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Effect of Oxygen Partial Pressure on the Optical Property of Amorphous Titanium Oxide Thin Films

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Abstract

Amorphous thin films of titanium oxide (TiOx) have been deposited on K9 glass substrates by dc reactive magnetron sputtering from a pure titanium target at different oxygen partial pressure. The structure and composition of these films have been characterized by x-ray diffraction (XRD), and x-ray photoelectron spectroscopy (XPS), respectively. The effects of the oxygen partial pressure on the composition and optical properties of amorphous TiOx thin films have been mainly investigated. Analyses of transmittance, reflectance, optical band gap of the films demonstrate that the oxygen partial pressure during the sputtering plays a very important role in their optical properties.

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Keywords: amorphous titanium oxide; magnetron sputtering; optical properties

1. Introduction

Titanium dioxide of non-stoichiometric ($TiO_{2-\delta}$) composition containing an excess of titanium is an n type semiconductor [1]. TiO_x has a wide band-gap and in thin film form presents very attractive features due to its high refractive index and transparency in a wide spectral range (350-1100 nm). Besides, this material shows good stability in adverse environments, all these properties are of great interest in various technological applications such as photovoltaics [2], electrochromics [3], chemical sensors [4], photocatalysis [5]-[6], optoelectronic devices [7], dielectric material of ultrathin capacitors [8] and self-cleaning windows [9].

In particular, amorphous TiO_x nanoparticles are only under intensive investigations for recent years by both of experiment [10] and computer simulation [11]. Though several methods have been developed to prepare amorphous TiO_x nanoparticles, such as aqueous peroxotitanate solution method, [12],

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microemulsion method [13], and supercritical carbon dioxide method [14], magnetron sputtering [15], very little is known about the optical properties of amorphous phase of TiO_x prepared by dc magnetron sputtering, which technique is of special interest because it is an industrial process applicable to large-area deposition and high quality films can be achieved even at low substrate temperatures. When the substrate temperature during deposition is low, amorphous TiO_x films are often observed [16].

In this paper, we report a study of effect of the oxygen partial pressure on some optical properties and the relation between the composition and the optical property of titanium oxide thin films prepared by dc reactive magnetron sputtering using an argon/oxygen mixture. The coatings have been deposited on K9 glass substrates at room temperature in order to obtain amorphous phase of TiO_x thin films.

2. Experimental Details

TiO_x thin films were deposited on K9 glass at room temperature with a conventional dc magnetron sputtering system consisting of a stainless-steel vacuum chamber (150 dm^3) evacuated with a turbomolecular pump backed by a mechanical pump giving an ultimate vacuum of order of 1×10^{-4} Pa. The magnetron source, running at a dc power of 150 W, was placed at a distance of 60 mm from the substrate and titled 30° away from the substrate normal. A resistive heater was mounted above the substrate so that the temperature, measured by a chromel-alumel thermocouple, could be varied from room temperature up to 800 ^{o}C. The water cooled Ti metal target (purity 99.995%, GRIKIN) of 8 cm was used for depositing the films. The mixed reactive sputtering gas of Ar (99.999%) and O_2 (99.995%) were controlled by two gas mass flux controllers, respectively. During sputtering, the total pressure was kept at 1.5 Pa, and the flux of Ar was 40 sccm (standard cubic centimeter per minute) while the flux of O_2 varied from 2 to 6 sccm. Prior to all the depositions, the substrates were ultrasonically cleaned with acetone, ethanol, and de-ionized water by an ultrasonic cleaning machine for 10 minutes and then were blown dry with nitrogen.

The phases present in the TiO_x thin films were analyzed by an X-ray diffractometer (X'Pert Pro MPD, PANalytical B.V.) using Cu Kα radiation (λ = 0.15406 nm) and operating at an accelerating voltage of 40 kV and an emission current of 35 mA. Data were acquired over the range from 20 to 70^{o} at a sampling width of 0.03^{o}. The XRD method was used to study the change of crystalline structure. Thickness of the as-deposited films was measured by profilometer (XP-2, Ambios Technology Inc.). The stoichiometry of titanium oxides was determined by x-ray photoelectron (XPS) spectra using x-ray photoelectron spectrometer (XSAM 800, Kratos) at room temperature with monochromatic Al Kα (hν = 1486 eV). The vacuum of the instrument chamber was 1×10^{-7} Pa. The binding energy was calibrated with reference to C 1s peak (285.0 eV). The optical transmission and reflection spectra of TiO_x thin films were recorded at room temperature by a double-beam spectrophotometer (UV-2550, Shimadzu Co.). The wavelength used in the experiment ranged from 300 to 800 nm.

