

Removal of a protective coating on Al by ion etching for high reflectance in the far ultraviolet

Juan I. Larruquet^{1,*} and Ritva A. M. Keski-Kuha²

¹Grupo De Optica de Láminas Delgadas, Instituto de Física Aplicada-Consejo Superior de Investigaciones Científicas, C/ Serrano 144, 28006 Madrid, Spain

²NASA/Goddard Space Flight Center, Code 551, Greenbelt, Maryland 20771, USA

*Corresponding author: larruquet@ifa.cetef.csic.es

Received 3 June 2008; accepted 4 July 2008;
posted 21 August 2008 (Doc. ID 96934); published 1 October 2008

The effect of ion etching on the reflectance of Al coatings in the far ultraviolet is investigated. Ion etching of an overlayer grown on Al was performed by applying 100–300 eV Ar⁺ ions using an ion gun. Ion etching was employed to remove the oxide naturally grown on an Al film that had been in contact with atmosphere. Ion etching was also used to remove part or all of the protective MgF₂ film on Al. The reflectance at 121.6 nm, H Lyman α line of the overlayer-removed Al surface was monitored after protecting it with a MgF₂ layer. Ion etching on both types of coatings resulted in an excellent reflectance value at 121.6 nm, whereas a reflectance loss was observed at longer wavelengths. © 2008 Optical Society of America

OCIS codes: 260.7200, 120.5700, 310.6860, 350.6090, 310.1515, 230.4170.

1. Introduction

Al coatings have an unparalleled normal incidence reflectance in the far ultraviolet (FUV, $\lambda < 200$ nm) spectral region above the Al plasma wavelength ($\lambda_p = 83$ nm). However, in presence of oxygen and/or water vapor, a thin oxide film readily grows on the Al surface that strongly absorbs FUV radiation and renders the oxidized Al coating useless. The use of protective coatings of MgF₂ and LiF extends the use of Al coatings down to 115 nm and 105 nm, respectively. Below these cutoff wavelengths, no transparent material has been found in nature for the protection of Al.

Since the propagation of FUV radiation requires vacuum due to the absorption of air, unprotected Al coatings could be maintained free from oxidation for some time if the application environment were under ultrahigh vacuum (UHV) conditions. There are various UHV environments in which the use of unprotected Al coatings might be practical for a certain time, such as optics placed in a synchrotron

beamline or in an on-orbit operating optical instrument for FUV astronomy.

In order to benefit from the high reflectance of unprotected Al films, a practical method that provides a pristine Al coating in the application environment must be developed. Several methods have been suggested to move toward the use of unprotected Al coatings in space astronomy, including on-orbit Al film deposition [1], and the use of a removable, volatile, aluminum protection (REVAP) [2].

Hass and Hunter [1] proposed the coating of telescope mirrors with Al once the instrument is placed in a high Earth orbit. This procedure would take advantage of the natural vacuum on the orbit in order to maintain the films free from oxidation. Such an application is a challenge, and it requires both laboratory research and coating demonstration in space. One issue is how to ensure a long enough operating time for a coating to accomplish the desired goals before the progressive Al oxidation reduces the performance. If the operating time of the Al coating is not long enough, a method to restore the reflectance of unoxidized Al would be required. The reflectance and the optical constants of unoxidized Al films in the FUV [3,4], the degradation of the FUV reflectance of Al

films exposed to controlled doses of molecular and atomic oxygen [5–7] (the latter being the most abundant oxidizing species in an Earth orbit of ~200–700 km altitude), and the effect of periodic recoatings with fresh Al over the partially oxidized surfaces [8] have been investigated. A few experiments have been performed on the deposition of Al coatings on-orbit [9,10], and this looks feasible, although challenging. *In situ* deposition of Al coatings in other environments, such as a synchrotron beamline, would be easier to implement.

The REVAP technique [2] proposes the use of a removable, volatile, protective coating to cover the Al surface during the time from the initial evaporation in the laboratory to the final protective coating removal by heating the coating in the application environment, such as outer space. This technique has not been demonstrated experimentally, and the available data [11,12] suggest that Al film reflectance may be degraded after the heating necessary to remove the protective coating if a temperature of ~500–520 K is achieved. A few other suggestions for the use of high FUV reflectance Al coatings have been mentioned [13], although these authors do not have information of any research along these lines.

A new technique able to provide with unoxidized Al coatings is proposed in the current paper; it is based on the capability of energetic ions to remove either a naturally grown oxide film or part or all the protective coating deposited on an Al film.

The evolution of surface morphology during ion sputtering is a complex phenomenon that may involve roughening or smoothing processes, and the resulting morphology is determined by a balance between them [14]. Processes involving ions have been used to enhance the reflectance of multilayer coatings in the extreme ultraviolet and soft x-rays. They include surface roughness smoothing and partial layer etching.

