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Synthesis of Thin Film Semiconductor Cu_2O-ZnO on Flourine Doped Tin Oxide with Electrodeposition Method for Solar Cell

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Abstract:*Semiconductor Thin Layers have been successfully synthesized through two-step electrodeposition using three electrodes potensiostatic producing Cu_2O-ZnO on FTO glass which is expected to be function as a electrode solar cell. Precursor used is an electrolyte solution which can produce ZnO as an n-type semicondutor and Cu_2O as a p-type semiconductor. The synthesized electrode was characterized by X-Ray Diffraction (XRD) to determine the size of crystals and the presence of compounds qualitatively compared with the literature. A thin layer of photocurrent test is performed to find that the thin layer has functioned as a semiconductor.In the application, the photoanode electrode and the carbon counter electrode generate current after irradiation with light energy using solar simulator 100 mWatt/cm^2.*

Keywords: *Two Step Electrodeposition, Photentiostate , Solar Cells*

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I. Introduction

Solar cells are a device that can directly transform the energy of solar radiation into electrical energy. A solar cell using a heterojunction semiconductor principle consists of a p-type semiconductor and a n- type. Semiconductors n junctions can transfer electrons because they have high mobility in carrying the load [1]. These materials include ZnS, CdS [2] and TiO_2. P junction has an excess hole that can be charged electrons from n junctions. Various p junctions include Ag_2O, NiO [3], Cu_2S [4].

The materials turned out to have some disadvantages such as not environmentally friendly and difficult to get raw materialnya. With the existence of such problems need a solution that is the need of materials semiconductor Cu_2O-ZnO raw material easy to obtain, environmentally friendly, cheap and abundant presence in nature. ZnO has a 3.2 eV band gap and has high mobility [5]. Cu_2O has a 2.1 eV band gap which is a nontoxic material, which is abundant in existence, so that when both are combined it will be a p-n junction semiconductor material that can be applied to solar panels [6].

An alternative method that can be used in the synthesis of a Cu_2O-ZnO / FTO semiconductor layer is electrodeposition using a potentiostat tool involving three electrodes. FTO acts as a working electrode, Ag / AgCl as a comparative electrode and Pt as opposing lectures, this method has advantages such as good sensitivity (10^{-12} to 10^{-1} concentration range), thickness and adjustable layer morphology [7], cheap [8], environmentally friendly, large deposition areas [9] and can be done at room temperature [1]. The materials used are also not necessary in large quantities and easily obtained, namely $CuSO_4.5H_2O$, $C_6H_8O_7.H_2O$, Zn (CH_3COO) 2.2H2O and KNO_3 as raw material. The electrodeposition process is carried out in two steps using two different fixed currents. The first electrodeposition was used to form a thin layer of Cu_2O and subsequently a second electrodeposition was made to form a ZnO thin layer.

In this research, the synthesis of thin layer electrode Cu_2O / ZnO in FTO using electrodeposition method and applying the result of thin layer synthesis on FTO for solar cell with efficiency value determination.

Characteristics of semiconductor layers to be synthesized to be known as the presence of Cu_2O and ZnO qualitatively and the size of the crystal grain so that the characterization by X-ray diffraction is done on semiconductor layer that has been synthesized.

II. Materials And Methods

Materials and Tools

a.The materials used in this research are $CuSO_4.5H_2O$ p.a (*Merck*), $Zn(CH_3COO)_2$ p.a (*Merck*), KNO_3 p.a (*Merck*), Citric acid ($C_6H_8O_7.H_2O$) p.a (*Merck*), NaOH p.a (*Merck*), Electrode Pt, electrode Ag/AgCl, FTO glass (*Sigma Aldrich, surface resistivity ~7Ω/sa*), Aquades, Aceton (*Merck*), pH universal (*Merck*), carbons

b.The tools used in this research are Potensiostat (CS 150), Multimeter (*Krisbow*), X-ray diffraction instrument (*PanAlytical*), *Hot plate,stirer* (*IKA C-MAG HS 7*), *Furnace* (*Naberthem*), analytical balance(*Ohauss*), Thermometer, Standard Research Tools (Herma and Pyrex), Multimeter (Krisbow), Cable and crocodile claws Lamp 100 mWatt/cm^2

