Investigations of the Causes of Expansion for Yttrium Oxide Films

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Abstract

Brigham Young University's Department of Physical and Astronomy's Thin Film Research Group has been studying the apparent expansion of yttrium oxide and scandium oxide when exposed to 7.27 eV excimer lamp. These films have more than tripled their initial thickness because of the exposure. Such expansion is quite unexpected. The excimer lamp used is very similar to UV cleaning lamps used to clean films and semiconductors in industry. It is therefore very important to understand this phenomenon. It has been previously found that reactively sputtered samples exhibit this expansion. Samples were grown and then analyzed using a tunneling electron microscope, ellipsometry, and spectral analysis. More samples were prepared and tested in various atmospheres in an attempt to isolate the catalysts or reactants needed for the phenomenon to occur. Evidence suggests that the presence of a gaseous species; perhaps oxygen or ozone is required in addition to the lamp for growth to occur.

Keywords: yttria, yttrium oxide, reactively sputtered, excimer lamp, electron microscope

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1 Introduction

1.1 Report Overview

It is proposed that the growth of thin films in yttrium oxide (commonly called “yttria” or Y_2O_3) is caused by gas acting as a glass forming agent. This report will attempt to establish the causes of yttrium oxide film growth, including the mechanisms for growth as well as the experimental evidence supporting it. This section in the report will show the importance of this research to the semiconductor industry, with the following sections explaining experiments and discussion on the experiment's results.

1.2 Interest in Yttrium Oxide for Semiconductors

Yttrium oxide is considered a potential substitute for silicon dioxide in metal-oxide-semiconductor devices as a primary gate dielectric material. [1] The increased need for miniaturized components is difficult to fulfill with silicon dioxide due to its low dielectric constant. Yttrium oxide has a high dielectric constant, allowing for smaller devices to be made. [2]

In addition to these properties, yttrium oxide possesses a bixbyite lattice structure, which is a face-centered cubic structure. [3] The lattice constant for this structure is 1.06 nm, which is roughly double that of silicon dioxide, 0.543 nm. This allows for junctions to have a low mismatch between the two materials. Silicon is therefore not greatly affected by the deposition of yttrium oxide on it, allowing semiconductors to retain many of the desirable material properties and structure. Such properties of yttrium oxide made it a good candidate for some applications within the semiconductor industry.

1.3 Application of Findings to Semiconductors

All of the growth recorded has been initiated by the use of a 7.2 eV excimer lamp. This lamp produces vacuum ultraviolet (VUV) light, which is used to clean surfaces for electronics. These photons are very high energy, and therefore react with many atoms in the atmosphere. VUV light can only travel about 1 cm in atmosphere before being totally absorbed. High energy photons such as those produced by this lamp react with atmospheric oxygen to produce atomic oxygen and ozone. The ozone and oxygen then interacts with hydrocarbons on the surface of the sample. Hydrocarbons convert to hydrocarbons of less molecular weight or into water and carbon dioxide, which readily leave the surface of the sample. Such lighter hydrocarbons and other molecules generally possess a higher vapor pressure, allowing the surface to be cleaned. [4]

This type of lamp is commonly used in the semiconductor industry because it easily cleans off the surfaces of silicon devices. Should a semiconductor contain yttrium oxide and be cleaned by this process, the results could be disastrous. Such semiconductor could potentially break, and some of the electrical properties of the semiconductor could change. Even small variations in the size of a doped layer or electrical properties in an area could easily result in an unusable or unreliable device. Understanding the expansion of yttrium oxide films is therefore important to preserving such devices.

1.4 First Observed Film Growth

The first observed film growth was in November of 2009, when a thin film of yttrium oxide on silicon was cleaned with a VUV lamp. After only 5 minutes of exposure to VUV light, the sample had changed its appearance. The color and surface of the sample had changed. The yttrium oxide film possessed a metallic, mirror like finish, which changed to a mottled finish with a brown hue. This visible change in color is often evidence of a change in thickness, as different wavelengths of light can be cancelled out by a film's thickness. Spectroscopic ellipsometry revealed that the change in color corresponded to a change in the film's thickness.

