Novel Nanostructured Coatings onto Particles by Atomic Layer Deposition, Their Method of Manufacture, and Feasibility of Scale and Economics

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ABSTRACT

Originally developed for the semiconductor industry, atomic layer deposition (ALD) has proven a useful coating technique for the modification of particle surfaces for a wide range of applications. Both conformal and non-continuous or segmented films have been deposited to prepare nanocomposites with a variety of intriguing properties. Particles have been coated in scalable fluidized bed reactors, and process economics are favorable. These application developments have enabled a new market for research and commercial particle ALD systems.

Keywords: atomic layer deposition, thin films, fluidized bed reactors, particles, surface modification

1. INTRODUCTION

Atomic layer deposition (ALD) is a widely accepted technique for growing thin, conformal nanoscale films. It is a gas-phase process that uses sequential, self-limiting surface reactions to deposit a continuous, dense film over the entire substrate surface. After the initial nucleation period of film growth, the film grows conformally over the entire substrate surface. The self-limiting nature of the surface reactions results in digital control over the film thickness with angstrom-level resolution. Established chemistries exist for a wide range of oxide and nitride materials, as well as metal and other films. These chemistries have also been expanded to include analogous metal alkoxides in a process known as molecular layer deposition (MLD).[1]

More recently, novel chemistries and post-treatments of ALD and MLD films have been shown to provide unique nanostructures on the surfaces of a variety of substrate types, including particles and polymers. On particles, these films can be used to create nanoscale composite materials with enhanced, designed properties, such as catalytic activity, increased dispersability, or enhanced stability.

ALD NanoSolutions will present a summary of recent advances in ALD nanocoatings onto particles. The discussion will also include the methods of manufacture, including the equipment used. Lastly, the topics of scalability and economics will be addressed.

2. DISCUSSION

2.1 Conformal Films

ALD films can have different nanostructures, which can in turn be used for a variety of applications when applied to particles. Standard conformal ALD films have the broadest suite of applications. Examples of particles coated with conformal nanoscale ALD films are shown in Figure 1. Note the uniformity and conformality of the films.

Uniform and pinhole-free films can be used as a barrier for protection of a substrate, to electrically insulate a substrate, or make a substrate more compatible with a matrix or resin material. The thinness of the ALD films means that the surfaces of the substrates can be modified while having minimal effect on the bulk properties of the particles. The degree of thickness control allowed by ALD enables novel applications of these types of coatings.

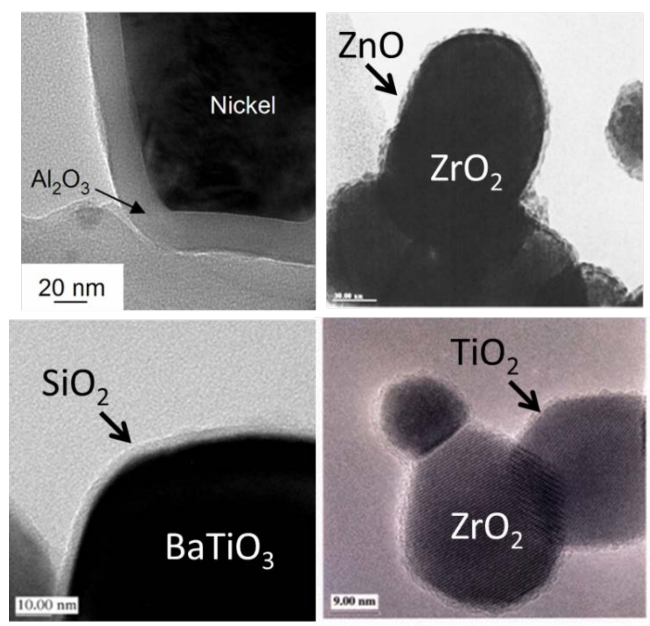

Figure 1. Examples of ALD-coated particle substrates

Figure 2 shows the effectiveness of ALD for the protection of metal particles from oxidation. Alumina films on the order of nanometers are able to significantly shift the temperature at which oxidation begins for copper and nickel. The performance of the barrier film is a function of the film thickness, meaning that the resistance can be tuned for specific applications.

