

Influence of deposition rate on the properties of ZrO₂ thin films prepared in electron beam evaporation method

Dongping Zhang (张东平), Meiqiong Zhan (占美琼), Ming Fang (方明),
Hongbo He (贺洪波), Jianda Shao (邵建达), and Zhengxiu Fan (范正修)

R&D Center for Optical Thin Film Coatings, Shanghai Institute of Optics and Fine Mechanics,
Chinese Science Academy, Shanghai 201800

Received January 8, 2004

ZrO₂ thin films were prepared in electron beam thermal evaporation method. And the deposition rate changed from 1.3 to 6.3 nm/s in our study. X-ray diffractometer and spectrophotometer were employed to characterize the films. X-ray diffraction (XRD) spectra pattern shows that films structure changed from amorphous to polycrystalline with deposition rate increasing. The results indicate that internal stresses of the films are compressive in most case. Thin films deposited in our study are inhomogeneous, and the inhomogeneity is enhanced with the deposition rate increasing.

OCIS codes: 310.1860, 310.6870.

Due to its attractive optical properties, such as low absorption of light, high index of refraction and transparent over a wide spectral range, ZrO₂ is a thin-film material of great interest for optical applications^[1-3]. It is frequently used as a high refractive-index material in multilayer optical coatings because it is hard, durable, and easily evaporated by electron beam. However, optical properties of ZrO₂ films strongly depend on deposition conditions such as substrate temperature, deposition rate, O₂ partial pressure, and other preparation parameters^[4,5]. A good understanding of the influence of the deposition parameters is vital to improve coating quality.

In order to find suitable deposition conditions with which the films need to be prepared to meet with the applications, we studied the influence of deposition rate on surface microstructure and the crystal structure of the films. In addition, the residual stress of the films, which can strongly affect the film adhesion and the other properties, plays an important role in many applications. Hence, the influence of the deposition rates on residual stress of ZrO₂ films has been studied in this report. A shortcoming of evaporated thin film layer of many metal oxide dielectric materials is the characteristic of a varying refraction index as a function of film thickness, and this variation is uncertainty^[6,7]. The occurrence of this inhomogeneity in practice can produce unpredictable results. The variation of inhomogeneity with deposition rate has studied as well in this paper.

In our experiments, BK7 glass substrates ($\phi 20 \times 1$ mm) were used. Before deposition the substrates were ultrasonically cleaned in petroleum ether and de-ionized water under 50°C for 10 minutes respectively to remove the contamination on the surface. Then the cleaned substrates were dried with high purity nitrogen gas. ZrO₂ films were deposited by electron beam thermal evaporated in an 800-mm vacuum chamber and the coating material was in tablet form. The vacuum chamber was baked under 300 °C for 2 hours. The chamber was evacuated to a base pressure of about 1.2×10^{-3} Pa. Ultrahigh

purity O₂ gas (99.99%) was used to backfill the chamber to pressure of 4×10^{-3} Pa during deposition to disrupt the sub-stoichiometry of ZrO₂ films. Before deposition, the coating material was adequate thermally degassed with a shutter blocking the vapor from the sample surface until the pressure stabilized. Film thickness was monitored by an optical monitor. The deposition rates were obtained by thickness divided deposition time, and the values varied from 1.2 to 6.3 nm/s by emission current changing.

Transmission spectra of the samples were measured with Lambda 900 spectrophotometer made by Perkin Elmer Company. Crystal structure analysis was carried out using a RIGAKU/MAX-3C x-ray diffractometer. Copper K α with 0.15406-nm radiation wavelength was used in measurement. The detector angle was incremented in 0.02° steps and data were gathered over an angle range from $2\theta = 20^\circ$ to 85° .

Generally, ZrO₂ has three crystal phases: monoclinic, tetragonal, and cubic^[8]. X-ray diffraction (XRD) analysis yields information on crystal size and phase. XRD spectra of the samples are shown in Fig. 1. The intense peak at about 30° is attributed to diffraction from

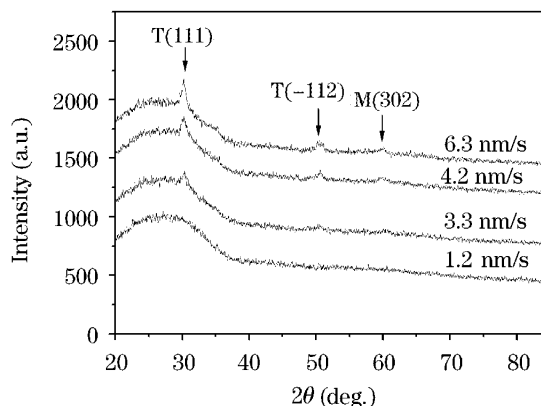


Fig. 1. XRD spectra of the samples.

