

UNIVERSITY of CALIFORNIA

SANTA CRUZ

**ATOMIC LAYER DEPOSITION OF ALUMINUM OXIDE**

A thesis submitted in partial satisfaction of

the requirements for the degree of

BACHELOR OF SCIENCE

in

APPLIED PHYSICS

by

Noel Mayur Dawson

May 30, 2010

The thesis of Noel Mayur Dawson is approved by

---

Professor Nobuhiko Kobayashi

Technical Advisor

---

Professor David Belanger

Thesis Supervisor

---

Professor David Belanger

Chair Department of Physics

## **Abstract**

This paper will cover the atomic layer deposition (ALD) of aluminum oxide on crystalline silicon and anodized aluminum substrates. A homemade ALD system is used with trimethylaluminum (TMA) and water as precursors to deposit uniform aluminum oxide thin films. Aluminum oxide thin films were deposited on the crystalline silicon substrates as the deposition temperature varied from 50 to 250° C to study the effects of deposition temperature on the deposition rate per ALD cycle. The presence of aluminum oxide was confirmed with energy dispersive spectroscopy. Measurement of film thickness was performed using ellipsometry. On the anodized aluminum substrates, that have pores formed spontaneously during the anodizing process, the deposition temperature was kept at 250° C while the number of cycles was varied to study the evolution of ALD aluminum oxide thin films on the pores. Scanning electron microscope (SEM) images were used to examine the aluminum oxide thin films covering the pores and the surface morphology of several samples.

## **Acknowledgements**

First and foremost I would like to thank God for all the grace and blessings which were bestowed upon me that aided in my completion of this thesis and the rigorous applied physics major. I would like to thank my thesis advisor Prof. Nobuhiko Kobayashi, to whom I'm forever grateful, without his support and belief in me this thesis could not have been completed. A special thanks to Drew Lohn, a graduate student whose guidance and countless hours of discussion have given me the knowledge and experience I needed to succeed in this and many other endeavors; you were a great mentor and have become a great friend. I would like to thank my second family in New York, Uncle Singh and Bommie Perima, you are a huge part of who I am today. I would like to thank my parents, siblings and friends without your support I would have no structure to hold me up when times got rough. I love you guys. Lastly, I would like to thank the Advanced Studies Lab at Ames Research Center for their help in this project.

This thesis is dedicated to the loving memory of Margaret M. Bernard, whose life was taken away too soon but who will always live on in our hearts. You inspire me.

# Table of Contents

<b>Abstract</b>	<b>I</b>
<b>Acknowledgements</b>	<b>II</b>
<b>Dedication</b>	<b>III</b>
<b>List of Figures</b>	<b>V</b>
<b>1. Introduction</b>	<b>1</b>
<b>Motivation</b>	<b>1</b>
<b>Background</b>	<b>1</b>
<b>2. Experiment</b>	<b>3</b>
<b>Setup</b>	<b>3</b>
<b>Deposition</b>	<b>4</b>
<b>3. Results and Analysis</b>	<b>6</b>
<b>Silicon substrate</b>	<b>6</b>
<b>Anodized aluminum substrate</b>	<b>10</b>
<b>4. Conclusion</b>	<b>12</b>
<b>5. References</b>	<b>14</b>
<b>Appendix A</b>	<b>15-17</b>
<b>Appendix B</b>	<b>18-22</b>

## List of Tables and Figures

Figure 2.1 ALD setup	2
Figure 2.2 Representations of the half-reactions between TMA, water, and the surface	5-6
Figure 3.1 SEM picture of deposition on sample at 50 and 250° C	7-8
Table 3.2 Summary of energy dispersive spectroscopy	8
Figure 3.3 Graph of growth per cycle versus temperature	8
Figure 3.4 SEM images of anodized aluminum substrate before and after deposition	11-12

# 1. Introduction

## Motivation

As the electronics and optics industry continue to shrink the size of devices, there is a need to be able to control the size of films with atomic precision. Atomic layer deposition (ALD) fulfills this need, enabling uniform thin films to be grown with the precision and accuracy of tens of angstroms. Furthermore, ALD gives us the ability to create structures which will enable us to exploit the nano-scale properties of different materials such as memristance [1]. ALD also allows us to correct the nano-scale defects of other processes, such as filling in the pores that occur in the anodizing process of aluminum. Thus, ALD has become an important process in the materials industry, giving us the ability to create new structures and novel solutions to old and new problems.

## Background

ALD originally known as atomic layer epitaxy (ALE) was developed by Dr. Tuomo Suntola at the University of Helsinki in 1974 for the development of thin zinc films in electroluminescent displays [2]. ALD is a chemical vapor deposition (CVD) process, however unlike usual CVD processes, the deposition rate is self-limited and the total film thickness depends on the number of ALD cycles rather than the exposure time. This is achieved by sequentially injecting the precursors into the reaction, thereby breaking down the chemical reaction into two self-limited half reactions. In a usual two precursor ALD for a binary alloy material the process is as follows: The first precursor is pulsed into the reaction chamber and forms a single monolayer on the surface of a substrate. Then an inert gas such as nitrogen or argon is injected in the reaction chamber to purge the residue of the first precursor and any bi-

product that remains unreacted. Subsequently, the second precursor is pulsed into the chamber which reacts with the initial monolayer of the first to form a target binary material one monolayer thick. Once again the chamber is purged with a nonreactive gas to complete one ALD cycle, and the cycle is repeated as many times as needed to achieve desired film thickness [3].

The ALD process offers unique advantages over the normal CVD process. First, the growth process is self-limiting, such that the amount of precursor injected with a pulse doesn't affect the deposition rate (thickness per cycle) as long as the surface of a substrate is completely covered.

In principle, the ALD process offers a deposition rate of one monolayer per cycle, giving unparalleled control over the film thickness. However, the deposition rate in the early stage of an ALD process can be less than a monolayer per cycle. The reasons for this are the limited number of reactive sites initially present on a substrate surface, and sluggish reaction kinetics due to the large size of the ligands in metalorganic precursors compared to the length scale over which surface atoms are arranged on a growing thin film [3]. Lastly, and maybe most importantly, the inherent nature of the ALD process allows it easily to be converted to a large scale process [3].

There are also drawbacks for the ALD process. For instance, a slow deposition rate of one monolayer per cycle is not apparently suitable for the needs of thick films. Another concern with the ALD process is the release of harmful chemicals into the environment during the half reactions, which is true of all CVD processes.



## 2. Experiment

### Setup

A home built ALD reactor (Fig. 2.1) was used in the experiments. Nitrogen with a flow rate of 20 sccm flowed through the system continuously. The reaction chamber is equipped with resistive metal plate heaters to heat up a loaded substrate. Trimethylaluminum, an aluminum precursor, was kept at a constant temperature (25° C) using a heated metal enclosure. Swagelok pneumatic ALD valves were used to pulse the precursors into the reaction chamber. The generation of a pulse (i.e., pressure transient) of the precursor is a result of the difference in pressure between the equilibrium vapor pressure of the precursor and the pressure equilibrated among the gas line and the reaction chamber. A Boc Edwards industrial dry chemical pump was used to maintain a low pressure in the reaction chamber.

