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Research paper

Influence of water volume and heating temperatures on type of phases and crystallite size of sol-gel thin films deposited without solvent

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Abstract

Sol-gel parameters such as solvent, heating temperature and water volume play a role on affecting phase and crystallite size of Titanium Dioxide (TiO_2) thin film. In this paper, the influence of water volume and heating temperature on phases and crystallite size were investigated. TiO_2 thin films deposited without solvent by varying water volume which is 32 ml (W_{32}) and 64 ml (W_{64}) and heated at various heating temperature. The phases of TiO_2 were analyzed by X-ray diffraction (XRD) and Raman Spectroscopy while crystallite size was calculated using Scherrer equation. Results show that when heating temperature at 500°C, W_{32} formulation exhibit anatase and rutile phases while W_{64} anatase and brookite phase were presence. Increment in heating temperature at 600°C, brookite phase in W_{64} formulation was transformed into rutile phase with crystallite size of 28.93 nm. Hence, the interest on preparing TiO_2 coating without solvent is an alternative method towards green process.

Keywords: *Anatase; Brookite; Raman; Solvent; XRD.*

1. Introduction

Recently, titanium dioxide (TiO_2) thin films have been intensively used because of their various applications such as gas sensor [1-2] and photocatalysts activities [3]. TiO_2 are known to exist in three crystalline phases; anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic). There are many techniques that can be used to prepare TiO_2 thin film such as sol-gel, chemical vapour deposition, chemical spray pyrolysis, hydrolysis deposition. In comparison to other methods, sol-gel is most commonly used for TiO_2 coating deposition because of its excellent mechanical and chemical stability. In addition, sol-gel method gives advantages of low cost, uniformity, easy processing and less time consuming.

The microstructure and properties of TiO_2 thin film depend upon particulars of sol-gel preparation parameter such as catalyst, heat treatment temperature, type of precursor and solvent used for the process. In reviewing works related to deposition of TiO_2 thin film, most research carried out are based on sol-gel preparation using solvent in the sol formulation. Solvent was known to affect the crystalline phase, microstructure and phtotoelectrochemical properties of the TiO_2 thin film. In such deposition, for example, Behnajady et al. [4] had studied on the effect of the solvent type onto the crystalline phases and size of TiO_2. It was found that isopropanol promotes growth of rutile with crystallite size of 22 nm as compared to ethanol and methanol. In the other hand, research done by Balaganapathi et al. [5] had carried out sol-gel preparation without solvent. It is reported that the TiO_2 produced consists of brookite with crystal size of 6 nm when heat treated at 400ºC. It was also stated that as the heat treatment increase at 500ºC, brookite and rutile phase are detected with the crystal size of 8 nm and 16 nm respectively. Thus, it is shown, TiO_2 synthesis, with or without solvent via sol gel method will affect transformation of the TiO_2 sample.

On the other hand, the characteristics of TiO_2 thin film produced is also depend on the heat treatment temperature and rate of TiO_2 hydrolysis. TiO_2 hydrolysis is influence by various reaction parameters such as water volume and sol catalyst. In the formulation of TiO_2 solution, H_2O: Ti ratio, known as the hydrolysis ratio r, is an important factor in governing the morphology, crystallinity and size of phase formation of the TiO_2 [6]. It is claimed that low hydrolysis ratio (H_2O: Ti) of 6:1 would lead to incomplete hydrolysis where anatase and rutile are produced. In contrast, higher hydrolysis ratio of (H_2O: Ti) of 100:1 will produced precipitation consist of anatase and brookite. Besides, Yoldas [7] claimed that the lower hydrolysis ratio tends to result in partial hydrolysis. Thus, higher hydrolysis ratios are necessary for complete or near-complete hydrolysis to take place. This is because lower hydrolysis ratio tends to produce amorphous phase due to slow diffusion of Ti alkoxides with higher alkyl group.

