

Effect of Microstructure of TiO₂ Thin Films on Optical Band Gap Energy

TIAN Guang-Lei(田光磊)^{1,2*}, HE Hong-Bo(贺洪波)¹, SHAO Jian-Da(邵建达)¹

¹R&D Center for Optical Thin Film Coatings, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800

²Graduate School of the Chinese Academy of Sciences, Beijing 100039

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TiO₂ coatings are prepared on fused silica with conventional electron beam evaporation deposition. After annealed at different temperatures for four hours, the spectra and XRD patterns of TiO₂ thin film are obtained. XRD patterns reveal that only anatase phase can be observed in TiO₂ coatings regardless of the different annealing temperatures, and with the increasing annealing temperature, the grain size gradually increases. The relationship between the energy gap and microstructure of anatase is determined and discussed. The quantum confinement effect is observed that with the increasing grain size of TiO₂ thin film, the band gap energy shifts from 3.4 eV to 3.21 eV. Moreover, other possible influence of the TiO₂ thin-film microstructure, such as surface roughness and thin film absorption, on band gap energy is also expected.

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Titanium dioxide is one of the most extensively studied transition-metal oxides. The preparation of TiO₂ thin films has received great attention during the past several decades because of its remarkable optical and electronic properties (refractive index, dielectric constant, and so on). Many different procedures for the preparation of thin films of titanium oxide materials have been reported.^[1,2] Thin films of titania (TiO₂) are frequently used for coatings due to their high refractive index and high stability, and its properties are known to be easily affected by the technological conditions of the deposition process such as the substrate temperature and oxygen partial pressure as well as by the post-deposition heat-treatment.^[3] In the previous research, it was observed that with the increasing annealing temperature, the band gap energy would gradually shift to small energy. Ultrafine polycrystal oxides with grain size in the nanometer range have received much attention because of the relationship observed between properties and microstructure.^[4-6] Such effects are primarily due to increasing interfacial area and size-dependent defect properties, which can enhance nonstoichiometry and reaction kinetics and are very important for such applications as in gas sensors, fuel cells, or ionic membranes.

The objective of this study is to determine the energy gap of nanocrystalline TiO₂ thin films by the use of optical absorption techniques and to correlate it with the thin film microstructure such as grain size, surface roughness and absorption posed by nonstoichiometry.

In our experiments, polished fused silica substrates were used. Firstly, the substrates were immersed to acetone for several hours to remove the oil pollu-

tion on the substrate surface, and then cleaned with petroleum ether at 353 K in ultrasound cleaner two times, 50 seconds per time. TiO₂ layers were deposited at a substrate temperature of 473 K by electron beam evaporation. The films were deposited by using the Ti₂O₃ crushed aggregates as the starting material whose purity is 99.99%, and before deposition run, the chamber was pumped to a base pressure of 7.3×10^{-3} Pa and oxygen was introduced to keep oxygen partial pressure to be 2.6×10^{-2} Pa. Oxide coatings with optical thickness of $8\lambda/4$ ($\lambda = 500$ nm) were deposited on fused silica under optical control. The post-deposition annealing of the films was performed in air at 573, 773, 973, 1173 and 1373 K for four hours, respectively. Microstructure of TiO₂ films was analysed by an x-ray diffractometer. The XRD method was used ex situ to study the change of the TiO₂ structure and grain size caused by post-deposition annealing. The optical transmittance of the samples was measured by a spectrometer LAMBDA900, through which we can study effect of annealing on the spectrum.

Figure 1 illustrates the XRD patterns of TiO₂ thin films as-deposited and annealed at different temperatures. The crystallization and grain growth of TiO₂ in the anatase phase is observed by the increasing and narrowing of the intensity of the diffraction lines as the annealing temperature increased. The analysis of the shape of x-ray lines has been used to determine the grain size for each specimen.

