Atomic Layer Deposition System Design

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Abstract

In the process of nanofabrication, deposition techniques are always extremely important. Factors such as large area, conformity and reproducibility can affect the end results dramatically. Using the technique of atomic layer deposition (ALD), large quantities of conformal film can be coated onto a wide array of substrate material with excellent repeatability. This technique also has the benefit of simple and accurate control over deposition thickness on the order of angstroms, allowing alternating monolayer stacks of particles to bond to a surface. Commercial products are available but extremely expensive. However, the theoretical setup for ALD is not that complicated. Therefore, the goal of this project is to design and build a working ALD system with focus on Al₂O₃ film deposition that costs a fraction of the retail price. In the end, the system is still incomplete requiring a few more key components before being operational.
Introduction

As technology continues to push the limits of electronics, demand for smaller and smaller devices increase. At the nanoscale, it becomes extremely important to be able to fabricate films of material with precise thicknesses and conformal coverage of the target surface.\textsuperscript{1-3} Development and implementation of atomic layer deposition (ALD) systems aim to accomplish these specifications.

ALD systems have evolved and advanced greatly in the last decade; to the point where several companies have arisen solely to manufacture them. However, the theory behind ALD is not very complicated, and therefore it is possible to design and build a custom system without relying on the manufacturing companies. Motivation for building a system from scratch is due to the high cost of purchasing a complete system.\textsuperscript{3} It is far more economical to construct due to the simple application needs such a system will provide.

My project will involve studying past research on ALD systems with a focus on Al\textsubscript{2}O\textsubscript{3}, which is cheap and an insulator, with the intention of being deposited across other devices for testing. After research, a design system will be created to minimize costs and fit with available equipment in the lab. Other parts will be purchased and
assembled. The final goal is to calibrate and test the system, with importance placed on attempting to produce similar results found in the literature.

**Thin Films**

Thin films are, by definition, a layer of material on the order of nanometers upwards to several microns in thickness. Depending on the material, application of thin films ranges from reflective coatings to intricate electronic interfaces. Because of the many uses of thin films, the techniques of deposition are very important. In general, there are two types of thin film deposition, chemical and physical.

In chemical deposition, a precursor liquid or gas is introduced onto the surface of interest, where then a reaction occurs bonding the precursor and the surface. This type of deposition tends to produce conformal films, or where the thickness of the film is uniform irrelevant of how rough the surface is. Common types of chemical deposition include chemical vapor deposition (CVD) and plating.

In contrast, physical deposition makes use of mechanical and thermodynamic interactions to produce thin films that are not actively bonded to the surface. In this technique, the film material is energized to vaporization and then allowed to travel to the cooler target surface where a solid film layer forms. Normally, physical deposition
is performed in vacuum to reduce collisions and allow the particles to travel as fast as possible to the film site. This tends to create directional deposition, where the surfaces perpendicular to the flow of particles have thicker films than parallel ones. Thermal evaporation, sputtering, and pulsed laser deposition are some of the common types of physical deposition.

**Atomic Layer Deposition**

Atomic layer deposition is a type of chemical deposition, implying that the film adheres strongly to the surface while maintaining conformity. ALD utilizes two alternating sequential (ABAB) gas exposures with a purging gas in between to ensure the two reactants do not mix. If we specify that the reactants are labeled as A and B with the purging gas as C, then a complete cycle of deposition is simply the introduction of these gasses in the order ACBC.\(^4\) Each of these reactant gases are required to be self-limiting, in the sense that after an initial reaction to the surface, no further reactions will occur between the reactant with itself and/or any products produced. After a complete cycle, the surface must also be reset to the original conditions to allow continued deposition. Because the deposition can be terminated successfully after a single layer of
deposition, it is able to produce monolayers of film as well as controlling the thickness of films based on the thickness of the monolayer.

ALD has many other advantages, such as large area uniformity. Since the deposition is a chemical reaction and self-limiting, large surface areas can be covered using this technique without much difficulty. This system has the benefit of being highly reproducible, and follows naturally from the requirement of needing many repeated cycles to build a thicker film. The temperature ranges for these depositions are also fairly low, ranging from 150°C to 400°C.

**ALD for Al₂O₃**

In production of Al₂O₃ thin films, reactant A is Trimethylaluminium (TMA), reactant B is water vapor (H₂O) and the purging gas C is nitrogen (N₂). When TMA is initially introduced to the deposition site, the reaction that occurs is

\[
\text{Al(CH}_3\text{)}_3 + \text{SiOH} \rightarrow \text{SiOAl(CH}_3\text{)}_2 + \text{CH}_4
\]  

where the substrate surface is made of silicon (Si). The substrate itself is covered in hydroxyl groups that come from the absorption of water vapor present in the air. After purging the system with nitrogen, the next reactant is introduced. The second reaction with water vapor is governed by

\[
2\text{H}_2\text{O} + \text{SiOAl(CH}_3\text{)}_2 \rightarrow \text{SiOAl(OH)}_2 + 2\text{CH}_4
\]
After this reaction, the surface of the film is primed for a new cycle of ALD due to the presence of hydroxyl groups. The byproduct of both of these reactions is methane (CH₄) which does not react with either film layers, and therefore carried out of the system during the next nitrogen purge.

