

DESIGNING, MODELING, MANUFACTURING, AND TESTING AN ATOMIC  
LAYER DEPOSITION SYSTEM

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by

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*I would like to dedicate my thesis to Mamani Mansoor and Baba Ali, the most loving and caring grandparents in the world. None of these could happen to me without their love, support, and existence in my life. The thoughtfulness and generosity I learned from them will always stay with me and I will forever be in their debt because of the happiness they brought to my life.*

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## **Abstract**

There are multiple techniques for depositing thin films in nanoelectronics and semiconductor industries. Each technique has its own advantage and disadvantage. Of the many techniques, chemical deposition is the most favorable since materials can be deposited in high aspect ratios and give full coverage across uneven surfaces. However the most conventional technique in chemical deposition, named chemical vapor deposition (CVD), has some limiting properties like high temperature and uncontrollable film growth. To have the advantage of chemical deposition and also being able to control film growth in monolayer resolution, a new technique has been introduced, named Atomic Layer Deposition (ALD). This technique gives a very good control on layer-by-layer film growth. It can work at low temperatures and high pressures. In manufacturing nanoantennas and MIM diodes there is a need, for having an ultra thin film with full coverage across select areas. ALD is a promising solution for ultra-thin film fabrication problems. In this work we designed, modeled, manufactured, and tested a novel ALD system. Our system is designed to do more exotic film depositions than the small-range accessible with industrially available ALDs.

A typical ALD process starts with entraining a precursor in a carrier gas that brings it inside the reactor where it adsorbs on the substrate's surface. The second step is removing the extra precursor from the chamber by purging it. The third step is adding another precursor gas to the reactor. The two precursors will react with each other on the substrate's surface. In the fourth step a purge is used to remove excessive precursors and by-products from the reactor chamber. A well-designed reactor for this process needs to have the ability to operate under high vacuum, high temperatures, and intense reactions. In the designed reactor within this project, a showerhead, a stage heater, a ceramic spacer, and stage holder were designed and manufactured. There are four gas inlets from a top flange that feed into showerhead, which helps better gas dispersion. Also in the showerhead each of the inlets can be used to bring different gases inside the reactor for CVD processes. The designed reactor is a cross reactor, which minimizes the gas entrapment. All the flanges were designed in a way to have good ability to control the

system.

The tubing in this system is used to bring precursors inside the reactor. To have a good control on the flow rate of precursors, individual mass flow controllers, i.e. four ALD Solenoid Valves, are used to regulate the flow of each precursor. Bubblers are used to contain precursors at the entry point of the gas delivery line. Each bubbler has a dipping tube that extends the length of the bubbler container to give the carrier gas the ability to entrain precursors and bring them inside reactor. ALD Valve-4 is designed in a way that can switch the system from ALD to CVD. This gives us the ability to have multiple depositions in different techniques in a single run. ALD Valve-3 is designed for vacuum bubblers in case there is a precursor with very low volatility or very sensitive to high temperatures.

Controlling the entire system, all at the same time, is crucial to the success of ALD. The parameters that needed to be controlled are temperature, pressure, gas flow, and each of the ALD Valves. There are five parts in the designed system that have separate thermocouples and heaters. Each of bubblers, tubings, the reaction chamber's body, and substrate stage can get to a separate temperature using PID controllers. Finally a box designed for all the PID controllers and relays to read all the temperatures side-by-side. In addition, there is a terminal box that connects all the tubings' heaters and chamber heaters together. Low vacuum pressure can be read by either of the two thermocouple gauges installed on the system. One of the thermocouple gauges reads the pressure of the reaction chamber and the other reads the pressure inside turbopump. To control gas flow and ALD Valves, a software program was developed that can send digital signals to DAQ cards and the cards can change it to analog signal and send to MFCs and Valves. A control box is designed that contains all the four DAQ cards and a circuit that gives us the ability to control the valves by low currents.

Finally the manufactured ALD was tested for process of depositing  $\text{Al}_2\text{O}_3$  on top of silicon substrate. The test were performed in two batches, EDS test were performed to prove the deposition of  $\text{Al}_2\text{O}_3$  also AFM test showed very flat films with 1.2 nm RMS were fabricated. The results of tests ensured the ability of the ALD to deposit films.

# 1. Introduction

Thin Film deposition is the technique of depositing a thin, flat film of a material with usually sub-micrometer thickness. This thickness can vary from micrometer scale to nanometer scale depending on the application. Nowadays thin film industries and nanoelectronic companies are in the frontline of commercial growth due to their fast influence in communication and information processing industry. The results of the expansion in thin film technologies can affect other industries like biotechnology, renewable energies and environmental science. Most of the future improvement in the mentioned industries is highly-dependent on advancement in thin film deposition technologies. (Ohring, 2001)

There are two major categories in thin film deposition techniques:

## 1. Depositions with chemical reactions:

- Chemical Vapor Deposition (CVD)
- Atomic Layer Deposition (ALD)
- Electrodeposition
- Epitaxy
- Thermal oxidation

In these processes the deposition of new film on the substrate happens due to a chemical reaction either in the environment of the reaction cell (chamber) or on the surface of a substrate. In this case there would be some by-products from the chemical reaction that can become a part of the deposited layer.

## 2. Depositions with physical process:

- Physical Vapor Deposition (PVD)
- Sputter Deposition

In these processes there are no chemical reactions and the deposited material physically moves on the substrate's surface.

It is usually possible to tailor the deposition process to satisfy the specific needs by changing the deposition process type, reactants, deposition equipment, and deposition environment. There are two major participants in this rapid growth of deposition technologies. The first is semiconductor industry which is interested in developing new technologies to manufacture smaller, faster and more durable devices; the second is the advances in characterization technologies which provides the ability to resolve a better understanding about the physics, chemistry and microstructure of the surface. (Werner Kern, 2001)

Regarding the significance of different deposition techniques on thin-film's quality; we tried to tailor a deposition technique, which allows us to produce ultra-thin films with minimum surface roughness to address the issues in nanoantennae and Metal-Insulator-Metal (MIM) diodes fabrication. In this text, first I am going to provide background about different deposition techniques in terms of their advantages and disadvantages. Then I will provide detailed information about Atomic Layer Deposition (ALD) systems; their different types, their mechanisms, kinetics, precursors, and applications. This discussion will provide the necessary background in which in which to present our design for an ALD/CVD system, which is customized for nanoantenna and MIM diode fabrication. I will present computational modeling and simulation of heat transfer and flow within my reactor which fed the designs various components of the ALD/CVD system. I will detail the machining, fabrications, and overview the process control systems. Lastly, I will speak to the quality of thin films produced by our homemade ALD/CVD interms of their surface roughness, deposition rate, and any existence of unwanted materials which have remained either in the thin film and/or ALD/CVD chamber.

## **1.1 Thin-Film Deposition Techniques**

Deposition techniques can be split into two branches: Chemical Vapor Deposition (CVD) and Physical Vapor Deposition (PVD). In PVD, a material evaporates or sputters on the surface with no chemical reaction. In CVD, volatile reactants are introduced which react with each other on the substrate surface to produce a thin layer. The precursors for

these processes are usually organo- or hybrid-compounds that have high vapor pressures at low temperatures. Both of the major deposition methods can be divided into variety of techniques. In the following we are going to discuss major physical and chemical deposition techniques that have been used in nanoelectronics fabrication. (Lesker, 2015)

### **1.1.1 Physical Vapor Deposition Techniques**

#### **1.1.1.1 Evaporation**

The purpose of this process is depositing a thin film of the selected material with atomistic control upon growth rate and film formation. Basically thermal energy induces a change in the physical state of the target material which then starts to evaporate or sublime. The evaporated material leaves the source and condenses on the substrate surface which forms a layer of the target material.

Major differences between PVD and CVD are:

1. Working with solid or molten sources, as CVD works with reactive gas or liquid phase precursors

2. Physical mechanisms

3. Ultra high vacuum for evaporation PVD to give the ability to evaporated material to reach the substrate without getting colliding with other gas molecules.

4. Absence of chemical reactants at the source and chamber environment in PVD (Ohring, 2001)

Generally there are three steps in any physical vapor deposition: creation of vapor from the source material; transport of the vaporized material to the substrate; condensation of the vapor on the surface of the substrate to produce the desired thin film. This process usually is housed in an ultra-high vacuum chamber to limit oxidation and maximize the deposition rate. The way evaporated material condenses on the substrate determines many physical properties of the deposited film. Nucleation and growth are the main steps in condensation part. In nucleation, the evaporated particles that reach the

surface lose their thermal energy and the substrate absorbs that energy. Depending on the amount of thermal energy, the deposited atoms may diffuse on the surface until thermodynamic equilibrium is reached. As the nuclei continued to form, they grow to a continuous sheet covering the substrate. The type of the bond and the energy of the bond, between substrate and deposited material, determines the strength of the bond between the two. During film growth the structure of thin film starts to develop. This structure can be described in terms like grain size, orientation, porosity, impurity content, and entrained gases. In some conditions high vacuum deposition processes are preferred over the other techniques to achieve the following properties:

- 1) High purity.
- 2) Good adhesion between the thin film and substrate.
- 3) Control over mechanical stress in the film.
- 4) Deposition of very thin layers, and multiple layers of different materials.
- 5) Low gas entrapment.

There are multiple parameters that one can control to change the properties of the thin film and get to the desired surface condition. The parameters one can control to achieve the specified goals are:

- 1) Kinetic energy of the evaporated atoms.
- 2) Substrate temperature.
- 3) Deposition rate of the thin film.
- 4) Augmented energy applied to the film during growth.
- 5) Gas scattering during transport of the vapor.

By changing these parameters thin film with different mechanical strength, optical reflection, electrical resistivity, and magnetic properties can be generated.

Heat can be delivered to the target material in several different ways like resistive heating, induction heating, and electron beam heating. The section that follows will discuss each of the different evaporation techniques.

#### 1.1.1.1.1 Resistance Evaporation

Electrical resistive evaporation is the simplest and most economical method of deposition between all kinds of PVD methods. In this method due to high resistivity in the filament by adding electrical energy at low voltage and high current the temperature of filament increases. The increase in filament's temperature causes the increase in target temperature which is in close contact with filament. By increasing the temperature, the target material starts to melt and evaporate. To prevent any unfavorable reaction and also increase the vapor pressure of targeted material, this process is contained in high vacuum or ultra-high vacuum chambers. These chambers are usually in glass bell jar in lab scale processes because they give high flexibility movement in chamber and cheap way to see inside the chamber. The filaments are usually made of refractory metals like Tungsten, Tantalum, etc. Filaments possess a high melting point (from 1000 °C to 2000 °C), a low solubility to the target material, high wettability, and also be highly resistive to thermal shocks.

#### 1.1.1.1.2 Induction Heated Thermal Evaporation

In this method a power supply generates Radio Frequency alternating current, the RF current goes through a conductive target material. This technique has many advantages like, low contamination in deposited films, and better control on deposition rate. The disadvantages in using this method is that the target material must be conductive, RF power supplies are typically very expensive, and there are possible chemical reactions between the target and crucible.

#### 1.1.1.1.3 Electron Beam Evaporation

In this method a heated filament generates an electron beam. This beam supplies

the necessary thermal energy to evaporate the target material. All of these systems have an anode and a cathode and they are usually categorized in self-accelerated and work-accelerated e-beam evaporators. (Bilto ft, 2002)

### **1.1.1.2 Sputtering**

Sputtering is one of the most popular thin film fabrication technologies. Although this technique of fabrication is widely used for metal depositions, in some cases it has been used for deposition of insulators. In this technique, accelerated ions hit the surface and force the surface atoms to detach from the surface and move toward the substrate where the ejected atoms can then condense on the substrate's surface and produce a thin film. A reverse process can be used to remove unwanted material from surface in this case the accelerated ions hit the contaminated surface and remove the unwanted material from the surface, this process is referred to as sputter etching. Sputtering is different from evaporation in many aspects and it results in deposition of more dense, conformal, and continuous film. As a result of acceleration potential inside the chamber the bombardment ion accelerates on the surface, this accelerated ion could produce from many different gases, but typically an inert gas is more favorable due to its non-reactivity. Argon is chosen because it is an inert gas and its molecular weight is close to the metals that are usually used in semiconductor industries like Ti, Al, and Cu. The required energy to accelerate the ions comes from the potential drop between the ionized gas and bombarded target. (Seshan, 2012) There are many different types of sputtering depositions; for brevity, three of the most common will be discussed here.

#### **1.1.1.2.1 DC Diode Plasmas**

DC Diode Plasma is the simplest among sputtering techniques. This process consists of two parallel plates (electrodes), a vacuum chamber and a power supply. A plasma discharge forms between the two plates which results in the movement of charged ions from the positive anode plate to the negative cathode plate. Due to the lighter mass of electrons they have higher velocity than gas ions, this higher velocity results in formation of a sheath layer next to the cathode. This sheath layer doesn't contain electrons and is the main cause of potential drop between cathode and anode. The

accelerated ions hit the target in cathode side causing newly ejected electrons, called secondary electrons. These electrons accelerate away from the plate and form an ionized gas either by hitting the neutral gas molecules directly or by elevating the Maxwellian velocity distribution of electrons already existing in the plasma through electron-electron scattering. (Rossnagel, 2003)

#### 1.1.1.2.2 RF Plasmas

To obtain a higher level of ionization and sputtering of cathode the DC power supply can be replaced by an alternating current RF source. The use of RF power results in a longer residence time which ultimately results in higher rate of ionization due to the higher number of collisions, and higher plasma density. RF plasmas can also be useful for sputtering insulated material, because it prevents the charge built up through alternating polarity of cathode. This alternating potential in the anode also allows for efficient sputter-cleaning. (Seshan, 2012)

#### 1.1.1.2.3 Magnetron Sputtering

In this technique, a permanent magnet is used so the secondary electron will be confined near the target surface which results in higher residence time of secondary electrons which results in higher ionization and denser plasma leading to higher deposition rates. (SM Rossnagel, 1987). Orbital motion magnetic sputtering is the most common form of magnetron sputtering because it provides a more uniform magnetic field and more conformal depositions.

### **1.1.2 Chemical Vapor Deposition**

Chemical vapor deposition is one of the most popular material processing techniques. This technology can be used for thin film deposition, ultra-high purity powder formation, and composite material production. It has been used to deposit a very wide range of materials, from pure elements to different sort of compounds. (Park, 2001)

The simplest way that CVD can be described is that it is a process whereby one or multiple precursor gases flow through a reactor to react and coat a heated substrate

surface. In this process, reactions can occur on or near the heated surface, which produces a thin layer of the desired material. Each reaction will have some by-products, which go to the vacuum chamber exhaust along with the unreacted precursors. Since CVD is one of the most popular thin film deposition methods and since there is much variety in the mechanisms required to produce the many materials one may wish to deposit, there are obvious multiple types of CVD methods. CVD can be performed in either hot-wall reactor or cold-wall reactor; it can be done at atmospheric pressure or high vacuum. It can be performed with different kinds of carrier gases or by not even using a carrier gas; and there is a wide range of temperatures, from 200-1600°C. Also there have been some enhancements in traditional CVD, which have led to production of other CVD systems using plasmas, ions, photons, etc. Using these new tools has given the ability to produce more conformal surfaces with higher deposition rates, and fewer contaminants and imperfections in the film. A major advantage of CVD is the quality of the deposited thin film surface, which usually gives a very conformal and more homogeneous surface. Another advantage is its ability to deposit films in areas possessing high aspect ratio holes in contrast with PVD which suffers from severe shadowing limitations, i.e. PVD requires a line of sight between the source and the desired area. Another advantage of CVD is the high purity of deposited material, which comes from the highly pure precursors. CVD also has some disadvantages. One of its major disadvantages is its precursors, which need to be volatile at room temperature. These precursors are generally highly toxic; corrosive, explosive, and/or extremely reactive; and expensive. These precursor characteristics place some restrictions in the choices of film deposition. In addition, sometimes when the films temperature is reduced after deposition, residual stresses can arise in the film which also lead to the potential for a lower stability in the film. (Park, 2001)

#### **1.1.2.1 CVD Processes**

A CVD process is a very complex process with reactions taking place in both the gas phase and on the surface. In figure 1-5 a simple illustration of the striation within the overall reaction process for a typical CVD process reaction is shown.

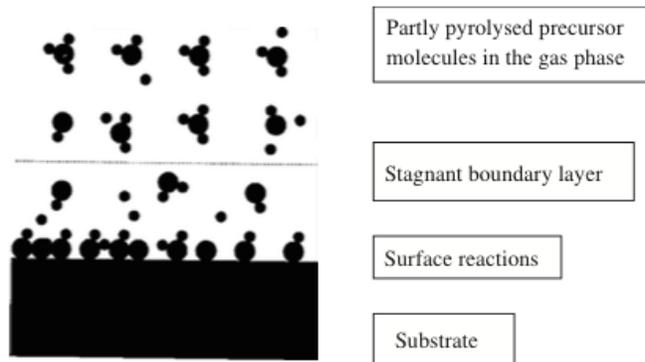


Figure 1-1 Simple schematic representation of MOCVD process (O'Brien, 1997)

The key steps in CVD processing is further illustrated in figure 1-6. These steps are(O'Brien, 1997):

1. Evaporation and transport of recursors
2. Reaction of precursors in gas phase
3. Transport of reactants to the substrates surface;
4. Adsorption of reactants on the surface;
5. Surface reaction leading to site growth, and nucleation
6. Desorption of byproducts

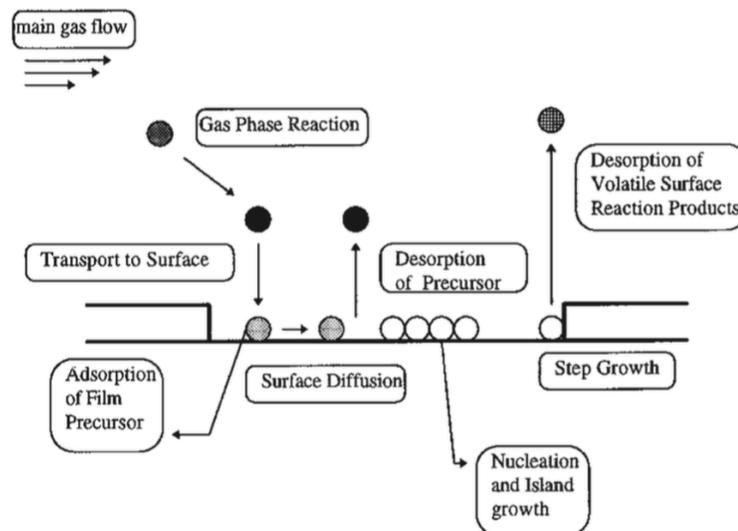


Figure 1-2 Precursor transport and reaction processes in CVD. (O'Brien, 1997)

In thermal CVD the film growth depends on several parameters like temperature, pressure within the system, and the chemistry of the precursors.

Both kinetic energy and mass transport play important roles in CVD systems. Having a constant temperature during the deposition process, uniform across the entire sample is very important to produce a homogeneous and complete deposited layer. By increasing the temperature there would be enough energy for surface and gas phase reactions so the process would only be limited by mass transfer. On the other hand increasing temperature to higher levels may lead to desorption of materials from substrate surface. Another important factor is pressure. In CVD systems pressure can vary from medium vacuum to atmospheric. Having lower pressure will lead the process to become more independent of gas phase reactions and in medium vacuums it only depends on the surface reactions.

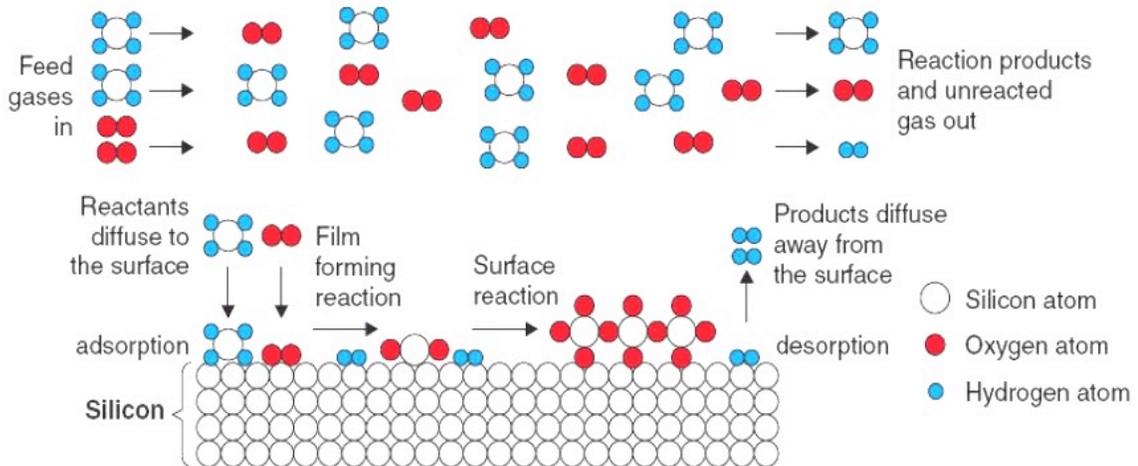


Figure 1-3 CVD deposition of second dioxide from silane

### 1.1.2.2 Different types of Chemical Vapor Deposition Systems

There are many different formats for CVD and there are many different classifications for these different kinds of systems. They can be classified based on their operating pressure like atmospheric pressure CVD (APCVD), Low-Pressure CVD

(LPCVD), and Ultrahigh Vacuum CVD (UHVCVD). Modern conventional CVDs are usually LPCVD or UHVCVD. There are also different plasma methods which include microwave plasma assisted CVD, Plasma Enhanced CVD (PECVD) and remote plasma enhanced CVD. There are also many other CVD techniques and systems for each especial application like Hot Filament CVD, Metallo-organic CVD, Rapid Thermal CVD, Atomic Layer Deposition (ALD) and many others.

Of all the different methods of chemical vapor deposition, ALD has been a center of focus in past couple of decades because it provides a very well-controlled method to produce a film deposited to an atomically specified thickness. Also, the growth of different multilayer structures is straightforward. Due to the sensitivity and precision of the equipment, it is very beneficial to those in the field of microelectronics and nanotechnology in producing small, but efficient semiconductors. ALD is typically run at lower temperatures along with using a catalyst, which drives thermochemically-favored reactions. The lower temperature is beneficial when working with fragile substrates, such as biological samples. Some precursors that are thermally unstable still may be used so long as their decomposition rate is relatively slow. (George, 2010) In the next chapter I am going to talk about ALD systems, their characteristics, precursors, applications, etc.