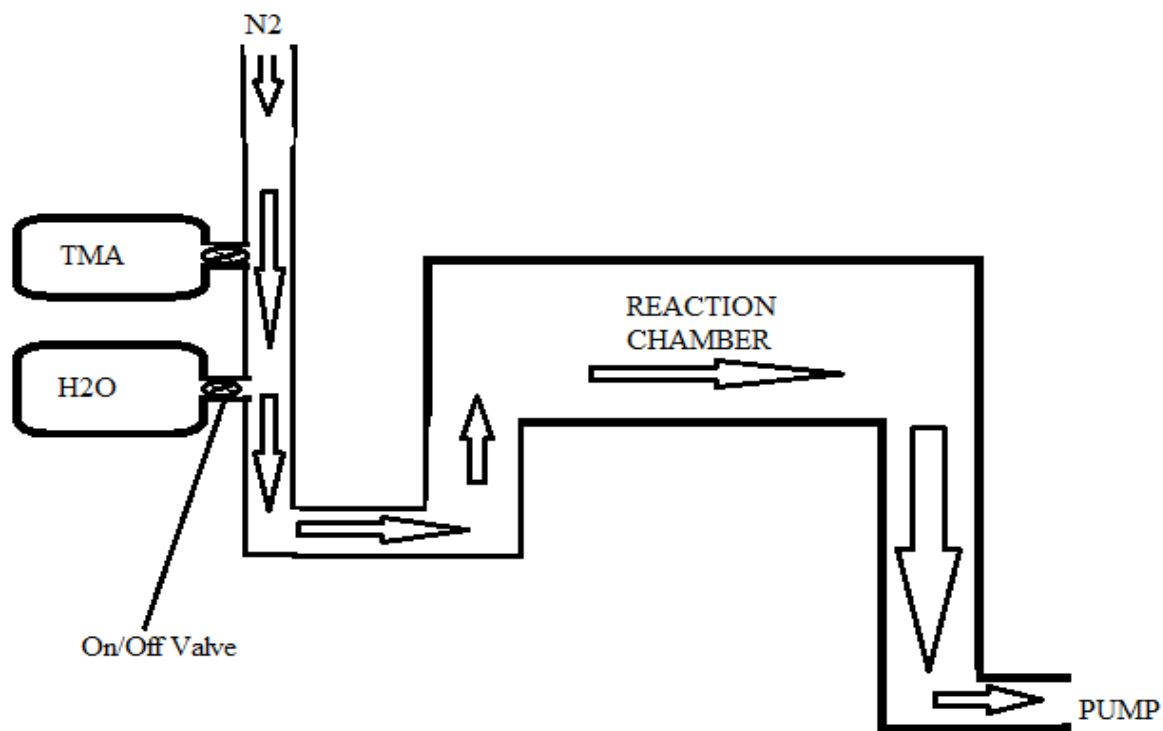


Figure 2.1 The ALD system.

## Deposition

For deposition of aluminum oxide, the precursors of trimethylaluminum (TMA) and water were used. These precursors were picked for their high volatility and reactivity upon mixture. The vapor pressure of TMA at 20° C is 8.7 Torr, and the vapor pressure of water at 20° C is 17.5 Torr. Both vapor pressures are sufficient to allow for a vapor pulse into the reaction chamber when the corresponding valve is open because the vapor pressure is higher than the base pressure of the reaction chamber and the associated gas manifolds. The base pressure is in the range of 180-250 mTorr. The TMA was maintained at 25° C for stable vapor pressure. The pulse duration of the TMA and water precursors was 200ms and there was a purge time of 8s between each pulse. . In a series of depositions of aluminum oxide thin films on Si substrates, the deposition temperature was varied from 50-250° C, while the number of ALD cycles was kept constant at 500 (except in the case of the 100 degree deposition where due to a limited amount of TMA the number of cycles were reduced to 63). ). On the anodized aluminum substrates the deposition temperature of aluminum oxide thin films was kept constant at 200° C (this specific deposition temperature was chosen based on the aluminum oxide growth rate calibrated on the silicon substrates), while the number of ALD cycles was varied from 400 to 800. Both of the substrates were cleaned with organic solvents before the deposition. The half-reactions for this process were described in a paper written by Widjaja and Musgrave [4] and are as follows (the asterisks show the surface species):



A graphical representation of the reaction is shown in Fig. 2.2a-c. This reaction according to the Widjaja and Musgrave is energetically favorable.

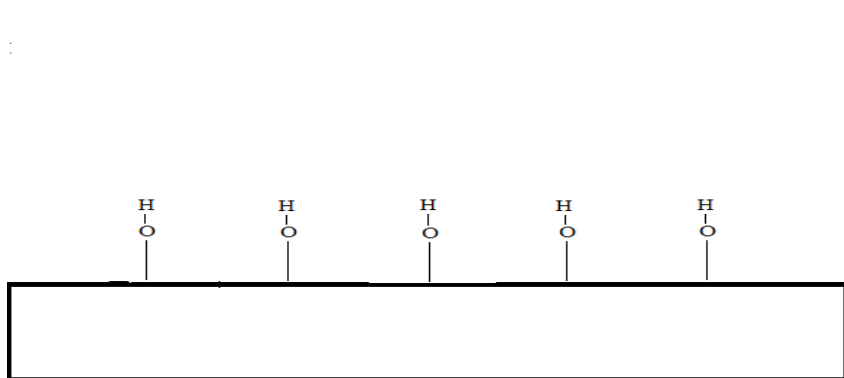


Figure 2.2a. The hydroxyl groups on the substrate surface before any pulse.

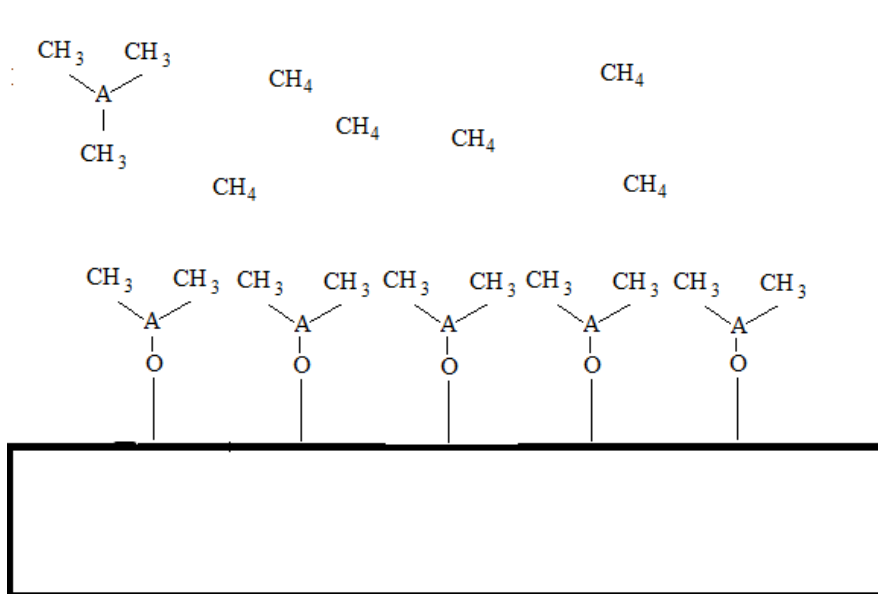


Figure 2.2b. After TMA pulse the TMA bonds to the surface hydroxyl groups releasing methane. The remaining TMA will not bind to the methyl groups on the surface therefore, the process is self-limiting.

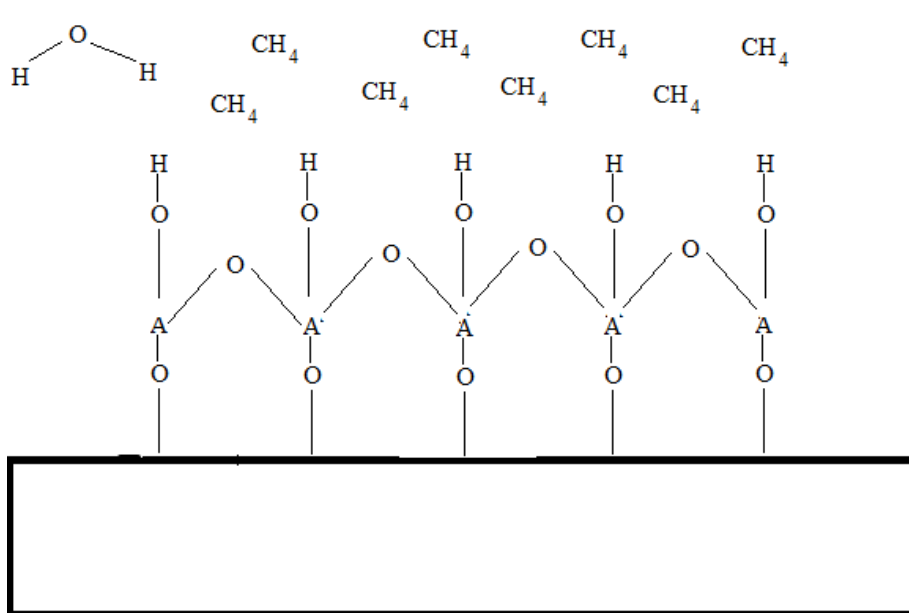


Figure 2.2c. After the water is pulsed two water molecules react with the each of the dimethyl aluminum surface species to form an oxygen bridge and a hydroxyl surface species and releasing methane. The remaining water will not react with the hydroxyl surface. Therefore, the reaction is self-limiting resulting in one monolayer of aluminum oxide per cycle.

