Technology Development for the Modification of High Aspect Ratio Geometries for Thermal and Environmental Control

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A key technology development driver in environmental control systems and next generation optics are discussed utilizing thin film development borrowed from the semiconductor industry. The optical and physical properties of spacecraft radiator coatings are dictated by orbital environmental conditions. For example, coatings must adequately dissipate charge buildup when orbital conditions, such as polar, geostationary or gravity neutral, result in surface charging. Current dissipation techniques include depositing a layer of ITO (indium tin oxide) on the radiator surface in a high temperature process. The application of these enhanced coatings must be such that the properties in question are tailored to mission-specific requirements. The multi-billion-dollar semiconductor industry has adopted Atomic Layer Deposition (ALD) for self-assembly and atomic-scale placement. ALD is a cost-effective nanoadditive-manufacturing technique that allows for the conformal coating of substrates with atomic control in a benign temperature and pressure environment. By using ALD, modification of these coatings can be accomplished during coating application preprocessing. The preprocessing is rendered directly on the coating dry pigment before binding. Through the introduction of paired precursor gases, thin films can be deposited on a myriad of substrates ranging from glass, polymers, aerogels, metals, powders, and other high aspect-ratio micro- and nano-structures. By providing atomic-level control, where single layers of atoms can be deposited, the fabrication of metal transparent films, precise nano-laminates, and coatings of nano-channels and pores is achievable. A method has been demonstrated for the ALD of In_2O_3 and films on a variety of substrates from Si(100) wafers, glass slides, and on Z93P pigments resulting in a direct spaceflight application. Results will be presented that verify the chemical composition of ALD pigments and charge dissipation properties when the pigment goes through its binding and coating process and we present early results of ALD for carbon nanotube formation and encapsulation.

Nomenclature

ALD	= *Atomic Layer Deposition*
In_2O_3	= *Indium Oxide*
SnO_2	= *Tin Oxide*
ITO	= *Indium Tin Oxide*
ESD	= *Electrostatic Discharge*
EMI	= *Electromagnetic Interference*
CVD	=*Chemical Vapor Deposition*
Sn	=*Tin*
In	=*Indium*

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I. Introduction

CHARGED Charged particles trapped by the Earth's magnetic field in the Van Allen radiation belts are the primary cause for the differential charging of spacecraft components. The Van Allen belts can vary in shape and radiation level due to solar variations and magnetic disturbances; they generally extend from approximately 1000 km to 6 Earth radii. If not dissipated, differential charging can lead to electrostatic discharge (ESD) between high potential and low potential components in spacecraft. ESD may cause electromagnetic interference and arcing resulting in damaged integrated circuits, blown fuses, electronics failures, operational anomalies and degradation of thermal control surfaces (Kauder 2005) (Gilmore 2002)

Differential charging can be a major concern in the case of nonconductive thermal control coatings used for spacecraft radiator panels. The main cause of differential charging on these components is the flux of low-energy electrons in the Van Allen belts since high-energy electrons easily penetrate the thin thermal coating and so do not cause charge buildup on the surface. The buildup charge is not completely compensated by low-energy protons due to their lower flux. The level of charging depends on factors such as flux intensity, specific coating material, surface contamination, and temperature. (Kauder 2005) One method to reduce differential charging is to apply a thin (∼200 ˚A) transparent conductive layer such as indium tin oxide (ITO) on nonconductive surfaces. Considering the relatively low electrical currents generated in orbit, typical 1×10−8 A/cm2, coatings with the sheet resistivity less than 105 Ω/ are sufficient to dissipate charge. (Kauder 2005)

An alternative to applying a conductive layer to the thermal coating surface is to modify the electrical properties of the thermal coating pigments before binding and spray application. The motivation for pre-processing the pigments is that this approach is not limited by the geometry of the spacecraft part to be coated, such as requiring a large deposition chamber to accommodate parts of different sizes making up the complete thermal radiator panels. (V. Dwivedi 2018)

