Indian Journal of Pure & Applied Physics
Vol. 52, February 2014, pp. 117-123

Temperature-dependent optical and mechanical properties of obliquely deposited MgF_2 thin films

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Received 1 February 2013; revised 12 November 2013; accepted 26 December 2013

The temperature-dependent optical and mechanical properties of magnesium fluoride (MgF_2) thin films with small columnar angles have been presented. Electron-beam evaporation method was used to prepare MgF_2 thin films with two different columnar angles of 6° and 24°. MgF_2 thin films were deposited on B270 glass substrates and silicon wafers, respectively. The temperature-dependent optical and mechanical behaviour of MgF_2 thin films with different columnar angles were obtained by elevated temperature in the range 30-110°C. The wavelength shift with temperature was measured by a spectrophotometer for evaluating the stability of obliquely deposited MgF_2 films. The microstructure and surface roughness of the MgF_2 thin films have been measured by scanning electron microscope (SEM) and atomic force microscopy (AFM). Characteristics for the temperature-dependent optical properties and biaxial residual stresses of MgF_2 thin films deposited at two different oblique angles have been measured and compared. The residual stress of MgF_2 thin films deposited on the B270 substrates has been plotted against the measurement temperature, both of the samples showed a linear dependence.

Keywords: Thin film, Electron-beam evaporation, Residual stress, Surface roughness

1 Introduction

Magnesium fluoride (MgF_2) has been widely used as an anti-reflection coating. It possesses several attractive features. For example, it transmits well from about 0.12 μm in the ultra-violet (UV) out to about 7 μm in the mid-infrared. It is highly stable against humidity and mechanical abrasion. MgF_2 thin films are widely used in optical coatings where a low refractive index layer is required and also for enhancing the reflectance of aluminium mirrors in the vacuum ultraviolet region[1]. However, MgF_2 films produced by vacuum evaporation at room temperature have a porous columnar microstructure[2,3]. Thus, they may exhibit low packing densities, causing extreme sensitivity to moisture in room air. The pores become filled with water when exposed to air, affecting detrimentally the stability of their optical and mechanical properties[4] and inducing undesired optical losses in the films[5].

Residual stress in thin films is very important factor for using a particular device[6]. The stress behaviour of thin films plays an important role in all optical coating applications. The mechanical properties of thin films are strongly dependent on the microstructure and chemical composition, and therefore, on the deposition technology. It is well known that mechanical stresses can be found in almost all thin films, regardless of the various deposition techniques used to produce them. The stress in a thin film is primarily composed of a thermal stress and an intrinsic stress[7]. The thermal stress is due to the difference in the thermal expansion coefficients between the coating and substrate materials. On the other hand, the intrinsic stress is induced by complex mechanisms that occur during the film-growth process that are not yet fully understood. To study thin film stress, it is necessary to understand the stress mechanisms and their effects. Many analyses assume an isotropic homogeneous stress distribution in the coating. In such a distribution, deformations of the substrate will be small as compared to the substrate thickness. However, residual stress in the film causes stress-induced substrate deformation that is not always isotropic. This indicates that the residual stress in such a film is not biaxially symmetry[8]. The differential curvature exhibits large variations with the magnitude of the variation depending on the deposition geometry and the distribution angles of the incoming vapour flux.

The temperature effect on the optical stability, biaxial residual stress and surface roughness of obliquely deposited MgF_2 thin film with small columnar angles has been investigated. MgF_2 films develop a tilted-columnar structure when these were deposited obliquely with the vapour incident at an angle with respect to the substrate normal. In the present work, characteristics for the optical properties and biaxial residual stress of MgF_2 thin films deposited at two different oblique angles are obtained by elevated temperature in the range 30-110°C. We perform *ex-situ* stress evaluation by measuring the substrate deformation before and after film deposition. Furthermore, the column angles of the MgF_2 films at various oblique angles are measured by a Scanning Electron Microscope (SEM). The cross-sectional SEM images of MgF_2 films deposited with different columnar angles can be obtained. The film's surface roughness is measured by an Atomic Force Microscopy (AFM).

