Electrical and Optical Properties of Nanostructured Titanium Dioxide (TiO_2) Thin Film Annealed At Different Temperatures

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Abstract – Nanostructured Titanium Dioxide (TiO_2) thin film has been synthesized using sol-gel method and deposited onto glass substrates using spin coating technique. These thin films then annealed at various temperatures. The electrical, optical and structural characterizations of the as deposited and annealed films were carried out using IV measurement with 4-point probe equipment, UV-Vis spectroscopy, atomic force microscopy (AFM) and scanning electron microscopy (SEM). From this study, it is known that, electrical properties were influenced by changes of annealing temperature. Resistivity of thin films was found to decrease as the annealing temperatures increase. Based on the readings from UV-Vis spectroscopy, it is found that transmittance properties of TiO_2 thin films increased as annealing temperatures increase. This result is supported by surface topography and morphology of the thin films which indicate grains size increasing as temperature increases.

Keywords: *Titanium Dioxide (TiO_2) thin film; annealing temperature; electrical properties; optical properties; structural properties*

1. Scope of Work

This research began with literature review on related to titanium dioxide. As much information was collected from journals, books or research papers. The literature review was focused on solution preparation methods, deposition techniques and characterization methods. After all data have been gathered, the TiO_2 solution was prepared using sol-gel method with 0.2 precursor concentration. Next step was depositing the solution onto glass substrates using spin coating technique. Then the TiO_2 thin films were annealed at various temperatures and each thin film was coated with gold electrode. The properties of the TiO_2 thin films were characterized using four method; IV-measurement, UV-Vis spectroscopy, AFM and SEM. All the results were gathered and finally this paper was written.

2. Objectives

The purpose of this research is to investigate the electrical properties of nanostructured TiO_2 annealed at different temperatures. The specific objectives of this research are:

1. To deposit the transparent nanostructured TiO_2 on glass substrates by using spin coating method
2. To study the electrical properties of nanostructured TiO_2 thin films annealed at different temperatures
3. To study the optical properties of nanostructured TiO_2 thin films annealed at different temperatures

3. Introduction

Titanium dioxide has arose much attention of chemists and physicists due to the capability of utilization in numerous industrial applications. TiO_2 is a wide band gap semiconductor material which has been under extensive investigations due to its applications in a variety of fields such as photoelectrolysis [1], photocatalysis [2], dye sensitized solar cells [3], gas sensor [4], optical fibers, electro chromic material for display devices [5], biomedical fields [6], etc. TiO_2 exists in different crystalline forms; anatase, rutile and brookite [9]. Many important applications of TiO_2 depend on its structural and optical properties [9]. Films with dense structure are good in solar cell applications where as porous films are better for gas sensors. Rutile phase has good stability and high refractive index which makes it suitable for protective coatings on lenses [7]. The anatase phase which has better response with ultraviolet photons is used for photocatalysis [2] where as amorphous TiO2 films are utilized in biomedical fields due to its blood compatibility [6]. Compared to others semiconductors, TiO_2 is favoured for such applications because apart from its high photo-activity, biologically and chemically inert, readily available and cheap [8]. Unfortunately, TiO2 with its bandgap around 3.2 eV, is activated only under ultraviolet (UV) light which possesses only a small fraction (about 8%) of the solar energy [11], [12].

The relationship between the DC current through an electronic device and the DC voltage across its terminals is called a current–voltage characteristic of the device. These characteristics are also known as I-V curves, referring to the standard symbols for current and voltage.

Electrical resistivity is a measure of how strongly a material opposes the flow of electric current. A low resistivity indicates a material that readily allows the movement of electrical charge. The resistivity of TiO_2 thin films can be measured using Solar Simulator according to the following equation for 4-point probe measurement [14]:

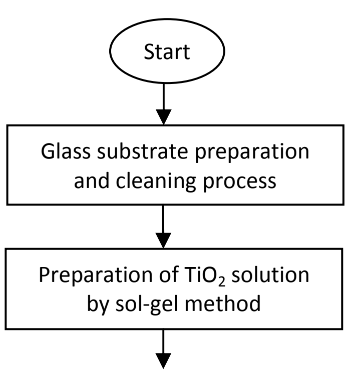
$$\rho_{\square}\left(\frac{\Omega}{\square}\right) = \frac{\pi}{ln\,(2)}\frac{V}{I} \tag{1}$$

