Optimization of MgF$_2$-deposition temperature for far UV Al mirrors

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Abstract: Progress towards far UV (FUV) coatings with enhanced reflectance is invaluable for future space missions, such as LUVOIR. This research starts with the procedure developed to enhance MgF$_2$-protected Al reflectance through depositing MgF$_2$ on a heated aluminized substrate [Quijada *et al.*, Proc. of SPIE **8450**, 84502H (2012)] and it establishes the optimum deposition temperature of the MgF$_2$ protective film for Al mirrors with a reflectance as high as ~90% at 121.6 nm. Al films were deposited at room temperature and protected with a MgF$_2$ film deposited at various temperatures ranging from room temperature to 350°C. It has been found that mirror reflectance in the short FUV range continuously increases with MgF$_2$ deposition temperature up to 250°C, whereas reflectance decreases at temperatures of 300°C and up. The short-FUV reflectance of mirrors deposited at 250°C only slightly decreased over time by less than 1%, compared to a larger decay for standard coatings prepared at room temperature. Al mirrors protected with MgF$_2$ deposited at room temperature that were later annealed displayed a similar reflectance enhancement that mirrors protected at high temperatures. MgF$_2$ and Al roughness as well as MgF$_2$ density were analyzed by x-ray grazing incidence reflectometry. A noticeable reduction in both Al and MgF$_2$ roughness, as well as an increase of MgF$_2$ density, were measured for films deposited at high temperatures. On the other hand, it was found a strong correlation between the protective-layer deposition temperature (or post-deposition annealing temperature) and the pinhole open area in Al films, which could be prevented with a somewhat thicker Al film.

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1. Introduction

The next challenges of the astrophysics community require more efficient optical coatings, particularly in the far UV (FUV, λ: 100-200 nm) [1-4]. Aluminum is the single material choice to efficiently reflect a broad spectrum ranging from the FUV to the infrared and beyond. In its pristine form, Al presents a very high reflectance, above 80% longwards of ~83 nm. However, the surface of Al films immediately oxidizes after contact with air; the thin but very absorbing oxide layer strongly degrades Al reflectance shortwards of ~200 nm; to avoid oxidation, a protective overcoating on Al is used.

Some fluoride films are transparent to the FUV radiation and are able to protect Al against oxidation. Hass and Tousey [5] discovered back in 1959 that Al films protected with MgF_2 kept a high reflectance in the FUV range, with a reflectance of 80% down to 121.6 nm (Hydrogen Lyman α line). Hunter *et al.* [6] reported the high reflectance of Al mirrors protected with either MgF_2 or LiF. More recently, new protective layers for Al have been utilized consisting in AlF_3 [7] or combinations of several fluorides [8]. LiF is the material with the shortest cut-off wavelength in Nature (around ~102 nm), but it is hygroscopic, hence Al/LiF mirrors performance is compromised if they are exposed to humid environments. When high reflectance down to 102 nm is not strictly required, useful protective materials for Al are AlF_3 and MgF_2, which present cut-off wavelengths at 113 and 115 nm, respectively; more specifically, MgF_2 has demonstrated to be a reliable protective coating for Al with high reflectance longwards of 115 nm, and effective after long periods of exposure to the atmosphere, with a long space heritage.

Best Al/MgF_2 mirrors are prepared by evaporation. Deposition conditions affect the final performance of the mirrors, such as background and quality of vacuum pressure, substrate

cleaning and roughness, Al and MgF$_2$ evaporation rates, and substrate temperature. The latter parameter is investigated in this work.

MgF$_2$ crystals are mostly transparent down to ~115 nm, with a minor residual absorption. Yet, the absorption of thin films of MgF$_2$ in the transparency range is several orders of magnitude higher than in MgF$_2$ crystals, and this absorption increases towards the cut-off wavelength. The absorption in thin films deposited by evaporation is related with the columnar growth that leaves room for water and contaminants [9]; columnar growth also generates scattering losses [10,11]. All this limits Al/MgF$_2$ mirror reflectance.