Surface roughness smoothing can be understood as a process of moving surface atoms located on a hill into the next valley, due to the smaller binding energy of the atoms at the former position. An important reflectance increase in the soft x-rays, based on a roughness decrease, was obtained for multilayers by ion polishing C-spacer layers and sometimes also metal scattering layers [15–17]; a roughness reduction through ion polishing was also obtained with metal/metal multilayers [18]. In these experiments, ion energies in the range 100–600 eV and grazing angles between ~10° and 45° were used, and a low dependence on these two parameters was reported. Puik *et al.* [19] reported an important roughness reduction, which resulted in a large soft x-ray reflectance increase, when etching 1.5 nm out of a total of 2.8 nm thick W layer in each W layer of a W/C multilayer. Voorma *et al.* [20] had a similar result by etching 3.8 nm out of a total of 8.5 nm thick Si layer in each Si layer of a Mo/Si multilayer in the extreme ultraviolet; the observed smoothing effect was attributed to relaxation through the viscous flow. Ion

energies and grazing angles used were 200 eV and 45° [19], and 2000 eV and 50° [20], respectively.

Low energy ion beam erosion of solid surfaces has proved a useful technique also for the generation of self-organized nanostructures. The ion beam parameters have been optimized to make ripple patterns on some materials, with selectable periodicity and amplitude [21]. The process involves sputtering and diffusion of surface defects based on thermally activated hopping [22].

A new application for ion techniques is proposed here, which consists of removing a protective overcoating to leave a high FUV reflectance Al coating. The experimental techniques used in this research are described in Section 2. Experimental demonstration of highly reflective Al coatings after removing the natural oxide film and part or all the MgF₂ protective film is given in Subsections 3.A and 3.B, respectively.

2. Experimental Techniques

A deposition chamber pumped with a cryopump was used to deposit both unprotected Al films and MgF₂-protected Al films by resistance heating evaporation; Al and MgF₂ films were deposited using W filaments and Mo boxes, respectively. A separate sputter deposition system pumped with a cryopump was used for MgF₂ deposition and for ion etching. The latter system was equipped with two 3 cm, Kauffman ion guns. One gun was used for deposition by ion beam sputtering (IBS), and it was directed to a water-cooled target placed at about 45° from the ion beam. The ion beam current and the ion energy could be controlled independently. The ions sputtered target atoms that impinged perpendicularly onto a water-cooled float glass substrate placed 10 cm away from the target. A 101.6 mm diameter, 99.997% purity, MgF₂ target was used. The Ar flow for IBS was 7.0 SCCM. The system was equipped with a second ion gun directed to the growing film for ion-assisted deposition or ion etching. In this gun an unfocused ion beam could be accelerated to energies in the 50–300 eV range. The ion-etching gun was operated with a 5.0-SCCM flow of Ar. For some experiments, when Al had to be protected immediately after the overcoating removal, Ar was set to flow simultaneously through the two guns in order to quickly overcoat the resultant film with a protective MgF₂ coating as soon as the etching process was finished. The ions impinged on the sample at a grazing angle of ~35°.

The base pressures in the sputtering and in the evaporation chambers were 4×10^{-6} Pa and 10^{-6} Pa, respectively. Typical total pressure in the sputtering chamber both during deposition and during ion etching was 4×10^{-2} and 6×10^{-2} Pa, respectively, and it was 10^{-5} Pa during deposition in the evaporation chamber. The deposition rates of evaporation deposited (ED) materials were ~20 nm/s for Al and 2–3 nm/s for MgF₂, and it was ~0.15 nm/s for IBS deposited MgF₂. The layer thickness was measured with a quartz crystal thickness monitor that was calibrated through a Topo-3D noncontact surface

profiler. All films investigated in this paper were deposited and their reflectance was measured at room temperature.

The samples were exposed to atmosphere for a few minutes before they were transferred to the reflectometer. Reflectance measurements were performed using a reflectometer–monochromator system described elsewhere [23].

3. Experimental Results and Discussion

A. Removal of the Natural Oxide Film Grown on Al by Ion Etching

Al films deposited by evaporation were exposed to normal atmosphere for about five minutes before being transferred to the sputtering/ion-etching chamber. Madden *et al.* [24] investigated the FUV reflectance of Al films aged under vacuum and in normal atmosphere. For a sample maintained under vacuum at a pressure of 5×10^{-5} Pa for 40 minutes, the reflectance at 121.6 nm H Lyman α line decreased from 0.85 to 0.66. Upon first contact to normal atmosphere, the reflectance of a freshly deposited Al film dramatically dropped below 0.50; the further reflectance decrease rate slowed down, and after ~ 2 hours it reached a value of ~ 0.40 , with a minimum reflectance decrease after that. The self-protective oxide film that grows on the Al outer surface after a prolonged contact to atmosphere has been reported to reach a final thickness of ~ 5 nm. In the present case, the oxide film that may have grown after the 5-minute exposure to atmosphere is estimated to range roughly between 1 and 3 nm.

The oxidized Al sample was ion etched in order to remove all the Al oxide film. Since an *in situ* reflectance capability was not available in the etching chamber, we decided to protect the resultant Al film *in situ* with a MgF_2 film, so that the sample could be transferred in air to the reflectometer; in this way the reflectance of Al after oxide etching could be measured at wavelengths longer than 115 nm, the MgF_2 cutoff. The protection of an Al coating has to be performed *in situ* immediately after deposition in order to avoid Al surface oxidation. A facility for MgF_2 deposition by evaporation was not available in the etching chamber; instead, IBS was available in this chamber, so that after oxide removal through etching, the resultant Al film was protected *in situ* with a ~ 24 nm thick film of IBS MgF_2 ; the latter is the optimum thickness to obtain the highest possible reflectance at the wavelength of 121.6 nm.

