Temperature Dependence of AlF$_3$ Protection on Far-UV Al Mirrors

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Abstract: More efficient and stable far ultraviolet (FUV) mirrors will enable future space observatories. Traditional FUV mirrors are based on MgF$_2$-protected Al. AlF$_3$ has been identified as a promising substitute for MgF$_2$ to prevent Al oxidation. Hence, the reflectivity, stability, and morphology of AlF$_3$-protected Al mirrors have been investigated as a function of deposition temperature of the AlF$_3$ film. In this work, it is shown how AlF$_3$ deposition temperature is an important parameter whose optimization ultimately yields valuable throughput enhancement and improved endurance to large storage periods. Al films were deposited at room temperature (RT) and AlF$_3$ protective layers were deposited at temperatures ranging from RT to 350 $^\circ$C. It was found that the optimum AlF$_3$ deposition temperature was between 200 and 250 $^\circ$C, yielding the largest FUV reflectance and a better stability of the mirrors, which had been stored in a desiccator environment. Increasing AlF$_3$ deposition temperature resulted in an increase in film density, approaching bulk density at 250 $^\circ$C. The morphology of Al and AlF$_3$ films as a function of AlF$_3$ deposition temperature was also investigated. The increase in the AlF$_3$ deposition temperature resulted in a decrease of both Al and AlF$_3$ surface roughness and in the growth of the grain width at the AlF$_3$ outer surface. It also resulted in a trend for the prevalent (111) planes of Al nanocrystals to orient parallel to the coating surface.

Keywords: mirrors; protective coatings; far ultraviolet; optical properties of thin films; space instrumentation

1. Introduction

The far ultraviolet (FUV; here it refers to the 100–200-nm spectral range) encloses spectral lines of many fundamental atom and ion species of H, C, N, O, etc.; observation at such spectral lines is key for the communities of astronomy and astrophysics [1–5], solar physics [6], as well as atmosphere physics. Aluminum is the material with the largest reflectance down to the FUV [7]. Bare Al grows a thin film of native oxide in the air or even under high vacuum, and this very thin oxide film fully degrades Al reflectance in the FUV. The fast oxidation of Al is a difficulty to obtain durable FUV high-reflectance mirrors, namely that reflectance is maintained over time. It is necessary that space-instrument optics be stable due to the high cost or impossibility of replacement. Both for the use of Al mirrors in space but also on earth, a transparent protective film is necessary to immediately overcoat the underlying Al film in order to avoid oxidation.

Most materials undergo strong absorption in the FUV; therefore, it is of paramount importance to have materials with very low absorption to protect Al. Oxides are typically transparent in the visible, but they start to strongly absorb shortwards of some cutoff wavelength. Fluorides are the materials...
that keep their transparency deeper in the FUV. LiF is the material in nature with its cutoff at the shortest possible wavelength of ~102 nm; nevertheless, LiF is a somewhat hygroscopic material, which complicates its practical application [8,9]; in spite of this, it has been recently used for narrowband FUV multilayers [10]. A fluoride with a short FUV cutoff of ~115 nm is MgF2 [11,12]; the high reflectance of MgF2-protected Al mirrors and their stability in normal atmosphere and in space environment has turned these mirrors into the most popular FUV coating for decades.

AlF3 is another fluoride with a FUV cutoff at 113 nm, which is at a slightly shorter wavelength than MgF2 cutoff [13]. In spite of this, it has received limited attention as a possible protective material for Al mirrors, probably because of the long successful experience with Al/MgF2 mirrors. Yet, various encouraging attempts to prepare AlF3-protected Al mirrors have been reported [13,14]. Al/AlF3 mirrors have been also prepared in which AlF3 was deposited by atomic layer deposition (ALD), although the samples were transferred in air from the Al evaporation chamber to the AlF3 ALD deposition chamber [15]. Al mirrors protected with a combination of several fluorides including AlF3 have been also attempted [14].

Al films for FUV mirrors are better deposited by means of thermal evaporation in vacuum and the substrate is typically at room temperature (RT). Regarding fluoride deposition by evaporation, coatings grow with large porosity when deposited at RT. Such porosity results in void sites that are able to accommodate contamination or water vapor molecules, which increases FUV radiation absorption. Porosity decreases when the fluoride is deposited on a heated substrate, and hence the film remains more stable and also more transparent. Therefore, it would be desirable to deposit the Al/fluoride coating on a heated substrate. However, the increased deposition temperature of an Al/fluoride coating results in FUV reflectance decrease, which is attributed to increased Al grain size and surface roughness [16–18]. Other fluoride deposition techniques, such as sputtering or ALD, result in less porous fluoride coatings; however, they involve increased absorption in the short FUV and/or they are difficult to combine with the deposition of the Al film.

