

Structure and optical properties of TiO₂ thin films prepared by glancing angle deposition

B. ZHAO, J. ZHOU*, Y. CHEN, Y. PENG

School of Energy Science and Engineering, Central South University, Changsha 410083, China

A new glancing angle deposition method was presented for fabricating TiO₂ films with engineered refractive index and low light absorption. With rotation of the substrate along the flux direction, the films possess small grain size and small nanorod diameter. The decrease of the grain size increases the optical transmittance in the visible light region, while the decrease of the nanorod diameter increases the optical transmittance in the ultraviolet region. The refractive index of the film decreases from 2.53 to 1.81 while the flux angle increases from 0° to 80°. This controllable refractive index allows the realization of grade-index profile.

(Received November 17, 2010; accepted November 29, 2010)

Keywords: Magnetron sputtering, Angle deposition, Titanium dioxide, Antireflection, Optical properties

1. Introduction

An antireflection (AR) coating is applied to the surface of a solar cell to minimize the light reflection and enhance the transmittance. Therefore, it can improve solar collection efficiency and the overall solar-to-electricity efficiency. In theory, there are two major types of AR coatings [1]. The first one is the single or multilayer quarter-wavelength film stacks [2]. This AR coating works only at a certain spectral range and at the normal incidence [3]. As solar radiation is broadband, the AR coating needs to be effective for the entire solar spectrum from ultraviolet and visible to IR wavelengths. The second one is the graded index (GRIN) AR coating [4], whose the refractive index changes gradually from the top to the bottom. The GRIN AR coating yields omnidirectional broadband antireflection characteristics, especially with the quintic index profile [5]. However, the difficulty in choosing materials for practicable control of index profiles has prevented the GRIN AR coating from practical applications.

The recently developed technique of glancing angle deposition (GLAD) allows the production of highly porous thin films [6]. As the refractive index is related to the porosity [7], GLAD method is a powerful method to tune the refractive index of AR coating [8]. The GRIN AR coating has been successfully prepared by GLAD method [3, 7, 9, 10]. With glancing angle deposition of TiO₂ thin films, an ultralow total reflectance at the surface of a solar cell of 1%–6% has been achieved by M. Kuo et al. [9]. M. F. Schubert et al have show that discrete multilayer coatings enable reflectivity far below values attainable by continuously graded coatings [10]. In these previously reported studies, TiO₂ thin films with different refractive

index are important components. However, the high optical absorption was observed in the films deposited by GLAD method [11-13]. This feature largely undermines the enhancement of conversion efficiency of solar cells. Few researches were to solve the problem. In this paper, the TiO₂ thin films with different refractive index were prepared by GLAD method, while the increase of optical absorption was suppressed. Besides, the reasons were tried to be explained.

2. Experimental

TiO₂ thin films were deposited by DC reactive magnetron sputtering of a Ti target of 99.99% purity with diameter of 100 mm at room temperature. The oxygen (O₂) and argon (Ar) were used as reactive gas and working gas respectively. The sputtering pressure was kept at 0.7 Pa, with an O₂ flow rate of 10 mL/min and an Ar flow rate of 90 mL/min. A turbo molecular pump was used to achieve a base pressure of 1×10^{-3} Pa. The target-to-substrate distance was kept constant at 85 mm. This distance can ensure the homogeneity of the films. The sputtering power was kept at approximately 400 W. Quartz glass with size of 25 mm × 25 mm × 1 mm was used as substrates. The substrates were ultrasonically cleaned in acetone, ethyl ethanol and deionized water for 15 min in sequence, then dried by N₂. The geometrical characteristics of the experimental setup are presented in Fig. 1. Incoming deposition flux angle α and tilted rod angle β were measured from the substrate normal. The GLAD was performed at the flux angle α of 0°, 30°, 60°, and 80°. In previously reported studies for GLAD, the substrates were fixed during deposition [12, 14]. In our experiment, the substrate can rotate along the line AB. For comparison,

the rotation speed ω was about 1.2 rad/s and 0 rad/s, respectively. The pre-sputtering was performed for 5 min to clean the surface of the titanium target, and then the TiO₂ thin films were deposited at room temperature for 50 min.

