Effect of multilayer on structural property and power conversion efficiency of DSSCs prepared by spin coating method

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Single layer and multi-layer TiO_2 thin films have been prepared by using simple sol-gel spin coating method. The prepared films are annealed at three different temperatures. The single layer TiO_2 thin films indicate that the films are amorphous in nature. But the multi-layer TiO_2 thin films annealed at 350°C exhibits crystalline nature with anatase phase. The result indicates that the crystallinity of the film improved with increase of annealing temperature and the number of coated layers. The dependence of photovoltaic efficiency of the dye-sensitized TiO_2 thin film solar cells (DSSCs) on the annealing temperature has been discussed using the photocurrent – voltage curves.

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1. Introduction

Titanium dioxide is considered as one of the most attractive photovoltaic material when compared with other various wide band gap semiconductors such as ZnO, SnO_2 and Nb_2O_5 [1-3]. TiO_2 has interesting properties like strong oxidizing power, non-toxicity, large excitation energy [4] and long term photo-stability [5] which makes it suitable for photocatalytic and photovoltaic applications. In addition to this TiO_2 also has some additional advantages like biocompatibility, thermal stability, low cost and easy availability. TiO_2 is commercially available and it is widely used in industrial applications, health care products and domestic applications such as paint pigmentation. The properties such as high refractive index, good chemical stability, amphoteric surface and low production cost are the main advantages for its broad use.

Titanium dioxide exists in three common forms namely: anatase, brookite and rutile. Among them rutile phase is the thermodynamically most stable phase, whereas anatase and brookite phases are metastable and get transformed to rutile on heating. The titania with rutile form has been widely used as pigments, cosmetic ingredients and catalyst support [6]. The brookite form has not attracted any attention from the investigators because of its instability at wide range of temperatures. The formation of a particular phase depends on the starting material used, deposition method and pH of the solution. But the transformation from one phase to another phase depends on the impurity content and annealing temperature.

Anatase form of TiO_2 is an attractive material for many applications such as transparent electrodes [7], gas sensors [8,9], antireflective coating in solar cells [10], photo-electrochemical cells [11], self-cleaning glasses [12] etc. Nanocrystalline TiO_2 thin film is being used as n-type electrode in dye sensitized photo-electrochemical solar cells and is a promising material for quantum dot sensitized solar cells. Anatase form of TiO_2 can absorb light below the wavelength of 400 nm because it has wide band gap energy of 3.2 eV. The absorption region of TiO_2 is easily extended to visible region by doping noble ions, transition metal ions or by sensitizing TiO_2 using organic dyes or semiconductor quantum dots. Anatase form of TiO_2 has been under intense research for many years because of its higher power conversion efficiency [13] and is much easier to adjust the absorption region compared with silicon solar cells. The anatase form of TiO_2 has a strong ionic character and is made of Ti^{4+} and O^{2-} ions. Irrespective of crystal structure it has Ti^{4+} ion surrounded by six O^{2-} ions that create a TiO_6 octahedral basic block. The conduction band is formed by the 3d orbitals of titanium and the valence band is formed by the 2p orbitals of oxygen. Therefore dye sensitized TiO_2 thin film solar cells have been under intense investigation and a number of research groups have reported encouraging results in such devices in recent years [14-16]. Several researchers have investigated the light emitting properties of TiO_2 films including ultra violet and visible region emission. TiO_2 is also used in non-electronic applications like optical brightener in wall colours, ingredient in sun cream and bone implants [17]. It is reported that structural imperfection and defects generally deteriorate exciton related recombination process and it is necessary to grow high quality films for high efficiency solar cell applications.

Anatase form of nanocrystalline TiO_2 thin film is usually prepared by various techniques, such as

evaporation [18], spray pyrolysis [19], chemical vapour deposition [20], sputtering [21], laser ablation [22] and sol-gel method [23, 24]. In the present study nanocrystalline TiO_2 thin films have been prepared by sol-gel spin coating technique. Because this technique has many advantages, like simple method, easy to control the parameters and deposition can be carried out at room temperature. This technique can be easily used for large area deposition at low cost and the thickness of the deposited layer can be readily controlled by varying the length of the deposition time. In the present study TiO_2 thin films have been prepared by using titanium tetra isopropoxide, absolute ethanol and acetic acid by sol–gel spin coating method. The oxide network of TiO_2 is formed by hydrolysis and condensation of alkoxides followed by polymerization at elevated temperatures. 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 [25]. Many factors such as crystallinity, particle size, surface area, number of layers or thickness of the film, amount of solvent used and preparation method strongly affects the properties of the prepared TiO_2 thin films [26].

