

# Rationale for the Auger Studies

---

- Multiple mechanisms have been formulated to explain the nucleation and growth of tin whiskers.
- The most dominant among them is the presence of compressive in-plane stress, which in the case of RT isothermal studies is considered to evolve from non-uniform reaction zone at the Sn-Cu interface (Lee & Lee - 1988), plus a mechanism that prevents such stresses from relaxing.
- The latter has been attributed by Tu in his now classical Phys Rev (1994) paper to a tenacious oxide layer that prevents the interface with the tin to serve as a good source or sink for vacancies. Thereby, stress relaxation is prevented and whiskers grow.
- Our own search shows that the literature on tin-oxides is not very abundant and indeed sometimes contradictory. Nevertheless, there must exist some basis for the oxide interface acting as a barrier to atomic deposition, since platings with grain boundaries parallel to the Cu-substrate have been found to minimize whisker growth.
- The rationale for our Auger studies was to obtain better insight on the oxide layer, and evaluate if Indium compromised the tin-oxide film, which thereby led to near complete elimination of tin whiskers.

# Experimental Details

---

- The Sn-In-Sn sample consisted of a multilayer deposition of approximate pure Sn (~500 nm)/pure In (~50 to 100 nm)/pure Sn(~500 nm) that was aged at 160 C for 45 minutes. *Vol. fraction 5 – 10%*.
- AES survey analysis was conducted at a point on the sample surface without sputtering and following various times of sputtering. This provided information on the oxide composition, and how the composition varied with depth from the free surface.
- Variation of composition at the sample surface (without sputtering) was estimated by choosing sampling at selected points on the surface.
- Composition variation analysis was also conducted following different times of sputtering, and sputtering followed by RT aging for a few days.
- Similar analyses were conducted on pure Sn and pure In samples that were prepared by vapor deposition using followed by heat treatment at 50, 145 and 160 C.

# Scanning Auger Microprobe Settings

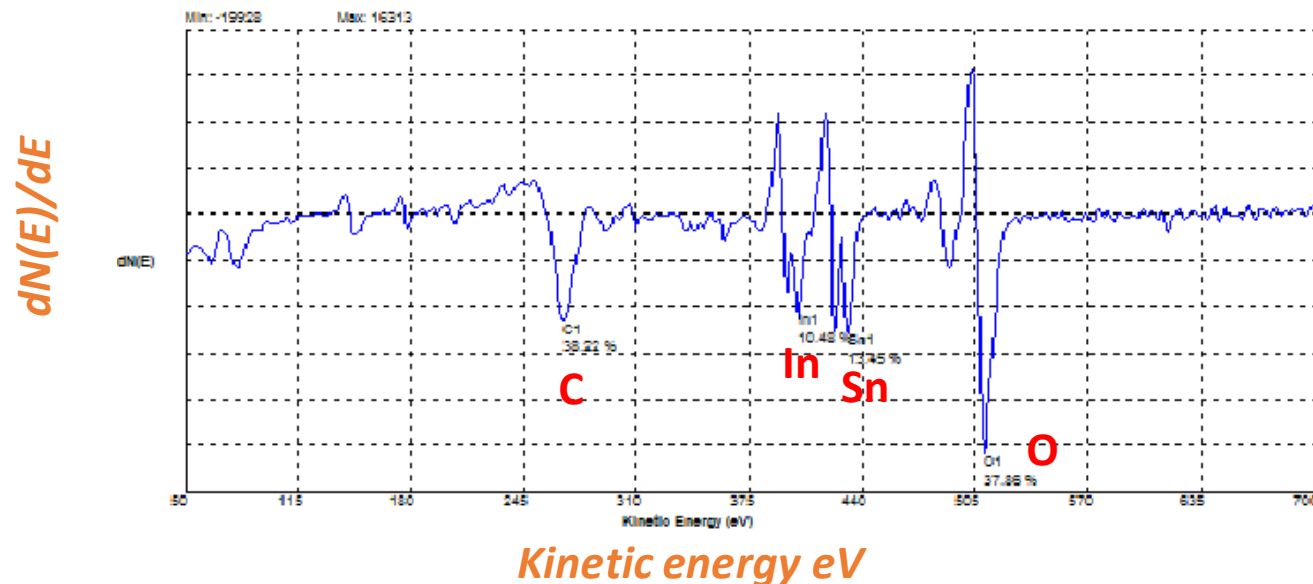
- Instrument: Perkin Elmer PHI 600 SAM
- UHV:  $2 \times 10^{-10}$  Torr.
- Electron gun: Electron gun with LaB<sub>6</sub> crystal & thermionic emission, **50-60  $\mu$ A** emission current.