To achieve the above goal, a deposition method is needed to conformally coat the micron- size radiator pigments. Furthermore, since the primary function of these pigments is to efficiently dissipate heat it is desired to coat them with the minimal amount of a conductive layer to avoid degradation of pigment optical properties. Atomic layer deposition (ALD) is a cost effective gas- phase nanoadditive-manufacturing technique that allows for the conformal coating of substrates with atomic control of film thickness.[(Puurunen 2014) (H. Salami 2017) (E. Ahvenniemi et al. 2017)] The self-limiting nature of ALD processes result in thin films that can be deposited on a myriad of substrates, from flat surfaces to those with significant topography. Recently, we have demonstrated that indium oxide (IO) and indium tin oxide (ITO) ultra-thin films can be uniformly grown on standard quartz and silicon substrates using ALD with trimethylindium (TMI), tetrakis(dimethylamino)tin (TDMASn), and ozone as precursors.[(A. U. H. Salami 2019)] Both IO and ITO are widely used as transparent conducting oxides in different applications including spacecraft component coatings.[(Kauder 2005) (J. W. Elam 2008)]

There are many groups who have successfully used ALD to coat particles with a range of size distributions for varying applications. Most of these studies have used fluidized bed (FB) reactor designs. For example, Wank et al, (J. R. Wank 2004)demonstrated the application of FB reactors for ALD experiments by coating Ni particles with alumina. They used the same alumina ALD process for coating boron nitride particles to increase their adhesion to epoxy resins. Hakim et al.[(L. F. Hakim 2005)] used a FB reactor to perform ALD of alumina on nano-sized silica particles. King et al.[(D. M. King 2008)] also used the same design to coat silica and titania nano-particles with zinc oxide films for applications in UV-blocking cosmetic particles. More recently Kaariainen et al.[(T. O. Kaariainen 2017)] used FB-ALD for coating acetaminophen particles for pharmaceutical applications. McNeary et al.[(W. W. McNeary 2018)] and Guo et al.[(J. Guo 2018)] also used FB-ALD to deposit titania and alumina nanostructures for catalyst synthesis.

While being the most promising method for large-scale ALD processing of particles, FB-ALD can require sophisticated reactor designs to assure proper fluidization of the particles and effective transport of ALD precursors. Likewise, when FB-ALD is used to coat lightweight nano-sized particles, a significant portion of each batch may be entrained in the carrier gas leading to a small recovery To avoid this issue Kikuchi et al. proposed an alternative ALD reactor design where particles were fixed on a substrate by applying an electrostatic potential and were mixed by a scraper attached to a rotator. This approach was proven successful in coating gold nano-particles with titania. Recently,

van Ommen has suggested a new design for particle ALD as a continuous process by passing the particles through a tubular reactor using a carrier gas and injecting the precursors in multiple downstream injection points (Ommen 2018).

II. ALD

ALD is a cost-effective nanoadditive-manufacturing technique that allows for the conformal coating of substrates with atomic control in a benign temperature and pressure environment. Through the introduction of paired precursor gases, thin films can be deposited on a myriad of substrates from flat surfaces to those with significant topography. By providing atomic layer control, where single layers of atoms can be deposited, the fabrication of metal transparent films, precise nano-laminates, and coatings of nano-channels and pores is achievable.

A characteristic of the surface adsorption and reaction mechanisms in ALD is that they are normally self-limiting, allowing for atomically accurate control of nanometer (nm) thickness and can be uniformly deposited on a myriad of substrates ranging from glass, polymers, aerogels, and metals to high aspect ratio geometries. Therefore, high uniformity and precise thickness control make ALD an attractive process for the creation of novel optical and other nano-scale devices. Thin films grown by ALD use alternating pulses of precursor gases where traditionally each gas contributes either a metal atom to the film or an oxygen, nitrogen or fluorine atom. An overview of the fundamental steps in the ALD manufacturing process can be illustrated in the following steps and in Figure 1.

