

Far ultraviolet optical properties of MgF₂ films deposited by ion beam-sputtering and their application as protective coatings for Al

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Abstract

Thin films of MgF₂ deposited by evaporation is a material widely used for its transparency in the far ultraviolet (FUV) down to ~115 nm. In this paper the optical properties of ion-beam-sputtered (IBS) MgF₂ in the FUV are investigated and compared with the standard MgF₂ films deposited by evaporation. A slightly higher transparency at the 121.6-nm, H Lyman α line was obtained for IBS MgF₂ films compared to films deposited by evaporation, which makes IBS MgF₂ a good candidate protective material for Al reflective coatings. Experimental work on Al films that were protected with a

thin evaporated MgF₂ film plus an IBS MgF₂ film to produce a protective coating with optimum thickness showed a reflectance at 121.6 nm that was higher by about 3% compared to the standard Al film protected with an all-evaporated MgF₂ film.

OCIS Codes: 120.4530 (Optical constants), 260.7210 (Ultraviolet, far), 260.7200 (Ultraviolet, extreme), 120.5700 (Reflection), 240.0310 (Thin films), 310.1620 (Coatings)

1. Introduction

MgF₂ is a material with a large number of applications in optics based on its low refractive index and on its transparency from the far ultraviolet (FUV, $\lambda < 200$ nm) to the IR. It is of particular interest as a protective overcoating on an Al film to obtain a high reflectance in the FUV above the MgF₂ cutoff wavelength (115 nm). MgF₂-protected Al deposited by thermal evaporation can achieve 85% reflectance at the 121.6-nm H Lyman α line, and this reflectance is limited by the radiation losses in the MgF₂ film. The MgF₂ film deposited by evaporation grows with a columnar structure and a low packing density. This imperfect structure results in higher radiation losses above the MgF₂ cutoff wavelength for the film compared to a single MgF₂ crystal¹. The transparency of MgF₂ films deposited by evaporation is continuously enhanced when the substrate is held at increasing temperatures up to 670 K due to the increase in the film crystallinity. In spite of the enhanced transparency, no significant change in the FUV reflectance of MgF₂-overcoated Al films was obtained for films deposited on a substrate heated up to 370 K, whereas a lower reflectance was obtained when deposited on a substrate heated at 420 K and above². This may be due to the conflicting growth requirements for the two films. A low-loss MgF₂ film can be best produced at high substrate temperatures, whereas a high reflectance aluminum film is destroyed at high temperatures^{1, 3, 4}. Thus Al protected with MgF₂ deposited by evaporation are regularly deposited on unheated substrates.

Compact films with a high packing density are regularly obtained for many materials using sputtering techniques. For some materials that have enhanced properties when deposited on heated substrates, similar enhancements can be obtained by sputter

deposition on room temperature substrates. In those cases, the high atom mobility in the hot growing film is replaced with the high energy of the sputtered atoms impinging on the growing film held at room temperature. Sputtering techniques are successfully employed for the deposition of single elements, compounds with two or more solid materials as well as oxides, nitrides, etc. The sputtering of compound materials in which one element is a gas at room temperature, such as oxides and nitrides, usually results in the deficiency of the volatile species unless reactive sputtering is performed with a partial pressure of a gas supplying extra atoms of the deficient species. The sputter deposition of fluorides is complicated because fluorine is a corrosive gas and that prevents the use of reactive sputtering in standard deposition chambers. In the past, attempts have been made to sputter MgF_2 but the results have been unsatisfactory because of loss of fluorine from compound decomposition^{5,6}. Research has been also performed on MgF_2 films deposited by evaporation with ion assisted deposition (IAD) in order to supply extra energy to the growing film^{7,8,9,10}. The IAD films showed an enhanced crystallinity, but the films had higher absorption above the MgF_2 cutoff wavelength, which was attributed to the presence of MgO related to the deficiency in F.