## 2 Atomic Layer Deposition and Characterization Techniques

### 2.1 Deposition Mechanism

Atomic Layer Deposition (ALD) is a different, newer method of CVD. In this method two or more precursors participate in the process in an alternating manner that is spaced by purging step. Figure 2-1 shows the process for a simple two precursors system. Aluminum Oxide ( $\text{Al}_2\text{O}_3$ ) deposition using Trimethylaluminum (TMA)  $\text{Al}(\text{CH}_3)_3$  and  $\text{H}_2\text{O}$  has been chosen because this is one of the precursor combinations used in the studies described in this thesis. The process consists of four major steps (1) precursor A (TMA) exposure; (2) purging of reaction product ( $\text{CH}_4$ ) and excess reactant; (3) precursor B ( $\text{H}_2\text{O}$ ) exposure and (4) purging of reaction product and excess reactant. In the cycle's first step, TMA vapor is exposed to a surface terminated with surface hydroxyl groups (Figure 2-1). Reaction of TMA with these surface sites produces O-Al bonds connected to two methyl groups (figure 2-2) on the surface.  $\text{CH}_4$  is produced as a byproduct, which is purged away along with any extra reactant, leaving a  $\text{CH}_3$  terminated surface at the end of step 2. The second precursor,  $\text{H}_2\text{O}$ , is then introduced which goes through a similar exchange reaction and byproduct ( $\text{CH}_4$ ) and extra water is purged away during step 4. At the conclusion of step 4 an  $\text{Al}_2\text{O}_3$  monolayer (or a partial monolayer) with a hydroxyl terminated surface very similar to the original surface at the start of step 1 is formed (Figure 2-3); this surface can undergo a similar sequence of steps to form another layer on top of the existing layer. Thus, the sequence consisting of 2 precursor pulses and 2 purge steps is termed one "cycle". The cycle is repeated in a sequential manner allowing layer-by-layer film growth. (George, 2010)

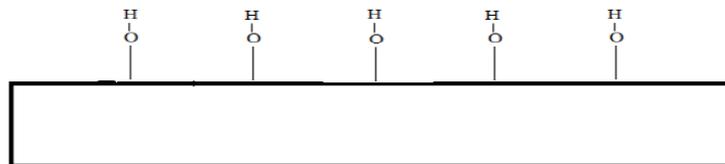


Figure 2-1 Hydroxyl groups on substrates surface

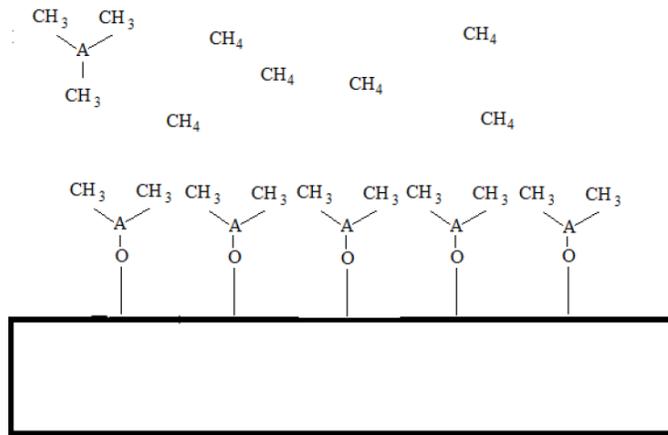


Figure 2-2 TMA bonds with H<sub>2</sub>O and reaction product is CH<sub>4</sub>

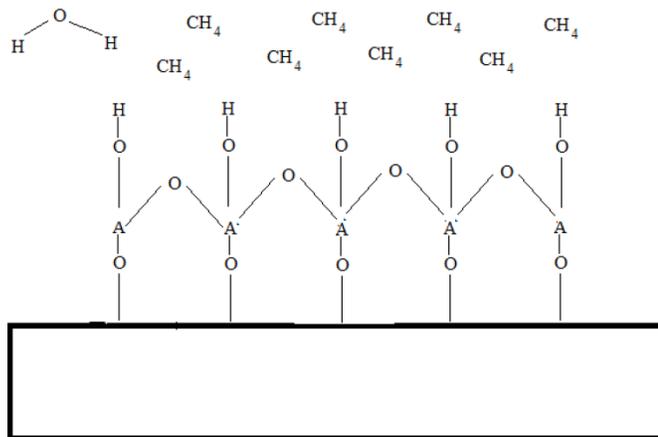


Figure 2-3 H<sub>2</sub>O purge, reaction between aluminum methyl groups with water results in production of aluminum oxide

It is very important to have sufficient flux of reactants in the process, since it prevents the process to be limited to mass transport and it only depends on adsorption and surface reactions. However the purge step should be long enough to eliminate the

possibility of gas phase reactions. In an ideal ALD process, materials can not be adsorbed on the previously adsorbed material, so after all the active sites filled by one material that material can't produce additional layers on top of the first layer. This is the major advantage of ALD which gives a self-limiting deposition on the surface; so after the cycle ends there would be only one layer of desired material. However it needs to be considered that for deposition of first layer due to nucleation and growth, the surface density of chemisorption sites may be different from further layer properties. Also since the adsorption is not limited by mass transport of precursors and it only depends on chemisorption, the deposition rate is constant over entire surface. This fact leads to very smooth surface, good step coverage, and a highly conformal thin film. Also the self-limiting film growth ensures good reproducibility and predictable scale-up. A general mistake in understanding ALD processes is that the deposition happens in a full monolayer followed by another full monolayer. In reality each cycle deposits 15-40% of a full monolayer. The reason for this behavior includes a limited number of active surface sites, and steric hindrance of bulky ligands. (Sinha, 2006)

## **2.2 Adsorption and Process Window**

### **2.2.1 Physisorption**

There are two basic types of adsorptions. Discussing them can give us a better understanding of ALD processes. First, depending on the substrate's surface and nature of precursor's gas, the bond strength between reactant and substrate surface can be different for various precursors and substrates. Second, the rate of adsorption can be very slow and finite. Physical adsorption (physisorption) is usually characterized by weak bonds (on the order of van der Waals forces) between the precursor and substrate. In thermal ALD the reaction occurs when both of the reactants are on the surface and the temperature is high enough to initiate the reaction. In all thermal ALDs temperatures are high enough to desorb weaker bonded monolayers. Because of this, thermal ALD usually takes advantage of chemisorbed monolayers of first precursors. All gases physisorb in a self-limiting monolayer if the temperature and pressure are in the proper range. The preferred condition for physisorption is moderate temperature and low pressure but if the

temperature is lower than expected there might be more than one layer of absorbed material and at low enough temperatures a liquid or solid film will be formed. As the temperature increases all other layers evaporate and a single monolayer will remain on the surface. Finally if the temperature is high enough the single monolayer will desorb from surface. Generally a monolayer of precursor will adsorb on a surface as long as the pressure is well below the precursor's saturation vapor pressure. Usually when precursors hit the surface and adsorb on it, they do not form a 100% complete monolayer, and this formation is highly dependent on temperature, pressure, and precursor concentration. The Langmuir isotherms detail this effect. These isotherms equate the rate of adsorption to the rate of desorption of gas molecules on a smooth surface. Also when a particle hits a bare space it sticks there and if it hits an occupied space it reflects back to the gas phase. However studying adsorption isotherms is very important in disciplines such as catalysis, but it plays a lesser role in ALD process since in this process, precursors cover an area at high enough pressure to form a complete monolayer. For example, nitrogen, which is a very common carrier gas for ALD process, at one millitorr, and at room temperature, will have a number density of  $\sim 3 \times 10^{13}$  molecules/cm<sup>3</sup>, and an impingement rate onto a surface of  $\sim 4 \times 10^{17}$  molecules/sec cm<sup>2</sup>. With a typical monolayer density of  $10^{15}$  molecules/cm<sup>2</sup> the impingement rate is  $\sim 400$  monolayers/sec. Therefore, there will be more than enough of a flux of gas phase species to the solid surface for a complete monolayer with 100% coverage to be formed. (Kääriäinen, 2013)

### **2.2.2 Chemisorption**

In chemisorption the reactant that has been absorbed on the surface forms a chemical bond with surface. In this case, the forces that holding the reactant on the surface are on the order of chemical bonds between atoms of a molecule. This kind of adsorption is important since sometimes the reaction between first and second reactant in ALD process needs to take place in high temperatures, however these temperatures may also result in desorption of physisorbed molecules. In this case the first reactant needs to be adsorbed and remain on the surface until the reaction is complete. (Kääriäinen, 2013)

Another important result of reactant's chemisorption in ALD process is that as the

reactant makes a bond with surface, it also makes a monolayer bond and any additional reactant that approaches within proximity of the surface will physisorb via a van der Waals interaction with the first monolayer that chemisorbed on the surface. However, the surface temperature will not allow physisorption to happen, therefore chemisorption bonding leads to a desirable single monolayer of reactants. (Kääriäinen, 2013)

### 2.2.3 Process Window

Understanding the process window for ALD is crucial in order to optimize the process and understand the kinetic of it in details. Figure 2-4 shows a typical ALD temperature window and indicates the self-limiting nature of ALD processes. There are different regions in this figure, which depends on ALD process's condition. Each characteristic region is explained as follows: (T. Suntola, 1994)

- L1 region: condensation of a reactant
- L2 region: activation energy-limited process
- W1 region: full monolayer saturation in each cycle
- W2 region: surface reconstruction during the deposition or steric hindrance between large precursor molecules
- H1 region: formation of non-volatile decomposition products from a reactant or a surface ligand
- H2 region: desorption of a monolayer formed or dissociation of a surface ligand

Since ALD growth rate is dependent on surface adsorption of precursors it is dependent on growth temperature which should be minimal as long as the process is in ALD regime. So the ALD window is characterized by a constant growth rate of one monolayer or sub-monolayer per cycle depending on the surface condition, chemistry, and size of precursor molecule. (T. Suntola, 1994)

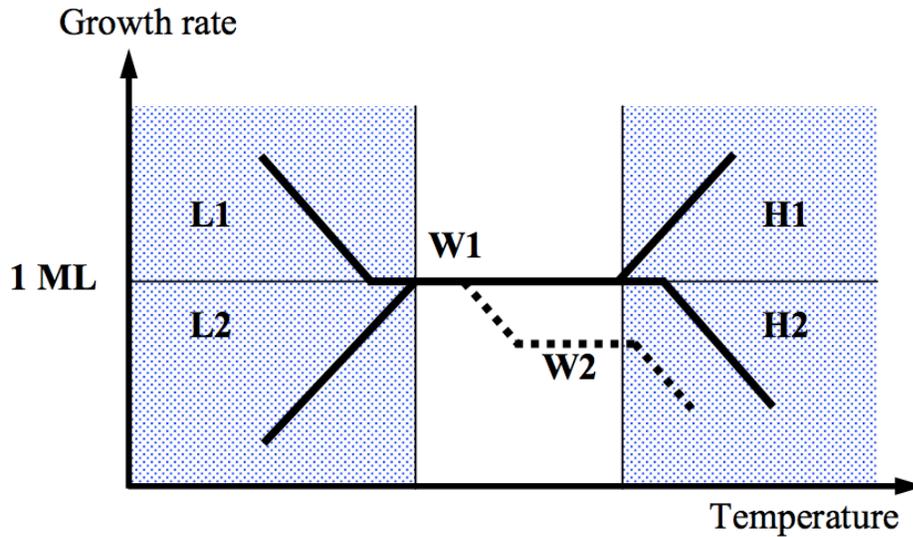


Figure 2-4 Temperature window of typical ALD process. ML stands for monolayer (T. Suntola, 1994)

Beside temperature, the design of a precursor delivery system is another key factor to characterize ALD process's behavior. Traveling-wave reactors, among many other reactor designs is a good starting point to characterize the ALD window and characteristic behavior of each precursor since it has a linear growth profile which depends on the flow direction (Figure 2-5). As can be seen from figure 2-5 insufficient dosing and purging along with desorption of precursors are the key factors which determine the film quality. Detailed explanation of each profile can be seen at caption of figure 2-5. If there is a good understanding about system and process's characteristics, then a near perfect uniformity on large-scale substrates can be achieved. Understanding the amount of dosing and the time for purging in delivery lines is as important as the temperature of substrate since all these characteristics need to work together to get a high quality film. (T. Suntola, 1994)

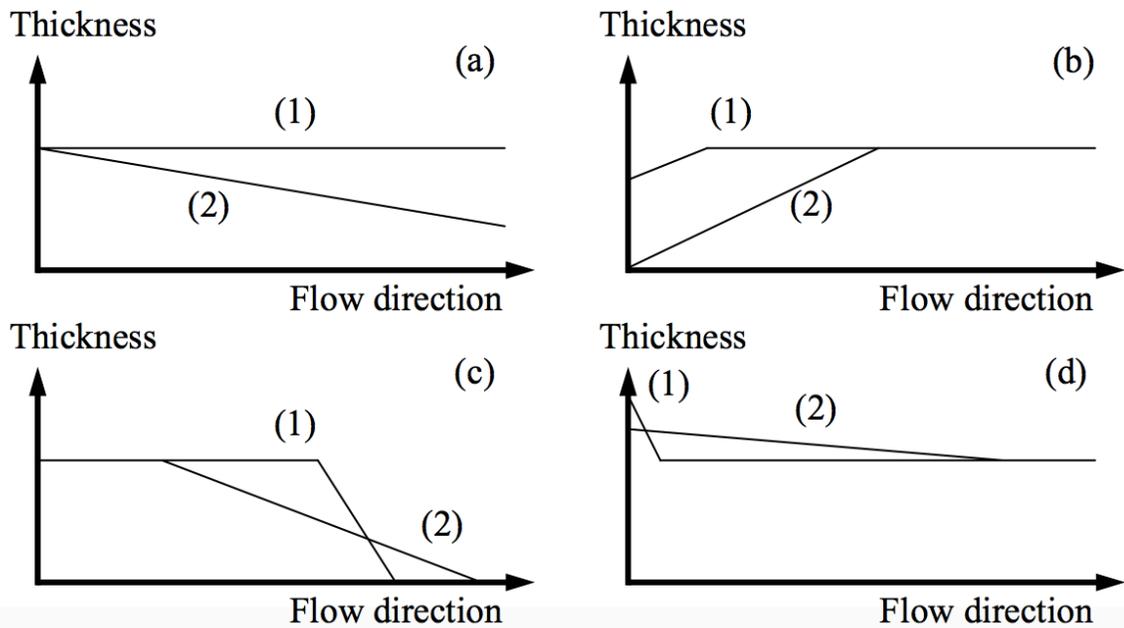


Figure 2-5 Characterization of the ALD process through the thickness profile in the direction of transport gas flow: (a) a good ALD process, (b) insufficient dosing of a reactant ((1) good and (2) poor reactivity), (c) desorption of formed monolayer ((1)slight and (2) strong desorption), and (d) insufficient purging ((1) slight and (2) strong effect of insufficient purging), CVD-like growth at the feeding end). (T. Suntola, 1994)

In contrast with CVD precursors, the precursors that need to be used in ALD should react aggressively with each other. On the other hand these precursors need to be stable within the processing temperature to avoid any decomposition and unfavorable reaction with other materials inside the reactor. (T. Suntola, 1994)

#### 2.2.4 Nucleation and Growth in ALD

To have a pinhole free ultra-thin film nucleation in ALD is very important. In case there is not a good bond between substrate and reactant, the nucleation may not happen or if it happens it only produce films in defected areas. This lack of uniformity can lead to island growth behavior in thin film production. After multiple ALD cycles the island might merge together and form a continuous film. Although in ultra-thin films there are usually not enough cycles and layers to cover all the islands. (George, 2010) Growth-per-cycle (GPC) is term that has been used for the amount of deposited material produced in a single ALD cycle and it is a function of three parameters: reactants, substrates surface, and reaction temperature. For many years the belief was that GPC is

constant during a process however recent research finds that due to the change in surface characteristics during the process, GPC can widely vary during the process. The effect of substrate surface can be seen in the beginning of the growth when the substrate is not fully covered by ALD grown film and by covering the substrate with ALD film the effect of substrate surface on GPC vanishes. ALD process can be divided into four classes to show different types of changes in the GPC (Figure 2-6). First, constant GPC, which is represented by a linear film growth (Figure 2-6 (a)). Second, a GPC that is higher at the beginning and becomes constant in steady region, which is called substrate-enhanced growth (Figure 2-6 (b)). Third, an initially lower GPC that increases to a steady growth, which is called substrate-inhibited growth (Figure 2-6 (c)). Fourth, a GPC that goes through a maximum and then decreases to steady GPC (Figure 2-6 (d)). The case with a gradual increase is referred to substrate-inhibited growth type 1, and the one with maximum in it is referred to as substrate-inhibited type 2. Substrate-inhibited type 1 has been observed for the  $\text{AlMe}_3/\text{H}_2\text{O}$ s (Me = methyl) process on silicon dioxide, and the  $\text{AlMe}_3/\text{NH}_3$  process on silica. Substrate-inhibited type 2 has been observed in many microelectronic fabrication processes like  $\text{ZrCl}_4/\text{H}_2\text{O}$  process on hydrogen-terminated silicon, the  $\text{AlMe}_3/\text{H}_2\text{O}$  process on hydrogen-terminated silicon, the  $\text{HfCl}_4/\text{H}_2\text{O}$  process on hydrogen-terminated silicon and on silicon dioxide, and the  $\text{TiCl}_4/\text{NH}_3$  process on silicon dioxide. Steady state in ALD is defined as when the GPC remains constant during processing. This is different from steady state in CVD since in ALD the constant amount of deposited material per cycle counts as the steady state. However in CVD the amount of deposited material per time needs to be constant to have a steady state CVD process. A brief comparison of steady state ALD and steady state CVD is given in Figure 2-6. (Vandervorst, 2004)

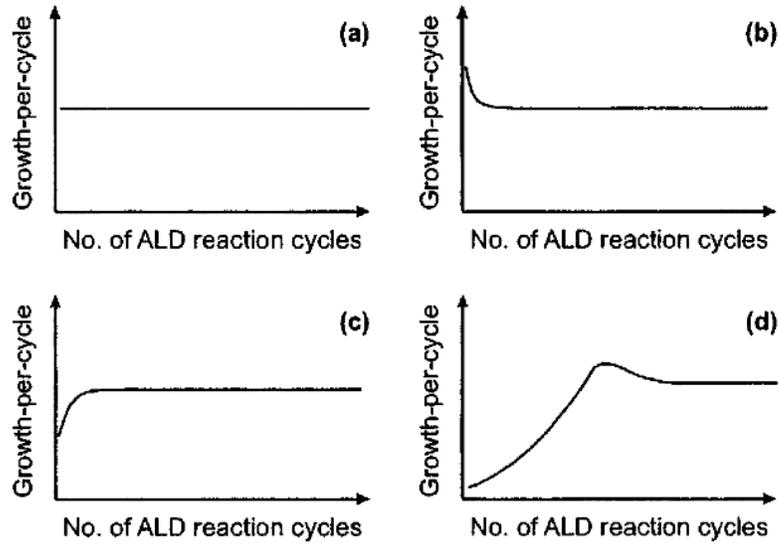


Figure 2-5 Proposed classification for the ALD processes:(a)linear growth,(b)substrate-enhanced growth,(c)substrate-inhibited growth of type 1, and(d)substrate-inhibited growth of type 2. (Vandervorst, 2004)

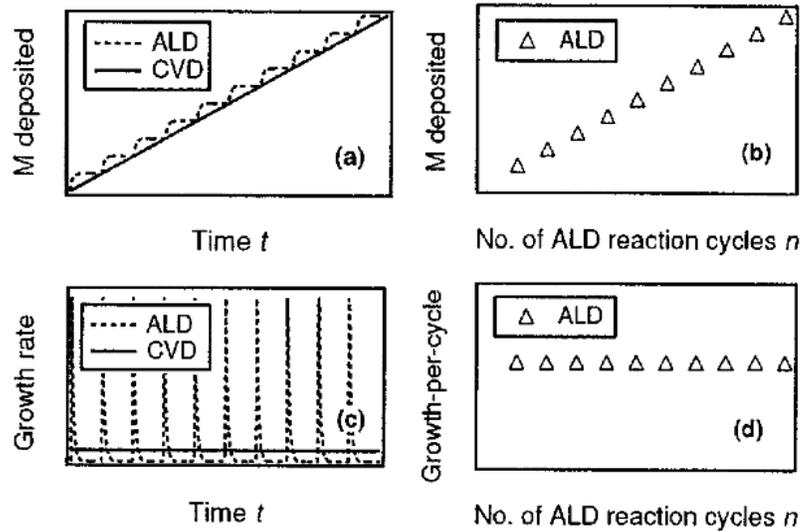


Figure 2-6 Comparison of steady ALD and steady-state CVD. Amount of M deposited  $c_M$  as a function of deposition time  $t$  (a) and the number of ALD reaction cycles  $n$  (b), the change in  $c_M$  with time, i.e., the growth rate(c), and the change in  $c_M$  and with the number of ALD reaction cycles, i.e., the GPC (d). (Vandervorst, 2004)

## 2.2.5 Materials for Atomic Layer Deposition

ALD can grow many different materials including metals, insulators, and semiconductors. Until now the major materials that have been deposited by ALD consist of pure elements, oxides, nitrides, and sulfides. Many of these materials have been grown in crystalline or amorphous phases. From table 2-1 it is obvious that there is a large selection of materials that can be deposited by ALD, however it is obvious that it is not yet possible to grow every material by ALD. (Richard W. Johnson, 2014)

Table 2-1 List of materials grown by ALD (Richard W. Johnson, 2014)

Elemental	Oxides	Nitrides	Sulfides	Other compounds
C, Al, Si, Ti, Fe, Co, Ni, Cu, Zn, Ga, Ge, Mo, Ru, Rh, Pd, Ag, Ta, W, Os, Ir, Pt	Li, Be, B, Mg, Al, Si, P, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Sr, Y, Zr, Nb, Ru, Rh, Pd, In, Sn, Sb, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, W, Ir, Pt, Pb, Bi	B, Al, Si, Ti, Cu, Ga, Zr, Nb, Mo, In, Hf, Ta, W	Ca, Ti, Mn, Cu, Zn, Sr, Y, Cd, In, Sn, Sb, Ba, La, W	Li, B, Mg, Al, Si, P, Ca, Ti, Cr, Mn, Co, Cu, Zn, Ga, Ge, As, Sr, Y, Cd, In, Sb, Te, Ba, La, Pr, Nd, Lu, Hf, Ta, W, Bi

Table 2-2 Available reactant groups for specific elements (Richard W. Johnson, 2014)

Elemental	Halides	Alkyls	Cyclopentadienyls	$\beta$ -diketonates	Other reactants
Mg, Mn, Zn, Ga, Cd, In, Sn	B, C, Ti, V, Cr, Mn, Cu, Zn, Ga, Ge, Zr, Nb, Mo, Cd, In, Sn, Sb, Hf, Ta, W, Pb	Be, Al, Si, Zn, Ga, Ge, Cd, In, Sn, Hg	Mg, Sc, Ni, Sr, Y, Zr, Ru, Lu, Os, Pt	Mg, Ca, Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Ga, Sr, Y, Zr, Ru, Pd, In, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Ir, Pt, Pb	Li, P, Ti, Fe, Co, Ni, Cu, Zn, Ge, As, Zr, Rh, Ag, Sb, Te, La, Pr, Yb, Hf, Ta, W, Ir, Pt, Pb, Bi

Selecting appropriate materials for ALD is very crucial. These materials need to facilitate the appropriate reaction pathway. Also, these materials need to act in a self-limiting manner during the adsorption process. These limitations may cause an extreme reduction in the number of materials that are available for ALD. A possible reactant precursor needs to be volatile enough to have vapor pressure in ambient temperatures or temperatures. Also while in gas phase it shouldn't decompose until it reaches and reacts on the substrate's surface. Surface reaction is preferred to be fast and irreversible to cause

fast growth. Neither the reactants nor the byproducts of reaction should etch or dissolve the substrate, growing film, or reactor itself. Small size reactants are also favorable to avoid steric hindrance. Finally the cost of reactants is another key factor in choosing the right precursor. Choosing the right precursor involves making a trade of between cost, availability, volatility, and reactivity. There are two major group of precursors: organics, and inorganics. Organic precursors generally are sources of pure elements and come in forms halides. Inorganic precursors more often are alkyls, alkoxides, amides, silyls and amidnates. Here the benefits and problems of some of these groups are discussed. Elemental reactants grow material with very high purity, however the number of elements with high vapor pressure in ambient temperatures is really limited. Halides are highly reactive with low steric hindrance and stable in wide range of temperature but reaction with halides usually release highly reactive by-product that can decrease the quality of the film and sometimes halides can incorporate in production of film. Alkyls are also highly reactive because of the bond between carbon and metals. Due to the high reactivity of halides  $H_2O$  can be used as counter reactant; however these materials decompose at high temperatures and are only available for small number of elements. B-Diketonates exist for large variety of elements but they are bulky and are not highly reactive so as a counter reactant they need a material more reactive than  $H_2O$  such as  $O_3$ . Alkoxides are thermally unstable and can decompose easily at moderate to high temperatures. Amides and Silyls have good reactivity but decompose at low temperatures. Table 2-2 shows the reactant groups that are currently available for a given element. There is also a selection of counter reactants that are appropriately suited to the metal reactants. For example, oxygen counter reactants include  $H_2O$ ,  $O_3$ ,  $O_2$ ,  $H_2O_2$ , and  $O$  from a plasma source. While  $O_3$  and  $O$  are very reactive and therefore can use lower deposition temperatures and enable the use of less reactive metal reactants, they are also more likely to oxidize the surface of the underlying substrate and create an unwanted interfacial layer. Despite being less reactive,  $H_2O$  is most commonly used for oxides, since it is gentler to the substrate surface and can withstand higher deposition temperatures without decomposing. (Richard W. Johnson, 2014)