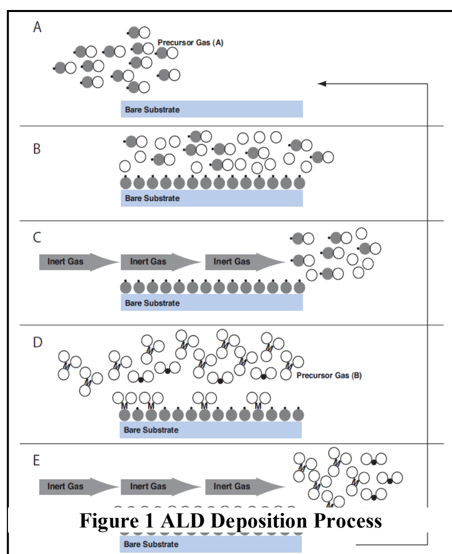


Figure 1 ALD Deposition Process

Step A: Precursor gas is pumped into a chamber containing a substrate.
Step B: Precursor gas chemisorbs on a substrate active site.
Step C: After a certain residence time the excess of the reactant precursor, which is in the gas phase or has been physisorbed on the reactor chamber walls or on the substrate, is pumped out the chamber with the aid of an inert gas.
Step D: A distinct second precursor then is pumped into the reactor chamber where it chemisorbs and undergoes an exchange reaction with the first reactant on the substrate.
Step E: This second reactant pulse results in the formation of a solid thin film; a second inert gas purge removes any excess gas from the chamber.

By repeating this cycle, controlled layer-by-layer growth is achieved. The inert gas that is pumped into the reactor between the precursor materials not only provides a separation between the precursors but ensures that a Chemical Vapor Deposition (CVD) type reaction does not occur in the gas phase. The separate and individual pulses of the precursors also allows this process to be scaled up to the desired dimensions of the substrate.

ALD Pigments

ALD is self-limiting because the surface reactions will terminate when reaction sites become inaccessible by depletion or by saturation with unreacted precursor ligands. An advantageous property of ALD is that the process is not line-of-sight; rather, any exposed surface with active sites will be coated. By taking advantage of these properties of ALD, pigments or powders can be coated conformally and with atomic-level control. A wide variety of materials have been deposited, including Al_2O_3 [(Ferguson 2000)], ZnO [(D. M. King 2008)], Co [(J.P Klesko 2016)], Pt, and Pd [(Mackus 2003)] on porous high surface area substrates powders and particles such as BN [(Ferguson 2000)]. SiO_2, Al_2O_3, opals [(Rugge 2003)] Au [(K. Kikuchi 2017)], and acetaminophen [(T. O. Kaariainen 2017)]. In all of these particular deposition chemistries the metals or metal oxides/nitrides are deposited with good thickness control and with complete encapsulation of the particulate substrate.

ALD Indium Oxide and ITO

The process of the deposition of ITO via atomic layer deposition can be separated into two distinct reaction chemistries for the surface production of indium oxide and tin oxide. A number of ALD process for In_2O_3 have been developed including the use $InCl_3$ with H_2O [(Asikainen 1994)] or H_2O_2 [(Ritala 1998)]. This process yields HCl as a corrosive

byproduct and requires a high growth temperature. Other processes that use hexalouroacetylacetonate, heptanedionate or acetylacetonate [(Elam 2006)] based indium precursors require plasma ALD processes as opposed to the simpler and conformal thermal methods to grow In_2O_3 films. For this investigation the growth of In_2O_3 films will be accomplished by using trimethylindium and ozone, as was done in a previously published study [(Mane 2016)]. The growth of SnO_2 films will be grown using tetrakis(dimethylamino)tin(IV), TDMASn and ozone. The combination of these precursors allows for a low growth temperature (100 °C) along with a common oxygen precursor to both processes, ozone. The common precursor simplifies the experimental procedures while yielding a novel method for the deposition of ITO.

III. Experimental Method

Figure 2 shows a schematic of the custom-built hot-wall ALD reactor used in this study. The reactor is a standard 4.5 in ConFlat cross with an inside diameter of 2.5 in. To measure the reactor pressure, one of the axis flanges is connected to a capacitance manometer (MKS Baratron). A multi-input dosing flange is attached to the second axis for introducing precursor pulses to the chamber. Semiconductor-grade pneumatic valves are placed on the precursor lines to control dosing. A gate valve separating the reactor from the pump is attached to the third-axis allowing for pigment particles to be exposed to the precursor gases for a set residence time. The forth axis flange was modified for particle processing via a rotary feed-through. The particles to be coated are placed inside a cylinder with the capacity to process batches of maximum 14 g, with walls consisting of a coarse mesh cage to provide rigidity and lined with a 55 micron Dutch weave mesh to prevent particles from escaping. The cylinder is capped with a KF40 aluminum flange attached to a rotating shaft. The internal shaft is attached to a Kurt J. Lesker magnetically coupled rotary motion feed- through with a co-axially mounted stepper motor. The stepper motor rotary speed is controlled by the applied voltage. The sample cylinder rotation prevents particle agglomeration and enables the precursor gases to react with the entire particle surface area. The reactor is maintained at 135 °C by a PID controller connected to a heating jacket covering the reactor walls. Z93 pigments were provided by AZ Technology Corporation with a mean particle size of 2 microns (Figure 2). all other details such as precursors used are the same as described in a previous article [(A. U. H. Salami 2019)].