Several Al samples were prepared and subjected to ion etching. The quality of a sample after the oxide removal was measured through the reflectance at 121.6 nm once protected with MgF_2 . The etching time was optimized by trial and error; the ion energy and the total beam current were set at 100 eV and 15 mA, respectively. Table 1 summarizes the relevant parameters of sample preparation. Figure 1 shows the dependence of the reflectance at 121.6 nm on the etching time for several samples prepared with an ion grazing angle of $\sim 35^\circ$. In the present conditions, the optimum etching time was determined to be ~ 800 s. A reflectance decrease was observed for 1200 s etching time, which may be caused by an increase in roughness due to prolonged etching.

Table 1. Main Parameters of the Different Etched Samples

Removal of Natural Oxide Grown on Al						
Sample Name	Initial Coating	Time Exposure to Air (min)	Ion Energy (eV)	Ion Current (mA)	Etching Time (s)	Thickness of Final MgF_2 Coating (nm)
S1	~ 65 nm Al	~ 5	100	15	150	~ 24
S2	~ 65 nm Al	~ 5	100	15	300	~ 24
S3	~ 65 nm Al	~ 5	100	15	500	~ 24
S4	~ 65 nm Al	~ 5	100	15	600	~ 24
S5	~ 65 nm Al	~ 5	100	15	800	~ 24
S6	~ 65 nm Al	~ 5	100	15	1200	~ 24
Total Removal of the MgF_2 Protective Coating on Al						
Sample Name	Initial Coating	Time Exposure to Dry Air (days)	Ion Energy (eV)	Ion Current (mA)	Etching Time (s)	Thickness of Final MgF_2 Coating (nm)
S7	~ 65 nm Al + ~ 7.5 nm ED MgF_2	1	300	15	80	~ 24
S8	~ 65 nm Al + ~ 7.5 nm ED MgF_2	6	300	15	52	~ 24
Partial Removal of the MgF_2 Protective Coating on Al						
Sample Name	Initial Coating	Time Exposure to Dry Air (days)	Ion Energy (eV)	Ion Current (mA)	Etching Time (s)	Thickness of Final MgF_2 Coating (nm)
HS1	~ 65 nm Al + ~ 10 nm ED MgF_2 + ~ 28 nm IBS MgF_2	0	N/A	N/A	N/A	~ 38
S9	~ 65 nm Al + ~ 10 nm ED MgF_2 + ~ 28 nm IBS MgF_2	5	300	15	42	~ 34
S10	~ 65 nm Al + ~ 10 nm ED MgF_2 + ~ 28 nm IBS MgF_2	5	300	15	142	~ 23

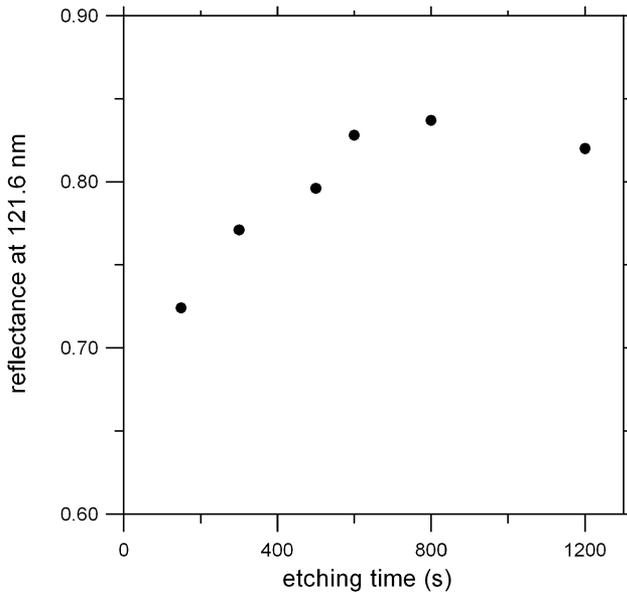


Fig. 1. Reflectance at 121.6 nm for samples S1 to S6 versus etching time. The samples were Al films that had been exposed to atmosphere prior to ion etching in vacuum. The samples were protected immediately after the ion etching with a ~ 24 nm thick, IBS MgF_2 film.

The preparation of an ED Al film immediately protected with an IBS MgF_2 film would be suitable for comparison purposes with the above etched samples; however, the vacuum chambers used in this research did not house both evaporation and IBS systems in a single chamber. Instead, the following comparison samples were prepared. A 7-to-10 nm thick ED MgF_2 film was deposited on an opaque Al film in the evaporation chamber. This film provided a temporary protection for the Al film in the transfer from the evaporation chamber to atmosphere and transferred quickly to the sputtering chamber where a thin film of MgF_2 was deposited by IBS on top of the Al/ MgF_2 bilayer in order to complete a total protective coating thickness of ~ 24 nm. These samples will be referred to as hybrid samples. More details on the hybrid samples can be found in Ref. [25].

