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RESEARCH ARTICLE

FABRICATION OF ZnO/Cu₂O AND TiO₂/Cu₂O HETEROJUNCTION SOLAR CELL USING SPRAY PYROLYSIS METHOD.

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Abstract

FTO-ZnO/Cu₂O-Cu and FTO-TiO₂/Cu₂O-Cu Solar cells were fabricated by electrodeposition of Cu₂O on the sprayed ZnO and TiO₂ films. The compositional, optical as well as electrical properties of the cell were studied using EDX, UV-Visible and Solar simulator respectively. The optical measurement shows that both ZnO and TiO₂ have higher transmittance when compared to Cu₂O. The band gap of Cu₂O, TiO₂, and ZnO, were found to be 2.32eV, 3.7eV and 3.75eV respectively. I-V characteristic curve confirm the rectifying behavior of the cells. The short circuit current density, open circuit voltage and efficiency of the cells were measured to be 0.093μA/cm², 0.0364V, 0.0076% and 5.8μA/cm², 0.03V, 0.037% for FTO-ZnO/Cu₂O-Cu and FTO-TiO₂/Cu₂O-Cu cells respectively.

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Introduction:-

Semiconductors oxides have attracted attention due to their potentials to serve as an alternative to silicon based solar cells, (Zulkiflee et al., 2016), (Fujimoto et al., 2013), (Jayathileke et al., 2007). Cu₂O is mostly p-type semiconductor oxides, having a cubic crystal structure with a space group of Pn3m, its direct band gap of 2.1eV make it possible to possess high optical absorption property in visible spectrum thereby become suitable material for high efficient solar cells. Moreover, Cu₂O is nontoxic, inexpensive, readily available and have low production costs which satisfy the environmental and economical requirements needed for large-scale applications in solar cell devices, gas and humidity sensors etc (Zulkiflee et al., 2016), (Jayathileke et al., 2007), (Pavan et al., 2015), (Saehana and Muslimin, 2013). Nowadays interest is focused on metal oxides heterojunction solar cell because of their advantage of a low price compared with silicon base solar cell (Pavan et al., 2015). Among the metal oxides materials, ZnO emerge to be a good candidate because of its peculiar properties over others, as they serve as a window layer to the Cu₂O layer. ZnO is a good electron acceptor n-types semiconducting material with a wide band gap ranged from 3.1eV to 3.37eV (Sharma, et al., 2012). This property enables it to have a reasonable number of applications in science and technological world such as optoelectronic devices (Light emitting diode, laser diode, photoelectrons, transistors etc) and solar cell (Fujimoto et al., 2013), (Abdullahi et al., 2016). Moreover, its free exciton binding energy of 60eV and transparency in 0.4-2μm optical wavelength range gives it more possibility to be utilized as liquid crystal display devices, electro luminescence and also as transparent conducting oxide materials (Chen, et al., 2009), (Kurunakaran, et al., 2011). In a similar manner, TiO₂ is a famous n-types materials with the wide band gap of more than 3eV having diverse functionalities as well as being a high efficient crystallites material with high dielectric constant.

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These materials can be utilized as microelectronic devices, photocatalyst, and also used as a heterojunction solar cell devices. (Zulkiflee et al., 2016), (Fujimoto et al., 2013), (Palmieri, et al., 2008), (Gu et al., 2013). With these remarkable properties and in line with its high index of refraction of 2.7 give it more chance of usage as multi layer interference filter, antireflection coating, optical wave guide as well as window layer to the high absorber layer material for solar cell applications (Oku et al., 2014), (Siripala et al., 2003), (Chergui et al., 2011). Many heterojunction solar cells made of Cu_2O have been reported using different methods. However, the efficiency of the cell is not that much. 0.15% efficient p- Cu_2O /n- TiO_2 thin film heterojunction solar cell has been fabricated using electrodeposition by (Hussain et al., 2012). (Saehana and Muslimin, 2013) reported 1.05% Performance improvement of $\text{Cu}_2\text{O}/\text{TiO}_2$ heterojunction solar cell by employing polymer electrolytes. (Minima et al., 2006) reported 1.4 and 1.52% $\text{ZnO}/\text{Cu}_2\text{O}$ solar cell using PLD and VAPE respectively. This work reported $\text{Cu}_2\text{O}/\text{ZnO}$ and $\text{Cu}_2\text{O}/\text{TiO}_2$ solar cells using spray pyrolysis method. This is due to its low cost process, easy means of deposition that can be up scale for the large area and vacuum medium is not needed during the deposition process.

