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Influence of annealing on structural and optical properties of *n*-TiO_2 thin films grown by sol-gel spin coating

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Abstract. The influence of thermal annealing to the properties of *n*-TiO_2 thin films fabricated by sol-gel spin coating has been investigated using X-ray diffraction (X-RD) and UV-Vis optical transmittance measurements. TiO_2 thin films were prepared by dissolving TiO_2 Nano-powders into a solvent of ethanol and it becomes sol-gel. The sol-gel of TiO_2 was deposited on indium tin oxide (ITO) substrate. Then, the TiO_2 the thin films were inserted into tube furnace for annealing in the temperature range of 300^{0}C to 500^{0}C during 60 minutes. Based on the x-ray diffraction results, the crystal structure of TiO_2 is anatase phase structures. The crystalline size of TiO_2 films after annealing at 300^{o}C was 46.6 nm and it slightly decreased to 46.2 nm after annealing at 500^{o}C. The optical transmittance value of TiO_2 film increased after annealing in comparison before annealing the TiO_2 film.

1. Introduction

Titanium dioxide (TiO_2) is an essential semiconductor material which used in many devises application such as photo catalysis, solar cell and photonic devices [1]. In addition to this, TiO_2 can be used in optical filters, antireflection coatings, and sensors [2]. This wide range of the application of TiO_2 is due to its unique electronic and structural properties. TiO_2 can be grouped into three crystalline phases: anatase, rutile, and brookite. Rutile is the most stable phase and it is usually obtained after annealing at temperature above 500^{o}C [3]. Also, TiO_2 is in the visible light region and its band gap is 3.0 eV for rutile and 3.2 eV for anatase crystalline phase.

Several methods have been performed to fabricate the TiO_2 thin films such as sputtering [4], chemical vapor deposition [5], and sol-gel process [6]. Among of these methods, sol-gel method offer several advantages including low cost to investigate the structural and optical characterization, and easy to control the chemical compound and deposition temperatures [4].

In this study, we investigate the structural and optical properties of TiO_2 thin films fabricated by sol-gel spin coating on indium tin oxide (ITO) substrates after thermal annealing at various temperatures. After annealing at different temperatures, the TiO_2 films were characterized using x-ray diffraction (X-RD) to study the structural properties such as the crystalline size and the strain of the films. Moreover, the UV-Vis spectrophotometer was performed to investigate the transmittance and the absorption of the TiO_2 thin films.

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2. Experimental Set-Up

TiO_2 thin films were prepared using-sol-gel method by dissolving TiO_2 Nano-powders into 10 ml ethanol. This solution was stirred on the magnetic stirred hotplate at 60^{0}C during 15 minutes with the speed rate of 1000 rpm. After the TiO_2 sol-gel formed, the ITO substrate was prepared where the TiO_2 sol-gel was fabricated on its surface. Previous study has reported similar precursor used to fabricate the TiO2 thin films [7].

Prior the sol-gel was coated on the ITO substrate; the substrate was cleaned with aquadest, ethanol and acetone during 15 minutes into each solution to remove the unwanted particles. Then, the first TiO_2 layer was coated on ITO substrates with a spin coating with a speed rate of 3000 rpm during 30 seconds. Next, the precursor solution was heated at 300^{0}C for 10 minutes at rapid thermal processor (RTP). The second TiO_2 layers were fabricated at the similar procedures with the first layer, so that the thin films forming the TiO_2 multilayers. Finally the TiO_2 thin films were inserted into the furnace for annealing process in the temperature range of 300^{0}C until 500^{0}C for 60 minutes. Figure 1 shows the flowchart for preparing TiO_2 multilayers thin film.

X-ray diffraction measurement was performed to study the crystalline properties of TiO_2 layers using a single scan diffractometer with Cu Kα (λ = 1.5406 Å) radiation and scanning range of 2θ between 20^o and 70^o. During the measurement, the current and the voltage of X-RD were maintained at 30 mA and 40 kV, respectively, and the scan speed was 2^o/min. The X-RD results were used to determine the crystalline size and the strain of TiO_2 layers using the Debye-Scherrer and William- Hall (UDM) formulation. The Optical transmittance measurements were carried out to characterize the optical properties of the films using a single beam UV-Vis spectrophotometer with a wavelength range of 250 – 800 nm.

