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Effects of Annealing Treatment on Optical Properties of Anatase TiO_2 Thin Films

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***Abstract*—**In this investigation, anatase TiO_2 thin films were grown by radio frequency magnetron sputtering on glass substrates at a high sputtering pressure and room temperature. The anatase films were then annealed at 300-600 °C in air for a period of 1 hour. To examine the structure and morphology of the films, X-ray diffraction (XRD) and atomic force microscopy (AFM) methods were used respectively. From X-ray diffraction patterns of the TiO_2 films, it was found that the as-deposited film showed some differences compared with the annealed films and the intensities of the peaks of the crystalline phase increased with the increase of annealing temperature. From AFM images, the distinct variations in the morphology of the thin films were also observed. The optical constants were characterized using the transmission spectra of the films obtained by UV-VIS-IR spectrophotometer. Besides, optical thickness of the film deposited at room temperature was calculated and cross-checked by taking a cross-sectional image through SEM. The optical band gaps were evaluated through Tauc model. It was observed that TiO_2 films produced at room temperatures exhibited high visible transmittance and transmittance decreased slightly with the increase of annealing temperatures. The films were found to be crystalline having anatase phase. The refractive index of the films was found from 2.31-2.35 in the visible range. The extinction coefficient was nearly zero in the visible range and was found to increase with annealing temperature. The allowed indirect optical band gap of the films was estimated to be in the range from 3.39 to 3.42 eV which showed a small variation. The allowed direct band gap was found to increase from 3.67 to 3.72 eV. The porosity was also found to decrease at a higher annealing temperature making the film compact and dense.

***Keywords*—**Titanium dioxide, RF reactive sputtering, Structural properties, Surface morphology, Optical properties.

I. INTRODUCTION

Over the last few decades, titanium dioxide (TiO_2) has been widely investigated recently for its interesting optical properties, electronic properties and good stability in the adverse environment. For its high refractive index, wide band gap and chemical stability, polycrystalline TiO_2 films are used for a variety of applications such as optics industry [1], dye-sensitized solar cells [2], dielectric applications [3], self cleaning purposes [4] and photocatalytic layers [5]. The highly transparent TiO_2 films have been widely used as anti-reflection coatings for increasing the visible transmittance in heat mirrors [6]. A heat mirror is a device that exhibits high transmittance at short wavelength combined with high reflectance at long wavelength, has been developed for reflecting the solar heat in a warm climate or to prevent the escape of indoor heating in a cold climate. A heat mirror is usually constructed as a multilayer of dielectric materials/metal/dielectric materials. Au, Ag, Cu, Al or metal like nitrides such as TiN or ZrN is used as metal layers. As a dielectric material, TiO_2 is one of the mostly used materials for the purpose of antireflection coatings [7-10].

TiO_2 can exist as an amorphous layer and also in three crystalline phases: anatase (tetragonal), rutile (tetragonal) and brookite (orthorombic). Only rutile phase is thermodynamically stable at high temperature. The refractive index at 500 nm for anatase and rutile bulk titania is about 2.5 and 2.7 respectively [11]. There are many deposition methods used to prepare TiO_2 thin films, such as electron-beam evaporation [12], ion-beam assisted deposition [13], DC reactive magnetron sputtering [5], RF reactive magnetron sputtering [2, 14], Sol-gel methods [15, 16], chemical vapor deposition [17] and plasma enhanced chemical vapor deposition [3]. The properties of the titanium dioxide films depend not only on the preparation techniques but also on the deposition conditions. PVD (Physical vapor deposition) technology is still a mainstream production tool for functional coatings. Sputter deposition techniques are widely utilized methods to obtain uniform and dense TiO_2 thin films with well-controlled stoichiometry. Heat-treatment is one of the utilized ways to obtain better optical properties of TiO_2 films [11, 18].

In this work, RF reactive magnetron sputtering was used to fabricate TiO_2 thin films with anatase phase on microscope slides substrates. In most past researches, the as-deposited

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films were prepared as amorphous and they showed the annealing effects on optical properties. Here, the attempts have been taken to produce anatase TiO_2 films on unheated substrates. Besides the films were taken for further annealing treatment. Hence, the effects of heat-treatment on optical properties were investigated in this paper.

