

**Atomic Layer Deposition on Nanoparticles in a
Rotary Reactor**

by

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PREVIEW

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Atomic Layer Deposition on Nanoparticles in a Rotary Reactor

Thesis directed by Prof. Steven M. George

Challenges are encountered during atomic layer deposition (ALD) on large quantities of nanoparticles. The particles must be agitated or vigorously mixed to perform the ALD surface reactions in reasonable times and to prevent the particles from being agglomerated by the ALD film. The high surface area of nanoparticles also demands efficient reactant usage because large quantities of reactant are required for the surface reactions to reach completion.

To address these challenges, a novel rotary reactor was developed to achieve constant particle agitation during static ALD reactant exposures. In the design of this new reactor, a cylindrical drum with porous metal walls was positioned inside a vacuum chamber. The porous cylindrical drum was rotated by a magnetically coupled rotary feedthrough. By rotating the cylindrical drum to obtain a centrifugal force of less than one gravitational force, the particles were agitated by a continuous “avalanche” of particles.

The effectiveness of this rotary reactor was demonstrated by Al_2O_3 ALD on ZrO_2 particles. A number of techniques including transmission electron microscopy, Fourier transform infrared spectroscopy, scanning Auger spectroscopy and x-ray photoelectron spectroscopy confirmed that the Al_2O_3 ALD film conformally coats the ZrO_2 particles.

Combining static reactant exposures with a very high surface area sample in the rotary reactor also provides unique opportunities for studying the surface chemistry during ALD. Sequential, subsaturating doses can be used to examine the self-limiting behavior of the ALD reactions in the rotary reactor. This dos-

ing method is the first demonstration of self-limiting ALD on bulk quantities of nanoparticles.

By combining these sequential, subsaturating doses with quadrupole mass spectrometry, ALD reactions can be analyzed from the gas phase using full mass spectrum analysis. The reaction products are present in a high enough concentration to discern a gas phase mechanism for reactions which previously only had surface studies as mechanism determination and characterization.

PREVIEW

If I had six hours to chop down a tree,
I'd spend the first four sharpening the axe.

—Abraham Lincoln

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Acknowledgements

I could easily write a chapter in this dissertation thanking everyone that has helped along this long road. Newton once wrote in a letter to Hooke, “If I have seen further, it is by standing on the shoulders of giants.” I’m not sure that I’ve seen further, but I know that anything that I have accomplished, is mostly due to the giants listed here.

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My lifelong friends Feet and Donnie have been there, literally, from day one. In another twenty-seven years, I know we will still be just as good of friends

as we always have been. I heard the guys at Webster's were in the process of updating their dictionaries with that golf pros picture of us under the definition of friendship.

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like the sky was the limit, and that I was encouraged to reach past that. Thank you for that encouragement and support.

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PREVIEW

Chapter 1

Introduction

In 1960, Richard Feynman, who later was awarded the Nobel prize in physics, presented a lecture entitled *There's Plenty of Room at the Bottom* on the idea of manipulating materials on the atomic scale [44]. At the time this was a largely unpopular lecture. It was taken by the audience as a farce, as the foundation for an epic science fiction novel – anything but science. It was such an innovative talk, that one scientist noted, “it was so visionary that it did not connect with people until the technology caught up to it.” [96] But today, nearly 50 years later, he's still right. There *is* plenty of room at the bottom, and with each passing day, it seems the bottom gets more and more spacious.

Many years after Feynman's legendary lecture, the word nanotechnology was coined. The prefix *nano*, literally small in meaning, brought with it a large wave of research at the atomic scale. The arrival of nanotechnology broke ground for the creation of new materials that had properties unlike anything ever seen before. Many of these materials followed only the laws of quantum mechanics, in sharp contrast to the classical laws of the macroscopic world.

For example, a semiconductor has a physical property, called the Bohr exciton radius. This radius is the average distance between electron-hole pairs in the crystal. When a semiconductor particle is smaller than the Bohr exciton radius, the electron-hole pairs are forced to be closer together than they would be nat-

urally, which drastically changes the electronic properties of the material. These particles are referred to as quantum dots. Through this quantum confinement, the bandgap of quantum dots can be altered by manipulating the particle size alone. These tunable structures can then be used in numerable optical and electronic applications. The constraints on confinement can be lifted in one or two dimensions creating quantum wires and quantum wells, respectively, each with seemingly limitless applications.

