APPENDIX A

INVESTIGATION ON P-N JUNCTION *I-V* CHARACTERISTICS OF p-Si/n-TiO_2

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Abstract— **The effect of annealing time on electrical properties and physical properties (surface morphology) of p-n junction between p-type silicon (Si) and n-type titanium oxide (TiO_2) were investigated. By varying the parameter of the annealing time, the TiO_2 thin films were deposited on silicon and glass substrates by using spin coating technique. Characterization were done using current-voltage *(I-V)* measurement, atomic force microscope (AFM) and Field Emission Scanning Electron Microscope (FESEM).The TiO_2 thin films were annealed at the 450°C. The annealing time varies from 30, 40, 60, 80, and 100 of minutes. The *(I-V)* measurement showed that at 80 minutes annealing time, the conductivity is higher than other annealing time. The AFM investigation showed roughness of thin film increase with longer annealing time. The result showed that the electrical properties and surface morphology of TiO_2 could be affected by changing the annealing time.**

Keywords—**PN Junction, Titanium Dioxide thin film, spin coating, annealing process.**

I. INTRODUCTION

The Titanium Dioxide (TiO_2) was of one of the most widely studied due to physical, optical and electrical properties and has many important applications such as solar cell, and sensor [1]. The TiO_2 are widely used in our life, such as pigment [2], in sunscreens [3, 4] paints [5], and toothpaste [6]. The transparent thin film of TiO_2 can be applied for coating such as for a solar cell application and self-cleaning glass. The research on TiO_2 solar cells are done because of the low cost and easy to fabricated [7]. Additionally there are many method to prepared the TiO_2 film such as thermal [8] or anodic [9] oxidation of titanium, electron beam evaporation [10], ion sputtering [11], chemical vapor deposition [12], including plasma-enhanced chemical vapor deposition [13] and the Sol-gel method [14, 15]. The sol-gel method has emerged as one of the most promising methods that will give sample with good homogeneity at low cost. Besides that preparing TiO_2 by the Sol - gel method, is not difficult, easy to control and low cost compared by using the physical vapor deposition (PVD) technique.

Since this research is done by sol-gel method or solution process, it has all the advantages over other method in term of purity, homogeneity, felicity and flexibility in introducing dopants in large concentration. According to Nafarizal Nayan et. Al., the annealing process and the number of layer are resulting have changing of crystalline and surface morphology of TiO_2 thin film. It says that, in XRD spectra of nanostructured TiO_2 thin film show the annealing process gives anatase structure [16]. Previous studies have shown the TiO_2 thin film have high band gap about (3.2-329) eV, and need (3.69-3.78) eV for allowed and forbidden direct transition [17].Pure TiO_2 has low conductivity due increasing the porosity will let less contact between the particles and less surface area for electron flow [18].

In this work the effect of annealing time on p-n junction p-Si/n-TiO_2 were studied. The TiO_2 thin film were prepared using sol-gel method and using spin coating technique on silicon and glass substrate. The annealing time were varied at 30,40,60,80 and 100 minute. The characterizations on electrical and physical were measure using solar simulator, Atomic Force Microscope (AFM) and Field Emission Scanning Electron Microscope (FESEM).

II. EXPERIMENTAL PROCEDURE

A. Preparation of substrate

The substrate used in this experiment is microscope glass and silicon p-type. The silicon and glass substrate were treated with acetone, methanol and distilled water in ultrasonic bath for 10 minutes each to remove the any particle on substrate. For the silicon substrate only, need to dip into hydrofluoric acid solution with ratio 1:10 (acid: water).Then, the glass and silicon substrate were blow with nitrogen gas for drying purpose and placing the substrate in sample holder.

B. TiO_2 solution

Using a sol-gel technique, TiO_2 thin film was prepared by mixing solution A and solution B. The solution A was prepared by mixing the 17.29ml absolute ethanol, 5.72ml nitric acid and 0.74ml of titanium Isopropoxide. The solution A was stir with 600rpm about 10 minute. Solution B that contains of 17.29ml absolute ethanol 4ml deionized water and one drop of triton x-100 need to mixing onto solution A after done with 10 minute. Then the solution was continuously stirred for 3 hours at room temperature.

