PREPARATION OF TITANIUM DIOXIDE VIA SOL GEL PROCESS: EFFECT OF MOLARITY CONCENTRATION

Hanis Binti Sutan Abd Latif Hamidi
Faculty of Electrical Engineering, Universiti Teknologi Mara (UiTM), 40450 Shah Alam, Selangor, Malaysia
Email: hanissutan@gmail.com

Abstract— **In this paper, TiO_2 thin film were deposited by using sol gel deposition process. The TiO_2 thin film prepared by sol gel method and utilizing titanium tetra (IV) isopropoxide, (TTiP) as precursor. This paper is focused on the effect of varying the precursor to the electrical properties, optical properties and surface morphologies. The molarity of the TiO_2 was varied by 0.01M, 0.05M, 0.10M, 0.15M, 0.20M and 0.25M. The electrical properties were characterized by 2 probes Solar Simulator while optical properties are observed by Uv-vis. The surface morphologies were examined by Atomic Force Microscope AFM. When increasing the molarity concentration of TiO_2, the conductivity increased while the resistivity decreased respectively. The photoresponsitivity shows that the highest molarity concentration has highest response to the present of UV light. For optical properties, the higher molarity concentration has lower transmittance. It effect to the absorbance coefficient and optical band gap. The surface morphology shows that the higher molarity concentration has the highest roughness and the best uniformity of the AFM result. Based on the result of the experiment, it can be conclude that the highest molarity concentration which is 0.20M of TiO_2 gave the best properties of electrical, optical and surface morphology.**

Keywords: TiO_2 thin film, sol gel, molarity concentration.

I. INTRODUCTION

In fabrication field, the TiO_2 have been investigated due to their remarkable chemical, optical and electrical properties. The TiO_2 gaining because of their interesting properties such as chemical stability, non-toxic, highly oxidative photogenerated holes, high energy conversion, high transparency and high refractive index [1, 2]. Nanoparticles of TiO_2 has a widely-known in many application such as antireflection coatings for photovoltaic cells and passive solar collectors[3], photocatalytic refinement of polluted air or wastewater and excellent degradation for organic pollutants[4]. 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 [5, 6].

There are several methods to prepare TiO_2 thin film. TiO_2 films can be synthesized by several deposition procedures including sol-gel [7, 8], chemical vapour deposition [9], electrophoretic [10], screen printing [11] and sputtering method [12]. Among the method available to prepare TiO_2 thin film, sol-gel is one of the most favorable methods because of several advantages such as ability varying properties of the thin film, cheaper, and convenient to coat on large areas [13]. Recently, researcher believe that the synthesized of thin film by sol gel method have big influence by composition of the precursor solution, the preparation conditions such as solution preparation arrangements, ageing temperature and time taken [14].

In this project, TiO_2 solution was prepared by sol gel method with different molarity of the precursor. The TiO_2 solution prepared with different molarity from 0.01M, 0.05M, 0.10M, 0.15M, and 0.20M. Then, the TiO_2 solution deposited onto glass substrate by using spin coating deposition. Further, the annealing process can restructure the particles of the thin film of the thin film, it has been reported that the crystal structural of the thin film was much better when the annealed catalyst was used if compared to the as deposited catalyst [15].

TiO_2 with its band-gap around 3.2eV, is activated only under ultraviolet (UV) light which possesses only a small fraction (about 8%) of the solar energy [16], [17]. In other's previous research, higher the concentration of the solution, the lower the band-gap [18]. The molarity will affect the absorption of light. It was already investigated that the low molarity causes low absorption that will influence the performance of organic solar cell.

II. OBJECTIVES

In this experiment, the main purpose are to conduct the preparation of TiO_2 thin film by using the sol gel process, to study the effect of molarity concentration in producing the TiO_2 thin film via sol gel process and characterize the electrical, optical and physical properties of the thin film performance.

III. SCOPE OF WORK

In this project, the scope of work consists the study of electrical properties by characterized the TiO_2 thin film with 4-Probes Solar Simulator. The study of electrical properties included the conductivity, resistivity and photoresponsitivity under illumination and in dark. While for optical properties, the study of optical band-gap and absorbance coefficient are conducted by using the Uv-vis spectroscopy. The surface morphology was characterized by using Atomic Force Microscopy to get the roughness and the uniformity of the TiO_2 thin film.