## 2.2.6 Different Reactor Types for ALD

To have a better understanding of process design for ALD systems there are two limiting types of ALD reactors. In one limit are reactors with no carrier gas. These reactors are exposed to the precursor vapor and after exposure the reactants are removed by the vacuum pump. This ALD reactor type can provide a very good coverage of reactants on the surface due to the high residence time, however evacuating the system at every step increases the process time drastically. At low pressures in molecular flow, random walks of molecules leads to long pumping time. In another limit there are ALD reactors with carrier gas that work in a viscous flow region. This flow is a continuous flow through the reactor. The carrier gas entrains the precursors and by passing through the reactor it shows a low residence time in the reactor. The advantage of using carrier gas and having viscous flow in the reactor is that it reduces the time of process comparing to molecular flow ALD system. (George, 2010)

Most ALD reactors operate at viscous flow and the optimum pressure for this kind of flow is around 1 torr. This optimum pressure is a trade-off between gas interdiffusion and entrainment. For instance, the interdiffusion coefficient of oxygen in nitrogen molecules is  $D_{12}=132 \text{ cm}^2/\text{s}$  at 1 Torr and  $0 \text{ }^\circ\text{C}$ . This interdiffusion coefficient is  $D_{12}=0.174 \text{ cm}^2/\text{s}$  at 1 atm and  $0 \text{ }^\circ\text{C}$  and that gas diffusion is inversely proportional to pressure,  $D \sim 1/P$ . The mean squared displacement,  $x^2$ , resulting from gas diffusion is  $x^2=6Dt$ , where  $t$  is time. Therefore, the mean displacement for  $\text{O}_2$  in  $\text{N}_2$  gas at 1 Torr and  $0 \text{ }^\circ\text{C}$  is  $x) 28 \text{ cm}$  in 1 s. This sizable mean displacement indicates that diffusion of reactants in  $\text{N}_2$  gas at 1 Torr is sufficient for removal of reactants and products from stagnant gas in the reactor in a reasonable time. (George, 2010)

1 Torr is high enough pressure for nitrogen to be an effective carrier gas. The mean free path,  $\lambda$ , between  $\text{N}_2$  molecules at room temperature is  $\lambda \sim 5 \times 10^{-3} \text{ cm}/P$ , where  $P$  is in Torr. This approximation reveals that the mean free path of  $\text{N}_2$  at 1 Torr is  $\lambda \sim 50 \text{ }\mu\text{m}$ . This small mean free path indicates that  $\text{N}_2$  gas is in viscous flow at 1 Torr and will effectively entrain reactants. Mean displacements may be too small for effective purging from stagnant gas at pressures higher than 1 Torr. (George, 2010)

There are also multiple gas flow designs in ALD reactors; cross-flow reactor is a kind that has parallel gas flow across the wafer. The showerhead brings the gas perpendicular to the wafer's surface by using a distributor plate. The gas then distributes radially across the surface. Also another category in ALD reactors is hot-wall and cold-wall reactors. In hot-wall the walls, stage, and tubings are all heated to substrates temperature. In cold-wall reactors, only substrate is heated and the walls remain at room temperature. (George, 2010)

## **2.3 Characterization Techniques**

### **2.3.1 Quartz Crystal Microbalance**

A Quartz Crystal Microbalance has the ability to measure the mass of material deposited on its surface. A QCM is made from a thin AT-cut quartz crystal sandwiched between two electrodes. The electrodes establish an electrical field across the crystal. The crystal would oscillate at its resonance frequency if appropriate electronics are used. The measured frequency is dependent on the combined thickness of quartz crystal and the thickness of deposited material. Due to the very sharp resonance, highly-accurate measurements can be made by using this method. The Sauerbrey equation defines the relationship between mass change and frequency change in Quartz Crystal Microbalance.

### **2.3.2 Atomic Force Microscopy**

Atomic Force Microscopy (AFM) can give information about samples surface at very-high resolutions. In AFM, a very sharp probe scans the substrate. This probe is made of silicon or silicon nitride with a very sharp tip. As the tip moves on the surface the laser on top of it can monitor its vertical movement. The movement of the laser spot on a photodetector gives a greatly exaggerated measurement of the movement of the probe. This set-up is known as an optical cantilever. The probe is moved over the sample by a scanner, typically a piezoelectric element, which can make extremely precise movements. The combination of the sharp tip, the very sensitive optical lever, and the highly precise movements by the scanner, combined with the careful control of probe-sample forces allow the extremely high resolution of AFM. The lateral resolution of the

image can be as small as the tip radius (typically 5-15 nm), and the vertical resolution can be on the order of subangstroms.

### **2.3.3 X-ray Photoelectron Spectroscopy (XPS)**

When a material is irradiated by X-ray, due to the excitation, electrons would eject from the surface. The emitted electron has a particular energy which is related to photon energy and binding energy of electron. This technique investigates the outer 5-10 nm of surface and it can be said that it is a surface sensitive technique. The spectra give information about the elemental composition, concentrations, and chemical environments. In Atomic Layer Deposition samples, this techniques can gives us information about the formation of oxides or nitride also about the possible contaminations on the surface.

### **2.3.4 Scanning Electron Spectroscopy (SEM)**

Using SEM, samples can be seen with resolutions up to 20 nm. This analysis has many different modes, which helps us to have a better understanding about the surface topography and elemental analysis. SEM works with an electron beam. When the beam hits the surface it excites electrons from the sample these electrons are collected by electron detectors. There are different types of electron detectors, which is applicable for different purposes like surface analysis or elemental characterization. Another great feature of SEM is EDS, which is short for energy dispersive spectroscopy; this technique helps us with identifying and quantifying the elements in the sample. EDS can work in low beam currents.

### **2.3.5 Auger Electron Spectroscopy (AES)**

A focused electron beam (3-20 keV) is scanned across the sample surface. Atoms near the surface are ionized, and a fraction of the ionized atoms relax via the Auger process. The spectrometer ultimately measures the kinetic energy distribution of a portion of the Auger electrons that are emitted from the sample. The technique is inherently surface sensitive because the majority of the measured Auger electrons originate in the outer 5-10 nm of the sample surface. The Auger spectra contain information about the

concentration and chemical environment (i.e. oxidation state) of surface and near surface atoms. Greater depths (up to a few microns) can be probed by coupling the technique with ion milling. Lateral distributions of elements can be measured with sub-micron resolution. This instrument is essentially an FESEM that provides surface elemental and chemical sensitivity. The detection limits are roughly 0.1-1 atomic percent within the information depth.

## **3 Design, Modeling, and Manufacturing of Atomic Layer Deposition system**

### **3.1 Introduction**

Due to the importance of ultra-thin films in nanoelectronics and the need to have new and exotic materials in monolayer scales, the need for instruments with ability to produce multiple different thin layers at the same time without breaking the vacuum is obvious. Designing a new type of ALD was crucial for us since we needed to try multiple different materials in thin films to get the best combination of materials for diodes and antenna. In designing many devices like diodes, having a conformal surface with very low roughness is the key for having a working, reliable device. Considering this requirement the best known deposition method to get this properties in a film is ALD, but using commercial ALDs can be troublesome since they only support particular depositions and don't let the user try to produce new materials for deposition. Also they are very expensive, and don't have the flexibility in design to add or improve extra features to the system. In regard to our project's need for deposition of new materials, we started designing a system with comprehensive control on each part of it, which can be used with many different precursors to deposit different types of layers. After the design phase and confirming it by modeling, using COMSOL, we started the manufacturing phase. In this phase we built the designed customized flanges, showerhead, stage, heater, tubing, bubblers, and put all together as a whole system. After this we needed controlling software to follow ALD program steps automatically, and give us the ability to control all the solenoid valves and MFCs simultaneously and independently. In this section we are going to talk about design, manufacturing, modeling, software programing, and testing our manufactured system.

### **3.2 Reactor Design and Manufacturing**

An ALD reactor consists of different parts, the first step in this design is the chamber, since knowing the size and shape of chamber can led us to design other parts.

The second step is designing the flanges to satisfy the needs of the system and the third step is designing showerhead, stage, and heaters. First, I am going to talk about the chamber design, then flange design, and at last all the parts that is placed inside the reactor.

### **3.2.1 Deposition Chamber**

One of the key factors in designing an ALD system is the shape and size of the reactor. The shape is really important due to the fact that the precursors can go anywhere inside the chamber and if there is a lot of surface area for them to adsorb, then contamination in the system can increase. Which means, if a precursor of material A stays in the chamber and we try to deposit material B then the existence of material A can led to serious contaminations in the material B's film. On the other hand the design should be in a way that no gas entrapment exists in the system so by using vacuum all the precursors can get out of chamber without trapping in a particular region. Also the size of the reactor is important because of the required space for all of the parts that we are going to put inside and required free space for future improvements. Regarding these two requirements, we decided to use a 4-way 14" \* 14" cross with 8" flanges on heads which gives us enough space to add showerhead, heater, stage, electrical connections, and thermocouple. Also due to its simple shape it has low surface area and low dead volume, which gives the ability to use many different precursors with no worries about film contamination. Using Comsol the flow pattern of viscous regime, and temperature distribution inside the cross reactor was investigated which shows appropriate velocity distribution around the substrate stage (Figure 3-1 to 3-3).

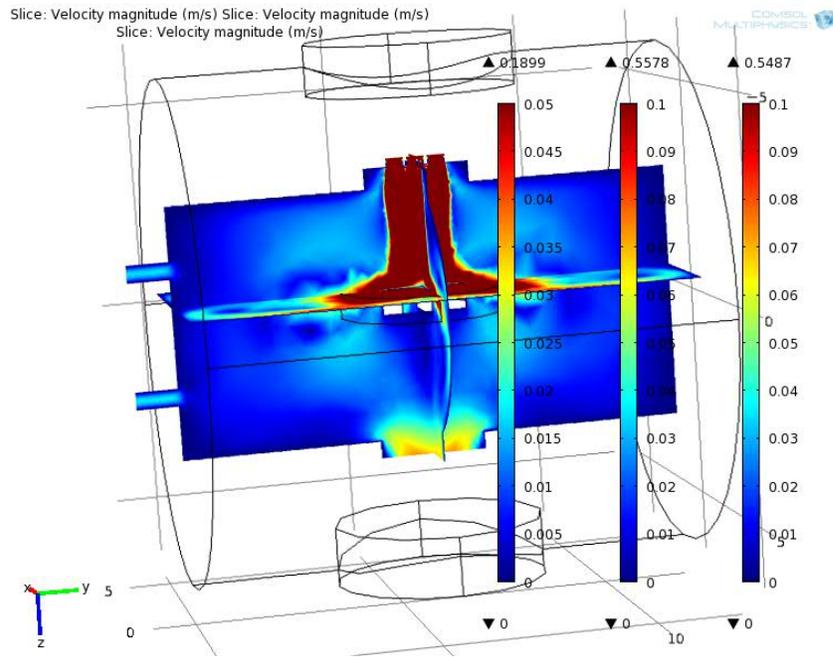


Figure 3-1 Comsol Viscous flow modeling inside reactor, 3D view

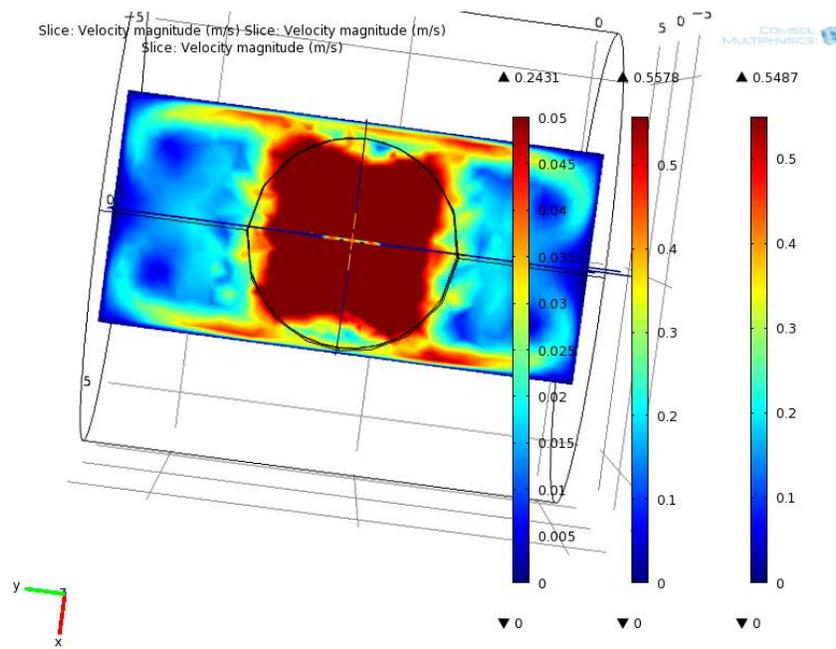


Figure 3-2 Comsol viscous flow modeling inside reactor, top view

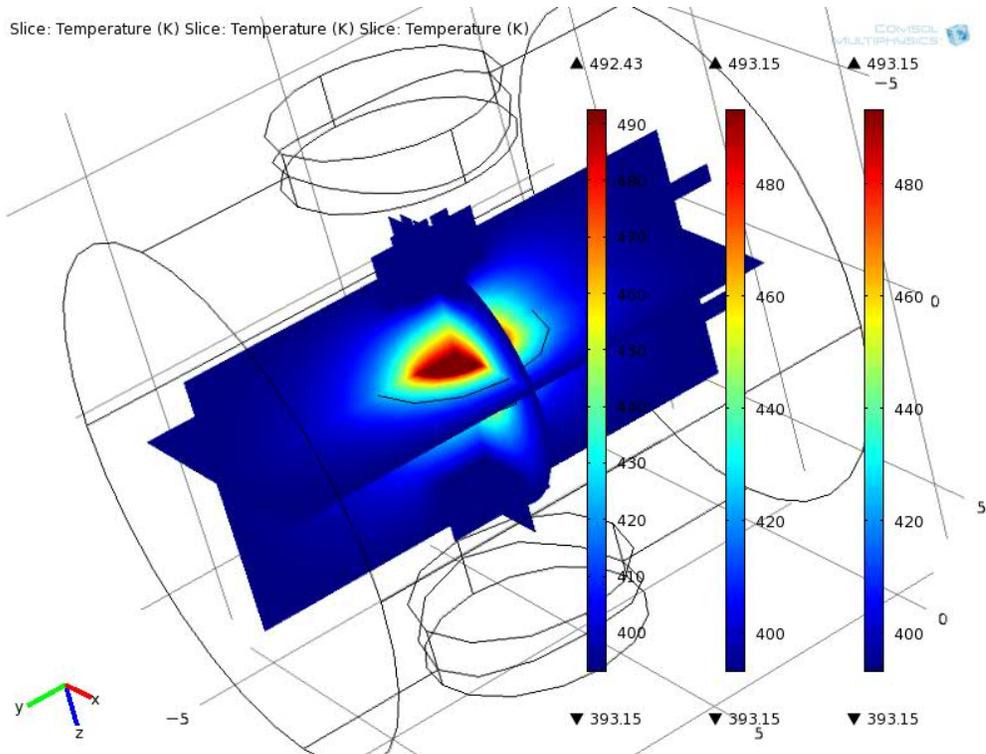


Figure 3-3 Comsol temperature distribution around stage modeling, 3D view

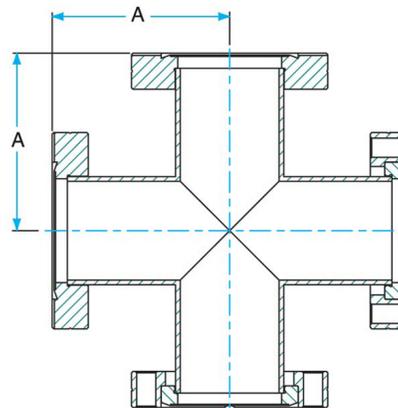


Figure 3-4 Chamber design

### 3.2.2 Flanges

The 4-way chamber connects to a turbopump on the bottom flange, to the precursor inlet and showerhead holder on the top flange, to the feedthroughs,

thermocouples, thermocouple gauges, and ion-gauge on one side, and the sample placing and removing gate on the final flange. For three of these sides there would be a special flange design to get us an actual reliable working system.

The top head flange needs to hold the showerhead and stage while it gives us inlet ports for precursor gases. To have the ability to switch the ALD system to CVD mode, a four-inlet structure has been designed as it can be seen in figure 3-6. This four-inlet structure gives us the ability to bring four different precursors at the same time to the chamber; also we can switch all the inlets so they connect together which gives the ALD mode. For this four-inlet structure four all way through holes, with 0.2505" diameter, were considered and four 3.88" long 1/4" diameter stainless steel tubes were used; so the tubes passes through the holes and were welded. Another important feature that this top flange has, is its ability to hold the showerhead, heaters, and stage which add up in weight to 10 lbs. To have a strict hold on the showerhead system a four-point holder has been designed. This four-point holder consists of 4, 5/16-24 threaded holes, 0.45" deep. By using whole thread rods all the downer parts can be connected and be held by the top flange. A 304 stainless steel flange were bought from Lesker and after welding it has been clean using Sparkleen, Acetone, and Methanol. Then it was connected to the vacuum for helium leak check around the welding points.

