Oxidation of Aluminum Under Various Thicknesses of Aluminum Fluoride

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ABSTRACT

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One of NASA's overarching goals is the Origins project, which explores both the universe and ways to better understand it. Of special concern is the extreme or vacuum ultraviolet (VUV or XUV, respectively) range, far past 10 eV (the current telescopes' observation limit). The growth rate of the aluminum oxide (Al_2O_3) under various protective coatings—specifically aluminum fluoride, First Contact Opticlean, and liquid nitrogen—is tested. Ellipsometry and SEM are used to understand more about the chemical composition of the created mirrors as a function of time. Results show a 9nm layer of AlF_3 on aluminum is a stable barrier layer against oxidation of aluminum.

Acknowledgments

This research would not have been possible without the help of Dr. David Allred, Dr. Steven Turley, and Paul Minson of the BYU Physics department, as well as Margaret Miles, former BYU graduate student and my mentor in our research group.

This paper would not have been possible without the support of Dr. Traci Neilsen of the BYU Physics department and my husband Aaron.

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Chapter 1   Introduction

Aluminum is an excellent candidate for broadband wavelength mirrors, however the growth of even 1nm of aluminum oxide significantly diminishes[1] its wide broadband reflectance capabilities[2,3]. Our goal is to figure out a solution and decide on a path to move forward.

1.1 Background: Interest in the Ultraviolet

NASA's upcoming missions[4] have a heavy emphasis on observing the universe across a wide band of wavelengths, spanning the infrared (IR) to the ultraviolet (UV). This more expansive form of observing can be done using the Large Ultra Violet/Optical/Infrared Surveyor (LUVOIR)[5,6], an 8-16 meter telescope mirror capable of reflecting extreme UV wavelengths, visible light, and IR radiation thus allowing an expansive collection of data beyond what is now possible. Figure 1.1 implies how limited our view of space would be if constrained to one or two wavelength ranges.
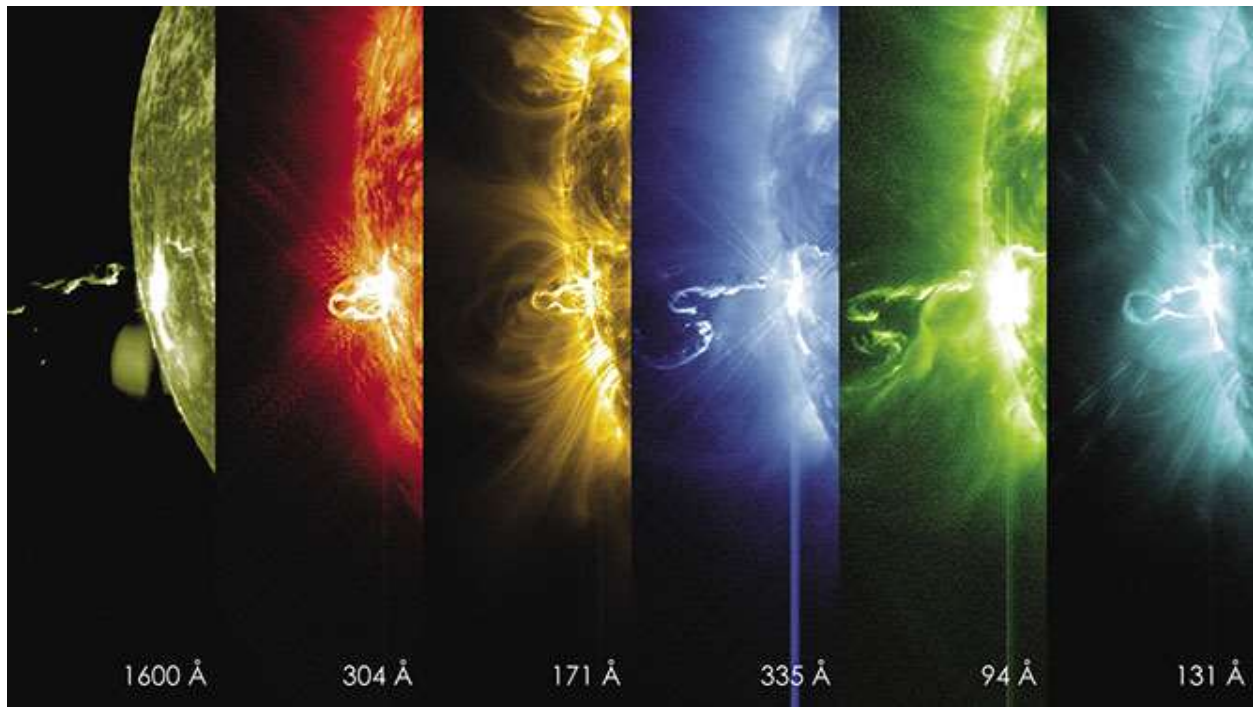
Figure 1.1 Images of the surface of the sun (same shot at the same time) at various wavelengths. Source: https://spinoff.nasa.gov/Spinoff2015/cg_5.html

