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INFLUENCES OF DEPOSITION TIME ON TiO_2 THIN FILMS PROPERTIES PREPARED BY CVD TECHNIQUE

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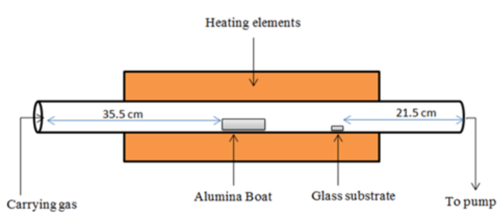
Graphical abstract



Abstract

Titanium dioxide (TiO_2) is known as a material with exceptionally good optical, mechanical and thermal properties. An increasing interest has been devoted to the study of TiO_2 because of their numerous applications in various industries. In this study, by controlling process parameters, TiO_2 thin films were successfully deposited on a glass substrate using chemical vapor deposition (CVD) technique. It has been fabricated using two source materials that are 99.9 % pure titanium and graphite powder at 1000 °C annealing temperature. The deposition time were observed at 1 hour, 2 hours and 3 hours. The TiO_2 thin films properties were characterized using X-Ray Diffraction (XRD), Atomic Force Microscope (AFM), Ultraviolet-Visible Spectroscopy (UV-Vis), Surface Profilometer (SP) and Current-Voltage (I-V) Measurement Tools. Based on XRD results, the intensity of mixed anatase, rutile, cotunnite type and TiO_2 was highest for 3 hours deposition time. AFM images reveal the crystalline morphology with average grain size of 151.662 nm. The band gap energy obtained from UV-Vis as well as thicknesses gained from SP and resistivity acquired from Current-Voltage (I-V) Measurement of deposited TiO_2 thin films were increasing with deposition time. It is vice versa for the conductivity of deposited TiO_2 thin films that is declining with increasing of deposition time. It can be concluded from the experimental results that the deposition time affects the TiO_2 thin films properties.

Keywords: Titanium dioxide, CVD technique, deposition time

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1.0 INTRODUCTION

TiO_2 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 TiO_2 are depends on the type of its crystallographic structure among others [1].

TiO_2 exhibits as various polymorphs for example; anatase, rutile and brookite. The stable rutile and metastable anatase are the most important polymorphs of TiO_2. 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.

Table 1 Standard deposition parameters

Parameter	Range
Regulator	50 A
Rate of gas flow	2.0 – 2.5 l/min
Level of rest time	5 minutes
Deposition temperature	1000 °C
Precursor concentration	0.5 g titanium : 0.5 g graphite

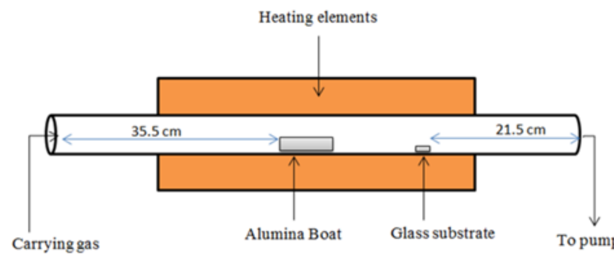


Figure 1 CVD tube furnace.

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 2θ 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, Shidmadzu) 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.

$$E_g = hc/\lambda \qquad (1)$$

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
λ = 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, α (refer equation 2) in order to calculate E_g of the deposited TiO_2 thin films.

$$\alpha = 1/t \ln(1/T) \qquad (2)$$

where;

α = 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.

$$\rho = \pi / \ln(2)(V/I) \quad (3)$$

Where;

ρ = resistivity
V = voltage
I = current

Whereas, the conductivity, σ of the TiO_2 thin films also can be calculated using the equation 4.

$$\sigma = 1/\rho \quad (4)$$

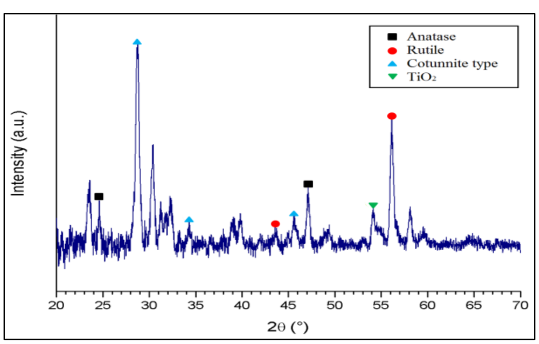
Where;

