Research Article

Optical and Structural Properties of Titanium Dioxide Films from TiO_2 and Ti_3O_5 Starting Materials Annealed at Various Temperatures

Shih-Chang Shei

Department of Electrical Engineering, National University of Tainan, No. 33, Section 2, Shu-Lin Street, Tainan 70005, Taiwan

Correspondence should be addressed to Shih-Chang Shei; scshei@mail.nutn.edu.tw

Received 29 August 2013; Accepted 8 October 2013

Academic Editor: Shouu-Jinn Chang

Copyright © 2013 Shih-Chang Shei. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

We investigated the optical and structural properties of titanium dioxide films deposited from Ti_3O_5 and TiO_2 starting materials by electron beam evaporation at annealing temperatures from 400°C to 800°C. We find that the refractive index of as-deposited films from Ti_3O_5 starting material is higher than that of as-deposited films from TiO_2 starting material. In addition, during thermal annealing, the refractive index fluctuates slightly as compared with TiO_2 films from TiO_2 starting material. This should be attributed to the fact that the deposited molecules had a higher packing density, such that the film was denser. The transmittance spectra of TiO_2 films from Ti_3O_5 starting material indicate that transmittance edge slightly shifts to longer wavelength with the annealing temperature increasing when compared with TiO_2 starting material, in which the transmittance spectra indicate that the transmittance edge strongly shifts to longer wavelength with the same annealing temperature increasing. These findings should be attributed to the absence of oxygen and scattering of rough surface.

1. Introduction

Titanium dioxide (TiO_2) film is extensively used as a high refractive index film material in optical coating. It is a perfect couple with SiO_2 which is commonly used as a low refractive index film material to make thin film multilayer dielectric coatings consisting of alternating layers of high and low refractive index materials [1–3]. Titanium dioxide films can be prepared by most reactive coating techniques such as evaporation, sol-gel, sputtering, and plasma-enhanced chemical vapor deposition. In the case of evaporation, preferably electron beam evaporation, which is one of the most traditional methods because of high efficiency and low cost, is extensively used in scientific researches as well as in practical production. When TiO_2 films are prepared from TiO_2 starting material with the electronic beam evaporation method, the film is loose with a refractive index 1.9, which is obviously lower than the refractive index of the bulk [4–6]. According to the literature, Duyar et al. reported that it is quite difficult to obtain films with reproducible and stable optical properties, in particular, for materials that exist in a

number of different stoichiometric forms of the system Ti-O. Whenever TiO , Ti_2O_3 , or TiO_2 is evaporated, the vapor may consist of various Ti-O combinations, which change as the evaporation continues. The refractive index of the deposited film, thus, is not constant because most Ti-O materials evaporate noncongruently. If, however, Ti_3O_5 is evaporated as starting composition, the only titanium species in the vapour is TiO , and the oxygen content in the vapour remains constant [7, 8]. Furthermore, the refractive index is higher than TiO_2 starting material due to the higher packing density [9]. Many researchers have reported the deposition of TiO_2 films from Ti_3O_5 starting material by electron beam evaporation. However, TiO_2 films are loosely packed which is caused by low molecular mobility. It indicates that the refractive index is lower than the bulk [9, 10]. Therefore, it is necessary for annealing to increase molecular mobility and make them more bulk-like. During annealing, thermal energy provides the mobility of the molecules, so the loose film becomes slimmer and increases the refractive index as the temperature increases. Many papers have reported that TiO_2 films from Ti_3O_5 starting material were annealed at rather low

FIGURE 1: Transmittance spectra obtained from (a) Ti_3O_5 and (b) TiO_2 starting materials at various thermal annealing temperatures.

