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Effect of Annealing Time of TiO_2 Thin Film Deposited by Spray Pyrolysis Deposition Method for Dye-Sensitized Solar Cell Application

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Abstract. Aim of this paper is to investigate the effect of annealing time of titanium oxide (TiO_2) thin film on structural and electrical properties. TiO_2 were deposited onto glass substrates by spray pyrolysis method. The thin films were annealed at three different annealing time; 1, 5 and 10 hours at 400°C. The structural and electrical properties were characterized using FESEM, I-V probe and solar simulator. Polycrystalline thin film with anatase crystal structure, as evidenced from X-ray diffraction pattern, was obtained with major reflection along (101). As anneal time increased the crystallite grain size is increased, thickness of TiO_2 decreased, power conversion efficiency, η increased from 0.0001% to 2.28% and percentage of IPCE increased at 520nm for transmission spectra of DSSC.

Introduction

The new solar cells are based on low cost and environment friendly materials and technology. Transparent oxide thin films are widely used materials in new generation solar cells. Most of these oxides such as ZnO, AZO, ITO, TCO or FTO are used as transparent electrodes [1–2]. Another intensively studied oxide is TiO_2, which is the most promising candidate for relatively low cost, simple manufacture and high-performance dye-sensitized solar cells (DSSC) [3–5]. Here, the prepared titanium dioxide film acted as active layer in a process similar to the photosynthesis [6]. The new development in the organic and hybrid solar cells performances of 9.8% in 2011 for organic solar cells and 11% for hybrid DSSC confirm that these new generation solar cells become one of the future solutions in energy conversion. Various methods could be employed for TiO_2 thin film deposition such as sol–gel, chemical vapor deposition, evaporation, sputtering, pulsed laser deposition, electro deposition, and spray pyrolysis. Spray pyrolysis deposition (SPD) systems present the advantages of a large area and low cost technology [7–8].

TiO_2 has attracted much attention in various fields of science and technology because of its remarkable optical and electronic properties. It has high refractive index and dielectric constant, and is transparent to visible light. TiO_2 thin films have successfully been used in photodecomposition of water, purification of environmental pollutants, and preparation of solar energy cells [9]. It has already been observed that the optical and electrical properties of TiO_2 films are substantially influenced by the thickness of the film [9]. In this paper, the effect of annealing time on structural, surface morphology and electrical properties of TiO_2 thin film by spray-deposited thin film are discussed.

Experimental/Methodology

Preparation of TiO_2 coating. The FTO glass was used as substrates and cleaned with acetone, ethanol and distilled water (1:1:1) by the ultrasonic method. TiO_2 thin films were deposited onto glass substrates using spray pyrolysis method.

TiO_2 solution used in this experiment is combination of TiO_2 transparent and TiO_2 P25 precursor solution. TiO_2 solution were prepared by adding required amount of titanium (IV) isopropoxide, ethanol, distilled water, glacial acetic acid and triton X-100 by mixing with magnetic stirrer. Then, TiO_2 P25 solution was prepared by mixing titanium dioxide (P25) with glacial acetic acid. Combination of TiO_2 transparent and TiO_2 P25 was mixed in a mortar. The TiO_2 thin films were deposited onto glass substrates by using SPD technique on hot plate at 150°C by using spray technique. The films were subsequently heated at 100°C for 30 minutes. Finally, the films were annealed at 400°C for 1 hour, 5 hours and 10 hours in the furnace to obtain the TiO_2 thin film.

Characterization of TiO_2 Thin film. The thicknesses measurements were performed by the surface profiler. Surface morphology was determined by FESEM (JEOL JSM-6380LA). The structural characterization was made by using Bruker D8 Advance Diffractometer. The IV measurement was performed using 2 points probe and a (Advantest R6243) source measuring unit. The performance of the DSC was examined under the illumination of a simulating solar light at an intensity of 100 mW/cm^2.

Results and Analysis

Structure Characteristics. XRD pattern of the film annealed for 1 hour, 5 hours and 10 hours at 400°C is shown in Figure 2. It is proven from the figure that the films annealed for shorter time are amorphous. Crystallinity of the film increase as the annealing time is increased. Peaks in XRD pattern are observed at 2θ values 25.35°, 38.96° and 48.1°, which assigned to [101], [112] and [200] planes, respectively. The calculation show that the observed crystalline peaks correspond to anatase TiO_2 phase. Angle peak in XRD pattern at 2θ=25.35° is attributed to 101 reflection of anatase.

