The effect of First Contact polymer storage on xenon difluoride passivated lithium fluoride on aluminum films

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ABSTRACT

Xenon difluoride passivated aluminum with a lithium fluoride overcoat (Al+XeLiF) mirror coatings are promising candidates for future space telescope missions due to their high reflectance down to 100 nm. The XeLiF mirror coating blocks aluminum oxidation. Aluminum oxide is undesirable since it significantly reduces the far UV (100-to-190 nm) reflectance. Cleaning techniques for this ideal coating require the balance of traditional surface cleaning with careful handling of the hygroscopic LiF. Photonic Cleaning Technologies' First Contact Polymers (FCP) are proven to clean and protect optical surfaces effectively. A specialized FCP formulation may be required for Al+XeLiF. We monitored Al+XeLiF changes under repeated application of four FCP formulations using variable angle spectroscopic ellipsometry (VASE), reflectance, and Atomic Force Microscopy (AFM). We also applied multiple FCP formulations to both Al+XeLiF and Al+LiF samples and stored them in different humidity environments to monitor potential protective qualities of each formulation. We observed that two FCP formulations can effectively protect Al+XeLiF in 40% RH without Al loss over half a year.

Keywords: Spectroscopic Ellipsometry, thin film characterization, humidity effects, lithium fluoride, aluminum, far ultraviolet, First Contact Polymer

1. INTRODUCTION

State-of-the-art fluoride protective coatings for aluminum, passivated lithium fluoride with xenon difluoride (XeLiF) and passivated magnesium fluoride with xenon difluoride ($XeMgF_2$), has been shown to be robust and resistant against environments of high humidity.[1] Aluminum (Al) has been a well-studied material for space telescope mirrors, as it has a high reflectance for the Lyman series (around 90 nm-to-130 nm). However, aluminum oxidation poses a significant threat, reducing the far-UV reflectance significantly. XeLiF and $XeMgF_2$ have been shown to protect Al from oxidation in humid environments.[1] Opaque Al+XeLiF is expected to be a prime candidate for the primary mirror coating of the Habitable Worlds Observatory,[1] and, with the exception of LiF's hygroscopicity[2,3] and susceptibility to electron radiation damage.[4,5] The Al+XeLiF coating has shown to be the ideal candidate for space telescope mirror coatings, as it is highly reflective in the far ultraviolet (far-UV).[1,6]

What is necessary for flagship missions in order to be successful? The Al+XeLiF must be as smooth as possible, less than 1 nm RMS roughness, to prevent polarization aberrations from ruining starlight suppression in the form of coronagraphy.[7] LiF recrystallization has been observed in the presence of humid environments due to its solubility of water and hygroscopic nature.[2,3] Capillary effects can cause moisture to condense from the environment even at low relative humidity (RH) if the surface is not smooth. This water can further roughen the surface through Ostwald ripening. Smaller crystals dissolve and large crystals grow larger from the solution on the surface.[2,3] In addition, the optical components must reach reflectance benchmarks. For the Habitable Worlds Observatory and other LUVOIR-inspired missions, 80% reflectance at the Lyman-α wavelength and

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70% at the Lyman-β wavelength is the minimum reflectance necessary. Al+XeLiF has shown 90% reflectance and Al+XeMgF$_2$ has shown 95% reflectance at the Lyman-α wavelength, while having an RMS roughness <1 nm. Al+XeLiF was also reported to achieve the 70% reflectance at 103 nm, around the Lyman-β wavelength. However, specifications require that the space telescope mirrors must remain smooth and as reflective as possible during manufacture, testing, assembly, and storage.

The effect of particulate and molecular contaminants for Lyα and Lyβ wavelengths can be significant, so the mirrors must be cleaned thoroughly. Contaminants may roughen the surface (in the case of particulate contamination) and impurities reduce reflectance. Therefore, the mirror must be carefully cleaned in a way that will not roughen the surface and will enhance rather than reduce the reflectance. The hygroscopic and fragile nature of LiF provides a unique challenge for any cleaning technique. The technique needs to (1) clean the mirror, (2) not cause damage to, or otherwise roughen, the mirror, and (3) not accelerate the oxidation of the Al film that produces the high far-UV reflectance that Al+XeLiF is known for.

Photonic Cleaning Technologies develops First Contact^{TM} Polymer (FCP), a blend of polymers and solvents that is spread onto optical components. The solution dries, trapping contaminants that are removed when the dried FCP is later peeled off the surface. Thus, the polymer is an 'apply-dry-peel' cleaning polymer, and has been shown to clean and protect optical components very effectively.[8–12] Our team has previously investigated the effects of applying FCP for repeated cleaning.[13] In that study, the surfaces were not stored under FCP. Of a given test cycle the FCP was present on the thin Al + XeLiF sufaces for only the 0.5 to 3 hours the FCP needed to dry (as discussed below). The samples were cleaned repeatedly over the course of 50 days. We found that for one formulation (labeled S3 in that work) Al thickness did not decrease over the 50 days. The tested sample was also observed to have maintained high reflectance in the far-UV. However, the long-term storage of Al+XeLiF in a FCP film was not considered in that study. In the present study, four different formulations were used, which we labeled S1, S2, S3, and S4. Incidentally, for Al+XeMgF$_2$, we have shown that two of the formulations, labeled in both this study and that study as S2 and S3, were successful in cleaning and are suitable for use as a long-term protective layer in dry environments for the entire five-month test.[14]

In this paper, we discuss the results of three experiments that delve into the question of the effects of FCP on Al+XeLiF or Al+LiF as a function of storage time. The three experiments were the long-term storage of FCP-applied Al+XeLiF samples in low humidity environments, the long-term storage of FCP-applied Al+XeLiF in 40% and 72% relative humidity (RH) environments, and the long-term storage of conventional Al+LiF deposited on silicon dioxide (SiO_2) samples in saturated humidity environments. We hypothesized that we would observe similar surface features as seen in our previous experiment. We also hypothesized that, due to the trace water in different FCP formulations, we could observe increased surface roughness and excess polymer adhesion in contrast with its behavior on typical optical components, such as silicon oxide-based films and surfaces.[8]

2. EXPERIMENTAL DETAILS

The first experiment: a (100) orientation silicon (Si) wafer coated with Al+XeLiF was sent to BYU from Goddard Space Flight Center several months before the experiment began. The coating was deposited by Dr. Quijada's team. Their reflectance studies on these samples and their initial reflectance are noted in their work.[1] Other members of this batch of samples were used by Lewis et al.[4,5] and Vawdrey et al.[13] At the time of the experiment, the thin Al+XeLiF coating thicknesses were measured to be approximately 25 nm of Al and around 11.5-to-14 nm fluoride layer thickness. The Al thickness is intentionally made around 70% thinner than the Al thickness used for future space telescope missions to aid in interpreting the ellipsometer measurements. Thin Al allowed the instrument's light to penetrate all layers of the thin film stack. Thus, film thickness changes became readily apparent. The fluoride thickness included around 2-to-3 nm AlF_3 from the XeF_2 passivation step and about 10-12 nm being LiF. The substrate is 1-to-2 nm of native silicon dioxide (SiO_2) on silicon (Si). The samples were free of surface scratches and had an RMS roughness of less than 1 nm when measured with atomic force microscopy (AFM).

We used a diamond scribe to cleave four 1-inch-by-1-inch samples. All samples were placed in 3-inch diameter Fluoroware containers. Double-sided tape was placed at the bottom of the sample holder to prevent samples from moving during transport. The samples were placed near the edges of the sample holder. In the case where

the samples were dislodged during transport, the samples were placed back into their respective places once we reached the destination.

Second experiment: We investigated two additional sample sets of Al+XeLiF. In each sample set, we had two 13 month aged Al+XeLiF on Si. The samples were $\frac{1}{2}$ inch by 1 inch and $\frac{1}{2}$ inch by $\frac{1}{2}$ inch. One sample had formulation S1 and the other had formulation S3. One of the sample sets were put into a 40% RH desiccator and the other was put into a 72% RH desiccator to understand the effects relative humidity may have on the samples.

Third experiment: We also evaporated Al+LiF at BYU on an 8-inch silicon wafer coated with 300 nm of SiO_2. The wafer was then cleaved into four equal pieces and kept on lint-free towels for about a week. One of the four wafer pieces was cleaved into five samples and were kept in the same desiccator as a <10% RH environment for about a week. FCP was applied to all but one sample (which served as the control of the experiment).