In spite of the overall negative effect on depositing the Al/fluoride coating on a heated substrate, a successful procedure was demonstrated by Quijada et al. [19,20] consisting in depositing the Al film on the substrate at RT, protecting it with an ultrathin fluoride film and heating up the incomplete coating to ~225 °C in order to complete the thickness of the fluoride protective film for large reflectance at short FUV wavelengths. The procedure was proved to work with MgF2, LiF [19,20], and also with AlF3 [21] protective coatings. Heating the mirror once the Al has been deposited in order to grow a more compact and transparent fluoride coating seems to preserve an acceptable, or even reduced, Al surface roughness.

The performance of Al/AlF3 mirrors has been reported so far for AlF3 protective coatings deposited at 250 °C [21]. The present research focuses on the dependence of Al/AlF3 mirror reflectance on AlF3-deposition temperature to look for a temperature range of FUV reflectance enhancement over RT-protected mirrors. It presents experimental measurements for mirrors aged up to 2 years. A comparable research was previously reported for Al mirrors protected with MgF2 [22]. Structural properties of these coatings are also presented, which includes surface roughness, AlF3 density, crystal-plane preferential direction and their dependence on AlF3-deposition temperature through X-ray reflectometry (XRR), atomic force microscopy (AFM), and θ–2θ (Bragg–Brentano) X-ray diffraction (XRD) as well as grazing incidence X-ray diffraction (GIXRD). The paper is organized as follows: Section 2 summarizes the experimental techniques used. Section 3 is divided into Section 3.1, which reports experimental results on reflectance as a function of deposition temperature, and Section 3.2, which presents structural data.

2. Materials and Methods

Samples were deposited in a 75-cm diameter, 100-cm height cylindrical stainless steel deposition chamber in an ISO6 clean room. Chamber was pumped with a Velco 250A cryo system (HSR Balzers, Balzers, Liechtenstein). Fore vacuum was made with an oil-free diaphragm pump and a turbomolecular
pump. Base pressure of the chamber was \(-3 \times 10^{-8}\) mbar. Previous to deposition, the chamber was heated to \(-150^\circ\)C for about thirty minutes in order to accelerate surface outgassing.

99.999\% pure Al and 99.99\% pure AlF\textsubscript{3} were evaporated from tungsten filaments and boats, respectively. Deposition rates were \(-10\) nm/s for Al and \(-1\) nm/s for AlF\textsubscript{3}. Film thickness was measured in situ with a quartz-crystal monitor that had been previously calibrated by profilometry. Substrates were 2 inch \(\times\) 2 inch pieces of BK7 floated glass polished to a root-mean-square (RMS) roughness of \(-0.5\) nm. Substrates were cleaned with organic solvents and cleaning was completed by means of a glow discharge in the deposition chamber.

Deposition was made as follows: A thin film of Al was deposited at RT and it was immediately protected with a 5-nm thick AlF\textsubscript{3} film that was deposited also at RT. Then the sample was heated in vacuum to the desired temperature, at which a further AlF\textsubscript{3} film was deposited to complete a total AlF\textsubscript{3} coating thickness of \(-26\) nm. The thickness was designed for higher reflectance at H Lyman \(\alpha\) (121.6 nm). During evaporation, pressure in the chamber momentarily increased to \(-10^{-6}\) and \(-3 \times 10^{-7}\) mbar with Al and AlF\textsubscript{3} deposition, respectively.

FUV mirror reflectance was measured in GOLD’s reflectometer (GOLD is the Spanish acronym for Thin Films Optics Group, Madrid, Spain), which operates in ultra-high vacuum (UHV) conditions. The reflectometer has a grazing-incidence, toroidal-grating monochromator, in which the entrance and exit arms are 146\(^\circ\) apart. The monochromator covers the 12.5–200-nm spectral range with two Pt-coated diffraction gratings that operate in the long (250 l/mm) or in the short (950 l/mm) spectral subranges. The reflectometer used a deuterium lamp to cover the present spectral range and a channel-electron-multiplier detector with a CsI-coated photocathode. Reflectance was obtained by alternately measuring the incident intensity and the intensity of the light beam reflected by the sample. Reflectance measurements were performed at 5\(^\circ\) from normal incidence.

