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Spectroscopic ellipsometry characterization of TiO_2 thin films prepared by the sol–gel method

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Abstract

TiO_2 thin films were prepared on SiO_2/Si(100) substrates by the sol–gel process. XRD results indicate that the major phase of TiO_2 thin films is anatase. The surface morphology and cross-section are observed by FE-SEM. The surface of thin films is dense, free of cracks and flat. The average grain size is about 60–100 nm in diameter. The thickness of single layer TiO_2 thin films is about 60 nm, which increases with the concentration of solution. Ellipsometric angles ψ, Δ are investigated by spectroscopic ellipsometry. The optical constant and the thickness of TiO_2 thin films are fitted according to Cauchy dispersion model. The results reveal that the refractive index and the extinction coefficient of TiO_2 thin films in wavelength above 800 nm are about 2.09–2.20 and 0.026, respectively. The influences of processing conditions on the optical constants and thicknesses of TiO_2 thin films are also discussed.

Keywords: A. Films; Sol–gel processes; C. Optical properties; D. TiO_2

1. Introduction

Titanium oxide (TiO_2) thin films are of significance in many industrial applications such as photocatalysts [1], sensors [2], filter materials [3], dye-sensitive solar cells [4] and anti-reflection films [5]. For anti-reflection application, it is important to know the optical properties of thin films, especially the refractive index, the extinction coefficient and the thickness.

For accurate measurement of optical constants and thickness, many attempts and theories were established. Chiu et al. [6] used heterodyne interferometry to investigate the phase difference between parallel and perpendicular polarization light that was due to the total internal reflection. The refractive index of the test medium could be obtained after substituting the phase difference in the Fresnel equations. Zheng and Kikuchi [7] proposed an analytical method to determine the refractive index and the extinction coefficient of a weakly absorbing thin films by measuring the reflectance extreme and corresponding transmittance of thin films at normal incidence. Ramadan et al. [8] modified the Lloyd's mirage setup to obtain the reference phase distribution for the interference pattern and to measure monotonically varying refractive-index profiles of planar waveguides. Hamza et al. [9] provided the first trial to measure the refractive index and thickness of polymeric thin films using Lloyd's interference.

One of the most important techniques is spectroscopic ellipsometry [10], which has been found favorably for the non-destructive characterization of thin solid films and bulk materials, especially semiconductors. This technique is of high sensitivity, high accuracy, of being able to easily in situ measure both optical constants and thickness simultaneously. In this paper, TiO_2 thin films were prepared on SiO_2/Si(100) substrates through the sol–gel process. Spectroscopic ellipsometry was used to determine the optical constants and the thickness of TiO_2 thin films. The refractive index, the extinction coefficient and the thickness of TiO_2 thin films were fitted according to Cauchy dispersion model. The influences of different preparation conditions on the optical constants and thickness of TiO_2 thin films were also discussed.

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2. Experimental procedure

2.1. Preparation of TiO_2 thin films

TiO_2 thin films were grown through the sol–gel process using tetrabutyl titanate as titanium source, 2-methoxyethanol as solvent, acetylacetone as a chelate to stabilize the solution. At first, appropriate amounts of acetylacetone were dissolved in 2-methoxyethanol. Meanwhile, 5 wt% glycerol aqueous solution was added to increase the viscosity of solution. Then, tetrabutyl titanate was added drop by drop to the solution at 80 °C. After stirring for 30 min, the solution was filtrated. Finally, the transparent and homogenous solutions with Ti^{4+} concentrations of 0.4, 0.5 and 0.6 mol L^{-1} 1 were obtained.

In the film coating stage, firstly the solutions with different concentrations were spin-coated on SiO_2/Si(100) substrates at the spinning rate of 2000 r min^{-1} for 30 s. Then the as-prepared wet films were heat-treated at 100 °C for 10 min to promote the gelation. Finally, the as-prepared wet films were annealed at 700, 725 and 750 °C for 3 h in air at the rate of 1.5 °C min^{-1} from room temperature.

2.2. Characterization

The phase structure of TiO_2 thin films was characterized by X-ray diffraction (XRD, RIGAKU, D/MAX-2400, Cu Kα). The morphology of TiO_2 thin films was investigated by field emission scan electron microscopy (FE-SEM, JEOL, JSM-6700F). The relationships of ellipsometric angle ψ–λ, Δ–λ of TiO_2 thin films were investigated by a spectroscopic ellipsometry (SE, J.A. Woollam Co. Inc., M-2000UI). The optical constants, the thickness of TiO_2 thin films were fitted using the Cauchy dispersion model.