Experimental:-

Cleaning step:-

Before the deposition, the substrate was emerged in to a sonicator containing 1g of Sodium loren sulphate mixed with distilled water for 6minutes followed by refluxing it with methanol using the sochcelet extractor to avoid any contamination. The bottle for the solvents was rinsed with the ethanol to remove any impurities.

Preparation of ZnO and TiO_2 films:-

N-type ZnO film is prepared first using 0.1M Zinc acetate (BDH) mixed with 50ml of pure ethanol, the mixture was stirred using a magnetic stirrer until the solute dissolved completely, 400 microliter of the solution was sprayed on top of FTO glass using electro dynamic spray pyrolysis machine at the rate of 2400 microlit/hr and a temp of 350°C. Similarly, TiO_2 film was prepared using 0.05M Titanium chloride (BDH) with 50ml of pure ethanol. The mixture was stirred using a magnetic stirrer and centrifuge for 20 minutes until all the titanium chloride dissolved completely, 400 microliter of the solution was sprayed on top of FTO glass substrate using electro dynamic spray pyrolysis machine at the rate of 2400 microlit/hr and a temperature of 450°C. For both ZnO and TiO_2 , the distance between the spray nozzle to the substrate was 8mm and the atomization voltage of 3500V was used.

Preparation of FTO-ZnO/ Cu_2O -Cu and FTO- TiO_2 / Cu_2O -Cu solar cells:-

P-type Cu_2O was electrodeposited on top of both ZnO and TiO_2 thin layers with 0.05M cupric sulfate and 3.0M lactic acid solution at a bath temperature of 60°C and electrodeposition potential of -0.6 mV for 20min. The pH was adjusted to 9 with the help of 0.1M NaOH. A graphite rod is served as a counter electrode and Ag/AgCl acted as a reference electrode. After deposition the samples were rinsed with distilled water, dried in air and a copper contact was stuck on the Cu_2O thin layer.

Results and discussion:-

EDX measurement:-

Prior to the completion of the cell deposition, the elemental analysis of ZnO and TiO_2 films was performed using Energy Dispersive X-ray (EDX) spectroscopy. Figure 1 show the EDX spectra of the films. The results comply with what is expected from the films deposition where by the composition of all the films deposited tallies with the outcomes of the EDX spectra. The spectrum contains all the expected elements and no impurity was found.