FUV reflectance was initially measured after \(-1\) h contact with the atmosphere, which will be referred to as fresh, and after various months and 2 years of aging. During this period of time, samples were stored in a desiccator.

A lambda-900 Perkin–Elmer double-beam spectrophotometer (Shelton, CT, USA) was used to measure specular reflectance and transmittance in the visible. Samples were situated at 8\(^\circ\) from normal incidence.

Samples were measured by XRR, XRD, and GIXRD at Centro de Asistencia a la Investigación, Universidad Complutense de Madrid, Madrid, Spain. The diffractometer was a PANalytical X’pert PRO MRD (Almelo, The Netherlands). The source was a Cu anode. For XRR measurements, Cu K\(\alpha\) line (0.154 nm) was selected with a graphite monochromator. Measurements were performed at grazing incidence angles with a step of 0.005\(^\circ\).

XRD was obtained using a conventional (Bragg–Brentano) \(\theta\)–2\(\theta\) scanning method. For GIXRD, the diffractometer was equipped with a parabolic X-ray mirror in the primary beam and a parallel plate collimator in the secondary beam; the primary beam impinged at a constant grazing angle of 0.5\(^\circ\). Both XRD and GIXRD scans were performed with a step of 0.04\(^\circ\) (20).

AFM analysis of surface topography and microroughness was performed with a high-resolution Agilent 5500 Scanning Probe Microscope (Santa Clara, CA, USA) in contact mode. The tip radius was 20 nm. AFM of 1 \(\times\) 1 \(\mu\)m\(^2\) size scan areas were obtained.

3. Results

3.1. Reflectance

We prepared a set of 8 Al/AlF\textsubscript{3} mirrors using temperatures ranging from RT to 350 \(^\circ\)C. AlF\textsubscript{3} film thickness was set at 26 nm for maximum reflectance at 121.6-nm H Lyman \(\alpha\) spectral line, an important line for astrophysics and solar physics. A first 5-nm thick AlF\textsubscript{3} layer was deposited on Al at RT and the complementary 21-nm thick AlF\textsubscript{3} film was deposited once the sample was heated at the desired temperature. Al thickness was set to approximately 70 nm. Two samples were prepared in each
vacuum cycle. The first sample was deposited at a larger temperature than the second sample; hence, the first sample was post-annealed at the second sample deposition temperature. For instance, M250 had AlF$_3$ deposited at 250 °C, and then it was let to cool down to RT. After that we prepared sample M150, so that M250 was annealed at 150 °C when M150 was being deposited. We assumed that post-annealing at a temperature significantly smaller than the deposition temperature should have negligible effects. Table 1 summarizes sample names and deposition temperature. For one sample, AlF$_3$ was deposited at 150 °C and it was later annealed in vacuum at 200 °C.

### Table 1. Sample deposition temperature.

| Sample Name | AlF$_3$ Depos. Temperature (°C) | Comments |
|-------------|---------------------------------|----------|
| M100        | 100                             | Same vacuum cycle |
| MRT         | RT                              |          |
| M150A $^a$  | 150 depos. + 200 annealing      | Same vacuum cycle |
| M200        | 200                             |          |
| M250        | 250                             | Same vacuum cycle |
| M150        | 150                             |          |
| M350        | 350                             | Same vacuum cycle |
| M300        | 300                             |          |

$^a$: Sample M150A was deposited at 150 °C and once completed, it was annealed at 200 °C.

Figure 1 shows FUV reflectance measured for the fresh mirrors after a short contact to the atmosphere of ~1 h. Samples with AlF$_3$ deposited at 300 and 350 °C displayed an uneven structure that was visible to the naked eye. An attempt to measure FUV reflectance resulted in values as low as ~10%, as well as a strong dependence on the specific spot over the sample so that these samples were not analyzed anymore. This result provides us with an upper limit for the AlF$_3$ deposition temperature, which must be between 250 and 300 °C.

![Figure 1](image1.png)  
**Figure 1.** Reflectance as a function of wavelength of fresh Al/AlF$_3$ mirrors, with the AlF$_3$ film deposited at the given temperatures.

