Deposition of Silica onto Carbon Nanotubes

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ABSTRACT

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The deposition of silica onto carbon nanotubes (CNTs) has significant applications in electronics, and their mechanical properties make them highly relevant in current materials research. Atomic Layer Deposition (ALD) is the preferred method for this deposition because the layer depth is easily controlled. However, because of the strength of the carbon–carbon bonds in the CNTs, functionalizing the surface requires impurities that the precursor (tris(dimethylamino)silane (3DMAS)) can bond to. The primary goal of this study is to deposit silica on CNTs using ALD and analyze the results using SEM imaging and EDX. The process used for ALD deposition of silica uses 3DMAS and ozone at 300°C in a vacuum in a Kurt J. Lesker ALD machine. This study demonstrates a growth per cycle (GPC) of around 0.015nm of silica deposition onto the walls of carbon nanotubes.

Keywords: Atomic Layer Deposition, silica, carbon nanotubes, ALD, CNT, 3DMAS, GPC

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Chapter 1

Introduction

There are numerous applications for depositing thin films on high aspect ratio materials, including carbon nanotubes (CNTs). More specifically, carbon nanotubes show significant promise when it comes to field emissions, energy storage, fibers, biomedical applications, etc. [1]

1.1 Motivation and Background

In this study, we enhance some of the applications of carbon nanotubes by depositing silica on these nanotubes to change their properties. The ability to change these properties can lead to significant application in projects with niche requirements. Atomic Layer Deposition (ALD) has shown significant promise in providing the tools to make the thin films of silica infiltration possible through a forest of CNTs. The process for ALD deposition of silica using Tris(dimethylamino)silane (3DMAS) is a well-researched process that uses ozone as the main oxidant for the silica deposition [2]. However, this process has not been done on CNTs. Carbon nanotubes are known to etch when exposed to ozone, so in this thesis I aim to demonstrate how to deposit silica on a porous high aspect ratio material—specifically, CNTs—using ALD of 3DMAS and ozone.

1.2 Physical Background: Atomic Layer Deposition and Carbon Nanotube Makeup

1.2.1 Atomic Layer Deposition

Atomic Layer Deposition was invented by two groups independently. [3] The first group that discovered ALD called it "Atomic Layer Epitaxy." This group was led by Dr. Tuomo Suntola, who was searching for a way to deposit ZnS for use on electroluminescent displays. He deduced a method using Atomic Layer Epitaxy rather than the typical thin film development methods such as sputtering. The other group that discovered ALD was Prof. Aleskovskii's group in the Soviet Union. As time progressed, the commercialization of ALD-capable machines turned this microchemistry into what it is today.

Atomic Layer Deposition is a type of chemical vapor deposition that is self-limiting in nature. This means that each precursor used in the process bonds much better to the previous layer rather than to itself. This allows for a single layer, roughly one molecule thick, to be generated for each dose of a precursor. The most basic form of an ALD process is in the form ABAB, where A represents one precursor and B represents a second precursor. This process is shown in Figure 1.1 for Al_2O_3. In this process, $Al(CH_3)_3$ is released into the reactor and chemisorbs onto the substrate. Then, after a short purge, H_2O is released into the chamber, which then bonds with the $Al(CH_3)_2$, leaving only hydrogen-terminated Al_2O_3. This process is repeated as many times as desired. [4] The deposition of silica using 3DMAS is a similar process; however, the main precursors are 3DMAS and ozone.

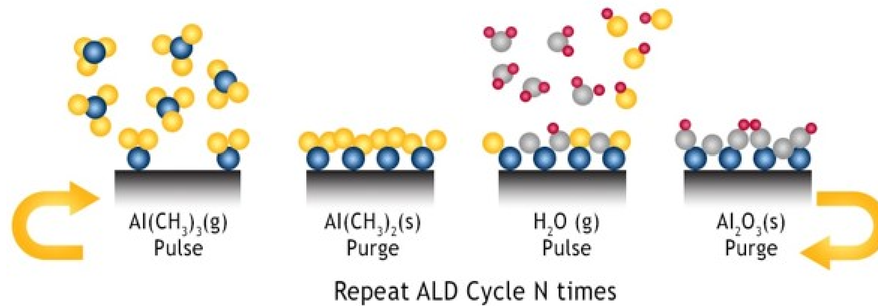

Figure 1.1 This figure illustrates the fundamental Atomic Layer Deposition (ALD) process used to deposit alumina (Al_2O_3) onto a silicon substrate. The process involves alternating pulses of a metal precursor and an oxidizing agent, with purges in between, to create uniform and conformal thin films at the atomic scale. This precise layer-by-layer growth mechanism is critical for coating complex surfaces and is foundational to many modern nanotechnology applications. (Source: [5]).

