Optics Express Vol. 29, Issue 5, pp. 7706-7712 (2

https://doi.org/10.1364/OE.418521

# Far UV-enhanced Al mirrors with Ti seed

**JUAN I. LARRUQUERT*, CARLOS HONRADO-BENÍTEZ, NURIA GUTIÉRREZ-LUNA, ÁLVARO RÍOS-FERNÁNDEZ, PALOMA LÓPEZ-REYES**

*GOLD-IO-CSIC Instituto de Óptica-Consejo Superior de Investigaciones Científicas*
*Serrano 144, 28006 Madrid, Spain*
**: j.larruquert@csic.es*

**Abstract:** A Ti seed film is investigated towards improving the far UV reflectance of Al/$MgF_2$ mirrors. Samples were initially coated with a Ti film in half of the area and they were later coated in the full area with an Al film and protected with $MgF_2$. All materials were deposited by evaporation. Samples were prepared with the $MgF_2$ layer deposited either at room temperature (RT) or at 225 °C. A 3-nm thick Ti seed film was seen to significantly reduce the reflectance dip of Al/$MgF_2$ mirrors centered at ~160 nm; this was attributed to a reduction of short-range surface roughness at the Al/$MgF_2$ interface, which is responsible for radiation absorption through surface-plasmon (SP) coupling. SP absorption was more efficiently reduced with a Ti seed on samples fully deposited at RT. A Ti seed as thin as 1 nm provided the largest SP absorption reduction, and the SP dip was almost completely removed.

**OCIS codes:** (230.4040) Mirrors; (260.7210) Ultraviolet, vacuum; (120.6085) Space instrumentation; (240.6680) Surface plasmons; (310.6860) Thin films, optical properties; (160.4670) Optical materials; (240.5770) Roughness

## 1. Introduction

Space observations in the far ultraviolet (FUV, wavelength in the ~100-200-nm range) for astrophysics, as well as for solar physics and atmosphere physics, require effective optics for optimum detection of the typically scarce photons. Broadband FUV mirrors have been overwhelmingly based on evaporation-deposited coatings of Al protected with $MgF_2$ since they were developed at the end of the 1950's [1]. The transparency of $MgF_2$ preserves Al high FUV reflectivity all the way from the infrared (IR) to the $MgF_2$ cutoff at ~115 nm. $MgF_2$ can be replaced with LiF to extend high FUV reflectance down to ~102 nm [2], although the instability of LiF in a humid environment complicates its practical application. A further fluoride, $AlF_3$, has been proposed recently to protect Al and it results in mirrors with an FUV reflectance almost as high as Al/$MgF_2$ [3,4,5].

Yet, Al/$MgF_2$ keeps as the reference broadband FUV mirror. Over so many years since these mirrors were first developed and until recently, their reflectance had been only slightly enhanced, based on improvements in vacuum technology, such as deposition chamber cleanliness. It has not been until the last years that Quijada et al. [6] reported an important advancement for these coatings. It consists in depositing the protective $MgF_2$ coating onto a heated Al film (except for the first few nm of $MgF_2$ in contact with Al). The procedure results in a significant FUV reflectance increase over the standard room-temperature (RT) deposition procedure, and such increase is remarkable in the range close to the $MgF_2$ cutoff. This reflectance increase can be attributed to the higher FUV transparency and lower porosity of the hot-deposited fluoride film. An optimum $MgF_2$ deposition temperature of ~250°C was found for largest FUV reflectance [7]. This procedure has been also proved successful on

Al/LiF [8] and $Al/AlF_3$ [5] mirrors. Some efforts have been attempted to deposit Al and/or $MgF_2$ and other fluorides by sputtering [9] and by atomic layer deposition [10,11], but up to now, they have not succeeded to match the FUV reflectance of evaporation-deposited mirrors.