Mirrors were stored in a desiccator and they were measured again after 4–8 months and after 2 years of aging. Figures 2 and 3 display FUV reflectance of middle- and long-time aged mirrors, respectively. Reflectance was also measured in the visible, which is displayed in Figure 4.
Figure 2. Reflectance as a function of wavelength of Al/AlF$_3$ mirrors aged of 4–8 months, with the AlF$_3$ film deposited at the given temperatures.

Figure 3. Reflectance as a function of wavelength of Al/AlF$_3$ mirrors aged of 2 years, with the AlF$_3$ film deposited at the given temperatures.

Figure 4. Reflectance in the visible as a function of wavelength of Al/AlF$_3$ mirrors aged of 1 year, with the AlF$_3$ film deposited at the given temperatures.
Hot-deposited AlF$_3$ results in mirrors with enhanced FUV reflectance compared to the mirror deposited at RT. Largest reflectance at the most demanding short FUV wavelengths was obtained at an optimum deposition temperature of 200–250 °C. Furthermore, aging somewhat increased reflectance enhancement over the RT sample, as the reflectivity of the latter decreased more over time than for mirrors deposited at high temperatures. Regarding reflectance in the visible range, no significant difference over the samples was observed. This behavior is similar to what was reported for Al protected with hot-deposited MgF$_2$ [22].

The sample that was protected at 150 °C and later annealed in vacuum at 200 °C resulted in a good aging behavior along with a relatively flat reflectance in the long FUV. No other coating was post-annealed at a temperature higher than deposition; hence, no further conclusion can be attained as to whether this was or not a fortuitously positive result.

We can compare the present results with those of del Hoyo and Quijada [21], who reported a reflectance at 121.6 nm of 90%; their samples were protected with AlF$_3$ deposited at 250 °C. The largest reflectance at 121.6 nm measured in the present research was 89.9% for the fresh 250 °C-sample, which reduced to 87.3% after a few months of aging. After two years of aging, the 200 °C-sample retained the largest reflectance at 85.5%. Such reflectance is not far from optimum results for the classical Al/MgF$_2$ mirrors [22].

All our samples presented a broadband reflectivity dip at ~160 nm, which is attributed to absorption due to the excitation of surface plasmons at the Al/AlF$_3$ interface. Surface plasmons are evanescent electromagnetic waves that propagate along the surface of the metal. For a free-electron-like metal such as Al, the surface-plasmon dip wavelength depends on the refractive index of the protective layer [23]. Since the dip is found close to what is observed for Al protected with MgF$_2$, the refractive index of AlF$_3$ and MgF$_2$ must be close to each other at ~160 nm. Surface-plasmon dip is superimposed in wavelength with a dip originated in the first destructive interference for the Al/AlF$_3$ coatings optimized at ~121.6 nm, which complicates discrimination between the two phenomena. The present results show a deeper reflectance minimum than the commented results of del Hoyo and Quijada [21], which suggests that the extra decay obtained here must be due to surface plasmon excitation since the interference effects should be approximately the same in the two pieces of research. Surface-plasmon excitation on mirrors like the present ones is permitted by the coupling of radiation wavelength with roughness at the Al/AlF$_3$ interface. Mainly roughness components with spatial wavelength shorter than radiation wavelength can contribute to the generation of surface plasmons [24]. This suggests that the present mirrors involve larger short-range roughness components than in Reference [21]. The Al film may better reproduce long-range substrate roughness components, whereas short-range roughness components may be most probably attributed to the film intrinsic roughness so that the difference observed in surface-plasmon excitation must reside in the Al film growth. Main deposition parameters are film thickness, deposition rate, and deposition and annealing temperature. No significant difference in film thickness or Al deposition rate is observed between the two mirror fabrication methods. For the same heating temperature, there might be a difference in the heating and cooling ramps. A difference between the two methodologies is substrate nature: quartz in [21] and glass here. It has been said above that substrate roughness should not govern surface-plasmon excitation at the Al/AlF$_3$ interface; however, the growth of the Al film in terms of crystallite size and preferential crystallite growth directions might be dependent on the crystalline or amorphous nature of the substrate, which might affect the resulting short-range roughness. Regarding the various deposition temperatures in the present research, a dip that is roughly similar in size was observed for the RT-, 200 °C- and 250 °C-deposited fresh samples, so that deposition temperature seems not to be an essential parameter, although samples protected at 100 and 150 °C display a relatively smaller dip. On the other hand, the sample that was protected at 150 °C and post-annealed at 200 °C had the smallest surface-plasmon dip over the present samples; the main difference over the other sample protected at 150 °C is the post-annealing process. In fact, it has been reported that post-annealing an Al film may result in films with the smallest excitation of surface plasmons [25]. Anyway, all present samples (except the RT
one) were annealed after Al deposition (for the deposition of the AlF$_3$ film), and the surface-plasmon reflectance dip was large instead.

