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Influence of temperature on structural and optical properties of nano-crystalline TiO_2 films prepared by Sol-Gel dip-drive coating

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Nanocrystalline TiO_2 thin films have been deposited on well cleaned glass substrates by Sol-Gel dip drive technique. The films have been prepared at pH = 9 and the prepared films are annealed at three distinct temperatures (350°C, 450°C, and 550°C) for one hour. The prepared films are characterized by XRD, EDAX, SEM and UV-Vis Spectrophotometer. The structural studies carried out reveals that the pristine films are amorphous in nature. The annealed films have been observed to be nanocrystalline in nature and the crystallinity has been observed to improve on annealing. The transmittance and absorbance spectra have shown that the films are transparent and band gap of the films are of the order of 3.26 eV.

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Keywords: TiO_2, Sol-Gel dip-drive coating, Band gap, Band structure, Effective mass of electrons and holes

1. Introduction

Nanocrystalline TiO_2 thin films are highly attractive in the development of materials area, due to their chemical stability, high refractive index, wide band energy gap, and high dielectric constant [1]. Titanium di-oxide nanocrystalline thin films find wide applications in the devices such as photo-voltaic, gas sensors, humidity sensors [2-4] and promising electrode material in dye-sensitized solar cells [5]. The property of TiO_2 thin films depends on the crystalline phase, roughness, porosity, and particle size. When the particle size is sufficiently small, it is possible to observe quantum size effects [6]. Good photo-catalytic activities of the TiO_2 films necessitate efficient photo-induced electron–hole pair generation and efficient charge separation, which requires in turn preparations of well-crystallized TiO_2 films, preferably in the anatase crystalline form [7]. TiO_2 thin films have been prepared by using chemical vapour deposition, sputtering, ion assisted electron beam evaporation, pulsed laser deposition technique and sol-gel method [8-11]. Out of these methods, the sol–gel method is simple, inexpensive, non-vacuum and low temperature technique for synthesizing films. This process offers many advantages like, excellent control of the stoichiometry of precursor solutions, ease of compositional modifications, customizable microstructure, ease of introducing various functional groups, requirement of relatively low annealing temperatures and possibility of coating over large area substrates. In order to prepare high quality nanocrystalline TiO_2 thin films with simple method, many researchers are using Sol-Gel dip coating technique. This research aims in identifying cost effective and simple deposition technique and the preparation and characterization of TiO_2 thin films for solar cell applications.

2. Experimental details

2.1 Preparation of precursor sol

Initially, diluted solution of ethanol (24.5 mL) was taken in a 50 mL beaker and titanium (IV) isopropoxide (2.5 mL) of 98% purity was added drop by drop into the solution. Then 0.25 mL of water was added drop by drop for hydrolysis and poly-condensation. To control the pH of the solution (pH=9) a small amount of ammonia was added in the solution. The expected pH values of the solution were confirmed by using digital pH meter. The final mixer solution was stirred at room temperature for three hours.

2.2 Fabrication and optimisation of dip-drive coating unit

Fig. 1 shows the schematic diagram of the newly, indigenously designed and developed dip-drive coating unit. The unit is fabricated to carry out the repeated dip coating and heat treatment (pre heating) for thin film preparation under vacuum (10^{-3} torr) condition. The simple unit consists of water reservoir vessel fitted with solenoid valve 1, water float vessel fitted with solenoid valve 2, floating beaker containing the clear solution in the water float vessel and immersed substrate holder cum heater. The complete set up is placed inside a glass chamber and evacuated to the vacuum of 10^{-3} torr using rotating pump.

In the beginning enough water is taken in the water reservoir and water float vessel and the solenoid valve 2 is adjusted to drip water, so that the decrease in the water level in the water float is in the order of 0.1 mm per min in the chamber. Opening the solenoid valve 2, thin film is deposited in the glass substrate. Once water in the water float vessel is completely drained, the substrate is heated and allowed to cool for half an hour. Opening the solenoid valve 1, water is filled in the float vessel. This is repeated two or three times for deposition.

