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ScienceDirect

Progress in Natural Science: Materials International 24 (2014) 218–225

Progress in Natural Science Materials International

www.elsevier.com/locate/pnsmi
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Original Research

Optical parameters induced by phase transformation in RF magnetron sputtered TiO_2 nanostructured thin films

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Received 30 January 2014; accepted 30 April 2014
Available online 2 June 2014

Abstract

Pure TiO_2 thin films were deposited onto quartz substrates using a ceramic TiO_2 target at an elevated substrate temperature of 573 K by RF magnetron sputtering, and an analysis of structural, optical and photoluminescence characteristics of the films upon phase transformation is reported in this paper. Structural investigations using X-ray diffraction revealed that the as-deposited film was amorphous in nature. Thermal annealing for 2 h at 873 K in air resulted in the formation of anatase phase, and a phase transformation to rutile was observed at 1073 K. An increase in grain size and an improvement in crystallinity were also observed on annealing. Rod- like rutile crystallites were observed in the SEM images of the film annealed at 1273 K. As-deposited films and films annealed up to 1073 K were highly transparent in the visible region with a transparency $>80\%$. Optical band gap of the films decreased upon thermal annealing which is attributed to phase transformation from amorphous to anatase and then to rutile. Optical parameters such as refractive index, optical conductivity and optical dielectric constant increased with increase in annealing temperature. Since rutile is the optically active phase, the superior refractive index of the film annealed at 1073 K along with its high transparency in visible region suggests the application of this film in antireflective coatings. Photoluminescence emission of maximum intensity was observed for the film annealed at 873 K, which exhibits anatase phase. Intense blue emission observed in this film makes it suitable for use in optoelectronic display devices.

Keywords: RF magnetron sputtering; TiO_2 thin films; Dislocation density; Optical conductivity; Photoluminescence

1. Introduction

Nanocrystalline titanium dioxide (TiO_2) thin films have been investigated extensively in recent years because of their potential use as a low cost material in photovoltaics [1], gas sensors [2], photocatalysis [3], smart windows [4], antireflection coatings [5], optical filters [6] and as dye-sensitized solar cells [7,8]. Moreover, these films have good mechanical, thermal and anticorrosive properties required for practical uses. The atmospheric concentration of oxygen and UV light are all that is needed to drive oxidation of virtually any organic molecules adsorbed at the TiO_2 surface. Since such redox processes can occur at room temperature under solar or artificial UV light, a number of practical applications have been suggested including photoelectron chemical cells [1], antifog windows [9], and various self-cleaning devices [10].

TiO_2 can exist in amorphous form and also in three crystalline forms – anatase (A), rutile (R) and brookite (B). These phases are well distinguishable in terms of their physical properties. Anatase and rutile phases are tetragonal in nature

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Peer review under responsibility of Chinese Materials Research Society.

Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.pnsc.2014.05.010

while brookite exhibits an orthorhombic structure. Films in amorphous phase are widely used for optical coatings because of its optical anisotropy. Also due to its unique blood compatibility, amorphous titania films are promising candidates in the biomedical field. Optical band gap is higher for anatase compared to that of rutile (3.2 vs 3.0 eV). Anatase phase is known to exhibit better photocatalytic activity and is preferred over rutile for photodecomposition of environmental pollutants [11,12]. The rutile structure is very compact and thermodynamically most stable phase at all temperatures, and has higher refractive index than anatase (2.7 vs 2.52, at 550 nm wavelength). Rutile phase exhibits better optical activity than anatase and is used for antireflective and dielectric applications [13,14]. High dielectric constant of the material enables the use of TiO_2 thin films in micro-electronic devices [15]. The variation in properties, exhibited by amorphous, anatase and rutile thin films, have generated much interest in the study of their growth mechanisms. Since the optical properties of TiO_2 films also show interesting variations influenced by oxygen defects, impurities and crystalline size, the method of deposition and post-deposition thermal treatments are very important in inducing the desired properties in thin films.

