Transparent Thin Film Dye Sensitized Solar Cells Prepared by Sol-Gel Method

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Transparent TiO_2 thin films have been prepared by sol-gel spin coating method. The sols used for deposition of thin films were prepared with different ethanol content. The effect of ethanol (solvent) concentration and annealing temperature on the performance of TiO_2 thin film solar cells has been studied. The results indicate that the as deposited films are amorphous in nature. TiO_2 thin films annealed at temperatures above 350 °C exhibited crystalline nature with anatase phase. The results also indicated that the crystallinity of the films improved with increase of annealing temperature. The high resolution transmission electron microscope images showed lattice fringes corresponding to the anatase phase of TiO_2. The band gap of the deposited films has been found to decrease with increase in annealing temperature and increase with increase in ethanol concentration. The dependents of photovoltaic efficiency of the dye-sensitized TiO_2 thin film solar cells (DSSCs) with the amount of ethanol used to prepare thin films was determined from photocurrent-voltage curves.

Key Words : Nanocrystalline TiO_2, Ethanol concentration, Sol-gel spin coating

Introduction

TiO_2 in the form of thin films has received a great deal of attention in recent years because of its application potential in different fields like dye sensitized solar cells, catalysts, gas sensors, transparent optical device, electrochromic displays, planar wave guides and optical coatings.[1-4] The structural, optical properties and power conversion efficiency of the dye sensitized TiO_2 thin film solar cells was influenced by many factors such as crystallinity, particle size, surface area and preparation methods.[5-9] TiO_2 thin films have been synthesized by various researchers using a wide variety of techniques such as chemical vapor deposition,[10] aerosol pyrolysis,[11] electrodeposition[12] and sol-gel method.[13-20] However, the sol-gel method offers some advantages compared to other solution methods, such as simple production of high purity films at low cost, homogeneity at molecular level and low temperature synthesis without degrading the organic functional groups. Wide band gap TiO_2 can absorb approximately 5% of sunlight; the lower quantum yield has limited its applications. Numerous studies have been carried out to improve the photo-response and some of the methods used to improve the photoresponse of TiO_2 films are dye sensitizing,[21-25] depositing noble metals,[26] surface modification,[27] and doping.[28] The properties of TiO_2 film can also be modified by varying the ethanol concentration because the ethanol concentration plays a major role in the formation of grains and hydrolysis of alkoxides. The oxide network of TiO_2 is formed by hydrolysis and condensation of alkoxides followed by polymerization at elevated temperatures.[29,30] The ease of decreasing or increasing the chain length of the alkyl group is being done easily by hydrolyzation of titanium alkoxides. These reactions give polymeric species

with -OH- or -O- bridges. The coordination of water to the metal is the first hydrolytic step, a proton on H_2O could then interact with the oxygen of an OR group through hydrogen bonding, leading to hydrolysis. The high reactivity of alkoxide water causes instantaneous precipitation. The stability of the sol can be increased by replacing water with acetic acid. Here acetic acid acts as a catalyst and also as a chelating agent. Acetic acid induces the initiating process of hydrolysis mechanism. Acetic acid is also used to modify the precursor's molecular structure.[31] In the present work the influence of ethanol concentration on the structural, optical properties of TiO_2 thin films and performance of dye sensitized solar cell has been studied. The effect of ethanol concentration on the grain size and band gap of TiO_2 thin films has been studied in detail in the present study. So far no work has been reported about the relation between the ethanol concentration and the performance of dye sensitized solar cells.

Experimental

Synthesis of Transparent TiO_2 Thin Films. Transparent TiO_2 thin films have been prepared by sol-gel spin coating method. Titanium tetra isopropoxide (Alfa Aaser 99.9%) has been used as the titania precursor, absolute ethanol (Hayman 99.9%) was used as a solvent, acetic acid was used a catalyst to control the pH of the solution and PEG 400 was used as a binder. The 0.1 M sol has been prepared using 1 mL of titanium iso-propoxide, 0.09 mL acetic acid and 10 mL ethanol. The mixed solution was stirred at room temperature for 3 h. The transparent solution obtained was then aged for 24 h and then used for the preparation of the films. It should be noted that cleaning of the substrate is important for proper

