Photocarrier dynamic measurement of rutile TiO₂ films prepared by RF magnetron reactive sputtering

Guangmiao Wan ^a, Shenwei Wang ^a, Ling Li ^a, Guangyao Mu ^a, Xue Yin ^a, Xinwu Zhang ^a, Ying Tang ^b, and Lixin Yi ^{a, *}

^a Key Laboratory of Luminescence and Optical Information, Ministry of Education, Institute of Optoelectronic Technology, Beijing Jiaotong University, Beijing 100044, China

^b School of Science, Beijing Jiaotong University, Beijing 100044, China

*Corresponding author.

Abstract

In this work, rutile titanium dioxide (TiO₂) films were prepared on quartz and SiO₂/Si substrates utilizing RF magnetron reactive sputtering technology. Crystal structure, surface morphology and optical property of these films were characterized to verify the obtainment of well crystalline rutile TiO₂ films. The dynamics of photocarriers were studied by using temporally resolved transient absorption measurements. The differential reflectivity as a function of pump fluence was investigated. We also directly obtained a carrier lifetime of about 286 ps. The absorption cross-section and the absorption coefficient of free carrier at 800 nm were $1.87 \times 10^{-17} \text{ cm}^2$ and 32.9 cm^{-1} , respectively.

Keywords: Rutile titanium dioxide; Sputtering; Thin films; Carrier dynamics; Free carrier absorption

1. Introduction

In recent years, titanium dioxide (TiO₂) has drawn great attention and been widely investigated due to its optical and electronic properties. TiO₂ thin films have various applications, such as photocatalysis [1], dye sensitized solar cells [2], biomaterials [3],

optical coatings [4], gas sensors [5], dielectric capacitors [6] and electrochromism [7]. It is known that TiO₂ has three types of crystalline phases, namely, rutile, anatase and brookite. Among them, rutile has superior properties for its higher thermal stability, refractive index and dielectric constant [8, 9].

To gain rutile TiO₂ films, several deposition techniques were developed, such as thermal oxidation [10], magnetron sputtering [11], chemical vapor deposition [12], roasting processing [13], spray pyrolysis [14], hydrolysis [15], chemical bath deposition [16], and sol-gel [17]. Among them, magnetron sputtering showed promise to improve the efficiency of producing rutile TiO₂ films. Recently, properties of rutile TiO₂ films have been studied by several groups. Gao et al. reported photocatalytic activities of rutile TiO₂ nanoflower arrays on mica particles [15]. Zemen et al. investigated self-cleaning and antifogging effects of TiO₂ films [18]. Sumita et al. researched photo-induced surface charge separation of highly oriented TiO₂ thin films [19]. However, to our knowledge, photocarrier dynamic of rutile TiO₂ film have not been studied.

In this paper, rutile TiO₂ films were prepared on quartz and SiO₂/Si substrates using RF magnetron reactive sputtering. Crystal structure, surface morphology and optical property of these films were investigated to verify the obtainment of rutile TiO₂. Photocarrier dynamic of the films was studied using transient reflectivity measurement.

2. Experimental

TiO₂ films were prepared on quartz glasses and silicon substrates with a 200 nm SiO₂ layer using RF (13.56 MHz) magnetron reactive sputtering on a Line 420 (Alliance Concept) with a titanium target (5N purity). The distance between the target and the substrate was 50 mm. The background pressure was 5.5×10^{-5} Pa in the process chamber. O₂

(5N purity) and Ar (5N purity) were used as reactive and working gases, respectively. And the Ar/O₂ flow ratio was kept constant at 15:5 (sccm/sccm). All depositions were carried out keeping RF power at 500 W without substrate heating. The working pressure was maintained at 0.1 Pa during sputtering. The thickness of the films was 70 nm. Finally, the films were annealed in O₂ (5N purity) for 1 h at 300°C, 400°C, 500°C and 600°C.

Crystal structures of films were characterized and analyzed by X-ray diffraction (XRD) and Raman spectroscopy. Surface morphologies of films were observed using scanning electron microscopy (SEM). Optical properties of films were measured by UV-Vis-NIR scanning spectrophotometer. Photocarrier dynamic of films deposited on SiO₂/Si substrates were tested by transient reflectivity measurement. All these measurements were made at room temperature.