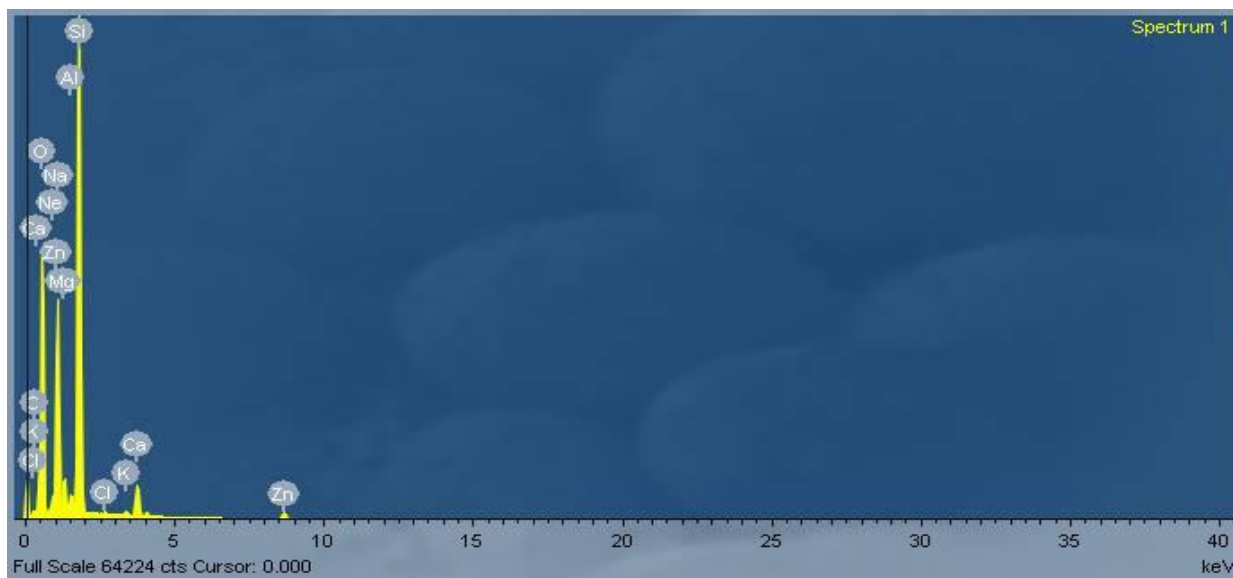


Figure 1a:- EDX Measurement of ZnO film

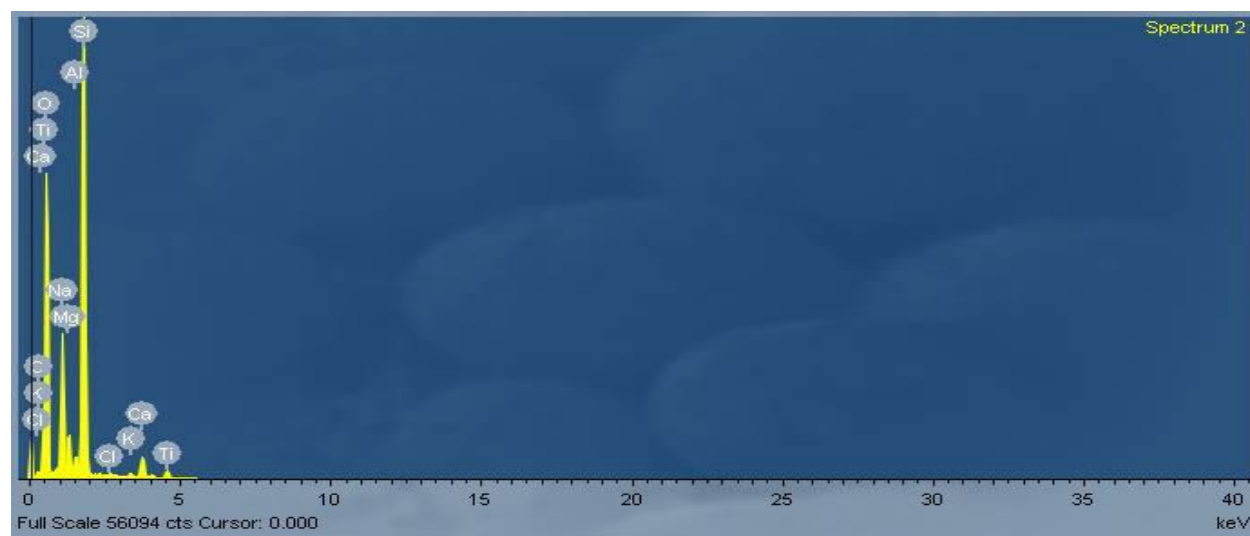


Figure 1(b):- EDX Measurement of TiO₂ film

Measurement of the thickness of the film:-

To measure the thickness of the film we used profilometer. The result is shown in figure 2(a) and (b) where the difference of height between the substrate and zone of the film covered gives the thickness of the film. It can be seen clearly from figure 2(a) and (b) that the difference is almost 100nm and 40nm for ZnO and TiO₂ respectively which show that the films are within nanometric scale.