The advent of nanotechnology has also brought with it an investment in theoretical work. This will inevitably help future generations pave the way towards understanding and exploiting these interesting new materials. In an exceptional coincidence, this theoretical research has coincided with the exponential increase in floating-point operations, or “flops”, capable by a computer processor. This has allowed theoretical code to be developed that utilizes a stratospheric number of flops, which could have taken an esteemed researcher’s entire life to complete if started during the 70’s, and now, reduced it to a graduate student’s lazy weekend worth of computation.

In recent years, the horizon of nanotechnology has changed. Materials have been synthesized on even the smallest of size scales. A large number of new nano words have even been introduced into the science lexicon for these materials – nanoparticles, nanowires, nanotubes, nanorods, etc. The horizon of nanotechnology is now shifting from synthesis of these nanomaterials, to creating new structures with these materials. A new question arises, just as the first question that was invariably asked upon the invention of the wheel, “But what can we *do* with this?”

For now, the answer to this question in terms of nanotechnology, is create composites and metamaterials.

Composite materials are created when materials are combined to make a

more complicated structure. This can be different materials laminated together, or a mixture of strategically placed materials. Think of a computer processor. It is made up of mostly silicon – the magical component in sand and most wine glasses. But the way the silicon is organized, the way it is assembled with dielectric materials, metal gates and interconnects is the key to its success as a computer processor.

Composite materials can be made using nanotechnology that drastically change the properties of a material. In a Science paper published in 2004, a nanolaminated material was created between repetitive Al_2O_3 and W layers so that the many interfaces scattered the phonons needed for heat transfer. This material transferred heat with an ultralow thermal conductivity due to the ability to create such small and ordered nanolaminates [19]. Using different bilayer spacings of the same Al_2O_3 and W nanolaminated structure, a material with the highest ever recorded reflection of x-rays was created [35]. Just think of all the different possibilities and permutations if we start to look at composites of materials other than Al_2O_3 and W!

Metamaterials are materials that gain their unique properties due to the structure of the materials contained within. They are a periodic array of substructures, much like a psuedo-crystal with a nano-sized structure as a basis. The elemental components of these materials are definitely important, but their structure is the key. Just as graphite and diamond are made up of the same elements, but have varied uses (and prices!), metamaterials are the psuedo-crystal extension of that same thought.

Metamaterials created using repetitive nanostructures of specific shapes like spheres, can guide light along paths, much like water through plumbing. The field that defines this interaction of nano-based metamaterials with light is called photonics. It has become such a popular emerging field, that the Nature Publishing

Group launched a topical journal, *Nature Photonics* in January of 2007, specifically aimed at this new field of research.

There are certainly many unexplored topics in the foundations of nanotechnology, but the state-of-the-art is heading in the direction of manipulation of nanomaterials to create new composites and metamaterials. These designer materials can be engineered to create the properties of interest for a certain application, even if the particular elements involved don't necessarily have those properties in the bulk, or even nano, scale.

The structure of nanomaterials can be altered in a number of ways to create composites and metamaterials. For example, nanosphere lithography permits patterning of repetitive spherical materials on a substrate of choice and is quite useful in photonics. A coaxial cable of nanometer diameter can be created by layering materials of different conductivities on a carbon nanotube. Novel, more effective, sunscreens can be created through nanolaminates of traditional ceramic sunscreen additives. The tie that binds most of these interesting applications together is the ability to deposit a conformal layer of material with nanometer dimensions onto a substrate, which doesn't necessarily have to be of nanometer dimensions.

Coatings in the macroscopic world are as ubiquitous in materials development as they are in everyday life. Just think how different life would be without the leather on the outside of a baseball, water sealant on the back patio or even fondant on a high-end wedding cake. Development of coatings for wear resistance, waterproofing and even aesthetics have allowed the quality of life to increase throughout the world. The development of this area is crucial to the advancement of nanotechnology, and will have a large impact on society and quality of life in the coming years.

With developing technologies such as the 32 nm node for computer processors, the energy saving photonic light bulb, and the passing of the carbon

nanotube's teenage years, it is safe to say that there is still plenty of room at the bottom, Dr. Feynman, to safely install a diving board.

1.1 Statement of Purpose

This dissertation is concerned with depositing conformal layers of materials onto nanoparticles using atomic layer deposition. The methods of coating nanoparticles will be examined and a novel approach to depositing conformal coatings on nanoparticles is designed and characterized. This technique is generalized and applicable to all small, particulate material of any shape and size.

