Stability of XeF_2 passivated Al plus LiF as possible coating for HWO

Devin M. Lewis[a], Tanner D. Rydalch[a], David D. Allred[a], Luis Rodriguez de Marcos[b], Manuel A. Quijada[c], Javier del Hoyo[c], and Mateo Batkis[c]

[a]Department of Physics and Astronomy, Brigham Young University, Provo, UT, 84602, USA
[b] Catholic University of America, Washington DC, USA
[c]NASA Goddard Space Flight Center, Greenbelt, MD, USA

ABSTRACT

A new deposition method developed by Goddard Space Flight Center fluorinates Al mirrors with XeF_2 followed by a LiF coating to create what they term Al+XeLiF. This in-situ, room temperature process produces mirrors with high reflectivity in a broad spectral range, from the FUV to the IR, and is reported to be stable in relative humidities of 30% and lower. These mirrors are envisioned for missions requiring sensitivity down to 100 nm wavelength such as the habitable worlds observatory. Because most mission integration and testing campaigns require prolonged exposure to lab environments, and launch sites experience high relative humidities (RH) on average, some at 80% RH. We investigate Al+XeLiF stability in a wider range of temperatures and humidities along with employing additional characterization techniques including atomic force microscopy and x-ray photoelectron spectroscopy. We found that Al+XeLiF is stable in environments up to 82%RH when kept at cooler temperatures (3°C and 21°C). However, this material is unstable when stored at 60°C, experiencing roughening and loss in reflection from resulting Al surface plasmon excitation.

Keywords: LiF, hygroscopic, Al mirror, FUV, AFM, environmental stability

1. INTRODUCTION

The next generation of space telescopes, including the habitable worlds observatory (HWO) will require broadband reflectance.[1] Aluminum (Al) is currently one possible material to achieve this spectral performance, but work is still being done to improve its reflectance in the far ultraviolet (FUV). When exposed to air, Al will oxidize. The resultant film absorbs light of wavelength shorter than 140 nm.[2] Even the low levels of atomic oxygen present at near Earth orbit is capable of reducing FUV reflectance.[3]

Metal fluoride layers have been employed to protect Al from oxidation while maintaining high reflection, such as on Hubble's mirrors. LiF has the widest bandgap of the commonly used metal fluorides and is thus desired for future missions.

However, LiF is hygroscopic, meaning it readily adsorbs water from the air. This property, combined with LiF's solubility in water, can result in LiF thin films reorienting when exposed to high humidity environments. This results in large performance loss of LiF-based mirror coatings. Protecting these LiF thin films from humid environments is challenging as optical systems cannot always be hermetically sealed while they are being integrated and tested. Integration can take weeks at a minimum and requires sufficient ambient oxygen for human presence. Hermetic sealing of a 6m-class OTA, such as envisioned for the HWO,[1,4] would be prohibitively expensive. The standard practice with smaller optics is to reduce the relative humidity around the mirrors through N_2 purging, with the objective of achieving humidity levels of less than 30%. However, a large-scale mirror surface area would require significantly more nitrogen to protect, which could present additional risks to human safety and electronic hardware. Therefore, it is desirable that coatings have good environmental stability.

Different LiF deposition techniques are being attempted to find a way to reduce the hygroscopicity of the material. Quijada *et. al.* at Goddard Space Flight Center (GSFC) have recently developed a formulation for

Further author information: (Send correspondence to D.M.L)
D.M.L.: E-mail: devinlewis131@gmail.com

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depositing LiF on an Al mirror that has among the highest reported Lyman α reflectance of similar film stacks.[5,6] They also report improved humidity stability of the LiF when exposed to humidities up to 50% relative humidity (RH). They produce this film by initially passivating the Al film with XeF_2 to form a thin, approximately 2.5-3 nm, layer of AlF_3 on the Al surface. The XeF_2 gas is then flowed continuously while the LiF is deposited via thermal evaporation to fluorinate any unbound Li atoms, resulting in a smoother surface. They call the product of this process Al+XeLiF.