II. EXPERIMENTAL DETAILS

Anatase TiO_2 thin films were prepared by RF magnetron sputtering system with a titanium target of 99.99% purity on microscope glass slides as substrates. Firstly, the target was pre-sputtered in an argon atmosphere in order to remove oxide layer. The sputtering was performed under a mixture of Ar (99.999%) and O_2 (99.999%) atmosphere at a ratio of 45:10 sccm supplied as working and reactive gases, respectively, through independent mass-flow controller. The sputtering chamber was evacuated down to 5×10^{-7} kPa by the turbomolecular pump and the working pressure was kept at about 3 Pa. Microscope glass slides were used as the substrates for thin films. Prior to deposition, the glass slides were sequentially cleaned in an ultrasonic bath with acetone and ethanol. Finally they were rinsed with distilled water and dried. The substrates deposited at room temperature with TiO_2 were annealed at 300 °C, 400 °C, 500 °C and 600 °C using an electric furnace for 1 h in air.

The crystalline properties of the TiO_2 films were analyzed by an X-ray diffractometer (Model-D5000, Siemens) using Cu K_α radiations (λ=0.15406 nm) and operating at an accelerating voltage of 40 kV and an emission current of 40 mA. Data were acquired over the range of 2θ from 20 to 80^o at a sampling width of 0.1^o and a scanning speed of 5^o min^{-1}. The XRD method was used to study the change of crystalline structure. For morphological investigations, AFM images were recorded using Nanoscope IIIa scanning probe microscope controller in a tapping mode.

The UV-visible-IR optical transmission spectra of TiO_2 thin films were recorded by a double-beam spectrophotometer (Jasco 570) in the range of 250-2500 nm. The measurements were taken at a normal incidence using a reference blank substrate. From the transmittance spectra, Swanepoel [19] methods were used to calculate the optical constants, absorption coefficient and optical band gap of the films. The film thickness was obtained from the optical transmittance spectra T(λ) using Swanepoel method. The thickness of a film is cross-checked by the SEM cross-sectional image.

III. RESULTS AND DISCUSSION

A. Structure

Fig. 1 illustrates the XRD patterns of TiO_2 films which were as-deposited at room temperature and annealed at different temperatures. From the figure, it was found that all the films were polycrystalline having anatase phase only. From diffraction patterns, it was observed that the films as-deposited, annealed at 300 °C, 400 °C, 500 °C exhibited characteristic peaks of anatase crystal plane (101), (200) and (211). It was found that anatase films were deposited and crystallized effectively for unheated substrate using P_{rf} of 250 W and working pressure of 3 Pa. The reason may be that the kinetic energy of the impinging particle is high enough to initiate crystallization. For the sample annealed at 600 °C, other characteristic peaks of anatase crystal plane (204) and (220) appeared, but the intensity of these peaks is very weak. It was observed that the intensities of the peaks of few anatase planes increased slightly with the increase of annealing temperature.

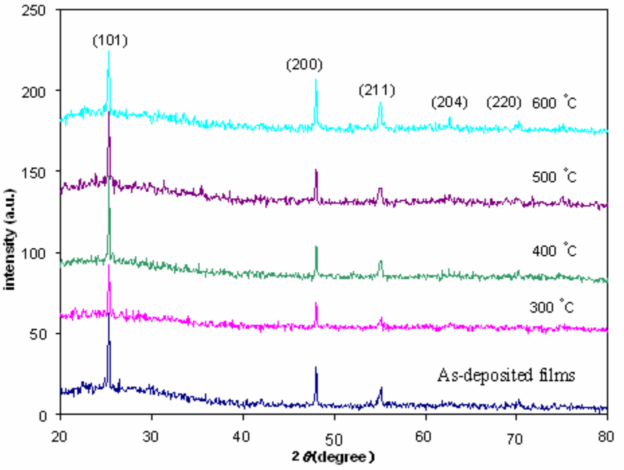

Fig. 1 XRD patterns of TiO_2 films deposited at room temperature and annealed at 300 °C, 400 °C, 500 °C and 600 °C

B. Morphology

The surface morphology of all the TiO_2 films is presented by AFM images in tapping mode shown in Fig. 2. All the TiO_2 films exhibit a smooth surface with uniform grains. As shown