As can be seen in the inset in Fig.1, the microstructure of the films strongly depends upon annealing temperature and the grain size can be varied from 23 nm to 59 nm over the temperature range of 573-1373 K. From this relationship of quantum con-

* Email: gltian@siom.ac.cn

finement between the grain size and band energy of thin films, the optical band gap energy was directly determined.

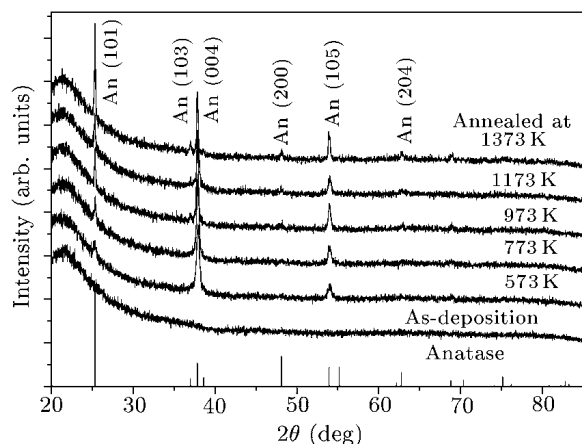


Fig. 1. X-ray diffraction patterns of TiO₂ thin films annealed at different temperature.

Table 1. Evolution of FWHM and grain size at An (101) and An (004) peak of TiO₂ coatings annealed at different temperatures.

Annealing temperature (K)	An (101)		An (004)	
	B (deg)	C (nm)	B (deg)	C (nm)
573	0.379	23.0	0.397	25.1
773	0.237	36.7	0.314	31.7
973	0.179	48.6	0.236	42.2
1173	0.151	57.6	0.292	34.1
1373	0.147	59.2	0.225	44.2

Figure 2 shows the optical transmittance of the coatings as-deposited and annealed at various temperatures in the wavelength range of 300 and 1200 nm at room temperature.

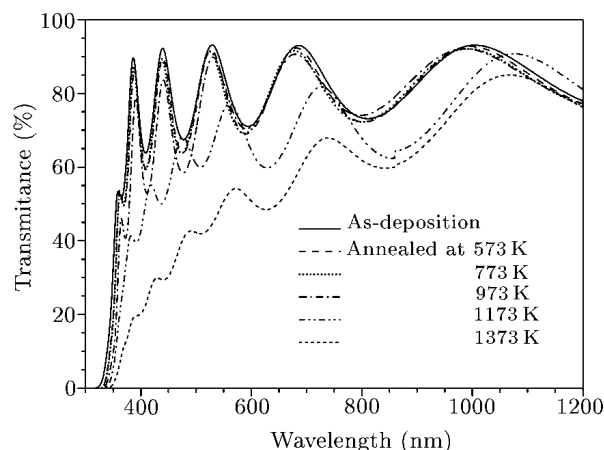


Fig. 2. Transmittance spectra versus wavelength for titania thin films as-deposited and annealed at different temperature for four hours.

Since TiO₂ is a semiconductor with a large band gap, the optical band gap E_g can be determined from absorption coefficient α . The sharp decrease in the transparency of the thin films in the UV region results from the fundamental light absorption of the semiconductor. The absorption coefficient α , which depends

on the wavelength λ , can be obtained by using the following relationship:^[7,12]

$$T = (1 - R)^2 e^{-\alpha d}, \quad (1)$$

where T is the transmittance, R is the reflectance, α is the absorption coefficient and d is the film thickness. Equation (1) is of course only valid close to the optical band gap of the material under the condition $\exp(2d) \gg R^2$. When the scattering effect is neglected, the absorption coefficient may be expressed by^[7,12]

$$\alpha \propto (h\omega - E_g)^m, \quad (2)$$

where E_g is the optical band gap. We have $m = 2$ for the indirect allowed transition, and $m = 1.5$ for the direct forbidden transitions.

