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Effects of deposition temperature on optical properties of MgF_2 over-coated Al mirrors in the VUV*

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Both long-term environmental durability and high reflectance of protected-Al mirrors are of great importance for developing the optical instruments in the vacuum ultraviolet (VUV) applications. In this paper, the dependence of spectral property and environmental durability of MgF_2 over-coated Al mirrors using a 3-step method on deposition temperature of the outermost MgF_2 layer are investigated in detail. Optics (reflectance), structure (surface morphology and crystalline), and environmental durability (humidity test) are characterized and discussed. The results show that both optical and moisture-resistant properties of MgF_2 over-coated Al mirrors are dependent on MgF_2 deposition temperature, and the optimal deposition temperature for the outermost MgF_2 layer should be between 250 °C and 300 °C for MgF_2 over-coated Al mirrors to have both reasonably high reflectance in the VUV spectral range and high moisture resistance for long lifetime applications.

Keywords: protected-Al mirrors, reflectance, vacuum ultraviolet, MgF_2

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1. Introduction

Optical coatings are indispensable in order to develop optical systems with the highest possible optical property. The best optical performance can be achieved by all-dielectric coatings. Due to the limited spectral band width of all-dielectric reflectivity mirrors, metal-based coatings are widely used in optical instruments. Among common mirror metals, including Al, Ag, Au, and Cu, Al is the only material choice in the vacuum ultraviolet (VUV) spectral range, due to its unique material properties such as a higher plasma frequency and no strong interband transitions in the interested wavelength range.[1] For this reason, Al coatings have been successfully applied to the Hubble Space Telescope (HST),[2] the Galaxy Evolution Explorer (GALEX),[3] and the FengYun III,[4] and will be used in the Large Ultraviolet Optical Infrared (LUVOIR)[5] and the Habitable Exoplanet Imaging Mission (HabEx).[6]

For the VUV applications, Al mirrors are strictly required to have high reflectance, low scattering, and high-environmental stability. The natural oxidation of Al severely degrades VUV reflectance owing to absorption loss,[7–10] hence a protected Al is normally used. For this reason, the fluoride materials with low intrinsic absorption, such us MgF_2, AlF_3, LiF, and $Na_5Al_3F_{14}$, have been widely used as the protective coatings. Up to now, the researches on protected Al coatings in the VUV spectral range have focused on the preparations of Al and fluoride films. By combining different materials (Al/MgF_2,[9,11,12] Al/AlF_3,[3] Al/LiF,[11,12] Al/$Na_5Al_3F_{14}$,[13] Al/LiF/AlF_3,[14] and Al/AlF_3/LiF/MgF_2,[7] *etc*.) and by using different deposition techniques (such as thermal evaporation (TE),[7,9,15] ion beam sputtering,[16] atomic layer deposition,[1,17,18] *etc*.), their optical property and harsh environmental durability have been extensively investigated. It has been demonstrated that Al/MgF_2 mirrors fabricated via TE present the best optical performance and environmental stability in the VUV spectral range. The resulting optical property of the mirror is strongly affected by the deposition conditions, such as purity of Al and MgF_2 layer, low roughness and clean substrate, background and quality of vacuum, Al and MgF_2 evaporation rate, and substrate temperature.

In the present work, TE is used to prepare MgF_2 protected Al mirrors in VUV spectral range under different MgF_2 deposition temperatures. The dependence of the optical performance, humidity sensitivity, and the microstructure-related properties (crystallization and surface morphology) of the mirrors on the MgF_2 deposition temperature are comprehensively investigated by VUV spectrophotometer, x-ray diffraction (XRD), and atomic force microscope (AFM). The effect of substrate heating time and quality of vacuum pressure on the MgF_2 over-coated Al are also evaluated.

