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Stability of lithium fluoride thin films as a function of humidity and temperature

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ABSTRACT

Aluminum mirrors protected by metal fluoride overcoats are crucial for FUV observations. Many contemplated missions specify optics elements with high reflectance down to 103 nm (Lyman beta). Lithium fluoride (LiF) has the highest band gap of any solid material and thus finds applications in FUV optics. However, LiF is difficult to work with because of its hygroscopic nature. The instability of these films was investigated by evaporating LiF onto silicon wafers and aging in environments with different relative humidities and temperatures. Samples were characterized using variable-angle spectroscopic ellipsometry (VASE) and atomic force microscopy (AFM). From these methods we found that storing LiF in a hot environment improved sample surface stability, and that in dry, hot environments, surfaces became more smooth after many hours in storage.

Keywords: lithium fluoride, aluminum mirror, protective coatings, hygroscopic, atomic force microscopy

1. INTRODUCTION

Aluminum (Al) has the highest plasma frequency among metals and is thus very useful in ultraviolet (UV) optics.[1] However, Al oxidizes when exposed to atmosphere, creating a film of aluminum oxide (Al_2O_3) opaque to the far UV range shorter than 140 nm.[2] To protect Al mirrors from oxidation and to maintain high reflectance, thin-film metal fluoride barrier layers are applied in situ. Among these, lithium fluoride (LiF) has the widest bandgap and can enable measurements at shorter wavelengths. However, due to its hygroscopic nature, LiF films visibly degrade when exposed to high humidity. At higher humidities LiF has been found to dissolve and redistribute across the surface of the sample.[3]

To further understand if the degradation of LiF films is dependent purely on water content in the air, which can be measured by dew point, we aged and characterized LiF films on silicon (Si) wafer pieces in environments with varying humidity and temperature. To avoid the complexity of LiF recrystallisation with Al_2O_3 and isolate the changes of LiF, this experiment was done only on bare Si.

1.1 Vocabulary

Since the vocabulary of processes these films experience may be unfamiliar to many, we begin with definitions.

Absorption: The collection of water within the body of a material/object.

Adsorption: The collection of water onto the surface of a material/object.

Capillary Action: Capillarity in small pores produces a pressure jump that can allow water to exist in vacuum-figure and equations. The Young-Laplace equation "describes the capillary pressure difference sustained across the interface between two static fluids, such as water and vacuum.".[4]

A conservative estimate of the jump in pressure going into the liquid phase is found using equations 1 and 2 with a contact angle $\vartheta = 45°$, a capillary radius a = 20 nm, and water's 20°C surface tension $\gamma = 0.0728$ N/m. $\Delta p = 5.1 \times 10^6$ Pa, or 50 atm. ϑ and γ need to be determined experimentally, as ϑ is not known and a saturated solution of LiF in water may alter ϑ and γ. The variable of these equations are also shown in Fig. 1. The large pressure jump is what causes pores and valleys in surfaces to fill up with water and is the driving force for LiF's

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hygroscopicity. This water dissolves some LiF and becomes a mode of crystal regrowth for LiF making up the film.

$$\Delta p = \frac{2\gamma}{R} \tag{1}$$

$$\Delta p = \frac{2\gamma \cos\theta}{a} \tag{2}$$

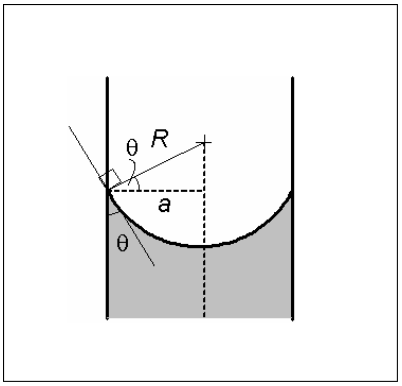


Figure 1. "Spherical meniscus with wetting angle less than 90°"[5]

Deliquescence: The tendency of a solid to adsorb moisture from the ambient atmosphere and dissolve in the condensed liquid. This is often seen with food coatings like the liquefaction of a doughnut's glaze in high humidity.

Efflorescence: Formation/deposition of solids left behind when water containing the solids evaporates . An example is the mineral deposits on rocks in dry regions.

Hygroscopcity: The tendency for a material to pull water out of the air.

