



Modification of Spaceflight Radiator Coating Pigments by Atomic Layer Deposition for Thermal Applications

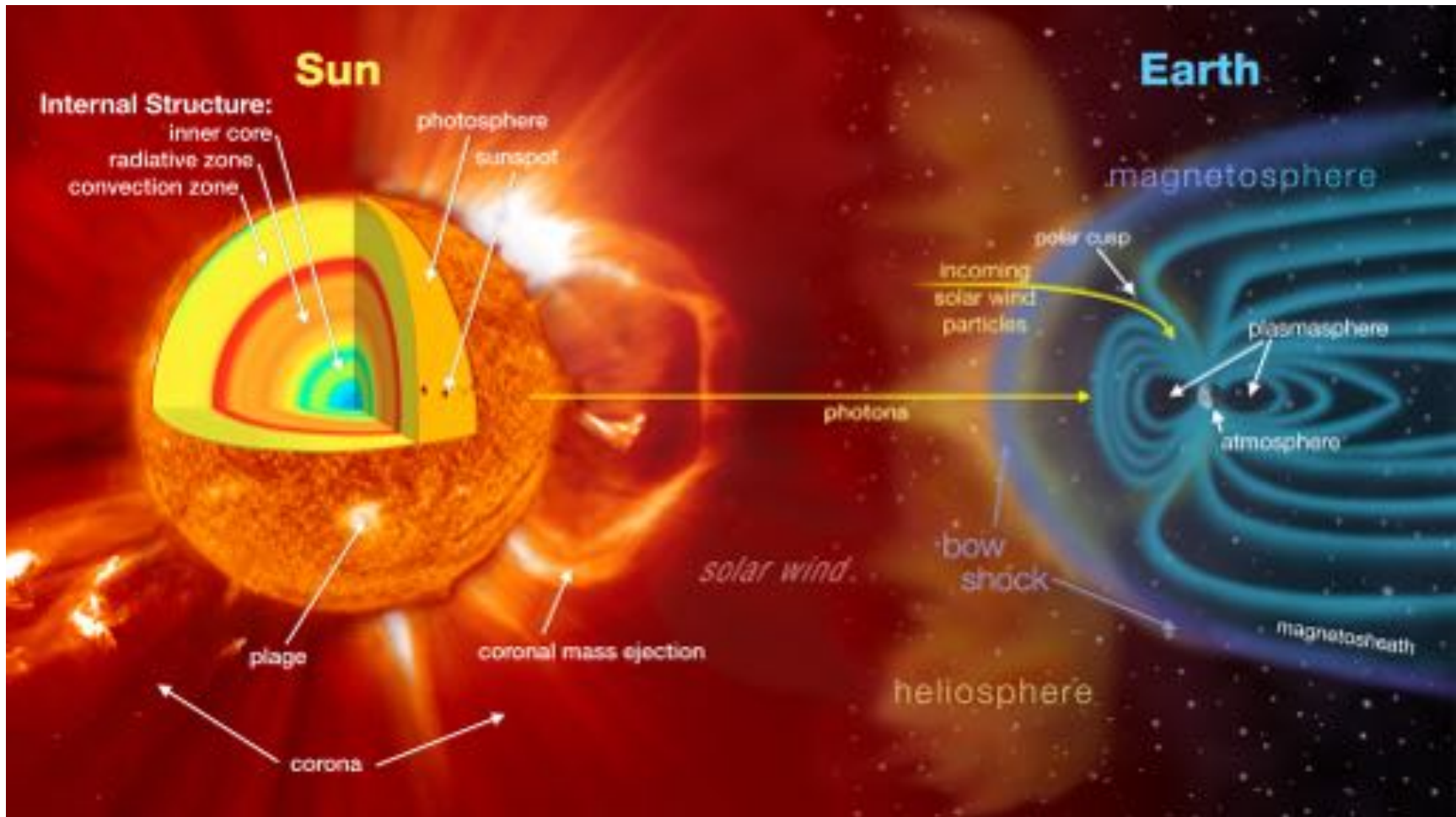
Vivek Dwivedi, Mark Hasegawa
NASA Goddard Space Flight Center

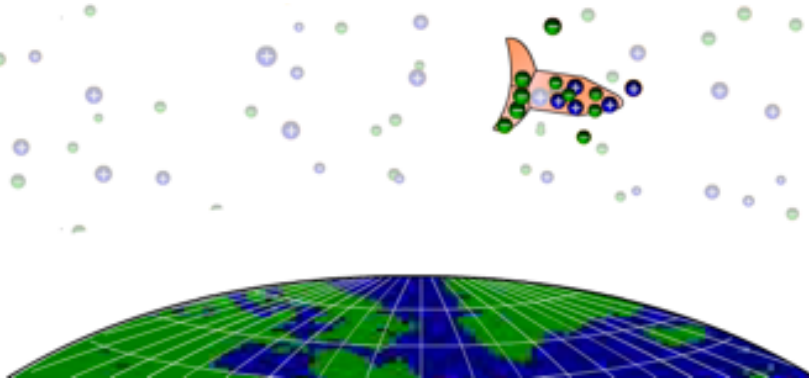
Presented By
Dr. Vivek H. Dwivedi

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Thermal & Fluids Analysis Workshop
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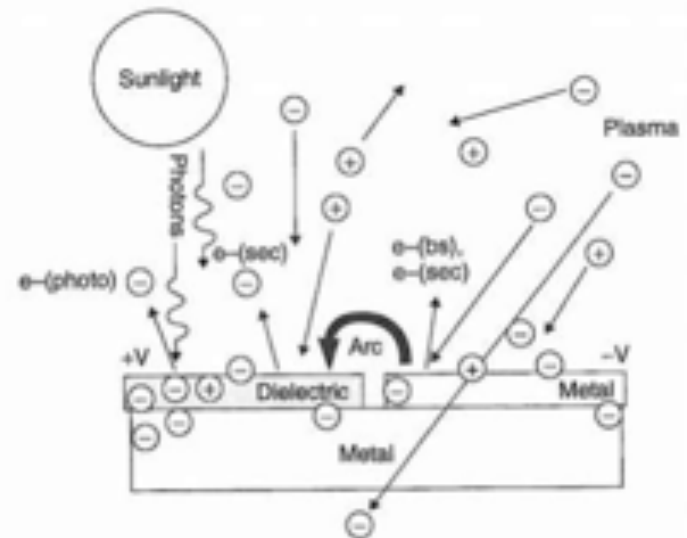
Sun – Earth Connection





Surface charging occurs from low-energy plasma and photoelectric currents.

During the eclipse (while in the shadow of the earth) phase of an orbit the spacecraft may negatively charge to tens of kilovolts and once the satellite emerges into sunlight a photoelectron emission may occur resulting in a potential discharge.