T(111) planes of ZrO_2 . The others are attributed to the diffraction from the monoclinic phase respectively. The intensity of monoclinic phase peaks is very weak. So the tetragonal is the dominant phase in the films. Under 1.2-nm/s deposition rate, there are almost no characteristic peaks and the film is amorphous. The characteristic peaks become emerging when deposition rate reaches 3.3 nm/s, and the intensity of the peaks increases with the deposition rate increasing. The changing of the XRD spectra indicates the films structure changed from amorphous to polycrystalline with deposition rate increasing. And the full width at half maximum (FWHM) of the diffraction peak changes with the deposition rate increasing slightly as well. According to the Scherrer formula^[9], the crystallite dimension could be expressed as

$$L = \kappa\lambda/(\beta \cos \theta), \quad (1)$$

where κ is a constant taken as 0.9, λ is 0.15406 nm of the copper $K\alpha$ radiation, θ is Bragg diffraction angle, and β is the FWHM of diffraction peak. The variation of the crystallite dimension with the deposition rate is shown in Fig. 2. The crystallite size increases with the deposition rate increasing, so it is reasonable to deduce that the surface roughness also increases with the deposition rate increasing.

Bragg equation was used in calculating the d_{111} lattice coefficient of tetragonal of the samples. Comparing with the results deduced from the JCPDS (Joint Committee on Powder Diffraction Standards) files from ICCD (International Center for Diffraction Data), obvious changes of the lattice coefficient are found of the samples, and these changes corresponding to the strain of the films are

$$\varepsilon_z = (d - d_0)/d_0, \quad (2)$$

where d and d_0 are strained and unstrained lattice coefficient respectively. So the average stress^[10] could express as

$$\sigma = (E/2\nu)\varepsilon_z, \quad (3)$$

where E is the Young's modulus of ZrO_2 taken as 135.24 GPa, ν is the poisson ratio^[11] taken as 0.36. The relations between the internal stresses and deposition rate are also shown in Fig. 2. The stress values are negative

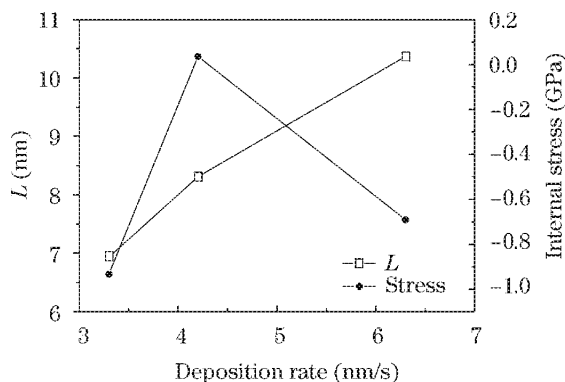


Fig. 2. Variation of crystallite dimension and internal stress with the rate of deposition.

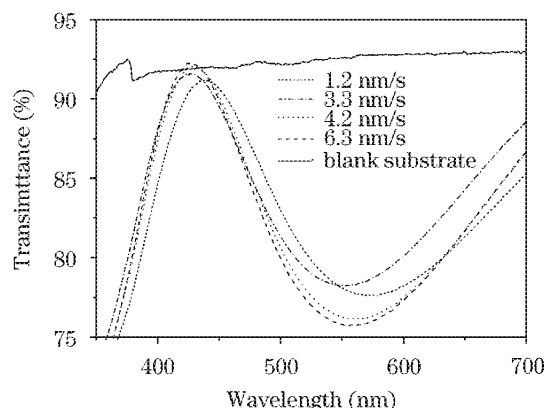


Fig. 3. Measured transmission spectra of the ZrO_2 thin films.

when the deposition rates are 3.3 and 6.3 nm/s that indicate a compressive stress in the films. Though the stress is tensile when the deposition rate is 4.2 nm/s, it is very close to zero. This indicates that the rate of 4.2 nm/s is the proper deposition rate to obtain the zero internal stress in ZrO_2 films.

The optical transmission spectra of the films are shown in Fig. 3. And the average refractive indices at 550-nm wavelength are deduced from their transmittance spectra in envelope method. The peak transmittance values are about 92% near the monitor wavelength, and they increase gradually with the deposition rate increasing. In 4.2- and 6.3-nm/s deposition rate cases, the transmittances are even beyond those of the blank substrate. This indicates that the ZrO_2 thin films deposited at high deposition rate have some antireflection coating properties. If the ZrO_2 layers are homogenous, the peak transmittance value will correspond to the transmittance of the substrate. The fact that it is higher indicates that the films are inhomogeneous, and the inhomogeneity of the films is strengthened with deposition rate increasing. This type of inhomogeneity is typical for many metal-oxide dielectric thin films, and electron-beam-deposited ZrO_2 films are known to be inhomogeneous as well. They have different refractive indices near the substrate and the outer surface respectively^[12]. So the hypothesis of a multilayer, which consists of many different homogeneous layers with different refractive index, could correctly explain the measured optical properties. The most successful model that explained the cause of the optical inhomogeneity in thin films is formulated by Harris *et al.*^[13]. They propose that index inhomogeneity results from a density gradient in the growth direction of the thin film. Klinger and Carniglia^[14] studied the optical and crystalline inhomogeneities of ZrO_2 films as the optical thickness increased from one to four quarter-wave at 600 nm. When the optical thickness is less than a quarter-wave, only the cubic phase appears. And films that are thicker than a quarter-wave optical thickness have both cubic and monoclinic phases. Their results show that the optical inhomogeneity behaves the same way as the crystalline inhomogeneity. In our experiment, for almost the same thickness of four samples, it is reasonable that the inhomogeneity refractive index of the films is result from the crystal phase variation with the different

