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Optical, microstructural and electrical studies on sol gel derived TiO_2 thin films

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TiO_2 thin films have many interesting optical, physical, electrical and chemical properties that offer many applications in different fields of science and technology. The sol-gel spin coating technique has immense advantageous; such as low cost, usage of very simple equipment and relatively easy process control method. The optical, structural, microstructural and electrical properties have been analyzed through four point probe, XRD, SEM, high resolution electron microscopy, AFM and UV-VIS-NIR spectrophotometer. This paper is a research article about the sol-gel spin coated TiO_2 thin film. The results will focus on the preparation and coating of TiO_2 thin films on glass substrate at different annealing temperatures.

Keywords: TiO_2, Sol gel, Spin coating, XRD, SEM, HRTEM, AFM

1 Introduction

The unique properties of TiO_2 such as high chemical stability and corrosion resistance make its superior from the other metal oxide materials. In recent years TiO_2 has become the most promising material in Nano technology and Nano science, because of having extensive interesting properties in the fields of medicine, catalysis[1] , dye-sensitized, gas sensor, waveguides applications[2] and optoelectronics devices[3]. It is used in anti-reflection coatings for optical devices due to its high refractive index. Furthermore used as a sunscreens, ointments toothpaste and pigment in paints[4]. The wide range applications of TiO_2 in different fields are due to its particle size, morphology and crystalline structure[5]. Various techniques have been used to prepare TiO_2 thin films; such as chemical vapor deposition, sputtering, hydrothermal and sol–gel process[1]. Among of all the other techniques, the sol-gel method has the most promising technique that offers many advantageous; such as low cost, capability of large coating size, usage of very simple equipment and relatively easily controlled method[6]. Moreover in photo catalysis, where high surface areas are required sol–gel processing allows the preparation of effective supported catalysts[7].This method is also used to produce TiO_2 thin films at lower temperatures in a relatively shorter processing time[8]. Through experiments it is realized that the properties of TiO_2 films strongly depend on the starting materials and process conditions. Many researchers have used sol-gel method to synthesize TiO_2; in 2004 Li *et al* [9] studied the "Preparation and characterization of nano-TiO_2 powder by sol-gel method" and analyzed the mean size of about 10 nm after calcinations. Similarly, Yu *et al.*[10] researched into the photo catalytic activity of nano-sized TiO_2 powders by sol-gel method, using $EtOH/H_2O$ solution. As results two phases such as anatase (75.1%) and brookite (24.9%) were obtained at 400 °C. The particle sizes (7.9 nm and 7.4 nm) were also obtained, respectively[10]. Furthermore Hemissi *et al.*[11] investigated "Optical and structural properties of TiO_2 Thin films". The optical band and dielectric constant were estimated to be 2.79 eV and 5.20 eV, respectively. Moreover Yuwono *et al.*[12] investigated "The Nano structural evolution of TiO_2 nanoparticles in the sol-gel derived TiO_2-polymethyl methacrylate Nano composites" by changing the coupling agent concentration, pH value, and water to alkoxide ratio. They found the significant enhancement in the nanocrystallinity of the TiO_2 phase in the resulting nano composites[12].

This paper reports on the investigation of the optical, microstructural and electrical properties of TiO_2 thin film prepared by sol-gel method deposited by spin coating. The optical, microstructural, electrical and the morphology of such material have been investigated by four point probe, XRD[13], SEM, high resolution electron microscopy[5], AFM and UV-VIS-NIR spectrophotometer[13].

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2 Experimental

2.1 The substrates, TiO_2 thin film solutions and equipment used in experiments

The TiO_2 thin film was prepared by sol-gel spin coated method as described in literature[5,14]. We have two solutions such as; precursor and hydrolysis. In our work, precursor is prepared by adding Tetrabutyl titanate ($Ti(OC4H9)_4$, TBOT) with ethanol. While on the other hand distilled water mixed with methanol is used as a hydrolysis solution. The sol-gel solution is prepared by adding precursor in the hydrolysis solution. We mixed and stirring these solutions at 100 °C temperature for 2 h. Glass was used as a substrate. This substrate was first heated at 200 °C for 20 min, and then cooled down to room temperature[14]. Then sol-gel prepared TiO_2 solution was spin coated on the prepared glass substrate. The spinning speed was kept 3000 rpm for 1 min. The coating thickness was kept (0~12 inch/min). Then the substrate was annealed at temperature 700 °C for 30 min. Finally we got the TiO_2 thin film on the glass substrate. The flow chart of the whole experimental work is shown in Fig. 1. The average crystalline size was estimated through powder X-ray diffraction (Philips PW-3710, Holland) instrument. Morphology and structure properties of TiO_2 thin films have been revealed through high resolution transmission electron microscopy (HRTEM). The morphology of the thin film has been observed on Philips XL-30 scanning electron microscope (SEM). Atomic force microscopy (AFM)[8] was used to estimate the roughness of the film. Optical properties were investigated through UV-VIS-NIR spectrophotometer. The resistivity and mobility were determined through four-point method[5].