2.1 Repeated apply-dry-peel storage tests

For the Al+XeLiF samples, we characterized the thickness with variable-angle spectroscopic ellipsometry (VASE) as well as the roughness and surface features with atomic force microscopy. These initial sets of measurements were used to create an ellipsometry model (See the Ellipsometry section). Once initial characterizaton measurements were performed, a FCP formulation was chosen for each sample. Each respective formulation was applied to their corresponding samples and left to dry in the lab environment (RH $<$ 10% to 30%) on a paper towel.

Once the formulations were dried, we stored the Al+XeLiF samples in a fluorware container and placed them in a $<$ 10% RH desiccator. Drierite (anhydrous $CaSO_4$) filled the bottom of this desiccator to control the RH environment, creating our dry ambient environment. For the higher RH samples (Both Al+XeLiF and Al+LiF), we stored them in a salt-induced saturated environment (100% RH) between measurements. During any measurement process, we would store the samples in a transport desiccator with RH <10% or use them in the lab environment. While FCP was being applied to the samples and while the FCP dried, the sample was left on a paper towel in the lab environment.

When it was time to make measurements, we would remove the dried FCP. This was done by placing a piece of chemically inert mesh ("FC-net") provided by Photonic Cleaning onto the sample near its edge so that a portion was beyond the sample edge and embedding the portion of the mesh on the sample into the first FCP layer by applying more FCP. If any FCP happened to fall onto the paper towel, the samples were moved to avoid FCP from clinging to the bottom of the sample. After about 0.5 to 1 hour of the second FCP layer drying, we would completely remove the FCP covering the sample by holding the sample in one hand and the embedded FC-net mesh in the other and peeling off the layer. We would then take VASE measurements of the samples.

2.2 Ellipsometry measurement

We used a J.A. Woollam RC-2 spectroscopic ellipsometer to measure the Ψ and Δ values. Ψ and Δ are defined by equation 1, where r_p and r_s are the Fresnel coefficients in the p- and s- polarized orientations, respectively.

$$\rho = \frac{r_p}{r_s} = \tan\Psi e^{i\Delta} \tag{1}$$

The experimental values of Ψ and Δ can be used to calculate the quantities N, C, and S, as shown in Equation 2. N, C, and S are components of the Mueller matrix of the measured samples assuming no anisotropy.[15]

$$N = \cos(2\Psi), C = \sin(2\Psi)\cos(\Delta), S = \sin(2\Psi)\sin(\Delta) \tag{2}$$

Changes in Ψ and Δ over time indicate changes in the film. The angles-of-incidence of each measurement were 50° to 80° in 5° steps. Every time we characterized a sample, we initially took a measurements in each of three different spots on the surface. The center of each measurement was usually near the bottom, middle and top of the sample center. After the first four peel-offs (31 days into the experiments), we began making six different VASE measurements. After the first three measurements, we would rotate the sample 90° and perform another three measurements.

We used J.A. Woollam's CompleteEase to create a model that utilized as parameters optical constants for each thin film in the stack. We then calculate the best fit of N, C, and S for the model. Based on the calculated N, C, and S values and the experimental N, C, and S values, a mean square error was calculated for every measurement. We considered a mean square error as close to 1 as possible to be an excellent fit for the Al+XeLiF samples. The Al+XeLiF model was able to get an MSE of around 1-to-2. For the Al+LiF samples, however, there is 300 nm of SiO_2 that create thin film interference that makes it difficult to fit Ψ and Δ exactly. Therefore, a mean square error beneath 10 is more than adequate to provide sufficient precision for layer thickness determination. The Al+LiF model we devised was able to achieve an MSE in the 2-to-6 range.

We paid attention especially to three quantities as the experiments progressed: (1) the MSE of the model, (2) the apparent LiF thickness, and (3) the Al thickness. For the Al+XeLiF samples, we performed the fits with a two-step process similar to Vawdrey et al.[13] This two-step process consisted of fitting the SE data for the LiF and Al thicknesses only and then using stoichiometry to infer the Al_2O_3 thickness using the approximation that 1.54 nm of Al_2O_2 is formed per 1 nm of Al lost. For the Al+LiF samples, due to the higher MSE, we only used a one-step process in fitting the LiF and Al thicknesses. The Al+LiF typically had a higher MSE than the Al+XeLiF samples due to thin film interference exhibited from the SiO_2 layer, typically 2.8-5.0 before any FCP treatment. Using multi-sample analysis, the parameters for the optical constants of both the LiF and Al for the Al+LiF samples were fit using the SE measurements before FCP was applied.

2.3 Atomic Force Microscopy

The AFM measurements performed for this experiment are fewer than made by Vawdrey et al.,[13] but were performed in the same manner. Three measurements (5 μm, 1024 pixels by 5 μm, 256 pixels) and one measurement at lower magnification (10 μm, 1024 pixels by 10 μm, 256 pixels) were made at a scan rate of 0.5 Hz. The integral gain, proportional gain, and amplitude setpoint were adjusted to get the highest quality images possible (See Vawdrey et al. for a more detailed description[13]).

3. RESULTS

FCP-cleaned Al+XeLiF and Al+LiF samples were visibly dust free after the first polymer application and removal. We observed a blue tint form on the surface of the S2 formulation sample after many cleaning cycles, however. AFM showed the formation of 'hillocks' on the Al+XeLiF surface in such cases. Such small features are expected to scatter more blue light more than red. Typically, the polymer peeled from the LiF-based coatings cleanly, in a manner similar to what is experienced with standard glass optical surfaces. However, occasionally the polymer adherence was greater and it was difficult to remove it from the surface. We were nevertheless able to remove it in the end. However, sometimes the mesh pulled out of the polymer leaving the FCP on the sample. This was taken as an indication that the second polymer layer needed to be dried longer.

We consider first the Al+LiF samples exposed to saturated air. The sample most affected was the control. It exhibited visible surface damage. The FCP-protected samples also exhibited some surface changes, but not as drastic as the control. The VASE measurements indicate that the Al layer in the samples. It optimized partially oxidized.

3.1 Repeated apply-dry-peel storage tests

3.1.1 Ellipsometry

For the purpose of this study, we focused on the quality of the thin-film stack and how well the samples retained their initial character. Following our two-step ellipsometry model, we report (1) the MSE of the modeled N, C, and S values compared to the experimental data, (2) the Al_2O_3 thickness predicted based on the loss of Al, and (3) the apparent LiF thickness. It should be noted that we had no control to compare the samples with. However, the long-term storage of Al + XeLiF samples has previously been investigated by Dr. Quijada's team.[1] It is known that the Al+XeLiF is extremely robust and resistant to degradation in laboratory environments. Therefore, we do not anticipate that the samples would be oxidized in the desiccator (<10% RH) or in the Utah's dry environment (20%-to-30% RH, with an exceptional excursion 50% RH in the spring).

