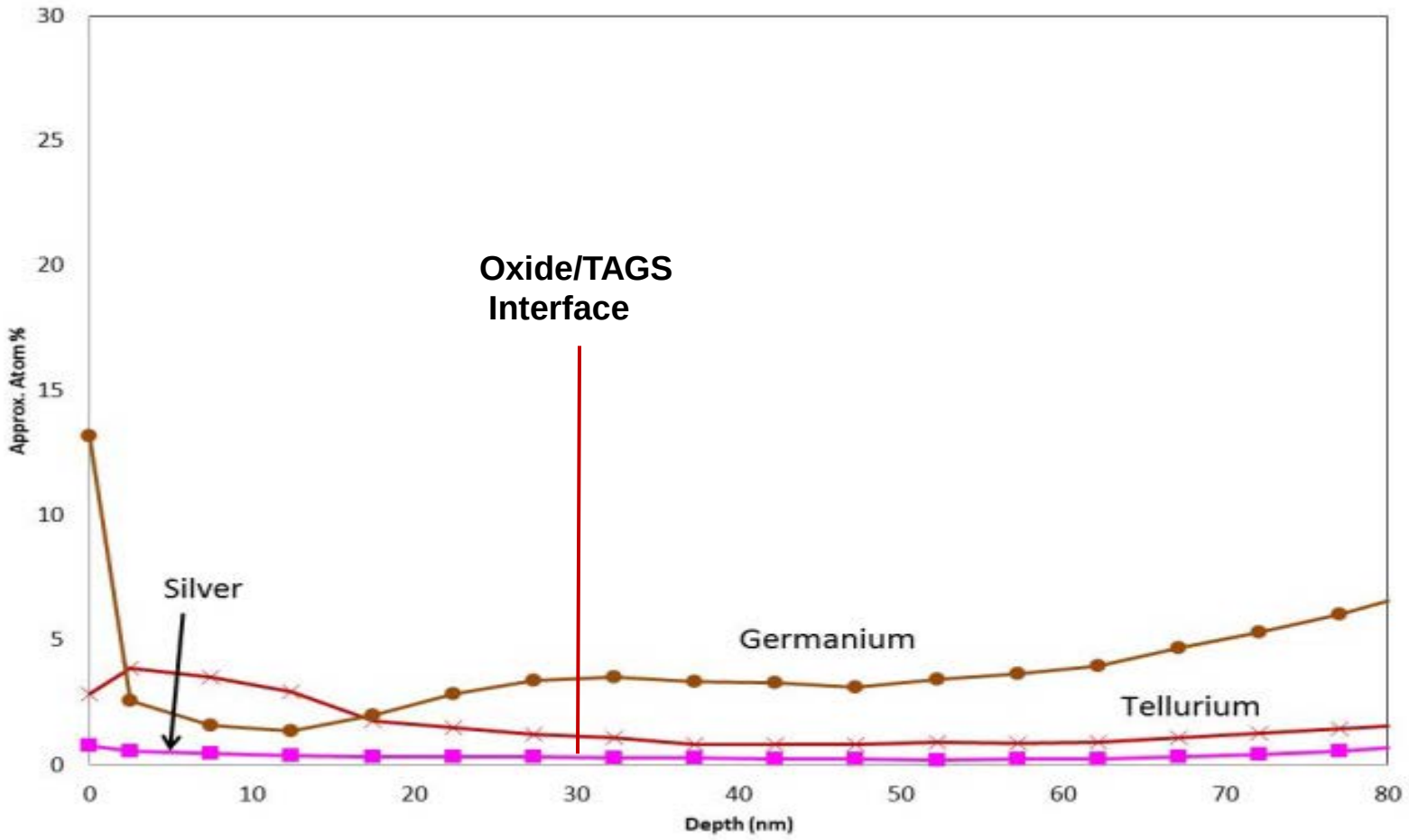