Aperture Number	Aperture Size	Typical Beam size
1	0.004"	250Å to 1100Å
2	0.004"	250Å to 1100Å
<b>3</b>	<b>0.008"</b>	<b>1100 Å to 1<math>\mu</math>m</b>
4	0.016"	1 $\mu$ m to 2 $\mu$ m
5	0.093"	High beam current mode

- Imaging: SED (Channeltron secondary electron detector) and ABS (absorbed current) imaging. *SED used here.*
- Spectrometer type: Full cylindrical mirror analyzer(concentric with electron gun) with resolution  $\Delta E/E = 0.6\%$ .
- Energy range: 0 to 3200 eV and energy increment of 1 eV over a counting period of 0.5 sec/eV. Here, *only scanned to 600 ev*, since an initial scan of surface to 1000 ev did not reveal the presence of Cu.
- Ion beam: Argon ion beam for sputtering at maximum ion beam current of 5  $\mu$ A at 3 keV. Beam size is 800 $\mu$ m to 200 $\mu$ m FWHM, variable at 5 cm from gun.
- Analyses details: Auger spectra elemental survey (multiplex), mapping, line scan (mapping), area scan, point scan and SEM.

# Results of AES Analyses of Sn-In-Sn: Heat Treated at 160 C

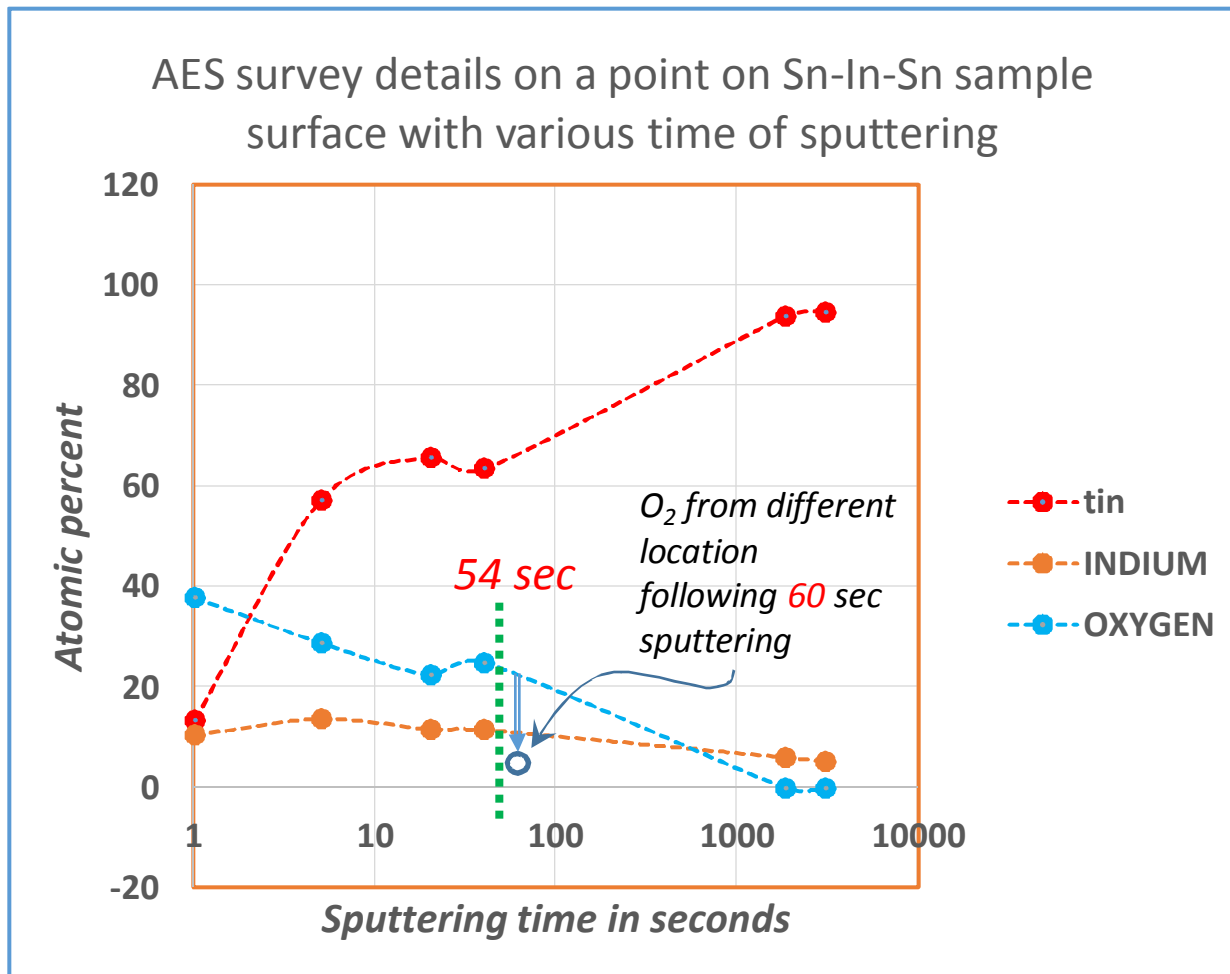
*AES analysis results on a point on the sample surface without any sputtering and with various time of sputtering.*