In the present paper we compare the FUV optical properties of evaporated and ion beam sputtered (IBS) MgF_2 films. We also analyze the protective properties of IBS MgF_2 on Al films for the highest possible reflectance at the 121.6-nm H Lyman α line. In Section 2 we describe the experimental techniques used. Section 3 is devoted to the experimental results obtained on the optical constants of MgF_2 both deposited by evaporation and IBS, and the reflectance of Al films protected with evaporated as well as IBS MgF_2 .

2. Experimental techniques

Two deposition chambers that were pumped with cryopumps were used in this work. One vacuum chamber was used to deposit Al and MgF₂ films by resistance heating evaporation and the other chamber was used to deposit MgF₂ by IBS. The IBS system was equipped with a 3-cm Kauffman ion gun that focused an Ar⁺ beam onto a water-cooled target placed at about 45° to the ion beam. An Ar flow of 7.0 sccm was maintained. The ions sputtered target atoms that impinged perpendicularly onto a water-cooled, float glass or MgF₂ crystal substrate placed 10 cm away from the target. A 101.6-mm diameter, 99.997% purity MgF₂ sputtering target was used. The base pressures in the sputtering and evaporation chambers were 4x10⁻⁶ Pa and 10⁻⁶ Pa, respectively. Typical total pressures during deposition were 4x10⁻² Pa in the sputtering chamber, and 10⁻⁵ Pa in the evaporation chamber. The deposition rates of evaporated materials were ~20 nm/s for Al, and 2-3 nm/s for MgF₂, and it was ~0.15 nm/s for sputtered MgF₂. The layer thickness was measured with a quartz crystal thickness monitor that was calibrated through a Topo-3D non-contact surface profiler.

Various samples were prepared in which in a first step an Al film was initially coated with a 7-to-10-nm thick MgF₂ film deposited by evaporation in order to protect the Al film from oxidation in the sample transfer to the IBS chamber, where in a second step a film of IBS MgF₂ was deposited to complete a total MgF₂ film thickness of ~24 nm for the highest possible reflectance at 121.6 nm. The sample with the uncompleted MgF₂ film was exposed to atmosphere for about five minutes.

The samples were exposed to atmosphere for a few minutes before being transferred to the reflectometer. Reflectance and transmittance measurements were performed using a reflectometer-monochromator described elsewhere¹¹. All films investigated in this paper were deposited on unheated substrates and their reflectance was measured at room temperature.

Two different types of substrates were used. 25.4-mm diameter, 3-mm thick MgF₂ crystal pieces were coated with MgF₂ for transmittance measurements. 50.8-mm x 50.8-mm x 2-mm float glass pieces were coated with single MgF₂ coatings or coatings of Al protected with MgF₂ for reflectance measurements.

3. Experimental results and discussion

A. OPTICAL CONSTANTS OF MgF₂

The normal incidence transmittance of ~25-nm thick MgF₂ films deposited by evaporation and by IBS on MgF₂ crystals was measured above the MgF₂ cutoff wavelength. The transmittance of the bare crystal substrate was also measured. The film+crystal/crystal transmittance ratio can be approximated by:

$$\frac{T_{fc}}{T_c} \approx \exp\left(-\frac{4\pi k_1 x_1}{\lambda}\right) \quad (1)$$

k_1 and x_1 stand for the extinction coefficient and thickness of the MgF₂ film, respectively. The above approximation takes into account that the reflectance at the

vacuum/crystal interface is small and assumes that the reflection coefficient at the interface MgF₂ film/MgF₂ crystal is negligible since the refractive index of the two materials can be expected to be close.

The extinction coefficient of the evaporated as well as the IBS MgF₂ film was obtained from the transmittance measurements on the bare crystal and on the crystal coated with a MgF₂ film using Eq. (1). Fig. 1 compares the extinction coefficient for MgF₂ deposited both by evaporation and by IBS. Two interesting results are observed in Fig.1. The extinction coefficient is slightly lower for the IBS film than for the evaporated film at 121.6 nm and below, showing that IBS films are slightly more transparent at the important H Lyman α line. However, k is higher for the IBS film above 125.4 nm, and the longer the wavelength up to 200 nm, the larger the difference. Deposition of MgF₂ films by RF planar magnetron sputtering resulted in films that absorbed in the visible, which was attributed to F deficiency. We also suggest that the higher absorption of our IBS films at wavelengths above 125.4 nm may be due to some F deficiency, whereas at short wavelengths close to the MgF₂ cutoff that stoichiometric MgF₂ starts to absorb, the suggested F deficiency might result in an relative absorption lowering.