adhesion of the films. The ITO conducting glass substrates were ultrasonically cleaned using NaOH and 2-propanol and rinsed with deionised water and then dried in hot air oven. The derived sol was spin coated on to glass substrates at a spinning speed of 3000 rpm for 35 seconds. The film was annealed at 100 °C for 10 min and then allowed to cool to room temperature. TiO_2 was again spin coated on the already coated TiO_2 film and heated at 100 °C for 10 min and then allowed to cool to room temperature. The spin coating, heating and cooling process was repeated five times in order to get thicker films as described in one of our earlier work.[32] The heating of the film in air after each deposition has been carried out to enhance the inorganic polymerization and stabilize the mesophases involved. The films were then dried at room temperature for 2 h and then annealed in air. The films have been annealed at 350 °C, 450 °C and 550 °C for 1 h. The same procedure was repeated for preparing the films using the other two ethanol (solvent) concentrations (15 mL and 25 mL) respectively.
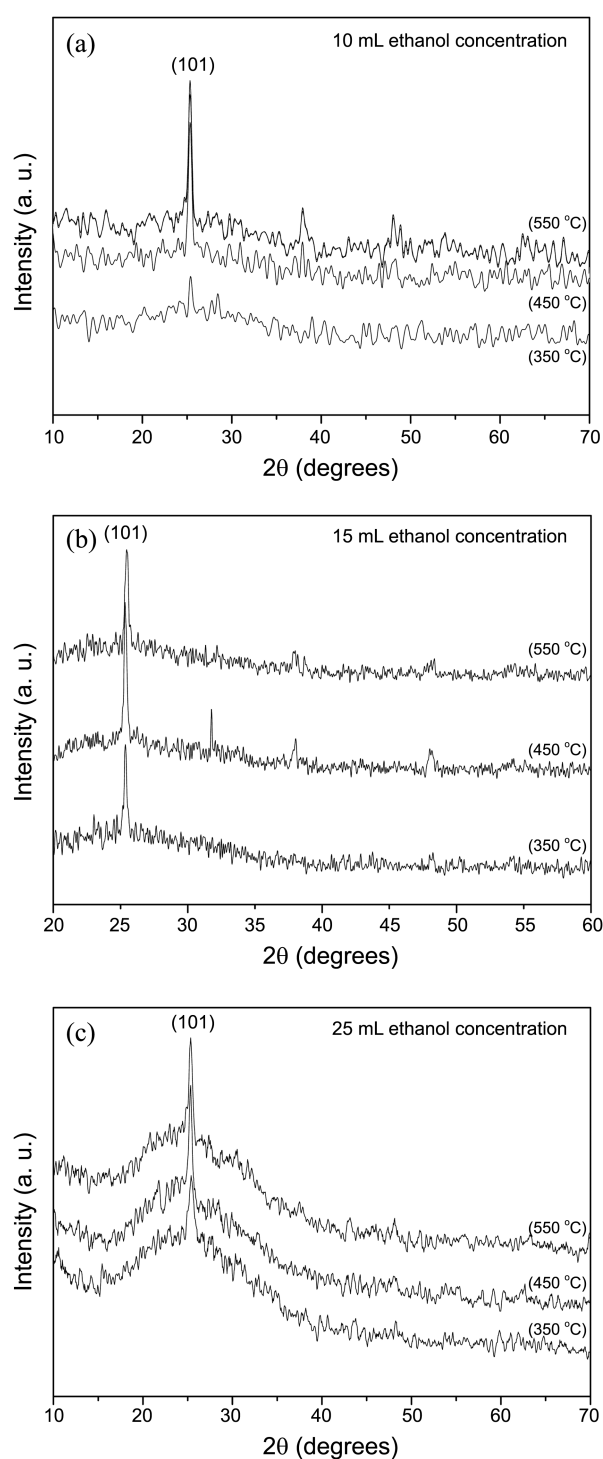
Manufacturing Transparent TiO_2 Thin Films-DSSC. For dye sensitized solar cell preparation, prepared TiO_2 thin film electrodes were immersed in a 3.0×10^{-4} M N719 dye solution at room temperature for 24 h, after that period the film was rinsed with anhydrous ethanol, and dried. A Pt-coated ITO electrode was then placed over the dye-adsorbed TiO_2 thin film electrode, and the edges of the cell were sealed with a sealing sheet (PECHM-1, Mitsui-Dupont Poly-chemical). A redox electrolyte, electron delivery, consisted of 0.5 mol KI, 0.05 mol I_2, and 0.5 mol 4-*tert*-butylpyridine was used as a solvent. Thickness of the films has been determined using gravimetric method and confirmed using stylus profilometer. The thickness of the deposited TiO_2 films has been found to lie in the range of 720-780 nm.

