

DETERMINING THE CAUSE OF YTTRIA FILM GROWTH DUE TO
EXPOSURE TO VACUUM-ULTRAVIOLET LIGHT

by

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DEPARTMENT APPROVAL

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ABSTRACT

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Brigham Young University's Thin Films Research Group has recently discovered that exposure of reactively sputtered yttria (Y_2O_3) films to 7.2 eV vacuum-ultraviolet (VUV) light results in a dramatic increase in the films' thicknesses. In some cases films swelled to nearly seven times their original thickness. Due to the high chemical stability of Y_2O_3 , this result was entirely unexpected. Determining the cause of this growth is an important issue since yttria is being considered as a material component in semiconductor devices and the light source used in this research is similar to cleaning lamps used in industry. We have experimentally determined that the film growth is not due to new deposition and is therefore a result of a change rendered to the sample itself. The growth cannot be attributed to oxidization of the yttria or the silicon substrate. Evidence suggests that VUV radiation is altering the structure of our Y_2O_3 samples, which is the main mechanism driving film growth.

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Chapter 1

Introduction

1.1 Report Overview

The purpose of this report is to identify the factors contributing to the growth of Y_2O_3 films when exposed to 7.2 eV VUV radiation. The following two sections (1.2-1.3) explain the relevance of this research to the semiconductor industry. Chapter 2 covers the collection and interpretation of data gathered from our research. Sections 2.1-2.2 explain the details of our deposition process and the events that led to the discovery of film growth. Initial theories about the causes of film growth are introduced and discussed in section 2.3. Current theories are covered in section 2.4. Chapter 3 explains our plans for future research. Chapter 4 consists of the conclusions that we have drawn from our data. Appendix A contains supplementary information on ellipsometry (a process used in our data collection).

1.2 Current Interest in Yttria in the Semiconductor Industry

Yttria (Y_2O_3) has recently been considered as a possible replacement for silicon dioxide (SiO_2) as the primary gate dielectric material in metal-oxide-semiconductor devices [1]. The low dielectric constant of SiO_2 imposes a restriction on the minimum thickness of silicon components, which limits the scaling down of electrical circuits. Y_2O_3 has a much higher dielectric constant, which would therefore allow for additional miniaturization [2]. Its lattice constant (1.06 nm) is also roughly twice that of silicon (0.543 nm), which results in a low lattice mismatch between the two materials [3]. A low lattice mismatch means that there can be a transition between two semiconducting layers without a change in the crystal structure. Thus it is possible to grow a layer of Y_2O_3 on top of SiO_2 without worrying about altering the molecular structure of the material. These characteristics make Y_2O_3 a prime candidate for integration into semiconductor components.

1.3 Applications of Our Findings to Semiconductor Research

The vacuum-ultraviolet light used in our research was generated by a 7.2 eV excimer lamp. This lamp is specifically designed to clean hydrocarbons off of sample surfaces. As its name suggests this lamp generates very short wavelength (high energy) photons. These photons are so energetic that they can only propagate about 1cm in the air before being absorbed. They also have enough energy to atomize the oxygen in the air. These oxygen atoms then bombard the surface of the sample. This either breaks up the “heavy” hydrocarbons into ones of a lower molecular weight or oxidizes

them completely into CO_2 and H_2O . All of these smaller molecules have higher vapor pressures, which means they can be removed from the sample much more easily [4].

This same type of lamp is used in the semiconductor industry for cleaning the surfaces of materials deposited onto silicon wafers. Expansion of yttria during cleaning would be unacceptable as it would alter the properties of individual components, resulting in device failure. Thus it is important to understand how, and why, yttria reacts to the cleaning process.

Chapter 2

Experimental Methods

2.1 Specific Details of Our Deposition Process

The yttria film samples used in our research were deposited onto silicon (Si) wafers by a reactive sputtering process. In this procedure, a blank silicon wafer is placed into a vacuum chamber. The chamber is then pumped down to a pressure on the order of 10^{-6} Torr. This ensures that the chamber is mostly free of unwanted molecules, which in turn increases the purity of the yttria layer deposited onto the wafer.

A low pressure also creates a long mean free path for yttria molecules during deposition. Mean free path is the average distance a molecule travels before experiencing a collision with another molecule or atom [5]. Therefore the longer the mean free path, the more likely a yttria molecule is to make it onto the surface of the silicon wafer during deposition. A picture of our deposition system is shown in Figure 2.1.

