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\(_2\) nanoparticles 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\(_2\) thin films were inserted into tube furnace for annealing in the temperature range of 300\(^\circ\)C to 500\(^\circ\)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\(^\circ\)C was 46.6 nm and it slightly decreased to 46.2 nm after annealing at 500\(^\circ\)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 devices 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\(^\circ\)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.
2. Experimental Set-Up

TiO₂ thin films were prepared using-sol-gel method by dissolving TiO₂ Nano-powders into 10 ml ethanol. This solution was stirred on the magnetic stirred hotplate at 60°C during 15 minutes with the speed rate of 1000 rpm. After the TiO₂ sol-gel formed, the ITO substrate was prepared where the TiO₂ 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 TiO₂ 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°C for 10 minutes at rapid thermal processor (RTP). The second TiO₂ layers were fabricated at the similar procedures with the first layer, so that the thin films forming the TiO₂ multilayers. Finally the TiO₂ thin films were inserted into the furnace for annealing process in the temperature range of 300°C until 500°C for 60 minutes. Figure 1 shows the flowchart for preparing TiO₂ multilayers thin film.

X-ray diffraction measurement was performed to study the crystalline properties of TiO₂ layers using a single scan diffractometer with Cu Kα (λ = 1.5406 Å) radiation and scanning range of 2θ between 20° and 70°. 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°/min. The X-RD results were used to determine the crystalline size and the strain of TiO₂ 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.

![Image](image_url)

*Figure 1. The flowchart of preparing the TiO₂ multilayers thin film, also the X-RD and UV-Vis measurements are included.*
3. Results and Discussion

3.1. Structural characterization

The crystalline properties of TiO\textsubscript{2} thin films were investigated using the X-ray diffraction measurements. Figure 2 shows the X-ray diffraction pattern of TiO\textsubscript{2} multilayers thin film after annealing at various temperatures from 300\textdegree C to 500\textdegree 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\textsubscript{2} thin film is the anatase crystalline phase structures (JCPDS: 00-021-1272). In addition to this, after annealing the film at 300\textdegree C, the X-RD patterns emerge at diffraction angle of 29.99\textdegree, 38.43\textdegree, 48.71\textdegree, 54.55\textdegree, 55.71\textdegree, 63.32\textdegree, and 70.90\textdegree which corresponded to the plane of (101), (004), (200), (105), (211), (204), and (220), respectively. However, after annealing the films at 400\textdegree C, the diffraction angle of TiO\textsubscript{2} thin films shift to 26.02\textdegree, 38.51\textdegree, 48.79\textdegree, 54.57\textdegree, 55.74\textdegree, 63.34\textdegree, and 70.91\textdegree, respectively at similar plane structures in the samples annealed at 300\textdegree C. In other words, there is a change of diffraction angle within the range of 0.2\textdegree to 0.8\textdegree after annealing the samples at 400\textdegree C in comparison to the samples that were annealed at 300\textdegree C.
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 ($10^{-3}$) |
| 300°C   |         |           |                   |           |                   |
| 25.99 (101) | 50.25 |
| 38.43 (004) | 53.23 |
| 48.71 (200) | 54.74 |
| 54.55 (105) | 52.22 | 54.17 | 46.6 | 0.24 |
| 55.71 (211) | 53.69 |
| 63.32 (204) | 57.04 |
| 70.90 (220) | 58.04 |
| 500°C   |         |           |                   |           |                   |
| 26.02 (101) | 48.07 |
| 38.51 (004) | 53.66 |
| 48.73 (200) | 51.09 |
| 54.57 (105) | 51.70 | 52.71 | 46.2 | 0.25 |
| 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],

$$D = \frac{k \lambda}{\beta \cos \theta}$$

(1)

where $k$ is a constant number, $\lambda$ is the x-ray wavelength (Cu Ka, $\lambda = 1.5406$ Å), $\beta$ is the full width at half-maximum (FWHM), and $\theta$ 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°C 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]

$$\beta_{hkl} \cos \theta = \frac{k \lambda}{D} + (4 \varepsilon \sin \theta)$$

(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 $(4 \varepsilon \sin \theta)$ 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 $0.24 \times 10^{-3}$ for the samples annealed at 300°C to $0.25 \times 10^{-3}$ 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.
3.2. Optical characterization

Figure 3 displays the optical transmittance of TiO$_2$ thin films before and after annealing at 300°C, 400°C, and 500°C 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 300°C, 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 500°C. It reduced from 40% to 15% after annealing at 500°C. 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 500°C 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°C annealed (c) 400°C annealed (d) 500°C annealed and (e) absorption spectra of TiO$_2$ films before and after annealing at 500°C.

4. Conclusion
We have studied the influence of the thermal annealing to the structural and optical characterization of TiO$_2$ 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°C, but the strain is slightly increased from 0.24x10$^{-3}$ at annealing temperatures of 300°C to 0.25x10$^{-3}$ after annealing at 500°C. The transmittance value of the TiO$_2$ increased after annealing the films at 300°C and it reduced when the annealing temperatures were further increased to 500°C.

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References

[1] Matthew N R, Morales E R, Cortes-Jacome M A, and Antonio J A T 2009 Solar Energy, 83, 1499
[2] Reddy B M, Ganesh I, Khan A, and Mol. J 2004, Catal A:Chemical, 223 295
[3] Abozovic N D, Mirenghi L, Jamkovic I A, Bibic N, Sojic D V, Abramovic B F, and Cmor M L 2009 Nanoscale. Res. Lett, 4 518
[4] Kajitvichyanukul P, Ananpattarachai J, and Pongpom 2005 Sci Technol Adv Mater, 6 352
[5] Ding Z, Hu X, Yue PL, Lu GQ, and Greenfield PF 2001 Catal Today, 68 173
[6] Pecchi G, Reyes P, Sanhueza P, and Villaseno 2001 Chemosphere, 43 141
[7] Khan M I, Bhatti K A, Qindeel R, Althobaiti H S, and Alonizan N 2017 Results in Physic, 7 1437
[8] Fallah H R, Ghasemi M, Hassanzadeh A, and Steki H 2006 Physica B, 373 274
[9] Pandiyarajan T, and Karthikeyan 2012 J. Nanopart. Res. 14 647
[10] Mekhnache M, Drici A, Hamideche L S, Benzarouk H, Amara A, Cattin L, Bernède J C, and Guerioune M 2011 Superlatt and Microstruc, 49 510
[11] Sengupta J, Sahoo R K, and Mukherjee C D 2012 Matt. Lett, 83 84
[12] Raoufi D, and Raoufi T 2009 Appl. Surf. Sci, 255 5812
[13] Matějová L, Cieslarová M, Matěj Z, Danis S, Peikertová P, Sihor M, Lang J, and Matějka V 2016 J. nanosci and nanotech, 16 504
[14] Giannakopoulou T, Todorova N, Giannouri M, Yu J, and Trapalis C 2014 Catal Today, 230 174