However, there has been little empirical assessment of how these Al+XeLiF coatings evolve when exposed to different humidity and temperature environments for extended periods of time. Hence, this manuscript studies the extended stability of these XeLiF coatings for the first time, and monitors optical and structural performance of samples over time. We perform a more extensive humidity and temperature experiment than was reported by Quijada *et. al.*, to better understand the stability limits of this new film.[5,6] This will increase the technology readiness level of this coating procedure with the aim to advance it towards flight ready status for the future HWO mission.

2. EXPERIMENTAL

We used the same formulation of Al+XeLiF to directly relate to and extend from GSFC's previous studies. Our characterization techniques included atomic force microscopy (AFM), vacuum UV (VUV) reflectance measurements, and x-ray photoelectron spectroscopy (XPS).

2.1 Sample Fabrication

We acquired samples from GSFC to use in this experiment. They thermally evaporated 30 nm of Al onto an 8" 100 Si wafer. This was followed by their fluorination processes to deposit a nominal 18 nm of LiF. Additional details about the chamber and deposition parameters can be found in Quijada's *et. al.* report.[5,6] A piece of the wafer was selected to keep at GSFC as a control in laboratory environment and the remainder was shipped to BYU in a nitrogen purged box. This minimized oxygen and humidity related degradation prior to the experiment.

2.2 Storage Environments

We stored samples in environments held at constant humidity and temperature. The temperature was controlled by placing desiccators in an oven (60°C), a temperature-controlled lab room (21°C), or a refrigerator (3°C).

Humidity was controlled by placing saturated salt solutions in the desiccators. This is a common method of controlling humidity because saturated salt solutions change the equilibrium vapor pressure of the solute. The exact RH attained is dependent on both the temperature of the ambient and the salt used to make the solution. We referenced Greenspan's[7] compilation of humidity tables to choose our salt solutions.

A total of 14 environments with different combinations of temperature and RH were selected for the experiment to achieve a wide range of combinations. In each case, the corresponding salt was dissolved in distilled water until the water was saturated. The desiccators meant to be stored at elevated temperature were then brought to the target temperature and more salt was added to ensure saturation. Drierite™ ($CaSO_4$) was used for the driest conditions and was simply placed in the bottom of the desiccator in a coarse, anhydrous form. These environments began with 3% RH but this increased to 20% RH by the end of the experiment after repeated opening and closing of the desiccator allowed the $CaSO_4$ to absorb moisture from lab air. This is remedied by heating the $CaSO_4$ in an oven for a week at 60°C. Table 1 is a list of all the experimental environments, conditions of those environments, as well as which material was used to control humidity.

All environments were made and given time to stabilize before samples were fabricated and shipped from GSFC, ensuring that samples could immediately be placed in their proper storage environments. Smaller wafers were cleaved from the wafer as-received from GSFC into approximately 2.5 cm by 5 cm wafers. Afterwards, sample wafers were characterized using AFM and placed in different environments.

When removing samples from any of the cold environments, it was essential to let them warm up in a dry, room temperature desiccator to avoid condensation. Any condensation present would likely dissolve the XeLiF, accelerating the aging process. A separate desiccator with the same environmental conditions as the desiccator for sample "a" (21°C and 3% RH) was used to do this as well as transport samples between labs to and from the different characterization instruments.

Table 1: Sample test mirror designations with the temperature and humidity that the sample was stored in. Humidity was controlled with saturated salt solutions, with the salt used given in the fourth column. The exception is $CaSO_4$, which was simply placed in an anhydrous form in the desiccator.

