

Effect of Annealing Temperature on the Structural and Optical Properties of TiO₂ Thin Film Prepared by Sol-gel Method

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Abstract

The effect of annealing temperatures on the surface morphology and optical properties of titanium dioxide (TiO₂) thin films deposited by spin coating on Silicon substrate was studied. The TiO₂ thin films deposited onto silicon substrates were annealed at different temperatures. The structural and optical properties were studied using scanning electron microscopy (SEM), X-ray diffraction technique (XRD) and optical ellipsometer. The results indicated that the structural properties of the TiO₂ thin films were changed with the increase in annealing temperature. The SEM investigation showed that as annealing temperature was increased, the grain and pores size were increased. The XRD patterns of the studied samples showed that rutile phase were found in a sample annealed at high temperature. The ellipsometry investigation shows that the refractive index increased while energy band gap decreased with the annealing temperature. The results showed that surface porosity, optical properties and surface morphology of TiO₂ could be affected by changing the annealing temperature.

Keywords: Thin film; Sol-gel; Spin coating; Annealing; TiO₂.

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1. Introduction

Titanium Dioxide, titania, TiO₂ is a promising wide band gap ($E_g > 3\text{eV}$) oxide material, and due to its unique properties such as non-toxic, inexpensive, highly photoactive, easily synthesized and handled, highly photostable, it has been subjected to extensive academic and technological research for decades [1,2].

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TiO₂ films are applicable for storage capacitor in integrated electronic, protective coatings, and optical components because of its high dielectric constant, hardness, and transparency. In order to improve the photocatalytic activity and optical absorption; study of nanosized TiO₂ is main focus [2]. TiO₂ is a large band gap semiconductor with exceptional stability that improves its importance in industrial applications. A TiO₂ thin film has a high refractive index due to which it has broad applications in optical coatings and waveguides [3]. TiO₂ normally occurs in three crystalline polymorphs: rutile (tetragonal), anatase (tetragonal), and brookite (orthorhombic) [4]. Both Anatase and Rutile phases are more common than the Brookite phase and have wide applications. Rutile is the most stable phase because of its high refractive index and density [5]. Particular phase formation of TiO₂ depends on the starting material nature, its composition, deposition technique, and annealing temperatures. TiO₂ thin films can be prepared by different methods including electron beam evaporation, Sputtering, Pulse Laser Deposition, Chemical Vapor Deposition, Polymer technique and sol-gel method [6-11]. The sol-gel is a quick and easy technique to produce homogeneous organic films with large surface areas. It is less demanding in terms of equipment and is thus less costly [12,13]. The main objective of this research is to use these thin films as electrodes in dye sensitized solar cells.

2. Experimental

The TiO₂ films were deposited on Silicon substrates by using spin coating deposition method. The silicon substrates were cleaned with acetone, methanol, and distilled water, followed by drying in an oven. The TiO₂ solution was prepared by mixing 50 mL deionized water and 3 mL acetic acid. Then one gram of TiO₂ nanopowder was added into the solution while vigorously stirring the solution. After that triton X-100 (one drop) was also added into the above solution. Then the solution was stirred continuously for 24 h at room temperature. The Si substrates were placed on spin coater and rpm value was fixed at 3000. The TiO₂ solution was dropped onto the substrates for 10 sec. The TiO₂ thin films were dried in the oven at 100°C for 10 min. After that, the films were annealed at 450°, 800° and 1000°C for 1 h in the furnace in air environment leaving one sample unannealed.

3. Results and Discussion

3.1. Structural characteristics

The structural and surface characteristics of TiO₂ thin films were studied in a scanning electron microscope (SEM). The microstructures of the as deposited sample and after being annealed at different temperatures are shown in the figure below (see Figs. 1a, 1b, 1c and 1d). It has been observed that as deposited TiO₂ thin film on silicon substrate has less grain size and pore area. Referring to Fig. 1b, the average grain size and pore area is increased. In Fig. 1c, the average grain size and the pores size of TiO₂ thin film is improved in a spherical shape. The average grain size and porosity at 1000°C is the highest among the sintered temperatures. This

shows that by increasing temperature the grain and pore size both increased which is in good agreement with the results by previous reported results [14,15]. These results showed that surface porosity and surface morphology of TiO_2 could be affected by changing the annealing temperature.

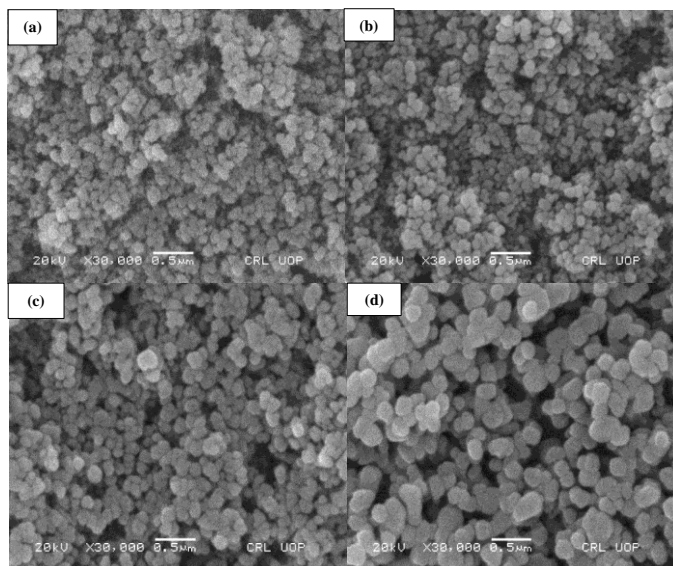


Fig. 1. (a), (b), (c) and (d) SEM images of TiO_2 thin films as-deposited and annealed at 450° , 800° and 1000°C using spin coater method at speed of 3000 rpm on silicon substrate respectively.

