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Microstructural evolution and optical properties of doped TiO_2 films prepared by RF magnetron sputtering

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Abstract

In this study, Y_2O_3 and Nb_2O_5 doped titanium dioxide (TiO_2) films on glass substrate were prepared using RF magnetron sputtering. The effects of dopants on the microstrucutral evolution and optical properties of TiO_2 films were investigated. The as-deposited films are amorphous, irrespective of films containing Nb_2O_5 or Y_2O_3. After annealing at 400 °C and above in pure oxygen, anatase phase was obtained for pure TiO_2 and Nb_2O_5 doped TiO_2 films. Y_2O_3 dopant retards the crystallization to a higher temperature. After annealing, the transmittance of the TiO_2 film is increased by Nb_2O_5 or Y_2O_3 addition. The higher transmittance of the doped samples can be correlated with their surface roughness.

Keywords: C. Optical properties; TiO_2 film; RF magnetron sputtering; Microstructural evolution

1. Introduction

Crystalline titanium dioxide (TiO_2) exists in three different forms: brookite, anatase, and rutile. Brookite, the orthorhombic phase, can be grown under hydrothermal conditions if sodium ions are present in the solution. Only anatase and rutile, which possess tetragonal structures, have been observed in thin film up to now. Anatase TiO_2 is a low temperature stable phase, which transforms to high temperature rutile structure at temperatures above 800 °C [1,2]. In addition, amorphous TiO_2 films are often observed when the substrate temperature during deposition is low [3]. Many studies have reported that the phase formation, microstructural evolution of the TiO_2 film depends on the substrate surface properties and the deposition conditions [1,9–13].

TiO_2 has many outstanding optical, electrical and chemical properties which make it suitable for variety of thin film application [4,5]. Rutile TiO_2 film has excellent optical transparency in the visible range, high refractive index, and chemical stability, which make it very attractive for use in optical coating (such as dielectric interference filters, multilayer mirrors and antireflective coating, etc.) [1,4,6]. Due to its high dielectric constant and high resistivity ($\rho \approx 10^{13}\ \Omega$ cm), it has drawn much attention for use in fabricating capacitors in microelectronic devices [7,8]. Recently, the rutile phase was found to be an important bio-compatible material, in particular for blood compatibility. Anatase TiO_2 are mainly used in chemical applications including photocatalysis, photochemical solar cell and as a gas sensor, e.g. for the detection of NO_2.

Though studies have attempted to understand how dopants impact on the photocatalytic and sensing effects of TiO_2 [12], rare information is available in the literature regarding the effects of dopants on the phase formation, microstructural evolution, and thus the optical properties of the TiO_2 thin films. In this work, the effects of Y and Nb dopants on the microstructural evolution and optical properties of TiO_2 films deposited on glass substrate, prepared using RF magnetron sputtering, were performed.

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Table 1
The structure of the pure and doped TiO_2 films, identified from XRD results, deposited on the glass substrate under Ar atmosphere, and subsequently annealed at different temperatures

Atmosphere	Target composition	Annealing temperature			
		As-deposited	400 °C	500 °C	600 °C
Pure Ar	TiO_2	Amorphous	Anatase	Anatase	Anatase
	TiO_2 + 2 m% Nb_2O_5	Amorphous	Anatase	Anatase	Anatase
	TiO_2 + 2 m% Y_2O_3	Amorphous	Amorphous	Anatase	Anatase

2. Experimental procedure

Y and Nb doped TiO_2 thin films investigated were prepared by RF magnetron sputter deposition. Deposition of thin films was done in a sputtering system equipped with a turbomolecular pump, achieving a base pressure of $<2 \times 10^{-7}$ Torr. Pure, Y_2O_3 doped, and Nb_2O_5 doped TiO_2 targets were prepared using TiO_2 (Showa Chemical, reagent grade) with 2 m% of Y_2O_3 or Nb_2O_5 (Fisher Scientific, reagent grade) powders. They were mixed in the methyl alcohol using polyethylene jars and ZrO_2 media. After drying, the powders were added with 3.5 wt.% of a 15% PVA solution and then pelletized into disc-shapes using a uniaxial pressure of 2 tons/cm^2. The samples were then heat treated at 550 °C for 6 h to eliminate the PVA, followed by sintering at the temperatures of 1400 °C for 4 h.