Another important feature of ALD is something called the ALD window, as shown in Figure 1.2. As seen from the process described above, ALD must be performed under conditions where the molecules follow a very specific bonding pattern. However, this does not always happen. If the reactor temperature is too hot, then the molecules could decompose and adsorb onto the substrate in undesirable ways; if the reactor temperature is too cold, then the molecules might not have enough energy to undergo the desired reaction.This is important to this study because it is important to have the temperature constraints of the atomic layer deposition process within the mechanical temperature range of the CNTs.

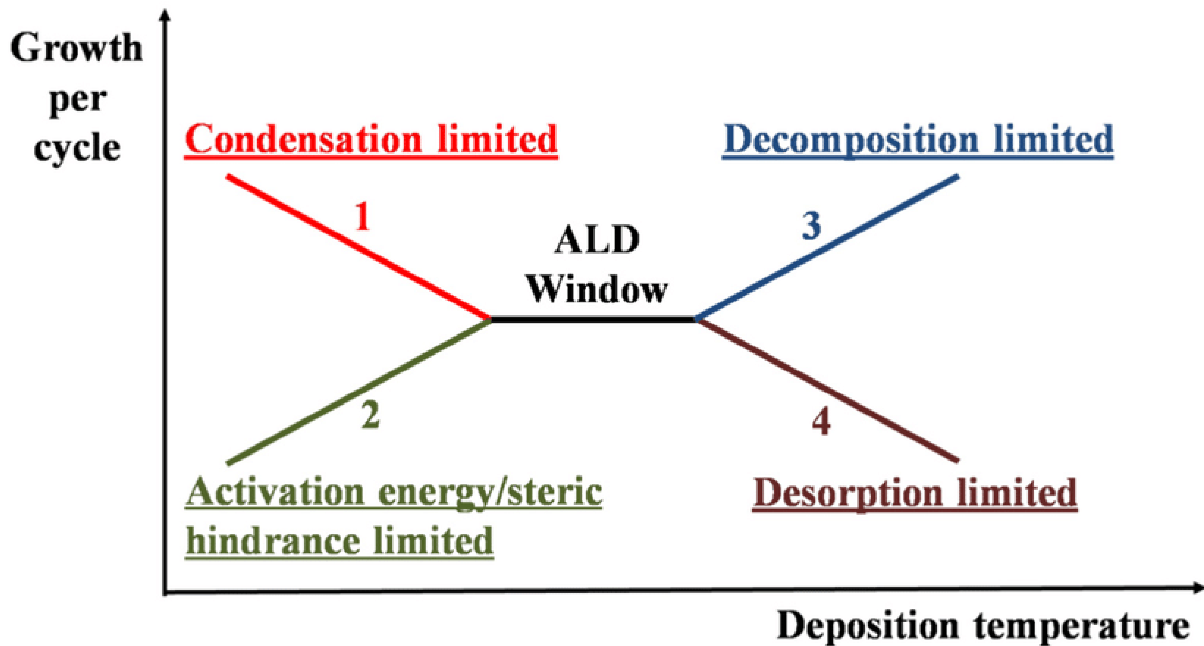

Figure 1.2 This figure shows the temperature "ALD window," where the deposition rate remains constant over a range of temperatures. Within this window, precursor reactions are self-limiting, enabling uniform, high-quality film growth. Operating outside the window can lead to incomplete reactions or unwanted chemical vapor deposition (CVD)-like behavior. Understanding and optimizing this window is critical for achieving consistent ALD coatings. (Source: [6]).

1.2.2 CNT Growth and Background

Carbon nanotubes, or CNTs, are a relatively recent discovery. They were first observed by Iijima and Ichihashi in 1991. [7] CNTs are nanomaterials composed of a two-dimensional lattice of carbon atoms, similar to graphite. This lattice is slightly curved and rolled into a cylindrical shape. Carbon nanotubes are typically classified into two categories: single-walled and multi-walled. In multi-walled carbon nanotubes (MWCNTs), several single-walled nanotubes are nested within one another, held together by van der Waals forces. Since their discovery, CNTs have attracted significant interest due to their unique mechanical and electrochemical properties.