3. Results and discussion

3.1. XRD analysis

The XRD pattern of TiO_2 thin films annealed at 700 °C with 0.5 mol L^{-1} solution is shown in Fig. 1. XRD result reveals that the major phase of TiO_2 thin films is anatase. The diffraction peak at 32.99° is assigned to Si(100). The average crystallite size of TiO_2 thin films according to FHWM data of each diffraction peak is calculated to be 40 nm in diameter by the Scherrer equation.

3.2. FE-SEM analysis

Fig. 2 shows the FE-SEM images of single layer TiO_2 thin films annealed at 725 °C with 0.5 mol L^{-1}. The surface of TiO_2 thin films is dense and free of cracks. The grain size of TiO_2 thin films is about 80 nm.

Fig. 3 shows the cross-section view of TiO_2 thin films. It is observed that the thicknesses of TiO_2 thin films annealed at 700 and 725 °C are 44 and 52 nm with 0.5 mol L^{-1} solution, respectively.

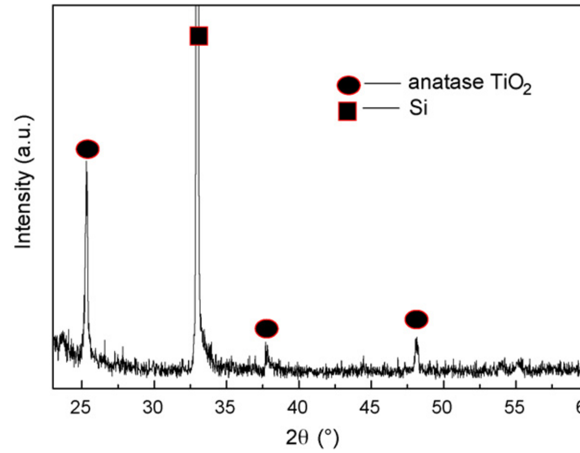

Fig. 1. XRD pattern of TiO_2 thin film annealed at 700 °C with 0.5 mol L^{-1} solution.

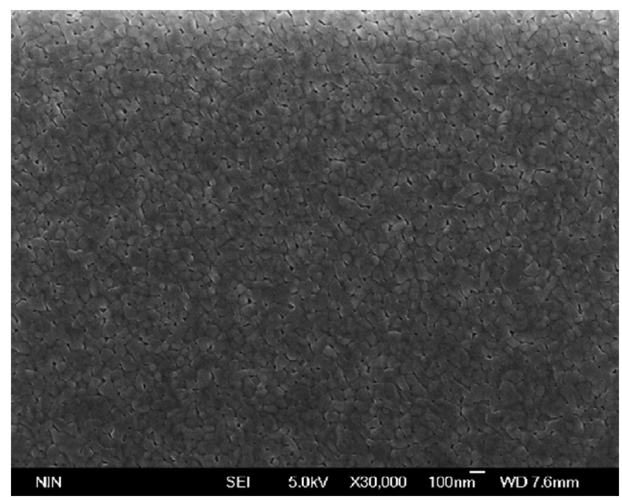

Fig. 2. FE-SEM images of TiO_2 thin films at 725 °C with 0.5 mol L^{-1}.

3.3. Optical constants and thickness of TiO_2 thin films

The complex reflectance ratio ρ of thin films is a function of ellipsometric factors of ψ and Δ. The fundamental equation of ellipsometry is described as follows:

$$\rho = \tan\psi e^{i\Delta} = f(n_1, n_2, n, \phi, d, \lambda, k) \quad (1)$$

where n_1, n_2 and n represent the refractive index of air, substrate and film, respectively. Φ and λ represent the incident angle and wavelength of incident light, respectively. d and k represent the thickness and extinction coefficient of thin films. In our experiment, the optical constants and thickness of Si substrate and SiO_2 layer were kept constant. The relationship of ψ–λ, Δ–λ were fitted under incident angle of 75° after adjusting n, d, k. Fitting the optical constants of thin films with a Cauchy dispersion model by ellipsometric parameters allow the determination of both thickness and optical constants of most transparent thin films. The mean square error (M.S.E.) is a destination function to evaluate the quality of the match between measured and model calculated data. M.S.E. could