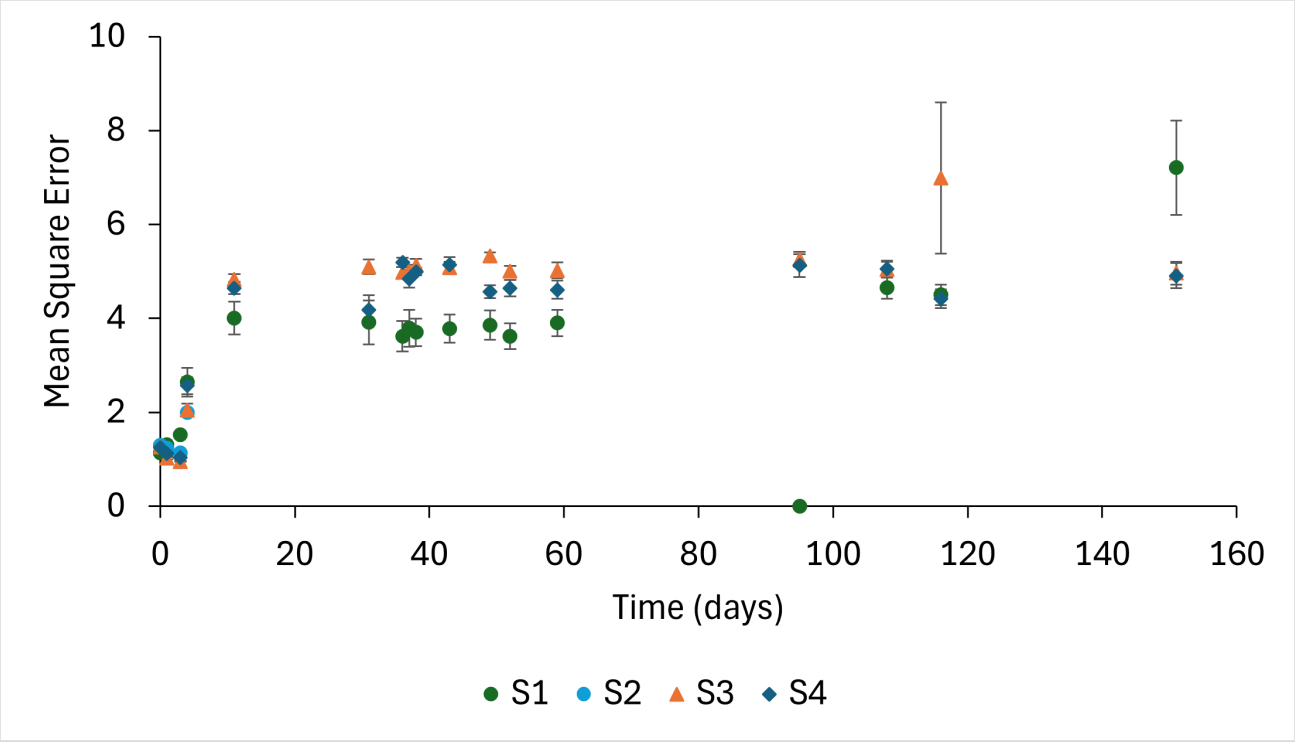


Figure 1: The mean square error (MSE) of all trials. Each data point is an average of all measurements of that sample performed on that day. The error bars are the standard error of the mean for each data point.

In Fig. 1, we observed the MSE values rise dramatically after 11 days of storage. The values of the MSE do not significantly rise after this time. The MSE indicates a change in the thin-film stack not explained by thickness adjustments of LiF, Al, or SiO_2. In Fig. 2, we observed a drastic increase in the Ψ values at photon energy 6 eV and higher near the end of the experiments for S1. S2 has dramatic changes to its Ψ values, so much so that in Fig. 4 and 3, we did not include it due to how poor the fit was to the data. S3 and S4 exhibited changes in that regime, but not as dramatic as S1 or S2. Still, the model did not fit near the end of the experiment with the same MSE as before. To try to understand what could cause the increase in Ψ values at the shortest wavelength shown in Fig. 2b, we created a Bruggeman effective medium approximation layer,[16] comprising Woollam's LiF, Woollam's H2O Pallik model, and Void. We found that this gave a more accurate fit than our current model. The water content and the void content were significant, indicating that moisture had restructured LiF into a porous structure 'hills' and 'canyons' and was still in the pores. Water could have arisen as a result of the FCP contact. Although the alumina content appears to saturate, the moisture could enter holes created by water in the LiF due to the Laplace pressure.[2]

The soft and hygroscopic nature of LiF is well known and has been investigated in state-of-the-art Al+XeLiF mirror coatings.[2–4] The coatings are robust and highly reflective in the far-UV.[1,6] FCP application has previously been shown to be effective at cleaning the Al+XeLiF without changing the thin film stack in a dry ambient.[13] FCP has been already shown to clean oxide surfaces effectively,[8] so being able to use FCP on Al+XeLiF samples would be effective. However, the FCP formulations need some optimizing to be able to store the Al+XeLiF in a disposable coating to reduce risk of particulate and molecular contamination. It was observed that there was a sharp increase in oxidation within 11 days of storage while in a dry ambient. It is not known if this is from the FCP treatment or if something external occurred to cause this effect. Further research must be performed to confirm the increase early onto the FCP film storage of Al+XeLiF in dry ambient conditions and as well as the features exhibited on the surface.

Interestingly enough, as shown in Fig. 5, there is very little oxide growth for the sample stored in 40% RH. We could see small changes for the 72% RH storage sample as shown in Fig. 6. The Ψ changes observed are

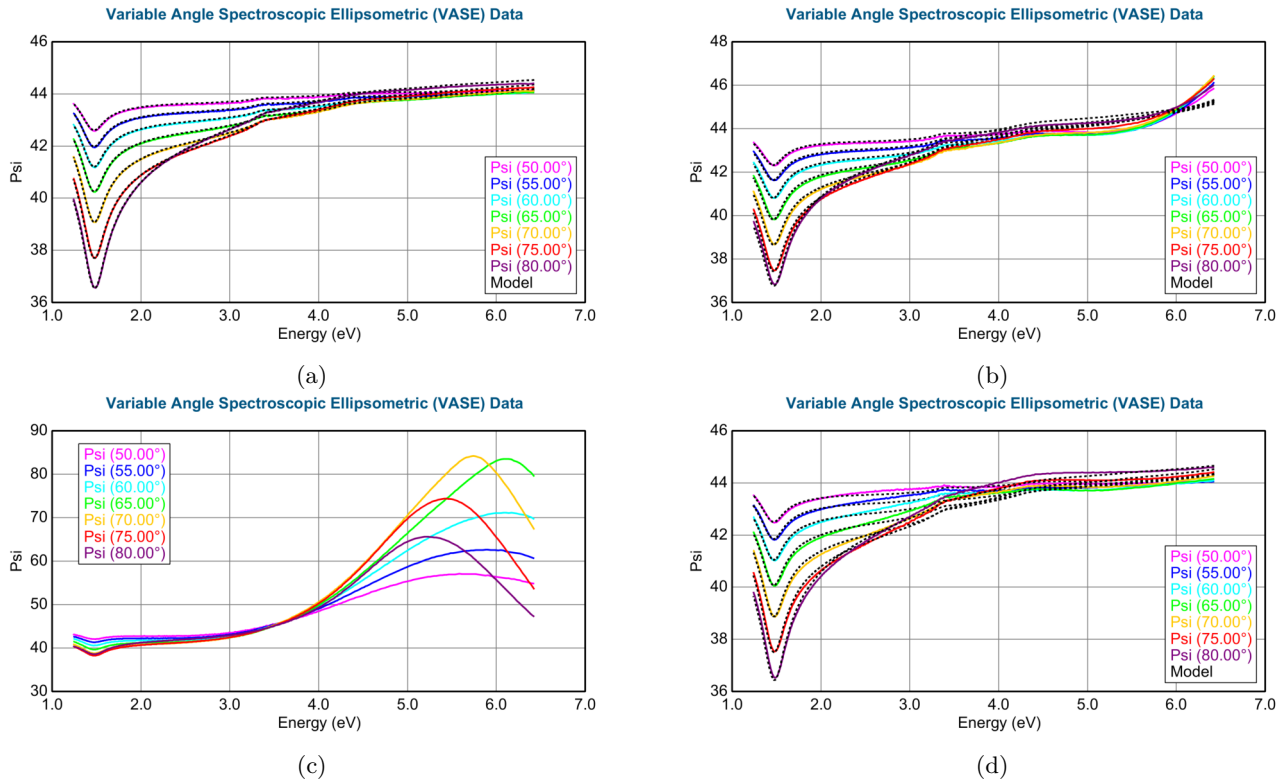


Figure 2: Ψ values as a function of photon energy: (a) S1 before FCP application and removal, (b) S1 after many FCP application/storage/removal cycles totaling about five months, (c) S2 after four months of FCP trials- for AFM see figure 8a, and (d) S3 after five months of FCP testing. The dotted lines are the calculated Ψ (CompleteEase) from our model and the solid lines are the experimental data at different angles of incidence.

similar to what was observed in the dry ambient. This indicates either oxidation of the aluminum or water creating and entering areas that have been restructured by water in the FCP or from the environment and left 'pits' or 'valleys' in their place. Why the difference in behavior between the sample of the first experiment and these? In addition to RH, the number of peel-off cycles differs. The samples stored at 40% and 72% RH were subjected to very few. Thus, storage results are promising for S1 and S3 in moderate RH environments.