Electrical conductivity is a measure of a material's ability to conduct an electric current. When an electrical potential difference is placed across a conductor, its movable charges flow, giving rise to an electric current. Conductivity is the reciprocal (inverse) of electrical resistivity, ρ, and has the SI units of siemens per metre ($S\cdot m^{-1}$). The relationship between resistivity and conductivity is shown by the following equation:

$$\sigma = \frac{1}{\rho} \tag{2}$$

4. Methodology

4.1 Flow chart of processes involved



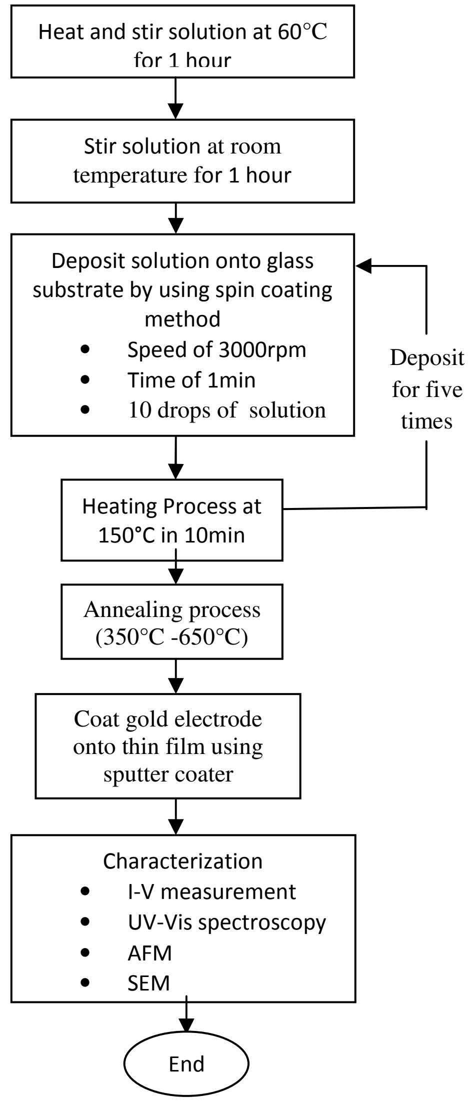


Figure 1: Flow chart for preparation and characterization of TiO_2 thin films

5. Experimental Procedure

5.1 Materials

These materials been used during the preparation of TiO_2 solution:

i. Titanium Butoxide (TTIB) acting as precursor
ii. Glacial asetic acid (GAA) as stabilizer
iii. Deionised water as a function of adding Oxygen (O_2) element into titanium butoxide for hydrolysis process
iv. Triton X-100 as a stabilizer to increase conductivity of films
v. Ethanol (ethyl alcohol) as a solvent

5.2 Preparation of TiO_2 solution

The TiO_2 solution was prepared using sol-gel method. All the materials mentions in section 5.1 above were mixed in a beaker in their specific order while stirring process was held on the hot plate stirrer:

i. The beaker was filled 50ml of ethanol
ii. 6.8ml of titanium butoxide was inserted into the beaker
iii. 5ml of glacial asetic acid poured into the solution
iv. 0.36ml of DI water
v. 1 drop of triton X-100
vi. Pour ethanol until solution is 100ml

Then, the solution was stirred in 60°C for 1 hour and in room temperature (37°C) for another 1 hour.

5.3 Thin film deposition method

The TiO_2 thin films were deposited onto glass substrates by using spin coating technique. Spin coater was set at a speed of 3000 rpm in 1 minute of time and the nitrogen (N_2) gas was supplied at 4 bars and 2 liter per minute. TiO_2 solution was dropped 10 times onto the substrates and then heated in the oven at 150°C for 10 minutes. 10 times drop and 1 time heating process was considered as 1 layer and this process were repeated for 5 times to get a 5 layer TiO_2.