Basic ellipsometry involves reflecting light of a known wavelength, polarization, and incident angle off of a sample. The changes to these variables are measured after the light has reflected off. Analyzing the changes of the reflected light allows for the calculation of many properties of the film, including thickness. [5] Closer inspection of this initial sample showed the starting thickness of the film to be about 24.7 nm (± 0.1 nm). The thickness of the film after 5 minutes of exposure resulted in a thickness of about 31.1nm (± 0 .07 nm). Thicknesses for cleaning surfaces usually decrease because of hydrocarbons being removed from the surface, and often the decrease in thickness is only a few nanometers. Expansion of the film, even by 6 nm, represents a 25.9% increase in thickness. Such expansion runs counter to intuition about the behavior of surfaces under VUV lamps.

1.5 Past Work

Devon Mortensen and several others have previously examined this phenomenon and have attempted to explain it. Their theories and work have provided a framework from which these experiments have built upon. Several theories have been developed to explain the expansion of the film, but many have been proven false by others. [6]

Investigations into the nature of this phenomenon have given data on the interplay of time and distance from the lamp on expansion. [6] Samples which have expanded have been annealed, resulting in those samples contracting back to their starting thickness or thinner. Annealed samples are also capable of the expansion under VUV light.

The first theory of expansion was that the expansion of yttrium oxide films was due to incomplete oxidation of yttrium in the reactive sputtering process. As the samples were created using reactive sputtering, it was thought the yttrium did not fully oxidize. Reactive sputtering involves creating plasma above a negatively charged yttrium target, thus removing individual atoms to float in the atmosphere. These atoms then react with oxygen, forming yttrium oxide, and then are deposited onto the surface of the sample. This process is performed in a vacuum system, disallowing for many external elements to corrupt the process. The incomplete oxidation theory claimed that the yttrium was incompletely oxidized, and that the VUV light allowed for completion of the oxidation process. Mortensen proved this theory false, showing that the recorded expansion was as much as 18 times the theoretical expansion limit for oxidation. [6] Oxidation of a sample during its exposure to VUV light could contribute to the overall increase in thickness, but it cannot account for the amount of expansion seen in samples.

The secondary theory of expansion involves the formation of another compound, potentially an yttrium ozonide which significantly increases volume. It is widely known that VUV lamps produce ozone, and it can be possible that the yttrium oxide reacts and forms an ozonide. Ozonide formation has been documented with group I and group II elements of the periodic table. [7, 8] Yttrium is a group III element, and the formation of an ozonide would be the discovery of a previously unknown chemical state. This new chemical state could have a large volume than the starting yttrium oxide film, but be a metastable state. Yttrium ozonide could decompose back into yttrium oxide but leave a structure which is much more stretched out.

This second theory would explain the expansion of yttrium oxide and the subsequent deflation of the film when annealed. Mortensen attempted to test this hypothesis, but drew no conclusive evidence from his attempts. A nitrogen-rich environment was used created in an attempt to eliminate any chances of creating ozone. The atmosphere created was not pure enough to eliminate all oxygen, and the observed growth of the sample seems to indicate that ozone is either not necessary or was present in the needed quantities for growth. [7]

2 Methods

2.1 Sample Creation

Samples for these experiments were created using reactive magneton sputtering. A vacuum system was used to control the environment where silicon (Si) wafers were sputtered onto. The procedure involved several steps, starting with a blank silicon wafer and an yttrium target in the vacuum chamber. Atmosphere from within the chamber was pumped out until the internal pressure, also called base pressure, was on the order of 10^{-6} Torr. Such a vacuum guarantees that the chamber is free of molecules which could change the constitution of the yttrium oxide layer.