2 Experimental Details

2.1 Thin films preparation

Thin films were deposited by conventional e-beam evaporation. Magnesium fluoride pellets were evaporated to deposit MgF_2 films on B270 glass and corning glass substrates, and silicon wafers. Each B270 glass substrate was polished on one side and ground on the other side. Prior to deposition, the substrates underwent ultrasonic cleaning in acetone and ethanol, and were then dried in a vacuum dryer. The MgF_2 films were deposited at the same time to avoid difference in the deposition conditions.

Figure 1 shows a schematic diagram of the thin film vacuum deposition system used for this study. The substrates were mounted at different positions onto the hemi-spherical substrate holder which was fixed about the vertical axis. The substrate surfaces located at different radial positions received nearly a similar flux of vapour species with different angles of incidence. The flux incident angle is defined as the angle between the incident flux and substrate surface normal. The distance between evaporation sources and substrate was 90 cm. The base pressure of vacuum system was kept below 6.0×10^{-6} torr. To promote formation of stoichmetric MgF_2 films at the substrates, argon (Ar) was introduced into the chamber at a flow rate such that the pressure during the deposition was 1.6×10^{-4} torr. A thermocouple was placed near the sample holder to monitor the chamber temperature. The substrate temperature was about 150°C. A quartz crystal monitor was used to control film thickness. The deposition rate was controlled at 1 nm/s.

2.2 Thin film measurements

MgF_2 thin films deposited on corning glass substrates were examined by transmission spectroscopy in the 350-1100 nm spectral range. The normal incident transmittance of the sample was measured by a spectrophotometer (SHIMADZU, Solid-Spec-3760). The optical constants of obliquely deposited MgF_2 films were determined by an ellipsometry.

To evaluate the anisotropic stress in a film, deformation must be measured in different directions, namely, the radial and tangential directions of the circular glass substrate. Biaxial deformation behaviour has not been reported widely, but several researchers have been done on the isotropic stress measurement. In this study, an improved method was used to overcome the above issues. The principle for measuring anisotropic stress by using an optical interferometry, fast Fourier transform technique[9] and Gaussian filter has been reported in a previous publication[10]. A modified Twyman-Green interferometer is used to measure the biaxial stress in the thin films, by measuring the fringes caused by deposition of the film on the B270 glass substrate. Figure 2 shows a schematic diagram of the residual stress measuring apparatus. The temperature of the sample was controlled in the range 30°-110°C. The interference fringes were recorded by a CCD camera.

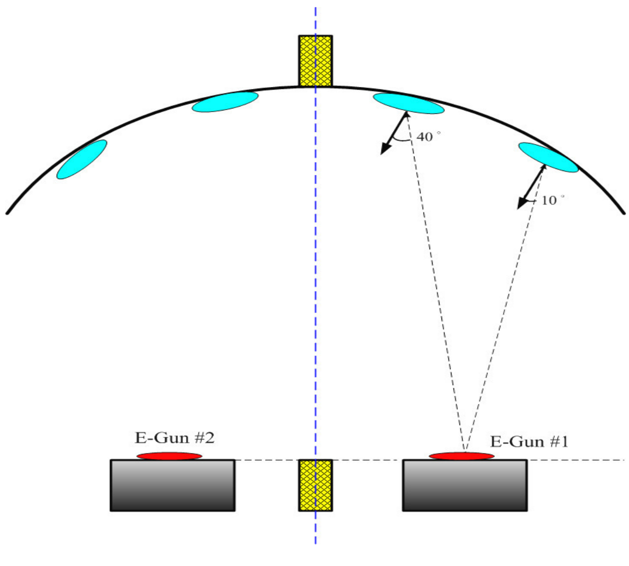

Fig. 1 — Schematic representation of the experimental set-up for thin film preparation