5.4 Annealing process

After the deposition process was completed, the thin films were annealed at different temperatures for 1 hour. These temperatures ranged from 350°C to 650°C. One thin film was not applied to any heat treatment in which called ‘as deposited’.

5.5 Gold electrode coating process

The TiO_2 thin films were coated with gold electrode by using sputter coater. The sputter coater was set to a current of 50mA and 2 minutes of time. The sputter vacuumed the chamber until the pressure is $2x10^{-1}$ mbar. Argon gas was purged into the chamber.

5.6 Characterization method

Finally, the thin films were characterized. There were 4 types of characterization that been used to study the characteristics of TiO_2 thin films. The electrical properties were observed by using I-V measurement by using 4-point probe equipment, optical properties by using UV-Vis spectrophotometer, surface morphology using SEM and surface topography by using AFM.

6. Results And Discussions

6.1 Electrical Properties of TiO_2 Thin Film

The electrical properties of nanostructured TiO_2 thin films were analyzed by performing IV measurement to the thin films. In order to measure the I-V characteristics, metal contact will be deposited onto nanostructured TiO_2 thin film. In this research gold was used as the metal contact. The reason gold used is gold is the standard metal contact used as finishing electrode onto samples. This is because it forms a good ohmic contact with materials. Figure below illustrates the thin film has been deposited with aurum.

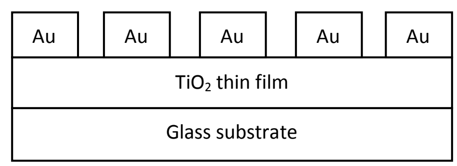


Figure 2: Electrode Au is coated onto TiO_2 thin films

The IV measurements were done using Solar Simulator. The measurement used a 4-point probe measuring system. This system can be used to measure either bulk or thin film specimen, each of which consists of a different expression.

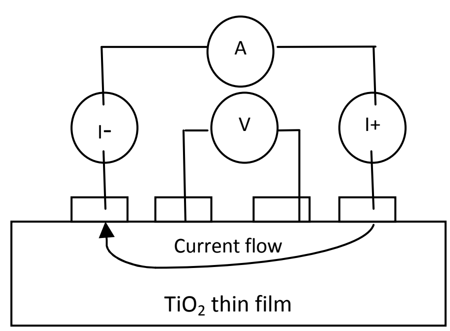


Figure 3: 4-point probe measurement using solar simulator

Figure 3 above shows how a 4-probe measurement operates. The outer two probes supply current and a voltmeter measures the voltage across the inner two probes. The resistivity was calculated using following equation [14]:

$$\rho_{\square}\left(\frac{\Omega}{\square}\right) = \frac{\pi}{ln\,(2)}\frac{V}{I} \qquad (1)$$

Where: ρ = resistivity
V = voltage
I = current
$\frac{\pi}{\ln 2}$= 4.53

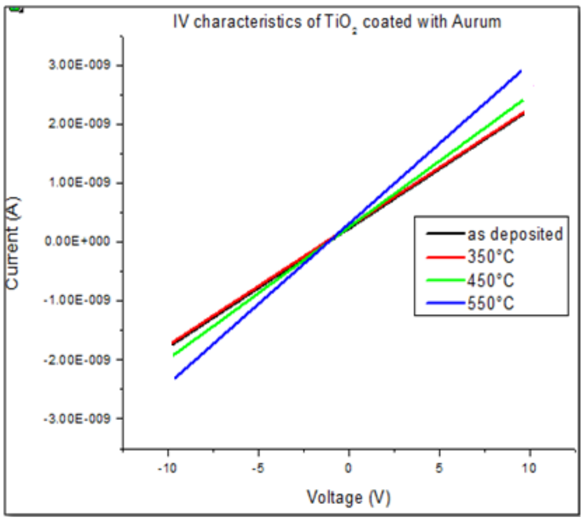


Figure 4: IV characteristics of nanostructured TiO_2 thin films annealed at different temperatures

Figure 4 shows the I-V characteristic of TiO_2 thin film deposited on glass substrate. The I-V characteristics were measured at various annealing temperatures. From the graph, it shown that the most conductive sample are 550°C followed with 450°C, 350°C and least conductive is as deposited thin film. As expected, the resistivity decreases with annealing. The decrease in resistivity with annealing temperatures can be explained as follows: the grain size increases with annealing temperature which leads to a decrease in grain boundaries and hence resistivity [9]. Larger grains size will provide higher surface contact between the TiO_2 thin films and electrode improving electron migration [10]. Annealing treatment also produces better physical attachment which improves the electronic contacts between all the particles of the thin films [10].