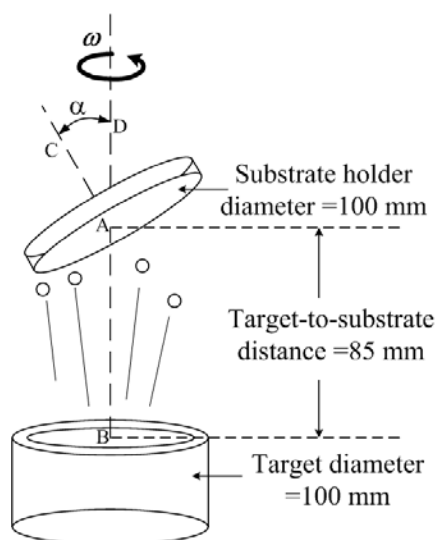


Fig. 1. Schematic representation of the GLAD system.

The crystal structures of the films were measured with Rigaku D/max 2500 VB+ XRD using Cu-K α radiation. The θ -2 θ scans range is between 10° and 90° with a step size of 0.01°. The cross-sectional morphology of the TiO₂ thin films was observed with Philips Sirion 200 field emission SEM. The samples were covered with gold for SEM operation. The thickness of the films was measured by SEM and Alpha-Step IQ type profiler. Optical transmittance spectra of the films were investigated at room temperature with TU-1800 type UV-VIS spectrophotometer, using air as a reference. From the transmittance spectra, the thickness and optical constants of the films were calculated using the Swanepoel method [15].

3. Results and discussion

3.1. X-ray diffraction measurements

Fig. 2 depicts the XRD patterns of the glancing angle deposited TiO₂ films with rotation speed of 0 and 1.2 rad/s. 'A' means anatase phase. The broad scattering peak occurring at 25° is from the substrate. As shown in Fig. 2, the anatase is main phase and exhibits a preferential orientation along the (1 0 1) plane. Anatase (1 0 1) peak shows a decrease in its intensity with increasing flux angle α . At the same flux angle α , the intensity of anatase (1 0 1) in Fig. 2a is higher than that in Fig. 2b. That means the anatase grain size decreases with increasing rotation speed

ω . That is because self-shadowing increase as increasing the flux angle α , and the surface diffusion decrease as increasing the rotation speed ω [6, 16]. These two effects restrain the growth of the crystal.

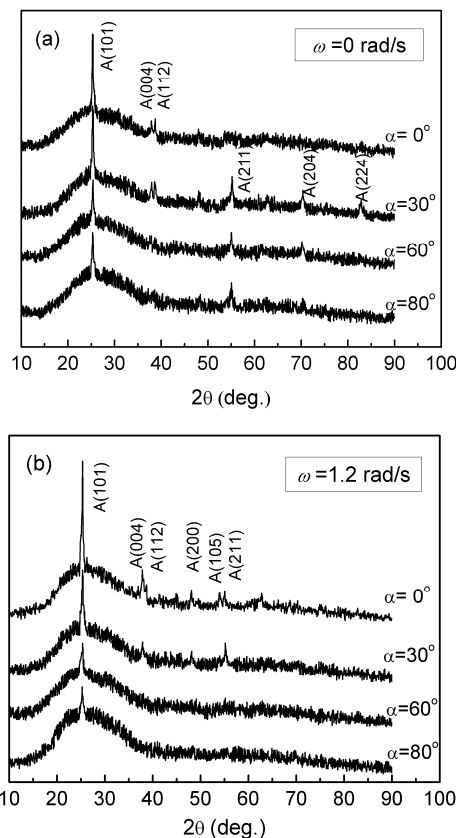


Fig. 2. XRD patterns for the TiO₂ films deposited at rotation speed of (a) 0 rad/s; (b) 1.2 rad/s.

