Conference Paper

Effect of Aging Time on the Synthesis of Fe-doped TiO_2 Thin Films by Spin Coating Method

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Abstract The synthesis of Fe-doped TiO_2 thin film using spin coating method was studied. Effects of aging time on the deposited thin film were investigated. Titanium butoxide ($C_{16}H_{36}O_4Ti$) as a precursor solution was mixed with the $FeCl_3$. Spin coating process was carried out on three types of precursor solution: (1) spin-coating process performed immediately after the precursor solution was made, (2) spin-coating process performed after solution was aged for 24 hours, (3) aged for 24 and (4) spin-coating after aging the precursor for 72 hours. Heating was carried out on the resulting thin film at temperature of 400°C. The morphology of TiO_2 layers was characterized using Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM). Elemental and phase composition of the films was determinedusing EDX and X-ray diffraction (XRD). We found that the best TiO_2 layer is obtained when spin-coating process is done after aging the precursor for 72 hours. The layer shows a more uniform particle distribution on the substrate and a more monodisperse particle size dominated by the anatase phase.

Keywords: TiO_2thin film, Fe doped TiO_2, spin coating, aging time.

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Received: 1 August 2016
Accepted: 18 August 2016
Published: 6 September 2016

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Selection and Peer-review under the responsibility of the ICoSE Conference Committee.

1. Introduction

TiO_2 coating has been investigated by many researchers because $TiO_2$is stable, non-toxic with band gap of 3.21 eV making it possible for photovoltaic [1] and photocatalytic [2] application. It is well known TiO2 nanoparticles with good physico-chemical properties are mainly dominated by three phasesnamely anatase, rutile and brookite. On a nanometer scale or in a thin layer form,TiO_2 nanoparticles are transparent and have a wide surface area [3]. To improve the performance of thin film $TiO_2$for photovoltaics application purpose such as dye sensitized solar cell, TiO_2 layer has been modified by the addingmetal dopant such as Fe [4] and Zn [5]. It is also reported that to improve the crystal size of TiO_2, treatment such as by varying aging time of the precursor can be performed [6].

Various methods has been reported to produce a thin layer of TiO_2such as electrophoretic deposition [7], electrodeposition [8], doctor blades [9], RF sputtering [10], sol gel [11], dip-coating [12], spin coating, etc. In this study, we use a spin coating method to deposit TiO_2 layer. The purpose of this research is to investigate the effect of aging time on the morphology and phase of Fe-doped TiO_2synhesized by spin coating method. From this study, it was found that the Fe-doped TiO_2 with aging time for precursor of 72 hours with annealing temperature of 400^{o}C produced better TiO_2 thin film. This finding may find useful in potential application in TiO_2 utilizing thin film such as photocatalytic and photovoltaic applications.

2. Experiment

Synthesis solution comprises a mixture of 13% vol. titanium (IV) butoxide ($C_{16}H_{36}O_4Ti$) (Aldrich 99.9%), 65% vol. ethanol, 4% vol. HCl, 5% vol. aquabidest (H_2O), and 13% vol. $FeCl_3$. All the ingredients were stirred for 1 hour with a magnetic stirrer C-Mag HS7. The solution was then divided into four portions. One portion was used in direct spin coating while the others were aged for 24, 48 and 72 hours prior to spin coating. Changes in aged solution were observed at a predetermined time. Spin coating parameters (rate of 2,500 rpm for 30 seconds) were the same for all samples. Deposition of TiO_2 layer was doneon microscope glass substrate. Prior to spin coating process, the glass substrateswere washed in the ultrasonic cleaner (Bransonic) for 30 minutes by using distilled water, then washed with acetone. The deposited layer was heated at a temperature of 400°C in the furnace. Characterization was performed using Scanning Electron Microscope (SEM + EDX) Hitachi S-3400N + Horiba-EMAX, Atomic Force Microscope (AFM) and X-ray Difraction (XRD) Shimadzu-7000.

3. Results and Discussion

Fig. 1 shows the typical morphology of the TiO_2 layer synthesized using spin coating technique from a solution of $C_{16}H_{36}O_4Ti$ that was aged for 72 hours, heated at a temperature of 400 °C. By using SEM technique, micrograph obtained at magnification of 40,000x shows that TiO_2 layer looks flat and solid. The thickness of the layers is estimated to be below 200 nm. All of the samples prepared regardless of its treatment and modification ((1) spin-coating process performed immediately after the precursor solution was made, (2) spin-coating process performed after solution was aged for 24 hours, (3) aged for 24 and (4) spin-coating after aging the precursor for 72 hours) have the same morphology when viewed with SEM prior to the aging time. In order to obtain clear information on the surface morphology of the TiO_2 layer, then AFM imaging (Fig 2) was later performed.

