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Atomic Layer Deposition Applications in Nanotechnology

Alexandra Burke
Taylor University

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Atomic Layer Deposition Applications in Nanotechnology
Senior Thesis Literature Review – CHE420
Ally Burke

Chapter 1: Introduction to Atomic Layer Deposition

Atomic Layer Deposition (ALD) is a thin film technique used to create controlled-depth layers of atoms on various surfaces.[1] The phrase "thin film" in the context of Atomic Layer Deposition refers to a thin layer of atoms that has been deposited on a target surface. This process is completed through a series of sequential half reactions, each reaction depositing a layer of atoms on the intended surface. These layers can be as thin as 1 atom or can be thicker depending on the cycle, and the contents of the layers can be specifically tailored depending on the system in question. This allows for a high degree of control in layer thickness and layer content. As technologies are becoming increasingly smaller, it has become necessary to create a technique which can create the thin layers required by these devices.[2,3] Nanotechnology as the name implies has reached sizes of nano-scale proportions. To add functionality to various nanotechnologies, such as nanotubes and nanoparticles, it has become necessary to design a highly precise mechanism for thin layer deposition. ALD, previously known as Atomic Layer Epitaxy (ALE), was introduced in 1977 by Suntola and Antson, who used it for depositing ZnS for flat panel displays.[3] ALE served as a way to accomplish highly precise monolayer deposition. As this process grew in popularity, the process began to be implemented without depositing elements epitaxially, which refers to the number of layers being deposited. Epitaxy implies that a single layer has been deposited, whereas modern ALD processes deposit more than one layer. This change in design led to the name change from Atomic Layer Epitaxy to Atomic Layer Deposition.[1] There are several ways Atomic Layer Deposition can be accomplished. ALD processes vary greatly; reactants, precursors, surfaces, and temperature windows can all be

tailored to the specific needs of the chemical system. Because of the variation within this process, there are many applications in various fields of chemistry.

Chapter 2: Methodology Behind Atomic Layer Deposition

Atomic Layer Deposition is a process that allows variety within how it is implemented. It is possible to finely tune individual pieces of each ALD method to fit whatever system is involved. Though there is variability within this process, there are some main guidelines that must be followed for success. The precursors involved need to have appropriate chemical properties for their intended use. This includes thermal stability, meaning the reactants must resist change when exposed to the temperature of the ALD process. Sufficient volatility for easy transport is also necessary. ALD reactions occur in the gas phase so it is necessary that the reactants are volatile to allow for quick reaction times. Appropriate surface chemistry to bind with the intended surface is also needed. Choosing half reactions that will react with the intended substrate is an important component of ALD process design. The reactants must also be complementary, which means the reactants within the two half reactions must interact in a way that is beneficial to the creation of the various layers. This allows for sequential layers that can bind irreversibly. If the half reactions were unable to react favorably with the intended surface and with each other, the process would be considered unsuccessful. It is also necessary for the reactants to react completely and irreversibly at the low temperatures required by this process.[2] ALD processes are generally completed at temperatures less than 350°C,[1] and some run at temperatures as low as 25°C,[6] though the temperature range varies with different processes. Temperatures outside the ideal temperature window tend to result in poor growth rates and non-ALD type deposition. These occur as a result of poor reaction kinetics and precursor

condensation, which occur at low temperatures, or thermal decomposition and rapid precursor desorption, which occur at high temperatures.[1]
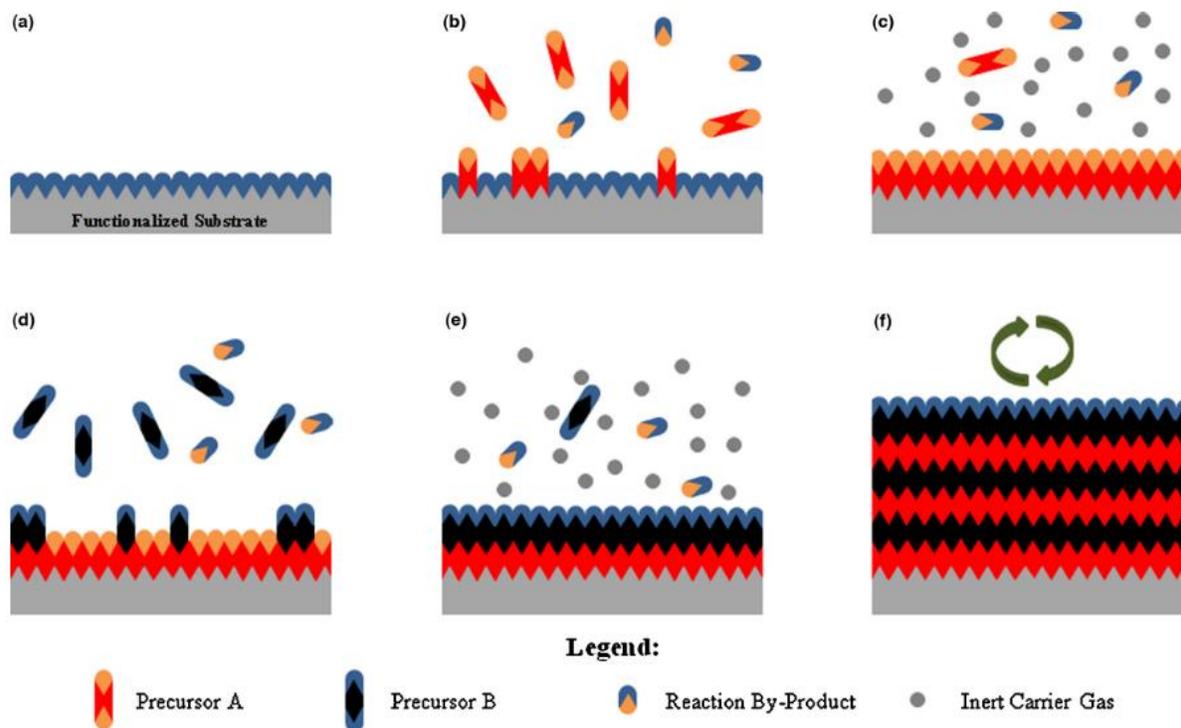
Figure 1: General functionality behind atomic layer deposition[1]