### 3. Results and Analysis

In the analysis of the silicon samples energy dispersive (EDS) was used for chemical analysis. The thickness of the silicon samples were measured by ellipsometry using a V-Vase Spectroscopic Ellipsometer made by J.A. Woollam Co. Inc. Scanning electron microscopy (SEM) was used to study surface morphology of the samples and to analyze film deposition on aluminum substrates. The results of this analysis are discussed in the sections below.

#### Growth on Silicon Substrates

The presence of aluminum oxide was confirmed with the use of EDS. The spectrum for each of the samples can be found in appendix A. The EDS could not be performed on the sample grown

at 50° C to get an accurate percent mass measurement but the presence of aluminum and oxygen was confirmed. A theory on why EDS did not work as well on the sample is that the resulting x-rays were scattered at large angles because of the rough surface morphology (Fig.3.1a) of the sample. As a result the number of x-rays collected by the detector was insufficient. It is also important to note that the sample grown at 100° C had a thinner film than usual at 19.6 nm because the number of cycles was limited to 63. The small excitation volume from which the x-rays were collected resulted in a low yield for the EDS signal. However, the presence of aluminum and oxygen was confirmed. The EDS results are summarized in Table 3.2.

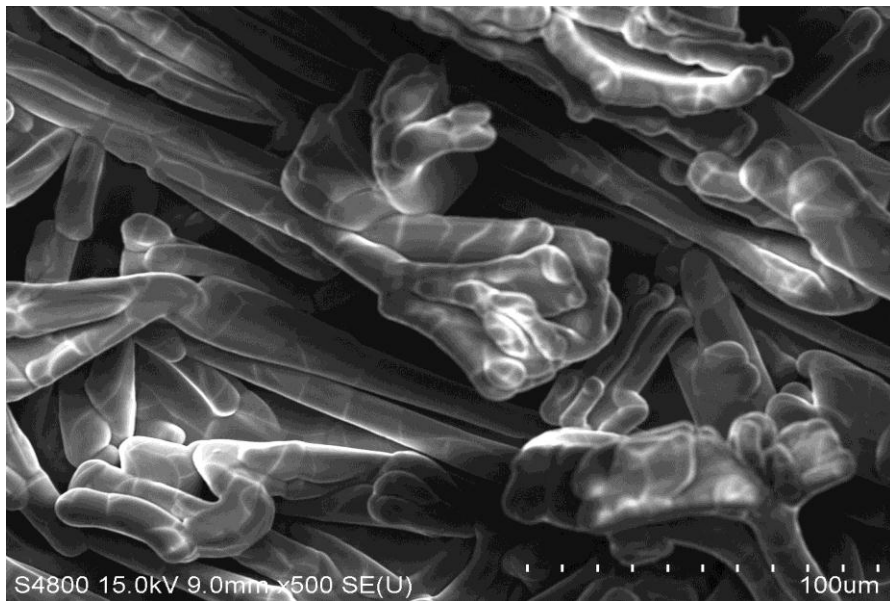


Figure 3.1a SEM. surface image of the 50° C sample.

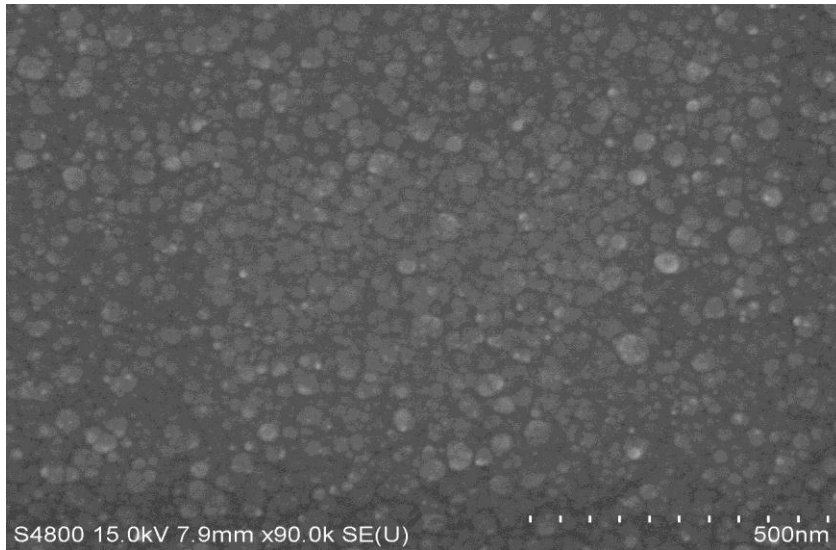


Figure 3.3b SEM surface image of the 250° C sample.

Growth Temperature(Celsius)	Mass Percentage		
	Aluminum	Oxygen	Silicon
50	NA	NA	NA
100*	<5%	<5%	90%
150	10%	40%	50%
200	10%	35%	55%
250	10%	40%	50%

Table 3.2 Summary of spectroscopy results for the silicon substrate samples. \*100 degree sample was deposited at only 63 cycles.

Ellipsometry provides a very robust way to make thin film thickness measurements that are accurate up to an atomic layer. The wavelength for the spectroscopy was scanned from 6000 to 14000 angstroms by steps of 1000, and the incident angle of the light was varied from 65 to 75 degrees by steps of 5 degrees. An accurate measurement for the sample with a deposition

temperature at 50 degrees could not be made using ellipsometry because the film was too thick and the surface was too rough. Therefore, the sample was imaged using a Hitachi TM 1000 tabletop scanning electron microscope and thickness measurements were extracted from the image shown in appendix B. The raw data for  $\Psi$  and  $\Delta$  along with the fitted model can be found in appendix B. A graph of growth per cycle of aluminum oxide versus deposition temperature is plotted in Fig 3.3 (one cycle consists of one water pulse and one TMA pulse).

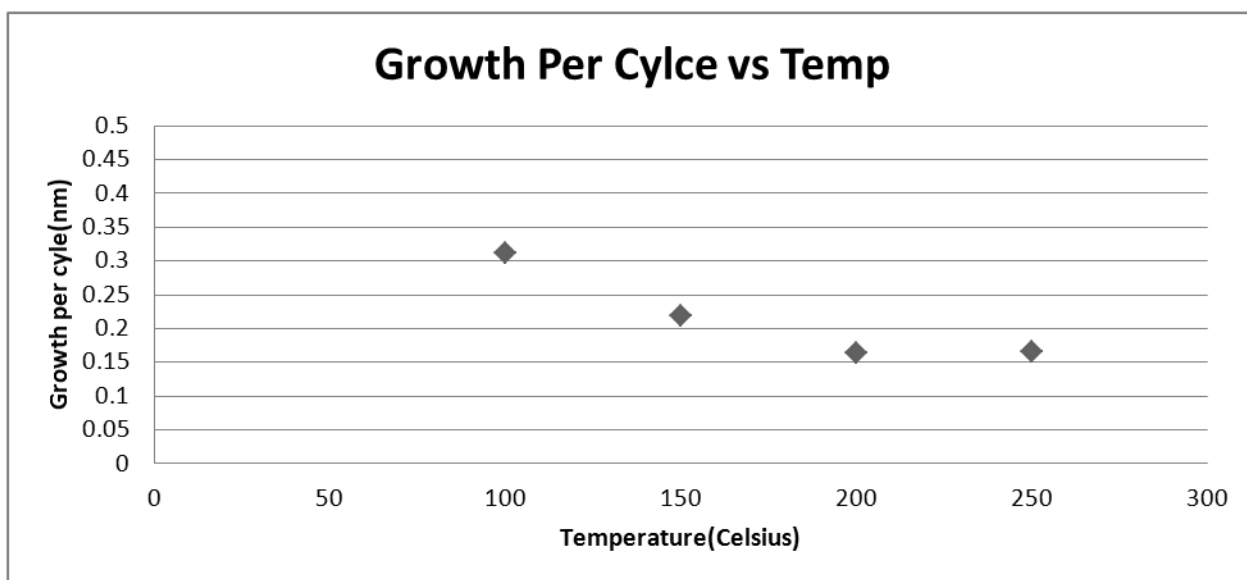


Figure 3.3 A graph showing growth per cycle versus deposition temperature. Note the growth at 50 degrees Celsius is out of range.