1.2 Motivation

In order to actually observe at all these wavelengths, the LUVOIR telescope needs a mirror that reflects well across this wide range. One candidate material for the mirror is aluminum because of its usefulness in reaching far into the XUV. It has been shown[1] that a pure aluminum surface reflects well into the XUV clear across to the IR wavelength range as desired for broadband reflection. However, aluminum oxidizes very quickly, and even 1nm of oxide on the aluminum significantly reduces the reflection effectiveness of the aluminum in the XUV from 90% (unoxidized) to 20% (1nm of oxide layer). Figure 1.2 shows this variability with wavelength. The problem then presents itself of how to keep aluminum unoxidized.
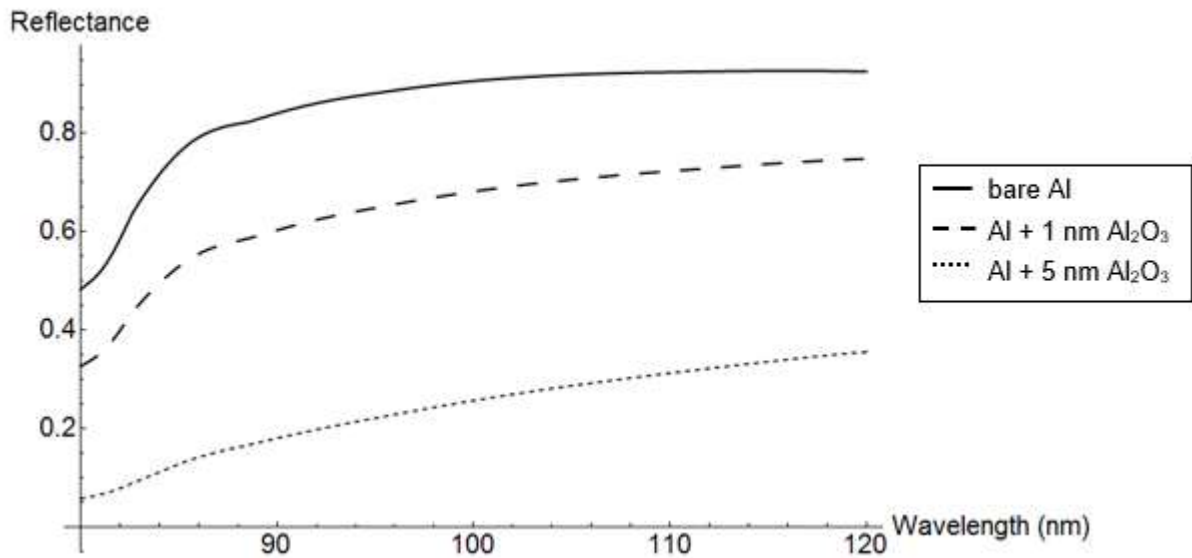
Reflectance

Figure 1.2 Calculated decrease in reflectance for the far XUV wavelengths as a function of oxide growth.

Several solutions have been proposed to this problem of decreased reflectivity. A mirror could be coated with aluminum in space, thus avoiding oxidation via earth's atmosphere all together. Or, a mirror could be made in situ under vacuum and then kept somehow under vacuum until reaching space, again avoiding exposure to atmosphere. Both of these ideas, however, are technically extremely difficult. Another idea would be to use a different material in the place of aluminum. The viability of this idea requires understanding how much reflectance is sacrificed by various amounts of oxide, and then comparing that reduction with the reflectance sacrificed by using the different material. The major concern with this proposal is knowing how fast and under what conditions aluminum oxidizes, or in other words, the rate of aluminum oxide growth under a protective layer.

1.3 Prior Work

Many broadband mirror coatings are being developed as solutions to aluminum's oxidation problem. Popular and promising among the many aluminum-coating options are fluorides, specifically lithium fluoride (LiF), magnesium fluoride (MgF_2), and aluminum fluoride (AlF_3). These are strong candidates because they are weak absorbers in the far XUV. In addition, our computational collaborators indicate that they will resist oxide growth. Work has been done[7,8,9] with LiF and MgF_2, but my work is strictly with AlF_3 on aluminum.