Ostwald Ripening: "Ostwald ripening is the phenomena in which smaller particles in solution dissolve and deposit on larger particles in order to reach a more thermodynamically stable state wherein the surface to area ratio is minimized".[6]

Partial Pressure (PP): The pressure that a gas would provide if it alone occupied a given volume. The ambient pressure is the sum of all partial pressures of all gases present.

Rayleigh scattering: Preferential scattering of higher energy light lending a blue hue to a material/object.

Relative Humidity (RH): The ratio of the partial pressure of water vapor to the vapor pressure of water in the local environment. Since both water's VP and PP are functions of temperature, RH values are in turn functions of temperature.

Vapor Pressure (VP): The pressure driving evaporation. VP is a function of temperature, and the higher the VP of a substance, the faster it evaporates.

2. EXPERIMENTAL

We deposited LiF films onto silicon wafer pieces using a Veeco® thermal evaporator. We did not deposit LiF on aluminum in order to minimize complicating factors, primarily, the oxidation of the aluminum film at the same time the fluoride film was changing. Prior to deposition, substrates were heated to 220° C to improve the uniformity of deposited material. Once the desired temperature was reached, LiF was evaporated at a rate of 0.3 Å/s which was monitored using an Inficon® quartz-crystal thickness monitor. The resulting films were

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nominally 18 to 20 nm thick. This thickness is optimal for enhancing reflectance of FUV mirrors in the Lyman β range.[7]

Samples were then placed in various environments with different levels of humidity and temperature. The list of all conditions is shown in Tab. 1 These conditions were controlled by placing desiccators in an oven or refrigerator and controlling their water content through Drierite® and/or leaving small amounts of standing water in the container.

Table 1. List of aging environments. Each different humidity percentage is the result of a different desiccator either placed in the 55°C oven or the 3°C refrigerator. Along with these, a control was kept at room temperature and 7-30% RH.

55°C	7% RH	15% RH	80% RH
3°C	26% RH	80% RH	85% RH

The aging process was then observed by periodically measuring samples using atomic force microscopy (AFM) and variable-angle, spectroscopic ellipsometry (VASE). AFM enables characterization of surface roughness and grain size while VASE is used to model what is happening in the film stack, giving information such as film thickness as well as percent water and voids inside the film.

3. RESULTS

Immediately after sample creation, films were measured using VASE. We were able to model this data to quantify the thickness of the LiF layer as well as the effect of surface roughness. This worked well for as deposited films and those that had not changed dramatically.[8,9] However, this approach no longer worked well when films seriously degraded, as seen in Fig. 2, and in Fig. 10 below. We found that AFM was able to accurately characterize LiF samples as they aged.

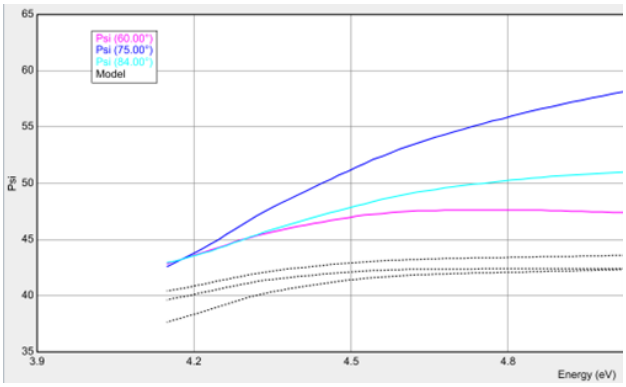


Figure 2. Ellipsometric ψ data from a sample aged 5 days in a humid environment (55 C 100% RH) together with an attempted fit to a model. The model provides an nonphysical fit and demonstrates that when a surface becomes discontinuous, VASE becomes an unsatisfactory method of characterization.

AFM is a known tool to measure surface roughness. By using it to measure grain size and surface roughness, we are also able to observe changes over time, including effects of water on the film. As a means of comparison, measurements were taken prior to any aging and can be seen in Fig. 3. Along with the AFM image seen in that figure there is a radial power spectral density function (RPSDF) graph. While changes can be seen in AFM images, their surface roughness can more easily be observed through RPSDF. RPSDF is the Fourier transform of the spatial autocorrelation function of a sample.[10] Spatial frequency (k) and distance (d) are related to each other by k= 2π/d.