The low pressure and corresponding dearth of molecules within the chamber ensures that the yttrium and yttrium oxide molecules have a long mean free path during deposition. A mean free path is the average distance a molecule or atom travels before colliding with another molecule or atom [5]. Longer mean free paths ensure that more yttrium oxide arrives on the wafer.

Once the base pressure was achieved, argon and oxygen are flowed into the chamber to produce an atmosphere for sputtering. A plasma composed mostly of argon was created and kept above the yttrium target by magnetic field. The magnetic field caused the plasma to bombard the yttrium target, ejecting yttrium into the atmosphere. The atomic yttrium then reacted with oxygen en route to, or after, collision with the silicon wafer. The reaction of yttrium with oxygen formed yttrium oxide. Deposition onto the surface is caused by the yttrium or yttrium oxide settling into the surface of the silicon wafer.

It is important to note that the difference between simple sputtering and reactive sputtering is the presence of oxygen during the deposition process. This phenomenon I studied does not work with sputtered yttrium oxide films; reactive sputtering must be used for these films to expand under VUV light.

2.2 Transmission Electron Microscope

A Transmission Electron Microscopy was used to analyze a sample of yttrium oxide removed from the target. Previous attempts by my group to deposit thin films on membranes had failed. Some part of the process, perhaps the pressure changes within the sputtering process are thought to be too extreme for most SiN TEM grids. A sample of expanded yttrium instead scraped with a surgical knife onto a carbon wafer, which was then placed into the tunneling electron microscope for analysis.

The microscope was also capable of analyzing samples crystal structure, using x-ray diffraction and chemical analysis via x-ray fluorescence. Both of these capabilities were used in addition to transmission electron microscopy in photos of the samples.

2.3 Isolated Atmosphere Experiment

To determine the effects of the atmosphere around the VUV lamp on the sample, a magnesium fluoride window was attached with Apiezon W compound to an aluminum tube. Opposing holes were drilled in sets of 2 staring at 1.27 cm away from the window. The sets of holes were placed 1.27 cm away from each other, going down the tube away from the window. All of the holes were then sealed. The tube was tested to see if the magnesium fluoride window still transmitted 7.27 eV photons with a transmittance test on a J.A. Woollam Ellipsometer. Upon the realization that it did, in fact, transmit VUV light the experiment continued.

First, spectroscopic ellipsometry was used to determine the starting thicknesses of samples. Samples were then placed inside the tube so that they could be exposed to the vacuum ultraviolet rays without encountering any of the atmosphere around the VUV lamp. The tube was placed, with the sample behind the window, so that the open end was 30 cm away from the VUV lamp and the magnesium fluoride window was placed very close to the VUV lamp.

In each run, the sample was allotted 10 minutes of exposure to VUV light through the window. Each run had a number of holes open. The first run had no holes open; second had the two furthest holes open, the third had the 4 furthest holes open, and so on. Their thicknesses were measured again using ellipsometry, and each sample was given another 10 minutes to expand under the same conditions. Finally, each sample was measured by ellipsometer after its final 10 minutes behind the magnesium fluoride window.

As a control to this experiment, the magnesium fluoride window retained its Apiezon W sealant and simply sat above the sample, but the sealant still isolated the sample from the tube. Shims of 0.1 mm thickness were added to raise the window by 0.1 mm between iterations of the experiment. In a second control, the magnesium fluoride window did not have the Apiezon W sealant on it and was placed above the sample.

2.4 Controlled Atmosphere Experiments

Three tests were used to determine the effects of the composition of the atmosphere on growth. The sample and the VUV lamp were placed inside of a sealed glove bag.

Specific gas was then pumped into the glove bag. Once the bag was full, these gases were pumped out until the bag was mostly empty, and then the bag was pumped full of a specific gas. Nitrogen, argon, and carbon dioxide atmospheres were selected. Nitrogen was selected because of the high content of nitrogen in air. Argon was a control, as it is an inert gas. Carbon dioxide was chosen so that atomic oxygen would form. Oxygen was not chosen because of the associated risk of explosion. Unlike past experiments, higher air purity was achieved by purging and filling a closed container with gas. [6] A custom-made glove bag was used. The glove bag had an intake tube and an outlet tube. The intake tube was hooked up to a container of compressed gas. The outtake tube was connected to a single-stage vacuum pump.

