Modification of Radiator Pigments by Atomic Layer Deposition (ALD)

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Motivation

- **Most white pigments do not dissipate electrical charge without a dopant or additive**
- **Two most commonly used dissipative thermal coatings (Z93C55 and AZ2000) rely on indium hydroxide or tin oxide as charge dissipative additives utilizing sol gel wet chemistry**
- **ITO formed locally on a macroscopic scale due to seeding and ITO crystal formation on the boundaries of the pigment grains. Thickness and dispersion throughout the coating are difficult to control.**

Instead of postprocessing the dissipative coating can we preprocess the dissipative coating before binding directly on the pigment itself?

Outline

- **Introduction to Thin Films and ALD**
- **Reactor Design**
- **Indium Oxide Chemistry**
- **Results**
- **Acknowledgements**
- **Questions**

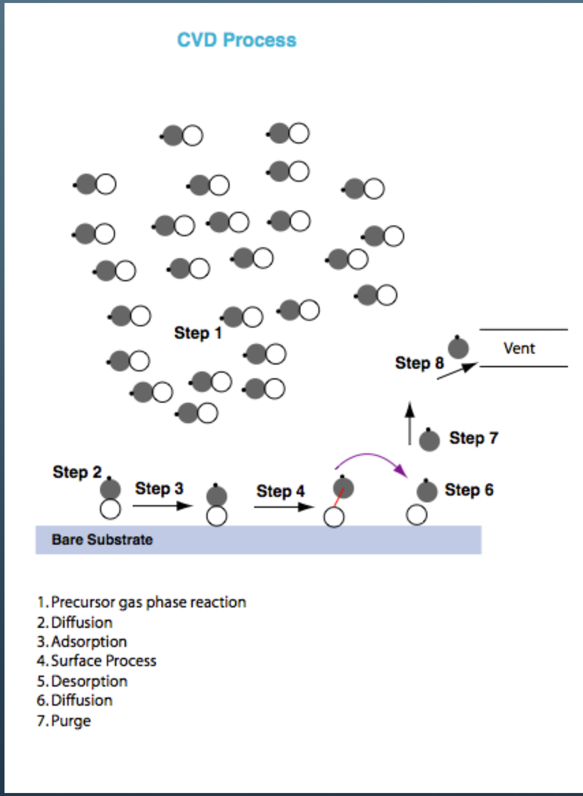
What is a Thin Film?

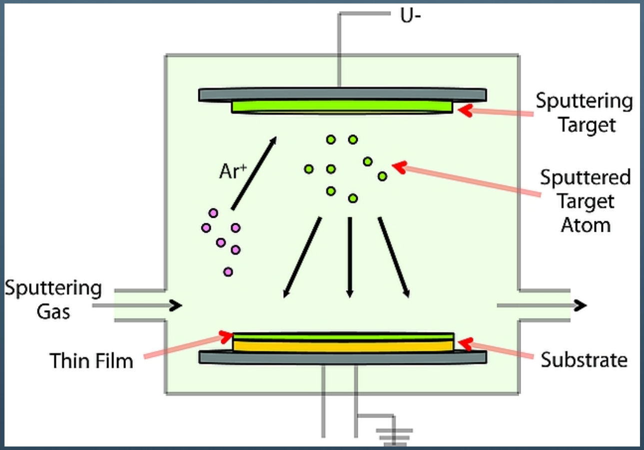
Thin film: thickness typically <1000nm.

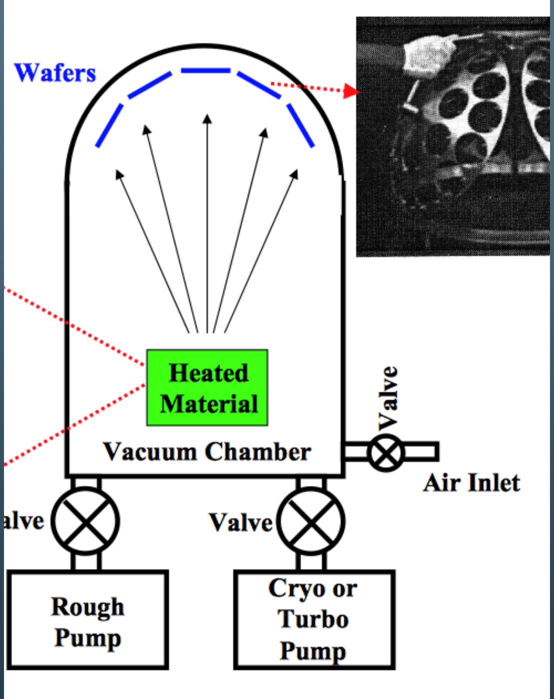
Special properties of thin films: different from bulk materials, it may be –

- Not fully dense
- Under stress
- Different defect structures from bulk
- Quasi - two dimensional (very thin films)
- Strongly influenced by surface and interface effects