For sputtering, argon as the working gas was at least 99.995% pure. Prior to deposition, the target was sputter-cleaned. The based line vacuum was less than 3×10^{-6} Torr. Working pressure was in the range of 5×10^{-3} Torr while RF power was 150 W. A pure Ar (40 sccm) atmosphere was used throughout the film deposition. Films were sputtered onto glass slide (KIMAX-75006) wafer without intentionally heating. During deposition, the substrate temperature reached to the range of 100–108 °C due to the thermal flow from the plasma. For the post-deposition annealing, film samples are heat treated at 400, 500, and 600 °C in O_2 atmosphere using RTA furnace (MILA-3000) with a heating rate of 1 °C/s. X-ray diffraction (XRD, Rigaku DMX-2200), scanning electron microscopy (SEM, Hitachi S4700), and energy dispersive spectroscopy (EDS) were used to confirm the formation of phases and characterize the microstructures of films. The surface morphology of the TiO_2 film was observed by mean of atomic force microscopy (AFM). Optical measurements were carried out using a double beam spectrophotometer (Perkin-Elmar Lambda 900 UV–vis/IR) over a range of wavelength λ from 200 to 900 nm. The light source is changed automatically, according to the region of measurements, e.g. in the visible and IR regions a xenon lamp, while in the UV region a deuterium lamp.

3. Results and discussion

The TiO_2 and doped TiO_2 films were prepared from pure TiO_2 and doped TiO_2 targets prepared using solid-state process. The effects of dopants and annealing temperatures on the structure of the TiO_2 films deposited on the glass substrate under Ar atmosphere, based on XRD results, are summarized in Table 1, and XRD patterns of films after annealed at 600 °C are indicated in Fig. 1. They indicate that the as-deposited films are amorphous, irrespective of films containing Nb_2O_5 or Y_2O_3. After annealing at 400 °C and above in pure oxygen, anatase phase was obtained for pure

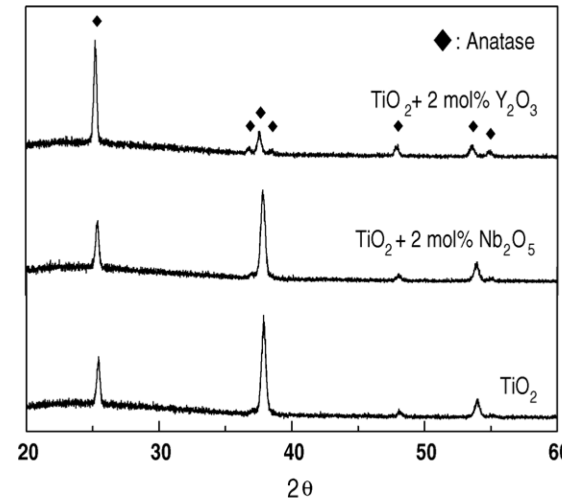

Fig. 1. XRD patterns for pure TiO_2 and Nb_2O_5 and Y_2O_3 doped TiO_2 films prepared on glass substrate under Ar atmosphere and subsequently annealed at 600 °C.

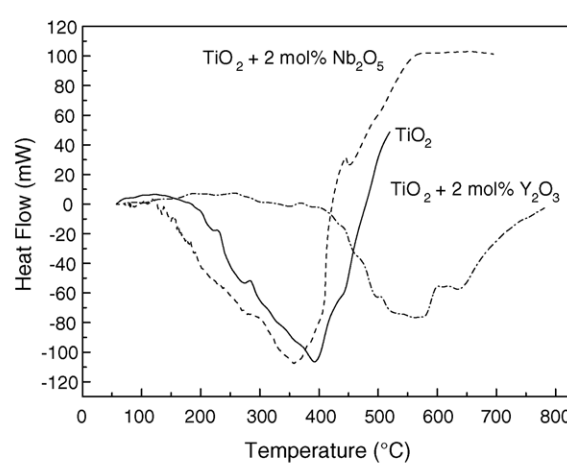

Fig. 2. DTA results for pure TiO_2 and Nb_2O_5 and Y_2O_3 doped TiO_2 films (heating rate: 10 °C/min).