Table 1: Resistivity and conductivity of nanostructured TiO_2 thin films at different annealing temperatures

Annealing temperature [°C]	*Resistivity, ρ (Ohm.m)*	*Conductivity, σ (Siemens/meter*
As deposited	*2.01E+10*	*4.97E-11*
350	*1.99E+10*	*5.02E-11*
450	*1.81E+10*	*5.52E-11*
550	*1.49E+10*	*6.71E-11*

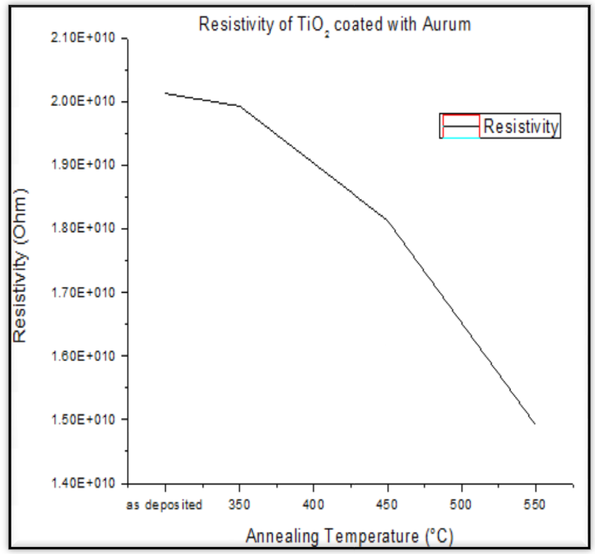


Figure 5: Resistivity of nanostructured TiO_2 thin films annealed at different temperatures

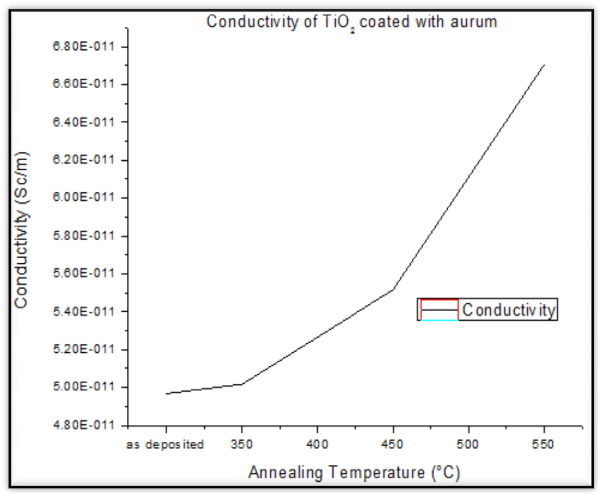


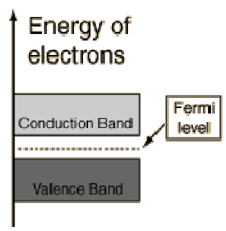
Figure 6: Conductivity of nanostructured TiO_2 thin films annealed at different temperatures

Conductivity of the TiO_2 thin film is the reciprocal (inverse) of resistivity, ρ, and has the SI units of siemens per metre ($S \cdot m^{-1}$). The relationship between resistivity and conductivity is shown by the following equation:

$$\sigma = \frac{1}{\rho} \qquad (2)$$

Where σ = conductivity
ρ = resistivity

From figure 6 and Table 1, it can be seen that the conductivity of TiO_2 thin films increased as the annealing temperature increased. This is due to decrease of resistivity which affected by grain size of TiO_2 as explained earlier. In terms of the band theory of solids, the conduction process is whether or not there are electrons in the conduction band; more electrons on conduction band more conductive a material is. Conductivity is increased when electrons in valence band supplied with external energy so that the electrons have enough energy to excite into conduction band [15].