Characteristic Auger peaks of the elements in analysis

- Carbon 272 eV - *this peak disappears following 5 sec of sputtering*
- Oxygen 510 eV
- Indium 411 eV
- Tin 430 eV

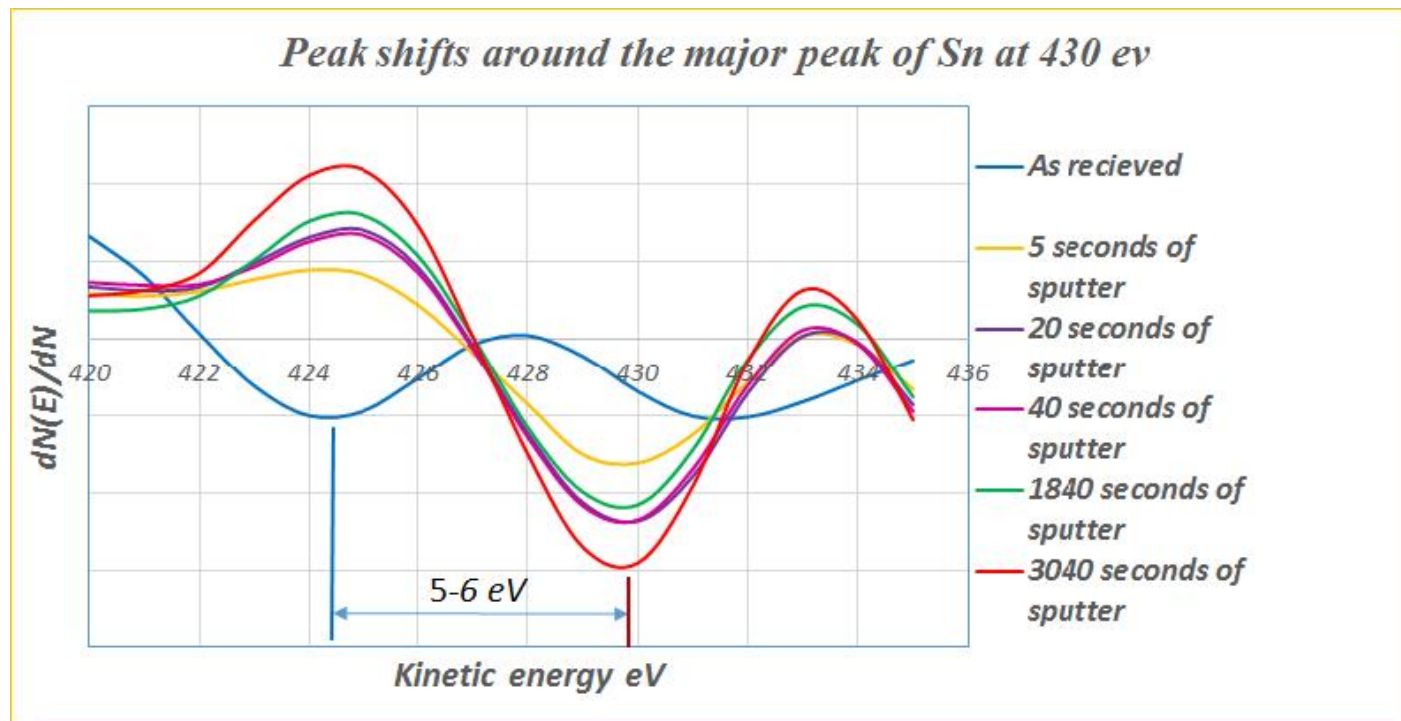
# AES Results Following Different Sputtering Times



- A pure Sn sample showed that the  $O_2$  peak disappeared in 54 seconds.
- With estimated sputtering rate of 0.5 nm/sec, the  $SnO_2$  oxide layer in *pure Sn* is estimated to be 27 nm, consistent with 20 nm mentioned in the literature. The Sn-In-Sn oxide layer is of similar thickness.
- About **14 -17 at.% of In** is observed in the oxide layer. This drops to about **8-10%** deep inside sample. In other locations, In reaches up to 20 at.%.

