Aging Studies of LiF Coated Optics for use in the Far Ultraviolet

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ABSTRACT

The Far Ultraviolet Spectroscopic Explorer (FUSE) is an astrophysics mission especially designed to access the quite rich spectral region between 90.5 nm and 118.7 nm with a high spectral resolving power.

The FUSE instrument contains four identical off-axis paraboloid telescope mirrors and four spherical diffraction gratings. Two mirrors and two gratings are coated with silicon carbide (SiC) and have a bandpass of 90.5 nm to 110.0 nm. The remaining two mirrors and gratings are coated with lithium fluoride (LiF) over aluminum (Al) providing about twice the reflectivity of the SiC at wavelengths larger than 105.0 nm but very little reflectivity below 102.0 nm.

The far ultraviolet reflectivity of the Al+LiF coated FUSE optics is very sensitive to moisture and molecular hydrocarbon contamination. To avoid degradation of the reflectivity all optics testing and handling has been carefully controlled to minimize the exposure of the coatmissfont.logings to ambient air. In general the optical surfaces were kept in nitrogen purged enclosures.

We report on a simple test program in which small Al+LiF witness mirrors were stored in different relative humidity (RH) environments in order to study the degradation of their reflectivity between 92.7 nm and 121.6 nm as a function of time. The results of this study were used to establish guidelines for storage and test environments for FUSE optics prior to launch. Our methods and results are then compared to a similar aging study performed by the NASA/GSFC Optical Thin Film Laboratory.

Keywords: FUSE, LiF, coatings, reflectivity, ultraviolet.

1. INTRODUCTION

The Far Ultraviolet Spectroscopic Explorer (FUSE) is a NASA "Principal Investigator-class" mission that was conceived to access the 90.5-118.7 nm spectral region with a high resolving power of $\lambda/\Delta\lambda$ = 24,000-30,000.

The spectral window viewed by FUSE will permit the study of many important atoms, ions, and molecules which cannot be investigated from the ground. In particular, the FUSE bandpass contains the important Lyman series of hydrogen which includes Ly_β=102.6 nm, Ly_δ=97.2 nm and Ly_γ=95.0 nm. Most of this spectral window is not accessible with the Hubble Space Telescope (HST), which contains optics that reflect light only at wavelengths longer than 115.0 nm. In addition to interstellar medium studies, observations in the far ultraviolet (FUV) wavelength range provide opportunities to answer important questions about many types of astrophysical objects, such as active galactic nuclei, quasars, hot stars, supernova remnants, planetary nebulae, cool stars and solar system objects.

One of the fundamental problems that will be addressed by FUSE is the abundance of deuterium in the present day Universe. FUSE will measure the abundance of deuterium in a multitude of galactic and extragalactic environments. These measurements will be used to test current theories of the chemical evolution of galaxies and the resulting degree of destruction of deuterium by stars, hence providing a better understanding of the amount of deuterium produced in the Big Bang. FUSE will also study the physical properties and map the distribution of hot gas within the Galaxy, by measuring the interstellar OVI absorption (λ=103.2 nm), as well as the nature and properties of the hot intergalactic medium, by measuring the absorption by HeII along the line of sight to several different quasars.

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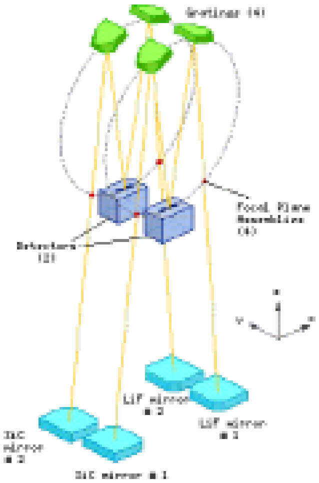

Figure 1. FUSE optical-layout

The FUSE satellite consists of the spacecraft and the science instrument. The instrument consists of four identical normal incidence off-axis paraboloid telescope mirrors that illuminate four spherical holographically ruled diffraction gratings (Fig. 1). The spectra fall then on two micro-channel plate detectors with delay line anodes. Two mirrors and two gratings are coated with silicon carbide (SiC) with a bandpass of 90.5 nm to 110.0 nm. The remaining two mirrors and gratings are coated with lithium fluoride (LiF) over aluminum providing about twice the reflectivity of the SiC at wavelengths larger than 105.0 nm but very little reflectivity below 102.0 nm (Fig. 2). The Optical Thin Film Laboratory at NASA/Goddard Space Flight Center (GSFC) applied all the coatings to the FUSE mirrors and gratings.

