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Illuminating the Degradation of Lithium Fluoride Mirror Coatings in Humid Environments

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ABSTRACT

Lithium fluoride (LiF) has the highest band gap of any solid material and thus find applications in far ultraviolet (FUV) optics. However, LiF is difficult to work with because of its hygroscopic nature, it can absorb water out of air. Surprisingly, little is known about what happens microscopically and the behavior of LiF thin films exposed in humid air. To shed light on this, LiF on bare Si wafers were deposited by resistive heating evaporation. Samples were then stored in various levels of humidity and were characterized using variable-angle, spectroscopic ellipsometry (VASE), atomic force microscopy (AFM), and scanning electron microscopy (SEM). When exposed to a relative humidity (RH) above 90%, LiF films undergo irreversible changes. The optical properties as determined by VASE and the structure as determined by SEM, irreversibly change. On the other hand, samples stored at a dew point of 250 K (4% RH room temperature), showed only small changes in ellipsometric constants. The ones stored at intermediate humidity 270 K (21% RH at room temperature) showed larger changes in ellipsometric constants. SEM showed that deliquescence as well as efflorescence is important in LiF thin films. In situ spectroscopic ellipsometric measurements using a controlled variable humidity environment showed a point at which changes in LiF moved from moisture absorption to complete deliquescence.

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

1. INTRODUCTION

The future of space exploration requires unprecedented UV sensitivity in spectroscopic instrumentation. A number of conceptual NASA missions will necessitate the production and use of thin film mirrors that meet that requirement. Lithium fluoride (LiF) barrier layers on aluminum substrates have proved promising for reflecting FUV wavelengths. However, LiF is hygroscopic and its properties as a transparent FUV window can be compromised. Furthermore, little is known about the behavior of LiF films in a human environment on a microscopic level, and we aim to correct that. Particularly, we wish to know how LiF is affected by humidity. We 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.

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 and >90% over most of the 0-14 eV range. Unfortunately, aluminum will oxidize quickly when exposed to air. Even under high-vacuum conditions, slow loss of vacuum ultraviolet (VUV) reflectance is observed [2]. 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 $0.01/\text{nm}^3$.

To overcome this difficulty, wide-bandgap, metal fluoride thin films have been deposited on the aluminum film before it is exposed to air. Of these, lithium fluoride has the widest bandgap of 13.6 eV (91.2nm). It is, however, hygroscopic and there are conditions where it cannot protect the aluminum for long periods of time. It also 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[4]. This allows the region of high reflectance to be expanded to slightly shorter wavelengths.

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2. EXPERIMENTAL

In this section, we will describe our 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

Our experiment depended largely on creating test samples that would allow us to answer scientific 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. LiF is often used as a barrier layer for front surface Al mirrors, but to isolate the effects of humidity on LiF by itself, LiF deposited onto substrates cleaved from polished Si wafers was the first study. These substrates were c.a. 2 x 2.5 cm. LiF deposited on hot substrates improves LiF surface smoothness and increases far UV transparency.[1,2] To accomplish this, substrates were attached to a substrate heater. This heater consisted of several thin rectangular 12V resistive heaters mounted side-by-side on a thin insulating plate which was in turn mounted to a larger platen which was 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 for this heater assembly. The platen was then placed back into the deposition and the chamber was evacuated for approximately 3 hours before beginning the deposition. It reaches a base pressure in the low 10^{-6} torr range.

The substrate heaters were then turned on, achieving 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. 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 with N_2. After samples were removed 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 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 and a sample was stored 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. In the fourth desiccator, a cigar box humidity 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 Fig. 1.

The humidity in open air changed much more than in other environments. It had RH (relative humidity values as low as 21% and as high as 43%. All other environments deviated in RH by +/- 1% from their average humidity. Because all samples were kept within the lab, temperature remained mostly constant for all samples, only deviating by +/- 1° C.

Because RH changes based on temperature conditions, we find it more informative to report data in relation to dew point. For this reason, the remainder of this paper will refer to the different samples by what dew point their storage environment was, but the correlating RH can be found in figure 1.

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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

Figure 1. Humidity environments with descriptions of environment and averaged measured humidity and temperature data along with calculated dew point.