In addition, the type of phase and crystallite size present in TiO_2 thin film produced via sol-gel is also governed by the heat treatment temperature. Previous research by Arier and Tepehan [8] revealed that the particle size of TiO_2 thin film increases with an increase of heat treatment. It is reported that when the heat treatment increases to 400ºC, brookite phase with crystallite size of 6.1 nm are produced. Besides, research done by Ranjitha et al. [9] observed an amorphous phase when TiO_2 sample was heated at 300ºC, while increased heat treatment at 400ºC and 500ºC results in the formation of anatase phase with the crystallite size in the range of 18-25 nm. Mutuma et al. [10] synthesized the TiO_2 samples via a modified sol-gel method had observed anatase phase with crystallite size of 10.9 nm and 18.2 nm respectively when heated at 200ºC and 600ºC. As the heat treatment increases to 800ºC, the anatase phase transforms into rutile phase with crystallite size of 46.5 nm. Based on this review, it is apparent that water volume and heating temperature are important in determining type of phases and crystallite size of TiO_2 thin film produced via sol-gel dip coating. Therefore, the influence of water volume and heating temperature on the type of phases and crystallite size of sol-gel thin films deposition without solvent are going to be investigated as an attempt to deposit TiO_2 thin film for green deposition process.

2. Experimental

TiO_2 coating were prepared by using titanium (IV) isopropoxide (TTiP) (Sigma-Aldrich Co.), hydrochloric acid (37% HCl) and deionized water as titanium precursor, acid catalyst and hydrolysis medium respectively. 4 ml of Titanium Isopropoxide (TTIP, 97%, Sigma Aldrich) was used as a precursor and 0.4 ml of hydrocholoric acid (HCl, 37%) was used as an acid catalyst during sol preparation. TTiP was addded dropwise into varied amount of 32 ml and 64 ml of deionized water. During hydrolysis reaction, HCl was addded into the solution. The solution was mixed and stirred constantly at room temperature (25ºC) using hot plate stirrer for 3 hours. Then, the solution was kept for 2 days for aging purpose. Formulations of sol are shown in Table 1.

Table 1: Formulation Used to Prepare TiO_2 Sol

Formulation	DI (ml)	TTiP (ml)	HCl (ml)
W_{32}	32	4	0.4
W_{64}	64	4	0.4

Glass slide was cut into a dimension of 30 mm x 10 mm. Before dipping, the glass substrates were cleaned in acetone and distilled water to remove organic impurities using ultrasonic bath for 10 minutes. Then, the glass substrates were dried at 110ºC for 2 hours in an oven. The glass substrates were dipped into TiO_2 sol and pulled at a constant speed of 30 mm/s and a dwell time of 5 second. After each dipping, the glass substrates were dried at room temperature for 30 minutes followed by drying in an oven at 110ºC for 30 minutes. Then, the dipping process was repeated for 10 times. The predetermined number of dipping process was referred in a recent study by Musa, et al. [11]. The TiO_2 thin films deposition with W_{32} and W_{64} formulation were heated at 500ºC and 600ºC. Then, for the purpose of studying brookite TiO_2 formation, TiO_2 thin films deposited with W_{64} formulation were heated by lowering heating temperature at 200ºC, 300ºC and 400ºC with a heating rate of 5ºC/min for 3 hours in the furnace.

2.1. Phase analysis

The X-ray diffraction (XRD) pattern was carried out using XPERT-PRO X-ray diffractometer over a scan range 20º-80º at a rate of 5º per min using Cu Kα radiation. The crystallite size of TiO2 thin films can be deduced from XRD lines broadening using Scherrer equa-tion (1). XRD pattern is used to deter-mine crystallite size of TiO_2 thin films.

$$L = K\lambda/[\beta\ (2\theta)\cos\theta] \quad (1)$$

Where L is the crystallite of TiO_2 thin films, K is a constant value (0.94), λ is the wavelength of X-ray (CuKα = 1.5406 Å) radiation, θ is the Bragg angle while β is the line broadening at half the maxi-mum intensity (FHWM).
Raman spectra was recorded at room temperature using Uniram 3500 spectrometer operating at 532 nm with incident power 20-30 mW. The spectral band was 100 μm and the integration time was 1s for each incremental step of 1 cm^{-1}.