In figure 1, the general process of Atomic Layer Deposition is outlined. Step (a) shows a functionalized substrate, which means it has been prepared to allow binding between Precursor A and the surface. In step (b), Precursor A has been exposed to the surface resulting in the binding between the two as well as Reaction By-Products being released. Excess Precursor A and Reaction By-Products are then purged by an Inert Carrier Gas. Precursor B then bombards and reacts with the surface, again resulting in Reaction By-Products being released. The Inert Carrier Gas is then added to remove the excess Precursor B and Reaction By-Products. These steps are repeated until the desired layer depth is achieved.[1] This general process is characteristic of all ALD processes.[6] This process of sequential, self-limiting half reactions is often referred to as binary reaction sequence chemistry. The binary reaction model operates under the assumption

that any surface has a finite number of reactive functional groups. The half reactions will continue as long as there are functional groups available for further reaction. After the half reaction has gone to completion and there are only newly produced functional groups available, the surface will no longer react with that particular half reaction, and the other half reaction should be applied to the surface. This concept can be demonstrated by the following half reactions.

$$(A) \ \ ZnCl^* + H_2S \rightarrow ZnSH^* + HCl$$

$$(B) \ \ SH^* + ZnCl_2 \rightarrow SZnCl^* + HCl$$
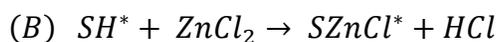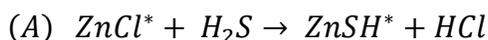
The asterisks in these reactions designate the surface species to be reacted with by the other reactants. Half reaction (A) exposes the zinc chloride surface to the precursor hydrogen sulfide, which deposits a thiol group onto the zinc surface, creating the new surface for reaction (B). The release of the chlorine from the zinc surface then results in the production of hydrochloric acid. Zinc is then re-deposited in half reaction (B) onto the new thiol surface via zinc chloride, re-chlorinating the surface, resulting in further production of hydrochloric acid. From one half reaction to the other, the surface functional group changes, which is characteristic of the self-limiting nature of binary reaction sequence chemistry. This sequential reaction sequence serves as an excellent example of the sequential binary reaction sequence.[7] The binary nature of ALD provides simplicity to this reaction process, and is one of the things which makes ALD advantageous over other deposition processes.

There are many other advantages to using Atomic Layer Deposition over other similar processes. With ALD processes, the conformality of the thin films is better than with other processes. This helps restrict the reaction to the surface, which refers to the outermost atomic layer. This promotes complete reaction of the entire surface.[1,3] There is also less of a need for the

reactant to be completely homogeneous in the deposition reactor, which allows these processes to be easily reproduced on a large scale for layers with a larger surface area without sacrificing conformality. It is also possible to avoid interference from gas phase reactions because the half reactions are separated into sequential processes. This adds to the effectiveness of this process.[2] Additionally, the subsequent cycles of ALD allow for uniform layer growth, which leads to thickness control of the deposited films. Layer thickness can be modified for different numbers of cycles. Generally, layers are less than 1 Angstrom thick per cycle, depending on which process is being used.[1,2] There is also flexibility in process design, ranging from temperature to reactants involved. This allows the process to be easily modified for a variety of needs.[2] Composition of the layers can also be controlled by combining multiple Atomic Layer Deposition processes, known as ALD 'super cycles.' Altering the ratios of cycles within these ALD super cycles can allow tailoring of the properties and film thicknesses of the deposition products. Examples of this include zinc tin oxide[8] and $SrTiO_3$.[1,9] In the process for zinc tin oxide, adjusting the super cycle ratios involved in the process alters the conduction behavior and optical properties of the film.[8] For $SrTiO_3$, the ALD processes for TiO_2 and $SrCO_3$ are alternated in a super cycle, resulting in a 1:1 ratio $SrTiO_3$ film.[9]

Atomic Layer Deposition seems like a good solution to growing needs in technology improvement. However, there are some disadvantages to using this process over others. It is possible for the deposition of contaminants to occur within the layers because of precursor side reactions. When compared with Physical Vapor Deposition (PVD), which is another process used to create thin films and is characterized by the reactant entering the condensed phase, switching to the vapor phase, and then condensing in thin films on a surface, there is some

variety in ALD regarding microstructures and morphologies within the layers. This is less of an issue in PVD, which may make that process more desirable.[2]

Issues also arise with the use of binary reaction sequence chemistry. One of the major issues with this reaction sequence is the difference between the pressures of the two precursors. This can occur because of insufficient pumping or purging flow between the two half reactions. This pressure difference can cause the film growth to be inconsistent, which ultimately affects the interpretation of the film growth per cycle. It is also difficult to optimize the reaction conditions for both half reactions. The optimal conditions for one of the half reactions may not be optimal for the other. This may be due to differences in reaction kinetics, pressure conditions, and temperature conditions of the two half reactions. Attempting to alter the conditions mid-ALD process to fully optimize each half reaction further complicates the process and is not practical. To accommodate this issue, ALD processes are often designed to occur at conditions that are suitable to both half reactions, though may not be optimal for either. Inhomogeneities within the functional group surface can also cause issues for ALD processes. Theoretically there should be a complete transition from one surface functional group type to the other. This would allow for complete reaction of each surface. It is difficult to create a surface without inhomogeneities, and as a result reaction times can take longer to allow for complete reaction of each surface. To account for this, interpretation of the layers includes the caveat that each layer may not be 100% homogenous.[7]