Sample Designation	Temperature	Relative Humidity	Control Material
a	21° C	3%	$CaSO_4$
b	21° C	33%	$MgCl_2$
c	21° C	40%	K_2CO_3
d	21° C	59%	NaBr
e	21° C	73%	$SrCl_2$
f	3° C	3%	$CaSO_4$
g	3° C	32%	$MgCl_2$
h	3° C	44%	K_2CO_3
i	3° C	60%	NaBr
j	3° C	82%	$SrCl_2$
k	60° C	3%	$CaSO_4$
l	60° C	29%	$MgCl_2$
m	60° C	50%	NaBr
n	60° C	62%	$SrCl_2$

2.3 Characterization

Originally, GSFC demonstrated that this film is resilient to two different humidity levels by showing minimal change in reflectance measurements. We use additional surface sensitive techniques to further probe the the structural changes occurring to the films. These methods include atomic force microscopy (AFM) and x-ray photoelectron spectroscopy (XPS).

2.3.1 Atomic Force Microscopy

Atomic force microscopy (AFM) is a characterization method that probes the surface of a sample to obtain a topographical map of a small region. From this information, the autocorrelation function of the surface can be calculated, which can be used to get other information. Of primary interest to us is the root-mean-squared (rms) surface roughness of the sample. Because LiF is hydrophilic it has a tendency to adsorb water from its ambient environment. This is most likely to happen at pores, which act as nucleation sites. Since more and larger pores appear when the rms roughness is larger, we take the rms surface roughness as calculated by Gwyddion to be a key indicator of film stability. Thus, we track this value over time.

During the measurement procedure, first, samples are removed from their storage environments and immediately placed and transported in a room temperature desiccator kept dry by using $CaSO_4$. Samples were removed from the transport desiccator for one hour during the measurement process. The lab room that the AFM measurements were taken in was nominally 21°C and RH = 20%. Three spots from the sample surface were randomly selected and scanned and the data were analyzed using the open source software Gwyddion. Using Gwyddion, the rms surface roughness of each scan was calculated and saved in an external Mathematica notebook. The rms roughness of each scan was averaged and the 1 σ standard deviation calculated. Figure 1 shows this data, with bars representing the 1 σ standard deviation.

The AFM used in this experiment is a Veeco™ Dimension 5000, with Aspire™ conical AFM tips, part number CT300R-25. Scans were made with a scan size of 2 µm x 2 µm, a scan rate of 0.5 Hz, a horizontal resolution of 1024 pixels and a vertical resolution of 256 pixels. All measurements were made in tapping mode.

2.3.2 UV Reflectance

The standard metric for mirror stability is its maintained reflection. GSFC has a McPherson 225 monochromator capable of taking wavelength dependent reflection data at near normal incidence over the range of 90-180 nm. They use a hydrogen plasma as a light source and scan through wavelength by rotating the diffraction grating. The end station used for sample manipulation is a McPherson model 121 goniometric sample chamber. Light

detection is done by converting the VUV photons to visible light with sodium a salicylate scintillator. This light was then detected with a photomultiplier tube.

2.3.3 XPS

XPS provides chemical analysis and stoichiometry of the different layers in the film stack. With its high surface sensitivity and ability to depth profile, it can illustrate changes happening in each layer. The XPS used in this experiment was a ThermoFisher K-alpha XPS with an Al K-α source. Analysis of XPS data was done with CasaXPS software.

3. RESULTS AND DISCUSSION

3.1 Atomic Force Microscopy

From each AFM scan taken during this experiment, the rms surface roughness was computed using Gwyddion. Fig. 1 shows the time evolution of the rms roughness for the three temperature groups. Each data point is the average rms roughness of three randomly selected points on the sample, scanned using AFM. Bars represent the 1 σ standard deviation of this value, to represent variations in surface roughness across the sample surface.