TiO_2 and Nb_2O_5 doped TiO_2 films. However, the first traces of the long range order did not appear in Y_2O_3 doped TiO_2 films until annealing at 500 °C. This manifests that Y_2O_3 dopant retards the crystallization to a higher temperature, which could be confirmed by the DTA results shown in Fig. 2. The onset of exothermic reaction, representing the crystallization temperatures of anatase phase, for pure TiO_2, Nb_2O_5 doped TiO_2, and Y_2O_3 doped TiO_2 are 392, 357, and 562 °C, respectively. Though a deviation in crystallization temperatures between XRD results and DTA results due to the difference in heating profiles of both analyses, the trends of the effect of dopants on the crystallization of TiO_2 films are evident. Previous study showed that rutile phase may form when the film was deposited on the Si substrate, especially under the presence of oxygen in the sputtering gas [14].

Fig. 3 shows the three-dimensional AFM image of the pure TiO_2 and Nb_2O_5 doped and Y_2O_3 doped TiO_2 films prepared on glass substrate under Ar atmosphere and subsequently annealed at 600 °C. The samples used in this analysis were deposited at the same substrate temperature (≈100–108 °C) and had the same film thickness (≈1000 nm). The corresponding surface roughnesses (root mean square roughness, R_{rms}) for the films were 8.87, 5.87, and 2.60 nm. Film doped with Y_2O_3 possesses smaller surface roughness compared with pure and Nb_2O_5 doped TiO_2 films.