The objective of the present work is to perform a systematic study about the importance of multilayer on the properties of TiO_2 thin films and the fabrication and study of nanocrystalline TiO_2 thin film solar cells.

2. Experimental

In the present study TiO_2 thin films with anatase phase has been prepared by using titanium tetra isopropoxide and ethanol by simple sol–gel spin coating method at room temperature. An attempt has been made to control the hydrolysis/condensation reaction in the sol–gel solution by using acetic acid. In spin coating method the properties of TiO_2 thin films are not only influenced by the post-annealing treatment, it also depends on number of layers deposited. TiO_2 thin films have been prepared onto well cleaned glass and ITO coated glass substrates by sol-gel spin coating method. In the present study titanium isopropoxide (Alfa Aaser 99.9%) has been used as the titania precursor, and the matrix sol was prepared by mixing titanium isopropoxide (TIP) with absolute ethanol (Aldrich 99.9%) and acetic acid at room temperature. A small amount of polyethylene glycol (PEG) was added as a binder.

Ethanol is used as a solvent and acetic acid acts as a catalyst controlling the pH of the hydrolysis/condensation reactions in sol–gel solution. The final mixture solution was stirred for about 3 hrs. The final composition of the solution was in the molar ratio of TIP: ethanol: acetic acid = 1:15:0.1 and the pH of the solution was 5.6. TiO_2 thin films have been prepared by spin coating method onto well cleaned glass substrates by using the prepared solution. The sol was introduced drop wise on the substrate, which was rotated at a speed of 3000rpm for 35 seconds resulting in the formation of thin film. The film was heated at 100°C for 10 minutes and then allowed to cool to room temperature. This forms the single layer TiO_2 thin films. Now the TiO_2 sol was again spin coated on the already coated TiO_2 thin film and heated at 100°C for 10 minutes 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 with good adherence to the substrate. This resulted in the formation of multi-layer TiO_2 thin films.

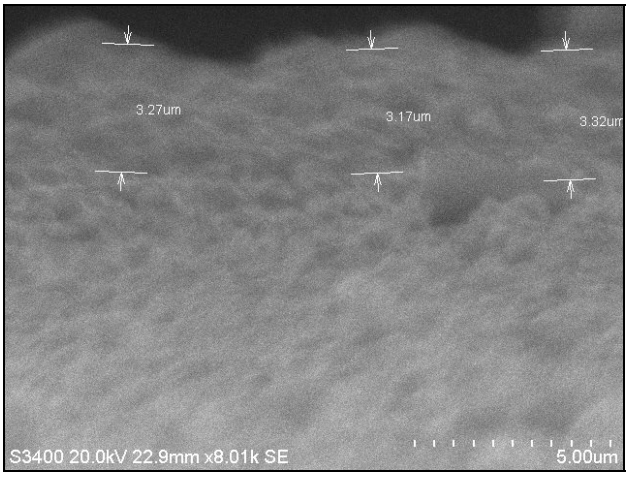

Fig. 1. Cross sectional SEM image of multi-layer TiO_2 thin film annealed at 450°C.

During the formation process of TiO_2, mono Ti–OH is formed during the hydrolysis reaction and Ti–OH aggregation results in the formation of crystalline nuclei and the primary particle size depends on the aggregation degree. Finally the particles in the film are oxidized and turned into oxide form during calcination and annealing at higher temperature promotes the formation of Ti–O–Ti anatase bonds. The pre-heat treatment at 100°C between each two cycles of spin coating 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 anatase nanocrystalline TiO_2 thin films.