At this point, the cycle is complete and a single monolayer of Al₂O₃ is deposited on the silicon substrate. Continuing the procedure to deposit a thicker film simply requires restarting the cycle with TMA and so forth. The reactions that govern further growth are

\[
\text{Al(CH}_3\text{)}_3 + \text{Al-OH} \rightarrow \text{Al-O-Al(CH}_3\text{)}_2 + \text{CH}_4
\]  

(3)

\[
2\text{H}_2\text{O} + \text{Al-O-Al(CH}_3\text{)}_2 \rightarrow \text{Al-O-Al(OH)}_2 + 2\text{CH}_4
\]  

(4)

The thickness of a single layer of Al₂O₃ is ~1.07Å and therefore also the thickness control of the system, allowing any multiple of this thickness to be theoretically produced. The crystal structure is shown in Figure 1, with a detailed 3D view that can be found at the site found under reference 6.
Design

The final setup design of my system is based strongly on those found in the literature, and is shown in Figure 2.

There are many components to the system, with there being three main sections. On the left is the vacuum pumping section, the middle is the deposition site and on the right are the precursors and their controllers.
Vacuum Pump Section

The vacuum pump is one available in the lab, an Edwards XDS series that has a particle filter (Figure 3B) used to trap excess reactants from the deposition process to prevent damage to the pump. This mechanical pump (Figure 3A) is connected to the top of a Kurt J Lesker (KJL) KF25 Tee (Figure 3C1) that allows three way connections through KF25 seals. The middle connection (Figure 3C2) is attached to an Edwards Speedivalve (Figure 3D) that allows coarse adjustments to the pressure of the system. The bottom Tee connection (Figure 3C3) is adapted to a \( \frac{1}{4}'' \) VCR tube (Figure 3E) that
attaches to a Swagelok metering valve (Figure 3F) and used as a fine tuning control of the system pressure. These two valves are attached to a KLJ KF25 Cross (Figure 3G) that connects to a manometer (Figure 3H) on one end and the rest of the system on the other end. The manometer is a KJL model, and is used to measure the pressure within the system and relay the information to a computer station. When a precise pressure is required, the coarse valve is first adjusted to be approximately the desired pressure, and then the fine tuning valve is adjusted to give us an exact pressure value. The deposition site will be maintained at a pressure of 0.1 Torr.

![Figure 4: Deposition site section with the key components labeled](image)

**Deposition Site Section**
Connecting from the vacuum pump section is a MKS KF25 to vacuum tube compression fitting (Figure 4A) that seals the quartz tube (Figure 4B) used as the deposition site. The quartz tube is housed within a heater (Figure 4C) that raises the temperature to 177°C, the deposition temperature. The other end of the quartz tube is a MKS vacuum compression fitting to KF40 adapter (Figure 4AD) to connect to the precursors/controllers section. Within the quartz tube, the sample substrate (Figure 4E) is placed, along with the quartz crystal microbalance (QCM) (Figure 4F). The sample and QCM are loaded into the quartz tube by removing the compression seal on the precursors/controllers section side.

The QCM is a device that measures changes in frequency that can be determined through changes in mass using Saeurbrey’s equation. These changes in frequency can then be correlated to changes in thickness confirmed through other techniques, such as Ellipsometry. By placing the QCM very close to the substrate, we can approximate the deposition rate by measuring the same rate on the surface of the QCM.
From the previous section, the compression to KF40 adapter is connected to a KJL KF40 Tee (Figure 5A1). The middle connection of this Tee (Figure 5A2) is connected to a ¼” VCR tube (Figure 5B) to a MKS mass flow controller (Figure 5C) that regulates flow rates of the reactant gases. The third end of the Tee (Figure 5A3) is used
to connect the backend of the QCM (Figure 5D). It contains the feed through that allows measuring of the crystal held within the quartz tube.

The mass flow controller is connected to a Swagelok union (Figure 5E) that allows the three gases to be regulated by the same controller. Each of the three union connections will be attached a Swagelok needle valve (Figure 5F). The needle valve is used to manually control the amount of gas flow into the system while ensuring no liquid reactant enters the system. The needle valves also ensure different pressures on either side of the valve. On the reactant side, the pressure will quickly raise to that of its vapor pressure, ~20 Torr for water and ~8.7 Torr for the TMA.