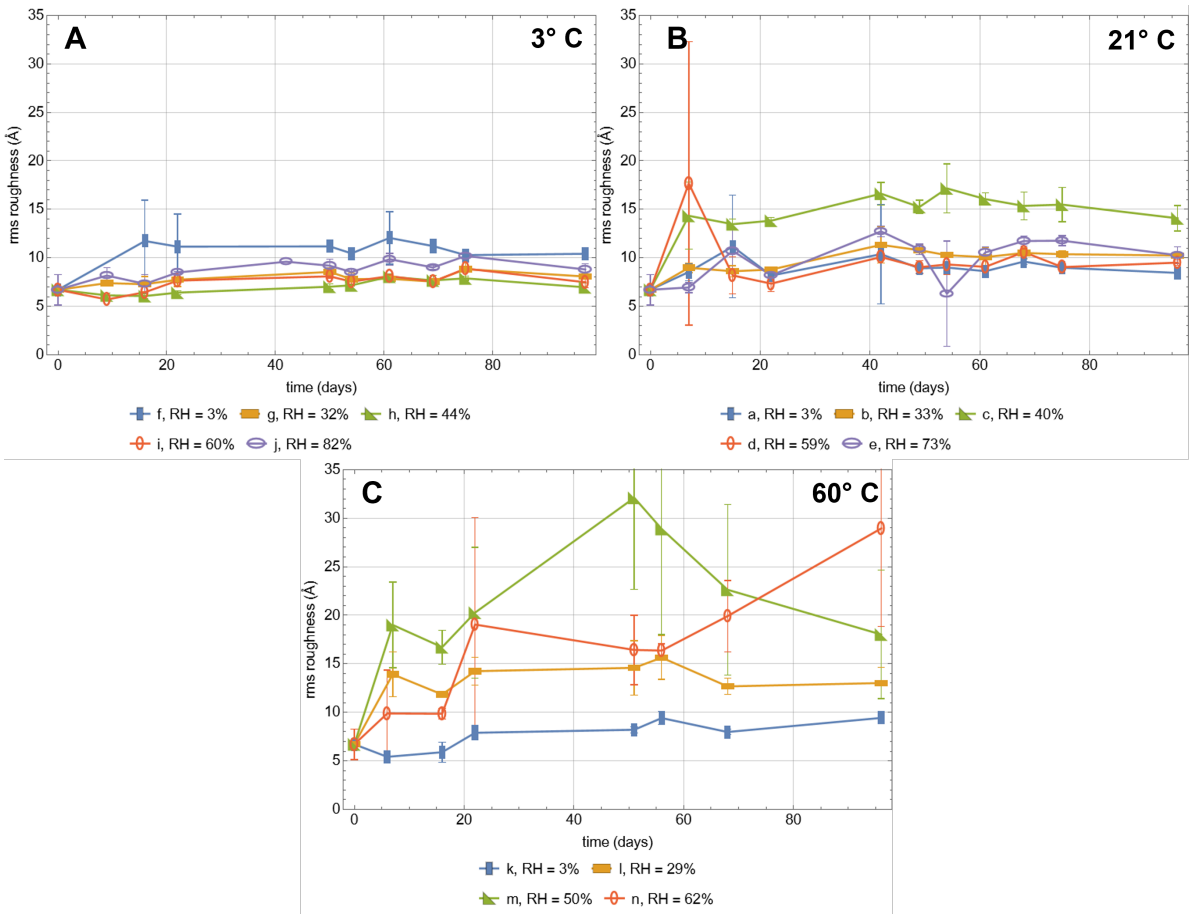


Figure 1: Average rms roughness over time grouped for samples stored in different temperature environments. (A) 3°C (B) 21°C (C) 60°C. At 3°C and 21°C rms roughness appears to be constant over time. This suggests that XeLiF thin films are more stable in colder temperatures.

As can be seen in Fig. 1A, XeLif thin films stored in a refrigerated environment (3°C) appear to be stable over a period of 3 months. There is an initial jump in rms roughness after the first scan for some samples such as

sample "c". Several scans were taken of the original wafer and averaged before cleaving into the smaller sample pieces. This average value was used as the starting point for all samples to reduce of samples to air before being placed in their environments. Where most samples appear to be stable within their error bars after the initial measurement, it is likely that they started with slightly different rms roughnesses.