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2. Experiment

2.1. Film preparation

All samples were prepared in a coating machine (ZZS800, Chengdu Nanguang Machinery Co. Ltd., China). This device was equipped with four thermal evaporators and two ceramic heaters. In the coating process a base pressure about 1.2×10^{-4} Pa was provided in the coating chamber with a cryopump set that ensured an oil-free environment for all depositions. The ultimate vacuum pressure was 8.0×10^{-5} Pa. In order to obtain a better vacuum and reduce the influence of water vapor on the properties of thin films, the vacuum coating machine with a polycold was a good choice. BK7 glasses ($\Phi 25.4 \times 4$ mm) with a root-mean-square surface roughness of approximately 0.5 nm were used as substrates and fixed above the evaporators. The distance between the evaporation source and substrate was about 450 mm. For deposition, the BK7 substrates were cleaned manually with alcohol and acetone. Tungsten-boat was used for the evaporation of high purity Al (99.999%), while MgF_2 grains (Merck) was deposited by molybdenum-boat evaporation. The deposition rate and physical thickness for each of the thin films were controlled by a quartz-crystal monitor, which was fixed at the top center of the deposition chamber. Deposition rates of 10 nm/s and 0.2 nm/s were for Al and MgF_2 layers, respectively. Deposition angles for both materials were smaller than 20°. A series of Al mirrors (each with a thickness of 80 nm) over-coated with a thin MgF_2 layer was deposited by a 3-step coating process. The main step of the method had been well outlined and documented in other literatures.[9,11,15] In order to enhance the reflectance at 121.6 nm, the total thickness of MgF_2 layer was set to be 25 nm. For the thin film design, optical constants of Al were obtained from the literature.[19] Parameters of MgF_2 films were determined from spectrophotometric measurements as presented in Ref. [20]. The substrate temperature and the holding time were varied for preparing the second MgF_2 layer. The deposition temperatures ranged from 25 °C to 350 °C. The holding time was set to be 0 and 120 min. The prepared sample types were summarized in Table 1. In the heating process, temperature and pressure profiles *versus* time are exhibited in Fig. 1. As temperature increased, the pressure significantly increased, which was caused by outgassing from the walls of the chamber. After fabrications, all samples were cooled to room temperature, and then the vacuum chamber was vented.

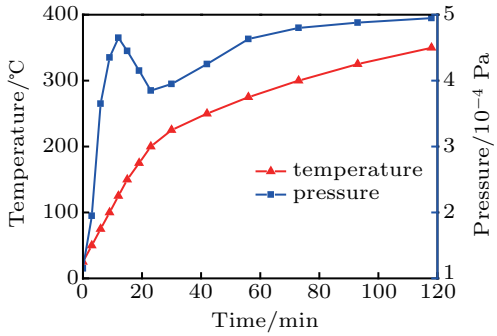


Fig. 1. Plot of substrate temperature and pressure *versus* time in coating chamber.

Table 1. Overview of prepared sample types.

Type	d_{Al}/nm	T_{sub}/°C	d_{1MgF_2}/nm	T_{sub}/°C	d_{2MgF_2}/nm	T_{sub}/°C	Heating time/min	Holding time/min
M1	80	25	25	25	—	—	0	0
M2	80	25	5	25	20	200	23	0
M3	80	25	5	25	20	250	42	0
M4	80	25	5	25	20	300	73	0
M5	80	25	5	25	20	350	118	0
M6	80	25	5	25	20	300	73	120