There are several methods for synthesizing CNTs, including the arc discharge method and the laser ablation method. However, the method used in this study is called the Chemical Vapor Composition method. [8] This technique relies on the decomposition of hydrocarbons onto a transition metal catalyst to form CNTs. The basic process of carbon nanotube growth using this method is shown in Figure 1.3.

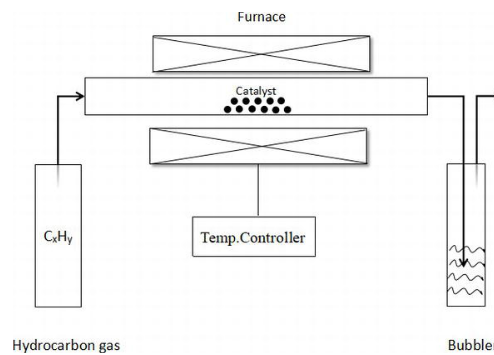

Figure 1.3 This image depicts the basic setup used in this study for growing carbon nanotubes, involving a quartz tube furnace and transition metal catalysts, based on chemical vapor deposition (source: [8]).

This study does not explore the detailed mechanism of CNT growth or the variety of usable transition metal catalysts; however, the paper by Xiao-Di Wang, K. Vinodgopal, and Gui-Ping Dai offers an excellent overview. [8] CNTs grown via this method are typically synthesized at around 750 °C. The growth process is highly sensitive to environmental conditions. In this study, the selected parameters produced MWCNTs ranging in height from approximately 200 to 500 nm. A close-up image of these CNTs is shown in Figure 2.1.

Chapter 2

Methods

In Chapter 2, the treatment of the multi-walled carbon nanotubes (MWCNTs) to layer silica on them was discussed. The results were analyzed using scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS).

2.1 Carbon Nanotube Growth

The method for growing MWCNTs begins with depositing 50 nm of Al_2O_3 onto a (100) silicon wafer via sputtering. We then used photolithography to pattern the wafer with a positive photoresist, AZ3330. Next, we used resistive thermal evaporation to deposit 4 nm of iron onto the wafer. After this, a protective coating of photoresist was applied. The wafer was then scored with a diamond scribe to etch lines, enabling the wafer to be snapped into 3-cm by 3-cm squares. To remove the photoresist and leave only the desired iron behind, we sonicated the wafer in N-Methyl-2-Pyrrolidone for 15 minutes. Afterward, the wafer was placed in a small plate of isopropyl alcohol and agitated for 1 minute. The same procedure was then performed using water from a Millipore Academic water purifier for another minute.

We performed CNT growths in a quartz tube furnace. The procedure for growing the CNTs in this tube furnace is as follows: The wafer is first heated to 750°C while only flowing hydrogen. At this point, ethylene is allowed to enter the tube at a flow rate of 338 sccm for ethylene and 311 sccm for hydrogen. The gases flow for 15 minutes, after which ethylene is shut off, and the furnace is allowed to cool to 200°C before removing the newly grown CNTs.

Next, we measured the diameters of the grown tubes using SEM imaging. At least five images were taken at different locations on the sample, as shown in Figure 2.1. The SEM was used in immersion mode with a beam energy of 5 kV and a beam current of 0.1 nA. The images were taken at a magnification of 200,000X to provide enough resolution for measuring the nanotubes with software like ImageJ. At least 100 measurements were made to obtain an accurate average diameter.

The measurement process is as follows: First, use the scale at the bottom of the SEM image to set the scale for converting pixels to your desired units. Then, zoom into a random MWCNT, draw a line covering the diameter, and use the measure tool to obtain a list of all diameters.

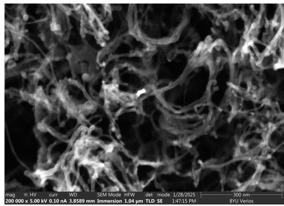

Figure 2.1 Scanning electron microscope (SEM) image showing the structure of multi-walled carbon nanotubes before atomic layer deposition (ALD) treatment. The nanotubes exhibit uniform diameters and clean surfaces.