IV. METHODOLOGY

A. Glass Substrate Preparation

Microscope glass was used in this project as the substrate for the thin film. The glass was cut about in dimensions of 2 cm x 2 cm. Then, the glass was cleaned with acetone in ultrasonic bath in 10 minutes, with ethanol in 10 minutes and lastly with di-ionized water in 10 minutes. Next step is blowing the glass substrate with N_2 gas. N_2 gas was used to blow the glass substrate to perform drying process [19]. The drying process was conducted to eliminate the contamination at the glass substrate.

B. TiO_2 Solution By Sol-Gel Method Preparation

Table below show the material that used included with their exact quantity for 50ml of 0.01M TiO_2 solution. Other molarities used different quantities of materials to provide the different molarity of TiO_2.

Table 1: Material used in preparing TiO_2 solution

Materials	Quantities	Function
Titanium tetra(IV) isopropoxide	0.142ml	As precursor
glacial acetic acid(GAA)	2.5ml	As a stabilizer or chelating agent
Ethyl alcohol (98.0%)	23.579ml	As a solvent
deionized water	0.2ml	as a function of adding the oxygen (O2)
Triton X-100	1 drop	As a surfactant

C. $Ti0_2$ Nanostructure Deposition

For deposition process, the TiO_2 solution was deposited onto the glass substrate by using spin coating method with 6000 rpm in 1 minute and 36 seconds. The deposition of TiO_2 thin film was done in 5 layers with 10 drops of TiO_2 solution for every layer. After deposited the layer, the substrate was carried drying process at 150° C in 10 minutes. The drying process was repeated until the 5 layers. The drying process is conducted to eradicate the solvent form TiO_2. Then after completing the deposition of the thin film, the substrate undergoes the annealing process at 450° C in 1 hour to restructure the crystalline structure of the thin film. Based on previous investigation, the anatase crystalline is formed at the annealing temperature between 500 - 600°C [19]. While at the annealing temperature above 700°C, the rutile crystalline is formed [19].

D. Metal contact deposition

A metal contact of gold (Au) 99.9% with 60nm thickness was deposited onto TiO_2 thin film. The deposition was conducted using metal sputter coater. The sputter coater was set with current of 50mA and time taken for sputtering operated was 4 minutes. Argon gas was used into the chamber with the pressure of 1x10-1 mbar. The Au metal contact is the most important part in electrical characterization because the metal contact responsible to give outside contact to the device. The Au metal contact performs as finishing electrode which gives good ohmic contact to the TiO_2 thin film. The ohmic state that a linear and symmetric current-voltage relationship for positive and negative voltages [20]. Moreover the ohmic contact includes the insignificant resistance compared with the bulk of the device [20]. The Au metal contact was chose rather other metal contact because of it properties which suitable to the TiO_2. The reason that the Au used in this project is the work function difference between thin film and metal contact materials. TiO_2 thin film has a work function of around 4.4 eV [21] and work function of Au are reported to be 5.28, [22]. Au metal contact is expected to have more electrons from TiO_2 thin film to transfer through the contact surface rather than other metal contacts.

E. Sample Characterization

After completing the deposition process of thin film, the sample was characterized to study their electrical properties, optical properties and their surface morphologies. The iv characterization was conducted by 2 probes Solar simulation to determine the electrical properties. The electrical properties characterization conducted under illumination and in dark to examine the phtoreponsitivity of TiO_2 thin film toward the present of UV light. Besides that the resistivity and the conductivity also examined to study in detail about the electrical properties. The optical properties were determined by using UV-vis spectrometer. The optical properties are including absorption coefficient, optical band-gap, transmittance and absorbance. The surface morphologies were examined by using Atomic Force Microscope AFM to determine its roughness and uniformity of the thin film.