Method of Preparation of electrolyte solution and electrodes

Solutions for the synthesis of Cu_2O are CuSO4.5H_2O and $C_6H_8O_7.H_2O$ solutions. 0.1 M $CuSO_4.5H_2O$ solution was prepared by weighing 1,25 grams of $CuSO_4.5H_2O$ and a solution of 0.2 M $C_6H_8O_7.H_2O$ was prepared by weighing 2.01 grams. Each ingredient was diluted with aquadest slightly separately and diluted on a 50 mL measuring flask. Then the solution is added with concentrated NaOH until the pH reaches 12.

Solution for ZnO synthesis required Zn $(CH_3COO)_2$ and KNO_3 solution. 0.1 M Zn $(CH_3COO)_2$ solution was prepared by weighing 1.09 grams Zn $(CH_3COO)_2$ and 0.4 M KNO_3 solution made by weighing 2.02 grams. Each ingredient was diluted with aquadest slightly separately and diluted on a 50 mL measuring flask. Then the solution was added with 1 M NaOH until the pH reached 8. Then the solution was heated to 65^{o}C for CuSO4.5H_2O solution and 70°C for Zn $(CH_3COO)_2$ solution after air bubbling was done for 20 min and then electrodeposition.

The potentiostat tool uses 3 electrodes. The opponent electrode used is Pt, the reference electrode used is Ag / AgCl, and the working electrode used is FTO (flourine doped tin oxide).

The FTO glass is cut to 2 x 1 cm. The deposition area is made up of 1x1 cm and the rest is covered with masking tape (the 1x1 part is used for the electrodeposition area). Glass was then washed with acetone for 10 minutes, followed by washing with ethanol 10 minutes and finally washed with 10 minutes aquades.

Two Step Electrodeposition

The electrodeposition process is carried out gradually, in which Cu_2O is deposited first in FTO. Heating to a temperature of 65 ° C of 0.1 M $CuSO_4.5H_2O$ and 0.2 M $C_6H_8O_7.H_2O$ solution while bubling for 20 minutes with pH 12. After that done linear sweep voltammetry command with a potential setting of 0 volts to -1.5 volts an application current of -0,0001 A. The current is used for electrodeposition within 1200 s.

Electrodeposition ZnO performed after electrodeposition Cu_2O. The electrodeposition preparation was carried out by heating to a temperature of 70 ° C of 0.1 M Zn $(CH_3COO)_2$ and 0.4 M KNO_3 solution while bubbing for 20 min with pH conditioning 8. After that linear sweep voltammetry was performed with a potential setting of 0 to - 3 volts obtained an application current of -0.002 A. The current is used for electrodeposition within an interval of 1200 s

Characterization with XRD

Characterization with X-ray diffraction was performed to determine the size of the crystal grains and the presence of Cu_2O-ZnO compounds qualitatively. Characterization by X-ray diffraction was performed on a synthesized thin layer electrode sample.

***Photocurrent* test**

After the synthesis focuses Cu_2O-ZnO / FTO, a photocurrent test is performed to determine that the semiconductor layer by coupling the surface layer on the glass as the working electrode, Pt as the opposing electrode and Ag / AgCl as the reference electrode. The test is performed with chop irradiation. This test uses sodium sulfate solution at pH 9 by conditioning using 0.1 M NaOH which is simulated by irradiation using lamps with 100 mWatt / cm^2 using a potential tool with a linear sweep voltammetry command with an initial potential of 0.1 volts and a final end of -1, 4 volts. In the irradiation done on off test for 10 seconds once.

Solar cell application

Once it is confirmed that the material is semiconductor then the J-V characteristic is then carried out by coupling the FTO as the working electrode (cathode) as well as the alloy between the opposing electrode and the reference electrode as the anode. Thin layer is carried out contact a carbon that serves for lighter current. The test was performed with two treatments in the initial potential range of -0.3 volts to 1.5 volts using a linear sweep voltammery program. The first treatment was initiated by a light with a power of 100mWatt / cm^2 in the initial potential range until the final potential. And the second treatment is done without giving the light from the initial potential to the final potential as well.