Sputtering is a specific method of thin film deposition that utilizes the creation of a plasma. The plasma, which consists of charged, localized argon atoms, is sustained by a very strong rare earth magnet. This magnetic field redirects the ionized atoms so that they crash into the surface of a target material. These high energy collisions eject

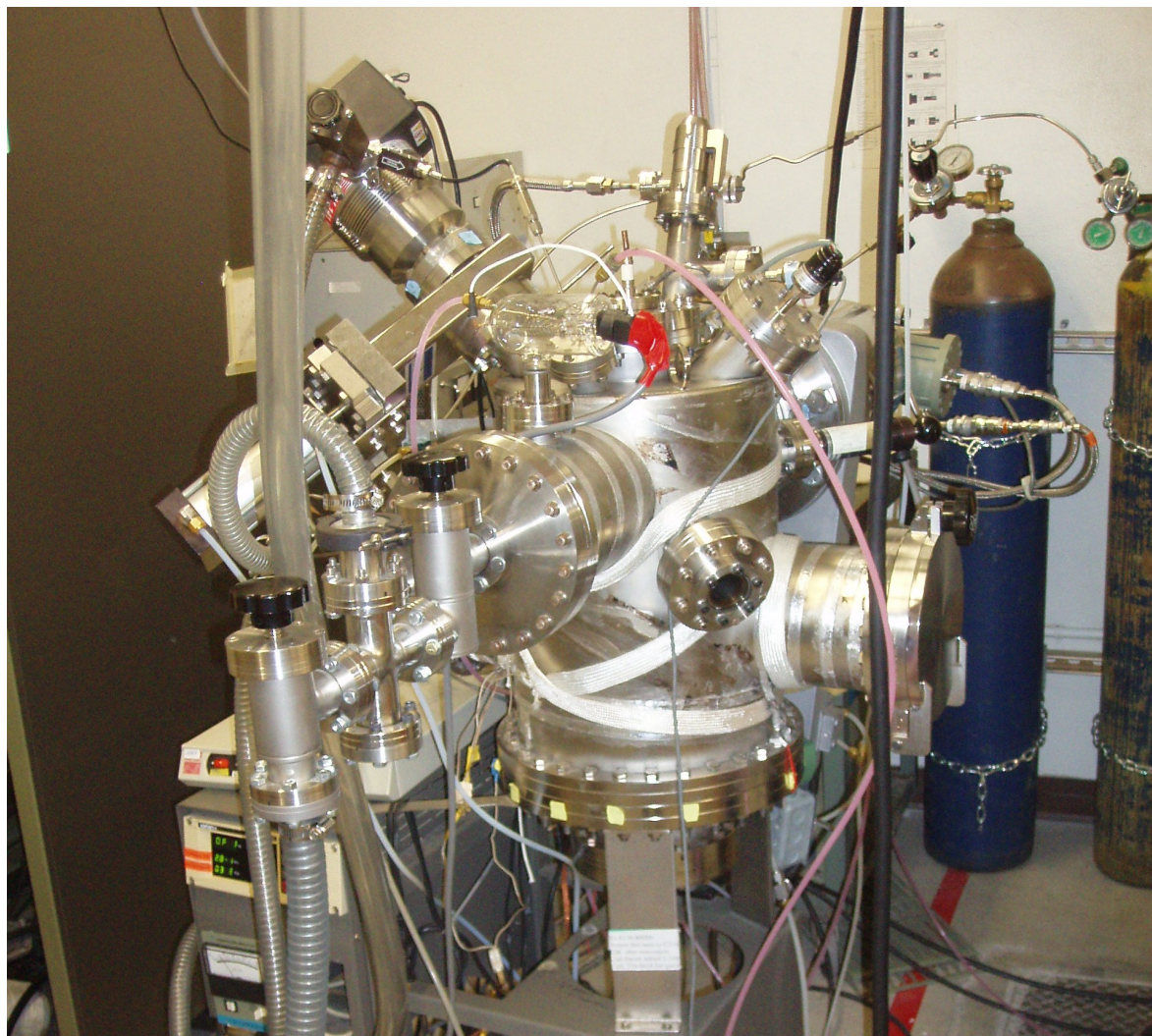


Figure 2.1 The vacuum system used to sputter Y_2O_3

particles from the target material which then float around in the vacuum chamber until they settle onto the surface of the silicon wafer [6].

Reactive sputtering refers specifically to the deposition of metal oxides from metal targets. In order to facilitate oxidation during the process a small amount of oxygen is flowed into the system. This allows the metal atoms to oxidize as they are collected on the surface of the silicon wafer.

2.2 First Observed Film Growth

The first observed film growth occurred with a Y_2O_3 sample created in November 2009. This film was placed under a VUV lamp in order to clean hydrocarbons off of the surface (a process detailed in section 1.3). After five minutes under the lamp the sample had noticeably changed in appearance. The surface appeared mottled and had acquired a brownish hue as can be seen in Figure 2.2. Analysis by spectroscopic ellipsometry suggested that this change in appearance was due to a corresponding increase in the thickness of the sample.