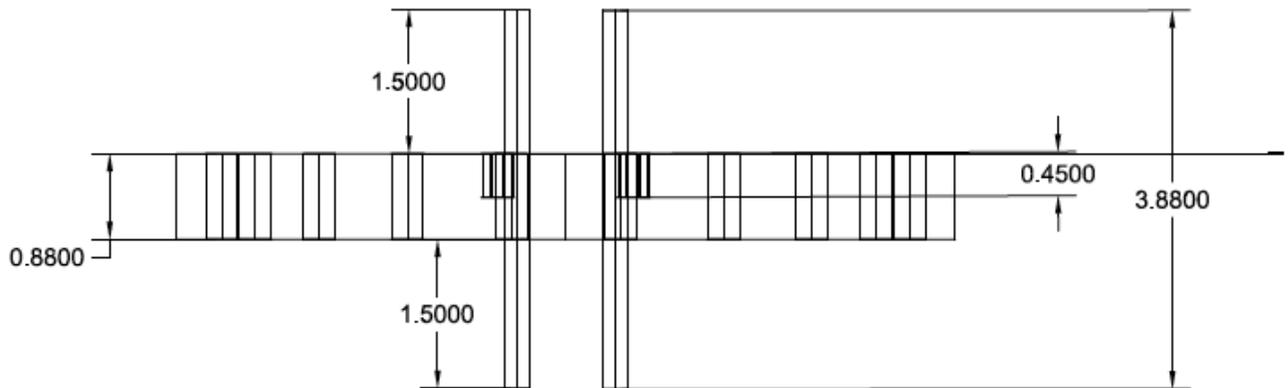


Figure 3-5 Top flange design, side view

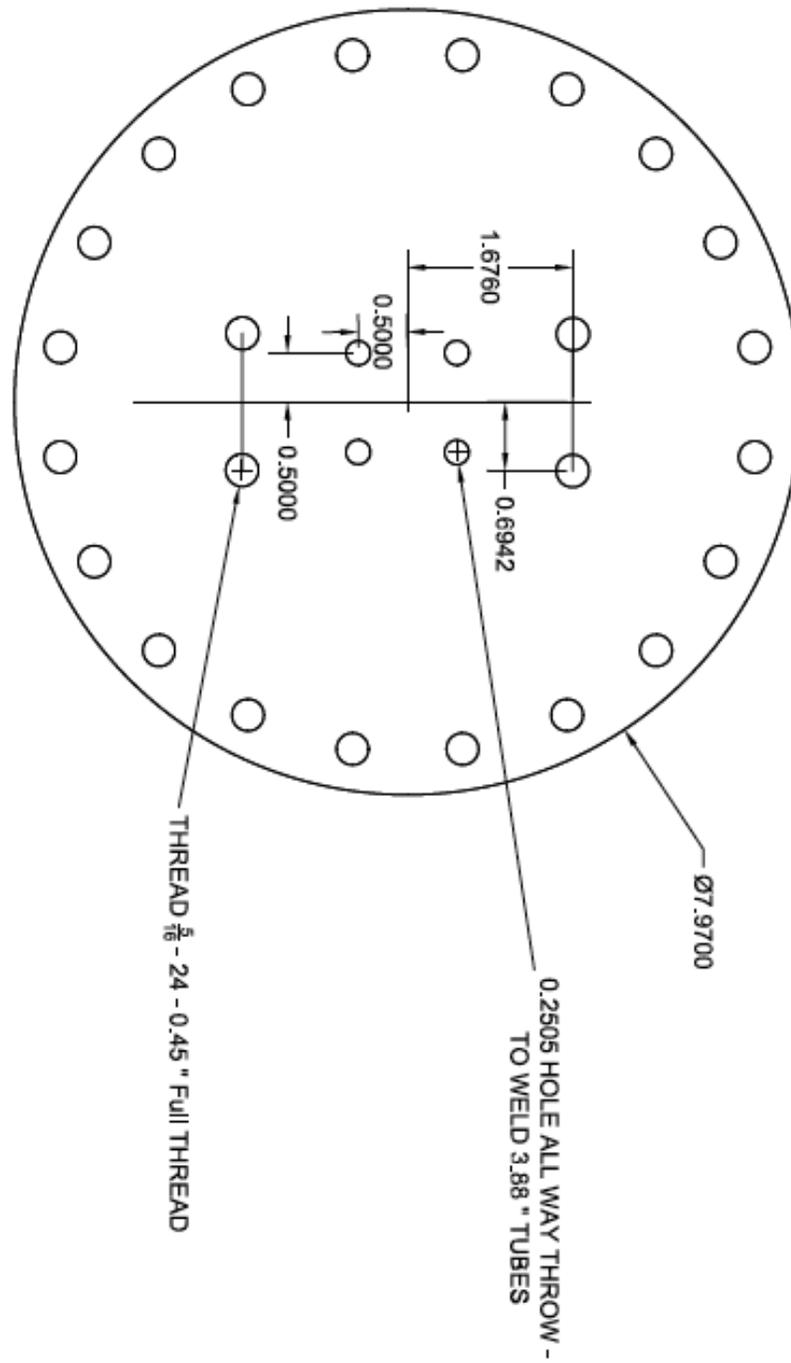


Figure 3-6 Top flange design, top view

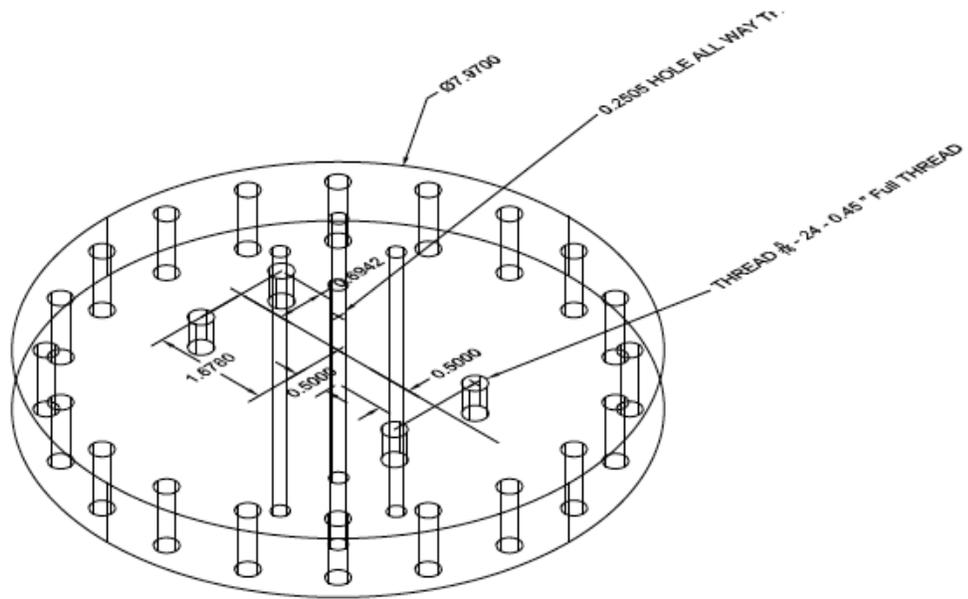


Figure 3-7 Top flange design, 3D view

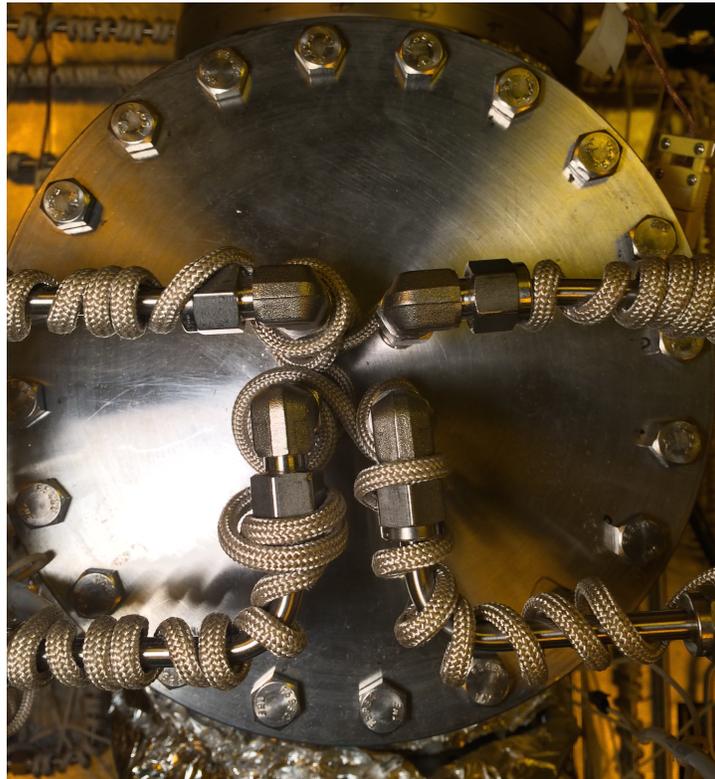
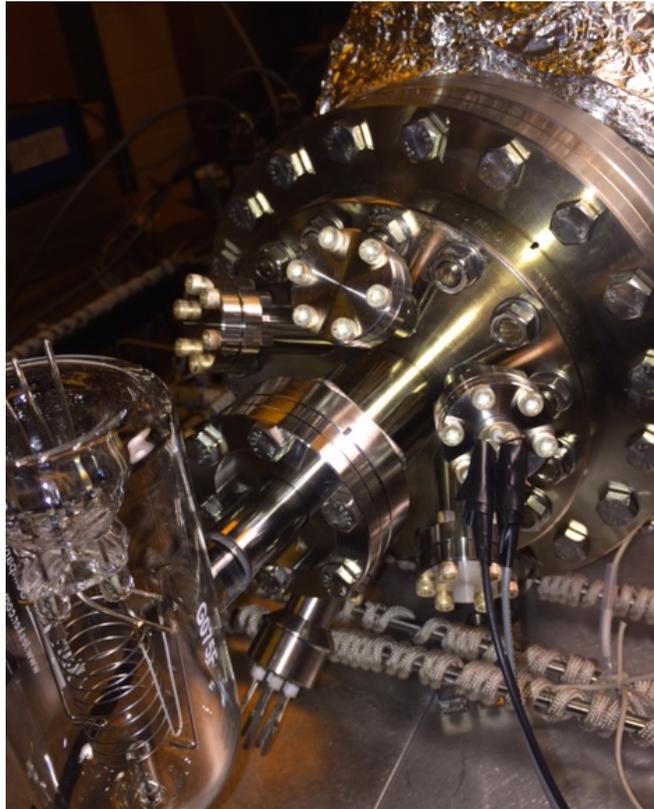


Figure 3-8 Top flange with L-connections

There are two side flanges, one of them act like a port for sample entrance which





**Figure 3-10 multiple angle port with thermocouple gauge, ion gauge, power feedthrough, and thermocouple feedthrough**

The other side's flange, which gives the access to inside of chamber, is a blank flange and needs to be opened and closed for each single use. A better solution for sample throughput is using from fast-entry vacuum door, shown at figure 3-11, which gives very easy access to inside of reactor and also a view port to see the inside. Another solution could be using a load lock assembly, which is a more expensive solution but it keeps the chamber under vacuum all the time and the user doesn't need to break the vacuum every single time to put the substrates in.



**Figure 3-11 Fast-Entry doors for easy access to the reactors inside.**

### **3.2.3 Showerhead**

Usually an inert gas carries the precursors to the reactor and one thing that is very important is even distribution of the carrier gas on the substrates surface. If the distribution doesn't happen equally on the samples surface then places that gets less of precursor grow slower and the other places grow faster, leading to a bumpy surface. To get the best gas distribution we designed a showerhead with 120 holes on it with 0.0045" diameter (Figure 3-12). Showerhead consists of 2 parts, upper part (Figure 3-12) and downer part (Figure 3-13). The upper part is a 4.5 CF flange, which has four gas inlets, 1.5" long. The upper CF flange seats on the downer part, with small holes on it. Two flanges are sealed by using 316 SS 5/16-24, 1.25" long bolts and torqued to 15 lb. ft. Finally the upper flange will connect to the chambers top flange using SS Swagelok tube fitting, bored-through union, 1/4 inch.

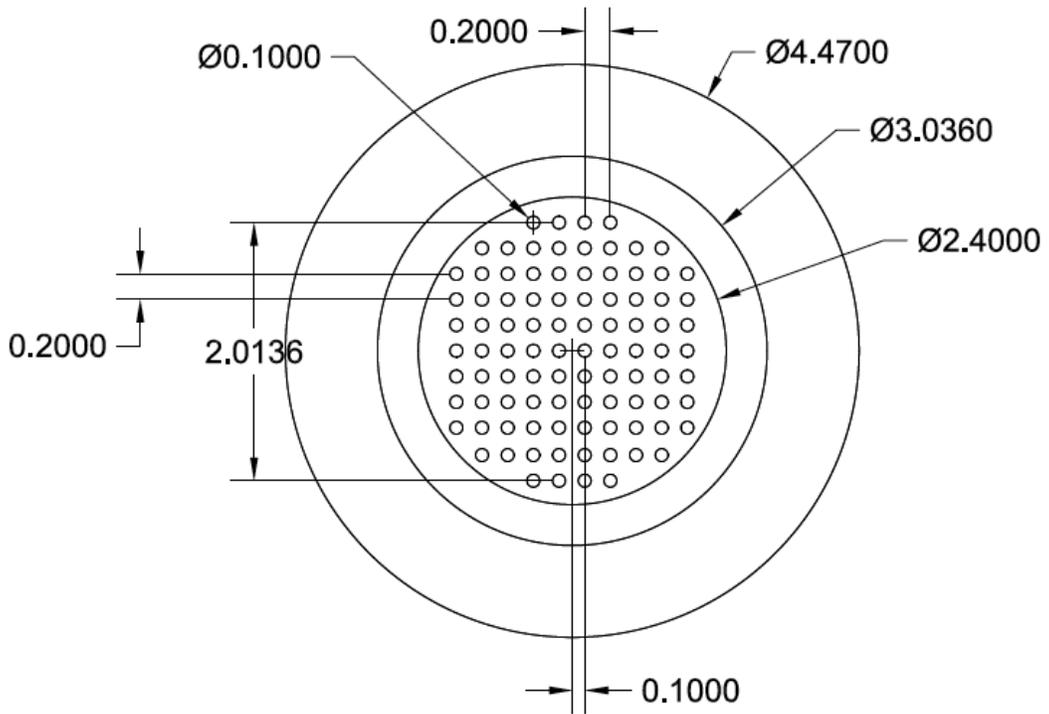


Figure 3-13 Carrier gas inlet, upper flange

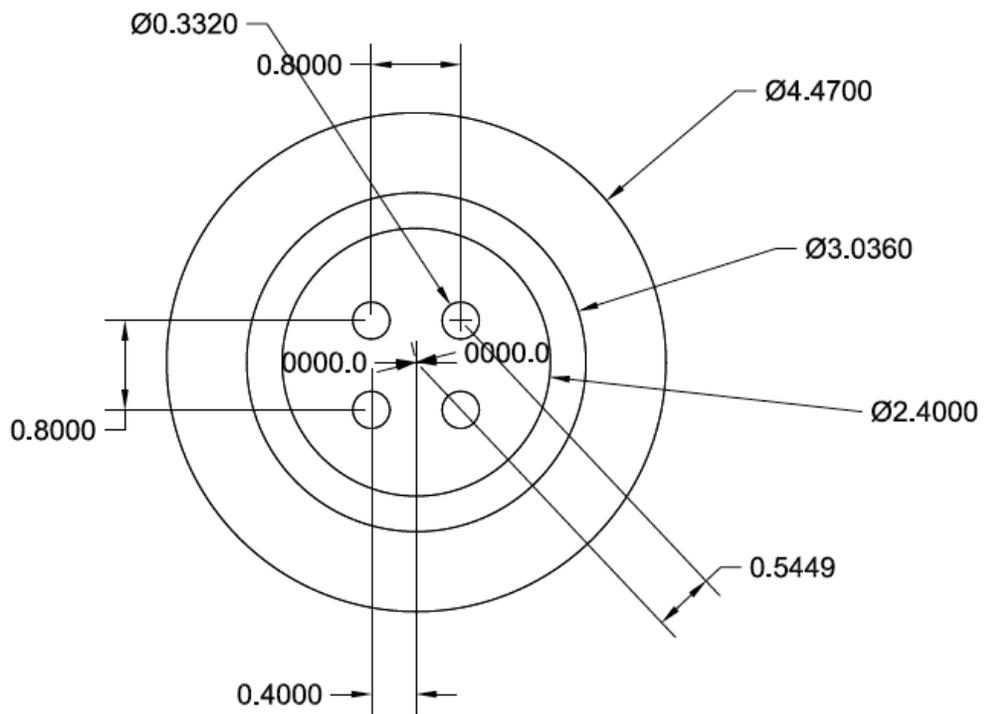


Figure 3-12 Showerhead holes, downer flange.

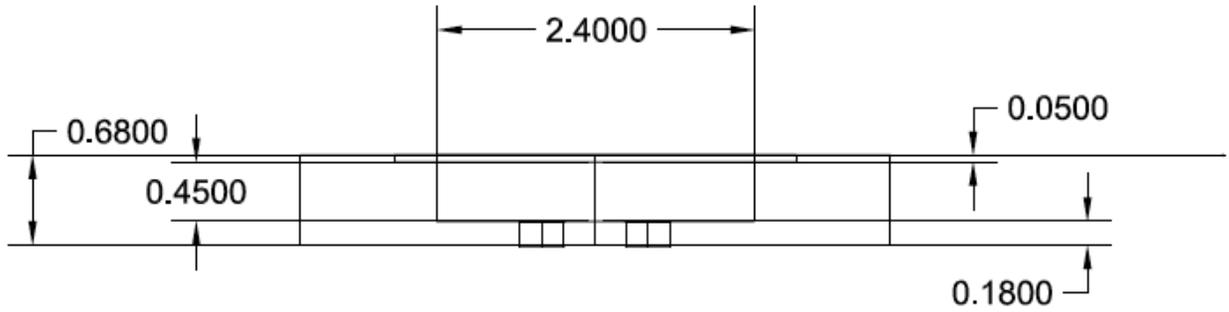


Figure 3-14 Showerhead, lower flange, side view

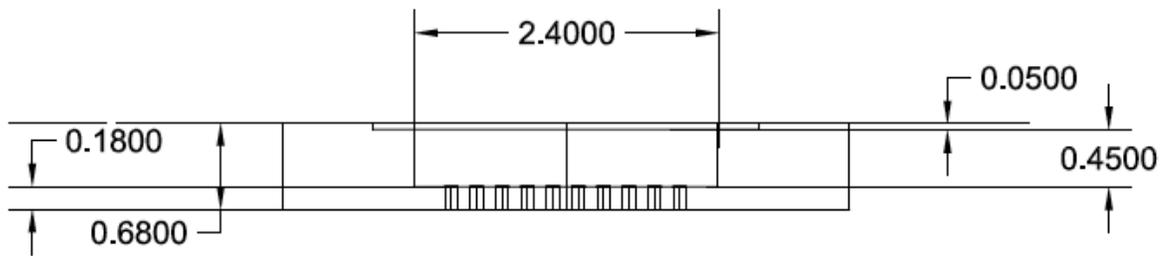


Figure 3-15 Showerhead, upper flange, side view

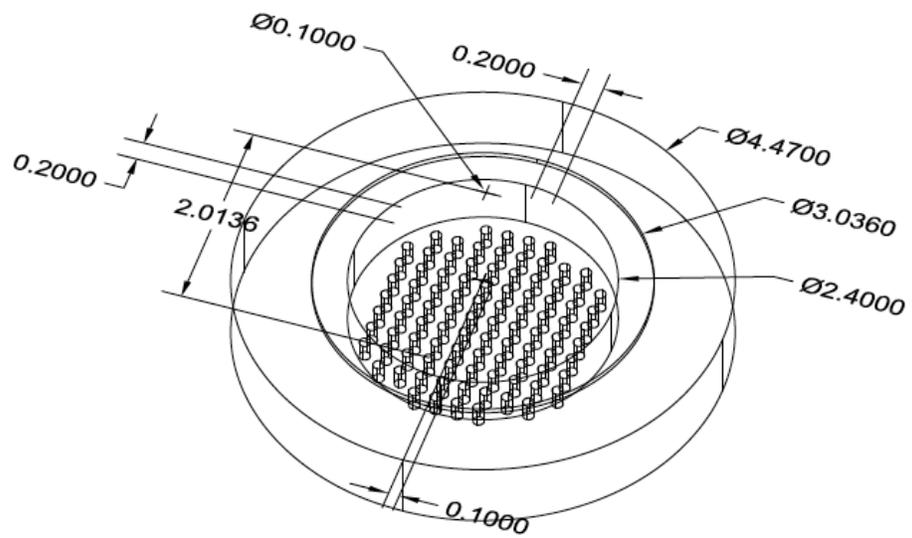


Figure 3-16 Lower flange, 3D view

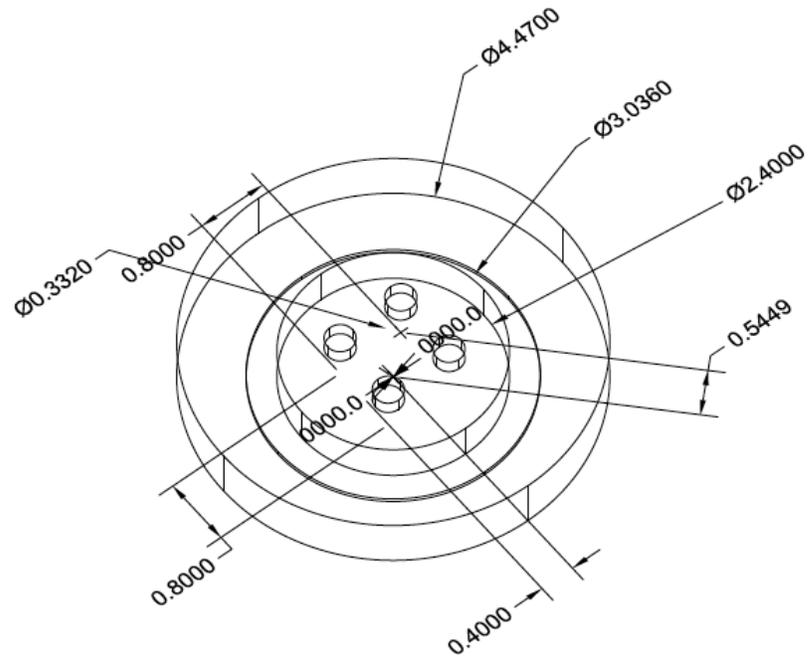


Figure 3-17 Upper flange with gas inlets, 3D view

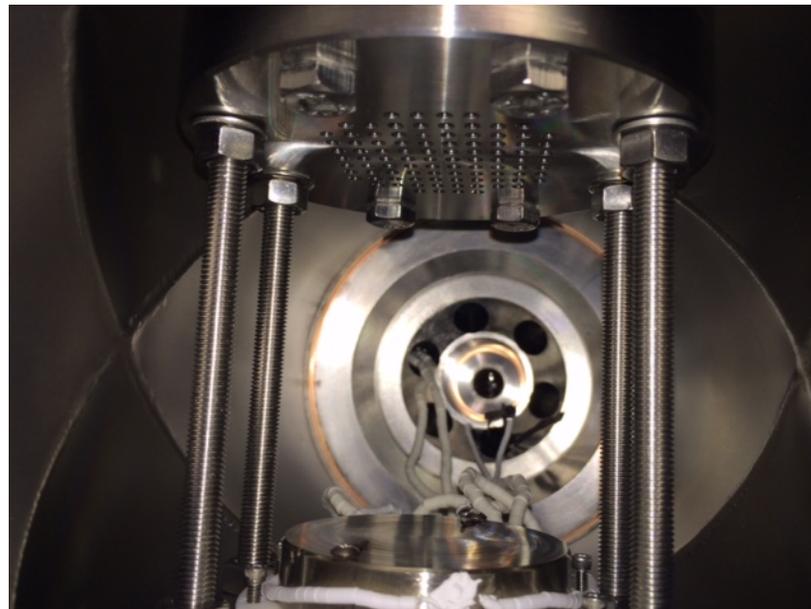


Figure 3-18 Manufactured showerhead



**Figure 3-19 Connection between upper flange and chamber's top flange, using Swagelok fitting**

### **3.2.4 Stage and Stage Heater**

In ALD systems the material that can be used inside the chamber is very limited, because of the chemical reactions, high vacuum, and high temperature condition. Regarding to these limitations, building a stage and stage heater that can fulfill the needs of an ALD system is very challenging. First step for us, was finding a way to hold the stage, and the heaters structure in the middle of chamber. So we decided to use from a 4.5" CF flange and tried to hold it with the full threaded rods that hold showerhead, figure 3-19. Figure 3-27, which is a Solidworks modeling for the combination of showerhead and stage, shows a better picture of the desired configuration. As it can be seen from the figures, 4 fully threaded rods come down from the chamber's top flange, first they connect the top and bottom flanges in showerhead and then come down to hold the stage, and stage heater structure.

Another challenge in designing the stage was the fact that the stage shouldn't have thermal conductivity with rest of the chamber, however there are 4 SS threaded rods that can transfer the heat from the stage to the showerhead, chamber's top flange and

ultimately chambers body. On the other hand to increase the flexibility of the system for future improvements it was favorable for us to electrically insulate the stage and stage heater from the rest of chamber. To solve this problem we needed a material that has thermal and electrical insulation properties, with low outgassing, low reactivity to different chemicals specially oxidizers, and thermally stable. The best option for the insulator layer was Macor ceramic. This ceramic can tolerate up to 1000 °C. Also it is nonreactive and it won't outgas in vacuum environment. Another important property of Macor is that it is machinable which give us the ability to machine it to our desirable shape. Figure 3-20 shows the designed Macor, as insulator layer. This layer connects to the bottom flange from one side and it bolts to the stage from the other side. It is very important that these connections are not the same so there is no electrical pathway from the stage heater to the bottom flange and rest of the chamber (Figure 3-22).

The stage heater, which holds the substrates on top of it, is also another part that needs to be designed in a way that spreads the heat in an equal manner so the temperature would be the same all over the stage. To satisfy this requirement a 0.5" thick stainless steel round disc with 2.5" diameter has been used for the stage and by making holes inside this disc for three cartridge heaters the stage can be heated, the design can be seen at figure 3-19. The cartridge heaters bought from McMaster-Carr in 1.5" and 2" long and 0.25" diameter. The cartridge heaters are insulated with magnesium oxide and enclosed in a 304 stainless steel cover. The heaters can go up to 550 °C and using three of them (Figure 3-26) gives an equal heat distribution on the stages surface. The stages temperature is read by an insertion K-type thermocouple that goes inside the stage disc for precise reading (Figure 3-26).