Z93 particles were processed in two sets of experiments. To investigate whether the IO film can nucleate and grow on the surface of the pigment particles, 600 ALD cycles were applied to a small batch of particles fixed in position by adhesion to a carbon tape. This experiment was performed using the optimized flow-type ALD recipe described previously [(A. U. H. Salami 2019)] consisting of 0.2 s and 0.1 s pulses of TMI and ozone and 30 s Ar gas purge after each precursor pulse. To study the effect of IO coating on the conductivity of the Z93 particles, the sample cylinder and rotatory feed- through were used to coat a 12 g batch of the particles. For this experiment, the sample cylinder was rotated at a constant rate of 20 revolution per minute through the application of 1.7 V to the motor. For each precursor pulse, the ALD process recipe cycled through four steps:

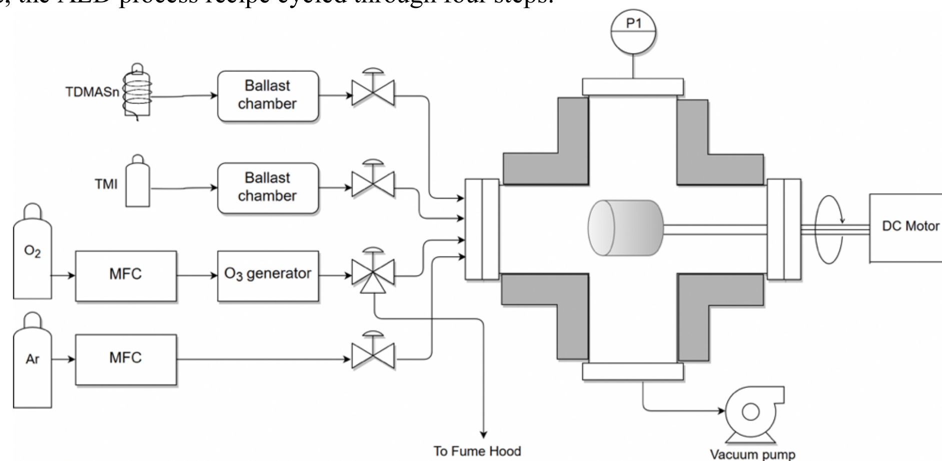
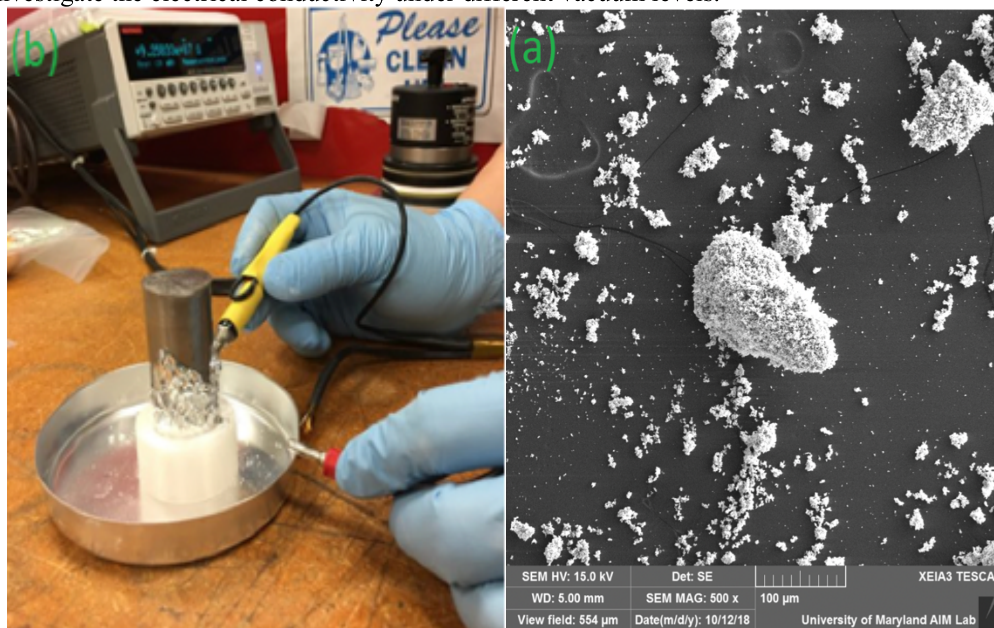


Fig. 2. Schematic of the house-built ALD reactor used to process Z93 pigments. The forth axis flange on the right side is configured for pigment particles processing via a rotary feed-through.