Characteristics and Photovoltaic Efficiencies for the Transparent TiO_2 Thin Films-DSSCs. The surface morphology of the films has been studied using scanning electron microscope (Hitachi S-500). The structural properties of the films have been studied using X-ray diffraction method (XPERT-PRO series with CuKα radiation as source). Optical characterization of the films has been carried out using the transmittance spectra recorded using UV-VIS-NIR spectro-photometer (Jasco V-570). Photocurrent-voltage (I-V) curves using white light from a xenon lamp (max. 150 W) using a sun 2000 solar simulator (ABE technology). Light intensity was adjusted using a Si solar cell to ~AM-1.5. Incident light intensity and active cell area were 100 mWcm^{-2} (one sun illumination) and 0.25 cm^2 (0.5 × 0.5 cm), respectively.

Results and Discussion

Characteristics of Transparent TiO_2 Films. Figures 1(a), 1(b) and 1(c) shows the X-ray diffraction pattern of the films prepared using 10 mL, 15 mL and 25 mL ethanol con-centrations and annealed at different temperatures. It should be noted that for all the three ethanol concentrations, the as deposited films are amorphous in nature and small peaks corresponding to the formation of nanocrystalline TiO_2 ap-

Figure 1. X-ray diffraction pattern of TiO_2 thin films prepared using different ethanol concentrations and annealed at different temperatures.

peared when the annealing temperature was increased above 350 °C. The intensity of the diffraction peaks has been observed to increase with increase of the heat treatment temperature. The observed peaks in the X-ray diffractogram correspond to specific lattice planes of the anatase phase of TiO_2 (JCPDS pattern no. 21-1272). The X-ray diffraction results indicate that nanocrystalline anatase TiO_2 thin films can be obtained when the spin coated films are subjected to

Table 1. Grain size of TiO_2 thin films prepared using different ethanol concentrations and annealed at different temperatures