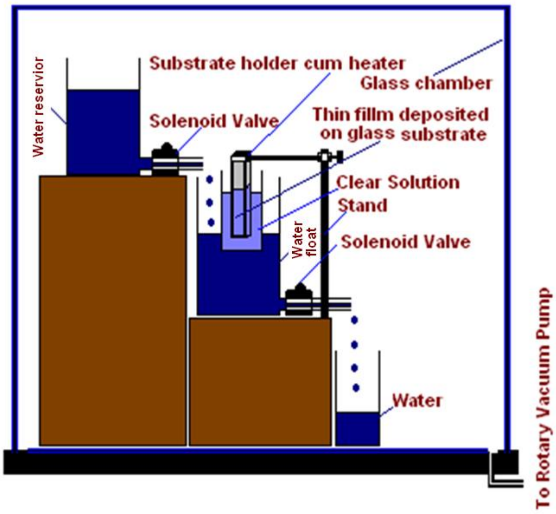

Fig. 1. Schematic diagram of the newly, indigenously designed and developed dip-drive coating unit.

2.3 Deposition of the films

Well cleaned glass substrates were fixed along the sides of the heater and placed just above the beaker containing sol-gel solution. The substrates were pre heated in the temperature range 200-250°C for ten minutes. The TiO_2 films were deposited using the above solution. Then the film was annealed at three different temperatures 350°C, 450°C, and 550°C for one hour and allowed to cool to room temperature. 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 labelled.

2.4 Characterisation of thin films

X ray diffraction (XRD) patterns of the films were recorded in the 2θ range from 20^o to 60^o with Philips Xpert pro with Ni filter and Cu K_α radiation. The morphology and features of the film were examined by scanning electron microscopy (Hitachi S-500). In the recent investigation, the presence of the elements in the prepared samples had been identified using energy dispersive x-ray analysis system attached with Hitachi S-500 scanning electron microscope. Optical characterization of the films had been carried out using UV–VIS–NIR spectrophotometer (Jasco V-570). 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) had been calculated using Scherrer formula. The strain (ε) was calculated for the slope of βcosθ versus sinθ plot using the relation,

$$\beta = \frac{\lambda}{D\cos\theta} - \varepsilon \tan\theta \qquad (1)$$

The dislocation density (δ) was calculated from the relation

$$\delta = \frac{1}{D^2} \qquad (2)$$

The absorption coefficient (α) was estimated from the optical transmittance spectra using the relation

$$\alpha = \frac{2.303 \log(100/T)}{t} \qquad (3)$$

where T is the Transmittance (in %) and t is the thickness of the film. All the graphs satisfied the condition for direct transition in the excitation process (i.e.) $\alpha = (E_v - E_i)^{1/2}$ for allowed direct transition, where E_v was the top of the valance band and E_i the initial state from which the transition was made. All the films exhibited direct band gap structure and their band gap values were found to be nearly 3.3eV [12].

3. Results and discussion

3.1 X ray diffraction

X-ray diffraction pattern has been used to investigate the phase of the prepared TiO_2 thin films. The X-ray diffraction pattern of TiO_2 thin films annealed at different temperatures is shown in Fig. 2. The diffraction pattern displays the coexistence of both amorphous and crystalline TiO_2 regions by showing the simultaneous presence of the broad hump in the low 2θ region demonstrating short range order and amorphicity. The diffraction pattern of TiO_2 film annealed at 350°C does not exhibit clear peaks indicating that the film is amorphous in nature, whereas the diffraction pattern of films annealed at 450°C and 550°C show small distinct peaks. This is due to the transformation from amorphous to crystalline on heat treatment. A strong peak occurs at $2\theta = 25.3°$ which corresponds to the (101) reflection and is in agreement with JCPDS data 21-1272 [13 - 15]. This shows that annealing of the samples at these temperatures have induced in some constructive features in the films. Further, increase in annealing temperature causes a significant dominate peaks of anatase TiO_2, which is consistent with the increasing crystallizing of the sample. The lattice parameters, particle size, strain and dislocation density of the prepared films have been calculated and tabulated in Table 1.

