

Degradation of Lithium Fluoride Mirror Coatings in Humid Environments

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ABSTRACT

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Lithium fluoride (LiF) has the highest band gap of any solid material and thus has many applications in far ultraviolet (FUV) optics. However, LiF is difficult to work with because of its hygroscopic nature, meaning it can absorb water out of air. Surprisingly, little is known about what happens microscopically and structurally to LiF thin films when exposed to humid air. To shed light on this, LiF was deposited on bare Si wafers by resistive heating evaporation and stored in various levels of humidity. Samples were characterized using variable-angle, spectroscopic ellipsometry (VASE), atomic force microscopy (AFM), scanning electron microscopy (SEM), and energy dispersive x-ray spectroscopy (EDS). Results show that LiF films exposed to a relative humidity (RH) above 90% undergo irreversible changes. These changes include optical properties as determined by VASE, the surface structure as determined by SEM, and the surface roughness as determined by AFM. On the other hand, samples stored at a dew point of -22°C (4% RH room temperature), showed only small changes in ellipsometric constants. The ones stored at intermediate humidity 4°C (21% RH at room temperature) showed larger changes in ellipsometric constants. SEM also showed that deliquescence as well as efflorescence occur in LiF thin films under higher humidity conditions.

Keywords: Fluoride Barrier Layers, Hygroscopic Materials, UV Optical Materials, Aluminum Mirror, Humidity Limits, Storage Procedures, Deliquescence

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Chapter 1

Introduction

The future of space exploration requires unprecedented FUV sensitivity in spectroscopic instrumentation. Astronomical bodies produce more UV energy at the beginning and late stages of their existences. By observing this energy people hope to learn more about the creation of galaxies. But, the ability to collect and learn from this energy is currently restricted by the limitations of reflective telescope mirrors. The selection of any of a number of currently conceptual NASA missions will necessitate the production and use of thin-film mirrors that exceed the current bounds.

Aluminum is the only material which can provide broad-band, IR-optical-UV reflectance. Bare, first-surface aluminum can (theoretically) provide >85% reflectance down to 89 nm. Unfortunately, aluminum will oxidize quickly when exposed to air. Even under high-vacuum conditions, slow loss of vacuum ultraviolet (VUV) reflectance is observed [1]. The aluminum oxide which forms, though only 3.5-5 nm thick, effectively blocks aluminum's high reflectance below 140 nm, which is the point at which sapphire's absorption constant rises above $0.01/\text{nm}^3$. The effects of oxygen on aluminum mirrors are so great that even environments with low oxygen can cause drastic changes. Even aluminum mirrors in low earth orbit will degrade from the low levels of oxygen present [2].

To combat the effects of oxidation, wide-bandgap, metal fluoride thin films have been deposited as a protective coating on the aluminum film before it is exposed to air. Of these fluorides, lithium

fluoride (LiF) has the widest bandgap of 13.6 eV (91.2 nm). It is, however, hygroscopic, meaning it absorbs water out of the air. Its properties as a transparent FUV window degrade over time as more water is absorbed.

1.1 Previous Work

Because of LiF being the most desirable protective layer optically for aluminum, many studies have been conducted in an attempt to optimize these films. It has been reported that depositing the films on a heated substrate and using a coating containing several layers allows the total thicknesses of the fluoride layers to be decreased without sacrificing the barrier properties of the overcoats [3]. This allows the region of high reflectance to be expanded to slightly shorter wavelengths.

Experiments have also been done to quantify the optical degradation of LiF as exposed to different levels of humidity. Two such experiment were done by John Hopkins University as well as a collaboration effort between NASA Goddard, JPL, and several other universities [1, 4]. They both found that FUV reflectance decreased quicker when exposed to higher humidities.

These studies, along with several others, have quantified the optical degradation of LiF coated mirrors. However, little is known about the behavior of LiF films on a microscopic level or if the effects of degradation are reversible, and I aim to correct that. I report on experiments which quantify the changes that occur in a LiF film over time due to its exposure to air at various humidity levels.

The results of this paper have also been published in the SPIE Astronomical Telescopes + Instrumentation 2020 conference proceedings [5]. I was the main author of that paper and I will be extracting from it information for this thesis.

Chapter 2

Experimental

In this chapter, I describe my experiment, including the process of deposition and characterization using spectroscopic ellipsometry, atomic force microscopy, and scanning electron microscopy. Each process has its own limitations, and it was therefore imperative that more than one method was used to characterize the thin film samples.

