Structural and Optical Properties of TiO₂ Thin Films Prepared by Sol-Gel Ultrasonic Dip-drive deposition

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TiO₂ thin films have been deposited onto well cleaned glass substrates by indigenously developed ultrasonic dip-drive coating method at different pH values 3 and 11 of the sol. After deposition, the films were annealed at three temperatures (350°C, 450°C and 550°C). X-ray diffraction results have shown that TiO₂ films are ploy-crystalline and have well defined anatase structure. The crystallites are preferentially oriented with (112) planes parallel to the substrate surface. The films have a high transparency (more than 75%) in the spectral range from 400 nm to 2500 nm. The analysis of absorption spectra show the direct nature of band to band transitions. The optical band gap energy ranges between 3.15 eV and 3.25 eV.

Keywords: TiO₂, Sol-Gel dip-drive coating, Band gap

INTRODUCTION

More attention has been given to the research of nano-materials. Compared with thin film and bulk materials, nanophase materials have unusual chemical, mechanical, optical, electrical and magnetic properties[1]. Titanium dioxide (TiO₂) semiconductor has a direct band-gap (Eg = 3.2 eV) with a large exciton binding energy, exhibiting near UV emission. TiO₂ is a bio-safe and bio-compatible material, and can be used for a variety of applications. It has attracted great attention in the fields of environmental purification, solar energy cells, photocatalysts, gas sensors, photoelectrodes and electronic devices. Catalytic applications of titanium dioxide have been studied for decades regarding the elimination of environmental pollutants and, more recently, for photocatalytic processes concerning the degradation of pollutants in air, water and soil [2-9]. There are many methods for preparing nano particles of TiO₂ sol-gel method [10], ball milling [11], chemical vapour deposition [12] and microemulsion [13] among them the sol-gel method show many advantages such as mild reaction conditions, less energy consumption, simple equipment and a large number of variable factors to control the morphology of the film [14].

Currently, the synthesis of TiO₂ by the sol-gel method has proven to be a very useful tool for photo-induced molecular reactions to take place on a titanium dioxide surface [15]. There are special variables that affect the photo-induced reactions, including particle size, phase composition, incident light and preparation method; for instance, anatase TiO₂ nanoparticles have shown higher photocatalytic activity than rutile TiO₂ [16]. Two types of mechanisms are involved in the TiO₂ thin film formation. The first one involves growth of the layer from individual atoms in solutions, which is referred to as the ion-by-ion process. The second one is the cluster-by-cluster growth, where the clusters form in solution by parallel homogeneous reactions. The basic idea of the present investigation is TiO₂ thin film preparation from the optimized amount of titanium (IV) isopropoxide, nitric acid and ammonia.

MATERIALS AND METHODS

Initially, diluted solution of ethanol (24.5 mL) was taken in a 50 mL beaker and titanium (IV) isopropoxide (2.5 mL) was added drop by drop into the solution. Then drops of water using syringe (0.25 mL) were added for hydrolysis and poly-condensation, and nitric acid (0.15 mL – 0.25 mL) was added to control precipitation in the solution. Controlled amount of ammonia was added to attain different pH values of the solution. The expected pH values of the solution were confirmed by using digital pH meter. The final mixed solution was stirred at room temperature for three hours. The transparent precursor solutions of different pH values were prepared for the deposition of thin films. Fig. 1 shows the schematic diagram of the newly indigenously designed and developed ultrasonic dip-drive coating unit. The unit is fabricated to carry out the repeated dip coating and heat treatment (pre heating) for thin film under ultrasonic environment. The simple unit consists of a fixed tall beaker containing water, floating beaker containing clear solution (sol), with immersed fixed substrate. The complete set up is placed inside an ultrasonic agitator. The withdrawal speed is fixed as 0.1mm/min by adjusting the knob in the side tube so as to have 30 drops per minute. Well cleaned and pre heated (in the temperature range 200-250°C for ten minutes) glass substrates were fixed with stand and immersed in the beaker containing sol-gel solution.