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 delta and psi 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 constants in the CompleteEASE®database; specifically, these were Si-JAW, SiO_2 JAW (silicon native oxide), and LiF (Sellmeier model).

Prior to the deposition, all substrates were characterized on the ellipsometer in order to quantify the thickness of native oxides present. The measurements were then modeled with a simple bilayer of SiO_2 on Si. The fitted SiO_2 thickness was then held constant in modeling all data after LiF was deposited onto the substrates.

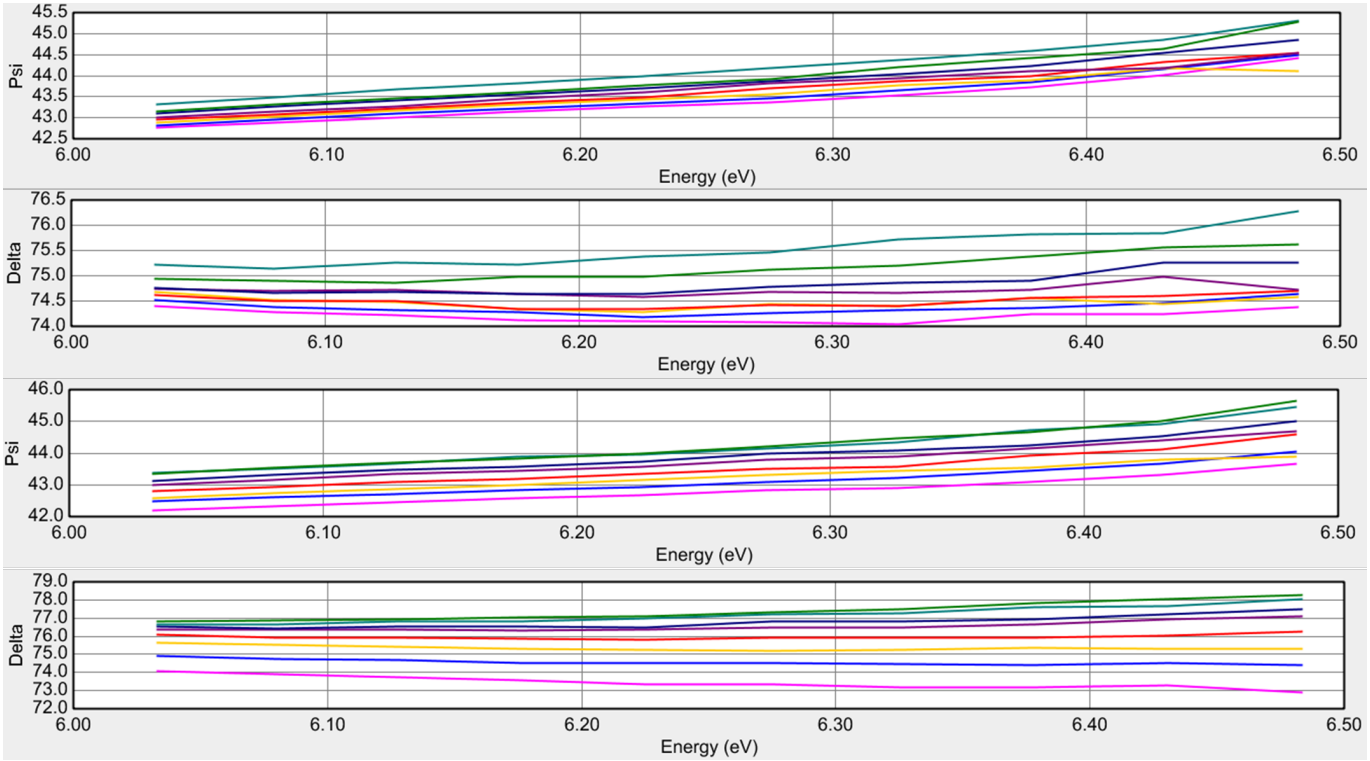


Figure 2. Delta and Psi data for sample stored in -22° C dew point (top Psi, second to top delta) and 15° C dew point (third Psi, bottom delta) over the energy range 6-6.5 eV. In all images delta and psi data are increasing over time. The earliest measurements are the lowest values with the most recent being higher.