2.1 Deposition of LiF Layers

This experiment depended largely on creating test samples that would allow me to answer questions about the degradation of the barrier layers. Although it was not necessary to create perfect mirrors for this experiment, it is important to understand the process of deposition, and know where some imperfections may manifest.

All films were deposited using a Veeco thermal evaporator. I hope to improve the use LiF when used as a barrier layer for front surface Al mirrors, but to isolate the effects of humidity on LiF I deposited LiF directly onto substrates cleaved from polished Si wafers. These substrates were nominally 2×2.5 cm. As mentioned in Section 1.1 LiF deposited on hot substrates exhibits improved surface smoothness and increased FUV transparency [1,3]. To accomplish this, substrates

were attached to a substrate heater. This heater consisted of several thin rectangular 12 V resistive heaters mounted side-by-side on a thin insulating plate which was in turn mounted to a larger platen positioned in the top of the evaporator chamber. There was a gap of about 6 mm between the substrate heater assembly and the platen. Aluminum foil was placed in this gap to block radiative heat transfer to the platen from this heater assembly. The platen was then placed back into the deposition and the chamber was evacuated for approximately three hours before beginning the deposition. The chamber achieves a base pressure in the low 10^{-6} torr range.

The substrate heaters were then turned on, reaching a temperature of about 220° C in about 5 minutes. Shutters and an Inficon quartz-crystal thickness monitor (QCM) allowed for precise control of film deposition (± 2 nm of desired thickness). By changing the voltage across the LiF boat, a deposition rate of 0.7 Å/sec as measured by the QCM was achieved. The shutter between the boat and substrates was then opened, and a nominal 180 Å LiF was deposited onto the substrates.

Immediately following the depositions, the chamber was vented and samples were removed. Afterwards they were promptly characterized in the John A Woollam M-200 Variable-Angle, spectroscopic ellipsometer. Measures to limit exposure to atmosphere between deposition and initial characterization were made. Because of limited availability, initial measurements of surface roughness using atomic force microscopy (AFM) took place within several days after deposition.

2.2 Sample Aging in Humidity

After initial characterization using ellipsometry, samples were moved to controlled humidity environments for studying aging. Four desiccators with different substances to control humidity were used while one sample was remained in open air as a control. In one desiccator fresh desiccant was used to establish a very low humidity environment. In two others, desiccant that had been exposed to different amounts of water vapor was used to create two different mid-range humidities.

Environment	Average Relative Humidity %	Average Temperature	Dew Point
Fresh Desiccant	4%	21 °C	-22 °C
Aged Desiccant	30.2%	21.5 °C	4 °C
Open Air	37.3%	21.6 °C	6 °C
Desiccant soaked in water	39.3%	21 °C	6 °C
Humidity Pillow	69.3%	21.3 °C	15 °C

Table 2.1 Humidity environments with descriptions of environment and averaged measured humidity and temperature data along with calculated dew point.

In the fourth desiccator, a cigar box humidification pillow was used to create a controlled high humidity environment. The humidity and temperature levels were measured for the duration of the experiment, averaged, and can be seen in Table 2.1.

The humidity in open air changed much more than in other environments. Open air had RH (relative humidity values as low as 21% and as high as 43%. All other environments deviated by $\pm 1\%$ in RH from their average humidity. Because all samples were kept within the lab, temperature remained mostly constant for all samples, only deviating by $\pm 1^\circ\text{C}$.

Since for the same water vapor partial pressure, the RH depends on temperature, I find it more informative to report data in relation to dew point. For this reason, in the remainder of this paper the various samples storage environment will be referenced to by its dew point. However, the correlating RH can be found in Table 2.1.

2.3 Ellipsometric characterization

Ellipsometric data was acquired using a J.A. Woollam M-2000, variable-angle, spectroscopic ellipsometer (J.A. Woollam Company, Lincoln, ME, USA) over the wavelength range of 190-1688 nm. The ellipsometer acquired Δ and Ψ data at 65° , 70° , and 75° . Measurements were taken intermittently over the space of 64 days. Data was subsequently modeled using the CompleteEASE[®] SE instrument analysis software. The optical constants for all layers were modeled with the optical

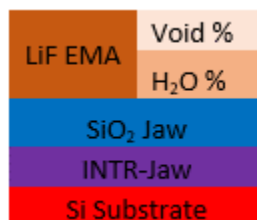


Figure 2.1 Film stack used in CompleteEASE ellipsometric modeling. It demonstrates the order of different film layers.

constants in the CompleteEASE[®] database; specifically, these were Si-JAW, SiO₂ JAW (silicon native oxide), and LiF (Sellmeier model).

