The effect of deposition time on the properties of titanium dioxide thin film prepared using CVD

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Abstract. This research aimed to investigate effect of deposition time on the structural, morphological properties and optical properties of the titanium dioxide (TiO2) thin film prepared using Chemical Vapour Deposition (CVD). This research involved two processes which are samples preparation process and characterisation process to fulfil the aim. The samples preparation process was done by synthesising TiO2 on indium thin oxide (ITO) substrates heated at 60°C substrate temperature. Titanium butoxide used as the precursor for this chemical reaction was volatilised at 210°C. Oxygen gas was flown at 1 litre per minute as the carrier gas. In order to study the effect of deposition time, the synthesise of the thin films were varied to 15, 30, 45 and 60 minutes. After synthesising process, the samples underwent thermal treatment via annealing process for 1 hour at 500°C. For the characterisation process, Raman Spectroscopy technique was employed to investigate the structural properties of the samples. Apart from that, Field Emission Microscopy (FEM) technique, which was performed via FE-SEM, was employed to investigate the morphologies of the samples. Other than that, UV-Vis spectrometry was employed to analyse the optical properties of the samples. Analysis of data from Raman spectroscopy displayed four Raman Shifts for each sample which confirms that the samples exhibit TiO2 of anatase phases. Whereas, images from FE-SEM displayed reduction of nanoparticle clusters on the samples as the rate of deposition time increases. Meanwhile, UV-Vis analysis displayed transmittance of the samples ranging between 50% to 80% transmittance and each sample exhibits the same optical band gap at 3.25 eV.

1. Introduction
The invention of thin film has marked significant changes in modern days technology especially in electronics and photonics field. The bulk size of transistors was able to scale down while the thinning of solar cells was made possible through this invention. Despite the importance of scaling down devices, economic and safety concern were heavily highlighted in fabrication. Therefore, researchers nowadays tend to look for alternative safe materials and method to fabricating thin film.

Recently, there have been a significant attention worldwide towards titanium dioxide (TiO2) as thin film materials because of the safe and economic properties of the materials. Anderson et al. stated that, the economic and non-toxic characteristics of TiO2 combines with the high photocatalytic efficiency and photochemical stability has prompted an extensive research interest globally [1]. The authors added that, nanoscale research has been going on for TiO2 where the characteristics of TiO2...
nanoparticle has been controlling to enhance the materials to suit specific applications. Khalifa & Mahmood shared similar opinions on the economic and non-toxic properties of TiO$_2$ [2]. The authors claimed that TiO$_2$ is preferable metal oxide in photocatalytic applications to support their opinion.

At the meantime, the fabrication methods for thin film have also been the subject of interest among researchers to produce high quality products. Thin films can be deposited through variety of methods which have two major branches which are the physical deposition and chemical deposition method. Prior literatures had extensively discussed various technique for depositing thin films. Kääriäinen et al. experimented on depositing TiO$_2$ thin films using atomic layer deposition, ALD [3]. Meanwhile, Evtushenko et al. employed sol-gel method for depositing their TiO$_2$ thin films [4]. Magnetron sputtering on the other hand, was employed by Pansila et al. to deposit TiO$_2$ thin films [5]. On the other hand, Rahim et al. [6], Lias et al. [7], Maruyama & Arai [8] and Khalifa & Mahmood [2] used CVD to deposit TiO$_2$ thin films.

CVD is the most prominent in term of economic term amongst all the other methods due to simplicity of the CVD device and process which able to yield good quality end products. Gupta described CVD processes are often used over other deposition technique because the high-purity deposits, substantial variety of chemical composition, moderately fine film adherence and excellent economy and process control [9]. The process for CVD was explained by Elshabini & Barlow who emphasised CVD technique depends on reactive carrier gas to deliver selected precursor to substrate where stable reaction product is produced through decomposition or gaseous reaction [10].

Another factor which influence the fabrication of thin film is time. A research by Shahadan et al. researcher identified that the deposition time influenced the properties of TiO$_2$ thin films deposited using solid precursor, 99.9% pure titanium powder through CVD technique [7]. The used of solid precursor had been analysed to promotes certain drawbacks especially in terms of time and energy consumption. Because of the high boiling point of solid, using solid as precursor has increases the deposition time which might not suit certain application which requires fast manufacturing process. Therefore, the main goal of this research is to seek the effects of deposition time on the structural, morphological and optical properties of TiO$_2$ thin films deposited on ITO glass using CVD technique with titanium (iv) butoxide as a precursor.