3. Results and discussion

3.1. X-ray Diffraction (XRD)

Fig. 1 shows the XRD pattern of as-deposited TiO_x films prepared at different oxygen partial pressure. As showed in Fig. 1, no sharp diffraction peaks of any crystalline phase appear in the deposited films, this indicates that all the films deposited of different oxygen partial pressure at room temperature are amorphous in structure. This result is in good agreement with the literature [17].

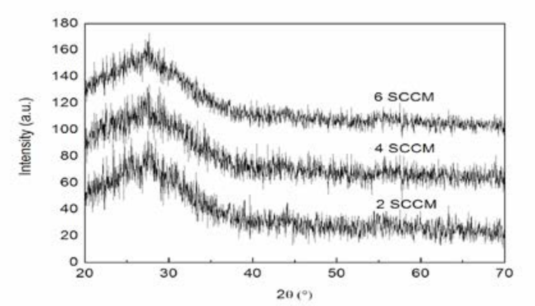
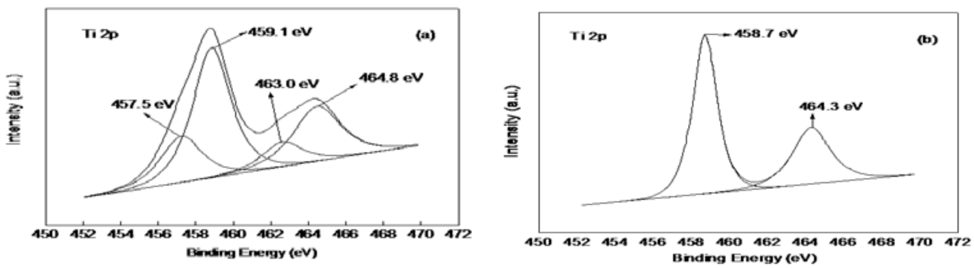


Fig. 1. XRD pattern of TiO_x thin films deposited at different oxygen partial pressure.

3.2. X-ray Photoelectron Spectra (XPS) Measurements

Fig. 2 shows the XPS spectra of Ti 2p energy level of TiO_x films deposited at the different oxygen partial pressure of 2 sccm and 6 sccm, respectively. The C 1s peak at 285.0 eV is used to calibrate the spectra. The spectra in Fig. 2(a) can be resolved into four Gaussian components. The Ti 2p3/2 peak at 457.5 eV and Ti 2p1/2 peak at 463.0 eV are attributed to Ti^{3+} while the peak Ti 2p3/2 at 459.1 eV and Ti 2p1/2 at 464.8 eV are attributed to Ti^{4+} [18]. This indicates that titanium oxide (TiO_x) but not titanium dioxide (TiO_2) films can be obtained by dc magnetron sputtering at the lower oxygen partial pressure. It is also clear that the Ti ions in sputtered TiO_x films are prominent in charge state of Ti^{4+}. The spectra in Fig. 2(b) can be only resolved into two Gaussian components. The Ti 2p3/2 peak at 458.7 eV and the peak Ti 2p3/2 at 464.3 eV are attributed to Ti^{4+}, and no peaks attributed to Ti^{3+} ions appear. Comparing the two XPS specra of deposited TiO_x films, it can be concluded that with the increasing of oxygen partial pressure, the oxygen content in TiO_x increases, too. In other words, using different oxygen partial pressure in reactive magnetron sputtering, different titanium oxide films could be obtained, as we all known, this is one of the merits for reactive sputtering. Therefore, we could control the stoichiometry of metal oxide films by this method, which is very important in the metal oxide semiconductor's electrical property [1].



(a) (b)

Fig. 2. The XPS spectra of Ti 2p energy level of TiO_x thin films deposited at different oxygen partial pressure: (a) 2 sccm, (b) 6 sccm.

3.3. Optical Properties

Fig. 3 and Fig. 4 show the transmission and reflectance spectra of as-deposited TiO_x thin films at different oxygen partial pressure. It can be seen that the transmittance of the TiO_x thin films increases as the oxygen partial pressure increases. When the oxygen partial pressure increases, the film structure changes from dense into porous, in this case, the film has more voids and part of the light can pass through the film without scattering and results in an increase of the transmittance. As shown in Fig. 4, the position of the reflectivity minimum shifts to longer wavelength, i.e., lower energy with the the increasing of oxygen partial pressure. This result is in good agreement with XPS analysis and the literature [19], which provides a quick way of determining the composition of the TiO_x films.