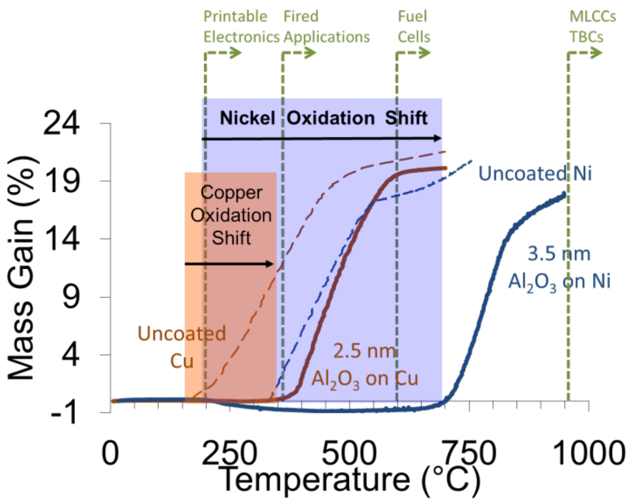

Figure 2. Oxidation barrier performance of alumina ALD films

Another example application of conformal ALD films is surge suppression. An ALD film can be used to precisely control the electron tunneling distance between conductive particles in a matrix. Fowler-Nordheim tunneling effects can then be exploited to achieve highly-nonlinear voltage response curves with fast response times. These varistors (variable resistors) can be tuned by varying the thickness of the ALD film. Figure 3 compares the performance of a traditional ZnO varistor to the tunable ALD quantum tunneling varistor. Note the absence of voltage overshoot, the sub-nanosecond response time, and the tunability of the ALD varistors. And because the ALD varistor functions via quantum tunneling, it can handle multiple voltage surges, whereas ZnO varistors cannot, since they undergo an irreversible chemical change (ZnO to Zn metal) as a result of the surge. The ALD varistor also has a significantly lower capacitance (on the order of 40 pF) as compared to a traditional ZnO varistor (on the order of 500 pF).

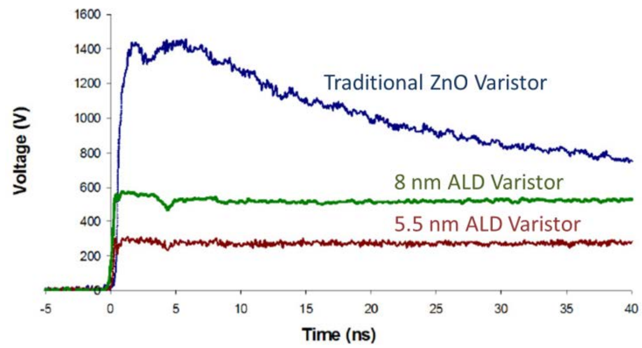

Figure 3. Voltage response to a 5 kV surge for a traditional ZnO varistor and two ALD quantum tunneling varistors

One final example of the performance of conformal ALD films is for increasing the compatibility of fillers with matrix materials. As an example, BN is used as a thermal filler in applications requiring UV transparency and low electrical conductivity. However, the BN surface is very inert, and is incompatible with resin materials. The result is an effective limitation on filler loading due to the viscosity of the filled material. Thin ALD films can convert the inert BN surface to a more compatible Al_2O_3 or SiO_2 surface, reducing the viscosity of the filled resin and allowing for higher loading levels, thus increasing the achievable thermal conductivities. Because the ALD films are nanoscale in thickness, they have minimal effect on the thermal conductivity of the filler. Figure 4 shows viscosity vs. shear data showing the ability of ALD films to increase the compatibility of the BN filler and the resin.

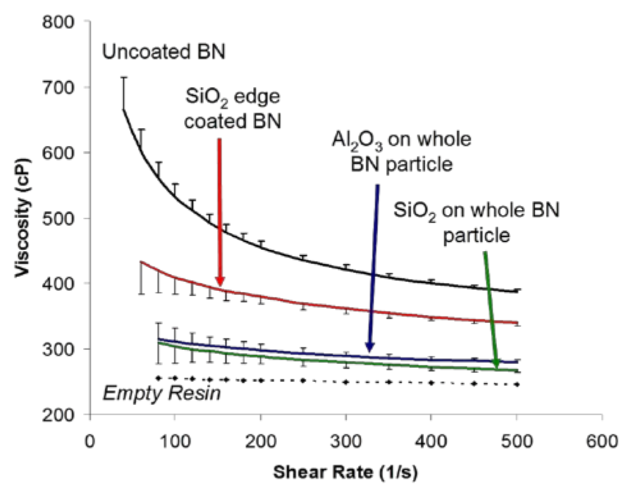

Figure 4. Example of the ability of ALD films to modify the viscosities of BN-filled thermal resins

2.2 Non-conformal or Segmented Films

ALD films can also be deposited non-conformally or with a segmented morphology. This is typically accomplished by limiting the number of ALD cycles performed on a substrate to fewer than the number of cycles required to nucleate a conformal film. Films of this nature

NSTI-Nanotech 2013, www.nsti.org, ISBN 978-1-4822-0581-7 Vol. 1, 2013

can be used to passivate the most reactive sites (such as surface defect sites) of a substrate while having minimal effect of more stable sites. This has proven useful in increasing the performance of Li-ion battery electrode materials. Selective deposition of ultra-thin Al_2O_3 films onto the electrodes passivates the reactive defect sites on the electrode, preventing the formation of the insulating solid-electrolyte interface (SEI) film. The result is an increase in the capacity retention of the battery (Figure 5). Whereas the battery made from the uncoated electrode loses about 85% of its starting capacity after 200 cycles, the battery made from the ALD-coated electrode has only lost about 20% of its starting capacity. This counterintuitive result of increasing the performance by placing a resistive material in an electrical system is just one instance of the unique and unexpected behavior ultra-thin ALD films can exhibit.