3.1.2 Atomic Force Microscopy

AFM measurements show a variety of effects which depend on which formulation used to preserve the surface of Al+XeLiF in FCP film. In Fig. 7, that the surface structure of S1 changes with many peel-off cycles over the first couple of months. Vawdrey et al. reported siimilar hillocks or blisters and provided XPS data that showed they were not FCP globules.[13] These features could be due to delamnination because of high polymer-to-surface adhesion. However, their exact nature is unknown. However, in Fig. 8, the sample applied with formulation S2 was observed to exhibit a higher density of these features. It is possible that the features are recrystallized LiF formed from Ostwald ripening,[2,13] as both high oxidation and a higher density of these features were observed. It could also be a combination of these possibilities. We also saw fewer features on the surface for the S3 formulation, which we observed in Vawdrey et al. to work better than the others in the case of apply-dry-peel with minimal storage with the FCP polymer.[13]

3.1.3 Far-UV Reflectance

Far-UV reflectance measurements of the samples were performed at Goddard Space Flight Center. Due to the fact that the thickness of the Al in the layer is only 30% of the thickness of the Al in the standard Al+XeLiF the reflectance is not as high as standard Al+XeLiF samples (such as shown in the work by Quijada et al.[1,6]). However, we found the reflectances to be dramatically lower than expected based on the measurements reported

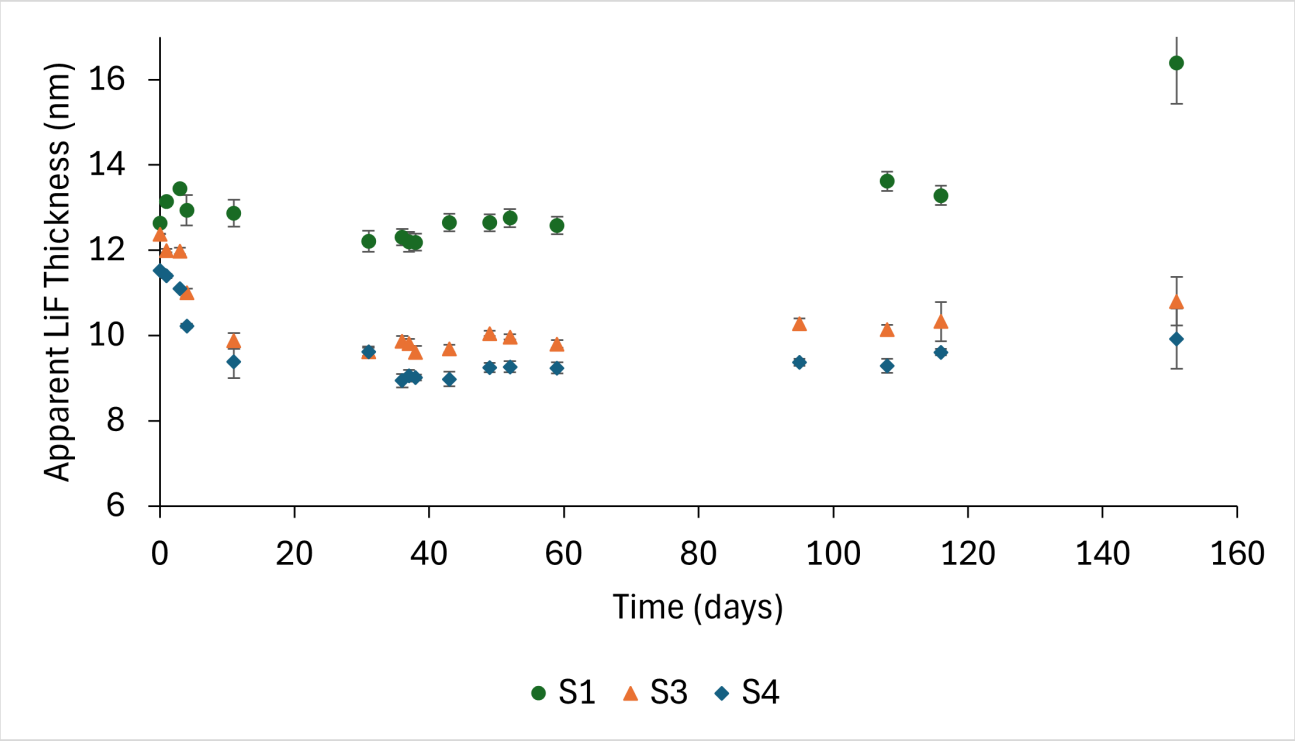


Figure 3: The apparent lithium fluoride (LiF) thickness for S1, S3 and S4. S2 is not shown due to the high MSE of the model. Changes in the apparent LiF thickness incorporates changes in the LiF as well as the roughness.

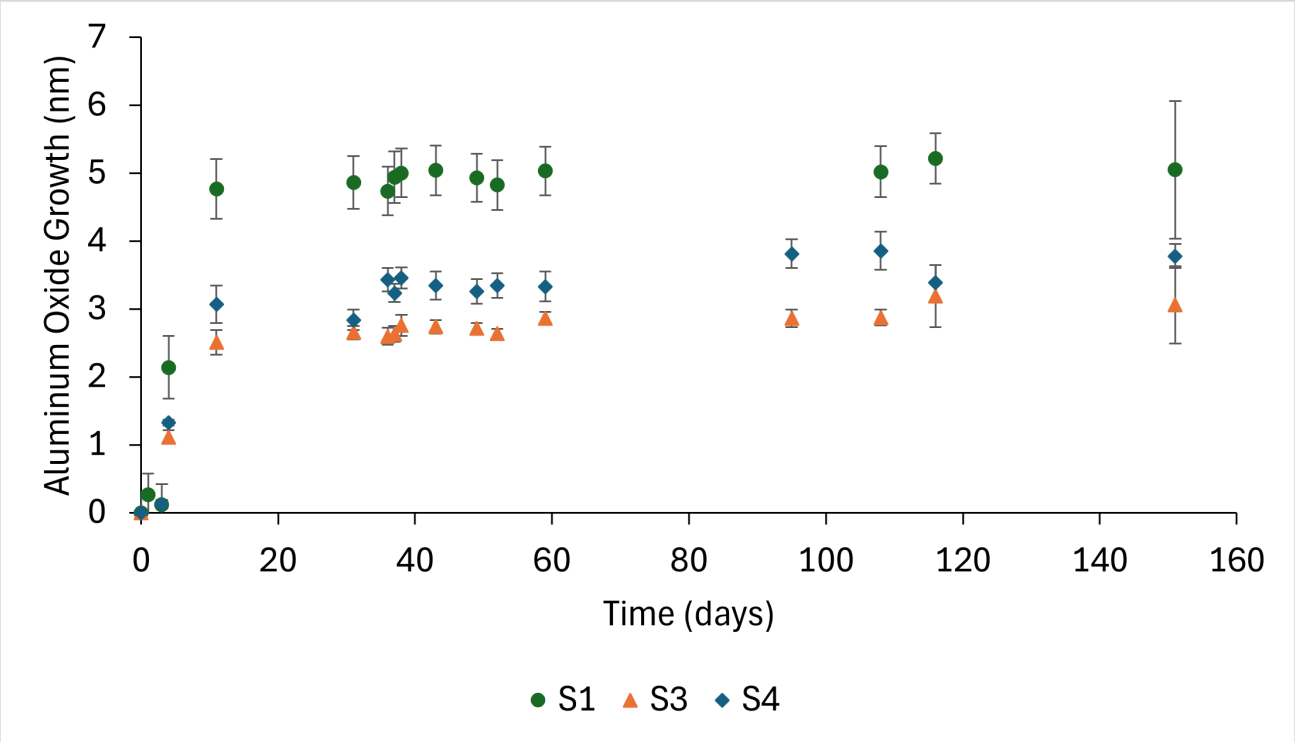
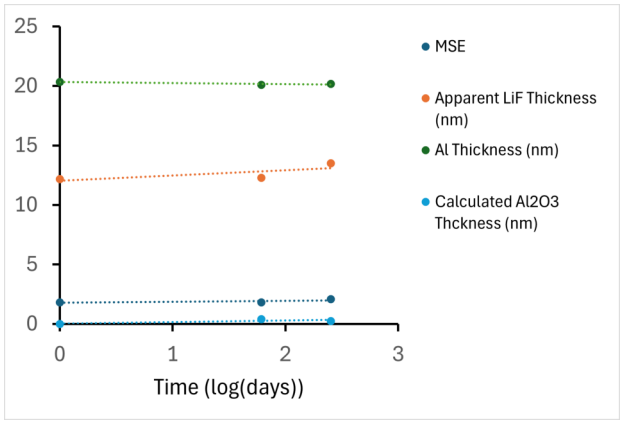
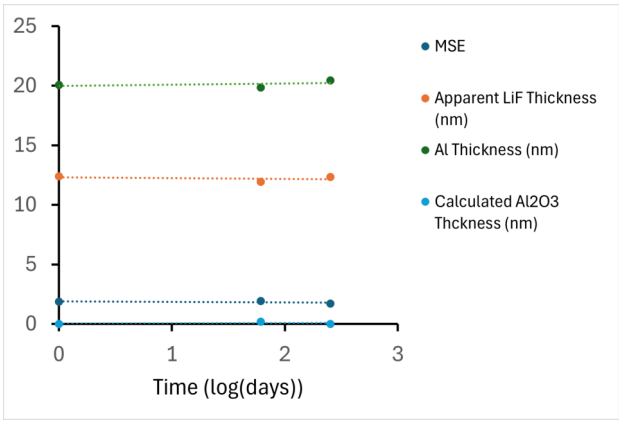


Figure 4: The calculated alumina (Al_2O_3) thickness for S1, S3 and S4. S2 is not shown due to the high MSE of the model. The Al_2O_3 thickness calculated is the loss of aluminum thickness from the initial measurement multiplied by 1.54.