The least conductive thin film is as deposited thin film. This thin film was not been applied with any heat treatment which means no additional energy applied to electrons at valence band. There are more electrons at valence band than conduction band so the conductivity is low.

The samples were annealed from 350°C until 550°C indicate improvements of conductivity according to the temperature applied. The highest conductivity can be found at thin film of 550°C which is the highest annealing temperature. This is because more energy supplied from the heat to the electrons making it easier to excite into conduction band.

6.2 Optical Properties of TiO_2 Thin Film

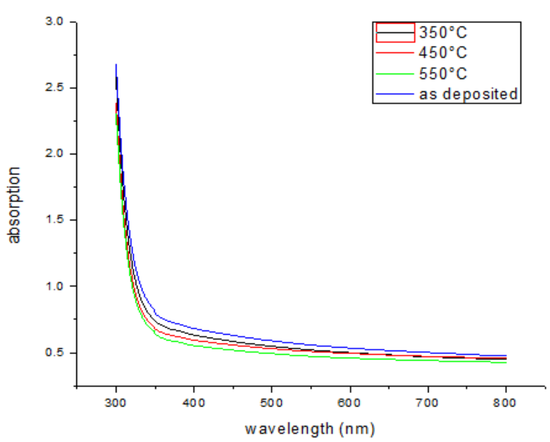


Figure 7: Absorption spectra

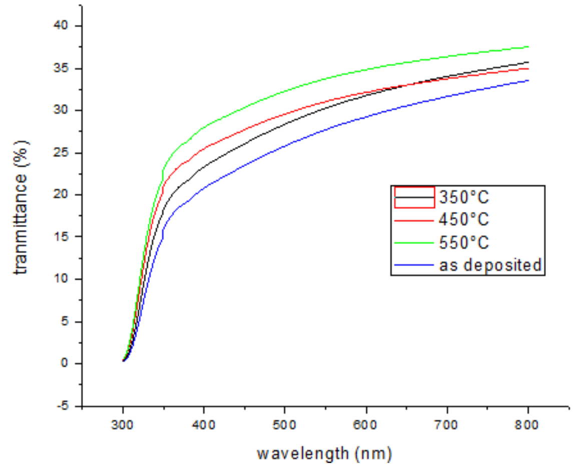


Figure 8: Transmittance spectra

The optical properties of TiO_2 thin films were observed using UV-Vis spectroscopy. From the results collected, it shows that the optical transmittance spectra of the thin films exhibited a transmission of only 25% to 35% in the visible region (400nm-800nm). The thin film annealed at 550°C has the highest value of transmission followed by 450°C, 350°C and as deposited. It is found that as the annealing temperature increase, the transmittance properties also increase. However; based on a study by P. Sudhagar et al; the transmittance supposedly to be decrease as the annealing temperature increase due to the annihilation of porous surface as result of the particles growth and densification [13]. This can be caused by cracks occurred in thin films which resulted from acids used in solution preparation and overheat on the thin films. These cracks may have influenced the growth and densification of particles of the thin films.

6.3 Structural Properties of TiO_2 Thin Film

6.3.1 Surface Topography

The surface topography of the thin films was observed by using Atomic Force Microscope (AFM). From the figures, it can be observed that recrystallization occurred due to annealing treatment. The surface of as deposited thin film is bulky, smooth and not uniform. As annealing temperatures increase, the surface topography of thin films becomes more uniform and the grain size becomes larger. From AFM, it also can be observed that the roughness of surface increased and the height variation becomes much larger as the annealing temperature increased. This trend is especially obvious when annealing temperature is 550°C. This can be related to high conductivity of this thin film. The more uniform and bigger grains produce better electron migration.