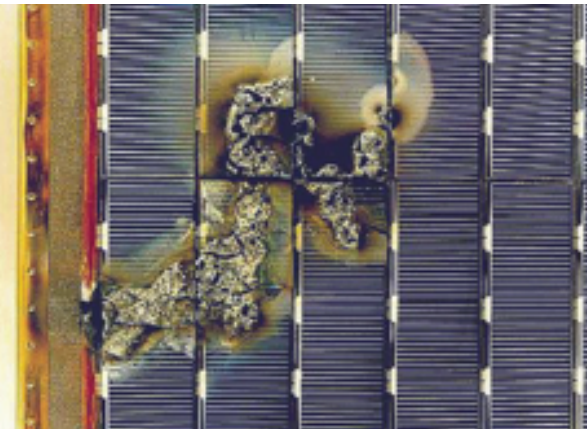
Garrett, H. B., Whittlesey, A. C.; GUIDE TO MITIGATING SPACECRAFT CHARGING EF

Spacecraft charging is the condition that occurs when a spacecraft accumulates excess electrons or ions. For a conducting spacecraft, the excess charges are on the surface. The term spacecraft surface charging (absolute charging) is used to clearly denote charging on the spacecraft surface as opposed to other charge distributions such as the voltage differences between electrically isolated parts of the spacecraft (differential charging).

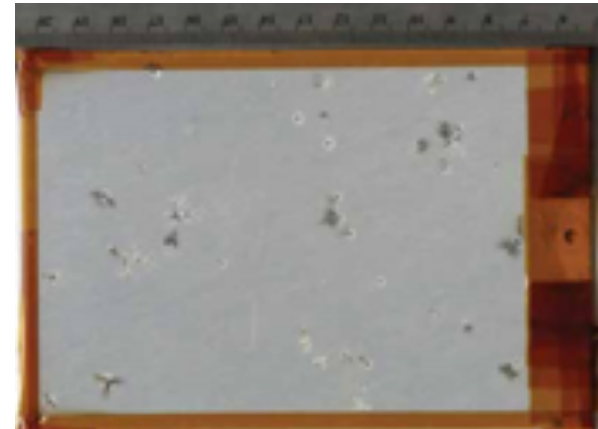
HAZARD

If a charge builds up that is too big for the spacecraft's material to hold, discharge arcs, which are essentially strong electrical currents, will occur.

And depending on where those arcs go, they can damage electronic components, destroy sensors, or damage important materials such as thermal control coatings.



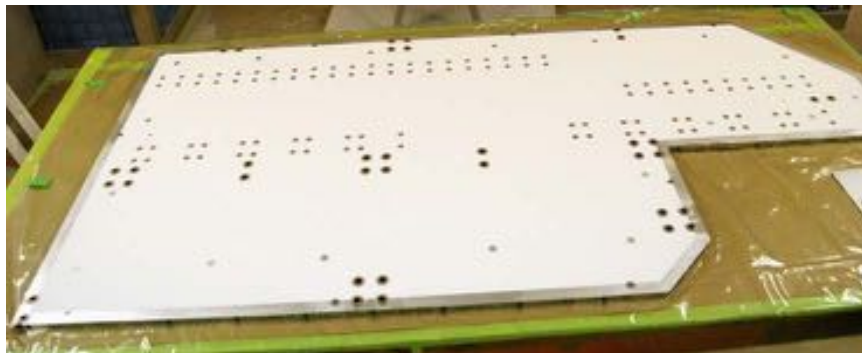
ESA EURECA satellite solar array sustained arc damage.
Credits: ESA



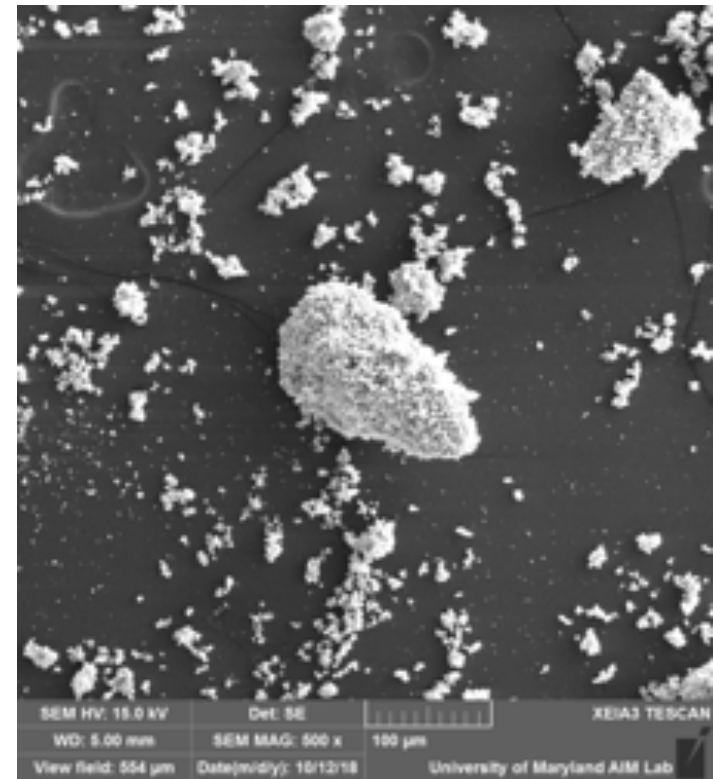
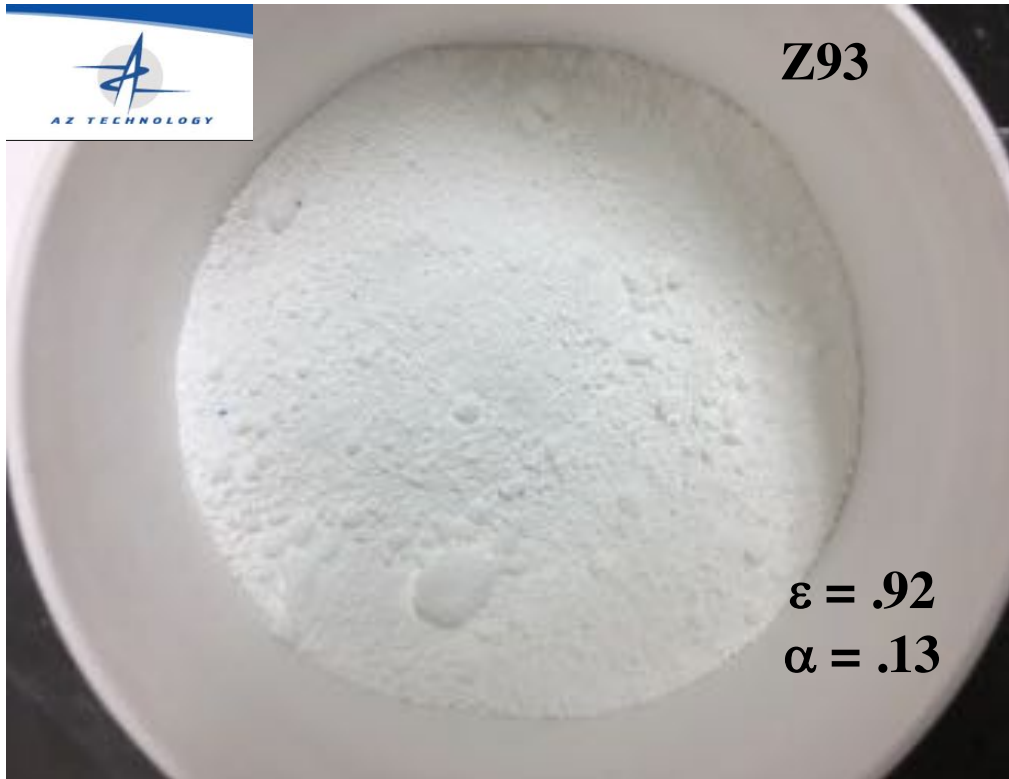
Arc damage in laboratory tests of the chromic acid anodized thermal control coating covering ISS orbital debris shield. Credits: NASA/T. Schneider