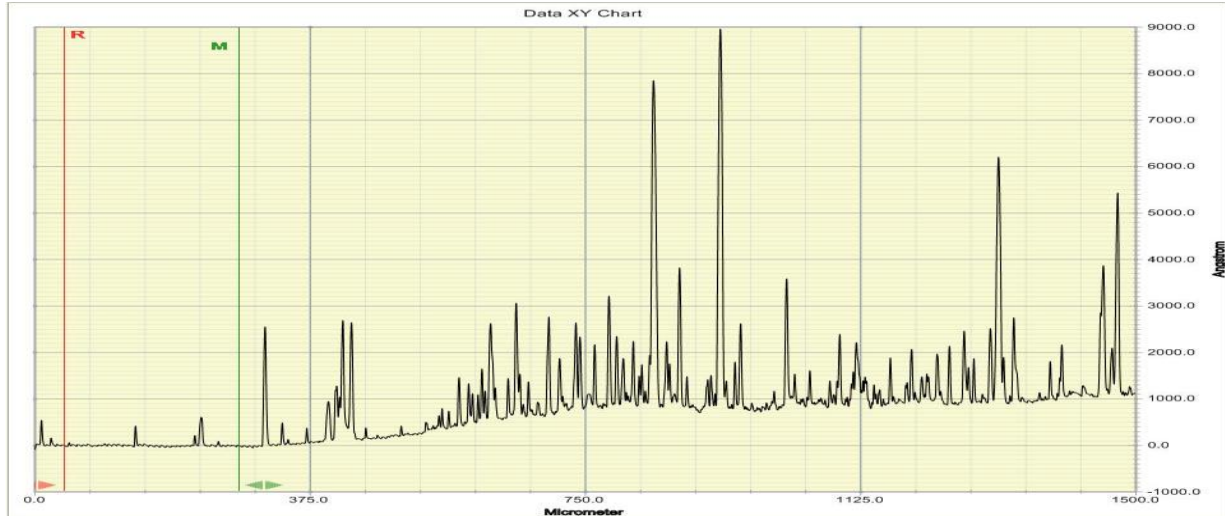
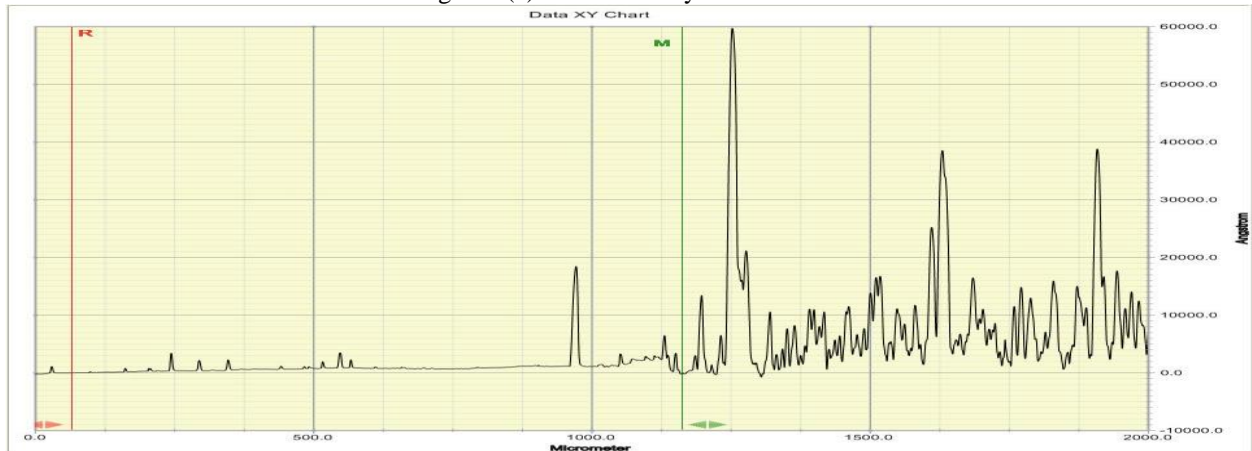


Figure 2(a): Profilometry of ZnO film

Figure 2:- (b) Profilometry of TiO₂ film

UV-Vis Spectroscopy:-

UV-Visible spectroscopy is used to study the optical transmittance, and band gap values, (E_g) of ZnO TiO₂ and Cu₂O films. The optical transmittance of the samples measured in the range of wavelength 250 to 1000nm reveals that ZnO and TiO₂ films have higher transmittance within the visible region (400-800nm) of almost 85 and 70% respectively when compared to that of Cu₂O with 20% transmittance. This indicate perfect match for ZnO and TiO₂ to be used as window layer while Cu₂O as the absorber layer (Madoun, et al., 2013).

To calculate the band gap (E_g) of the films we use the well known Tauc relation (Joshi and Saxena 2003), (Shimadzu.,), (Abdullahi et al., 2016) given as

$$\alpha h\nu = A (h\nu - E_g)^n \quad \dots\dots\dots(1)$$

where α is linear absorption coefficient, ν is light frequency, and A is the proportionality constant. The power of the parenthesis, n is taken equal to 1/2 for direct band gap materials, the absorption coefficient α is determined using

$$\alpha = \frac{1}{d} \ln \left(\frac{(1-R)^2}{T} \right) \quad \dots\dots\dots(2)$$

where d is the thickness of the film, R and T are the reflectance and the transmittance respectively (Abdullahi et al., 2015) .

Figure.3 show the graph of $(\alpha h\nu)^2$ vs $h\nu$. A straight line is fitted for the straight segment. The extrapolation of this straight line to the axis of abscissa ($h\nu$ axis) gives the band gap values. The values were 2.32eV, 3.7eV and 3.75eV

for Cu_2O , TiO_2 and ZnO respectively, which are within the range of the theoretical results (Pavan et al., 2015)., (Siripala et al., 2003).