The desired gas was pumped into the glove bag until the glove bag was full. A valve was then used to stop the flow of compressed gas into the glove bag. The pump on the outtake tube was then activated, removing most of the gas from the glove bag. Once the bag was mostly deflated, the pump was disengaged. The glove bag was filled once again, making the glove bag full of a specific type of air plus a mixture from the previous atmosphere. This process was repeated until the desired purity was reached.

Once the atmosphere within the glove bag reached the desired level of air replacement, the samples were positioned within 2 cm to the VUV lamp. The lamp was activated for 10 minutes, allowing the samples time to expand. The samples were then analyzed using spectroscopic ellipsometry to determine their thickness.

The glove bag for testing the effects of a mostly nitrogen atmosphere was emptied and refilled 5 times. Every time it was vacated, the bag pumped down to about 1/3 its original volume. Thus the atmosphere within the glove bag had a nitrogen purity calculated to be about 99.5%. The VUV lamp required nitrogen or air cooling, so the intake line was hooked up to the VUV lamp and the exhaust was allowed to be introduced to the atmosphere of the glove bag. The sample was then exposed to the 7.2 eV light for 10 minutes. Once the 10 minutes expired, the sample was then removed and analyzed by the ellipsometer.

Due to the fact that the VUV lamp needs air or nitrogen cooling, two more lines were introduced to the glove bag after the nitrogen atmosphere experiment. These lines hooked up to the intake/outtake valves of the VUV lamp. All gasses which cool the VUV lamp are in an air-tight system. Atmospheric nitrogen was used to cool the lamp and was expelled outside of the glove bag.

The glove bag for the argon atmosphere was similarly purged and refilled 8 times. Every time it was evacuated, the bag was pumped down to about half its full volume. The atmosphere within the glove bag was calculated to have a purity of about 99.6% argon. Once the atmosphere within the glove bag reached the desired purity, the valve to the argon tank was sealed and the sample was placed under the lamp. After 10 minutes of exposure, the sample was removed and an ellipsometer was used to determine its apparent oxide thickness.

To test the effects of a CO_2 atmosphere, the bag was vacated and refilled 8 times. As in the argon run, the glove bag was vacated to about half of its full volume. After refilling the atmosphere 8 times, the atmosphere was calculated to have a purity of around 99.6% CO_2. A sample was then placed under the lamp for 10 minutes. Once the 10 minutes elapsed, the sample was removed and analyzed with an ellipsometer to determine the final apparent oxide thickness.

3 Results

3.1 Transmission Electron Microscope

Initial observations indicate that the expanded layer was very spongy, as seen in figure 3.1.1. The lack of distinct, whole sections and the continual curling of the piece indicate that there are no strong crystalline structures on this scale. The vertical lines apparent on the broad surface of the sample may have be indicative of a crystalline structure or points at which the sample bent as it was cut.

Figure 3.1.1 Initial View of Expanded Yttrium Oxide Film

More detailed examination of the edge of this sample is revealed in figure 3.1.2, below. This figure shows that there is no obvious crystalline structure to the expanded yttrium oxide film. If there was structure, one would expect to see plains of atoms or hexagonal structures. X-ray diffraction shows that there is no set structure, but only one ring, in figure 3.1.3.

Such a diffraction pattern, with one ring, is typical of amorphous solids. It indicates a strong, but not consistent, distance between nearest neighbor atoms. The lack of any other rings indicates there is no long-range order; otherwise strong secondary rings would appear. This supports the observation the expanded yttrium oxide is a spongy, void-filled material.