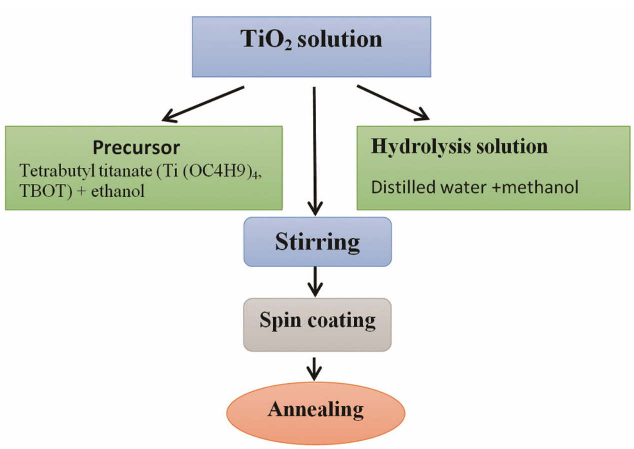

Fig. 1 – Flow chart of experimental work

3 Results and Discussion

3.1 Structural properties

X-ray diffraction (XRD) pattern of TiO_2 thin film annealed at 700 °C shown in Fig. 2. According to investigations of Pawar *et al.*[5]; it was showed that rutile phase (*R*) was along at 2θ = 27.600, 36.180, 39.120 and anatase phase (*A*) was along the [101] direction shown in Fig. 2. According to Sabataityteÿ et *al.* through spray pyrolysis technique for the layer deposition, at 500 °C annealing temperature anatase phase obtain. On the other hand, spin coating technique leads to the formation of anatase phase after annealing at 450 °C; and the rutile crystalline structure[5] was observed after annealing at temperatures higher than 700 °C. While on the other hand scanning electron microscopy (SEM) has been used to investigate the surface morphology of the TiO_2 thin film shown in Fig. 3. It has been investigated through micrograph

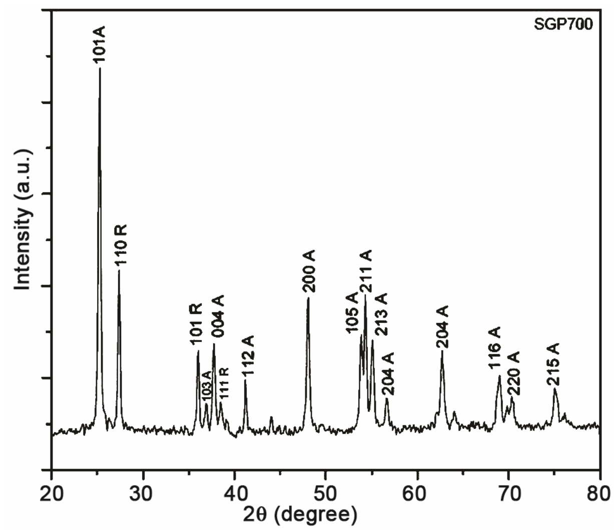

Fig. 2 – X-ray diffraction (XRD) pattern[5] of TiO_2 thin film annealing at 700 °C

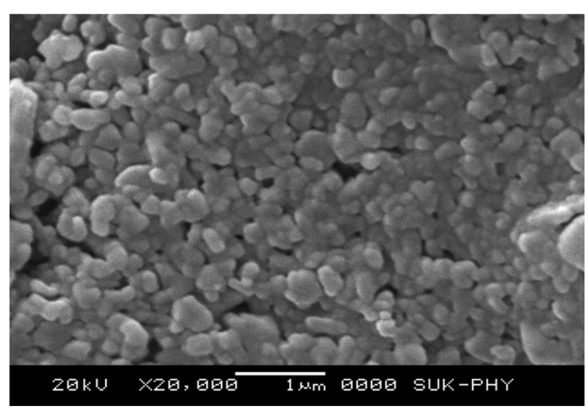

Fig. 3 – Surface morphology[5] of TiO_2 nanoparticle film annealing at 700 °C

that the average grain size is the 60 nm at 700 °C annealing temperature[5]. According to Hemissi *et al.*[11] the surface morphology of the TiO_2 nanoparticle film annealed at 600 °C, clearly shows that nanoparticles have extra-fine structure, with an average grain size of 20 nm shown in Fig. 4. Both these results show that by increasing annealing temperature the average grain size increase. The increase in grain size may be due to deficiency of oxygen on the surface.

