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Effects of Ion Assistance and Substrate Temperature on Optical Characteristics and Microstructure of MgF_2 Films Formed by Electron-Beam Evaporation

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Magnesium fluoride thin films were prepared by electron-beam evaporation and ion-assisted deposition (IAD). The effects of ion assistance and substrate temperature during deposition on the optical properties and microstructure were studied. The grain size, the crystallinity and the surface roughness of MgF_2 films deposited without ion assistance all decreased with substrate temperature. MgF_2 films deposited with IAD exhibited small grains, rough surfaces, fluorine deficiencies and large optical losses in the 200–500 nm wavelength range when bombarded with argon ions. [DOI: 10.1143/JJAP.45.5027]

KEYWORDS: MgF_2, ion-assisted deposition, substrate temperature, optical property, microstructure, crystallinity, surface roughness, fluorine deficiency, optical loss

1. Introduction

Thin films of magnesium fluoride, MgF_2, are extensively adopted in optical coatings because the compound has a low refractive index and relatively high chemical and mechanical durabilities. MgF_2 is particularly effective as a coating against UV and deep-UV light because it has a large energy band gap.[1–5] MgF_2 films prepared by vacuum evaporation have a columnar structure, which is typically porous and has a packing density on the order of 0.72.[6] The density of this film was found to increase by either heating the substrate to 250–300 °C, or using an ion-assisted beam during the deposition of the film.[7,8] Ion-assisted deposition (IAD) is an energetic process that provides great advantages and it is easy to perform using conventional equipment. The main advantage of ion-assisted processes is the increase in the packing density of the films, making them more bulklike, enabling robustness against moisture.[9–15] Alvisi *et al.* reported that the ion-assisted electron-beam evaporation approach gave MgF_2 films high environmental stability.[8] Kennemore and Gibson studied the effects of ion-beam processes when coating MgF_2 onto substrates at ambient temperature and the increased resistance against abrasion and the adherence of films during argon-ion bombardment deposition.[16] However, Martin *et al.* reported that oxygen-ion assistance increased the extinction coefficients of MgF_2 films at wavelengths < 180 nm.[7] Therefore, in this work we study how ion assistance and substrate temperature affect the optical characteristics and microstructure of MgF_2 films.

2. Experimental Methods

Thin films of MgF_2 were prepared in an electron-beam evaporation system equipped with a Kaufman ion source for IAD. Films were deposited on fused quartz at substrate temperatures of 150 and 250 °C without ion assistance and at a substrate temperature of 250 °C in IAD. MgF_2 was employed as a starting material. The vacuum chamber was pumped down to a base pressure of 5×10^{-4} Pa. Argon was the working gas for the ion source and the flow rate was 8 sccm. The pressure was maintained at approximately 8×10^{-4} Pa in deposition without ion assistance and at 1.33×10^{-2} Pa in IAD. The ion-beam voltage was 300 V and the ion current density was $20\,\mu A/cm^2$ when the ion source was operational. Films were deposited at a rate of $0.2\,nm\,s^{-1}$ and the thickness was optically measured 765 nm.

All of the samples were observed using a Perkin Elmer Lambda 900 spectrometer with an error of under 0.1% in transmission over the spectral range from 200 to 800 nm. The composition of the deposited films was analyzed using an Oxford Inca Energy 400 energy-dispersive X-ray spectrometer (EDS) on a JEOL JSM-6700F field emission scanning electron microscope (FE-SEM). The microstructure was analyzed using a JEOL JEM-200CX transmission electron microscope (TEM). The crystalline structure of the films was studied using a Siemens D5000 X-ray diffractometer (XRD) with a copper anode. The rms surface roughness of the films was determined using a Digital Instruments Nanoscope II atomic force microscope (AFM). The scanned area was $3 \times 3\,\mu m^2$.

3. Results and Discussion

3.1 Transmission measurements

Figure 1 presents the transmittance spectra of MgF_2 films deposited on fused quartz without ion assistance at substrate temperatures of 150 and 250 °C. Figure 1 also presents the transmittance spectra of IAD MgF_2 film at a substrate temperature of 250 °C. MgF_2 film deposited with ion assistance at a substrate temperature of 250 °C has a larger optical loss over the 200–500 nm range than do films deposited without ion assistance at substrate temperatures of 150 and 250 °C. These results indicate that ion assistance does not reduce the deep-UV loss of MgF_2 films but yields films that are more absorbant than those prepared by evaporation on substrates at 150 and 250 °C. This observation is consistent with the results of Kennemore and Gibson[16] and Martin *et al.*[7] Kennemore and Gibson reported a slight shift in the UV absorption edge toward longer wavelengths for the IAD MgF_2 film.[16] This shift occurred at 270 nm as the absorption rose to 3% at 200 nm. Martin *et al.* reported an increase in the extinction coefficient over the 107.5–180 nm wavelength range exhibited by MgF_2 films prepared by oxygen and argon IAD.[7]