The TEM is also capable of chemical analysis via x-ray fluorescence. The results are recorded in figure 3.1.4. There are strong lines for yttrium, oxygen, molybdenum, and copper. The sample holder is mostly composed of copper, molybdenum, and iron, which accounts for the peaks for these elements. Further analysis of these counts revealed a stoichiometry of 2 yttrium atoms for every 3 oxygen atoms, which is the chemical formula for yttrium oxide.

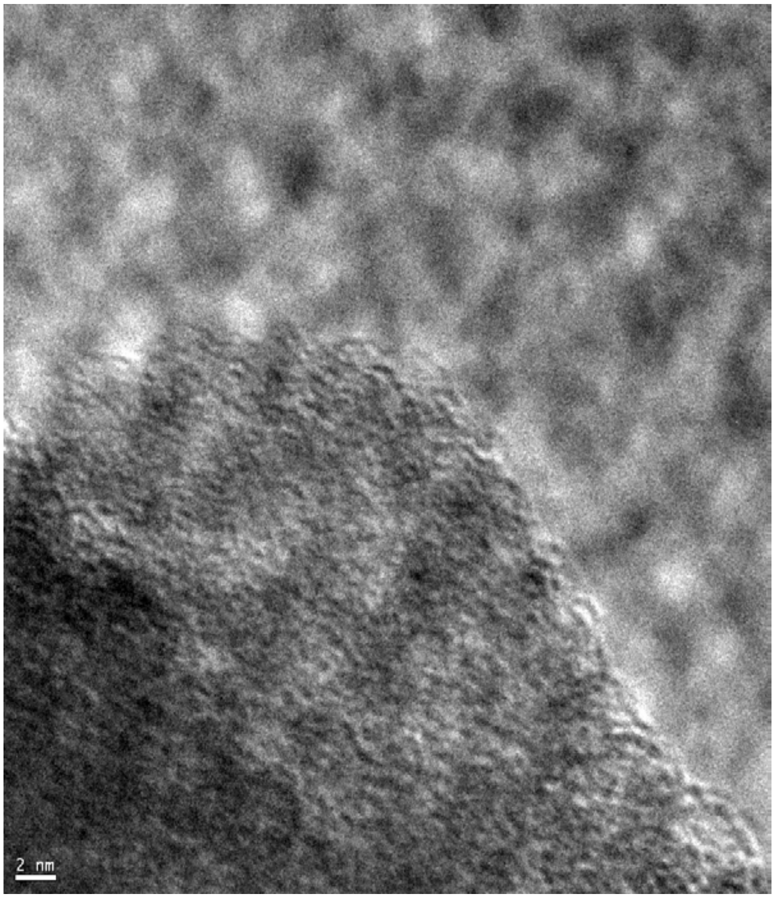

Figure 3.1.2 Edge of Film

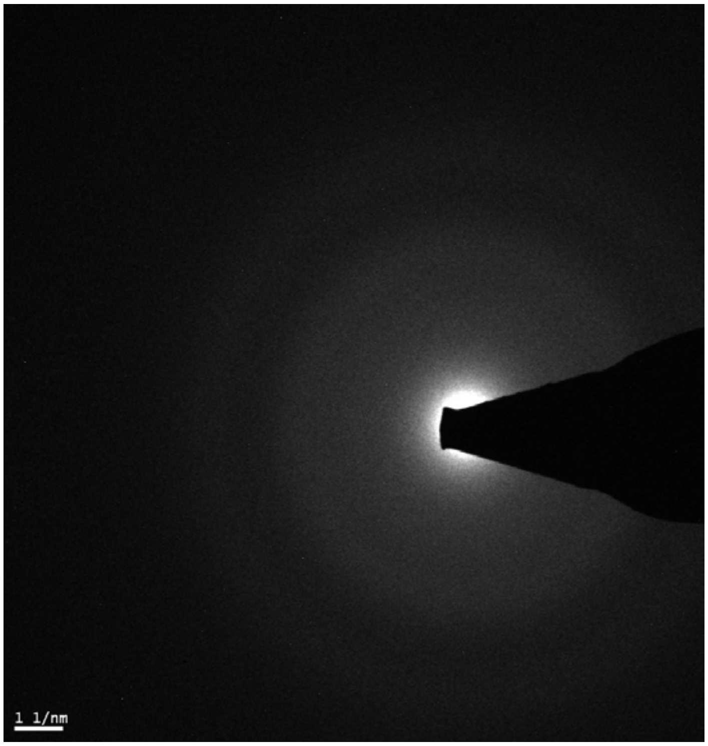

Figure 3.1.3 X-Ray Diffraction Pattern of Expanded Yttrium Oxide Film

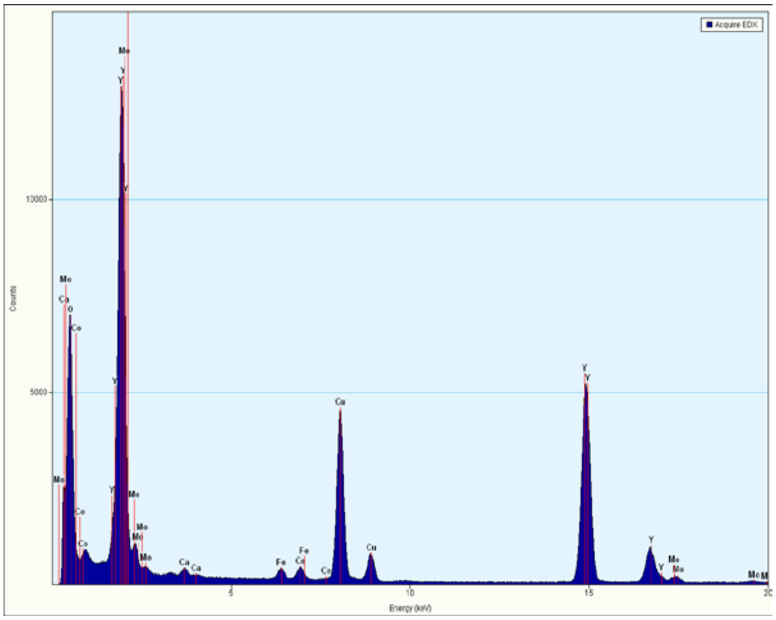

Figure 3.1.4 Chemical Spectroscopy Results

3.2 Isolated Atmosphere Experiments

The first results from this test indicated that no growth occurred. Samples showed very little variation in thickness. They generally did not grow at all, even with all holes open. The variant of this experiment was then devised to see if the Apiezon W wax compound was affecting the expansion of the thin film. It was soon found that the wax compound used to seal the tube prevented the expansion. In the control run without the wax, the thin film grew as previously expected.

The control run also showed a very interesting pattern. This particular sample was smaller than the magnesium fluoride window, and was not well centered under the window. Expansion occurred around the outside edge of the sample, and not as much in the middle of the magnesium fluoride window. This is either due to the way the weight was distributed on the sample or due to some other effects, like the ability of air to penetrate the sample.

3.3 Controlled Atmosphere Experiment

The thin film in the nitrogen atmosphere started at 17.009 ± 0.357 nm thick and expanded to a thickness of 17.880 ± 0.0376 nm. This change in thickness is well within the error range, meaning that no significant growth occurred.

The thin film in the argon atmosphere started at 17.880 ± 0.0376 nm and grew to a thickness of 22.011 ± 0.0683 nm. This change in thickness is outside of the error range, and represents about 23.1% increase in film thickness.

The thin film for the carbon dioxide atmosphere started at 20.024 ± 0.066 nm. After 10 minutes of growth, the thickness was 12.545 ± 0.0787 nm. The film decreased its thickness by approximately 37%.

The control started at 24.783 ± 0.135 nm, and expanded to a thickness of 50.056 ± 0.26 nm. The controls expansion was about 102% larger than the starting thickness.

