

Sains Malaysiana 45(8)(2016): 1197–1200

Effect of Annealing Temperatures on TiO₂ Thin Films Prepared by Spray Pyrolysis Deposition Method

(Kesan Suhu Sepuhlingap ke atas Filem Nipis TiO₂ Disediakan melalui Kaedah Semburan Pemendapan Pirolisis)

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ABSTRACT

Titanium dioxide (TiO₂) nanoparticles thin film has been successfully synthesized by a spray pyrolysis deposition method by using an air compressor on a fluorine-doped tin oxide (FTO) substrate and was annealed at different temperature. TiO₂ is the most common oxide as an electrode in dye sensitized solar cell (DSSC) which still has chances of improvements to increase its efficiency as an electrode. The efficiency of a DSSC was relatively low but modifications on every part of a DSSC were currently in research progress and an increase in adsorbed dye molecules was considered a potential. Thus, the influences of annealing temperature on structural and morphological properties of TiO₂ have been studied using X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM), respectively, while the efficiency of the films in a solar cell was studied by a solar simulator. The FESEM result showed several degrees of porosity obtained by varying the annealing temperature. The crystallinity of TiO₂ investigated by XRD showed that the crystallinity of the TiO₂ thin films was generally unaffected by the annealing temperature. The relationship between the properties and the efficiency of the films as an electrode was also studied.

Keywords: Crystallinity; electrical properties; semiconductor; spray deposition; surface morphology; thin films; TiO₂

ABSTRAK

Filem nipis nanopartikel titanium dioksida (TiO₂) telah berjaya disintesis oleh kaedah pemendapan semburan pirolisis dengan menggunakan pemampat udara pada substrat fluorin-terdop timah oksida (FTO) dan telah disepuhlingap pada suhu yang berbeza. TiO₂ adalah oksida yang paling biasa digunakan sebagai elektrod dalam sel solar pekapencilup (DSSC) yang masih mempunyai peluang untuk penambahbaikan bagi meningkatkan kecekapannya sebagai elektrod. Kecekapan DSSC adalah agak rendah tetapi pengubahsuaian pada setiap bahagian DSSC masih dalam proses penyelidikan dan peningkatan dalam jumlah molekul pewarna yang terjerap dianggap berpotensi untuk meningkatkan kecekapan DSSC. Pengaruh suhu penyepuhlingapan pada sifat struktur dan morfologi TiO₂ telah dikaji dengan menggunakan pembelauan sinar-X (XRD) dan pelepasan medan mikroskop elektron pengimbas (FESEM) manakala kecekapan filem dalam sel solar telah dikaji oleh simulator suria. Keputusan FESEM menunjukkan beberapa darjah keliangan diperolehi dengan perubahan suhu penyepuhlingapan. Kehabluran TiO₂ yang dikaji oleh XRD menunjukkan bahawa kehabluran filem nipis TiO₂ tidak terjejas oleh suhu penyepuhlingapan. Hubungan antara sifat dan kecekapan filem sebagai elektrod juga telah dikaji.

Kata kunci: Filem nipis; morfologi permukaan; penghabluran; semburan pemendapan; semikonduktor; sifat elektrik; TiO₂

INTRODUCTION

Dye sensitized solar cell (DSSC) is a more economical alternative to the p-n junction photovoltaic devices currently used today. DSSC differs from the p-n junction solar cells in as uses only one type of semiconductor as a charge carrier transport while p-n junction solar cells uses two types of semiconductor for light absorption and charge carrier transport. In DSSC, light is absorbed by dye sensitizer molecules which were adsorbed onto the semiconductor surface. An array of different dyes can be used in DSSC as approached in previous research (Khalil 2012). Photo-induced electron injection takes place in the dye and the excited electrons will then travel into the conduction band of the semiconductor and to the charge collector. The charges will reach the transparent electrode and continue to travel along the external circuit before

reaching the counter electrode. The counter electrode was lined with a thin sheet of electrocatalytic conductive metal (Roy-Mayhew et al. 2010). The electrolyte located in between the two electrodes will carry the charges back from the counter electrode to the working electrode by redox reaction. The positively charged sensitizer molecules will receive the electrons to become neutral again thus completing the circuit (Grätzel 2003).

Titanium dioxide (TiO₂), also known as titania, is one of the most widely used oxide materials as the photoelectrode/photoanode of a DSSC. This was due to its wide band gap, stability and versatility. TiO₂ also delivers the highest photo-conversion efficiency and is abundant in nature. The surface area of the TiO₂ plays an important role in increasing the efficiency of the solar cell as larger surface area means more adsorbed dye (Nakade et al. 2003). In this

paper, the TiO_2 thin film was prepared by spray pyrolysis deposition method (Perednis & Gauckler 2005). Annealing process allows organic substances to evaporate from the samples thus making it thinner and more porous (Hasan et al. 2008). The films fabricated were annealed at different temperature using a furnace.