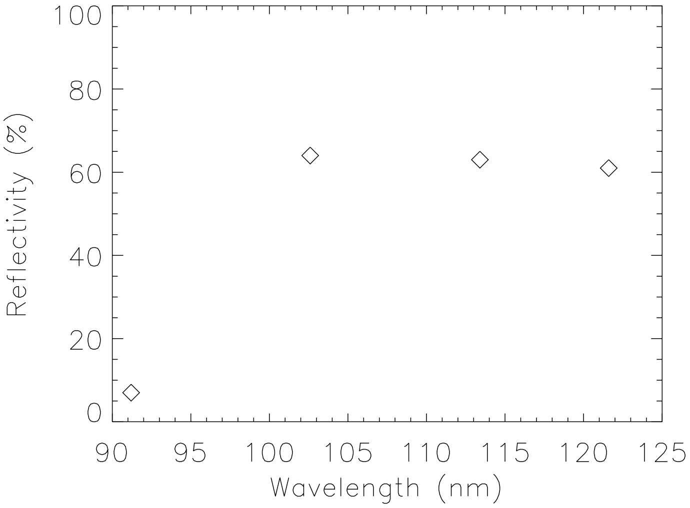

Figure 2. Reflectivity vs. wavelength for LiF mirrors

The lithium fluoride over aluminum coatings used in the FUSE mirrors posed enormous technical challenges. In particular, the LiF overcoating is hygroscopic and therefore exhibits reflectance deterioration with exposure to water vapor. Because of this, no other space missions have used this type of coating since 1972, when the third Orbiting Astronomic Observatory mission, *Copernicus*, was launched.

2. CONTAMINATION

The far ultraviolet reflectivity of the Al+LiF coated optics is very sensitive to moisture and molecular hydrocarbon contamination. A molecular contaminant deposition of only 0.5 nm thickness on these surfaces can seriously degrade the instrument performance. The humidity control for the lithium coated optics is much more stringent than that of the rest of the satellite which can be kept at a 30% to 50% relative humidity. To maintain the efficiency of the instrument on orbit, the average effective area can not decrease by more than 20% per year, taking into account all possible sources of contamination.[2] Therefore attempts were made to keep the optical surfaces in environments with less than 30% relative humidity.

These contamination issues were a main concern during the design phase of FUSE and many elements were included to control or prevent contamination. These include barriers, temporary and permanent covers, use of low-outgassing materials, selection of inherently clean fabrication processes, minimization of the use of organic materials and extensive use of nitrogen purging, amongst others. Strict control of all ground operations from integration through launch was established in order to reduce the risk of molecular contamination by: careful selection and placement of all organic materials, direct venting of outgassed by-products and thermal-vacuum bake-outs.

With the purpose of monitoring the reflectivty of the flight optics and the environments to which they were exposed a "witness mirrors" plan was established. This was accomplished by fabricating small mirrors with coatings similar to the flight optics. These can then be handled much more easily than the flight optics due to their reduced size, and in addition removes all the problems associated with measuring the reflectivity of large and fragile flight hardware. Nevertheless, the flight optics still went through a reflectivity baseline measurement.

The witness mirrors are truly representative of the flight optics surfaces. They were fabricated at the same time, to the same tolerances, and using the same process. There are several types of witness mirrors. Flight witness mirrors are defined as those that have been coated at the same time as the flight optics and have been exposed to the same environments. Test witness mirrors are those that are used to verify an environment in advance of flight hardware exposure. Control witness mirrors are used to monitor shipping and handling environments when the flight or test witness mirrors are not in the environment being sampled.

2.1. Molecular Contamination

Hydrocarbon molecular contamination can produce complicated effects since there may be significant wavelength dependence to the loss of reflectivity. The requirements for FUSE are based on modeling done by GSFC. Multilayer calculations were performed in order to estimate the reflectivity both before and after contamination of the optical surfaces with various thicknesses of a contaminant.[3] Based on these calculations, limits were set on the allowable levels of molecular contamination (Table 1).