1.3.1 Prior work at BYU

Our research group has been trying to find practical barrier layers for aluminum that will still allow reflectance far into the XUV. My mentor, Margaret Miles[10], worked on both AlF_3 and MgF_2 as protective coatings of aluminum, but her Master's thesis focused on the roughness of the AlF_3 thin film to help prevent oxidation growth on the aluminum. Other previous work has included genetic algorithms to see what combinations of metals are most effective, and multiple layers underneath the pure aluminum thin film for other reflectance properties, among other things. The past few papers[11] have discussed both (1) a layer as a protective barrier that is thick enough to protect against oxidation of the aluminum and thin enough to be transparent in the far XUV range, and (2) a layer that can be removed by etching or another similar process once reaching space.

My research in knowing how thick an AlF_3 protective coating needs to be to decisively prevent oxidation growth, aids both paths of future research.
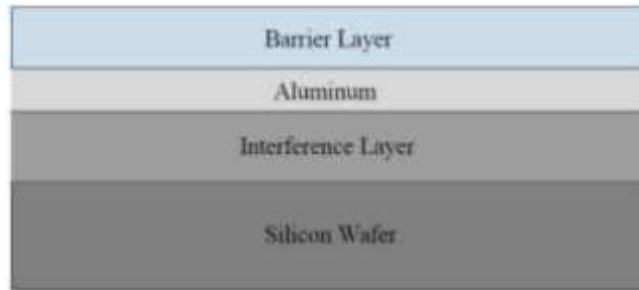
Figure 1.3 Cross section of possible mirrors.

1.4 Thesis Overview

Thus, deep space observation may be possible using a mirror made of aluminum without an oxide layer. Our goal is to make a mirror and covering layer in situ in a vacuum system. Chapter 2 describes the experiment that explores the efficacy of using aluminum fluoride as this barrier layer against oxidation. In actuality, 20 nm of aluminum are thermally evaporated and then coated with 9 nm of AlF_3 as a barrier layer against oxidation. Ellipsometry is used to track the growth, if any, of an aluminum oxide (Al_2O_3) layer between the aluminum and AlF_3 over time, which indicates if our AlF_3 layer is thick enough to resist oxidation of the aluminum. Our results showed almost no growth of an oxide layer, proving that our AlF_3 layer is indeed thick enough. To ensure the validity of our data, we also used scanning electron microscopy (SEM) to check our sample chemical composition. Chapter 3 describes the analysis of the information we gathered, and concludes with the plans for future work.

Chapter 2   Methodology

Here I describe how the experiment explores the efficacy of using aluminum fluoride as this barrier layer against oxidation. Section 2.1 discusses how I evaporated the thin films of aluminum and AlF$_3$, and section 2.2 explores the data collection techniques for both ellipsometry and the SEM.

2.1 Evaporation of thin film aluminum and aluminum fluoride

Our goal is to create a thin film of unoxidized aluminum under a protective layer of aluminum fluoride (AlF$_3$). A Denton model DV-502A thermal evaporator was used with two separate heating/evaporating sources (Fig. 2.1). The aluminum was deposited by evaporating an aluminum wire with resistive heating of a multistrand tungsten filament. Next the AlF$_3$ was deposited by evaporation of AlF$_3$ pellets as prepared by Pure Tech, Inc. using heating of a tungsten boat. To minimize the risk of oxidation of the freshly deposited aluminum, the AlF$_3$

layer was evaporated in quick succession. Two different thicknesses of CVD-deposited silicon nitride (Si_3N_4), 100 – 2000 nm thick, on the silicon wafers act as the substrates of our thin films. These wafers were then affixed to a rotating sample stage to await deposition of the aluminum and AlF_3. The point of the rotating stage is to achieve a more uniform deposition layer.

Next, the thickness was determined for the aluminum and AlF_3 thin films and those parameters were then programmed into the Denton monitor. The thickness is determined by measuring the thickness of the layer deposited on an Inficon quartz crystal monitor (which is in close proximity to the rotating sample stage for accuracy) linked to the shutter and the amount of time passed since evaporation and subsequent deposition of each metal.

In order for the aluminum to be deposited without being subject to oxygen or normal atmospheric gases, the chamber must be pumped down. Our deposition chamber was initially pumped down to the mid 10^{-6} torr range, and during evaporation and deposition rose to the 10^{-5} torr range. This rise in pressure is assumed to be due to water vapor being released from the sides of the chamber walls as they were radiated. After both aluminum and AlF_3 metals were deposited as thin films, we vented the chamber.