The possible presence of pinholes was measured through transmittance in the visible range, which is plotted in Figure 5. The smallest measured transmittance can be considered as a top limit of the pinhole fractional open area. Curves in Figure 5 corresponding to temperatures of 100, 150, and 250 °C display a shape with a minimum in the visible which is typical for the transmittance of an Al film. Samples involving temperatures of RT, 200 °C, and 150 °C + annealing at 200 °C display a relatively flat transmittance shape in the ~400–800-nm range, which suggests a transmittance limited by pinholes. Therefore, the pinhole open area seems to approach $10^{-5}$ for the latter three samples, but it is well below $10^{-6}$ for the former ones. There seems not to be any correlation between the specific temperature and the sample being limited by pinholes, so that the increased number of pinholes in some samples might arise from other unknown factors, such as local defects at the substrate or imperfect substrate cleaning. The present result contrasts with the important correlation observed between MgF$_2$-deposition temperature and the presence of pinholes in Al/MgF$_2$ coatings [22]. Furthermore, the pinhole open area is overall smaller in the present research. The apparently erratic presence of pinholes found here combined with the relatively short statistics both here and in Reference [22] might be at the root of the contrasting results between the two pieces of research.

![Figure 5. Transmittance versus wavelength of Al mirrors protected with AlF$_3$ deposited at the given temperatures.](image)

3.2. Structural Properties

Samples were measured with XRR. These data were fitted using IMD Software (version 5.04) [26] from which information on interface and surface roughness and AlF$_3$ density was obtained along with film thickness. Experimental data were fitted up to ~1°. Figure 6 displays XRR data and fits for some samples. In the fits, the density of Al was set at 2.7 g/cm$^3$.

Figures 7–9 display AlF$_3$ density as well as Al-AlF$_3$ interface and outermost AlF$_3$ surface roughness obtained from XRR fits. AlF$_3$ density displays a trend to monotonously grow with deposition temperature. Fluoride films are known to grow with a reduced packing density due to the presence of pores, which originates in the low mobility of condensing molecules at film growth on a low-temperature substrate. Evolution of AlF$_3$ density with deposition temperature can be interpreted as an increase of packing density, with the film approaching bulk density of ~2.88 g/cm$^3$.

Al surface roughness displays a continuous trend to decrease with increasing temperature. This surface-roughness decrease may be compatible with the growth of larger crystallites with temperature [27]. As for AlF$_3$ surface roughness, there is a roughness decrease up to the temperature range of 150–200 °C; the small increase at 250 °C might be within the uncertainty range.
**Figure 6.** Fits of X-ray reflectometry (XRR) data for Al mirrors protected with AlF$_3$ deposited at room temperature (RT) (a), 150 °C (b), and 250 °C (c).

**Figure 7.** AlF$_3$ density calculated from XRR fits versus AlF$_3$-deposition temperature.

**Figure 8.** Al-AlF$_3$ RMS interface roughness calculated from XRR fits versus AlF$_3$-deposition temperature.
The outer surface topography was measured by means of AFM. Three samples were measured: mirrors with AlF3 deposited at RT, 100 °C, and 250 °C. Topography data were processed using WSxM software (version 9.1) [28]; the following functions and algorithms were applied: flatten, plane filter, and Gaussian smooth. Figure 10 displays the measured topography of these samples.