The optical constants (n , k) of the two species of MgF₂ films at wavelengths 121.6 nm and below were obtained from reflectance measurements as a function of the angle of incidence for MgF₂ films deposited on glass substrates. Since the MgF₂ films were not opaque, the reflectance of the vacuum/ thin film/ glass substrate multilayer had to be taken into account in the optical constant calculation. The complex amplitude reflectance of the vacuum /MgF₂ film /glass substrate multilayer can be expressed by:

$$r^{s,p} = \frac{r_{01}^{s,p} + r_{12}^{s,p} \exp\left(\frac{4\pi i N_1 x_1 \cos \theta_1}{\lambda}\right)}{1 + r_{01}^{s,p} r_{12}^{s,p} \exp\left(\frac{4\pi i N_1 x_1 \cos \theta_1}{\lambda}\right)} \quad (2)$$

where $r_{ij}^{s,p}$ are the Fresnel reflection coefficients at the ij interface ($i,j=0$ -vacuum-, 1 - thin film-, 2 -glass) for both parallel (p) or perpendicular (s) electric vector. θ_1 is the complex propagation angle through the film, which is given by Snell's law. $N_1 = n_1 + ik_1$ is the complex refractive index of MgF₂ film. The radiation emerging from the monochromator onto the sample is partially polarized. The influence of polarization on the reflectance can be described by a single parameter that will be referred to as the degree of polarization p :

$$p = \frac{I_p - I_s}{I_p + I_s} \quad (3)$$

where I_p and I_s indicate the fraction of the incident intensity with the electric vector parallel or perpendicular, respectively, to the plane of incidence. With this notation, the reflectance (ratio of reflected to incident intensity) of the multilayer vacuum/ thin film/substrate for a certain degree of polarization is given by:

$$R = \frac{1+p}{2} R_p + \frac{1-p}{2} R_s \quad (4)$$

where R_p and R_s are the reflectance for p and s polarization, respectively, i.e., $R_s = |r_s|^2$, $R_p = |r_p|^2$ as they are given in Eq. (2).

The search for the optical constants of the MgF₂ film was made by the minimization of the following merit function:

$$s_j^2 = \sum_{i=1, \dots, m} \{ R^{\text{exp}}_{\theta(i)} - R[\theta(i), n_j, k_j, p] \}^2 \quad (5)$$

where $R^{\text{exp}}_{\theta(i)}$ is the reflectance measured at the angle of incidence $\theta(i)$, and $R[\theta(i), n_j, k_j, p]$ is the calculated reflectance for the trial set (n_j, k_j) of optical constants in the iteration j , and for the partial polarization of the beam p as defined in Eq. (3). The reflectance as a function of the angle of incidence was measured for films of MgF₂ deposited both by evaporation and by IBS on float glass substrates. The number of angles of incidence m equaled 6 (15°, 30°, 45°, 60°, 75°, and 83°, all of them in the horizontal plane of incidence of the reflectometer). The degree of polarization p of the monochromator and the optical constants of glass, which were used in the calculation of the optical constants of MgF₂, were previously obtained from reflectance measurements performed on uncoated float glass substrates; these reflectance measurements were performed as a function of the angle of incidence in two perpendicular planes of incidence: a horizontal and a vertical plane.

A plot of the optical constants of MgF₂ films deposited both by evaporation and by IBS is shown in Fig. 2. At 121.6 nm the extinction coefficient obtained from transmittance measurements was used as a known parameter and the figure of merit given by Eq. (5) was optimized only through the variation of n . The extinction coefficient data between 125.4 nm and the cutoff wavelength that were represented in Fig. 1 were also included in Fig. 2. From Fig. 2 we observe that the optical constants over the 57.9-121.6 nm

range for MgF₂ films deposited by the two techniques are close and the differences are mostly within the error bars.