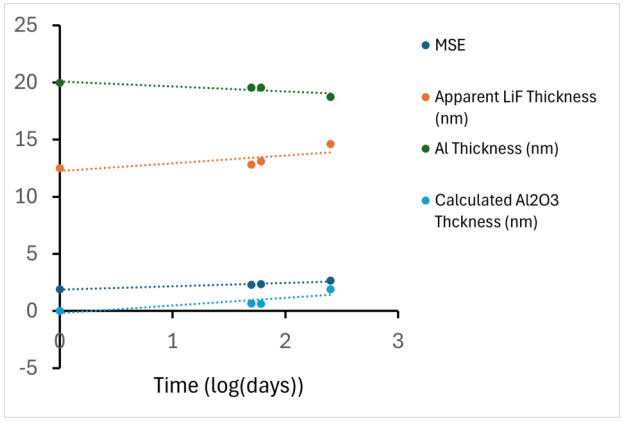


(a)

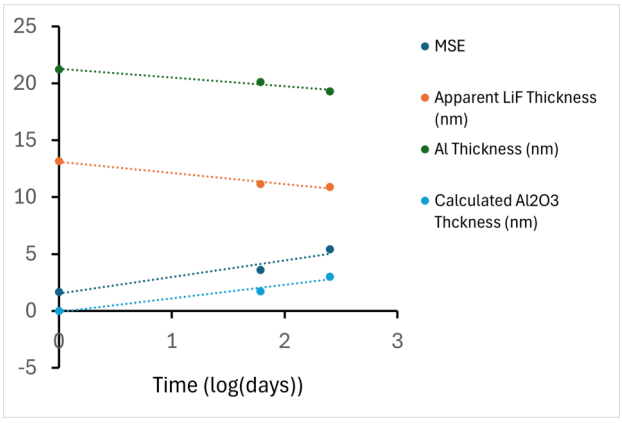


(b)

Figure 5: Layer thicknesses as determined by VASE for Al+XeLiF stored with a protective FCP film (a) S1 formulation and (b) S3 formulation. These samples were stored at an RH of 40% but without multiple FCP application and peel-off events. Unlike samples stored in a dry ambient environment and subjected to multiple FCP applications and peel-offs, there was little oxide growth in five months.



(a)



(b)

Figure 6: The thickness of layers in Al+XeLiF as determined by VASE for a sample protected by an FCP film and stored at 72% RH. (a) Shows layer thickness for samples coated with the S1 formulation, while (b) show thickness for the sample with the S3 formulation. There is a slight decrease in the aluminum thickness with time. Thus, the alumina thickness is inferred to increase.

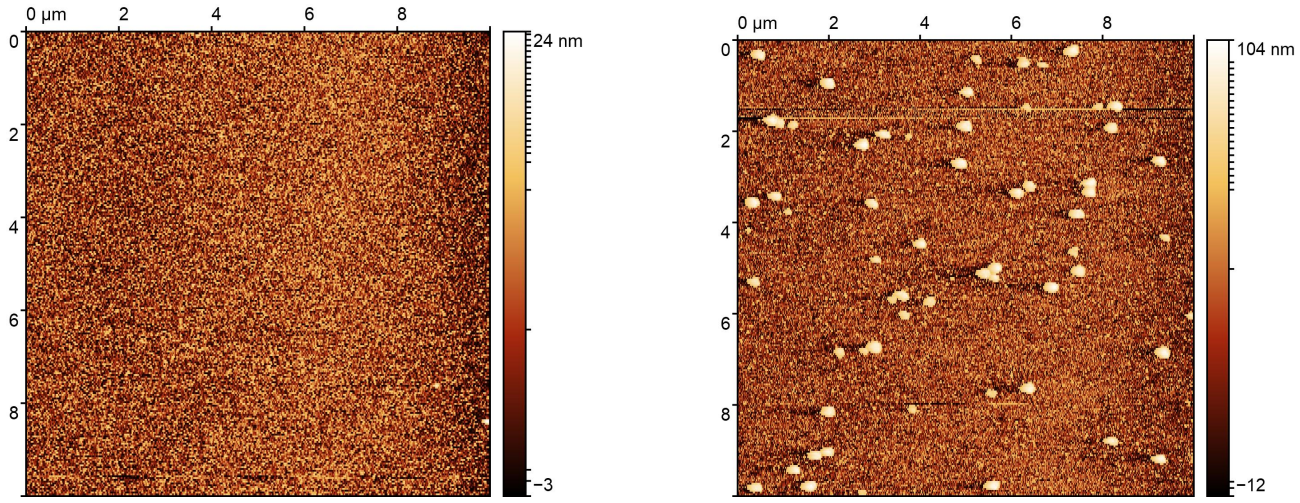
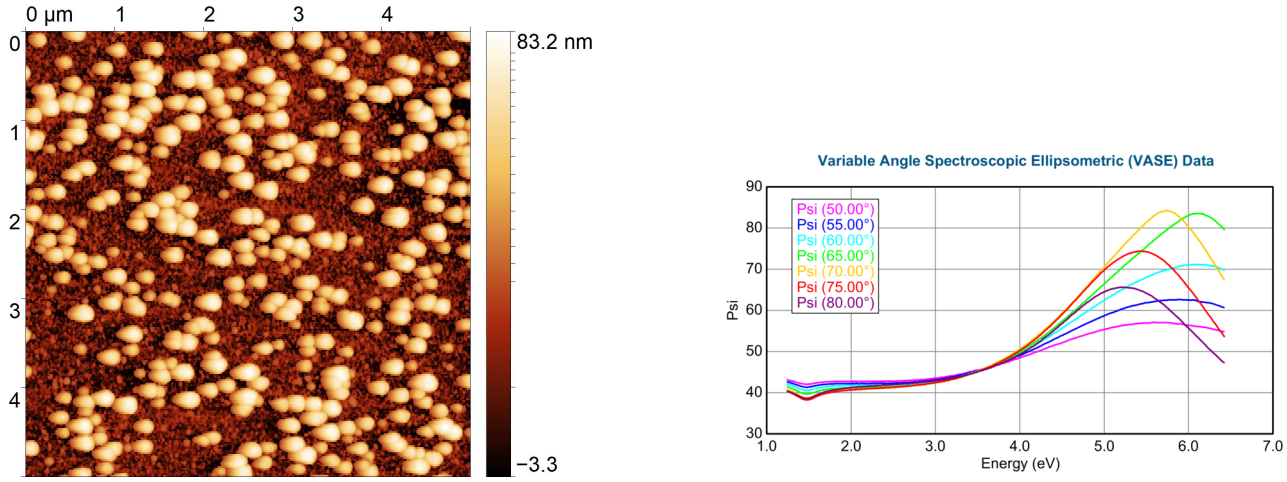


Figure 7: AFM picture of the surface of Al+XeLiF sample (a) prior to cleaning with FCP formulation S1 and (b) after a month of cycling. Note the difference in vertical scale. Hillocks are on the surface in b. It is unclear whether these are film delamination from the repeated peel-off cycles or an effect of prolonged storage in the FCP.



(a) (b)

Figure 8: (a) 5 μm $\times$ 5 μm AFM scan after around two weeks of storage and (b) Ψ values after four months of storage corresponding to the sample that was applied with formulation S2.