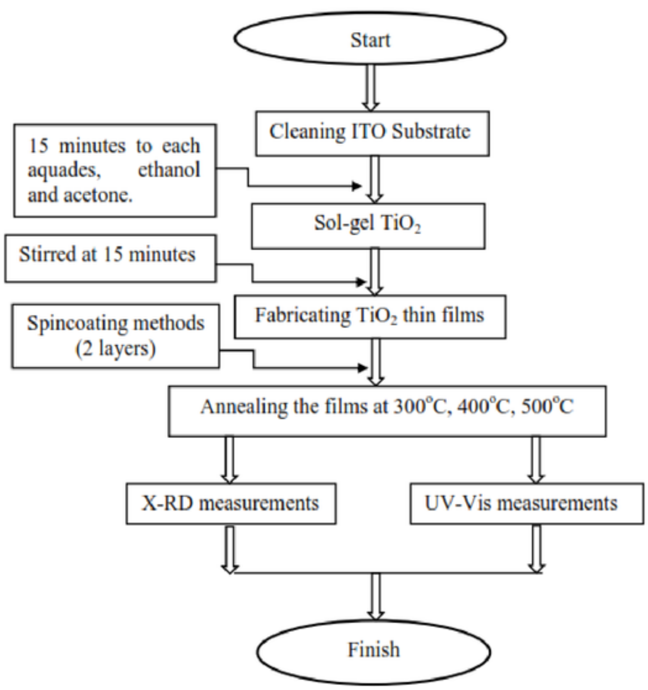

Figure 1. The flowchart of preparing the TiO_2 multilayers thin film, also the X-RD and UV-Vis measurements are included.

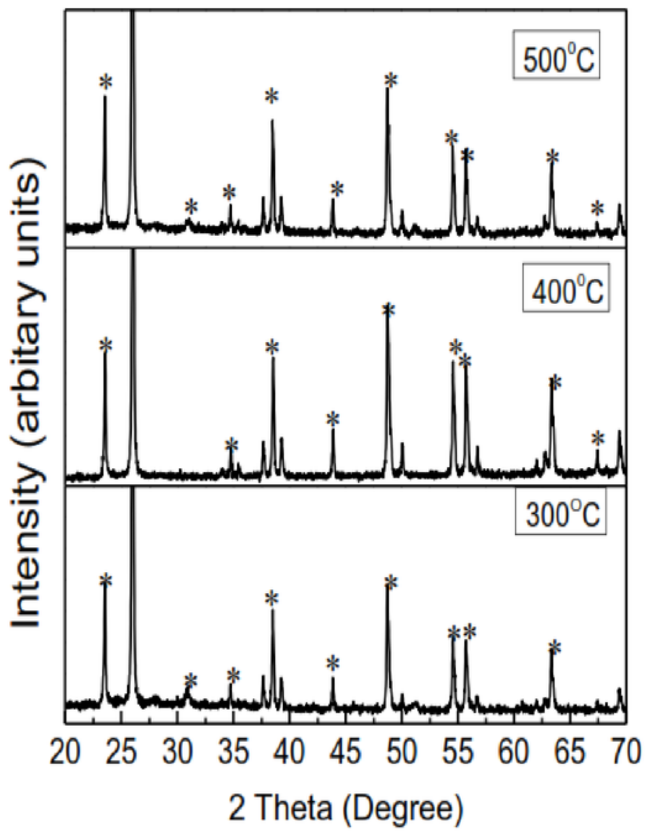

Figure.2.The X-ray diffraction patterns (X-RD) of TiO_2 multilayer thin films after annealing at different temperatures from 300⁰C until 500⁰C during 60 minutes.

3. Results and Discussion

3.1. Structural characterization

The crystalline properties of TiO_2 thin films were investigated using the X-ray diffraction measurements. Figure 2 shows the X-ray diffraction pattern of TiO_2 multilayers thin film after annealing at various temperatures from 300°C to 500°C during 60 minutes. As shown in this figure that, the intensity of diffraction peak was well determined. Also the bandwidth (FWHM) of the peak is small. The results indicated that the TiO_2 thin film is the anatase crystalline phase structures (JCPDS: 00-021-1272). In addition to this, after annealing the film at 300^0C, the X-RD patterns emerge at diffraction angle of 29.99^0, 38.43^0, 48.71^0, 54.55^0, 55.71^0, 63.32^0, and 70.90^0 which corresponded to the plane of (101), (004), (200), (105), (211), (204), and (220), respectively. However, after annealing the films at 400^0C, the diffraction angle of TiO_2 thin films shift to 26.02^0, 38.51^0, 48.79^0, 54.57^0, 55.74^0, 63.34^0, and 70.91^0, respectively at similar plane structures in the samples annealed at 300^0C. In other words, there is a change of diffraction angle within the range of 0.2^0 to 0.8^0 after annealing the samples at 400^0C in comparison to the samples that were annealed at 300^0C.