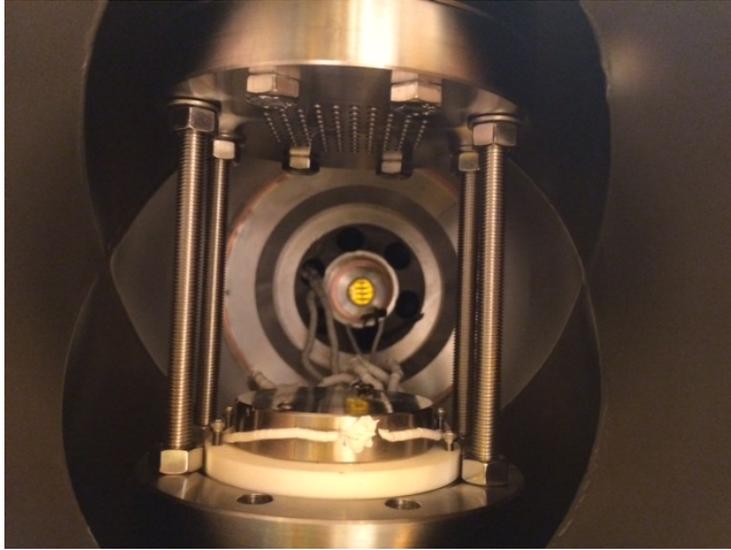


Figure 3-20 Showerhead and Stage holder configuration

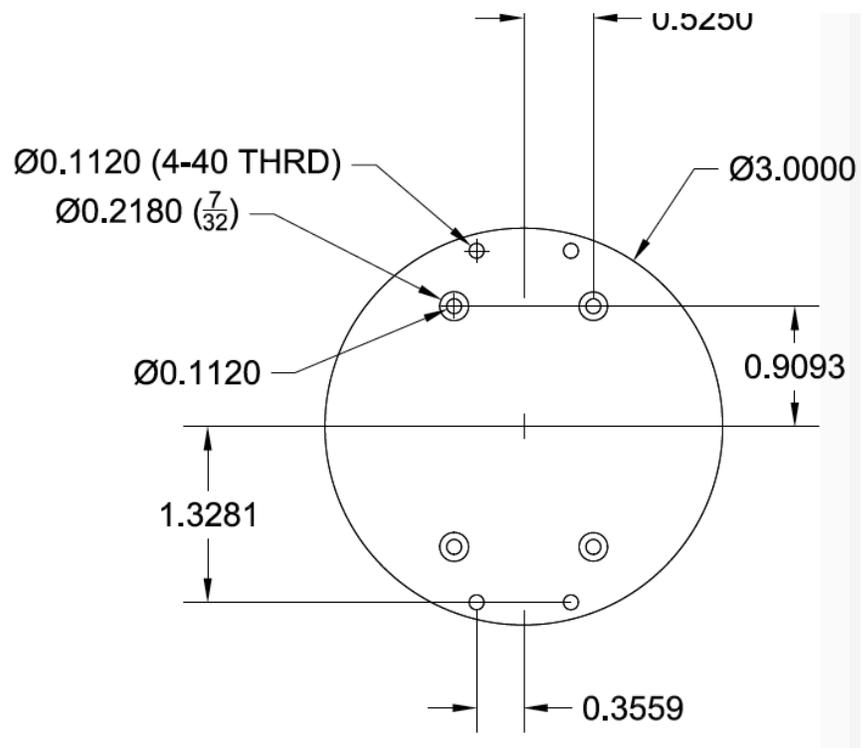


Figure 3-21 Macor Ceramic, top view

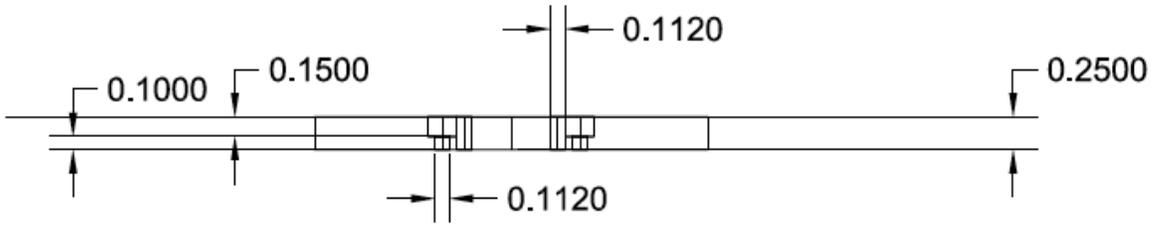


Figure 3-23 Ceramic Design, Side view

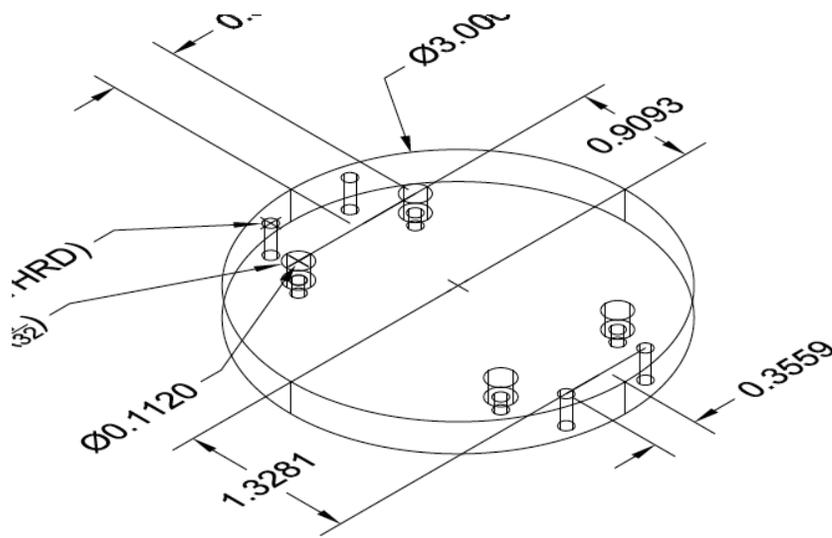


Figure 3-22 Macor Design, 3D view

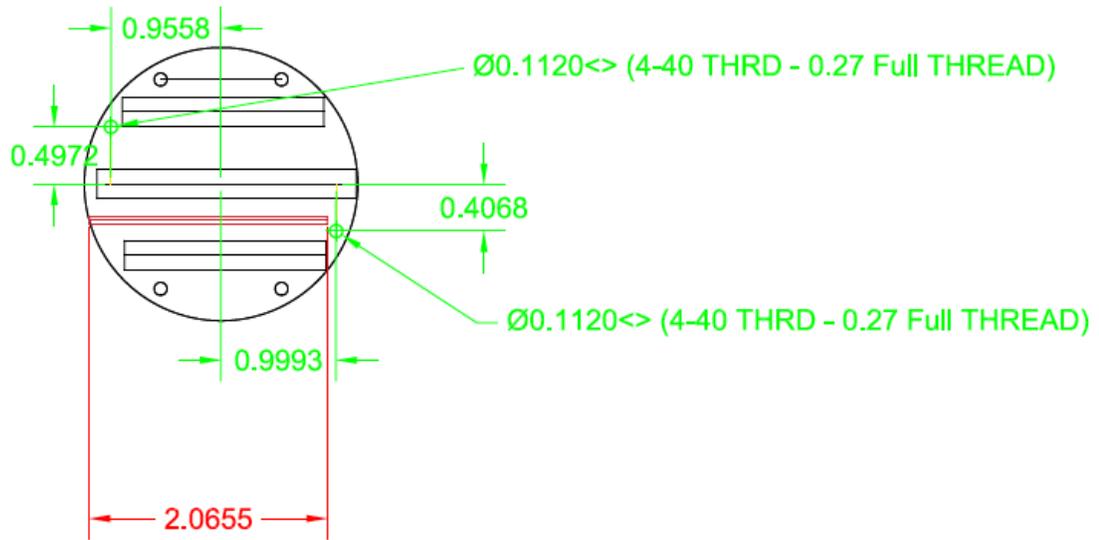


Figure 3-26 Stage design to hold cartridge heaters and thermocouple

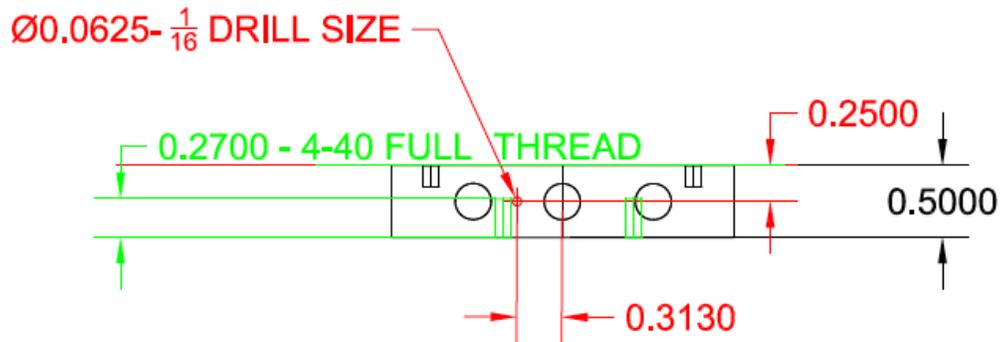


Figure 3-25 Stage design, side view

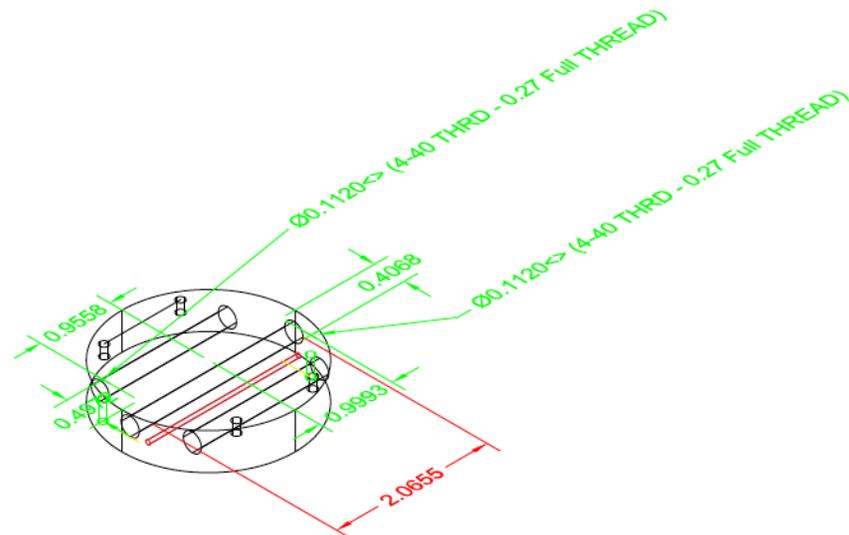


Figure 3-24 Stage design 3D

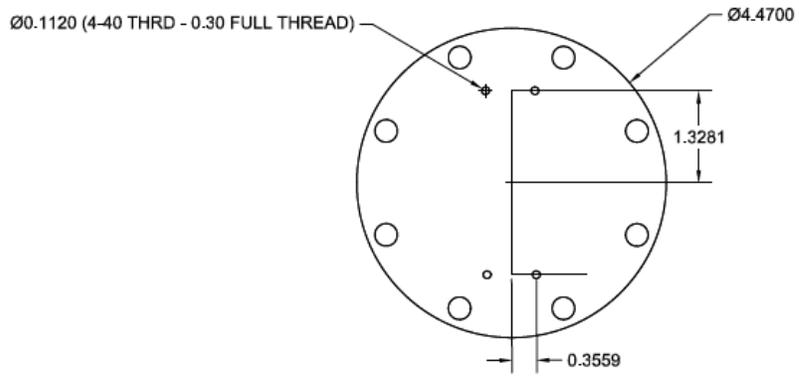


Figure 3-28 Holder flange on the bottom , top view

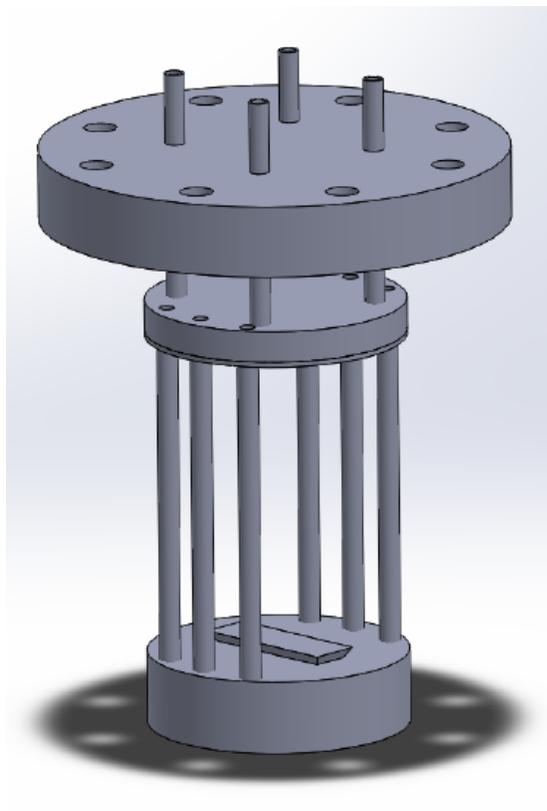


Figure 3-27 Solidworks modeling for the combination of showerhead and stage holder

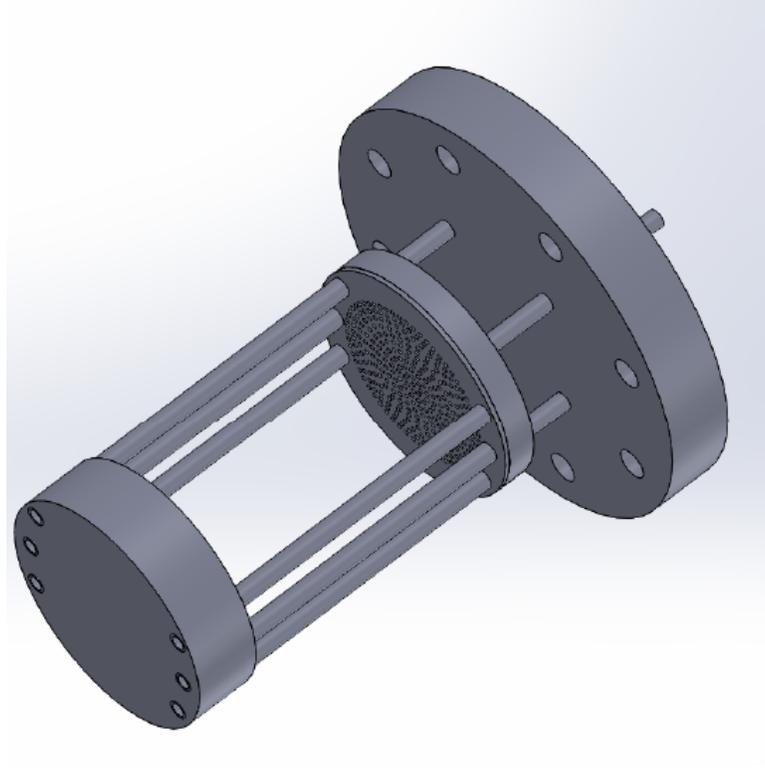


Figure 3-29 Solidworks modeling for the combination of showerhead and stage holder

### 3.3 Precursors' Delivery Line

Designing a controllable, flawless delivery system for ALD is crucial due to the fact that all the controlling valves, bubblers, and MFCs are in this part of system and they all need to work harmonically to improve the film quality and avoid contaminations either in bubblers or in tubings. In this section we are going to talk about bubbler's design and manufacturing, ALD valves, tubing, and mass flow controllers.

#### 3.3.1 Mass Flow Controllers

Between many steps that need to exist to deliver the carrier gas to the chamber the first stop is Mass Flow Controller. Mass Flow Controllers work on the basis of heat transfer laws and first law of thermodynamics. When the gas enters the instrument it divides into two pathways one goes to the sensor tube and the other is laminar flow bypass. The pressure drop caused by laminar flow bypass forces a small amount of flow

to go through the sensor tube. (Figure 3-30 and 3-31) Two RTD controllers around sensor tube brings a constant amount of heat to the flowing gas, the temperature difference between two coils shows the mass flow. A servo control valve then controls the mass flow by opening or closing the valve. In ALD systems the maximum flow rate is usually 100 sccm so we decided to use from Sierra Trek 830, with maximum capacity of 100 sccm. We also used from a 4 channels MFC power supply/Controller, model 954 Sierra, which gives us the ability to turn the MFCs on and control their flow.

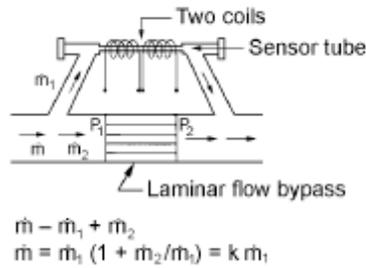


Figure 3-30 Flow through the transducer (Sierra)

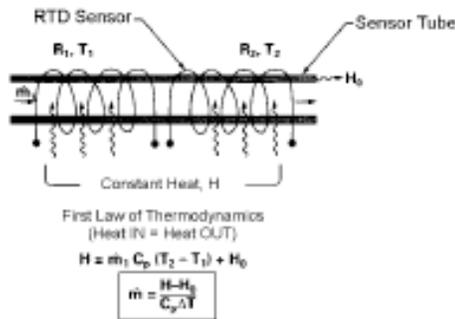


Figure 3-31 Flow Measuring Schematic (Sierra)

### 3.3.2 Bubblers

Due to the required vapor pressure for ALD precursors most of these chemicals are exist in liquid phase and to transfer them to the chamber there should be a mechanism that let the gas passes throw the precursor liquid and bring the precursor's vapor to the chamber. The devices that can help the carrier gas to bring precursors to the chamber are known as bubblers. Bubblers usually consist of 3 ports, one of them is the inlet port that let the carrier gas flow inside the bubbler, this port is connected to a dipping tube which let the gas goes all the way down to the bottom of precursor liquid. Reaching the bottom let the gas to path throw liquid and entrain the precursor with itself when it reaches the outlet port. The third port is used as pressure measurement port and also feed port, so there is no need to open the flanges each time we need to add precursor, also the pressure built up can be monitored using this port.

The designed bubbler (Figure 3-29) consists of one 4.5” CF blank flange in which the ports and dipping tube is welded. A counter bored 4.5” CF flange is used to weld to a 2 “ tube which makes the container of precursor, the container's capacity is 800 ml. All materials are 316 Stainless Steel and a copper gasket is used to close the bubbler head to 15 lb. ft. torque.

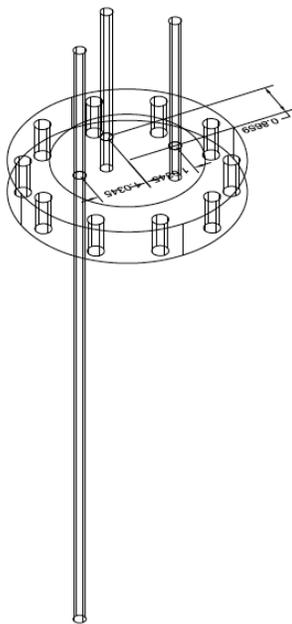
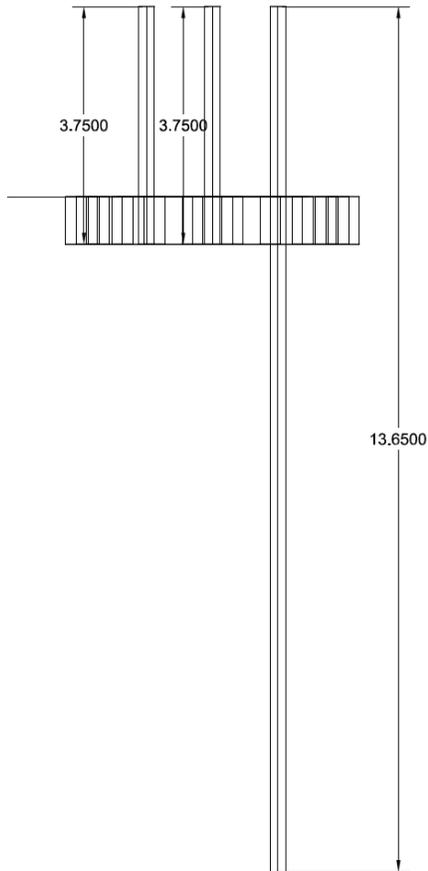
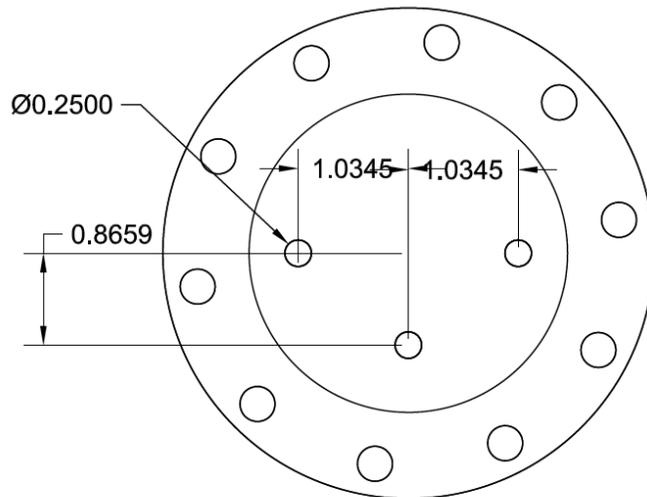


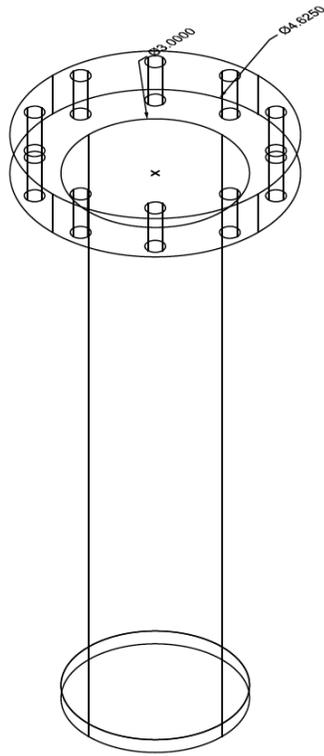
Figure 3-32 Bubbler's top part design, 3D view



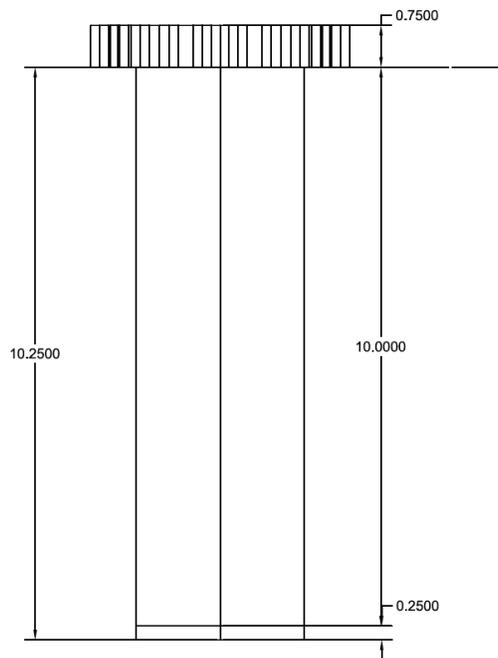
**Figure 3-33 Bubbler's top, side view, the dipping tube goes all the way down to the bottom of container**



**Figure 3-34 Bubbler's top, top view, 3 ports for gas inlet, gas outlet, and filling port**



**Figure 3-36 Bubbler's bottom part, a 2 inch tube welded to a 4.5 inch CF flange.**



**Figure 3-35 Bubbler's bottom part, side view**

### **3.3.3 Valves**

#### **3.3.3.1 ALD Diaphragm Valves**

For the designed system we needed four solenoid valves to give us sufficient control on the pulses and purges. In the case of ALD systems, precursor chemicals are usually highly corrosive and reactive so choosing all stainless steel valves are desirable. On the other hand base on the solenoid valve structure it is very hard to find a valve that is all stainless steel and they are mostly consist of polymer rings as sealers. These valves need to have ultra long life cycles because for a 1nm of deposition each one of them need to open and close around 10 times. Also need to have high flow coefficient so the pressure drop caused by the valve doesn't affect the process. In addition they should tolerate high temperatures up to 200 °F. High temperatures in the valve and tubing is needed to prevent condensation of precursors on the walls. To satisfy all these requirements ALD 3 Swagelok valves were purchased. These valves consists of 2 parts one is a pneumatic actuator and the other is an electrical actuator. The pneumatic actuator acts with pressurized air and if the air pressure goes higher than 10 psi it opens the valve to let the carrier gas flow. To control the pneumatic actuator, electrical actuator is used. Electrical actuator acts like a solenoid valve and when there is enough current inside the circuit, it lets the pressurized air to flow inside the pneumatic actuator, and the pneumatic actuator opens due to the pressure. The valve opening and closing time in these valves is less than 5ms and they are made from 316 Stainless Steel to have maximum compatibility to ALD processes.



**Figure 3-37 ALD Valve with electronic actuator**

### **3.3.3.2 Nupro Gas Metering Valve**

Nupro valve is used on the bypass line, which goes straight to the reactor. Using this valve gives the ability to have a very controlled neutral gas flow for purging the chamber in case of power outage or purging the molecular sieve to avoid the pressure drop inside the trap. Lesker Nupro straight valve was purchased for this application that can tolerate temperatures up to 200 °C, has a flow coefficient of 0.03, and made from 316 Stainless steel.