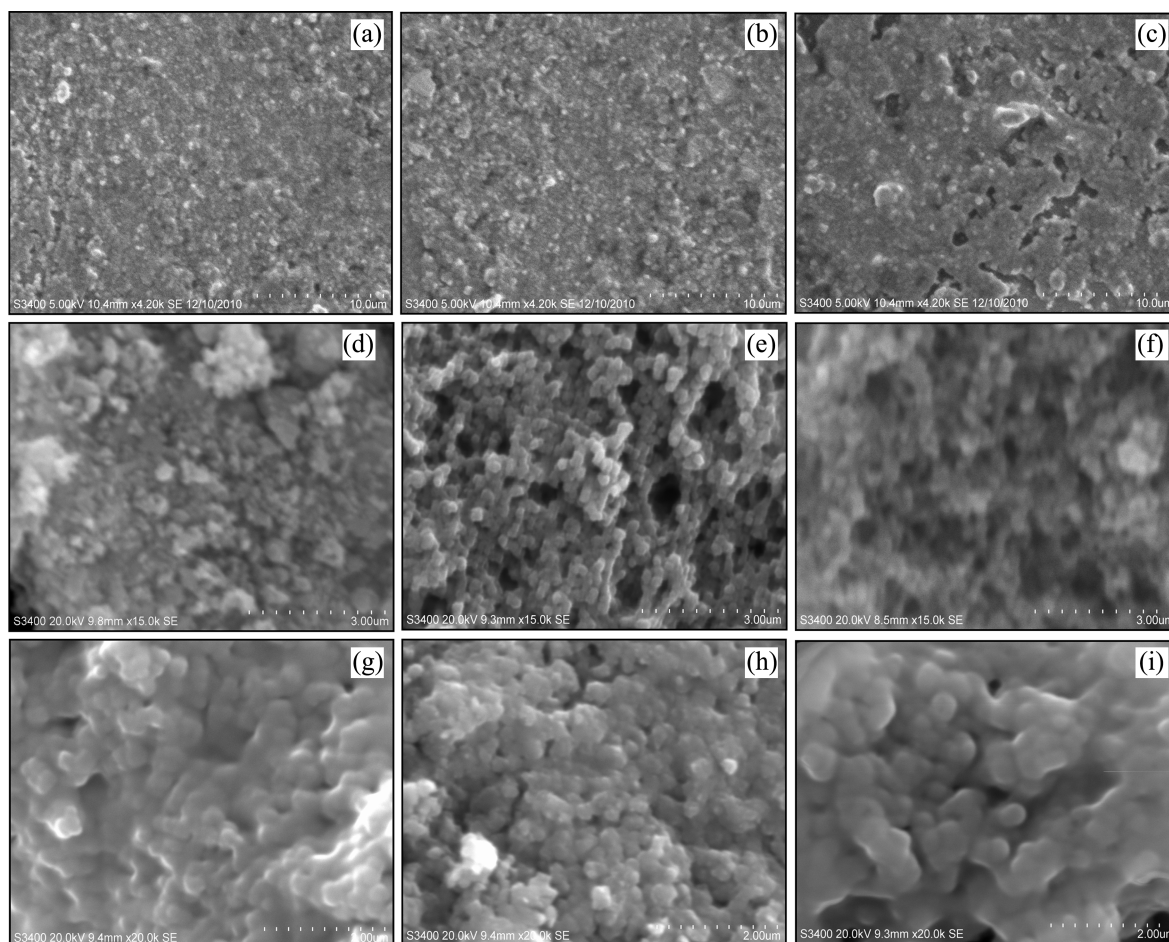| Annealing temperature (°C)	Grain size for different ethanol concentration		
	10 mL	15 mL	25 mL
350	15 nm	12 nm	8 nm
450	19 nm	17 nm	10 nm
550	22 nm	21 nm	11 nm

heat treatment.