Spectroscopic ellipsometry is a useful way of characterizing the thickness and optical properties of a sample by observing how it affects light incident upon it [7]. Light of a known polarization and intensity is reflected off of the sample and then measured. Based on how the light is changed it is possible to determine the characteristics of the sample. For a more rigorous explanation of ellipsometry refer to Appendix A.

Before VUV exposure the film (including the supposed hydrocarbons) was measured at 24.7 ± 0.1 nm. After the five minute VUV treatment its thickness was measured at 31.1 ± 0.07 nm. This is a change of over 6 nm, which amounts to a 25.59% increase from the original thickness of the material. Since the film thickness was expected to decrease as a result of the hydrocarbons being removed from the surface,



Figure 2.2 A yttria sample after exposure to VUV radiation

the immediate question became: What caused the film to grow?

2.3 Theories of Film Growth

2.3.1 Theory I: Oxidization of Yttrium

Our initial thought was that our yttrium sample was not completely oxidized. As previously explained, this particular sample had been prepared through a reactive sputtering process. This means that instead of using a yttrium oxide target, we used a yttrium target. Oxygen was then flowed into the system during the deposition process, which allowed the yttrium to oxidize as it deposited onto the substrate. As stated before, the VUV lamp atomizes oxygen in the air, meaning there is abundance of oxygen atoms surrounding the sample. If the yttrium film was not fully oxidized,

it would react with this extra oxygen to form yttrium oxide.

To test this theory we first needed to establish some reasonable upper bound on the expected film growth. The situation allowing for the largest possible growth would be if the sample went from completely unoxidized (yttrium) to completely oxidized (yttria), while expanding only upwards. Knowing the thickness of the sample and the density of yttrium it is possible to calculate the number of yttrium atoms in the sample:

$$N_Y = \frac{M_{Total}}{m_Y} = \frac{\rho_Y A t}{m_Y}, \quad (2.1)$$

where N_Y is the number of yttrium atoms, M_{Total} is the total mass of the film, m_Y is the mass of a single yttrium atom, ρ_Y is the density of yttrium, A is the cross-sectional area of the wafer, and t is the film thickness.

We can then calculate the number of oxygen atoms that could be captured by the sample in the formation of yttrium oxide. Since the ratio of oxygen to yttrium in Y_2O_3 is 3:2, there will be $1.5 N_Y$ atoms of oxygen added to the sample. Now using the density of yttria we can work backwards to find the new thickness of the material:

$$t' = \frac{M'_{Total}}{\rho_{Y_2O_3} A} = \frac{N_Y m_y + N_O m_O}{\rho_{Y_2O_3} A} = \frac{N_Y m_y + 1.5 N_Y m_O}{\rho_{Y_2O_3} A} = N_Y \frac{(m_Y + 1.5 m_O)}{\rho_{Y_2O_3} A}, \quad (2.2)$$

where t' is the new film thickness, M'_{Total} is the new total mass, $\rho_{Y_2O_3}$ is the density of yttria, N_O is the number of oxygen atoms, and m_O is the mass of an atom of oxygen.

By inserting equation 2.1 into equation 2.2 this reduces to:

$$t' = \frac{\rho_Y A t}{m_Y} \frac{(m_Y + 1.5 m_O)}{\rho_{Y_2O_3} A} = (1 + 1.5 \frac{m_O}{m_Y}) \frac{\rho_Y}{\rho_{Y_2O_3}} t. \quad (2.3)$$

Using this equation we calculated the upper bound of expected film growth to be 3.3 nm. The actual film growth, however, was 6.3 nm.

This theory immediately presented serious limitations since the experimental result well exceeded (by a factor of two) the maximum value of the theoretical. And