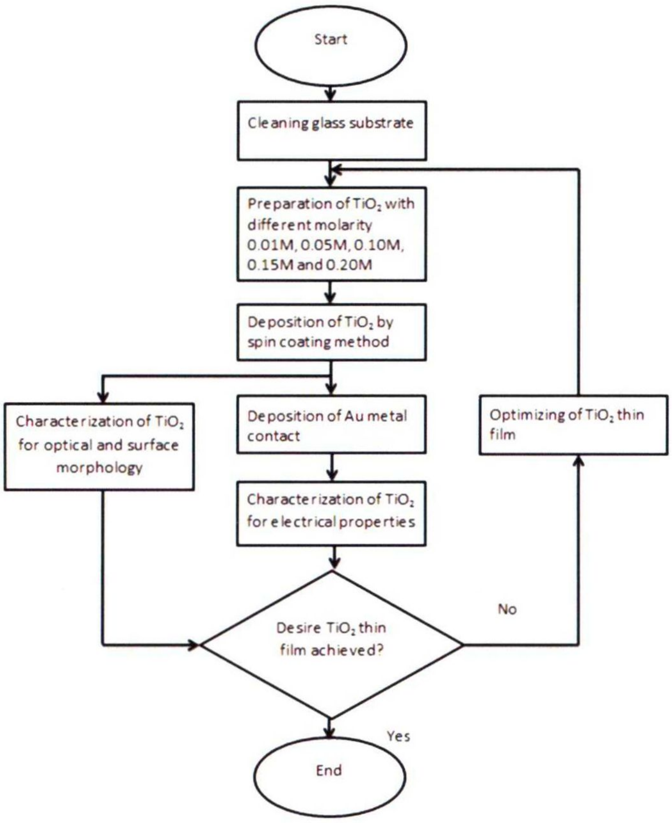

Figure 1: The flow chart

Figure above shows that the steps that have been used to synthesized the TiO_2 by using the sol gel method.

V. RESULTS AND DISCUSSIONS

A. Elctrical Properties

I-V characteristic was measured by using 2-probes Solar Simulator. The I-V was characterized under illumination and in dark condition. TiO_2 is a material which has a very low conductivity it is required the deposition metal contact onto the samples as electrodes [23]. The graph plotted shows that the IV curves between -10 V to 10 V with different molarity of TiO_2. Three time reading of IV characteristic was observed for every sample and the average of the reading was calculated. The curves show that the different of TiO_2 molarity give major effect to the IV characteristic. The conductivity and resistivity have calculated by referring the IV characteristic for under dark and under illumination. The characterization under illumination are conducted to study of the ability of TiO_2 to perform with UV light present. With the ability to perform in UV light better than in dark, the TiO_2 can be applied to the organic solar cell.

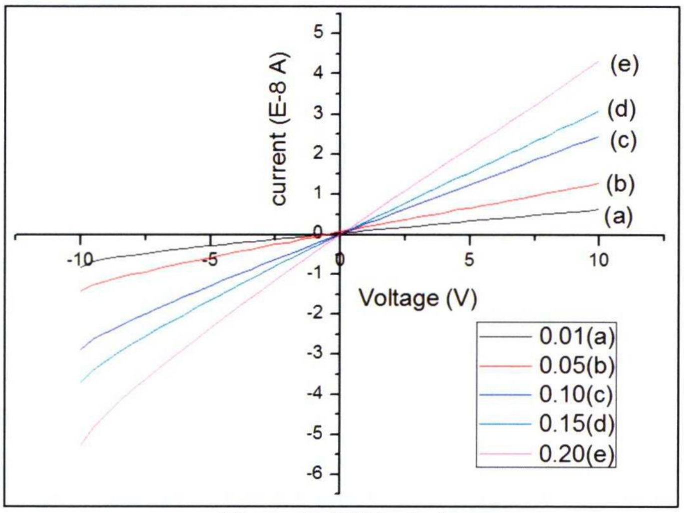

Figure 1: I-V in dark

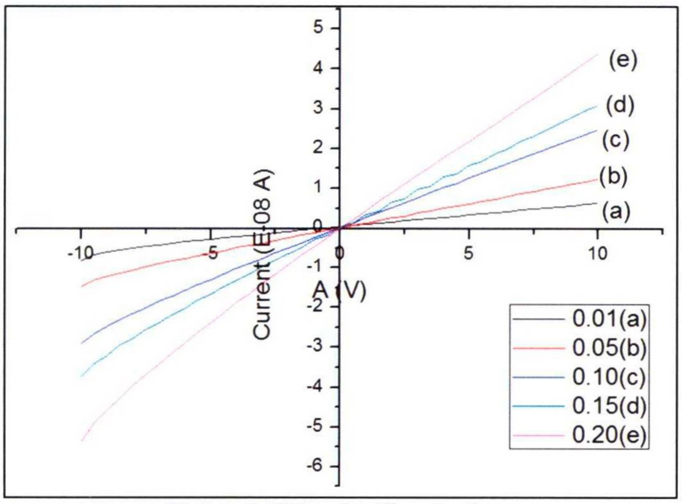

Figure 2: IV under illumination

The graph plotted shows that the I-V characteristics of TiO_2thin films at different molarity under illumination and in dark condition. The resistivity and conductivity graph in dark and illumination was plotted by using formula below.