Surface roughness can be evaluated through power spectral density (PSD) function. PSD provides information about the contribution of the different spatial frequencies to surface roughness. PSD is defined by [29,30]:

$$PSD(f_x, f_y) = \lim_{L \to \infty} \frac{1}{L^2} \left| \int_{-L/2}^{L/2} \int_{-L/2}^{L/2} h(x,y) e^{-2\pi i (f_x x + f_y y)} dx dy \right|^2$$  \hspace{1cm} (1)

where $f_x$ and $f_y$ are the spatial frequencies in $X$ and $Y$ directions, $L$ is the sampling length, and $h(x,y)$ represents the surface profile height at each point over the surface. Since no preferential direction is expected for the coating growth, a simplified 2-D isotropic form of PSD can be used by expressing it in polar coordinates and by averaging it over the $2\pi$ azimuth angle $\theta$:

$$PSD(f) = \frac{1}{2\pi} \int_0^{2\pi} PSD(f, \theta) d\theta$$  \hspace{1cm} (2)

PSD calculated for the three mirrors is represented in Figure 11. The three curves are very close to each other; PSD is slightly smaller for the 250 °C-protected mirror in the spectral range above ~20 μm$^{-1}$. 

Figure 9. Outermost AlF3 RMS surface roughness $\sigma$ calculated from XRR fits versus AlF3-deposition temperature.

Figure 10. Atomic force microscopy (AFM) images for Al mirrors protected with AlF3 deposited at RT (a), 100 °C (b), and 250 °C (c).
RMS surface roughness $\sigma$ can be obtained from PSD through [31]:

$$\sigma^2 = 2\pi \int_{f_{\text{min}}}^{f_{\text{max}}} \text{PSD}(f) f df$$

(3)

where $f_{\text{min}}$-$f_{\text{max}}$ stands for the spatial frequency range in which PSD function is determined. Calculated $\sigma$ depends on the spatial frequency bandwidth used in the integration. Substrate roughness contribution can be expected to dominate PSD in the low spatial frequencies, whereas the coating is expected to dominate it in the high spatial frequencies [32]. Hence, we have divided our frequency range of integration in Equation (3) into two subranges separated at 20 $\mu$m$^{-1}$, since the three curves in Figure 11 have approximately common values below that frequency. The result of integrating PSD for the three mirrors in the two subranges provides RMS roughness parameters for the low- and for the high-spatial frequencies, which can be roughly attributed to the substrate and to the film, respectively. $\sigma$ calculated in the full-frequency range and in the two frequency subranges is given in Table 2. Even though $\sigma$ in the full-frequency range is similar for the three mirrors, a decrease of the large-frequency $\sigma$ component can be seen for the 250 °C-protected mirror. The observed high-frequency $\sigma$ reduction at the largest temperature is consistent with $\sigma$ decrease for the outer AlF$_3$ interface obtained from XRR fits.

Table 2. RMS roughness ($\sigma$) and autocorrelation length $T$ for protective AlF$_3$ film deposited at various temperatures.

| Parameter                              | Protective Layer Deposition Temperature |
|----------------------------------------|-----------------------------------------|
|                                        | RT           | 100 °C       | 250 °C       |
| $\sigma$ full range $^a$              | 1.1          | 1.3          | 1.1          |
| $\sigma$ high frequencies (film) $^a$ | 0.6          | 0.6          | 0.4          |
| $\sigma$ low frequencies (substrate) $^a$ | 1.0          | 1.1          | 1.0          |
| $T$                                    | 18           | 20           | 23           |

$^a$: in nm.

Surface roughness can be also characterized by means of the autocorrelation function $\text{ACF}(\tau)$, which is defined in the spatial domain:

$$\text{ACF}(\tau) = \lim_{L \to \infty} \frac{1}{L} \int_{-L/2}^{L/2} h(r)h(r+\tau)dr$$

(4)

$\text{ACF}$ enables us to compare a data set $h(r)$ with a translated version of itself $h(r + \tau)$ [28,29]. In Equation (4) we assumed again the absence of any preferential direction. $\text{ACF}$ was calculated with
the present AFM data for the three mirrors and it is displayed in Figure 12. Data were normalized as ACF(τ)/ACF(0).

![Normalized ACF curves of Al/AlF3 mirrors with the protective AlF3 film deposited at room temperature (RT), 100, and 250 °C.](image)

Figure 12. Normalized ACF curves of Al/AlF3 mirrors with the protective AlF3 film deposited at room temperature (RT), 100, and 250 °C.