The trend seen in Fig. 3.3 can be understood by invoking the kinetics of the reactions.. The growth per cycle of the 50° C sample is ~ 350 times larger than those of the other samples. The scanning electron micrograph of the 50° C sample shown in Fig. 3.1a is non-uniform, and the deposition mode is clearly not ALD in contrast to the 250 ° C sample shown in figure 3.1b. The surface morphology of the 50° C sample is rough and easily rubs off the silicon substrate, which suggests that at such a low temperature the TMA did not chemically adsorb onto the

silicon and just physically condensed on the surface [5]. TMA physically adsorbed on the growth front, reacting with water readily to form aluminum oxide loosely attached to the substrate, but the deposition was not self-limiting and thus formed very thick aluminum oxide with very rough morphology. At deposition temperatures of 100° C and above chemisorption is achieved on the silicon substrate and deposited aluminum oxide surfaces. The continuous reduction in the growth per cycle at temperatures above 100° C up to 200° C can be attributed to the corresponding decrease in concentration of the OH groups on the surface due to an increase in the temperature [6]. The 200° C and 250° C film thickness stays constant to within 2% indicating that the film growth is truly self-limited and is independent of the deposition temperature. The temperature was limited to less than 300° C for this study because the breakdown temperature of TMA is 300° C. At this temperature the breakdown of TMA would cause the growth to be dependent on the amount of precursor pulsed into the chamber and would not be self-limiting as in other chemical vapor deposition processes.

### **Growth on Anodized Aluminum Substrates**

Since anodized aluminum is aluminum oxide. The detection of deposition on the substrate could not be confirmed by a chemical analysis of the surface. Instead SEM was used to image the sample before and after deposition Fig 3.4a-c.



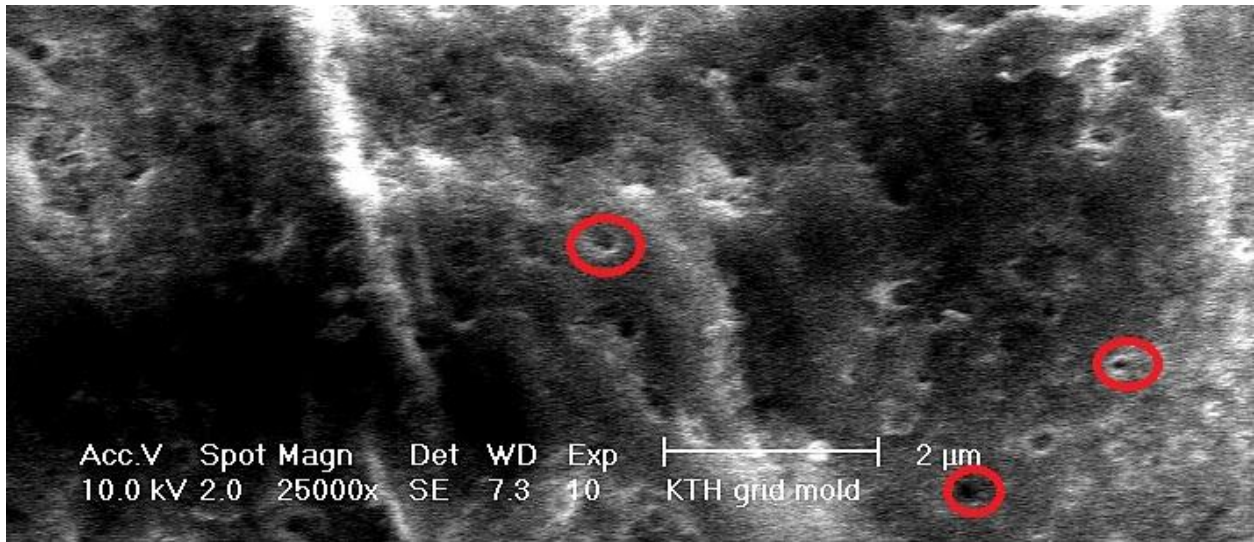


Figure 3.4a. Anodized aluminum substrate before deposition.

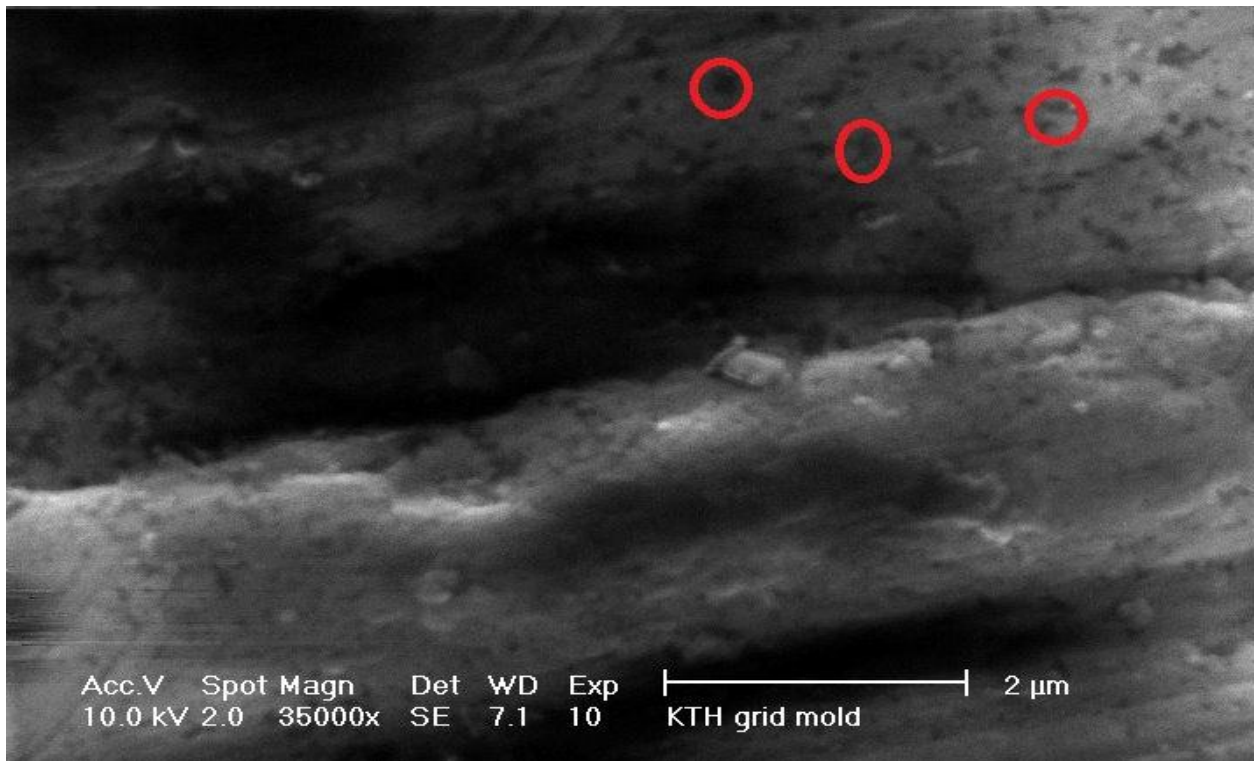


Figure 3.4b. Anodized aluminum after 400 cycles.