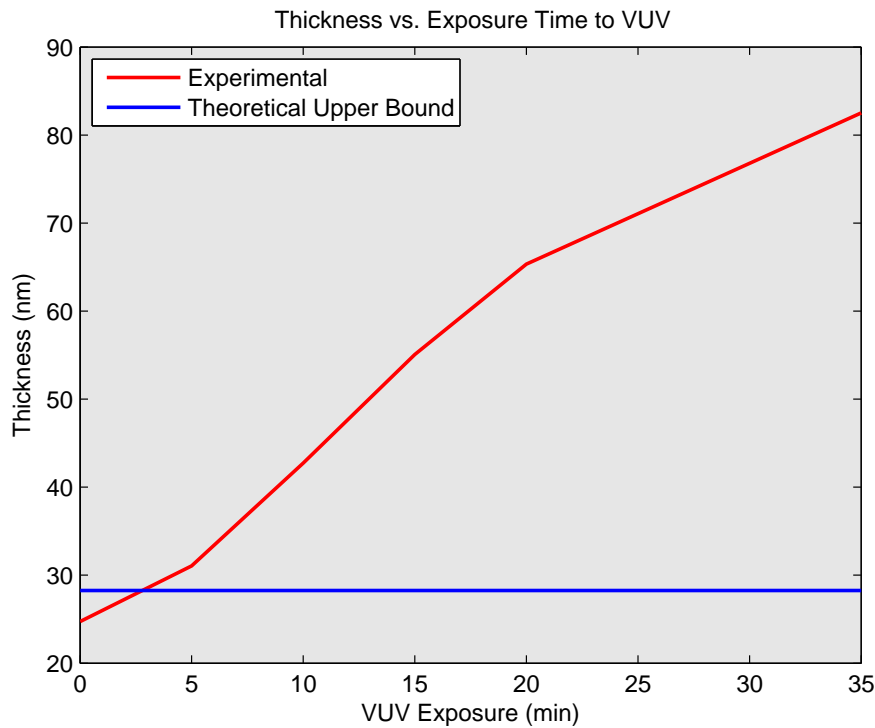


Figure 2.3 Film growth vs. VUV exposure time

this was after only five minutes of exposure. As you can see from Figure 2.3, as VUV exposure time increased the theory became less and less suitable. The film thickness increased to as high as 82.5 ± 0.3 nm.

Thus after 35 minutes of exposure, the observed growth jumped from twice the expected value to nearly eighteen times the upper theoretical limit. Therefore, while the theory of yttrium oxidation could possibly be accounting for a small percentage of the growth, it is inadequate in explaining all of the change.

2.3.2 Theory II: New Deposition

Our second theory was that the VUV lamp could be depositing new material onto the sample. It would not be probable that it was depositing more yttrium since yttrium is a rare earth element that is not readily abundant in large concentrations. However,

it is possible that the VUV photons were knocking molecules off the support base and these molecules were finding their way onto the sample. As previously stated, the VUV photons can only propagate about 1cm before being absorbed. With this in mind we placed the sample as close as possible to the lamp using a support base of glass microscope slides. This may have put the slides close enough to the lamp to interact with the VUV photons. If the photons were knocking molecules off of these slides it could have provided a source of new material to be deposited onto the film.

A simple way to test this idea was to subject a blank silicon substrate to the same treatment and look for film deposition. Since this theory contributes the growth to the lamp and glass slides and not the sample itself, growth should occur regardless of the sample being used.

Before any VUV treatment, we measured the thickness of material on top of the silicon substrate, which would be composed of silicon dioxide and hydrocarbons, to be 2.1 ± 0.008 nm. The thickness of this layer of material as a function of VUV exposure time is shown in Figure 2.4. After twenty total minutes the thickness settled down to 1.9 ± 0.01 nm, which is less thick than it was in the beginning. This type of behavior is exactly what you would expect if the VUV lamp was simply cleaning the hydrocarbons off of the surface.

Notice that after five minutes the thickness increased to 2.2 ± 0.009 nm (an increase of 0.3 nm). This data could suggest that material was being added to the wafer. However, since this increase was very slight and measurements at later exposure times showed a decrease in thickness, it is more likely that the supposed increase can be attributed to non-uniformity of the silicon surface. Due to the lack of a lasting increase in the thickness of the silicon witness, it does not seem that the VUV lamp is enabling new deposition onto yttrium oxide samples.