3.2 Microstructural properties

Figure 5 shows the high resolution image of TiO_2 thin film. HRTEM results revealed that grain diameter was in ranged from 2-3 nm. Surface morphology of the thin film was observed through AFM imaging shown in Figs 6 and 7. According to Xiaodong *et al.*[14] the surface roughness increased after annealing temperature. The root mean square roughness (R_q) of the surface is less than 1 nm and increases with the increasing annealing temperature. These results revealed that the regular shaped grains develop on the surface of the substrate. The obtained values of root mean square roughness at 500 °C and 700 °C is R_q=0.464 nm and R_q=1.356 nm, respectively. At 700 °C annealing temperatures, the grains combine with each other and make denser coatings. It was also observed that grain size become larger at that temperature but the basic structure remains un-changed[14]. These obtained results were also confirmed by Senain *et al.*[8]. Surface morphology of TiO_2 thin film before and after the annealing can be shown in Fig. 8 The roughness of thin film was increased from 0.341-1.690 after the annealing process[8]. Both these results confirmed that surface roughness increased after annealing. The actual size of the surface remains same but the grain size become larger after annealing. As a result the surface roughness increases.

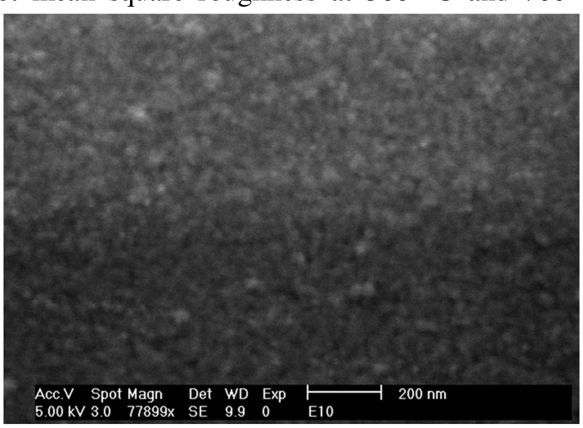

Fig. 4 – SEM microscopy[11] of TiO_2 nanoparticles annealing at 600 °C

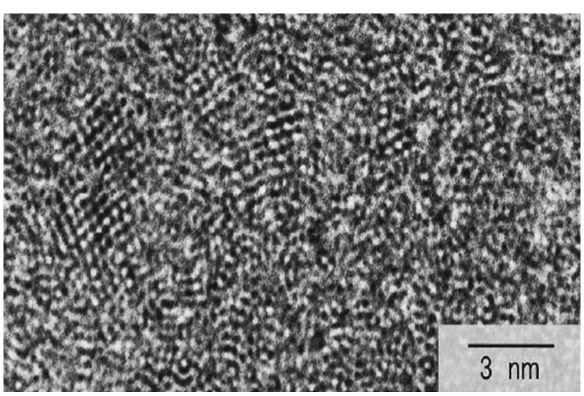

Fig. 5 – High resolution TEM image[5] of TiO_2 thin film annealing at 700 °C

3.3 Optical properties

Band structure and band gap energy (E_g) has been studied through optical transmission spectra. Figure 9 shows the reflection and transmission spectra of thin films annealed at 700 °C temperature. Pawar *et al.*[5]