2.2. Film characterization

The reflectance for each of all Al mirrors was measured in the spectral range 115 nm–220 nm in steps of 0.1 nm and at an incident angle of 10° by using a high-precision ML6500 VUV spectrophotometer (Laser Zentrum Hannover, Germany). The nominal measurement accuracy of the VUV spectrophotometer is ±0.3% for the reflectance. In order to avoid the absorption of oxygen, moisture and hydro-carbon contamination, the spectrum was measured under vacuum environment with a pressure below 1.0×10^{-3} Pa. The surface morphology was characterized by using a Dimension 3100 atomic force microscope, performing in a tapping mode for imaging surface over scanning size of 5 μm square with 256×256 data points. Crystalline structure was evaluated with a Philips X'Pert-MRD x-ray diffraction. The start and end incident angle were 10° and 80°, respectively, in steps of 0.01°. Moreover, in order to study the humidity sensitivity of the as-deposited Al mirrors, samples were accelerated the ageing process in a custom humidity control chamber held at temperature of 50 °C and relative humidity of 95 ± 3% for 12 h, 24 h, and 36 h, respectively. After humidity experiments, the spectral performances of Al mirrors were measured and corresponding degradation of the reflectance was determined.

3. Results and discussion

3.1. Optical properties

Figure 2(a) shows the measured reflectance spectra of the MgF_2 over-coated Al mirror with different deposition temperatures. To reduce the influence of stochastic variation in the layer thickness and random measurement error on the result of optical performance ranking, in each case, a spectrally averaged reflectance has been obtained for ranking purposes. Therefore, the reflectance at 121.6 nm is calculated by averaging the measured spectra from 121 nm to 122 nm (with 11 data points) and exhibited in Fig. 2(b), while the VUV reflectance is averaged in the wavelength region of 115 nm–220 nm (Fig. 2(c)). When the deposition temperature is between 25 °C and 250 °C, the spectral performance is improved with the increase of substrate temperature. Above 250 °C, the application of the higher deposition temperature leads the reflectance to significantly drop down. The experimental result is in agreement with that in Ref. [9].

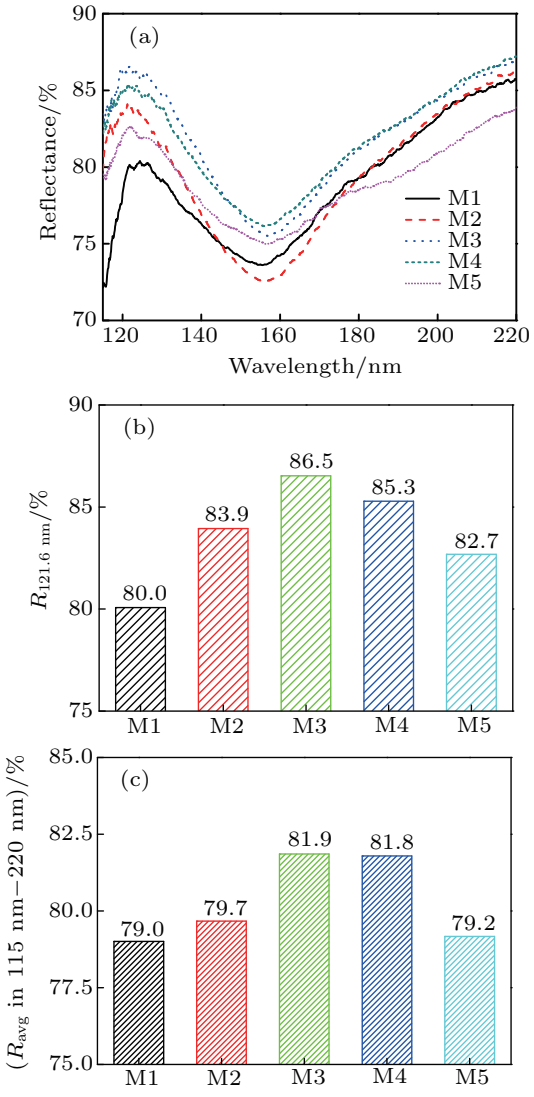


Fig. 2. (a) Spectral performance, (b) reflectance (121.6 nm), and (c) average reflectance (115 nm–220 nm) of MgF_2 over-coated Al mirrors with various substrate temperatures.