3. Results and discussion

3.1. Influence of water volume

Fig. 1 shows the XRD pattern of TiO_2 thin film deposited with W_{32} and W_{64} formulation heat treated at 500ºC and 600ºC. TiO_2 thin film deposited with W_{32} formulation shows the presence of mixture anatase and rutile phase (Fig. 1(a)(i)). The peak corresponding to anatase presence (JCPDS No: 01-071-1167) is identified at angle of 25.3º, 48.0º, 53.8º and rutile phase (JCPDS No: 01-072-4813) at angle of 27.1º and 56.5º. TiO_2 thin film deposited with W_{64} formulation (Fig. 1(b)(i)), shows the presence of mixture anatase and brookite. The peak corresponding to anatase phase (JCDPS No: 01-070-7348) is identified at angle of 25.3º, 48.0º and 55.0º whereas the presence of brookite (JCDPS No: 00-029-1360) is observed at and 31.9º. The type of alkyl groups in the alkoxide in addition to the H_2O: Ti ratio affects the forming reactions. This is due to the Ti alkoxides with higher alkyl groups are slower to hydrolyse and diffuse [4]. W_{64} formulation gave the fastest hydrolysis ratio and diffusion with the addition of excess water. Based on the result, it can be seen that W_{64} formulation with hydrolysis ratio (H_2O: Ti) of 64:4 resulted in the higher rate of hydrolysis reactions produced mixture of anatase and brookite. This result is consistent with study done by [3] which had found that the mixture anatase and brookite phase are produced during hydrolysis reaction when the hydrolysis ratio of H_2O: Ti is increased.

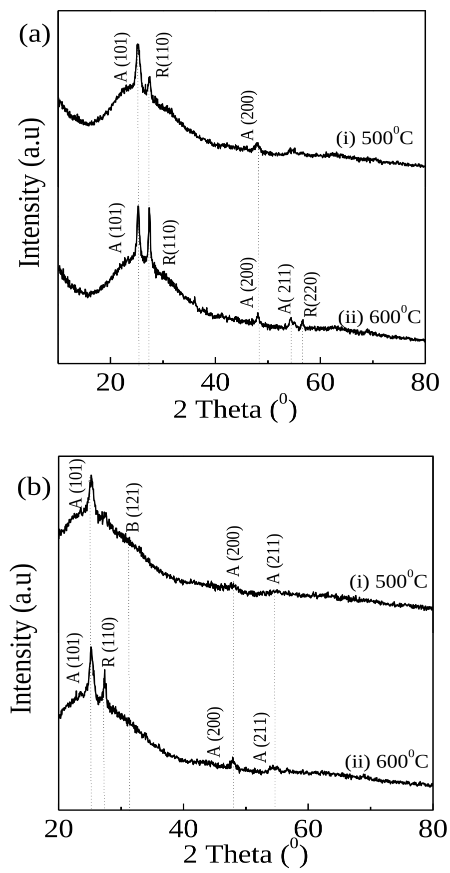

Fig. 1: XRD Patterns of the TiO_2 Thin Film Deposited with (A) W_{32} and (B) W_{64} Formulations Heated at (i) 500ºC and (ii) 600ºC (A=Anatase, R=Rutile and B=Brookite).

Raman spectra of TiO_2 thin film deposited with W_{32} and W_{64} formulation heat treated at 500ºC and 600ºC are shown in Fig. 2. For W_{32} formulation with hydrolysis ratio (H_2O: Ti) of 32:4 shows anatase band at 144 cm^{-1}, 394 cm^{-1}, 513 cm^{-1} and 633 cm^{-1} and brookite phase also has been detected (Raman band = 196 cm^{-1}, 247 cm^{-1}, 329 cm^{-1}, 365 cm^{-1}) as shown in Fig. 2(a)(i). Meanwhile, W_{64} formulation with a hydrolysis ratio (H_2O: Ti) of 64:4 as shown in Fig. 2(b)(i) shows the presence of mixture anatase and brookite phase. The existence of brookite phase as in Figure-1(b)(i) is consistent with Raman spectra located at 139 cm^{-1}, 190 cm^{-1}, 318 cm^{-1}, 390 cm^{-1} phase whereas characteristics bands at 512 cm^{-1} and 632 cm^{-1} are reported to anatase TiO_2 phase. However, for TiO_2 deposited with W_{32} formulation, brookite phase was detected by using the Raman spectra but no brookite peak was observed through XRD. The reason of the low intensity XRD peak of brookite phase is due to small crystallite size of brookite.