The FUV reflectance obtained in [6] at the important FUV spectral line of H Lyman α (121.6 nm) is close to the calculated reflectance of $Al/MgF_2$ mirrors with bulk $MgF_2$ optical constants, so that little room for improvement has been left in the short FUV, close to the $MgF_2$ cutoff. But there is still room for improvement at longer FUV wavelengths, where $Al/MgF_2$ mirrors display a reflectance dip peaked at ~160 nm. This is attributed to absorption through excitation of a resonant surface-plasmon (SP) mode, and it is remarkable in free-electron metals. Coupling between the incoming wave and the SP mode is made through the metal surface roughness [12]. For a nearly free-electron-metal like Al and for radiation incident from vacuum, the dip is peaked at $\sim\sqrt{2}\lambda_p$, where $\lambda_p$ stands for the free-electron-metal (volume) plasma wavelength (83.5 nm for Al). When light impinges on the metal surface from a dielectric material with $\varepsilon_1$ dielectric constant, the dip is shifted to longer wavelengths according to $\sim\sqrt{1+\varepsilon_1}\lambda_p$ [12,13]. Hence the SP dip is nominally peaked at $\lambda_{sp}$ =153 nm for $MgF_2$ on Al [14]. In practice, the real dip is often peaked at a slightly longer wavelength and it extends to a relatively wide band; the width increases with the metal damping constant [15]. SP absorption is induced by surface-roughness spatial wave vectors that are larger than the light wave vector [15]. This means that light coupling to SP is induced by short-range roughness, which can be intuitively visualized as granular structures that are narrower than the light wavelength. The long-range roughness components induce light scattering.

The roughness of Al films can be somewhat reduced by depositing the Al film at a high deposition rate [16]. Recently, Stempfhuber et al. [17] observed significant roughness reduction in Al films deposited on seed layers of Ti and Cu. Calculations in [17] showed a large reduction of the scatter losses; such reduction was larger for Ti-seeded than for Cu-seeded Al films. The average grain size of the Ti-seeded Al was seen to increase compared to unseeded Al, whereas surface roughness strongly decreased, so that roughness statistical distribution was significantly modified. [17] reported FUV reflectance measured for non-protected Al films that had been intentionally oxidized in an oxygen plasma. For such samples, an increase in FUV reflectance was observed for the Ti-seeded Al films compared to the non-seeded ones. In [17], the higher reflectance of the Ti-seeded Al film was attributed partly to a thinner aluminum oxide layer and partly to decreased plasma resonance in the grain boundaries. However, due to Al oxidation, the increased reflectance did not compensate for the reduced reflectance of the oxidized Al mirror compared with standard $Al/MgF_2$ mirrors.

The present research advances towards removing the FUV reflectance dip of $Al/MgF_2$ mirrors. The start point is the results of [17], except that the Ti-seeded Al film is immediately protected with $MgF_2$ to preserve the high FUV reflectance of Al, so that the effect of Ti seeding on the reflectance of high-performance $Al/MgF_2$ mirrors can be ascertained. Ti-seeding was performed for Al films protected with $MgF_2$ deposited both at RT and at 225°C, the two temperatures attempted in [17]. Section 2 presents the experimental techniques used in this research. Section 3 compares the FUV reflectance measured for $Al/MgF_2$ mirrors with and without Ti seed layers of various thicknesses. The FUV reflectance enhancement enables to estimate the reduction of the SP absorption.

## 2. Experimental techniques

Coatings were deposited in a 75-cm diameter, 100-cm height, oil-free high-vacuum deposition chamber pumped with a cryo pump; the chamber is located in an ISO6 clean room. Samples were divided into two areas; one of them was masked with a shutter while the other area was coated with an ultrathin Ti film. After Ti deposition, the shutter was removed and both areas were immediately overcoated with a common ~70- and ~25-nm thick Al and $MgF_2$ layer, respectively, so that any difference over the two areas could be attributed to the Ti seed. All three layers were immediately deposited one after the other without breaking vacuum. One sample was divided into three areas with different Ti film thicknesses over the three areas and a common Al and $MgF_2$ overcoating. Two samples were protected with the $MgF_2$ film deposited at RT, whereas for one sample, the procedure reported in Refs. [6,7] was followed, i.e., Al was initially protected with a 5-nm thick $MgF_2$ film deposited at RT and the additional 20 nm of $MgF_2$ were deposited after the partly-coated sample had been heated to 225°C. 50.8 mmx50.8 mm pieces of polished, floated BK7 glass substrates with a nominal roughness of 0.5 nm were used. 99.999% pure Al, VUV-grade $MgF_2$, and 99.99% pure Ti were deposited by evaporation techniques. Al was evaporated from W filaments, whilst $MgF_2$ and Ti were evaporated from W boats. Deposition rates were ~12 to 20 nm/s, ~1 to 2 nm/s, and 0.1 to 0.2 nm/s for Al, $MgF_2$, and Ti, respectively, as measured with a quartz crystal microbalance. Base pressure was $10^{-6}$ Pa and it increased up to $\sim 5\times10^{-5}$ Pa during deposition.