In the beginning, clear solution is taken in floating beaker and it is allowed to float in the fixed beaker (with enough water) then stop cock is adjusted to drip water, so that the decrease the water level in the fixed water beaker is in the order of

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Fig. 1. Schematic diagram of ultrasonic dip-drive coating unit

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mm/min. Once water in the fixed beaker is drained up to the spout, the thin film deposited substrate is heated and allowed to cool for half an hour. The procedure is repeated for three to six times to increase the thickness of the films. Thin film were post heated in conventional furnace at different temperatures of 350°C, 450°C, and 550°C for one hour and allowed to cool to room temperature in the furnace. Transparent homogenous films with high adherence to the substrates and excellent chemical as well as mechanical stability were finally obtained. The deposited films were collected and labeled. X-ray diffraction (XRD) patterns of the films were recorded in the 2θ range from 20° to 80° with Philips Xpert pro with Ni filter and Cu Kα radiation. The investigations of surface morphology of films on the glass substrate were carried out using Scanning Electron Micrograph (SEM Hitachi 63400N). Optical transmittance and absorption data of the films were measured in the range of 120 - 2500 nm using a JASCO-370 spectrophotometer. The thickness of the films was measured by multiple beam interference technique and the thicknesses were found to be in the range 800-900 nm. The crystalline size (D) are calculated using Scherrer’s formula from the full width at the half maximum (β) using the relation \( D = \frac{0.94\lambda}{\beta \cos \theta} \).

The strain (ε) is calculated for the slope of ρ cosθ versus sinθ plot using the relation, \( \beta = \frac{\lambda}{D \cos \theta} - \varepsilon \tan \theta \). The dislocation density (δ) is calculated from the relation \( \delta = \frac{1}{D^2} \). The lattice parameter (a & c) of the crystal are determined by using the relations \( \frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \), where (hkl) is the Miller indices of the predominant peaks. The absorption coefficient (α) is estimated from the optical transmittance spectra using the relation \( \alpha = \frac{2.303}{t \log_{10}(T)} \), where T is the Transmittance (in %) and t is the thickness of the film. All the graphs satisfy the condition for direct transition in the excitation process (ie) \( \alpha = (E_t - E_v)^{\frac{1}{2}} \) for allowed direct transition, where \( E_v \) is the top of the valence band and \( E_t \) the initial state from which the transition is made. All the films exhibit direct band gap structure and their band gap values are found to be nearly 3.3 eV.

**RESULTS AND DISCUSSION**

Fig.2 shows the XRD patterns with SEM images of TiO₂ thin films annealed at 350°C, 450°C, and 550°C. The XRD patterns in general have exhibited lesser degree of crystalline. The crystalline phase present in these films is identified as anatase structure of TiO₂ as shown in figure 4 as per JCPDS 861155, 861156, and 861157 [17]. The intensity of the peaks corresponding to the planes (101) and (200) enhances as the annealing temperature of the films increases and the 2θ values of the XRD peaks are closure to other experimental data [18-24]. Importantly a preface orientation is seen along the (101), and (200) planes in all the annealed films. This shows that annealing of these samples at these temperatures have induced in some constructive features. Further, increase in annealed temperature causes a significant dominate peaks of anatase TiO₂, which is consistent with the increasing crystalizing of the sample. The lattice parameters, particle size, strain and dislocation density of the films deposited from XRD graphs are determined, it is found that the size of the particle increases with the annealing temperature in all films also with higher pH values and the results are in agreement with the SEM results.

**CONCLUSION**

Platinum Sol-gel dip drive coating is a very economical and a versatile technique to deposit homogeneous and good quality thin films. The film thickness can be increased by repeating the deposition cycle of dip coating. We have showed that a deposition cycle which involves curing the film at 100°C for ten minutes after each dip coating, it is a very practical approach to obtain uniform and smooth TiO₂ films with...
desired thickness. The change from amorphous-to-crystalline nature occurs after annealing at 450°C. A detailed study of the structural, optical properties of the films using various experimental tools provided an insight into the effect of post deposition annealing on the properties of the films. The major observations of this study can be summarized as follows. The grain size showed dependence on annealing temperature indicating re-crystallization. Band gap of the film decreased from 3.4 to 3.32 eV while annealing from 350 - 550°C, which is higher TiO2 films prepared at different pH values 3 and 11 at different post annealing temperatures. In all the cases the films are found to be transparent above (50-70 %) in the visible range with the sharp absorption edge at 300 nm. The electrons and holes are important parameters describing the most carrier transport properties in the film. The high band gap observed in this study can be correlated with the nano-crystalline nature of the films, which could be a result of the film preparation and curing procedures adopted. The as deposited films are porous and found to dense as annealing temperature increases.

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