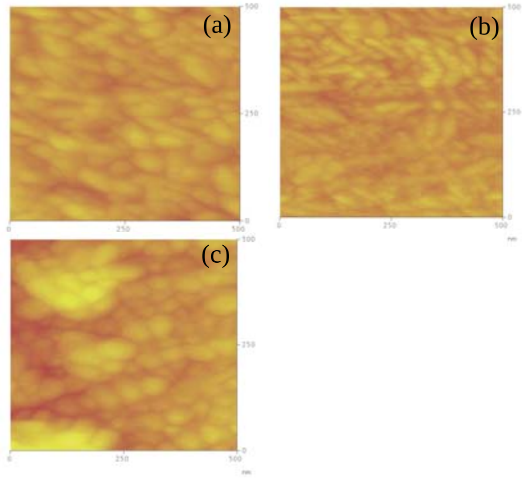

Fig. 2 AFM images of TiO_2 films deposited at room temperature and annealed: (a) As-deposited, (b) 300 °C and (c) 600 °C

in Fig. 2, the surface morphology reveals the nano-crystalline TiO_2 grains, which combine to make denser films significantly with the increased temperatures. Annealing up to 500 °C does not impart a significant change in structure. At temperatures of 600 °C the grains get larger but the basic structure remains unchanged. The films were mainly made of spherical particles. From the images, it was observed that the surfaces of the films exhibited a certain degree of roughness and the film came rougher when the annealing temperature increases.

C. *Optical Properties*

In this work, the optical thickness is evaluated for the as-deposited film as 315 nm which is in good agreement with the cross-sectional image by SEM shown in Fig. 3.

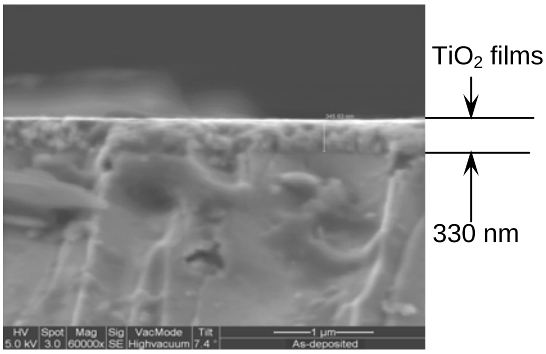

Fig. 3 SEM cross-sectional image of the as-deposited film

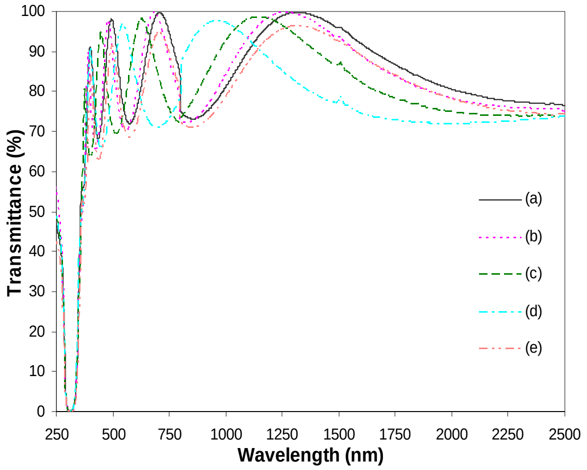

Fig. 4 Transmittance spectra of TiO_2 films: (a) as-deposited at room temp. (b) annealed at 300 °C, (c) 400 °C, (d) 500 °C and (e) 600 °C

In this work, from Fig. 4, it is found that average transmittance of as-deposited and annealed TiO_2 films is about 85% in the visible region with respect to reference blank glass substrate. Annealing shows a slight decrease in transmittance with the increase of annealing temperature. The films annealed at 600°C shows a significant decrease in visible light transmittance. It may be attributed to the light scattering effect for its higher surface roughness. It is observed that average transmittance of as-deposited TiO_2 films in the visible spectral region is found above 80% for films on glass and quartz substrate [12, 20]. TiO_2 films annealed at a higher temperature shows a lower transmittance [12]. Because annealing treatment causes a film surface to be more rough which scatters light.