FUV reflectance was measured in GOLD's (GOLD is the Spanish acronym for Thin Films Optics Group) reflectometer. The reflectometer 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 subranges. The reflectometer used a deuterium lamp to cover the present spectral range and a channel-electron-multiplier detector with a CsI-coated photocathode. FUV reflectance was measured at 5° from normal incidence. Reflectance in the near UV (NUV) to the infrared (IR) was measured with a lambda-900 Perking–Elmer, double-beam spectrophotometer, which operated at 8°.

Samples were measured first after a short contact to atmosphere of ~1 hour and again after ~one month of ageing in a desiccator.

## 3. Results

Research started by reproducing the 3-nm thick Ti seeds reported in [17]. Two Al/$MgF_2$ samples were prepared, one (S2) at RT and one (S1) with the $MgF_2$ protective coating deposited at 225 °C following Quijada's procedure [6,7]. For the two samples, half substrate was pre-coated with a 3-nm Ti film, as described in Section 2. Fig. 1 displays the reflectance measured in both areas for the samples aged of one month. A common fact is observed on films deposited at the two temperatures: the area seeded with Ti presents a remarkable reflectance increase over the non-seeded coating at the SP range, which is interpreted as a reduction of SP absorption. The largest reflectance increase was obtained at ~165 nm. No significant difference between seeded and unseeded coatings was found at short FUV wavelengths close to the $MgF_2$ cutoff. This can be interpreted as that the short-range roughness components have been reduced on the seeded mirror, with no appreciable modification of the long-range roughness components.

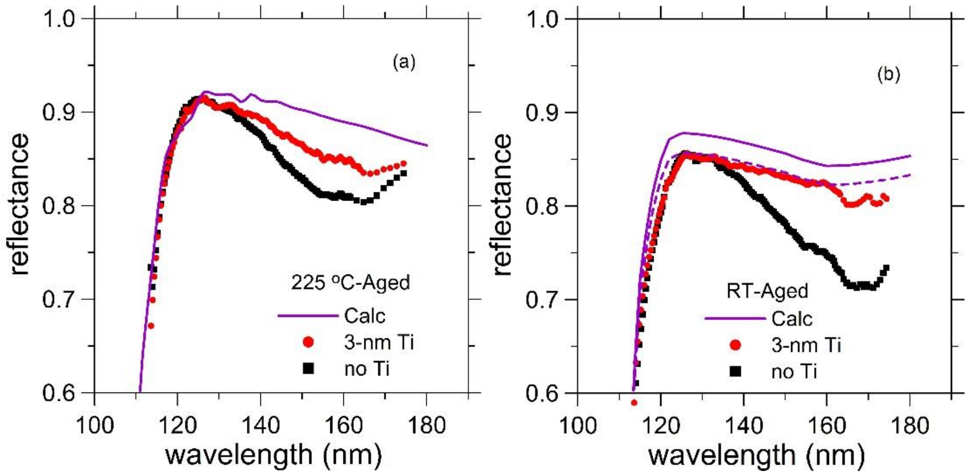


Fig. 1. Reflectance of Al mirrors with the $MgF_2$ protective layer deposited at 225 °C (a) and RT (b). One half of each mirror was pre-coated with a 3-nm thick Ti film and the other half was not pre-coated. Calc stands for calculated reflectance using the optical constants of Al [18,19] and of $MgF_2$ deposited either at 250 °C [14] [(a) 25-nm thick] or at RT [20] [(b) 27-nm thick]. Dashed line: reduced calculation (see text).