The reflectance at 121.6 nm obtained for the sample etched for 800 s was 0.837, which is a remarkably high value, very close to the optimum reflectance measured for Al films that had not been exposed to air before protecting them with MgF_2 (hybrid samples), which averaged ~ 0.85 [25]. Hence the oxide film and any contaminants were practically 100% removed. Figure 2 shows the reflectance as a function of wavelength for a sample that was ion etched for 600 s with the aforementioned ion parameters. In the figure we also show the reflectance of a hybrid sample and of an ED MgF_2 -protected Al film.

Two interesting features are observed in Fig. 2. At 121.6 nm and below, the reflectance of the etched sample is similar to, and even higher than, the one of the nonetched sample. This proves that the full

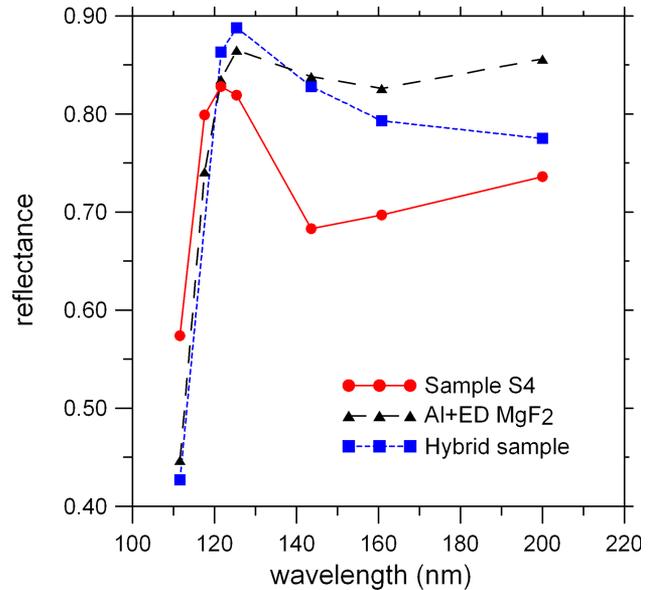


Fig. 2. (Color online) Reflectance as a function of wavelength for sample S4 with an Al film that was exposed to atmosphere prior to undergoing ion etching in vacuum, and it was protected immediately after the ion etching with a ~ 24 nm thick, IBS MgF_2 film. The reflectance of nonetched Al samples protected with ED MgF_2 as well as with hybrid MgF_2 is also shown for comparison.

oxide film and any contaminants on the Al surface were removed by ion etching. However, the reflectance at 125.4 nm and above was lower for the etched than for the nonetched samples. The reflectance for hybrid samples is also somewhat lower than for the ED samples at 143.6 nm and above, which was explained through higher losses at these wavelengths in the IBS MgF_2 [25]. Since the etched samples were protected with a ~ 24 nm thick IBS MgF_2 , versus ~ 14 – 17 nm thick IBS MgF_2 for the hybrid samples (the rest of the protective layer was ED MgF_2), the former samples are expected to undergo larger losses at longer wavelengths. However, this cannot solely explain the large reflectance loss of Fig. 2, which is peaked between 143.6 and 160.8 nm for the different samples prepared.

The extra reflectance loss can be explained by means of surface plasmon excitation in the Al film. The etching process is suggested to enhance short-range surface roughness; this etching-enhanced roughness would help surface plasmons to couple to the electromagnetic waves, resulting in a reflectance loss. The surface roughness is described by its power spectral density (PSD) [26]; only PSD roughness components with frequency $k > \omega/c$ (or equivalently, only surface roughness of spatial range shorter than the wavelength) are actually involved in the excitation of surface plasmons. In contrast, the roughness spectral components with $k > \omega/c$ are involved in roughness-induced light scattering [27]. A parameter called the surface plasma wavelength λ_{sp} is defined as the wavelength around or above which surface plasmons can be excited with light impinging on a rough surface. λ_{sp} is given by

$$\lambda_{\text{sp}} = \lambda_p \sqrt{1 + \varepsilon}, \quad (1)$$

where λ_p is the Al volume plasma wavelength, and ε is the dielectric constant of the MgF_2 coating that protects the Al film. By applying Eq. (1) and using a value of ~ 2.19 for ε [28], λ_{sp} amounts to ~ 148 nm. The wavelength at the peak of reflectance loss depends on the surface PSD, as well as on the metal optical constants. For Al, the wavelength at the reflectance loss peak may be at or somewhat above λ_{sp} [29], which is consistent with the reflectance dip in Fig. 2.

The ions impinging on the Al film in the process of removing the oxide seem to have caused a short-range structural change, thus enhancing the surface plasmon excitation, which results in the large reflectance loss in Fig. 2 centered between 143.6 and 160.8 nm. This structural change may consist of some Al crystallization. The long-range roughness did not increase, since the reflectance at 121.6 nm and at shorter wavelengths is comparable to the case of nonetched samples. Therefore the Al surface roughening after oxide etching will not result in the degradation of the point spread function, and of an Al/ MgF_2 mirror, but it will reduce the efficiency around λ_{sp} .

A similar reflectance dependence on wavelength was obtained for Al coatings deposited by IBS and later protected with MgF_2 [30]. In that case, a reflectance dip obtained for IBS Al coatings was attributed to an increase of the short-range roughness, which was responsible for surface plasmon excitation. In [30], Al surface roughening effect may have been due to the higher average energy of the Al atoms impinging on the growing film for IBS versus ED coatings; in the present case, the roughening effect may have been due to energy supplied by the ions impinging on the growing film in the etching process.