C. Deposition of TiO_2 thin film

The TiO_2 solution was deposited onto substrate by using spin coating technique. The spin coater was set at 3000 rpm and drops the solution for 10 times by using a dropper. After that, the samples were heated at 100 °C for 10 minute to dry the thin film in furnace. The process of coating and heating was repeated by five times. After that, the sample was carried to annealing process at 450 °C in difference minutes. The TiO_2 thin film were annealing at 450 °C for 30, 40, 60, 80, and 100 minutes.

D. Characterization on physical properties

The surface topology of TiO_2 thin film was characterizes used Atomic force microscope (AFM) at the room temperature. The AFM gives the information about the roughness of the TiO_2 thin film. The thickness of TiO_2 thin film was measured by using Veeco Dektak 150.

E. Characterization on Field Emission Scanning Electron Microscope (FESEM)

Besides that TiO_2 thin film also was characterizes using Field Emission Scanning Electron Microscope (FESEM) to determine the surface morphology.

F. Characterization on UV-VIS spectrometer

The optical transmission spectra were recorded in the range from 200nm to 800nm by using UV-VIS spectrometer. From the information of the transmittance by plotting the graph between $(ahv)^2$ versus hv. The ahv is an optical band gap meanwhile hv is photon energy.

G. Chacterization on Current Voltage

The electrical properties of p-n junction p-Si/n-TiO_2 are measure using current-voltage *(IV)* measurement. 2-point probe that connected to a source meter was used to measure the *I-V* p-n junction p-Si/n-TiO_2 . Figure 1 below shows the schematic structure of the TiO_2 thin films which has gold (Au) on top of the thin film, which is used as a metal contact for *I-V* measurement. The process deposit Au metal on the silicon substrate is set at 60nm thickness by using electron beam thermal evaporation machine.

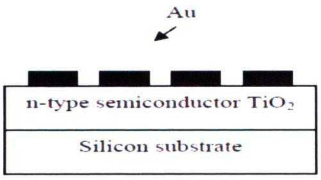


Figure 1. Diagram of Au metal contact on the silicon substate

From the *I-V* curve, the information of resistivity and conductivity can be obtained from equation in Table 1.

TABLE 1. EQUATION FOR RESISTIVITY AND CONDUCTIVITY

RESISTIVITY	$p = \frac{Rwt}{L}(\Omega.cm)$
CONDUCTIVITY	$\sigma = \frac{1}{\rho}(\Omega.cm)^{-1}$

The value of resistance is obtaining from the gradient of IV curve. Where the ρ is resistivity, W and L is a width and length of metal contact and t is thickness of the thin film. The conductivity is inverse of resistivity that show ability of material conduct electric.

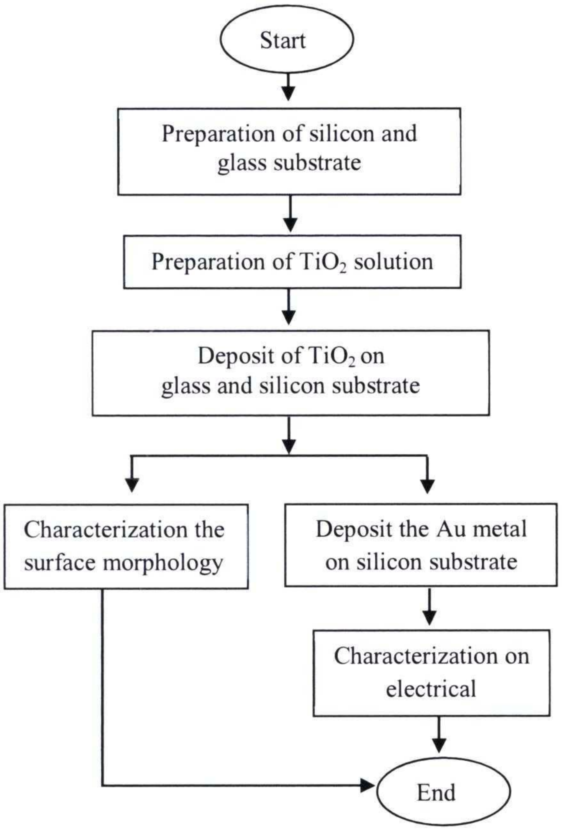


Figure 2 shows the experiment procedure to prepare the samples.

