



## INFLUENCE OF TiO<sub>2</sub> THIN FILM ANNEALING TEMPERATURE ON ELECTRICAL PROPERTIES SYNTHESIZED BY CVD TECHNIQUE

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### ABSTRACT

Titanium dioxide (TiO<sub>2</sub>) thin film deposited onto a glass substrate by varying the parameter of annealing temperature using chemical vapor deposition (CVD) technique to investigate the electrical properties. TiO<sub>2</sub> thin film annealed at the temperature of 300°C, 800°C and 1000°C before characterizations done using Atomic Force Microscope (AFM), X-Ray Diffraction (XRD), Ultraviolet-Visible spectroscopy (UV-Vis), Field Emission Scanning Electron Microscope (FE-SEM) and two point probe I-V measurement. The effects of anneal temperature on TiO<sub>2</sub> thin film surface morphology and electrical properties were studied intensively. The results obtained indicate that when a chemical modification were done, the properties of the TiO<sub>2</sub> thin film changed as well. From the AFM image, the roughness of TiO<sub>2</sub> thin film surface morphology increased as the annealing temperature increased. The electrical properties on the other hand, also increased as the temperature increased. Vice versa, the resistivity of the TiO<sub>2</sub> thin film decreased as annealing temperature increased. As expected, it is found that, heat treatment affecting TiO<sub>2</sub> surface morphology in term of roughness and indirectly changed the resistivity of TiO<sub>2</sub> due to the temperature applied on the thin film.

**Keywords:** titanium dioxide (TiO<sub>2</sub>), CVD technique, annealing temperature, electrical properties.

### INTRODUCTION

An increasing interest has been devoted to the study of TiO<sub>2</sub> because of their numerous applications in electronic devices. The advantages derived from TiO<sub>2</sub>, benefit various industries but the crystallization structure of TiO<sub>2</sub> influences the application of TiO<sub>2</sub>. Chemical modification done by thermal treatment can result in a wide range of new properties and gives strong effect on parameters such as surface morphology, optical properties and electrical properties

Naturally, TiO<sub>2</sub> obtained as powder consists of a mixture of amorphous and crystalline phase. TiO<sub>2</sub> form in three crystalline phases, brookite, anatase and rutile (M. S. P. Sarah *et al.*, 2010). The anatase phase were more stable at low temperature between 400°C to 700°C and also exist as metastable phase known to be useful for photocatalysis application which it has a better response to ultraviolet photons (Jianguo Yu *et al.*, 2001). At the temperature of 900°C, the TiO<sub>2</sub> thin film changed into rutile phase completely (Ya Qi Hou *et al.*, 2003). Rutile phase has a high chemical stability and suitable for optical coating applications (Dongsun Yoo *et al.*, 2007; S. Amor *et al.*, 1997; C. Su *et al.*, 2004).

To synthesis TiO<sub>2</sub> thin film, several technique can be used such as chemical vapor deposition (CVD), sol-gel deposition, spin coating and spray pyrolysis (M. Alzamami *et al.*, 2013). However, CVD technique consider as a promising method for the preparation of high quality thin films over a large surface area with well controlled composition and low defect density (SangChul Jung *et al.*, 2013).

Any heat treatment applied on the TiO<sub>2</sub> thin film can produce a new structural form such as morphology and particle size, which affecting the electrical properties of the thin film (M. K. Ahmad *et al.*, 2010). Thus, annealing temperature plays an important role because it strictly depends on the material properties.

The purpose of this research to prepare and synthesis TiO<sub>2</sub> thin film onto glass substrate and investigate TiO<sub>2</sub> thin film annealing temperature effects on the electrical properties.

### EXPERIMENTAL PROCEDURE

#### Preparation of substrate

2cm x 2cm glass slide is used as substrate. Then, the glass substrate is placed into a beaker filled with acetone solution. The process of cleaning substrate was done using sonic energy by placing the beaker into Power Sonic405 about 5 minutes at 50°C.

Substrate cleaning is very important before deposition process because this allows the cleaning and removal of submicron particles from the substrate. The presence of impurities after deposition process can be reduced. Finally, the glass substrate rinsed with deionized water (DI water) and blew with nitrogen gas for drying purposes.

#### Preparation of source materials

As source material for deposition process, 0.5g of 99.9% pure titanium and graphite powder weighted. These



powders later were mixed well. Then, the mixture was placed in an alumina boat and spread uniformly.

### Deposition of TiO<sub>2</sub> thin film

A CVD technique used to deposit TiO<sub>2</sub> thin film. An alumina boat contained a mixture of pure titanium and graphite placed in the middle of a CVD chamber while the glass substrate placed 17.5 cm away from chamber outlet. Gas flow rate and regulator set at 2.0-2.5 L/min and 50A respectively.