FIGURE 2: Refractive index obtained from (a) Ti_3O_5 and (b) TiO_2 starting materials at various thermal annealing temperatures.

temperature [11–13]. For example, Chen et al. reported that TiO_2 films were deposited from Ti_3O_5 starting material by ion-assisted deposition. The refractive index increased with the substrate temperature from 150°C to 250°C; they thought that the deposited molecules had greater surface mobility, so the film was denser, with a higher refractive index. They also found that the refractive index with the substrate temperature of 150°C increased from 100°C to 200°C during annealing and declined as the annealing temperature decreased from 200°C to 300°C. Such a variation was caused by the loss of oxygen below 200°C during annealing and by the capture of oxygen as the temperature was increased above 200°C. Therefore,

some suboxides (TiO_x) were separated from titanium oxide and oxidized during annealing. These findings revealed that the film was too loose to have a large surface area, which made it lose and capture oxygen easily at a substrate temperature of 150°C [12]. Jaing et al. reported that TiO_2 films were deposited from Ti_3O_5 starting material by ion-assisted deposition. They showed that the refractive index fluctuated irregularly with the annealing temperature below 350°C. However, the refractive index increased with the annealing temperature from 350°C to 450°C; they thought that the film became denser as the annealing temperature increased above 350°C because the refractive index showed the densification of the

FIGURE 3: Cross-sectional view by SEM of the TiO_2 films from (a) Ti_3O_5 and (b) TiO_2 starting materials annealed at 400°C, 600°C, and 800°C.

film. This was due to the loss of oxygen and large thermal energy during annealing at temperatures of over 350°C [13]. According to the open literature, little further research was devoted to discuss the fluctuation of refractive index and the phenomenon of cutoff wavelength shift to longer wavelength when TiO_2 films from Ti_3O_5 starting material were annealed at above 400°C. The main aims of this research were to investigate the effect of annealing temperature on the theoretically explained reason for cutoff wavelength shift to long wavelength. We also compared with from TiO_2 starting material.

2. Experiment

TiO_2 films were deposited upon double-polishing sapphire substrate at room temperature by electron beam evaporation. Ti_3O_5 and TiO_2 were used as the starting materials, and the deposition rate was about 0.13 nm/s. The vacuum chamber was pumped to a base pressure of less than 5×10^{-5} torr before deposition, and the working pressure was kept at approximately 4×10^{-4} torr throughout the deposition process. During deposition, thickness controller with a quartz oscillator was used to monitor the thickness of TiO_2 films, which deposited at about 190 nm. Finally, TiO_2 films were annealed from 400°C to 800°C in step 200°C for 30 min by furnace in air environment. The crystallization of the film was analyzed by an X-ray diffraction meter (XRD). The thickness of the film was observed by a field emission scanning electron microscopy (JSM7000). The refractive index and transmittance were measured by n&k analyzer (n&k analyzer 1280). XPS surface analysis was performed using an Auger Electron Spectroscopy (JAMP9500F) employing an $\text{Mg K}\alpha$ X-ray source. The surface roughness was observed by atomic force microscopy (AFM). The root mean square (RMS) surface roughness values were obtained using the software which comes with the instrument.

3. Results and Discussion

Figure 1(a) presents the transmittance spectra of TiO_2 film from Ti_3O_5 starting material during thermal annealing. The