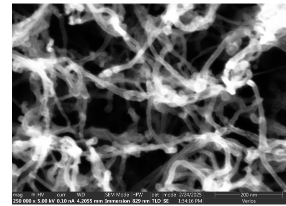

Figure 2.2 SEM image showing the multi-walled carbon nanotubes after silica deposition via atomic layer deposition (ALD). A clear increase in diameter and slight surface roughness are observed compared to the untreated sample.

2.2 Ozone Treatment

To functionalize the surfaces of the CNTs and increase the nucleation of the ALD, this study performed an Ozone treatment. The MWCNTs were then placed in a commercial Kurt J. Lesker ALD-150LX system. While the sample was in this system, ozone was flowed at room temperature for 30 minutes at an average concentration of 7% and a flow rate of 200 sccm.

2.3 Atomic Layer Deposition (ALD)

Thermal ALD of silica was performed using the same ALD-150LX system. This system's process chamber has a 6" plate that can be heated to 500°C. The chamber is connected to a rotary roughing pump by a pneumatic roughing valve. Throughout the process, the chamber maintains a flow of carrier gas to carry any precursor to the chamber without causing reactions. This study used ultra-high purity nitrogen. In this study, a 3DMAS precursor was attached to one source, and ozone was attached to another source. Both of these sources flow into the top of the chamber during their respective cycles.

After cleaning the MWCNTs with ozone, the chamber was heated to 332°C. The lines leading to the chamber were also heated to avoid deposition on the walls of the lines. Once all heaters reached their setpoints, the silica deposition process began. The process was as follows: 1000 ms pulse of 3DMAS, 1000 ms purge, 15000 ms dose of ozone, and 10000 ms purge. This process was designed to ensure complete saturation on the nanotubes. The time required to reach saturation depends on the shape of the CNTs [9]. The machine ran for 75 cycles before venting the chamber and removing the sample from the heated plate.

Lastly, the sample was placed on a stub and imaged using SEM to measure the diameters of the CNTs. The diameters were measured using ImageJ and the same methods mentioned earlier in the Methods. EDX was also performed in the same machine to determine the chemical makeup of the

sample. It is important to have one sample without silica deposition and one with silica deposition for comparison. Additionally, imaging should be done from one of the thicker parts of the sample to avoid scattering electrons to areas that are not being imaged.

Chapter 3

Results

The results of this study demonstrate the successful deposition of silica onto the carbon nanotubes (CNTs). As shown in Table 3.1, the average diameter of the nanotubes increased from 10.71 nm to 12.48 nm after the ALD treatment. The standard deviation also increased slightly, from 2.18 nm to 2.71 nm, indicating some variation in the treatment.

The energy-dispersive X-ray spectroscopy (EDX) spectra, shown in Figures 3.1 and 3.2, provide further confirmation of the silica deposition. In the spectrum of the untreated CNTs (Figure 3.1), the major peak corresponds to carbon (C), with minimal signals from oxygen (O) or other elements. After the ALD treatment, the spectrum of the CNTs (Figure 3.2) shows a significant increase in both silicon (Si) and oxygen (O) peaks, indicating the presence of silica on the nanotubes.

	Before Treatment	After Treatment
Measurements	125	141
Average Length (nm)	10.71	12.48
Standard Deviation	2.18	2.71

Table 3.1 This table shows the data from the diameters of the nanotubes. The average diameter increased after the treatment.