MgF$_2$-film absorption can be reduced by deposition on a heated substrate [12], or, alternatively, by post-deposition annealing [13]. This reduced absorption is desired as a means to improve MgF$_2$-protected Al reflectance. Hutcheson *et al.* [14] studied the effect of substrate deposition temperature on the reflectance of Al/MgF$_2$ and Al/LiF mirrors. However, for Al/MgF$_2$ mirrors, they reported no increase of reflectance with substrate temperatures below 100°C, and a decrease of reflectance for temperatures above 100°C. The reason for this negative result may be that the benefit of depositing the MgF$_2$ film on a heated substrate, which increases its transparency, is neutralized by the fact that Al grows rougher when deposited on a hot substrate [15], resulting in a mirror with smaller reflectance than when deposited onto a substrate at room temperature. Deposition on a heated substrate was more successful for Al/LiF, with an important increase at 100°C. Post-deposition mirror annealing was reported to provide some reflectance enhancement. Adriaens and Feuerbacher [13] annealed Al/MgF$_2$ and Al/LiF mirrors at 300°C for 60 h. Particularly for Al/MgF$_2$ mirrors, they reported an increase of reflectance between 107 nm and 123 nm, but also a decrease of reflectance longwards of 123 nm in annealed mirrors in comparison with non-annealed mirrors.

In spite of the mostly negative results reported above, Quijada *et al.* [16,17] obtained a dramatic reflectance enhancement on Al films protected with MgF$_2$ deposited at 220°C. They circumvented the problem of Al roughening by depositing the Al film at room temperature (RT) and later heating the mirror to overcoat it with MgF$_2$. To avoid Al partial oxidation during heating, a very thin film of MgF$_2$ was quickly deposited on the Al film at RT, and the MgF$_2$ film was deposited to complete the optimum thickness once the aluminized substrate with the ultrathin protection was hot. 220°C was the deposition temperature that was reported.

In this research we investigate the reflectance enhancement of Al/MgF$_2$ mirrors as a function of MgF$_2$-deposition temperature following the deposition procedure reported in Quijada *et al.* [16,17]. We explore the temperature range between RT and 350°C. An alternative way to obtain enhanced-reflectance mirrors based on post-deposition annealing of RT-deposited mirrors has been also investigated. The effect of substrate temperature on the Al and the MgF$_2$ thin film roughness as well as on the density of the latter material is also studied, along with the growth of pinholes in the Al layer as a function of substrate temperature.

This paper is organized as follows: Section 2 describes the experimental techniques for mirror deposition and characterization. Section 3.1 reports mirror reflectance as a function of deposition or post-annealing temperature; measurements on aged samples are also presented. Section 3.2 displays the effect of deposition temperature on the roughness and density of Al and MgF$_2$ films and the dependence of pinhole open area in Al layers with deposition temperature.

2. Experimental setup

Al/MgF$_2$ mirror coatings were prepared in a 75-cm diameter, 100-cm height cylindrical stainless steel deposition chamber, pumped with a Velco 250A cryo system. The chamber is placed in an ISO-6 clean room. This chamber uses a diaphragm plus a turbomolecular pump for the fore-vacuum; both pumps are oil free. In order to accelerate degassing, a bake out (chamber internal walls temperature of up to ~180 °C, measured with a K thermocouple) was made. Chamber base pressure was ~1x10^{-6} Pa. During evaporation, pressure increased to between 5x10^{-6} Pa and 10^{-5} Pa. Films of Al and MgF$_2$ were deposited by evaporation using W multi-stranded filaments (Al) and W boats (MgF$_2$). Material purity was 99.999% for Al and VUV-grade for MgF$_2$. The sources

and materials were outgassed before mirror deposition. Film thickness was measured with a quartz-crystal monitor, which had been previously calibrated through ellipsometry and profilometry measurements. Deposition rates were ~6.5 nm/s for Al films and ~1.2 nm/s for MgF_2 films. The source-to-substrate distance was ~70 cm.

