Journal of Physics and Chemistry of Solids 123 (2018) 266–270

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs

Optical properties of TiO_2 thin films with crystal structure

Manil Kang[a], Sok Won Kim[a,*], Hyo Yeol Park[b]

[a] Department of Physics, University of Ulsan, Ulsan 44610, Republic of Korea
[b] Electronics and Communication Semiconductor Applications, Ulsan College, Ulsan 44610, Republic of Korea

ARTICLE INFO

Keywords:
TiO_2
Anatase
Rutile
Spectroscopic ellipsometry
Optical band gap

ABSTRACT

The optical properties of TiO_2 thin films with polymorphs were investigated by spectroscopic ellipsometry (SE) and transmittance measurements. Films were prepared by RF sputtering and e-beam evaporation and post-annealing, and their microstructures were examined by SEM and XRD. The results reveal that the crystal structure of the TiO_2 film is strongly affected by the post-annealing temperature. The optical constant spectra of the films showed a gradual change above 3.5 eV. As the crystal structure of the film changes from amorphous phase to rutile phase, the extinction coefficient spectra are enhanced and shift toward lower energy. The direct band gap energies obtained by SE measurements were well matched with those obtained by transmittance measurements. The SE analysis was supported by comparison of the measured and calculated transmittances of the films, and both spectra showed good agreement over the entire spectral range.

1. Introduction

Since the discovery of photolysis using titanium dioxide (TiO_2), intensive research on photocatalytic applications has been performed due to the low cost and high activity of the material [1–3]. TiO_2 is used in a wide range of applications, such as photocatalysis, sensor devices, and dye-sensitized solar cells [4–6]. TiO_2 is also used in paints and self-cleaning coatings [7,8].

Generally, the physical properties of metal-oxide films including TiO_2 film are affected by their crystal structure and morphology and are strongly dependent on the growth method [9–13]. TiO_2 thin film can be grown to various crystal structures such as amorphous, anatase, rutile, and brookite phases. Many applications using TiO_2 thin film depend on its structural and optical properties. TiO_2 thin film is widely used in photocatalysis, coatings on lenses, and self-cleaning windows [8,14,15]. For these reasons, TiO_2 thin films are extensively studied.

TiO_2 thin film with anatase phase has a variety of possible applications in environmental protection because it can photocatalytically degrade organic compounds under ultra-violet (UV) radiation [16,17]. TiO_2 thin film with rutile structure has good compatibility with blood and can be used in artificial heart valves [18]. TiO_2 thin films are also important optical films for the visible range due to their high reflective index, high transparency, and a wide band gap [19].

In application fields such as optical lenses and interference mirrors [20], analysis of optical properties of TiO_2 films with crystallization is very important, because a change of optical properties due to crystallization debases their performance. Thus, in this study, we report the optical properties of TiO_2 polymorph films characterized by spectroscopic ellipsometry (SE) and transmittance measurements. The complex refractive index and optical band gap of the films were obtained by SE measurements, and the optical band gap of the films was compared with that obtained by transmittance measurements. To verify the SE analysis, the transmittance of the films was calculated using the optical constants obtained by the SE measurements and compared.

2. Experiments

TiO_2 thin films were prepared using an RF sputtering system and a TiO_2 (99.99%) disk target with a 5-cm diameter. Sputtering was performed at an RF power of 120 W. The TiO_2 films were grown on a quartz substrate at room temperature for 120 min. The distance between the target and substrate was 10 cm. The sputtering gas was Ar with 99.999% purity, which was injected into the chamber with a flow rate of 20 sccm. The base pressure of the chamber was less than 6.67×10^{-3} Pa, and the working pressure was approximately 1.33×10^{-1} Pa. To obtain amorphous and anatase TiO_2 films, the prepared films were post-annealed using a tubular furnace at temperatures of 550 °C for 120 min in air. Also, rutile TiO_2 films were prepared by using e-beam evaporation and post-annealing. TiO_2 grain with 99.9% purity was used as target material, and evaporation was conducted at a substrate temperature of 200 °C and at a deposition rate of 0.25 nm/s. The deposited films were post-annealed using a tubular

* Corresponding author.
E-mail address: sokkim@ulsan.ac.kr (S.W. Kim).

https://doi.org/10.1016/j.jpcs.2018.08.009
Received 17 March 2018; Received in revised form 2 August 2018; Accepted 10 August 2018
Available online 11 August 2018
0022-3697/

