Crack-Free TiO$_2$ Thin Film via Sol-Gel Dip Coating Method: Investigation on Molarity Effect

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Abstract. Titanium dioxide, (TiO$_2$) is transparent to visible light and excellent in optical transmittance. In this experiment, TiO$_2$ thin films have been fabricated on glass substrates by sol-gel dip coating method. Sol-gel dip coating technique can provide corrosion protection performance and can produce thick coating. Due to the thick coating, the possibility to get a crack thin film is high. Therefore, this paper is to investigate a crack-free TiO$_2$ thin film for optical sensor application where it is needed the most. The films were subjected to different molar concentration solution with 0.01M, 0.05M, 0.10M, 0.15M and 0.20M. The thin films are then characterized by field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM), surface profiler and UV- VIS NIR spectrometer. From this study, a crack-free of TiO$_2$ thin film was obtained and this thin film could be used for optical sensor application later.

1. Introduction

TiO$_2$ is a wide band-gap semiconductor that is of interest for different kinds of optical applications. Some of the examples are photocatalysts, optical spacers in polymer photovoltaic cells, and optical sensors [1]. TiO$_2$ is also an important commercial element because of its characteristics which are highly transparent and high refractive index ($n=2.6142$) [2]. Example of TiO$_2$ applications are pigment in paints and coating materials in optical thin films. The distinct properties of TiO$_2$ as its high refractive index and photocatalytical activity lead to high types of applications in various areas such as electronics sensing optics and catalysis [3]. Due to excellent optical transmittance in the visible range [4], transparency over a wide spectral range and high reflective index and the absorption of UV light [5], TiO$_2$ films become essential in optical films. The distinct properties of TiO$_2$ make a particular sensing purpose can be reached with the types of TiO$_2$ phase [6], composition and nanostructure feature are decisive factors for sensor performance [7].

In previous work, it was reported that the preparation and characterization of TiO$_2$ films have been largely used due to increasing number of applications in optics [8]. Chemical vapour deposition, sputtering and sol-gel is some of the method to prepare TiO$_2$ materials [9]. A flexible method like sol-gel method can control the uniformity and thickness of the thin film, and thermal stability of high surface area material [10]. Sol-gel method has many benefits such as very simple in operation [11], can be used for deposition of substrates, and easily anchored on the substrate [12]. On top of that, this method enables the modification of the structure and the microstructure of the deposited TiO$_2$. The properties of the sol-gel TiO$_2$ thin are highly dependent on the structure, thickness and the density of the deposited layers [13]. These features are predominantly manipulated by the sol composition, the sol viscosity and the withdrawal speed in the dip coating process [14].

Researchers have studied that controlling of the viscosity is very important in the deposition process. The controlling of parameter includes characteristics of the solution such as ionic concentration, conditions of heating and withdrawal speed, where this is compulsory in order to acquire crack-free
films [15]. From observation, the thin film thickness is directly proportional to the viscosity of the precursor sol [16]. Moreover, the appearance of cracks occurred when the critical value for thickness of the thin films is reached [17]. In fact, withdrawal speed has to be controlled to prevent the thickness of the films producing cracks and bubbles after annealing [18]. Furthermore, by using sol-gel dip coating technique, the microstructure of the film can be easily controlled by changing the solution composition and deposition condition. These parameters also were influenced to obtain a crack-free TiO$_2$ thin film [19]. There are a few types of crack that have been recognized. Rosette is one type of crack where it is short and branching from the center [20]. This type can be observed over the whole surface of the thin film and occurs at lower viscosities. The other type of crack is a long straight line and these cracks obtained from solution with higher viscosity [21].

This research is to investigate the crack-free thin film by sol-gel dip coating technique with different molar concentration. After optimizing the characteristics of TiO$_2$ thin films based on optical properties, surface morphology, topographic surface and thickness of the film, the TiO$_2$ thin film will be used for optical sensor application.

2. Methodology

2.1. Glass Substrate Preparation
The glass was cut with the size of 2 cm x 2 cm. Then, it was cleaned with acetone in ultrasonic bath, followed by ethanol and lastly with di-ionized (DI) water for 10 minutes. Lastly, it was blew with N$_2$ gas for drying purpose.

2.2 TiO$_2$ Solution by Sol-Gel Method Preparation
The starting material used was Titanium (IV) Isopropoxide (TTIP). The molarity of the precursor was varied from 0.01M, 0.05M, 0.1M, 0.15M and 0.2 M. Glacial acetic acid and Triton-X were added to the solution as stabilizer and surfactant respectively. Small amounts of DI water were also added to increase the hydrolysis reaction rate.

2.3 Deposition of TiO$_2$
TiO$_2$ thin films were deposited on a glass substrate by pulling it from the solution at constant withdrawal speed and dip speed of 10 mm/s by using the dip coater equipment, Precision Dip Coater. The dipping cycles was set at 15 cycles. The glass was attached at the holder perfectly to prevent it from falling in the solution. The thin films were dried at 100$^\circ$ C for 30 minutes in a chamber furnace, PROTHERM (PLF 160/25). It was then undergoes the annealing process at 450$^\circ$ C for 2 hours to restructure the crystallinity of the thin film.

2.4 Sample Characterization
The samples were characterized using atomic force microscope (AFM, Park System XE-100) for structural images. Meanwhile, the thicknesses have been measured using Dektak 150 Stylus Veeco Dektak 750 Surface Profiler. As for the surface morphology, FESEM was done using JEOL JSM-7600F. The optical properties were studied using UV-Visible (Vis)-near infrared.
3. Results and discussions

A. FESEM

Figure 1 shows the FESEM micrographs of the surface morphologies of the TiO$_2$ thin film for each molarity. It can be observed from the FESEM images that the films are free from the crack. The grain size of all the samples were also measured.