50.8-mm square, 3-mm thick floated glass substrates were used; they had been polished to a roughness of ~0.5 nm rms. Substrates were degassed in vacuum before deposition. Deposition was made as follows. A thin film of Al was deposited, and immediately protected with a ~4.5-nm thick MgF_2 film at room temperature. Then the substrate was heated to the desired temperature and more MgF_2 was deposited to complete the coating thickness of ~24 nm for highest reflectance at 121.6 nm. Process time of Al heating and cooling was minimized to prevent Al oxidation. Some Al/MgF_2 mirrors were deposited at room temperature and immediately post-annealed in vacuum. The annealing procedure reproduced the temperature ramp for MgF_2 deposition at the same target temperature; the annealing time at the nominal temperature was 12 min.

Reflectance measurements in the FUV were performed on mirrors that had been in contact with laboratory air typically for 1 hour, which will be referred to as fresh, and on the same mirrors, stored for months in a desiccator.

FUV reflectance was measured in GOLD's (Spanish acronym for Thin Film Optics Group) reflectometer, which operates under UHV conditions (base pressure ~$1x10^{-8}$ Pa). It has a grazing-incidence, toroidal-grating monochromator, in which the entrance and exit arms are 146° 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 sub-ranges. The reflectometer operates either with a deuterium lamp or with spectral lines that are generated in a windowless discharge lamp. For the latter, the lamp is fed with various pure gases or gas mixtures with which the lamp can generate continuous spectra or many spectral lines to cover the spectral range of interest. The beam divergence is ~1.5 mrad. The sample holder can fit samples up to 50.8 x 50.8 mm^2. The detector was a channel electron multiplier with a CsI-coated photocathode. Reflectance was obtained by alternately measuring the incident intensity and the intensity reflected by the sample; reflectance uncertainty is estimated as ±1%. Reflectance measurements were performed at 5° from normal incidence.

A Lambda-900 Perkin-Elmer double-beam spectrophotometer was used to measure regular transmittance and specular reflectance with the universal reflectance accessory, respectively. For reflectance and transmittance measurements, samples were situated at 8° and 1.5° from normal incidence, respectively, and the spectral ranges of measurements were 185-1100 nm and 350-400 nm, respectively.

Selected samples were measured by grazing incidence x-ray reflectometry (XRR) at Centro de Asistencia a la Investigación, Universidad Complutense de Madrid. The diffractometer was a PANalytical X`pert PRO MRD. The source was a Cu anode under 45 kV discharge. The Cu Kα (λ=0.154 nm) line was selected by means of a graphite monochromator. Measurements were performed at grazing incidence angles from 0.15° to 2.5°, with a step of 0.005°.

3. Results

3.1. Reflectance

A set of 11 Al/MgF_2 mirrors were prepared using substrate temperatures ranging from RT to 350°C. Nominal thickness was ~70 nm for Al films and ~24 nm for MgF_2 films, in order to maximize reflectance at 121.6 nm. Table 1 summarizes sample names, deposition/annealing temperature, and MgF_2 film thickness, which was measured *a posteriori* for selected mirrors by fitting XRR measurements. Samples deposited on hot substrates or post-annealed are named starting with D or A, respectively.

Table 1: Deposition/annealing temperature and thickness of samples

Sample	MgF$_2$ hot deposited/Mirror annealed	Temperature (°C)	MgF$_2$ thickness (nm)	Comments
D-RT		22	23.4	Room temperature
D-100	Hot depos.	100	23.2	
D-186	Hot depos.	186	23.1	
D-216	Hot depos.	216	18.6	Incorrect MgF$_2$ thickness
D-250	Hot depos.	250	23.4	
D-250-2	Hot depos.	250	23.5	
D-300	Hot depos.	300	-	
D-350	Hot depos.	350	-	
A-150	Anneal.	150	23.4	Deposited at RT and annealed
A-150-2-2xAl	Anneal.	150	-	Deposited at RT and annealed, double Al thickness
A-250	Anneal.	250	23.2	Deposited at RT and annealed