transmittance decreased weakly as the annealing temperature was increased to 400°C. In contrast, as the annealing temperature was increased to 600°C, the transmittance increased and the spectra shifted back to shorter wavelengths. On the other hand, the transmittance decreased slightly and the spectra shifted to longer wavelength as the annealing temperature was increased to 800°C. Figure 1(b) presents the transmittance spectra of TiO_2 film from TiO_2 starting material during thermal annealing. As the annealing temperature was increased to 400°C and 600°C, the transmittance decreased and the spectra shifted to longer wavelength. On the other hand, as the annealing temperature was increased to 800°C, the transmittance decreased and the spectra shifted to longer wavelength. Figure 2 plots the refractive index versus wavelength and annealing temperature. As shown in Figure 2(a), the refractive index rose as the annealing temperature was increased to 400°C but declined as the temperature was increased further from 400°C to 800°C. Such a variation was attributed to the loss of oxygen as the annealing temperature decreased below 400°C. The film contained some lower suboxides that were attributable to the titanium oxide [11]. As the annealing temperature was raised from 400°C to 800°C, the film captured oxygen from the air to yield the oxide. This finding is explained below with reference to XPS measurement. As shown in Figure 2(b), the refractive index rose as the annealing temperature increased to 800°C but declined as the annealing temperature decreased below 800°C. This finding is also explained below with reference to the XPS measurements. From measured results, we can find that the refractive index of as-deposited films from Ti_3O_5 starting material is higher than that of films as-deposited from TiO_2 starting material. In addition, it should be noted that the refractive indexes shown in Figure 2(b) fluctuate strongly as compared with those measured refractive indexes shown in Figure 2(a). This should be attributed to the fact that the deposited molecules had a higher packing density, such that the film was denser [9]. This finding is illustrated below with reference to SEM measurement. Thus, Ti_3O_5 material used as the starting material should be good choice for a high refractive index film. Figures 3(a) and 3(b) show the thickness of the TiO_2 films from Ti_3O_5 and TiO_2 starting

FIGURE 4: XPS spectra of TiO_2 films annealed at various temperatures: (a) $\text{Ti } 2p^{3/2}$ and (b) O1s from Ti_3O_5 starting material and (c) $\text{Ti } 2p^{3/2}$ and (d) O1s from TiO_2 starting material.

materials at different annealing temperatures, respectively. As shown in Figure 3(a), as the annealing temperature increased to 800°C, the loose film became less slim. On the other hand, as shown in Figure 3(b), as the annealing temperature increased to 800°C, the loose film became slimmer. Due to the aforementioned reason, from Figure 3(a), it is clear that the TiO_2 film from Ti_3O_5 starting material has higher packing density. In contrast, in Figure 3(b), it is apparent that the TiO_2 film has lower packing density.

As shown in Figure 4, X-ray photoelectron spectroscopy (XPS) measurement was used to certify both the binding energy of the $\text{Ti } 2p$ line and variation of the O1s line. The peaks at 458.8 and 457.8 eV in the spectra correspond to Ti^{4+} and Ti^{3+} , respectively [14]. Figure 4(a) shows that the binding energy of the $\text{Ti } 2p^{3/2}$ peak from 458.8 eV as-deposited, to 457.8 eV, 400°C annealed, corresponds to a transition from Ti^{4+} to Ti^{3+} ; this indicates that titanium oxides lost oxygen, exhibiting the properties of the lower suboxides. On the other hand, the binding energy (458.8 eV) of the film annealed at

600°C reveals that the film captured oxygen from the air to yield the oxide [11]. Figure 4(b) reveals that the O1s line (near 529.9 eV) varies with the annealing temperature. The peak at lower binding intensity, 529.9 eV, for the film annealed at 400°C is attributed to defective oxides. In contrast, the peak at higher binding energy, 529.9 eV, for the film annealed at 600°C is attributed to oxides. As shown in Figure 4(c), the $\text{Ti } 2p^{3/2}$ peak from 458.8 eV as-deposited, to 457.8 eV, 800°C annealed, corresponds to a transition from Ti^{4+} to Ti^{3+} ; this indicates that titanium oxides lost oxygen, exhibiting the properties of the lower suboxides. On the other hand, the binding energy (458.8 eV) of the film annealed at 600°C reveals that the film captured oxygen from the air to yield the oxide [14]. Figure 4(d) reveals that the O1s line (near 529.9 eV) varies with the annealing temperature. The peak at lower binding intensity, 529.9 eV, for the film annealed at 800°C is attributed to defective oxides. In contrast, the peak at higher binding intensity, 529.9 eV, for the film annealed at 600°C is attributed to oxides.