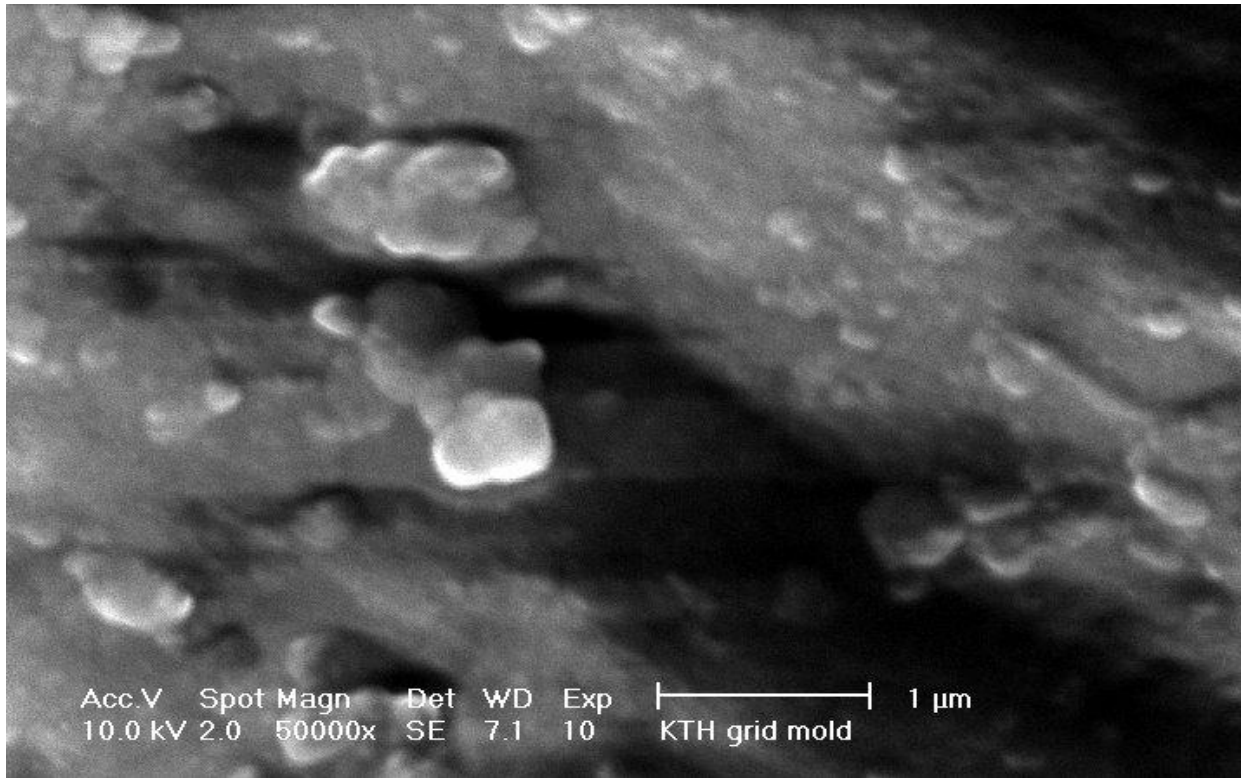


Figure 3.4c. Anodized Aluminum after 800 cycles.

In Fig. 3.4a the pores that naturally occur in the anodizing of aluminum can be seen with a diameter of a couple hundred nanometers and a few of them are circled. ALD deposition of an aluminum oxide thin film conformably covers the entire anodize aluminum surface, thus the diameter of the pores is expected to be reduced after the deposition. After 400 ALD cycles, the pores are considerably reduced in size although their presence is still noticeable and a few are again circled in Fig. 3.4b. After 800 ALD cycles (Fig. 3.4c), the surface is smooth and the pores are non-existent, confirming deposition of aluminum oxide on an anodized aluminum substrate.

#### 4. Conclusion

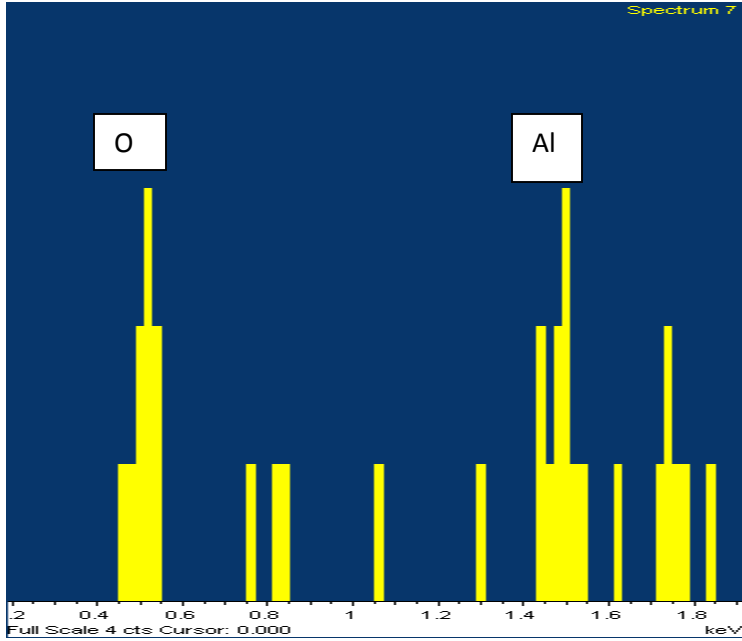
Deposition of aluminum oxide by ALD was demonstrated on both silicon substrates and anodized aluminum substrates. The deposition on silicon substrates was studied by varying the deposition temperature. The ALD mode was identified above 200° C up until the breakdown temperature of TMA. It has been suggested that for other metal oxides the growth per cycle will drastically fall at a temperature below the decomposition temperature due to desorption at the surface [5], but we did not see this in the deposition of aluminum oxide.. Furthermore, it has been shown that ALD can be used to create structures on the nanometer scale. In this thesis it was demonstrated by using ALD to create plugs for nano-sized pores in anodized aluminum. The crystal structure of the resulting films grown by ALD has not been examined in the paper although it would be of interest to study. Further study should be conducted in the deposition of other transition metals by ALD for the creation of novel device structures such as nanotubes, nanowires, heterojunctions, and unique combinations of them. ALD has given us the ability not only to create these structures but to also control the size of these structures to atomic precision. ALD of metal oxide gives us the opportunity to exploit the unique properties of materials at the nano-scale.

## References

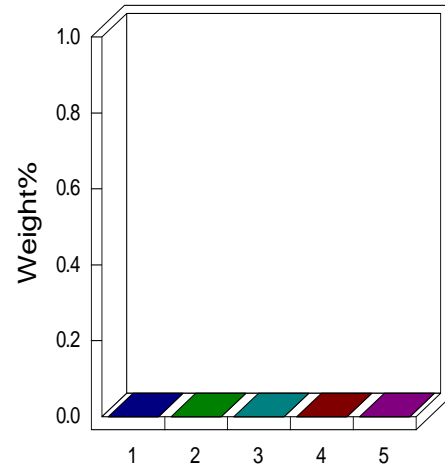
1. Dmitri B. Strukov, Gregory S. Snider, Duncan R. Stewart & R. Stanley Williams. "The missing memristor found." *Nature* 453 (2008), p. 80-83.
2. Tuomo Suntola & Jaakko Hyvarinen. "Atomic Layer Epitaxy." *Ann. Rev. Material Science* 15 (1985), p. 177-95.
3. Markku Leskela & Mikko Rital. "Atomic layer deposition (ALD): from precursors to thin film structures." *Thin Solid Films* Volume 409 Issue 1 (2002), p. 138-46.
4. Yuniarto Widjaja & Charles B. Musgrave. "Quantum chemical study of the mechanism of aluminum oxide atomic layer deposition." *Applied Physics Letters* Volume 80 Number 18 (2002), p.3304-6
5. Jill S. Becker. "Atomic layer deposition of metal oxide and nitride thin films." PhD Thesis, Harvard University, Cambridge MA 2002. Print.