Table 1. Limits for allowable levels of molecular contamination.

	Ground LiF thickness	In flight (per year) thickness
Telescopes	0.5 nm	0.15 nm
Gratings	0.5 nm	0.15 nm

2.2. Water Vapor Contamination

The exposure of the Al+LiF coated optics to water causes a severe loss of reflectance, in particular in the wavelength region from 100.0 nm to 105.0 nm. This exposure causes a permanent change of the lithium fluoride surface. This change is distinctively different from molecular contamination which simply coats the surface. The existence of only very limited data on the behavior of the LiF coatings in different humidity environments led us to conduct a test program that is described below.

3. JHU - AGING STUDY OF LITHIUM COATED OPTICS

Although there was a long term lithium fluoride aging study at GSFC (described briefly in section 4) we felt it was necessary to have more data on the behavior of the lithium fluoride coatings in a broader range of humidity environments. With this purpose a lithium fluoride coating aging study was established at the Johns Hopkins University (JHU). The glass substrates were coated in the same facility as the flight optics using a similar process. The different humidity environments simulated, the process used to measure the reflectivity and the results obtained are described below.

3.1. Optics Coating Procedure

Eighteen 25 mm diameter by 3mm thickness borosilicate float glass witness mirrors were coated at the NASA/GSFC Optical Thin Film Laboratory facility. The coating process included a glow discharge during which 14.8 nm of lithium fluoride were deposited over 62.2 nm of aluminum. The eighteen mirrors were numbered 1 through 18. The reflectivity of two of them, 1 and 16 was measured shortly after the film deposition occurred for reference purposes, (Table 2). The reflectivity of the lithium fluoride coatings was expected to decrease slightly for the first few days after the coating occurs, stabilizing afterwards. This reflectivity degradation is typical of both SiC and LiF newly coated optics.

Table 2. Reflectivity of witness mirrors 1 and 16 shortly after being coated.

Mirror ID	102.5 nm	116.2 nm	121.6 nm
1	67.9%	72.3%	71.6%
16	68.7%	70.3%	71.0%

After being coated all the mirrors were stored inside nitrogen purged containers which were then sealed inside a polyethylene bag with desicate capsules. They were then stored inside a desiccator until they were transported to our laboratory at JHU.

3.2. Relative Humidity Simulation

After arriving at JHU a baseline reflectivity measurement was made, the mirrors were then grouped in pairs and each pair was stored in a different humidity environment.

Table 3. Distribution of mirrors through the different humidity environments and salts used to produce them.

Mirror Id	Measured RH	Specified RH[1]	Salt
3, 10	26%	20%	Potassium Acetate (CH_3COOK)
4, 11	42%	35%	Chromium Trioxide (CrO_3)
5, 12	52%	45%	Potassium Nitrite (KNO_2)
6, 13	78%	65%	Magnesium Acetate ($Mg(C_2H_3O_2)_2$)
7, 14	40% - 70%	-	Room
8, 15	5% - 30%	-	Desiccator

Humidity environments corresponding to 26, 42, 52 and 78% relative humidity (RH) were produced using different salts (Table 3). A solution of water and salt in a closed container reaches an equilibrium where its vapor pressure maintains a constant humidity in the air above it. The humidity inside is then measured with a sensor attached to the lid of the containers used. The sensor used has a 2% accuracy at 25° Celsius. This process allows a quick RH measurement without the need of opening the containers.

For the pair of optics that was stored in the desiccator, the RH varied between 5 and 30%, reaching this maximum value when the desiccator was opened to remove the optics for reflectance measurements. For the pair of optics that was stored at room RH the humidity varied according to the weather outside. Because the duration of this study covered all seasons, we will assume that the RH ranged between $10 - 70$ % based on periodic measurements in the lab.

3.3. Reflectivity Measurements

The system used to measure the reflectivity consists of a monochrometer, where the light beam is produced and collimated, and a reflectometer where light is reflected off the witness mirrors and measured. The monochrometer, a *McPhearson* model $255MI$, is a grazing incidence instrument capable of providing monochromatic light of up to 200.0 nm (using a $300line/mm$ grating).