One of the other major limitations associated with Atomic Layer Deposition is the rate at which the cycles occur. Generally, only a fraction of a monolayer is deposited in one cycle. This causes deposition rates to generally fall in the range of $100 - 300$ nm hour^{-1}. Because such thin layers are added one at a time, it takes longer to achieve the same goal when compared with

other similar processes that do not require a cyclical process for deposition.[2] The slow reaction rates associated with ALD make it an impractical solution for creating micrometer-thick layers. Rather, this method should be reserved for the creation of nano-scale layers. Implementing ALD on such a small scale means that the slow reaction rate is not much of an issue. This slow growth rate can also be compensated for by using a single ALD process on large amounts of substrates. This large-scale production can improve the efficiency of ALD processes. Slow growth rates can also be optimized by changing reactor types. There are a few different types of common ALD reactors which can be characterized by two limiting types: the use of a pump and the use of a carrier gas. The first type is characterized by the lack of a carrier gas and often throttled pumping is implemented to transport the gases. After exposure of the surface to the precursors, the excess reactants are then removed by evacuating the reactor using a pump. This method allows the reactants to remain in the reactor for longer periods of time, which can be efficient, but the evacuation times for this method can be slower than normal because of the absence of a purging gas. The other major type of ALD reactor is characterized by the presence of a carrier gas flowing through the reactor. This carrier gas flows continuously to the pump, and the reactants with sufficient vapor pressures can be added to the carrier gas stream. This carrier gas improves the efficiency of ALD processes by allowing continuous movement of the reactants and products of the half reactions. This helps to decrease ALD cycle times when compared with the other method.[10] Reaction times can also be optimized by altering ALD process variables such as temperature, reactant volatility, and other variables discussed previously.[3]

When designing a new Atomic Layer Deposition method, it is important to take each of these variables into account to produce the most efficient deposition process. ALD has diverse functionality which allows it to be useful in the production of various technologies. For example,

atomic layer deposition has useful applications in nanotechnology, specifically in the production of nanotubes and nanoparticles. The high precision of ALD makes it a good solution to the growing needs in the field of nanotechnology.

Chapter 3: Current Applications of Atomic Layer Deposition in Nanotechnology

Atomic Layer Deposition is a technique that has characteristics that work well for nanotechnology. Properties such as accurate and simple layer thickness control, uniformity over large areas, good conformity and reproducibility, multilayer processing capability, and high-quality layer production at relatively low temperatures are all useful in nanotechnology production.[11,12] Studies have shown that thickness accuracy of Atomic Layer Deposition processes is well-maintained up to around 100 nm and the conformality and uniformity of ALD over large areas make it possible for deposition on substrates of complex shapes, such as those encountered in nanotechnology.[11] These characteristics make ALD a viable technique for nanotechnology production. As technology has been decreasing in size, the need for precision at an atomic level has increased. Due to the chemistry of ALD processes, they have the ability to self-assemble layers, meaning that the reactions proceed without external stimuli.[1] This is useful for ease of use when it comes to nanotechnology applications, and it continues to build the argument that ALD is an excellent thin film building technique to be used in nanotechnology.

Chapter 4: Use of Atomic Layer Deposition in Nanotube Production

Nanotubes are hollow tubes with walls formed by one-atom-thick sheets, which can be composed of various types of atoms. Most often they are composed of carbon, which are known as carbon nanotubes. Nanotubes are categorized as single-walled nanotubes (SWNT) and multi-walled nanotubes (MWNT). Single-walled nanotubes are characterized by their ability to conduct a charge. Some nanotubes also have optoelectronic properties, which refers to the

combination of electronics and light. These properties are important to the functionality of single-walled nanotubes, so it is important that any ALD processes applied to these nanotubes preserve these properties. It is also necessary that as the deposition is taking place, the nanotubes be agitated to obtain high gas conductance. This helps improve the efficiency of the ALD process by ensuring that the nanotubes are evenly coated. If the nanotubes were allowed to remain stagnant, the nanotubes may become stuck together and the layers would not be conformal.[10]

Nanotubes provide an additional degree of freedom when compared to wires. Not only can length and diameter be varied, but thickness can also change with the use of Atomic Layer Deposition. This can be achieved in a variety of nanotubes, such as carbon and ferromagnetic nanotubes. Variation in the thickness of the nanotubes can add different functions to the nanotubes in the form of differing functional groups on the surface of the tubes.[13] Changing the thickness and characteristics of the walls of the nanotubes via ALD provides increased functionality to these already functional nanotechnologies, optimizing their ability to perform.

Atomic Layer Deposition on single-walled carbon nanotubes is useful because it prevents adversely affecting the electrical properties of the nanotubes. Also, the low temperature and high precision of the ALD process prevent any physical damage to the nanotube.[5] High temperatures could potentially cause damage to the chemical bonds that make up the nanotube, and the high precision of ALD prevents any chemical changes which may damage the nanotube walls. Atomic Layer Deposition is also desirable for coating carbon nanotubes because it allows optimization of the nanotube's characteristics and it is able to create improved functionality for future technology, which is the ultimate goal of optimizing their functionality.[5,14] For carbon nanotubes,

the conductance and optoelectronic properties are of value, so an ALD process would be

considered successful if either of these properties were improved.