# Peak Shift/Chemical Shift Results:

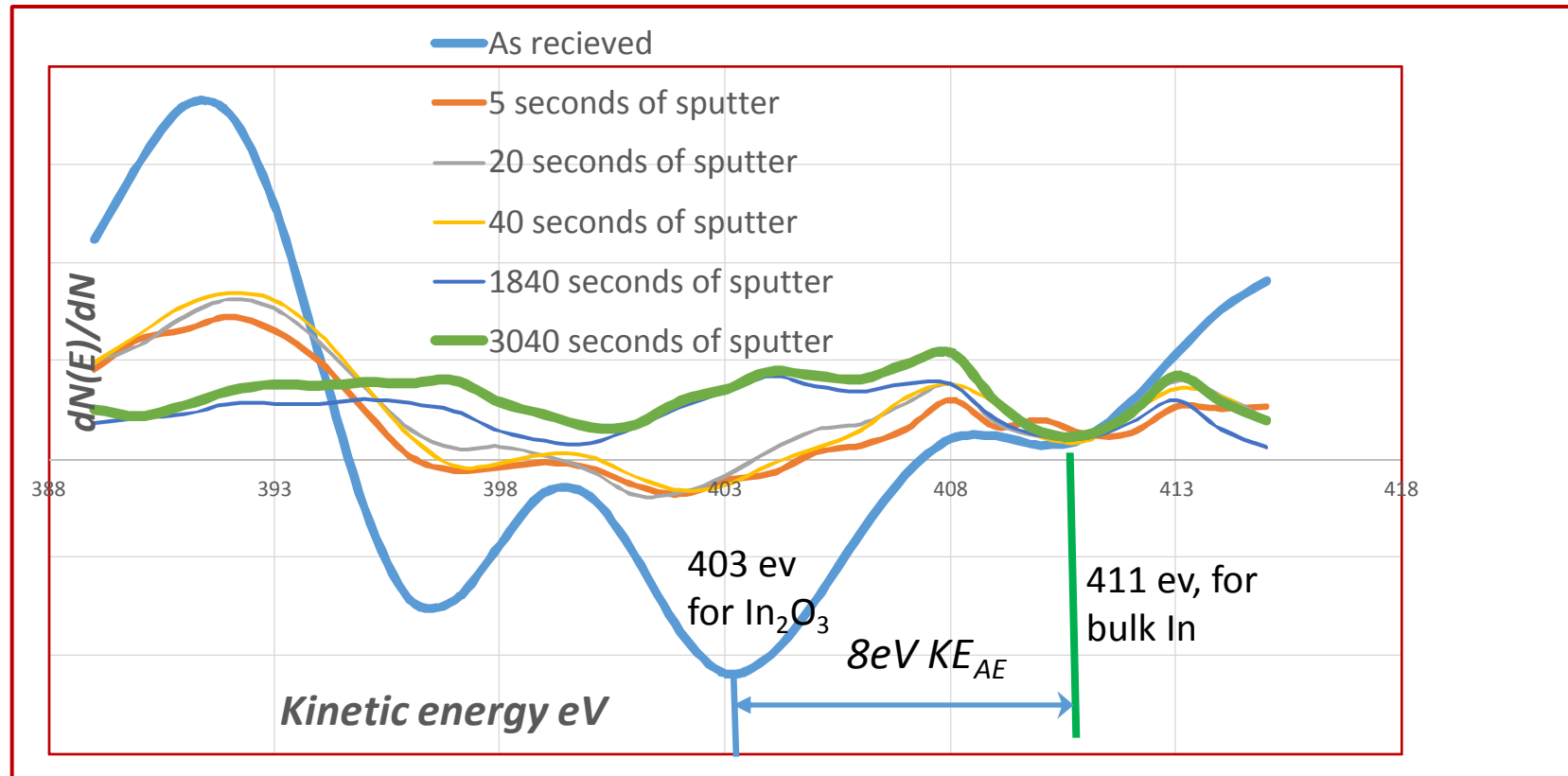
- $\text{SnO}_2$  in the Oxide Layer



- From the bulk of the sample (red line) to the surface (blue line), the major Sn Auger peak at 430 eV goes to a lower kinetic energy range by about **6 eV**. This peak shift occurs due to the binding energy from oxygen bonding at the valence band and also likely influenced by intermetallic oxide with indium at the sample surface.
- The literature data for the peak shift in  $\text{SnO}_2$  from Sn is about 6 eV – *M. Batzill & U. Diebold, The surface and materials science of tin oxide, Prog. Mat. Sc., 2005, 47-154.*