Prior to the deposition, the thickness of native oxides present on each substrates was determined ellipsometrically. Measurements were modeled with a simple bilayer of SiO₂ on Si. The fitted SiO₂ thickness was then held constant in modeling all data after LiF was deposited onto the substrates.

Changes in Ψ for samples stored in different conditions are illustrated in Fig. 2.2. It can be seen that optical changes are occurring in samples stored in even the best conditions but with much larger changes occurring in samples stored in higher humidities, as expected. However, in all samples these changes are more pronounced in the highest energy (UV portion).

In VASE analysis, it is customary to create an optical model of the films and to fit thickness etc. to attempt to capture what such changes could mean. Since LiF is hygroscopic, it is natural to try to add the effect of water on the LiF. An effective median approximation (EMA) was thus used to attempt to understand the changes in the LiF with time. The EMA employed is the Bruggeman approximation. The possibility of voids was also included in the EMA layer. A schematic of the film stack used in modeling is shown in Fig. 2.1. Because the index of water is similar to LiF, attempts to model and quantify the changes in layer thickness were unsatisfactory. To achieve better quantification of changes in the sample composition, other tools, such as SEM, were necessary.

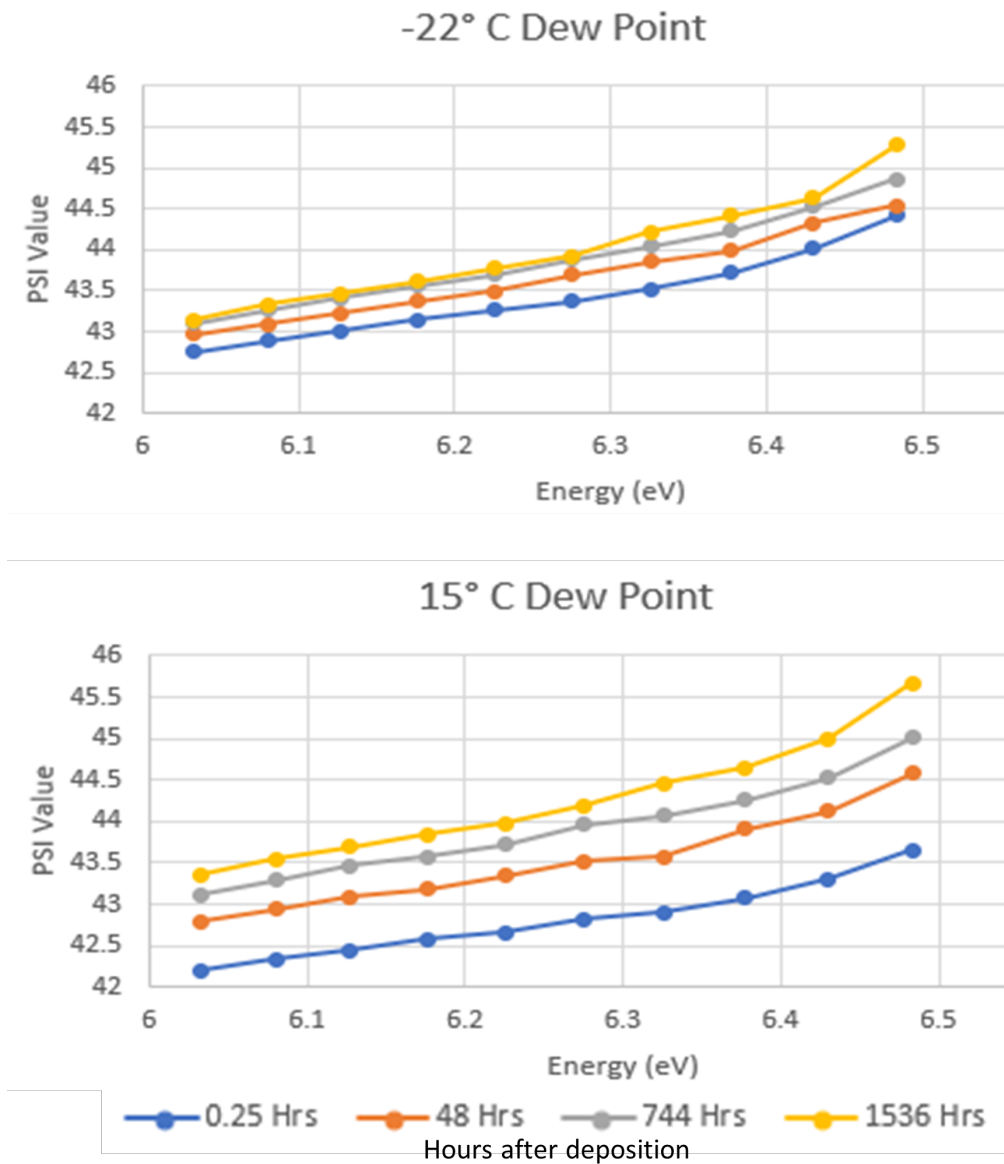


Figure 2.2 Ψ data for sample stored in -22° C dew point and 15° C dew point. Even though the range of data taken extends from 0.8-6.5 eV only 6-6.5 eV is shown to better highlight the changes. In all images Ψ data are increasing over time. The earliest measurements are the lowest values with the most recent being higher.