= – —

Where I= current
V=voltage
w= width of metal contact
t=thickness of thin film and metal contact
l=distance between metal contact

For calculate the conductivity, below equation was used:

Where = resistivity

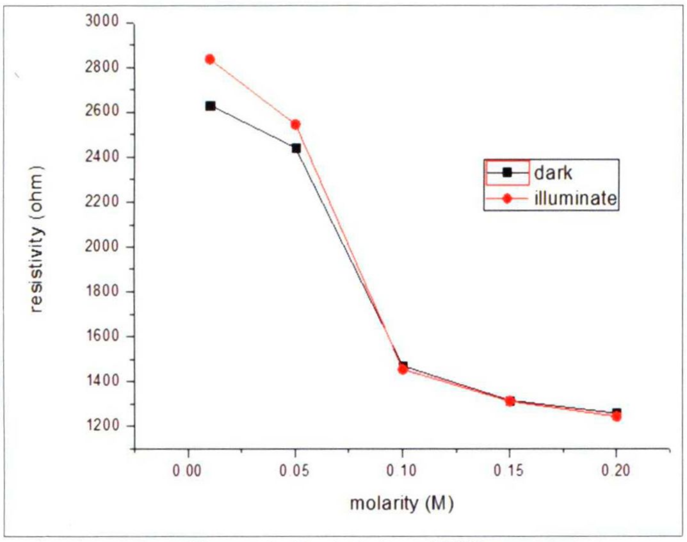

Figure 3: Resistivity of TiO_2

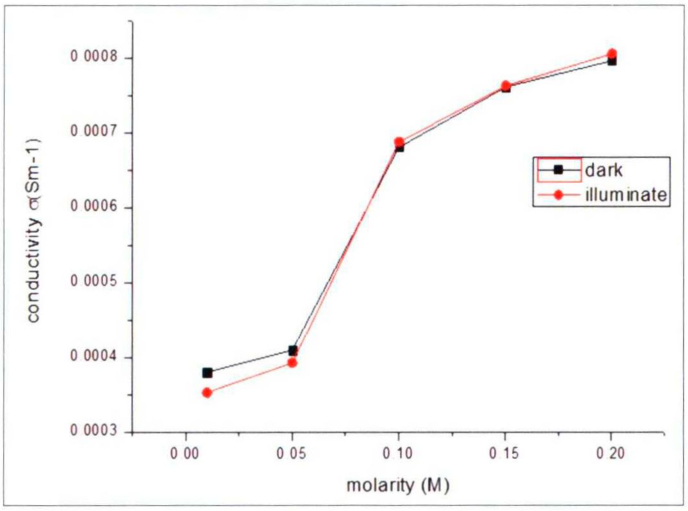

Figure 4: Conductivity of TiO_2

Figure 3 shows that the increasing molarity of precursor affect to the decreasing the resistivity for both in dark and under illumination. Meanwhile, when the resistivity of TiO_2 is decreasing, it can lead to increasing of TiO_2 conductivity. The conductivity under illumination condition was slightly different from the conductivity in dark condition. Based on figure 4, it shows that the conductivity under illumination is little bit higher compare to the conductivity in dark condition. This is because TiO_2 thin film is sensitive to light. The earlier researches summarized that the photoconductivity performance under illumination and in dark it is predicted the photocurrent produced under illumination is much higher compare to in dark condition [24]. As increasing the molarity of the TiO_2, the resistivity of the TiO_2 is decrease based on previous research [18]. The higher molarity of the TiO_2 will result to higher grain size of the TiO_2 thin film [25]. Therefore, the larger grains size will affect to higher surface contact between the TiO_2 thin films and electrode hence give effective migration of electron.