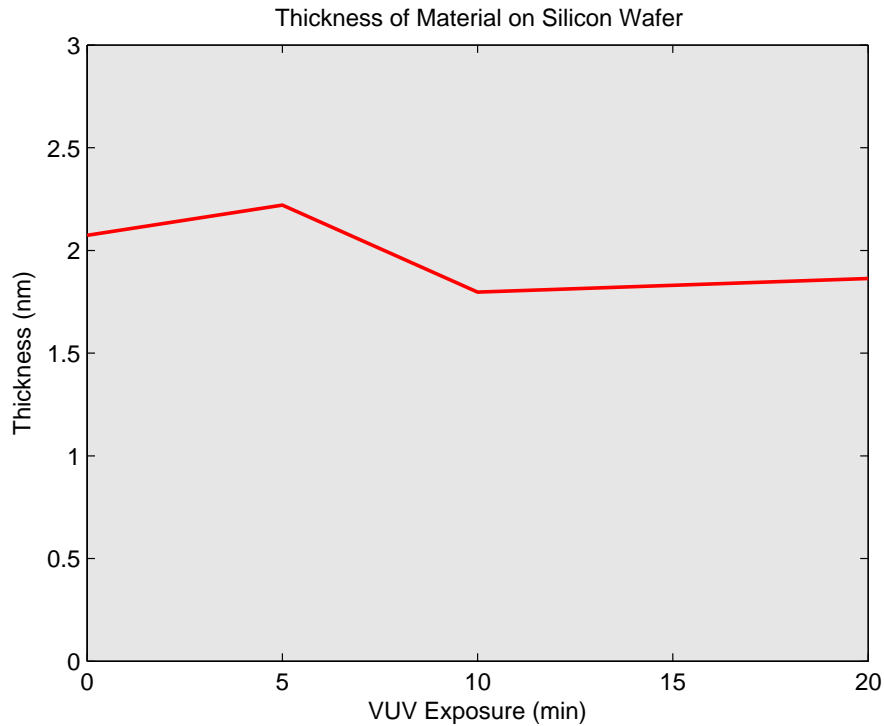


Figure 2.4 Thickness of film on blank silicon wafer vs. VUV exposure time

2.3.3 Theory III: Oxidization of Silicon Substrate

If nothing is being added to it the sample the only other possibility is that what is already there is somehow being altered. Our next thought was that the yttrium oxide could be catalyzing the oxidation of the silicon wafer underneath. As explained in section 1.3, the VUV lamp generates atomized oxygen. In addition to colliding with the sample surface, the atomic oxygen (O) interacts with the molecular oxygen (O_2) still in the air to form ozone (O_3).

Silicon readily oxidizes (since SiO_2 is a more stable configuration) and it has previously been found that SiO_2 can be grown by exposure of Si to ozone [8]. Using the same method as in section 2.3.1 we found that the maximum change in thickness

due to silicon oxidization would be:

$$t' = \left(1 + 2\frac{m_O}{m_{Si}}\right)\frac{\rho_{Si}}{\rho_{SiO_2}}t, \quad (2.4)$$

where m_{Si} is the mass of a silicon atom, ρ_{Si} is the density of silicon, ρ_{SiO_2} is the density of silicon dioxide, and t is now the original thickness of the silicon wafer, which is around 1 mm. Using this equation we found the upper bound of the growth to be 1.9×10^6 nm. As you can see, the experimental result falls well within the bounds of film growth provided by this theory.

To test this theory we decided to take a closer look at how the optical constants of our yttria sample were changing as a function of VUV exposure time. We chose to look specifically at the index of refraction at a photon energy of 2.4 eV (516 nm wavelength). This is green light, which is close to the middle of the visible range. At this energy yttrium oxide has an index of refraction of 1.94. Silicon dioxide on the other hand has a much lower index at 1.47. Because of this difference the formation of silicon dioxide would lower the effective total index of the overall material.

To determine the optical constants of our film we fit our ellipsometry data using a Cauchy model, which is a dispersion model of the form:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}, \quad (2.5)$$

where A is the index in the infrared range (which is approximately constants), B and C are fitting parameters, and λ is the wavelength of the light incident upon the sample. In Figure 2.5, you can see that even before VUV exposure the index was at 1.60, which is not close to yttrium oxide (1.93).

To account for this, we reasoned that our deposition process was not perfect. Instead of uniform layers, some void formation occurs. Within these voids are pockets of air or water. Since air and water have indices lower than yttria (approximately 1.00 and 1.33 respectively), their presence in a yttria film would lower the effective index

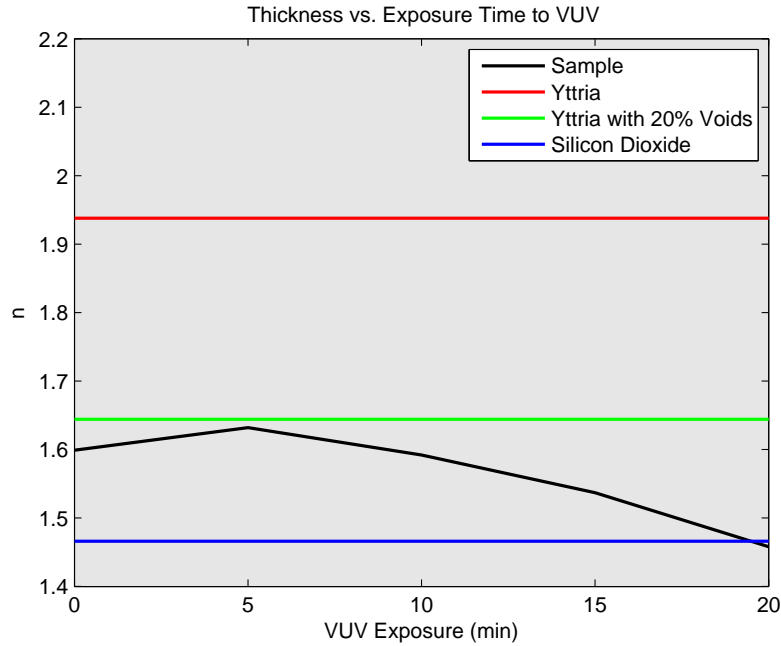


Figure 2.5 Index change of yttria sample

Index of refraction of the yttria sample vs. VUV exposure time

of the sample considered as a whole. To model this structure we used an effective medium approximation (EMA) model with 80% yttrium oxide and 20% voids (see section A.3 for an explanation of EMA). This put the index at 1.64, which was much closer to the starting index of the sample.