III. RESULT AND DISCUSSION

A. Electrical Properties

Figure 3 shows the graphs of electrical properties of TiO_2 thin film deposited on silicon substrate. The film exhibited diode properties due to p-n junction or called depletion region is created between TiO_2 thin film and p-type silicon substrate. Figure 3 (a), (b), (c), (d), and (e) shows the *I-V* measurement at annealing 30, 40, 60, 80 and 100 minutes. Figure 3 (a), (b), (c), (d), and (e) shows the *I-V* curve under illumination have high current compare with dark. This happen due to the electron gain energy by absorbing the light [19].The process measurement under illumination, the UV light passes through the TiO_2 thin film and generate the electron –hole pair when the energy of the UV light is absorbed [19].The result at 30 minutes annealing time exhibit more p-n junction behavior compare with other annealing time .During the TiO_2 thin film annealing for 40 minute, there are huge difference of current on the current under illumination and dark. Figure 3 shows that, the 80 minute annealing time gives the high current compare other minute. The sample that anneal at 80 minute annealing time, behaves as a resistor due to the insufficient hole- blocking [20].

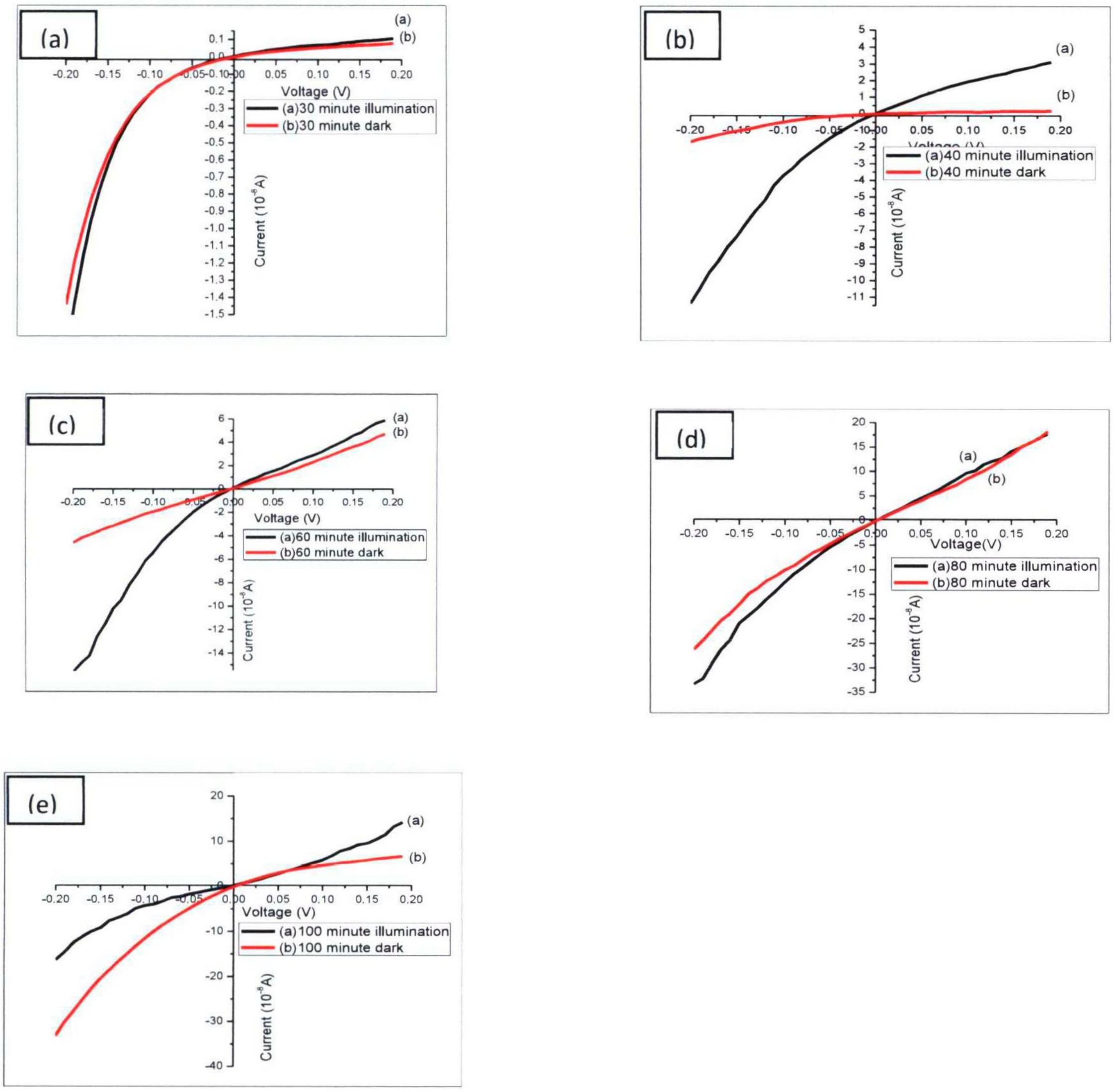


Figure 3. (a),(b),(c),(d),(e) i-v characteristics TiO_2 thin film deposited on silicon substrate at 30,40,60,80 and 100 minutes.

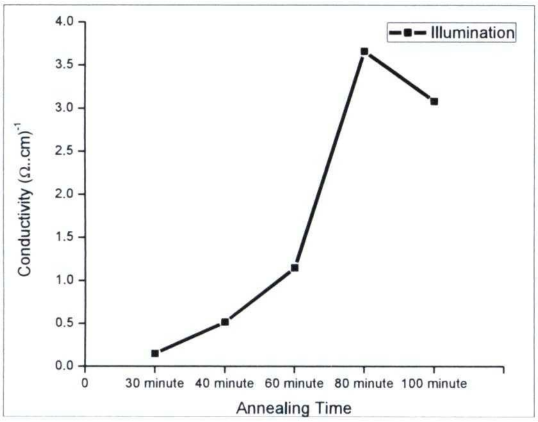
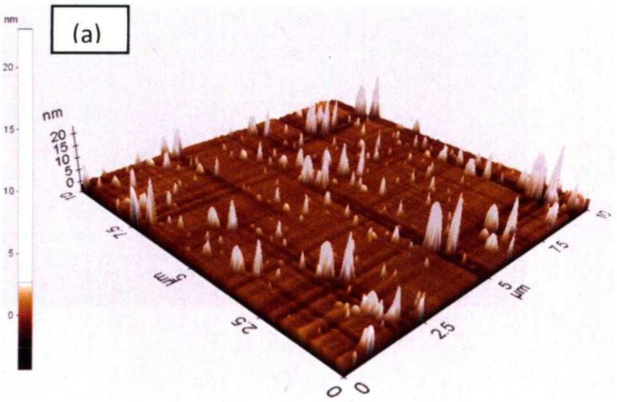


Figure 4. Conductivity of 30,40,60,80 and 100 minute annealing time

Figure 4 shows the conductivity of the 30, 40, 60, 80, and 100 minute annealing time. From the figure, it shows that increasing the annealing time to 80 minutes increased the conductivity of TiO_2 thin films due to grain size were improve with longer period of the annealing time. At the 100 minutes annealing time, the conductivity of the TiO_2 thin films decreased due to the TiO_2 thin films became rougher and decrease the contact surface of the thin film. The electrical properties decreased due to the electron mobility decrease with less contact surface of TiO_2 thin films.

B. Surface topology

Figure 5 shows the surface topology of TiO_2 thin films on the silicon substrate. From the image of AFM, the surfaces of TiO_2 thin films are changings due to the influence of annealing time. From the images, the sample with 100 minutes annealing time has more peak structure compared with 30 minutes annealing time.