3.2. Cross-sectional morphologies observed by SEM

SEM images for some samples are shown in Fig. 3. It is observed that the glancing angle deposited films exhibit a tilted nanorod structure. The films have a good homogeneity in microstructure. The rods of the films deposited at $\omega=0$ rotation are 'fan-out' in the direction perpendicular to the deposition flux. In the Fig. 3a and Fig. 3b, the rod diameter is about 100 nm. For the Fig. 3c and Fig. 3d, the rod diameter is about 10 nm. The nanorod diameter of the films deposited at $\omega=0$ is much larger than that of the films deposited at $\omega=1.2$ rad/s. The nanorod diameter of the films deposited at $\omega=0$ gets larger as increasing the angle α . However, that of the films deposited at $\omega=1.2$ rad/s has no significantly change. At $\omega=1.2$ rad/s, the growing interface can be exposed to the incident flux from any angle because the substrate is continuously rotated during a deposition. Therefore some

part of the growth front will be interrupted due to the change of the shadowing direction and the other part will become a preferred growing front during a rotation [17, 18].

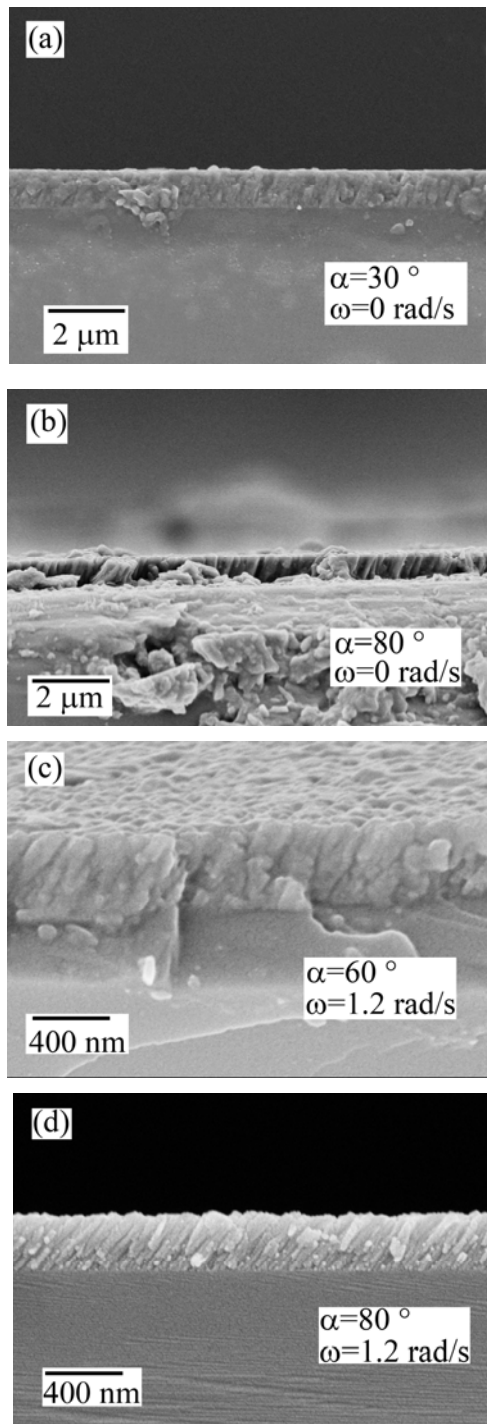


Fig. 3. Cross-sectional SEM images for the TiO_2 films deposited at: (a) $\alpha=30^\circ$, $\omega=0$ rad/s; (b) $\alpha=80^\circ$, $\omega=0$ rad/s; (c) $\alpha=60^\circ$, $\omega=1.2$ rad/s; (d) $\alpha=80^\circ$, $\omega=1.2$ rad/s.