2. Methodology

In order to achieve the goal, the research was split into three processes which are the substrate preparation, thin films deposition and thin films characterisation.

2.1. Substrate preparation

Prior to depositing the TiO$_2$ thin film, the substrate was prepared by cutting the ITO substrate into 1.5 cm x 2.0 cm. The substrates were then washed with soap to remove impurities. Next, the substrates were immersed in deionised (DI) water and bathed in ultrasonics for 10 minutes at 60°C. Next, the substrates were immersed in acetone and again bathed in ultrasonic for 10 minutes. After that, isopropyl alcohol (IPA) was used to remove the acetone residue through immersing the substrates in IPA and bathed in ultrasonic for another 10 minutes. The substrates were then let to dry in dry oven for 5 minutes before proceeding to the CVD step. The setup for deposition process using the double zone CVD is clearly illustrated in the Figure 1 to prepare the thin film samples. Additionally, since this research aimed to study the effect of deposition time, the deposition time were varied at 15, 30, 45 and 60 minutes.
The deposition of the thin film was done by first, heating the substrate in the second zone of the CVD to 60°C. The current supply for the second zone should be set to 50 mA. This process should take approximately around 15 to 20 minutes because the CVD will need to stabilise the temperature. When the substrate reaches 60°C, 1 ml of titanium (iv) butoxide was dispensed using pipette inside alumina boat was inserted into first furnace and was heated to 210°C. The distance between the substrate and precursor should be kept constant at 30 cm. After the titanium butoxide was inserted inside CVD, the ends of the quartz tube were plugged with carrier gas holder at the first-zone end while exhaust holder at the second zone end. The current supply for the first zone should be set to 50 mA. The heating of precursor should take around 15 to 20 minutes as the CVD need to stabilise. After the temperature reached 210°C, oxygen gas was flown at the rate of 1 litre per minutes. The flow rate was adjusted using oxygen gas flow rate. The deposition time should start as soon as the oxygen was flown inside the CVD. When the desired deposition time was reached, the deposition process should be stopped in the reverse order. Oxygen supply was first halted. This is followed by reducing the temperature of both zones to 27 °C. Meantime, the current should be set to 0 mA. The substrate and alumina boat can be removed after the temperature for both zones reach 27°C. After that, the samples were annealed for 1 hour at 500°C.

In order to study the effect of deposition time on the structural, morphological and optical properties of TiO₂ thin film prepared using CVD, the thin films were characterised via multiple instruments. Raman spectroscopy was used to analyse the structural properties of the TiO₂ thin film. Field emission scanning electron microscope (FE-SEM) was used to analyse the surface morphology of the TiO₂ thin films. The optical properties of the TiO₂ thin films, the transmittances were measured using ultraviolet visible (UV-Vis) spectrometer. The transmittances were also used for determining the band gap of the thin films.
3. Results and discussion

The findings from all characterisation process are discussed briefly in this section.

3.1. Structural properties

Analysis from Raman Spectroscopy found that there are 4 Raman shifts being presented. The Figure 2 shows the Raman shifts for every sample of TiO$_2$ thin films meanwhile, the Table 1 recorded the details of the Raman shifts. Based on the Table 1, For the 15 minutes-deposited thin film, the Raman shift for the first E1g band was observed to be 154.339 cm$^{-1}$ this was followed by the first B1g band, A1g + B1g band and E1g bands which are observed to be 414.165, 526.166 and 651.525 cm$^{-1}$ respectively.

As displayed by the Table 1, for the 30 minutes-deposited thin film, the Raman shift for the first E1g band was observed to be 151.197 cm$^{-1}$. This was followed by the first B1g band, A1g + B1g band and E1g bands which were observed to be 408.070, 523.158 and 642.632 cm$^{-1}$ respectively.

Referring Table 1, the 45 minutes-deposited thin film, the Raman shift for the first E1g band was observed to be 151.197 cm$^{-1}$. This was followed by the first B1g band, A1g + B1g band and E1g bands which were observed to be 405.019, 514.128 and 639.666 cm$^{-1}$ respectively.

According to the Table 1, 60 minutes-deposited thin film, the Raman shift for the first E1g band was observed to be 148.055 cm$^{-1}$. This was followed by the first B1g band, A1g + B1g band and E1g bands which are observed to be 401.969, 511.117 and 636.698 cm$^{-1}$ respectively.

Tuschel, states that the anatase TiO$_2$ should occupies 6 Raman shifts which indicated tetragonal crystal system of anatase TiO$_2$ which belongs to the group D194h [11]. However, the typical Raman discussed in literature by Chu et al. stated that the typical anatase phase of TiO$_2$ are peaking at 144, 394, 514 and 636 cm$^{-1}$ of Raman [12].