FIGURE 5: Partial enlarged drawing of transmittance spectra from (a) Ti_3O_5 and (b) TiO_2 starting materials in the wavelength region between 300 and 350 nm.

FIGURE 6: Surface morphology ($2 \times 2 \mu\text{m}$) by AFM of TiO_2 films from (a) Ti_3O_5 and (b) TiO_2 starting materials annealed at 400°C , 600°C , and 800°C .

In order to investigate the phenomenon of cutoff wavelength shift to longer wavelength, the partial enlarged drawing of transmittance spectra from Ti_3O_5 and TiO_2 starting material in the wavelength region between 300 and 350 nm is shown in Figure 5. As shown in Figure 5(a), the transmittance spectra indicate that the transmittance edge slightly shifts to longer wavelength with the annealing temperature increasing. Compared with TiO_2 starting material, the transmittance spectra indicate that the transmittance edge strongly shifts to longer wavelength with the same annealing temperature increasing as shown in Figure 5(b). It can be interpreted that both scattering and absorption loss increase as a result of surface roughness increase and absence of oxygen. The scattering loss results from surface roughness and bulk defects such as particles and microcracks. But the scattering loss posed by

surface roughness, namely, surface scattering loss (SSL), plays a principal role in general. If the value of the root mean square roughness is σ , we can deduce the transmission scattering loss that can be expressed as [15]

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

where T_0 is the transmittance of ideal smooth interface and n_0 and n_1 are the refractive index of interface bilateral dielectric. On the other hand, the relationship between absorption coefficient and concentration of free carriers can be written as [14]

$$a = \frac{Ne^2\lambda_0^2}{\varepsilon_0 m^* 8\pi n c^3 \tau}, \quad (2)$$

FIGURE 7: Influence of annealing temperature on RMS roughness of TiO₂ films from Ti₃O₅ and TiO₂ starting materials.

FIGURE 8: Optical band gap of as-deposited, annealed at 400°C, 600°C, and 800°C.

where a is absorption coefficient, N is the concentration of free carrier, n is the refractive index, m^* is the effective mass of free carrier, τ is relax time, and λ_0 is absorption wavelength. So the total optical loss I_{loss} of the transmittance at cutoff wavelength should consist of absorption α_a and scattering (SSL)_t:

$$I_{\text{loss}} = \alpha_a + (\text{SSL})_t. \quad (3)$$

Thus, based on the analysis above, we can conclude that the cutoff wavelength shift results from absence of oxygen

FIGURE 9: X-ray diffraction patterns of TiO₂ films from Ti₃O₅ and TiO₂ starting materials annealed at different temperature.

and scattering of rough surface. Clearly, the cutoff wavelength shift has great dependence on the surface topography. Therefore, we can acquire important information of surface topography. The evolution of surface topography by AFM of TiO₂ films from Ti₃O₅ and TiO₂ starting materials was illustrated in Figures 6(a) and 6(b), respectively, and the experimental results evidently indicated that surface topography depends strongly on the thermal treatment. The relationship between the root mean square (RMS) roughness by AFM and annealing temperature is shown in Figure 7. It is found that RMS of TiO₂ films from Ti₃O₅ starting material increases from 1.02 nm as-deposited to 1.08 nm at 400°C, and if the annealing temperatures increase further, the RMS value increases as well and reaches 4.22 nm for 800°C. It is also found that the grain size also grows from 40 nm to 101 nm. In contrast, it is found that RMS of TiO₂ films from TiO₂ starting material increases from 1.17 nm as-deposited to 1.25 nm at 400°C, and if the annealing temperatures increase further, the RMS value increases as well and reaches 1.91 nm for 800°C. The grain size also grows from 45 nm to 66 nm. Due to the aforementioned reason, we can find that TiO₂ film from TiO₂ starting material is very serious cutoff wavelength shift with the annealing temperature increasing. In contrast, the TiO₂ film from Ti₃O₅ starting material is less cutoff wavelength shift with the same annealing temperature increasing.