Other Deposition Techniques



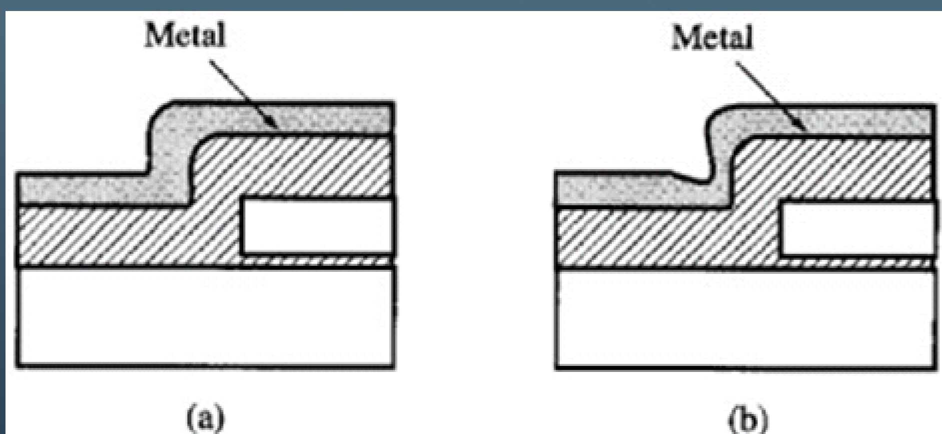




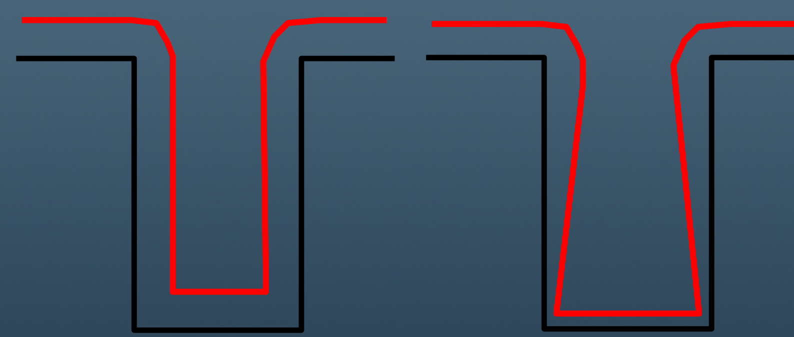
Common Denominator

- Deposition only occurs on substrates that “see” the target.
- Plasma process can damage the substrate
- Poor thickness control
- Poor Step Control
- High Pressure High Temperature Environment

Step Coverage Example



conformal non-conformal



Step coverage of metal over non-planar topography.
(a) Conformal step coverage, with constant thickness on horizontal and vertical surfaces.
(b) Poor step coverage, here thinner for vertical surfaces.

Atomic Layer Deposition

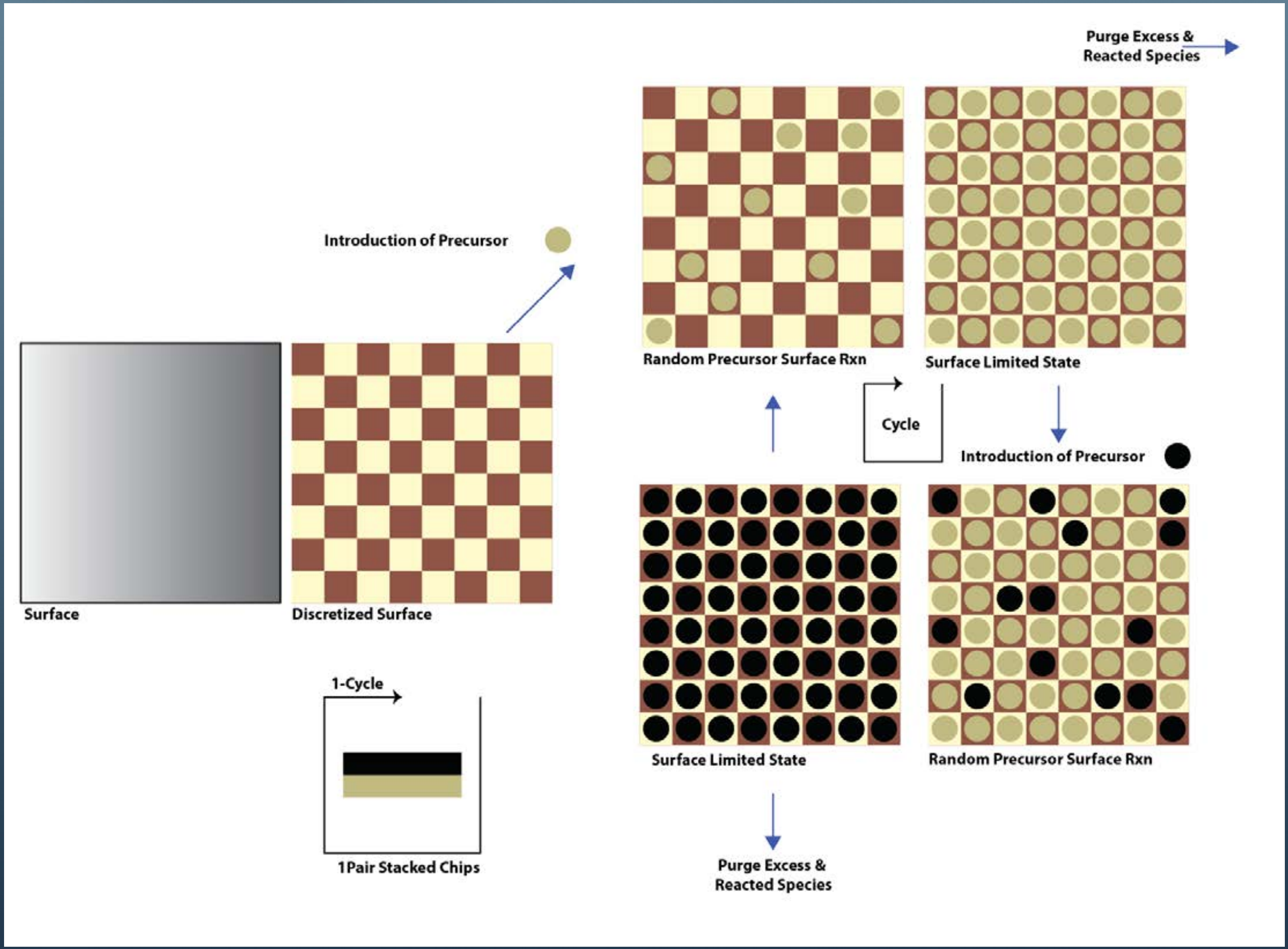
Atomic
Layer
Deposition

A thin film"nanomanufacturing" tool that allows for the conformal coating of materials on a myriad of surfaces with precise atomic thickness control.