Figure 5 shows that the responsivity of TiO_2. The responsivity define that the ability of the material response to present of UV light. The current at 10V was used to plot the responsivity graph of the TiO_2 thin film. Based on the calculation, the higher molarity which is 0.20M has the highest responsivity. As a result the higher molarity of TiO_2 affect to the higher responsivity toward UV light compare to the other molarity of TiO_2 thin film.

$$\text{Responsivity} = I_{illumination} / I_{dark}$$

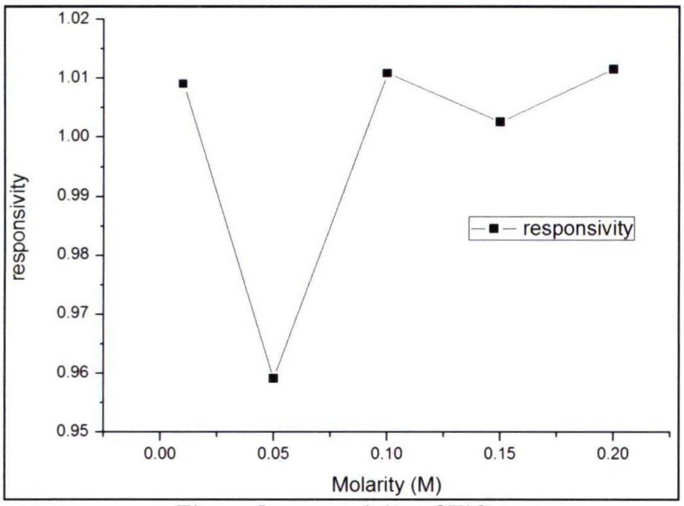

Figure 5: responsivity of TiO_2

B. Optical Properties

The optical properties of the deposited TiO_2 thin films were studied on the transmittance and absorbance measurements using the UV-VIS spectrophotometer. Transmittance spectra were measured at the wavelength range of 300 – 850nm. The TiO_2 films spectra display high visible transmittance, up to 94.61% at the lowest molarity of the TiO_2 thin film. The TiO_2 thin film with the highest molarity has the lowest visible transmittance which is 53.42%. For the transmittance spectra at 0.05M, 0.1M, 0.15M and 0.20M shows that the 84.50%, 79.00% and 78.00% respectively. Refer to the transmittance spectrum, the optical transmittance give high slope at 350 nm of wavelength, which was the reason the optical transmittance was collected at 350nm. The lowest molarity of the TiO_2 will affect the highest transparency while the highest molarity will affect the lowest transparency of the thin film. From the thickness of the thin film, higher the molarity, the condition of the films will be not transparent compared to the low molarity [18]. Because of the transmittance are different due to its molarity, the absorption of light also changing with varies of the molarity. Based on the result, the transmittance of 0.20M of TiO_2 has the lowest transparency while the 0.01M of TiO_2 has the higher transparency.

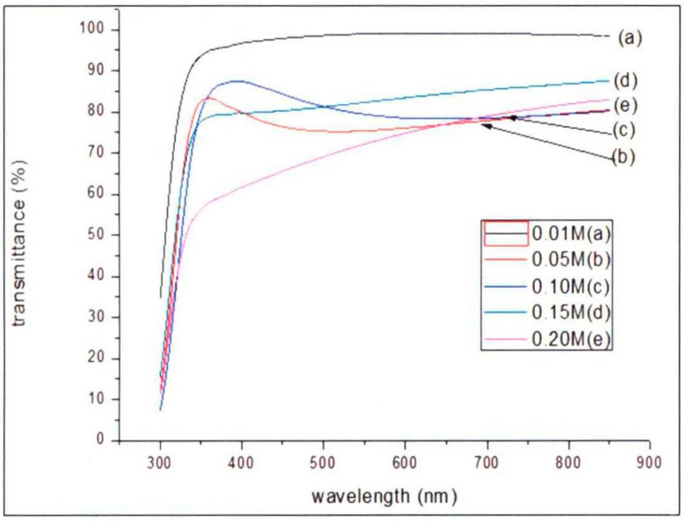

Figure 6: Transmittance spectra

With the different value of transmittance it will effect to its optical band gap. The optical band gap was obtain by plotting the plotting $(\alpha * hv)^2$ against photon energy (hv) for direct band gap since the TiO_2 perform direct optical band gap. Based on the graph plotted, the optical band gap for 0.01M, 0.05M, 0.10M, 0.15M and 0.20M are 3.97eV, 3.94eV, 3.92eV, 3.90eV and 3.83eV respectively. By referring the graph plotted, the higher molarity of TiO_2 produce the nearest to the theoretical optical band-gap as already investigate, TiO_2 have the larger band gap which is 3.2eV and it can absorb UV-light [26]. Some researcher predict that the low molarity of TiO_2 generate the higher optical band-gap hence the large different form the theoretical optical band-gap [27].

