INFLUENCE OF TiO\textsubscript{2} THIN FILM ANNEALING TEMPERATURE ON ELECTRICAL PROPERTIES SYNTHESIZED BY CVD TECHNIQUE

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ABSTRACT
Titanium dioxide (TiO\textsubscript{2}) 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\textsubscript{2} 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\textsubscript{2} 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\textsubscript{2} thin film changed as well. From the AFM image, the roughness of TiO\textsubscript{2} 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\textsubscript{2} thin film decreased as annealing temperature increased. As expected, it is found that, heat treatment affecting TiO\textsubscript{2} surface morphology in term of roughness and indirectly changed the resistivity of TiO\textsubscript{2} due to the temperature applied on the thin film.

Keywords: Titanium dioxide · CVD technique · Annealing temperature · Electrical properties

INTRODUCTION
An increasing interest has been devoted to the study of TiO\textsubscript{2} because of their numerous applications in
electronic devices. The advantages derived from TiO\textsubscript{2} benefit various industries but the crystallization structure of
TiO\textsubscript{2} influences the application of TiO\textsubscript{2}. 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\textsubscript{2} obtained as powder consists of a
mixture of amorphous and crystalline phase. TiO\textsubscript{2} 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 (Jiaguo Yu et al., 2001). At the temperature of
900°C, the TiO\textsubscript{2} 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\textsubscript{2} thin film, several technique can
be used such as chemical vapor deposition (CVD), sol-gel
deposition, spin coating and spray pyrolysis (M. Alzamani
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\textsubscript{2} thin film
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\textsubscript{2} thin film onto glass substrate and investigate
TiO\textsubscript{2} 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$_2$ thin film

A CVD technique used to deposit TiO$_2$ 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$_2$ 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$_2$ 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 (Eg) of the sample.

Field Emission Scanning Electron Microscopy (FE-SEM)

The topography of TiO$_2$ 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$_2$ 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.

RESULT AND DISCUSSION

Surface morphology study

Characterizing TiO$_2$ thin film using AFM, by setting scanning size to 3 µm the surface morphology and roughness of TiO$_2$ sample obtained. Figure 1 shows an AFM image of TiO$_2$ thin film after annealing process was done.

The changes on surface morphology clearly can be observed. Upon TiO$_2$ 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.

![Figure 1](image-url)
At high temperature, 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 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 TiO$_2$ particle easily can be determined. FE-SEM image obtained at the magnifier of 50kx. Figure 2 shows FE-SEM image of TiO$_2$ thin film after the annealing process was done.

![Figure 2](image1.png)

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

From FE-SEM image, the presence of 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 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 TiO$_2$ thin film.

**Band gap energy study**

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

![Figure 3](image2.png)

Figure 3: UV-Vis graph of TiO$_2$ thin film anneal at (a) 300°C, (b) 800°C and (c) 1000°C

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

$$E_g = \frac{h \cdot c}{\lambda}$$

where: $E_g$ = band gap energy
From the result collected, showed that the annealed TiO$_2$ 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$_2$ thin film band gap energy estimated about 3.3eV to 3.4eV compared to a commercialized TiO$_2$ thin film, the band gap energy slightly lower about 3.2eV (K. M. Reddy et.al., 2002).

The absorbance of TiO$_2$ 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$_2$ thin film unable to investigate the electrical properties especially the resistivity of the samples.

The resistivity calculated using the following equation:

\[
\rho = \frac{\pi V}{\ln (2) I}
\]

Where : 
- \( \rho \) = resistivity
- \( V \) = voltage
- \( I \) = current

\[ \frac{\pi}{\ln (2)} = 4.53 \]

Relationship between resistivity and conductivity shown below:

\[
\sigma = \frac{1}{\rho}
\]

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$_2$ 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 properties.
CONCLUSION
Deposition of TiO\textsubscript{2} 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\textsubscript{2} 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\textsubscript{2} nanoparticles on glass substrate. Upon the TiO\textsubscript{2} thin film subjected to high temperature, the formation of large cluster is reduced. Existing of crack on TiO\textsubscript{2} 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\textsubscript{2} 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\textsubscript{2} thin film band gap energy is 3.2eV. As the temperature is increased, the absorbance of TiO\textsubscript{2} 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\textsubscript{2} thin film from one grain to the other.

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REFERENCE