Next the samples are quickly taken out of the chamber, and one of each type of wafer is either put in the liquid nitrogen, optically coated with First Contact Opticlean, or left exposed to air atmosphere. Limiting the exposure of the thin films to only these three situations allows us to compare the oxidation rate under different circumstances. Our hypothesis is that the sample in liquid nitrogen will have an oxidation growth rate that is considerably retarded compared to the control sample. However, this topic and information is here referenced only for future work (section 3.5), since it is not the subject of my thesis project.
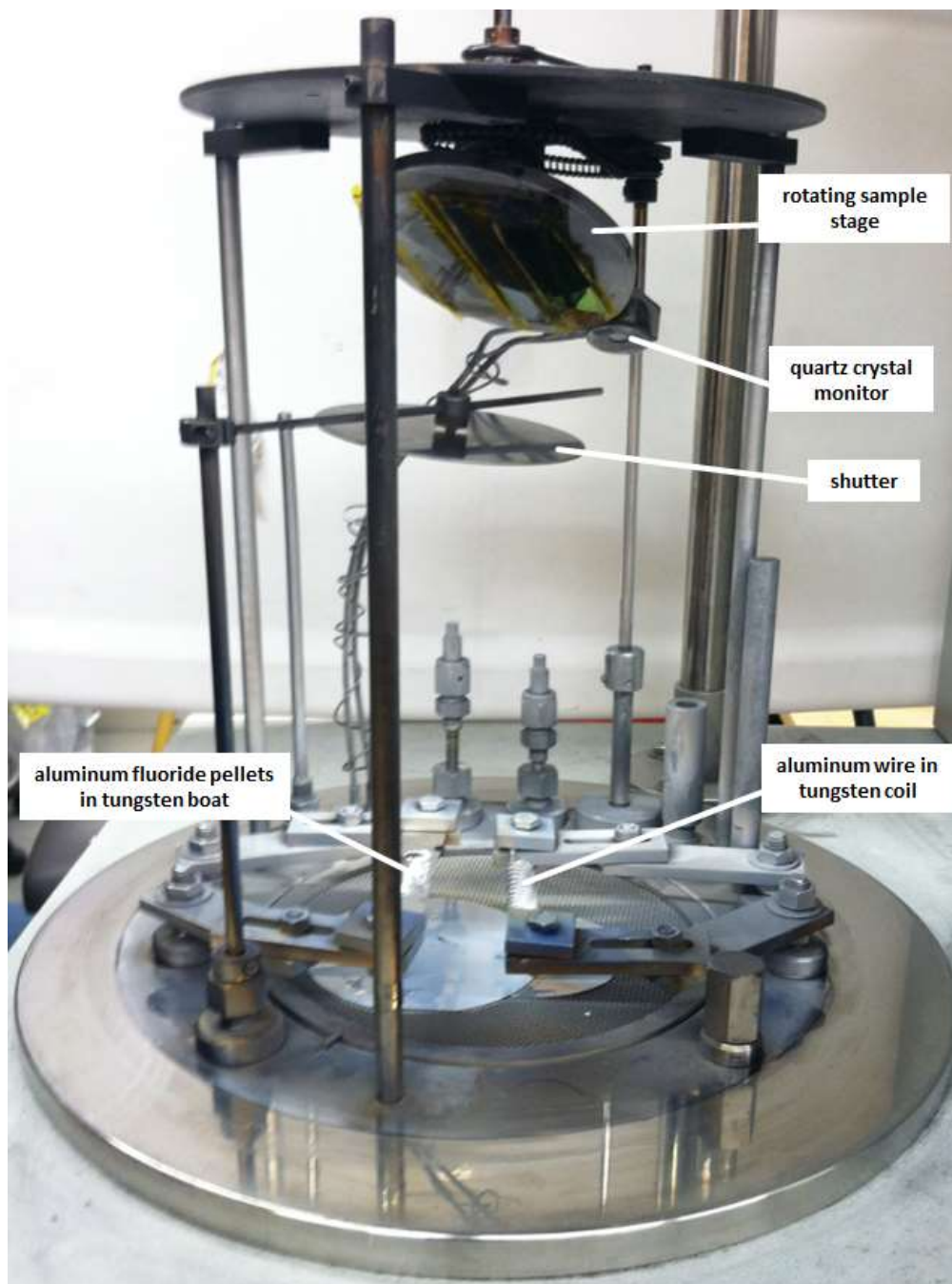
Figure 2.1 The setup of our Denton evaporation chamber.

2.2 Data Collection

The goal and purpose of using both ellipsometry and scanning electron microscopy (SEM) is to better understand the optics of the thin films created, and the to make sure we have actually created what was intended on a chemical-composition basis. With both the what and why, respectively, the thin films' usefulness can be better understood.