# Peak Shift/Chemical Shift Results:

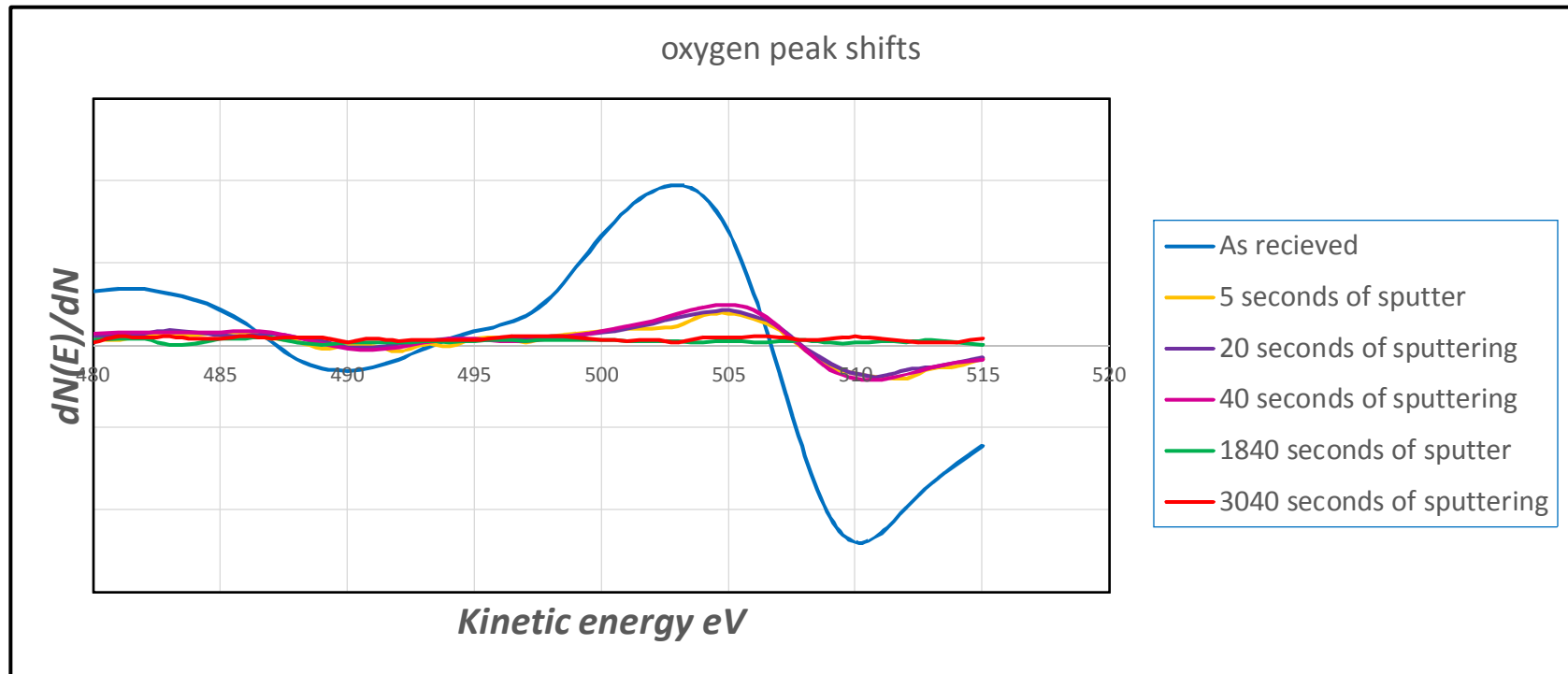
-  $\text{In}_2\text{O}_3$  in the Oxide Layer



The peak shift for  $\text{In}_2\text{O}_3$  in our Sn-In-Sn sample is measured at about 8 eV. This is consistent with literature data for pure In and its oxide.

- *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*, ed. D. Briggs and M.P. Seah, John Wiley & Sons, 1983.