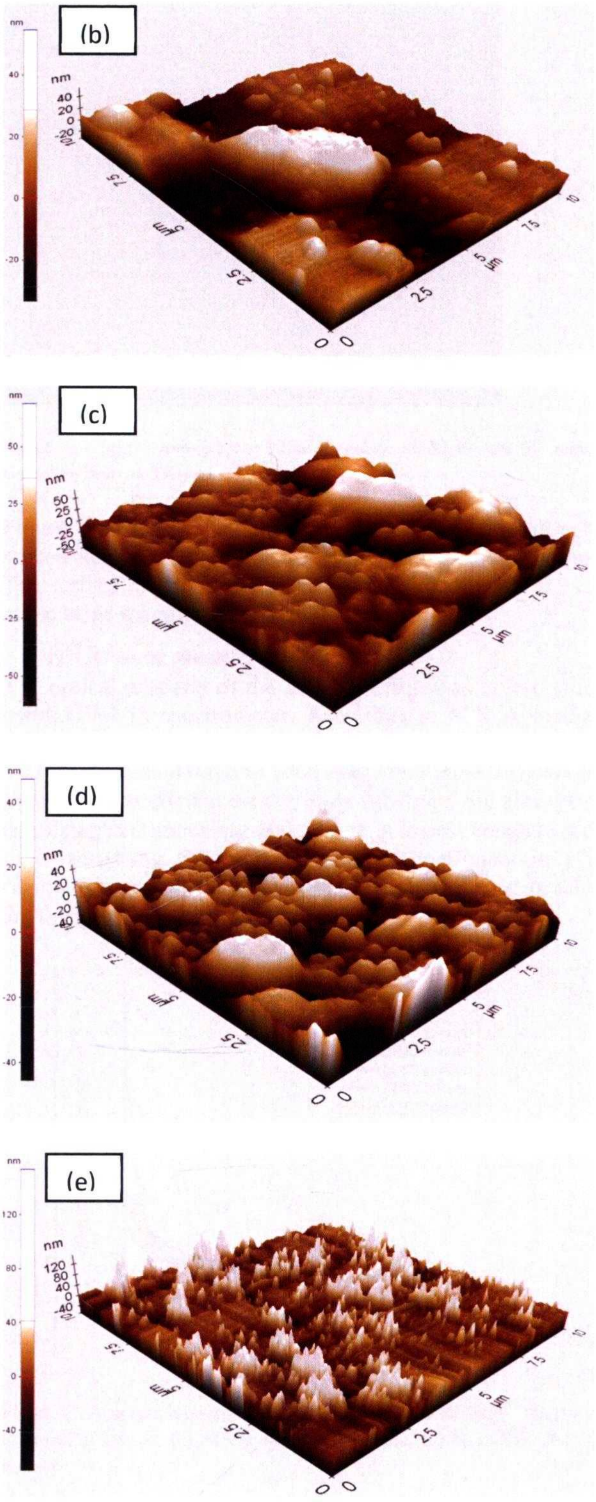


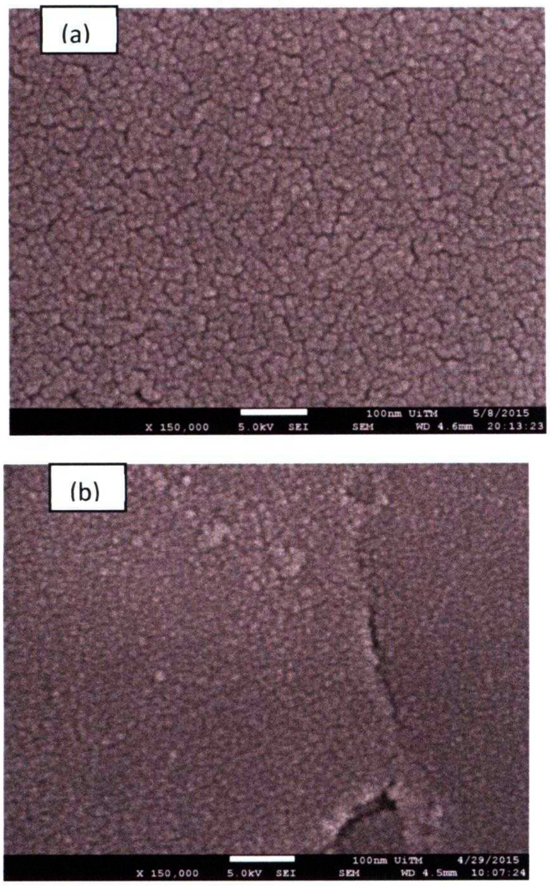
Figure 5. (a),(b),(c),(d) and (e) are AFM image at 30,40,60,80 and 100 minute annealing time on TiO_2 thin film.