The XeLiF thin films stored in a room temperature environment (21°C) also appeared stable as observed in Fig. 1B. However, Fig. 1C shows that films stored in an oven (60°C), exhibit a sharp increase in rms roughness, which stays elevated. The exception to this is sample k (60°C, 30% RH) which exhibits a slow increase in rms roughness. The most likely explanation for this difference is the lack of water available to dissolve the LiF of the film. Since LiF's solubility increases with temperature, if water is available to collect on the film at an elevated temperature, the water should dissolve the XeLiF.

The changes in rms roughness are drastic and very evident in topographical maps. This is shown in Fig. 2. The sample stored at 21°C shows a slight enlarging of some crystallites, whereas the sample stored in 60°C shows large features and plateaus that vary in thickness, up to twice that of the original LiF layer. This is indicative of film failure, where the XeLiF would no longer protect the Al layer from oxidation.

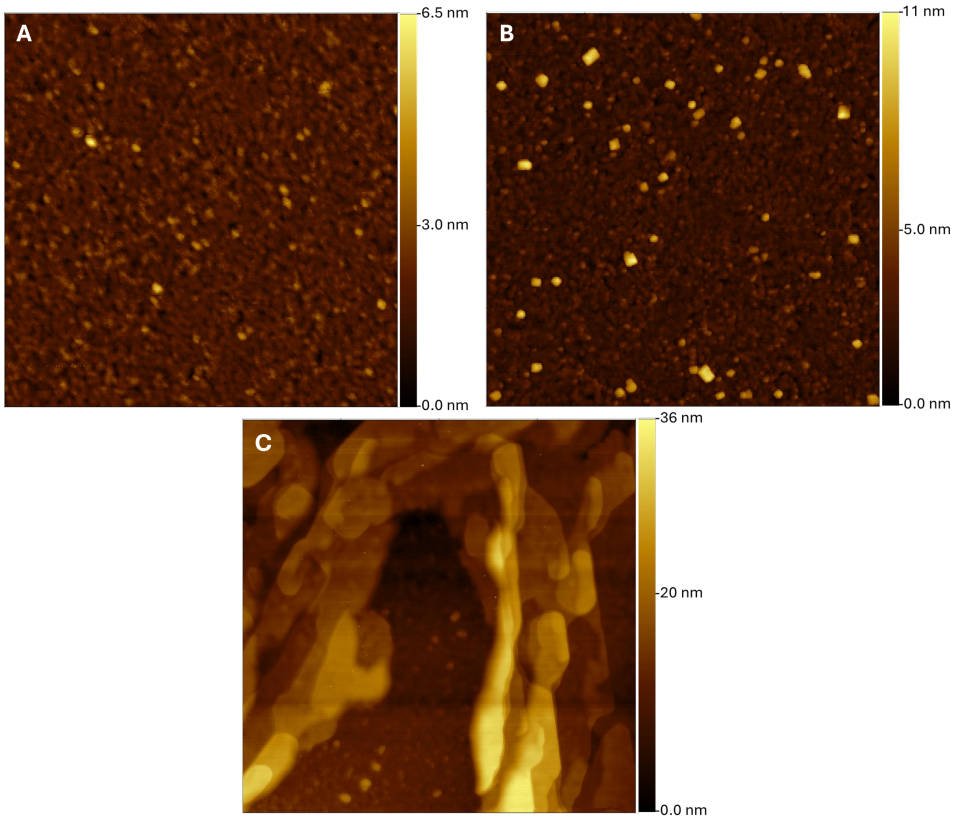


Figure 2: AFM topographical maps of (A) sample before experiment started (B) sample "a" stored in 21°C 3% RH for 2.5 months (c) sample "m" stored in 60°C 50% RH. Both samples were aged for 2.5 months.