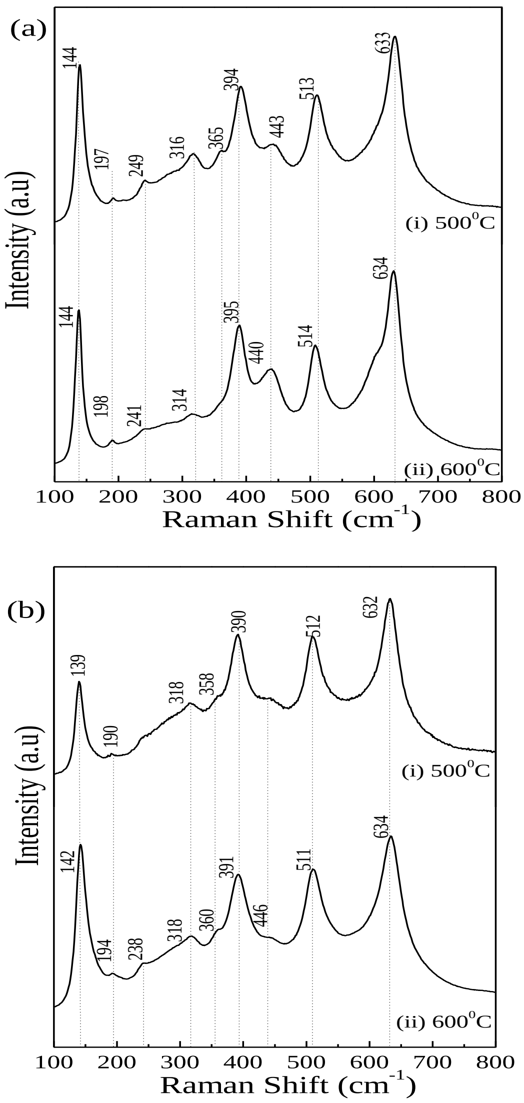

Fig. 2: Raman Spectrum of the TiO_2 Thin Film Deposited with (A) W_{32} and (B) W_{64} Formulations Heated at (i) 500ºC and (ii) 600ºC (A=Anatase, R=Rutile and B=Brookite).

Fig. 3 shows that the crystallite sizes of TiO_2 thin film deposited with W_{32} and W_{64} formulation. In particular, the crystallite sizes produced with W_{32} formulation are larger as compared with crystallite sizes produced with W_{64} formulation. The crystallite sizes of anatase with W_{32} formulation and W_{64} formulations produced are 17.28 nm to 14.41 nm respectively when heat treated at 500ºC. This is due to W_{32} formulations with a lower hydrolysis ratio (H_2O: Ti) of 32:4 contribute to slow rate of hydrolysis reaction. The slow hydrolysis reaction controlled the formation of large crystallite sizes of TiO_2 in [6].