As shown in Figure 8, the direct optical band gap values (Eg) are 3.43, 3.43, and 3.4 eV for TiO₂ films from Ti₃O₅ starting material annealed at 400°C, 600°C, and 800°C, respectively. On the other hand, the direct optical band gap values (Eg) are 3.52, 3.51, and 3.33 eV for TiO₂ films from TiO₂ starting material annealed at 400°C, 600°C, and 800°C, respectively. From the graph, it is clear that the optical band gap of TiO₂ films is obviously affected by the absence of oxygen and scattering of rough surface. Specifically, the optical band gap of TiO₂ films from TiO₂ starting material from 3.53 eV as-deposited, to 3.33 eV, 800°C annealed, indicates serious absence of oxygen. In contrast, the optical band gap of TiO₂ films from Ti₃O₅ starting material from 3.43 eV

as-deposited, to 3.4 eV, 800°C annealed, indicates serious scattering of rough surface.

Figure 9 presents the X-ray diffraction patterns of the TiO₂ film from TiO₂ and Ti₃O₅ starting materials deposited onto the sapphire substrate and annealed at different temperature. The films are amorphous before annealing. At 400°C, 600°C, and 800°C the preferred (101) orientation reveals that the film exhibited a single phase anatase structure [11, 13, 14, 16]. In addition, there were two weak diffraction peaks, anatase (200) and (211), appearing in the pattern of TiO₂ films annealed at 400°C, 600°C, and 800°C. The crystallization of the TiO₂ films was evidently improved by annealing. After annealing, the structure of the TiO₂ film was in the anatase phases with the preferential crystalline orientation of (101). We can assume that the as-deposited films are amorphous due to the low mobility of molecules depositing on the cold substrate. We can find that the TiO₂ films from Ti₃O₅ starting material have strong diffraction peaks at 400°C, 600°C, and 800°C.

4. Conclusion

In this study, we deposited TiO₂ films from Ti₃O₅ and TiO₂ starting materials onto sapphire substrate with electron beam evaporation and then annealed as the temperature increased from 400°C to 800°C. We find that the refractive index of as-deposited films from Ti₃O₅ starting material is higher than that of films as-deposited from TiO₂ starting material. In addition, during thermal annealing, the refractive index fluctuates slightly as compared with TiO₂ films from TiO₂ starting material. This should be attributed to the fact that the deposited molecules had a higher packing density, such that the film was denser. The transmittance spectra of TiO₂ films from Ti₃O₅ starting material indicate that transmittance edge slightly shifts to longer wavelength with the annealing temperature increasing. Compared with TiO₂ starting material, the transmittance spectra indicate that the transmittance edge strongly shifts to longer wavelength with the same annealing temperature increasing. These findings should be attributed to the absence of oxygen and scattering of rough surface. The optical band gap of TiO₂ films from TiO₂ starting material from 3.53 eV as-deposited, to 3.33 eV, 800°C annealed, indicates serious absence of oxygen. In contrast, the optical band gap of TiO₂ films from Ti₃O₅ starting material from 3.43 eV as-deposited, to 3.4 eV, 800°C annealed, indicates serious scattering of rough surface.