3.2 Reflectance

The number of times samples could be measured with GSFC's monochromator was limited because of the challenges of environmental control when shipping. For this reason, one reference sample was measured at GSFC at the beginning of the experiment and kept there in a box in lab air while all other samples were sent to BYU. After 2.5 months of storage in the various environments, a selection of samples were sent back to GSFC for reflectance measurements. These measurements are seen in Fig. 3.

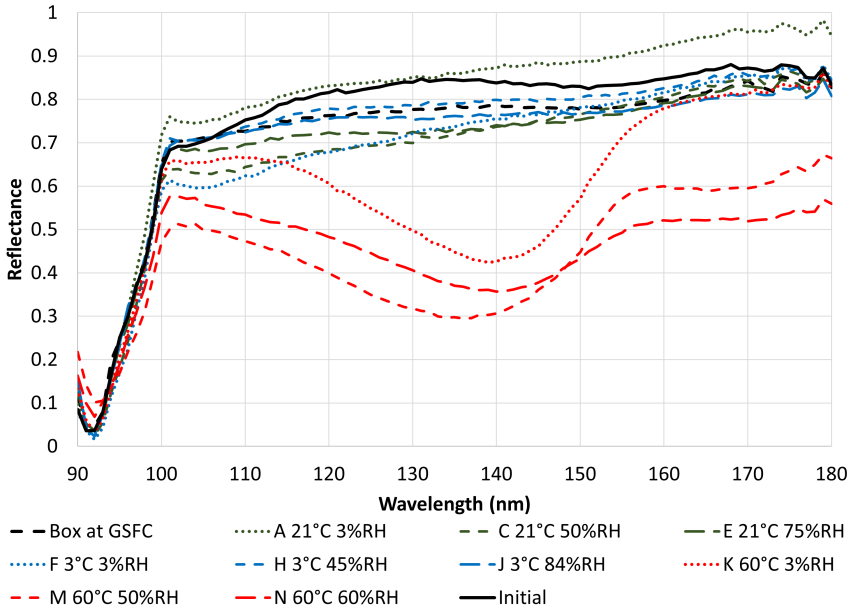


Figure 3: Reflectance measurements at near normal incidence for 9 samples after aging for 2.5 months. The solid black line is the reflectance of a witness coupon cleaved and measured at GSFC before the rest of the wafer was shipped to BYU. The dashed black line is the same witness coupon kept by GSFC and aged in ambient air.

Of immediate note is the apparent increase in reflectance of the sample stored in 3% RH at room temperature. This change in reflectance is likely due to thickness non-uniformity across samples, introduced during deposition. Thus, we cannot conclude that deviations in reflectance from the reference sample are due to sample degradation without more measurements further into the experiment. However, the three samples stored at 60°C show a large dip in reflectance centered near $\lambda = 140$ nm, a feature independent of thickness non-uniformity. These dips in reflectance appear to be Al surface plasmon excitation[8] due to the roughening seen in Fig. 2C.

To further check if the roughness was the source of plasmon excitation a simulation was done. The Al layer was assumed to be flat and roughness from sample "m" (60°C and 50% RH) as seen in Fig. 1C and Fig. 2C was used. This simulation calculated the expected reflectance at 106 nm and 140 nm wavelengths and returned 52% and 39% reflectance respectively. These results relatively match the data seen in Fig. 3 and confirms the hypothesis that the dips in reflectance are due to Al surface plasmon excitation.

3.3 XPS

We etched through the LiF and AlF_3 layers of the film stack with the Ar ion gun in our XPS. Scanning over the Al 2p region revealed the presence of two peaks, one for Al metal and one that corresponds with Al_2O_3, as seen in Fig. 4. To avoid damaging samples still being aged, this measurement was taken on one of several extra samples stored in conditions similar to those for sample "a" (21°C and 3% RH).