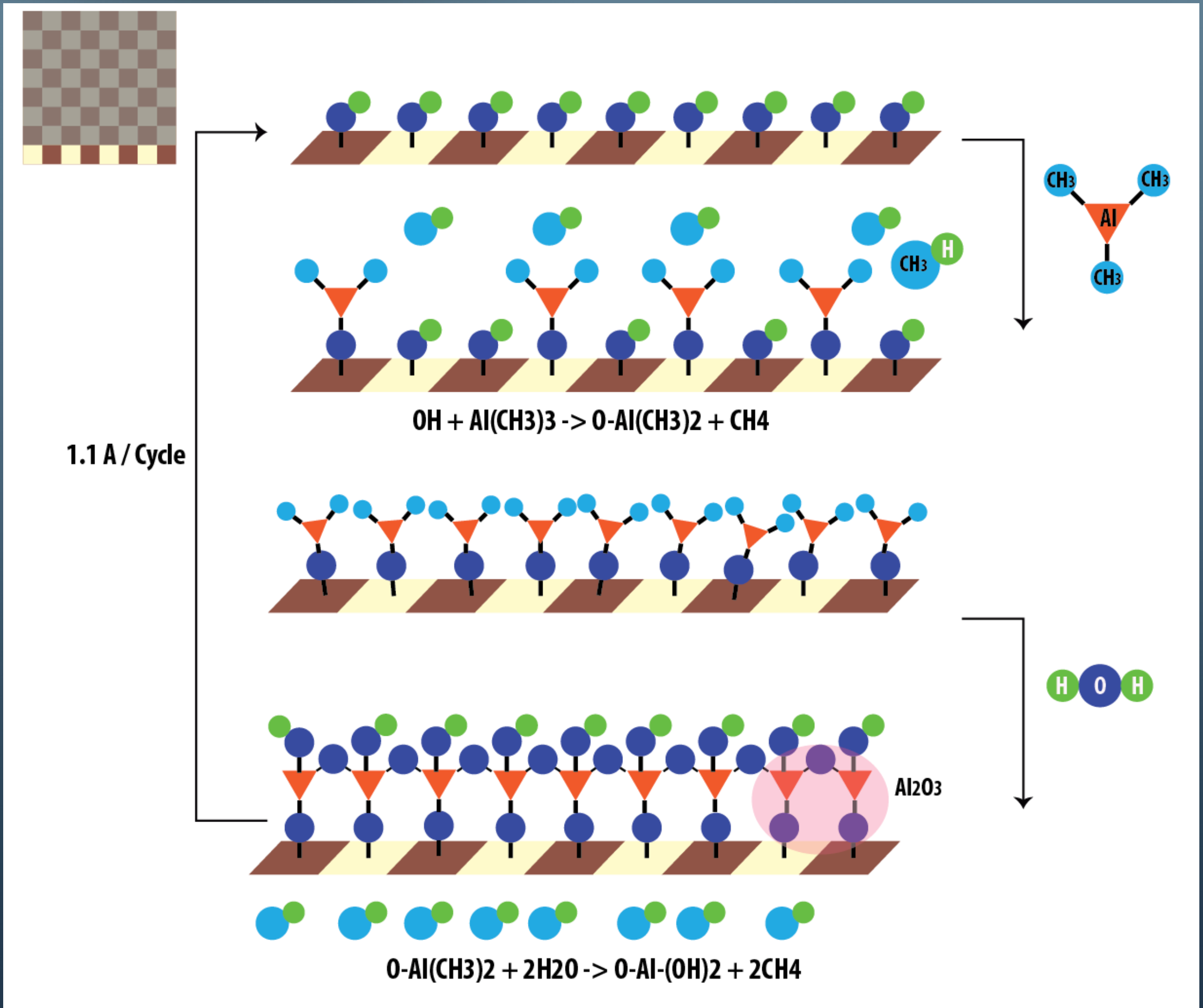
Based on:

- **Paired gas surface reaction chemistries**
- **Benign non-destructive temperature and pressure environment**
  - **Room temperature -> 250 °C (even lower around 45 °C)**
  - **Vacuum**

ALD Analogy (Checkers)

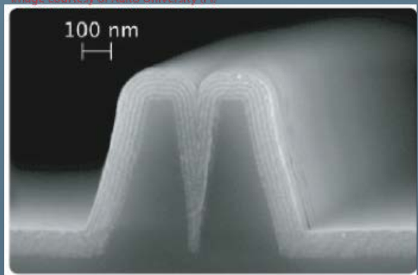


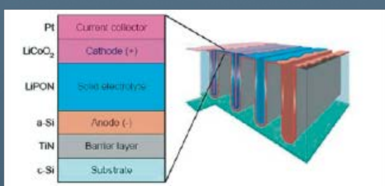
ALD Analogy Chemistry



ALD Advantageous Property

Artificial trench filled with an ALD nanolaminate
Image courtesy of Aalto University (FI)

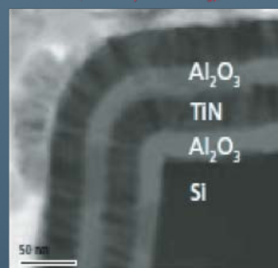




Schematic of a 3D battery integrated in a Si- substrate. The cross-section shows the various functional layers in the battery stack as well as the candidate materials.
Knoops, H.C.M. et al., ECS Trans., 25 (2009) pp. 333-344