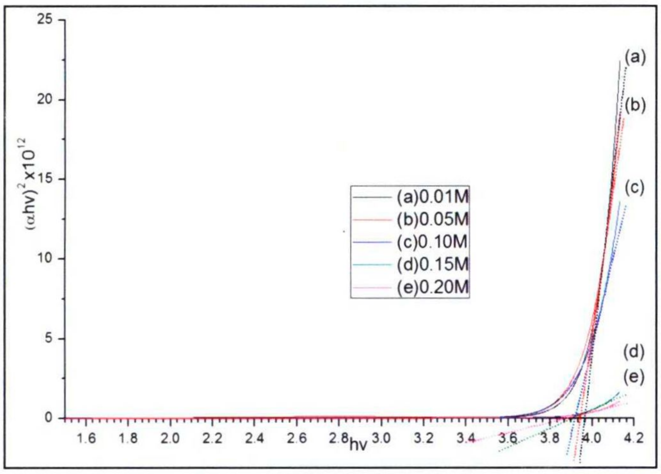

Figure 8: Optical band gap

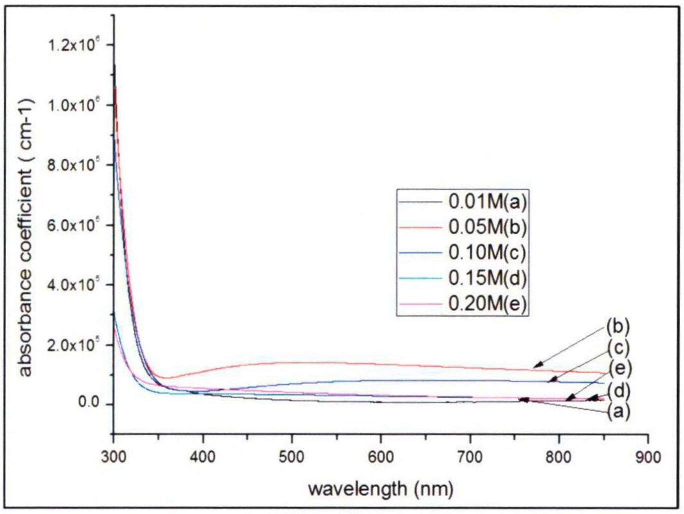

Figure 9: Absorption Coefficient

For absorbance coefficient, the graph was plotted by using the formula $\alpha = (1/t) * ln\ (1/T)$. It shows that with the different transmittance spectra, it would effect to the absorption coefficient. Based on the calculation of the absorption coefficient, the different of molarity which are 0.01M, 0.05M, 0.10M, 0.15M and 0.20M have $4.77 \times 10^4\ cm^{-1}$, $14.81 \times 10^4\ cm^{-1}$, $9.62 \times 10^4\ cm^{-1}$, $3.81 \times 10^4\ cm^{-1}$ and $4.43 \times 10^4\ cm^{-1}$ respectively. The absorption coefficient state that how far the material of light of a certain wavelength can penetrate before it is absorbed. Material with high absorption coefficient will give result to higher absorption of light and the transparency of the wavelength due to thin of the semiconductor material. Materials with higher absorption coefficients more readily absorb photons, which excite electrons into the conduction band.

C. Surface Morphology

The thickness of the TiO_2 thin film with different molarity from 0.01M, 0.05M, 0.10M, 0.15M and 0.20M are increasing uniformly from 9.24 nm to 79.7 nm. Table below show that the result from Atomic Force Microscope AFM with different molarity.

Table 2: Thickness of thin film

MOL	0.01M	0.05M	0.10M	0.15M	0.20M
Average (nm)	9.24	19.9	29.0	60.6	79.7

Based on the average of the TiO_2 thin film thickness, the higher TiO_2 molarity, will affect the increasing of the thickness of the thin film. The different of TiO_2 thin film thickness will affect to the TiO_2 grain size, roughness, porosity and uniformity. The surface morphology of the TiO_2 thin film was characterized by using Atomic Force Microscopy AFM. The different molarity TiO_2 thin film obviously effect to it's the surface morphology. The lowest molarity 0.01M give result the smallest roughness of 2.2nm while the higher molarity 0.20M gives the best uniformity and highest roughness about 7.66nm. Uniformity of the particle size across the thin film is important because the nanoparticle size significantly affects the electrical conductivity of the film [28]. With the highest uniformity at the highest roughness, there are providing the higher surface contact of the TiO_2. With the highest surface contact of the TiO_2, result to higher conductivity of thin film.

