INFLUENCES OF DEPOSITION TIME ON TiO₂ THIN FILMS PROPERTIES PREPARED BY CVD TECHNIQUE


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1.0 INTRODUCTION

TiO₂ which is also acknowledged as titania is the naturally occurring oxide of titanium. It is well known material with exceptionally outstanding optical, mechanical and thermal properties which has high refractive index (~2.5); transmit in the visible excellently, also high stability in electrical and chemical. The properties and application of TiO₂ are depends on the type of its crystallographic structure among others [1].

TiO₂ exhibits as various polymorphs for example; anatase, rutile and brookite. The stable rutile and metastable anatase are the most important polymorphs of TiO₂. Attracted attention for its significant photo catalytic activity, anatase is stable at low temperatures between 400 °C to 700 °C and will converts irreversibly to rutile at elevated temperatures. Rutile has high chemical stability and more suitable for optical coating application [2].
The studies of TiO$_2$ thin films have recently attracted much interest because of its various applications, such as photo-catalysis, optical coating, sensors, integrated optics, metal-cutting industry, or microelectronic devices [1-5]. Researchers are working on numerous techniques in order to prepare good quality of TiO$_2$ thin films which are not all can produce it [5-11]. In order to obtain the most optimized TiO$_2$ thin films, CVD technique is used because it is a well known deposition method that produces better quality of thin films [8].

CVD technique is a promising way to deposit TiO$_2$ thin films with great control because it is well known for large scale deposition and high quality of grown TiO$_2$ thin films [13-15]. The properties of deposited TiO$_2$ thin films can be varied and controlled by proper optimization of preparation parameters. The preparation parameters are annealing temperature, deposition time, precursor concentration, level of rest time and position of substrate [16-17].

Fundamentally, the application of TiO$_2$ thin films is biased by its structural, morphology, optical and electrical properties [12]. So, this study is conducted in order to find the suitable key factor of TiO$_2$ thin films deposition parameter in terms of deposition time.

2.0 METHODOLOGY

2.1 Material Preparation

99.9 % pure titanium powder with size 45-63 µm (Vistec Technology Services) and graphite powder natural GRG with assay 85 % (Avondale Laboratories) were used as the source material with ratio 1:1. The materials were mixed and put into alumina boat and ready for CVD process.

2.2 Experimental Setup

Customized made CVD furnace from Vistec Technology Services is the equipment used to conduct CVD experiment. Table 1 shows the standard deposition parameters that will be taken into account during deposition process.

Alumina boat and glass substrate were placed inside the CVD tube furnace system according to Figure 1. Alumina boat was inserted inside CVD tube furnace from left side with distance of 35.5 cm whereas the glass substrate was inserted from right side with distance of 21.5 cm. Both were placed in the centre of CVD tube furnace where the heating elements were able to distribute the heat evenly.

![Figure 1 CVD tube furnace.](image)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regulator</td>
<td>50 A</td>
</tr>
<tr>
<td>Rate of gas flow</td>
<td>2.0 - 2.5 l/min</td>
</tr>
<tr>
<td>Level of rest time</td>
<td>5 minutes</td>
</tr>
</tbody>
</table>

2.3 Sample Characterization

The usages of X-Ray Diffraction (XRD)(AXS D8, Bruker) are to identify crystalline phases and orientation, to determine structural properties and to determine atomic arrangement. After the samples of 1 hour, 2 hours and 3 hours of deposition time were examined under XRD, the peaks of TiO$_2$ such as anatase, rutile and cotunnite type were obtained indicating that TiO$_2$ thin films were successfully deposited on glass substrate using CVD technique. The results were gained by scanning 20 in the range of 20° - 80°.

Atomic Force Microscope (AFM) (XE-100 Series, Park System) is designed to measure local properties such as height, friction and magnetism with a probe. To acquire an image, the AFM raster will scans the probe over a small area of the sample and measuring the local property simultaneously. UV-Vis (UV 1800, Shimadzu) equipment was used to gain the absorbance and transmittance spectrum of deposited TiO$_2$ thin films. From these spectra, band gap energy ($E_g$) of TiO$_2$ thin films can be calculated. Equation 1 shows the formula to calculate $E_g$ by obtaining wavelength value from the absorbance spectra.

$$E_g = \frac{hc}{\lambda}$$

where:

- $E_g$ = band gap energy
- $h$ = Planck’s constant = 6.626 x 10$^{-34}$ J.s
- $c$ = speed of light = 3.0 x 10$^8$ m/s
- $\lambda$ = wavelength

Surface Profilometer (SP) (Alpha Step IQ) was used to obtained thickness of the deposited TiO$_2$ thin films. The thickness is required in order to calculate the absorption coefficient, $\alpha$ (refer equation 2) in order to calculate $E_g$ of the deposited TiO$_2$ thin films.

$$\alpha = \frac{1}{t} \ln(1/T)$$

where:

- $\alpha$ = absorption coefficient
- $t$ = thickness
- $T$ = transmittance

A small region of the samples was etched using hydrogen fluoride solution for SP characterization.
There is a boundary between deposited TiO$_2$ thin films and glass substrate can be used for SP characterization. Three spotted area of every sample were examined to obtain the average thickness of TiO$_2$ thin films.