TABLE 2. SURFACE ROUGHNESS AND THICKNESS OF THIN FLIM

	30 minute	40 minute	60 minute	80 minute	100 minute
Surface roughness (nm)	0.522	9.193	11.268	13.096	14.096
Thickness (nm)	83.87	73.34	62.69	57.32	52.01

Table 2 shows that, the surface roughness and thickness of TiO_2 thin film. The roughness of the TiO_2 thin film was measured by using AFM. The roughness of TiO_2 thin film is increase within increasing of annealing time. The increasing roughness of TiO_2 thin film is due to the increasing of grain size on the TiO_2 thin film. The thickness was decreasing within increasing of annealing temperature.

C. Surface morphology



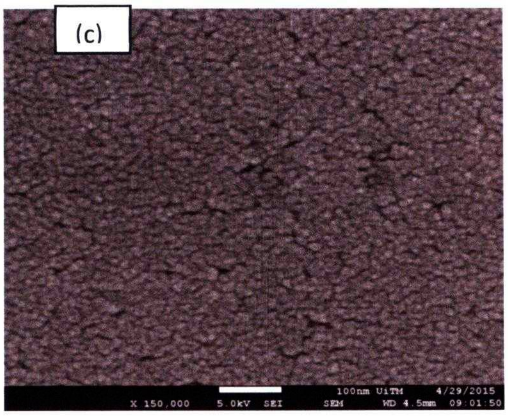


Figure 6. (a),(b) and (c) are FESEM image at 30,40 and 60 minute annealing time on TiO_2 thin film

Figure 6 shows the FESEM images of TiO_2 thin film on silicon substrate at 30, 40 and 60 minute annealing time. The surface morphology of the TiO_2 thin film was observed at the same magnification 150000.

D. Uv-vist measurement

The optical property of the TiO_2 thin film was investigating using UV-VIS spectrometer. According to M.K Ahmad et. Al, the range of visible region in transmission spectra of the TiO_2 is between 450nm to 1000 nm [21]. Figure 7 shows the absorption coefficient on the glass substrate, the absorption coefficient for annealing 100 minute is lowest compare with other annealing time. The absorption coefficient in UV-region decreased with increasing of annealing time, because the thicknesses of thin film were decrease.

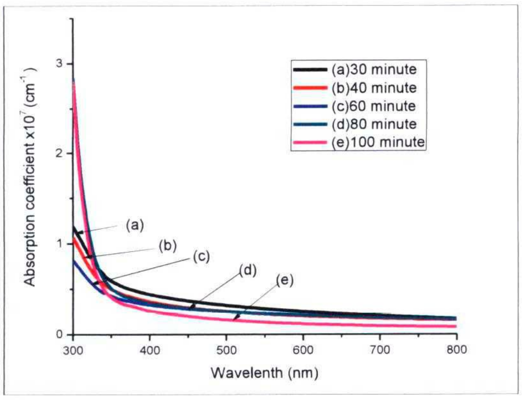


Figure 7. Absorption coefficient of TiO_2 thin film at difference annealing time (a) 30 minute, (b) 40 minute, (c) 60 minute, (d) 80 minute and 100 minute.