The crystallite size of the films annealed at 350 °C, 450 °C and 550 °C has been calculated using the Scherer formula[33] and the obtained values are shown in Table 1. The grain size is found to increase with increase in annealing temperature. The pre-heat treatment at 100 °C after each spin coating process induces generation of more nuclei. This facilitates the subsequent crystal growth process, accompanied by the diffusion of titania species towards the nucleated grains resulting in grain growth and formation of nanocrystalline anatase TiO_2 thin films.
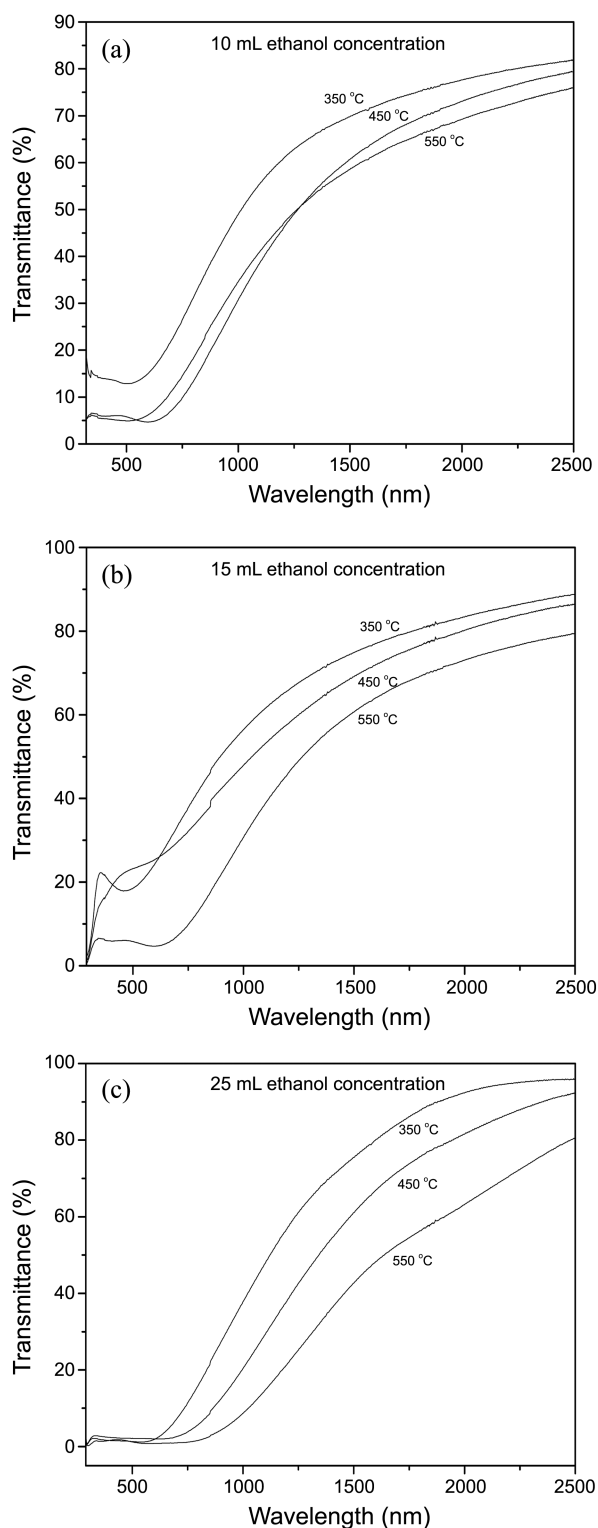
The scanning electron microscope images of the TiO_2 films prepared using different ethanol concentration and annealed at different temperatures is shown in Figures 2(a-i).

The images show that the films annealed at higher temperatures exhibit a better crystallinity. The increase in ethanol concentration has been found to affect the surface morphology of the films and it also reduces the agglomeration of particles. Films annealed at higher temperature are found to exhibit a more clear surface morphology. The films annealed at 350 °C contain pores and grains of smaller size. When the annealing temperature is raised to 450 °C and 550 °C, the grain size is found to increase. The SEM image of the TiO_2 film shows the formation of nanosized smooth grains all over the surface with meso-sized pores in between the grains. Such type of porous structure resulted due to the nucleation and coalescence of small particles. The presence of pores is due to the evaporation of polyethylene glycol (PEG) and other complexing agent at higher temperatures.