In the reflectometer vacuum system a sample holder that holds up to two mirrors can be moved vertically from the outside allowing for measurement of the incident or reflected light. An $AMPTEK$ photon detector/electron multiplier is mounted in an arm that is supported by a rotating flange, which rotates the detector between incident and reflected positions. When at the incident position the detector faces the beam directly, measuring the total number of photons on the beam. When at the reflected position, the detector makes an angle of 15 degrees with the incident beam, and the sample holder is mounted in such a way that the angle of incidence is 7.5 degrees. This layout allows the detector to "see" the reflected light without blocking the incident beam. The output of the detector (electron pulses per second) is then converted to counts per second with an universal counter. The monochrometer side produces and collimates the light beam. A *Quantatec* flow-through nitrogen lamp produces a variety of wavelengths for which the selection of a particular one is made by moving a synchronous motor that moves the lamp on a rail that changes its angle of incidence to the diffraction grating while keeping the aperture stop on a *Rowland* circle. After the light is collimated with a concave diffraction grating and aperture stop, it reaches the reflectometer side where it goes directly to the detector, when counting incident photons, or is reflected off the optics into the detector, when counting reflected photons. A $Varian\ turbo - V550$ pumping station is used to keep the pressure in the monochrometer below 10^{-5} torr.

A typical measurement run includes loading the sample holder with the optics into the system and then pumping down both the reflectometer and monochrometer chambers, independently of each other. When the pressure in both chambers reaches 10^{-5} torr the lamp is turned on and a gate valve between the monochrometer and the reflectometer is open. After the lamp has warmed up, the wavelength at which the measurement is to be made is selected. A measurement of the incident light is performed by lowering the mirrors holder to a position that allows light to go through and rotating the detector to the position that faces the beam directly. Next, a measurement of the reflected light is done by rising the holder until the desired mirror is in the path of the light beam and rotating the detector until it intercepts the reflected beam. This procedure is then repeated for each mirror to be measured, at each wavelength.

For each measurement of the incident and reflected beams a total of ten, ten seconds integration time photon counts are taken.

3.4. Results

The results of our reflectivity measurements as a function of time are shown Figure 3, for each wavelength at which the reflectivity (R) was measured, with the different RH environments labeled. The horizontal axis represents the period of time elapsed since the mirrors were initially coated. The first data point corresponds to a baseline reflectivity measurement that was made before the mirrors were placed in the containers. To calculate the amount of time a mirror spent inside a certain RH environment 9 days have to be subtracted from the time indicated in the x-axis, as the mirrors were kept in a desiccator cabinet while the RH environments were being prepared.

Although not represented in Figure 3 the reflectivity of all witness mirrors was also measured at 92.7 nm. At this wavelength the reflectance of the LiF coatings is intrinsically low ($<$ 10 %). Still, the effect of the highest RH environment (78%) was clearly seen on the behavior of mirror 13. This mirror starts out with a reflectivity of 7% in the beginning of the aging study and drops to 2% 50 days later, while for the mirrors in the other RH environments the minimum reflectivity obtained at this wavelength was 6%.

As Figure 3 displays for 102.5 nm and 113.4 nm a similar general trend is seen for mirrors 14 and 15 on one side and mirrors 11 and 12, on the other.

There are many systematic effects that possibly contribute to the scatter observed in the reflectivity measurements:

1. *Lamp output/stability* - The output of the lamp depends sensitively on the pressure inside the lamp. For a small range of pressures (0.01 torr) the lamp's output can vary by more than a factor of 2. Its output is relatively stable if enough time is allowed for the lamp to warm up.

2. *Linear feedthrough* - The sample holder that holds the optics to be measured is moved in the vertical direction with the use of a linear feed-through that is operated from the outside of the vacuum system. Although designed to move only in the vertical direction this instrument has shown a small amount of rotation (< 30 degrees) as the holder is moved in the vertical direction. This rotation of the feedthrough only happens for certain vertical positions, that were avoided during this study.

3. *Slit aperture* - The width of the entrance and exit slits determines the FWHM of the lamp's spectrum, how resolved the different wavelengths are and more importantly the size of the beam.

New data has been recently obtained for all mirrors (Table 4). Because the experimental setup was modified[*] since the last reflectivity measurements shown on Fig. 3 these last points are not shown on that figure.