After five minutes under the lamp, the index increased slightly, but as time continued the index got lower and lower, approaching the index of silicon dioxide. Thus it seemed that the theory of silicon oxidation was viable.

To further test this theory we placed the sample into a furnace. If the silicon had oxidized then putting it in a furnace would not cause the thickness to go back down. As previously stated silicon dioxide is a very stable configuration. Therefore putting it in the furnace would not cause the silicon to revert back to an unoxidized state.

We placed a piece of the sample that had been exposed to the VUV light and had reached a thickness of 98.3 ± 0.2 nm into the furnace for 2 hours at 500 °C. It

was then removed and immediately measured. It was found that the thickness had dropped significantly, down to 16.9 ± 0.02 nm. This is a decrease of 82.76%. Due to this dramatic change in thickness, the theory of silicon oxidation could not possibly be a proper explanation for the behavior of our yttria sample.

2.4 Current Theories

2.4.1 The Popcorn Effect

Our data seems to suggest that the structure of the yttrium oxide itself is somehow being altered. One possible factor for this change involves the voids within the sample. If water is settling in these voids the VUV photons would be of sufficient energy to boil it. This would create an effect similar to popping popcorn, where internal pressure from water vapor forces outward expansion.

2.4.2 Formation of Yttrium Ozonide

Another possibility is the formation of a previously unknown yttrium ozonide chemical state. As stated in section 2.3.3, use of the VUV lamp in air leads to the formation of ozone. There have been published reports of ozonide formation with group I and group II elements of the periodic table [9, 10]. Yttrium is a group III element. Thus it could be that there is some sort of yttrium ozonide forming. The formation of the ozonide would likely expand the internal structure of the sample. If the ozonide later decomposed back into yttrium oxide (which it would do if yttrium ozonide is not a stable configuration) the structure would be left stretched out. This would account for both the increase in film thickness due to VUV exposure and its subsequent decrease when placed in a furnace.

We have attempted to test this theory by performing the VUV exposure in a nitrogen rich atmosphere. The thought here is that if there is no oxygen there can be no creation of ozone. Thus if the film were to still grow it would not be due to ozonide formation. This test was conducted by placing the lamp into a glove box and then purging the box several times with nitrogen. After 20 minutes of exposure in the nitrogen environment, a reactively sputtered yttria sample increased from 23.4 ± 0.08 nm to 182.4 ± 0.2 nm. This result would seem to suggest that ozone is not a contributing factor in yttria film growth.

We quickly realized though that while the nitrogen purge certainly reduces the oxygen content in the glove box, it does not eliminate it completely. Thus we cannot conclusively state that the film growth is not due to the formation of yttrium ozonide.

Chapter 3

Results and Discussion

Although our research has narrowed the range of possible explanations, there is still no conclusive theory on the mechanisms driving yttria film growth due to VUV light exposure. The results, however, have been qualitatively duplicated by several additional reactively sputtered yttria samples (the growth of each of these samples is summarized in Figure 3.1). Therefore we know that the growth is not due to some irreproducible anomaly of the original film.

3.1 Future Research

3.1.1 Monitoring Oxygen Content in the Glove Box

In order to obtain conclusive results on the theory of yttrium ozonide formation we need to be able to more closely monitor the oxygen content in our glove box. One possible way to do this is to place a zinc-air battery in the glove box. This type of battery, like most batteries, is electro-chemical which means that it generates electrical voltage through the conversion of energy from chemical reactions. A zinc-air battery relies on the oxidization of zinc using oxygen in the air. Thus if the amount

Sample Number	VUV Time (min)	Pre-VUV Thickness (nm)	Post-VUV Thickness (nm)	% Growth	Notes
100520	15	8.20	53.75	555.8	
100608	10	17.82	77.44	334.7	
100610b	5	25.88	48.81	88.7	1/8" from lamp
100610d	5	22.88	66.91	192.5	1/4" from lamp
100610e	5	21.76	92.55	325.2	1/2" from lamp
100713a	10	21.66	26.67	23.1	Nitrogen purge
100713c	20	23.01	182.03	691.2	Argon purge

Figure 3.1 Summary of yttria film growth from multiple samples

of oxygen is decreased there will be less zinc oxidization. This decrease in chemical reactions will in turn decrease the voltage output by the battery. Since voltage is an easily measureable quantity, we can use this relationship to determine the amount of oxygen present in our system.