B. IBS MgF₂ PROTECTIVE FILMS ON Al FOR HIGH REFLECTANCE AT 121.6 nm

According to the extinction coefficient data shown in sub-section 3-A, IBS MgF₂ is a good candidate to protect Al films for high reflectance at least at 121.6 nm and below. The vacuum chambers used in this work did not house both evaporation and IBS systems in a single chamber. Therefore, the preparation of an evaporated Al film protected with an IBS MgF₂ film was not possible since Al is readily oxidized unless quickly overcoated in vacuum. In spite of this, we were able to proceed in the following way. A 7-to-10-nm thick MgF₂ film was deposited by evaporation on an opaque Al film in the evaporation chamber. The sample was removed from the chamber to atmosphere and transferred quickly to the IBS chamber where a thin film of MgF₂ was deposited by IBS on top of the Al/ MgF₂ bilayer in order to complete a total MgF₂ film thickness of ~24 nm for the highest possible reflectance at 121.6 nm. These samples will be referred to as hybrid samples. 7 nm was the minimum thickness considered for temporary Al protection during the sample transfer to the IBS deposition chamber. Additionally, standard bilayers with a ~24-nm thick MgF₂ film deposited by evaporation in a single run on opaque Al films were prepared for comparison purposes. The same substrates were used for both types of coatings. Fig. 3 shows the reflectance as a function of wavelength for each kind of coating. The highest reflectance for both kinds of samples was obtained at 125.4 nm. At 121.6 and 125.4 nm the reflectance of the sample with a MgF₂ film deposited first by evaporation and then by IBS was higher than for a single

protective film deposited by evaporation, whereas the opposite was true at 143.6 nm and above. This result is consistent with the results of sub-section 3-A on the higher (lower) transparency of IBS- versus evaporated-MgF₂ at short (long) wavelengths.

Ten hybrid samples of evaporated+IBS-MgF₂ protected Al films were prepared, which gave a reflectance at 121.6 nm ranging between 0.866 and 0.837, averaging 0.850. The reflectance at 121.6 nm for the seven samples prepared in this work with ~20-24-nm thick, all-evaporated MgF₂ film on Al ranged between 0.835 and 0.804, averaging 0.816. The optimum film thickness for evaporated MgF₂ was difficult to achieve at the high deposition rate, but the largest thickness error for evaporated MgF₂ films is expected to result in a reflectance lowering at 121.6 nm of ~0.01. Summarizing, all the hybrid samples had higher reflectance at 121.6 nm than those with all-evaporated MgF₂. The reflectance at 121.6 nm for the samples with all-evaporated MgF₂ on Al was not the highest achievable (an optimum reflectance of ~0.85 is achievable). However, the hybrid samples were prepared with a bottom MgF₂ layer deposited in the same conditions than for the all-evaporated Al/ MgF₂ samples and hence the former samples were not optimum either. A hybrid sample prepared using an optimized process (both evaporation and IBS) could provide an even higher reflectance. Furthermore, the Al film of the hybrid samples might have been slightly oxidized in the transfer from the evaporation to the IBS chamber because of the small thickness of the protective film. As an example, a sample of Al protected with a 9.9-nm thick MgF₂ film deposited by evaporation had a reflectance of 0.597 (121.6 nm) and 0.315 (83.5 nm) after 2-h storage in a desiccator. Reflectance reduced to 0.557 (121.6 nm) and 0.232 (83.5 nm) after a 24-h storage in a desiccator, which can be explained by the partial oxidation of the underlying Al film through the thin MgF₂ film, which did not provide 100% protection.

Nevertheless, the samples of 7-10-nm thick IBS MgF₂ on Al were exposed to air only for about five minutes in the transfer to the IBS chamber, and, according to the high reflectance measured, oxidation must be negligible. A lower deposition rate for evaporated MgF₂ is known to provide Al/ MgF₂ coatings with lower FUV reflectance. However, even though MgF₂ films were deposited at a much lower rate by IBS than by evaporation, the reflectance of the hybrid samples was higher.