The destructive nature of depth profiling made it difficult to take multiple measurements as samples were aged. Because of this, it could only be used to establish the presence of Al_2O_3 and not to quantify the time evolution of Al_2O_3 thickness.

In previous studies, Al_2O_3 has been observed to grow underneath thin fluoride films using variable angle spectroscopic ellipsometry.[9] We similarly took periodic ellipsometric measurements of these samples as done in past LiF humidity experiments.[10] We observed no Al_2O_3 growth on the samples stored at 3°C and 21°C. The large surface changes of the samples stored at 60°C made it difficult to model in ellipsometry. However, because

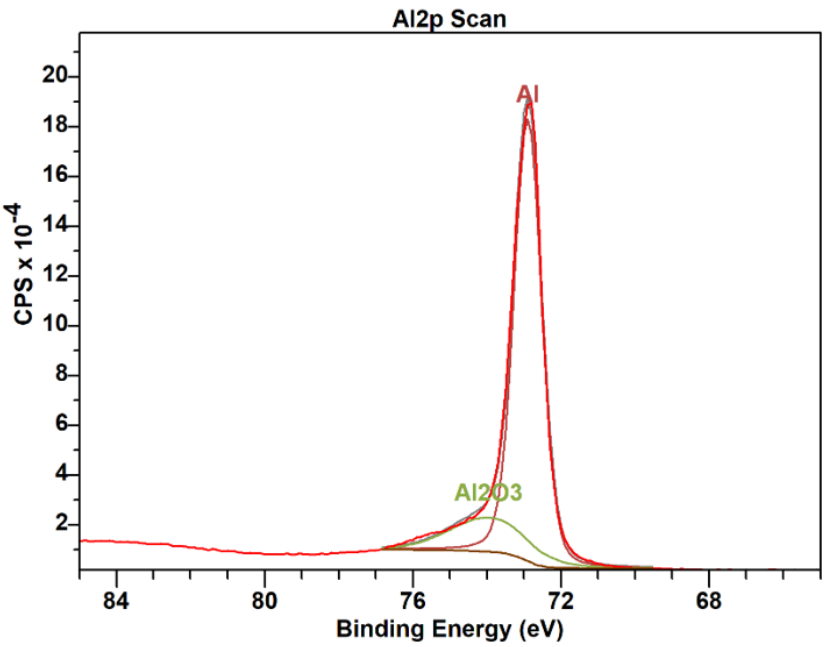


Figure 4: XPS scan of extra wafer piece stored in 21°C and 3% RH for five months. This scan is over the Al 2p range after etching through the LiF and AlF_3 layers.

no cutoff reflection is seen in Fig. 3 that would correspond to an optically thick Al_2O_3 we assume that there was no significant Al_2O_3 in this sample set as well. It is likely that the Al_2O_3 observed in XPS grew during deposition from residual oxygen in the chamber.

4. CONCLUSIONS

Al+XeLiF is unstable in heated conditions and most stable in a cooled environment. Al_2O_3 causes a characteristic cut off of reflectance in the VUV.[2] Since this is not observed in any reflectance profiles, we conclude that XeLiF protects Al from oxidation, even when shown to degrade at the surface in heated conditions. However, the resulting rougher surfaces from heated storage cause Al surface plasmon excitation, which creates a dip in the reflectance of Al+XeLiF mirrors. While our 60°C environment is not representative of any natural environment, many mission launch sites regularly experience temperatures up to 40°C and similar degradation may occur.

Room temperature and cooled environments preserve Al+XeLiF mirrors at all humidities tested (up to 82% RH). Since clean rooms generally have 45-65% RH to preserve electrical components, this means that Al+XeLiF is stable in most clean room conditions.

From these results, temperature appears to play a larger affect in degradation than humidity alone. If elevated temperatures can be avoided then Al+XeLiF is capable of of withstanding elevated humidities up to 82% RH at least.

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