2.2.1 Ellipsometry

After the samples were removed from vacuum, the thin films were then characterized using ellipsometry to observe if any oxide grew between the deposition layers, and to gage the true thicknesses of the deposition layers. This ex-situ characterization data was taken using a John A. Woollam M2000 variable-angle, spectroscopic ellipsometer with photon energies of 1.2 - 7 eV (Fig. 2.2). To obtain the ellipsometry data, the incident and reflected light were calibrated at the highest, two middle, and lowest angles. At each of these angles, the reflected light was properly recorded and calibrated. Data was obtained from approximately 60 degrees from normal to Brewster's angle, and finished at near 80 degrees from the vertical. Successive sets of the same data were taken and various increasing intervals to show growth or decisive lack of growth of an Al_2O_3 layer, thus allowing a trend over time to be determined.

Using the computer program VASE, we determined the thicknesses of the thin films by parameter equations. By constraining some variables and allowing the program to determine other variables through iteration cycles, the thicknesses of the thin films was determined.
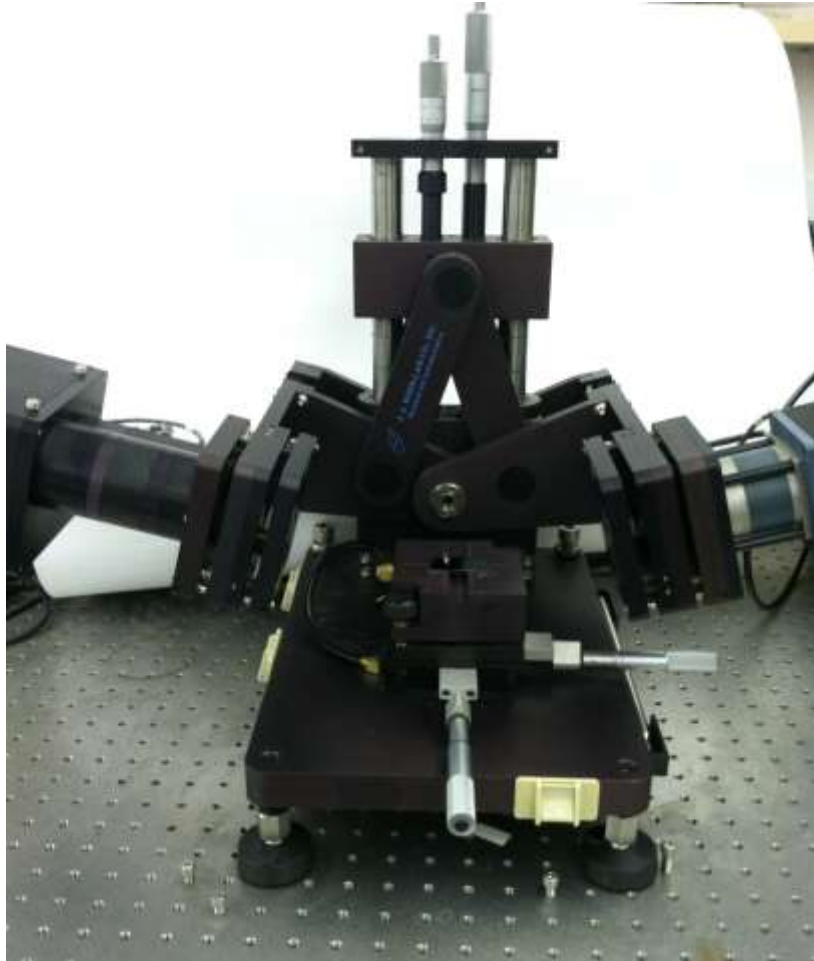
Figure 2.2 The setup of the J.A. Woollam Ellipsometer with a sample on the stage. The arm on the left is the incident light, and the right arm captures the reflected light from the sample.