![Figure 2](image-url)  
**Figure 2.** The Raman spectra for the synthesised thin films. The label (a), (b), (c), and (d) are for the 15, 30, 45 and 60 minutes deposited TiO$_2$ thin films respectively.
Table 1. The Raman spectra for the synthesised thin films.

| Deposition time (minutes) | Raman Shifts (cm⁻¹) |
|--------------------------|---------------------|
|                          | $E_{1g}$  | $B_{1g}$  | $A_{1g} + B_{1g}$ | $E_{1g}$ |
| 15                       | 154.339   | 414.165   | 526.166           | 651.525  |
| 30                       | 151.197   | 408.07    | 523.158           | 642.632  |
| 45                       | 151.197   | 405.019   | 514.128           | 639.666  |
| 60                       | 148.055   | 401.969   | 511.117           | 636.698  |

3.2. Morphological properties

The Figure 3 shows the FE-SEM images for the TiO₂ thin films under 5000 magnification at 5.0 kV.

According to the images taken from FE-SEM analysis, the 15 minutes deposited TiO₂ thin films produced the highest clusters of TiO₂ nanoparticles. This is followed by 30, 45, and 60 minutes deposited TiO₂ thin films respectively.

Since the deposition of the TiO₂ thin films using CVD included annealing process, which is known for crystal modification, it can be said that the crystal growth process is influenced by the deposition time.

Based on the findings, the shortest deposition time reveals more cluster growth of nanoparticles. Meanwhile, the nanoparticles clusters were observed to be decreasing as deposition time increases.

Figure 3. The FE-SEM images for the TiO₂ thin films under 5000 magnification the labels (a), (b), (c) and (d) indicates 15, 30, 45 and 60 minutes deposited film respectively
3.3. Optical properties and band gap
The Figure 4 shows the transmittance spectra for TiO\textsubscript{2} thin films deposited using CVD for 15, 30, 45 and 60 minutes. In general, all the deposited TiO\textsubscript{2} thin films show a lesser than 80\% and greater than 50\% transmittance. Hence, all the TiO\textsubscript{2} thin films deposited appears translucent.

The 15 minutes deposited TiO\textsubscript{2} thin films shows the highest percentage of transmittance which exceeds 70\%. On the other hands, the 60 minutes deposited TiO\textsubscript{2} thin films shows the lowest percentage of transmittance reaching not more than 65\%. This suggest that the deposition time influence the transmittance of TiO\textsubscript{2} thin films. The longer the deposition time lower the transmittance of TiO\textsubscript{2} thin films.

Meanwhile, the band gap for all films were determined via Tauc Plot. The band gap of the TiO\textsubscript{2} thin films show a constant band gap trend as the TiO\textsubscript{2} thin films being deposited from 15 minutes to 60 minutes. The 15, 30, 45 and 60 minutes deposited TiO\textsubscript{2} thin films show the same band gap values which are at 3.25 eV. The fundamental band gap recorded in various literature on TiO\textsubscript{2} thin films is 3.2 eV. The 0.5 eV difference from the findings can be assumed mainly because of several defects in the samples.

![Figure 4](image)

*Figure 4. The UV-vis spectra for the TiO\textsubscript{2} thin films labelled (a), (b), (c) and (d) for 15, 30, 45 and 60 minutes deposition time*

4. Conclusion
According to the analysis of structural, morphological and optical analysis from Raman Spectroscopy, FE-SEM imaging and UV-vis spectrometry, the relationship between deposition time and these properties can be configured. On structural level, the deposition time influence the stress of TiO\textsubscript{2} thin films. Increasing deposition time reduces the stress of TiO\textsubscript{2} crystalline while reducing the deposition time increases the stress of crystalline in TiO\textsubscript{2}. Besides that, on morphological scale, it can be said that, longer deposition time allows less clustering of nanoparticles of TiO\textsubscript{2} thin films growing on ITO substrate after annealing vice versa. On the other hand, on optical scale, the translucency of TiO\textsubscript{2} thin films are declining over time when deposited using CVD while the correlation between band gap and deposition time is that the band gap of TiO\textsubscript{2} thin films deposited using CVD are unaffected by the deposition time.
Acknowledgement
The author would like to express their thanks to the Microelectronics and Nanotechnology-Shamsuddin Research Centre (MiNT-SRC), Universiti Tun Hussein Onn Malaysia (UTHM) for providing facilities to run the research.

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