Atmosphere	Starting Thickness	Ending Thickness	Percent Expansion
Control	24.783 ± 0.135 nm	50.056 ± 0.26 nm	101.98%
Nitrogen	17.009 ± 0.357 nm	17.880 ± 0.0376 nm	5.12%
Argon	17.880 ± 0.0376 nm	22.011 ± 0.0683 nm	23.10%
Carbon Dioxide	20.024 ± 0.066 nm	12.545 ± 0.0787 nm	-37.35%

Figure 3.3 A summary of the results of controlled atmosphere tests.

4 Discussion

4.1 Review

The TEM and X-ray diffraction results conclusively show that the expanded yttrium oxide film is an amorphous solid. Spectroscopy reveals that the stoichiometry remains the same for the sample as a whole, meaning that no permanent chemical change occurs. The change could be very easily explained by the presence of a glass forming compound in the atmosphere. The controlled atmosphere experiments clearly show that nitrogen and argon are not the glass forming agent. VUV lamps are known to produce ozone as a byproduct, and oxygen is the second largest component of the atmosphere.

The results of these experiments point to oxygen and ozone being a key factor. Even small amounts of ozone can lead to significant growth of an yttrium oxide film. There is no direct evidence of an yttrium ozonide forming, but there is significant evidence that points to ozone being a glass forming agent. The shrinking of the film in carbon dioxide can be attributed to formation of carbon monoxide, which could “eat away” at the film, but perhaps a different mechanism is responsible.

The fact that annealed samples also exhibit this phenomenon indicates that the expansion could be due to a phase change or the dissolution of crystal structure. Instead of being well ordered, it could be that the presence of ozone with VUV light allows yttrium oxide to overcome energy barriers and lose its crystalline structure. As it loses its crystalline structure, the solid becomes less well-packed, and then becomes larger without changing its stoichiometry.

Previous experiments have used simple purging methods to purify and atmosphere. This method of purification does not allow for atmospheres to reach high levels of purity, and there may have been enough of the glass-forming agent to produce expansion. The amount of different components of air in the glove bag for both the argon and nitrogen atmosphere were assumed to be that of normal atmospheric air. The actual stoichiometry of air before purification was unknown, and that may result in the varying results.

4.2 Further Research

Further research should concentrate on the effects of oxygen on expansion of yttrium oxide films. Varying the oxygen content of the glove bag via filling and pumping out gas would be ideal. Using a zinc-air battery in the glove bag can produce an accurate estimate of the amount of oxygen present. This type of battery relies on atmospheric oxygen to produce a voltage difference, and it would be a simple matter of calibration and measuring voltage while running the experiment.

Producing a sample of reactively sputtered yttrium oxide on a TEM grid would also help test the theory that yttrium oxide becomes an amorphous solid when exposed to ozone. If an unexpanded sample of yttrium oxide displays the familiar bixbyite structure, then it would lend support to the phase-change hypothesis. If the unexpanded yttrium oxide is an amorphous solid, it could be because it is forming yttrium ozonide. This theory could also be further pursued by examining more annealed samples, which should have the bixbyte structure.

5 Conclusion

It appears that the expansion of yttrium oxide is caused exclusively by the application of vacuum ultraviolet light and the presence of ozone. It appears that any agent which would intercept or more readily react with ozone or the 7.27 eV light could prevent expansion. Small amounts of oxygen interacting with the lamp could produce enough ozone to create expansion. The expansion itself may be a product of the yttrium oxide losing its well-ordered crystalline structure in exchange for an amorphous configuration. Further research should focus on the relationship between ozone, vacuum ultraviolet light, film thickness, and time.

The use of yttrium oxide in the semiconductor industry should be aware of this phenomenon. It has been shown that even fractions of a percent of oxygen can cause yttrium to swell, which could be harmful to semiconductor devices. Using a plasma cleaner would be preferable and perhaps the most cost effective way to avoid the swelling. Alternatively, creating an atmosphere which readily reacts with radical oxygen and ozone would also prevent the welling from occurring.

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