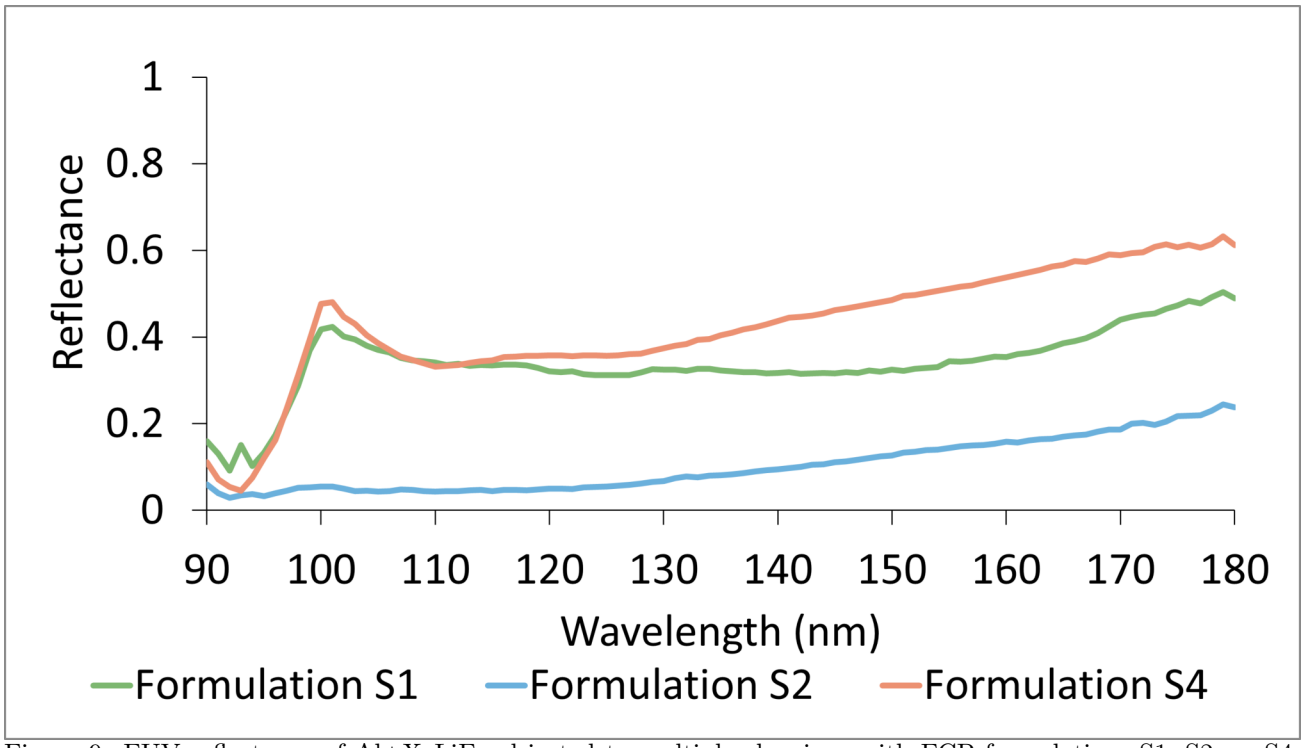


Figure 9: FUV reflectance of Al+XeLiF subjected to multiple cleanings with FCP formulations S1, S2, or S4. Note the reflectance at Lyman-α (121.6 nm) and Lyman-β (102.6 nm) are much lower than measured and reported elsewhere. The target reflectance is to be greater than 60% at the Lyman-β and 80% at the Lyman-α. This low reflectance is indicative of damage to the Al+XeLiF. VASE and AFM also detected changes to the thin-film stack that could cause low FUV reflectance.

in Vawdrey et al.for sample cleaned with but not stored in FCP,[13] As far-UV reflectance is the key indicator for success with these samples, the formulations used on our tests may be unsuitable for the longterm storage of Al+XeLiF samples in the case of multiple peel-off. However, the situation for few peel-off events may be different as seen in the second experiment.

The samples were expected to have a reflectivity around 80%. For S1 and S4, we observed that the reflectivity dropped to around 40%. This reflectance drop is indicative of aluminum oxidation due to its high absorbance in the FUV. It is important to note that S2 had a reflectance less than 5% on the Lyman-β line. This is indicative that the particular formulation we tested had a significantly negative effect with Al+XeLiF, likely because moisture from the FCP formulation got into the LiF top layer, affecting the Al. We do not have data for S3.

3.2 Long-term storage of LiF+Al with FCP

The Al+LiF samples (experiment 3) were different in nature, as they were lacked the uniformity and robustness of Al+XeLiF. However, understanding the FCP-applied Al+LiF samples will help future endeavors in undersanding the effects of Al+XeLiF in high-humidity storage. The saturated environment caused visible damage to the control. While the FCP-stored LiF+Al+SiO_2 samples did exhibit some surface changes, we observed less water damage on the surface.

Unlike the VASE measurements for the Al+XeLiF, the VASE measurements for the Al+LiF were only fit once with the model. The roughness was assumed to be small (1 nm), and we assumed there was no Al oxidation for the purpose of the fit. Therefore, any changes in the apparent LiF thickness (See Fig. 12) indicated changes in the material above the Al layer, including any oxidation, moisture caused recrystallization of the LiF films, and/or an increase in its roughness.