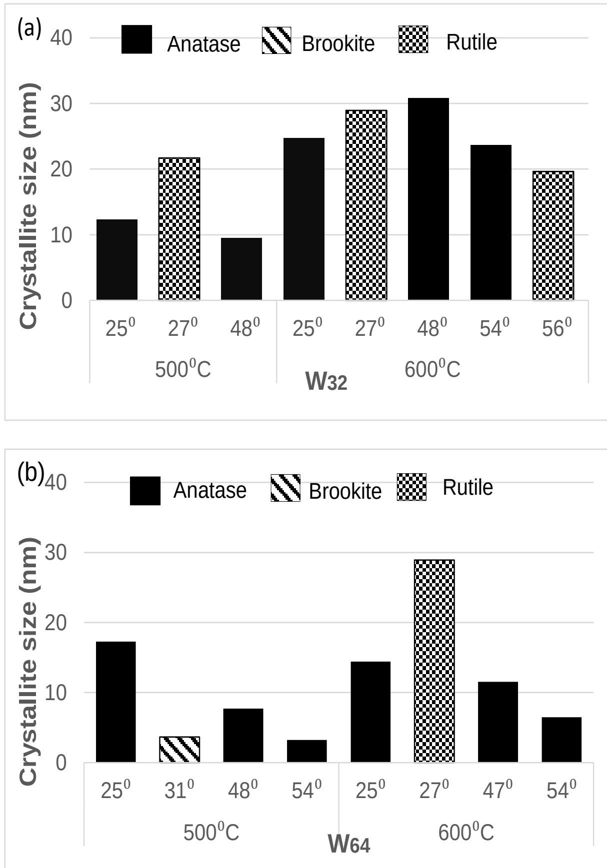

Fig. 3: Crystallite Size of the TiO_2 Deposited with (A) W_{32} and W_{64} Formulation Heated at 500°C and 600°C.

3.2. Influence of heating temperature on W64

The TiO_2 thin film deposited with W_{64} formulation was further studied to investigate brookite phase transformation at lower heating temperature. Fig. 4 shows the XRD pattern on phase transformation of TiO_2 deposited with W_{64} sample was heated at temperature ranging from 200ºC to 600ºC. Fig. 4 (i) and (ii) show presence of only anatase phase. The anatase phase (JCDPS No: 01-070-7348) are identified at angle of 25.3º, 48.0º and 54.0º. Further increase in heat treatment at 400ºC and 500ºC (Fig. 4 (iii) and (iv)), a mixture of brookite and anatase phase are presence with small peak corresponding to brookite presence (JCDPS No: 00-029-1360) is identified at 31.9º whereas, anatase phase (JCDPS No: 01-070-7348) at angle of 25.3º, 48.0º and 55.0º is observed. At higher heating temperature at 600ºC, a mixture of anatase and rutile phases are presence. The anatase phases (JCPDS No: 01-071-1167) are indentified at angle of 25.2º, 48.0º, 53.8º and rutile phase (JCPDS No: 01-072-4813) is observed at angle of 27.1º and 56.5º. This means that brookite phase is not identified at higher temperature of 600ºC due to the formation of rutile phase. These results indicated increases heating temperature.

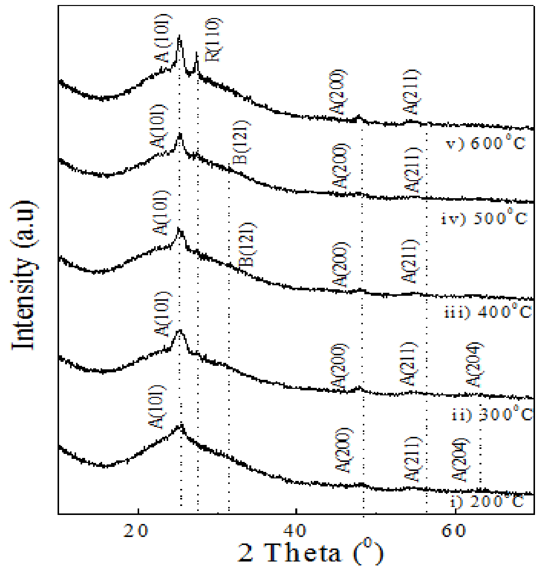

Fig. 4: XRD Patterns of the TiO_2 Thin Films Deposited with W_{64} Formulation Heated in the Range of 200ºC - 600ºC (A = Anatase, B = Brookite, R = Rutile).

Fig. 5 shows the Raman spectra of the TiO_2 thin films deposited with W_{64} formulation heated at different temperature (200ºC-600ºC). Fig. 5 (i) shows the presence of anatase phase (Raman band= 145 cm^{-1}, 394 cm^{-1}, 511 cm^{-1} and 632 cm^{-1}). Fig. 5 (ii) also shows similar results with anatase is identified at 146 cm^{-1}, 395 cm^{-1}, 511 cm^{-1} and 632 cm^{-1}. Further increases heat treatment at 400ºC (Fig. 5 (iii)) and 500ºC (Fig. 5 (iv)) shows the presence of a mixture brookite (Raman band = 190 cm^{-1}, 191 cm^{-1}, 318 cm^{-1} and 390 cm^{-1}) and anatase located at 141 cm^{-1}, 511 cm^{-1} and 633 cm^{-1}. At higher heat treatment of 600ºC, it shows peaks related to anatase (Raman band= 144 cm^{-1}, 194 cm^{-1}, 511 cm^{-1} and 634 cm^{-1}) and rutile (Raman band= 238 cm^{-1} and 446 cm^{-1}) are identified.