Table 4. Reflectivity data for all mirrors obtained at t= 716 days.

RH	Mirror ID	104.8 nm	106.7 nm	121.6 nm
26%	10	58%	60%	52%
42%	11	42%	44%	48%
52%	12	52%	54%	50%
78%	13	0%	0%	0%
Room	14	50%	60%	52%
Desiccator	15	67%	68%	58%

4. NASA/GSFC OPTICAL THIN FILM LABORATORY AGING STUDY

For the purpose of comparing our study with theirs, we briefly describe a similar aging study established at NASA. This long term study, established in 1996 and conducted by Jeffery Gum and Charles Fleetwood at the NASA/GSFC Optical Thin Film Laboratory studied the ultraviolet reflectivity degradation of a lithium fluoride over aluminum film structure.

Eight glass slides were coated at the above facility, by a process similar to the one used for the flight optics, and their reflectivity was periodically measured with a McPhearson 225 reflectometer. The slides, named A though H were stored in different environments, that are described below (Table 5).

Table 5. Distribution of slides through different environments.

Slide ID	Environment
A, B	Desiccator, together in slide box
C, D	Open environment for first month (max RH= 52%, then desiccator with A and B
E, F	Sealed and nitrogen purged clean room bag
G, H	Sealed and nitrogen purged clean room bag for first month, then desiccator with A and B

4.1. Measurements

The reflectance measurements are shown in Figure 3, as a function of time for each wavelength, with the different environments labeled. The horizontal axis represents the total amount of time elapsed since the optics were initially coated, which is (within a few hours) the amount of time that the optics spent in the different environments.

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[*] Nitrogen used in the lamp was replaced by argon, producing brighter lines but at different wavelengths.