Figure 3(a-c) shows the optical transmittance spectra of the TiO_2 films prepared using different ethanol concentration and annealed at different temperatures. For a particular annealing temperature (consider 350 °C annealed films), the transmittance of the films is found to increase with increase of ethanol concentration. This is due to the fact that increase of ethanol concentration reduces the grain size and the amount of light scattered from the film surface decreases. It
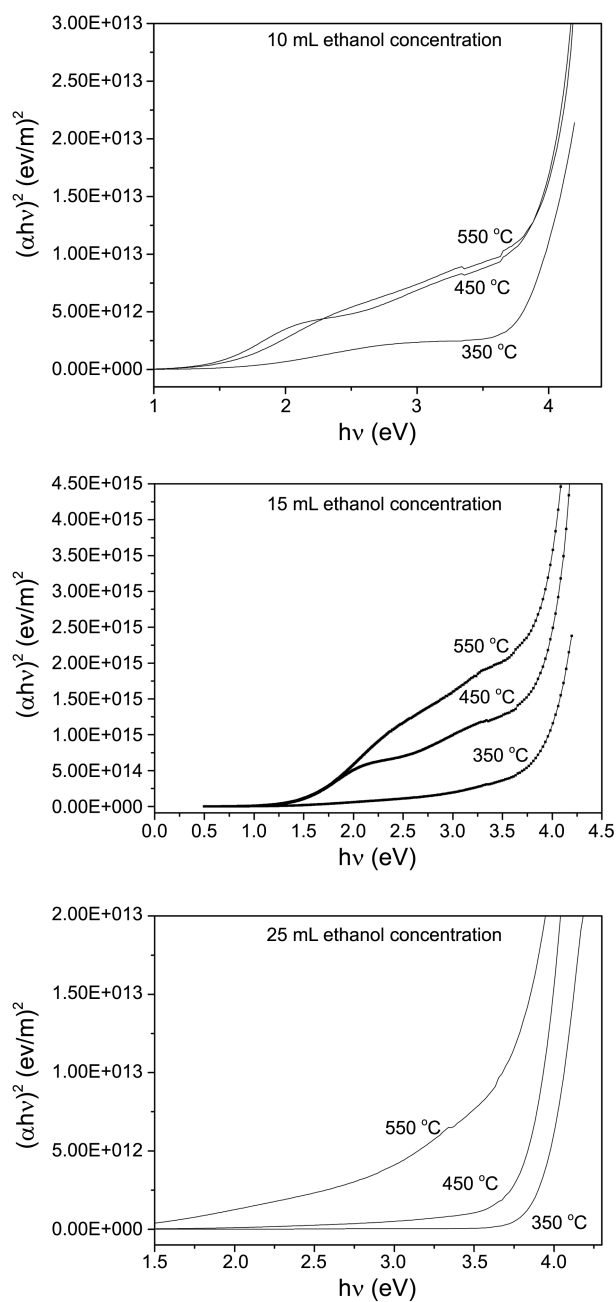

Figure 2. (a, b, c) SEM images of TiO_2 thin films prepared using 10 mL ethanol concentration and annealed at 350 °C, 450 °C and 550 °C respectively. (d, e, f) SEM images of TiO_2 thin films prepared using 15 mL ethanol concentration and annealed at 350 °C, 450 °C and 550 °C respectively. (g, h, i). SEM images of TiO_2 thin films prepared using 25 mL ethanol concentration and annealed at 350 °C, 450 °C and 550 °C respectively.

Figure 3. Transmittance spectra of TiO$_2$ thin films prepared using different ethanol concentrations and annealed at different temperatures.

Figure 4. Plot of hν *vs* (αhν)^2 of TiO$_2$ thin films prepared using different ethanol concentrations and annealed at different temperatures.

is also observed that for a particular ethanol concentration (consider 10 mL ethanol concentration), the transmittance of the films decreases with increase of annealing temperature. This can be ascribed to the formation of larger particles on the surface of Ti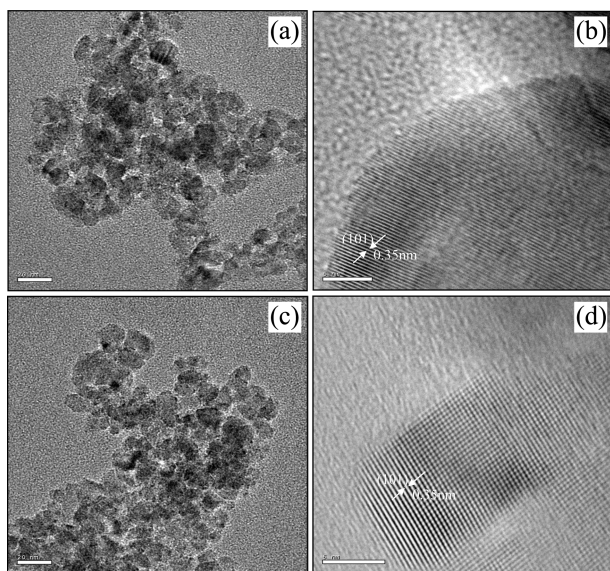O$_2$ thin films, which causes the scattering of light. The transmittance spectra also shows that the absorption edge shifts towards longer wavelength with increase in heat treatment temperature and this shift of absorption edge can be attributed to the growth of TiO$_2$ crystallites on annealing.