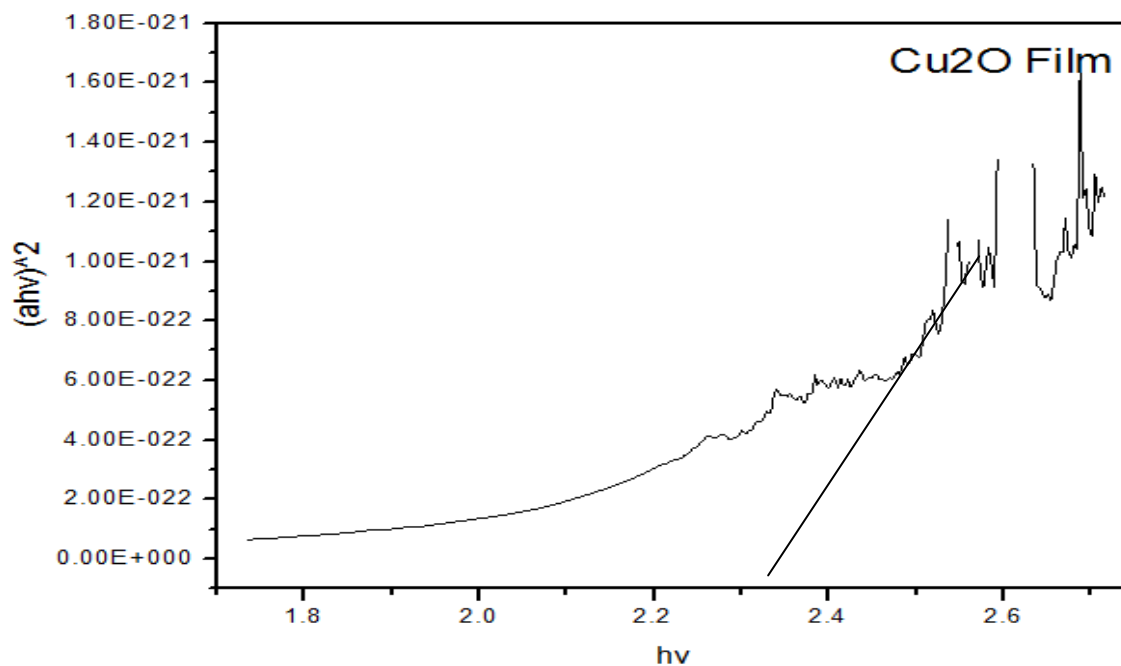


Figure.3:- (a) $(ah\nu)^2$ plot against $h\nu$ for Cu_2O films

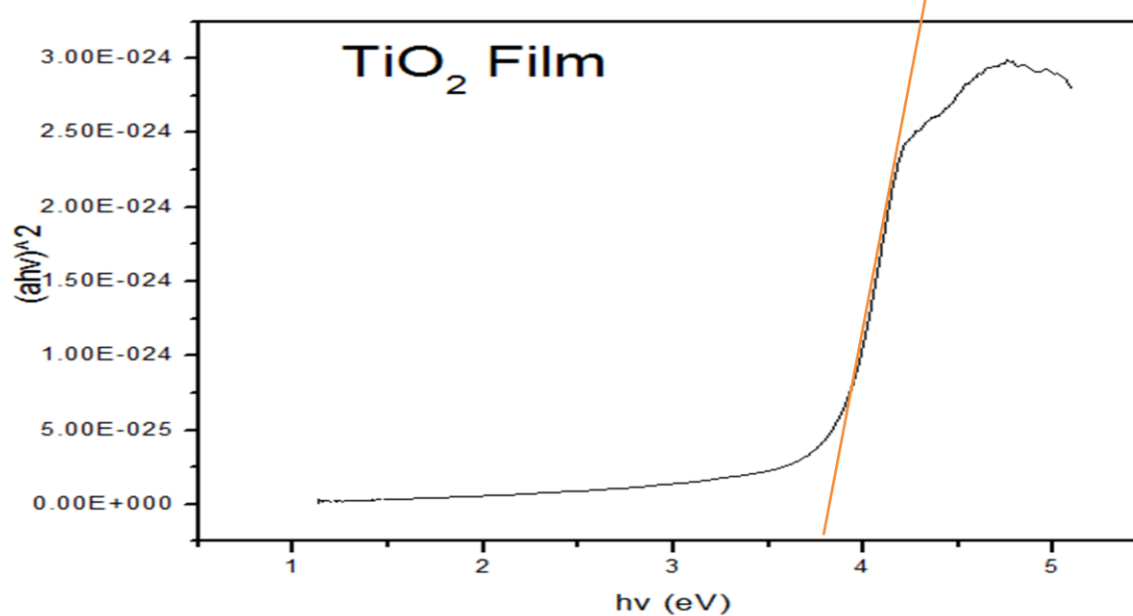


Figure 3(b):- $(ah\nu)^2$ plot against $h\nu$ for TiO_2 films

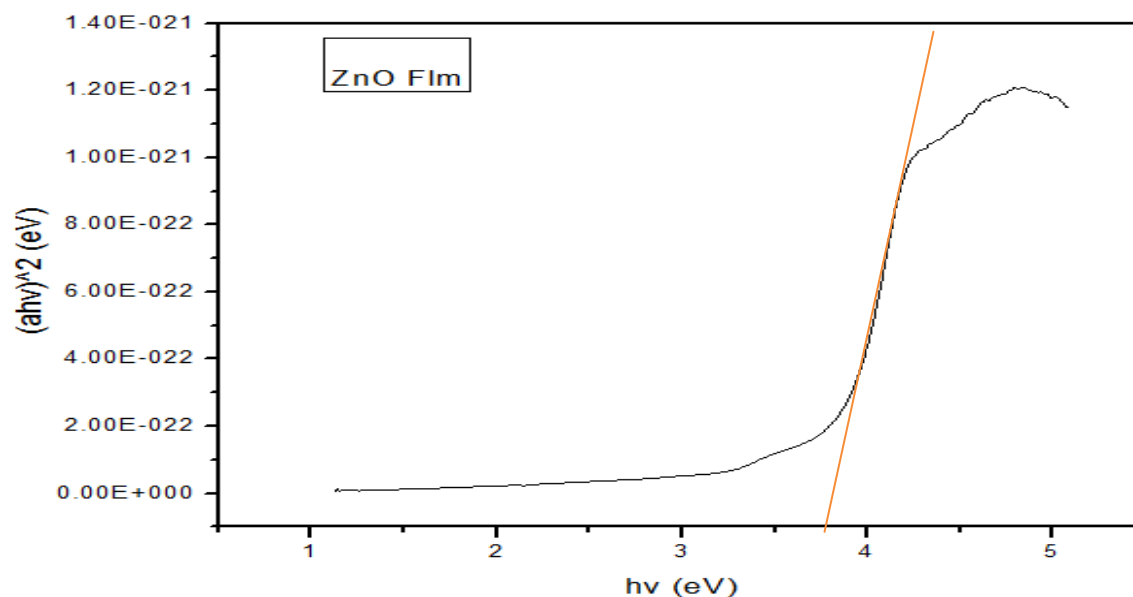


Figure 3:- (c) $(ahv)^2$ plot against $h\nu$ for ZnO films

Electrical measurement:-

I-V characteristic of the cells were investigated in dark and under illumination using a calibrated AM 1.5 Solar simulator Controller (Newport, Oriel instruments, Model: 69922) with a light intensity of 100mWcm^{-2} and a computer controlled digital source meter (Keithley, Model: 2400). Figure 4 shows the I-V characteristic curve of both 1.5 by 1.5cm FTO-ZnO/Cu₂O-Cu and FTO-TiO₂/Cu₂O-Cu solar cell. It can be seen that the heterojunction shows a rectifying behavior whereby under relatively low forward voltages the current increases exponentially, the short circuit current density, open circuit voltage and efficiency of the cells were determined to be $0.093\mu\text{A/cm}^2$, 0.0364V , 0.0076% and $5.8\mu\text{A/cm}^2$, 0.03V , 0.037% for FTO-ZnO/Cu₂O-Cu and FTO-TiO₂/Cu₂O-Cu solar cells respectively. This indicates that FTO-TiO₂/Cu₂O-Cu cell is having better efficiency than FTO-ZnO/Cu₂O-Cu cell. The result is comparable to that of (Fujimoto et al., 2013) and (Siripala et al., 2003) with 0.0073% and 0.05% respectively, and less than that of (Jeong, et al., 2008) and (Hussain et al., 2012) with 0.41% and 0.15% respectively.