### **3.3.3.3 Ball Valves**

There are multiple ball valves used in the lining of the ALD system. Three ball valve on top of each bubbler that control gas inlet, gas outlet, and precursor entrance. Two additional ball valves, help the bubblers reach the vacuum pressure that the rest of the system is in. These valves are all stainless steel with Swagelok connections and 0.25” diameter fitting.

### **3.3.4 General Design of Tubing**

In designing tubings in an ALD system three factors must be considered. First, all

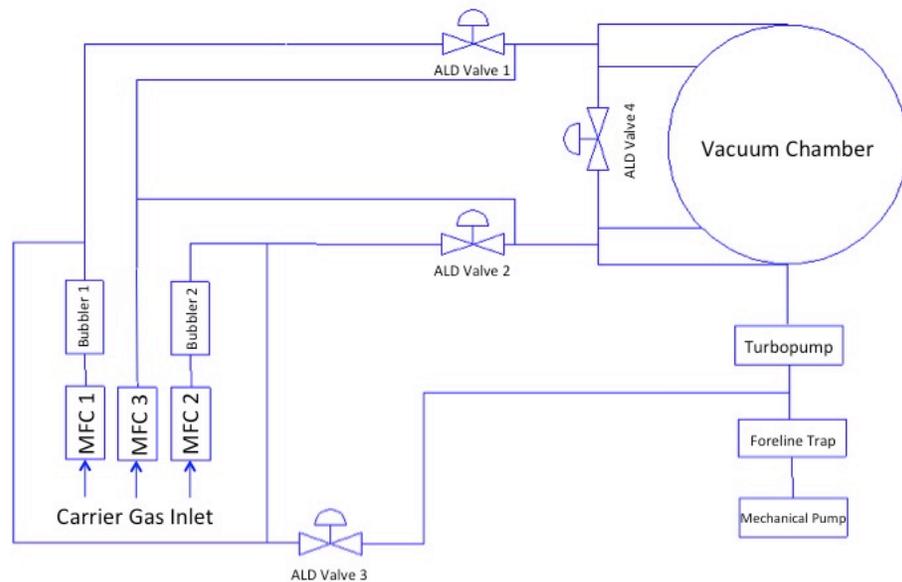
the tubings, connections, and valves need to be stainless steel to prevent any unfavorable reaction. Second, all the tubings in need to be in a design that can purge after each step to keep the tubes clean and prevent from reaction inside tubes. Third, all the tubings should prevent back-flow from one bubbler to the other bubbler, that can be very dangerous due to high reactivity of precursors. To prevent the back flow ALD 3 Swagelok valves are used which automatically switches off after each pulse.

In general the carrier gas, which can be Argon, and Nitrogen goes to MFCs. MFCs allow particular flow of gas to pass through which can be controlled either by reader-box or ALD software. Then carrier gas goes inside the bubbler and comes out of it with a little fraction of vaporized precursor. After that the gas reaches the ALD valve, and if it is that particular precursor's turn to go inside the chamber the ALD valve will automatically turn on to let the gas path through (Figure 3-38).

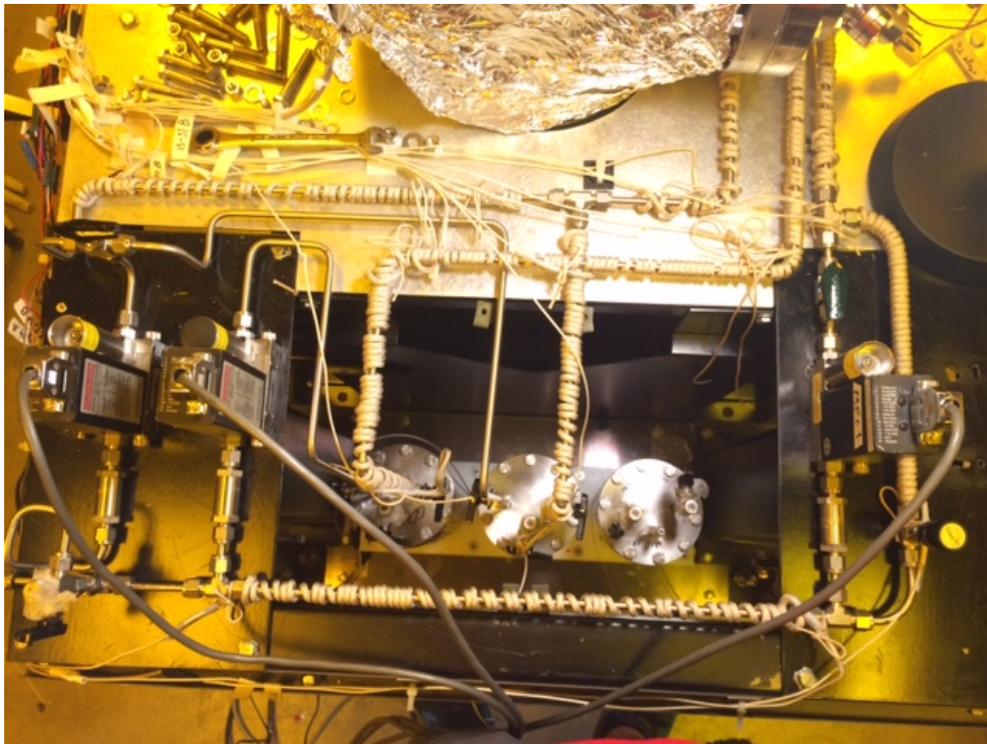
In our system there are three MFCs each of them has used for particular reason. From figure 3-39, the left MFC belongs to the oxidizer line. Usually the oxidizers in ALD process are either  $H_2O$ , or  $O_3$ , or  $O_2$ . Since  $H_2O$  is liquid in room temperature it needs to be filled in a bubbler, so the carrier gas paths through  $H_2O$  to entrain it and bring it inside chamber. The other most common oxidizers are in gas phase and do not need to go through bubbler, so for these oxidizers there are two 3-way valve at each end of first MFC that can switch from the carrier gas to oxidizer gases. The second MFC, belongs to the chemically reactive precursor. The carrier gas goes through the MFC, inside the bubbler, through the ALD valve and goes inside the reactor. The third MFC from left belongs to the purging line. From the figure 3-39, there is a bypass line beside this MFC, which gives the ability to purge the system manually. The purging gas goes through this MFC, and goes straight inside the reactor.

There are 4 ALD valves in this system (Figure 3-40), ALD 1, belongs to the precursor-1 line, and it automatically turns on and off depending on the required step. ALD 2 valve belongs to the precursor-2 line, and for ALD mode it only opens when ALD 1 is off, but for CVD mode it opens simultaneously with ALD 1. ALD 3 is designed to reduce the pressure inside the bubblers, also purging the bubblers with inert gas without

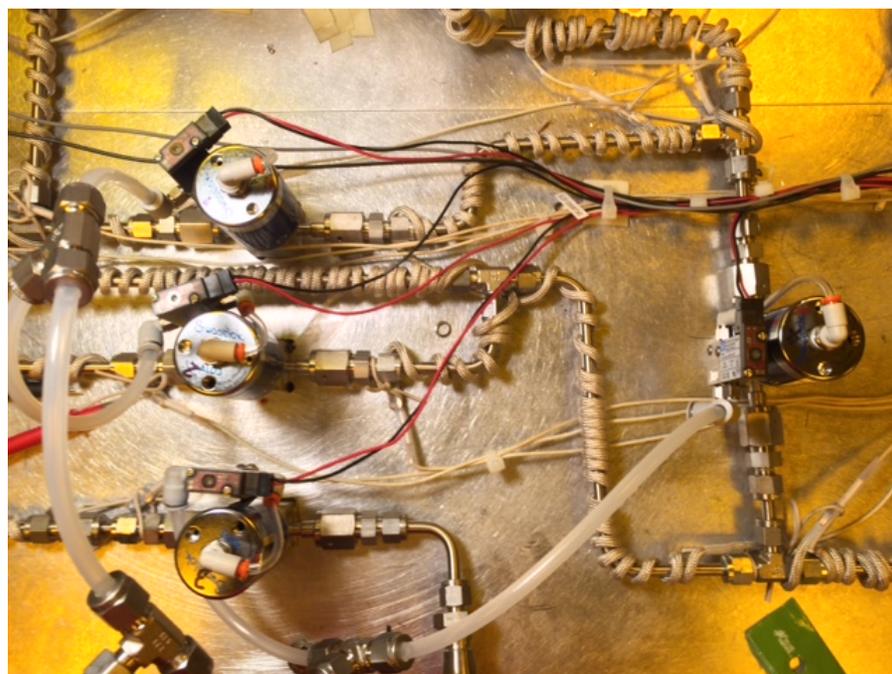
flowing the exhaust inside the chamber. Two manual valves on top of the picture in figure 3-36, let us vacuum each bubbler separately to prevent mixing between two precursors. ALD 4 valve is the switch between ALD mode and CVD mode. In CVD system both of the reactants exist in the reactor at the same time, so to be able to have a CVD process we needed to bring each precursor separately inside the reactor. If the precursor meet each other before the reactor they would react inside the tubings and it would cause serious contaminations in the linings. When ALD 4 is closed, two precursor lines go inside the reactor separately and at the same time, which gives us a CVD process, then if we open ALD 4 valve and change the system to pulse and purge program then from all the four reactor inlets only one precursor can enter at each pulse. Having the ability to have both CVD, and ALD system at the same time gives us the ability to fabricate exotic layers, like fabricating a graphine layer in CVD mode and growing Niobium on top of it using ALD mode.



**Figure 3-38 Simple schematic of MFCs and ALD Valve arrangement**



**Figure 3-39 Mass Flow Controllers, and purge bypass arrangement**



**Figure 3-40 ALD valves arrangement, the valve on left top: valve 1, left middle: valve 2, left bottom: valve 3, right: valve 4**

### 3.4 Vacuum

Usually ALD systems work under atmospheric to low vacuum pressures, around  $10^{-3}$  Torr to 760 Torr. To get to the desired pressure most of the systems have double stage rotary vane pump which can get up to  $10^{-3}$  Torr. In our system we used a combination of Rotary pump and turbopump. The main reason we used the turbopump is that it can give us the vacuum that we cannot get from a mechanical pump. It goes down to  $10^{-8}$  Torr, which is very close to the pressure of Auger Electron Spectroscope. This low pressure is desirable for us if we would like to add our ALD system to the current AES system we have. This would allow us to check the quality and topography of fabricated film immediately after the process without breaking the vacuum. On the other hand since there is a need to try different kind of precursor to get the best combination of materials for diodes, antennas, and metamaterials, different kind of precursors would go inside the reactor and after a while the contamination gets higher and higher, having access to high vacuum gives the ability to bring the pressure very low and evacuate all the unwanted material from the chamber by going to higher vacuum and baking the system.

The turbopump was made by Pfeiffer model no. TPU 300. This model needs a water-cooling system. It has a 8 inch CF flange connection on top of it and to have a good control on turbopump's effect on chamber there is a 8 inch gate valve on top of turbopump on the bottom of chamber. Opening and closing the gate valve can result in decreasing and increasing the pressure of chamber.

The rotary vane pump first connects to a foreline trap, which prevents the oil mist to travel inside the turbopump and chamber. After the trap there is a Tee connection that from one side it goes to the turbopump to decrease the pressure of chamber to a point that turbopump can start to work, the other connection goes to ALD 4 valve to reduce the pressure inside the bubblers and purging the bubblers.

Helium leak detection was done using Alcatel ASM 110 Leak detector. This process was one of the most complicated processes in this project since there was over 40 connections, 40 ft. of tubing, 15 valves, and 11 con-flat flanges. Leak detection process started with PVC tubes, foreline trap, Tee connection and secondary PVC tube. Then it gets to check the leaks in turbopump connections; and after that check leaks of the chamber, which contains the leak for all the flanges. At the end the leaks for tubings and bubblers was checked and it gave up to  $10^{-3}$  torr vacuum by just using mechanical pump.



**Figure 3-41 foreline trap and Tee connection arrangement. The mechanical pump can pull the vacuum from both bubblers, and chamber.**

To read the system pressure two thermocouple gauges and an ion gauge are used. Thermocouple gauges can read the pressure to as low as  $10^{-3}$  Torr, and there are two of them in this system, one of them is located on top of the gate valve in the bottom of chamber, which reads the pressure inside the chamber. The other one is placed on the turbopump to give the pressure inside the pump; knowing this pressure would help us to figure out the best time to turn the turbopump on. There is also an ion gauge, which measures the pressures under  $10^{-3}$  Torr. This gauge is used when the turbopump is on and it can read pressures as low as  $10^{-12}$ .

## 3.5 Temperature Controllers and Heaters

Bringing the ALD system to particular temperature is crucial for many reasons. Tubings temperature should all be constant and high enough to prevent precursors from condensing on the walls. Bubbler temperatures should be in a range to give high enough vapor pressure of precursors. The chambers temperature needs to be in a range to prevent precursor condensation and also in a range to give enough heat to the precursor gas to prepare it for reaction; having high enough temperature is especially significant in CVD mode because during CVD, part of the reaction happens in the gas phase. The Substrate stage is the most important heating element in this system since it gives enough energy for chemisorption of reactants, which leads to surface reactions and thin film production.

### 3.5.1 Heaters

To heat up the chamber body and bubbler bodies heat tapes produced by Amtex is used. For each of the bubblers a 10ft. Amtex heat tape with 58-ohm resistivity is used. These heat tapes can reach up to 450 °C and by using glass fiber insulation and aluminum foil cover they can prepare an isothermal environment to have a steady vapor pressure inside bubblers. To cover the chamber body by heat tape, two 10ft., two 8ft., and two 6ft. heaters are used. These heaters are all connected in parallel and controlled by a PID controller.

To heat up the 40 ft. tubings, heat ropes from Omega are used. These heat ropes are in different lengths 6 ft., 8 ft., and 10 ft. They are very flexible to cover all the tubings, connections, and valves in between. Having all the tubing at the same temperature helps us because having cold or hot spots in tubings will result in decomposition of precursors or condensations of them. These heaters can reach up to 450 °C and they cover all the connections from the MFCs to the chamber. In this system we used eleven 10ft. long, six 8ft. long and three 6ft. long heat ropes. All of these heat ropes are connected in a special arrangement to release the same amount of heat.

For heating the substrate three high power cartridge heaters from McMaster-Carr were used. These heaters placed inside a 0.5" thick stainless steel rod to have optimum

heat distribution (Figure 3-23). They can go up to 550 °C and each of them covered by stainless steel sheath and connected in parallel to distribute same amount of heat anytime they turn on.

### **3.5.2 Heaters Terminal Box**

Since there are over 29 heaters in this system connecting them in a controlled manner is very important. The tubing part has 20 heaters and they all need to get the same amount of power per length to have the same heat distribution. Connecting all 20 heaters in parallel can be an option but having all of them in this configuration would need up to 80 Amps which is hard to provide and unnecessary for our system. So to get to lower Amps and still having enough power to get to our desired temperature the combination of heaters, shown at figure 3-42 is suggested. This combination was built in a 17” \* 17” enclosure box, using fourteen, 6 row, terminals and jumpers (Figure 3-43). Having heaters on tubings side is very important because if there is only one cold spot in our 40 ft. system then the gas will condense there and would result in very bad quality in thin film fabrication.

In this enclosure box (Figure 3-43) the first column from right belongs to chambers body heaters all these heaters connected in parallel. One side of each circuit goes to plug and the other part goes to PID controller box, which can be seen at figure 3-44.

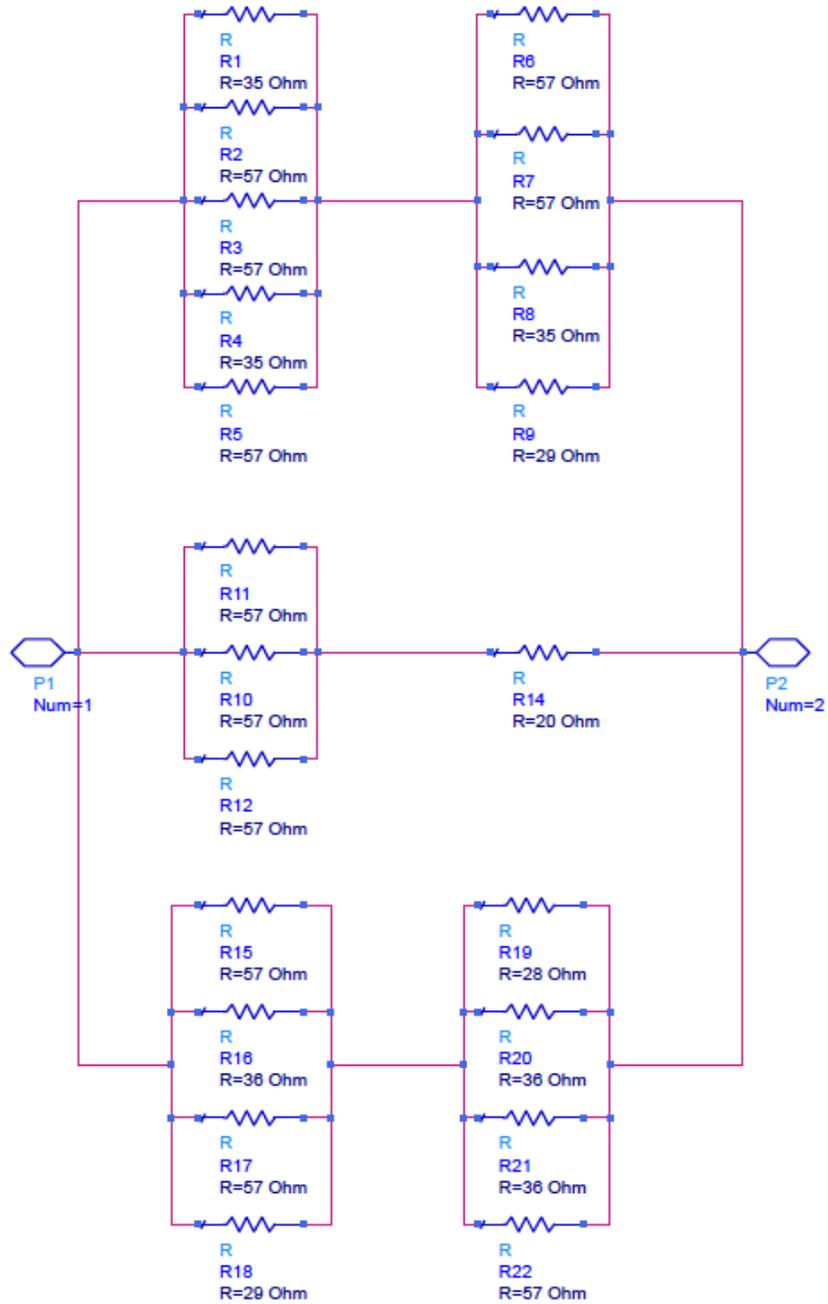
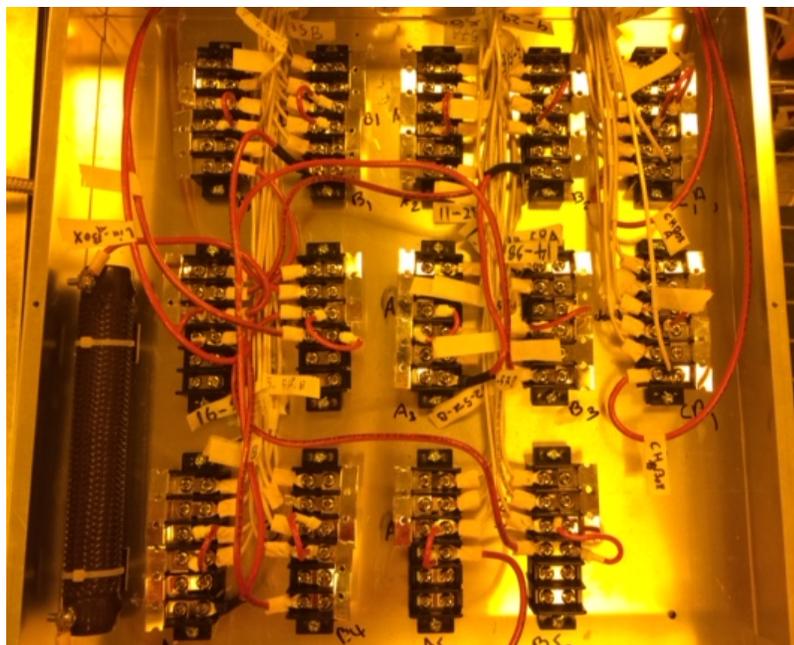


Figure 3-42 Tubings' heaters configuration to get optimum amount of heat and prevent energy lost



**Figure 3-43 Terminal box for tubings and chamber's body heaters**

### **3.5.3 Thermocouples**

To have a full control on temperatures in different parts of our system we used from K-type thermocouples. These thermocouples can go up to 1000 °C and sensitive to 1 °C changes. For tubings, chamber body, and two bubblers we used Omega self-adhesive K-type thermocouples, which has a good adhesion properties on stainless steel. For the stages thermocouple we used a bare thermocouple with 20 gauge wires, since using the one with sleeves would result in outgassing and unfavorable reactions inside the chamber. We covered the bare thermocouple with Omega ceramic fish holes, which prevents the thermocouple wires from having connection with chamber's body.

### **3.5.4 PID Controller Box**

Since getting the system to right temperature in each part is crucial we used 6 different PID controllers, each belonging to a part of the system. One for each bubbler, one for the chamber body, one for stage heater, one for tubing, and one for regeneration

of the molecular sieve in the foreline trap. It is important to have a good control on the bubbler temperatures since this temperature will control the vapor pressure of precursors. Each of the bubblers connects to a separate thermocouple. Each thermocouple goes to a PID controller in PID controller box (Figure 3-45); the PID controller compares the adjusted temperature and read temperature and if bubbler's temperature is lower than adjusted temperature it switches the relay on so the current can pass through the bubbler heater. The same procedure happens to control the temperature of the chamber body and tubing.

For the heater stage inside the chamber a thermocouple feedthrough is used, because of the vacuum inside the chamber. This feed through is attached to a 1.33" CF flange and the flange connects to one of the heads in our multiple port 8" CF flange.

PID controllers read the temperature from thermocouples and compare it with their adjusted temperature; if the adjusted temperature is higher than current temperature then they turn the relay on. The relays are 25 Amps double side 20-300 VAC. Once the PID controller sends a current to the switch side of the relay (Figure 3-45), number 3 and 4, then the relay turns on and let the current pass through from port 1 to port 2.

All PID controllers are CN 743 series, bought from omega and they connected in parallel using terminals, shown at top left corner of figure 3-45.