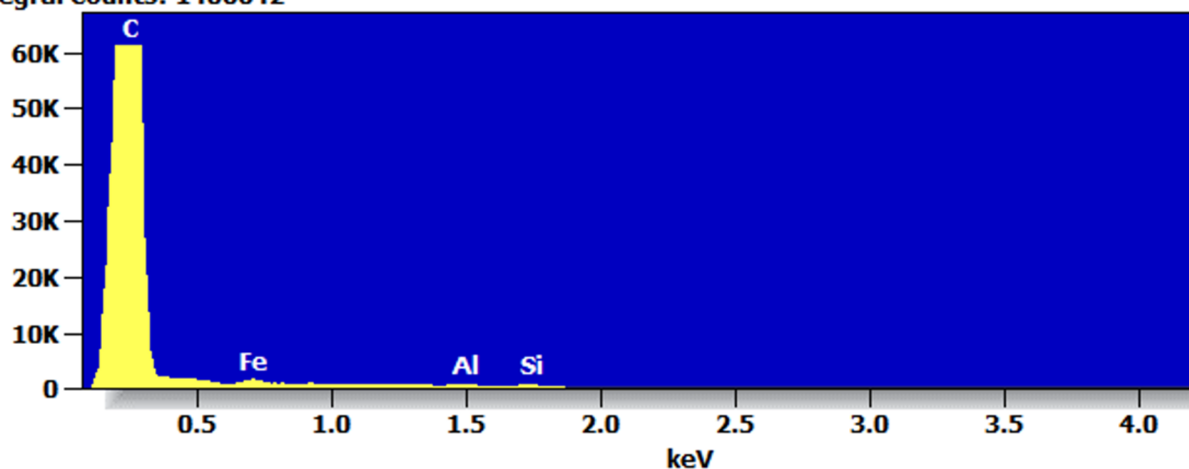

Figure 3.1 Energy-dispersive X-ray spectroscopy (EDX) spectrum of the untreated carbon nanotube sample, with major peaks corresponding to carbon and minimal traces of oxygen or other elements.

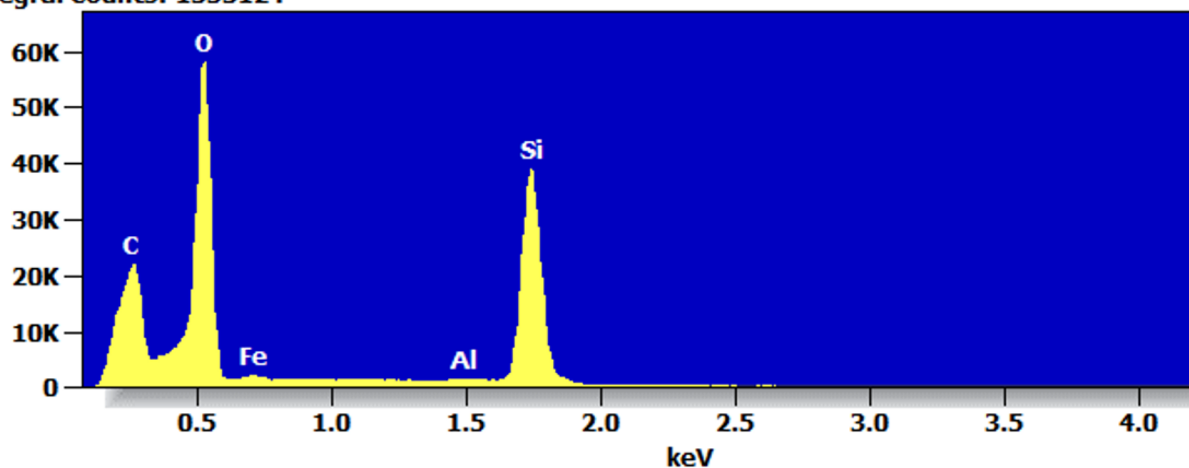

Figure 3.2 EDX spectrum of the carbon nanotube sample after silica deposition by ALD, showing a notable increase in silicon and oxygen signals, confirming successful coating.

Chapter 4

Analysis and Conclusion

The measurements taken from the diameters of the two groups of carbon nanotubes show a clear difference. A two-tailed unpaired t-test on this data yields a P value of less than 0.0001, indicating that the two data sets are statistically significant. The standard error used in the calculation was 0.304. The only difference between the two samples is the Atomic Layer Deposition (ALD) process, which allows us to conclude that the ALD process successfully deposited a layer of material onto the nanotubes. While we expect this diameter difference to be due to silica deposition, we cannot definitively conclude this from diameter measurements alone. This uncertainty arises from the sensitivity of the ALD process, which can transition from ALD to CVD under certain conditions, as discussed in the introduction.

To confirm the chemical change, EDX analysis was conducted. The samples were imaged at areas with dense nanotube forests, around 20 microns wide, to minimize electron scattering. The results clearly show a shift in the carbon-to-silicon ratio, as illustrated in Figures 3.1 and 3.2. This confirms that silica deposition is responsible for the change in the nanotube diameters, further supported by the increased oxygen content.

The growth per cycle (GPC) of the 3DMAS process on bare silicon is approximately 0.04 nm. However, in this study, we observed a GPC of about 0.0126 ± 0.304 on nanotubes, which

is significantly lower than expected. This discrepancy is likely due to a nucleation delay on the carbon nanotubes. The nucleation delay is caused by a lack of bonding sites. Future studies could investigate the effect of varying the number of cycles to see if the GPC improves and whether the nucleation delay is indeed responsible for the low GPC.

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