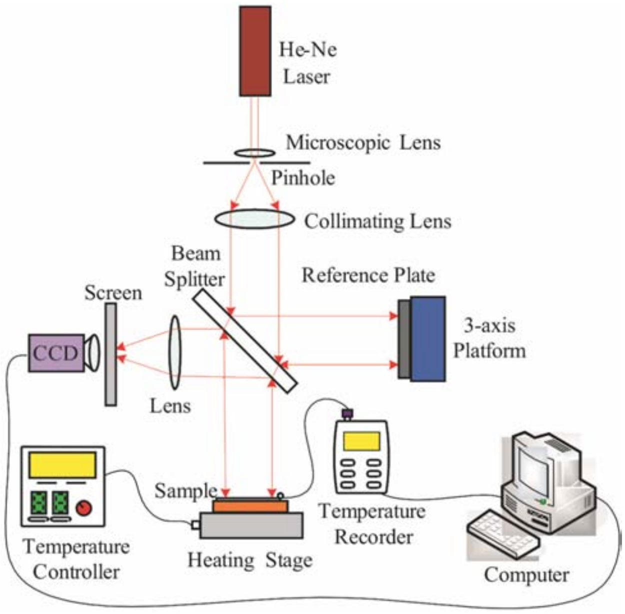

Fig. 2 — Schematic illustration of the residual stress measuring apparatus

The change in the deformation of the substrates after deposition indicated strain in the films, which in turn is a measurement of stress in the film. Film stress measurements were performed by determining substrate curvature before and after deposition and a custom-made stress analysis program. By this method, the accuracy on the residual stress value was estimated to be about 1.6%. The commonly used Stoney equation[11] for evaluating the residual stress in thin films is calculated by:

$$\sigma_f = \frac{E_s}{6(1-\nu_s)}\frac{t_s^2}{t_f}\left(\frac{1}{R_2}-\frac{1}{R_1}\right) \qquad \ldots (1)$$

where σ_f is the residual stress in the thin films, E_s and ν_s are the Young's modulus and Poisson's ratio of the substrate, respectively, t_s is the thickness of the substrate and t_f ($t_f << t_s$) is the film thickness, R_1 and R_2 are the radii of curvature of the substrate measured before and after deposition of films. The above Stoney equation requires the basic assumption that the residual stress in a film is isotropic. For an elastically anisotropic structure, the biaxial stress in thin films can be expressed[12] by:

$$\sigma_x = \frac{1}{6}\frac{E_s}{1-\nu_s^2}\left(\frac{1}{R_x}+\frac{\nu_s}{R_y}\right)\frac{t_s^2}{t_f} \qquad \ldots (2)$$

$$\sigma_y = \frac{1}{6}\frac{E_s}{1-\nu_s^2}\left(\frac{1}{R_y}+\frac{\nu_s}{R_x}\right)\frac{t_s^2}{t_f} \qquad \ldots (3)$$

where σ_x and σ_y are the biaxial stresses in the thin films, R_x is the radius of curvature in the x-axis (i.e. tangential) direction and R_y is the radius of curvature in the y-axis (i.e. radial) direction.

The residual stresses, σ_f, included both the intrinsic stress (σ_i) produced during film deposition and the thermal stress (σ_{th}) due to thermal expansion mismatch between the film and the substrate. The residual stress can be written as:

$$\sigma_f = \sigma_i + (\alpha_s - \alpha_f)\frac{E_f}{1-\nu_f}(T_1 - T_2) \qquad \ldots (4)$$

where α_f and α_s are thermal expansion coefficients of the film and the substrate, respectively. E_f, and ν_f are Young's modulus and Poisson's ratio for the film. $E_f/(1-\nu_f)$ is defined as the biaxial elastic modulus of the film. T_1 is stress measurement temperature and T_2 is deposition temperature. From Eq. (4), it can be readily shown that the slope of the measured stress-temperature curve is equal to:

$$\frac{d\sigma_f}{dT} = (\alpha_s - \alpha_f)\frac{E_f}{1-\nu_f} \qquad \ldots (5)$$

As the intrinsic stress does not depend on the measurement temperature, the thermal stress can be calculated from the temperature dependence of the residual stress.