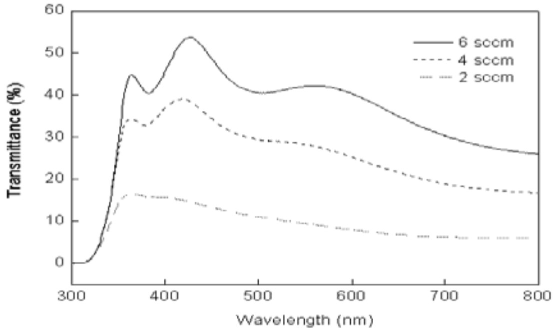


Fig. 3. Optical transmittance as a function of wavelength of TiO_x thin films deposited at different oxygen partial pressure.

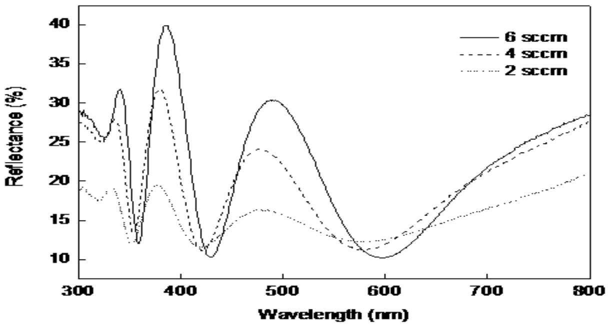


Fig. 4. Optical reflectance as a function of wavelength of TiO_x thin films deposited at different oxygen partial pressure.

Since titanium dioxide is a semiconductor with a large band gap, the optical band gap E_g can be determined from absorption coefficientα. The absorption coefficientα, which depends on the wavelengthλ, can be obtained by using the relation [20].

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

where T is the transmittance, R is the reflectance, α is the absorption coefficient and d is the film thickness which was measured by the profilometer. As the increasing of oxygen partial pressure, the thickness of the TiO_x thin films decrease obviously, i.e., 300 nm (2 SCCM), 280 nm (4 SCCM), 255 nm (6 SCCM), respectively. The drop in deposition rate is due to oxidation of the target, which is a typical characteristic of dc reactive sputtering.

Equation (1) is valid close to the optical band gap of the material under the condition exp $(2\alpha d)>>R^2$. From Equation (1), the absorption coefficient α could be deduced by:

$$\alpha = -d^{-1}\ln\,[T/\,(1-R)^2] \quad (2)$$

Above the threshold of fundamental absorption, the dependence of α on incident light energy is given by the expression [21]:

$$\alpha h\nu = \alpha_0(E-E_g)^m \quad (3)$$

where $E=h\nu$ is the photon energy, E_g is the optical band gap and $\alpha 0$ is a constant which does not depend on E. Since TiO_x is a semiconductor with a direct band gap but dipole-forbidden transitions, the value of m can be used as 3/2 [22].

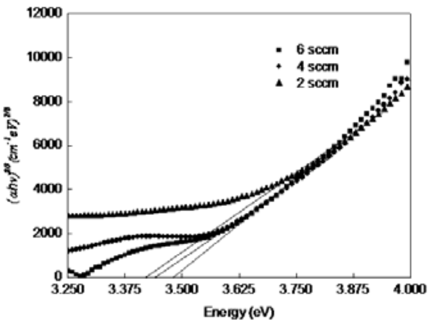


Fig. 5. Optical band gaps for as-deposited TiO_x thin films at different oxygen partial pressure.

From the Fig. 5, it is observed that optical band gap for the as-grown TiO_x thin film at room temperature decreases from 3.45 eV to 3.42 eV, which is not obvious with the increase of oxygen partial pressure in our experiments. However, these results have shown clear optical blueshift of the absorption edges comparing to bulk TiO_2 (Anatase: 3.2 eV, Rutile: 3.0 eV) which can be explained by the quantum-size (Q-size) effect, i.e., the small size of titanium oxide nanoparticles raises the conduction band and lowers the valance band, finally cause a blueshift of the band gap [23]-[24].

4. Conclusions

Amorphous titanium oxide (TiO_x) thin films have been prepared by dc reactive magnetron sputtering at different oxygen partial pressure. The composition and optical properties of the sputtered films such as transmittance, reflectance and optical band gap of the sputtered films have been investigated, i.e., with the increasing of oxygen partial pressure, the oxygen content of the TiO_x films increases, which make the transmittance of the TiO_x thin films increase and the position of reflectivity minimum has a red shift. Because of quantum-size effect, the optical band gap of deposited TiO_x films is found to have a blueshift comparing to bulk TiO_x, and with the increasing oxygen partial pressure, it decreases from 3.45 eV to 3.42 eV.

Acknowledgment

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