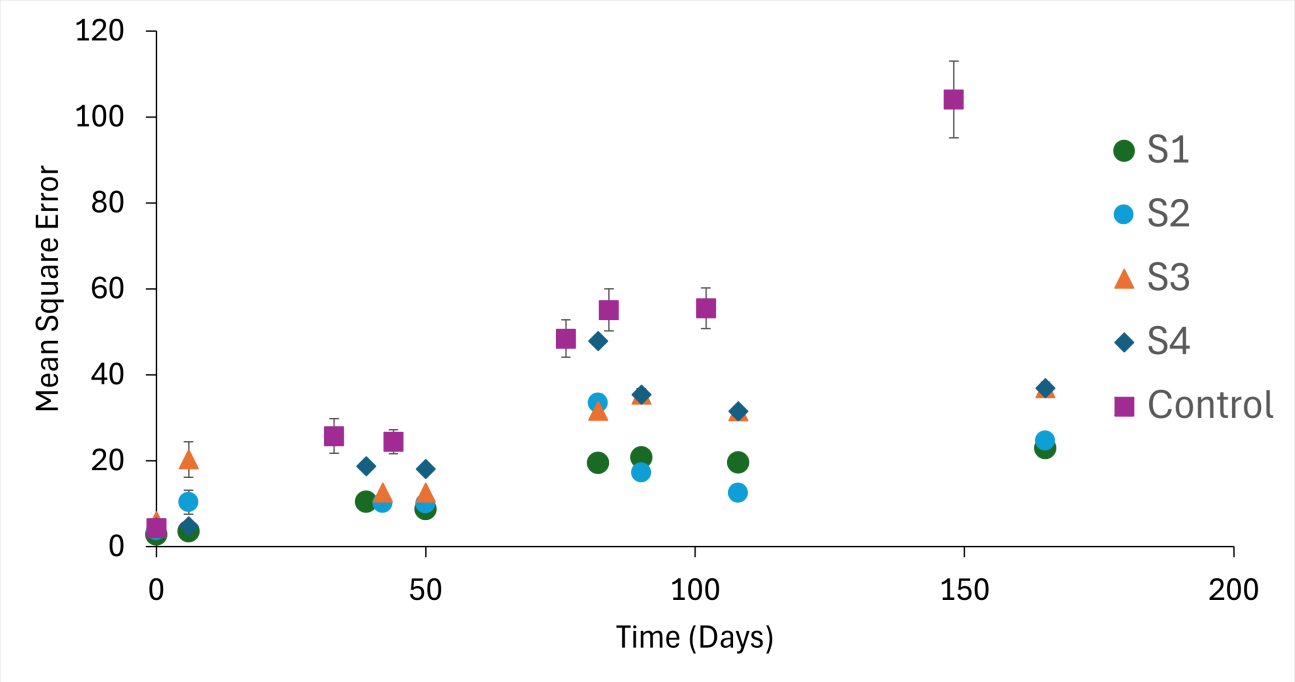


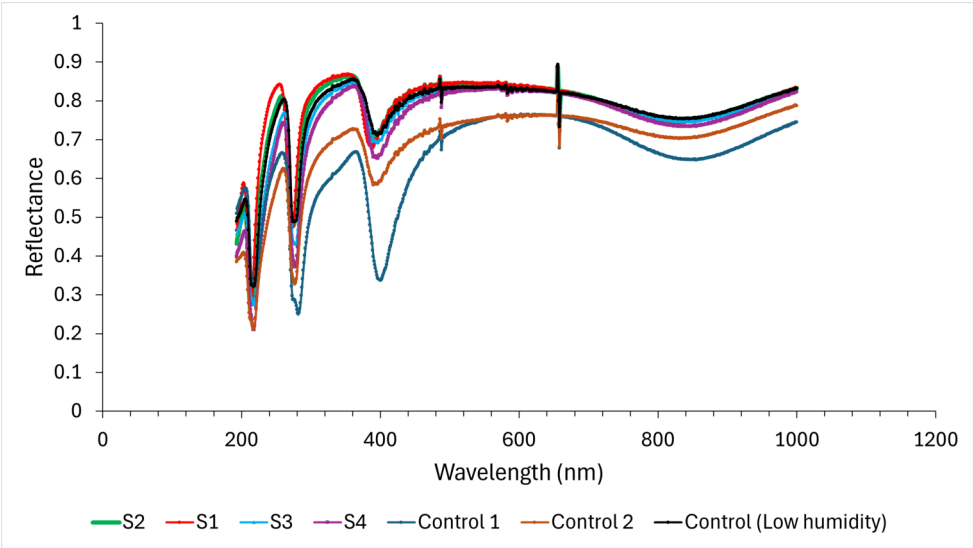
Figure 10: The MSEs for the VASE measurements of Al+LiF samples that were left in the saturated (100% RH) environment. Significant increase in MSE indicates the thin-film stack has changed significantly compared to the initial measurements.

In Fig. 10, 12, and 13, we observed that the model had a high MSE, which reveals that the best-fit N, C, and S values did not fit the experimental N, C, and S values well. We currently do not have a model able to account for the thin-film interference precisely. The modeled values, therefore, are just approximations of the actual thin film thicknesses. If we tried fitting the Ψ values from 1.25 eV to 5 eV instead of 1.25 eV to 6.425 eV, we were able to get a better fit. Our future research will include an improved model for the LiF+Al+SiO_2 samples.

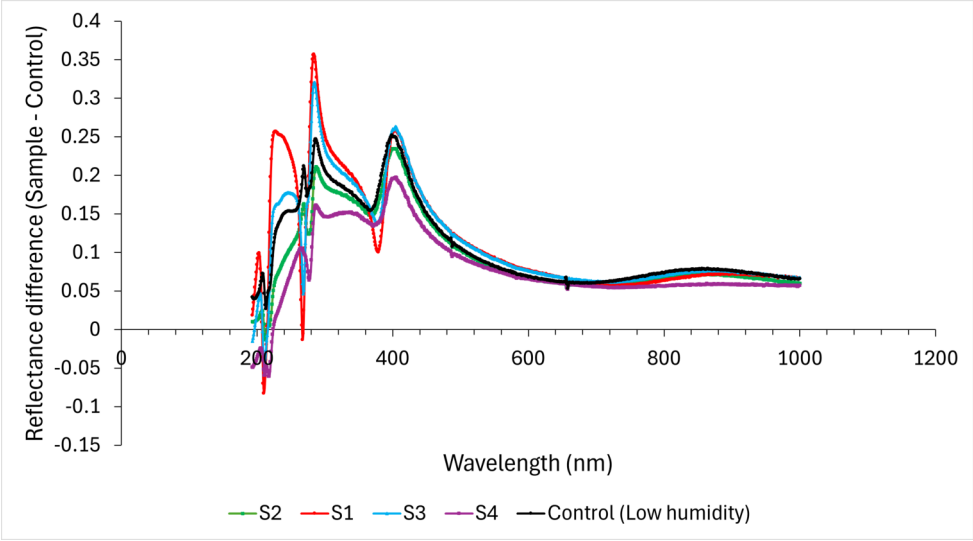
4. DISCUSSION

For the Al+XeLiF samples stored in FCP film in a dry ambient environment, we observed low far-UV reflectance, multiple dome-like features, and a sharp increase of Al_2O_3 thickness near the beginning of the experiment in a dry ambient. Typically, this would mean that the current formulations of FCP are not suitable for storing Al+XeLiF in. However, the success of Al+XeLiF+FCP storage in 40% RH provides evidence that there is likely a polymer from the FCP family that will allow for longterm Al+XeLiF+FCP storage. The VASE and AFM data suggest that multiple peel-offs may be the cause for the significant increase in hillock surface features. However, Vawdrey et al. previously determined that one can clean Al+XeLiF multiple times with formulation S3 without any Al loss while maintaining high far-UV reflectance. Thus, the results reported here are somewhat at variance with this. The experiment in a dry ambient could be repeated to determine if the increase in MSE within the first 11 days is reproducible. However, at the present, none of the four FCP formulations tested can be said to be suitable for longterm storage in a dry ambient of Al+XeLiF+FCP subjected to multiple FCP applications and peeloffs. However, experiment two indicates that, with only three FCP applications and peel offs, longterm storage of Al+XeLiF+FCP (S1 or S3) at 40% RH, may be possible. VASE showed no thin-film stack changes, indicating no significant aluminum oxidation over half a year. This lines up with the cleaning of Al+XeLiF in the dry ambient studies in Vawdrey et al.,[13] as we also found S3 was suitable to clean the surface repeatedly without any problems in a dry ambient. However, FUV reflectance measurements on these aged samples need to be made to see if reflectance is still high.

The Al thickness reduction from prolonged exposure to the FCP film appeared to be a consistent problem until saturation. However, the reduction in reflectance was significant in the far-UV. We assume the aluminum



(a)



(b)

Figure 11: The (a) reflectance of LiF+Al+SiO_2 samples and the (b) reflectance differences between the FCP-stored samples and the control in humid environments. The reflectances are nearly all higher than the average of the controls. There was 36 days in between the initial measurement and the final measurement.

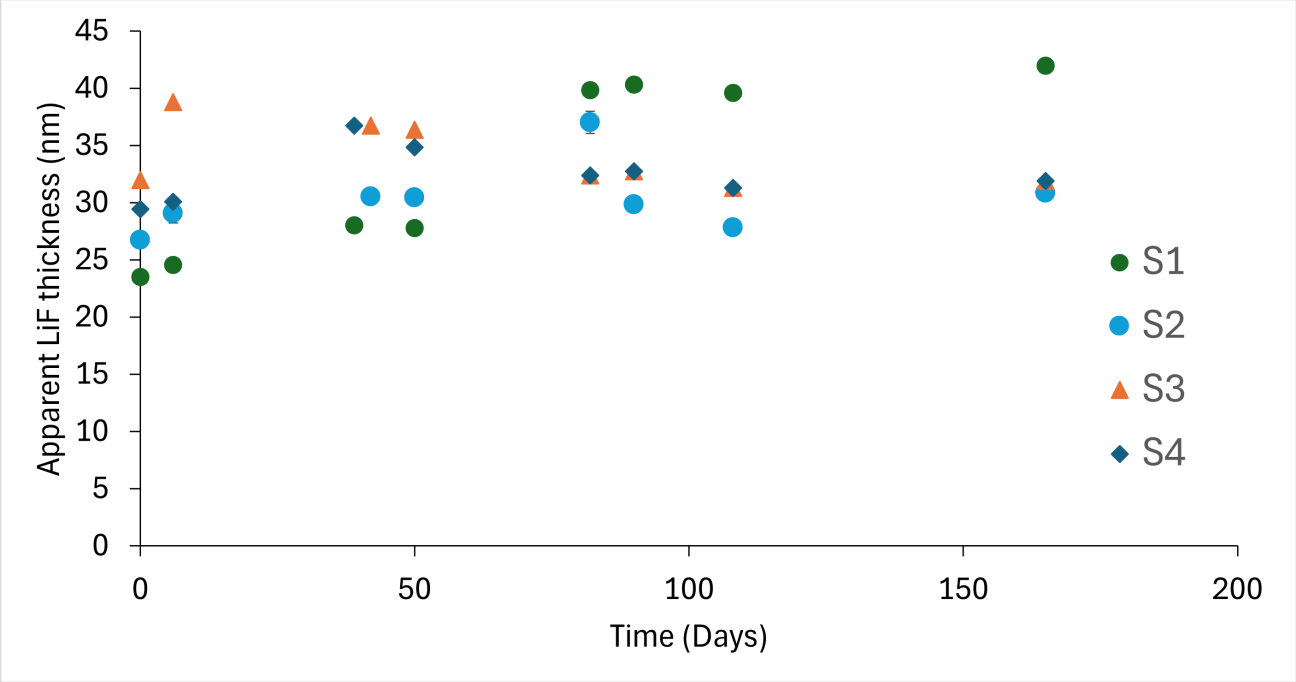


Figure 12: The apparent LiF thickness in the Al+LiF samples that were left in the saturated (100% RH) environment. Due to similarities in the dispersion curve with LiF, AlF_3, and Al_2O_3, thickness changes in the apparent LiF could indicate thickness in any of these layers. It could also include any surface damage caused from high polymer-to-surface adhesion.