1. Close the gate valve and shut off the Ar flow into the chamber.
2. Pulse TMI for 0.2 s (or ozone for 0.1 s).
3. Keep the gate valve closed and the Ar flow shut off for TMI (or ozone) exposure for 5 s.
4. Open the gate valve and restart Ar flow to purge the chamber of excess precursors and byproducts.

Note that the pulse time for TMI and ozone was set to 0.2 s and 0.1 s corresponding to the saturating dose obtained for flat substrates.

Upon processing, the pigments were compressed lightly by hand and held in place by a 3D- printed electrically insulating hollow Nylon/Teflon annulus spacer held on an aluminum plate. A stainless steel rod with 1 in diameter and 3 in height was placed on top of the spacer and compressed by approximately 5 lbf. This setup, shown in Figure 3, is then biased with voltages varying from 1 to 100 V using a Keithley 6517B electrometer with a built-in source and resistance measurement. Following resistivity measurements in air, the set-up was transferred to a vacuum chamber to investigate the electrical conductivity under different vacuum levels.



(a) (b)

Fig. 3. The scanning electron microscope image of commercial Z93 heat radiator pigments (a), bulk resistivity measurements of a compressed batch of coated pigments (b).

IV. Results and Discussion

Figure 4 shows the scanning electron microscope (SEM) images of and Si substrate and Z93 pigments coated in the first set of experiments described with 600 ALD cycles of exposure to TMI and ozone in a regular flow-type ALD process. As it can be seen, IO film is able to nucleate and grow on the surface of Z93 particles confirming the possibility of the encapsulation with a thin-layer of IO. Furthermore, the structure of the IO coating is similar to that of the IO film deposited on a standard silicon substrate during the same experiment resulting in a ∼30 nm thick film. The film appears to be polycrystalline with the grain size of ∼20 nm; this agrees with the crystallization of IO films reported in the literature at 135-140 °C. [(J. A. J. W. Elam 2011)]

Energy Dispersive X-ray Spectroscopy (EDS) analysis also was performed to confirm the pres- ence of indium in the coated sample. Figure 5 clearly shows the presence of indium. Note that the Zn signal originates from the pigment itself, and O signal results from both the IO film and the Z93 pigments.

As mentioned, the primary function of Z93 or other materials used for thermal control coatings is to efficiently dissipate waste heat. These coatings are required to have high emissivity and low solar absorptivity. Therefore, it is

desirable to apply the minimum level of coating on their surface to maintain their original optical properties.[1] In our previous study, we concluded that using our precursor system, 100 ALD cycles was sufficient to produce a continues uniform IO thin-film with conductivity that satisfies the criteria required to avoid charge buildup and the subsequent ESD (A. U. H. Salami 2019) while retaining on average ~90% transparency in visible range.