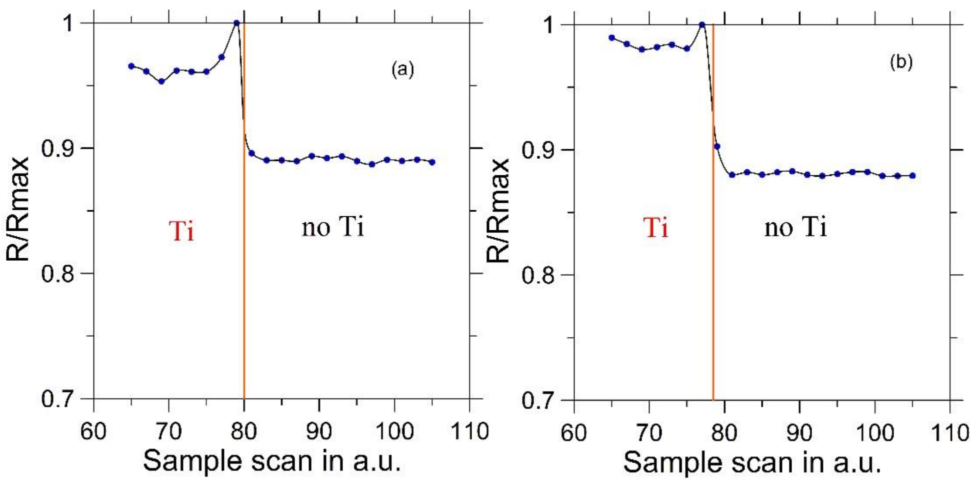


Fig. 2. Normalized reflectance at ~160 nm versus sample scan for Al mirrors with the $MgF_2$ protective layer deposited at 225 °C (a) and RT (b). One half was pre-coated with a 3-nm thick Ti film and the other half was not pre-coated. A line is plotted to indicate the separation between the seeded and the unseeded areas.

To make sure that the Ti seed was making the difference, the samples were scanned in reflectance with the deuterium doublet at ~160 nm, not far from the dip peak. Fig. 2 displays reflectance as a function of the position across the two mirrors. A clear change is observed at the edge between the seeded and the unseeded areas for both samples, so that reflectance is mostly constant over each area and a steep change is observed at the transition between the two areas. In contrast, no significant reflectance variation was observed when the scan was performed at 121.6 nm.

These results are compatible with Ref. [17], where a decreased plasma resonance for the Ti-seeded Al was inferred from the topography measured with SEM and AFM. The distinct topography observed for unseeded and Ti-seeded Al in [17] was remarkably explained in terms of the higher surface free energy of Ti compared to the native oxide of the Si wafer substrate and in terms of the close bond energies of Al-Al and Ti-Al. Both features were proposed to result in more nucleation sites for Al and in decreased diffusion of Al on the seeded substrates, which would result in Stranski-Krastanov growth mode and in a decreased surface roughness [17]. The present substrates were glass, which can be expected to have a close surface free energy to the native oxide of Si. A further source of reflectance enhancement was attributed in [17] to a thinner aluminum oxide of the Ti-seeded sample, but this fact does not apply here due to the protective effect of the $MgF_2$ layer.

A slight reflectance increase can be observed in Fig. 2 on both samples at the edge of the seeded area, which was interpreted as a further reflectance increase towards the extinguishing presence of Ti in the transition from the 3-nm Ti layer to the no-Ti area. This evidence suggested that a thinner Ti film might be even more effective in reducing short-range roughness and SP absorption. Hence a sample (S3) with three areas coated with 1-, 2-, and 3-nm thick Ti films was prepared. The full sample was coated with a common Al and RT-deposited $MgF_2$ film. Fig. 3 displays the FUV reflectance on the three sample areas: the smallest SP absorption dip was found on the area with 1-nm thick Ti film. The dip was also smaller for the 2-nm- than for the 3-nm-thick seeded area. Hence a Ti film as thin as 1 nm was the most effective to reduce SP absorption and hence to reduce Al short-range roughness. A similar ultrathin seed was reported for Ge-seeded smooth Ag films [21]. Fig. 3 also displays a sample scan at the deuterium doublet crossing the three areas. The figure confirms that there are three distinct areas with increasing reflectance for decreasing Ti-seed thicknesses. For this sample, each Ti deposition was performed with a shutter that covered the other two areas, in a way that there were tiny gaps between adjacent seeded areas. At these small gap areas, the sample was masked during Ti deposition, but, since the shutter was a few centimeters away from the sample, the transition between the seeded area and the adjacent masked area may be smooth, with slight presence of Ti on the edge of the masked area. This residual presence of Ti may explain the sudden reflectance increases at the edges of the 2-nm thick film and at the edge of the 3-nm thick film. Fig. 3.b displays a deep minimum reflectance at the gaps between adjacent seeded areas. This value is somewhat smaller than for the non-seeded area of the other sample deposited at RT (S2). This raises the question whether there might be a modified growth dynamics when a residual Ti thickness thinner than 1 nm is present.