Generally, the reflectance of MgF_2 over-coated Al mirror in the VUV is influenced mainly by the absorptance and scatterring of the prepared layer system. Absorptance is due to the fact that both MgF_2 and alumina have non-negligible absorption in the VUV region. As mentioned in Refs. [11], [21], and [22] a high substrate temperature is preferred to prepare the low-absorption MgF_2 film. Obviously, the absorption of MgF_2 film is not the main reason for reducing the reflectivity of Al mirrors prepared with a substrate temperature above 250 °C. On the other hand, the waiting period for the substrate to reach the expected temperature in between depositions of Al layer and MgF_2 layer will cause the fresh Al surface to be oxidized and contaminated due to its interacting with gas released from the chamber wall. The influence of released gas on reflectivity of Al mirror will be discussed and experimentally verified below. Moreover, scatterring strongly depends on the structure and the surface quality of the layer. In order to comprehensively analyze the source of the discrepancy in optical performance of samples prepared at different deposition temperatures, characterizations of crystalline structure and surface topography are necessary.

3.2. Microstructure

3.2.1. Crystalline structure

Crystalline structures of the MgF_2 over-coated Al mirrors deposited on BK7 substrates are revealed by XRD patterns, as presented in Fig. 3. For the prepared Al mirrors at various substrate temperatures, the main peak appears at (111) of each Al films, whereas no crystal peak is detected from none of MgF_2 films. According to our previous research results,[20] the grain size of MgF_2 film fabricated at a small deposition angle is larger than 30 nm, and hence the thickness of the experimentally prepared MgF_2 film is not enough to crystallize. On the other hand, as the substrate temperature increases from 25 °C to 350 °C, the positions of XRD peak are observed at $2\theta = 38.43°$, $38.49°$, $38.53°$, $38.55°$, and $38.57°$, respectively. The shift of the peak position to a large angle is due to the thermal stress of thin films. The thermal stress is caused by the difference between the thermal expansion coefficients of the film and substrate materials and also by the temperature difference between deposition temperature and ambient environmental temperature. In addition, the grain size (D) of the Al film is calculated from the main XRD peak using the Scherrer equation: $D = 0.94\lambda/(\beta\cos\theta)$, where λ is the x-ray wavelength, β is the full width at half maximum of the main peak for the XRD pattern. The determined grain size for each of all evaporated Al films is about 65 nm. Obviously, the thin MgF_2 layer succeeds in preventing the Al layer from forming large crystal grain in a high temperature environment.

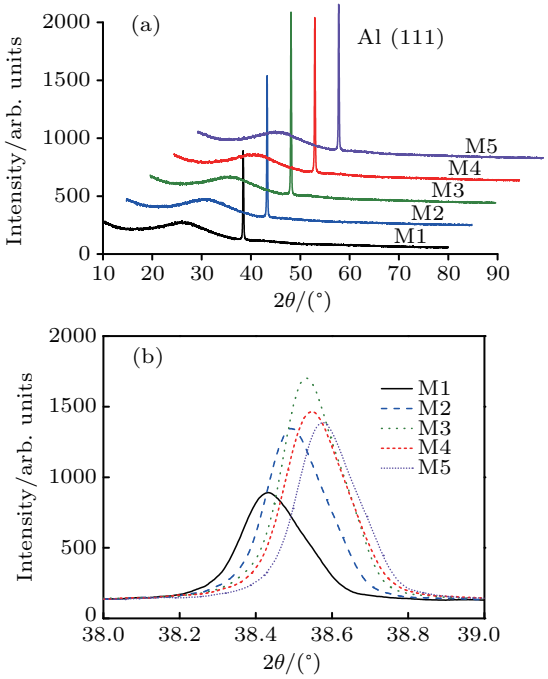


Fig. 3. (a) X-ray diffraction patterns of MgF_2 over-coated Al mirrors prepared at various substrate temperatures and (b) (111) crystal phase profile of samples.