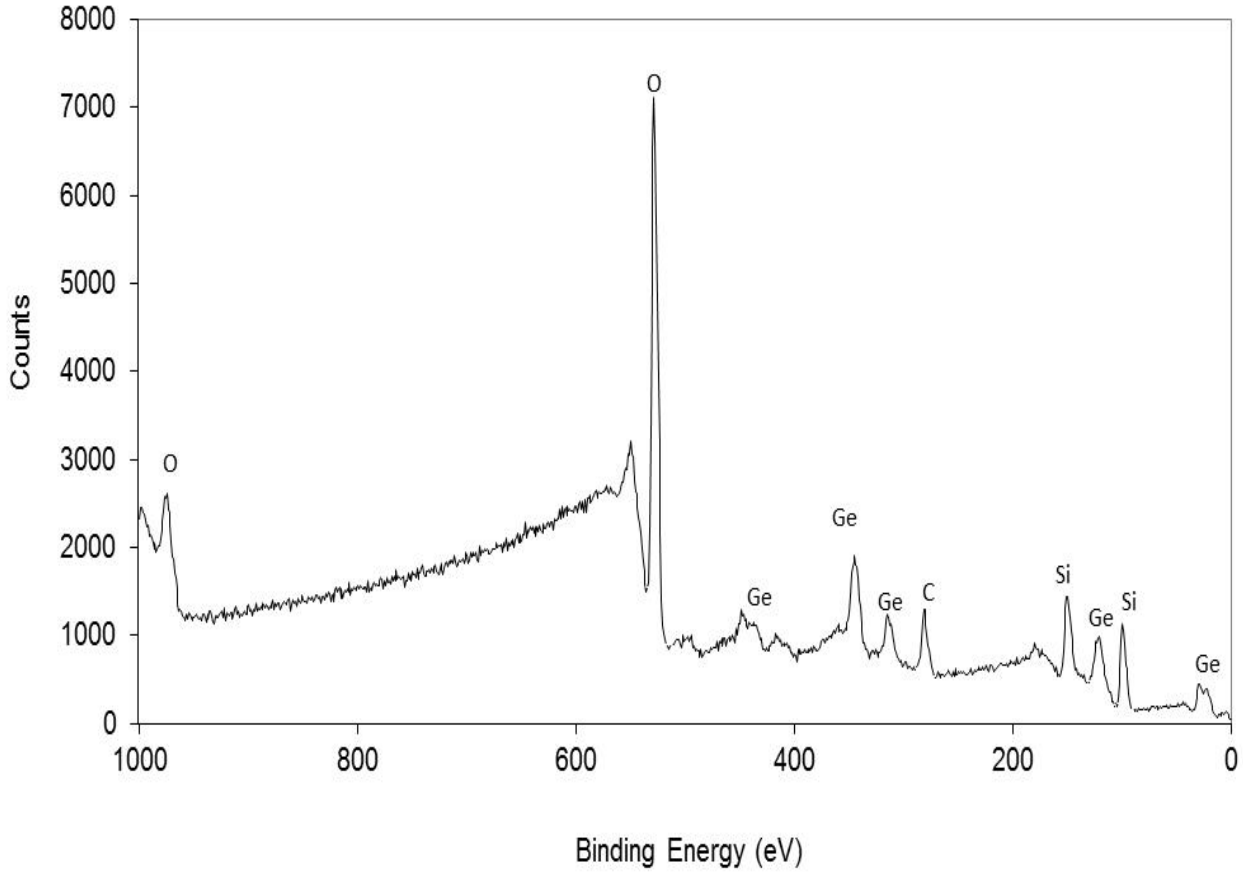