![Figure 1](image_url)

Figure 1. FESEM image of TiO$_2$ thin film at different molarity (a) 0.01M, (b) 0.05M, (c) 0.10M, (d) 0.15M, and (e) 0.20M

Figure 1(a) shows that there was no surface to show crack-free of TiO$_2$ thin film. This was due to the lower molarity of solution. When the solution was prepared, the viscosity of the solution is too low. This can be seen where the glass substrate shows very transparent features after completing the dip coating process. The glass substrate was very transparent and looks as the same as glass before the glass was coated. Even though, 6nm of platinum was coated on the glass and the image was zoom in, there is still no structure on the image view. However, the image started to show a crack-free surface of TiO$_2$ thin film at 0.05M, 0.10M, 0.15M and 0.20M, Figure (b), Figure (c), Figure (d) and Figure (e) respectively.

As seen in Table 1, the distribution of the grain size of the thin film is depending on molarity. It was observed that when molarity is increasing, the grain size also increasing. By analyzing and characterizing the grain size of each molarity, it can be seen that the grain size of the lowest molarities of 0.01M cannot be determined. This is because the size of the grain for 0.01M is too small due to TiO$_2$
thin film is very transparent. However, when the molarity is 0.05M, it tends to agglomerate and the grain size is 116nm which is the smallest grain size. The agglomeration is due to mixing technique by using the magnetic stirrer that the solution was not stirred continuously that makes nanoparticles easily agglomerates [22]. Besides that, the agglomeration is significantly influenced by film thickness and agglomeration easier occurs when the film thickness is thinner [23]. When the molarity is 0.10M, the grain size was increased by 137 nm. Moreover, when molarities are 0.15M and 0.20M, the grain size are 145nm and 152nm respectively which gives grain size bigger than the other molarity. For 0.15M, it can be seen that the grain growth more on the surface of thin film and quite uniform than the other molarity. It was observed that higher the molarity of TiO$_2$, the uniformity of the surface morphology is better.

| Sample | Molarity (M) | Average Grain Size (nm) |
|--------|--------------|-------------------------|
| A      | 0.01         | Too small               |
| B      | 0.05         | 116                     |
| C      | 0.10         | 137                     |
| D      | 0.15         | 145                     |
| E      | 0.20         | 152                     |

**B. Topographic Surface**

Figure 2: AFM image for 0.15M sample

Figure 2 shows the AFM topographic images of TiO$_2$ thin film after annealing at 450º C temperature for 0.15M sample. The scanning area is 10um x 10um. The surface roughness was measured to study the morphology evolution. The value of the surface roughness at this molarity is 157.094 nm and thickness is 802.01 nm. Due to 0.15M is much more uniform than the other sample, so the roughness of this sample was measured. In the previous research, it was reported that when the molarity of the solution is increasing, the roughness of the thin film is decreasing [24]. By referring to Figure 2; the film is quite uniform with not much porosity, so that the roughness was low.

**A. Optical properties**

**UV- Vis Analysis**

Figure 3 shows the transmittance of each sample in the wavelength range from 300 to 800 nm. The transmittance value is taken at wavelength around 350 nm. At 0.01M, the optical transmittance value is almost 100.0% which gives the highest reading than the other molarity. The glass substrate is too transparent after the dip-coating process and look like a clean glass. When the sample was characterized
by using UV-Vis spectrometer, the transmittance value was higher because the coating of TiO$_2$ solution is so thin and therefore it cannot be determined by the laser. The transparency starts to decrease for 0.05 M with 60 T%. However, the transmittance values do not show any trend of decreasing when it increase to 75 T% and 85 T% for 0.1 M and 0.15 M respectively. While, 0.20M shows transmittance value 65 T%.

![Transmittance spectra of the TiO$_2$ thin films at different molarity](image1.png)

Figure 3: Transmittance spectra of the TiO$_2$ thin films at different molarity

Figure 4 represents the absorbance spectra of each sample measured by using UV-VIS spectrometer. It can be seen that all the samples have a different absorption edge in the range wavelength of 300 nm to 800 nm. The lowest absorbance belongs to 0.01 M samples with almost 0.00 a.u at 350 nm. Meanwhile, the absorbance value for 0.05M is 0.23 a.u. At 0.1M and 0.15M, the absorbance value is decreasing to 0.13 a.u and 0.03 a.u respectively. But, at 0.2M the absorbance value tends to show increment with the reading 0.2 a.u. The results show no trend for both transmittance and absorbance spectra due to the not well prepared samples. However, the results follows the theory where, the higher the optical transmittance value; the lower absorbance value [25].

![Absorbance spectra of the TiO$_2$ thin films at different molarity](image2.png)

Figure 4: Absorbance spectra of the TiO$_2$ thin films at different molarity

4. Conclusion

The fabrication of TiO$_2$ thin film was successfully prepared on glass substrate by using sol-gel dip coating technique. It can be observed that sol-gel dip coating technique was a suitable method to produce a crack-free of TiO$_2$ thin films. For FESEM images, the higher the molarity of solution, the uniformity of the surface morphology is better. It shows that 0.15M is quite uniform and the grain growth more on the surface of the thin film. Moreover, based on the FESEM result, 0.15M shows low
and quite uniform with not much porosity sample. For UV-Vis result, it can be prove that this work follows the theory; high transmittance, low absorbance.

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