Further research may lead to minimizing this surface roughening in order to obtain the highest possible FUV reflectance. The process could be optimized with respect to the different etching parameters: ion energy, ion fluence, ion impingement rate, ion impingement angle, and ion species.

The technique of oxide removal with ions may find applications in the field of FUV optics, and, more specifically, for the use of unprotected Al-coated optical elements, such as mirrors and perhaps gratings, to be used in synchrotron environments or in space operating astronomical instruments. This technique may have some advantages over *in situ* Al deposition scheme. Thus, Al deposition by evaporation in space over a substrate that had been cleaned in the lab months or even years before launch would probably require some *in situ* ion cleaning technique to obtain a high quality coating. Therefore, oxide removal in space, involving only an ion technique, may be considered a simpler method than Al deposition in space for the development of nonprotected Al coatings for the FUV. The oxide removal may be thought of as a technique used periodically to restore a high reflectance

on Al films that became oxidized or contaminated after a certain time. An Al film should allow periodical oxide-etching processes; the Al film must be thick enough because every oxidation/etching process will result in a certain Al mass loss. Research would be required to investigate whether a repeated etching process might cause a higher damage in the film.

Another possibility would be to protect the Al film with a certain protective coating that would be etched off with an ion technique once the optical instrument is placed on a high orbit. MgF_2 might be such a protective coating. This possibility is analyzed in Subsection 3.B. Further applications in FUV optics can be envisioned for the ion-etching technique on other materials that undergo limited surface oxidation which results in performance reduction, such as IBS SiC or B4C coatings used for FUV optics. They might also benefit from oxide removal by ion etching.

B. Ion Etching on a MgF_2 Protective Layer

The ion-etching technique may be used to remove all or part of a protective coating. Such a technique would be useful in the case when a protective film has to be removed, or when the protective film thickness is too thick for a desired application. In this subsection we report experiments to remove a MgF_2 protective layer on Al both partly and completely by means of an ion beam.

Let us start with the complete removal of a MgF_2 protective layer. Two samples consisting of an ED Al film and a protective ~ 7.5 nm thick ED MgF_2 film were deposited in a single run. The two samples were etched for different times with 300 eV Ar ions and a total ion current of 15 mA. One sample was etched for 80 s; the dose was calculated to approximately remove the whole MgF_2 layer. The other sample was etched for 52 s; the dose was calculated to remove most of the MgF_2 layer, leaving a ~ 2.5 nm thick MgF_2 film over Al. In both samples, the resultant Al layer was immediately protected with IBS MgF_2 to complete a ~ 24 nm thick MgF_2 layer. The relevant parameters of sample preparation are also given in Table 1.

The reflectance measured for these samples is plotted in Fig. 3. A high FUV reflectance is obtained for both samples. At 121.6 nm, somewhat higher reflectance is obtained for the sample that underwent lower ion fluence; the reflectance difference between the two samples increased somewhat with wavelength. The sample exposed to 80 s ion fluence shows a reflectance decrease at 143.6 nm, almost as high as the sample for which oxide was removed (Fig. 2). Hence, when all MgF_2 layer is etched, Al seems to roughen in a way similar to the one described in Subsection 3.A, and the reflectance loss is attributed again to surface plasmon excitation through short-range roughening. The sample exposed to 52 s ion fluence displays a smaller reflectance loss at long wavelengths, which is explained in that the

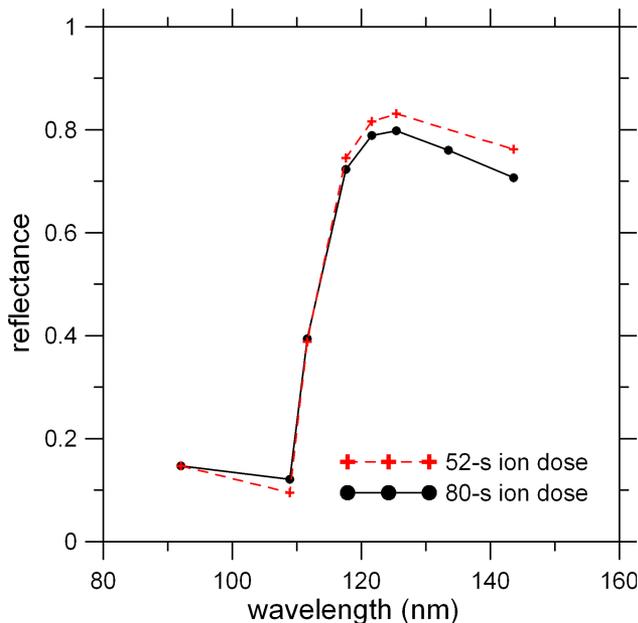


Fig. 3. (Color online) Reflectance as a function of wavelength for samples S7 and S8 consisting of an Al film protected with a 7.5 nm thick, MgF_2 film that was etched away with Ar ions. S7 was exposed to ions over 80 s in order to remove all the MgF_2 , whereas S8 was exposed over 52 s to remove all but ~ 2.5 nm MgF_2 . Both samples were protected immediately after the ion etching with a ~ 24 nm thick, IBS MgF_2 film.