FUV reflectance of a selection of fresh mirrors is shown in Fig. 1. Samples were stored in a desiccator, and were measured again after 4 to 8 months. Fig. 2 displays the reflectance of aged mirrors both in the FUV and extended to the near IR.
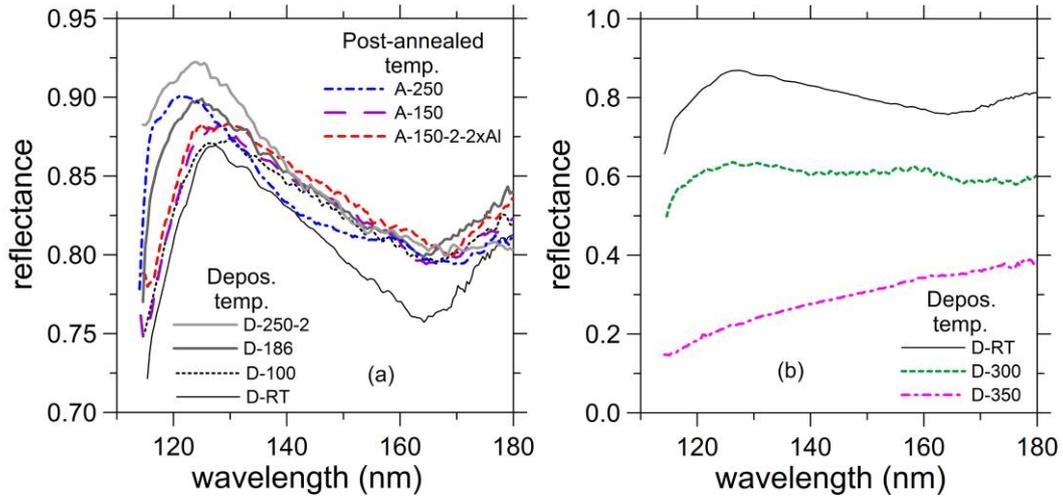

Fig. 1. Reflectance as a function of wavelength of fresh Al/MgF$_2$ mirrors for MgF$_2$-film deposited or fresh sample post-annealed at different temperatures (in degrees Celsius). a: samples with deposition or annealing temperatures≤250°C. b: samples with MgF$_2$ deposited at temperatures≥300°C compared to the one deposited at room temperature

Figure 3 displays the reflectance of fresh and aged mirrors as a function of substrate temperature at the important wavelength of 121.6 nm (a), and also displays the average reflectance in the 115-185 nm range (b). In both figures, reflectance is averaged among samples deposited at the same substrate/annealing temperature.

Figure 3 shows a correlation for fresh and aged samples between substrate temperature and reflectance at both 121.6 nm and in the full FUV range. For fresh samples, the maximum reflectance values at 121.6 nm, 0.895, 0.900 and 0.916, were achieved on samples A250, D250 and D250-2, respectively, where MgF$_2$ layers were deposited/annealed at 250°C. These reflectance values of fresh samples at 121.6 nm are above what is regularly obtained for mirrors