$I$-$V$ measurement (Oriental Instrument) was used to determine the electrical characteristics of the deposited TiO$_2$ thin films. First of all, the samples need to be coated with metal contact by using sputter coating in order to measure the sheet resistivity by plotting an $I$-$V$ graph. For this study, gold (Au) was used as metal contact. From the $I$-$V$ graph, the resistivity of TiO$_2$ thin films can be obtained using equation 3.

$$\rho = \pi / \ln(2) (V/I)$$

(3)

Where;

- $\rho$ = resistivity
- $V$ = voltage
- $I$ = current

Whereas, the conductivity, $\sigma$ of the TiO$_2$ thin films also can be calculated using the equation 4.

$$\sigma = 1/\rho$$

(4)

Where;

- $\sigma$ = conductivity
- $\rho$ = resistivity

3.0 RESULTS AND DISCUSSION

3.1 X-Ray Diffraction (XRD) Analysis

Figure 2 shows the peaks obtained from varied deposition time starting from 1 hour, 2 hours and 3 hours, respectively. The results of XRD indicate that the TiO$_2$ thin films, which were annealed at different deposition times, have all four crystalline phases; anatase, rutile, cotunnite type and TiO$_2$ but more peaks per phases were gained as the deposition time increases.

The intensity of the peaks of TiO$_2$ crystalline phases and orientation were obtained clearly for the longest deposition time of TiO$_2$ thin films preparation. This result is clearly shown in Figure 2. It means that the structural properties of TiO$_2$ thin films were greatly affected at 3 hours of deposition time.

3.2 Atomic Force Microscope (AFM) Analysis

Figure 3 shows the surface morphology of TiO$_2$ thin films deposited by varying the deposition time and Table 2 displays the average roughness and grain size of TiO$_2$ thin films. The average roughness ($R_a$) of 1 hour, 2 hours and 3 hours deposition time are 89.500 nm, 105.050 nm and 172.600 nm respectively. The average grain size of 1 hour, 2 hours and 3 hours deposition time are 149.851 nm, 151.505 nm and 153.630 nm respectively. This result shows that the $R_a$ and grain size increases with increases of deposition time. To sum up, the uniformity and roughness of deposited TiO$_2$ thin films increasing with the deposition time due to existing large grain size.
Table 2 Average roughness and grain size of TiO$_2$ thin films

<table>
<thead>
<tr>
<th>Deposition time</th>
<th>Average roughness ($R_a$)</th>
<th>Average grain size</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 hour</td>
<td>89.500 nm</td>
<td>149.851 nm</td>
</tr>
<tr>
<td>2 hours</td>
<td>105.050 nm</td>
<td>151.505 nm</td>
</tr>
<tr>
<td>3 hours</td>
<td>172.600 nm</td>
<td>153.630 nm</td>
</tr>
</tbody>
</table>

3.3 Ultraviolet-Visible Spectroscopy (UV-Vis) Analysis

From the result shows in Table 3, $E_g$ values are the highest at 3 hours deposition time compared to 1 hour and 2 hours deposition time. This is maybe due to high intensity of anatase and rutile diffraction peaks which depending on increasing of the deposition time.

Table 3 Band gap energy of TiO$_2$ thin films

<table>
<thead>
<tr>
<th>Deposition Time</th>
<th>Direct Band Gap Energy, $E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 hour</td>
<td>3.00</td>
</tr>
<tr>
<td>2 hours</td>
<td>3.02</td>
</tr>
<tr>
<td>3 hours</td>
<td>3.04</td>
</tr>
</tbody>
</table>

3.4 Surface Profilometer (SP) Analysis

The average thickness of 1 hour deposition time is 4.781 µm and it is increases to 6.136 µm for 2 hours deposition time. The average thickness for 3 hours deposition time is the highest among all which is 7.942 µm. It is concludes that the longest deposition time produces the thickest TiO$_2$ thin films using CVD method.

3.5 Current-Voltage (I-V) Analysis

Figure 4 displays the I-V graph of 1 hour deposition time, 2 hours deposition time and 3 hours deposition time respectively.
The resistivity values increases from 2.518 x 10^3 Ω cm with an increase of deposition time. However, the conductivity of deposited TiO2 thin films decreases with increases of deposition time.

The results show that the highest conductivity was obtained for 1 hour deposition time indicates that the electrical properties of deposited TiO2 thin films were optimized at a parameter of 1 hour deposition time. TiO2 thin film at 1 hour deposition times have smaller band gap among all, so the energy required to excite an electron from valence band to conduction band also the minimum which make it the most conductive TiO2 thin film.

4.0 CONCLUSION

Deposition of TiO2 thin films successfully fabricated onto glass substrate by varying the deposition time. Characterization through AFM showed that the roughness of TiO2 thin films was increased as the deposition time increased. AFM images also reveal the crystalline morphology with average grain size of 151.662 nm. The optical properties were inspected using UV–Vis by obtaining the absorbance and transmittance spectrums of every samples. The band gap energy is the highest at 3 hours deposition time.

The thicknesses of deposited TiO2 thin films were increased with increment of deposition time. Same goes to the resistivity that is also rises with time. However, the conductivity of deposited TiO2 thin films was decreased as the deposition time increased.

It can be concluded from the experimental results that the deposition time affects the TiO2 thin films properties.

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