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Effects of Annealing Temperature of TiO_2 Thin Film Deposited by Spray Pyrolysis Deposition Method for Dye-Sensitized Solar Cell (DSSC) Application

Noor Kamalia Abd Hamed[1, a],Nur Ain Adam[1, b], Mohd Khairul Ahmad[1, c]

[1]Microelectronics and Nanotechnology-Shamsuddin Research Center (MiNT-SRC), Universiti Tun Hussein Onn Malaysia, 86400, Parit Raja, Batu Pahat, Johor, Malaysia.

[a]mel_leya@yahoo.com, [b]ainadam@ymail.com, [c]akhairul@uthm.edu.my

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Abstract. Titanium dioxide (TiO_2) thin films have been fabricated and deposited on FTO glass substrates by spray pyrolysis deposition (SPD) method. The TiO_2 thin films were annealed at four different temperatures for an hour. The temperature was set at 100°C, 300°C, 400°C and 500°C. Surface morphology and electrical properties of TiO_2 thin films were investigated using FESEM and 2 point- probe I-V measurement, respectively. The FESEM result shows that the grain size of the TiO_2 increases when annealed temperature increases. For XRD test shows that the crystallinity improved with the increasing of annealing temperature. When the annealing temperature increases, the electrical properties of TiO_2 also change. The result shows that the optimum temperature for annealing of TiO_2 thin film was 400°C.

Introduction

Titanium dioxide is known as a crucial material as it is extensively used as pigment in paints and coating materials in optical thin films. This is due to its high transparency and high refractive index and also its chemical durability in the visible and near IR region [1]. Titanium dioxide occurs in nature as minerals rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic) [2]. There are varieties of applications of TiO_2 for examples photo-catalyst, optical filter, gas sensor, optical filter, antireflection and dye-sensitized solar cell (DSSC). TiO_2 thin film can be fabricated using many different techniques such as sol-gel, DC magnetron sputtering, chemical vapor deposition, spin-coating and spray pyrolysis deposition (SPD) method [3]. For current experiment, spray pyrolysis were chosen to fabricate the thin film because of its simplicity, commercial viability, potential for cost-effective mass production and for large area deposition [4]. Temperature will affect parameters, for example particle size, morphology and crystallinity[1]. The optimization of annealing process will influence the structure of TiO2 thin film to obtain an appropriate phase composition. This study focuses on the effect of annealing temperatures on TiO2 thin films prepared by spray pyrolysis deposition (SPD) method in terms of structure, surface morphology and electrical properties.

Experiment

FTO glass of two different dimensions which are (2.5cm x 1cm) and (2.5cm x 2.0cm) was used as a substrates. The FTO glass substrates were cleaned with deionised water, methanol and acetone with ratio (1:1:1) in the ultrasonic bath for 10 minutes. The TiO_2 transparent solution was prepared by mixing 5 ml of glacial acetic acid, 3 ml of titanium (IV) Isopropoxide (TTIP), 1 droplet of triton X-100, 30 ml of ethanol and 3 ml of deionised water. By using magnetic stirrer with 500 rpm speed, the solution was stirred for 10 minutes. Then, the TiO_2 solution was prepared by combining the TiO_2 transparent solution with 5.5ml of acetic acid and 0.3 g of P25. This solution was stirred in a porcelain bowl for 10 minutes.

After that, the TiO_2 thin film was fabricated onto the substrates by using spray pyrolysis deposition (SPD) method on a hotplate set at 150°C. The distance between the spray nozzle and the substrates was set at 15 cm and the solution volume was 20 ml. All the samples were heated at

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100°C for 30 minutes. Later, each sample was annealed at temperatures 300°C, 400°C and 500°C for an hour. The samples of the TiO2 thin films were characterized by using Field Emission Scanning Electron Microscope (FESEM), XRD and 2 point- probe I-V measurement.

Result and Discussion

X-ray diffraction (XRD) characterization

XRD results of the thin films annealed at 100°C, 300°C, 400°C and 500°C was shown in Figure 1. The amorphous phase of TiO_2 thin films was obtained at lower temperatures of annealing process. Crystallinity of the thin films increase when annealed temperature increases. The peaks in XRD pattern are observed at 2 theta values of 25.28°, 37.80 ° and 48.05 ° which related to 101, 004 and 200 planes. The crystalline peaks of the graph are anatase peaks. When the temperature increases, the full width half maximum (FWHM) of the peaks becomes smaller and the peak at 101 become sharper. This shows better crystallinity. Table 1 shows the crystalline size of the thin films. The crystallitesize was calculated by using the Scherrer's formula below.

$$D = \frac{K\lambda}{\beta\ cos\theta} \tag{1}$$

Where K=1 is the shape factor, λ is the X-ray wavelength of CuKα radiation, θ is the Bragg's angle and β is the full width at half maximum of the peaks.The result shows the thin film annealed at 400°C have the highest crystallinity size.