The deposition of a ~24-nm thick MgF₂ film using only IBS and the optimization of the IBS MgF₂ deposition process may result in a further reflectance enhancement for MgF₂ protected aluminum at 121.6 nm. Further research would be needed to find out whether the films deposited by IBS are stoichiometric or deficient in F. In the latter case, the long-term stability of an F-deficient film under atmospheric conditions should be investigated. Short-term reflectance aging studies performed on a few hybrid samples showed that they were stable.

The high reflectance of samples with IBS MgF₂ deposited at a low rate is an advantage for applications in which a thin and precise MgF₂ film thickness is required. For instance, for high reflectance multilayer and narrowband antireflection coatings for the ~50-125 nm spectral range^{12,13}. In these applications the fast deposition necessary to obtain high quality MgF₂ films deposited by evaporation is an issue when a precise thickness of ~10 nm or thinner is required.

Conclusions

The optical properties in the FUV of IBS MgF₂ have been measured for the first time. IBS MgF₂ films were shown to have FUV optical properties close to those of MgF₂ deposited by evaporation. The main differences were that IBS films were slightly more transparent at the important H 121.6-nm, Lyman α line, but the radiation losses for IBS-MgF₂ were larger at longer wavelengths.

Due to the enhanced transparency at 121.6 nm, Al films that were protected with a thin evaporated MgF₂ film plus an IBS MgF₂ film to produce a combined ~24-nm thick protective film showed a reflectance at 121.6 nm that was higher by about 3% than that of a standard Al film protected with an all-evaporated MgF₂ film. However, at 143.6 nm and above a standard Al film protected with an all-evaporated MgF₂ film had a higher reflectance based on the higher transparency of MgF₂ deposited by evaporation. The highest reflectance measured at 121.6 nm was 0.866. The current results suggest that process optimization may produce coatings with even higher reflectance at 121.6 nm. An optimization is envisaged by depositing a 24-nm thick IBS MgF₂ protective overcoating on an evaporated Al film, the MgF₂ film deposited in the same vacuum chamber and in a single run.

Al films protected with IBS MgF₂ are proposed as more efficient coatings than the standard Al/evaporated MgF₂ at wavelengths close to 121.6 nm, which is an important spectral line for astrophysics.

Acknowledgments

Felix T. Threat is acknowledged for the preparation of samples of Al films protected with evaporation-deposited MgF_2 . This research was supported by NASA Office of Space Science grant RTOP 344-01-23. It was performed while Juan I. Larruquert held a National Research Council- NASA/ Goddard Space Flight Center Research Associateship, on leave from Instituto de Física Aplicada, Consejo Superior de Investigaciones Científicas, Spain.

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Figure Captions

Fig. 1. The extinction coefficient as a function of wavelength of evaporated and IBS MgF_2 films.

Fig. 2. The optical constants as a function of wavelength of evaporated and IBS MgF_2 films.

Fig. 3. The reflectance as a function of wavelength for Al films that were protected with MgF_2 deposited both by evaporation in a single film, and by evaporation of a thin film followed by an IBS film to complete a 24-nm thick protective film.