A dedicated structure whose purpose is the rejection of waste heat to deep space

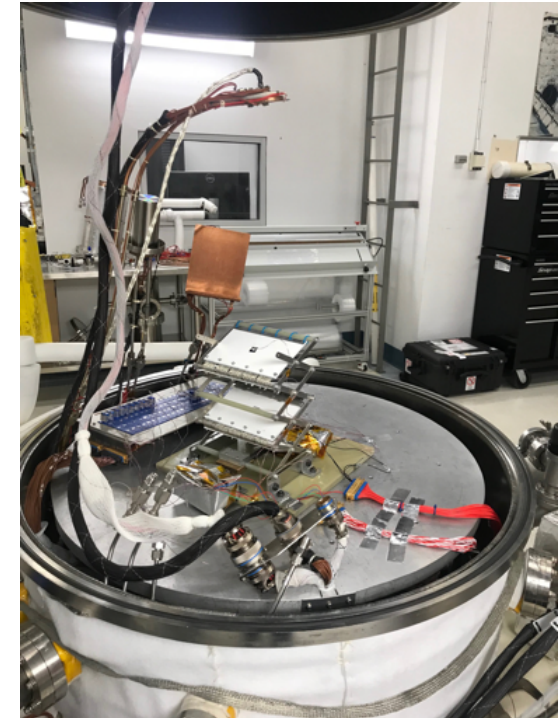
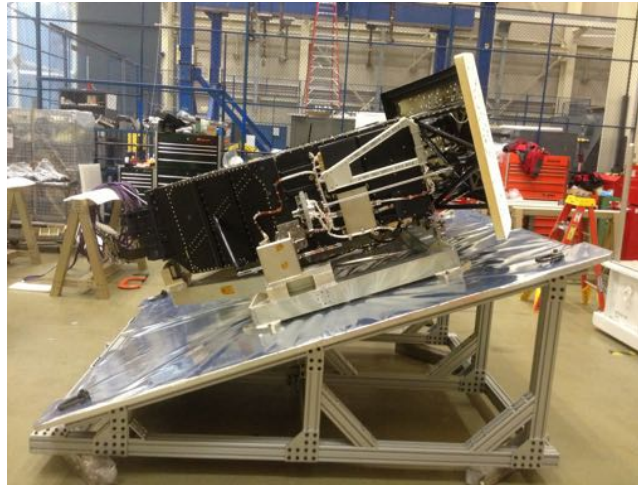
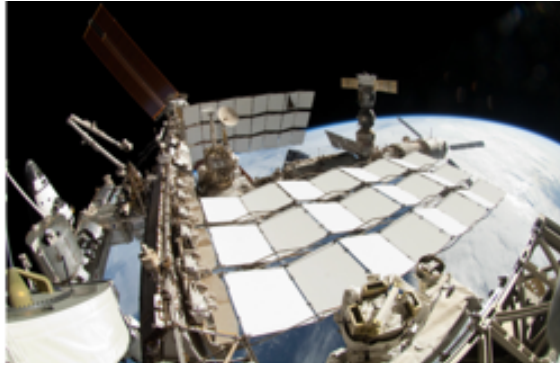
- Coated with high emissivity coating to maximize heat rejection potential
- May be coated with high or low solar absorptivity coating depending on view to solar sources
- If not existing structure, then supports are needed
- **Coatings** – films, tapes, paints, etc. applied to surfaces to obtain the desired thermo-optical properties for thermal control
 - Thermo-optical properties are intrinsic to the material itself (e.g. white paint, black paint, Kapton, etc)
 - a – Solar Absorptivity – percentage of sun energy (Direct Solar, Albedo [e.g. reflected solar]) absorbed
 - e – IR Emissivity – percentage of planet energy (Planetshine) absorbed
 - *Also a measure of emissive capability of a surface to reject heat via IR radiation*
 - Because the (electrically) insulating pigment can become differentially charged in LEO or GEO orbits a mitigation technique is needed to “bleed” it off



Radiator with White Paint Coating



Radiator - Vary in Size



Origami Inspired



The space station's radiator system, which is a critical component of the active system, consists of seven panels (each about 6 by 12 feet)