However, there are also problems with using ALD for layer deposition on carbon

nanotubes. Because of the inert nature of the surface of the nanotubes, it is difficult to perform

direct deposition. Instead, some have attempted to create casings for the nanotubes using

supporting substrates to grow the layers.[14] Creating these casings around the nanotubes can limit

the functionality and flexibility of the nanotubes. Because this technique limits the functionality

of nanotubes, finding a better, more functional technique for making the nanotube more

susceptible to Atomic Layer Deposition became necessary. Rather, a liquid-based technique was

attempted that would functionalize the SWNT through covalent bonding, but this proved to be

too tedious and impractical to be a good solution to the problem. This technique also changed the

hybridization of the nanotube, which caused the loss of some optoelectronic properties, which

had to be re-established using post-ALD heat treatments.[5,15] To solve these problems, a new,

simpler technique was designed. Treatment with nitrogen dioxide gas and trimethylaluminum

(TMA) vapor serves as a less destructive ALD process than the previously attempted

methods.[5,15]
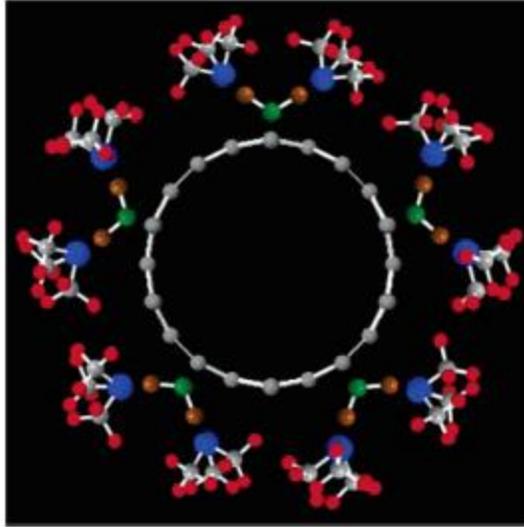
Figure 2: Proposed mechanism for NO_2 – trimethylaluminum vapor ALD process[5]

In figure 2, we see the proposed mechanism for the nitrogen dioxide – trimethylaluminum ALD process. This process consists of a dose of NO_2 to bind directly with the nanotube walls, a purge using an inert gas to remove excess reagents and reaction by-products, a dose of TMA to bind with the new oxygen functional groups on the surface, and another purge using inert gas to remove excess reagents and reaction by-products. After the initial deposition of NO_2, the nitrogen dioxide is absorbed onto the SWNT carbon wall via attraction between the carbon and nitrogen atoms, which is the most stable configuration for absorbed NO_2. The TMA is then absorbed onto the NO_2 surface via the TMA half reaction. The oxygen atoms are attracted to the aluminum atoms, creating a self-terminating layer around the nanotube with the outer methyl groups as the surface functional groups of the SWNT. This cycle was repeated 50 times inside a vacuum, followed by a dose of Al_2O_3 for further stabilization of the layer. This was completed at 25°C, and after this was completed the temperature was increased to 225°C and another dose of Al_2O_3 was applied for even further stabilization.[5]
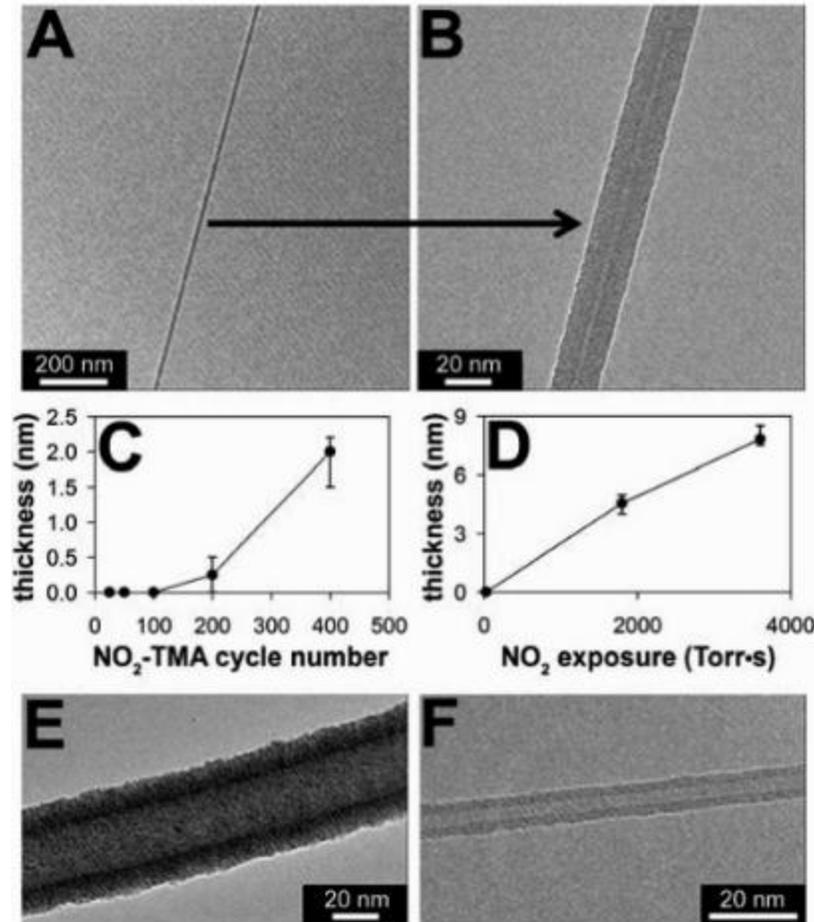
Figure 3: (A) Transmission electron micrograph of single-walled carbon nanotube coated with Al_2O_3 (B) Same image of carbon nanotube with 10x magnification (C) Graph of layer thickness versus number of ALD cycles (D) Graph of layer thickness versus NO_2 exposure (E) SWNT coated in Al_2O_3 (F) SWNT coated in Al_2O_3[5]