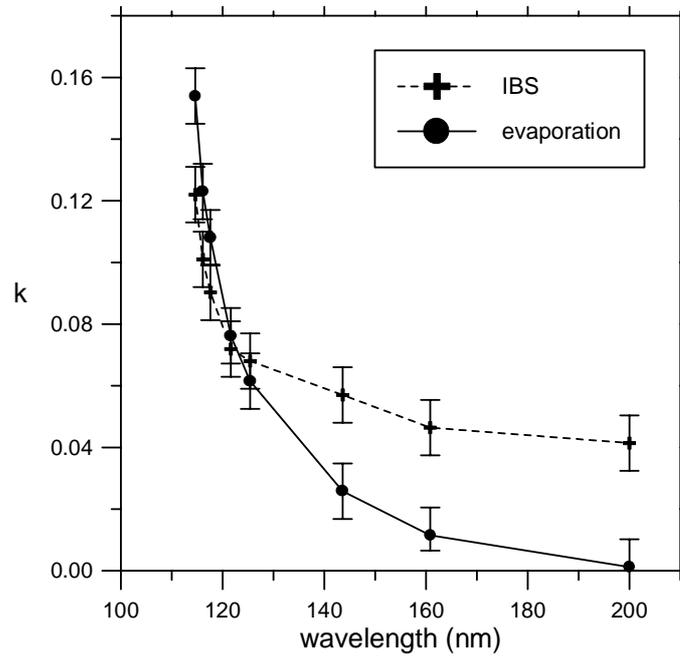


Fig. 1
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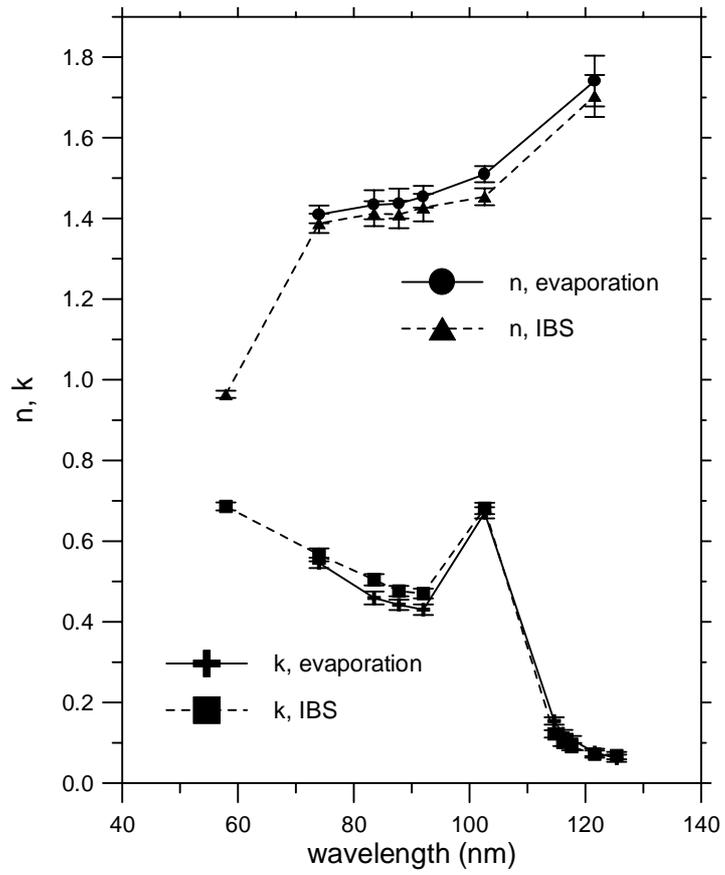


Fig. 2
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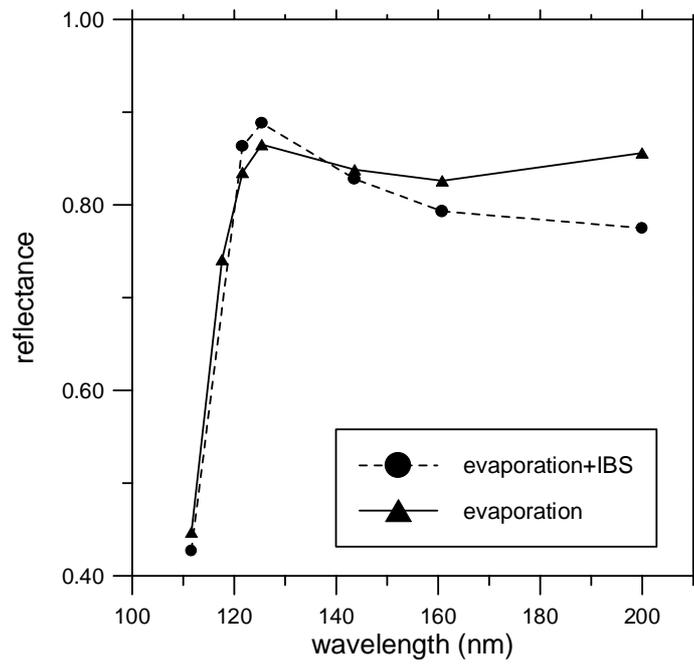


Fig. 3
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