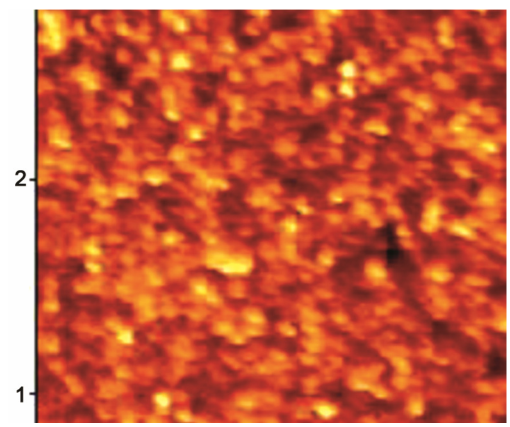

Fig. 6 – 2-D AFM images[14] of TiO_2 thin film at 500 °C annealing temperature

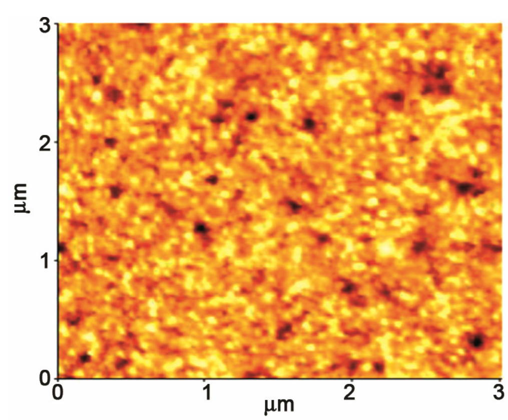

Fig. 7 – 2-D AFM images[14] of TiO_2 thin film at 700 °C annealing temperature

investigated that when spectrum reached at high energies level transmission become decreases due to inter band absorption. These results revealed that the optical absorption coefficient is a function of incident photon energy of TiO_2 thin film[5]. The absorption coefficient α can be written as:

$$\alpha hv = B\left(hv - [E_g)]^{2} \qquad \ldots (1)$$

where E_g = optical band gap, m= transition level. The factor B depends on the transition probability and can be taken constant[5]. Let Y= αhv and Y' be the first derivative of Y with respect to photon energy, from Eq. (2) we can obtain:

$$\frac{Y}{Y`} = \frac{hv - E_g}{m} \qquad \ldots (2)$$

Y and Y' are determined from experimental data; m is slop and E_g is the intercept of the linear plot Y/Y' versus hv. The plot of Y/Y' as a function of photon energies of thin films which is annealed at 700 °C can be shown in Fig. 10. Through these investigation the obtained value of slope and band gap energy are m=1/2 and E_g =3.24 eV, respectively[5]. Xiaodong *et al.*[14] investigated that the refractive index increased with increasing annealing temperature as shown in Fig. 11. The results obtained from calculations and measurements over the 400~1000 nm wavelength region. The results revealed that the refractive index increases with annealing temperature from 1.98-2.57. The rapid increase of refractive index at 700 °C temperature might due to the thermal induced growth of the grains which increased the packing density[14].

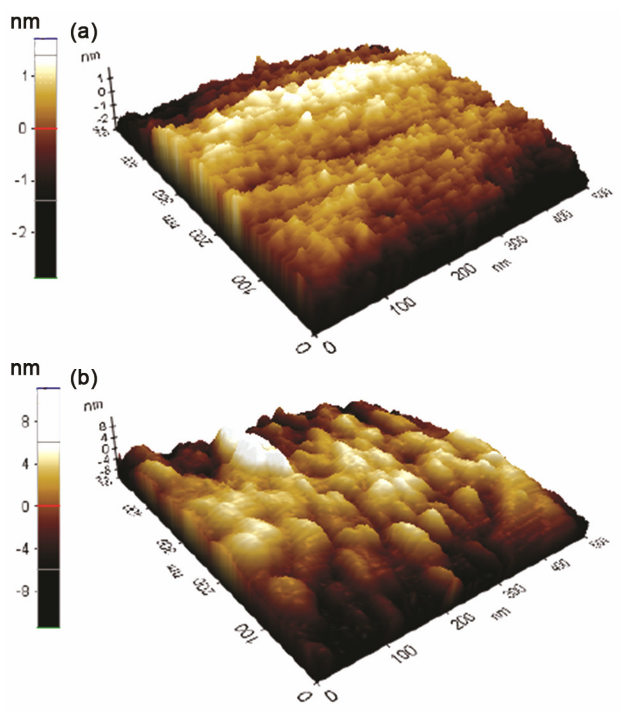

Fig. 8 – AFM image[8] of TiO_2 thin film (a) before and (b) after annealing process

3.4 Electrical properties

The electrical properties of TiO_2 thin films have been observed through four point probe. According to Pawar *et al.*[5] TiO_2 thin films annealed at 700 °C is *n*-type semiconductors and free electron density of these semiconductors[5] is 7.7×10[13] cm-3. In the same year these results were also confirmed by Senain *et al.*[8] The obtained results of resistivity of TiO_2 thin film before and after the annealing process can be