One feature of aging was observed in a sample that had been stored in a warm humid environment (55°C 80% RH). As it was being, the sample dried out. Features were observed to sharpen in AFM images shown in Fig. 4.

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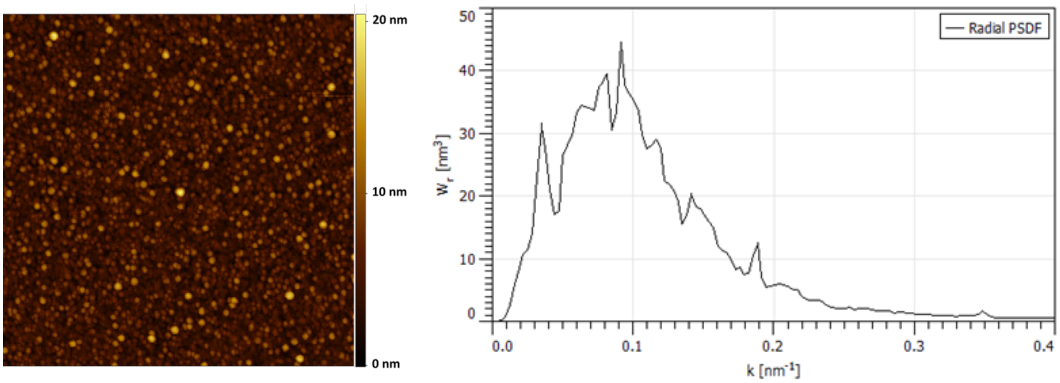


Figure 3. Left: AFM image taken of control sample before any aging could occur. Right: RPSDF of same sample. The gaussian shape suggests a fairly random distribution in the size of surface features.

The globular nature of features in the first image is interpreted as a surface coated with a film of water which disappears as the film dries in the cooler and dryer AFM room (20°C 20% RH), resulting in sharper images.

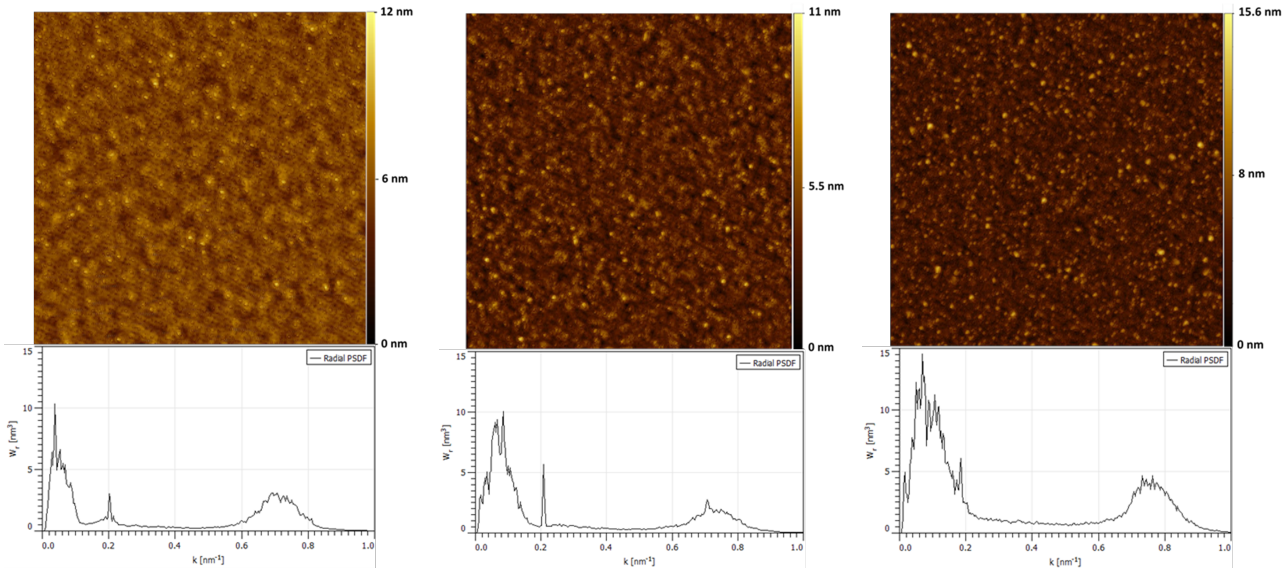


Figure 4. 2x2µm AFM scans of 20nm LiF stored in 55°C 80% RH. These images exhibit the sample drying out once removed from the humid environment. Top Left: AFM image of a sample 30 min after removal from storage, note the globular shape of surface features. Top Middle: scanned 50 min after removal from storage, note the increased sharpness of surface features. Top Right: scanned 70 min after removal from storage, note features are raised and sharpest. Bottom Row: corresponding RPSDF's.