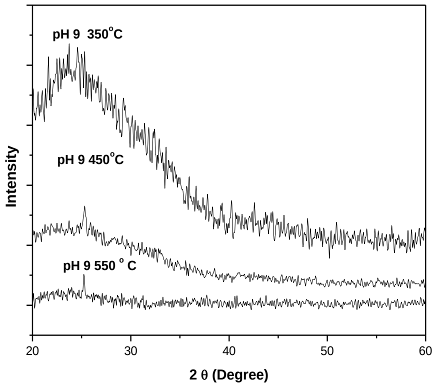

Fig. 2. XRD patterns of TiO_2 thin films annealed at 350°C, 450°C, and 550°C.

Table 1. Structural properties of TiO_2 thin films prepared at different pH values and annealing temperatures.

Annealing temperature (°C)	**Lattice parameter (Å)**		**Particle size (D) (nm)**	**Strain (ε) (x 10^{-4} lines^{-2} m^{4})**	**Dislocation density (δ) (x 10^{15} lines m^{-2})**
	a	c			
450	3.898	9.534	29.534	14.292	1.147
550	3.898	9.534	29.524	14.361	1.147

3.2 Compositional analysis

Energy dispersive x-ray analysis (EDAX) pattern of TiO_2 thin film prepared at pH = 9 and annealed at different temperatures is shown in Fig. 3. The compositions of the films are very close to the expected TiO_2 structure [15, 16].

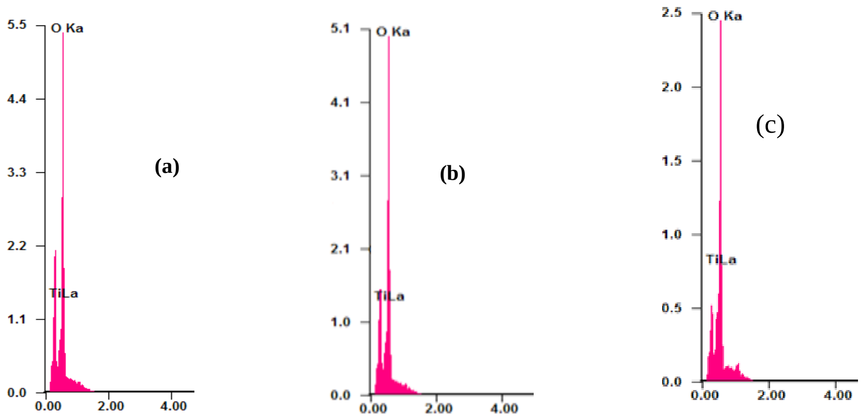

Fig. 3. EDAX pattern of TiO_2 thin films annealed at different temperatures.

3.3 Morphological studies

The scanning electron microscope image of the TiO_2 thin films annealed at 550°C, recorded at 5 KV with 30 K magnification is shown in Fig. 4. The SEM micrograph of the prepared films shows large crystalline grains distributed uniformly. This shows that annealing at higher temperature is favourable for the grain growth. The particle sizes in SEM micrographs of all the films are measured and mean values of the particle sizes are found to be 30.7nm which are very close to the XRD results.

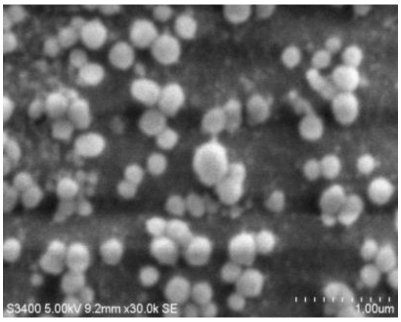

Fig. 4. SEM image of TiO_2 thin films annealed at 550°C.