In thin film form, TiO_2 is technologically important for use as light emitting devices and flat panel displays and hence the luminescence properties of the material have attracted much interest. Luminescence emission from TiO_2 nanopowders and nanowires has been reported in the literature [16,17]. The photoluminescence (PL) properties of rare-earth doped TiO_2 thin films have been reported by some authors [18–20]. Liu et al. [21] have reported PL emission in pure TiO_2 thin films on quartz substrates prepared by DC magnetron sputtering. They have concluded that post-deposition annealing can enhance PL properties of pure TiO_2 thin films. Huang et al. [22] have reported that incorporation of nitrogen in TiO_2 thin films deposited on Si(100) wafers enhances their visible PL significantly.

Structural control constitutes one of the major challenges in the design of suitable coating process for use in specific applications. In the present study, RF magnetron sputtering was used to deposit thin films. RF magnetron sputtering can produce highly uniform films having good adherence to the substrate. The method also offers the advantage of depositing films on a large area and on large scale which makes the method suitable for industrial applications [23]. Various parameters such as sputtering pressure, sputtering power, substrate temperature, and $Ar:O_2$ ratio can alter the structural and optical properties of thin films prepared by the sputtering method. The crystalline phases and microstructure are temperature dependent and hence post-deposition annealing has to be carefully carried out to enable the use of TiO_2 thin films for practical applications. This study aims to present a detailed analysis of the optical and photoluminescence properties of RF magnetron sputtered TiO_2 thin films, which have undergone structural changes due to post-deposition thermal annealing.

2. Experimental

The target used in the experiment was prepared by traditional ceramic process as described in our earlier paper [23]. The sputtering and post-deposition annealing conditions used in the study are given in Table 1. The as-deposited films are coded as T0 and the films annealed at 873, 973, 1073 and 1273 K are coded T873, T973, T1073, and T1273 respectively. All the films exhibited good adherence to the substrate. No cracking or peeling of the films was observed even after annealing at 1273 K.

Structural properties of the films were examined by standard X-ray diffraction (XRD) technique (Bruker AXS D8 Advance). Surface morphology was characterized by scanning electron microscopy (SEM) (Jeol Model JSM-6390LV) and atomic force microscopy (AFM) (SPA-400, SII, Inc. Japan – non contact mode). Optical transmission spectra were recorded in the wavelength range 300–900nm using a spectrophotometer (JASCO V- 550). Photoluminescence spectra was recorded in the wavelength range 350–600 nm using a spectroflurometer (Perkin-Elmer LS 55) employing a 40 W Xenon lamp as the excitation source. The samples were excited at 320 nm.

3. Results and discussions

3.1. Structural studies

Fig. 1 shows the XRD patterns of as-deposited and annealed TiO_2 thin films deposited at RF power 300 W and sputtering pressure 0.01 mbar. The as-deposited films were amorphous in nature, whereas the films annealed at 873 K showed the presence of anatase (101), (004) and (200) peaks at $2\theta = 25.35$, 37.86 and 48.19°, respectively. (101), (004), (200) and (105) peaks of the anatase at $2\theta = 25.28$, 37.93, 48.16 and 53.68° respectively, and a weak (110) peak of the rutile at $2\theta = 27.77°$ were observed in the film annealed at 973 K. Rutile (110), (101) and (211) peaks were observed at $2\theta = 27.45$, 36.07 and 54.48°, respectively, for the films annealed at 1073 K. For the film annealed at 1273 K, the diffraction peaks of (110), (111), (211) and (220) planes corresponding to rutile phase were observed at $2\theta = 27.93$, 41.89, 54.09 and 55.87°, respectively. During thermal annealing, the rearrangement of Ti and O atoms was such that the unit cell of TiO_2 tries to attain more stable and defect free configuration. Though anatase and rutile are tetragonal in nature, the value of c/a is closer to that of the most stable cubic lattice ($c/a = 1$) for rutile phase (0.65) than that for anatase ($c/a = 2.51$). Thus thermal annealing at higher temperatures (> 1073 K) favors the complete phase transformation to rutile [13].

Table 1
Sputtering and post-deposition annealing conditions.

Sputtering gas	Argon
Sputtering pressure	0.01 mbar
RF power	300 W
Substrate temperature	573 K
Sputtering time	3 h
Substrate used	Quartz
Annealing temperature	873, 973, 1073, 1273 K
Annealing time	2 h
Annealing atmosphere	air