The autocorrelation length \( T \) is defined as the distance at which ACF decays to a certain fraction of ACF(0). The physical meaning of \( T \) is related with the grain width. For random rough surfaces, two common functions are used to fit the autocorrelation function: Gaussian and exponential function. A somewhat more general function, also containing the above ones, can be used [33,34]:

\[
ACF(\tau) = ACF(0)e^{-|\tau|^2\alpha}
\]  

(5)

where \( \alpha \) specifies the type of statistical distribution of surface irregularities; Gaussian distribution stands for \( \alpha = 1 \) and exponential distribution for \( \alpha = 1/2 \). For the set of functions described by Equation (5), it is convenient to define the autocorrelation length \( T \) as the distance at which ACF decreases from its maximum to 1/e. This decay is used here to define \( T \).

\( T \) calculated for the curves of Figure 12 is given in Table 2. There is a moderate increase in grain width with AlF3-deposition temperature. The obtained width increase may have originated at the AlF3 protective film but most probably at the thicker Al film [27].

Summarizing roughness data, \( \sigma \) from XRR has been seen to decrease all the way with deposition temperature for the Al/AlF3 interface and to decrease up to \(-150 \, ^\circ\text{C}\) and not to vary significantly above that temperature for the outer AlF3 interface. As per AFM, the average grain width on the outer surface has been seen to increase with AlF3 deposition temperature, whereas surface roughness has been seen to decrease at the largest temperature of \(250 \, ^\circ\text{C}\). Grains in a film are often expected to grow with temperature; from XRR measurements, we have seen that there is an increase in AlF3 packing density with AlF3-deposition temperature up to close to 100% at \(250 \, ^\circ\text{C}\); the decrease in porosity must occur simultaneously with the trend to grow larger crystals at higher temperatures.

X-ray diffraction measurements were performed both in the \(\theta-2\theta\) geometry (XRD) and at grazing incidence (GIXRD). Due to the deep penetration of X-ray radiation, much deeper than the coating thickness, most diffracted photons in the \(\theta-2\theta\) geometry correspond to interaction with the substrate. To reduce this parasitic contribution and to increase the signal coming from the coating, geometry can be changed to grazing incidence, in which the incoming beam impinges at a constant grazing angle and the detector scans the diffraction angle. \(\theta-2\theta\) spectra provide information for crystal planes parallel to the sample surface, whereas GIXRD, with a fixed primary beam and a rotating secondary beam, collects photons diffracted from families of planes that are tilted with respect to the sample surface. Crystal planes in the coating were identified from diffraction spectra using Panalytical X-Pert Plus software package (version 2.2.5), which compares measured data with the International Tables for Crystallography database.
\( \theta-2\theta \) XRD spectra for mirrors with the AlF\(_3\) film deposited at RT, 100, and 250 °C are shown in Figure 13. For all three samples, a single Al (111) peak is observed; it is the most stable orientation because it has the lowest surface energy [35,36]. Al (111) peak integrated area, normalized to the full curve area, is given in Table 3. Peak integrated area shows a strong increase from the RT coating to the 100 °C-protected coating, with a further increase to the 250 °C-protected one.

![XRD spectra](image)

**Figure 13.** XRD spectra for mirrors protected with AlF\(_3\) deposited at RT (a), 100 °C (b), and 250 °C (c).

**Table 3.** Al (111) peak integrated area measured in the \( \theta-2\theta \) geometry for mirrors protected at the given temperatures.

| Protective Layer Deposition Temperature | Integrated Area \(^a\) |
|----------------------------------------|------------------------|
| RT                                    | 0.010                  |
| 150 °C                                | 0.043                  |
| 250 °C                                | 0.061                  |

\(^a\): normalized to the full area.