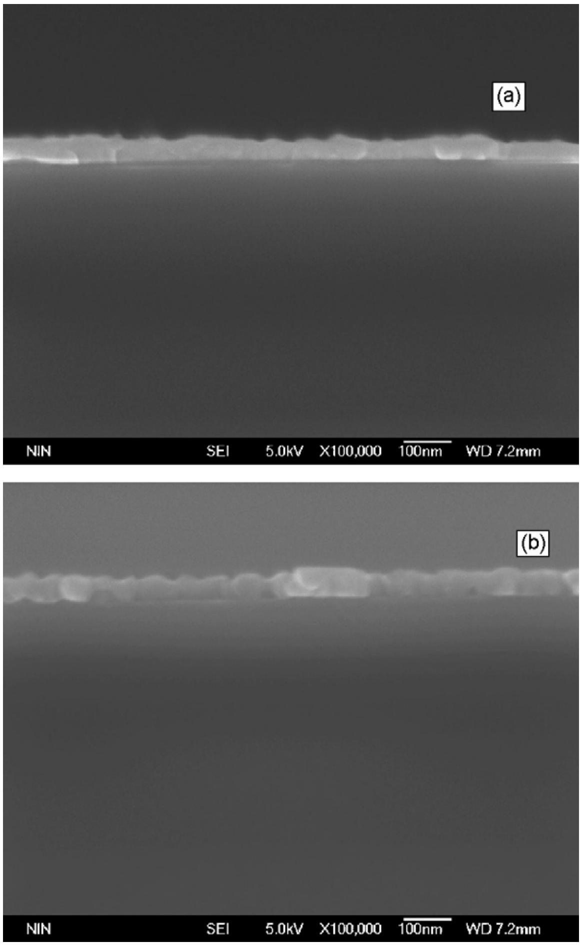

Fig. 3. FE-SEM images of cross-section of TiO_2 thin films annealed at 700 °C (a) and 725 °C (b) with 0.5 mol L^{-1} solution.

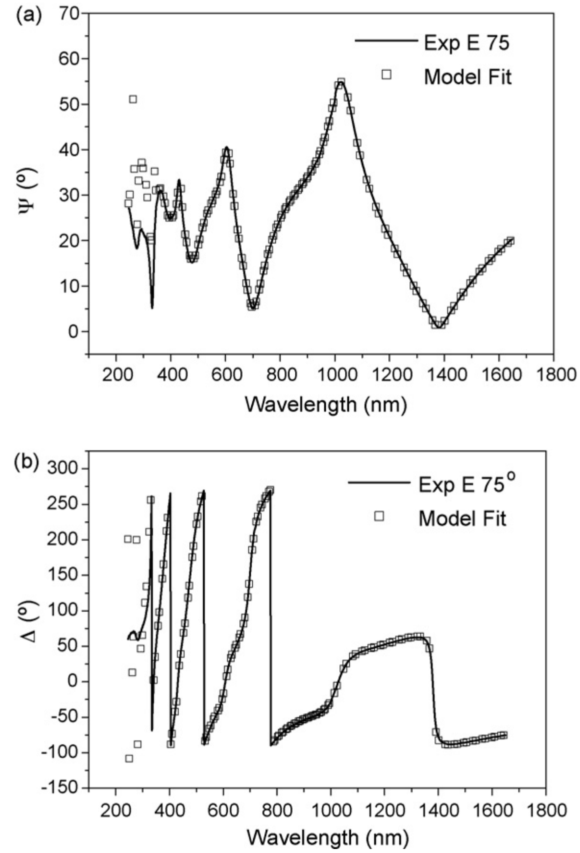

Fig. 4. Experimental and fitting results of Ψ–λ (a) and Δ–λ (b) of single layer TiO_2 thin films annealed at 700 °C with 0.5 mol L^{-1} solution.

be described as follows:

$$\text{M.S.E.} = \frac{1}{2N-M}\sum_{i=1}^{N}\left[\left(\frac{\psi_i^{\text{mod}} - \psi_i^{\text{exp}}}{\sigma_{\psi,i}^{\text{exp}}}\right)^2 + \left(\frac{\Delta_i^{\text{mod}} - \Delta_i^{\text{exp}}}{\sigma_{\Delta,i}^{\text{exp}}}\right)^2\right] = \frac{1}{2N-M}x^2 \quad (2)$$

where Δ and ψ represent the ellipsometric factors, superscript ''mod'' means the calculated data and superscript ''exp'' means the experimental data. N represents the number of (ψ, Δ). M is the number of variable parameters. σ is the standard mean square deviation.