Atomic force microscopy (AFM) micrograph of Fe doped TiO_2 sample was later carried out to study the thickness and uniformity of the particles grown. Fig 2(a) shows amicrograph of TiO_2 layer synthesized from a solution ofsol-gelspin coating process, done directly without aging using spin-coating process. The image was taken immediately after the solution was made, without heating treatment. It is clearly visible that the film obtained forms two different layers that have uneven thickness. No grain of TiO_2particles is visible because the paste contains a lot of water. The absence of TiO2 aggregates viewed is also due to the incomplete formation of TiO_2 aggregates via Ostwald ripening process. After heating treatment at 400°C (Figure 2b.), the surface of the layer began to be filled by TiO_2 particles. Despite having uneven distribution,

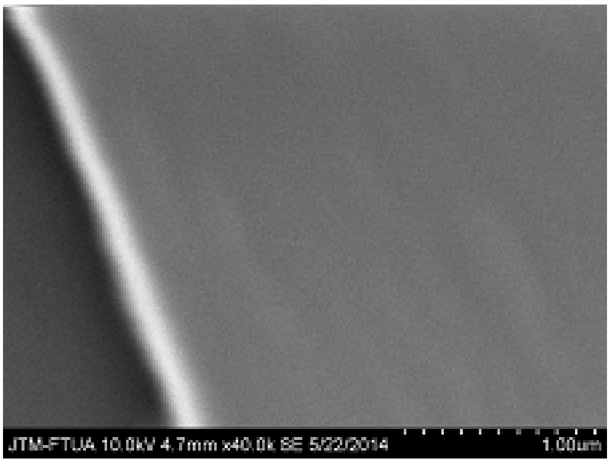

Figure 1: Scanningelectronmicroscope image of TiO_2 layer synthesized from solution of $C_{16}H_{36}O_4Ti$ with aging time for 72 hours and heated at a temperature 400∘C.

Sampel	Element	Mass %	Atom %
Before heating 400°C	Cl	531	5.05
	C	6.83	9.93
	Ti	5633	48.42
	Fe	29.38	29.25
	O	2.15	7.35
After heating 400°C	Cl	3.26	4.96
	C	5.97	3.08
	Ti	58.68	55.70
	Fe	28.04	23.91
	O	4.14	12.35

Table 1: The elemental composition of TiO_2 layer for the precursor solution aged for 72 hours.

particlebuildupoccursin someparts of the surface.We found that the best TiO_2 layer is obtained when spin-coating process is done after aging the precursor for 72 hours. The layer shows a more uniform particle distribution on the substrate and a more monodisperse particle size dominated by the anatase phase.

Fig. 2c displays TiO_2 layer produced after the spin coating sol gel solution after aging for 46 hours. Similar to Fig. 4a, here the layer thickness is still uneven and the formed two layers were still in dry pasta shape. When the sample is heated at a temperature of 400 °C (Fig 2d), the surface of the TiO_2 layer began to form evenly. The particles produced ware almost uniform in size on the order of ten nanometers. When the synthesis is done after aging the precursor for 72 hours (fig 2e), the layer of TiO_2 produced a more even distribution. The surface looks more delicate because particles are smaller than before. This shows that aging of the precursor for 72 hours produces a good TiO_2 layer. Aging treatment affects the size and agglomeration of particles [4]. If TiO_2 layer is heated at 400 °C, it will form a homogeneously-distributed layer with a more uniform thickness across the surface of the substrate (fig 2f).

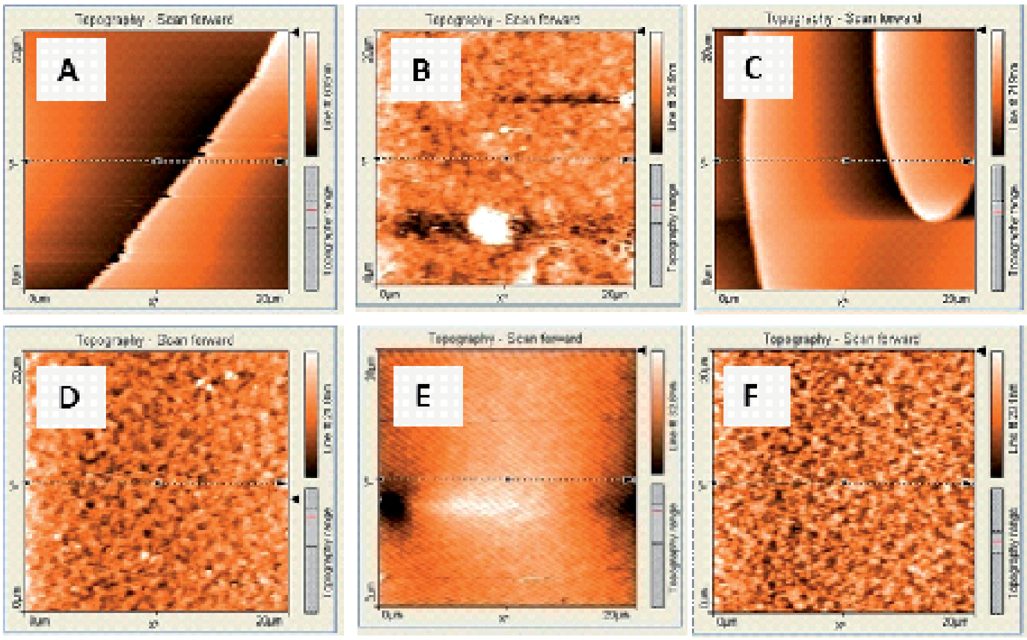

Figure 2: Atomic force microscopy micrograph of TiO_2 layer synthesized by spin coating method: a. without aging and without heating, b. without aging but heating at 400◦C, c. with aging for 48 hours without heating, d. with aging for 48 hours and with heating at 400◦C, e. after aging 72 hours but without heatingand f. After aging 72 hours and heating 400°C.