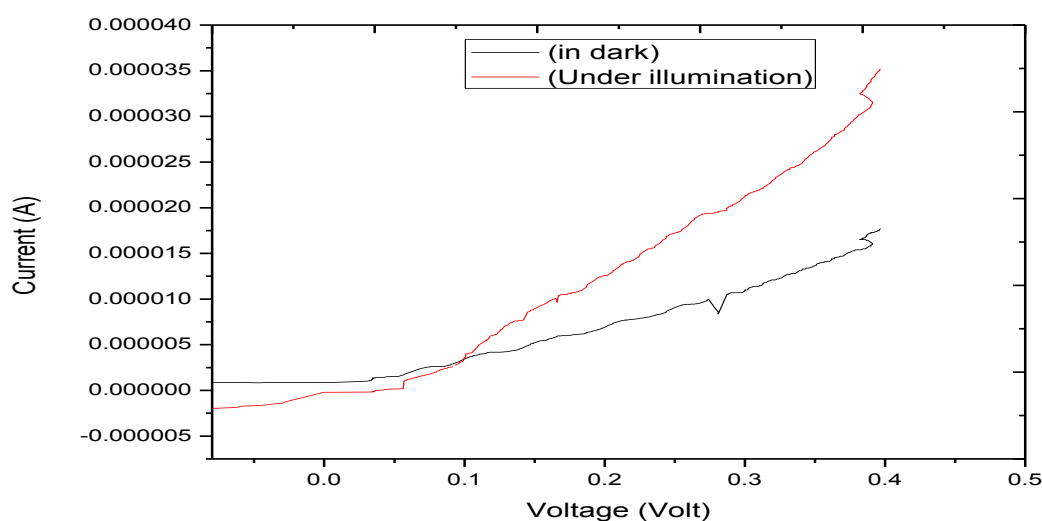


Figure 4(a):- I-V characteristic of FTO-ZnO/Cu₂O-Cu solar cell

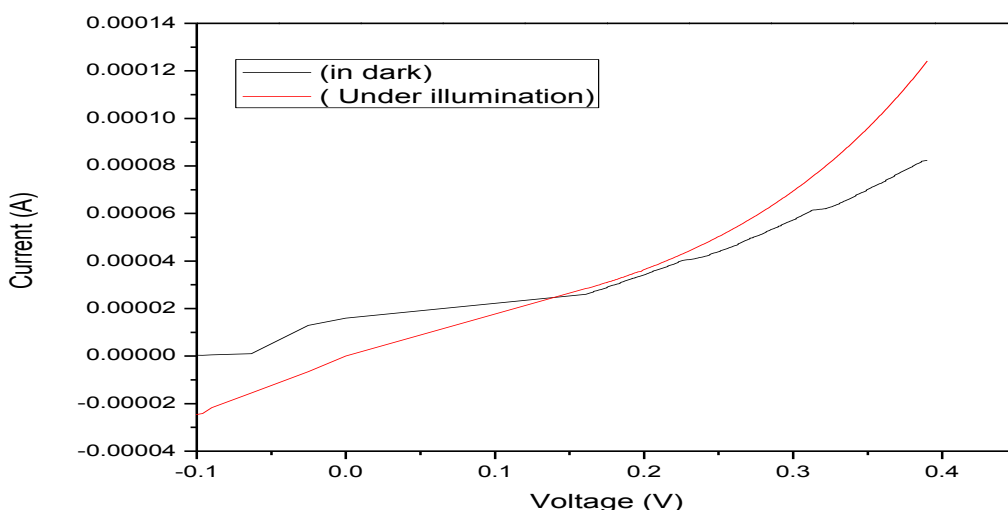


Figure 4(b):- I-V characteristic of FTO-TiO₂/Cu₂O-Cu solar cell

Conclusion:-

FTO-ZnO/Cu₂O-Cu and FTO-TiO₂/Cu₂O-Cu solar cells were successfully fabricated by electro deposition of Cu₂O on top of the sprayed pyrolysis ZnO and TiO₂ films. The optical measurement shows that both ZnO and TiO₂ have higher transmittance when compared to Cu₂O, which clearly indicate their perfect match to be utilized as a heterojunction solar cell. The band gaps of Cu₂O, TiO₂, and ZnO, were found to be 2.32eV, 3.7eV and 3.75eV respectively. I-V characteristic curve confirm the rectifying behavior of the cell. The short circuit current density, open circuit voltage and efficiency of the cells were measured to be 0.093μA/cm⁻², 0.0364V, 0.0076% and 5.8 μA/cm⁻², 0.03V 0.037% for FTO-ZnO/Cu₂O-Cu and FTO-TiO₂/Cu₂O-Cu cells respectively.

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References:-

1. Abdullahi, S. S., Y. Koseoglu, S. Guner, S.Kazan, B.Kacaman C.E. Ndikilar (2015). Synthesis and characterization of Mn and Co codoped Zinc oxide nanoparticle. *Superlattice and microstructure* July 03 021 342-352.
2. Abdullahi, S.S., S.Guner, Y. Koseoglu, I.M Musa, B.I Adamu, and M. I. Abdulhamid. (2016). Simple method for the determination of band gap of a nanopowdered sample using Kubelka Munk theory *journal of the Nigerian association of Mathematical Physics*, Volume 35 May pp241-246.
3. Abdullahi, S.S., S. Ahmad and S. Isiyaku (2016) Synthesis and Structural characterization of Fe doped CoZnO nanoparticles *Bayero Journal of mathematical physics*.
4. Chen, J., D.Chen, J.Heb, S. Zhang, Z.Chen (2009). The microstructure, optical, and electrical properties of sol-gel-derived Sc-doped and Al-Sc co-doped ZnO thin films. *Applied Surface Science* 255 9413-9419.
5. Chergui, Y., N. Nehaoua and D. E. Mekki (2011). Comparative Study of Dye-Sensitized Solar Cell Based on ZnO and TiO₂ Nanostructures, *Solar cells - Dye-Sensitized devices*, ISBN:978-953-307-735-2.
6. Fujimoto, K., T. Oku, T. Akiyama and A. Suzuki (2013). Fabrication and characterization of copper oxide-zinc oxide solar cells prepared by electrodeposition *Journal of Physics: Conference Series* 433 012024.
7. Gu, Y.Z., H.L.Lu, Y.Geng, Z. Y. Ye, Y. Zhang, Q.Sun, S.Ding and D.W.Zhang (2013). Optical and microstructural properties of ZnO/TiO₂ nanolaminates prepared by atomic layer deposition *Nanoscale Research Letters*, 8:107.
8. Hussain, S., C. Cao, Z. Usman, Z.Chen, G. Nabi, W. S. Khan, Z. Ali, F.K. Butt, T. Mahmood (2012). Fabrication and photovoltaic characteristics of Cu₂O/TiO₂ thin film heterojunction solar cell *Thin Solid Films* 522 430-434.