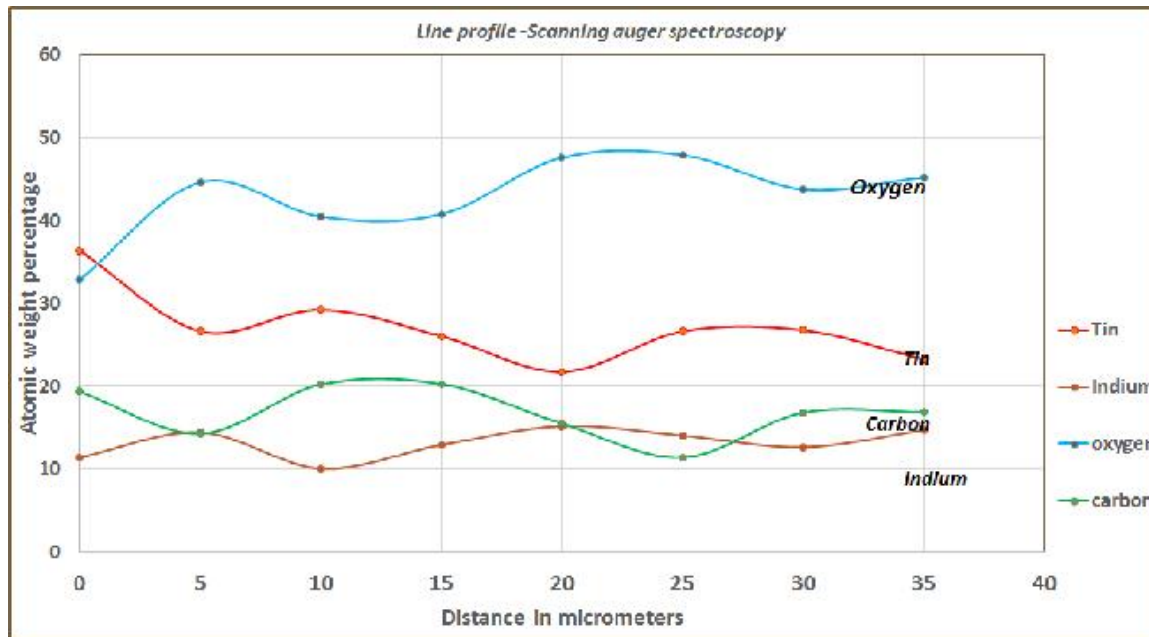
# Oxygen Peak Shift: No Observable Peak Shift



- *There is no significant shift observed in the oxygen energy peak with sputtering. The major oxygen peaks observed from the experiments (510 eV) are about 7eV different from that of the reference data seen in Perkin Elmer Physical Electronics division Auger spectra data base (Oxygen in MgO with 503 eV).*