The transient reflectivity measurement setup is shown schematically in Fig. 1. A Ti:sapphire laser is used to emit 100 fs pulses at 80 MHz with a central wavelength of 800 nm. A portion of the output is reflected by a beamsplitter and focused to a beta barium borate (BBO) crystal to generate the second harmonic at 400 nm. This beam is used as the pump pulse. The other portion of the output is used as the probe pulse. Then, the two beams are guided by some beamsplitters and focused to the sample surface through a microscope objective lens with a spot size of about 2 μm. To measure the differential reflectivity as a function of the probe delay, defined as the time delay of the probe pulse with respect to the pump pulse, we change the length of the probe arm by moving a retroreflector in the probe arm.

The reflected probe beam is sent to one photodiode of a balanced detector. A portion of the probe beam is reflected to the other photodiode and used as reference beam, before

entering the sample. The balanced detector outputs a voltage which is proportional to the difference between the powers of the two probe beams. With the pump beam blocked, we can regulate the power of the reference beam to set the outputs as zero. The relative change of reflected probe beam is defined as the differential reflectivity, $\Delta R/R_0 = (R-R_0)/R_0$, where R and R_0 are the reflectivity of the probe beam with and without the pump beam, respectively.

3. Results and discussion

3.1 Crystal structure

XRD patterns of the TiO₂ films that deposited on quartz substrates and annealed in O₂ for 1 h at various temperature ~~was~~ **are** shown in Fig. 2a. The obtained diffraction peaks were identified by comparison with JCPDS file no. 21-1276. The diffraction peak intensity of (110) plane became stronger as the annealing temperature increased. What's more, (210) and (220) planes of rutile TiO₂ appeared when the annealing temperature exceeded 500°C. The average crystal size of TiO₂ films is estimated by Scherrer's equation [20] as follows:

$$D = 0.89\lambda/\beta\cos\theta \quad (1)$$

where D denotes the average crystal size of TiO₂ films, $\lambda = 0.154$ nm is the X-ray wavelength of Cu K α , β is the full width at half maximum intensity (FWHM) and θ is the Bragg's angle of the peak. The average crystal size of the TiO₂ film annealed in O₂ for 1 h at 600°C is 74 nm.

Fig. 2b shows Raman ~~spectrum~~ **spectra** of the prepared films. Typical rutile bands can be observed at 235, 447, and 612 cm⁻¹. As the annealing temperature increasing, **the** improvement of intensities of the Raman bands indicates an enhancement of crystallinity of the films.

3.2 Surface morphology

Surface morphologies of the films by SEM images are shown in Fig. 3(a-e). It can be observed that the ~~film~~ as-deposited ~~film~~ has a fairly smooth surface (Fig. 3a). Whereas, grain aggregation appeared after the film was annealed and the average crystal size of TiO₂ films became larger as the annealing temperature increased, which agrees with Agnarsson [21]. And Fig. 3e shows that the TiO₂ film annealed at 600°C has an average crystal size of about 70 nm, which is consistent with the result of XRD.

3.3 Optical Property

A spectral transmittance measurement was implemented and the optical band gap of the TiO₂ film was ascertained. As is shown in Fig. 4a that shapes and intensities of transmittance spectra of samples are approximate. But, red shift of transmittance spectra was observed as the annealing temperature increased. The TiO₂ film has an average transmittance of 80.2% in the range of 400-760 nm after annealed at 600°C in O₂ for 1 h. The fluctuation of transmittance curve is caused by interference of multiple reflections between the two surfaces of the thin film [22].

The optical band gap of TiO₂ films can be calculated based on the basis of UV-vis absorption edge by the Tauc equation [23]:

$$\alpha h\nu = A(h\nu - E_g)^n \quad (2)$$

where $h\nu$ is the photon energy, A is a constant, E_g is the optical band gap, n is a number that determined by the nature of transition and has values of 2 and 1/2 for indirect and direct transitions, respectively. And α is the optical absorption coefficient and can be calculated using the formula [24]:

$$\alpha = -\ln T/d \quad (3)$$

where T is the transmittance and d is the thickness of the films. Optical band gap value can be extrapolated in a standard manner from a plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$, by drawing a intercept of the tangent to the curve. Fig. 4b indicates that optical band gap values of the TiO_2 films as-deposited and annealed in O_2 for 1 h at various temperature are 3.08, 3.12, 3.10, 3.06 and 3.02 eV, respectively. The optical band gap value of the film annealed at 600°C is consistent with theoretical value of rutile [25].

