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Influence of annealing temperature and number of layers on the properties of nanocrystalline TiO₂ thin films: Structural & Optical investigations

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Abstract: Fabrication of TiO₂ thin films was carried on microscopic glass substrates by sol-gel spin coating method using Titanium tetra isopropoxide (TTIP) as an initiating inorganic precursor. Films with different post annealing temperatures and varying number of layers were coated. It has been observed from XRD study that the size of crystallites of TiO₂ film was found to increase with increase in both annealing temperature and number of coatings. UV-Visible spectrometric measurements revealed that the transmittance of the film and the band gap values, calculated from Tauc's relation, were found to decrease with increase in both film thickness and annealing temperatures. Two emission peaks at 485 nm & 502 nm were observed in Photoluminescence spectrum of all the films. Changes in the surface morphology of the films were investigated using FESEM studies. The resistivity decreases with increase in number of coatings. The obtained results show that the post annealing temperature and the number of coatings have influence over the physical properties of TiO₂ thin films.

Keywords: TiO₂ thin films; Sol-gel process; Spin coating method; XRD; UV-Visible; Photoluminescence; FESEM & Resistivity.

Introduction and Experimental:

Titanium dioxide (TiO₂) is one of the most extensively studied transition metal oxide. TiO₂ possess excellent properties such as chemical resistance, mechanical strength, transparency and insulating properties [1]. Sol-gel deposition method is employed to coat TiO₂ films for good film homogeneity, low processing temperature, large area coating and low equipment cost [2].

In the present work, TiO₂ thin film was prepared using titanium tetra isopropoxide (TTIP) by sol-gel spin coating technique. 1 ml of TTIP was mixed with 10 ml of ethanol and stirred for 10 minute using magnetic stirrer to obtain a milky white solution. To this mixture 1 ml of acetylacetone was added and stirred for 30 minute. Again 10 ml of ethanol was added to the solution and stirred vigorously for 3 hours. The prepared sol was kept in open air for 48 hours for aging to form the gel. The gel was dropped onto the clean glass substrate, and rotated at a speed of 3000 rpm for 10s by using a spin coater. The coated film layer was dried at 150°C for 10 minutes in a muffle furnace. The process of spinning and drying was repeated for two more times to obtain a 3 coating film. Finally the coated films were annealed at 450°C for 1 hour. Similarly 5 coating films were

prepared. In order to study the changes in detail two more films were prepared with 3 and 5 coatings but with a post annealing temperature of 550°C.

This paper deals with the study of structural and optical properties of TiO₂ thin films prepared by varying number of coatings at two different post annealing temperatures and the surface morphology and the resistivity of the films were also analysed.

Results and Discussion:

Structural Analysis

X- ray diffraction analyses of the films were carried out to study the structure of the films. From Figure 1(a) & (b) it is observed that the single coated film was amorphous in nature. The most dominant peak with (1 0 1) orientation is observed for all the films other than single coating. For the film with 3 coatings annealed at 450°C along with dominant peak, another peak of (2 0 0) orientation is alone present. All the observed orientations which correspond to tetragonal structure with anatase phase match well with JCPDS file No- 21-1272. Less intense diffraction peaks of (0 0 4), (2 0 0), (1 0 5), (2 1 1) and (2 1 3) orientations are also observed for all other films.

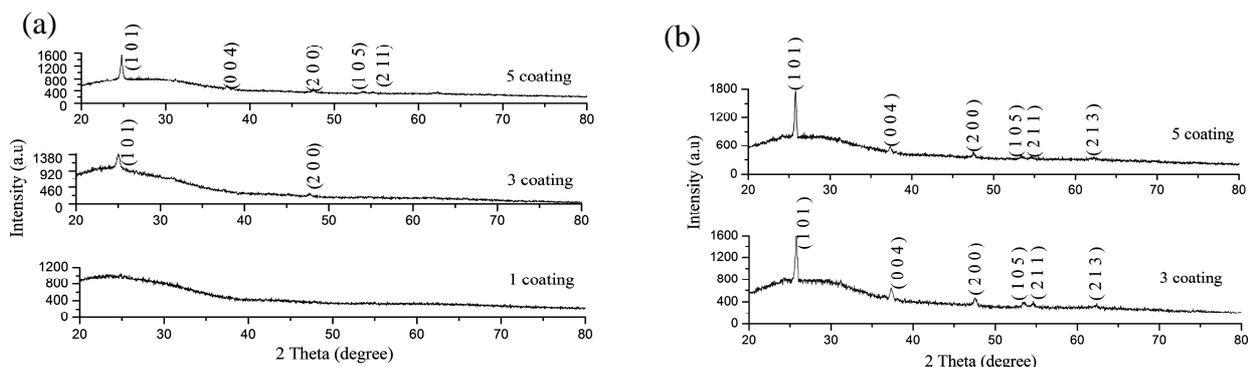


Figure 1(a) and (b) XRD patterns of TiO₂ thin films prepared at 450°C & 550°C

For the film with 5 coatings annealed at 450°C and the films with 3 & 5 coatings annealed at 550°C, in addition to anatase phase, (2 1 1) orientation of rutile phase (JCPDS file No-21-1276) was also observed. The Crystallite sizes calculated using the Debye Scherrer formula for the films annealed at 450°C with 3 and 5 coatings are 6.3 nm, 8.2 nm and for the films with 550°C are 7.4 nm and 19 nm respectively. The peak intensity and crystallite size increases with increase in both annealing temperature and number of coatings. Thus the crystallinity of TiO₂ thin film depends on the growth conditions and number of layers.