3.3. Transmittance spectra of TiO_2 films

Fig. 4 shows the transmittance spectra in UV-VIS region of and TiO_2 thin films glancing angle deposited on glass substrate at different rotation speed ω . Transmittance in ultraviolet region decrease a lot as increasing the flux angle α in Fig. 4a, while the transmittance does not change significantly in Fig. 4b. This because the rod diameter in the films deposited at $\omega=0$ rad/s is about 100 nm, the feature size is similar to the wavelength of ultraviolet, the Mie and Rayleigh scattering in short wavelength increase largely [3]. While, the feature size of the films deposited at $\omega=1.2$ rad/s is about 10 nm, the Mie and Rayleigh scattering can be neglected. Moreover, the grain size of the films deposited at $\omega=0$ rad/s is larger than that of the films deposited at $\omega=1.2$ rad/s. That means the scattering loss owing to crystallization in the films deposited at $\omega=0$ rad/s is larger than that deposited at $\omega=1.2$ rad/s. This is why the visible light transmittance in the films deposited at $\omega=0$ rad/s is lower than that of the films deposited at $\omega=1.2$ rad/s [14]. Briefly, the high optical absorption in the films deposited by GLAD method was successfully suppressed.

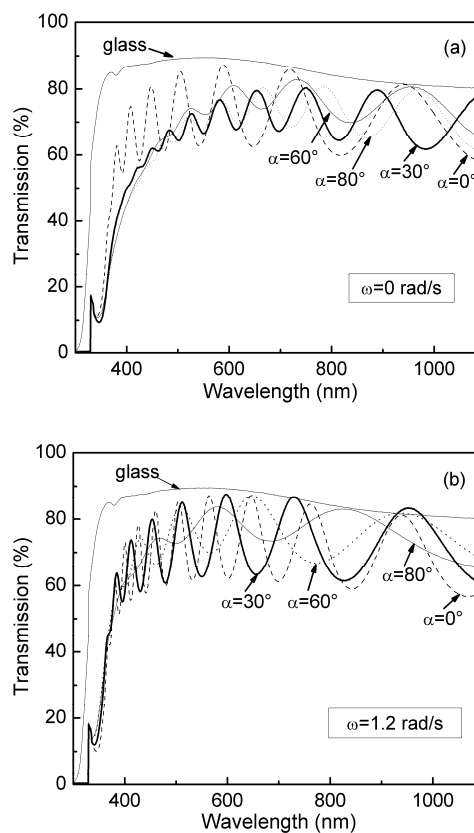


Fig. 4. Transmittance spectra for the TiO_2 films deposited at rotation speed of (a) 0 rad/s; (b) 1.2 rad/s.

3.4. Optical constants of TiO₂ films

To appreciate our method's ability to adjust refractive index of thin films, the refractive index of the films deposited at $\omega = 1.2$ rad/s was calculated by the Swanepoel method [15]. Fig. 5 plots the refractive index of the TiO₂ films as a function of the wavelength. It can be seen that the refractive index of the films decreases as increasing the flux angle α . This is caused by the formation of nanostructures in the films deposited by the GLAD method. For example, the refractive index of the film at 550 nm decreased from 2.53 to 1.81 when deposited at 0° and 80°, respectively. This controllable refractive index allows the realization of almost any grade-index profile [9]. Beside, GLAD deposited at $\omega = 1.2$ rad/s successfully suppress the increase of the light absorption. It indicates that this method can broaden the application of a material as AR coatings.

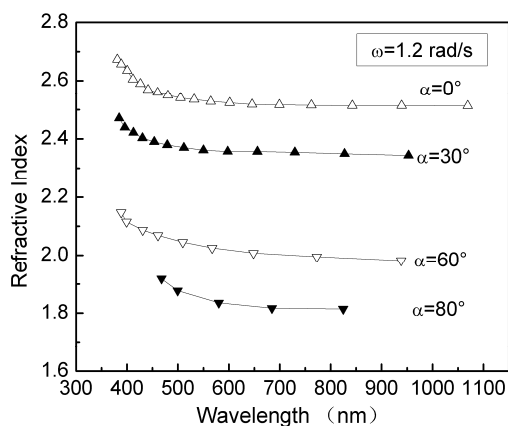


Fig. 5. The refractive index spectra of the TiO₂ films deposited at $\omega = 1.2$ rad/s.