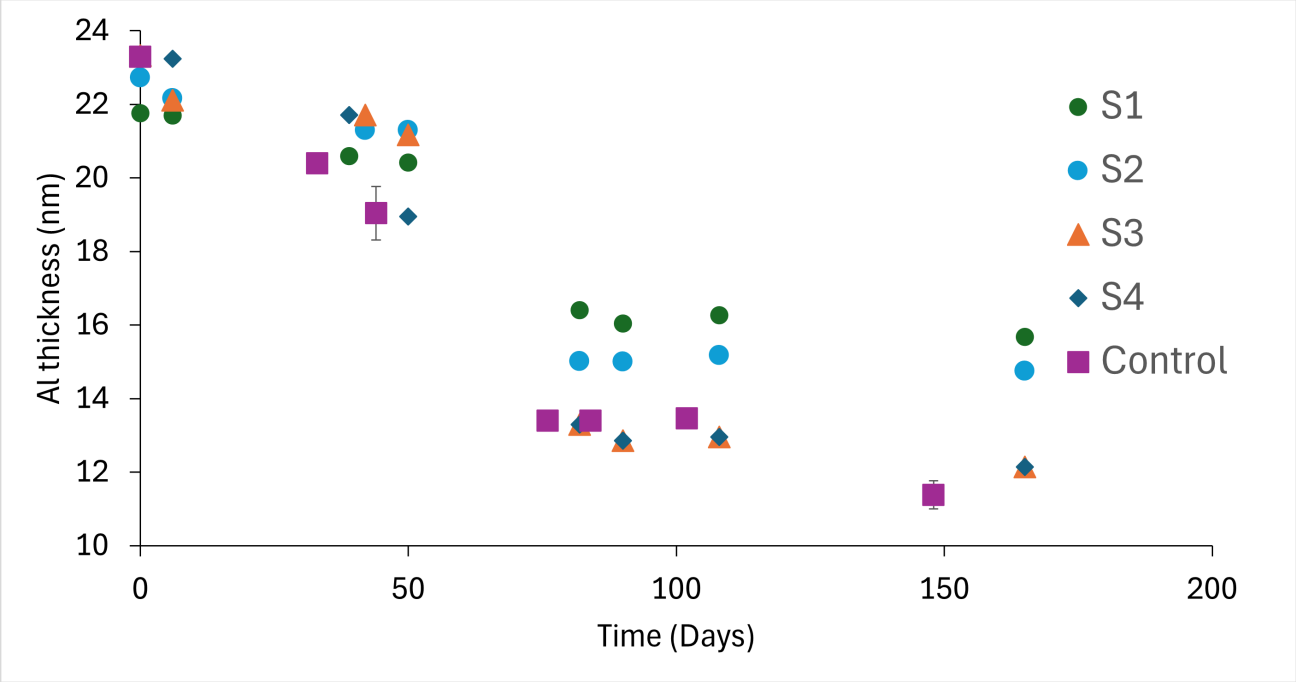


Figure 13: The Al thickness of the Al+LiF samples that were left in the saturated (100% RH) environment. Loss of aluminum indicates an increase in Al_2O_3. A loss of 4 nm of Al produces $>$ 6 nm of oxide which is enough to destroy the stack's FUV reflectance.

oxidation due to prolonged exposure to the FCP is the reason why the reflectance reduced significantly, as it has been shown that Al+XeLiF is highly resistant to oxidation in high humidity environments.[3]

The hillock features on some samples from the first experiment after they have been subjected to multiple FCP application/removal cycle was reported previously.[13] These features were speculated to either be substrate/thin film interfacial cavities forming from polymer-to-surface peel-off stress or crystallization of the LiF from water in the FCP. Therefore, both polymer-to-surface adhesion and water content are suspect in causing the likely changes. The changes in MSE observed in Fig. 1 are mostly due to changes in the SE data over a limited energy range, such as that shown in Fig. 2 for S1. Other samples show the Ψ values either increase dramatically as well at 6-6.5 eV or spread out, possibly indicating the presence of a new material with an absorption edge just above that energy, further in the FUV. This something could be alumina forming on the aluminum and/or water getting into the LiF layer. alternatively blistering could occur. It is more likely to have caused the features observed in Fig. 8. As AFM has not been performed on the 40% RH and 72% RH samples. It is not known if those samples exhibited any hillock features.

5. CONCLUSION

The soft and hygroscopic nature of LiF is well known and is being investigated as to how its properties may affect state-of-the-art Al+XeLiF mirror coatings.[2–4] These coatings are robust and highly reflective in the far-UV.[1,6] Some FCP formulations have previously been shown to be effective at cleaning the Al+XeLiF without changing the thin-film stack in a dry ambient environment.[13] A standard FCP formulation has already been shown to clean oxide surfaces effectively,[8] so being able to use FCP to clean and protect Al+XeLiF samples for storage is desirable. However, the current FCP formulations may need some optimizing to allow the storage of a Al+XeLiF mirror in a disposable coating that reduces the risk of physical damages as well as soiling via particulate and molecular contamination. In one set of multiple application and removal of FCP experiments it was observed that there was a sharp increase in the quantity of oxide within 11 days of storage in a dry ambient environment. Reproducing the experiment could confirm or deny the increase early onto the FCP film storage of Al+XeLiF in dry ambient conditions and as well as probe the origin the hillocks (blisters) observed via AFM on the surfaces.

We also observed that Al+XeLiF samples stored with one of the two formulations (S1 and S3) can only be stored at a 40% RH without significant oxidation for several months. It appears that only one formulation can be used to clean and store the Al+XeLiF. Although Al + XeLiF was found to retain high reflectance when applied with FCP for a short period of time from a previous experiment,[13] storing samples in FCP can cause increased roughness and oxidation. Hillocks formed possibly from internal stress from high polymer-to-surface adhesion during peel-off or recrystallization from the trace water content in the FCP. This causes a drastic reduction in the far-UV reflectance of our samples. Our study shows evidence that using FCP currently developed to store samples in a protective layer can be effective under the right humidity conditions (ie. 40% RH) and minimal peel-offs. More research should be conducted to create a new FCP formulation that will perform well with Al+XeLiF in all humidity conditions.

Our Al+LiF do appear to suggest that the FCP may be able to reduce the effect saturated environments may have on LiF. The visible degradation of the control compared to the samples applied with FCP suggests that FCP did play a protective role with the samples. However, the aluminum still exhibited oxidation. Future experiments will need to investigate new FCP formulations that can clean the surface, be removed without any problems, and remain on the sample for long periods of time as a protective coating.

FCP is a promising candidate for cleaning and protecting state-of-the-art mirror coatings like Al+XeLiF. Factors such as adhesion and water content can be adjusted in the development phase of the new polymer. However, until further research is performed, multiple formulations can be used to clean it a single time,[13] one formulation can be used to clean the mirror coating multiple times over the course of months,[13] and no formulations can be used to stored the Al+XeLiF in a dry ambient environment. Two formulations were found to be effective in 40% humidity, which is surprising considering the dry ambient results. No formulations were found to be effective at completely mitigating aluminum loss in 72% RH conditions. Future research will investigate customized formulations on Al+XeLiF in higher humidity as well as research into the sudden increase in alumina growth in the dry ambient.

ACKNOWLEDGMENTS

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6. CONFLICT OF INTEREST

We report that James Hamilton is the CEO of Photonic Cleaning Technologies, the company that makes First Contact Polymers.

7. DATA AVAILABILITY

Data have been archived locally and are available upon reasonable request.

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