References

- [1] S. J. Chang, C. F. Shen, M. H. Hsieh et al., "Nitride-based LEDs with a hybrid Al mirror +TiO₂/SiO₂ DBR backside reflector," *Journal of Lightwave Technology*, vol. 26, no. 17, pp. 3131–3136, 2008.
- [2] C. Yang, H. Fan, Y. Xi, J. Chen, and Z. Li, "Effects of depositing temperatures on structure and optical properties of TiO₂ film deposited by ion beam assisted electron beam evaporation," *Applied Surface Science*, vol. 254, no. 9, pp. 2685–2689, 2008.
- [3] Y.-C. Liu, Y.-F. Lu, Y.-Z. Zeng, C.-H. Liao, J.-C. Chung, and T.-Y. Wei, "Nanostructured mesoporous titanium dioxide thin film prepared by sol-gel method for dye-sensitized solar cell," *International Journal of Photoenergy*, vol. 2011, Article ID 619069, 2011.
- [4] A. D. Barros, K. F. Albertin, J. Miyoshi, I. Doi, and J. A. Diniz, "Thin titanium oxide films deposited by e-beam evaporation with additional rapid thermal oxidation and annealing for ISFET applications," *Microelectronic Engineering*, vol. 87, no. 3, pp. 443–446, 2010.
- [5] J. Shin, K. Lee, J. Koh et al., "Hydroxyapatite coatings on nanotubular titanium dioxide thin films prepared by radio frequency magnetron sputtering," *Journal of Nanoscience and Nanotechnology*, vol. 13, no. 8, pp. 5807–5810, 2013.
- [6] E. D. Palik, *Handbook of Optical Constants of Solids*, Academic Press, Washington, DC, USA, 1991.
- [7] Ö. Duyar, F. Placido, and H. Zafer Durusoy, "Optimization of TiO₂ films prepared by reactive electron beam evaporation of Ti₃O₅," *Journal of Physics D*, vol. 41, no. 9, Article ID 095307, 2008.
- [8] F. Waibel, E. Ritter, and R. Linsbod, "Properties of TiO_x films prepared by electron-beam evaporation of titanium and titanium suboxides," *Applied Optics*, vol. 42, no. 22, pp. 4590–4593, 2003.
- [9] H. Selhofer, E. Ritter, and R. Linsbod, "Properties of titanium dioxide films prepared by reactive electron-beam evaporation from various starting materials," *Applied Optics*, vol. 41, no. 4, pp. 756–762, 2002.
- [10] F. X. Wang, C. K. Hwangbo, B. Y. Jung, J. H. Lee, B. H. Park, and N. Y. Kim, "Optical and structural properties of TiO₂ films deposited from Ti₃O₅ by electron beam," *Surface and Coatings Technology*, vol. 201, no. 9–11, pp. 5367–5370, 2007.
- [11] C.-C. Lee, H.-C. Chen, and C.-C. Jaing, "Effect of thermal annealing on the optical properties and residual stress of TiO₂ films produced by ion-assisted deposition," *Applied Optics*, vol. 44, no. 15, pp. 2996–3000, 2005.
- [12] H.-C. Chen, C.-C. Lee, C.-C. Jaing, M.-H. Shiao, C.-J. Lu, and F.-S. Shieu, "Effects of temperature on columnar microstructure and recrystallization of TiO₂ film produced by ion-assisted deposition," *Applied Optics*, vol. 45, no. 9, pp. 1979–1984, 2006.
- [13] C.-C. Jaing, H.-C. Chen, and C.-C. Lee, "Effects of thermal annealing on titanium oxide films prepared by ion-assisted deposition," *Optical Review*, vol. 16, no. 3, pp. 396–399, 2009.
- [14] J. Yao, J. Shao, H. He, and Z. Fan, "Effects of annealing on laser-induced damage threshold of TiO₂/SiO₂ high reflectors," *Applied Surface Science*, vol. 253, no. 22, pp. 8911–8914, 2007.
- [15] G. Tian, L. Dong, C. Wei, J. Huang, H. He, and J. Shao, "Investigation on microstructure and optical properties of titanium dioxide coatings annealed at various temperature," *Optical Materials*, vol. 28, no. 8–9, pp. 1058–1063, 2006.
- [16] X. Cheng, S. Hu, P. Zeng, T. Kuang, G. Xie, and F. Gao, "Structure and properties of TiO₂ films prepared by ion beam assisted deposition," *Surface and Coatings Technology*, vol. 201, no. 9–11, pp. 5552–5555, 2007.