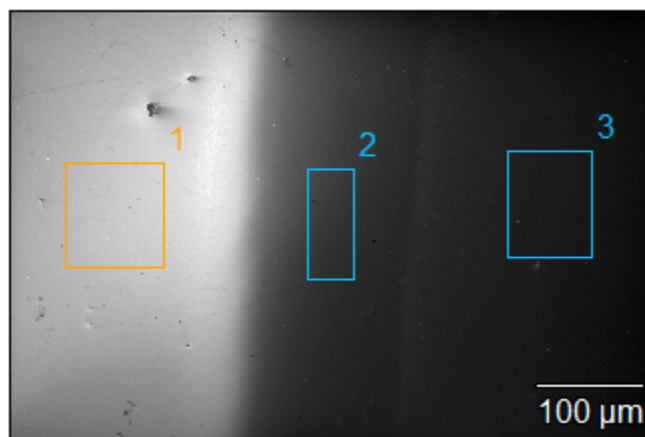


Figure 2.3 SEM image of sample stored in an environment of -22°C dew point. The image was taken with beam energy 3 keV. The three labeled rectangles are areas where EDS was performed (see Fig. 2.4).

2.4 SEM Characterization

The SEM used was a ThermoScientific Verios G4 UC SEM with an attached EDAX energy-dispersive X-ray (EDX) analyzer a ThermoScientific Pathfinder XEDS System add on. The XEDS attachment allowed for energy dispersive x-ray spectroscopy (EDS) of samples and for quantification of the different elements within the film. Because lithium and hydrogen do not produce x-rays EDS cannot detect them. Materials such as H_2O and LiF were quantified using oxygen and fluorine characteristic x-rays, respectively. EDS was performed on the samples stored in -22°C and 15°C dew point environments. Fig. 2.3 is an SEM image of the -22°C sample. The color differentiation are shadows arising from clips in the deposition chamber that held the substrate to the platen. These prevented LiF from being deposited in the darker regions. EDS was performed separately on each of the rectangles shown in Fig. 2.3. The data collected provides the number of characteristic x-rays from each section. Fig. 2.4 shows the comparison of counts between area 1 and area 3 of Fig. 2.3.

As was expected, no fluorine is present in section 3. However, an unforeseen problem arose when oxygen counts did not go to zero. This situation makes it difficult to accurately quantify