Each of the needle valves is connected to a Swagelok electropneumatic actuating solenoid ball valves (Figure 5F). These are valves designed to only activate in the presence of an electric current, which opens the valve by activating a compressed air line. This seemingly roundabout method is designed to account for unforeseen power outages. In the case of a power outage, the loss of electric current will deactivate the compressed air which in turn closes the ball valve. This effect is apparently not achievable with electrical valves alone. From these solenoid valves a VCR tube is fitted that then connects to the gas containers. Each of the containers will possess their own ball valve or regulator to allow manual shut off of the gases.
Safety

The issue of safety in this project is important due to the dangers of the TMA precursor. The MSDS for TMA lists that the chemical can cause severe burns if physical contact is made. The chemical is also highly flammable, reacts violently with water, and can spontaneously ignite in air. To ensure safety, the entire system will first be leak tested with helium. In this process helium is allowed to flow through the entire system, and a mass spectrometer is used to detect if there is any leakage anywhere. The entire system will also be housed within a walk in fume hood, to help ventilate out the gas in case of a leak. Beyond these safety measures, the handling of this chemical in this project should not require anything more. Goggles, gloves, and lab coats should also be used to provide extra protection.

Current Progress

The system is currently ~80-90% complete. Due to communication issues with one company, the QCM device still has not been purchased. The solenoid valves have only recently arrived, and was discovered that they are several pounds in weight, and since the quartz tube will be approximately a foot off the table, a stand needs to be made to support the devices. Compressed air is available within the fume hood; however, it must be split in some way to provide air to each of the three solenoid
valves. These valves also require electrical inputs that are controllable by a computer for automation. The following are images of the setup equipment that are currently available. Some of the parts are not connected together due to lack of space. Once the supports are placed, room will be available to make all of the connections.

Figure 6: Overview of the setup area with the three different sections in separate pieces
Figure 7: Precursors/Controllers section containing the solenoid valves needed to allow automation
Results in Literature

While the system is incomplete and therefore no data can be collected ourselves, it is useful to understand the kinds of results we expect and wish to find.

Average Al₂O₃ Thickness in a Single Cycle

![Graph showing Al₂O₃ thickness over time](image)

Figure 8: Average Al₂O₃ thickness in a single cycle showing most of the film thickness arises from the first reactant TMA

In Figure 8, the Al₂O₃ film thickness is measured as a function of time. This is also correlated to the mass deposited as measured by the QCM used in their system. The
thickness is averaged over one hundred runs. The TMA deposition accounts for a large fraction of the thickness of the film, with water vapor making up a far smaller percentage. The film thickness appears to be ~1.1 Å.

Figure 9 shows the \( \text{Al}_2\text{O}_3 \) thickness per cycle. This graph shows that the thickness increase is extremely linear, which is what we would expect since each cycle...

![Graph showing Al₂O₃ thickness per cycle](image)

**Figure 9:** \( \text{Al}_2\text{O}_3 \) thickness per cycle over a hundred cycles shows a strong linear relation
cycle should produce 1.07Å of film. The discrete steps observed in the data show that the film is being deposited in layers. These observations reinforce our knowledge that a termination of the deposition process after any complete cycle will leave a conformal film whose thickness is easily determined. The slope of this line is where the estimation of the thickness control for the system originates.

Al₂O₃ Growth Rate in Varying Deposition Times

Figure 10: Al₂O₃ growth with varying exposure times. While one variable is being tested, the other remains constant.
Figure 10 analyses what happens to the Al₂O₃ growth rate when the deposition times of the TMA and H₂O are varied away from their starting values of 1 second. While one exposure time is being varied, the other is being held constant at the original 1 second. What is found is that under both circumstances, the growth rate saturates at ~1.2Å/cycle. The saturation occurs after 3 seconds for varying H₂O times and after 8 seconds for varying TMA times. These results are found to be consistent with previous works and ex situ ellipsometry measurements.

**Al₂O₃ Growth Rate in Varying Purge Times**

Figure 11: Al₂O₃ growth with varying purge times. While one variable is being tested, the other remains constant.
In Figure 11, Al₂O₃ growth rates are measured while purge times after reactant exposure are varied. As in the previous test, while one time was being varied, the other time remained constant at its original value, in this case 5 seconds. During these experiments the exposure times of the precursors remained constant at 1 second. It is found that purge times less than 1 second for H₂O and 0.5 seconds for TMA causes large spikes in the Al₂O₃ growth rate. This is attributed to the fact that the purge times are insufficiently long enough to remove all particulates of the previous reactant before the next reactant is introduced. The mixing of the precursors causes a reaction that produces CVD, which is undesirable. To ensure this does not occur, purge times greater than 1 and 0.5 seconds for H₂O and TMA, respectively, are required.

In a separate test, this same ALD growth was performed where only the sample substrate is heated and not the entire deposition site, it was determined that a purge time greater than 15 seconds was needed to avoid the CVD effect. This is an important observation, and luckily our system by default causes the entire deposition site to be heated.
Future Work

The first thing that must be accomplished is the completion of the set up with the supports and secondary equipment. Once this has been accomplished, we would like to reproduce these results. Having done that, the implementation of this technique in other work being done in the lab will become viable.

Because I was unable to finish my project as originally planned, I will also need to prepare detailed information about the parts purchased, the system design, and all the things I have learned and observed for my successor. Hopefully my notes will allow him/her to finish what is left of this project quickly and easily.

Acknowledgements

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References


3. Cambridge Nanotech 2003