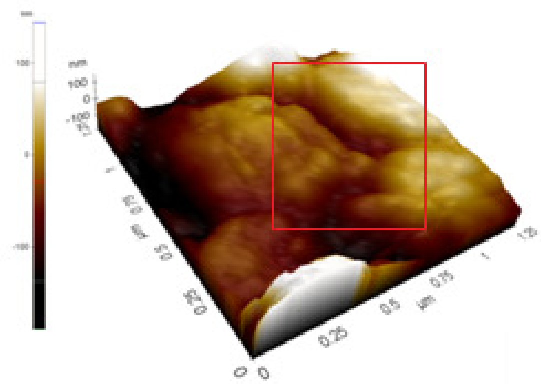


Figure 9: As deposited

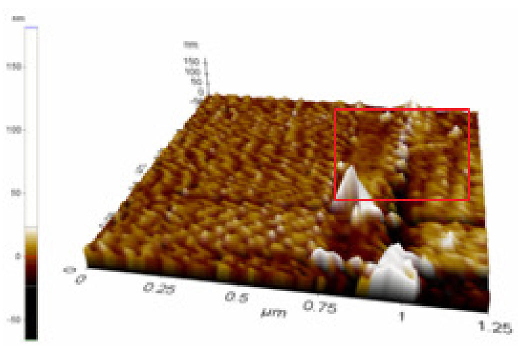


Figure 10: 350°C

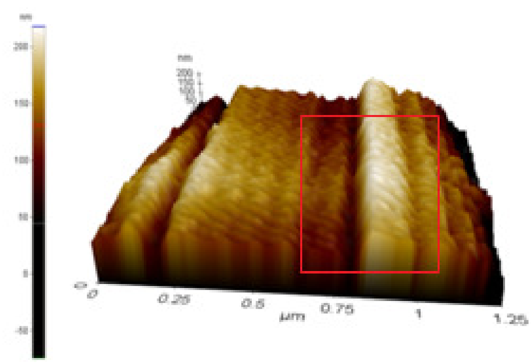


Figure 12: 450°C

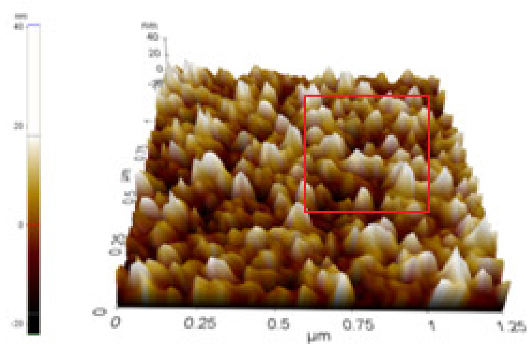


Figure 12: 550°C

6.3.2 Surface Morphology

The surface morphology of the thin films was observed by using Scanning Electron Microscopy (SEM). The SEM images show that the presence of TiO_2 nanoparticles combined together and formed a thin film. Based on the observation, the cluster size is starting to reduce as the annealing temperature increased. Hence**,** high electrical properties can be obtained. The crystalline clusters will give high quality in electrical properties due to electron in the thin film which can easily move to one another.