3.2.2. Surface morphology

Figure 4 shows the root mean square (RMS) roughness values of MgF_2 over-coated Al mirrors. The measurement results show that the RMS roughness of samples decreases as the deposition temperature increases. This is due to molecular migration and surface diffusion of MgF_2 films, which gives rise to a smooth surface morphology during a high temperature growth. According to the classical structure zone model,[23] thin film is modeled as a function of T_s/T_m, where T_s is the substrate temperature and T_m is the melting temperature of material. It can be found that when the substrate is at room temperature, the T_s/T_m is 0.19 (the melting temperature of MgF_2 is 1266 °C), which is placed in zone T. The T_s/T_m values of other samples are 0.31, 0.34, 0.37, and 0.40, respectively, which are placed in zone II. More thermal energy gives rise to more molecular migration and surface diffusion. Consequently, there are more smooth surfaces and fewer voids in the zone II microstructure than in the zone T microstructure. In general, the fewer the voids, the better the environmental stability of thin film will be. It is in good agreement with the following experimental result.

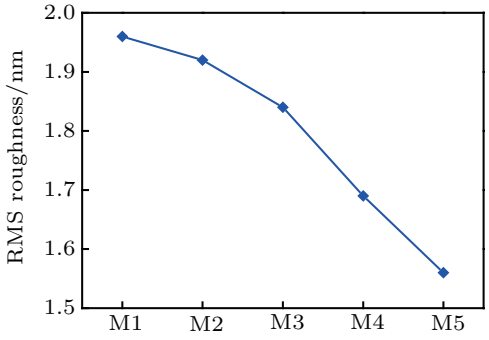


Fig. 4. Roughness values for prepared Al mirrors.

3.3. Humidity sensitivity

Traditional TE technique is used to prepare MgF_2 film with a columnar growth and a low material packing density. It provides a large free volume for accommodating the contaminations such as water. Condensed water not only leads the film to enhance the absorption and reduce the reflectance but also causes its lifetime to shorten. Therefore, it is necessary to improve the quality of the Al mirrors under harsh humidity conditions. The measured average reflectance and the relative reflectance degradation as a function of humidity test time of all Al mirrors are presented in Fig. 5. It is found that for all samples the optical performance in VUV range degrade dramatically. The averaged reflectance values of as-deposited Al mirrors at room temperature and 300 °C are as high as 79.0% and 81.8%, and decrease to 66.1% and 78.9% after 36 h of aggressive humidity testing, respectively, indicating 16.4% and 3.5% less reflectivity degradations for the two samples tested in the same environments. Moreover, as indicated in Fig. 5(b), a higher deposition temperature will be favorable for obtaining better humidity stability due to denser microstructure in the MgF_2 layer than lower deposition temperature. For the films degraded by harsh humidity test, ultraviolet ozone and high temperature annealing treatments can be used to restore their performances as reported in Ref. [9]. Taking into consideration the optical property and environmental durability of Al

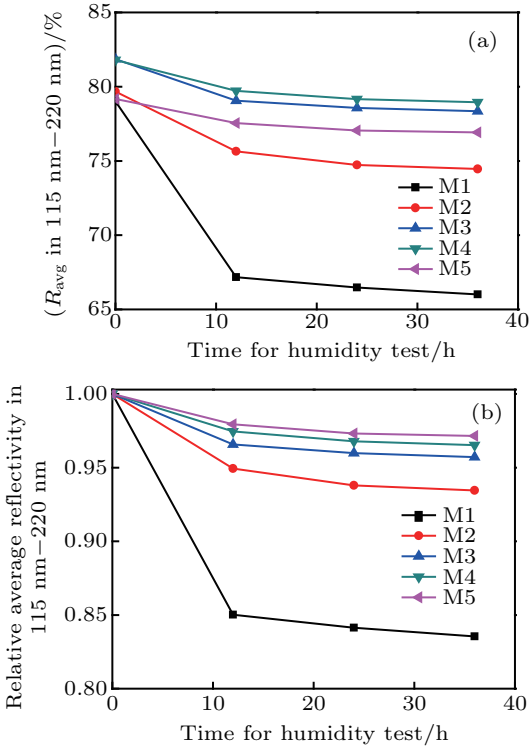


Fig. 5. Plots of average reflectance (115 nm–220 nm) (a) and relative average reflectivity degradation (b) *versus* humidity test time.

mirrors for the VUV applications, the best deposition temperature of the outermost MgF_2 film is in a range between 250 °C and 300 °C.