Table 1. The structure parameters of TiO_2 Thin films after annealing at 300°C and 400°C

Samples	2θ	(hkl)	Scherrer Method [8]		William Hall Plot-Method [9] Uniform Deformation Method (UDM)	
			Size (nm)	Average Size (nm)	Size (nm)	Strain (x10^{-3})
300°C	25.99	(101)	50.25	54.17	46.6	0.24
	38.43	(004)	53.23			
	48.71	(200)	54.74			
	54.55	(105)	52.22			
	55.71	(211)	53.69			
	63.32	(204)	57.04			
	70.90	(220)	58.04			
500°C	26.02	(101)	48.07	52.71	46.2	0.25
	38.51	(004)	53.66			
	48.73	(200)	51.09			
	54.57	(105)	51.70			
	55.74	(211)	54.63			
	63.34	(204)	55.81			
	70.91	(220)	54.01			

X-ray diffraction measurements results were used to determine the crystalline size (D) of the TiO_2 thin film using the Debye-Scherrer equation [8],

$$D = \frac{K\,\lambda}{\beta\cos\theta} \qquad (1)$$

where k is a constant number, λ is the x-ray wavelength (Cu Kα, λ = 1.5406 Å), β is the full width at half-maximum (FWHM), and θ is the Bragg angle, respectively. Based on figure (1), the crystalline size of TiO_2 film was calculated using the plane structures that having high intensity. This means that a small intensity does not take into account to determine the crystalline size of the films. We take the TiO_2 samples after annealing at 300°C and 400 to calculate the crystalline size. Based on the Debye-Scherrer formulation, the crystalline size of TiO_2 was 54.17 nm after annealing at 300°C and it reduced to 52.71 nm after annealing at 400°C (see table 1). In order to confirm these results, the William-Hall (UDM) was also used to calculate the crystalline size and the strain of the films using the equation [9]

$$\beta_{hkl}cos\theta = \frac{k\alpha}{D} + (4\varepsilon\, sin\theta) \qquad (2)$$

The calculation of the crystalline size and strain in TiO_2 films by using the UDM methods are assumed that the strain is uniform in all crystallographic direction in which the properties of the materials are independent of the direction along which they are measured [9]. Based on the UDM equation, the term of $\beta_{hkl}cos\theta$ is plotted against $(4sin\theta)$ would give the slope and y-intercept of the fitted line where the slope represent to the strain and the y-intercepts represents the crystalline size of TiO_2 films, respectively. Figure 2 displays the UDM plot of the fitted line of the equation (2) for the TiO_2 thin film after annealing at 300°C and 500°C. Based on the fitted line, the crystalline size of the film was 46.6 nm that annealed at 300°C and 46.2 nm for annealing at 500°C. In the case of the strain of the films, it increased from 0.24x10^{-3} for the samples annealed at 300°C to 0.25x10^{-3} after annealing the samples at 500°C. Figure 3 shows that the crystalline size of the TiO_2 films reduced as the annealing temperature increased, while the strain was negative indicating that the strain might be due to the shrinkage of the lattice parameters of the films.

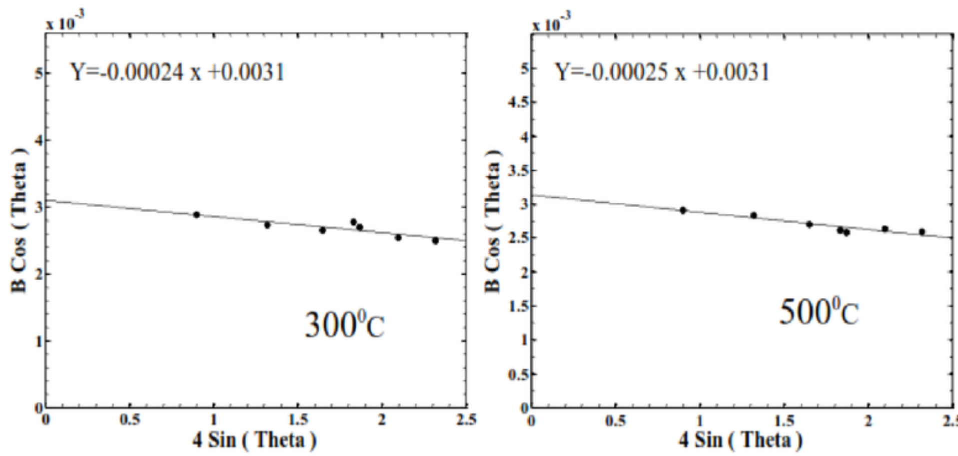

Figure.3. The William-Hall (UDM) analysis of TiO_2 mulitilayer thin films that annealed at various temperatures 300ºC, and 500ºC for 60 minutes. From the fitting data, y-intercept represents the crystalline size and the slope represents the strain of the films.