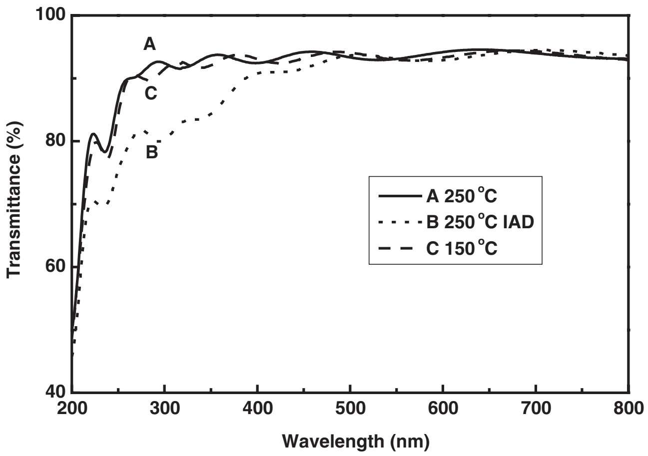


Fig. 1. Transmittance spectra of MgF_2 films deposited on fused quartz at substrate temperature of 250 °C without and with ion assistance, and at substrate temperature of 150 °C without ion assistance.

Table I. Stoichiometric Mg : F ratio of MgF_2 films.

Film	Mg : F
Evaporated (250 °C)	1 : 1.9
Evaporated with IAD (250 °C)	1 : 1.7
Evaporated (150 °C)	1 : 1.9

3.2 Energy-dispersive spectrometry

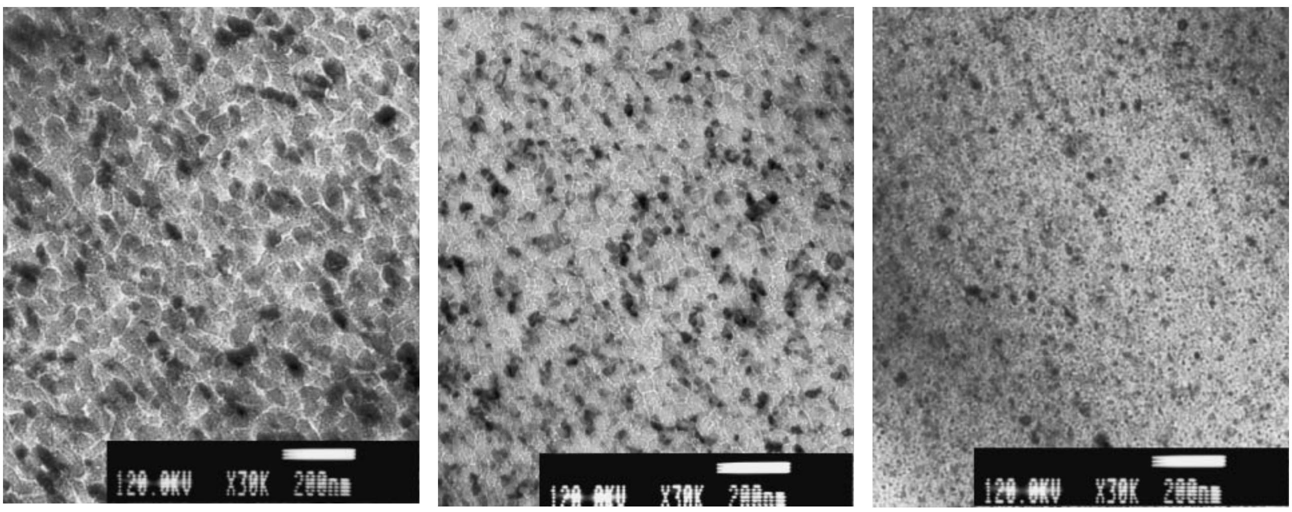
The fused quartz substrates studied using EDS comprise only two elements—silicon and oxygen. Therefore, the stoichiometric Mg : F ratio can be determined from EDS measurements of MgF_2 films deposited on fused quartz substrates. Table I presents the results. The sample prepared without ion assistance is slightly deficient in fluorine, probably because of thermal decomposition during heating at the source. The IAD MgF_2 film exhibits the greatest fluorine deficiency, because of the preferential sputtering of the fluorine during argon-ion bombardment deposition. The removal of the fluorine enables oxygen to bond with magnesium in the growing film. Kennemore and Gibson[16] and Martin *et al.*[7] studied the presence of MgO in MgF_2 films deposited with ion assistance using Rutherford backscattering spectrometry (RBS). The fluorine deficiency and the presence of MgO in the MgF_2 films deposited with ion assistance are considered to be partially responsible for the high optical loss of the films in the 200–500 nm wavelength range.