The center of the broad peak on the left side of the RPSDF figures moves towards greater spatial frequency, as seen in the progression of the bottom row in Fig. 4. This suggests that features are becoming refined as surface water evaporates. Although the image taken after 70 min resembles the "before aging" sample in Fig. 3, its RPSDF shows it is smoother and possesses a narrower low-k RPSDF than as deposited.

Surprisingly, this sample as dried bears a striking resemblance to the as-deposited sample in Fig. 3. However, a few differences are worthy of note. Firstly, the magnitude of the height scale is different. In AFM images, the color-gradient scale automatically adjusts to match the maximum height and the minimum depth in the image. Thus, it should be noted that the height scale in Fig. 4 is smaller than in Fig. 3, indicating smaller surface features. Additionally, the relevant RPSDF of Fig. 4 indicates the same, with a W_r peak of no greater value

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than 15 nm^3, while the RPSDF of Fig. 3 peaks at a value of about 45 nm^3. This may indicate that storing a LiF film in a sufficiently high temperature ambient can offset and potentially reverse the effects of high humidity.

The RPSDF images in Fig. 4 exhibit a bump at k = 0.7 in every chart. This corresponds with a distance of about 9 nm. The origin of this feature is unknown, but observed in all samples, and is suspected to be an artifact leftover by the AFM.

The apparent stabilizing effect of hot environments appears most pronounced in dry conditions. In this experiment, the 55°C 7% RH and the 3°C 80% RH environments have very similar water contents, yet very different outcomes as seen in Fig. 5. The immediately visible result is the large difference in height scales. The sample stored in warm conditions has a height scale six times smaller than that of the the cold sample and half the size of the as made sample seen in Fig. 3. This suggests that the film stored in the warm dry ambient has become smoother than samples imediatley post deposition.

Grain size and shape in Fig. 5 are also telling, but of great relevance to this analysis are the RPSDF charts in Fig. 6, which shows that the heated sample has a W_r value of no greater than about $3nm^3$, while the cooled sample has a peak of $W_r > 450\ nm^3$, a difference of two orders of magnitude. An immediate observation is to regard storage a dry environment as a method of preservation.

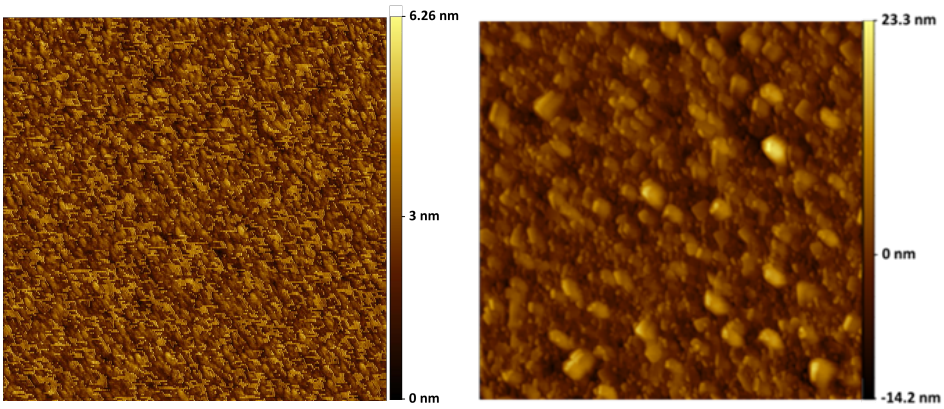


Figure 5. 18nm LiF aged in two environments with a height scale set to the same range. Left (55 C 7% RH, 167 days): Sample shows rolling hills of small range. Right (3 C 80% RH, 151 days): Surface has large features whose scale dwarfs the heated sample. It can be observed that large features have deep valleys next to them, which are presumably the result of large features growing at the expense of smaller ones.