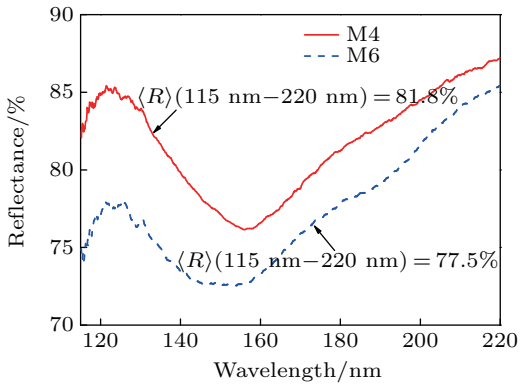


Fig. 6. Spectral performance of MgF_2 over-coated Al mirrors deposited at 300 °C for different holiding times.

As already well documented in Ref. [11], the 3-step method for Al mirror preparation in VUV is based on the following considerations: firstly, Al layer grown with a high temperature is quickly contaminated by forming alumina and tends to rough surface morphology as crystal grain increases. Thus, the substrate at room temperature favors the fabrication of Al film. Secondly, MgF_2 film deposited at high temperature produces a higher-density structure with lower absorption. Last but not least, between depositions of Al film and outermost dielectric layer, a very thin MgF_2 layer is employed to cover the as-deposited Al film as soon as possible in order to protect it from forming oxidation and large crystal grain. Based on the previous experimental results, it is clear that neither the absorption of MgF_2 layer nor scattering in coating system is the main cause for the decrease in optical property of Al mirror prepared at temperature above 250 °C. The remaining reason is that the 5-nm-thick MgF_2 layer deposited by the second step may not completely prevent the fresh Al layer from being contaminated. As presented in Fig. 1, the higher the deposition temperature, the longer the heating time and the higher the pressure in the chamber is. It means that the probability of residual gas pollution increases. To further confirm the observation, the outermost MgF_2 layer with a holding time of 120 min (type M6 in Table 1) is prepared during deposition. In the case, an obvious spectral drop of the mirror is determined and the performance in the VUV spectral range is significantly worse than that of M4 as shown in Fig. 6. Due to the insertion of a constant temperature step in the heating process, the averaged reflectivity decreases from the initial 81.8% to 77.5%, even worse than the M5 reflectivity (79.2%). Therefore, improvement of Al mirrors fabricating process should focus on an optimal trade-off between intrinsic absorption of the MgF_2 film and protection of the metal surface from interacting with contaminants. In future studies, many process parameters must be optimized, including MgF_2 layer thickness in step 2 of the coating process, heating time for the substrate to reach the target temperature, residual gas species and pressure in the chamber, *etc*.

4. Conclusions

Based on a 3-step approach, experiments with MgF_2 over-coated Al mirrors deposited at different substrate temperatures are analyzed and discussed. Spectrophotometer, AFM, and XRD are used to investigate the dependence of the optical and structural properties, and environmental durability on the deposition temperature. In this study, optical performances and environmental stabilities for Al mirrors prepared at substrate temperatures between 250 °C and 300 °C are improved significantly compared with those obtained from the ambient deposition technique. It has been shown that film properties of Al mirror may also be enhanced by diminishing the gas released from the chamber. Therefore, it is necessary to optimize the production machine and relevant components. These results would be of great importance for preparing the high-performance Al mirrors in the VUV applications.

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