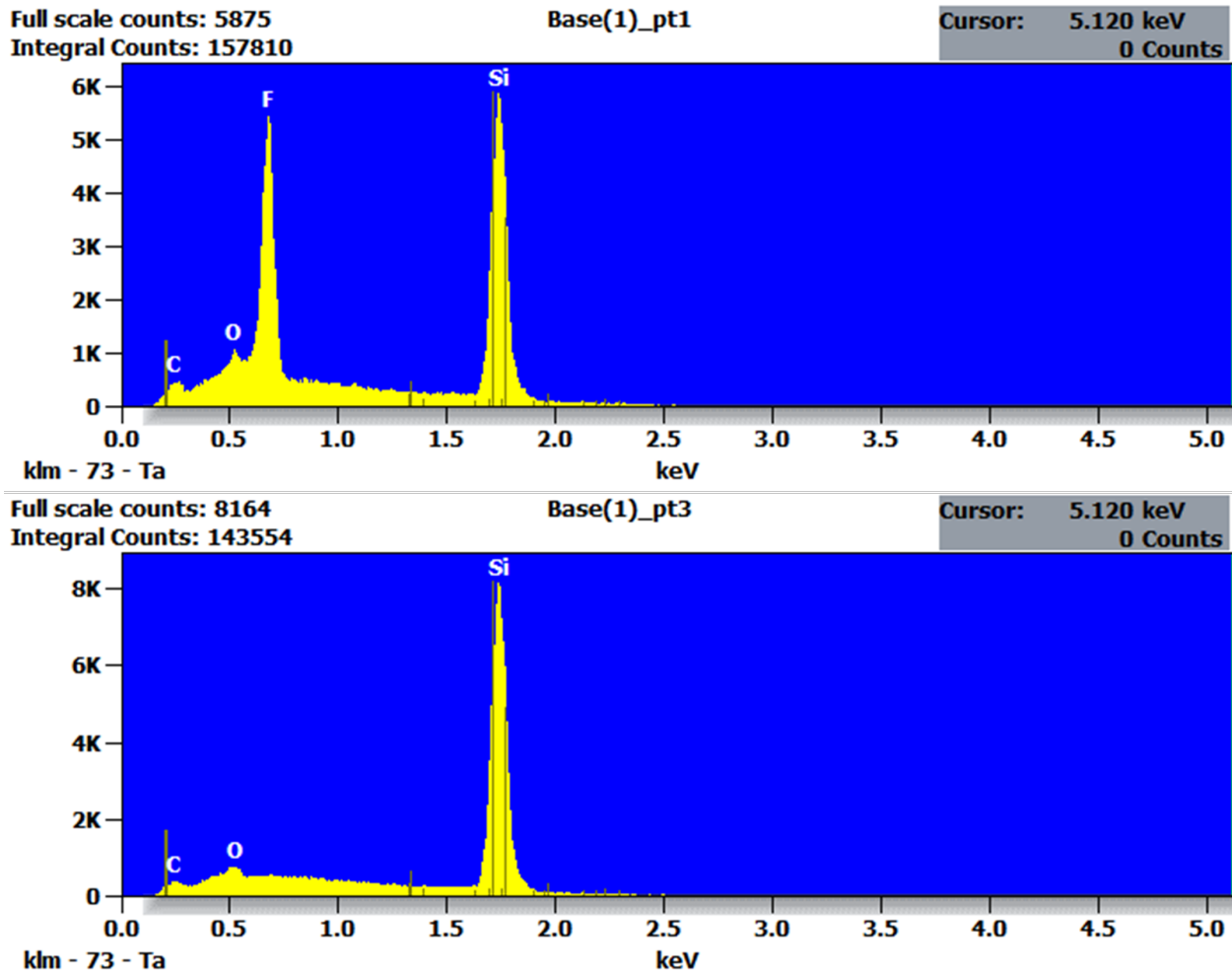


Figure 2.4 EDS counts of the sample from Fig. 2.3. The top shows the counts from area 1 and the bottom shows the counts for area 3. The results of area 2 are intermediate between the counts of regions 1 and 3 and are not displayed in this paper.

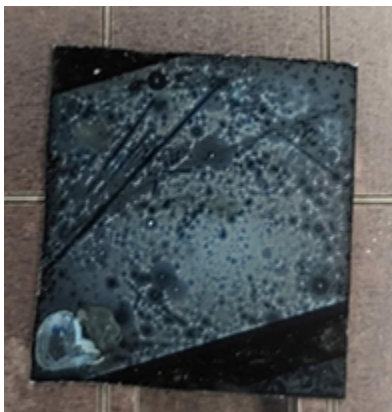


Figure 2.5 LiF on Si wafer stored in a water saturated environment for a week.

changes in oxygen levels between samples because one cannot rule out the possibility that more native SiO_2 has formed or that the amount of SiO_2 is constant across the sample.

The most reliable way to quantify the water in the LiF film is to deposit LiF onto a substrate that won't oxidize. That cannot be a bare Si wafer, because native oxide inevitably forms on Si substrates. It was decided that gold would be the most viable option for this objective. Following a similar deposition process to the LiF deposition, around 26 nm of gold was deposited onto a 20 cm Si wafer. 2×2.5 cm samples were then cleaved and approximately 18 nm of LiF was deposited onto these substrates following the same deposition process for LiF. Samples were again stored in the previously described controlled humidity environments.

After a day of controlled storage, the samples under -22°C and 15°C dew point storage conditions were characterized using EDS. By making measurements with a beam energy of 2 keV the interaction volume was confined to the gold and LiF layers. This was verified by a lack of characteristic Si x-rays detected. 6.31% of detected x-rays were oxygen in the 15°C dew point sample and respectively 5.62% in the -22°C dew point sample. This shows the expected trend of higher water absorption in higher humidity environments.