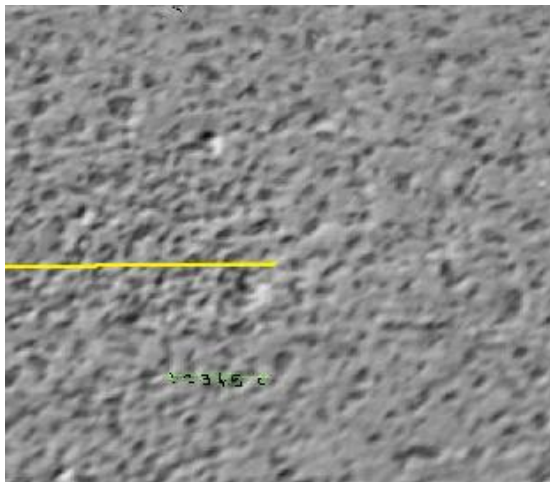


# Variation of Auger Spectra at the Surface Prior to any Sputtering

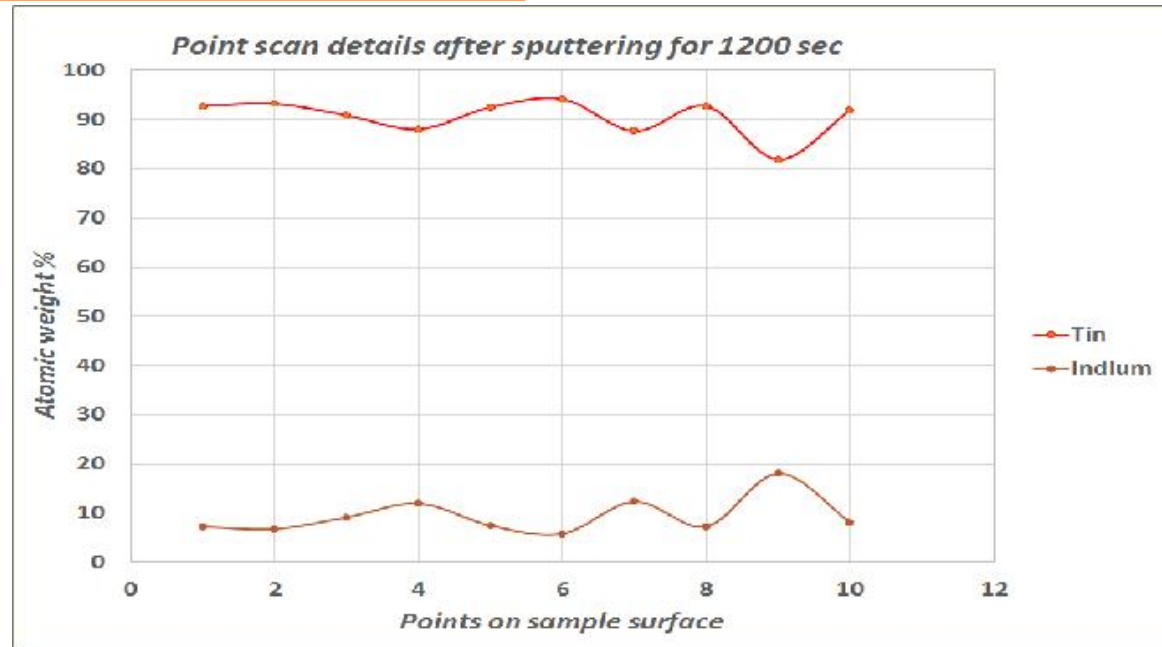


- Measurements conducted along a line about 5  $\mu\text{m}$  spaced apart.
- There is an oscillatory behavior with approximately *out-of-phase* variation of Sn and In composition.
- The overall atomic concentration of In lies at 14%. This is well below that observed in ITO of about 34.5%.

# Variation of Auger Spectra Following 1200 seconds of Sputtering

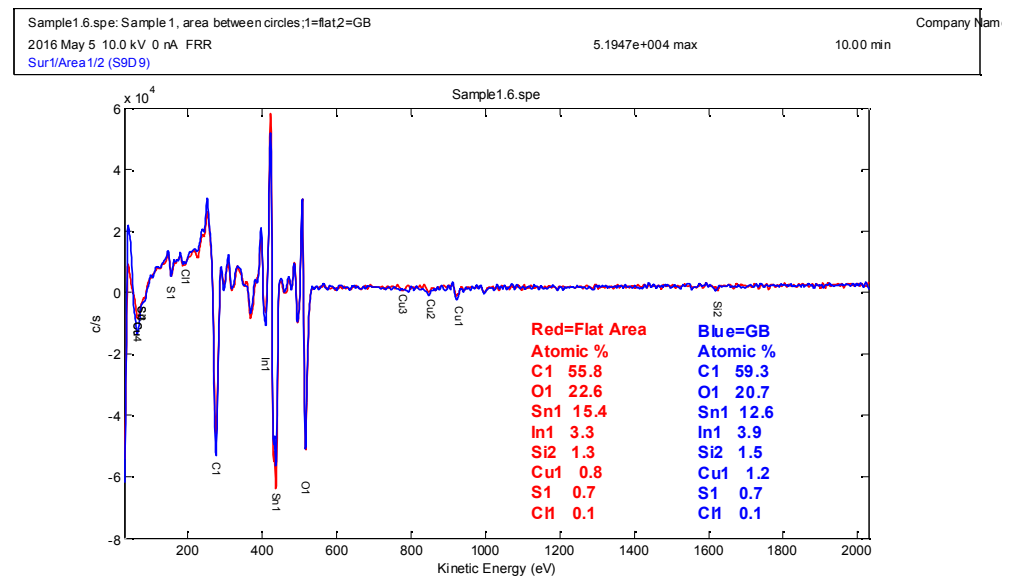
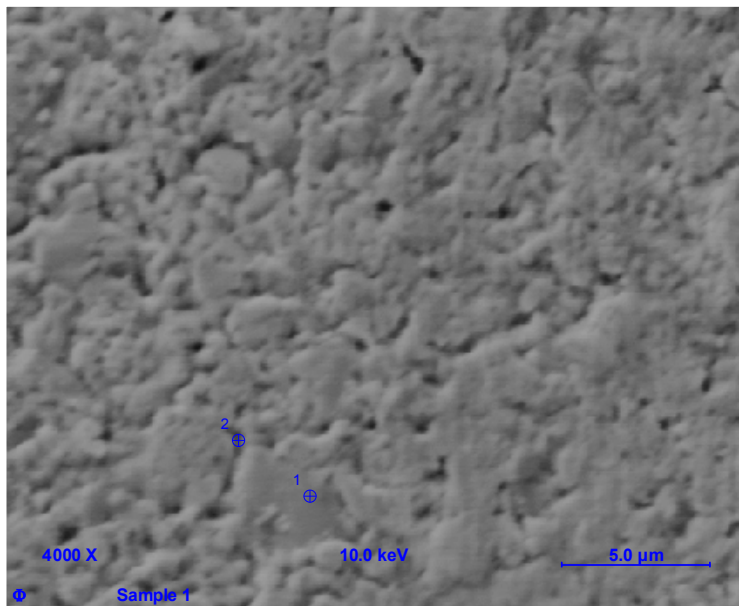


Auger spectra at equidistant points at about 2  $\mu\text{m}$  spacing along the yellow line.