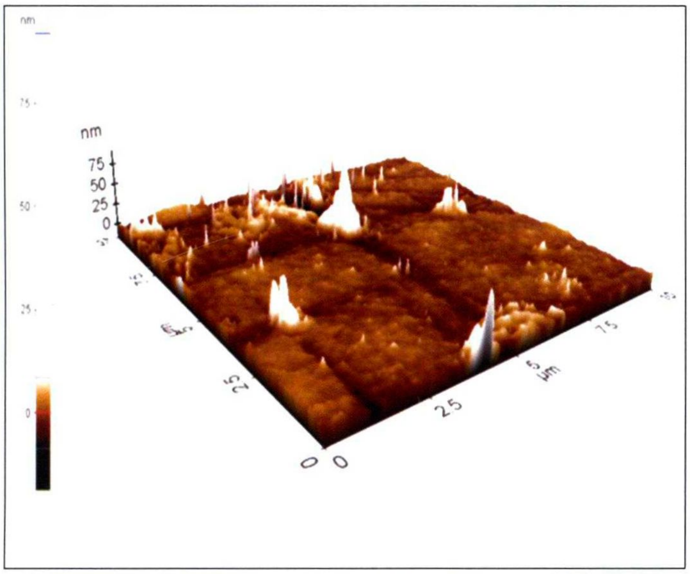

Figure10: AFM result of 0.01M TiO_2 thin film

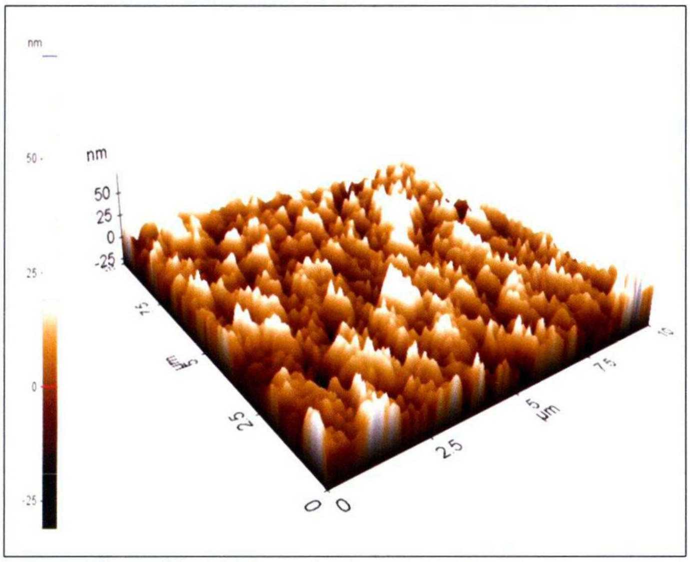

Figure11: AFM result of 0.20M TiO_2 thin film.

VI. Conclusion

It can be summarized that TiO_2 thin film preparation has successfully synthesized by using the sol gel method. Moreover, the study of varying the molarity of the precursor in sol gel method has been conducted. In addition, the characterization of TiO_2 including electrical, optical properties and the surface morphology is done at the end of the experiment. For electrical properties, when increasing of TiO_2 molarity, the conductivity of the TiO_2 also rapidly increases while the resistivity was decrease. The conductivity of TiO_2 thin film under illumination little bit higher compare to conductivity in dark condition. The higher the molarity will increase the thickness of the TiO_2 thin film. Based on the observation of the optical properties, increasing the molarity of the TiO_2 solution, the transmittance spectra decrease rapidly over the wavelength between 300 to 850nm. The surface morphology of the TiO_2 has the lowest molarity have the lowest roughness while the highest molarity of TiO_2 has the highest roughness and the most uniformity. Finally, based on the result of the experiment, the 0.2M of TiO_2 has the best properties due based on its higher conductivity, the nearest value of optical band-gap with the theoretical value, high absorbance coefficient, higher roughness and most uniform surface morphology.

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