To better understand the structural changes of LiF films, several samples were made following the same deposition process on Si wafers and allowed to age in 99% RH until complete film failure.

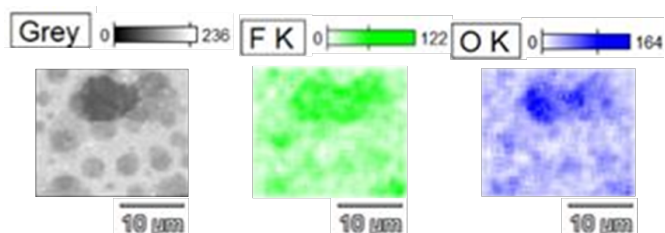


Figure 2.6 (Left) grayscale SEM image of area observed with EDS, (Middle) EDS image showing concentrations of Fluorine counts across the defined region of the sample, (Right) EDS image showing concentrations of oxygen counts.

After a week in this environment, the resulting film failure is visible on the sample surface as seen in Fig. 2.5. The broad stripes seen at the top and bottom of the figure are shadows where there is no LiF. Clips which held the substrate to the sample stage during deposition prevented LiF from being deposited in those areas. These stripes seem relatively unaltered compared to the middle section where LiF is present. Closer inspection of the EDS image revealed that the LiF film is no longer uniform or even continuous across the surface. Fig. 2.6 shows that LiF has pulled together, creating pockets of a higher concentration of LiF and water. This failed sample successfully demonstrates that LiF's affinity for water can compromise the integrity of thin-film LiF. This is an example of deliquescence. The moisture that the film pulls out of the air dissolves the film, allowing concentrations of LiF to shift and pool together. When the sample is removed to a reduced humidity environment, water evaporates off the sample, leaving the surface in a new blotchy state. This process, called efflorescence, is comparable to salt water evaporating from a moist area, leaving a surface with scattered white streaks.

To ensure that these changes were consistent across samples without native oxides as mentioned above, the experiment was repeated on gold, a material that does not oxidize or absorb water. An initial gold layer was deposited on a Si wafer before the LiF deposition took place. Measures were taken to ensure the gold layer would be thick enough so the interaction volume of the electron beam did not go through to the native SiO_2 . Afterwards, LiF-coated samples were subjected to

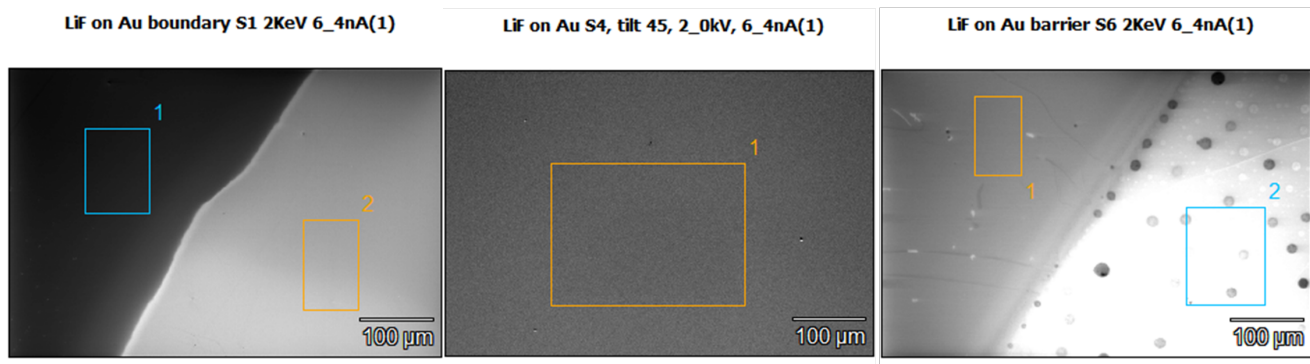


Figure 2.7 The darker left side (left and right) is the area of the sample with only gold whereas the right side is LiF on gold. The middle sample is entirely LiF on gold. (Left) stored in -22°C dew point, (Middle) stored in 15°C dew point, (Right) stored in 99% RH.

the humidity aging process. Visually, a similar pattern of circles is seen across the surface of the sample in a saturated environment as displayed in Fig. 2.7. This pattern only seems to occur in samples exposed to extreme levels of saturation. This observation further supports the observation that deliquescent materials have a tipping point RH above which total material failure occurs. EDS analysis of the dark regions on the failed sample and the regions immediately surrounding them showed that there was often evidence of carbon-based particles in the centers of these pool-like structures.