Epitaxial Growth

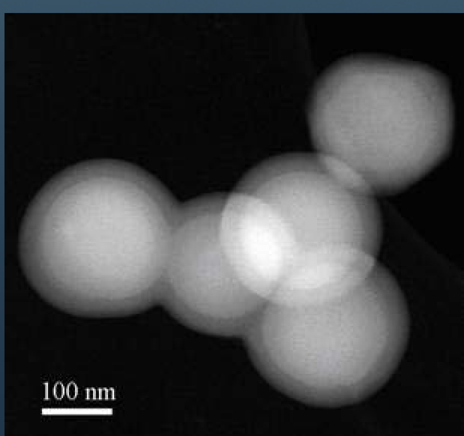
Multilayer consisting of:
Al2O3 - 25 nm
TiN - 20 nm
Al2O3 - 25 nm
Dr. Fred Roozeboom, NXP Semiconductors Research and
Dr. Erwin Kessels, University of Technology, Eindhoventd

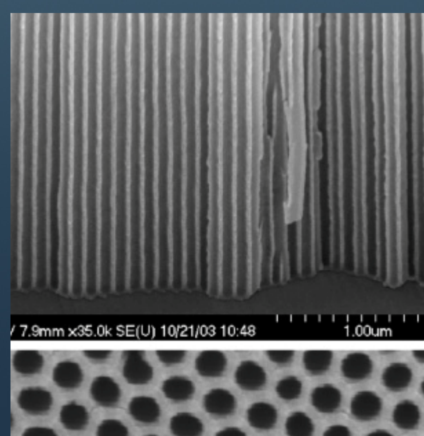


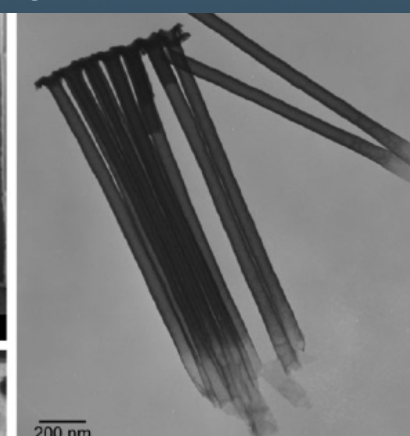
Batch Process

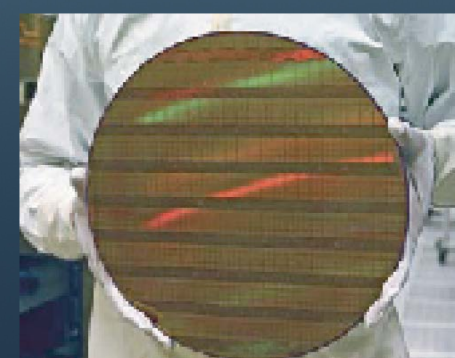
Coating Silver with Aluminum Oxide
http://www.glassonweb.com/

Substrate Independence









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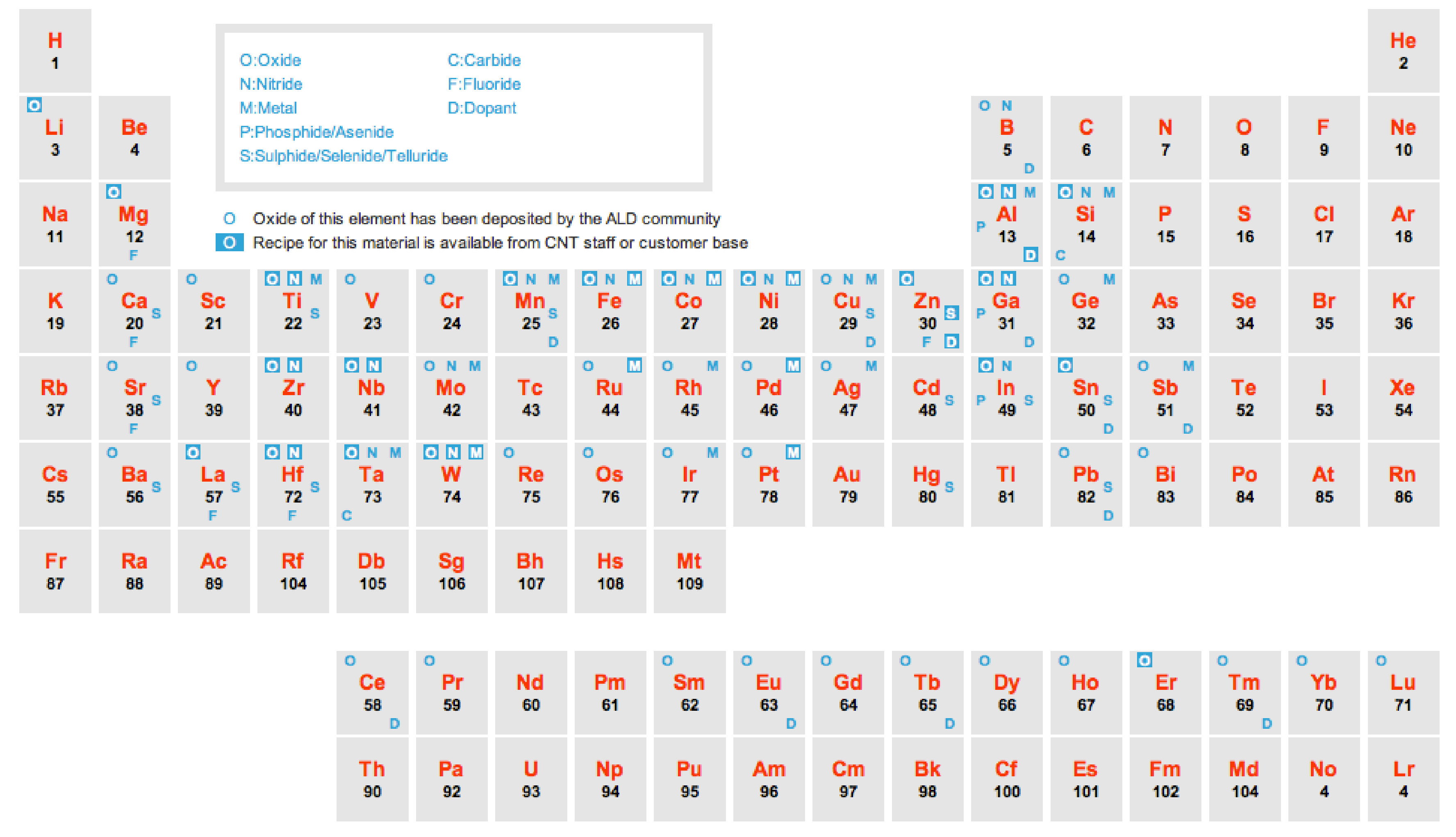
ALD Material Systems