~ 2.5 nm thick film of MgF_2 remaining on the Al film reduced the Al roughening effect produced by ions.

As an application, the ion-etching technique could be used to completely remove a protective coating once the optics is placed in its final environment, such as for in space FUV astronomy with pure Al coatings. If a MgF_2 protective coating is deposited immediately after Al deposition on Earth, the protective coating could be etched away with an ion-etching technique once the instrument is in space. This procedure resembles the REVAP process, described in Section 1, but now the removal of the protective film would not be performed through heating, but through ion etching.

Let us now address the removal of part of the MgF_2 protective coating on Al by ion etching. Figure 4 shows the reflectance of an Al film that was first overcoated with a 10 nm thick ED MgF_2 film and overcoated with a ~ 28 nm thick IBS MgF_2 film. The 38 nm thick hybrid protective coating was too thick for the purpose of providing the highest reflectance at 121.6 nm, far from the ~ 24 nm optimum thickness. In order to reduce the protective film thickness, the ion-etching technique was used. The sample was exposed to two successive ion-etching doses maintaining the ion energy and the total beam current constant at 300 eV and 15 mA, respectively. The sample was first ion etched for 42 s, its reflectance was remeasured, and it was placed back in the sputter-etching chamber and further ion-etched for another 100 s. The relevant parameters of sample preparation are also given in Table 1. The reflectance

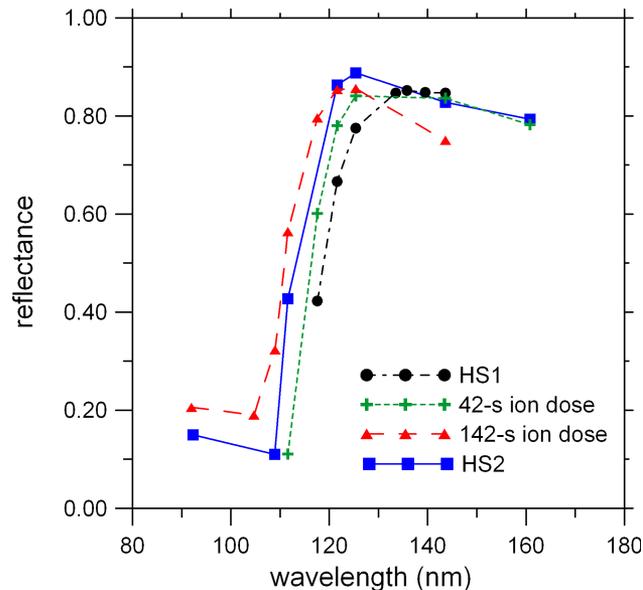


Fig. 4. (Color online) Reflectance as a function of wavelength of an Al film protected with a ~ 38 nm thick hybrid MgF_2 film (HS1), and for the same sample after exposure to two ion-etching doses: 42 s (S9) and 142 s (S10). The reflectance of a hybrid sample of Al protected with a total ~ 24 nm thick MgF_2 film (HS2) that was not etched is also shown for comparison.

after the two etching processes is shown in Fig. 4. As an effect of the ion-etching processes, the reflectance peak shifted toward shorter wavelengths, as expected for a MgF_2 film that is getting thinner and closer to the optimum thickness. After the second etching process, the reflectance measured at 121.6 nm was 0.854, which is comparable to the reflectance of the hybrid samples optimized at 121.6 nm that were not ion etched, averaging 0.850 [25]. Therefore the technique of overlayer removal by ion etching was successful in enhancing the 121.6 nm reflectance of Al mirrors protected with MgF_2 when the protective coating was too thick.

The reflectance of the 142 s etched sample was even higher below 121.6 nm than that of an optimum, nonetched hybrid sample. This is attributed to a MgF_2 film somewhat thinner than 24 nm (thus enhancing the short wavelength reflectance) and to the slightly lower losses for the IBS MgF_2 compared to ED MgF_2 at or below 121.6 nm [25]. The reflectance at 143.6 nm for the 142 s etched sample is lower than for the ~ 24 nm thick hybrid sample. The reflectance loss might be partly attributed to MgF_2 film thickness deficiency, but once more, also to surface plasmon excitation induced by short-range surface roughening. The reflectance loss is somewhat smaller than for the samples in which all the aluminum oxide or all the MgF_2 overlayer was removed by ion etching. This may be explained in terms of a different efficiency in the surface plasmon excitation for the two types of samples. The local damage due to ion impingement for the partially removed MgF_2 overlayers must be preferentially produced on the MgF_2 film, and to a lower extent on the underlying Al film, whereas for the oxide-etched or the all- MgF_2

etched samples the damage is directly produced on the resultant Al film.