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

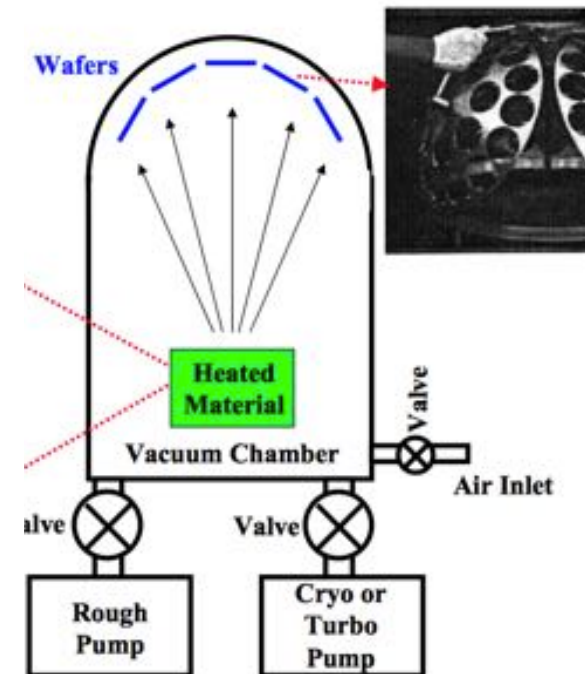
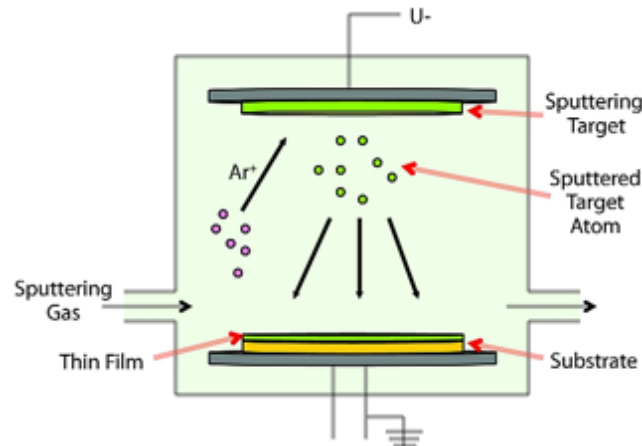
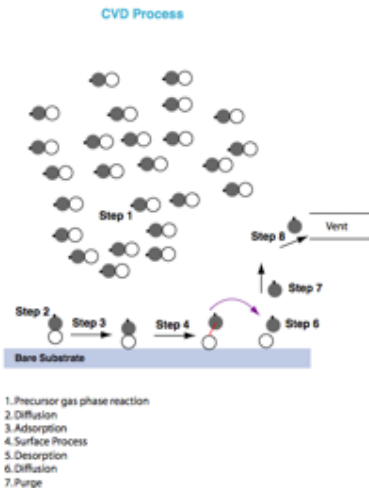


Wide Field Planetary Camera 2 (WFPC2) that was installed on the Hubble Space Telescope in December 1993, and removed during the last servicing mission in 2009

Thin film: thickness typically $<1000\text{nm}$.

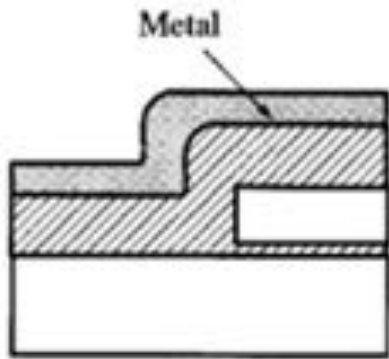
Special properties of thin films: different from bulk materials, it may be –

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

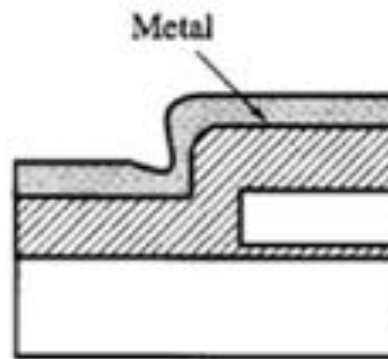


- Deposition only occurs on substrates that “see” the target.
- Plasma process can damage the substrate
- Poor thickness control
- Poor Step Control
- High Pressure High Temperature Environment

Step Coverage Example

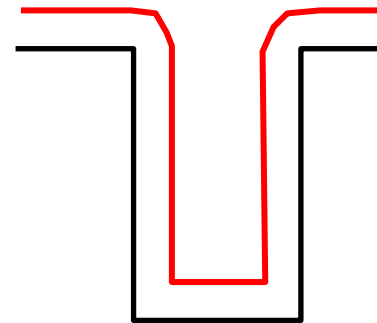


(a)

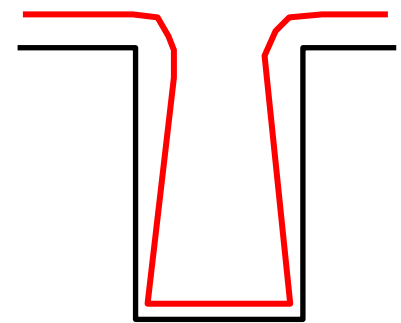


(b)

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



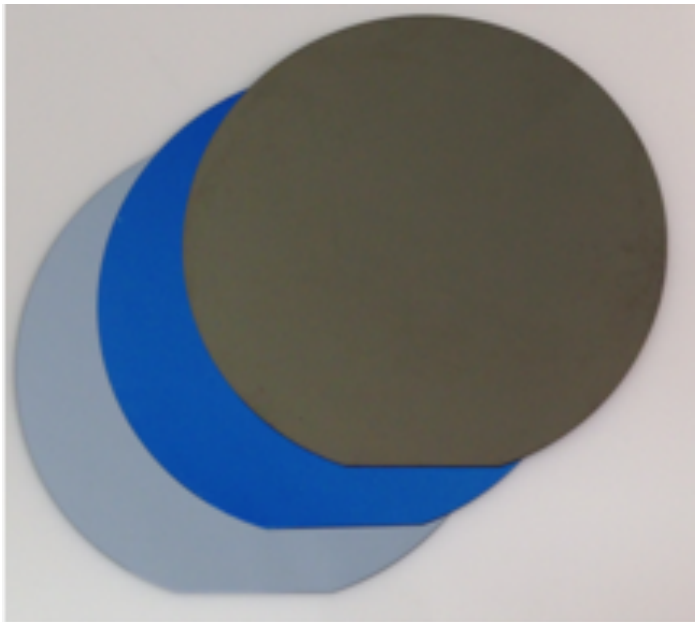
A thin film “nanomanufacturing” tool that allows for the conformal coating of materials on a myriad of surfaces with precise atomic thickness control.

Based on:

- **Paired gas surface reaction chemistries**
- **Benign non-destructive temperature and pressure environment**
 - **Room temperature $\rightarrow 250^{\circ}\text{C}$ (even lower around 45°C)**
 - **Vacuum**

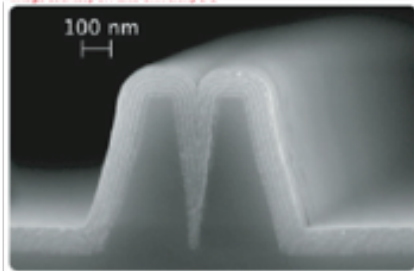
Precursor A + Precursor B → Solid film + Gas by-products

Cyclic operation: A → purge → B → purge → A → purge → ...