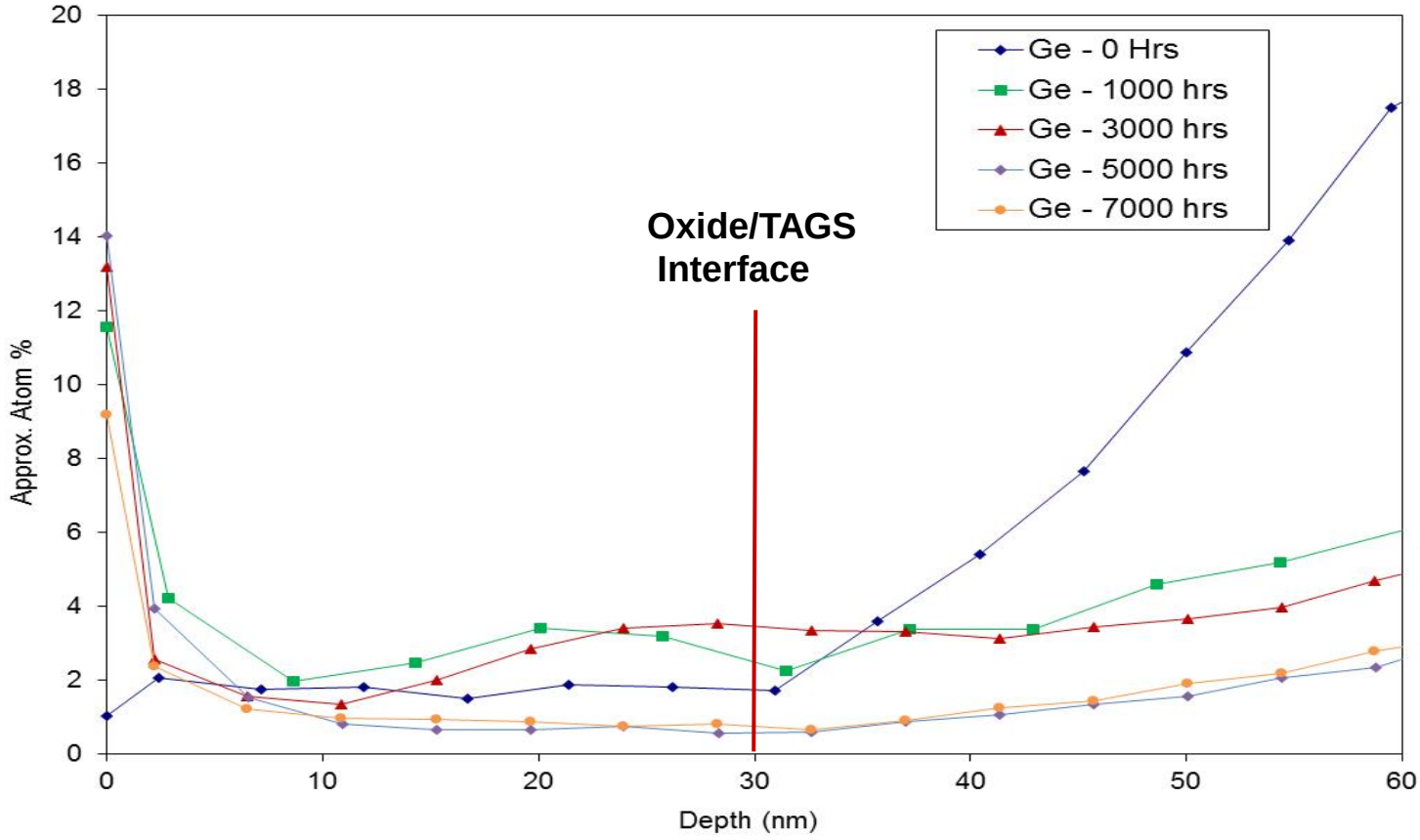
Results – ALD Al_2O_3 Coated Tags-85

XPS surface scan of the inside of an ampoule used to age an ALD Al_2O_3 coated TAGS-85 specimen at 350°C for 3000 hrs



Sublimation Suppression Coatings - Results

Changes in AES depth profile of ALD Al_2O_3 coated TAGS-85 specimens as a function of exposure time at 350°C