3.1.2 TEM Imaging and Electron Diffraction

The next step in testing the theories detailed in section 2.4 is to utilize tunneling electron microscope (TEM) imaging. This will be able to reveal more about the structure of our sample and how, or if, it is changing. Not only does the TEM offer extremely highly resolution imaging of our samples, but it can also perform electron diffraction. By shooting a beam of electrons through our Y_2O_3 samples and observing how and where the electrons diffract, or scatter, we can deduce the lattice structure of our material. If yttrium ozonide were forming it would change the lattice structure of our sample. We would then be able to observe this lattice change as a corresponding change in the diffraction pattern.

Unfortunately, regularly used copper TEM grids have so far been unable to hold up to the oxygen atmosphere used in our sputtering process. By the time the deposition is finished the carbon film on the back of the grid has been completely oxidized away. Since the yttria settles onto the carbon film, this effectively destroys any deposition we might have had. There is, however, some new research that might provide a solution to this problem. Dr. Robert Davis of BYU and his research group have recently manufactured TEM grids composed of carbon nanotubes instead of copper. We are currently running tests to see if these new grids are capable of withstanding reactive sputtering.

Chapter 4

Conclusions

The mechanism driving the growth of yttria films due to VUV exposure appears to be an internal rather than an external change. Yttrium oxidization, while possibly contributing to some of the growth, cannot be the primary cause of the change. Experimental tests have also ruled out new deposition and oxidization of the silicon substrate as viable explanations for film growth. Instead our evidence suggests that the structure of our yttria samples is being altered by the VUV radiation. In order to better understand the nature of this change, we propose that yttria samples be studied using high resolution microscopy and electron diffraction.

Bibliography

- [1] Semiconductor Industry Association, *The International Technology Roadmap for Semiconductors*, (Sematech, Austin, 1999).
- [2] J. X. Zhang, G. Ceder, T. Maxisch, W. K. Chim, and W. K. Choi , “Native Point Defects in yttria and relevance to its use as a high-dielectric-constant gate oxide material: First-principles study,” *Physical Review B* **73**, 104101 (2006).
- [3] E. K. Evangelou, C. Wiemer, and M. Fanciulli, “Electrical and structural characteristics of yttrium oxide films desposited by rf-magnetron sputtering on n-Si,” *Journal of Applied Physics* **94**, 1 (2003).
- [4] E. Strein and D. D. Allred, “Eliminating carbon contamination on oxidized Si surfaces using a VUV excimer lamp,” *Thin Solid Films*, **517** (3), 1011-1015 (2008).
- [5] P. A. Tipler and G. Mosca, *Physics for Scientists and Engineers*, 6th ed. (W. H. Freeman and Company, 2008), p. 578.
- [6] R. V. Coleman and K. Lark-Horovitz, *Solid State Physics*, Vol. 11 (Academic Press, Inc., New York, 1974), pp. 643-645.
- [7] J. Peatross and M. Ware, *Physics of Light and Optics*, (Unpublished, 2010), p. 154-155.

- [8] C. K. Fink, K. Nakamura, S. Inchimura, and S. J. Jenkins, "Silicon oxidation by ozone," *Journal of Physics: Condensed Matter* **21**, 183001 (2009).
- [9] S. Ramanathan, D. Chi, P. C. McIntyre, C. J. Wetteland, and J. R. Tesmer, "Ultraviolet-ozone oxidation of metal films," *Journal of the Electrochemical Society* **150**, 5 (2003).
- [10] T. Nakajima, T. Tsuchiya, and T. Kumagai, "Rubidium metavanadate formation at room temperature under vacuum ultraviolet irradiation from metal-organic compositions," *Applied Surface Science* **255**, 9787 (2009).
- [11] *Guide to Using WVASE32™*, (J. A. Woollam Co., Inc.) pp. 24-25.
- [12] *Guide to Using WVASE32™*, (J. A. Woollam Co., Inc.) p. 49.
- [13] *Guide to Using WVASE32™*, (J. A. Woollam Co., Inc.) pp. 47-48.

Appendix A

Ellipsometry

A.1 Spectroscopic Ellipsometry

Ellipsometry is a powerful and sensitive method of determining the thickness and optical constants of a thin film. This is done by measuring the change in polarization of a light beam after reflection from the film surface. In order better characterize the thickness and constants, data is taken over a range of incident angles and a spectrum of wavelengths. This particular process of measurement is referred to as spectroscopic ellipsometry.