As the incident and reflected light off the sample was recorded, VASE graphed the results as a complex number in polar coordinates (magnitude and angle) as seen graphed in green in Fig 2.3. The parametric fitted data equations as mentioned previously is graphed in red. The more consistent the green and red graphs, the more confident we are that we have correctly characterized the thin film layers.
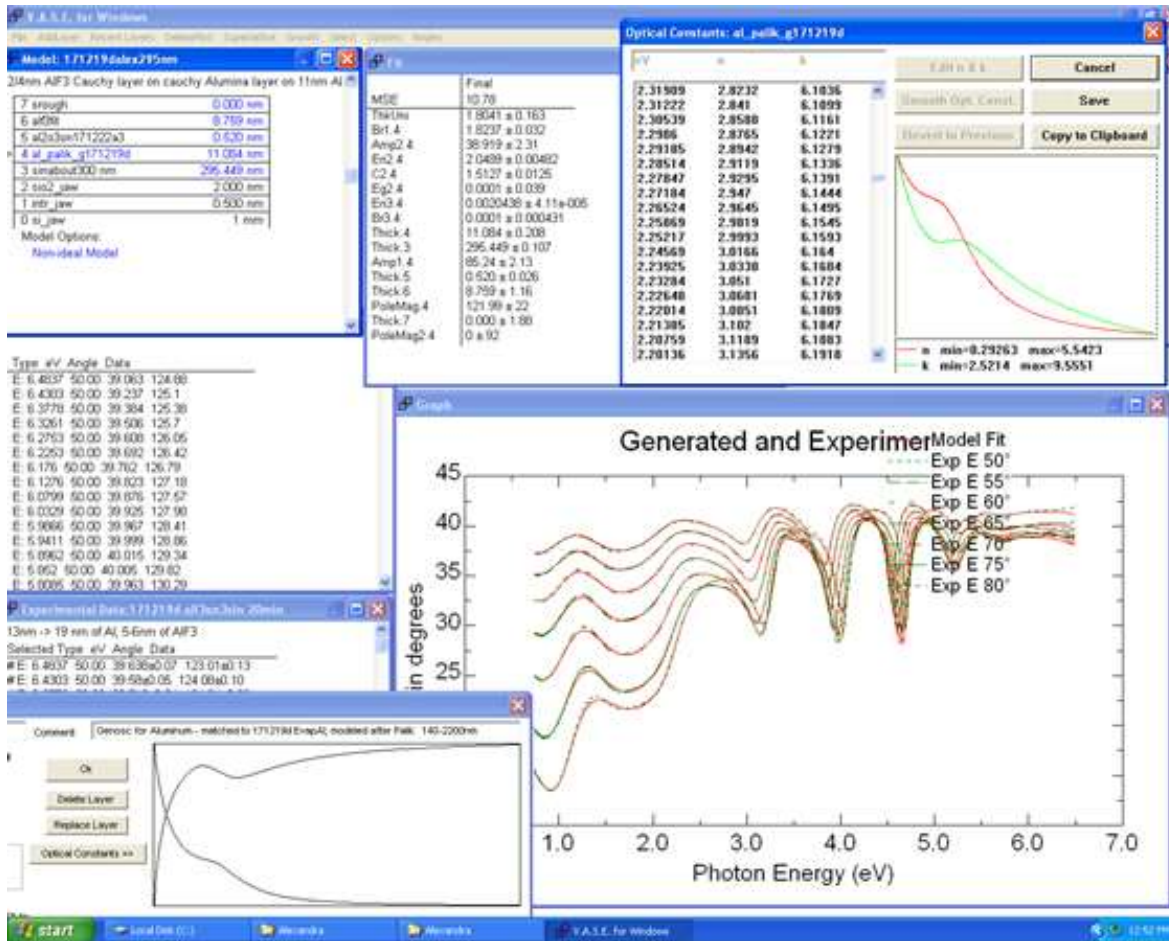
Figure 2.3 Screenshot of our ellipsometry data for a given sample, this one of Sample-171219d. The dialog box with the graph has the experimental data graphed in green and the fitted data graphed in red. In the top left corner are the constraints we can choose to either set or allow the VASE program to try and decide based on various other constraints given to it. In the top-middle dialog box we see the error bars for the variables VASE was trying to fit. This is an observation of the sample after 48+ hours.

2.2.2 SEM

The goal of scanning electron microscopy (SEM) electron dispersive x-ray (EDX) is to decisively determine the chemical content of composition of the samples and then through a program connected with the microscope, analyze that data taken (analysis will be done in chapter

3). The purpose of the SEM EDX data was to confirm our thickness of layers, and to determine if there is anything missed using ellipsometry.

The SEM data was taken with the help of a specialist, Paul Minson. Standard SEM procedures were used for the SFEG, a model of SEM microscope using the EDX technique. The software used to collect the data was called Team Software from the company EDAX. From the results of the SEM chemical analysis data, we get both graphical (Fig. 3.1) and table data (Table 3.3) as shown in chapter 3, to help confirm the chemical composition. Efforts were made to take ellipsometry data and SEM data from the same basically the same location on each respective sample, thus ensuring consistency of the thin film.

As referenced from the term 'electron dispersive x-ray' (EDX), the SEM data is taken using an electron beam, where the instrument directs and bombards a small patch of the sample surface with electrons. The rebounded electrons allow an image to be taken and elemental analysis to be made. The process is extremely time and magnification sensitive however, as the longer and closer we observe the sample, the more adventitious carbon can contaminate the sample. In our case, this is especially dangerous as carbon often traps with it oxygen which can then create the oxide layer we are trying so hard to avoid.

Thus, the methodology of ellipsometry characterization and SEM chemical analysis have been explained. In chapter 3 we will analyze these results and discuss their meaning.

Chapter 3   Analysis and Discussion

Here I discuss and analyze both the characterization data gathered using the ellipsometer

(section 3.1) and the chemical analysis data from the SEM (section 3.2), and then conclude with

the plans for future work.