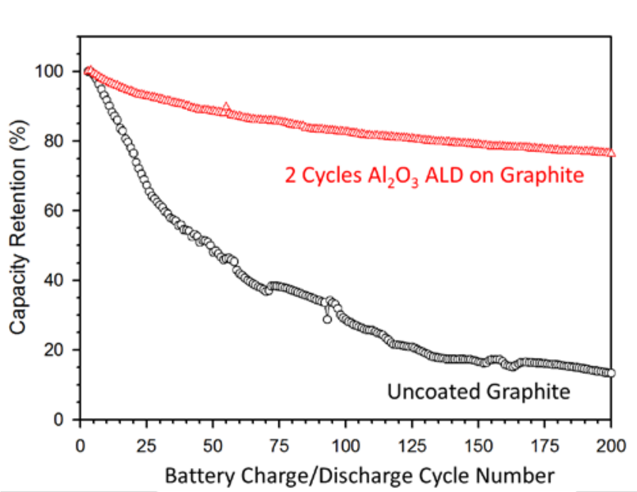

Figure 5. Improved charge/discharge stability for a Li-ion battery made using ALD-coated electrodes

Other novel nanostructures can also be created through ALD. While metals can be deposited conformally by ALD, they typically exhibit long nucleation phases. As a result, ALD can be used to deposit them as distributed islands over a substrate surface. This results in a very high active surface area for the deposited materials. This film morphology is highly attractive for catalytic applications. ALD has been used to deposit highly active Pt, Pd, and other catalytic metals onto supports. Figure 6 shows an example of nanoclusters of Pt on high surface area TiO_2. Other porous nanostructures deposited by ALD have been shown to act as stabilizing mesh over catalyst particles, preventing the sintering of the catalysts and the resulting loss in activity.

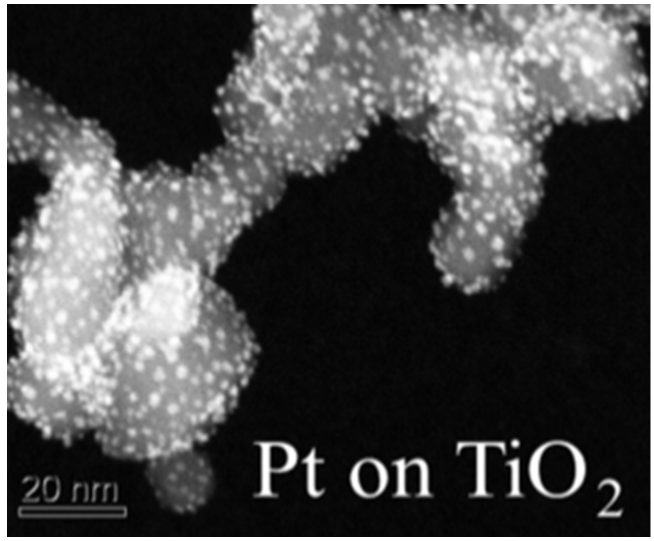

Figure 6. TEM image of a TiO_2 nanoparticle coated with nanoclusters of Pt (bright spots)

2.3 Scalable Deposition Systems

ALD has initially been commercialized in the semiconductor industry using batch tools to coat silicon wafers and other low-surface area substrates. Those tools are not suitable for the coating of large amounts of high surface area powders. In order to prevent the agglomeration of particles during the coating process at static contact points, which would cause defects in the continuous films and ruin the performance in some applications, reactor designs that continually agitate the particles during the coating process are necessary. This is commonly done with a fluidized bed or rotary reactor. Both types fluidize the material throughout the entire coating process while gases are introduced and removed from the system. Both reactor types have been used and scaled in a variety of industries for the processing of very large amounts of material.

Being a gas-phase process, ALD is inherently scalable and comparable to many similar gas/solid reaction processes that already exist for particles. The gas phase nature also allows for ALD processes to use standard vessels and equipment used for particle handling. For example, fluidized beds are commonly used at very large scale. ALD has already been demonstrated at both the lab (100 ml) and pilot (8 liter) scales for fluidized bed processing. Work at both scales indicates that further scale up should be possible.

Economics must also be considered when looking at new technologies. Modeling has shown that major cost drivers for an ALD process are substrate surface area, number of cycles, and precursor cost. Depending on annual production volume, labor may or may not be a driving factor. For typical combinations of substrate properties and production volumes, coating costs can range anywhere from tens of cents per kilogram to dollars per kilogram. Given the possible performance improvements of ALD coated materials, this increased cost can be absorbed by a wide range of applications.

CONCLUSIONS

ALD on particles can provide unique opportunities to control surface chemistry or create new composite materials. These techniques can create a wide variety of structures to suit many different commercial applications from batteries, to catalysts, to novel pigments. These materials can be produced at any scale needed for the application in a cost effective manner. The application developments have generated a new market for research and commercial particle ALD systems.

REFERENCES

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NSTI-Nanotech 2013, www.nsti.org, ISBN 978-1-4822-0581-7 Vol. 1, 2013