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Changes in psi and delta for samples stored in different conditions are illustrated in figure 2. It shows 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).

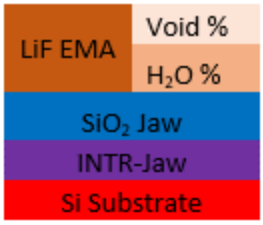


Figure 3. Film stack used in CompleteEASE ellipsometric modeling

In VASE 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 use 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 Figure 3. Because the index of water is similar to LiF, attempts to quantify the gradual changes in the psi and delta are unsatisfactory. To achieve better quantification of changes in the sample composition, other tools, such as SEM, are necessary.

2.4 SEM Characterization

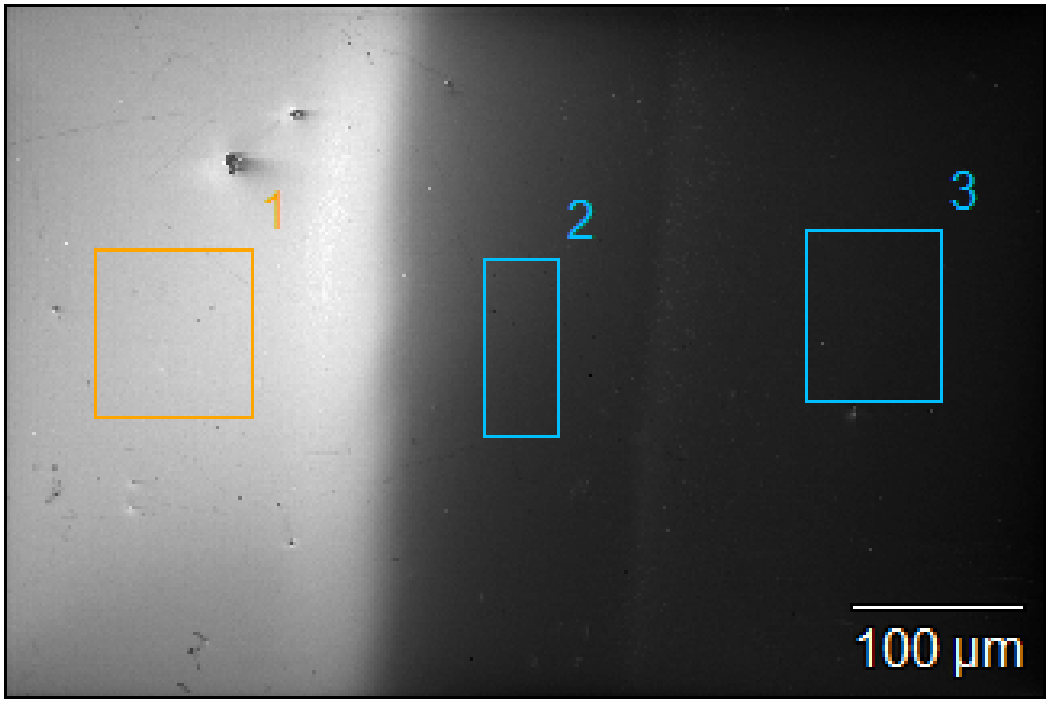


Figure 4. SEM image of sample stored in an environment of -22° C dew point. The image was taken with beam energy 3 keV. The three labeled rectangles are regions where EDS was performed (see figure 5).

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.

EDS was performed on the samples stored in -22° C and 15° C dew point environments. Figure 4 is an SEM image of the -22° C sample. The color differentiation comes from clips in the deposition chamber that were

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holding the substrate to the platen. It prevented LiF from being deposited in the darker regions. EDS was performed separately on each of the rectangles shown in figure 4. The data collected provides the number of characteristic x-rays from each section. Figure 5 shows the comparison of counts between area 1 and area 3 of Figure 4.