A digital instruments NanoScope III-a Atomic Force Microscopy (AFM) was used to study the microstructure of evaporated columnar thin films. The atomic force microscopy is a useful tool for observing the surface topography of these interesting surfaces. The AFM measurement was performed *ex-situ* after deposition. Any surface roughness can be quantitatively identified by the root-mean-squared (RMS) roughness. The studied surface images were 1×1 μm in area. RMS roughness and other statistical parameters were determined from these images by using a computer program. In addition, the structure information of the thin films can also be obtained by a HITACHI S3000 scanning electron microscopy (SEM). In this study, columnar growth structures can be observed in evaporated MgF_2 films grown with different oblique columnar angles.

3 Results and Discussion

3.1 Microstructure

When thin films are deposited onto stationary substrates with the flux arriving at a non-normal angle (α) under conditions of limited adatom diffusion, and columnar angle (β) is produced. The columnar angle (β) is always smaller than the vapour oblique incidence angle (α), and is dependent upon several factors including material and deposition conditions. The α-β relationship may be affected by the substrate temperature[13]. This relationship is complex and poorly understood, although a number of attempts at understanding and quantifying this relationship have been presented. The empirical formula of "tangent rule", tan $\alpha = 2\tan\beta$, is a simple relationship based on near normal deposition and gives very poor results[14] for α greater than about 50°.

From the SEM studies of thin films, variations in the columnar microstructure in thin films have been described qualitatively. Figure 3 shows typical cross-sectional SEM images of MgF_2 films deposited with different columnar angle. The MgF_2 thin films exhibit a columnar microstructure that is somewhat porous. The films have a mixture of columnar structures and pores. Here the films deposited with vapour oblique incidence angles of α=10° and 40° correspond to the columnar angles of $\beta = 6°$ and 24°, respectively.

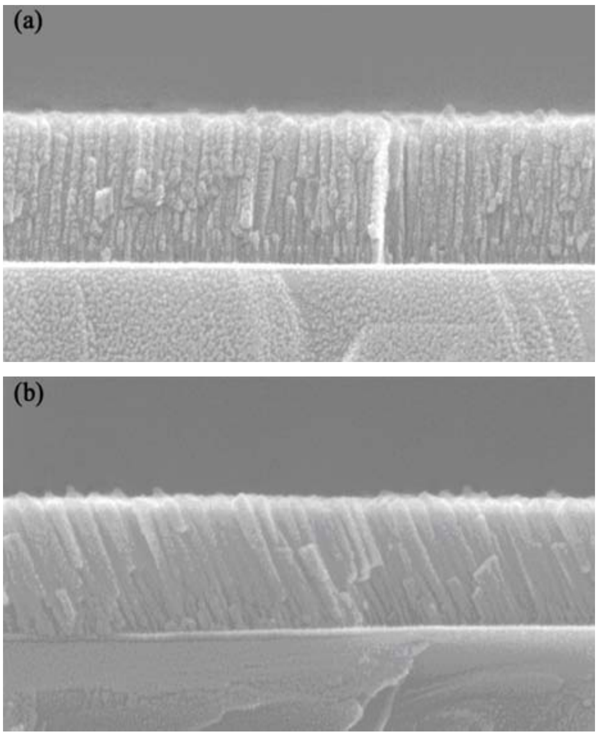

Fig. 3 — Cross-sectional SEM images of MgF_2 thin films deposited at different columnar angles: (a) β=6°; (b) β=24°