The physical properties of TiO_2 material are greatly influenced by the methods of deposition and annealing temperatures. Annealing temperature can transform an amorphous TiO_2 to anatase and then to rutile as it increases. Generally, TiO_2 thin films will be amorphous at the point of deposition and later become anatase after annealing at the temperatures between 300°C and 600°C. Since anatase is metastable, it can transform to rutile after annealing at the temperatures from 700°C to 1000°C. Annealing of TiO_2 can also improve their surface morphology and crystallinity. Annealed TiO_2 will become porous as the solvent used in deposition process evaporated; leaving porous structure on the surface of the material. It was also reported that annealing of the films makes the grain size becomes larger, lowers the transmittance of the film, increase the value of refractive index and allowed indirect optical band gap (Hasan et al. 2008).

METHODS

TiO_2 solution was prepared by mixing TiO_2 P25 powder with acetic acid in a mortar. The mixture was grinded until thoroughly combined. Then, diluted acidic anatase TKC-303 was added into the mortar and the solution was well mixed before transferred into a lightproof bottle. Ethanol and Triton X-100 were added into the solution as

solvent and surfactant, respectively. The bottle was then placed into an ultrasonicator for 30 min. Fluorine-doped tin oxide (FTO) substrates used were aligned on a hotplate with the temperature set at 150°C. The TiO_2 solution was sprayed onto the substrates using a regular airbrush with the distance between the nozzle and the substrate fixed at about 10 cm. The spraying process was done with left to right motion until the solution was finished. The samples were left to dry at room temperature before annealed with controlled temperature ranges from 300°C to 600°C. The characterization of the samples was done using field emission scanning electron microscopy (FESEM) for the surface morphology, x-ray diffractometer (XRD) for the crystal structure and the crystal phase of the samples, surface profiler for the thickness of samples and Solar Simulator to measure the efficiency of the samples as the working electrode of a DSSC.

RESULTS AND DISCUSSION

Figure 1 shows the FESEM images of the samples annealed at different temperature. The size of the particles ranges from 25 to 40 nm. The porosity of films seems to increase as the annealed temperature increases. The particles also seem to have agglomerated as the annealing temperature increases and resulting in increase of particle size which were still of nanometer size. From the FESEM images, it can also be seen that the grains becomes larger and were well connected and distributed and is thick enough that no FTO particles can be seen. It can be deduced that the annealing temperatures can alter the evaporation rate of organic substances which results in more evaporation as

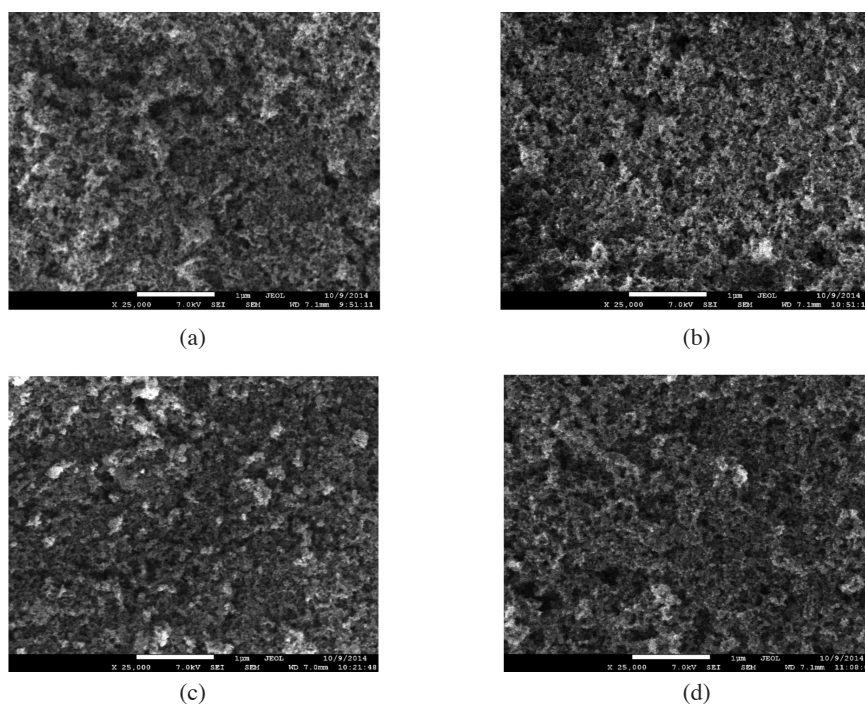


FIGURE 1. FESEM images of TiO_2 thin films annealed at (a) 300°C, (b) 400°C, (c) 500°C and (d) 600°C

the temperature increased; thus making the film more porous. The organic substances in this context come from ethanol; which only served as solvent for the deposition process. Porosity of the thin films is important as the film becomes more porous, the surface area of the film will increase. An increase in surface area will ensure more dye molecules to attach thus increasing the number of excited electrons.