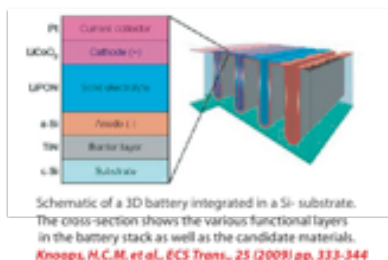
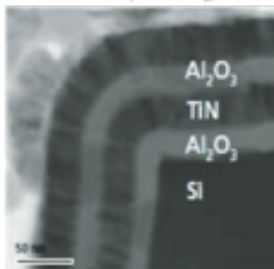
**... equivalent to a 60 μm layer
over a city-sized wafer**

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



Epitaxial Growth

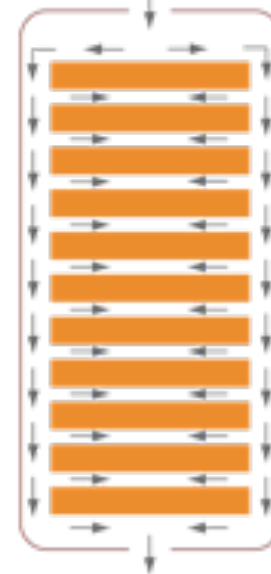
Multilayer consisting of:
Al₂O₃ - 25 nm
TiN - 20 nm
Al₂O₃ - 25 nm
Dr. Fred Roozeboom, NXP Semiconductors Research and
Dr. Erwin Kessels, University of Technology, Eindhoven



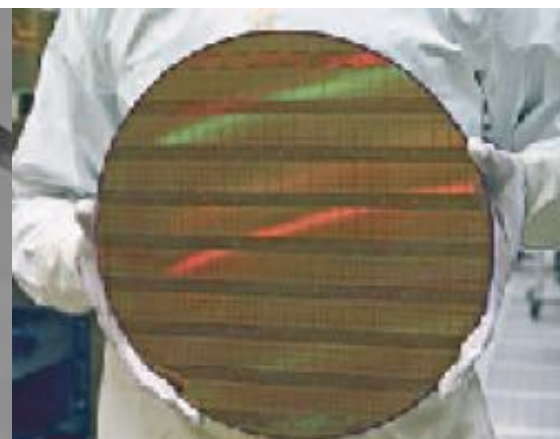
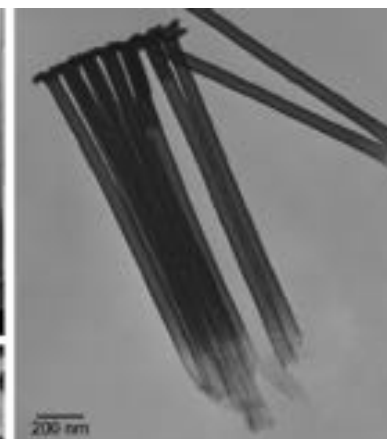
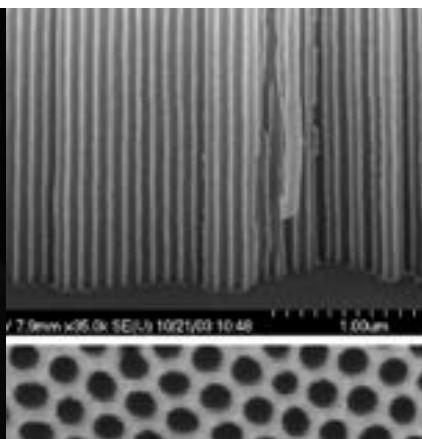
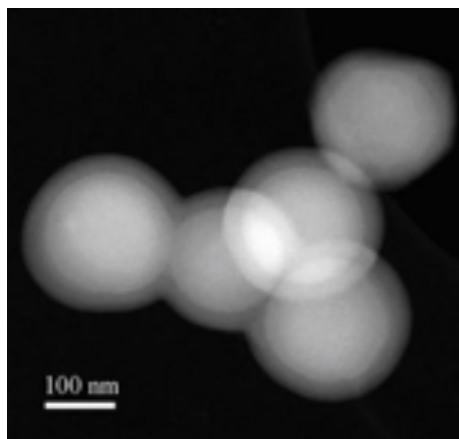
Batch Process



Coating Silver with Aluminum Oxide
<http://www.glaconwebb.com/>



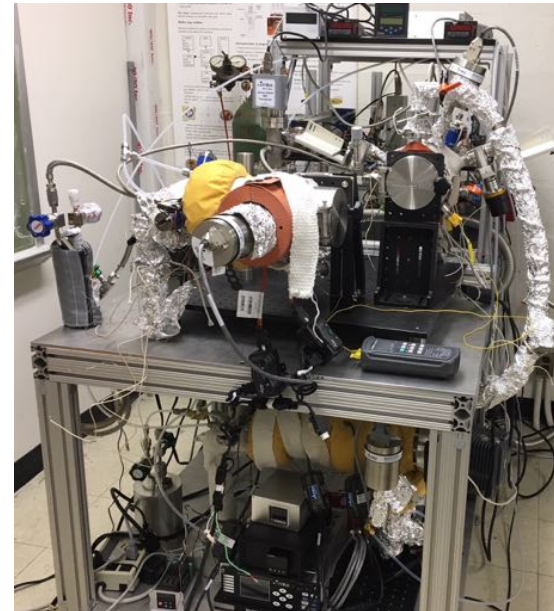
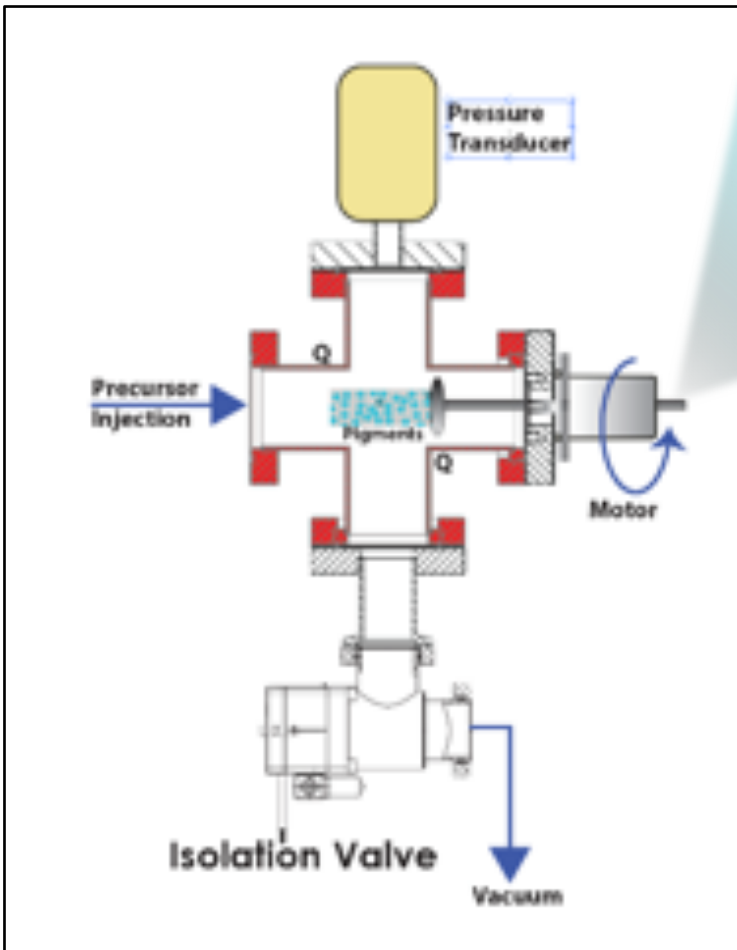
Substrate Independence