3.2. Optical characterization

Figure 3 displays the optical transmittance of TiO_2 thin films before and after annealing at 300⁰C, 400⁰C, and 500⁰C respectively. It can be seen from this figure that the transmittance value of the films before annealing was lower than that the films after annealing. After annealing at 300⁰C, the transmittance value of the films increased around 40%. The increase of the transmittance value after annealing indicates that there is an improvement of the crystalline of the TiO_2 films. Although, there is increasing of the transmittance value, however, this number is lower than that other thin film such as ZnO fabrication using sol-gel spin coating technique [10-12]. Also, it is shown in figure 3 that the transmittance value reduced significantly after annealing the films at 500⁰C. It reduced from 40% to 15% after annealing at 500⁰C. This result is probably due to the saturation of crystalline forming at high annealing temperatures. In other words, during at high annealing temperatures, it might be happened that defects could be generated and formed as the cluster or the defects agglomerated in the interface, thereby reducing the transmittance value of the TiO_2 thin films. Our results have confirmed with the previous results that the transmittance value of the TiO_2 markedly reduced in the ultra violet region. The reduction of the transmittance was attributed to a semiconducting nature of TiO_2 thin films due to the existence of the band gap [13].

Figure 3e shows the absorption spectra of the TiO_2 thin films. It can be shown in figure 3e that there was a strong absorption edge in range of wavelength smaller than 290 nm. Before annealing the films, the absorption edge was smaller than that the films after annealing at 500⁰C at the wavelength range <290 nm. The absorption spectra of the TiO_2 thin films indicate that there is an energy transition of electron-holes from the valence to the conduction bands [14]. Therefore, based from the optical transmittance and the absorption spectra indicates that TiO_2 thin films is preferable as absorbing the light.

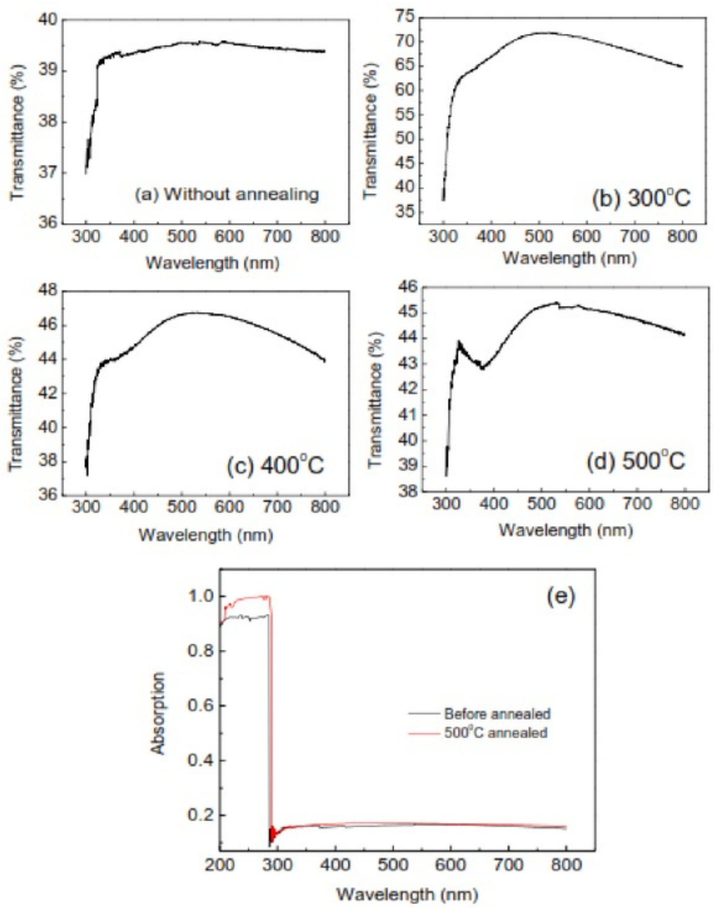

Figure 4. The optical transmittance of TiO_2 thin films (a) before annealing (b) 300^0C annealed (c) 400^0C annealed (d) 500^0C annealed and (e) absorption spectra of TiO_2 films before and after annealing at 500^0C.

4. Conclusion

We have studied the influence of the thermal annealing to the structural and optical characterization of TiO2 films at various temperatures from 300°C to 500°C for 60 minutes. The TiO_2 thin films were fabricated on the ITO substrate using sol-gel method. The X-ray diffraction results show that the TiO_2 thin films is anatase phase structures where the crystalline size of this film reduced after annealing the films at 500^0C, but the strain is slightly increased from $0.24x10^{-3}$ at annealing temperatures of 300^0C to $0.25x10^{-3}$ after annealing at 500^0C. The transmittance value of the TiO_2 increased after annealing the films at 300^0C and it reduced when the annealing temperatures were further increased to 500^0C.

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