As for Figure 2, the result showed that the TiO_2 thin films fabricated were anatase corresponding to the peaks of the spectrum. The peaks found at 2θ values of 25.3° , 37.89° , 47.89° and 54.82° corresponds to the anatase planes (101), (004), (200) and (211), respectively. The pattern agrees with the JCPDS data file for anatase (PDF-04-0477). FTO peaks were also found at 37° which corresponds to FTO planes (200) matched with the JCPDS data file for FTO (PDF-46-1088). Since TiO_2 P25 powder contains 25% of rutile, rutile peaks were found at 27.45° , 36.09° , 41.23° and 54.32° which correspond to rutile planes (110), (101), (111) and (211), respectively, supported by JCPDS data file for rutile (PDF-03-9171). The spectrum for all samples showed good crystallinity with the changes of annealing temperature shows little effect on crystallinity. The deposited sample also showed good crystallinity with no significant difference with the annealed samples. Therefore, it can be said that the crystallization of the film occurred during the deposition process.

Although the XRD peaks show significant crystallinity for all the samples, the I-V graph as shown in Table 1 shows that there is a significant difference in the current density (mA/cm^2) for each samples with the one annealed at 600°C delivering the highest current. I-V measurements were done after the assembly of the DSSC. TiO_2 thin films were immersed in N719 ruthenium dye overnight before assembled with Pt counter electrode and iodide electrolyte. The DSSC was exposed in the solar simulator with the exposure equals to the irradiance of the sun with forward bias from -1V to 1V . One of the strategies to improve the conversion efficiencies was to increase light harvesting efficiency by increasing the amount of dye molecules on the electrodes using thick TiO_2 films. As for the dye adsorption to increase, the effective surface area must be increased. A thick nanocrystalline film may, however, increase charge recombination between injected electrons and electroactive agents arising from low drift mobility of electrons in the film (10^{-4} - $10^{-7}\text{cm}^2/\text{Vs}$), which limits the conversion efficiency (Kang et al. 2003). By referring to Figure 3, it can be seen that the thickness for the film annealed at 600°C is the lowest. This data agrees to the statement mentioned before. FESEM results also supplied the sample for 600°C has the highest porosity thus provided higher effective surface area. It can be said that the efficiency is not affected by the crystallinity but surface morphology of the TiO_2 thin film.

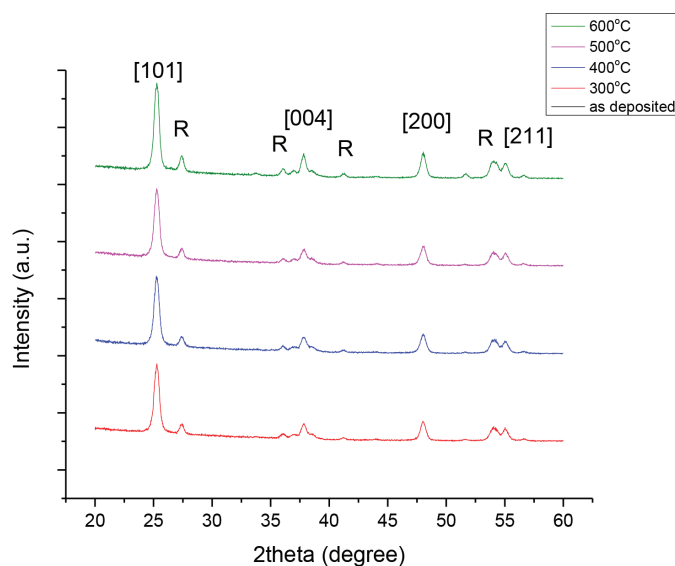


FIGURE 2. XRD spectrum of TiO_2 thin films annealed at different temperatures

TABLE 1. I-V measurements of DSSC with TiO_2 samples annealed at different temperatures