The ion-etching technique can be useful to reduce the thickness of a film that was grown thicker than desired. For instance, the ED MgF₂-protected Al films with the highest reflectance at 121.6 nm are obtained when the MgF₂ film is deposited at a high rate, such as ~4 nm/s; this high rate complicates depositing a precise film thickness. In case a too thick MgF₂ film had been deposited, ion etching could be used to remove the extra thickness. The technique can be also used with multilayers. For instance, multilayer coatings based on MgF₂ that were optimized for the highest possible reflectance at 83.4 nm and simultaneously zero reflectance at 121.6 nm [31], as well as for the highest possible reflectance at 91.2 nm regardless of the reflectance at 121.6 nm [32], have been prepared. For these multilayers, ~10 nm and ~16 nm thick MgF₂ films, respectively, were required. The deposition of such thin films, particularly for the application of zero reflectance at 121.6 nm, was challenging, and the reflectance at 121.6 nm varied over one order of magnitude with only minor film thickness differences. For this application the ion-etching technique might be used after MgF₂ (and perhaps other material) deposition in order to set the correct film thickness. This would allow preparing multilayer coatings close to optimum with a high reflectance or reflection/suppression ratio.

4. Conclusions

Ion etching using an ion beam has proved to be a successful technique to modify and enhance high reflectance FUV coatings. Three particular cases were investigated:

- Oxide removal with 100 eV Ar⁺ ions of an Al oxide film grown on the Al film after exposure to normal atmosphere. Such a coating, once protected with a MgF₂ film for FUV reflectance monitoring purposes, had a reflectance at 121.6 nm, almost as high as the standard Al protected with MgF₂. A large reflectance loss of the etched samples in the 143.6–200 nm spectral range was attributed in part to surface plasmon excitation in the Al film due to short-range surface roughening induced by the ion impingement.
- Total removal of a MgF₂ protective coating on Al with 300 eV Ar⁺ ions. After MgF₂ coating removal, this coating was also protected with a new MgF₂ film, and it had a reflectance at 121.6 nm almost as high as the standard Al protected with MgF₂. A large reflectance loss in the 143.6–200 nm spectral range was also attributed to surface plasmon excitation in the Al film due to short-range surface roughening induced by the ion impingement.
- Partial removal of a MgF₂ protective coating on Al. This method was applied to reduce the MgF₂ film thickness protecting the Al coating that was thicker than the optimum value of 24 nm required for the highest possible reflectance at 121.6 nm. After etch-

ing with 300 eV Ar⁺ ions, the sample had a reflectance at 121.6 nm as high as similar coatings with the correct MgF₂ film thickness that had not been ion etched. As in the previous application, a certain reflectance loss at 143.6 nm was attributed in part to surface plasmon excitation in the Al film, slightly damaged by the ion impingement on the outer MgF₂ film.

This research was supported by NASA Office of Space Science grant RTOP 344-01-23 and by the Spanish National Programme for Space Research, Subdirección General de Proyectos de Investigación, Ministerio de Ciencia y Tecnología, project ESP2005-02650. The experimental work was performed while Juan I. Larruquert held a National Research Council–NASA/Goddard Space Flight Center Research Associateship.

References

1. G. Hass and W. R. Hunter, "Calculated reflectance of aluminum-overcoated iridium in the vacuum ultraviolet from 500 Å to 2000 Å," *Appl. Opt.* **6**, 2097–2100 (1967).
2. W. M. Burton, "Removable volatile protective coatings for aluminized mirrors used in far-ultraviolet space astronomy," *J. Phys. D* **16**, L129–L132 (1983).
3. J. I. Larruquert, J. A. Méndez, and J. A. Aznárez, "Far ultraviolet reflectance measurements and optical constants of unoxidized Al films," *Appl. Opt.* **34**, 4892–4899 (1995).
4. J. I. Larruquert, J. A. Méndez, and J. A. Aznárez, "Optical constants of aluminum films in the extreme ultraviolet interval of 82–77 nm," *Appl. Opt.* **35**, 5692–5697 (1996).
5. J. S. Edmonds, C. N. Maldé, and S. J. B. Corrigan, "Measurements of the far ultraviolet reflectivity of evaporated aluminum films under exposure to O₂, H₂O, CO, and CO₂," *Vacuum* **40**, 471–475 (1990).
6. J. I. Larruquert, J. A. Méndez, and J. A. Aznárez, "Far UV reflectance of UHV prepared Al films and its degradation after exposure to O₂," *Appl. Opt.* **33**, 3518–3522 (1994).
7. J. I. Larruquert, J. A. Méndez, and J. A. Aznárez, "Degradation of far ultraviolet reflectance of aluminum films exposed to atomic oxygen. In-orbit coating application," *Opt. Commun.* **124**, 208–215 (1996).
8. J. I. Larruquert, J. A. Méndez, and J. A. Aznárez, "Life prolongation of far ultraviolet reflecting aluminum coatings by periodic re-coating of the oxidized surface," *Opt. Commun.* **135**, 60–64 (1997).
9. A. V. Bruns, G. M. Grechko, A. A. Gubarev, P. I. Klimuk, V. I. Sevast'yanov, A. B. Severny, and K. P. Feoktistov, "Spectroscopy of solar active regions performed from Salyut-4," *Izv. Krym. Astrofiz. Obs.* **59**, 3–30 (1979).
10. J. A. Aznárez, J. A. Méndez, J. L. Sacedón, and M. Sánchez-Avedillo, "EDMO: experimental deposition of materials in orbit," *Preparing for the Future Newsletter* (ESA Publications, 1998), Vol. 8, Issue 3, pp. 12–14.
11. Yu. I. Dymshits, V. A. Korobitsyn, and A. A. Metel'nikov, "Effect of heating on the reflectivity of aluminum coatings in the vacuum ultraviolet," *Sov. J. Opt. Technol.* **46**, 649–651 (1979).
12. J. A. Méndez, J. I. Larruquert, and J. A. Aznárez, "Preservation of FUV aluminum reflectance by overcoating with C₆₀ films," *Appl. Opt.* **39**, 149–156 (2000).
13. M. Grande, "Prospects for producing normal incidence aluminum reflectors in the 800 Å to 1200 Å range," Internal Report RAL-84-037 (Rutherford Appleton Laboratory, 1984).