Fig. 4 is the experimental and fitting results of Ψ–λ and Δ–λ of TiO_2 thin films annealed at 700 °C in the region of 245–1700 nm. It is obvious that the fitting results match very well with the experimental results in the region of 350–1700 nm. When the wavelength of incident light is less than 350 nm, a visible deviation between the fitting results and the experimental results was observed. In spectroscopic ellipsometry measurement, the underlying assumptions are (i) low absorption in the test wavelength, and (ii) surface uniformness in the region of incident light spot. Because of 3.2 eV (370 nm) band gap of anatase TiO_2 bulk crystal, the absorption will increase at the wavelength less than 370 nm. As a consequence, the obvious deviation appears at the wavelength less than 350 nm.

Fig. 5 is the fitting result of optical constants of TiO_2 thin films annealed at 700 °C with 0.4, 0.5 and 0.6 mol L^{-1} solutions. In Fig. 5, a similar tendency was observed according to the curves of reflective index and extinction coefficient. The reflective index and extinction coefficient are almost invariant in the mid-IR region from 800 to 1650 nm. When wavelength is less than 800 nm, the reflective index and extinction coefficient gradually increase with the decrease of wavelength and sharply increase at wavelength less than 350 nm. This wavelength threshold is corresponding to the band gap of anatase TiO_2 bulk crystal (3.2 eV). The value of reflective index of TiO_2 thin films annealed at 700 °C with 0.6 mol L^{-1} solution is about 2.09–2.13 in the wavelength range of 800–1650 nm. At the same time, the reflective index will increase with the decrease of the concentration of solution. It indicates that the porosity of TiO_2 thin films increase with the concentration of solution. The extinction coefficient is about 2.0×10^{-2} to 3.5×10^{-2} at the wavelength range of 800–1650 nm and increase with the concentration of solution. We believe that more pores are left in TiO_2 thin films after volatilization of organic materials with the thickness of thin films. As the consequence, the reflective index will decrease and the extinction coefficient increases with the porosity of thin films.

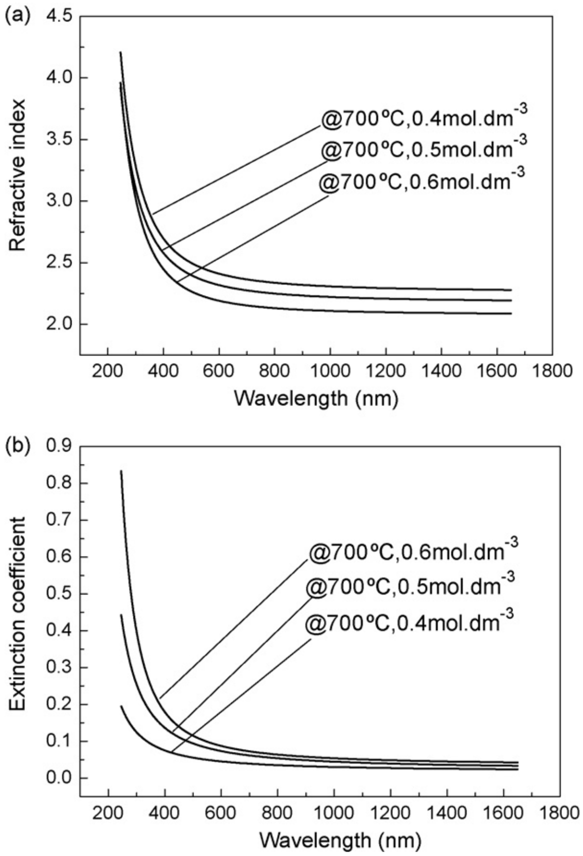

Fig. 5. Reflective index (a) and extinction coefficient (b) of single layer TiO_2 thin films annealed at 700 °C with different concentrations of solution.

The thickness fitted according to ellipsometric parameters of TiO_2 films annealed at 700, 725 and 750 °C with 0.5 mol L^{-1} solution are 48.2, 53.2 and 56.0 nm, respectively. The M.S.E. values of TiO_2 thin films above-mentioned are 51.15, 42.36 and 31.4, respectively, which are acceptable if applied as anti-reflection films in mid-IR region.

4. Conclusions

TiO_2 thin films were prepared through a sol–gel process. The main phase of TiO_2 thin films is anatase with mean crystallite sizes of about 80 nm. The thickness of single layer TiO_2 thin films is about 60 nm, which increase with the concentration of solution. The fitting results according to the ellipsometric spectroscopy indicate that the optical constants increase with the decrease of wavelength. The reflective index decreases with the concentration of solution. On the contrary, the extinction coefficient increases with the concentration of solution.

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