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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, $\eta$ 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,

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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.

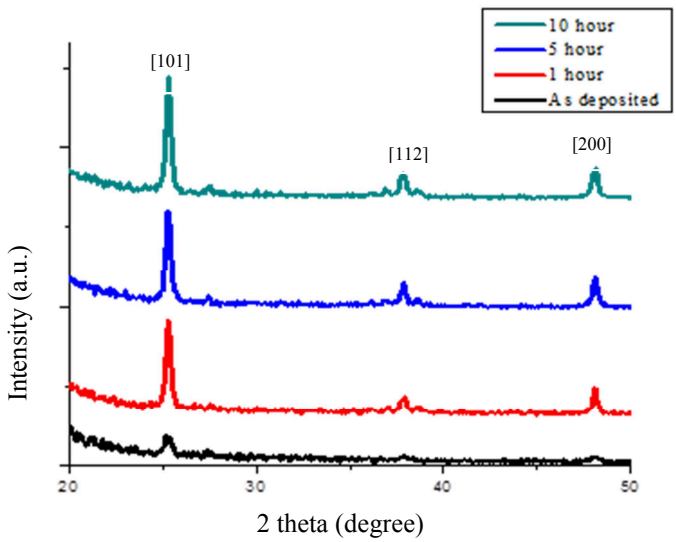


Figure 2 XRD pattern of $TiO_2$ film annealed for as deposited, 1, 5 and10 hours at $400^0$C.

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

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

Where $\lambda$ is the wavelength of incident X-ray radiation (Cu Kα = 0.15406nm), β is the line width at half maximum height, and $\theta$ 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.

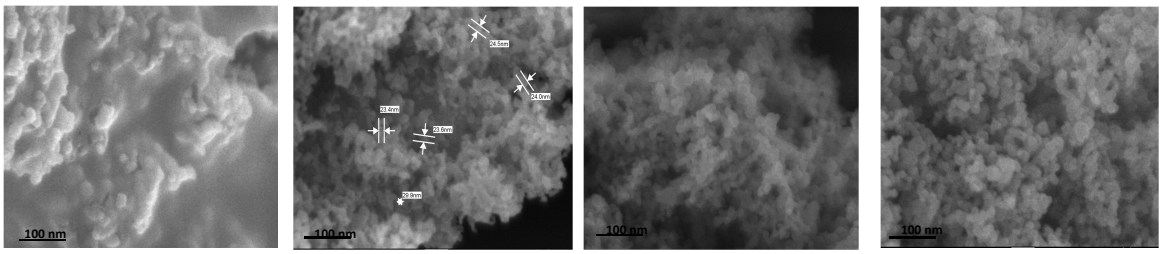


Figure 3 FESEM images of the samples (a) As deposited, (b) $AT_{1hour}$, (c) $AT5_{hour}$, (d) $AT_{10hour}$.

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

| Sample | Thickness, t [nm] | Sheet resistance, Rs [x10$^9$Ω/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.**

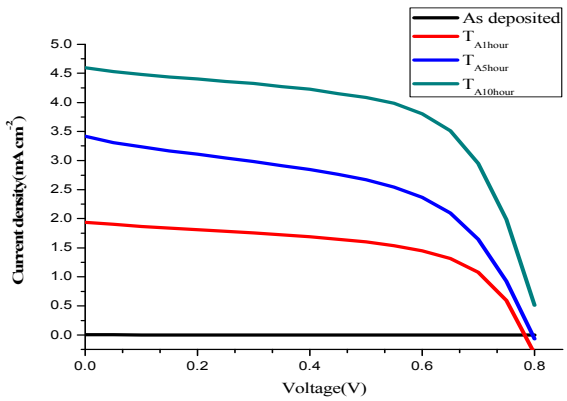


Figure 4 Photocurrent-voltage characteristics of DSSC composed of $TiO_2$ layer deposited by spraying on FTO substrate for as deposited, $AT_{1hour}$, $AT_{5hour}$ and $AT_{10hour}$.

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.

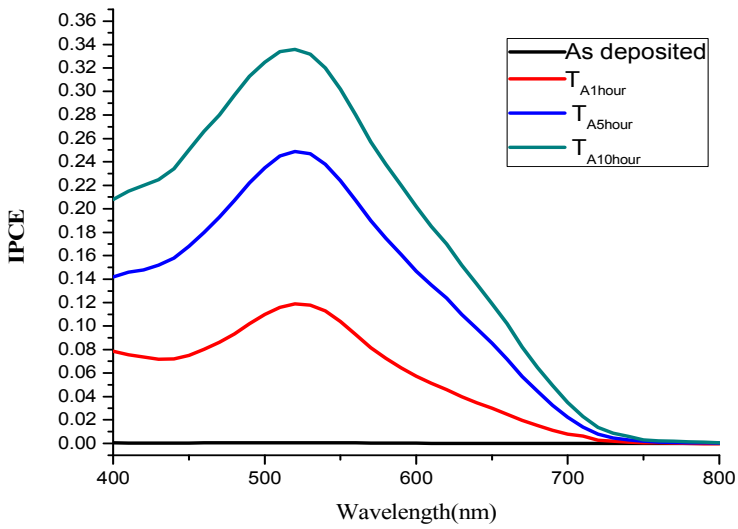


Figure 5 IPCE of DSSC as a function of the wavelength in the range of 400 – 800 nm.

## 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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