The EDX results (Table 1) show that a thin layer that was heated to 400 °C produced more atomic percentage of Ti and O atoms. This finding indicates that the annealing process enhanced the formation of TiO_2 nanoparticles. From EDX elemental mapping performed, the presence of Fe elements indicates that Fe was successfully doped into TiO_2 nanoparticles.

Fig. 3 shows the X-ray diffraction pattern of thin film layer of TiO_2 synthesized using precursor solution of $C_{16}H_{36}O_4Ti$ that was aged for 48 and 72 hours and annealed at a temperature 400 °C (the same samples with Fig.2d and Fig.2f). From here, it can be clearly seen that the main peak for anatase of (101) and (004) was obtained at a diffraction peak of 25.28 and 37.81° [2]. The diffraction peak obtained is in agreement with the standard for JCPDS of TiO_2 anatase (File no 21-1272). From here we can see that finer and smoother obtained for sample prepared at longer aging time of $C_{16}H_{36}O_4Ti$ that is 72 hours. This might due to the fact that the longer aging times provide much more reaction time to produce more TiO_2 nanoparticles according to Ostwald ripening process. From the spectra obtained, it can be clearly seen that there is no other TiO_2 phase observe in the XRD pattern. The presence of neither Fe element nor Fe alloy was seen in both of the spectra also indicating that the Fe might exist is such small amount. It is expected as the Fe elements trace in the EDX elemental mapping composition is also quite small. This phenomena obtained reflects that the Fe doping in both TiO_2nanoparticles prepared at both aging time is successfully performed. The peaks obtained at both 21° and 30.58° are from ITO coated glass substrate (JCPDS file no 88-2160).

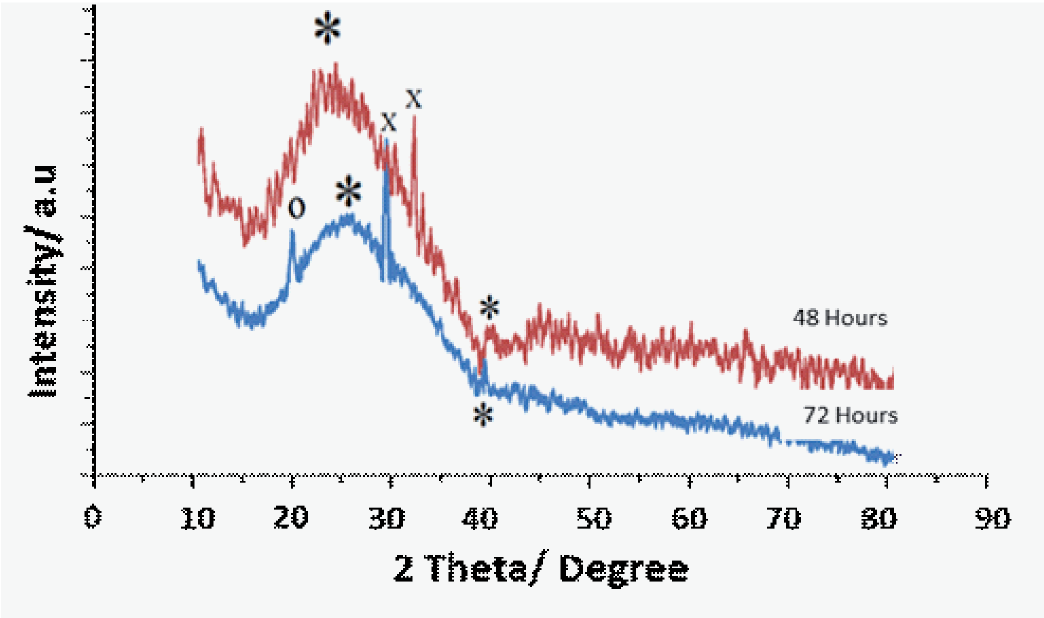

Figure 3: XRD pattern of TiO_2 films synthesized with aging time solution for 48 and 72 hours, both of samples were annealed at 400°C.

4. Conclusion

Fe doped TiO_2 thin film has successfully synthesized using spin coating method by preparing an aged precursor solution of $C_{16}H_{36}O_4Ti$. From this work, it was found that the precursor solution of $C_{16}H_{36}O_4Ti$ aged at 72 hours produced better thin film anatase TiO_2 compared to $C_{16}H_{36}O_4Ti$ aged at 48 hours judging from its AFM image and XRD spectrum. It is expected that the film produced may find use in potential application such as dye sensitized solar cell.

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