In the deposition process of TiO<sub>2</sub> thin film two types of gas used. Argon gas was used at the beginning of the deposition process as carrier gas to remove residue gases in the CVD chamber before the process of deposition took place. Argon gas does not react with the other gas or materials since argon gas classified as noble gases.

Argon gas then replaced with oxygen gas when the targeted annealing temperature achieved at 300°C, 800°C, and 1000°C. The process of deposition kept for 1 hour before cooling process was done.

## CHARACTERIZATION

### Atomic Force Microscope (AFM)

Characteristics through AFM done to obtain sample structure information including roughness value. The changes of force created between the tips and sample surface produced three dimensional images. The process of scanning done in directions of x-axis and y-axis.

### Ultraviolet-Visible spectroscopy (UV-Vis)

UV-Vis performed to investigate the band gap energy of the TiO<sub>2</sub> thin film sample. The fundamental of absorption edge defined when a sharp increase in absorptivity at the absorbed energies close to the band gap energy that exhibit as an absorption edge of the absorbance spectrum in UV-Vis. The absorbance against wavelength graph offer important information which can be used to calculate the band gap energy (E<sub>g</sub>) of the sample.

### Field Emission Scanning Electron Microscopy (FE-SEM)

The topography of TiO<sub>2</sub> thin film obtained through FE-SEM analysis. FE-SEM capable to examine the sample surface area at a magnification of 10x to 300kx.

### I-V analysis

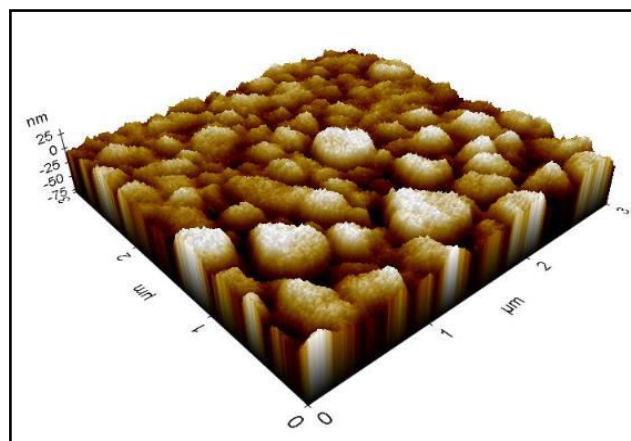
The electrical properties of TiO<sub>2</sub> thin film analyzed using two-point probe I-V measurements. Metal contact deposited on the sample surface in order to measure the sample resistivity by plotting an I-V curve. For this research, platinum (Pt) is used as metal contact.

## RESULTS AND DISCUSSIONS

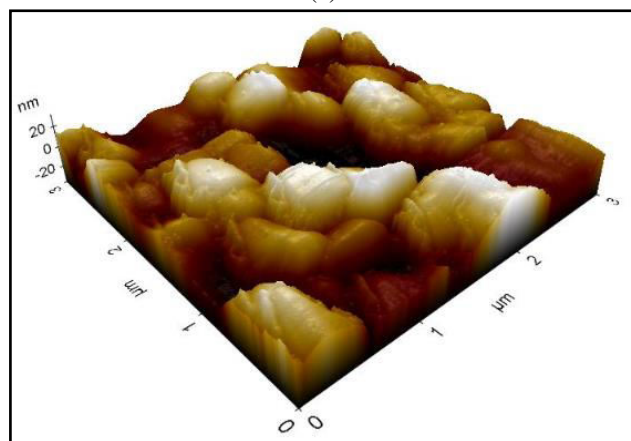
### Surface morphology study

Characterizing TiO<sub>2</sub> thin film using AFM, by setting scanning size to 3 μm the surface morphology and roughness of TiO<sub>2</sub> sample obtained. Figure-1 shows an AFM image of TiO<sub>2</sub> thin film after annealing process was done.