3.2 Thermal-optic properties

The thermal induced shift of transmission spectra of MgF_2 thin films with different deposition angles are measured by the spectrophotometer as shown in Fig. 4. We observed that both films have a higher transmittance at the elevated temperature from 30°C to 110°C. Fig. 4(a) shows that an optical transmittance of MgF_2 thin film increases from 93.2% to 95.7% at wavelength of 537 nm for the columnar angle of 6°. Figure 4(b) shows that MgF_2 thin film is deposited at the columnar inclination angle of 24°, its transmittance increases from 93.8% to 96.6% at wavelength of 537 nm. Because the packing density is low for the GLAD films, the thin films with some voids are sensitive to exposure to moisture and demonstrate a spectral shift from vacuum to air. The spectra shift has been attributed to the change in optical thickness of thin films. For an elevated

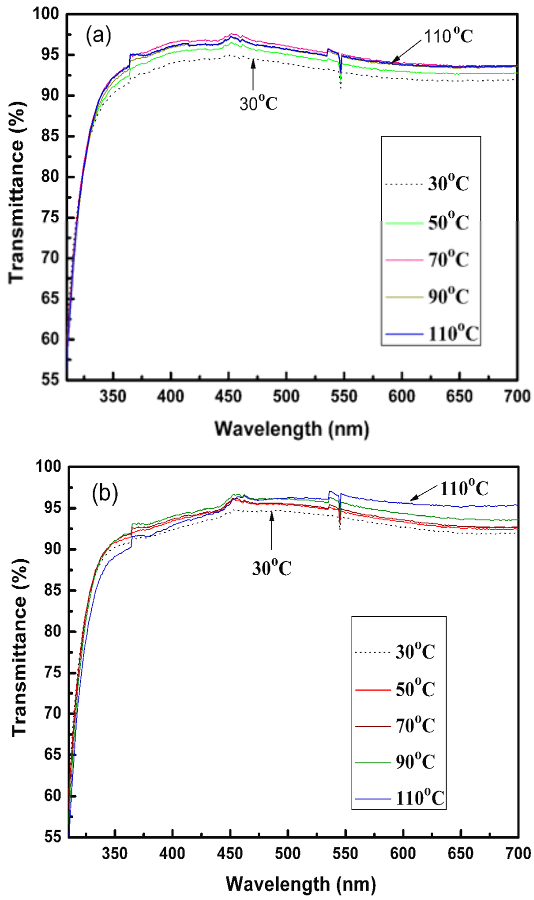

Fig. 4 — Transmission spectra of oblique deposited MgF_2 thin films with different elevated temperatures for (a) β=6°; (b) β=24°

substrate temperature, water removal from the voids between columns decreases the optical thickness due to the difference of refractive index between water (n=1.33) and air (n=1.00).

3.3 Biaxial residual stress

The biaxial stress in thin MgF_2 films was investigated for different columnar inclination angles. The temperature-dependent stress behaviour of MgF_2 thin films was obtained by the elevated substrate temperature in the range 30°-110°C. Since the thermal stress is caused by the difference between the thermal expansion coefficients of the film and the substrate, and by the temperature difference between deposition temperature and ambient environmental temperature. We see a slight linear increase of tensile stress during heating. By heating, the samples will cause the water in void to evaporate out of the film, leading to increase the tensile stress. The tensile residual stress in MgF_2 films varied from 0.053 to 0.953 GPa for the columnar angle of 6°; while the residual compressive stress of-0.034 GPa transited to a tensile stress of 0.908 GPa for the columnar angle of 24°, as shown in Fig. 5. A measure of the anisotropy was obtained by the ratio σ_y/σ_x of stresses along y and x directions, where σ_x was the stress component in the tangential direction and σ_y was the stress component perpendicular to that. The anisotropy was particularly significant in the case of the higher columnar angle. To demonstrate the anisotropic stresses more clearly, we have plotted the ratio of the biaxial stresses σ_y/σ_x as a function of heating temperature. Figure 6(a) shows the biaxial ratio of two stress components for the columnar angle of 6° was σ_y/σ_x=1.051±0.824. Figure 6(b) shows the biaxial ratio of two stress components for the columnar angle of 24° was σ_y/σ_x=0.614±1.138. Thus, the standard deviation of the biaxial stress ratio σ_y/σ_x was small for MgF_2 thin films with a lower columnar angle. When the columnar angle was high, the higher features geometrically shadowed the nearby lower regions of the films; thus the atomic shadowing was greatly enhanced. This produced a porous columnar microstructure and a tensile stress[15].