deposited at room temperature and they also surpass the value of 0.866 reported for Al mirrors protected with ion beam sputtered-MgF$_2$ [18], and are in the range of the values reported by Quijada *et al.* [16] for the mirror whose MgF$_2$ film was deposited at 220°C. After months of storage in desiccator, samples A250, D250 and D250-2 retained a reflectance at 121.6 nm of 0.892, 0.898, and 0.904 respectively. Though FUV reflectivity enhancement with deposition/annealing temperature is remarkable in fresh samples, it is even larger in aged samples, as mirrors deposited at high temperatures overall aged better than the one deposited at RT.
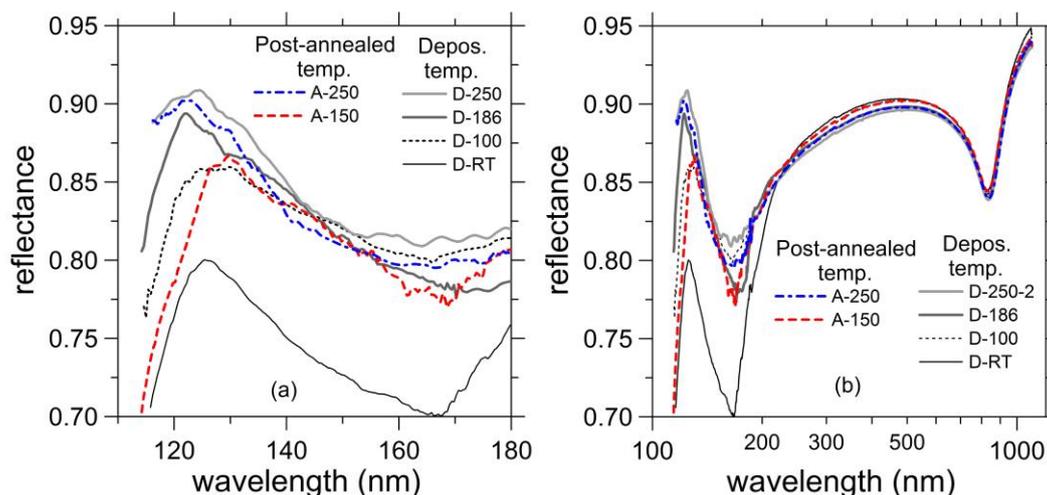
Fig. 2. Reflectance of aged samples. a: FUV reflectance versus wavelength. b: Reflectance versus wavelength (log axis) extended to the near IR
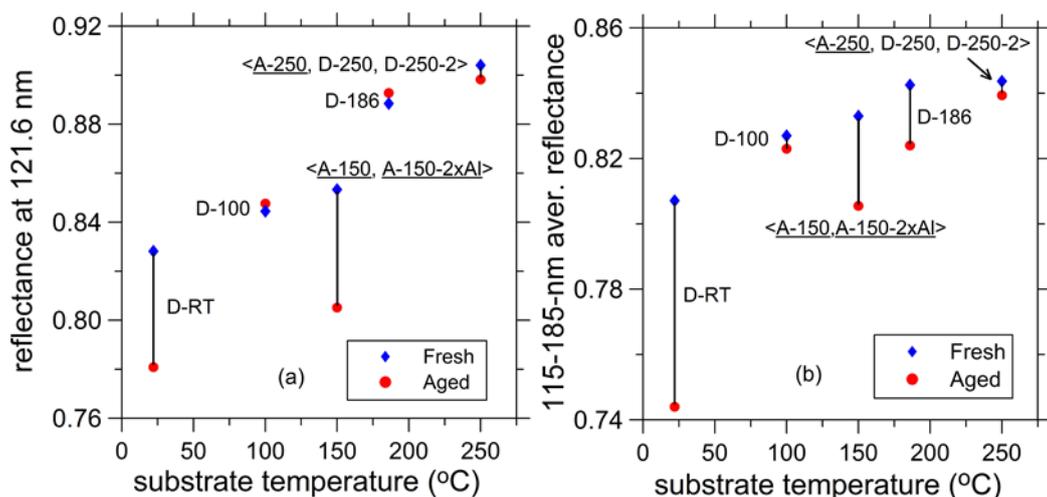

Fig. 3. Reflectance at 121.6 nm (a) and average FUV reflectance in the 115-185-nm range (b) of Al/MgF$_2$ mirrors vs temperature. Reflectance is averaged among samples deposited/annealed with the same temperature. Labels of annealed samples are underlined

Figure 1 shows that at 300°C and above, reflectance of mirrors plummeted. Reflectance at 121.6 nm (average FUV reflectance) of fresh samples D300 and D350 were 0.619 and 0.194 (0.616 and 0.300), respectively. This result states that 250°C is close to the optimum deposition temperature of MgF$_2$ for highest reflectance, and 300°C is already beyond the temperature limit and results in significant reflectance degradation.

Figure 1 also displays that samples D250 and A250, one with MgF$_2$ film deposited at 250°C and the other deposited at RT and post-annealed at the same temperature, have a close reflectance in a band including 121.6 nm. Such similarity, along with the simplicity of the post-

annealing procedure compared to the other procedure, makes the post-annealing a promising technique. The overall FUV reflectance enhancement obtained here for annealed films contrasts with the reflectance increase below 123 nm but reflectance decrease above this wavelength obtained by Adriaens and Feuerbacher [13]; their annealing temperature of 300°C, higher than in the present research, and their much longer annealing time of 60 h, might not be the optimum parameters to obtain an overall FUV reflectance enhancement.