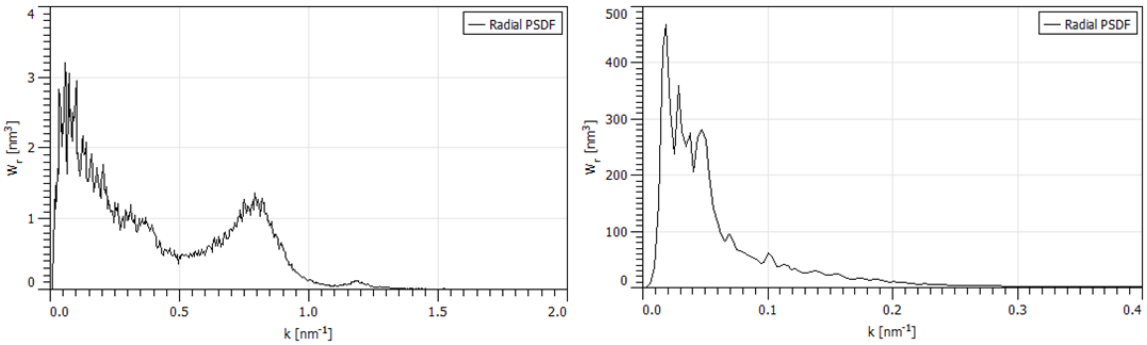


Figure 6. RPSDF of a samples shown in 5. Left: sample stored in 55 C 7% RH. The very small value of W_r suggests that surface features are kept small. Since W_r peaks at low k, it can be inferred that the largest features are still infrequent. Right: sample stored in 3 C 80% RH. The increase in W_r at low k indicates a reordering of the sample surface such that large features are infrequent, but more dominant than smaller features.

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However, the reported results for cold samples may be compromised by the possibility of water condensing onto the surface when it was removed from the cold environment. We attempted to prevent this by allowing samples to warm up to room temperature in a dry desiccator but the elimination of any condensation cannot be ruled out.

Comparing Fig. 5 to Fig. 3 reinforces the observation that LiF stored in a hot ambient remains stable, while a film in colder environments undergo coarsening in almost any other humidity environment. It is our observation that samples stored in an ambient of 55 °C in any humidity underwent no dramatic coarsening. Even when the sample stored in 80% RH in the warm ambient, as seen in Fig. 7, coarsening was minor. The sole exception being a sample stored in complete saturation (55 °C 100% RH) as seen below in Fig. 8.

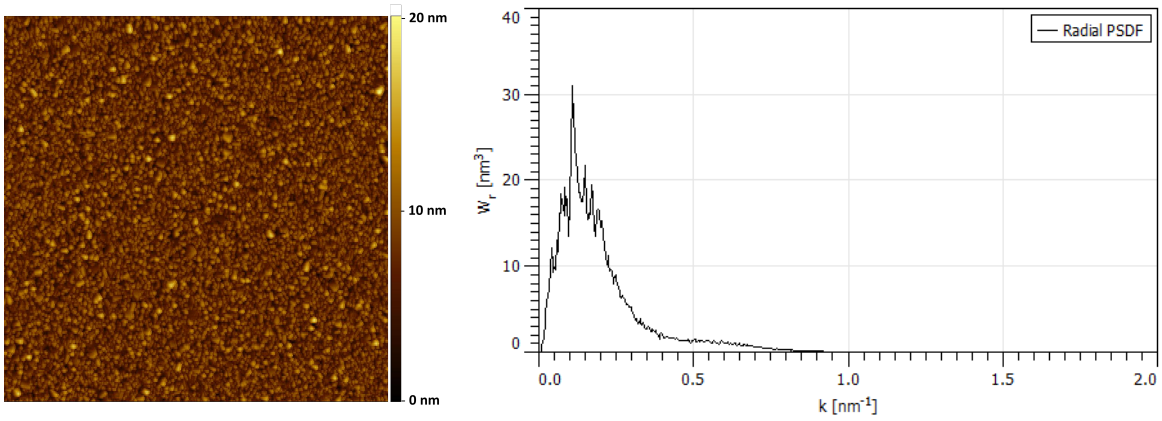


Figure 7. Left: AFM image of a sample aged 20 days in 55°C 80% RH. Possesses many more small surface features than in an unaged control (see Fig. 3). Right: RPSDF of same sample. The overall shape resembles that of the RPSDF of an unaged control (see Fig. 3), but with a lower peak in W_r, suggesting smaller surface features overall.