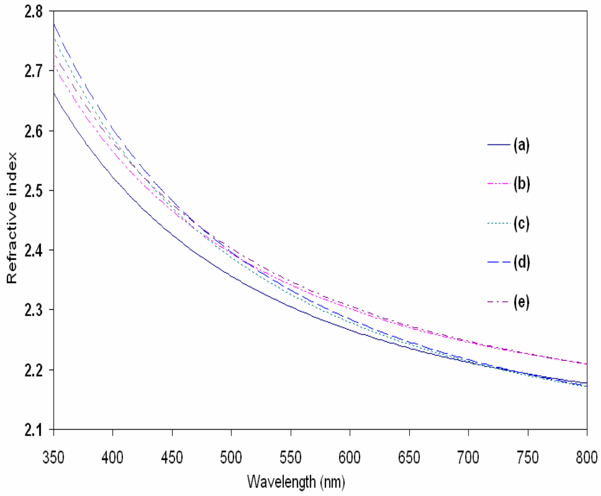

Fig. 5 Refractive index of TiO2 films: (a) as-deposited at room temp. (b) annealed at 300°C, (c) 400°C, (d) 500°C and (e) 600°C

The curves of refractive index and extinction coefficient for as-grown and annealed TiO_2 films are shown in Fig. 5 and Fig. 6. Here, it is found that the refractive index at 550 nm for as deposited, annealed at 300 °C, 400 °C, 500 °C and 600 °C are 2.31, 2.34, 2.33, 2.33 and 2.35 respectively. This trend shows an increase of the value of refractive index with higher annealing temperature. The increase may be attributed to higher packing density and change in crystalline structure. From Fig. 6, the extinction coefficient is also found to increase as the treatment temperature is increased. In the visible region, all the films exhibit very low extinction coefficient. Few researchers reported that the as-deposited or annealed anatase TiO_2 films had refractive index in the range of 2.10-2.50 and annealing treatment caused refractive index to increase due to the enhancement of crystallization [11, 13, 18].

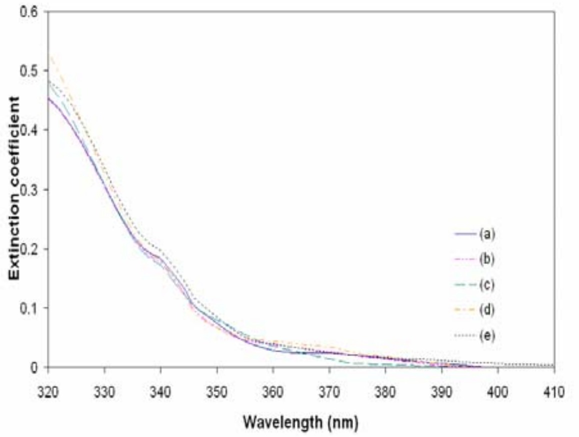

Fig. 6 Extinction coefficient of TiO_2 films: (a) as-grown at room temp. (b) annealed at 300 °C, (c) 400 °C, (d) 500 °C and (e) 600 °C

To quantify the optical band gap of films, Tauc Model[21] is employed in the high absorbance region of the transmittance specta

$$\alpha h\nu = A\left(h\nu - E_g\right)^r \tag{1}$$

where α is the absorption coefficient, $h\nu$ is the photon energy, E_g *is the optical band gap,* A is a constant which does not depend on photon energy and r has four numeric values (1/2 for allowed direct, 2 for allowed indirect, 3 for forbidden direct and 3/2 for forbidden indirect optical transitions). In this work, direct and indirect band gap was determined by plotting $(\alpha h\nu)^{1/2}$ vs. $h\nu$ and $(\alpha h\nu)^2$ vs. $h\nu$ curves respectively, with the extrapolation of the linear region to low energies. From Fig. 7**,** it was observed that indirect optical band gap increases from 3.39 eV to 3.42 eV with the increase of annealing temperature up to 600 °C. This increase may be attributed to the improvement of crystallinity of anatase phase. In the research, the indirect band gap results are in good agreement with the findings of Amor et al. [14]. For evaluating allowed direct band gap, the curves used are shown in Fig. 8. From Fig. 8, it is estimated that the direct optical band gap for the as-deposited film and annealed at 300 °C, 400 °C, 500 °C and 600 °C are 3.67, 3.68, 3.70, 3.72 and 3.68 eV respectively. Here the increase of direct band gap with the increase of annealing temperature is also observable. It was reported that for as-deposited and annealed TiO_2 films, direct optical band ranges from 3.50 to 3.80 eV [12, 13].