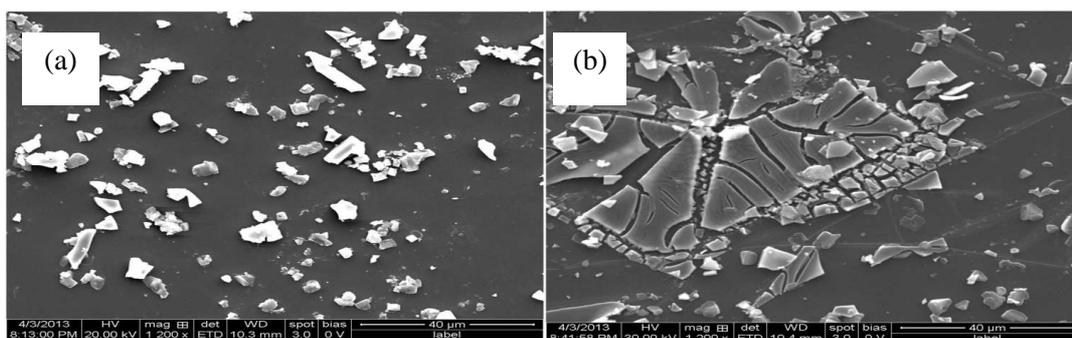


Figure 2(a) and (b) FESEM images of TiO₂ film annealed at 450°C & 550°C with 5 coatings

The surface morphological observations were done by FESEM. Figure 2 (a) and (b) shows the surface morphology of TiO₂ thin films with 5 coatings annealed at 450°C and 550°C. Figure 2(a) shows scattered particles on the surface and Figure 2(b) shows agglomerated particles with non-homogeneous cracks.

Optical Analysis

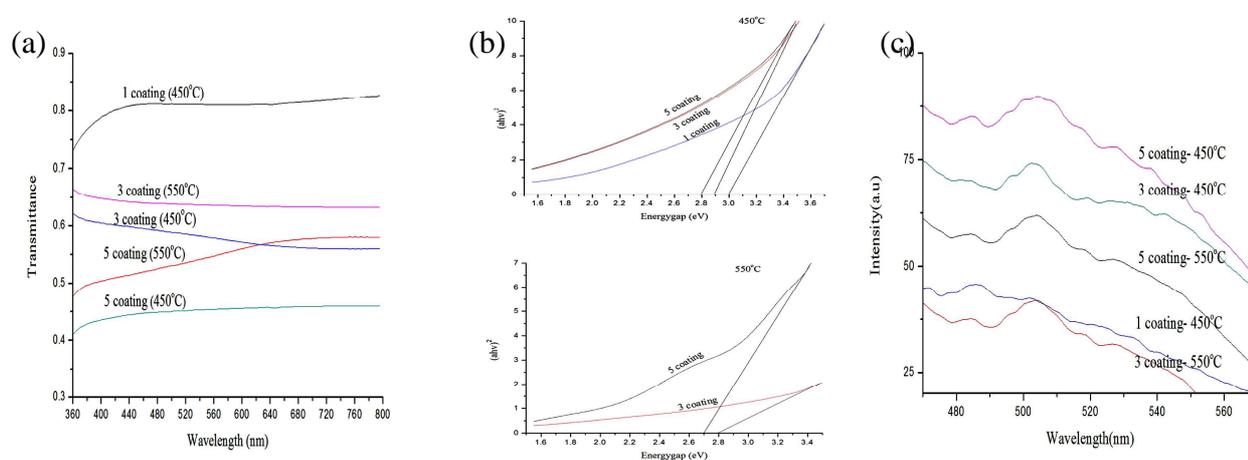


Figure 3(a),(b) and (c) optical Transmittance, energy gap & PL spectrum of TiO₂ thin films

From UV-Visible study, it is observed that the optical transmittance reduces as the number of layers and correspondingly thickness of the film increases. The films annealed at 550°C have better transparency than the films annealed at 450°C for same number of coatings. The energy gap values calculated from Tauc's relation for films annealed at 450°C with 1, 3 & 5 coatings are 3 eV, 2.9 eV, and 2.8 eV and for 3 and 5 coating films annealed 550°C are 2.8 eV and 2.7 eV. The energy gap value decreases with increase in both the number of coatings and the post annealing temperature. Photoluminescence spectra of TiO₂ thin films show two visible emission peaks at 485 nm and 502 nm and the PL peak intensity decreases with increase in annealing temperature. The emission peak at 485 nm is attributed to impurities and defects [3].

Electrical Analysis

The electrical resistivity of the samples is found to be at the range of MΩ. The high value of resistivity may be due to chemisorption of large number of oxygen molecules at surface grain boundaries. The absorbed oxygen will produce potential barrier which hinders the electrical transport. The resistivities of the films with 3 coatings are 1.52 MΩ and .74 MΩ for 450°C and 550°C annealing temperature respectively. Similarly the resistivities of the films with 5 coatings are .90 MΩ and .41 MΩ for 450°C and 550°C annealing temperature. Thus the resistivity decreases nearly half the value with increase in annealing temperature. The resistivity decreases also with increase in number of coatings and it is so as the increase in number of layer increases the cross sectional area of the films.

From the obtained results we observed that the post annealing temperature and the number of layers influence the physical properties of TiO₂ thin films.

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