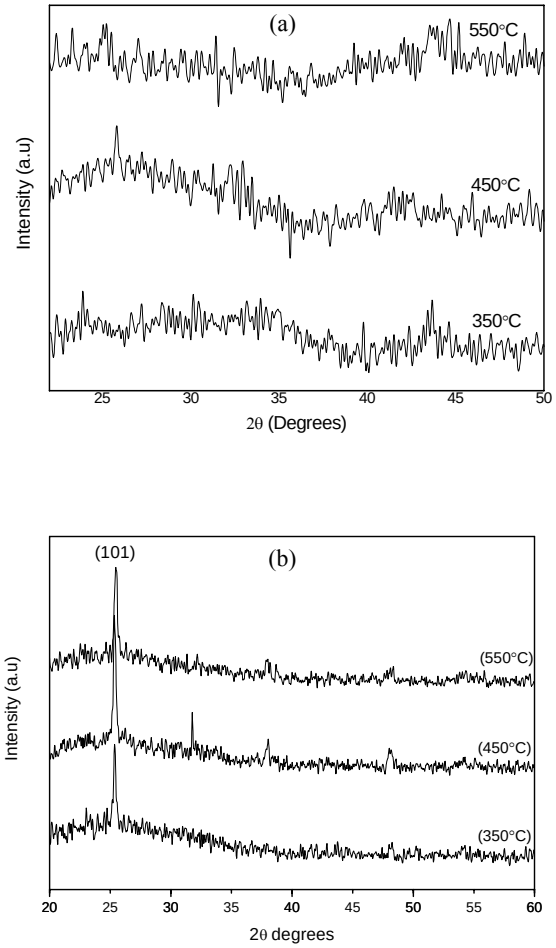

Fig. 2. X-ray diffraction pattern of (a) single layer and (b) multi-layer TiO_2 thin films annealed at different temperatures.

The heating of the film after each deposition in air is carried out to enhance the inorganic polymerization and stabilize the mesophases involved. The films were then dried at room temperature for 2 hrs and then annealed in air. Both the single layer and multi-layer TiO_2 thin films are annealed at 350°C, 450°C and 550°C for 1 hr using a heating rate of 2°C/min. The thickness of the multi-layer film has been determined using gravimetric method and verified using surface profilometer and was in the range of 3–3.5μm. The thickness of the film was also confirmed by cross sectional scanning electron microscope image and the average value was 3.25μm. Figure 1 shows the cross sectional SEM image of multilayer TiO_2 thin film annealed at 450°C. By using the prepared single layer and multilayer TiO_2 thin films dye sensitized solar cells have been fabricated as described in one of our earlier works [27]. In cell assembly section, both the single layer and multilayer TiO_2 thin film electrodes were immersed in a $3.0x10^{-4}$ M N719 dye solution at room temperature for 24 hrs, after that period the film was rinsed with anhydrous ethanol and dried. A Pt-coated ITO electrode was then placed over the dye-adsorbed electrode, and the edges of the cell was sealed with a sealing sheet (PECHM-1, Mitsui-Dupont Polychemical) by heating with hot plate at 100°C for 2 minutes. A redox electrolyte consists of 0.5 mol KI, 0.05 mol I_2, and 0.5 mol 4-tert-butylpyridine was used as a solvent and a drop of electrolyte solution was injected into the drilled hole in the counter electrode and is driven into the cell. Finally, the hole is sealed using additional cello tapes and the size of the electrodes used was 0.25 cm^2 (0.5 x 0.5 cm).

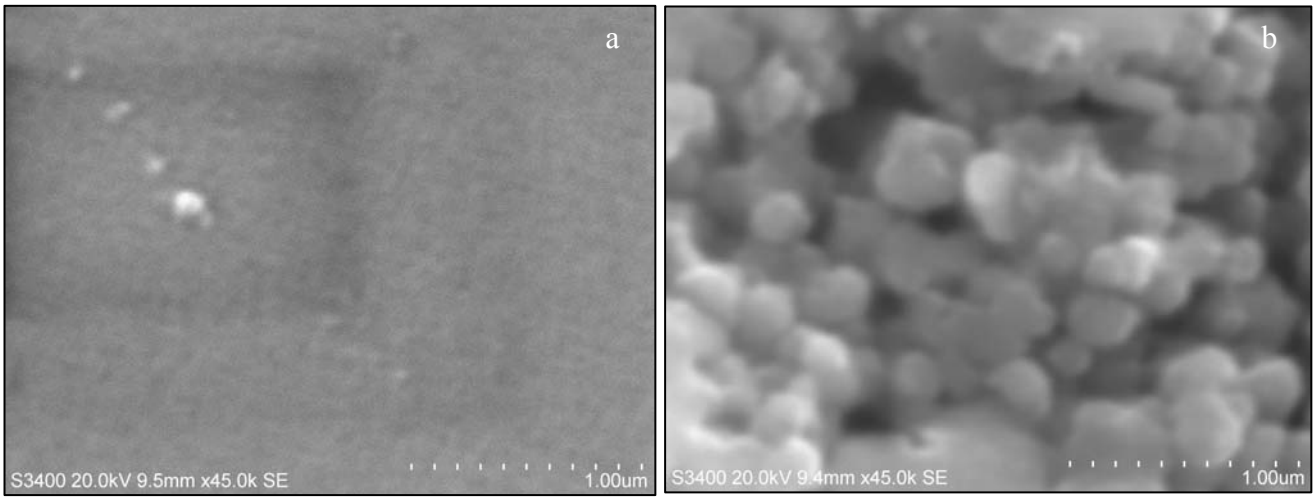

Fig. 3. SEM image of (a) single layer and (b) multi-layer TiO_2 thin film annealed 450°C.