The samples were measured in an extended spectral range. Fig. 4 displays reflectance from the FUV to the IR for the same samples displayed in Figs. 1 and 2. Measurements were performed after ~1-month sample ageing in a desiccator. Measurements show a slightly larger reflectance at the Ti-seeded mirrors that extends all the way to the visible and even to the IR. The connection range between the two instruments is not smooth for some curves, which may originate mostly in uncertainties in the long FUV range measurements due to a low signal, and to a lesser extent in uncertainties in the NUV range measurements.

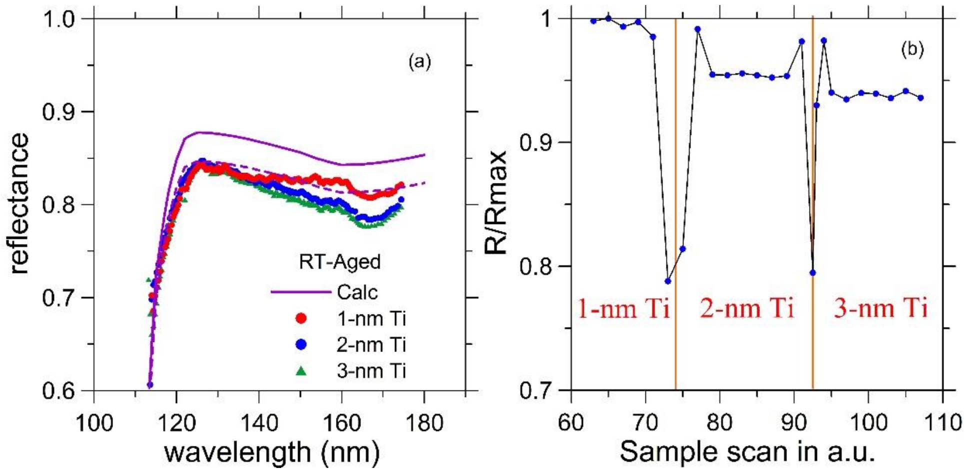


Fig. 3. Reflectance of an Al mirror with the $MgF_2$ protective layer deposited at RT. The sample was pre-coated on 3 areas with 1-, 2-, and 3-nm thick Ti film. (a): reflectance versus wavelength. Calc stands for calculated reflectance using the optical constants of Al [18,19] and of 27-nm thick $MgF_2$ deposited at RT [20]. Dashed line: reduced calculation (see text). (b): normalized reflectance at ~160 nm versus sample scan; lines are plotted to indicate the separation between the areas seeded with 1-, 2, and 3-nm thick Ti film.

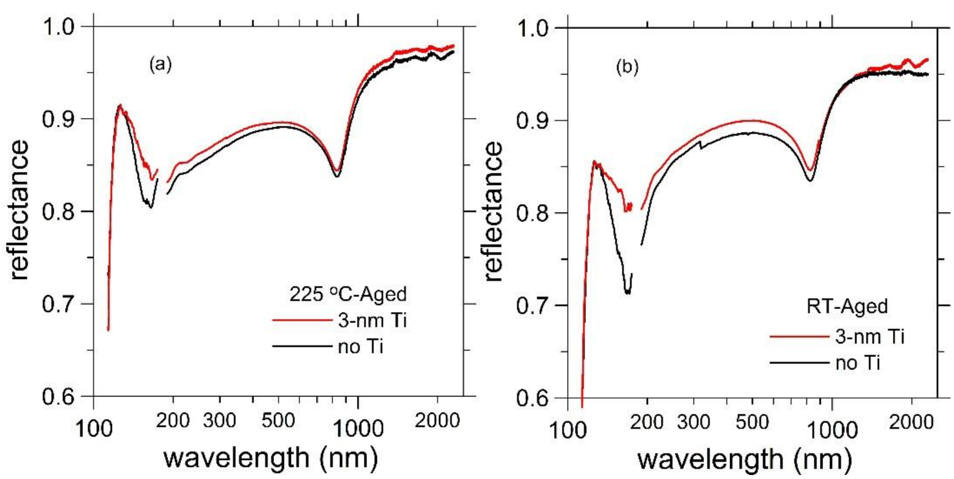


Fig. 4. Reflectance vs. wavelength from the FUV to the IR of Al mirrors with the $MgF_2$ protective layer deposited at 225 °C (a) and RT (b). One half was pre-coated with a 3-nm thick Ti film and the other half was not pre-coated.