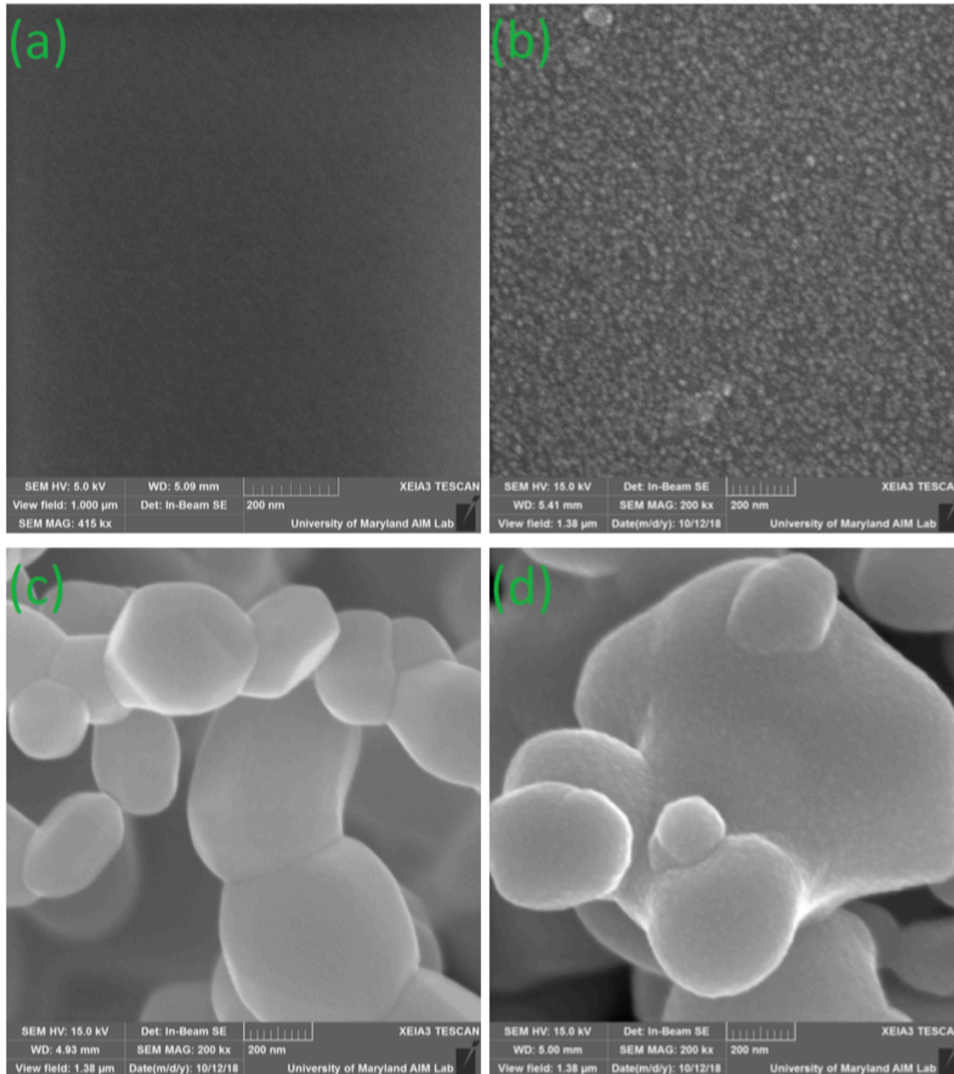


Fig. 4. SEM images showing the IO thin-films deposited with 600 ALD cycles at 135 ◦C in a regular flow-type ALD process. Clean uncoated Si wafer (a), IO film deposited on the Si wafer (b), original uncoated Z93 particles (c), coated Z93 particles (d).