# Appendix A

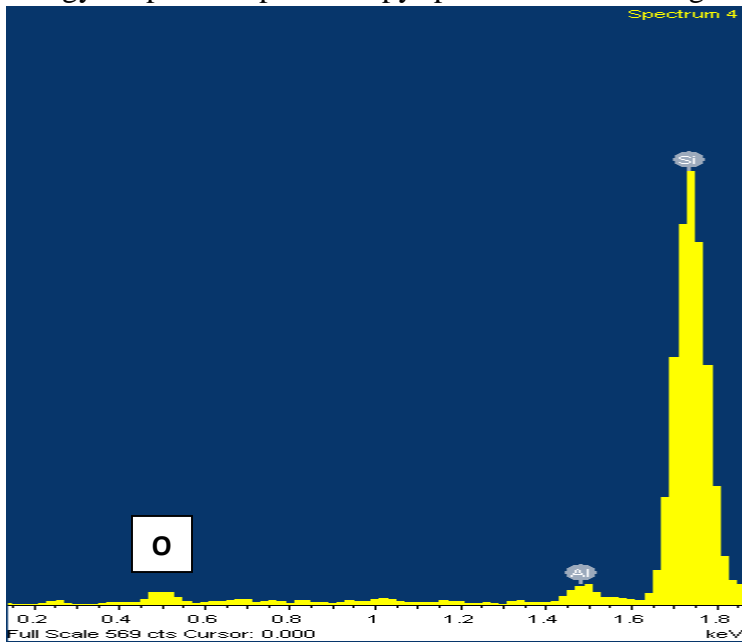
Energy dispersive spectroscopy spectrum for 50° C growth



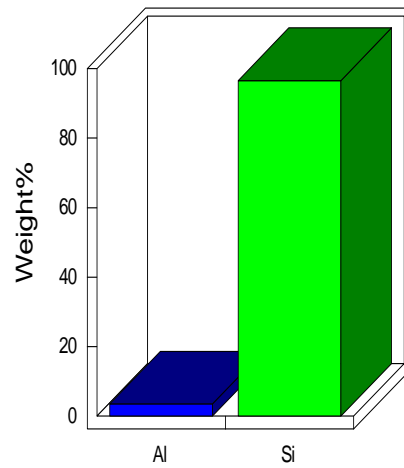
No Quantitative results



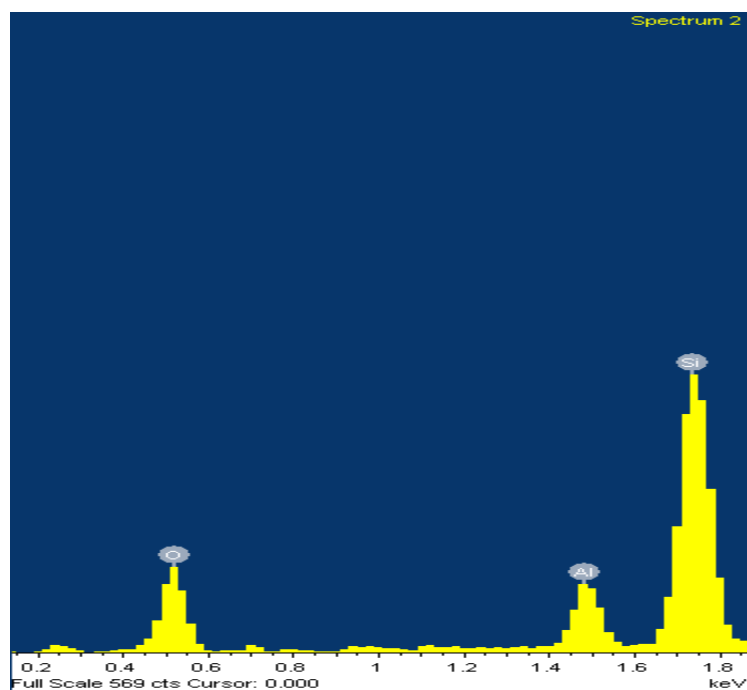
Energy Dispersive spectroscopy spectrum for 100° C growth



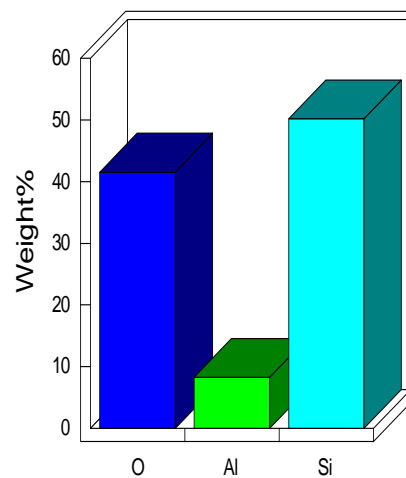
Quantitative results



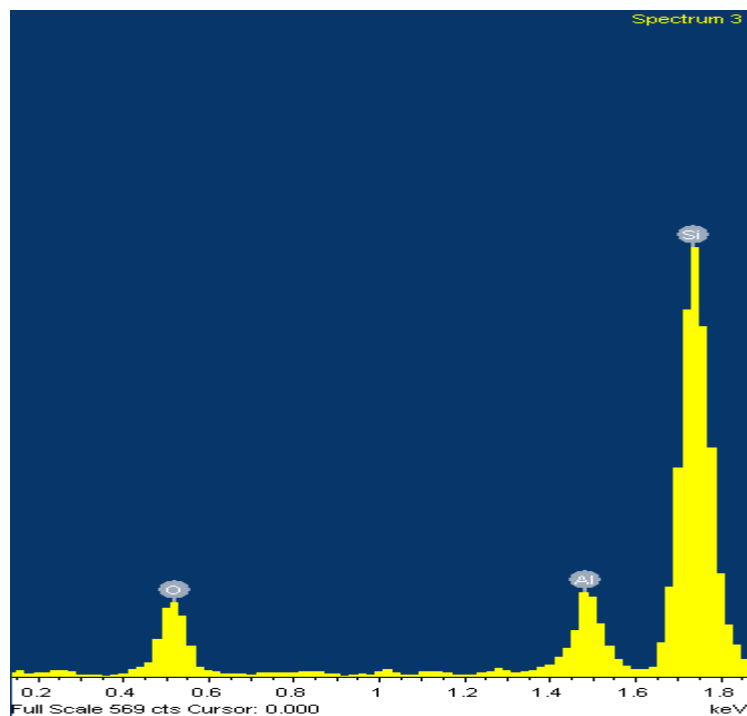
Energy dispersive spectroscopy spectrum for 150° C growth