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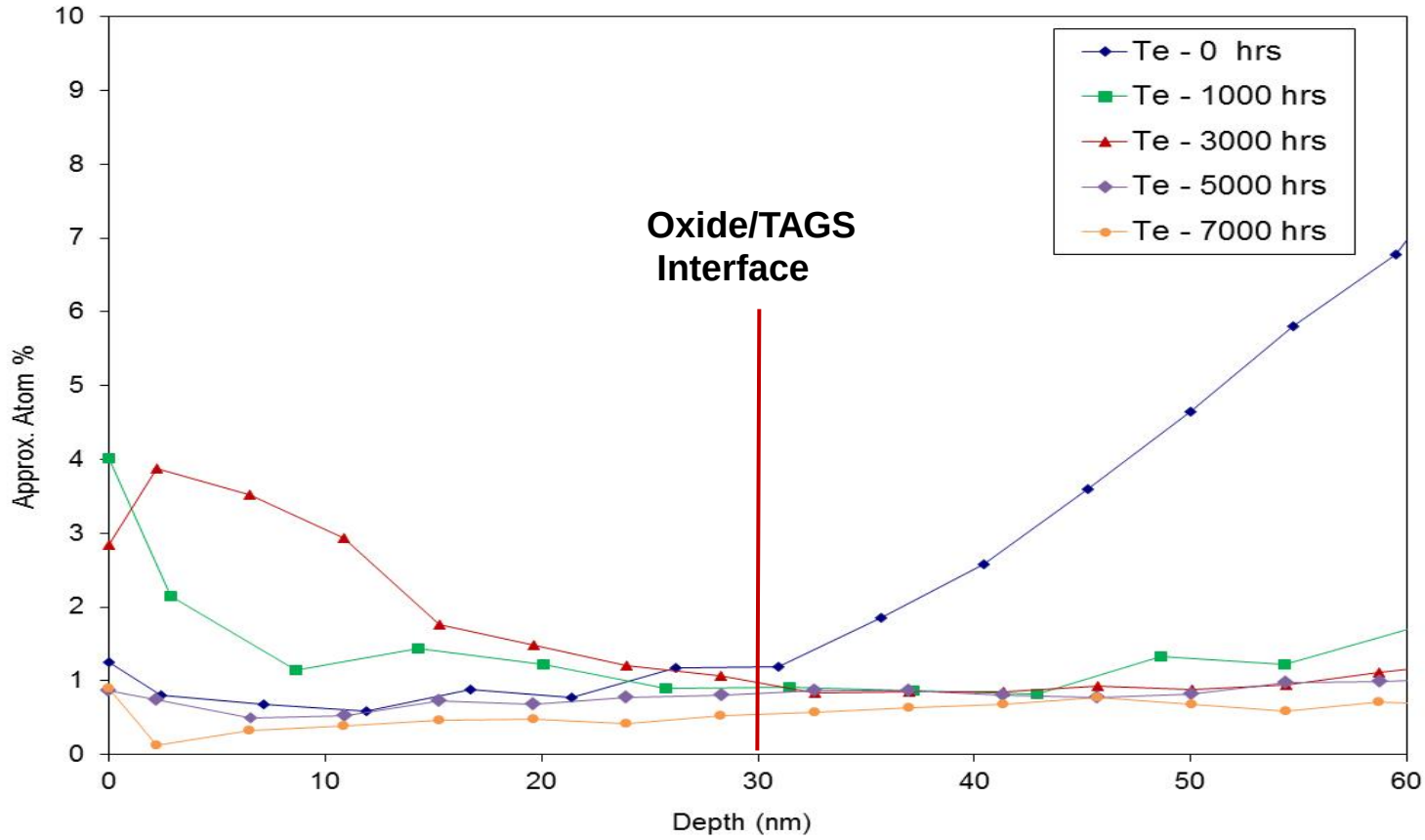