3.1 Ellipsometry Analysis

In this section I discuss the results of the research and what they explicitly and implicitly

imply. This is done primarily by use of tables and figures.

Table 3.1   Parametric characterization data, modeled by VASE. Parameters I specified (based on
prior experience) are in black, and parameters allowed to be fitted by VASE are in blue. Data
taken 48+ hours after deposition.

7 srough	0.000 nm
6 alf3fit	8.759 nm
5 al2o3on171222a3	0.520 nm
4 al_palik_g171219d	11.084 nm
3 sinabout300 nm	295.449 nm
2 sio2_jaw	2.000 nm
1 intr_jaw	0.500 nm
0 si_jaw	1 mm

Table 3.2 Mean Square Error (MSE), modeling fitting parameters and their corresponding uncertainties for the sample discussed in Table 3.1. The optical constants of Al were fit in the modeling.

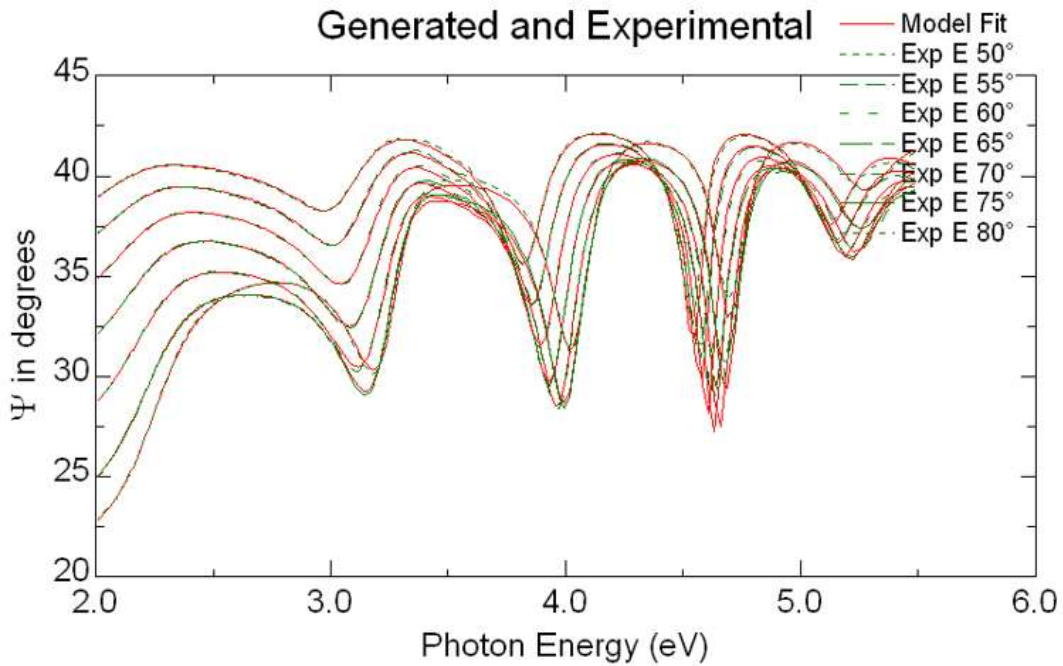|	Final
MSE	10.78
ThkUni	1.8041 ± 0.163
Br1.4	1.8237 ± 0.032
Amp2.4	38.919 ± 2.31
En2.4	2.0489 ± 0.00482
C2.4	1.5127 ± 0.0125
Eg2.4	0.0001 ± 0.039
En3.4	0.0020438 ± 4.11e-005
Br3.4	0.0001 ± 0.000431
Thick.4	11.084 ± 0.208
Thick.3	295.449 ± 0.107
Amp1.4	85.24 ± 2.13
Thick.5	0.520 ± 0.026
Thick.6	8.759 ± 1.16
PoleMag.4	121.99 ± 22
Thick.7	0.000 ± 1.88
PoleMag2.4	0 ± 92

Figure 3.1 Ellipsometric plot. The green curves are measured, the red curves are the plot generated for the given and fitted thickness parameters. Angles given from normal incidence.

To be able to say with confidence that we have correctly characterized the sample using spectroscopic ellipsometry, the various thicknesses in Table 3.1 must make sense and the uncertainties for the parameters in the MSE in Table 3.2 must be within reason. If these two conditions are satisfied, as they are in the above tables, then we look at the graph such as the one provided in Fig 3.1 and confirm that the red fitted curves do indeed follow the green experimentally measured curves. In this case, we see that the thickness of the Al_2O_3 (the oxide growth) is negligent (maybe 0.5 nm), telling us that the protective coating layer is thick enough to prevent oxidation indefinitely.