The structural properties of the prepared single and multi-layer TiO_2 thin films have been studied using X-ray diffractometer (PANalytical). The surface morphology feature of the prepared samples has been studied using Hitachi S-500 scanning electron microscope. Fourier transform infrared spectroscopy analysis of the prepared sample was analyzed using the instrument ABB Bommn, MB 3000, Canada. The photocurrent-voltage (I-V) were measured using white light from a xenon lamp (max. 150 W) using a sun 2000 solar simulator (ABE technologies). Light intensity was adjusted using a Si solar

cell to ~AM-1.5 and the incident light intensity was 100 mWcm^{-2} (one sun illumination).

3. Results and discussion

X-ray diffraction technique has been used to study the structural properties of the prepared TiO_2 thin films. The single layer TiO_2 thin films are found to be very thin and amorphous in nature. The X-ray diffraction pattern of the single layer TiO_2 thin film is shown in Figure 2(a). The diffraction pattern shows no peaks clearly depicting that the films formed using a single coating are amorphous in nature and it has been found that even annealing does not help the nucleation and growth of the grains. So in the present study multi-layers have been deposited onto glass substrates. The X-ray diffraction pattern of the multi-layer TiO_2 thin film annealed at different temperatures is shown in Figure 2(b). The presence of very small peaks in the 350°C annealed film shows that nucleation of grain has started. The presence of more intense peaks in the 450°C and 550°C annealed samples shows that the grains have started to grow on annealing and the films are of nanocrystalline nature. The observed peaks correspond to the (101), (112) and (200) plane of anatase TiO_2 and is in agreement with JCPDS data (21-1272). These peaks indicate that the prepared TiO_2 thin films are of anatase phase. The diffraction pattern shows that the intensity of the peaks increases with increase of annealing temperature. This is due to the improvement in the crystalline nature of the prepared TiO_2 thin films on annealing. The peaks are observed to become narrower with annealing indicating the grain growth on annealing. The lattice parameter values a and c have been calculated using the relation

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \qquad (1)$$

and the calculated values are a = 3.728Å, c = 9.513Å and are in good agreement with the standard values. This clearly shows that the prepared TiO_2 thin films are of anatase phase. No peaks corresponding to the rutile or brookite phase has been observed in the X-ray diffraction pattern. The diffraction pattern of the film annealed at 350°C show very small reflection peaks of anatase phase, which indicates the formation of very small crystallites. The intensity of these diffraction peak increases with an increase of the heat treatment temperature, which is evident from increased intensity of (101) reflection and reduced full width at half maximum (FWHM). This is due to the transformation from amorphous to crystalline nature on heat treatment. The crystallite size has been determined using Scherer's semi-empirical formula and the calculated values are 15, 19 and 22 nm respectively. When the annealing temperature increases the particle size increases and this is due to the grain growth which occurs on annealing.

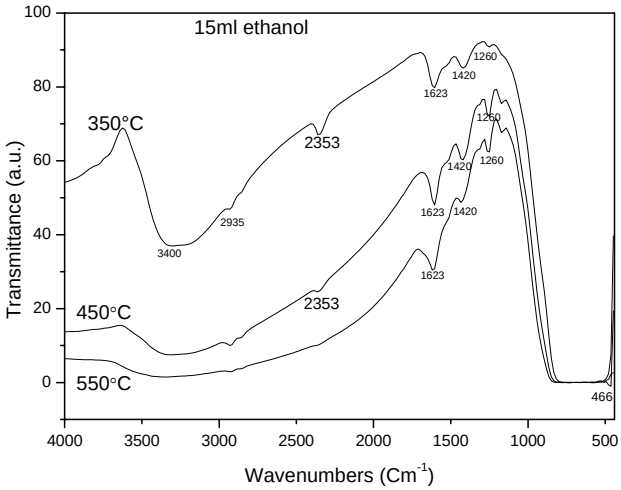

Fig. 4. FTIR spectra of multi-layer TiO_2 thin films annealed at different temperatures.