An evaluation parameter for the reduction of SP-absorption through a Ti seed would be desirable. Reflectance was calculated using the optical constants of Al and $MgF_2$ assuming smooth interfaces; calculated reflectance is also plotted in Figs. 1 and 3.a. For samples deposited at RT, measured reflectance is lower than calculations even at short wavelengths, which may be attributed to mirror ageing, to roughness-induced scattering, and also to uncertainties in the optical constants and in the reflectance measurements. To help the eye compare calculations and measurements, calculated reflectance was reduced with a constant factor until matching the measurements at short wavelengths, where there must be no SP absorption, and the reduced calculation was plotted with a dashed line in Figs. 1.b and 3.a. In

Fig. 1.a, the reflectance at the SP range for the seeded mirror is approx. halfway between the reflectance of the non-seeded mirror and calculated reflectance, so that the 3-nm thick Ti seed for the Al mirror protected at 225°C reduces the SP dip by almost one half. For the Al mirror protected at RT, the dashed line is mostly coincident with the Ti-seeded mirror reflectance in Fig. 1.b, so that the 3-nm thick Ti seed almost fully suppresses the SP dip, except longwards of ~160 nm, but our FUV measurements have larger fluctuations there, most probably due to low radiation intensity. For the Al mirror protected at RT with 3 Ti-seed thicknesses, the 3- and 2-nm thick seeds are somewhat less effective to reduce SP absorption than in Fig. 1.b, which may be attributed to uncontrolled differences from sample to sample (including deposition rates, partial pressures of gases in the chamber, and substrate roughness and cleanness), whereas the 1-nm thick Ti seed fully suppresses the SP dip. Hence, SP absorption is progressively more effectively removed from 3- towards 1-nm thick seed. According to the present results, a 1-nm thick Ti film is proposed as the optimum seed film thickness that almost completely removes the SP dip in Al mirrors.

## Conclusions

The deposition of a 3-nm thick Ti seed before depositing an Al mirror protected with $MgF_2$ results in a significant reflectance increase at the SP resonance, which is interpreted as a strong reduction of short-range surface roughness and hence of the SP absorption thereof. This reduction is largest in a band centered at ~160 nm, but extends to the IR with a slight reflectance increase all the way. The SP reduction was obtained for Al mirrors protected with a $MgF_2$ layer both deposited at 225 °C as well as at RT. The SP reduction with the Ti seed was larger for the RT-deposited mirror than for the 225 °C-protected mirror. A still thinner Ti seed film was seen to further enhance such SP reduction, and a 1-nm thick Ti seed film was seen to approximately remove completely the SP reflectance dip for a sample deposited at RT. No significant evolution in terms of the SP dip reduction due to the use of a Ti seed was observed for samples after 1 month of ageing in a desiccator.

Al films with reduced roughness are associated in the literature with high deposition rates, which complicates the deposition of a homogeneous layer with the target thickness. The use of a Ti seed indicates that such a high deposition rate may not be necessary to deposit coatings with small SP absorption.

## Acknowledgments

We gratefully acknowledge José L. Bris and Joaquín Campos for spectrophotometry measurements in the NUV to IR. This research was funded by Secretaría de Estado de Investigación, Desarrollo e Innovación (PID2019-105156GB-I00).

## Disclosures

The authors declare no conflicts of interest.

## References

[1] G. Hass and R. Tousey, “Reflecting coatings for the extreme ultraviolet,” J. Opt. Soc. Am. **49**, 593-602 (1959).