3.2 SEM Analysis

The data in Fig 3.2 proves chemically that the sample is we have what we expected to create, and that the amount of oxide growth layer is minimal at best. Chemical and structural data obtained via scanning electron microscopy (SEM) coupled with energy-dispersive x-ray spectroscopy (EDS), and in some cases, atomic force microscopy, can be used to constrain which layers are present and their roughness.

Table 3.3   EDAX Smart Quant Results: the program's best guess at how much each element is present in percentages.

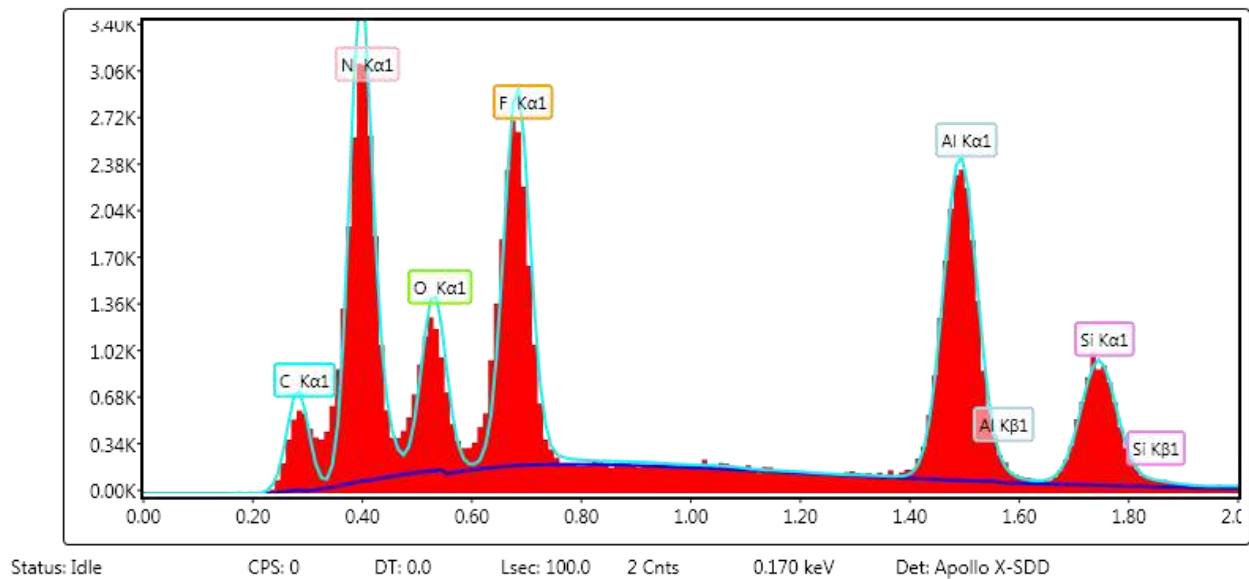| Element	Weight %	Atomic %	Net Int.	Error %	Kratio
C K	3.96	6.44	33.46	11.78	0.0301
N K	34.72	48.34	240.70	9.10	0.3154
O K	2.88	3.51	37.74	11.77	0.0247
F K	0.84	0.86	12.89	16.00	0.0074
AlK	30.58	22.10	197.06	12.58	0.2780
SiK	27.01	18.75	103.96	15.82	0.2442

Figure 3.2 Example of SEM experimental data (red) to fitted model (cyan). Elements in the box above the corresponding peaks. Blue line represents background noise level.

3.3 Discussion

My results are compared to Margaret Miles' data[10]. Margaret showed that a 2.4 nm aluminum fluoride layer does not prevent aluminum from oxidation but does significantly retard the oxide growth – decreasing the oxide layer thickness from 1 nm in less than an hour to 0.9 nm over 116 hours. By contrast, my sample of 9 nm of AlF_3 appears to completely halt the oxidation growth based on our observation of 150-200 hours. The combination of these findings will confirm to NASA the range at which aluminum oxidizes slowly and doesn't oxidize at all.

3.4 Conclusion

We have shown that 9 nm of AlF_3 on bare aluminum is thick enough to retard oxidation growth upwards of 200 hours, and so we assume indefinitely. This is progress for our research group as we continue to find the best optimized mirror for broadband, UV/optical/IR reflectivity.

3.5 Future Work

Future work can be done to further optimize the thickness of the thin film for which Al_2O_3 is completely retarded.

As I mentioned back in section 2.1, future work would be well worth the effort to examine the possibilities of First Contact Opticlean as another protective barrier option against

oxidation on top of the AlF_3 and aluminum. Exploration of the effectiveness of submerging the freshly coated aluminum/AlF_3 in liquid nitrogen as a means of halting oxidation growth should also be researched.

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