TiO$_2$ Thin Film via Sol-Gel Method: Investigation on Molarity Effect

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Abstract. We have systematically investigated the current-voltage ($I-V$), absorbance and optical band gap of TiO$_2$ thin film prepared through varying the molarity of the TiO$_2$ precursor by sol-gel spin coating technique. In addition to the electrical and optical characteristics, the surface morphology was examined by using Atomic Force Microscope (AFM). From the image of the AFM, we were able to observe the uniformity of the TiO$_2$ thin film. From the experimental results, we found that the uniformity of the TiO$_2$ thin film is optimized at 0.2M sample. It is also found that, as the molarity increased, there is tendency of the resistivity to decrease. Not only that, the absorbance measurement and optical band gap also gave its best value for 0.2M sample. Therefore, in this work it is concluded that 0.20M of TiO$_2$ gave the best characteristics for all measurements.

1. Introduction
A lot of works were done on TiO$_2$ due to its interesting properties such as chemical stability, non-toxic, highly oxidative photogenerated holes, high energy conversion, high transparency and high refractive index [1]. Nanoparticles of TiO$_2$ are widely-known in many applications such as antirefection coatings for photovoltaic cells and passive solar collectors [2], photocatalytic refinement of polluted air or wastewater and excellent degradation for organic pollutants [3]. Moreover, the TiO$_2$ thin film deposited on conducting glass can be used in new types of solar cells which are liquid and solid dye-sensitized photo-electrochemical solar cells [4, 5].

There are several methods to prepare TiO$_2$ thin film. TiO$_2$ films can be synthesized by several deposition procedures including sol-gel [6, 7], chemical vapour deposition [8], electrophoretic [9] [10], screen printing [11] and sputtering method [12]. Among the methods available to prepare TiO$_2$ thin film, sol-gel is one of the most favorable methods. The advantages of using this method are able to vary the properties of the thin film, cheaper and convenient to coat on large areas [7]. Researchers found that the molarity effect and the preparation conditions such as solution preparation arrangements, ageing temperature and time taken [13] have effect on the TiO$_2$ properties.

In this work, the thin films were fabricated by a sol–gel method combined with spin coating technique on glass substrate. The concentration amounts of TiO$_2$ in the solution were kept at 0.01M, 0.05M, 0.10M, 0.15M, and 0.20M. The annealing procedures applied to achieve the higher electrical conductivity of the TiO$_2$ thin films. The effects of different molarity of the films are discussed.
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. The last step is blowing the glass substrate with N\textsubscript{2} gas for drying purpose.

2.2 TiO\textsubscript{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\textsubscript{2}
The TiO\textsubscript{2} solution was deposited on the glass substrate using spin coating technique with 6000 rpm for 1 minute and 36 seconds. The deposition was done for 5 times with 10 drops of TiO\textsubscript{2} solution. The deposited thin film was then dried at 150º C for 10 minutes to vaporize the solvent. The drying process was repeated for 5 times. It was then undergoes the annealing process at 450º C for 1 hour to restructure the crystallinity of the thin film.

2.4 Metal contact deposition
A metal contact of gold (Au) 99.9% with 60nm thickness was deposited on TiO\textsubscript{2} thin film. The deposition was conducted using metal sputter coater. The sputter coater was set with current 50mA and time taken was 4 minutes. Argon gas was purged into the chamber with pressure 1x10\textsuperscript{-4} mbar. Au was chosen rather than other metal because of its properties; the work function difference between thin film and metal contact materials.

2.5 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. The optical properties were studied using UV-Visible (Vis)-near infrared. Current-voltage measurement has also been carried out for all the samples using two point probes Bukoh Keiki (CEP-2000) Spectral Sensitivity Analyzing System Solar Simulator.