The scanning electron microscope image of single and multi-layer TiO_2 thin films, annealed at 450°C is shown in Figure 3. Compared with single layer film, multi-layer TiO_2 thin film contains more pores and smaller grains on the surface. The presence of pores is due to the evaporation of polyethylene glycol (PEG) and other complexing agent at higher temperatures. But the single layer film does not contain any pores and grains on the surface, which is due to lesser thickness of the film (500nm). This small thickness layer does not help for the nucleation and growth of the grains.

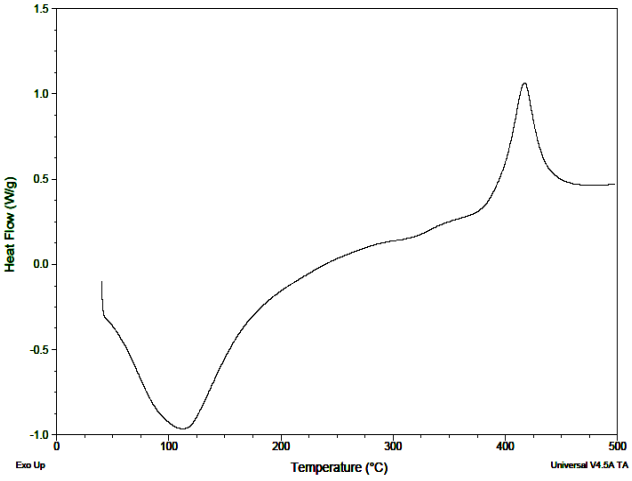

Fig. 5. DSC curve of multi-layer TiO_2 thin film annealed at 450°C temperature.

Fourier Transform Infrared (FTIR) spectroscopy is a promising method for observing molecular vibrations. Figure 4 shows the FTIR spectra of multi-layer TiO_2 thin films annealed at different temperatures. The band in the transmission spectra (absorption peaks) at 466 cm^{-1} is that of TiO_2. The thin films annealed at 350°C have features in

the O–H stretching vibration region with a broad band centred at 3400 cm^{-1}. The band at 3400 cm^{-1} is predominant for the film annealed at 350°C and as the annealing temperature increases, the band decreases which indicates the removal of the adsorbed water from TiO_2 [28]. This feature has been assigned to the O–H stretch of hydrogen bonded hydroxyls on the anatase TiO_2 surface. A reaction with a hydroxyl anion is thought as the initial step of the photo-oxidation of water. Since the TiO_2 sol layer has a relatively small hardness and soft surface, it seems to be easy to dissociate the water or oxygen molecules from the sol surface. The hydrate water vibration peak at 1623 cm^{-1} is still observable. This may be related to water bound to TiO_2 or may be due to the presence of reduced oxidant salt species or TiO_2 in a hydrate form. The band at 466 cm^{-1} is due to Ti-O-Ti stretching mode and the band at 3400 cm^{-1} is due to the presence of hydroxide group [29] that cannot be avoided in the sol-gel method. The film annealed at 350°C exhibited a prominent band at 3400 cm^{-1} when compared to the films annealed at 450°C and 550°C, and this is due to the removal of hydroxide group on annealing at higher temperatures. The intense band below 1210 cm^{-1} is due to Ti-O-Ti vibrations. The slight shift of the band to the lower wave numbers and sharpening of the Ti-O-Ti band on annealing may be due to the increase in size of the nanoparticles. In addition, the surface hydroxyl groups in TiO_2 increases with the increase of annealing temperature. There is no band centred at 1389 cm^{-1} which clearly shows the absence of the C-H bond in the TiO_2 film. Also, there are no additional bands present in the spectra corresponding to the alkoxy groups. This reveals that the addition of acetic acid has not introduced any residual impurities on the surface of TiO_2. There is a small absorbance band at 2353 cm^{-1} corresponding to the various hydroxyl groups present in the film, which is due to the addition of polyethylene glycol (PEG) in the solution. When the annealing temperature increases, the intensity of the band decreases and this is due to evaporation of polyethylene glycol at higher temperatures.