- Gordon, Roy (2008). Atomic Layer Deposition (ALD): An Enable for Nanoscience and Nanotechnology. PowerPoint lecture presented at Harvard University, Cambridge, MA.
- Elam, Jeffrey (2007). ALD Thin Film Materials. Argonne National Laboratory

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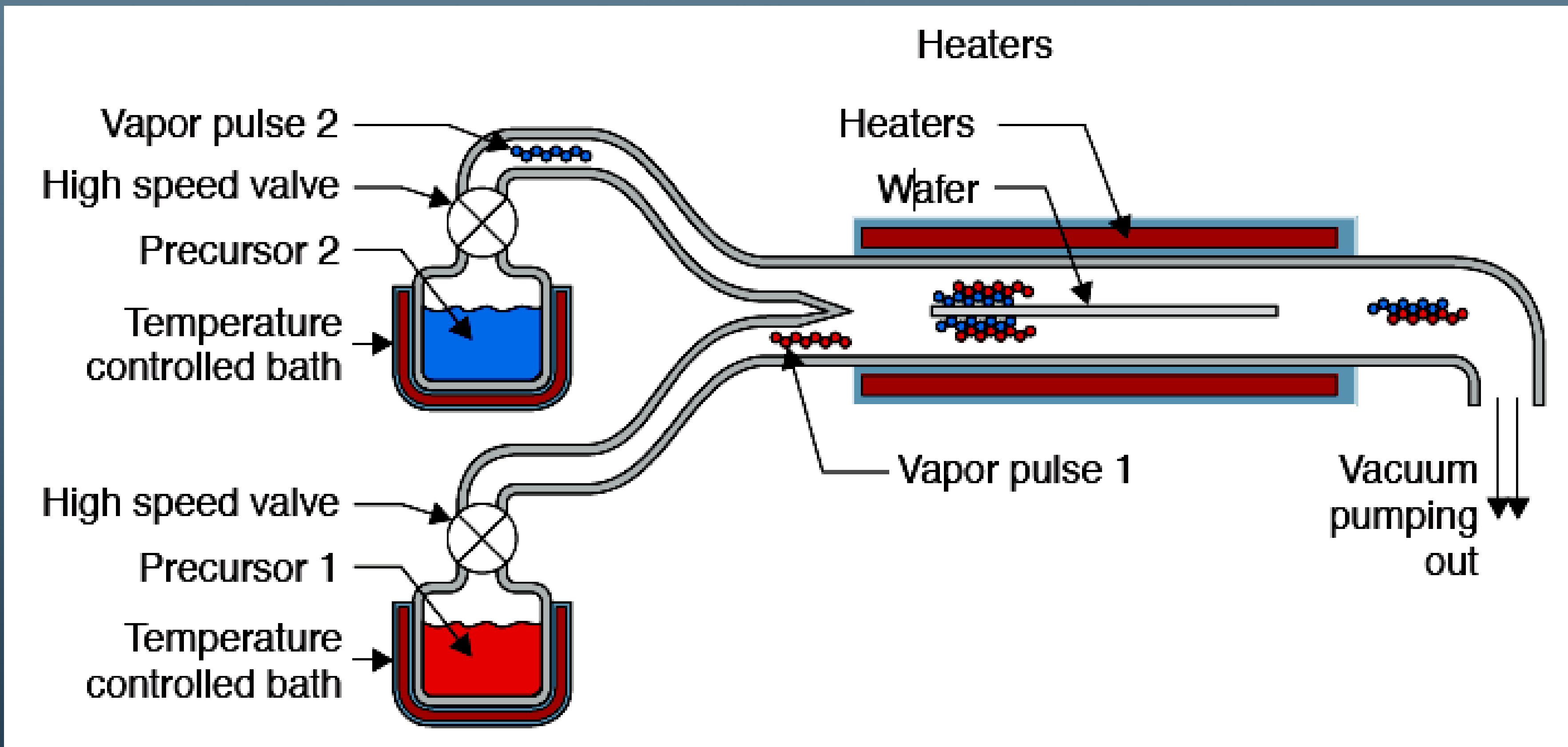
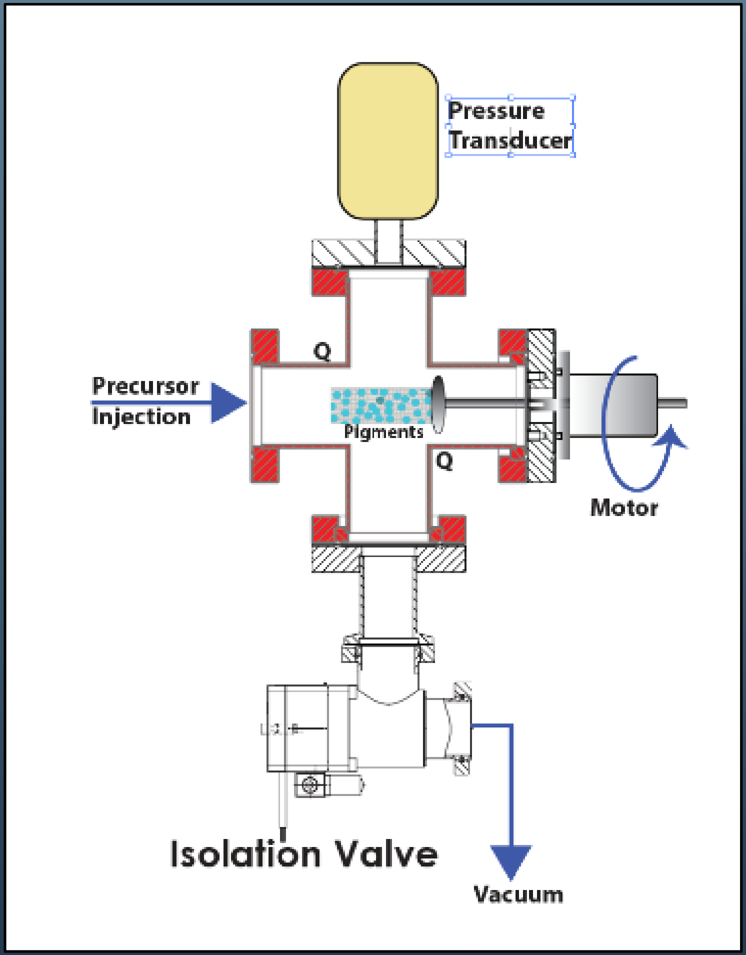
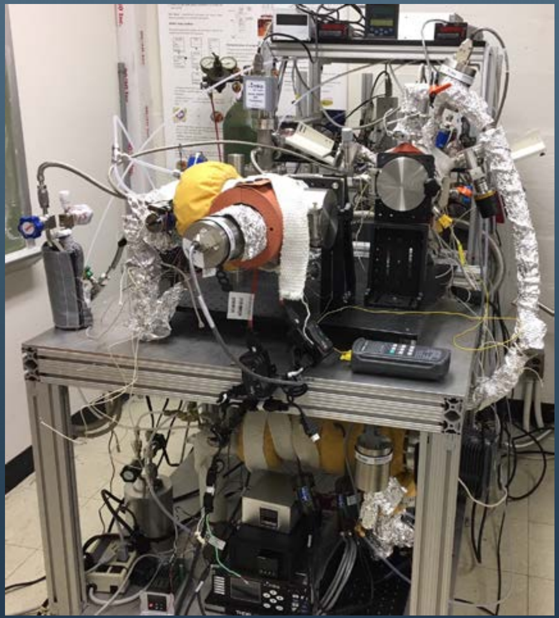
Basic Reactor