The effects of polarization and reflection on the light beam can be expressed using Jones vector formalism:

$$E_D = [Analyzer\ Matrix][Sample\ Matrix][Incident\ Light\ Vector], \quad (A.1)$$

where E_D is the electric field of the light incident on the detector [11]. The ellipsometer used in our research employs two polarizers, one before reflection from the sample and one in the analyzer. The first polarizer simply creates a beam with both s and p-polarized components (polarized at some angle θ). The Jones vector of the incident

light is therefore:

$$\begin{bmatrix} \cos \theta \\ \sin \theta \end{bmatrix}. \quad (\text{A.2})$$

The Jones vector of the light that arrives at the detector is then:

$$\begin{aligned} E_D &= \begin{bmatrix} \cos^2 \phi & \sin \phi \cos \phi \\ \sin \phi \cos \phi & \sin^2 \phi \end{bmatrix} \begin{bmatrix} -\tilde{r}_p & 0 \\ 0 & \tilde{r}_s \end{bmatrix} \begin{bmatrix} \cos \theta \\ \sin \theta \end{bmatrix} \\ &= \begin{bmatrix} -\tilde{r}_p \cos \theta \cos^2 \phi + \tilde{r}_s \sin \theta \sin \phi \cos \phi \\ -\tilde{r}_p \cos \theta \sin \phi \cos \phi + \tilde{r}_s \sin \theta \sin^2 \phi \end{bmatrix}, \end{aligned} \quad (\text{A.3})$$

where ϕ is the angle of the analyzer polarizer and \tilde{r}_p and \tilde{r}_s are the complex Fresnel coefficients [7].

Of course the physical quantity measured at the detector is not the electric field, it is the intensity. The intensity, however, is proportional to the square of the electric field. Thus the intensity measured at the detector (I_D) is:

$$I_D \propto |E_D|^2 = |\tilde{r}_p|^2 \cos^2 \theta \cos^2 \phi + |\tilde{r}_s|^2 \sin^2 \theta \sin^2 \phi - \frac{(\tilde{r}_p^* \tilde{r}_s + \tilde{r}_p \tilde{r}_s^*)}{4} \sin 2\theta \sin 2\phi. \quad (\text{A.4})$$

Rather than solve for the Fresnel coefficients directly, it is the convention in ellipsometry to solve for the ratio of the coefficients in the following manner:

$$\tilde{\rho} = \frac{\tilde{r}_p}{\tilde{r}_s} = \tan \psi e^{i\Delta}. \quad (\text{A.5})$$

Thus ψ , which contains the amplitude information, and Δ , which contains the phase information, replace the Fresnel coefficients. Because these values apply only to relative amplitudes and phases they offer greater reproducibility [11].

A.2 Mean Squared Error

The ellipsometric data collection and analysis in our research was performed with WVASE32TM software. This program uses the ψ and Δ data at a number of angles

and wavelengths to fit for the thickness and optical constants of a thin film sample. The quality of a fits is expressed in terms of its mean squared error (MSE), which is a measure of how closely the model fits the experimental data. The formula for MSE is:

$$\text{MSE} = \frac{1}{2N - M} \sum_{i=1}^N \left[\left(\frac{\psi_i^{mod} - \psi_i^{exp}}{\sigma_{\psi,i}^{exp}} \right)^2 + \left(\frac{\Delta_i^{mod} - \Delta_i^{exp}}{\sigma_{\Delta,i}^{exp}} \right)^2 \right], \quad (\text{A.6})$$

where N is the number of (ψ, Δ) data pairs, M is the number of variable parameters in the given model, σ is the standard deviation of the experimental data points, and *exp* and *mod* refer to the experimental data and the model data respectively [12].

For a perfect fit the MSE would approach unity. In practice, however, this is highly improbable. As such, a MSE of less than 10 is typically considered to be a reliable fit, although in some instances fits with higher MSE values can still produce an accurate measurement of thickness.

A.3 Effective Medium Approximation

An effective medium approximation (EMA) is a type of model that bases the physical properties of a material on the properties of its constituent components. In the case of optics, an EMA can be applied to determine the optical constants of an inhomogeneous thin film layer. This model states that the constants are some sort of an average of the constants of the materials that compose the layer.

The simplest EMA is a linear interpolation. As its name suggests this method models the optical constants of a composite layer as a linear combination of the individual parts. In this case the index of each part is weighted by its relative volume. In mathematical terms this model states that the complex index, $\tilde{\epsilon}$, of the composite

material is:

$$\tilde{\varepsilon} = f_A \tilde{\varepsilon}_A + f_B \tilde{\varepsilon}_B + \dots = \sum_i f_i \tilde{\varepsilon}_i, \quad (\text{A.7})$$

where $\tilde{\varepsilon}_i$ is the complex index of the i th component material and f_i is its corresponding volume fraction [13]. This, of course, imposes the condition that:

$$\sum_i f_i = 1. \quad (\text{A.8})$$