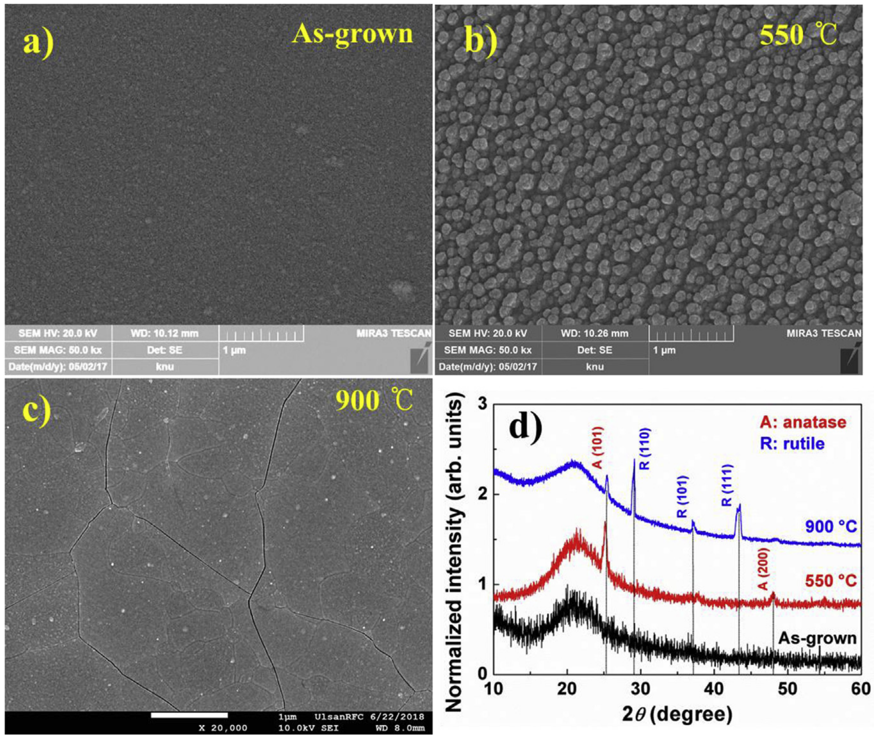

Fig. 1. Surface morphologies of the TiO_2 films with different post-annealing temperature: (a) as-grown film, (b) film post-annealed at 550 °C, and (c) film post-annealed at 900 °C. (d) XRD patterns of the as-grown TiO_2 film and TiO_2 films post-annealed at 550 and 900 °C.

furnace at temperatures of 900 °C for 180 min in air.

The ellipsometric constants (Ψ and Δ) of the films were measured by a spectroscopic ellipsometer (Jobin-Yvon, Uvisel UV/NIR). SE measurements were conducted over a photon energy range of 0.75–4.5 eV at an incident angle of 70°. The measured Ψ and Δ of the films were analyzed using an optical model based on the Bruggeman effective medium approximation (BEMA) [21,22]. The optical model of the TiO_2 films consisted of three layers: a surface layer, a film layer, and a substrate. The double new amorphous (DNA) formula combined with two oscillators was used to describe the dispersion in the optical constants of the films. The transmission spectra were measured using UV-visible spectrophotometry in the wavelength range of 300–1100 nm. The microstructures of the films were investigated using a scanning electron microscope (SEM; JEOL, JSM6335F) at an operating voltage of 10 kV and an X-ray diffractometer (XRD; Rigaku, D/MAX-Rc) with Cu Kα radiation. The XRD measurements were performed using a 2θ method at an interval of 0.02°.

3. Results and discussion

Fig. 1(a)–1(c) show the surface morphologies of the TiO_2 films with post-annealing. As the post-annealing temperature increases, the films show considerable variation in their surface morphology. The film post-annealed at 550 °C shows grain growth indicating crystallization, and the morphology of the film post-annealed at 900 °C shows a dense surface, and the grains observed in the film of 550 °C disappear.

Fig. 1(d) shows the XRD pattern of the as-grown TiO_2 film and TiO_2 films post-annealed at 550 and 900 °C. The as-grown TiO_2 film has an amorphous structure with no diffraction peaks. The pattern of the TiO_2 films post-annealed at 550 °C shows peaks that belong to the anatase phase of TiO_2, and the film post-annealed at 900 °C mostly has rutile phase [23–25]. As shown in Fig. 1(d), the peaks at 2θ values of 29.18°, 37.24°, and 43.33° correspond to reflections in the (110), (101), and (111) planes of the TiO_2 rutile phase, respectively.

Fig. 2(a) and (b) show the optical transmission spectra of the TiO_2

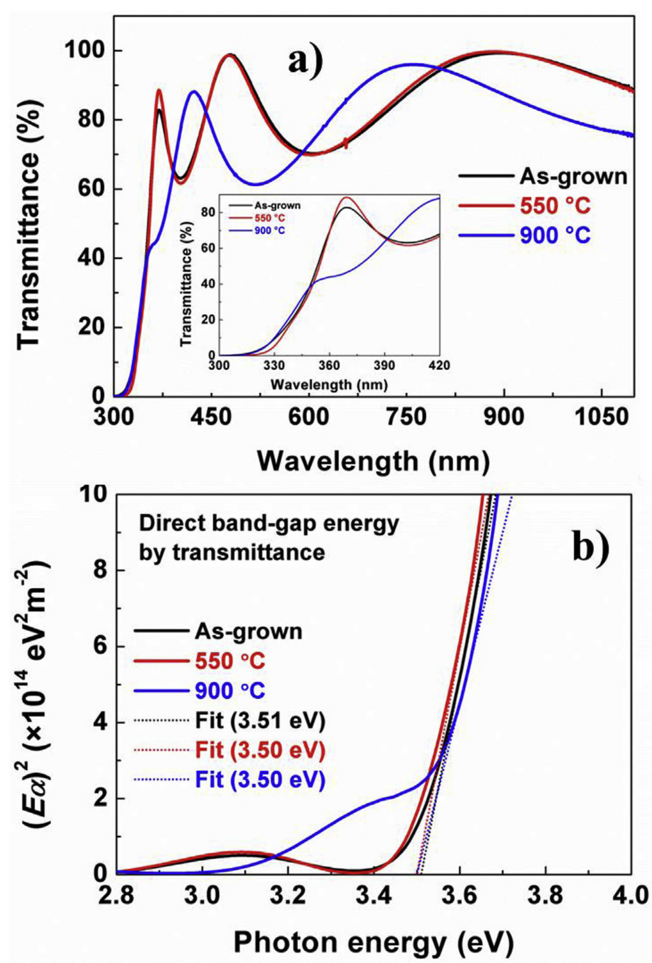

Fig. 2. (a) Optical transmission spectra of TiO_2 polymorph films (inset: enlarged spectra). (b) Direct band gap energy calculated from the transmission spectra.