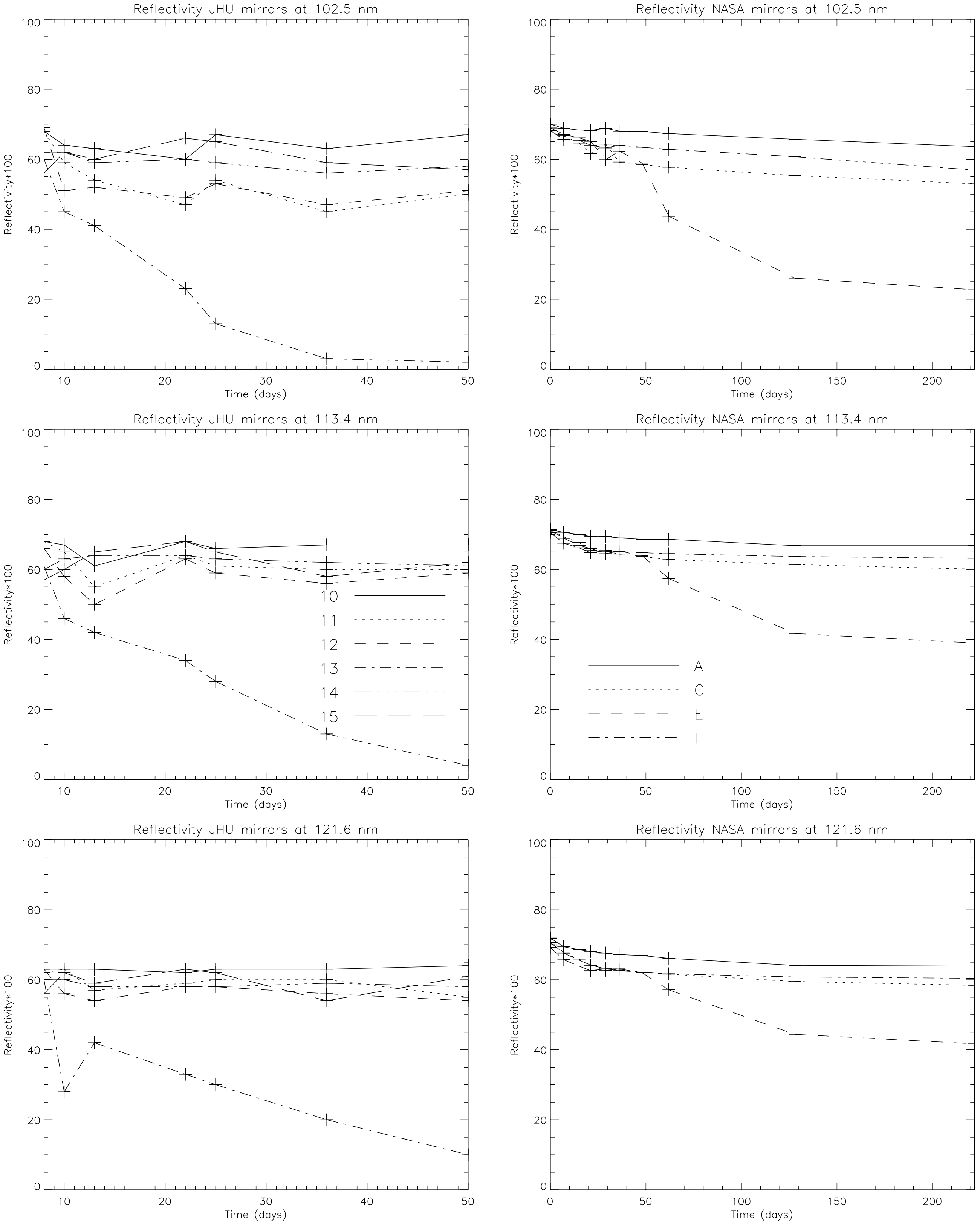

Figure 3. Reflectivity as a function of time for the JHU and NASA aging studies

5. DISCUSSION

5.1. JHU aging study

As expected mirror 13, the one stored in the highest humidity environment (78%), has suffered the severest reflectivity degradation. In fact, the last measurement (Table 4) indicates that this mirror has now 0% reflectivity.

Taking into account only the data for the first two months (Fig. 3), mirror 10 (26%RH) has suffered the least reflectivity loss. However when we consider the data on Table 4, we see that this mirror behaves better than the one stored at room RH, but not as well as the one stored in the desiccator.

Surprisingly, the mirrors stored at 42% RH (mirror 11) and 52% RH (mirror 12) show a consistently worse behavior than mirror 14 which was stored at room RH. Periodic RH measurements in the lab showed that several times the RH was above 60% and on average above 55% during the first two months of the study. Because of the process used to simulate the different RH environments (chemicals) it is possible that somehow this salts have reacted with the coatings and contributed to a degradation of the reflectivity that would not be seen otherwise. Further work will be done to investigate this possibility.

5.2. NASA/GSFC Optical Thin Film Laboratory aging study

Mirror A, the sample kept in the desiccator, seems to be the one that has experienced the least reflectivity degradation over the course of their study.

It is clear from looking at the plot for mirror C when this mirror was transferred from an open room environment to a desiccator, around day 30, contrary to expectations the reflectivity decreased slightly, but stabilized very rapidly.

Mirror E, which was kept in a sealed and purged clean room bag, is the one that had the severest reflectivity loss. Mirror H was kept in the same type of bag as mirror E but after one month it was transferred to a desiccator. It seems that somehow some moisture might have been sealed inside bag E, especially around the measurement made around day 50, when the reflectivity drops substantially. The reflectivity keeps dropping until day 128 after which it stabilizes. This seems to indicate that after a mirror has been exposed to a certain RH, its reflectivity drops a certain amount, but if the mirror is then stored in dry environment the reflectivity stops dropping. For mirror C the RH was always $< 52\%$ and since this mirror doesn't show the same behavior as mirror E, which suffered a much more severe reflectivity loss, this seems to imply that E was not contaminated by ambient air humidity, reinforcing the idea of moisture contamination in the sealed bag.

Mirror H, which was kept inside a purged and sealed cleanroom bag and later transferred to a desiccator behaved similarly to mirror A, but its reflectivity decreased more than that of A.

We should not forget though that some of this drop in reflectivity might be due to the characteristic behavior of freshly coated optics, and that because these mirrors have been stored in dry environments this common reflectivity degradation took place on a larger timescale.

From these two studies we can conclude that the shorter wavelengths are the most sensitive ones to moisture contamination and keeping these type of coatings stored in a desiccator is the best way to preserve their reflectivity.

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For more information about the mission see the FUSE webpage at http://fuse.pha.jhu.edu/.

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