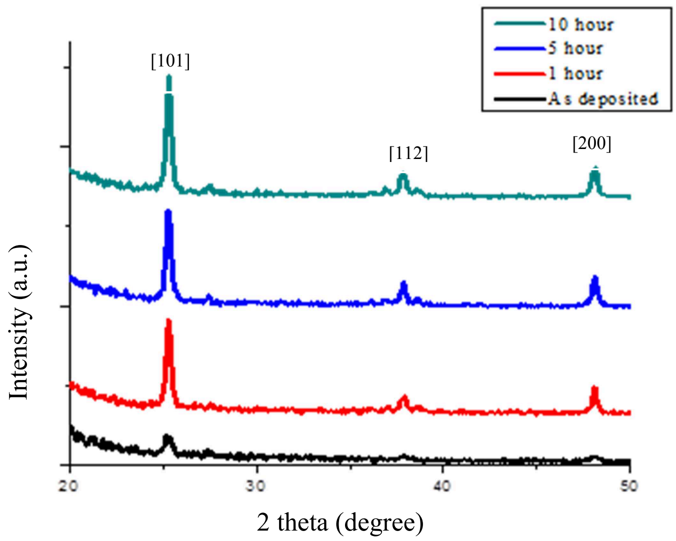

Figure 2 XRD pattern of TiO_2 film annealed for as deposited, 1, 5 and10 hours at 400^{0}C.

The crystalline size is deduced from Debye Scherrer's formula [9];

$$D_{(101)} = \frac{0.9\lambda}{\beta cos\theta} \quad (1)$$

Where λ is the wavelength of incident X-ray radiation (Cu Kα = 0.15406nm), β is the line width at half maximum height, and θ is the Bragg's diffraction angle corresponding to the peak (101) peak.

The crystallite size increases from 0.267 to 0.623nm with substrate temperature as in Table 1. This is due to the fact that smaller grains tend to have surfaces with sharper convexity and gradually disappear by feeding the larger grains, as annealing time increase. The net effect is the grain growth. Figure 3 show that the sample AT_{10hour} has larger crystallite size than other samples.

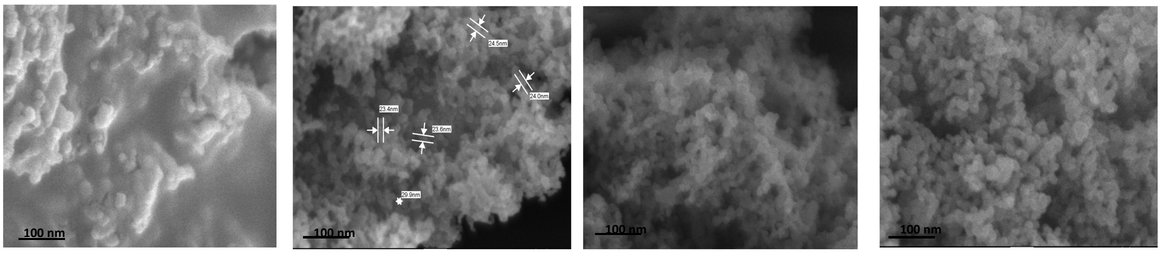

Figure 3 FESEM images of the samples (a) As deposited, (b) AT_{1hour}, (c) $AT5_{hour}$, (d) AT_{10hour}.

Table 1 Effect of annealing time on properties of spray-deposited TiO_2 thin film.

Sample	Thickness, t [nm]	Sheet resistance, Rs [$x10^9\Omega/m^2$]	Resistivity, ρ [Ω.µm]	Crystallite size, $D_{(101)}$ [nm]
As deposited	10.00	2.04	2.64	0.26
AT_{1hour}	25.44	2.59	7.21	0.46
AT_{5hour}	16.80	2.21	4.32	0.47
AT_{10hour}	14.12	2.13	3.61	0.62

Electrical Properties. The data obtained from two-point probe method, which was applied on the produced film indicates that the film have a high resistance. Table 1 shows annealing time dependence of resistivity (ρ) for all annealed films, supporting the semiconducting behavior. The resistivity was measured using relation [9], where V is the applied voltage, I the current and t the film thickness of the film.

$$\rho = \frac{\pi}{In2}\left(\frac{V}{I}\right)t \quad (2)$$

The values are listed in Table 1. It shows that the resistivity decrease with decreasing film thickness. Thus, the increment of annealing time was accompanied by a decrement of film resistivity.

Performance of DSSC-Photocurrent voltage of DSSC.