Analysis of the layers via transmission electron micrograph (TEM) proved that the layer thickness was consistent and as deep as expected from the number of cycles completed. Part A of figure 3 is a TEM micrograph of an SWNT coated in Al_2O_3 and part B is the same image magnified to show the uniformity of the deposited layer. This helps confirm that this ALD process was successful in depositing the expected layers with uniform and conformal thickness. The graph in part C shows that as the number of cycles implemented increases, the layer thickness begins to approach a positive linear slope. This is helpful information when attempting to control the layer thickness. The layer thickness can be easily predicted as the number of cycles

increases, which provides a higher degree of control when designing and tuning this ALD process. The graph in part D shows that increased NO_2 exposure causes a linear increase in layer thickness, which again can help determine the appropriate amount of reactant to use to create specific layer depths. Parts E and F also show uniform layer thickness on the carbon nanotubes as a result of the parameters outlined above.[5]

Further study of this ALD process has shown that the addition of H_2O allows growth past the self-terminating monolayer of NO_2 and TMA.[5] Later studies of this ALD process have shown this modification to be useful, so it is important to mention this change.[10,16] Without this addition, the layer thickness remains constant for nearly the first 100 cycles.

$$(A) \quad AlOH^* + Al(CH_3)_3 \rightarrow AlOAl(CH_3)_2{}^* + CH_4$$

$$(B) \quad AlCH_3{}^* + H_2O \rightarrow AlOH^* + CH_4$$
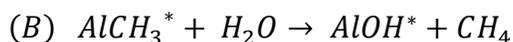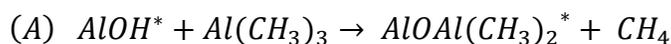
Following the initial deposition of NO_2, cyclical exposure to TMA mixed with H_2O causes the methyl groups (which previously caused the lack of layer growth) to be cleaved via the H_2O, leaving hydroxyl groups in their place. The TMA can react further with the hydroxyl groups via a similar cleavage mechanism, increasing the layer thickness. After surpassing the 100th cycle of NO_2 – TMA deposition, imperfections in the methyl groups on the outer surface result in increased layer thickness. This results in a porous SWNT, which is in turn reacted with by NO_2 and TMA, resulting in increased layer thickness.[5] This process can be used for increased rates of layer growth but seems more difficult to control than the previously discussed methods. If the goal of this method is to create thick layers this modification may be helpful, but if only a monolayer is needed, the original method without the addition of water may be more appropriate.

Once the SWNT has been functionalized using the outlined ALD process and stabilized through Al_2O_3 exposure, the coated structure can then be used as a foundation for growing other

materials through other ALD cycles, such as nitrides, sulfides, and metals and their corresponding oxides. Characteristics of the nanotubes involved can be varied to produce more specialized products for more specific ALD processes. Through this study, a successful ALD process for functional optimization of carbon nanotubes, which is no longer tedious and is practical for large-scale use, has been developed. Furthermore, minimized covalent bonding preserves the optoelectronic properties of the SWNT, and changes in conduction have been minimized.[5] Because the conductive and optoelectronic properties of the nanotubes have been maintained, this process can be considered successful. Conductance and optoelectronic properties of nanotubes are not the only valuable assets this nanotechnology affords. There are also potential applications in high-density data storage via the magnetic properties of ferromagnetic nanotubes.[13]

As mentioned before, nanotubes provide an extra degree of freedom when compared to wires: thickness. Nanotube thickness can affect the mechanism involved in the overall magnetic response, which can be useful in high-density data storage. Previous difficulties in producing ferromagnetic nanotubes include difficult synthesis of nanotubes in nanometer proportions, granular tube structures, and inconsistencies in thickness and diameter. To resolve these issues, ALD can be applied to porous tubes, resulting in smooth nanotubes with controlled and mutable geometries. For the production of iron oxide nanotubes, H_2O and iron(III) tert-butoxide complex were implemented sequentially.[13]
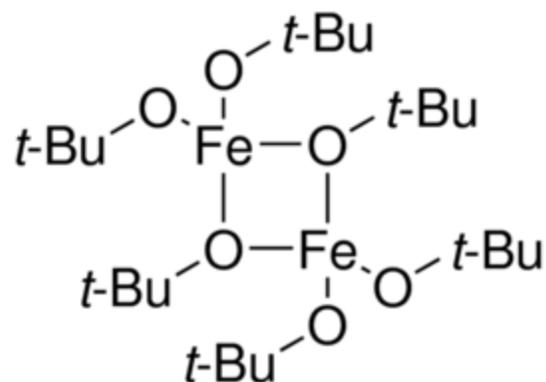
Figure 4: Chemical structure of iron (III) tert-butoxide complex which is used in the ALD process for Fe_2O_3 nanotubes[13]

A self-ordered porous anodic alumina membrane was used as the surface for the ALD reaction.

After being exposed to the cycles of H_2O and iron(III) tert-butoxide complex, the surface of the

nanotubes is evenly coated with Fe_2O_3.[13]
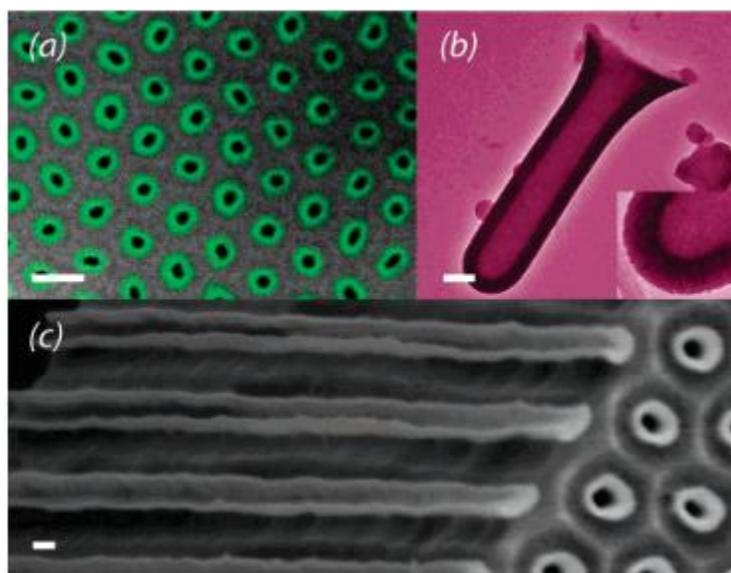
Figure 5: (a) Scanning electron microscopy of nanotubes coated with Fe_2O_3 (b) Transmission electron microscopy of nanotubes coated with Fe_2O_3 (c) Cross section of nanotubes coated with Fe_2O_3[13]