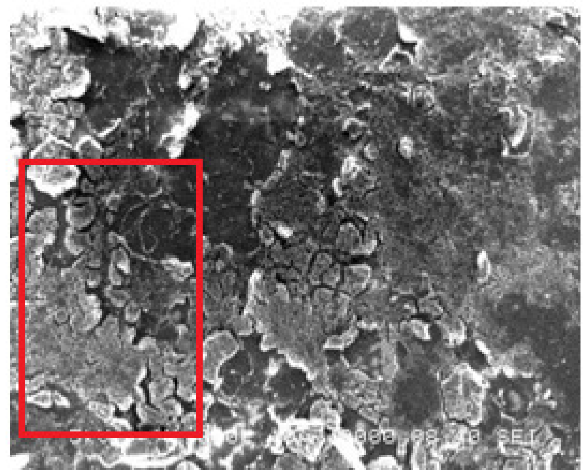


Figure 13: As deposited at magnifier of 1kx

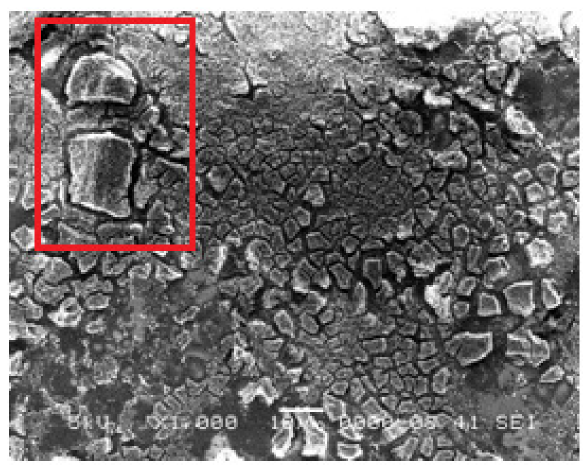


Figure 14: 350°C at magnifier of 1kx

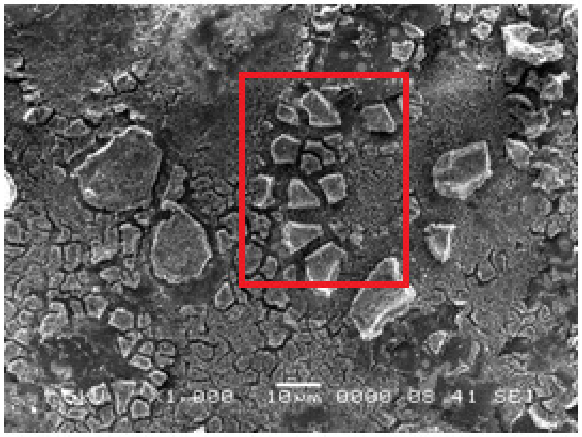


Figure 15: 450°C at magnifier of 1kx

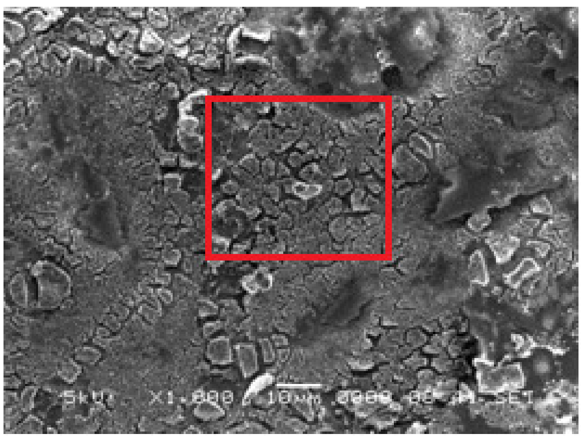


Figure 16: 550°C at magnifier of 1kx

7. Conclusion

A nanostructured Titanium Dioxide thin film has been successfully synthesized by depositing TiO_2 solution; which prepared by sol-gel method; onto glass substrates by using spin coating technique. These thin films were annealed at different temperature except one. The electrical, optical, and structural properties of TiO_2 thin films were investigated and analyzed.

For electrical properties, it can be concluded that the resistivity of TiO_2 thin films decreased and the conductivity increase as the annealing temperature increased. Hence, the most conductive sample is thin film annealed at 550°C. Meanwhile, the 550°C thin film also give the most transmission value in optical properties. It is believed that when temperature increases, the transmittance also increase. As for the surface topography, the trend of uniformity and roughness is increasing as the annealing temperatures increase, thus giving the 550°C thin film as the most uniform surface topography. The SEM images illustrate that increasing temperatures will produce smaller cluster size but overheating may produce cracks.

The major observations of this study can be summarized as annealing treatment applied clearly affecting the properties of TiO_2 thin films. These changes of properties concluded as due to the growth of grains size of the films. As the temperature increase the grains size also increase which leads to a decrease in grain boundaries. But, overheating these thin films can caused cracks and may affect the properties in different ways. These thin films with large grains size of are preferred for use in solar cell application.

8. Future Development

In order to improve the properties of TiO_2 thin films, an improve solution preparation method is therefore necessary such as varying the materials used. Using better deposition technique could also produce better film characteristics. For example, varying the parameters for the spin coating or change to another technique like dip-coating.

9. Acknowledgement

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