σ = conductivity
ρ = resistivity

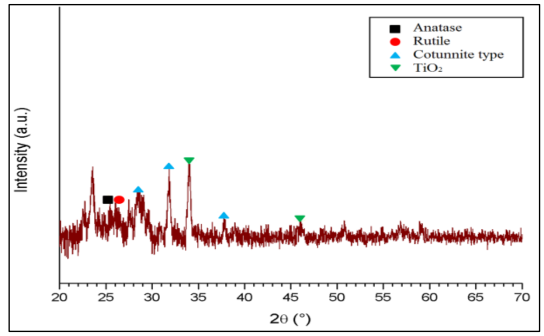
3.0 RESULTS AND DISCUSSION

3.1 X-Ray Diffraction (XRD) Analysis

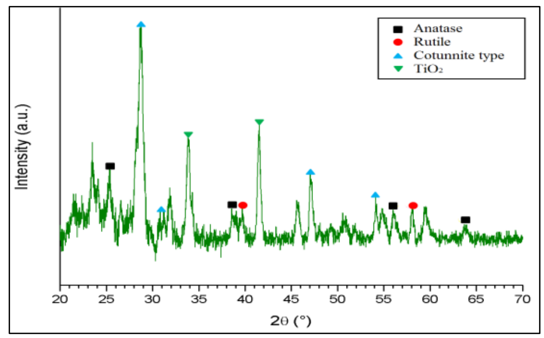
Figure 2 shows the peaks obtained from varied deposition time starting from 1 hour, 2 hours and 3 hours, respectively. The results of XRD indicate that the TiO_2 thin films, which were annealed at different deposition times, have all four crystalline phases; anatase, rutile, cotunnite type and TiO_2 but more peaks per phases were gained as the deposition time increases.



(a) 1 hour



(b) 2 hours



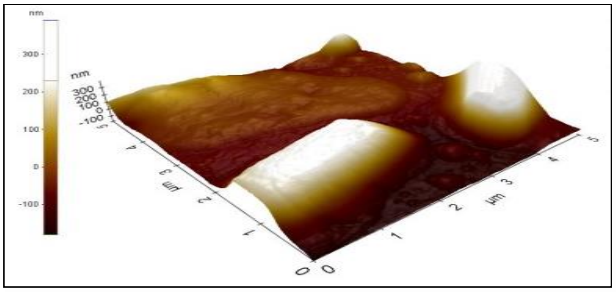
(c) 3 hours

Figure 2 XRD spectra for three different deposition times

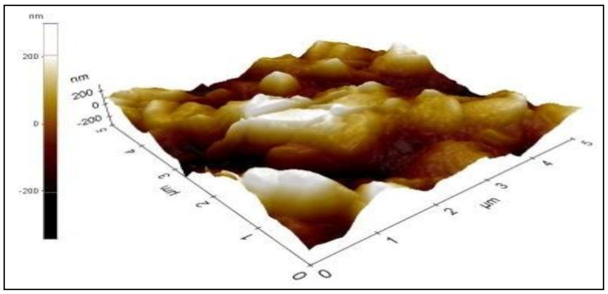
The intensity of the peaks of TiO_2 crystalline phases and orientation were obtained clearly for the longest deposition time of TiO_2 thin films preparation. This result is clearly shown in Figure 2. It means that the structural properties of TiO_2 thin films were greatly affected at 3 hours of deposition time.

3.2 Atomic Force Microscope (AFM) Analysis

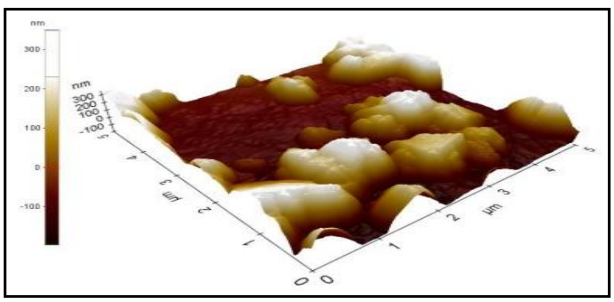
Figure 3 shows the surface morphology of TiO_2 thin films deposited by varying the deposition time and Table 2 displays the average roughness and grain size of TiO_2 thin films. The average roughness (R_a) of 1 hour, 2 hours and 3 hours deposition time are 89.500 nm, 105.050 nm and 172.600 nm respectively. 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.