Part (a) of figure 5 shows a scanning electron microscopy of the nanotubes embedded in the

alumina template. Part (b) of figure 5 shows a transmission electron microscopy of a coated

nanotube. The magnified section in the bottom right corner of part (b) shows the smoothness of

the coating. Part (c) shows a scanning electron microscopy of the Fe_2O_3 nanotubes embedded in the template. Each of these images helps to confirm that this ALD process was successful in depositing smooth, consistent layers. Further analysis will show us whether the ALD process was successful in improving the functionality of these ferromagnetic nanotubes.[13]

X-ray photoelectron spectroscopy confirmed that the material built up on the substrate was in fact Fe_2O_3, though the authors do note there was an unexpectedly large quantity of carbon within the layers. This may be due to residual tert-butoxide complexes which were not hydrolyzed with their first exposure to water. Theoretically, when the tert-butoxide complexes are first exposed to water are completely hydrolyzed, but this was not the case for this study. The amount of carbon decreases with layer depth, which the authors claim does not affect the functionality of the nanotubes, though this may be something to be considered in future studies of this mechanism. The Fe_2O_3 tubes were then reduced with a mixture of H_2 and Argon gas to produce Fe_3O_4. The study did not provide the exact reaction mechanism for this conversion, but for visualization purposes the following is the general concept of this reaction.[13]

$$Fe_2O_3 + H_2/Ar \rightarrow Fe_3O_4$$
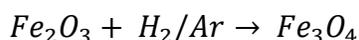
Reduction of the iron(III) to iron(IV) was accomplished via electron exchange with the hydrogen gas. To protect the air-sensitive Fe_3O_4, a thin layer of polystyrene was applied to the surface to prevent degradation during handling of the nanotubes. The Fe_3O_4 tubes behaved as ferromagnets, which was the ultimate goal of this ALD process.[13]

This synthetic approach allows variable geometries for these ferromagnetic nanotubes. It is possible to control the strength and functionality of the ferromagnets using variable thickness and variable geometries for the substrate of the ALD process. As the thickness of the nanotube walls increases, the magnetic response of the ferromagnetic surface increases. This well-

controlled synthesis of ferromagnetic nanotubes has provided improved functionality to these

nanotubes, which proves that Atomic Layer Deposition is an appropriate process for the

production of improved nanotechnologies. Further study and understanding of this specific

process is necessary before harnessing this technology for high density data storage, but there is

potential in this area of study.[13]

**Chapter 5: Use of Atomic Layer Deposition in Nanoparticle Production**

Atomic Layer Deposition is also useful in other areas of nanotechnology production.

Nanoparticles are a form of nanotechnology which have a variety of uses including biomedical

and industrial applications. Atomic Layer Deposition is useful for the production of

nanoparticles because it can be highly controlled for the nanometer-scale size of the particles and

because it is highly tunable to whatever type of nanoparticle is in question.

The use of ALD on nanoparticles can be helpful for modifying the surface chemistry of

the original particles and for retaining the properties which make the particles useful, such as

optical, mechanical, and conductive properties. When performing Atomic Layer Deposition on

particles, it is important that the particles be in motion to prevent the particles from becoming

stuck together and to allow the ALD process to produce conformal, uniform layers. Often the

bed of particles will be fluidized to prevent the particles from becoming stagnant. Fluidization of

the particle bed causes constant agitation of the particles, preventing them from sticking together

during deposition. This does not completely prevent aggregation of the particles, however any

clumps of particles remain dynamic and the exchange of particles between clumps prevents them

from sticking together.[10]

Noble-metal particles supported on metal oxide surfaces are an excellent example of

ALD used to produce functional nanoparticles.[17] These particles form potential metallization

materials for microelectronic applications.[18] These nanoparticles can also be used as catalysts for electrochemical, photochemical, and thermal processes.[4,17] The nanometer-scale of the nanoparticles can contribute to efforts to save energy and efforts to reduce pollution. Because of the benefits of these nanoparticles, there is a need to create a scalable synthetic method for their mass production. A paper by Christensen *et al.* has provided some insight into a process for this production. For this process, strontium titanate ($SrTiO_3$) nanocubes were used as the surface for the deposition of platinum atoms.[17] Recent studies have shown that the combination of platinum and strontium titanate has shown potential as a method of production of efficient catalysts, which can be used for a variety of things such as combustion and as a photocatalyst for fuel production, Because of the benefits these catalysts can provide, attempting to build a process for this type of catalyst is important.[19,20]