3. Results and discussions

3.1 Surface morphology and thickness
Table 1 shows the thickness of TiO\textsubscript{2} thin film with different molarity from 0.01M, 0.05M, 0.10M, 0.15M and 0.20M. The thickness are increasing from 9.24 nm, 19.9 nm, 29.0 nm, 60.6 nm and 79.7 nm respectively. It is found that as the thickness increase it will affect the electrostatic contact between solute particles [14]. The particles become larger and resulted in increasing the probability of more solute particles to be grouped creating agglomerate particles. This result was supported by structural analysis.

| Molarity (M) | Thickness (nm) |
|-------------|----------------|
| 0.01        | 9.24           |
| 0.05        | 19.9           |
| 0.1         | 29.0           |
| 0.15        | 60.6           |
| 0.2         | 79.7           |
Figure 1 shows the AFM images of the TiO$_2$ thin films. The images shown are for samples at 0.01M and 0.2M. The lowest molarity give the less roughness with 2.2nm while the higher molarity 0.20M gives the best uniformity and highest roughness about 7.66nm. This was probably due to scattering mechanism in which influence the particle size. Uniformity of the particle size across the thin film is important because the nanoparticle size significantly affects the electrical conductivity of the film [15]. With the highest uniformity of the thin film, there are providing higher surface contact of the TiO$_2$ thin film and resulted in higher density and in return, producing high conductivity of the thin film.

![AFM images](image)

Figure 1: AFM images for a) 0.01 M, b) 0.2 M

3.2 Electrical Properties

Figure 2 shows the current-voltage ($I$-$V$) characteristics under illumination (100 mWcm$^{-1}$, AM 1.5) of the TiO$_2$ thin film with different molarity. The TiO$_2$ samples exhibit a linear and symmetrical curve, indicating ohmic contact characteristics between the thin films and the Au metal contact [16]. From the figure, we could see that the molarity strongly influences the $I$-$V$ characteristics. When the molarity of TiO$_2$ is 0.2 M, the thin film exhibited the highest current (4.5x10$^{-8}$ A). On the other hand, the current at 0.1 M is approximately 0.5x10$^{-8}$ A. The electrical resistivity of the thin film was calculated from the $I$-$V$ curve and was plotted and shown in Figure 3. The resistivity decreases with the increment of molarity and reaches a minimum value at 0.2M. The high density of TiO$_2$ causing an increase of electron carrier concentration. This will contribute to the high electrical conductivity.

![I-V measurement plots](image)

Figure 2: $I$-$V$ measurement plots of TiO$_2$ thin film
3.3 Optical Properties
Figure 4 represents the absorbance spectrum of the prepared samples. High molarity and low molarity concentration samples show comparable absorbance spectrum behavior. When the molarity concentration reaches 0.2M, the absorbance shows a significant increment in the Vis region. It is a known fact the molarity increment can improve the absorbance of TiO$_2$ by relating it with high density of TiO$_2$ particles. High molarity concentration of TiO$_2$ can produce a much thicker thin film as in Table 1 [17]. Therefore, the photon energy will be absorbed more, thus increasing the absorbance value in the Vis region. Minimum absorbance value implies that electron did not absorb the photon energy. This means that the electrons are transmitted or reflected [18]. Meanwhile, Figure 5 shows the optical band gap for 0.1M and 0.2M samples. The optical band gap energy (E$_g$) is derived assuming direct transition of electron between the edges of the valence band and the conduction band. From the extrapolation of the graph in Figure 5, the band gap energy for 0.01M and 0.2 M are 3.9eV and 3.7eV respectively. The value for optical band gap that has been reported elsewhere is 3.2 eV [19]. With the molarity concentration being analyzed in parallel with the optical band gap properties, the significant relationship between this parameter can be concluded; the results showed that high molarity exhibited lower optical band gap.
Conclusion
As a conclusion, TiO$_2$ thin film with different molarity has been successfully prepared using the solution based method. 0.2M shows the roughest surface as compared to 0.01M. Not only that, $I-V$ results also shows the highest current for the same sample. In conjunction to that, the results for the rest of the characterizations also show that 0.2M gives the same trends.

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