Plot of (αhν)^2 versus photon energy (hν) of TiO$_2$ films prepared using different ethanol concentrations and annealed at different temperatures are shown in Figures 4(a-c). The band gap values of the TiO$_2$ films prepared using different ethanol concentrations and annealed at different temperatures are given in Table 2. The estimated values are in agreement with the reported values.[34,35] The crystalline

Table 2. Band gap value of TiO₂ thin films prepared using different ethanol concentrations and annealed at different temperatures
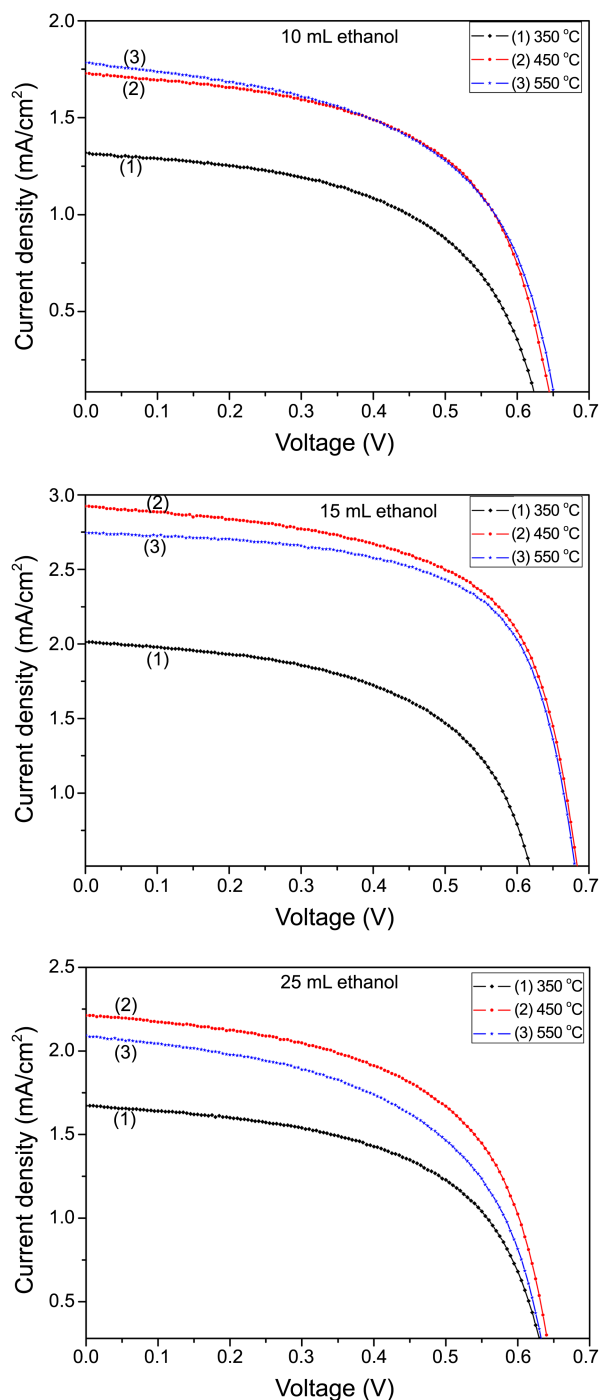
Annealing temperature (°C)	Band gap for different ethanol concentration (eV)		
	10 mL	15 mL	25 mL
350	3.53	3.81	3.91
450	3.42	3.66	3.77
550	3.33	3.48	3.49

Figure 5. HRTEM images of TiO₂ thin films prepared using (a, b) 15 mL and (c, d) 25 mL ethanol concentrations and annealed at 450 °C.

structure and particle size of the spin coated TiO₂ thin film has also been studied using high-resolution transmission electron microscope. For that the TiO₂ films were peeled out from the substrate and dissolved in acetone. The solution was sonicated for 24 h.

The high-resolution transmission electron microscope image of the spin coated TiO₂ films prepared using 10 mL and 15 mL ethanol and annealed at 450 °C is shown in Figures 5(a, b) and 5(c, d). Using the particle number (frequency %) and the average particle diameter of the particles in the high-resolution transmission electron microscope image the particle size has been calculated and is found to be 20 nm. This is in agreement with the X-ray diffraction results. The images show spherical and elongated shaped particles with roughly uniform in size of about 20-30 nm. High resolution TEM images show that each of these larger particles are the agglomeration of smaller particles, with nanostructured domain. The films exhibit lattice fringes and using the fringes the d-spacing has been calculated and is found to be 0.35 nm. On comparing the d-spacing with standard JCPDS data it is observed that the d-spacing corresponds to the (101) plane of anatase TiO₂.