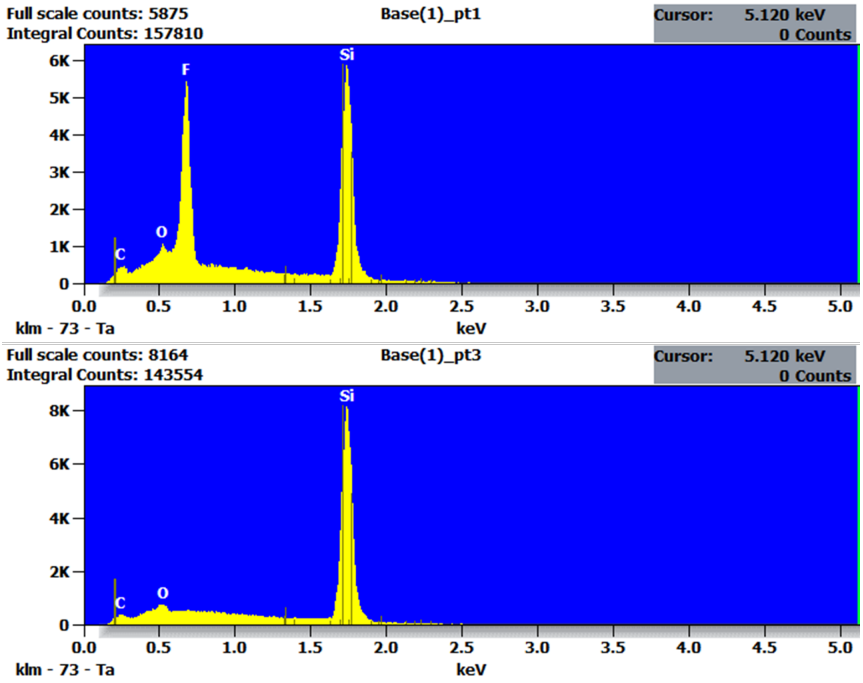


Figure 5. EDS counts of the sample from figure 4. The top shows the counts from rectangle 1 and the bottom shows the counts for rectangle 3. The results of rectangle 2 are intermediate between the counts of regions 1 and 3 and are not displayed in this paper.

As was expected, no fluorine is present in section 3. However, an unforeseen problem arose when oxygen counts didn't go to zero. This will make it difficult to accurately quantify changes in oxygen levels between samples because we can't rule out the possibility that more native SiO_2 is forming 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 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. 2x2.5 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 2KeV 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. After a week in this environment, the resulting film failure is visible on the sample surface as seen in Figure 6. The broad stripes seen at the top and bottom of the figure are where clips held the substrate to the sample stage during deposition. These clips prevented LiF from being deposited in those areas. These stripes seem relatively unaltered compared

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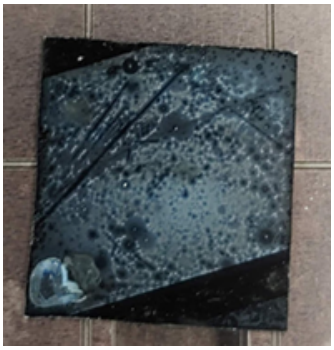


Figure 6. LiF on Si wafer stored in a water saturated environment for a week.

to the middle section where LiF is present. Closer inspection through EDS revealed that the uniformity of the surface is compromised. Figure 7 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 compromises the integrity of the sample surface.