The above equation resulted in a good fit for the spectra in the region obtained for all annealing TiO₂ thin film specimens. The similar results have been obtained for optical absorption studies for BaCeO₃:Y^[8] and also for semiconducting materials. The absorption coefficient above the threshold of fundamental absorption follows the $(E - E_g)^2$ energy dependence of indirect allowed transition by $\alpha^{1/2}$ on photon energy E , as illustrated in Fig. 3. The extrapolated optical absorption gaps of the thin films have been determined, and thus we obtain the band gap energy of the TiO₂ thin films annealed at different temperatures. It can be seen that the optical band gap energy decreases (from 3.38 to 3.21 eV) when the annealing temperature increases.

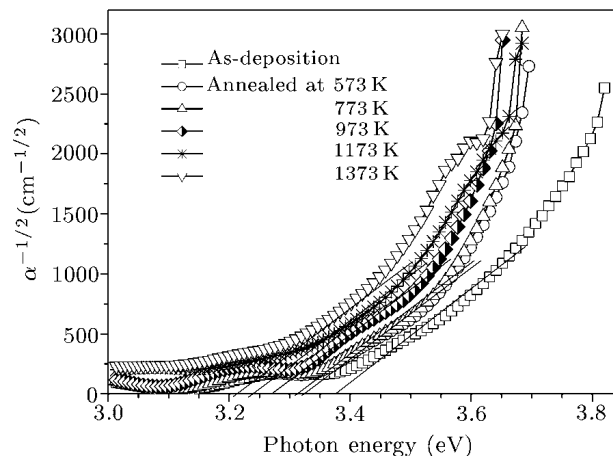


Fig. 3. Optical absorption coefficient α versus band gap energy of TiO₂ thin films with different annealing temperatures.

Figure 4 shows the relationship between the band gap energy and the microstructure. It can be seen that the experimental band gap energy distributes around the theoretical curve other than that of thin films as-deposited and annealed at 573 K. When quantum confinement is present, the expression for the band gap

energy is derived by^[6,9]

$$E_g = E_g^0 + \frac{h^2 \pi^2}{2d_g^2} \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right] + d_g \left[p - \frac{1.8e^2}{\epsilon} \right], \quad (3)$$

where E_g^0 denotes the band gap energy for the bulk material with large grain size ($d_g \gg \infty$) and m^* terms are the electron and hole effective masses, e is the charge of electron, ϵ is the dielectric constant and p represents the polarization term.

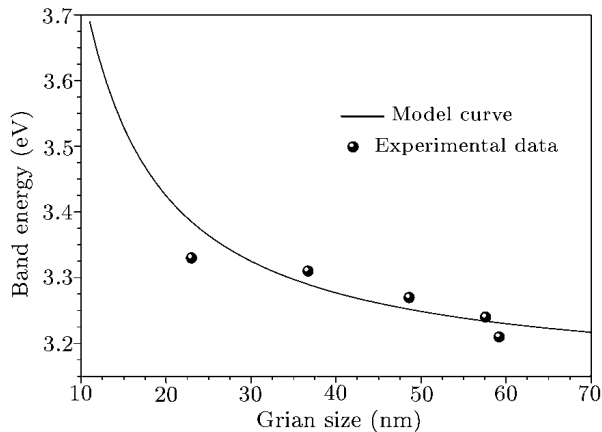


Fig. 4. The band gap energy of TiO₂ thin films versus their microstructures.

Although this figure indicates that the general trend predicted by model correlates with the experimental data, there are small deviations from the experimental results. It can be attributed to surface scattering and absorption of thin films.