3.4 Photocarrier dynamic

We confirmed that well crystalline rutile TiO_2 films were obtained after annealed at 600°C in O_2 , through the measurements mentioned above. Then, photocarrier dynamic of the films deposited on SiO_2/Si substrates were studied, since opaque substrates are necessary in a by transient reflectivity measurement. The differential reflectivity is was measured with a pump pulse of 400 nm and a probe pulse of 800 nm. With a pump fluence of $59 \mu\text{J cm}^{-2}$ and an absorption coefficient of $1.66 \times 10^4 \text{ cm}^{-1}$ at 400 nm referring to Eq. 3, the carrier density could be calculated as $1.76 \times 10^{18} \text{ cm}^{-3}$ by using the formula [26]:

$$N = \alpha f e^{-\alpha z} / (h\nu) \quad (4)$$

where N is the carrier density, f is the pump fluence and z is the optical passing depth into the sample. It can be seen from Fig. 5a that the signal reaches a peak at about 2.3×10^{-4} near zero probe delay, meaning that the photocarriers injected by the pump pulse result in a maximal signal level instantaneously. The decay of the signal remains about hundreds of ps and could be fit by a biexponential function, as shown in Fig. 5a as the red curve.

Since the probe photon energy (1.55 eV) is smaller than the bandgap of rutile TiO_2 ,

interband absorption is forbidden. Instead, free carrier absorption (FCA) occurs. In this case, the probe photon could be absorbed, and the free carriers that excited to the conduction and valance bands by the pump pulse will be excited up to higher energy levels of the respective bands. The total absorption coefficient of the probe photon could be written as [27]:

$$\alpha_T = \alpha + \sigma N \quad (5)$$

where α is an absorption coefficient unrelated to carriers, σ is the absorption cross-section of free carrier and could be calculated using the formula [27]:

$$\Delta R/R_0 = \sigma L N \quad (6)$$

where L is the thickness of the films, and σN is the absorption coefficient of free carrier. By using the values of parameters mentioned above, the absorption cross-section and the absorption coefficient of free carrier at 800 nm are $1.87 \times 10^{-17} \text{ cm}^2$ and 32.9 cm^{-1} , respectively.

In order to study the influence of the photocarrier density on the dynamics, we repeated the measurement with different values of pump fluences. As shown in Fig. 5b, a linear relationship between the pump fluence and the peak value of the signal is observed, which indicates the absence of the exciton quenching effect.

Fig. 5c shows the biexponential fit results of the signals. It can be observed that time constants are independent of the pump fluence, which means that the dynamics of the photocarriers are not impacted by multicarrier processes. The time constant of about 286 ps can be attributed to the lifetime of the photocarriers.

4. Conclusions

Rutile TiO_2 films have been deposited on quartz glasses and SiO_2/Si substrates by RF

magnetron reactive sputtering technology. Crystal structure, surface morphology and optical property of these films were characterized to verify the obtainment of well crystalline rutile TiO₂ films. The dynamics of photocarrier of rutile TiO₂ films were studied by using a temporally resolved transient absorption measurement. The differential reflectivity as a function of pump fluence was investigated. The decay of the signal could be fit by a biexponential function. The time constant of about 286 ps can be attributed to the lifetime of photocarriers. The differential reflectivity here resulted from FCA of the probe pulse. The absorption cross-section and the absorption coefficient of free carrier at 800 nm are found be $1.87 \times 10^{-17} \text{ cm}^2$ and 32.9 cm^{-1} , respectively. In addition, a linear relationship between the pump fluence and the peak value of the signal was observed.

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Figure captions

Fig. 1 Schematics of the experimental setup to measure differential reflectivity.

Fig. 2 (a) XRD patterns (b) Raman spectra of the TiO₂ films as-deposited and annealed in O₂ for 1 h at various temperature.

Fig. 3 Surface morphologies by SEM images of the TiO₂ films as-deposited and annealed in O₂ for 1 h at various temperature.

Fig. 4 (a) UV-vis transmittance spectra (b) absorption spectra plotted as $(\alpha h\nu)^{1/2}$ versus $h\nu$ of the TiO₂ films that deposited on quartz substrate as-deposited and annealed in O₂ for 1 h at various temperature.

Fig. 5 (a) Differential reflectivity as a function of the probe delay, measured with a pump pulse of 400 nm and a probe pulse of 800 nm. The red curve represents a biexponential fit to the black curve, with two time constants of 34 and 252 ps, respectively. (b) The peak value of the signal as a function of the pump fluence. (c) The decay time constants measured with different pump fluences.

1 **Fig. 1**

3 **Fig. 2**

5 **Fig. 3**

1 **Fig. 4**

2

3 **Fig. 5**

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