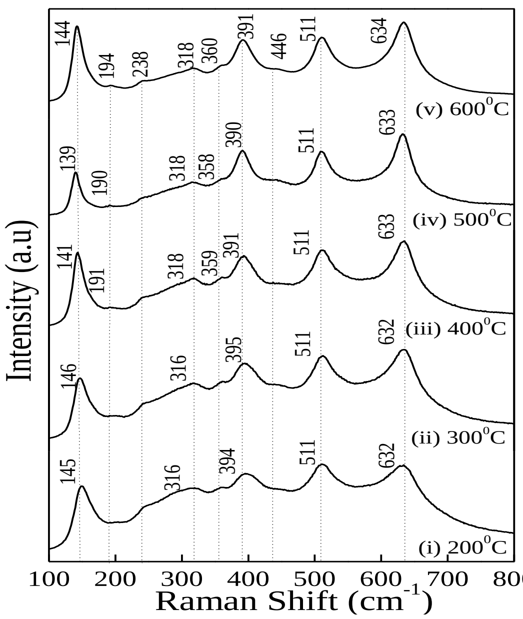

Fig. 5: Raman Spectra of TiO_2 Thin Films Deposited with W_{64} Formulation Heated in the Range of 200°C-600°C.

Fig. 6 shows the crystallite size of the TiO_2 thin film with W_{64} formulation. TiO_2 thin film heated at 200ºC produced anatase phase at angle of 25.3º with crystallite sizes of 8.65 nm respectively. However, when TiO_2 thin film heated at higher temperature of 600ºC, the crystallite size of anatase phase at angle of 25.3º becomes larger (14.41 nm). In contrast, TiO_2 thin films heated at 400ºC resulted in the brookite phase with crystallite size of 2.73 nm at angle of 31.9º. Increase heat treatment at 500ºC, the crystallite sizes of the brookite phase becomes larger to 3.66 nm. This can be deduced that the increased heating temperature increased the crystallite size of TiO_2 thin film.

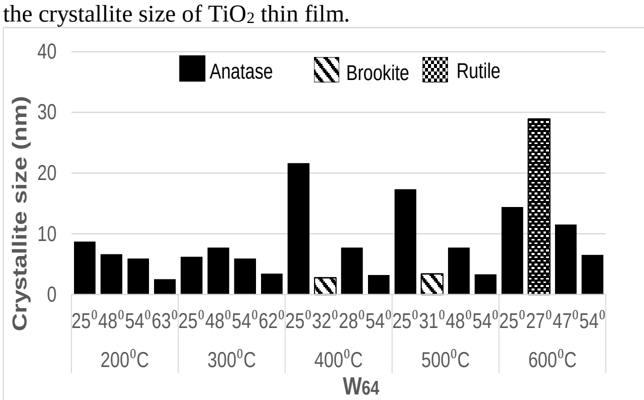

Fig. 6: Crystallite Sizes for TiO_2 Coating Deposited with W_{64} Formulation Heated in the Range of 200°C-600°C.

4. Conclusion

The TiO_2 thin film was successfully deposited via sol-gel dip coating method without solvent. The water volume and heating temperature play as decisive roles in determining phase content and crystallite size in TiO_2 thin film. When deposited with W_{32} formulation, it mainly consists of anatase and rutile phase while with W_{64} formulation, the mixture of anatase and brookite phase are produced when heated at 500ºC. It has been found that crystallite size of anatase phase at angle 25.3º decreases with increase in water volume from W_{32} to W_{64} formulation. However, when increasing the heating temperature at 600ºC, brookite phase of TiO_2 thin film deposited with W_{64} formulation transformed into rutile phase while anatase phase remains unchanged. Consequently, the effort towards green deposition process can be achieved with no utilization of solvent in obtaining phases and crystallite size of TiO_2 thin film needed for photocatalytic activity.

Acknowledgement

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