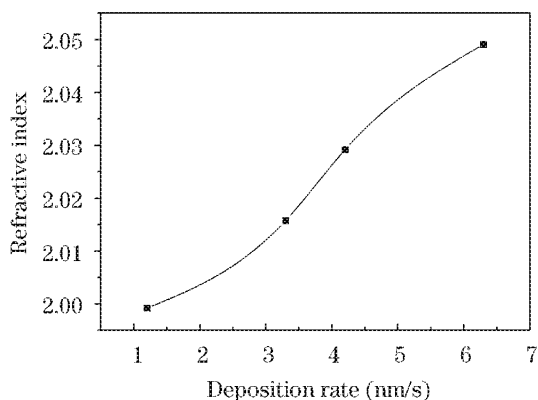


Fig. 4. Relations between diffraction index and rate of deposition.

deposition rate. The difference of the crystal phase means the difference variation of the crystalline inhomogeneity with the film thickness increasing at different deposition rate.

The refractive index data are indicative of the film density, and the relations between the average refraction index and the deposition rate are shown in Fig. 4. We could see the increasing of average refraction index with the deposition rate increasing. Therefore the packing density of the films is enhanced with deposition rate increasing because of almost a linear relationship between packing density and the refraction index of the film^[15].

In conclusion, we analysed the influence of the deposition rate on the characters of ZrO_2 thin films, which were deposited in electron beam thermal evaporation method. With the deposition rate increasing, the crystal structure changed from amorphous to polycrystalline, and the crystallite size of the films also increased. Internal stresses in ZrO_2 films are compressive in most cases, and zero internal stresses of the ZrO_2 films could be obtained by choosing the proper deposition rate. Electron-beam-deposited ZrO_2 films are to be inhomogeneous and the high de-

position rate will strengthen the inhomogeneities. The refractive indices of thin film increase with deposition rate increasing as well.

The authors would like to thank Mr. W. B. Wang for the XRD measurement experiment. D. Zhang's e-mail address is zdp@mail.siom.ac.cn.

References

1. S. Y. Shao, Z. X. Fan, J. D. Shao, and H. B. He, *Thin Solid Films* **59**, 445 (2003).
2. N. L. Zhang, Z. T. Song, S. Xing, Q. Wan, C. L. Lin, *Chin. J. Lasers* (in Chinese) **30**, 345 (2003).
3. D. Li, G. H. Ma, W. M. Huang, and S. X. Qian, *Acta Opt. Sin.* (in Chinese) **22**, 688 (2002).
4. P. T. Gao, L. J. Meng, M. P. dos Santos, V. Teixeira, and M. Andritschky, *Appl. Sur. Sci.* **173**, 84 (2001).
5. W. Heitmann, *Appl. Opt.* **7**, 1541 (1968).
6. H. J. Cho and C. K. Hwangbo, *Appl. Opt.* **35**, 5545 (1996).
7. J. P. Borgogno, F. Flory, P. Roche, B. Schmitt, G. Albrand, E. Pelletier, and H. A. Macleod, *Appl. Opt.* **23**, 3567 (1984).
8. N. K. Huang, Z. R. Feng, and D. Z. Wang, *Thin Solid Films* **221**, 9 (1988).
9. H. P. Klug and L. E. Alexander, *X-Ray Diffraction Procedure* (2nd ed.) (Wiley, New York, 1974) p. 550.
10. N. G. Ferreira, E. Abramof, E. J. Corat, and V. J. Trava-Airoldi, *Carbon* **41**, 1301 (2003).
11. W. W. Kriegel and H. Palmour III, *Mechanical Properties of Engineering Ceramics* (Interscience, New York, 1961) p. 583.
12. P. J. Martin, *J. Mat. Sci.* **21**, 1 (1986).
13. M. Harris, H. A. Macleod, S. Ogura, E. Pelletier, and Vidal, *Thin solid films* **57**, 173 (1979).
14. R. E. Klinger and C. K. Carniglia, *Appl. Opt.* **24**, 3184 (1985).
15. H. K. Pulker, *Coatings on Glass* (Elsevier, Amsterdam, 1984) p. 322.