EDS analysis was performed on the dark circles of the 99% RH sample to elucidate their composition. The analyzed areas are shown in Fig. 2.8. Region 2 in that image highlights a particle-like structure in the center of the circle. The EDS done in Fig. 2.9 shows that this particle is sodium and carbon based, or in other words, foreign to the film. This feature was seen in many of the surrounding circles. It is possible that particles accumulating on the film surface stimulate water accumulation and film degradation.

Further observation of Fig. 2.8 and Fig. 2.9 show that LiF counts are low to none outside of these dark circles. This further supports the idea that LiF pools together once it experience total deliquescence. Ostwald ripening or related phenomena might be the mechanism but needs to be

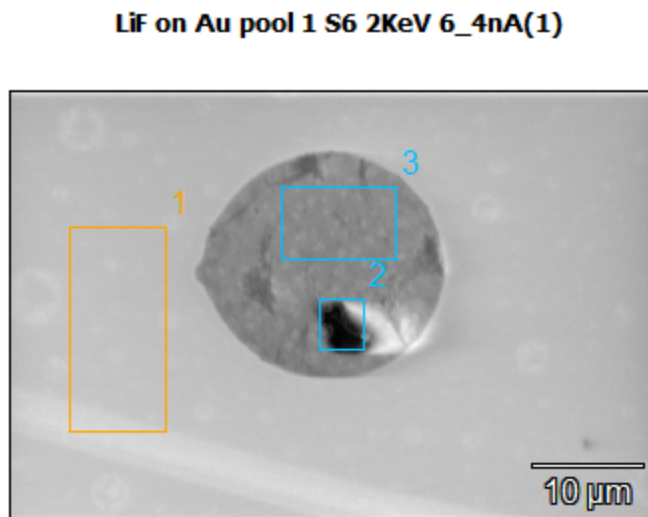


Figure 2.8 This is a zoomed in image of one of the dark pools seen in the failed sample of Fig. 2.7. EDS counts for region 1 and 2 can be seen in Fig. 2.9.

further investigated.

2.5 AFM Characterization

To understand overall changes of surface structure for each sample over time, samples were measured on an atomic force microscope (AFM) after deposition and then again about three months later. This quantifies changes in surface roughness due to changes in the LiF film.

The AFM produces a root mean square (RMS) roughness value that is used as the standard value for roughness. Measurements were made in three separate areas of each sample to study surface uniformity. The averages of the RMS measurements is shown in Fig. 2.2. The change in roughness for the sample stored in -22°C dew point is essentially 0. The roughness at three months is slightly smaller than its initial measurement but the difference is so small that it is within measurement error bars.

The time delay between deposition and initial characterization was a concern. Because of