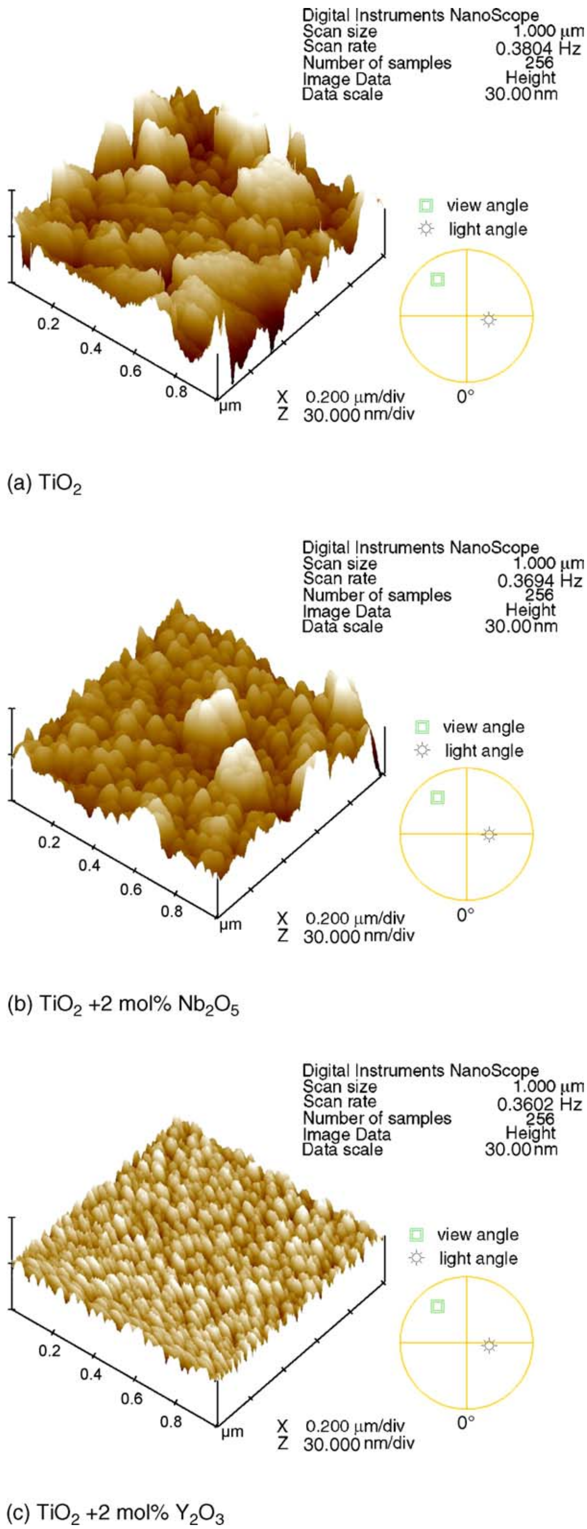

Fig. 3. The three-dimensional AFM image of (a) pure TiO_2, (b) Nb_2O_5 doped TiO_2, and (c) Y_2O_3 doped TiO_2 films prepared on glass substrate under Ar atmosphere and subsequently annealed at 600 °C.

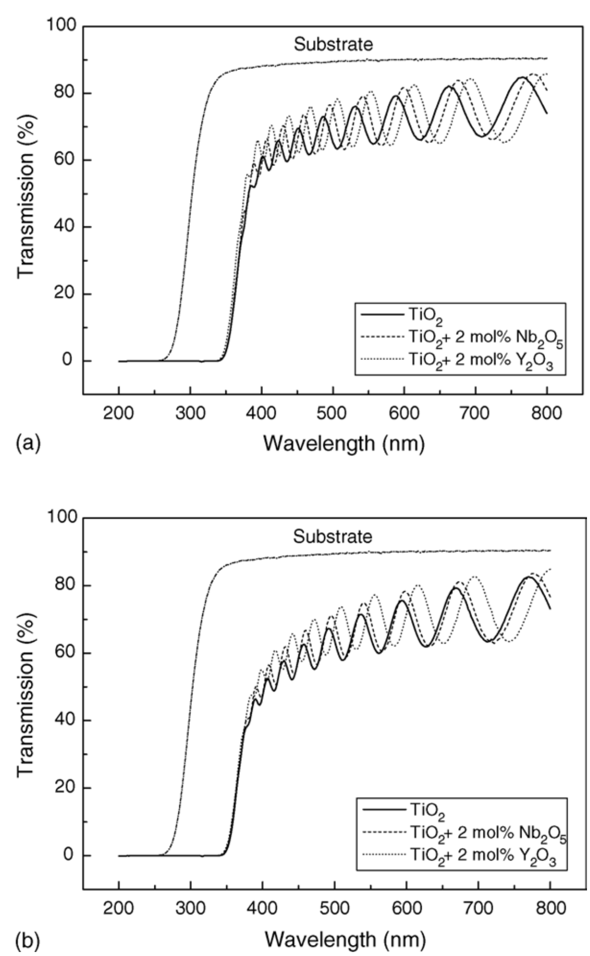

Fig. 4. The transmittances of the (a) as-deposited and (b) subsequently annealed at 600 °C for pure TiO_2 and Nb_2O_5 andY_2O_3 doped TiO_2 films prepared on glass substrate under Ar atmosphere.