Photovoltaic Efficiencies of the Transparent TiO₂-DSSCs. The J-V characteristics of the dye sensitized TiO₂ thin film solar cells prepared using different amount of ethanol are shown in Figure 6(a, b and c). The unit cell area

Figure 6. *J-V* characteristics of transparent thin film dye sensitized solar cells prepared using different ethanol concentrations and annealed at different temperatures.

is fixed at 0.25 cm². The solar cell parameters like fill factor (FF) and efficiency (η) have been calculated using the Eqs. (1) and (2).

$$FF = J_{max} \times V_{max} / J_{sc} \times V_{oc}, \tag{1}$$

$$\eta(\%) = P_{out}/P_{in} \times 100 = J_{max} \times V_{max}/P_{in} \times 100 = J_{sc} \times V_{oc} \times FF^{36} \tag{2}$$

The calculated solar cell parameters are given in Table 3. For

Table 3. Power conversion efficiency of transparent TiO_2 thin film solar cells prepared using different ethanol concentrations and annealed at different temperatures

Ethanol concentration (mL)	Annealing Temperature (°C)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	□ %
10	350	0.625	1.316	0.891	0.603
	450	0.667	1.725	0.572	0.644
	550	0.670	1.784	0.555	0.643
15	350	0.657	2.009	0.572	0.741
	450	0.706	2.920	0.655	1.308
	550	0.702	2.738	0.672	1.271
25	350	0.662	1.670	0.567	0.615
	450	0.669	2.213	0.585	0.843
	550	0.641	2.087	0.624	0.787

all the ethanol concentrations, the power conversion efficiency of the cell increases with increase of annealing temperature and at higher temperature (550 °C) the efficiency gets decreases. For all the cases the efficiency is higher at 450 °C. This may due to the formation of well crystallite size and more pores present in the surface of the film. The presence of pore in film is confirmed by the SEM images. The presence of more pores on the surface of the films enhances more adsorption of dye molecules which in turn increase the overall power conversion efficiency. But the films prepared using 10 mL ethanol gives very less efficiency this may due to more agglomeration of TiO_2 particles on the surface of the film, this may due to presence of higher amount of precursor particles in the sol. This agglomeration reduces the dye adsorption and also the performance of the cell. But in the case of 25 mL ethanol, even agglomeration is less, the thickness of the film play important role for dye adsorption. *i.e.* thickness of the film prepared using 25 mL ethanol and annealed at 450 °C is 730 nm, which is less compared with the film prepared using 15 mL ethanol and annealed at 450 °C, this may due to dilution of sol. However, when the amount of ethanol was increased from 10 mL to 15 mL, the photoelectric efficiency was increased and the photovoltaic efficiency of 1.3%. It was remarkably increased to an efficiency of twice than that of the solar cells prepared at other amount of ethanol concentrations. These results confirm that the amount of ethanol used to prepare TiO_2 thin films greatly affects the photoconversion efficiency of DSSCs.

Conclusion

TiO_2 thin films with anatase phase have been prepared by sol-gel spin coating method using different ethanol (solvent) concentrations. All the prepared films were annealed at three different temperatures 350, 450 and 550 °C respectively. The annealed films have been found to exhibit anatase phase. The grain size has been observed to decrease with increase in ethanol concentration and can be considered as a means to control grain growth. The optical band gap has been observed

to decrease with increase in annealing temperature and increase with increase in ethanol concentration. The power conversion efficiency of the TiO_2 thin films annealed at 450 °C shows maximum efficiency compared with other films. Although the efficiencies obtained with these results are still below the current requirements for large scale practical applications, the results are useful to prepare uniform crystallite size with meso pores and may initiate additional studies oriented towards the surface modification of the TiO_2 films.

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