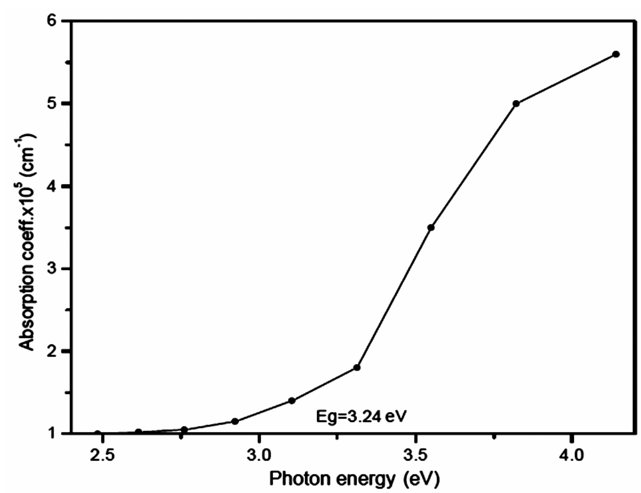

Fig. 9 – Optical absorption coefficient function[5] of incident photon energy of TiO_2 thin film annealing at 700 °C

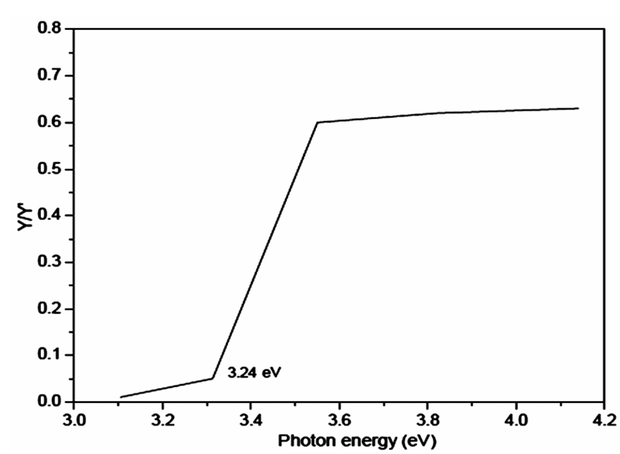

Fig. 10 – Plot of Y/Y′ as a function of photon energies[5] of TiO_2 annealing at 700 °C

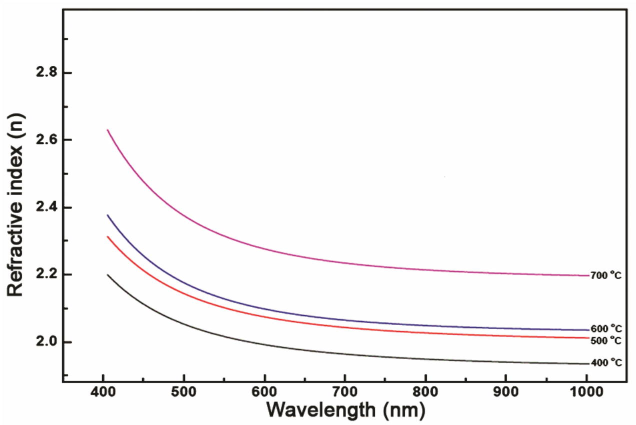

Fig. 11 – Refractive index dispersion[14] of TiO_2 annealing at different temperatures

Table 1 – Resistance and resistivity of TiO2 thin film before and after annealing process[8]

	Before anneal	After anneal
Resistance (Ω)	5.00E+08	8.00E+07
Thickness (*µm)*	0.5	0.4
Resistivity (Ω.cm)	2.34E+04	3.20E+03

seen in Table 1. Both these results show that the resistivity decreases after annealing. This is due to the increasing in the grain boundaries and also due to the oxygen deficiency in the surface after annealing.

4 Conclusions

The sol-gel technique is relatively easy process control method. A review of TiO_2 thin films prepared by sol-gel spin coating technique was carried out. The general procedure includes the preparation of TiO_2 thin films and its deposition on glass wafer by spin coating method. The optical, structural, microstructural and electrical properties have been analyzed through four point probe, XRD, SEM, high resolution electron microscopy, AFM and UV-VIS-NIR spectrophotometer. Through X-ray diffraction pattern it has been revealed that anatase to rutile phase change took place after increasing annealing temperature from 500-700 °C. Scanning electron microscopy (SEM) results show that grain size become lager from 20-60 nm when we increased the annealing temperature from 600-700 °C. The increase in grain size might be due to deficiency of oxygen on the surface and increase in the grain boundaries. Surface morphology has been observed from AFM images. These results revealed that when annealing temperature increased from 500-700 °C, the surface roughness also increased from R_q=0.464–1.356 nm, but the basic structure remains un-changed. An optical transmission spectrum shows that transmission decreases and refractive index increases with annealing temperature, from 1.98-2.57. The rapid increase of refractive index at 700 °C temperature might due to the thermal induced growth of the grains which increased the packing density. Four point probe results also analyzed that resistivity decreases after annealing. This is due to the increasing in the grain boundaries and also due to the oxygen deficiency in the surface.

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