ALD For Radiators - Pigments





In_2O_3 and SnO_2 Chemistries

ALD of multi-material systems such as ITO requires that the films, in this instance metal oxides with ozone as the common oxidizer, have a deposition window that corresponds to an ALD growth window common to each precursor system.

$In(CH_3)_3 + O_3 \rightarrow In_2O_3$

$TDMASn + O_3 \rightarrow SnO_2$

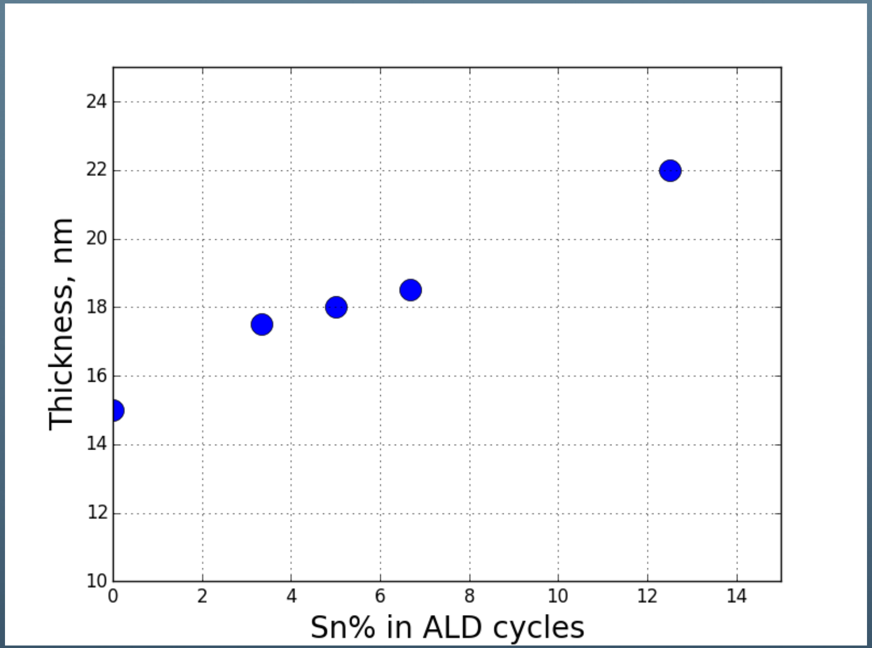
For “standard 5%” Sn doped indium oxide we apply a super cycle

$$\left.\begin{array}{r} 19\,[\mathrm{In(CH_3)_3} + \mathrm{O_3}] \\ 1\,[\mathrm{TDMASn} + \mathrm{O_3}] \end{array}\right\} = m\ \mathrm{In_2O_3} \cdot \mathrm{SnO_2}$$