Sample	Voc (V)	Isc (mA/cm^2)	Fill factor	Efficiency (%)
As deposited	0.765	1.492	0.604	0.689
300°C	0.765	4.333	0.629	2.085
400°C	0.785	5.657	0.664	2.947
500°C	0.795	4.191	0.667	2.220
600°C	0.788	6.915	0.673	3.668

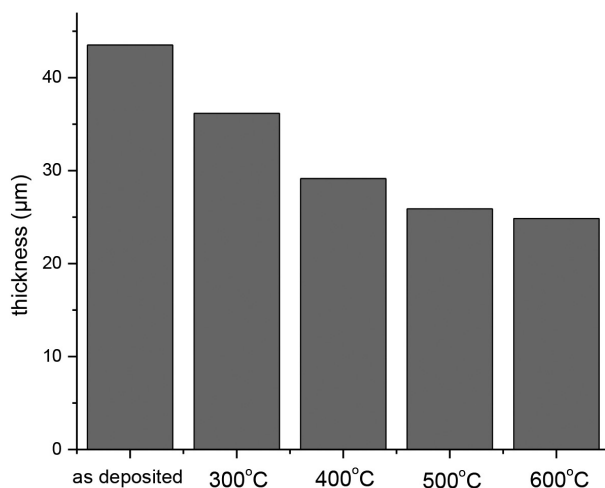


FIGURE 3. Thickness of TiO₂ thin film annealed at different temperature

Furthermore, when grain size becomes larger, electron movement between the TiO₂ particles improves. Therefore, the resistivity of the TiO₂ thin films decreased as the annealing process improves electronic contacts between the TiO₂ particles and also between the TiO₂ particles and FTO particles. While increasing the annealing temperature will increase the effective surface area, it will also increase the surface roughness of the thin film and decrease the contact surface between particles of the film. With less contact surface, electron mobility will decrease; thus decreasing the efficiency of the DSSC (Ahmad et al. 2010).

CONCLUSION

TiO₂ thin films was successfully fabricated using spray pyrolysis deposition method. The effects of different annealing temperatures on structural and morphological properties as well as the influences of the properties on the efficiency of the thin films have been studied. The results showed that the efficiency TiO₂ as the photoelectrode in DSSC was influenced by the surface morphology and porosity of the thin film. Further studies are needed on other parts of the DSSC as well as to improve the electron mobility of TiO₂.

ACKNOWLEDGEMENTS

The authors would like to thank the MiNT-SRC, University Tun Hussein Onn, Geran Insentif Penyelidikan Siswazah, GIPS (vot. U225), Fundamental Research Grant Scheme, FRGS (vot. 1275) and Explatory Research Grant Scheme, ERGS (vot. E025) grants for financial and technical supports.

REFERENCES

Ahmad, M.K., Halid, M.L.M., Rasheid, N.A., Ahmed, A.Z., Abdullah, S. & Rusop, M. 2010. Effect of annealing

temperatures on surface morphology and electrical properties of titanium dioxide thin films prepared by sol gel method. *Journal of Sustainable Energy & Environment* 1: 17-20.

Grätzel, M. 2003. Dye-sensitized solar cells. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* 4(2): 145-153.

Hasan, M.M., Haseeb, A.S.M.A., Saidur, R. & Masjuki, H.H. 2008. Effects of annealing treatment on optical properties of anatase TiO₂ thin films. *International Journal of Chemical and Biological Engineering* 1(2): 92-95.

Khalil Ebrahim Jasim. 2012. Natural dye-sensitized solar cell based on nanocrystalline TiO₂. *Sains Malaysiana* 41(8): 1011-1016.

Kang, M.G., Ryu, K.S., Chang, S.H., Park, N.G., Hong, J.S. & Kim, K.J. 2003. Dependence of TiO₂ film thickness on photocurrent-voltage characteristics of dye-sensitized solar cells. *Bull. Korean Chem. Soc.* 5(25): 742-744.

Nakade, S., Saito, Y., Kubo, W., Kanzaki, T., Kitamura, T., Wada, Y. & Yanagida, S. 2003. Enhancement of electron transport in nano-porous TiO₂ electrodes by dye adsorption. *Electrochemistry Communications* 5(9): 804-808.

Perednis, D. & Gauckler, L.J. 2005. Thin film deposition using spray pyrolysis. *Journal of Electroceramics* 14(2): 103-111.

Roy-Mayhew, J.D., Bozym, D.J., Punckt, C. & Aksay, I.A. 2010. Functionalized graphene as a catalytic counter electrode in dye-sensitized solar cells. *ACS Nano* 4(10): 6203-6211.

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Received: 20 April 2015

Accepted: 12 October 2015