When the vapour flux arrives at an oblique angle from the substrate normal during thin films deposition by e-beam evaporation, and when the adatom mobility is sufficiently limited to create a columnar microstructure, the resulting stress is tensile and anisotropic. We found that the surface roughness increases as the columnar inclination angle increases. The surface roughness also increases if an oblique incidence angle is increased. Figure 7 shows AFM micrographs of MgF_2 thin films deposited with different columnar inclination angles. The rms surface roughness is 3.806 nm for $\beta = 6^{\circ}$ and 3.951 nm for

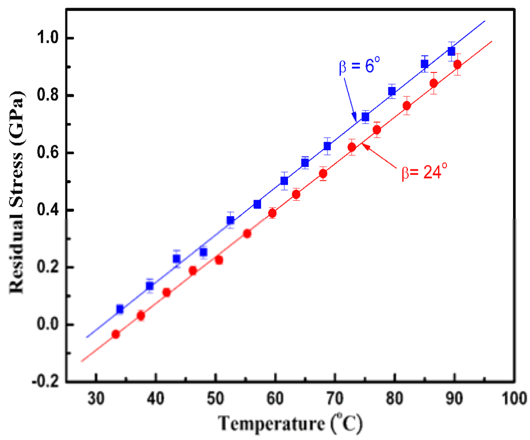

Fig. 5 — Stress-temperature curves of MgF_2 films deposited at two different columnar angles

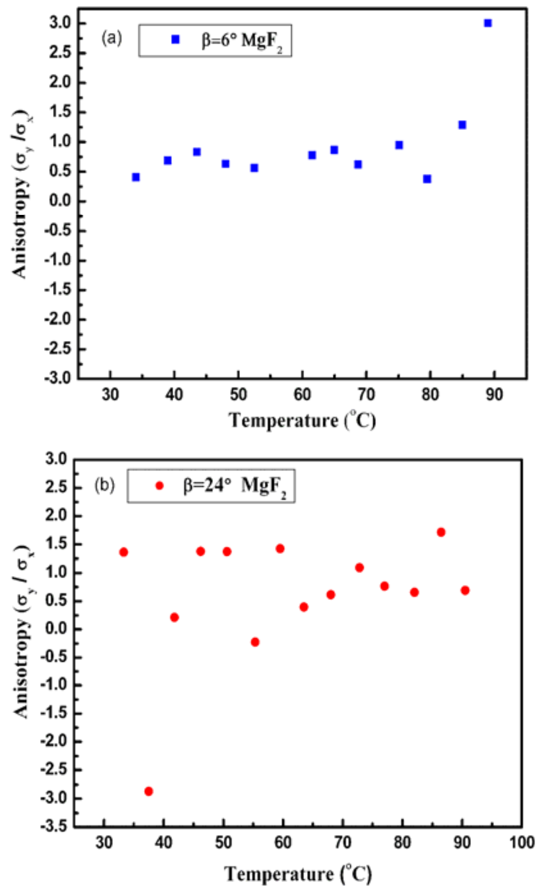

Fig. 6 — Biaxial stress σ_y/σ_x of MgF_2 thin films deposited with different columnar angles: (a) β=6°; (b) β=24°