Experimental Procedures

- The first set of experiments were conducted on flat substrates for the ALD of In_2O_3 and ITO, the films were deposited on a variety of substrates including n-type Si(100) wafers for thickness measurements and glass microscope slides for sheet resistivity determination.
- The In_2O_3 ALD on the particle substrates was applied to Z93P pigments provided by Alion Science and Technology; these particles had a mean size of 2 microns.
- Thickness and conformity of the ALD films on the Si wafers of In_2O_3 and ITO were measured using a J.A. Woollam M-2000D Spectroscopic Ellipsometer. The sheet resistivity of the ALD films on the microscope glass substrates was measured using a Lucas Signatone S-302 four-point probe
- The bulk resistivity of the ALD deposited pigment system is measured in air after the formation of a pellet of 1 in. diameter and a thickness of approximately .5 in. The pigment is compressed lightly by hand and held in place by a 3D printed electrically insulating hollow nylon/Teflon annulus spacer held on an aluminum plate.   Resistivity was measured in air and vacuum.

Results



As the percentage of SnO_2 cycles is increased, the overall thickness of the film also increases from 15 nm at 0% SnO_2 cycles to 23 nm at 12.5%. The 15 nm of the pure In_2O_3 film corresponds to .5 A/cycle; this matches literature values within a reasonable degree of error. The growth rate increases as a function of SnO_2 cycles to a rate of .77 A/cycle at 12.5%. This growth rate increase is attributed to the higher growth rate of ALD SnO_2.

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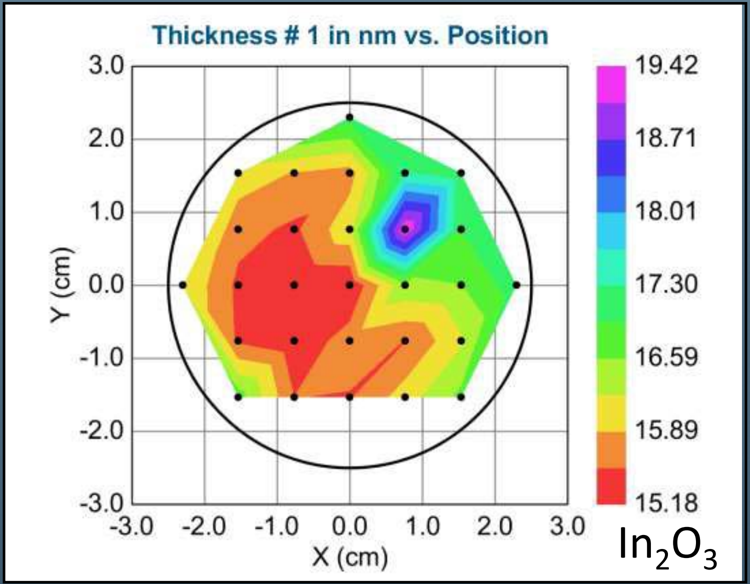
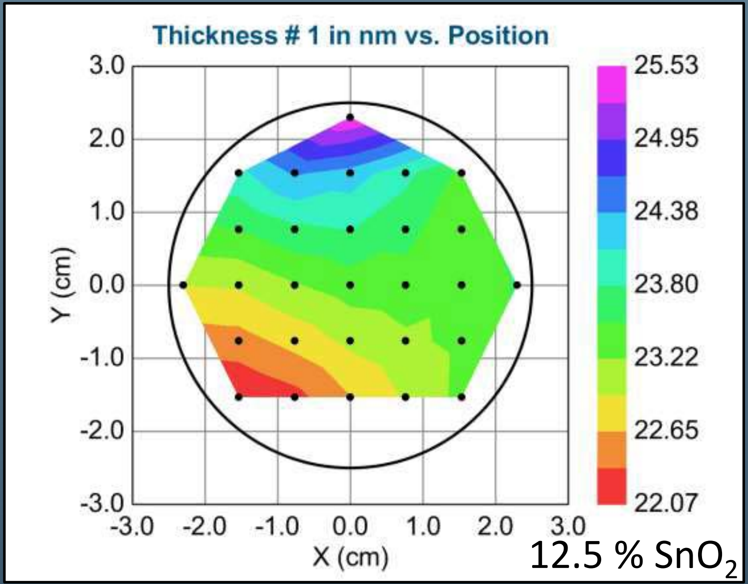
Results

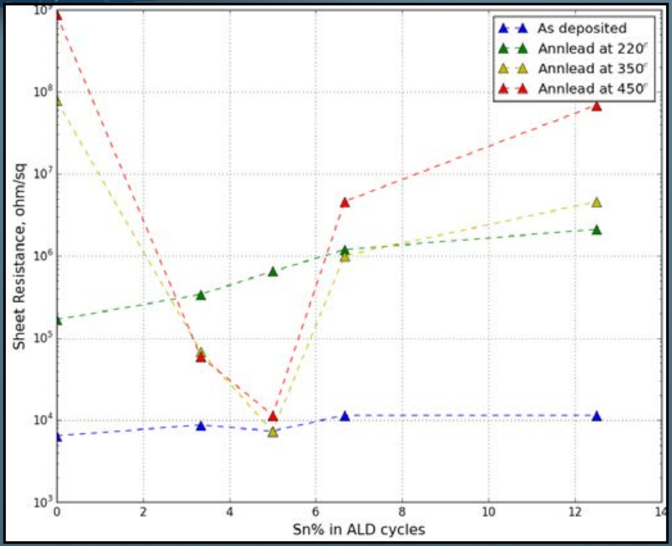


In_2O_3



12.5 % SnO_2

Results



- ALD of ITO, In_2O_3 films are deposited with an amorphous structure and crystallinity increases as a function of annealing temperature (H. Morikawa, 2000).
- The resistivity change is the same between annealing in a vacuum or air environment (S. Chan, 2015).
- In the above figure, as-deposited In_2O_3 possesses the best sheet resistivity. This result follows literature values showing its resistivity being lower than that of ITO thin films. An interesting aspect of these results is that a very thin film, <5 nm of indium oxide will maintain a constant level of conductivity regardless of tin doping.
- The effect of tin doping in ultrathin films is not well understood, while for thicker films tin doping allows for the tin atom to replace oxygen vacancies in the bulk indium oxide structure at an optimum percentage, thus changing its resistivity.