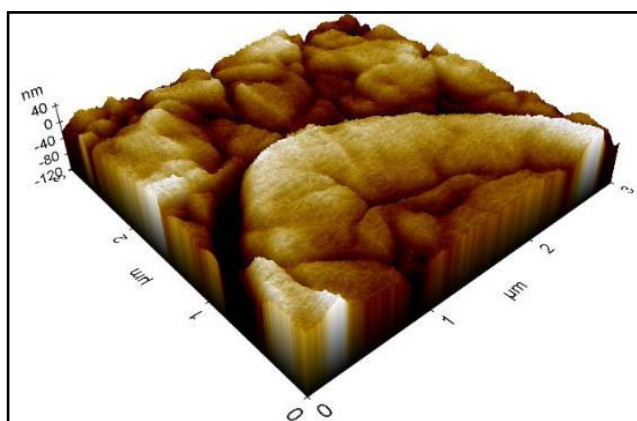
The changes on surface morphology clearly can be observed. Upon TiO<sub>2</sub> thin film subjected to high temperature, the roughness and grain size increase. At temperature of 300°C the average roughness obtained is 7.686 nm but increased to 9.248 nm at 800°C and 13.356 nm at 1000°C.



(a)



(b)

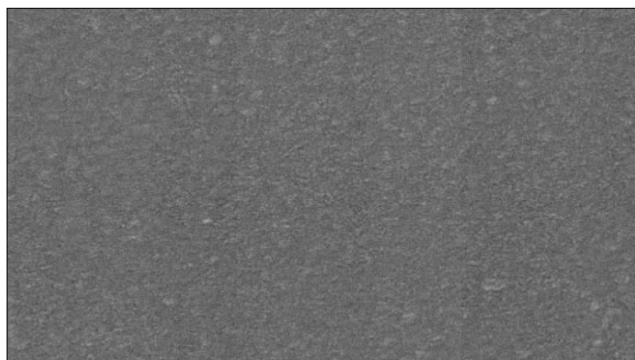


(c)

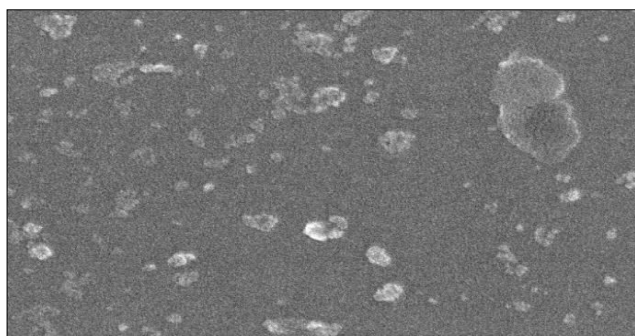
**Figure-1.** AFM image of  $\text{TiO}_2$  thin film anneal at (a) 300°C, (b) 800°C and (c) 1000°C.

At high temperature,  $\text{TiO}_2$  thin film surface become rougher due to exiting of large grain size. The movement of electrons can be improved from one grain to another grain within the  $\text{TiO}_2$  thin film as the grain size increased at high temperature.

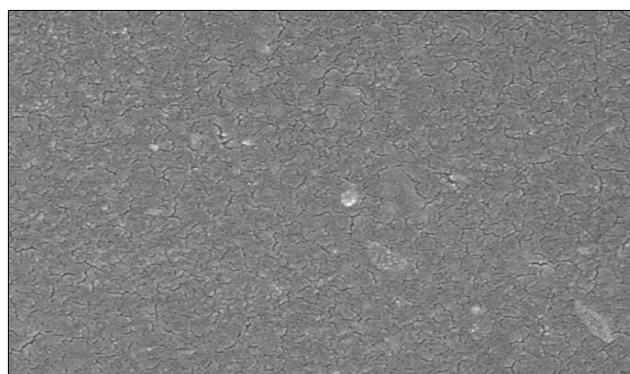
Beside AFM, FE-SEM also a method used to investigate the surface morphology of sample surface. Through FE-SEM, the presence of  $\text{TiO}_2$  particle easily can be determined. FE-SEM image obtained at the magnifier of 50kx. Figure-2 shows FE-SEM image of  $\text{TiO}_2$  thin film after the annealing process was done.



(a)



(b)



(c)

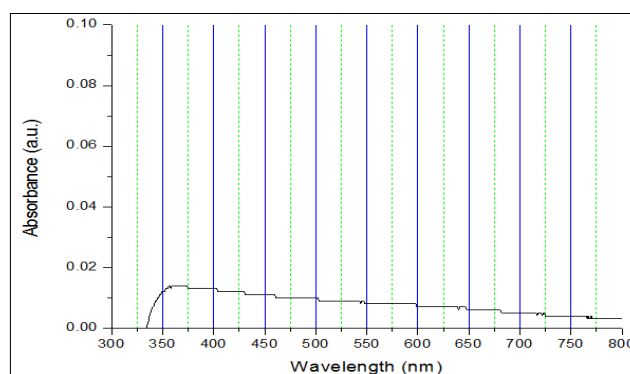
**Figure-2.** FE-SEM image of  $\text{TiO}_2$  thin film anneal at (a) 300°C, (b) 800°C and (c) 1000°C.