Atomic Layer Deposition is also useful for catalyst production when compared with other catalyst production methods because it is more precise and cleaner than some other methods.[21,22] For the production of these nanoparticle catalysts, platinum layers on the strontium titanate nanocubes were built up using alternating half reactions of (methylcyclopentadienyl)trimethyl platinum(IV) and oxygen.
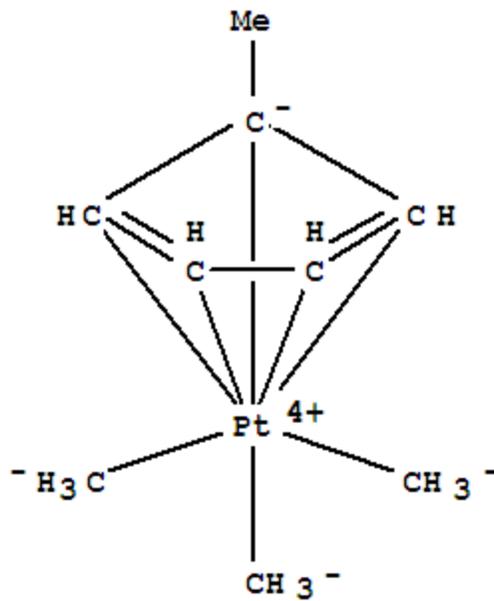
Figure 6: Chemical structure of (methylcyclopentadienyl)trimethyl platinum(IV) which is used in the ALD process for platinum nanoparticle production[17]

Through analysis via scanning electron microscopy (SEM), the morphology and dispersion of

the nanoparticles before and after platinum coating were studied.[17]
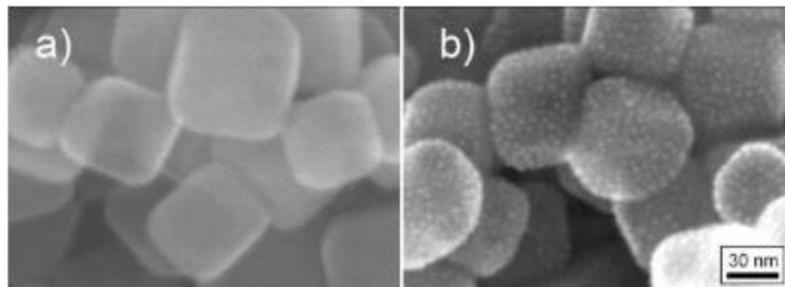

Figure 7: a) Scanning electron microscopy of the nanoparticles before deposition b) Scanning electron microscopy of the nanoparticles after 3 ALD cycles[17]

Part a) of figure 7 shows a scanning electron microscopy of the particles before deposition and

part b) shows another SEM after 3 ALD cycles of the platinum complex and oxygen. As you can

see in part b), the platinum particles have been evenly distributed across the strontium titanate

nanocubes, causing the nanoparticles to appear granular. Continued ALD cycles will produce

complete coverage across all of the nanocubes.[17]

This study was conducted to investigate the steady-state increase of layers as the number

of cycles increases. Study of early stages of growth was not investigated at this time, but because

the study proved successful for producing these nanoparticles, further studies may be conducted

later. The dispersion and size of the nanoparticles were further studied using small angle x-ray

scattering and wide-angle x-ray scattering.[17]
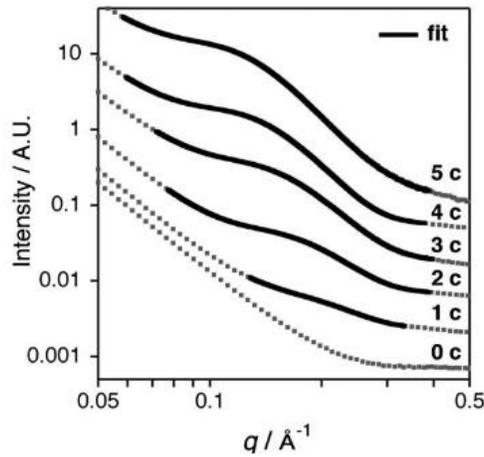
Figure 8: Single angle x-ray scattering of nanocubes after varying numbers of ALD cycles[17]

Figure 8 shows the single angle x-ray scattering of the non-coated nanocubes and the following

addition of subsequent cycles. This data shows us the interparticle scattering interference for the

platinum particles. The interference leads to a peak whose position yields the interparticle

spacing, denoted as D, by using the following equation.

$$D = \frac{2\pi}{q_p} \tag{1}$$

Essentially, this data tells us the change in dispersion of the platinum nanoparticles as the cycles

proceed. The interparticle spacing increases linearly as the number of cycles increases, which

can be seen in equation 1. By inputting different values of q_p into equation 1, we can see that as

q_p decreases, D will increase. This linear increase of the particle spacing indicates that the density of the particles per unit area is decreasing, which is due to the particles coalescing.[17]

Nanoparticles of this size are likely to show a size-property relationship in relation to the chemical activity of the nanoparticles. With these platinum nanoparticles, as the size of the particle increases, the catalytic activity changes slightly. This is because as the initial layers of platinum are being deposited, they are oxidized by the surrounding environment, resulting in an abundance of Pt-O bonds. As the cycles continue and the layers increase, this changes to an abundance of Pt-Pt bonds as the amount of platinum increases. This change results in differing catalytic activity.[17] Depending on the desired activity of the nanoparticle catalysts, different numbers of cycles may be used to produce varying types of platinum bonds. This study contributes to the idea that Atomic Layer Deposition can be varied for different catalytic characteristics. The results seen in this study are consistent with findings by others who have attempted this same ALD process.[4] This is encouraging because it shows that this process is viable for nanoparticle production.