The transmittances of the as-deposited films are shown in Fig. 4(a), and those after annealing at 600 °C are shown in Fig. 4(b). The transmittance of a bare substrate is also given for comparison. The films were deposited at the same substrate temperature (≈100–108 °C) and had the same film thickness (≈1000 nm). All films are transparent in the visible and near-IR region. Typically the increased thickness may lead to a decrease in the transmittance of the oxide film. The transmittance of the TiO_2 film is increased by the Nb_2O_5 or Y_2O_3 addition. Since all films consist of anatase phase and similar grain size, the higher transmittance of the doped samples can be correlated with their surface roughness. The film uniformity reduces the loss of light due to scattering and results in the increase in the transmittance. Carefully comparing the transmittances of the as-deposited films (Fig. 4(a)) and the annealed films (Fig. 4(b)), the transmittances of the as-deposited films are higher than those of the films after annealing, due to the higher density and refractive index of the crystallized anatase phase. The absorption thresholds for the films slightly move to lower wavelength with the dopant addition. The value of the optical band gap, E_g, were found by fitting $(\alpha h\nu)^2$ versus $h\nu$ to the experimental data of the films (Fig. 5(a) and (b)). From the linear part of these dependence, the extrapolated optical band gaps were obtained for each curve [15,16]. The E_g for pure TiO_2, Nb_2O_5-doped, and Y_2O_3-doped TiO_2 films for as-deposited and annealed films are 3.22, 3.23, and 3.27 eV, and 3.20, 3.21, and 3.22 eV, respectively. Though the results of the band-gap for the TiO_2 films in literature [17–19] still spread over a wide range of values, the differences in E_g due to the annealing as well as the dopant additions in this study are not evident.

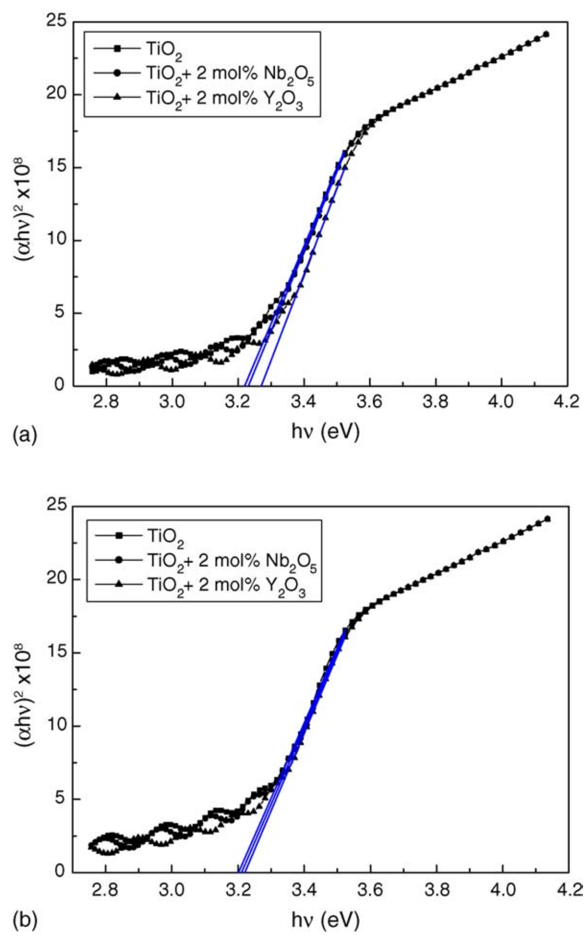

Fig. 5. Analysis of optical transition: $(\alpha h\nu)^2$ as a function of photon energy $h\nu$ for (a) as-deposited and (b) annealed at 600 °C pure TiO_2, Nb_2O_5 doped TiO_2 and Y_2O_3 doped TiO_2 films.

4. Summary

In this study, Y and Nb doped TiO_2 films on glass substrates were prepared using RF magnetron sputtering. The XRD results indicated that Y_2O_3 doped in the TiO_2 films inhibits the crystallization of anatase phase on the subsequent annealing, which was verified by DTA result. Film doped with Y_2O_3 has the smallest surface roughness among pure TiO_2 and doped TiO_2 films. All films are transparent in the visible and near-IR region. The transmittance of the TiO_2 film is increased by Nb_2O_5 or Y_2O_3 addition due to the better film uniformity which reduces the loss of light due to scattering. The absorption thresholds for the doped films slightly move to lower wavelength compared with the pure TiO_2 film, though the difference in energy gaps is trivial.

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