9. Jayathileke, K. M. D. C., W. Siripala and J. K. D. S. Jayanetti (2007). Donor and Acceptor density Variations in Electrodeposited Cuprous Oxide Thin Films Institute of Physics – Sri Lanka *Proceedings of the Technical Sessions*, 23 55-59.
10. Jeong, S. S., A. Mittiga, E Salza, A.Masci, S. Passerini (2008). Electrodeposited ZnO/Cu₂O heterojunction solar cells *Electrochimica Acta* 53 2226–2231.
11. Joshi, G.P., Saxena, N. S. (2003). Band gap determination of Ni–Zn ferrites *Bullutein Material Science*. 26 (4) 387–389.
12. Karunakaran, C., V. Rajeswari, P. Gomathisankar (2011).Optical, electrical, photocatalytic, and bactericidal properties of microwave Synthesized nanocrystalline Ag-ZnO and ZnO Solid State Sciences 13 923-928.
13. Madoun, M, et al., (2013). Temperature effect on structural and opto electronic properties of Bi₂S₃ nanocrystalline thin films deposited by spray pyrolysis method, *materials science in semiconductor Processing*, 04.004.
14. Minami,T.; Miyata, T.; Ihara, K.; Minamino, Y.; Tsukada,S.(2006). Effect of ZnO film deposition methods on the photovoltaic properties of ZnO-Cu₂O heterojunction devices. *Thin Solid Films*, 494, 47–53.
15. Oku T., T. Yamada, K. Fujimoto and T.Akiyama(2014).Microstructures and photovoltaic properties of Zn(Al)O/Cu₂O-based solar cells prepared by spin-coating and electrodeposition coatings, 4, 203-213; doi:10.3390/coatings4020203.
16. Palmieri, V., C. Pira, L.Oleksiyi (2008).Study of thin film solar cell based on Copper Oxide substrate by DC Reactive Magnetron Sputtering. *Laboratori Nazionali di Legnaro Anno accademico*.
17. Pavan, M. S., Rühle A. Ginsburg D. Keller H.Noabarad .P.M.Sberna, D.Nunes , R. Martins A.Y.Anderson, A. Zaban, E.Fortunato (2015). TiO₂/Cu₂O all-oxide heterojunction solar cells produced by spray pyrolysis *Solar Energy Materials Solar Cells* 132 549–556.
18. Saehana, S. and Muslimin (2013) Performance Improvement of Cu₂O/TiO₂ Heterojunction solar cell by Employing Polymer Electrolytes *International Journal of Engineering & Technology IJET-IJENS Vol:13 No:06* 83.
19. Sharma, V.K., M.Najim, A.K.Srivastava, G.D.Varma (2012). Structural and magnetic studies on transition metal (Mn,Co)doped ZnO nanoparticles *Journal of Magnetism and Magnetic Materials* 324 683–689.
20. Shimadzu. Measurements of band gap in Compound semiconductors, band gap determination from the diffuse reflectant spectra *spectrometric analysis No. A428*.
21. Siripala, W., A. Ivanovskaya, T. F. Jaramillo, S. B. Eric W. M. Farland (2003). A Cu₂O/TiO₂ heterojunction thin film cathode for photoelectrocatalysis *Solar energy materials & solar cells* 77 229–237.
22. Zulkiflee. N. S., R. Hussin, J. Halim, M. I. Ibrahim, M. Z. Zainal,S. Nizam and S.Abdulrahman (2016). Characterization of TiO₂, ZnO, and TiO₂/ZnO thin films Prepared by sol-gel method *Journal of Engineering and Applied Sciences*.