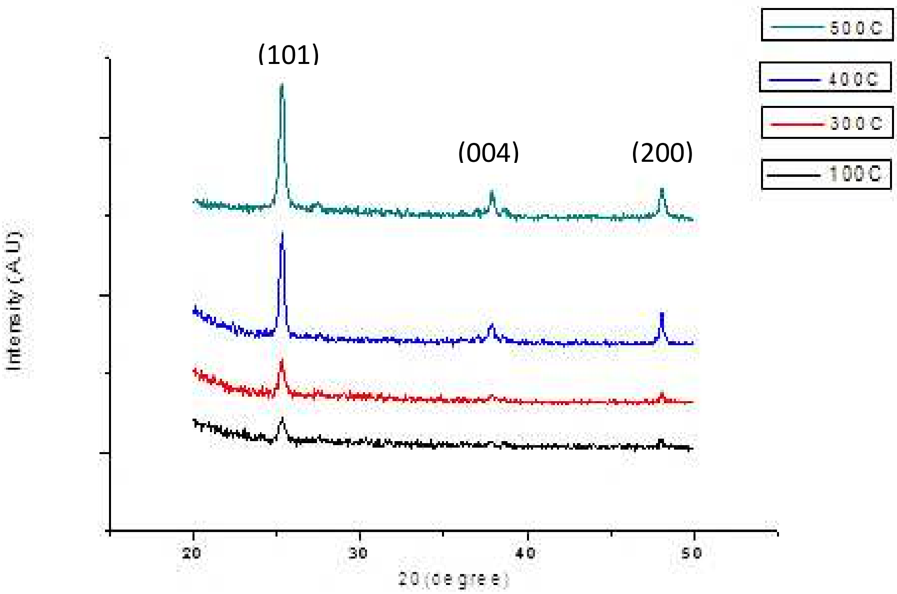

Figure 1. XRD spectra of TiO_2 thin film annealed for 1h at four different temperatures.

Table 1.Crystallite size for different temperatures

Anneal Temperature (°C)	100	300	400	500
FWHM	0.39	0.36	0.32	0.33
Crystallite Size (nm)	39.90	43.48	49.90	48.55

Surface Morphology

FESEM was used to study on their surface morphology. Surface morphology of the samples after being annealed at 4 different temperatures was shown in Figure 2. The average grain size for the films is about less than 25.0 µm as the P25 powder was used. At 400°C and 500°C, the result shows that the TiO_2 thin film contains a large amount of particles due to the small size of TiO_2 particle formed on the surface thus makes a larger surface area. The formation of polycrystalline thin films also started at higher temperature. It will create more dye molecules adsorbed onto the TiO_2 particles. The dye molecules are responsible for the light-to-electricity conversion efficiency of the DSSC.