Table 1. Power conversion efficiency of dye sensitized TiO_2 thin film solar cells

Annealing Temperature (°C)	Layer	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	□ %
350	Multi-layer	0.657	0.503	0.572	0.741
450	Single layer	0.596	0.276	0.542	0.089
	Multi-layer	0.706	0.731	0.655	1.308
550	Multi-layer	0.702	0.685	0.672	1.271

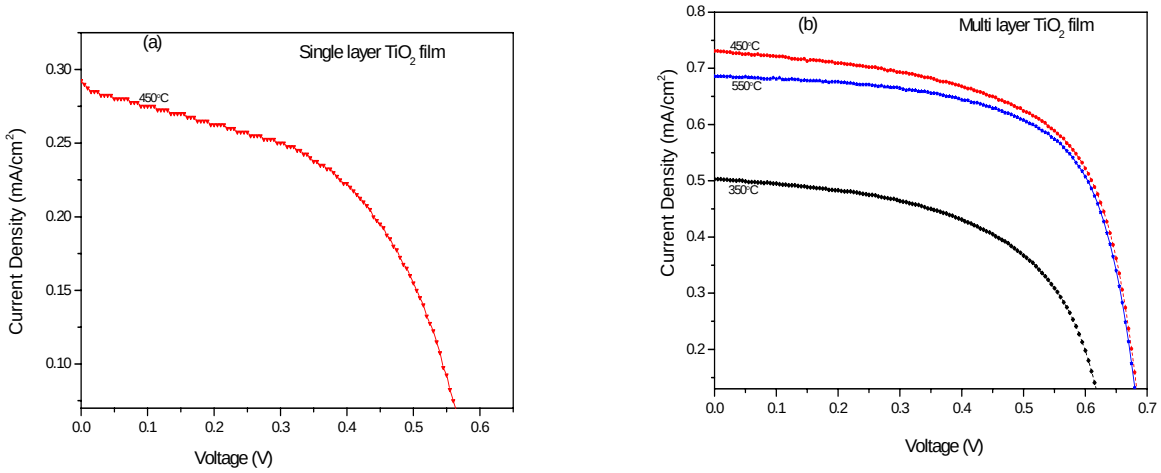

Fig. 6. J-V characteristics of dye sensitized solar cells prepared using (a) single layer TiO_2 thin films annealed at 450°C and (b) multi-layer TiO_2 thin films annealed at different temperatures.

Differential scanning calorimetric study was carried out to identify the crystallization temperature. Figure 5 shows the differential scanning calorimetric curve of multi-layer TiO_2 thin film annealed at 450°C. The curve shows two singularities: an endothermic peak spreading from 50 to 175°C, which corresponds to the evaporation of water, the thermal decomposition of ethanol or the combustion of the acetic acid and certain elements which constitute the alkoxide. The exothermic peak appearing at 425°C is associated with a weight loss that is probably due to crystallization of TiO_2. This indicates that the TiO_2 film

decomposes and crystallizes at a temperature as low as 425°C [30].

Fig. 6(a,b) shows the photocurrent-voltage (I-V) characteristics of dye sensitized solar cell prepared using single and multi-layer TiO_2 thin films annealed at different temperatures. Table I shows the power conversion efficiency and the important solar cell parameters of dye sensitized TiO_2 thin film solar cells. It is observed that the samples annealed at 450°C shows short-circuit current density (J_{sc}) of 1.52 mA/cm^2 and conversion efficiency (CE) of 1.308%, which is high compared to the solar cells prepared at 350°C and 550°C. It is due to the presence of well granular nanoparticles on the surface of the film. This nanoparticles adsorb more dye molecules resulting in an increase in the generation of electron-hole pairs and therefore the short-circuit current density. It is noteworthy to mention that the decreased J_{sc} in 550°C is due to higher series resistance of the ITO/TiO_2 multilayer structure, increased diffusion length for photo excited electrons and easy charge recombination. The films annealed at 350°C also shows smaller J_{sc}, it may due to the reduction of dye absorption area or presence of very less number of nanoparticles on the film surface.

4. Conclusion

Single layer and multilayer TiO_2 thin films with anatase phase have been prepared by sol–gel spin coating method. All the prepared films were annealed at three different temperatures. The single layer TiO_2 thin film indicates that the films are amorphous in nature. Multi-layer TiO_2 thin films annealed at 350°C and above exhibited crystalline nature with anatase phase. The X-ray diffraction result clearly shows that the crystallinity of the film improved with increase of annealing temperature. Dye-sensitized TiO_2 thin film solar cells (DSSCs) prepared using 450°C annealed TiO_2 film was observed to exhibit a better efficiency.

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