The reflectance increase of mirrors deposited at high temperatures is attributed to a summation of two effects: MgF_2 transparency enhancement based on porosity reduction and the reduction in roughness of both MgF_2 and Al films, which are analyzed in sub-section 3b.

All samples displayed above present a broadband reflectivity dip at ~166 nm, which is attributed to the excitation of Al surface plasmons. The surface-plasmon dip central wavelength depends on the optical constants of the protective layer [19] and for MgF_2 it is close to the above wavelength. Surface plasmon dip is superimposed with a destructive interference dip centered at close wavelengths for mirrors optimized at 121.6 nm. The depth of the surface-plasmon dip is strongly dependent on Al surface roughness. In the present samples, no straightforward correlation has been found between the depth or the center wavelength of the dip and the deposition/annealing temperature. A second dip in reflectivity is present at ~830 nm and it is due to an interband transition of Al.
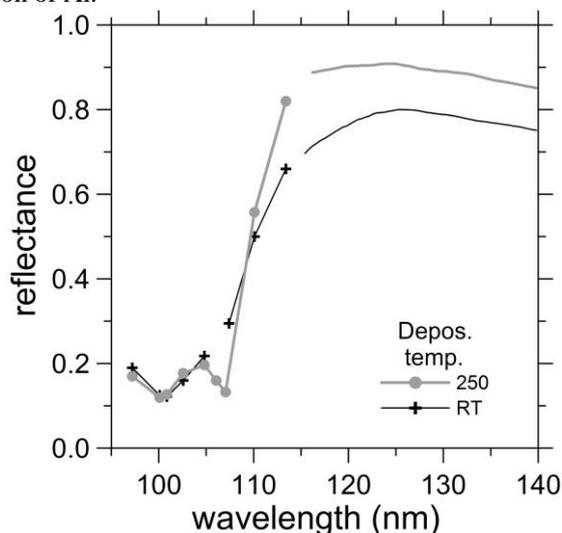

Fig. 4. Reflectance down to 97.2 nm of aged samples deposited at room temperature (DRT) and at 250°C (D250-2)

Reflectance of aged samples deposited at room temperature (DRT) and at 250°C (D250-2) were measured down to 97.2 nm, which is displayed in Fig. 4. The reflectance of both samples is quite similar in the short wavelength range, whereas they separate longwards of ~109 nm, where reflectance enhancement due to deposition substrate temperature is significant. Applications targeting spectral lines at wavelengths down to 110 nm, such as C III, Si II or S III, may benefit from the present reflectance enhancement on MgF_2–protected Al mirrors, mainly in humid environments where LiF-protected Al mirrors are known to degrade. In this respect, it is remarkable the reflectance enhancement reported for Al films protected with hot-deposited LiF, either uncoated [17] or coated with a thin outer protection for LiF [20].

3.2. Density, roughness, and pinholes.

Several samples were analyzed by XRR in order to evaluate the dependence of density and surface roughness on deposition/annealing temperature. A model for each mirror was built using IMD software [21] and it was fitted to experimental data. Main fitting parameters were Al and MgF_2 thicknesses and surface root-mean-square (rms) roughness along with MgF_2 film density.