According to Young Ug Ahn et al, the TiO_2 thin film prepared at 400-600°c have high transparency in visible range of light [22].

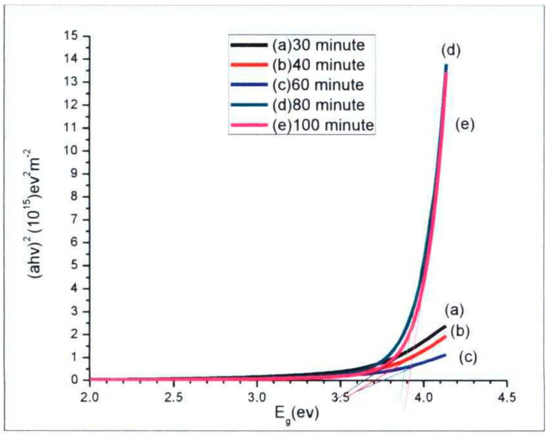


Figure 8. Energy band gap for 30,40,60,80 and 100 minute annealing time.

Figure 8 above show the energy band gap of the TiO_2 that annealing at difference time. The energy band gap graph (Eg) can be estimated by plotting $(ahv)^2$ versus hv. Extrapolating the straight line part of the plot to the photon energy axis. The energy band gaps for annealing process are given in Table 3 .Tables 3 shows the increasing of the band gap within increasing of the annealing time.

TABLE 3. ENERGY BAND GAP FOR TIO_2 THIN FILM

Annealing Time (minute)	Energy band gap (ev)
30	3.6
40	3.65
60	3.7
80	3.85
100	3.9

IV. CONCLUSION

TiO_2 thin films have been successfully deposited onto silicon and glass substrates by the spin coating technique and annealed at different minutes. The surface topology, electrical properties and surface morphology of the TiO_2 thin film were investigated by using AFM, IV measurement and FESEM. For electrical properties, the current intensity increase from 30 minute to 80 minute annealing time, but decrease at 100 minute annealing time. It can be concluded that, the increasing of the annealing time will decrease the resistance value but at the some point the resistance will increase again due to the surface to roughness and decrease of the contact surface. The sample at 30 minutes annealing time exhibit more p-n junction behavior compare to other annealing time. From the surface topology, within increasing of annealing time, the roughness of the TiO_2 thin film will increase. By referring the electrical properties and surface topology, the TiO_2 thin film is suitable to be used as solar application and as photodiode. The result of *I-V* curve shows that the TiO_2 thin films react well with illumination light and dark.

FUTURE RECOMMENDATION

Based on investigation has been done, there are several recommendation to improve the electrical and physical properties by considering using TiO_2 doped with Copper (Cu). By doping process the photocatalytic will improve over using pure TiO_2 nanoparticles.

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REFERENCES

[1] X. Chen and S. S. Mao, "Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications," *Chemical reviews,* vol. 107, pp. 2891-2959, 2007.

[2] G. Pfaff and P. Reynders, "Angle-dependent optical effects deriving from submicron structures of films and pigments," *Chemical reviews,* vol. 99, pp. 1963-1982, 1999.

[3] L. Liu and X. Chen, "Review pubs. acs. org/CR Titanium Dioxide Nanomaterials: Self-Structural Modi? cations."

[4] R. Zallen and M. Moret, "The optical absorption edge of brookite TiO_2," *Solid State Communications,* vol. 137, pp. 154-157, 2006.

[5] J. H. Braun, A. Baidins, and R. E. Marganski, " TiO_2 pigment technology: a review," *Progress in organic coatings,* vol. 20, pp. 105-138, 1992.

[6] X. Chen, M. Schriver, T. Suen, and S. S. Mao, "Fabrication of 10 nm diameter TiO_2 nanotube arrays by titanium anodization," *Thin Solid Films,* vol. 515, pp. 8511-8514, 2007.

[7] V. Thavasi, V. Renugopalakrishnan, R. Jose, and S. Ramakrishna, "Controlled electron injection and transport at materials interfaces in dye sensitized solar cells," *Materials Science and Engineering: R: Reports,* vol. 63, pp. 81-99, 2009.