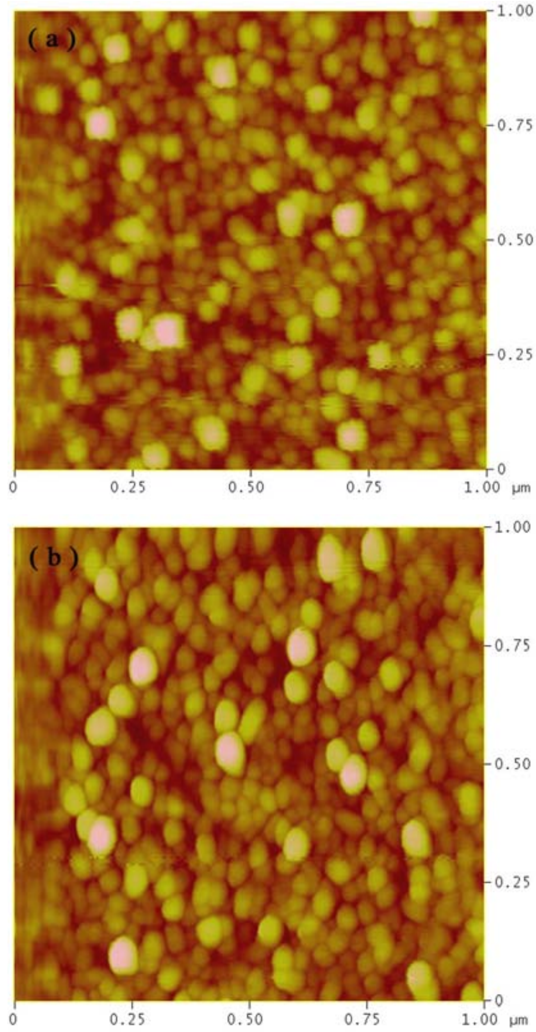

Fig. 7 — AFM micrographs of MgF_2 thin films deposited at different columnar angles with an rms surface roughness of: (a) 3.806 nm for β=6°; (b) 3.951 nm for β=24°

β = 24°. The surface roughness level of the MgF_2 films deposited with a columnar angle of 6° is lower than those of corresponding films made with a columnar angle of 24°. This result demonstrates that the larger incident angle leads to an increase in the surface roughness of thin film during the deposition process.

Since the microstructure of thin films is different from that of the bulk material. It was realized that most vapour deposited films had loosely packed structures resulting from low atom (molecule) mobility which resulted in the columnar microstructure and voids. This structure has great influence on the optical and mechanical properties of the films. Structure-related optical properties of thin films have been studied[16-18] and their results show that the looser the packing of the columns (i.e. higher porosity), then the lower the refractive index. The structure of many evaporated thin films is dominated by the columnar microstructure. This microstructure consists of columns that often extend from the substrate to the surface of the film. Some optical film properties are affected by this columnar structure. Movchan and Demchishin[19] proposed a structure zone model based on the formation of structure zones in condensates, which were dependent on the ratio of substrate temperature to material melting temperature. The cross-sectional morphologies are comparable with the zone 1 structure of the structural zone model, which is caused by the limited mobility of the incoming atoms during oblique deposition[20]. Zone 1 films are characterized by tapered columns separated by voids. Thin films with this type of structure are pores. Although the structure zone model is only qualitative, it is useful in guiding the choice of deposition condition.

4 Conclusions

The temperature-dependent stress behaviour of MgF_2 films has been studied. The results reveal that obliquely deposited MgF_2 thin films developed distinct states of residual stress which is dependent on deposition geometries and elevated substrate temperatures. The residual stresses of MgF_2 films deposited with different columnar angles are plotted against the measured temperature, showing a linear dependence. When the columnar angle of MgF_2 films was increased, the higher stress anisotropy exhibits as the substrate temperature increases from 30° to 90°C. During the measurement of optical transmittance versus the elevated temperature by an ultraviolet-visible spectrophotometer, it is also observed that the transmission spectra of MgF_2 thin films with different columnar angles have a higher transmittance as the temperature increases.

Acknowledgement

The authors gratefully appreciate the support of the National Science Council of Taiwan, the Republic of China, under projects number NSC 100-2221-E-035-053 and NSC 99-2221-E-035-061.

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