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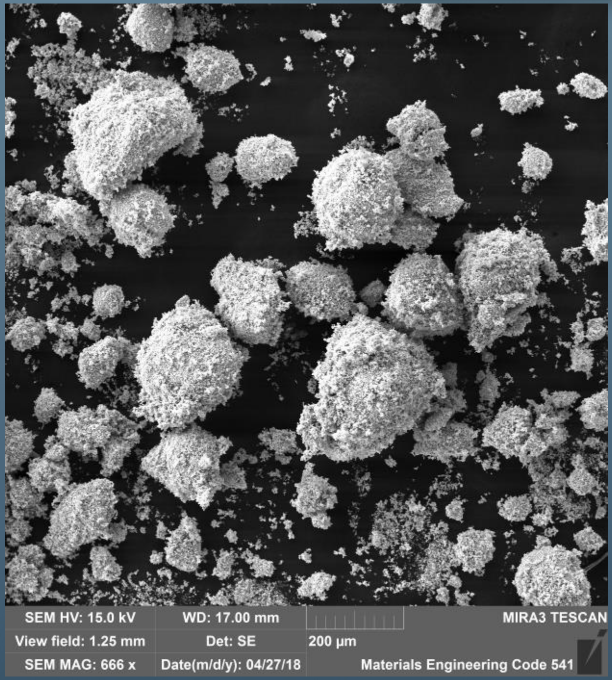
Results



SEM Of Uncoated Z93 Particles

Spectrum Label	Zinc Oxide Particles	Indium Oxide Coated
C	57.73	73.72
O	33.23	24.76
Zn	9.04	1.28
In	-	0.23

XPS of Particle Composition

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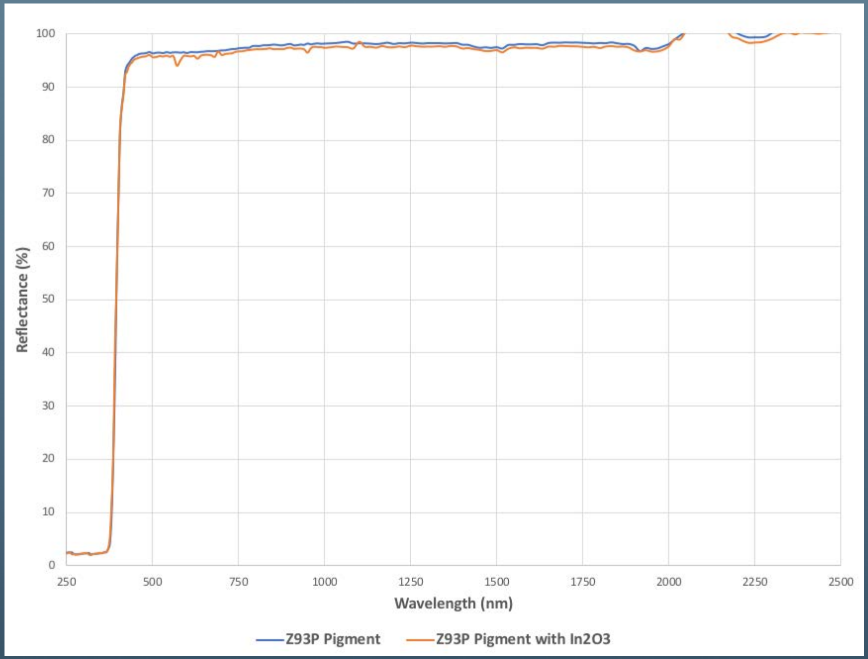
Results

Pressure (Torr)	Sample	Voltage (V)	R (ohms)
7.60E+02	In_2O_3 ALD Z93	40	1.30E+08
	Z93	40	5.10E+08
7.00E+01	In_2O_3 ALD Z93	40	1.60E+08
	Z93	40	8.00E+10
7.00E-02	In_2O_3 ALD Z93	40	1.80E+08
	Z93	40	1.80E+11
6.00E-02	In_2O_3 ALD Z93	100	7.00E+07
	Z93	100	6.00E+10

As vacuum is increased the resistivity of the Z93 pigment powders increases several orders of magnitude while the indium oxide treated Z93P pigment remains relatively stable. This increase in resistivity can be attributed to either the removal of moisture within the bulk powder or the compression of the powder filling the void space allowing for an increased number of conduction paths.

Results



Reflectance measurements were taken on lightly compressed pellets of the untreated and indium oxide treated Z93P pigment and show approximately one percent reflectance differences across the solar spectrum

Acknowledgments

Adomaitis Research Group

Mark Hasegawa

References

S. Chan, M. L. (2015). The Effect of Annealing on Nanothick Indium Tin Oxide Transparent Conductive Films for Touch Sensors. *Journal of Nanomaterials*.

H. Morikawa, M. F. (2000). Crystallization and electrical property change on the annealing of amorphous indium-oxide and indium-tin-oxide thin films. *Thin Solid Films*, 61-67.