4. Conclusions

A new GLAD method has been presented for fabricating the TiO₂ films with engineered refractive index and low light absorption. The grain size decreases as increasing the flux angle α and the rotation speed ω . The rod angle β increases as increasing the flux angle α . With rotating the substrate along the flux direction, the films possess small grain size and small nanorod diameter. The decrease of the grain size develops the optical transmittance in the visible light region, while the decrease of the nanorod diameter develops the optical transmittance in the ultraviolet region. Thereby, the high optical absorption in the films deposited by GLAD method is suppressed. The refractive index of the film deposited at $\omega = 1.2$ rad/s for a wavelength of at 550 nm decreased from 2.53 to 1.81 when the flux angle increases from 0° to 80°. This controllable refractive index allows the realization of

almost any grade-index profile.

Acknowledgement

This work is supported by the Hunan Province Key Project of Science and Technology (Project no.08FJ1002).

References

- [1] W. Zhou, M. Tao, L. Chen, H. Yang, *J. Appl. Phys.* **102**, 103105 (2007).
- [2] J. Ni, Y. Zhu, S.H. Wang, Z.C. Li, Z.J. Zhang, B. Q. Wei, *J. Am. Ceram. Soc.* **92**, 3077 (2009).
- [3] J. Q. Xi, M. F. Schubert, J. K. Kim, E. F. Schubert, M. Chen, S.-Y. Lin, W. Liu, J. A. Smart, *Nat Photonics* **1**, 176 (2007).
- [4] A. Mahdjoub, L. Zighed, *Thin Solid Films* **478**, 299 (2005).
- [5] W.H. Southwell, *Opt. Lett.* **8**, 584 (1983).
- [6] D. Vick, L. J. Friedrich, S. K. Dew, M. J. Brett, K. Robbie, M. Seto, T. Smy, *Thin Solid Films* **339**, 88 (1999).
- [7] S. R. Kennedy, M. J. Brett, *Appl. Opt.* **42**, 4573 (2003).
- [8] R. Teki, M. K. Datta, R. Krishnan, T. C. Parker, T. M. Lu, P. N. Kumta, N. Koratkar, *Small* **5**, 2236 (2009).
- [9] M.-L. Kuo, D. J. Poxson, Y. S. Kim, F. W. Mont, J. K. Kim, E. F. Schubert, S.-Y. Lin, *Opt. Lett.* **33**, 2527 (2008).
- [10] M. F. Schubert, D. J. Poxson, F. W. Mont, J. K. Kim, E. F. Schubert, *Appl. Phys. Express* **3**, 082502 (2010).
- [11] Z.-P. Yang, L. Ci, J. A. Bur, S.-Y. Lin, P. M. Ajayan, *Nano Lett.* **8**, 446 (2008).
- [12] H. Y. Yang, M. F. Lee, C. H. Huang, Y. S. Lo, Y. J. Chen, M. S. Wong, *Thin Solid Films* **518**, 1590 (2009).
- [13] R. T. Kivaisi, *Thin Solid Films* **97**, 153 (1982).
- [14] M. F. Cansizoglu, R. Engelken, H. W. Seo, T. Karabacak, *Acs Nano*, **4**, 733 (2010).
- [15] E. Márquez, J. Ramírez-Malo, P. Villares, R. Jiménez-Garay, P. J. S. Ewen, A. E. Owen, *J. Phys. D: Appl. Phys.* **25**, 535 (1992).
- [16] M. Mansour, A. S. Keita, B. Gallas, J. Rivory, A. Besnard, N. Martin, *Optical Materials*, **32**, 1146 (2010).
- [17] D.-X. Ye, T. Karabacak, B. K. Lim, G.-C. Wang, T.-M. Lu, *Nanotechnology*, **15**, 817 (2004).
- [18] N. Starbov, K. Starbova, *J. Optoelectron. Adv. Mater.* **11**(9), 1093 (2009).

* Corresponding author: jicheng@mail.csu.edu.cn