Continuing to age samples in even harsher environments brought about more visible coarsening as seen in Fig. 8 and Fig. 9. When stored in a water saturate environment the film becomes discontinuous as visible in the AFM image and as demonstrated in the RPSDF with the high value of W_r at a low value of k. This discontinuity is so prevalent that it is visible without the assistance of microscopy. Fig. 10 shows that samples stored in both saturated environments, both become discontinuous to the point of scattering in the visible spectrum. This is apparent by the blueish white light reflected off the LiF surface also known as Rayleigh scattering.

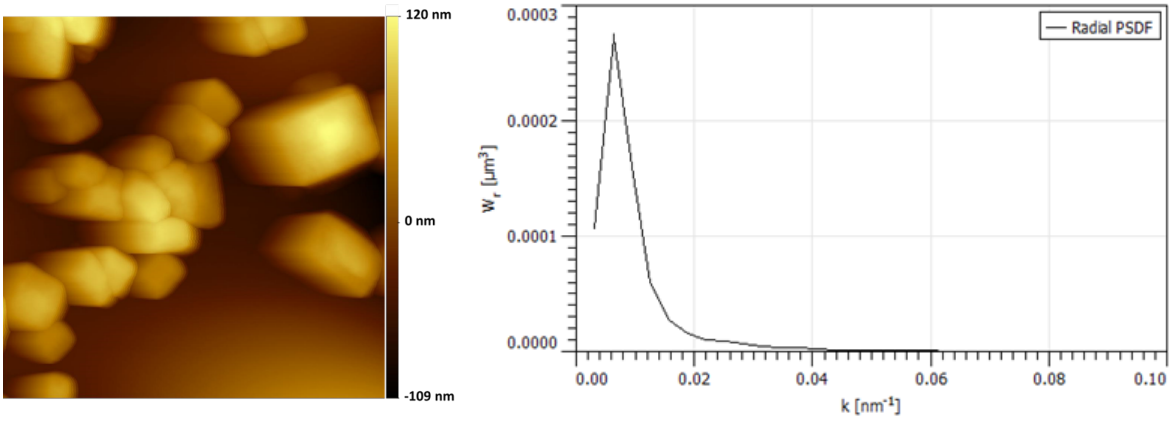


Figure 8. Left: AFM image of a sample aged 6 days in 55°C 100% RH. Such exposure has degraded the film to the point of being discontinuous. Right: RPSDF of same sample. A peak at such a high value of W_r with a low value of k demonstrates that the surface has reordered such that the dominant features are large and infrequent.

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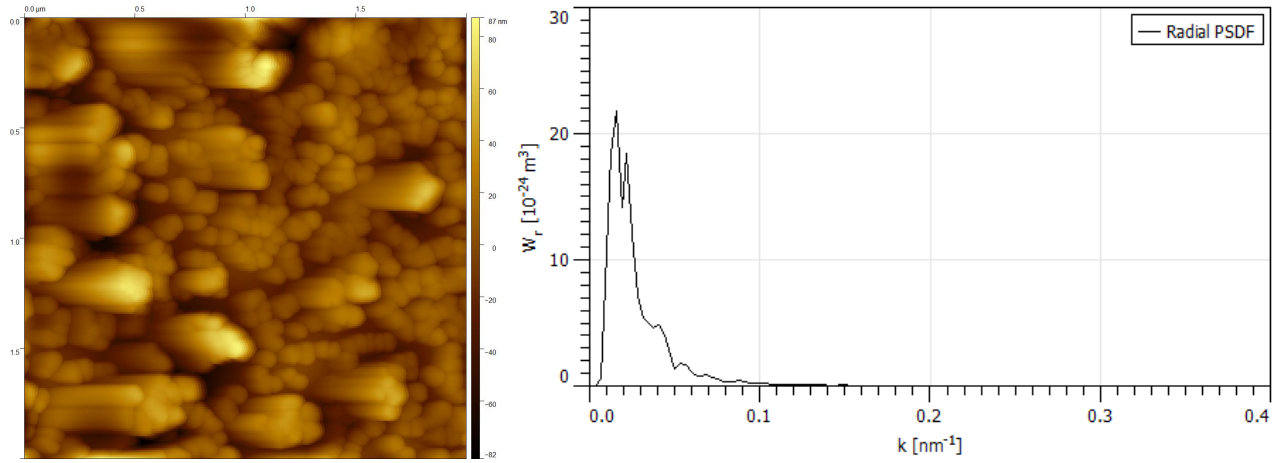