3.2. XRD results

Fig. 2 shows XRD patterns for TiO_2 thin films. The spectrum of as deposited film shows well defined diffraction peaks and possesses an Anatase and weakly brookite structure. There is no significant changes occurs in XRD peaks up to 4500°C . The intensities of the peaks of few TiO_2 planes changes slightly with the increase of annealing temperature and become rutile if the annealing temperature reaches to 10000°C which is good agreement with the results by Yoo *et al.* [16]. They reported only rutile structures of the samples annealed above 8000°C at 11000°C by conventional thermal annealing (CTA) of the TiO_2 thin films prepared by RF magnetron sputtering. It was also observed that at the high annealing temperature ($10,000^\circ\text{C}$) the intensities of the peaks increase due to which the FWHM of the peaks reduced, and by reducing the FWHM, the crystallite size increased (according to Scherrer formula). These results are in agreement with the SEM data presented above.

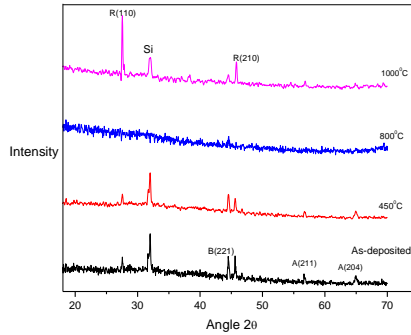


Fig. 2. XRD patterns for the samples as-deposited, annealed at 450°C, 800°C and 1000°C.

3.3. *Optical characteristics*

Optical properties (Refractive index and Band gap energy) were investigated from the data collected from optical Ellipsometer.

In Fig. 3, we show the refractive index (n) at the surface of the samples over the wavelength range of 350-800 nm. Increasing the annealing temperature the gradual increase in the value of “ n ” can be seen. It can also be seen that the value of “ n ” decrease with increasing the wavelength. This increase in “ n ” with annealing temperature is attributed to the increase in packing density and crystallinity of the films which are also evident from the thickness measurement and XRD analysis. These results are in good agreement with the results obtained by Rahman *et al.* [3] and the results obtained by Kaduory [17] and Al-Obaidi [18].

The energy gap value depends on the films deposition conditions and its preparation method which influences in the crystalline structure [19]. The reason of variation in energy gap is by making variations in the structural and other properties of the deposited films.

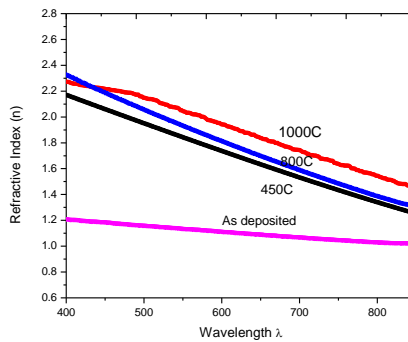


Fig. 3. Variation of Refractive Index with wavelength for different annealed samples.

Optical Energy Gap (E_g) can be calculated by extrapolating the straight line part of the curves $(\alpha h\nu)^2$ with energy axes ($h\nu$) i.e. $(\alpha h\nu)^2 = 0$ we evaluated the band gap of the TiO_2 thin films, as shown in Fig. 4. From the Figure it can be observed that E_g is decreased with the increase of the annealing temperature. The result obtained is consistent with the reported literature [20]. Annealing led to increased levels of localized near valence band and conduction band and these levels ready to receive electrons and generate tails in the optical energy gap and tails is working toward reducing the energy gap, or can be attributed decrease energy gap to the increased size of particles in the films [21] or we can say that decrease in the bang gap energy occur with increasing the annealing temperature is due to the lowering of interatomic spacing.

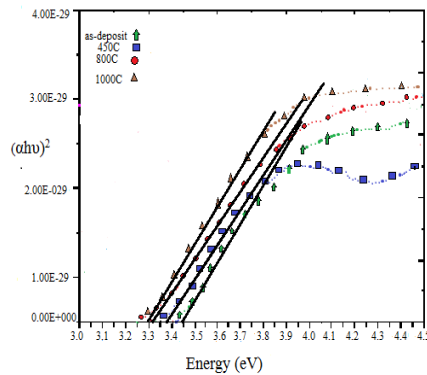


Fig. 4. $(\alpha h\nu)^2$ as a function of photon energy.

4. Conclusion

Titanium dioxide (TiO_2) thin films were deposited by spin coating technique on Silicon (Si) substrates. The effect of annealing temperatures on the surface morphology and optical properties were studied by using SEM and XRD and optical properties were studied by optical ellipsometry. The XRD result indicated that as the annealing temperature was increased the grain and pore size was increased. The SEM investigation showed that at higher annealing temperature the grains were well shaped i.e. spherical. The optical investigation shows that the value of refractive index and band gap changes with the annealing temperature.

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