Another example of Atomic Layer Deposition in nanoparticles is coating zirconia nanoparticles with alumina films. Previous research by other authors has proven that this process of producing Al_2O_3 films via ALD processing is efficient and self-limiting.[10,16] The main reason this reaction sequence is considered efficient is because of the strength of the Al – O bond. This allows the half reactions to occur quickly and irreversibly.[10] Hakim *et al.* performed this study in hopes of proving that nanoparticles can be uniformly and consistently produced in large-scale proportions using this same ALD process. Layers of Al_2O_3 were deposited on the zirconia nanoparticles using alternating half reactions of trimethylaluminum vapor and H_2O.[23]

$$(A) \quad AlOH^* + Al(CH_3)_3 \rightarrow AlOAl(CH_3)_2{}^* + CH_4$$

$$(B) \quad AlCH_3{}^* + H_2O \rightarrow AlOH^* + CH_4$$
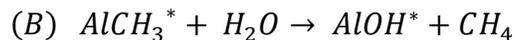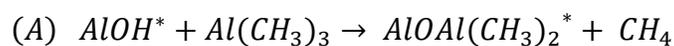
The asterisks within each half reaction denote the surface that the reactants will react with. As the trimethylaluminum vapor was applied to the aluminum hydroxide surface, the aluminum hydroxide was dehydrogenated resulting in the production of the aluminum oxide complex in half reaction (A) and methane. A previous study of this same ALD process was able to confirm the production of the aluminum hydroxide surface and the formation of the new aluminum methyl surface via Fourier-transform infrared spectroscopy.[10] This study is comparable with the nanoparticle research done by Hakim *et al.* because both processes used the same deposition half reactions and variations in temperature and pressure. This proves that this method of producing the new aluminum methyl surface is viable. The new aluminum methyl surface was then bombarded with water resulting in the production of the aluminum hydroxide surface and more methane. This process resulted in the desired Al_2O_3 layers.[23] Again, similar studies of this same ALD process were able to confirm the loss of the aluminum methyl surface and subsequent gain of the aluminum hydroxide surface, which is indicative of a cyclic process.[10] Further analysis of the nanoparticles via transmission electron microscopy proved that the desired layers had been deposited on the nanoparticles.[23]
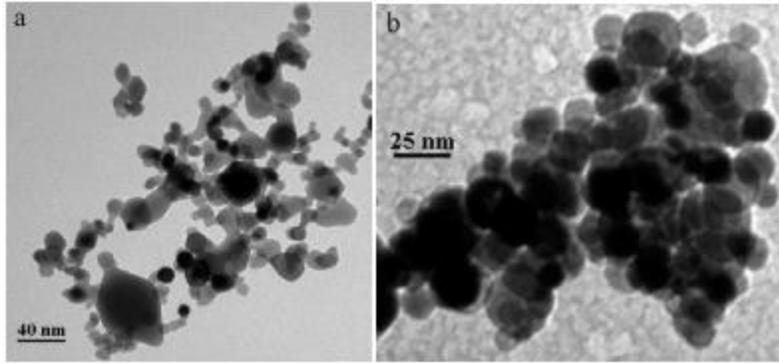
Figure 8: (a) and (b) Transmission electron micrographs of zirconia nanoparticles before deposition of Al_2O_3[23]
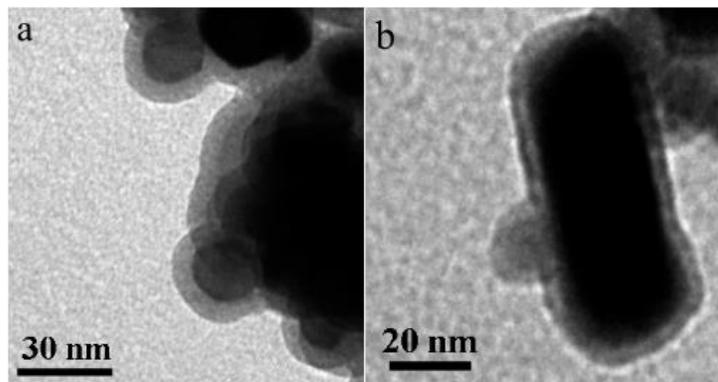
Figure 9: (a) and (b) Transmission electron micrograph of zirconia nanoparticles after 50 ALD cycles[23]

In figure 8 we see the nanoparticles before any ALD process has been applied to them. Figure 9 shows a magnified view of the nanoparticles after having undergone 50 ALD cycles. As you can see, there is a layer of Al_2O_3 present on the surface of the nanoparticles, which shows us that this technique was successful in depositing conformal and uniform layers of Al_2O_3 on the zirconia nanoparticles. These nanoparticles now have increased oxidation resistance and increased surface reactivity, achieving the goal of optimizing the functionality of the nanoparticles.[23]

Through investigating what Atomic Layer Deposition looks like in various examples of nanotechnology, it has become apparent that ALD is a viable process for producing improved functionalization within nanotechnology. Also, through seeing the various reactions involved in

each example, it has become apparent that ALD is a versatile technology. With the high precision and control of Atomic Layer Deposition, this process can continue to improve nanotechnology in the future.

Chapter 6: Conclusions

As the size of technology has been decreasing, as seen with the surge of nanotechnology production, it has become necessary to design processes to deposit thin layers of atoms on these technologies. In several cases, such as with various types of nanotubes and nanoparticles, this deposition has the potential to improve the functionality of these already functional nanotechnologies. Not only does ALD provide a way to deposit thin films of atoms, it also allows for current properties of the deposition substrates to be improved or maintained. The ability to maintain control over such minute processes speaks to our level of understanding of these chemical reactions. This method of thin film deposition is relatively new to the scientific community, the first instance of this process being implemented occurring in the 1970's.[24] Great advances have been made with ALD technology for it to be as advanced as it is today. As technology continues to improve, further methodology and process designs will need to be created to improve ALD technology. Atomic Layer Deposition is currently at a stage where it is most useful for nanotechnology, which is due to its slow reaction rates and atomic levels of precision. However, with improved understanding and implementation of this technology, it may become practical to use this technology for larger scale productions. Before this can happen, it is necessary that the current reaction rates are increased, otherwise this would be impractical and inefficient compared to other deposition processes. Until that time comes, Atomic Layer Deposition has many practical uses in the field of nanotechnology and it can fulfill current production needs.

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