Figure 9. Left: AFM image of a sample aged 6 days in 3°C 100% RH. Such exposure has degraded the film, greatly, but in a different way than in Fig. 8. Right: RPSDF of same sample. A peak at such a high value of W_r with a low value of k demonstrates that the surface has reordered such that the dominant features are large and infrequent, but not to the same degree as in Fig. 8.

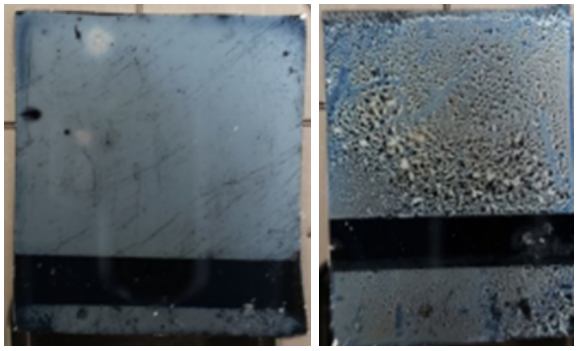


Figure 10. 20 nm LiF samples stored in saturation. Left: stored in 3°C 100% RH. Right: stored in 55°C 100% RH. The dark bar at the bottom of each image is where the substrate was held to the platen in the deposition chamber so no LiF was deposited there.

It should be noted that Fig. 8 displays a pattern of grain coarsening whereby large cubic structures form, separated by bare substrate material. Fig. 9 showcases a similar phenomenon, but one in which large surface features grow to dominate the sample, but with smaller grain structures of similar size separating the largest structures. In turn, it appears that the smaller structures are separated by bare substrate. Thus in both cases, within 6 days of storage two LiF films stored in saturated conditions degraded to the point of discontinuity, but the film stored in a 55 °C ambient underwent a greater degree of change. This change is reflected in macro-scale changes discernible to the naked eye as in Fig. 10, where patches of bare substrate can be observed, in addition to the scattering mentioned earlier.

It is yet unknown what exact mechanism allows for such a phenomenon when in other humidity conditions, an ambient of 55 °C has preserved the quality of LiF films. We suspected that when water is available in such large quantities, as in these completely saturated environments, a layer of water several times thicker than the film collects over the surface of the sample. It may be that in less saturated environments, water may have a more difficult time collecting onto the film via capillary action in a hot ambient, but in this case there is now a high abundance of water coating each surface. Since the solubility of LiF in water increases with temperature, the 55 °C ambient is better able to dissolve and transport LiF, providing a more efficient mechanism for the degradation of the film.

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4. CONCLUSIONS

19 ± 1 nm LiF on silicon samples were stored in various environments for periods of time up to 151 days. The surface grains were observed via AFM to coarsen in both hot and cold, both dry and moist storage environments. However, lower grain growth was seen in the hot dry environment while greater coarsening was observed in cold environments. These changes were quantified by preparing radial power spectral density function (RPSDF) charts of the AFM data. This suggests that storing LiF films in a heated ambient can preserve film integrity. Whether this is true for aluminum mirrors protected by LiF was not reported here and is the subject of ongoing research.

A key finding is that films stored in a hot, dry environment for 167 days actually became more smooth than the unaged sample. Thus, storage in a hot, dry environment could preserve the quality of a film for various purposes, potentially making LiF films viable as a protective layer. Because of threat of static electricity to electronic components optical components containing metal fluoride barriers will not be stored in ultradry environments. Thus, being able to store them in a warmer ambient with the same RH may improve stability.

This study also provides guidance in studying moisture-sensitive thin films and in understanding hygroscopicity and deliquescence at nanometer scales. AFM Surface images of changes, coupled with RPSDF has proven a useful tool in studies of film aging. Capillary theory is heuristically useful in understanding the observed changes. water will fill pores in hydrophilic films and may coat The drying of a LiF thin-film sample stored at elevated temperature at high humidity over the course of several hours of AFM measurements are particularly striking.

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