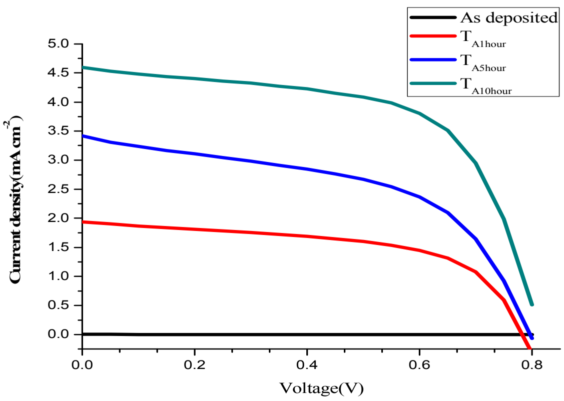

Figure 4 Photocurrent-voltage characteristics of DSSC composed of TiO_2 layer deposited by spraying on FTO substrate for as deposited, AT_{1hour}, AT_{5hour} and AT_{10hour}.

Table 2 Power conversion efficiency and ICPE percentage of TiO_2 thin film solar cell prepared by different annealing time at 400°C.

Sample	V_{OC} (V)	J_{SC} (mA.cm^{-2})	FF	η (%)	ICPE (%)
As deposited	0.473	0.00139	0.164	0.00011	0.063
AT_{1hour}	0.782	1.94	0.572	0.87	11.9
AT_{5hour}	0.796	3.42	0.521	1.42	24.9
AT_{10hour}	0.813	4.59	0.611	2.28	33.6

Figure 4 illustrates the photocurrent density-voltage of the DSSC by using the TiO_2 film fabricated by spray pyrolysis deposition technique under the illumination of a simulating solar light. The solar cell parameters such as fill factor (FF) and efficiency (η) have been calculated using equation (3) and (4) [12].

$$FF = J_{max} \times \frac{V_{max}}{J_{sc}} \times V_{oc} \quad (3)$$

$$\eta(\%) = J_{max} \times V_{oc} \times FF^{36} \quad (4)$$

The calculated solar cell parameters are given in Table 2. The power conversion efficiency of the cell increase with increase of annealing time. The higher efficiency is 2.28% for 10 hour annealing time. This may due to formation of well crystalline size and more pore present in the surface of the film. The presence of pore in film is confirmed by the FESEM image. This result confirms that the annealing time used to prepare TiO_2 thin film greatly affects the photo-conversion efficiency of DSSC due to the high surface area from its fabrication.

Incident photo-to-current conversion efficiency (IPCE) of DSC. Figure 5 shows the dependence of the IPCE on the wavelength in the range between 400 nm to 800 nm for samples AT_{1hour}, AT_{5hour} AT_{10hour}. The percentage of IPCE increased when annealing time increased at 520 nm. If we take into account the reflection by conduction of FTO, the IPCE is close to 100% [11]. Referring to Table 2, it shows that the high J_{SC} and the η of the DSC are related to the high IPCE value.

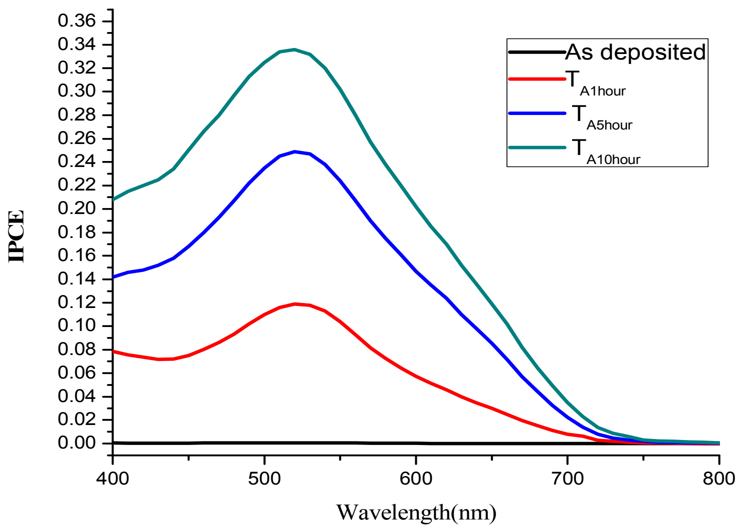

Figure 5 IPCE of DSSC as a function of the wavelength in the range of 400 – 800 nm.

Conclusions

TiO_2 thin films with anatase phase have been prepared by SPD method using different annealing times. All the prepared films were annealed at three different annealing times for 1 hour, 5 hours and 10 hours. The annealed films with increased annealing time have been found to exhibit anatase phase. The grain size has been observed to increase with increased annealing time and can be considered as a mean to control grain growth. The transmittance spectra have been observed to increase with increased annealing time. The 2.28% power conversion efficiency of the TiO_2 thin film annealed for 10 hours shows maximum efficiency compared to other films. This result clearly suggests that the contact between TiO_2 nanoparticles in the nanocrystalline deposit significantly influences the cell's performance. It can be considered that the controlling of the particle contact through deposition condition benefits the improvement of DSC performance.

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