[8] M. Kozlowski, P. Tyler, W. Smyrl, and R. Atanasoski, "Anodic TiO2 Thin Films Photoelectrochemical, Electrochemical, and Structural Study of Heat-Treated and Modified Films," *Journal of The Electrochemical Society,* vol. 136, pp. 442-450, 1989.

[9] H. Kangarloo, S. Rafizadeh, and B. Salami, "Optical properties of titanium oxide nano layers," in *Proceedings of the 3rd WSEAS international conference on Engineering mechanics, structures, engineering geology,* 2010, pp. 305-309.

[10] M. Lottiaux, C. Boulesteix, G. Nihoul, F. Varnier, F. Flory, R. Galindo, *et al.,* "Morphology and structure of TiO_2 thin layers< i> vs.</i> thickness and substrate temperature," *Thin solid films,* vol. 170, pp. 107-126, 1989.

[11] A. Benyoucef, A. Benyoucef, F. Lapostolle, D. Klein, and B. Benyoucef, "Structural and morphological study of TiO2 magnetron sputtering thin film for a photovoltaic application," *Revue des Energies Renouvelables ICRESD-07 Tlemcen,* pp. 61-65, 2007.

[12] K. Yeung and Y. Lam, "A simple chemical vapour deposition method for depositing thin TiO_2 films," *Thin Solid Films,* vol. 109, pp. 169-178, 1983.

[13] L. Williams and D. Hess, "Photoelectrochemical properties of plasma-deposited TiO_2 thin films," *Thin Solid Films,* vol. 115, pp. 13-18, 1984.

[14] J. Livage, "Sol-gel chemistry and electrochemical properties of vanadium oxide gels," *Solid state ionics,* vol. 86, pp. 935-942, 1996.

[15] B. A. Morales, O. Novaro, T. Lopez, E. Sanchez, and R. Gomez, "Effect of hydrolysis catalyst on the Ti deficiency and crystallite size of sol-gel-TiO2 crystalline phases," *Journal of materials research,* vol. 10, pp. 2788-2796, 1995.

[16] I. Senain, N. Nayan, and H. Saim, "Structural and electrical properties of TiO2 thin film derived from Sol-Gel method using titanium (IV) butoxide," *International Journal of Integrated Engineering,* vol. 3, pp. 1-35, 2010.

[17] Y. Chiba, A. Islam, Y. Watanabe, R. Komiya, N. Koide, and L. Han, "Dye-sensitized solar cells with conversion efficiency of 11.1%," *Japanese Journal of Applied Physics,* vol. 45, p. L638, 2006.

[18] M. A. Anderson and H. Kikkawa, "Titanium Dioxide Ceramic Membrane Made More Electroconductive By Incorporation Of Niobium Dopant," ed: Google Patents, 1991.

[19] T.-Y. Tsai, S.-J. Chang, T.-J. Hsueh, H.-T. Hsueh, W.-Y. Weng, C.-L. Hsu, *et al.*, "p-Cu2O-shell/n-TiO2-nanowire-core heterostucture photodiodes," *Nanoscale research letters,* vol. 6, pp. 1-7, 2011.

[20] J. Jhaveri, S. Avasthi, G. Man, W. E. McClain, K. Nagamatsu, A. Kahn, *et al.*, "Hole-Blocking Crystalline-Silicon/Titanium-Oxide Heterojunction with Very Low Interface Recombination Velocity," in *Photovoltaic Specialists Conference, 20l3., Conference Record of the Thirty Ninth IEEE*, 2013, p. 2923296.

[21] M. K. Ahmad, N. Rasheid, W. Zaki, W. Suhaimizan, A. Zain Ahmed, S. Abdullah, *et al.*, "Fabrication of transparent titanium dioxide thin film at low temperature by Sol-gel Spin Coating Method."

[22] L. R. Paez and J. Matousek, "Properties of sol-gel TiO~2 layers on glass substrate," *CERAMICS SILIKATY,* vol. 48, pp. 66 71, 2004