The models were fitted to experimental data up to ~1°. All measurements were done on aged samples. Fig. 5 displays the roughness values of MgF_2 and Al films (a) and the MgF_2 film density (b) obtained from the fittings, as a function of deposition/annealing temperature. Samples deposited at temperatures higher than 250°C and sample A150-2xAl were not measured.
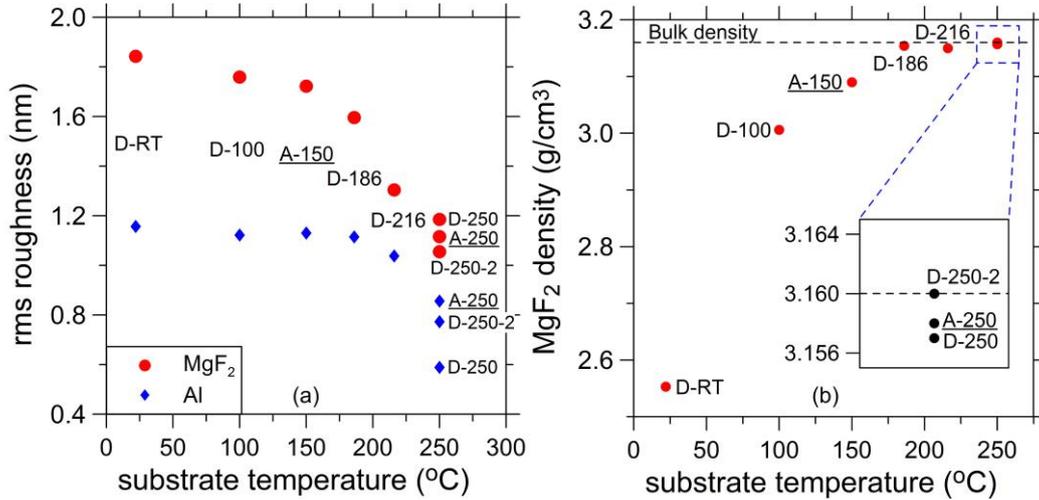

Fig. 5. Roughness values of MgF_2 and Al films (a) and MgF_2 film density (b) as a function of deposition/annealing temperature. Labels of annealed samples are underlined. Measurements were performed on aged samples

The present roughness analysis shows that Al/MgF_2 mirrors either heated for MgF_2-film deposition or post-annealed in vacuum have a reduced Al and MgF_2 surface roughness in the temperature range from room temperature up to 250°C. Films in mirrors deposited at 250°C are remarkably less rough than films deposited at room temperature. The trend seems to have two different regions. From RT to ~186°C, the differences in roughness for both films, particularly for Al, are relatively small. However, beyond ~186°C, roughness reduction in films of both materials is more pronounced. We want to highlight the smoothening effect of temperature on Al films: even though depositing Al on hot substrates results in rough films, as reported in Ref. [15], post-deposition annealing results in Al film smoothening. In contrast to Ref. [15], in the present work all Al films were deposited at room temperature and heated *a posteriori*. Endriz and Spicer also found a smoothening effect of Al films through annealing [22]. Regarding scattering losses, they are expected to be relatively small, according to the rms roughness values plotted in Fig. 5.a. Calculations of scattering losses at 121.6 nm, relative to the reflectance of a smooth bilayer, range between 1% (using rms roughness of the room-temperature sample) to 0.3% (using roughness of a sample deposited at 250 °C); calculations were performed with IMD code [21] and with available optical constants of Al and MgF_2.

Figure 5 (b) shows that density of MgF_2 films increased with substrate temperature from ~81% of bulk density (3.16 g/cm^{-3}) for the film deposited at room temperature up to ~100% of bulk density for the films deposited at 250°C. This result is compatible with those reported in Ref. [9]. Density increase must be due to a reduction of voids in the film, leaving less room for water and contaminants and thus reducing MgF_2 extinction coefficient values as reported by Wood II *et al*. [12]. This density increase may be at the origin of the smaller reflectance degradation over time of Al mirrors protected with MgF_2 deposited at hot temperatures.

Al films, as well as films of other materials, typically include some pinholes. In order to analyze the effect of substrate temperature in the development of pinholes, transmittance measurements were performed on aged samples in the range between 350 nm and 400 nm, longwards of BK7 glass substrate cutoff wavelength. The 350-400-nm average transmittance for each sample is displayed in Fig. 6. All Al films have the same nominal thickness of 70 nm. Only sample A150-2xAl was made with double Al film thickness, which is discussed below. At