- There is no oxygen present following 1200 seconds of sputtering.
- The peaks for In variation in the plot are about 3  $\mu\text{m}$  apart, which is close to the grain size of 1-2  $\mu\text{m}$ . Thus, the In excess may lie at grain boundaries, although Auger nanoprobe would be required to establish this correlation.

# Nano Auger Probe Results – Preliminary Findings



The preliminary results suggest possible enrichment of In at grain boundaries, but confirmatory tests are necessary.

# Effect of RT Exposure Following 1800 sec Sputtering

---

## Sputtering for 1800 sec:

- Results in: (a) complete loss of oxygen in the Auger trace, and, (b) the concentration of In comes down to 7-8 at. % from as high as 15-17 at.% in the original oxide layer. The former is about the bulk composition of the Sn-In alloy.

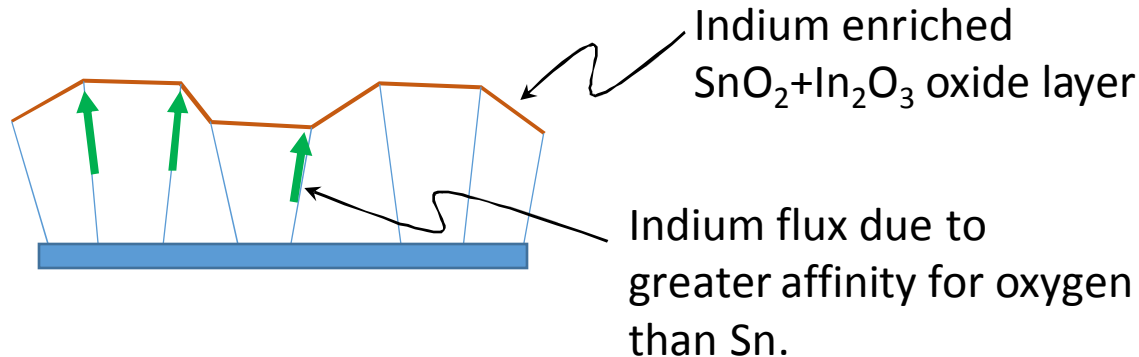
## Following RT Exposure in air for 10 days:

- When the above sputtered sample was exposed to air at RT for 10 days and followed up with Auger analysis, we observe once again tin and indium oxides at the surface, with the In concentration back up to 15 at.%, the value in the as heat treated state.

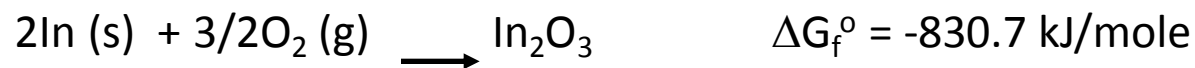
- Thus, the Indium appears to have greater affinity for oxygen at the surface than Sn. This also explains why the concentration of In dropped from the surface to the bulk in the initial sputtering run on the heat treated material.

# Possible Mechanism of Indium Enrichment at the Oxide Layer

---



- Grain boundary diffusion dominated flux.
- Standard Free Energy of Formation:



- The higher free energy reduction associated with the indium oxide compared to tin oxide likely explains why In concentration is enhanced in the oxide layer.

# Recent Results: Heat Treatment May Not be Necessary for Indium Enrichment in the Oxide Layer

---

- Preliminary results for Indium doped Sn electroplating shows enriched  $\text{In}_2\text{O}_3$  at the surface even in un-heat treated Sn-In-Sn samples.
- However, in this case, only SnO and  $\text{In}_2\text{O}_3$  is observed, and no  $\text{SnO}_2$ .
- Electroplated **Pb-Sn** material (acidic MSA bath) exhibits SnO and PbO at the oxide layer.

# Conclusions from AES Results

---

- A goal of this effort was to understand the mechanisms that may be responsible for the dramatic decrease in whisker growth rate in the In containing Sn plated sample.
- The Auger studies show that there is a greater concentration of In at the surface, leading to the formation of  $\text{In}_2\text{O}_3$ .
- The peak shift data for both Sn and In are consistent with literature data, which suggests that the formation of complex oxides like ITO are unlikely, and if present, such oxides are present in very small quantities.
- The variation of Sn and In composition exhibit variations. The period of variation is similar to the grain size, approximately 1 – 2  $\mu\text{m}$ .
- *It is likely that the presence of both Sn and In oxides reduce the high tenacity that is observed in pure tin coatings. The oxide-metal interface can thus serve as a good source or sink for vacancies, leading to an effective mechanism for stress relaxation and whisker mitigation.*