From FE-SEM image, the presence of  $\text{TiO}_2$  nanoparticles on glass substrate can be observed but it is too small. The image in Figure-2(c) showed presence of crack on the  $\text{TiO}_2$  thin film at the temperature of 1000°C.

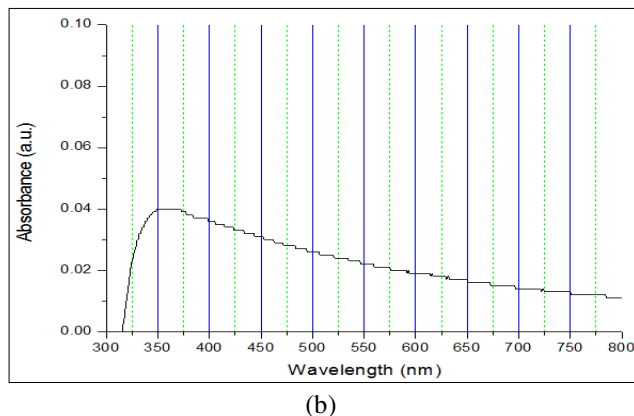
The results obtained probably caused by condition of thin film produced during the process of deposition is too thin. The formation of a crack affects the cluster size and indirectly reduce the movement of electrons due to the low quality of  $\text{TiO}_2$  thin film.

### Band gap energy study

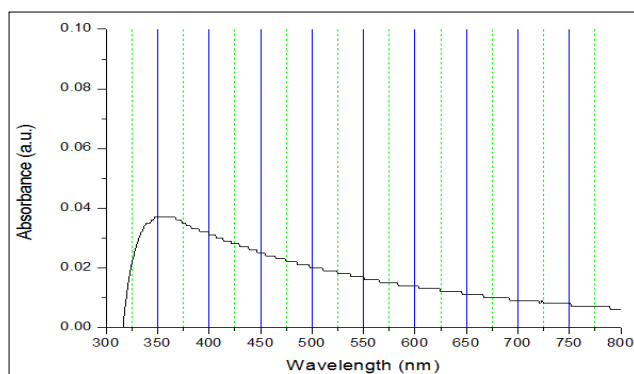
Investigation of band gap energy on  $\text{TiO}_2$  thin film sample were studied through UV-Vis spectroscopy by obtaining absorption spectra as shown in Figure-3.



(a)



(b)



(c)

**Figure-3.** UV-Vis graph of TiO<sub>2</sub> thin film anneal at (a) 300°C, (b) 800°C and (c) 1000°C.

Band gap energy ( $E_g$ ) calculated using the following equation:

$$E_g = h * C / \lambda \quad (1)$$

Where:  $E_g$  = band gap energy

$h$  = plank's constant

=  $6.626 \times 10^{-34}$  Joules sec

$C$  = speed of light

=  $3.0 \times 10^9$  meter/sec

$\lambda$  = wavelength

From the result collected, showed that the annealed TiO<sub>2</sub> thin film at 1000°C has the highest value of band gap energy, 3.38eV followed by 800°C, 3.34eV and 300°C, 3.32eV.

Studies by K. Madhusudan Rendy *et al.* claimed that for a synthesized TiO<sub>2</sub> thin film band gap energy estimated about 3.3eV to 3.4eV compared to a commercialized TiO<sub>2</sub> thin film, the band gap energy slightly lower about 3.2eV (K. M. Reddy *et al.*, 2002).

The absorbance of TiO<sub>2</sub> thin film increased as the annealing temperature increased. This probably due to the particle size and surface roughness increased with the annealing temperature.

### Effect of electrical properties

Electrical properties were fundamental and critical parameters to be investigated. Performing I-V measurements using two-point probe to the TiO<sub>2</sub> thin film unable to investigate the electrical properties especially the resistivity of the samples.

The resistivity calculated using the following equation:

$$\rho = \frac{\pi}{\ln(2)} \frac{V}{I} \quad (2)$$

Where:  $\rho$  = resistivity

$V$  = voltage

$I$  = current

$$\frac{\pi}{\ln(2)} = 4.53$$

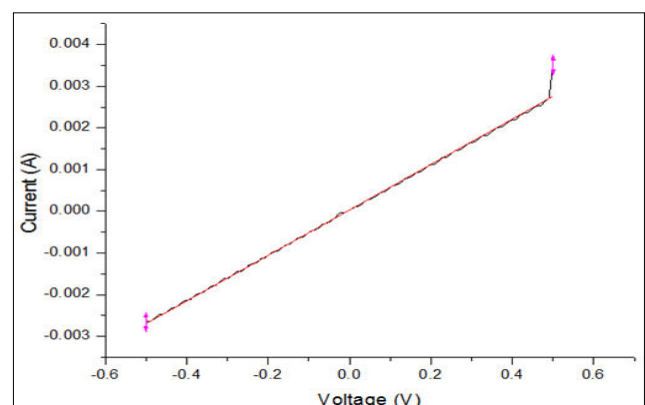
Relationship between resistivity and conductivity shown below:

$$\sigma = \frac{1}{\rho} \quad (3)$$

Where :  $\sigma$  = conductivity

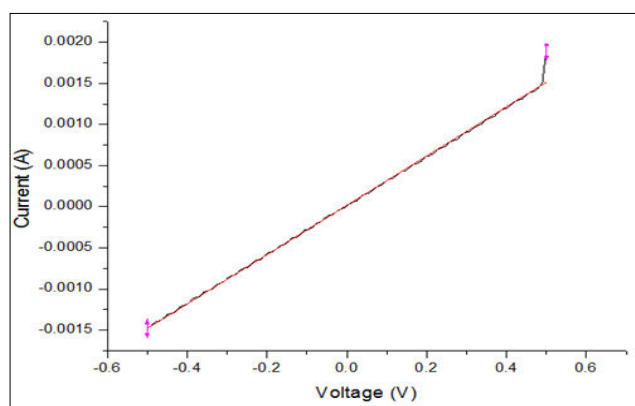
From the graph shown in Figure-4 and data collected in Table-1, it was noticed that the resistivity decreased with increasing of annealing temperature but the conductivity was increasing with annealed temperature.

This collection of data proved that at high temperature the conductivity is high due to the formation of good TiO<sub>2</sub> crystalline structure after the process of heat treatment. External energy provided during the process of annealing improved the movement of electrons from a grain to another grain. A good crystalline structure combined with the formation of larger grain size promises a better electrical property.

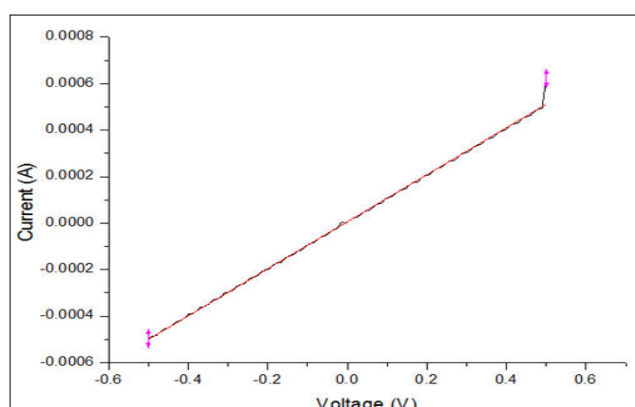


(a)





(b)



(c)

**Figure-4.** I-V graph of TiO<sub>2</sub> thin film anneal at (a) 300°C, (b) 800°C and (c) 1000°C.

**Table-1.** The resistivity and conductivity of TiO<sub>2</sub> glass substrate annealed at a temperature of 300°C, 800°C and 1000°C.

Annealed temperature (°C)	Resistivity (Ωcm)	Conductivity (S/cm)
300	24.701	40.484
800	13.552	73.790
1000	4.578	218.436

## CONCLUSIONS

Deposition of TiO<sub>2</sub> thin film successfully fabricated onto a glass substrate by varying the annealing temperature using the CVD technique. The surface morphology showed the roughness of the TiO<sub>2</sub> thin film surface increased with the temperature due to the existing of large grain size. Movement of electrons can be improved from one grain to another grain.

Characterization through FE-SEM showed the presence of TiO<sub>2</sub> nanoparticles on glass substrate. Upon the TiO<sub>2</sub> thin film subjected to high temperature, the

formation of large cluster is reduced. Existing of crack on TiO<sub>2</sub> thin film will decrease the quality of the thin film and indirectly affect the electron movement.

The optical properties investigated using UV-Vis by obtaining the band gap energy for each TiO<sub>2</sub> thin film annealed at different temperature. The band gap energy obtained in the range of 3.3eV and 3.4eV compared to the commercialized TiO<sub>2</sub> thin film band gap energy is 3.2eV. As the temperature is increased, the absorbance of TiO<sub>2</sub> thin film also increased.

The electrical properties showed when the annealing temperature increased, the resistivity decreased and conductivity increased. An increase in grain size affects the electrical properties and improve the migration of electrons within the TiO<sub>2</sub> thin film from one grain to the other.

## ACKNOWLEDGEMENT

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