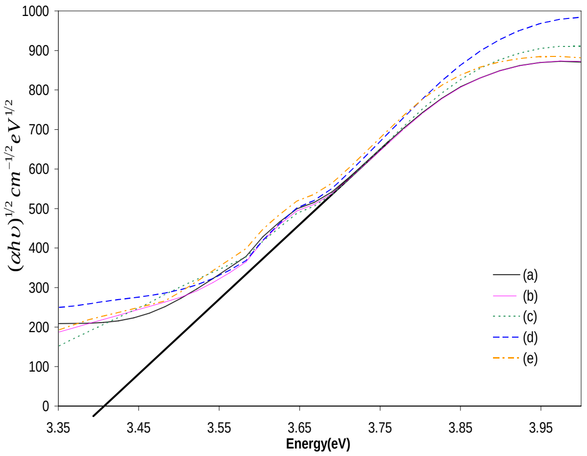

Fig. 7 $(\alpha h\nu)^{1/2}$ versus energy curves of TiO_2 films: (a) as-grown at room temp. (b) annealed at 300 °C, (c) 400 °C, (d) 500 °C and (e) 600 °C

The porosity (the volume of pores per volume of film) of the titania films depends on the refractivity of the film layer. To estimate the porosity ratio, the expression used is given below [11],

$$P = 1 - (n_p^2 - 1)\big/(n^2 - 1) \tag{2}$$

where n_p is the refractivity of the porous thin films; n is the refractivity of bulk TiO_2. From Eq. (2), the porosity ratio tabulated from the refractive index at a wavelength of 550 nm is shown in Table I. From the data, it is found that the porosity ratio decreases with the increase of annealing temperature.

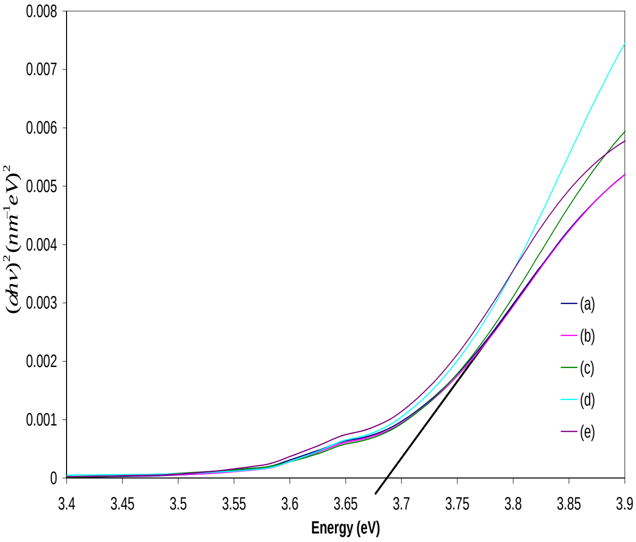

Fig. 8 $(\alpha h\nu)^2$ versus energy curves of TiO_2 films: (a) as-grown at room temp. (b) annealed at 300 °C, (c) 400 °C, (d) 500 °C and (e) 600 °C

TABLE I
POROSITY OF AS-GROWN AND ANNEALED TiO_2 FILMS

Samples	Refractive index at wavelength 550 nm	Porosity ratio (%)
As-grown film	2.31	19.0
Annealed at 300 °C	2.34	16.4
Annealed at 400 °C	2.33	17.2
Annealed at 500 °C	2.33	17.2
Annealed at 600 °C	2.35	15.5

IV. CONCLUSION

The anatase phase titanium dioxide thin films have been produced by RF reactive sputtering method on unheated glass substrates. The crystallization is found to increase slightly in the annealed films. AFM images also support the slow growth of crystallite sizes for the as-grown films and annealed films from 300 to 600 °C. The TiO_2 films are highly transparent in the visible range and annealing treatment causes slight decrease in visible transmittance. The film annealed at 600 °C have the least transmittance among the films. For as-grown and annealed TiO_2 films, the refractive index at 550 nm wavelength increases and ranges from 2.31 to 2.35 which is close to bulk anatase material. The extinction coefficient increases with the increase of treatment temperature. It is observed that the allowed indirect optical band gap of the films increases from 3.39 to 3.42 eV with the increase of annealing temperature. And the allowed direct band gap is found to increase from 3.67 to 3.72 eV.

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