3.3 Transmission electron microscopy

A transmission electron microscope (TEM) was employed to observe the grain size of MgF_2 films. Figures 2(a) and 2(b) present bright-field TEM micrographs of MgF_2 films deposited onto substrates at 250 °C by evaporation both without and with IAD. Figure 2(c) also presents a TEM micrograph of MgF_2 film prepared by evaporation at a substrate temperature of 150 °C. These high-resolution micrographs enable accurate measurements of the sizes of individual grains. MgF_2 films deposited at a substrate temperature of 250 °C without and with ion assistance have gains around 48 and 32 nm thick, respectively, as shown in Figs. 2(a) and 2(b). The grains in the MgF_2 film prepared at a substrate temperature of 150 °C are too small to be determined from Fig. 2(c). The TEM micrographs indicate that the grain size in columns in MgF_2 films increases with substrate temperature because the heating of substrates provides thermal energy. The TEM micrographs also indicate that the grains in MgF_2 films deposited with ion assistance are smaller than those in the MgF_2 films deposited without ion assistance at a substrate temperature of 250 °C. Argon-ion bombardment prevents the growth of the columnar structure in MgF_2 films.

3.4 X-ray diffractometry

The crystallinity of MgF_2 films was studied using an XRD system. Figure 3 presents the XRD patterns of the MgF_2 films of all studied samples. MgF_2 films with a randomly oriented crystalline structure were obtained under all deposition conditions. The XRD patterns of all samples exhibit peaks that correspond to the MgF_2 (110), (111), and (211) planes. The peaks that correspond to the MgF_2 (210),



(a) (b) (c)

Fig. 2. TEM micrographs for MgF_2 films prepared (a) at substrate temperature of 250 °C without ion assistance, (b) at substrate temperature of 250 °C with ion assistance and (c) at substrate temperature of 150 °C without ion assistance.

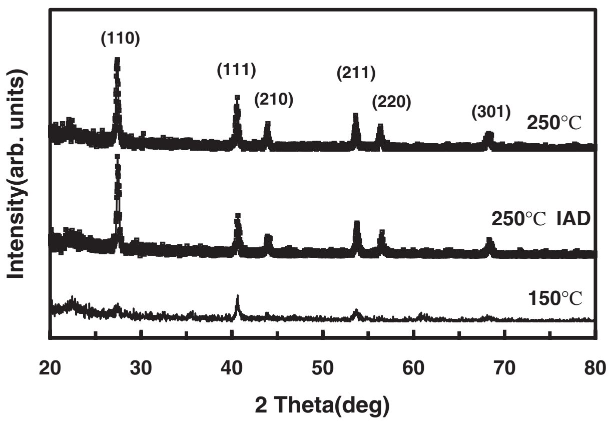


Fig. 3. XRD patterns from MgF_2 samples.

Table II. Rms surface roughness of MgF_2 films.

Film	rms (nm)
Evaporated (250 °C)	6.3
Evaporated with IAD (250 °C)	7.3
Evaporated (150 °C)	5.0

(220), and (301) planes are stronger in the XRD patterns of the films deposited at a substrate temperature of 250 °C both without and with ion assistance. In particular, Fig. 3 shows that the MgF_2 film deposited at a substrate temperature of 150 °C has weak crystalline peaks, whereas the MgF_2 film deposited at the substrate temperature of 250 °C yields strong crystalline peaks, regardless of whether IAD was used. The crystallinity of MgF_2 films depends mainly on substrate temperature, even in the case of argon-ion bombardment. The crystallinity of MgF_2 films prepared by IAD is slightly less than that of films prepared without ion assistance at a substrate temperature of 250 °C.

3.5 Atomic force microscopic analysis

AFM was employed to determine the rms surface roughness of MgF_2 films of all examined samples. Table II summarizes the results. The rms surface roughness of MgF_2 films prepared at a substrate temperature of 150 °C is lower than that of MgF_2 films prepared at 250 °C, indicating that the surface roughness of MgF_2 films increases with substrate temperature. At a substrate temperature of 250 °C, the rms surface roughness of MgF_2 films deposited with ion assistance exceeded those of MgF_2 films deposited without ion assistance, as presented in Table II. The scattering is well known to be proportional to rms surface roughness. The rough surface of MgF_2 films deposited with ion assistance is partially responsible for the large optical loss in the 200–500 nm wavelength range.

4. Conclusions

The optical characteristics and microstructure of magnesium fluoride films deposited by evaporation depend on the effects of argon-ion bombardment and substrate temperature. X-ray diffractograms indicated that the crystallinity of MgF_2 films depends primarily on substrate temperature, even in the case of argon-ion bombardment. TEM micrographs showed that the size of the grains in columns in MgF_2 films increases with substrate temperature. TEM micrographs also showed that the grains in MgF_2 films deposited with ion assistance are smaller than those deposited without ion assistance at a substrate temperature of 250 °C and that argon-ion bombardment prevents the growth of columns in MgF_2 films. The EDS measurements revealed that the stoichiometric fluorine ratio of MgF_2 films prepared by IAD is lower than those of MgF_2 films deposited without ion assistance owing to the argon-ion bombardment. The removal of fluorine enables oxygen to bond to the magnesium in the MgF_2 films. AFM observations showed that the surface roughness of MgF_2 films increases with substrate temperature. The AFM results demonstrated that MgF_2 films deposited with IAD have rough surfaces. The transmittance spectra from 200 to 500 nm indicated that the optical loss of IAD MgF_2 films exceeds that of films deposited without ion assistance. Accordingly, the optical loss was caused by the absorption associated with fluorine deficiency and scattering from rough surfaces.

Acknowledgments

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