14. S. Rusponi, C. Boragno, and U. Valbusa, "Ripple structure on Ag(110) surfaces induced by ion sputtering," *Phys. Rev. Lett.* **78**, 2795–2798 (1997).
15. E. Spiller, "Smoothing of multilayer x-ray mirrors by ion beam polishing," *Appl. Phys. Lett.* **54**, 2293–2295 (1989).
16. E. Spiller, "Enhancement of the reflectivity of multilayer x-ray mirrors by ion polishing," *Opt. Eng.* **29**, 609–613 (1990).
17. H. J. Stock, G. Haindl, F. Hamelmann, D. Menke, O. Wehmeyer, U. Kleineberg, U. Heinzmann, P. Bulicke, D. Fuchs, and G. Ulm, "Carbon/titanium multilayers as soft-x-ray mirrors for the water window," *Appl. Opt.* **37**, 6002–6005 (1998).
18. K. Soyama, W. Ishiyama, and K. Murakami, "Enhancement of reflectivity of multilayer neutron mirrors by ion polishing: optimization of the ion beam parameters," *J. Phys. Chem. Solids* **60**, 1587–1590 (1999).
19. E. J. Puik, M. J. van der Wiel, H. Zeijlemaker, and J. Verhoeven, "Ion etching of thin W layers: enhanced reflectivity of W-C multilayer coatings," *Appl. Surf. Sci.* **47**, 63–76 (1991).
20. H. J. Voorma, E. Louis, F. Bijkerk, and S. Abdali, "Angular and energy dependence of ion bombardment of Mo/Si multilayers," *J. Appl. Phys.* **82**, 1876–1881 (1997).
21. B. Ziberi, F. Frost, Th. Höche, and B. Rauschenbach, "Ripple pattern formation on silicon surfaces by low-energy ion-beam erosion: experiment and theory," *Phys. Rev. B* **72**, 235310 (2005).
22. E. Chason, W. L. Chan, and M. S. Bharathi, "Kinetic Monte Carlo simulations of ion-induced ripple formation: dependence on flux, temperature, and defect concentration in the linear regime," *Phys. Rev. B* **74**, 224103 (2006).
23. J. F. Osantowski, "Reflectance and optical constants for Cer-Vit from 250 to 1050 Å," *J. Opt. Soc. Am.* **64**, 834–838 (1974).
24. R. P. Madden, L. R. Canfield, and G. Hass, "On the vacuum-ultraviolet reflectance of evaporated aluminum before and during oxidation," *J. Opt. Soc. Am.* **53**, 620–625 (1963).
25. J. I. Larruquert and R. A. M. Keski-Kuha, "Far ultraviolet optical properties of MgF₂ films deposited by ion-beam-sputtering and their application as protective coatings for Al," *Opt. Commun.* **215**, 93–99 (2003).
26. J. M. Elson, J. P. Rahn, and J. M. Bennett, "Relationship of the total integrated scattering from multilayer-coated optics to angle of incidence, polarization, correlation length, and roughness cross-correlation properties," *Appl. Opt.* **22**, 3207–3219 (1983).
27. E. Kretschmann and E. Kröger, "Reflection and transmission of light by a rough surface, including results for surface-plasmon effects," *J. Opt. Soc. Am.* **65**, 150–154 (1975).
28. P. Laporte, J. L. Subtil, M. Courbon, M. Bon, and L. Vincent, "Vacuum-ultraviolet refractive index of LiF and MgF₂ in the temperature range 80–300 K," *J. Opt. Soc. Am.* **73**, 1062–1069 (1983).
29. J. G. Endriz and W. E. Spicer, "Study of aluminum films. I. Optical studies of reflectance drops and surface oscillations on controlled-roughness films," *Phys. Rev. B* **4**, 4144–4159 (1971).
30. M. Fernández-Perea, J. I. Larruquert, J. A. Aznárez, A. Pons, and J. A. Méndez, "Vacuum ultraviolet coatings of Al protected with MgF₂ prepared both by ion-beam sputtering and by evaporation," *Appl. Opt.* **46**, 4871–4878 (2007).
31. J. I. Larruquert and R. A. M. Keski-Kuha, "Multilayer coatings for narrowband imaging in the extreme ultraviolet," *Appl. Opt.* **40**, 1126–1131 (2001).
32. J. I. Larruquert and R. A. M. Keski-Kuha, "Multilayer coatings with high reflectance in the EUV spectral region from 50 to 121.6 nm," *Appl. Opt.* **38**, 1231–1236 (1999).