3.4 Optical studies

Fig. 5 shows the optical transmittance spectra of the prepared TiO_2 thin films annealed at different temperatures. It shall be noted that the transmittance of the films decreases with the increase of the annealing temperature. This may be due to the formation of larger particles on the surface of TiO_2 thin film, which causes the scattering of light. All the films are found to be transparent above (50-70%) in the visible range with the sharp absorption edge at wavelength of about 380 nm, which is very close to the band gap of TiO_2 (3.26 eV). Fig. 6 shows the corresponding plot of $(\alpha h\upsilon)^2$ versus $h\upsilon$ and the extrapolation of the linear portion to the abscissa are the band energy gap of the film. The band gap energy of the films is found to be decreasing from 3.39 to 3.26eV.

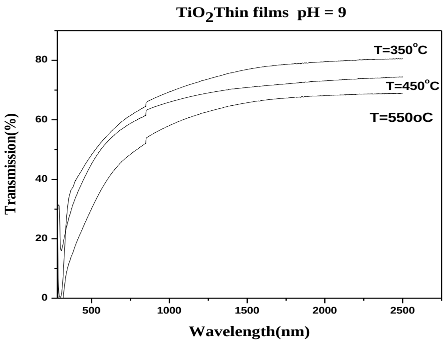

Fig. 5. Transmission spectra of TiO_2 thin annealed at different temperatures.

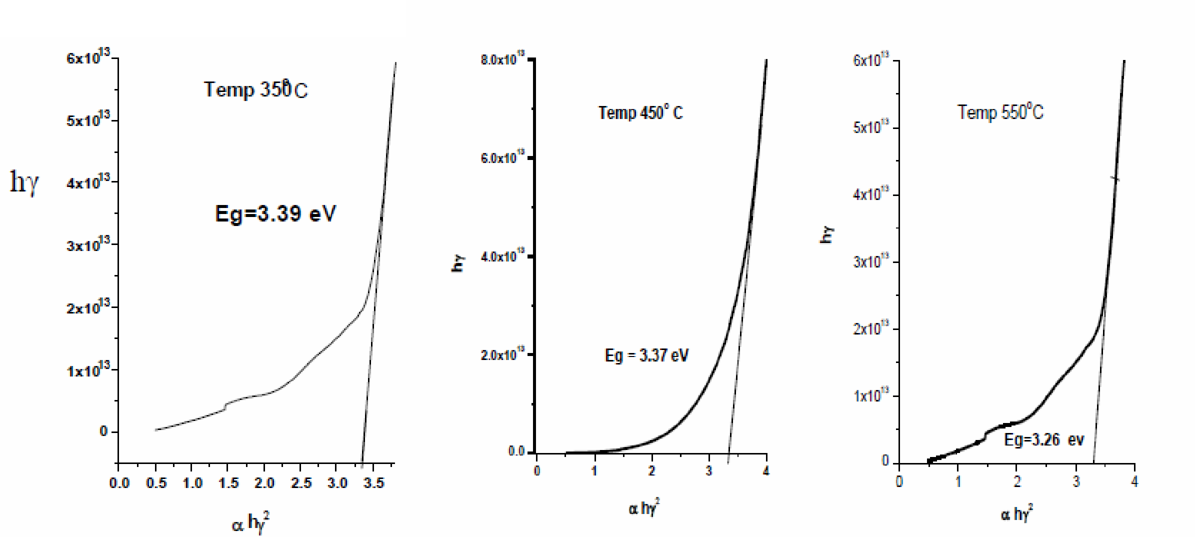

Fig. 6. Plot of $(\alpha h\upsilon)^2$ versus $h\upsilon$ of the TiO_2 thin films annealed at different temperatures.

4. Conclusions

Nanocrystalline TiO_2 thin films with anatase phase have been prepared by sol–gel dip drive coating method at comparatively low temperatures. The anatase phase has been identified using X-ray diffraction method. The change from amorphous-to-crystalline nature occurs after annealing temperature above 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. Band gap of the film decreased from 3.39 to 3.26 eV while annealing from 350-550°C. 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 adopted curing procedures.

Acknowledgments

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