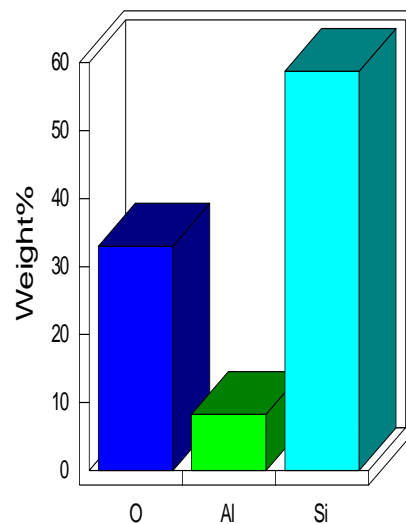
Quantitative results



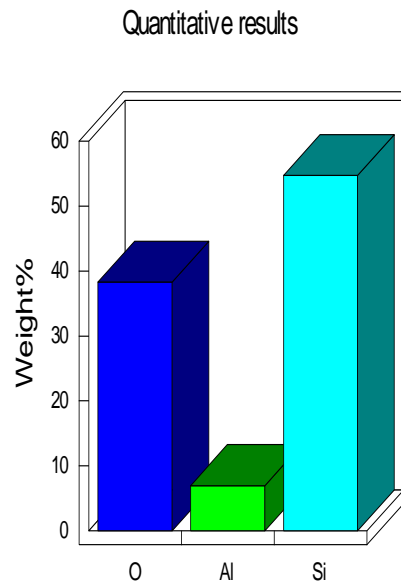
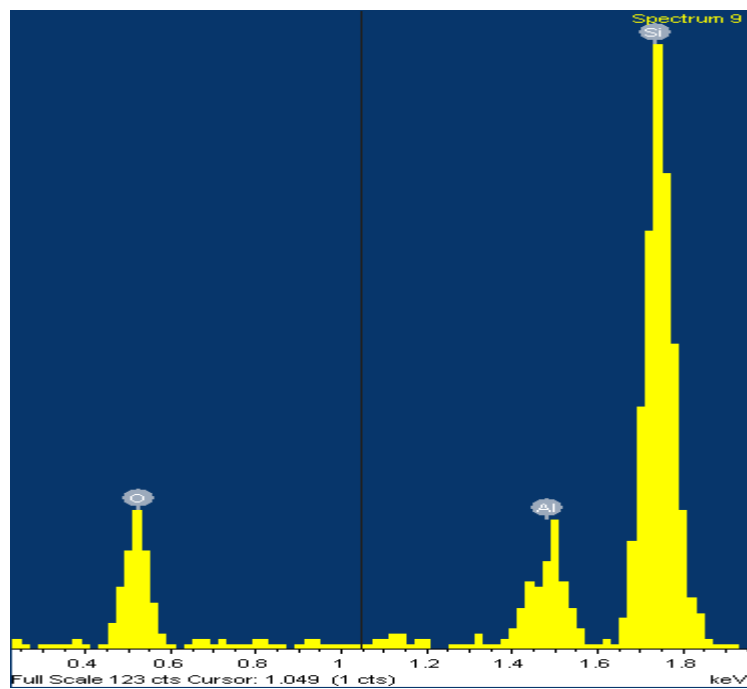
Energy dispersive spectroscopy spectrum for 200° C growth