It will also be shown that this method can be extended to determine mechanisms of atomic layer deposition reactions from the gas phase. By utilizing subsaturating doses coupled with quadrupole mass spectrometry, the gas phase products of the atomic layer deposition reactions can be determined. This allows correlation of the surface species to gas phase species which can lead to a mechanism for the reaction.

The ability to deposit very thin and conformal films on structures, independent of shape, is the main theme of this dissertation. This is one of the first steps in being able to make designer composites and metamaterials of any shape, size or material.

Chapter 2

Relevant Background Information

2.1 Thin Film Deposition

Many industries rely on a multitude of deposition techniques to accurately deposit thin films of various dimensions and morphologies onto many different substrates [105]. These thin films can vastly change the optical, electromagnetic, chemical and mechanical properties of a material, while leaving the bulk properties largely unchanged. Many chemically different thin films can also be specifically arranged using fabrication techniques to create devices, such as computer processors.

In recent years, considerable energy and effort has been devoted to multidisciplinary research involving thin film deposition methods and chemistries. The focus of most of this newer research has been largely driven by the International Technology Roadmap for Semiconductors (ITRS) which identifies the future needs and challenges presented to the microelectronics industry [1]. This requires thinner, more perfect and conformal thin films of both metals and dielectrics, with tighter size restrictions each passing year.

For example, in 2007, at the time of this writing, the size of each metal oxide semiconductor, field effect transistor (MOSFET) structure has to be 65 nm or smaller as dictated by the ITRS. By 2012, each transistor has to be 36 nm to keep up with the slated demand. This size includes the metal gate as well as the

dielectric layer, as well as any seed or diffusion barrier layers necessary for proper functioning of the device. These requirements, while seemingly insurmountable, are slated to be met with current technology until 2010. After that, new thin film deposition technologies and chemistries will be required to meet needs.

While the major driver of these techniques has been the microelectronics industry, thin film deposition has a multitude of other uses. Thin films can be deposited as catalytic layers [75], optical materials [27], biocompatible materials [109], as well as corrosion resistant layers [115] on a multitude of substrates. The ability to modify the surface of materials has an immense number of applications.

So far, the definition of the word thin has been quite ambiguous. When speaking of the microelectronic devices, the word thin means something of nanometer thickness whereas to an atmospheric chemist, thin could easily describe the thickness of the ozone layer, which is about 15 km [94]. In this context the word thin will be used to denote a film that can be deposited with nanometer, or sub-nanometer, control even if the resulting deposited layer is microns or larger in thickness.

Thin film deposition can either be carried out using physical or chemical methods [105]. Physical methods deposit thin films through a thermodynamic driving force. A typical example of physical deposition is thermal evaporation of metals. Chemical methods deposit thin films through chemical reactions. These reactions can be performed in the gas or liquid phase. There are also some techniques, such as plasma processes, that are hybrids between purely physical and purely chemical-based deposition methods.

The most common type of physical deposition, is physical vapor deposition (PVD) [105]. This type of deposition involves evaporating a material into the gas phase and condensing it onto a substrate. This method provides for uniform deposition onto many types of substrates, but is a line-of-sight chemistry, mean-

ing that the evaporating material to be deposited has to have a line-of-sight to the substrate to deposit on it. Substrates that are not entirely flat will not be deposited on conformally and regions that received no deposition will look like shadows.

Chemical deposition involves depositing materials in which a chemical reaction is involved in creating the thin film. Chemical-based processes include electroplating and sol-gel chemistries where liquid chemistries are involved, as well as gas phase chemistries like chemical vapor deposition (CVD) and atomic layer deposition (ALD). Chemical methods of thin film deposition tend to not be line-of-sight and can deposit on the entire surface of the substrate regardless of shape.

As size scales are decreased in thin film deposition the conformality and step-coverage of the thin films is of great concern. These types of deposition are explained in Figure 2.1. Step-coverage is the ability of a chemistry to deposit isotropically along the sidewalls of a step. As shown in Figure 2.1a, the deposition is nonisotropic and favors the upward facing surfaces, whereas Figure 2.1b shows a very good step coverage. Conformality is the ability of the chemistry to not only have good step-coverage, but also deposit in a very uniform thin film. Examples of bad and good conformality are shown in Figure 2.1c and d, respectively.

To fulfill the goal of this dissertation and deposit thin films on particles, the deposition has to be conformal over the entire particle surface. For this, the logical choice is chemical-based methods of deposition. This leaves a choice between liquid and gas phase deposition techniques. Since the particles are so small, and intimate contact between the fluid and solid phases is required, a gas phase chemistry such as CVD or ALD is necessary.