Figure 3-44 Temperature controller box, front view

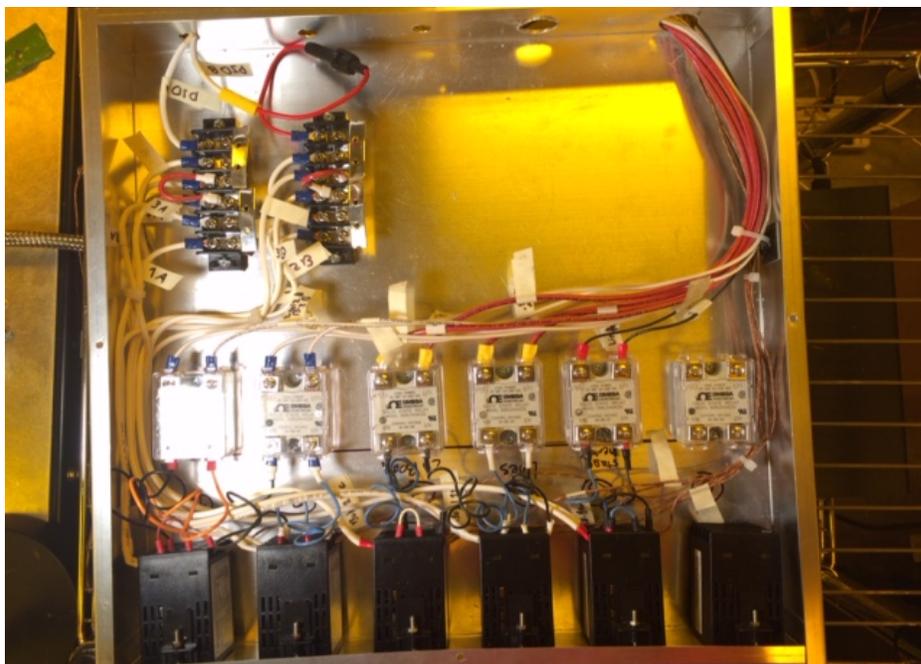


Figure 3-45 Temperature controller box, top view

## 3.6 Flow Controlling and Programming

The most important part of an ALD system is flow control. Controlling the carrier gas is crucial since in ALD mode each of the precursors need to reach the reactor separately in different time segments and there is a need for purge after each pulse of precursors. Controlling the flow is plausible by having solenoid control valve and mass flow controllers and software, which can synchronize all these instruments; giving them the ability to work simultaneously or individually in any time segment that we assigned for them. To manage MFCs and ALD Solenoid Valves we used Data Acquisition Cards to read them and having the ability to change the position of the valves and flow of the flow controllers.

### 3.6.1 Data Acquisition Cards

To be able to read all the valves and MFCs and control them we needed to have a connection between the programmed software and these instruments. Data acquisition cards give us the ability to make these connections. DAQ cards' jobs are converting

physical parameters into electrical signals, convert sensor signals to digital signals, and convert analog signals to digital signals. The last one, converting analog data to digital, is very important for us since both our valve systems and mass flow controllers are working with analog signals. So the cards are converting the analog input of these instruments to digital signals to give the software ability to understand their condition and also convert the digital signals from software to analog signals so the software can control them.

In this system four USB-6001 DAQ cards from National Instrument were purchased. Each of these cards has 8 analog inputs, 2 analog outputs, 20 KS/s, and 14-bit resolution. Since 7 analog output slots were needed for 4 ALD valves and 3 MFCs, and each of the DAQ cards has two of them we at least needed four DAQ cards. It can be seen from figure 3-46 that, DAQ-1 connected to MFC1 and MFC2, DAQ-2 connected to MFC3, DAQ-3 connected to ALD valve 1 and ALD valve 2, and DAQ-4 connected to ALD valve 3 and ALD valve 4.

### **3.6.2 ALD Valves**

The first step for controlling the flow is controlling the ALD valves. The way that these valves work was discussed in section 3.3.3.1. In this section the way that each valve can be managed individually is going to be discussed. To be able to control the valves with Labview software, we needed to send on/off signals to Data Acquisition Cards and these card in their output send a DC voltage if we needed to open the valve and they cut the DC voltage if it needs to be closed. The current that shows up at the output of DAQ cards doesn't have enough power to turn the valves on, so we needed to use relays to solve this problem. ALD valves turn on at 24 V and 0.150 Amps and DAQ cards have an output voltage of around 10 V. So we used from DC/DC solid state relays. These relays switch on if they receive an electrical current from DAQ cards and when they switch on they let the electrical current from port 3 to port 4 flow. There are 4 ALD valves and each of them needs to go to a separate solid state relay (Figure 3-46). A small electrical circuit was designed to connect each ALD valve individually to a relay and from there to a DAQ card. Finally all ALD valves connected in parallel to a 24 V 750 milliamps power source with a 750 milliamps inline fuse to protect valves' electronics.

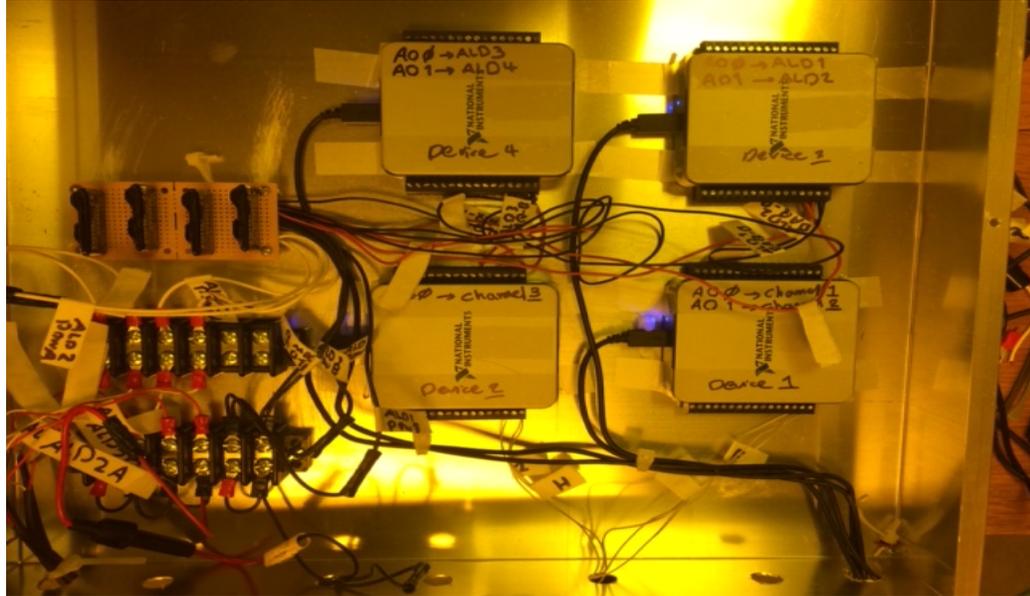


Figure 3-46 MFCs and ALD valves control box

### 3.6.3 MFC Read Box

All mass flow controllers initially connect to a MFC read box. This box is able to control each mass flow controller manually or remotely by computer. Here a Sierra 904 Flo-Box unit is used, this system has 5 different channels, which is able to connect up to five different MFCs. Flow set point for controllers can come either from the box's front panel or via the back panel I/O interface. Using the side-trek, MFCs also incorporate valve purge/monitor/off functions from the back panel I/O connector.

Each MFC flow rate is shown on the front panel LCD. The back panel I/O interface is connected to DAQ cards. From the DAQ card a set point signal can be sent to I/O connector to control the flow of each MFC. Also there is a switch on read box's back panel, which converts manual to automatic in case there is a need to control MFCs in manual mode.

### 3.6.4 Labview Software

Using the Labview software, a data acquisition and control program has been developed that gives us the ability to control valves and MFCs in a cycle process or

individually. The designed program has two modes: process mode and control mode. In control mode (Figure 3-47) each instrument can be controlled separately. When we choose a number for MFCs flow or a position for valves a digital signal goes from software to DAQ card. In DAQ card the data converts to an analog signal and becomes the input for the chosen instrument. Also the analog data regarding the position of MFCs can be transferred to digital signals and read by software which gives us the right chart on figure 3-47. In process mode (Figure 3-48) there are 8 steps. In each step all of the valves and MFCs can have a value to operate. There is a timer which shows how long each step is going to last. The program starts from step one and goes step by step until the last step. At the end of the last step, if the number of cycles that has been set by user is bigger than the number of cycles software counted, the process continues.

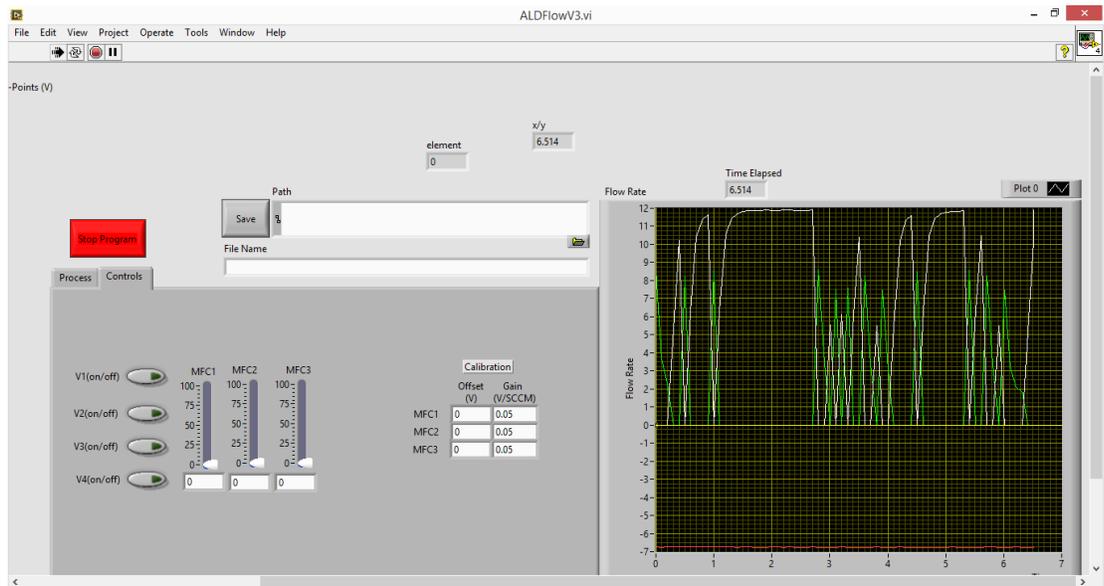


Figure 3-47 Labview software, control mode

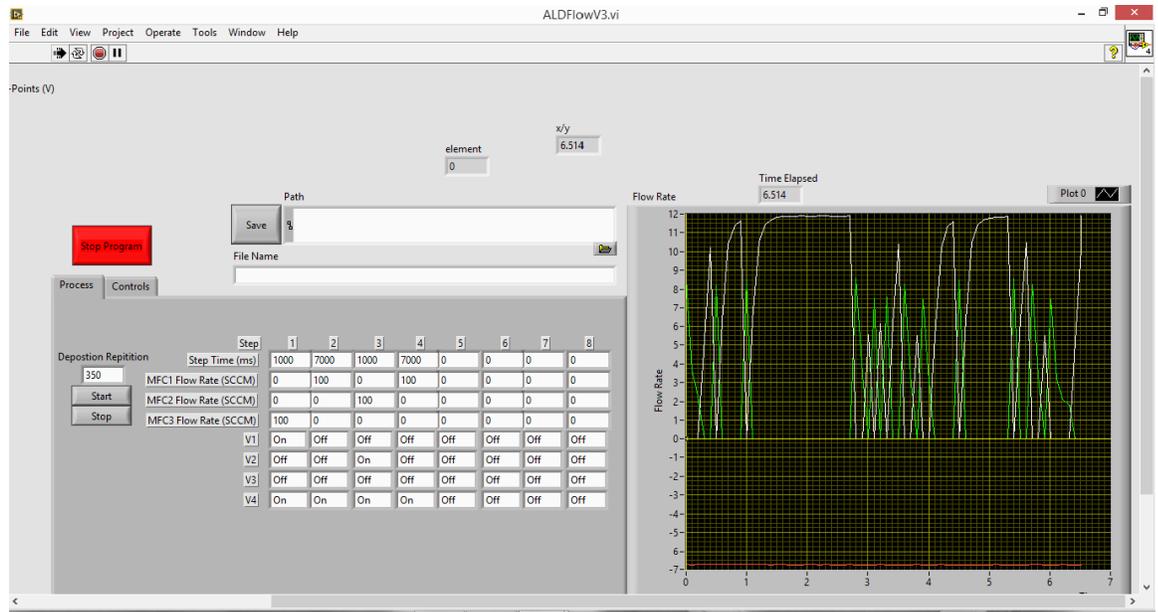


Figure 3-48 Labview software, process mode

### 3.7 Testing ALD and Characterization of Films

After all the modeling, designing, and manufacturing parts, the fabricated ALD system needed to be tested to make sure it is functional for nano-scale depositions. To do this a reference material was chosen so it makes it easy to compare the film growth with multiple available literature references. Also SEM, AFM, and EDS tests have been done on the sample to have a good understanding about the deposited film.

#### 3.7.1 Deposited Material

To test the designed ALD system,  $\text{Al}_2\text{O}_3$  was chosen as the first material to deposit, since there are abundant references on this material's ALD process and the contamination of this ALD process is by far less than other ALD processes. In this process there are two precursors, the first is Trimethylaluminum (TMA), and the second one is  $\text{H}_2\text{O}$ . Usually in ALD systems precursors are chosen based on their volatility and this is the same case in this experiment. To have a constant rate we kept both of the bubblers at constant 25 °C. To avoid condensation on the walls we set the tubings at 35 °C. Also to avoid condensation on chamber's wall the temperature was set to 40 °C. The

stage temperature was set to 150 °C. Also the software was set on 350 cycles. Each cycle contains 4 different steps in it, the first step was a TMA pulse for 1000ms. The second step was 4000ms of argon purge. The third step was a H<sub>2</sub>O pulse for 1000ms. The fourth step was an argon purge for 4000ms. In the first batch two different types of samples were put inside the chamber. One was a silicon substrate and the other was silicon with 100 nm of aluminum on top. In the second batch the substrate was silicon and there were changes in pressure, flow time, and flow rates between the first and second round. In the first round the pressure inside the bubbler was around 1.5 Torr. However, in the second round test the pressure was 760 Torr inside the bubbler. Also in the first round the flow rate was 100sccm in all MFCs, but in second round the flow rate was 30sccm for precursors' MFCs'. One more change was decreasing the time of each precursor step from 1000 ms to 200ms. The reason we are interested in playing with the bubbler pressure and flow rates is that by changing the pressure we can change the vapor pressure of precursor and dosing of reactant in the precursor line. The two step surface reaction in this process is shown below reactions (George, 2010). The asterisks mean the materials are on the surface.



Equation 3-1 and 3-2 shows what reactions happen during each step of the process. First TMA is pulsed and it reacts with hydroxyl groups on the surface of substrate. This reaction results in production of Al-O-Al-(CH<sub>3</sub>)<sub>2</sub> and release of methane gas. The remaining TMA in the chamber will not bond with methyl groups and this results in a self-limiting reaction. In the water pulse, water reacts with the TMA and results in production of an oxygen bridge and a hydroxyl group.

ALD prepared samples were characterized by using AFM, and SEM and their characteristics are shown in the next subsection.

### 3.7.2 Characterization

To validate the functionality of the Manufactured ALD system, two batches of samples were prepared. The first batch belongs to the condition that the stage temperature is 150 °C and bubbler temperature is 25 °C. In this batch the pressure inside the reactor is  $3.5 \times 10^{-2}$  Torr and the pressure inside the bubblers is 1.5 Torr. At this pressure water and TMA can turn to vapor easily and this results in high doses of precursors in each pulse. Also precursors may start to boil at this pressure, which results in moving some parts of precursors as liquid to the chamber. After the ALD process each sample was analyzed. Figure 3-49 and 3-50 belongs to the  $\text{Al}_2\text{O}_3$  on top of silicon, it is obvious that there is island growth for the first batch samples. At the island edges the crystalline form of the growth is obvious. This type of growth is expected in ALD processes however it is not the favorable growth since multiple crystal growths may result in a very rough surface. The grains are obviously large which may be caused by very high dose of precursors during the process.

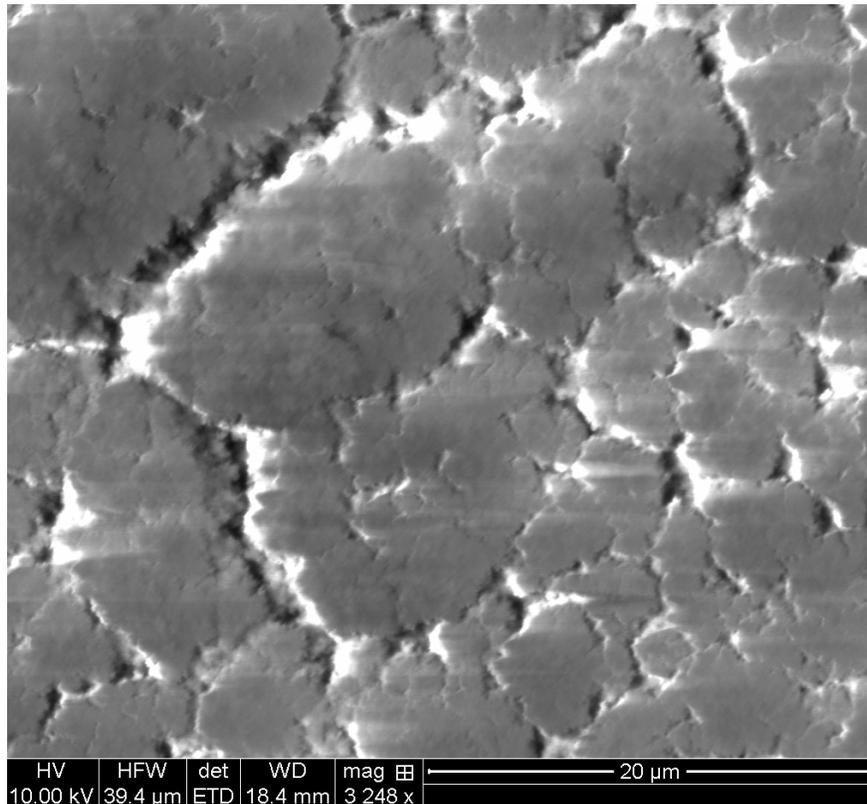
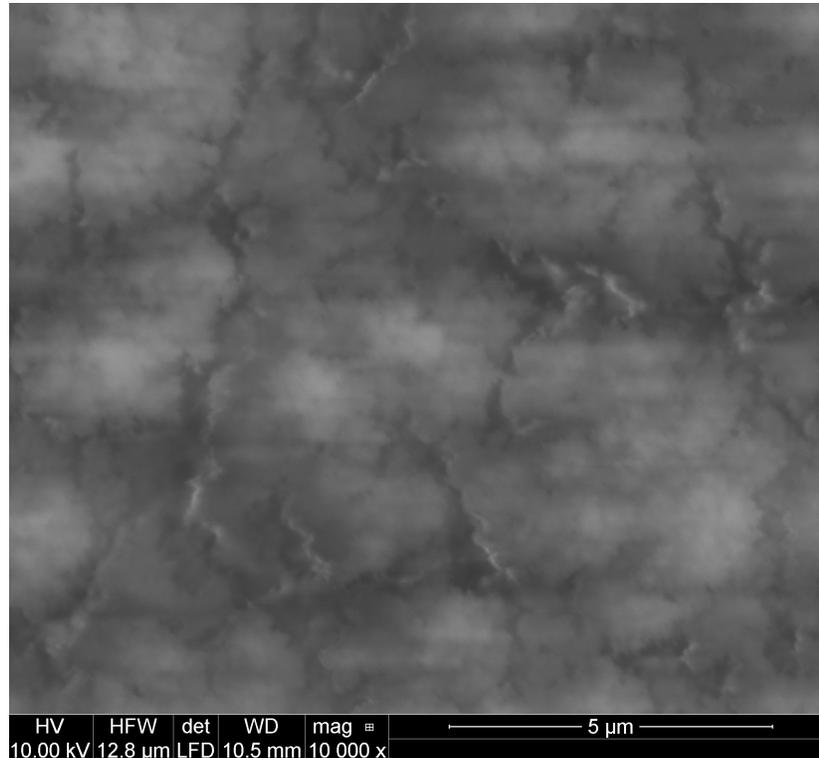


Figure 3-49 Atomic Layer Deposition of  $\text{Al}_2\text{O}_3$ , first batch, silicon substrate

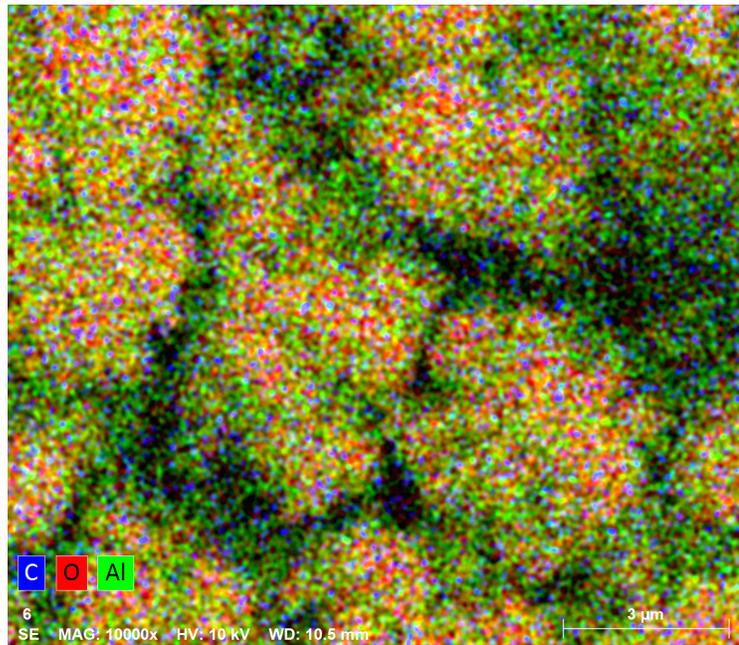


**Figure 3-50 Atomic Layer Deposition of Al<sub>2</sub>O<sub>3</sub>, first batch, silicon substrate, 10000 Magnification**

The second sample in batch-one belongs to a silicon substrate with 100nm of Aluminum on top. Here the growth happens on a surface of aluminum. The growth of Al<sub>2</sub>O<sub>3</sub> happened on this substrate where there was no chemical bond between the deposited layer and the substrate and the deposited layer was easily removed by pressurized nitrogen. This might happened due to the lack of chemisorption between aluminum and TMA at the beginning of process, which results in formation of a non-stick Al<sub>2</sub>O<sub>3</sub> layer.

To make sure of having aluminum oxide on the surface, an EDS test was performed to see the existence of elements on the wafer and the distribution of elements. Figure 3-48 shows all the elements the EDS detector detected on the sample. Figure 3-49

to 3-51 shows the distribution of each element on the sample. Figure 3-52 shows the peak of each element which shows very strong peaks for Aluminum and Oxygen. The percentage of Aluminum is 68% and percentage of oxygen is 31%, there is also a small peak of carbon, which can be attributed to the SEM chamber contamination or sample contamination. As can be seen the ratio of Aluminum to Oxygen is not three to two in this measurement. This can happen due to the low thickness of deposited material, since EDS can also detects Silicon and Oxygen in SiO<sub>2</sub> substrate as part of the surface analysis. Another factor that can affect atomic percentage calculation is eliminating peaks with particular energy, which resulted in eliminating the energy peak belonging to Silicon and also any energy peak higher than 2.0 KeV.