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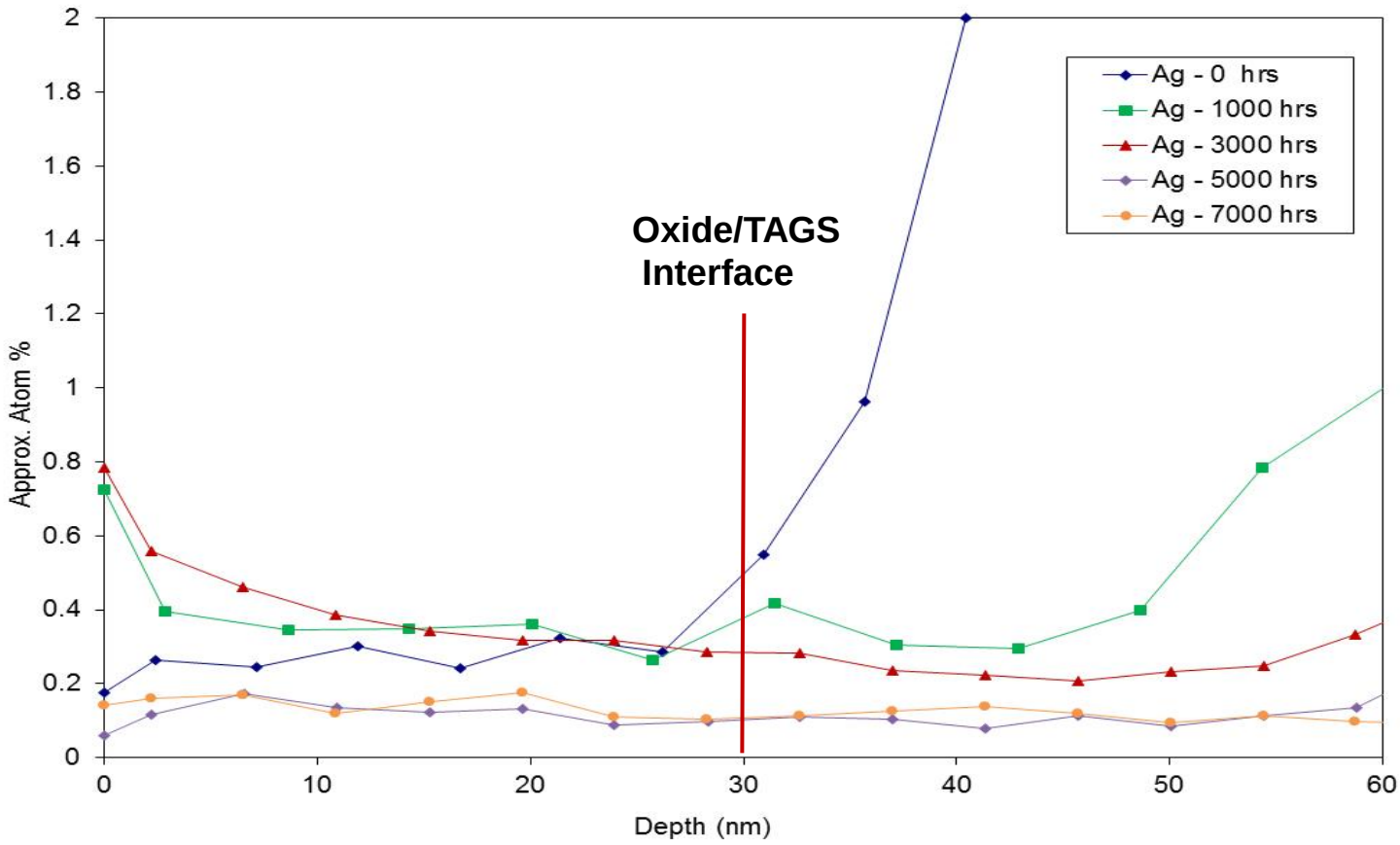

Ongoing Investigations

- **Addition of a thin ALD barrier coating (2-3 nm) of HfO_2 between the TAGS/Al_2O_3**
  - Further inhibit the migration of Germanium
- **Incorporation of a thermal gradient during testing between 150-350°C**
  - Specimens will also be exposed to Aerogel and Min-K insulation

- **Thermal cycling from RT-350°C at 5°C/min for 10-cycles**
  - Validate how the coatings would behave during performance testing at TESI before MMRTG fueling operations at the INL

Discussion/Summary

- Results are based on first-order coupon-level demonstrations
- ALD Al_2O_3 coating demonstrated a significant reduction of the diffusion of Ge, Te, and Ag from the TAGS-85 surface thru the Al_2O_3 coating at 350°C for durations up to 7000 hours
- ALD offers a novel, inexpensive, and fast technique to retard the sublimation-induced deterioration of TAGS-85

Acknowledgements

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Sublimation Suppression Coatings

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Questions?