deposition/annealing temperatures of 100°C and below, the measured transmittance is ~10^{-5} and can be assigned to a perfect 70-nm thick Al film with no pinholes, so that the pinhole fractional open area can be roughly estimated as the excess of transmittance above 10^{-5}. Fig. 6 shows a strong correlation between substrate deposition/annealing temperature and pinhole open area. Samples prepared at optimal temperature of 250°C for FUV reflectance result in a transmittance of ~10^{-3}, which is taken as the pinhole open area for this temperature. Sample A150-2xAl was made with double Al film thickness (140 nm) to check if the thickness increase had an effect on the presence of pinholes. A 350-400-nm average transmittance of ~10^{-7} was measured for the sample with double Al thickness, which is well below the general trend. Its real transmittance could have been even lower since 10^{-7} is close to the noise threshold of the spectrophotometer. In contrast, sample A150, identical to A150-2xAl except that it had the standard Al thickness of 70 nm, displays a transmittance slightly above 10^{-5}, so that the pinhole open area started to be noticeable in that sample. Summarizing, the pinhole open area seems to increase significantly with temperature, but this increase might be strongly attenuated with the use of a thicker Al film. The sample deposited at 300°C, is farther away from the general trend, whereas sample D350, deposited at 350°C, displays a far larger transmittance. This suggests a complex degradation process that starts at ~300°C. All samples were observed in the optical microscope by transmission. Microscopy measurements were done with common magnification under a 50x objective (bright field); resolution is estimated at ~0.8 microns. Pinholes were not resolved in the microscope for any sample, except for sample D350, which indicates that pinhole size grew with temperature at least at the present highest temperature. Indeed, sample D350 was semi-transparent under naked-eye observations. No further effort was performed to study the samples involving temperatures $\geq$ 300°C due to their low FUV reflectance.
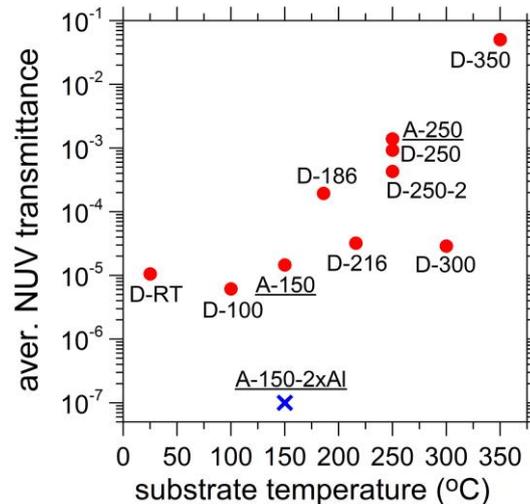

Fig. 6. Average transmittance in the 350-400 nm spectral range as a function of MgF$_2$ deposition/annealing temperature. Labels of annealed samples are underlined. Samples were measured after 4 to 8 months of storage in desiccator

The increase of FUV reflectance but also of pinhole open area with temperature are two conflicting processes, which may require a compromise between the two. Some presence of pinholes are not expected to invalidate a mirror for most applications as long as pinholes do not result in coating degradation and pinhole open area, and the associated scattering and transmittance losses, are negligible. The positive result on pinhole reduction obtained by increasing the Al film thickness provides a direction to try to overcome the pinhole issue. The possible roughness increase with Al film thickness in this thickness range is not expected to be significant [23]; in fact, the reflectance of the two twin samples, one with 70- and the other with 140-nm thick Al film, are very similar, the one with double Al thickness being slightly more reflecting (probably due to measurement uncertainty).

Conclusions

A monotonous FUV reflectance enhancement with deposition temperature up to 250°C has been obtained for Al films deposited at room temperature and heated to deposit the protective MgF_2 film. A similar enhancement was obtained on post-annealed mirrors that had been deposited at room temperature. Mirrors deposited or post-annealed also resulted in a lower reflectance decrease over time than standard coatings prepared at room temperature. A reflectance of ~90% at 121.6 nm was measured both for coatings with the MgF_2 film deposited at 250°C and for samples post-annealed at this same temperature. Analysis of XRR measurements showed that MgF_2 film density increased from ~81% of the bulk density for the film deposited at room temperature to close to MgF_2 bulk density for films deposited or post-annealed at 186°C and above. Furthermore, both Al and MgF_2 surface roughness decreased with deposition/annealing temperature and the reduction was particularly noticeable above 186°C. The pinhole open area was seen to increase with film deposition/annealing temperature through NUV transmittance measurements but this negative effect could be mitigated by increasing Al film thickness.