[2] D. W. Angel, W. R. Hunter, R. Tousey, and G. Hass, “Extreme ultraviolet reflectance of LiF-coated aluminum mirrors,” J. Opt. Soc. Am. **51**, 913-914 (1961).
[3] F. Bridou, M. Cuniot-Ponsard, J. M. Desvignes, M. Richter, U. Kroth, A. Gottwald, “Experimental determination of optical constants of $MgF_2$ and $AlF_3$ thin films in the vacuum ultra-violet wavelength region (60–124 nm), and its application to optical designs,” Opt. Commun. **283**, 1351–1358 (2010).
[4] S. Wilbrandt, O. Stenzel, H. Nakamura, D. Wulff-Molder, A. Duparré, N. Kaiser, “Protected and enhanced aluminum mirrors for the VUV,” Appl. Opt. **53**, A125–A130 (2014).
[5] N. Gutiérrez-Luna, B. Perea-Abarca, L. Espinosa-Yáñez, C. Honrado-Benítez, T. de Lis, L. V. Rodríguez-de Marcos, J. A. Aznárez and J. I. Larruquert, “Temperature dependence of $AlF_3$ protection on Far-UV Al mirrors,” Coatings **9**, 428 (2019).
[6] M. A. Quijada, S. Rice, and E. Mentzell, “Enhanced $MgF_2$ and LiF over-coated Al mirrors for FUV space astronomy,” Proc. SPIE **8450**, 84502H (2012).
[7] L. V. Rodríguez-de Marcos, J. I. Larruquert, J. A. Méndez, N. Gutiérrez-Luna, L. Espinosa-Yáñez, C. Honrado-Benítez, J. Chavero-Royán, B. Perea-Abarca, “Optimization of MgF2-deposition temperature for far UV Al mirrors,” Opt. Express **26**, 9363-9372 (2018).
[8] M. A. Quijada, J. del Hoyo, and S. Rice, “Enhanced far-ultraviolet reflectance of $MgF_2$ and LiF over-coated Al mirrors,” Proc. SPIE **9144**, 91444G-1 (2014).
[9] 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).
[10] J. Hennessy, K. Balasubramanian, C. S. Moore, A. D. Jewell, S. Nikzad, K. France, and M. Quijada, “Performance and prospects of far ultraviolet aluminum mirrors protected by atomic layer deposition,” J. Astron. Telesc. Instr. Syst. **2**(4), 041206 (2016).
[11] B. Fleming, M. Quijada, J. Hennessy, A. Egan, J. del Hoyo, B. A. Hicks, J. Wiley, N. Kruczek, N. Erickson, and K. France, “Advanced environmentally resistant lithium fluoride mirror coatings for the next generation of broadband space observatories,” Appl. Opt. **56**(36), 9941-9950 (2017).
[12] B. P. Feuerbacher and W. Steinmann, “Reflectance of evaporated aluminium films in the 1050-1600 Å region, and the influence of the surface plasmon,” Opt. Commun. **1**, 81-85 (1969).
[13] J. M. Elson K. H. Ritchie, “Diffuse scattering and surface-plasmon generation by photons at a rough dielectric surface,” Phys. Stat. Sol. (b) **62**, 461-468 (1974).
[14] L. V. Rodríguez-de Marcos, J. I. Larruquert, J. A. Méndez, J. A. Aznárez, “Self-consistent optical constants of $MgF_2$, $LaF_3$, and $CeF_3$ films,” Opt. Mater. Exp. **7**, 989-1006 (2017).
[15] 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).
[16] 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**(12), 4144-4159 (1971).
[17] S. Stempfhuber, N. Felde, S. Schwinde, M. Trost, P. Schenk, S. Schröder, and A. Tünnermann, “Influence of seed layers on optical properties of aluminum in the UV range,” Opt. Express **28**, 20324-20333 (2020).
[18] E. Shiles, T. Sasaki, M. Inokuti, and D. Y. Smith, “Self-consistency and sum-rule tests in the Kramers-Kronig analysis of optical data: applications to aluminium,” Phys. Rev. B **22**(4), 1612–1628 (1980).
[19] D. Y. Smith, E. Shiles, M. Inokuti, *The optical properties of metallic aluminum*, in *Handbook of Optical Constants of Solids* (E. D. Palik. ed., Academic, 1985).

[20] Unpublished data.
[21] V. J. Logeeswaran, N. P. Kobayashi, M. S. Islam, W. Wu, P. Chaturvedi, N. X. Fang, S. Y. Wang, and R. S. Williams, “Ultrasmooth silver thin films deposited with a germanium nucleation layer,” Nano Lett. **9**(1), 178-182 (2009).