H 1	<div><div>O: Oxide N: Nitride M: Metal P: Phosphide/Arsenide S: Sulphide/Selenide/Telluride</div><div>C: Carbide F: Fluoride D: Dopant</div></div>																He 2														
<div>Li 3</div>	Be 4																	<div>B 5</div>	C 6	N 7	O 8	F 9	Ne 10								
<div>Na 11</div>	<div>Mg 12</div>																	<div>Al 13</div>	<div>Si 14</div>	P 15	S 16	Cl 17	Ar 18								
<div>K 19</div>	<div>Ca 20</div>	<div>Sc 21</div>	<div>Ti 22</div>	<div>V 23</div>	<div>Cr 24</div>	<div>Mn 25</div>	<div>Fe 26</div>	<div>Co 27</div>	<div>Ni 28</div>	<div>Cu 29</div>	<div>Zn 30</div>	<div>Ga 31</div>	<div>Ge 32</div>	<div>As 33</div>	<div>Se 34</div>	<div>Br 35</div>	<div>Kr 36</div>														
<div>Rb 37</div>	<div>Sr 38</div>	<div>Y 39</div>	<div>Zr 40</div>	<div>Nb 41</div>	<div>Mo 42</div>	<div>Tc 43</div>	<div>Ru 44</div>	<div>Rh 45</div>	<div>Pd 46</div>	<div>Ag 47</div>	<div>Cd 48</div>	<div>In 49</div>	<div>Sn 50</div>	<div>Sb 51</div>	<div>Te 52</div>	<div>I 53</div>	<div>Xe 54</div>														
<div>Cs 55</div>	<div>Ba 56</div>	<div>La 57</div>	<div>Hf 72</div>	<div>Ta 73</div>	<div>W 74</div>	<div>Re 75</div>	<div>Os 76</div>	<div>Ir 77</div>	<div>Pt 78</div>	<div>Au 79</div>	<div>Hg 80</div>	<div>Tl 81</div>	<div>Pb 82</div>	<div>Bi 83</div>	<div>Po 84</div>	<div>At 85</div>	<div>Rn 86</div>														
<div>Fr 87</div>	<div>Ra 88</div>	<div>Ac 89</div>	<div>Rf 104</div>	<div>Db 105</div>	<div>Sg 106</div>	<div>Bh 107</div>	<div>Hs 108</div>	<div>Mt 109</div>																							
																		<div>Ce 58</div>	<div>Pr 59</div>	<div>Nd 60</div>	<div>Pm 61</div>	<div>Sm 62</div>	<div>Eu 63</div>	<div>Gd 64</div>	<div>Tb 65</div>	<div>Dy 66</div>	<div>Ho 67</div>	<div>Er 68</div>	<div>Tm 69</div>	<div>Yb 70</div>	<div>Lu 71</div>
																		<div>Th 90</div>	<div>Pa 91</div>	<div>U 92</div>	<div>Np 93</div>	<div>Pu 94</div>	<div>Am 95</div>	<div>Cm 96</div>	<div>Bk 97</div>	<div>Cf 100</div>	<div>Es 101</div>	<div>Fm 102</div>	<div>Md 104</div>	<div>No 104</div>	<div>Lr 104</div>

- 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

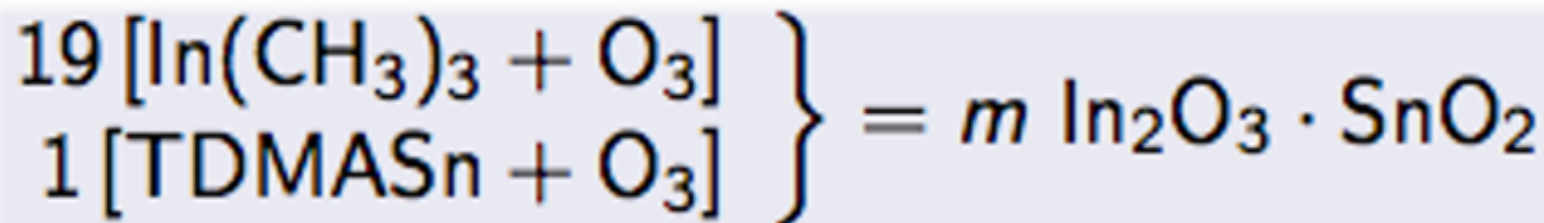
ALD For Radiators - Pigments



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.