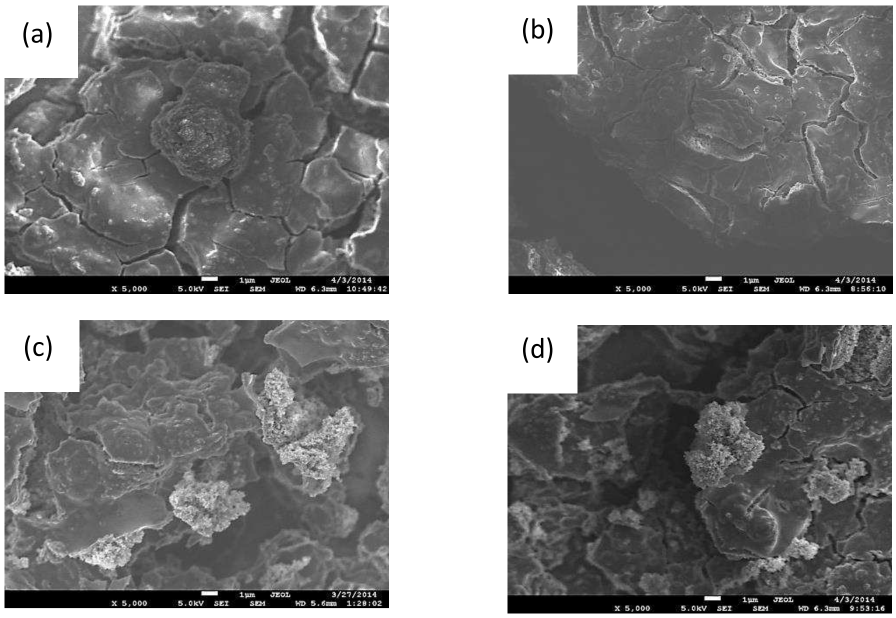

Figure 2.FESEM surface morphology of TiO_2 thin film annealed at 4 different temperatures for 1h (a) 100°C (b) 300°C (c) 400°C (d) 500°C

Electrical properties

I-V analysis was conducted to measure the electrical properties of the TiO_2 thin film by using 2-point probe. Resistivity is calculated as follows:

Resistivity, ρ

$$\rho = R_s . t \tag{2}$$

Sheet resistance, R_s

$$R_s = \rho / t \tag{3}$$

R_s is sheet resistance and t is thickness. The value of R_s was obtained from I-V graph as in Figure 3 while t value was obtained by measuring the thickness of TiO_2 thin film by using a surface profiler.

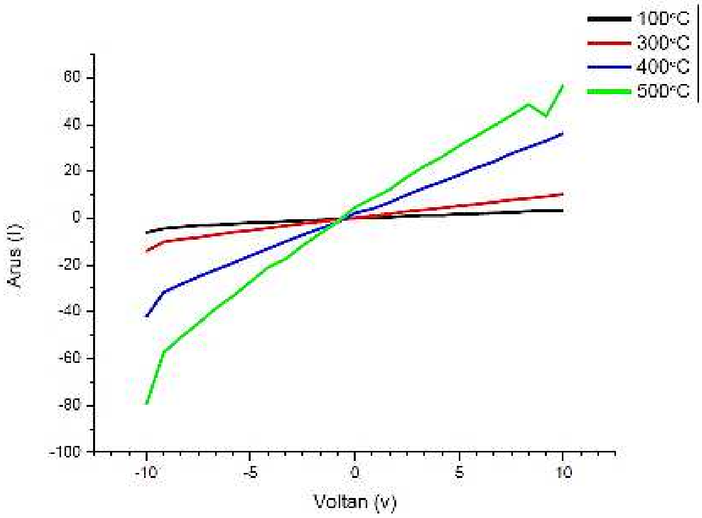

Figure 3.I-V analysis measurements at four different temperatures

Table 2.Resistivity at four different temperatures for 1hour

Temperature (°C)	Resistance Sheet (Ω/cm^2)	Thickness (m)	Resistivity(Ω)
100	0.400	1.00 $x10^{-05}$	4.00 $x10^{-06}$
300	1.086	3.27 $x10^{-05}$	35.56 $x10^{-06}$
400	3.591	2.54 $x10^{-05}$	91.36 $x10^{-06}$
500	6.025	2.22 $x10^{-05}$	133.76 $x10^{-06}$

Previous study shows that resistivity and annealing temperatures are not parallel to each other as resistance decreases when the annealing temperature increases [5]. However, it depends on the grain size. When grain size becomes larger, electron movement from particles to other particles improves. Therefore, the resistivity of TiO_2 thin films supposed to decrease after the annealing process was done but the results of resistivity at four different temperatures shown in Table 2 does not agree with this theory. Instead, the resistivity increases with increasing temperature value.

This is due to non-homogeneous thickness of surface area of TiO_2 fabricated on the glass as shown in Table 2. The thickness affects the resistivity value.

Conclusion

Titanium dioxide thin films are successfully fabricated onto FTO glass substrates using spray pyrolysis deposition (SPD) method which annealed at four different temperatures. The effect of the crystallinity, surface morphology and electrical properties has been studied. The structured of TiO2 thin film has undergone annealing process which changed from amorphous phase to anatase phase and improved the crystallinity. FESEM shows that the higher annealing temperature will result to higher surface area of the TiO_2 thin films deposited on the glass. The grain size increased when the annealing temperature increased. The increment of resistivity of the TiO_2 thin films with higher temperatures does not follow the theory due to non-homogeneous thickness of surface area of TiO_2 fabricated on the FTO glass.

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