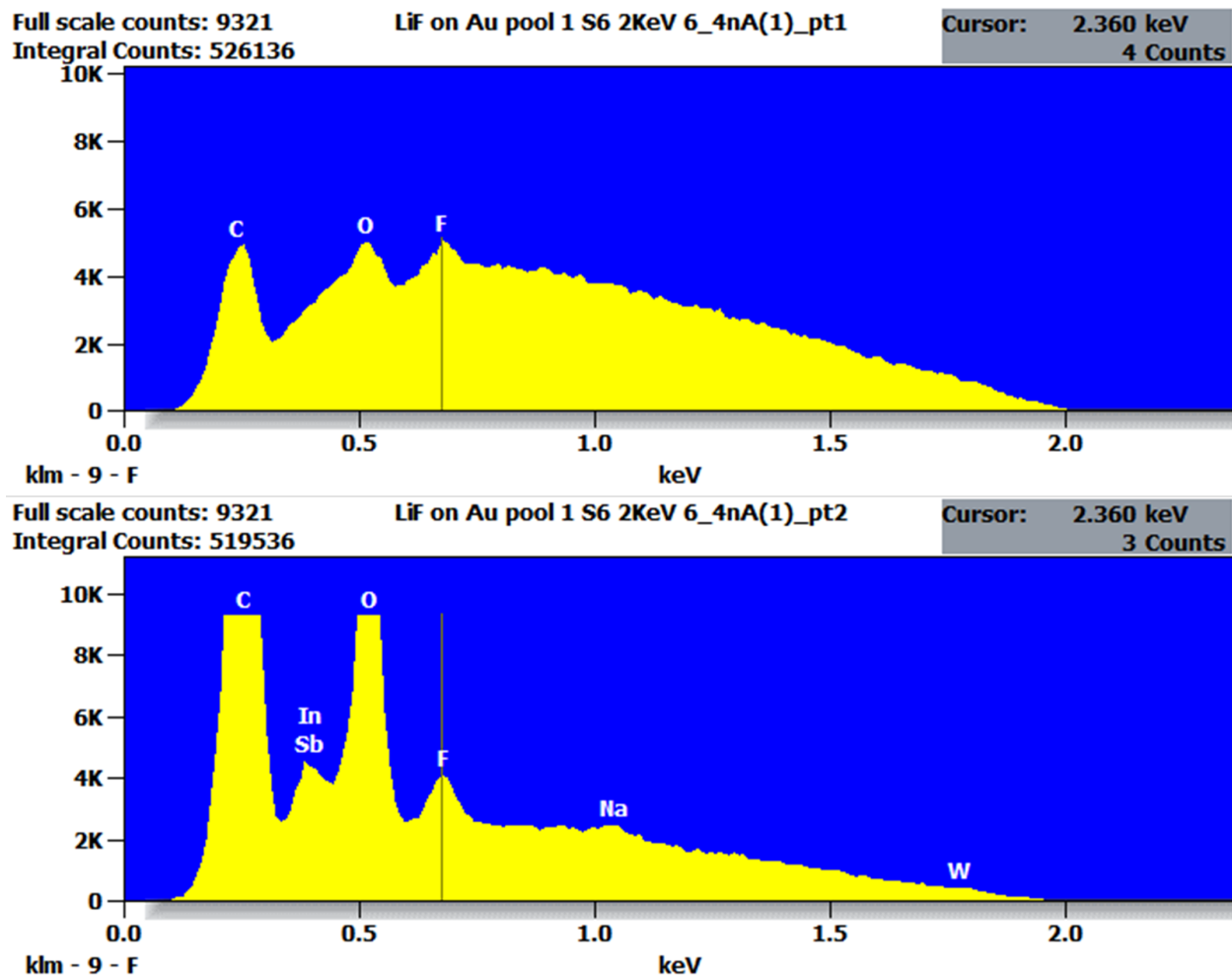


Figure 2.9 The top image corresponds with region 1 in Fig. 2.8 and the bottom corresponds with region 2.

Storage Dew Point	Roughness After Deposition	Roughness After ~80 days	Net Change
-22 °C	1.38±0.08 nm	1.26±0.07 nm	-0.12 nm
4 °C	1.55±0.36 nm	1.99±0.08 nm	0.44 nm
6 °C open air	2.89±0.59 nm	4.67±0.47 nm	1.78 nm
6 °C controlled humidior	1.07±0.02 nm	1.28±0.11 nm	0.21 nm
15 °C	0.9±0.09 nm	3.92±0.65 nm	3.01 nm

Table 2.2 AFM data of each sample taken within a week of sample deposition and then again approximately 90 days later.

equipment limitations not all samples were measured on the day of deposition and some were measured as much as several days later. This gave some samples time to change before an initial measurement could be taken. This could account for the much larger starting RMS roughness of the sample stored in open air with the dew point of 6° C. As mentioned in section 2.2, because it was stored in open lab air, it was subject to drastic humidity fluctuations. This could account for the large change in roughness observed.

Chapter 3

Discussion of Results

The experiment used a number of characterization methods to probe the hygroscopic limits of LiF films at room temperature. As was expected, if the dew point is low enough, here found to be $< 6^{\circ}\text{C}$, changes were negligible. However, at $> 6^{\circ}\text{C}$ (see the 15°C dew point sample, for example) the samples roughened significantly and for samples exposed to saturated air (99% humidity) the LiF is drastically altered. The LiF bunches up leaving a large fraction of the surface uncoated. Large features surrounded by regions lacking LiF are seen. I suggest that there is a critical humidity level at which total film failure occurs. This was seen in AFM data as a large increase in surface roughness and in SEM with the formation of dark circles on the sample (Fig. 2.5). How this depends on environmental temperature should be investigated.

This data may be especially important in areas with periodic high humidity such as Maryland, Virginia, Texas, Alabama, and Florida in the U.S. where it is not unusual to experience dew points above 15°C . In order to construct functional LiF thin film mirrors that may be used for spectroscopic instrumentation, the humidity in the environment must be controlled. In future work I hope to identify at what point this total film failure actually happens. Furthermore, I would like to quantify the effect of the film failure on its abilities to reflect in the far ultraviolet by depositing LiF on Al mirrors.

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