GIXRD spectra were obtained for the same three samples and they are displayed in Figure 14. GIXRD spectra for the RT sample display many Al peaks; that is why we extended the angular range to 140°. The presence of all Al peaks suggests that Al has a polycrystalline grain structure. If we combine this result with the XRD spectrum for the RT sample, we can conclude that the Al film has a polycrystalline structure with some trend to orient the (111) planes parallel to the sample surface. There is only one possible peak of AlF\(_3\), (113), but it is superimposed with Al (200) peak. For the mirror protected at 100 °C, only GIXRD peaks of Al (111), Al (220) (again, AlF\(_3\) (113) peak could appear superimposed with it), and Al (311) remain, with the (220) turning prevalent. For the mirror protected at 250 °C, there is an overwhelming presence of Al (220) peak, and only a tiny Al (111) peak, and an almost undetectable Al (311) peak are left. Hence Al (111) peak dramatically decreases with the increase of AlF\(_3\)-deposition temperature and at the same time a strong increase of Al (220) peak is obtained with this same temperature increase; a similar trend was observed in a previous research for Al mirrors protected with MgF\(_2\) films [37]. In fact, the observed behavior may be independent of the particular protective coating on Al, and the specific AlF\(_3\)-deposition temperature could be interpreted as a post-annealing temperature of the already deposited Al film.
With XRD spectra we collect photons diffracted by families of crystal planes that are parallel to the sample surface. Hence the increased integrated intensity with rising temperature that we measured for the Al (111) crystal planes suggests that these planes have an increasing trend with temperature to grow parallel to the sample surface. On the other hand, GIXRD collects photons diffracted from families of planes that are tilted with respect to the sample surface; if the incidence angle is $\alpha$ (measured from the sample surface; here $\alpha = 0.5^\circ$) and the secondary beam is deviated $\theta$ upon diffraction, the planes contributing to diffract in that direction are tilted $\theta - \alpha$ from the sample surface towards the primary beam. Hence the Al (220) crystal plane that becomes prevalent in GIXRD spectra for increasing deposition temperature is calculated to be tilted $32.1^\circ$ from the sample surface toward the primary beam. This value is not far from the angle between crystal planes (111) and (220) in an fcc crystal, which is $35.3^\circ$. These two close angles suggest that the prevalent Al (220) GIXRD peak at 100 °C- and 250 °C-protected mirrors may correspond to the same crystals that diffract the Al (111) peak in the $\theta$–2$\theta$ XRD spectra, assuming these crystals are merely tilted $35.3^\circ - 32.1^\circ = 3.2^\circ$ with respect to the sample surface; this angle may be a lower limit of the disorder angle of the Al (111) crystals with respect to the sample surface.

Regarding AlF$_3$, only (113) peak could be identified, at most, in samples where AlF$_3$ was deposited at RT and 100 °C, and none at 250 °C. For polycrystalline AlF$_3$, (113) peak is the second prevalent peak, behind (012) at 26.5°, which is not present in the GIXRD spectra. So, the peak observed can be most probably assigned to Al (200) peak. The small thickness of the AlF$_3$ protective layer of ~26 nm may partly explain the small intensity of AlF$_3$ peaks. GIXRD spectra obtained for AlF$_3$ suggests a small crystallinity.

Combining the present results with those obtained from AFM and XRR data, we can conclude that unheated Al is polycrystalline with some trend to orient the (111) peak parallel to the sample surface; by heating the deposited Al film in the process to protect it with AlF$_3$, Al undergoes a change in the crystallization pattern, with a strong trend for the prevalent Al (111) planes to orient parallel to the coating surface, along with a porosity reduction of the AlF$_3$ film, a reduced internal Al/AlF$_3$ interface.
and external AlF₃ interface roughness, a reduced PSD at high spatial frequencies, and increased autocorrelation length.

4. Conclusions

Al mirrors with high FUV reflectance have been obtained with AlF₃ protective coatings. The dependence of FUV reflectance with AlF₃-deposition temperature was investigated and a temperature range of 200–250 °C for mirrors with the largest FUV reflectance was obtained. Reflectance enhancement of hot-deposited AlF₃–protected mirrors in comparison with RT-deposited mirrors was seen to increase upon sample aging in a desiccator due to the larger reflectivity decrease in the latter. Even though aging resulted in some FUV reflectance decrease, a reflectance at 121.6 nm as high as 85% was measured for a mirror aged of 2 years. Such reflectance is not far from the optimum performance of the classical Al/MgF₂ mirrors.

RMS roughness of Al/AlF₃ interface and of the outermost AlF₃ surface was seen to mostly decrease with increasing AlF₃-deposition temperature, while AlF₃ packing density, as well as grain width in the AlF₃ outer surface, increased.

A strong correlation between the orientation of Al crystallites and AlF₃-deposition temperature was observed. For coatings deposited at RT, the Al film had a polycrystalline structure with some trend to orient the (111) planes parallel to the sample surface. The increase of AlF₃-deposition temperature resulted in an increased trend for the prevalent Al (111) crystal planes to orient parallel to the coating surface. Such preferential orientation is attributed to the post-annealing of the Al film (which was performed for AlF₃ protection on a heated substrate) more than to the deposition of the AlF₃ film at the heated substrate since, in fact, no significant crystallinity was observed for AlF₃ at any temperature.

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