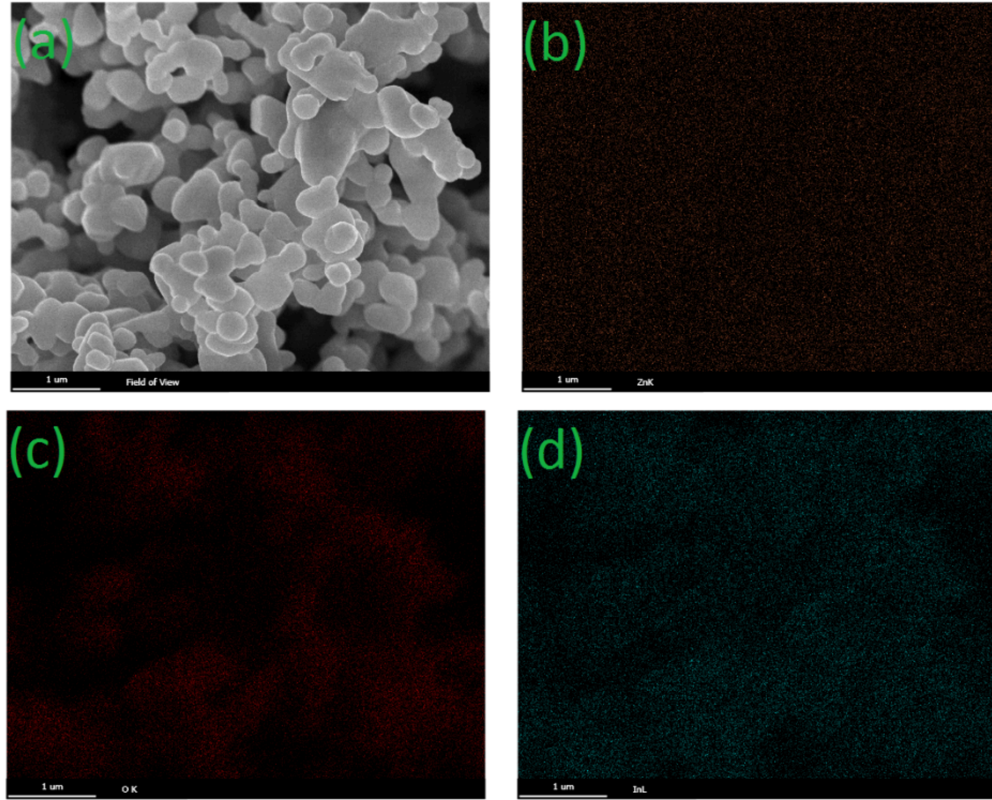


Fig. 5. EDS scan of coated Z93 particles deposited with 600 ALD cycles at 135 ◦C in a regular flow-type ALD process. Image of the mapping area (a), Scan for Zn (b), O (c), and In (d). The black background is the carbon tape used for fixing the particles.

Table 1 compares the bulk resistance in ambient pressure of the original uncoated Z93 pigment particles and a sample coated with 100 ALD cycles. It also is important to check for potential degradation of electrical properties in various environments, therefore, the bulk resistance measurements were also performed under vacuum.

The effect of the indium oxide coating can be clearly seen as the resistivity has been decreased almost with a factor of 4. As the vacuum level is increased, the difference between the resistivity of indium oxide coated and original pigments becomes more significant. This can be partially attributed to either the removal of the moisture within the bulk powder or the compression of the powder filling the void space allowing for a clearer conduction path. Figure 5 shows the reflectance of the original and processed Z93 sample coated with 100 ALD cycles of indium oxide. As it can be seen, the processed pigments have retained their original reflectance.

Pressure (Torr)	Sample	Applied voltage	R(Ohms)
$7.60\times10^{+2}$	coated Z93	40	$1.30\times10^{+8}$
	original Z93	40	$5.10\times10^{+8}$
$7.00\times10^{+1}$	coated Z93	40	$1.60\times10^{+8}$
	original Z93	40	$8.00\times10^{+10}$
7.00×10^{-2}	coated Z93	40	$1.80\times10^{+8}$
	original Z93	40	$1.80\times10^{+11}$
6.00×10^{-2}	coated Z93	100	$7.00\times10^{+7}$
	original Z93	100	$6.00\times10^{+10}$

Table 1. Bulk resistance of uncoated Z93 pigments and the sample coated with 100 ALD cycles under different vacuum levels.

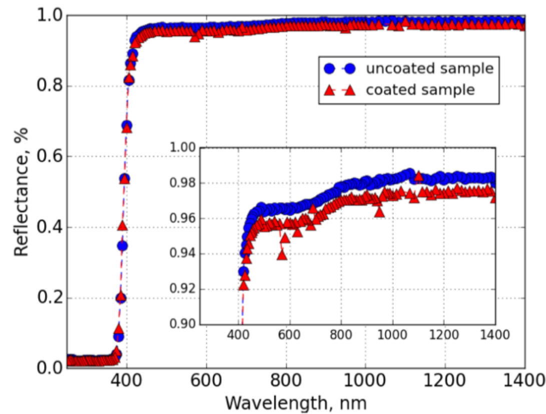


Fig. 6. The reflectance spectrum of the original and processed Z93 sample coated with 100 ALD cycles of indium oxide.

V. Conclusions

Ultra-thin indium oxide films deposited by Atomic Layer Deposition (ALD) using trimethylindium and ozone were shown to nucleate and grow on the surface of commercial Z93 thermal control pig- ment particles. The sample coated using 100 ALD cycles showed significant decrease in resistance; while under vacuum the resistance was 3 orders of magnitude lower than that of the uncoated sam- ple. Reflectance measurements of coated and original samples showed no significant degradation of optical properties. These results suggest that the ALD of indium oxide and potentially indium tin oxide can provide an alternate solution to avoid charge buildup and resulting electrostatic discharge in spacecraft thermal control coatings.

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