**Figure 3-51 All elements EDS map**

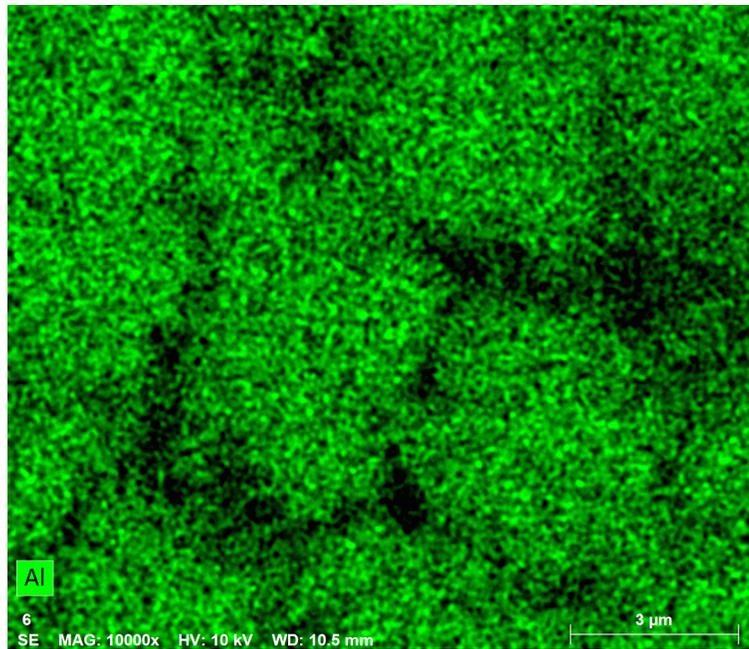


Figure 3-52 Aluminum EDS map

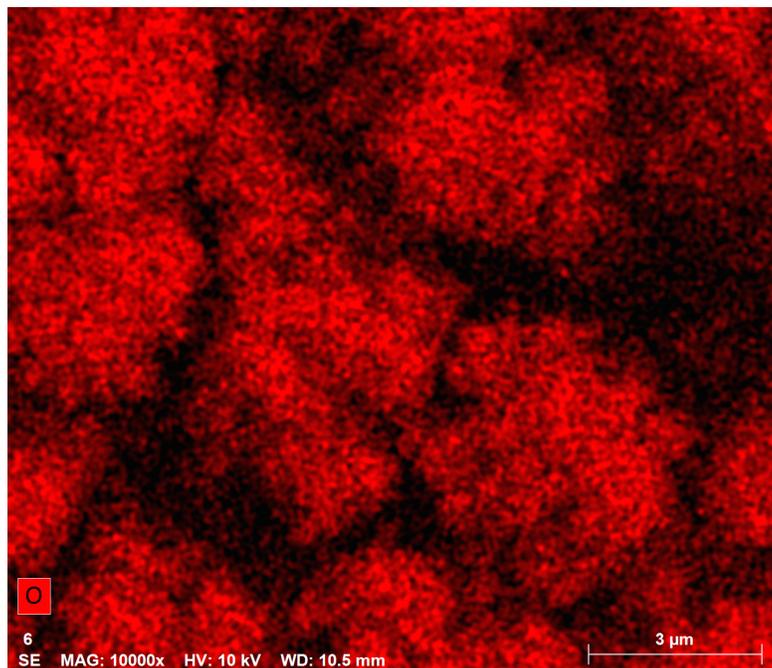


Figure 3-53 Oxygen EDS map

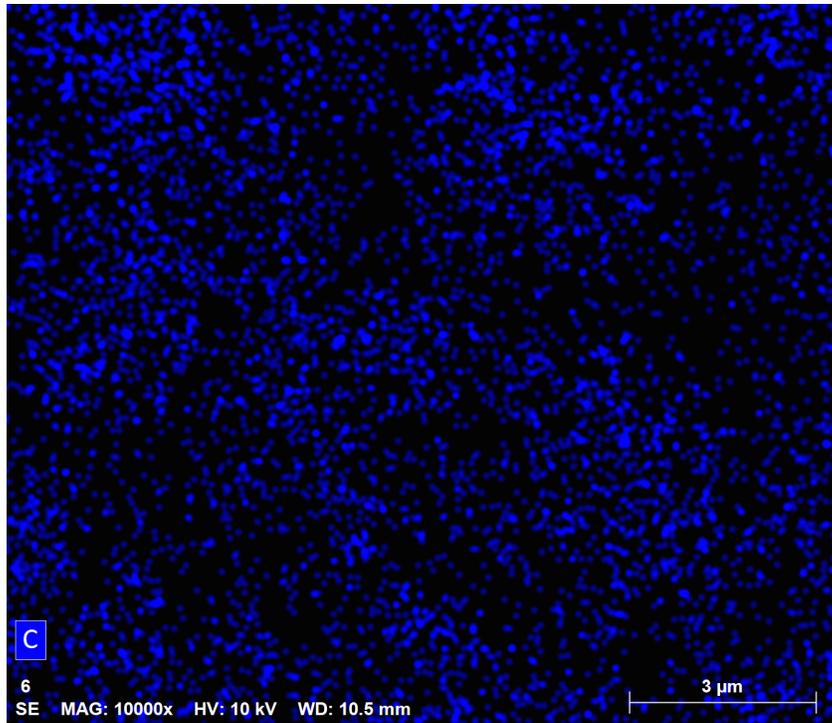
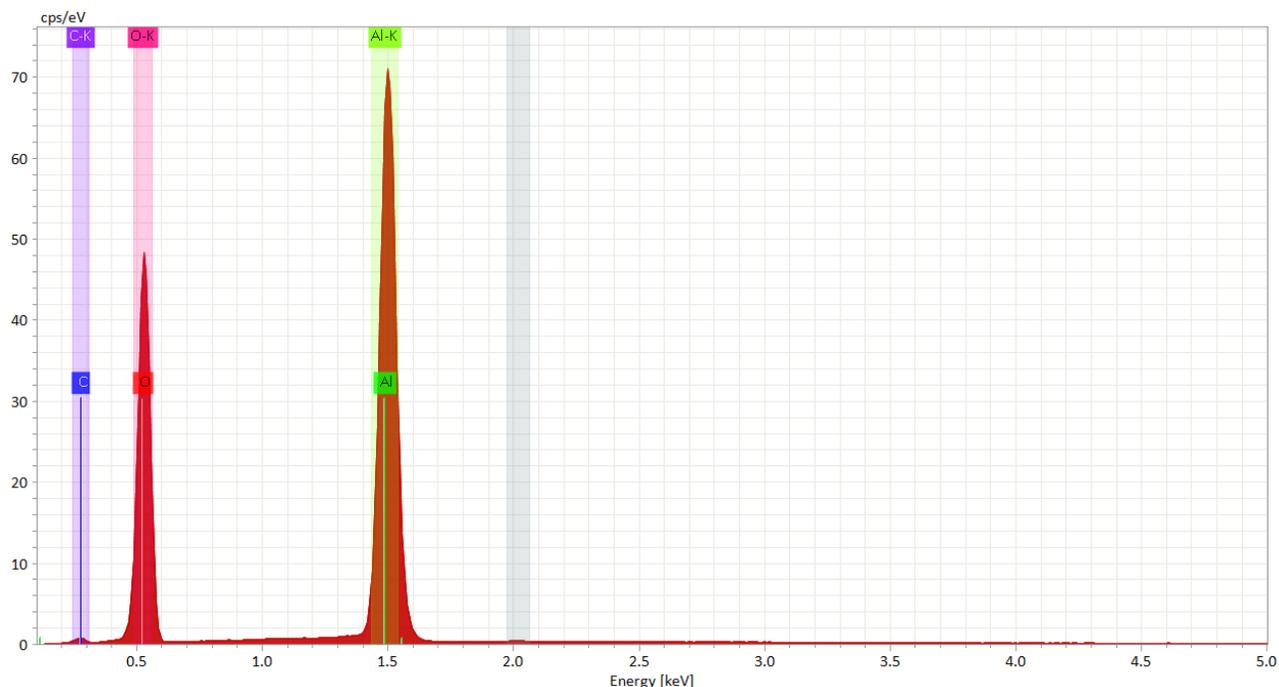


Figure 3-54 Carbon EDS map

Table 3-1 Percentage of each element

Element	At. No.	Line s.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]
Carbon	6	K-Serie	0	0	0	0
Oxygen	8	K-Serie	255682	1.006616428	56.23317147	68.42196983
Aluminium	13	K-Serie	341185	0.783459433	43.76682853	31.57803017
			Sum	1.790075861	100	100



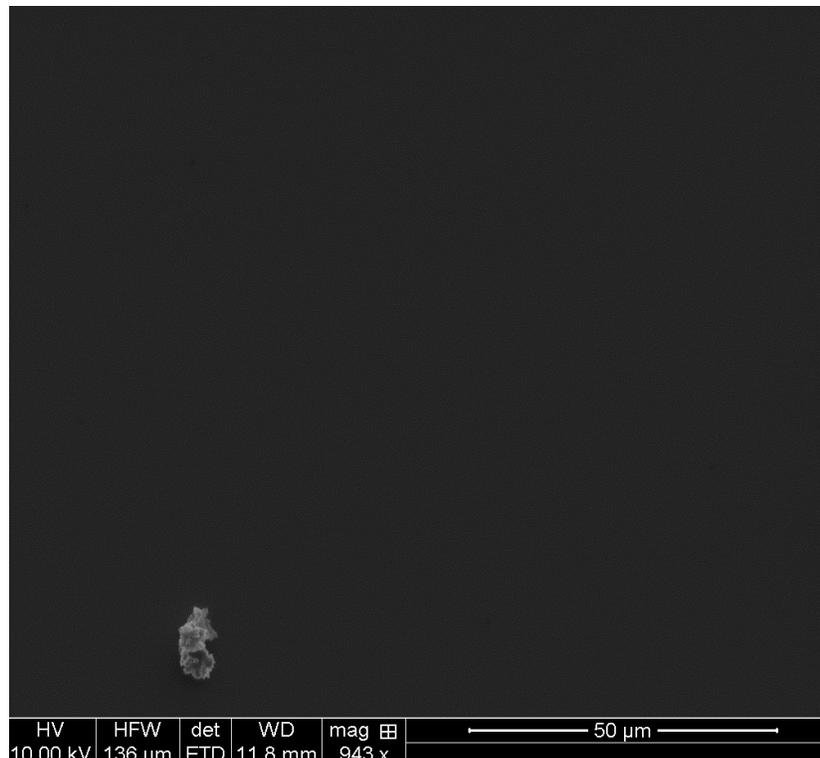
**Figure 3-55 Elemental peak from EDS**

In the second batch or batch-two, the process varied the pressure of the chamber, and all temperatures are the exact same as batch-one additional differences are the pressure in bubblers, flow rates, and pulse time. The bubbler pressure in this batch tried to remain at atmospheric pressure. This pressure is high enough for both of the precursors since the vapor pressure for TMA at 25 °C is 8.7 Torr and for water at 25 °C is 17.5 Torr. These pressures are high enough for vapor pulses inside the reactor. Changing the pressure gives a lower dosing per cycle, which results in a smoother surface. It also prevents the precursors from boiling inside the bubbler and bringing liquids inside the chamber. Also the pulse time for precursors decreased to 200ms and the flow rate stayed at 20 sccm. Figure 3-56 shows the SEM pictures for batch-two sample and there is no island growth on the wafer.

To understand the exact smoothness of surface AFM analysis was performed on the batch-two sample and the result is shown at figure 3-49. The deposition in batch-two shows a much smoother surface with 1.2 nm RMS (Figure 3-54). This roughness is comparable to the similar works in literatures like Steven George et al. with 5 Angstrom

roughness (M. D. Groner, 2004).

Another factor we needed to check in our system is the thickness of the film. To see if the thickness we can get from this system with particular condition matches with the thickness from literature under the same conditions. To measure the thickness another AFM test was performed and the result can be seen from figure 3-59 to 3-60. For this test we used the scratch method. In this method by using a blade, a scratch was made since normal blades can not scratch silicon substrate, a jump happens in AFM test due to the scratch and it shows the film thickness. The thickness for a 350 cycle ALD with 150 °C temperature from our AFM test is about 56 nm, which is comparable to 43 nm mentioned in the literature for 300 cycle of ALD process. (M. D. Groner, 2004)



**Figure 3-56 SEM picture for batch-two sample**

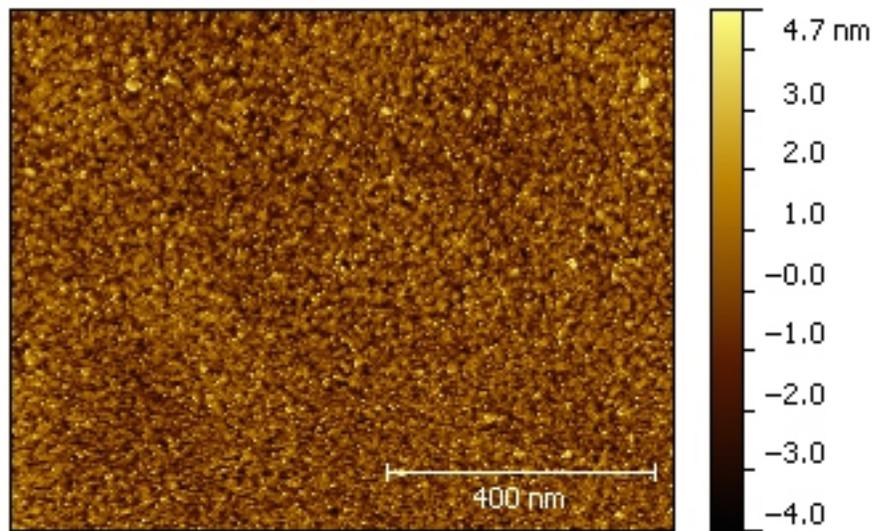


Figure 3-57 AFM measurement for batch-two sample

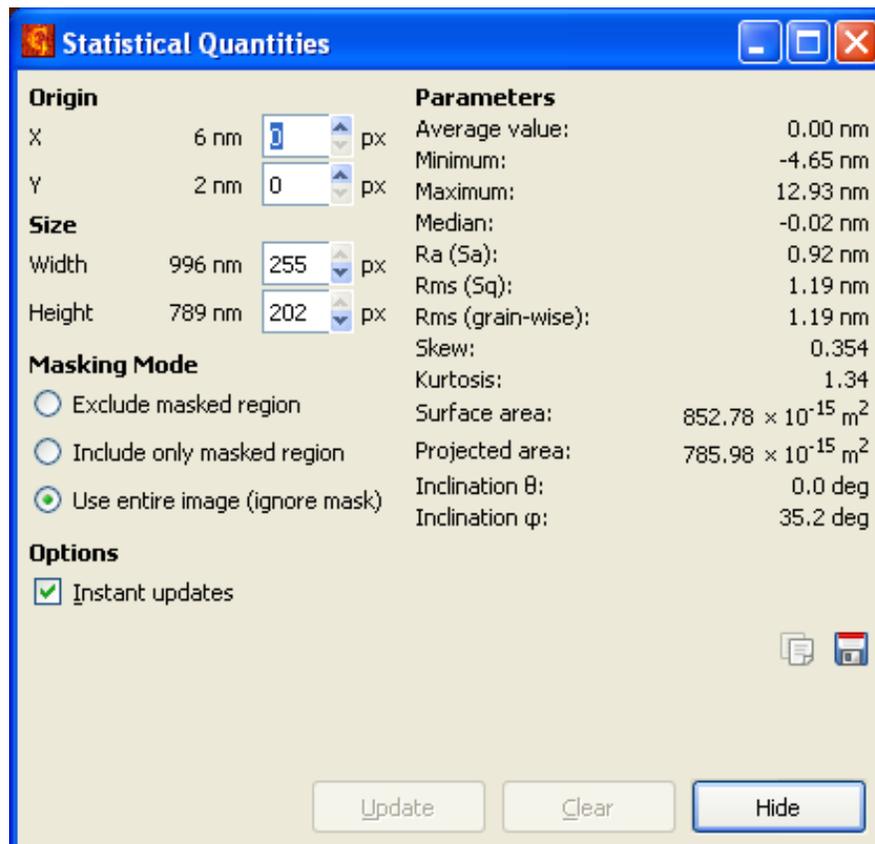


Figure 3-58 Statistical quantities of surface roughness analysis

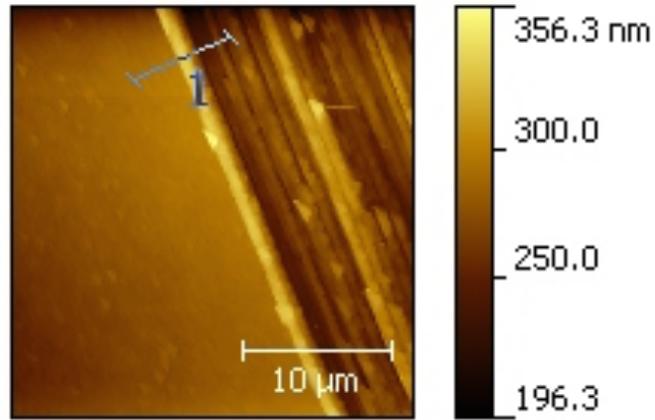


Figure 3-59 Film thickness measurement using AFM

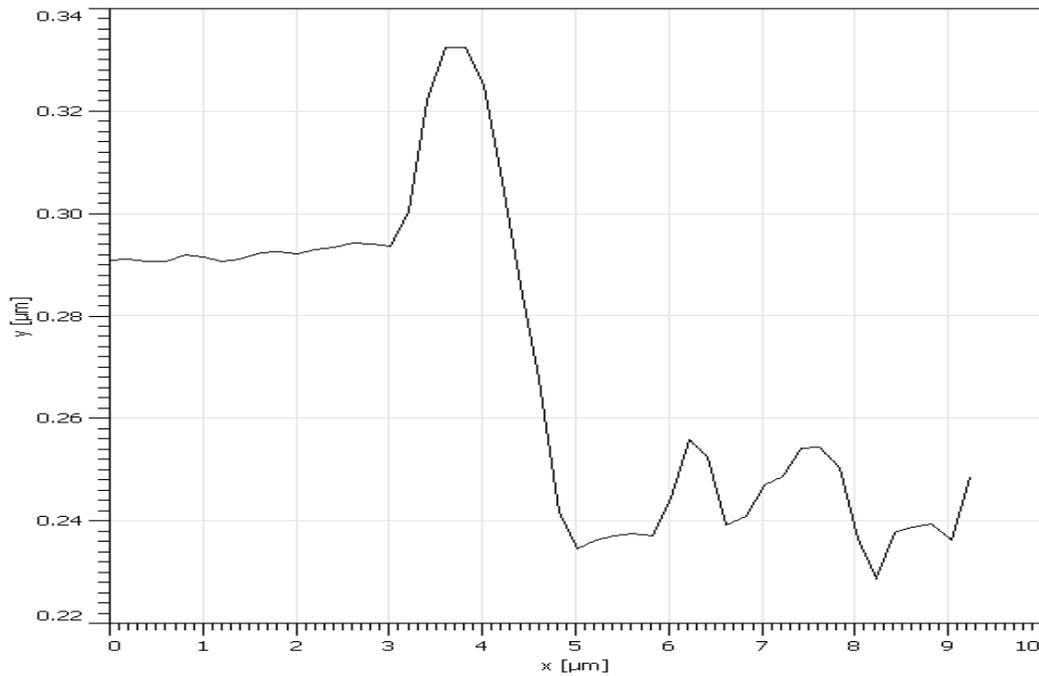


Figure 3-60 Step due to the scratch on sample's surface that gives film thickness

## 4 Conclusions and Future Work

### 4.1 Conclusions

An atomic layer deposition system was designed, modeled, manufactured, and tested. The design of the ALD system needed to be in a way that all of the parts can work together and match each other perfectly. A reactor, showerhead, flanges, heater stage, and stage holder were designed in a way that can fit together and work together perfectly inside the chamber. The manufacturing of each part needed a meticulous sight and great understanding of how different parts are going to work together. The stage heater was designed to contain three cartridge heaters in it to have a very even temperature all over the surface. The showerhead has four gas inlets, which gives it a very good gas distribution capability. The Macor ceramic can easily remove the stage heater from the stage holder for any services. The reactor is designed in a way to have minimum precursor entrapment in it. With the exception of Macor ceramic, which is used as a spacer between stage heater and stage holder the rest of reactor's parts are all 316 stainless steel which gives a durable and reliable device for systems with chemical reactions in them.

The tubings are all designed in a way to give us the ability to switch our ALD system to CVD. Also the design considered having 3 bubblers. All bubblers were designed in a way that they can hold up to 800ml of precursors, they all have a dipping tube which goes on the bottom of the container and causes precursors to entrain in gas. In the tubing design, there are three mass flow controller and four ALD Solenoid Valves. Valve 3 in this system gives us the ability to reduce the pressure inside the bubblers. Reducing pressure helps us to work with precursors that have low volatility or precursors which are temperature sensitive.

The system contains two different vacuum pumps; one mechanical pump and one turbopump. The mechanical pump can get the chamber's pressure as low as 30 mTorr while the turbopump can get to  $10^{-6}$  Torr. This high vacuum is not necessary for ALD processes but it gives the ability to clean the system from volatile materials and by-

products very well. Also it gives the ability to connect ALD to AES without breaking the vacuum. A foreline trap is used between mechanical pump and turbopump to prevent the pump oil mist from going back to chamber. A gate valve is also placed between the turbopump and chamber. This valve helps us to use it as a throttle valve to control the pressure inside the chamber.

All of the tubing, bubblers, chamber, and stage need to have a controllable temperature, because drastic temperature differences between different parts can lead to condensation or decomposition of the precursor. There are thermocouples inside the chamber, on the chamber's body, on the bubblers, and tubing to give us the ability to read the temperatures. Also all of these parts are somehow covered with heaters. The thermocouples send the temperature to a PID controller and the controllers compare it to set point temperature. If the set point is higher, PID controller turns on the relay so the current can pass through heaters to get them warmer. For this purpose a PID controller box was designed. In this box there are six PID controllers and six Solid State Relays. Also there are 2 terminals which gives the ability to turn all the controllers on and off at the same time. Each PID controller belongs to one particular part of the system. There is one for the chamber body, one for tubing, one for the stage heater, and one for each bubbler.

To control the flow of precursors there are 4 solenoid valves and 3 MFCs. Each of them needs to be controlled in a way to perform in process mode or control mode. To control each of the MFCs or solenoid valves they need to be readed by computer and get orders from it. Data Acquisition Cards can connect physical instruments to computer. Here we used 4 DAQ cards to have 8 analog output. From each analog output we can send a signal to one of our instruments. MFCs work in a range of numbers so the analog signal is in a range from 0 to 5 V. However, valves are on/off instruments and they only need a small current from the analog output to turn the relay on for ALD Valves. To help these instruments work simultaneously, a Labview software was designed with process mode and control mode. In process mode all of the MFCs and valves work in an assigned order to complete all the steps one after another and in control mode each of these instrument can be controlled manually, which gives a very good control on the system

specially while adjusting the pressure.

Finally the manufactured ALD was tested to see if it is capable of thin film production. Two batches were tested. Batch-one, which had a very low pressure inside the bubbler, showed the island growth with crystalline structure. An EDS analysis was performed and it proved the deposition of  $\text{Al}_2\text{O}_3$  on the silicon substrate. Another ALD process was performed under the name batch-two. The conditions were the same as batch-one except the pressure inside the bubblers remained at around atmospheric pressure, the flow rate was 20 sccm and the pulse time for precursors was 200ms. In this case a much smoother surface was fabricated with a 1.2 nm RMS. The thickness of this sample was measured and it was about 50 nm, which was very close to the measurements reported in literature.

## **4.2 Future Work**

The manufactured ALD is an instrument, which is designed to do exotic depositions. This instrument has the capability to work under high vacuum; it is able to work with highly unstable or very low volatility precursors. It could switch between ALD and CVD by one click and can do each of these processes one after another without breaking the vacuum. It can connect to AES to have direct analysis without vacuum break or using its ion gun to improve the surface properties. That being said, the next step for this instrument is to start targeting deposition of materials that are desirable for antenna or diode fabrication, which are hard to manufacture by conventional ALDs. Another work that needs to be done is moving the system to a dust free environment like a clean room to avoid contaminations. Also the performance of this instrument can be improved a lot by connecting it to AES.

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