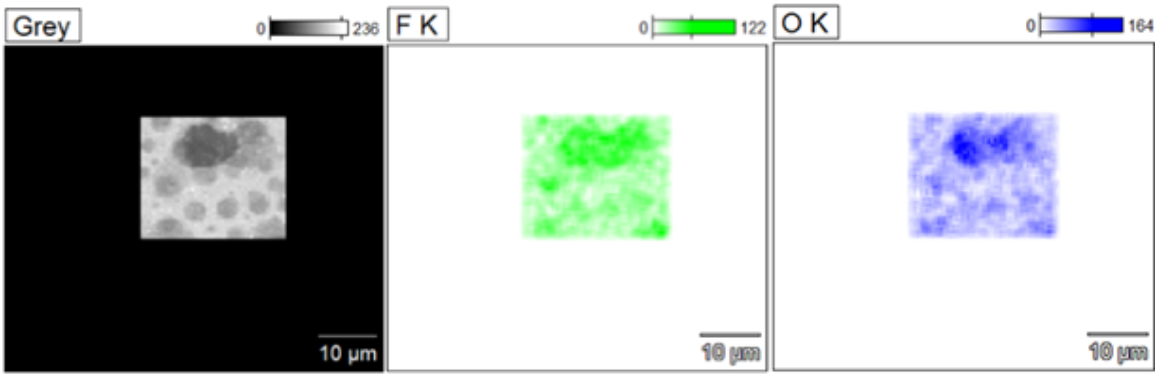


Figure 7. (Left) grayscale SEM image of area observed with EDS, (Middle) EDS image showing concentrations of Fluorine counts across the defined region of the sample, (Right) EDS image showing concentrations of oxygen counts.

To ensure that these changes were consistent across samples without native oxides, this was repeated on gold. Visually, a similar pattern of circles is seen across the surface as displayed in Figure 8 which only seems to occur in samples exposed to extreme levels of saturation. This further supports the trend in deliquescent materials to have a tipping point RH where total material failure occurs. Further investigation was then done on the dark regions of the sample to understand its composition.

Further EDS investigation was done on the dark circles of the 99% RH sample to understand their composition. In many of the circles there is a darker region which EDS reveals to be an organic compound. It is possible that particles accumulating on the film surface stimulate water accumulation and film degradation.

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 our 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 Figure 9. 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

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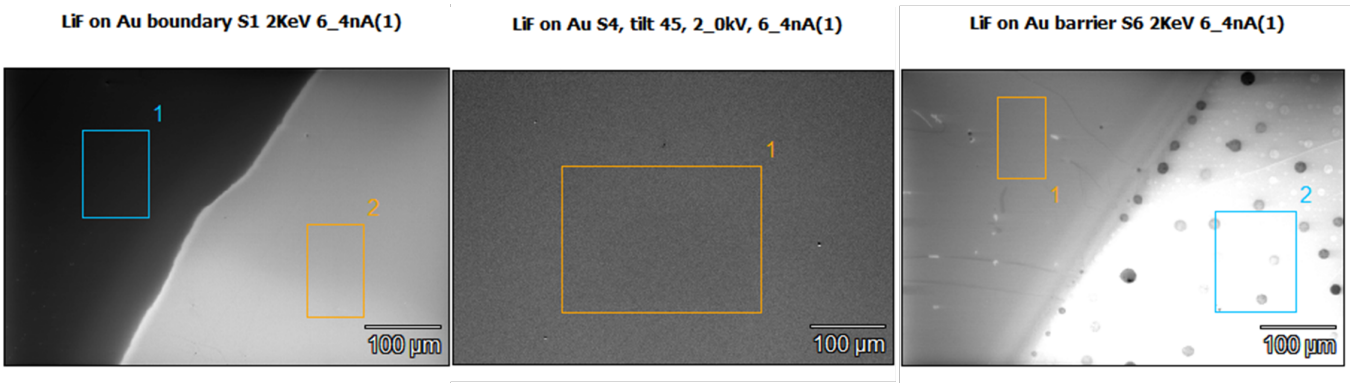


Figure 8. The darker left side (left and right) is the area of the sample with only gold whereas the right side is LiF on gold. The middle sample is entirely LiF on gold. (Left) stored in -22° C dew point, (Middle) stored in 15° C dew point, (Right) stored in 99% RH.

but the difference is so small that it is within the error bars. The time delay between deposition and initial characterization was the source of a concern. Because of 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.

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 humidor	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

Figure 9. AFM data of each sample taken within a week of sample deposition and then again approximately 90 days later.

3. SUMMARY

Our experiment used a number of characterization methods to probe the hygroscopic limits at room temperature of LiF films. As we expected, if the dew point is low enough-here found to be <6°- changes were minor at most. However at >6°C- see the 15° C dew point sample, for example- the samples were observed to roughen and for sample exposed to saturated air (99% humidity) the LiF is drastically altered. The thin film nature of the coating vanishes. Large features surrounded by regions lacking LiF are seen. We 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. 6). 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 are not uncommon. 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 we hope to identify at what point this total film failure actually happens. Furthermore, we would like to quantify the effect of the film failure on its abilities to reflect in the far ultraviolet.

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