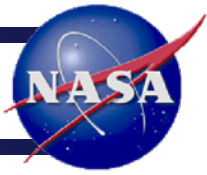


For “standard 5%” Sn doped indium oxide we apply a super cycle





Experimental Procedures

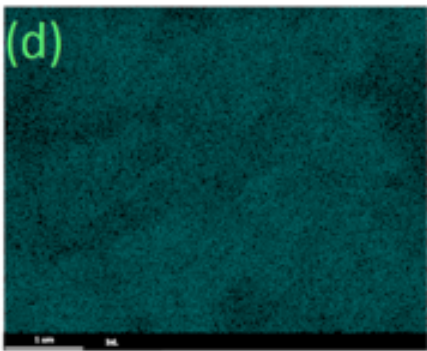
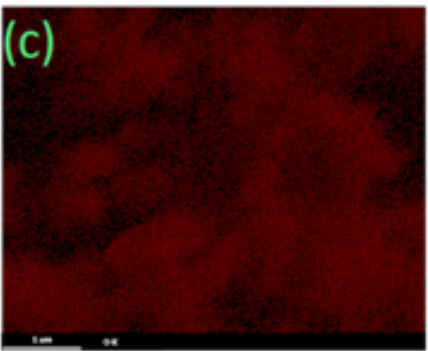
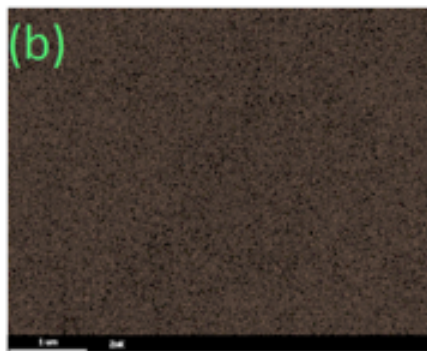
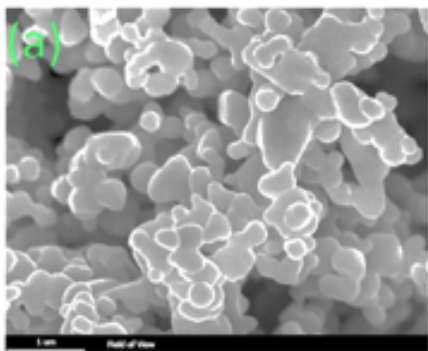
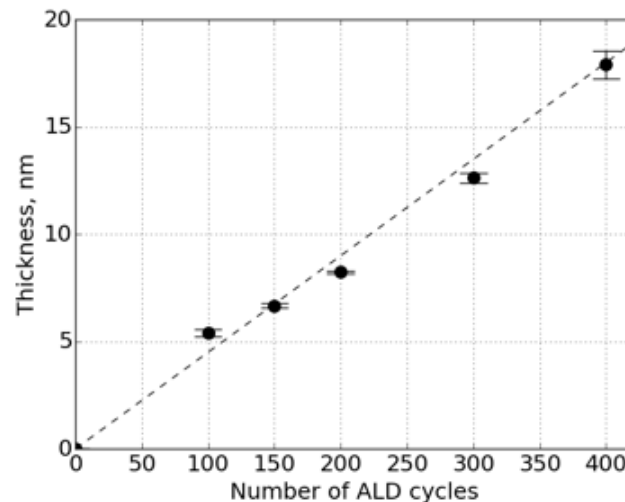


- The first set of experiments were conducted on flat substrates for the ALD of In_2O_3 and ITO, the films were deposited on a variety of substrates including n-type Si(100) wafers for thickness measurements and glass microscope slides for sheet resistivity determination.
- The In_2O_3 ALD on the particle 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.

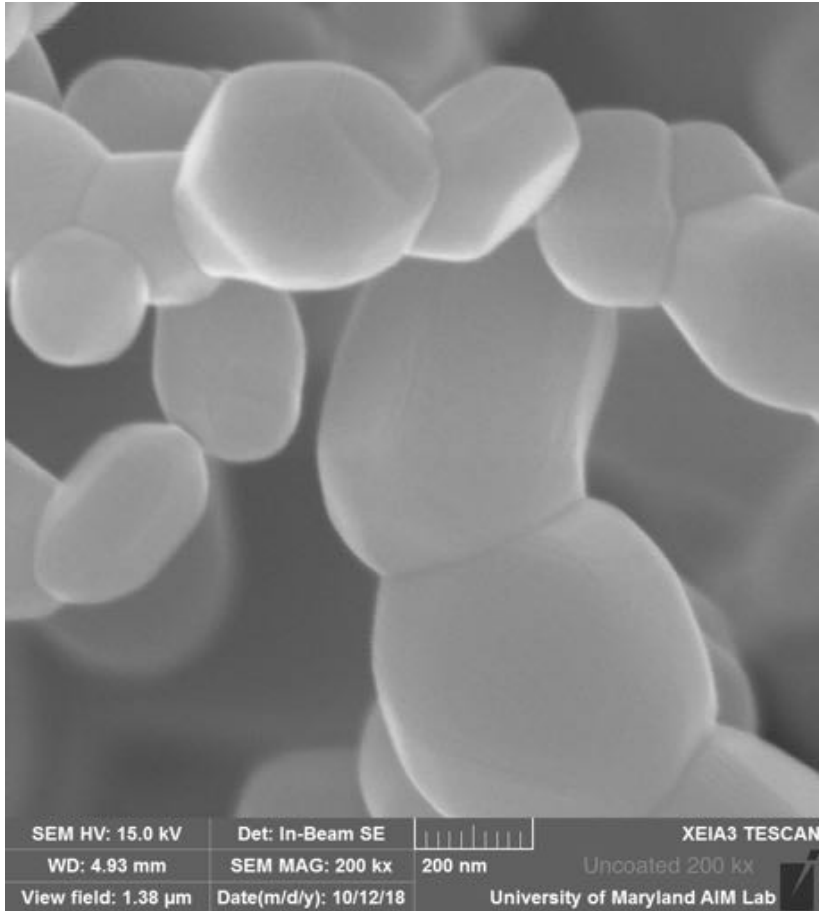
The growth Vs. the number of ALD cycles confirms a self-limiting gpc 0.46 Å/cycle for indium oxide.

A saturated growth was observed to result in gpc of 0.55 Å/cycle independent of the process temperature.

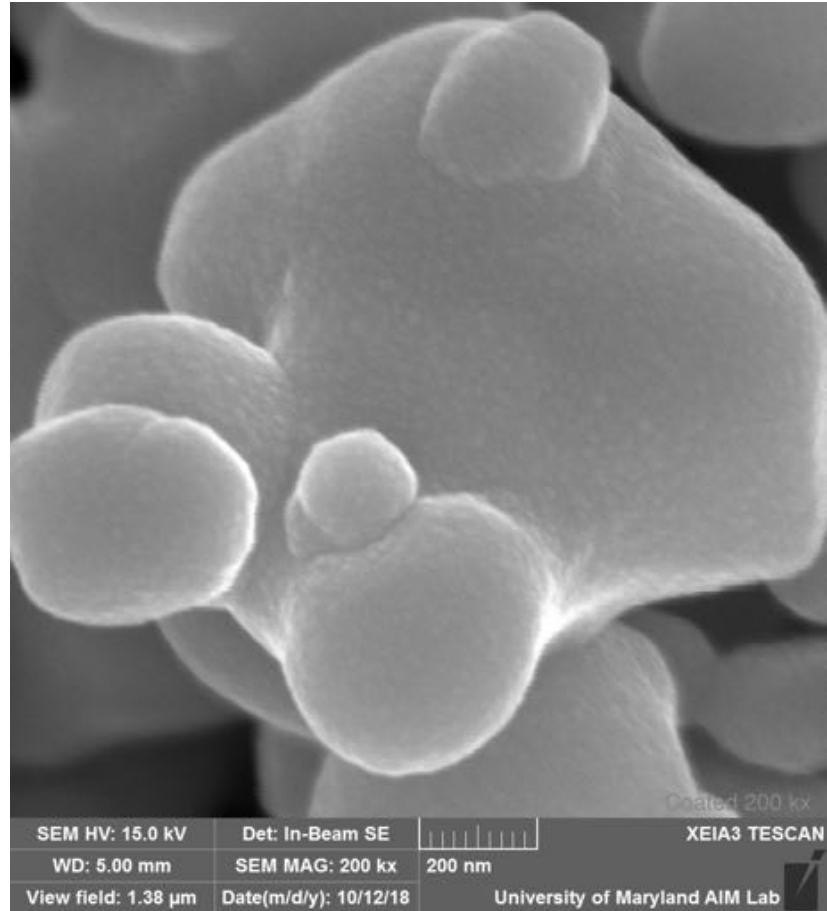
At 413K small crystal grains are formed 20nm in size. This is consistent with the onset of crystallization reported for similar system.