If the value of the rms roughness is σ , then based on the Kirchhoff diffraction integral we can deduce reflectivity of rough interface as follows:^[10]

$$R_s = R_0 \exp \left[- \left(\frac{4\pi}{\lambda} \sigma n_0 \right)^2 \right], \quad (4)$$

then the transmissivity scattering loss can be expressed by^[10]

$$(SSL)_t = T_0 \left\{ 1 - \exp \left[- \left(\frac{2\pi}{\lambda} \sigma (n_1 - n_0) \right)^2 \right] \right\}, \quad (5)$$

where T_0 is the transmittance of ideal smooth interface, n_0 and n_1 is the refractive index of interface bilateral dielectric, and σ is the root mean square roughness of surface. It is obvious that the surface morphology of thin films has some effect on optical transmissivity, and especially this influence is rather evident in the short wavelength range. Figure 5 shows the rms roughness of the TiO₂ film surface by an atomic force microscope (AFM), and the rms roughness of thin film surface is so great that it decreases the transmissivity. Therefore, it is believed that the scattering contributes to the increase of the optical band gap energy, and moreover the absorption resulting from non-stoichiometry should also be responsible for the changes of the shape of the fundamental absorption

edge,^[11] which result in deviations from the theoretical results.

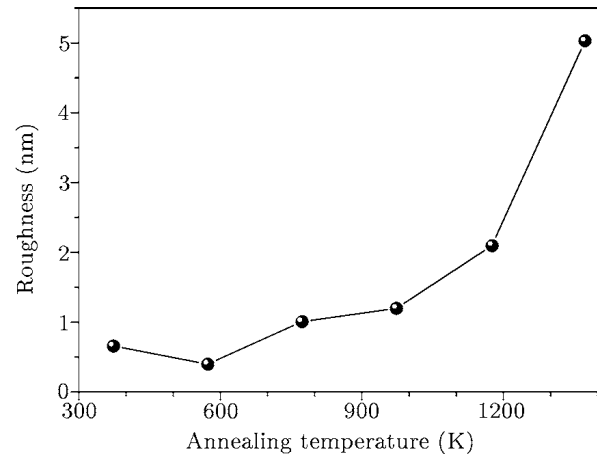


Fig. 5. The influence of annealing temperature on rms roughness of titania thin films. The rms roughness is calculated on the z scale from the AFM images.

In conclusion, TiO₂ thin films were prepared on fused silica substrates with conventional electron beam evaporation deposition. With the increasing annealing temperature, the grain size of TiO₂ thin films also grew. It has been found that there is a close relationship between their band gap energy and the grain size, which can be attributed to quantum confinement. A little deviation from the experimental results as well as other influences of the TiO₂ film microstructure such as scattering and absorption on band gap energy has also been discussed. The rms roughness of the TiO₂ film surface has been measured by an atomic force microscope (AFM), and other references and our analysis show that scattering and absorption contribute to the deviation from the theoretical results.

References

- [1] Weinberger B R and Garber R B 1995 *Appl. Phys. Lett.* **66** 2409
- [2] Mikhelashvili V and Eisenstein G 2001 *J. Appl. Phys.* **89** 3256
- [3] Radecka M, Zakrzewska K, Czternastek H and Sapinski T 1993 *Appl. Surf. Sci.* **65/66** 227
- [4] Chiang Y M, Lavik E B, Kosacki I, Tuller H L and Ying J Y 1996 *Appl. Phys. Lett.* **69** 185
- [5] Kosacki I and Anderson H U 1996 *Appl. Phys. Lett.* **69** 4171
- [6] Kosacki I, Petrovsky V and Anderson H U 1999 *Appl. Phys. Lett.* **74** 341
- [7] Asanuma T, Matsutani T, Liu C, Mihara T and Kiuchi M 2004 *J. Appl. Phys.* **95** 6011
- [8] He T, Ehrhart P and Meuffels P 1996 *J. Appl. Phys.* **79** 3219
- [9] Brus L E 1984 *J. Chem. Phys.* **80** 4403
- [10] Beckmann P and Spizzichino A 1963 *The Scattering of Electromagnetic Waves from Rough Surfaces* (New York: Pergamon)
- [11] Ting C C and Chen S Y 2000 *J. Appl. Phys.* **88** 4628
- [12] Martin N, Rousselot C and Rondot D 1997 *Thin Solid Films* **300** 113