(a) 1 hour



(b) 2 hours



(c) 3 hours

Figure 3 AFM surface morphology of TiO_2 thin films at different deposition time

Table 2 Average roughness and grain size of TiO_2 thin films

Deposition time	Average roughness (R_a)	Average grain size
1 hour	89.500 nm	149.851 nm
2 hours	105.050 nm	151.505 nm
3 hours	172.600 nm	153.630 nm

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

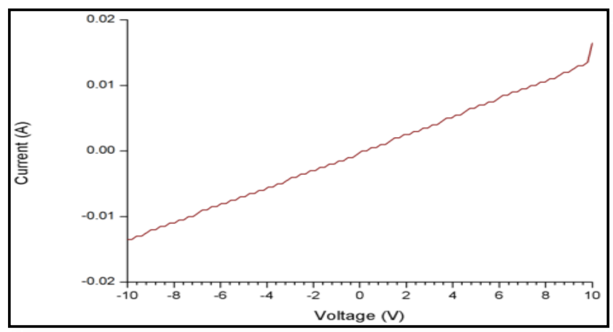
Deposition Time	Direct Band Gap Energy, E_g (eV)
1 hour	3.00
2 hours	3.02
3 hours	3.04

3.4 Surface Profilometer (SP) Analysis

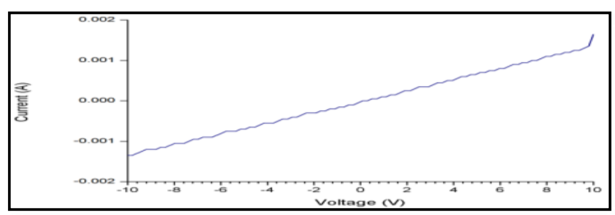
The average thickness of 1 hour deposition time is 4.781 µm and it is increases to 6.136 µm for 2 hours deposition time. The average thickness for 3 hours deposition time is the highest among all which is 7.942 µm. It is concludes that the longest deposition time produces the thickest TiO_2 thin films using CVD method.

3.5 Current-Voltage (I-V) Analysis

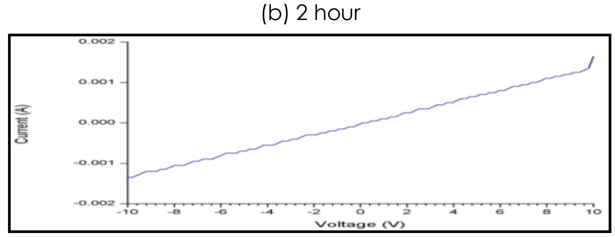
Figure 4 displays the *I-V* graph of 1 hour deposition time, 2 hours deposition time and 3 hours deposition time respectively.



(a) 1 hour



(b) 2 hour



(c) 3 hour

Figure 4 I-*V* graph for three different deposition times

Table 4 Resistivity and conductivity of TiO_2 thin films

Deposition Time	Resistivity, ρ ($x10^3$ Ω.cm)	Conductivity, σ ($x10^{-6}$ S/cm)
1 hour	2.518	397.141
2 hours	26.661	37.508
3 hours	133.305	7.502

The resistivity values increases from $2.518x10^3$ Ω.cm with an increases of deposition time. However, the conductivity of deposited TiO_2 thin films decreases with increases of deposition time.

The results shows that the highest conductivity was obtained for 1 hour deposition time indicates that the electrical properties of deposited TiO_2 thin films was optimized at parameter of 1 hour deposition time. TiO_2 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 TiO_2 thin film.

4.0 CONCLUSION

Deposition of TiO_2 thin films successfully fabricated onto glass substrate by varying the deposition time. Characterization through AFM showed that the roughness of TiO_2 thin films were 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 TiO_2 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 TiO_2 thin films was decreased as the deposition time increased.

It can be concluded from the experimental results that the deposition time affects the TiO_2 thin films properties.

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