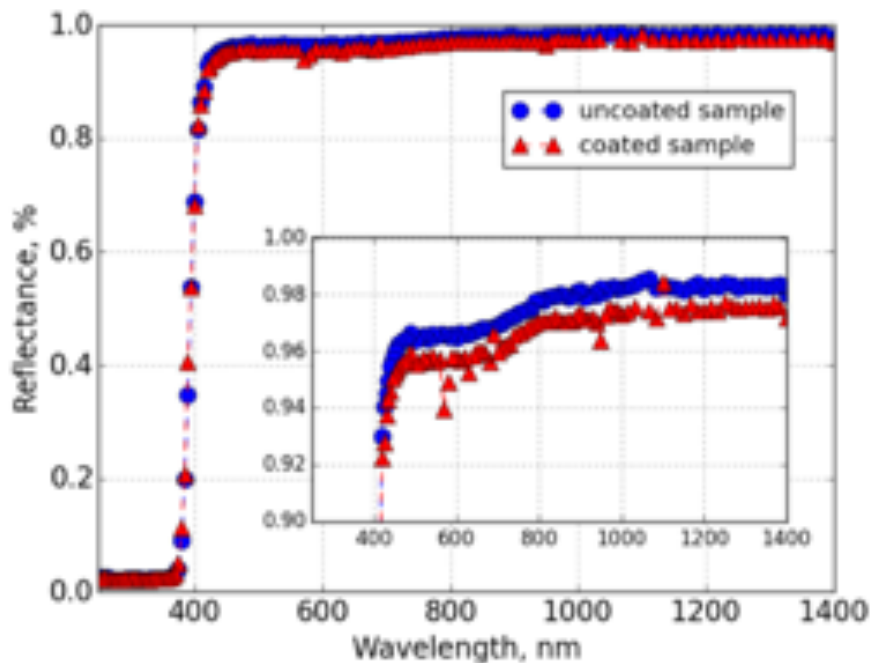
EDS scan of coated Z93 particles deposited with 600 ALD cycles at 135 °C in a regular flow-type ALD process. Image of the mapping area (a), Scan for Zn (b), O (c), and In (d). The black background is the carbon tape used for fixing the particles.



Uncoated Pigment



Coated Pigment



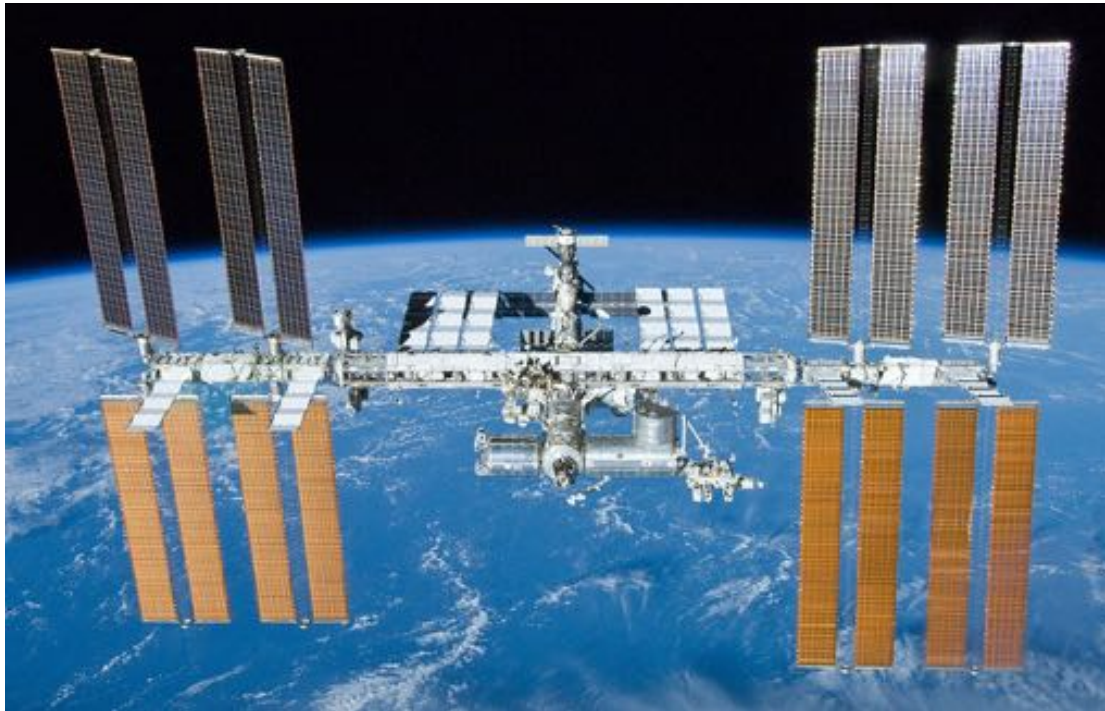
Reflectance measurements were taken on lightly compressed pellets of the untreated and indium oxide treated Z93P pigment and show approximately one percent reflectance differences across the solar spectrum

	BOL (Cold Case)	
	Absorptivity (α)	Emissivity (ε)
Z93	0.13	0.92
Coated Z93	0.14	0.92



Pressure (Torr)	Sample	Applied voltage	R(Ohms)
7.60×10^{-2}	coated Z93	40	$1.30 \times 10^{+8}$
	original Z93	40	$5.10 \times 10^{+8}$
7.00×10^{-1}	coated Z93	40	$1.60 \times 10^{+8}$
	original Z93	40	$8.00 \times 10^{+10}$
7.00×10^{-2}	coated Z93	40	$1.80 \times 10^{+8}$
	original Z93	40	$1.80 \times 10^{+11}$
6.00×10^{-2}	coated Z93	100	$7.00 \times 10^{+7}$
	original Z93	100	$6.00 \times 10^{+10}$

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.



The Materials ISS Experiment Flight Facility (MISSE-FF) with MISSE Sample Carriers (MSCs) in the fully open position exposing samples/experiments to the harsh environment of space in low-Earth Orbit (LEO). Image courtesy of Alpha Space.



An earlier MISSE mission

Many Thanks