Quantitative results

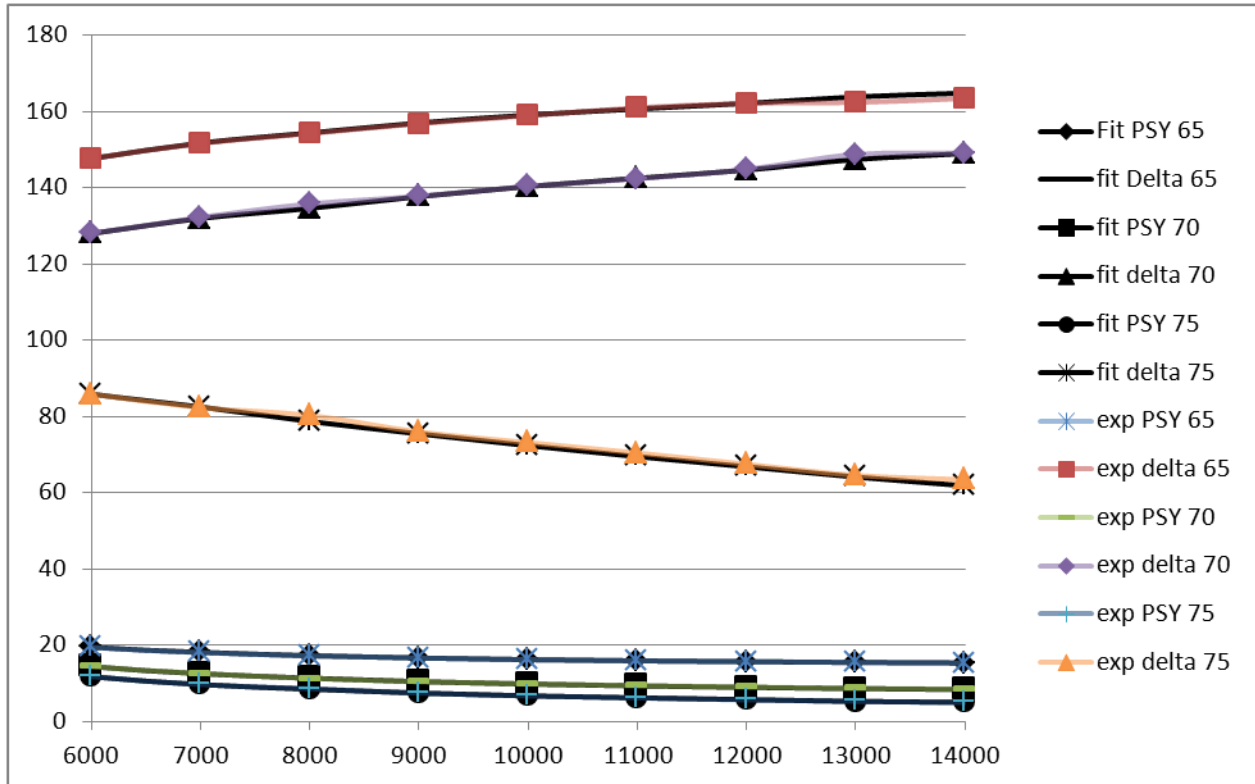


# Energy dispersive spectroscopy spectrum for 250° C growth



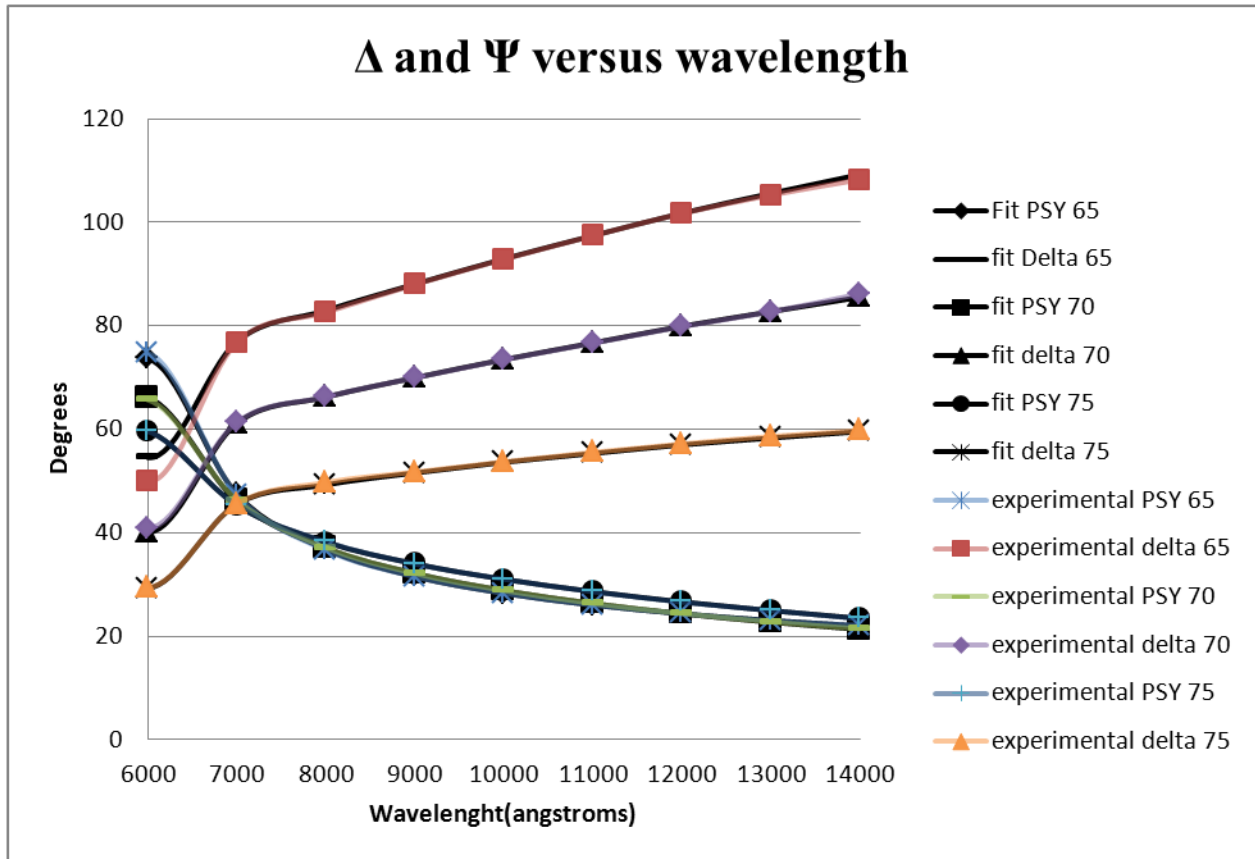
## Appendix B

$\Delta$  and  $\Psi$  for 100° C growth determined thickness 19.6nm

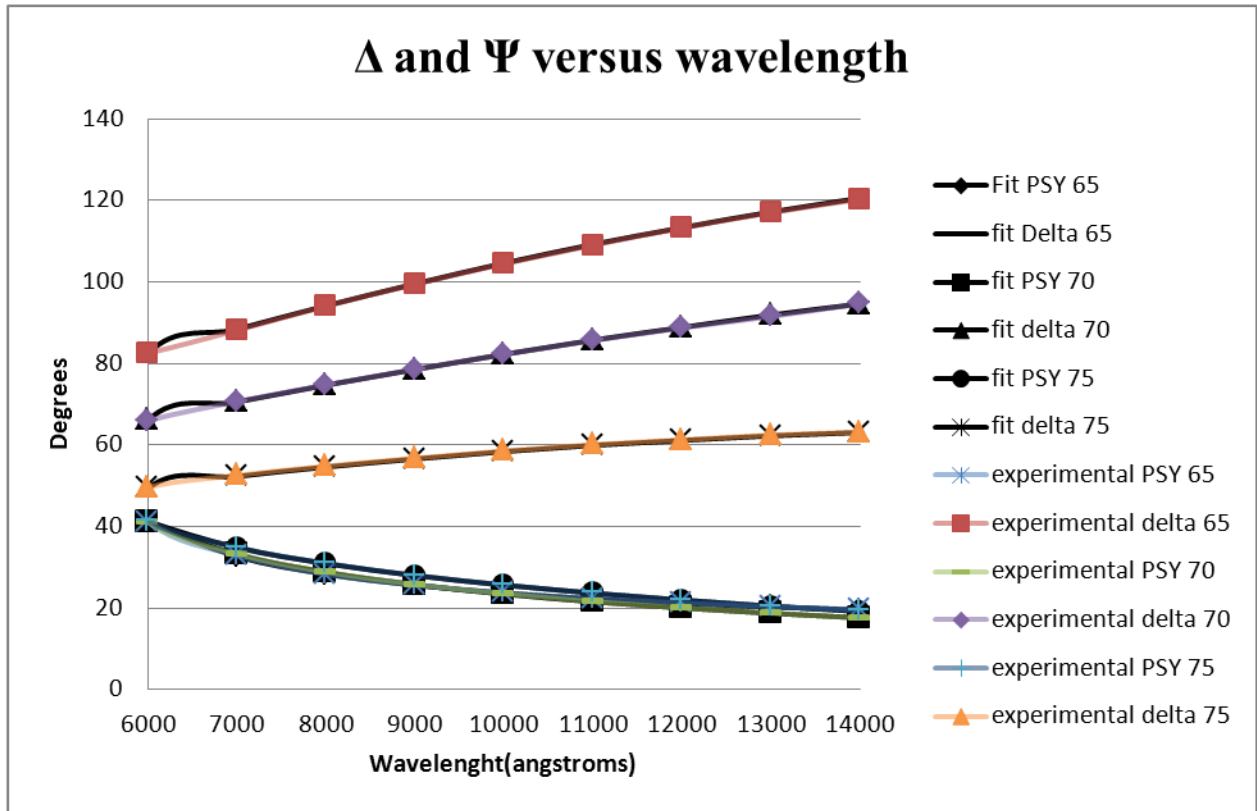




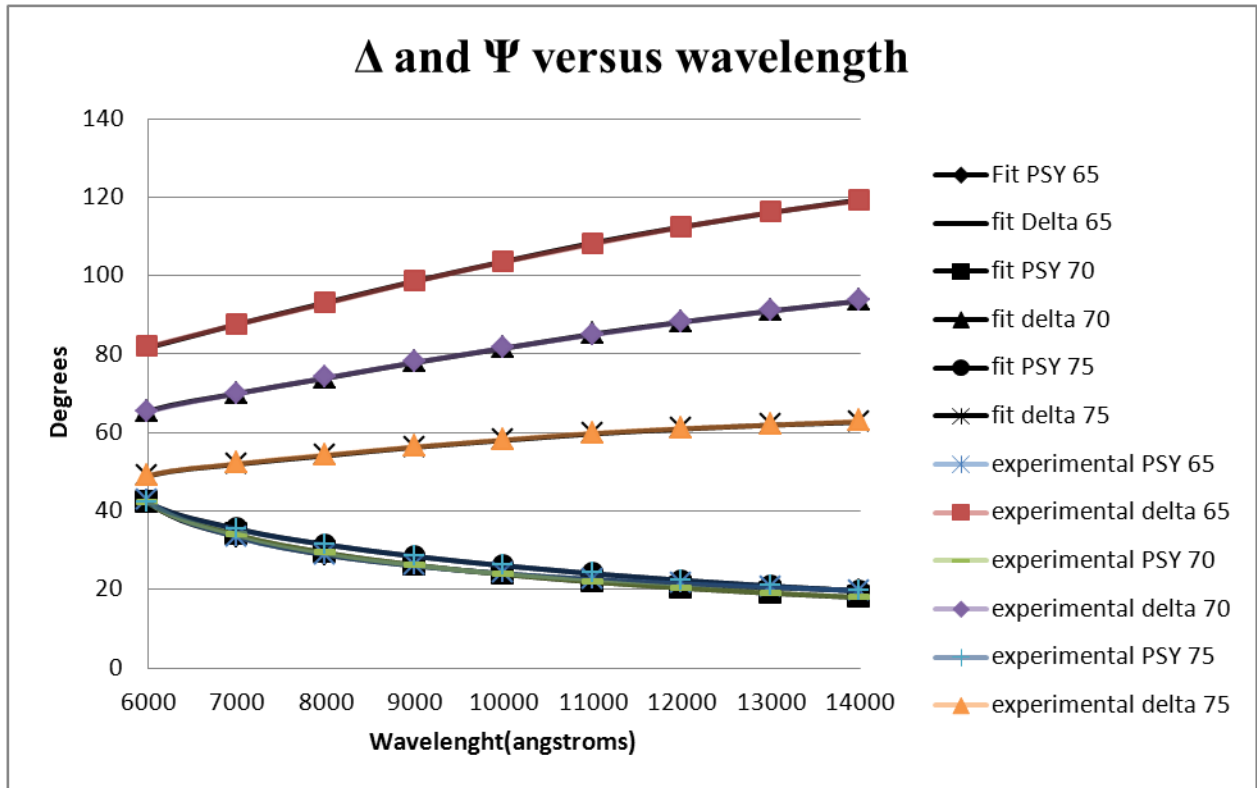
$\Delta$  and  $\Psi$  for 150° C growth determined thickness 109.3nm



$\Delta$  and  $\Psi$  for 200° C growth determined thickness 81.4nm



$\Delta$  and  $\Psi$  for 250° C growth determined thickness 82.7nm



SEM image of 50° C growth to estimate thickness around 30 μm. This is side view image the smooth light surface is the silicon substrate and the dark rough surface is the deposition.