III. Result And Discussion

Determination current application

The purpose of determining the flow of application is to determine the minimum external currents that must be supplied to the electrolysis cell to cause the electrolysis process to proceed continuously. In the

determination of the application flow using the Linear Sweep Voltammetry (LSV) stage, scanning at potential between ranges is 0 to -0.8 volts with scan rate of 10 mV per second.

The application current determination can be seen from the first high current spike area and plot the potential area of Cu_2O formation at a potential of about -0.4 to -0.65 volts. From the curve obtained an application flow of -0,001 A. In the potential area between -0.4 volts to -0.65 volts is a potential area of Cu_2O formation, and in areas greater than -0.65 V is a potential area of Cu metal formation [10]. From the curve can be known the value of application flow is -0.1 mA

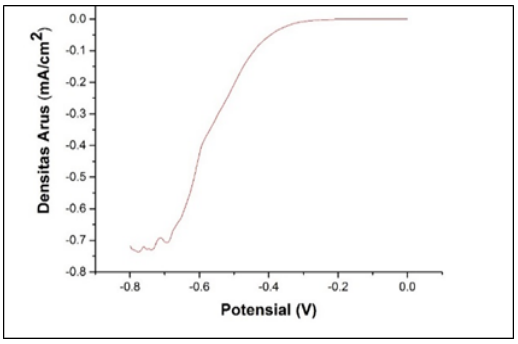


Fig.1 Determination potential application of curve Cu_2O

In determining the Current of ZnO applications using the Linear Sweep Voltammetry (LSV) stage, scanning potential between ranges is 0 to -3 volts with scan rate of 10 mV per second

Based on the graph in figure III.1 shows that at the -2 mA the ZnO has already begun to form. The application current determination can be seen from the first high current spike area and plot the potential area of ZnO formation at a potential of about -2.11 volts. From the curve obtained an application flow of -2 mA. at a potential region of -2.5 volts which is a potential region of ZnO formation, and in regions greater than -2.5 V is a potential area of Zn metal (Izaki and Omi, 1996). From the curve can be known the application flow value is -2 mA

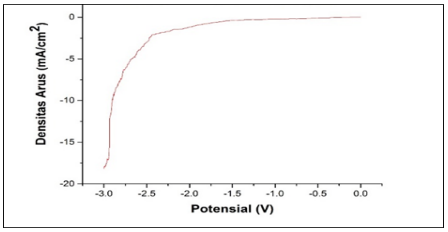


Fig.2 Determination potential application of curve ZnO

Two Step Electrodeposition

The electrodeposition carried out for the synthesis of this semiconductor layer in two steps is carried out by a separate deposition process or each material deposited in a different solution with different application streams. The electrodes used are FTO glass as working electrode, Pt as opposing electrode and Ag / AgCl for comparator electrode.

The FTO glass used is 2 x 1 cm, but the area used for electrodeposition is only 1x1 cm in size so the rest is covered with masking tape. The FTO glass is a fluorine-doped conductive layer of oxo-transparent oxide oxide, meaning that the FTO glass is a transparent material that can carry an electric current, therefore it can be used as an electrode in an electrodeposition system.

The electrodeposition process is carried out gradually, first electrodeposition Cu_2O first, then on the same FTO glass ZnO is deposited after the electrodeposition process Cu_2O completed.

a.Elektrodeposition of Cu_2O

$CuSO_4.5H_2O$ as the Cu source which will be reduced to the cathode, NaOH for the pH regulator to obtain an alkaline environment with pH 12 and $C_6H_8O_7.H_2O$ as a complexing agent. The complexing agent acts as a Cu^{2+} ion stabilizer and prevents the formation of Cu $(OH)_2$ precipitate by forming Cu^{2+} complexes with citric acid wherein Cu is still in desired oxidation state during the electrodeposition process.

The formation of Cu_2O coating on the FTO glass by electrodeposition is reinforced by giving the oxygen bubbling treatment into a solution of $CuSO_4.5H_2O$ and heating to a temperature of 65^oC. The oxygen bubbling process aims to increase the concentration of dissolved oxygen in the sample so as to increase the

chances of formation of hydroxide ions from the oxygen reduction reaction in the FTO glass layer and the heating is carried out so that the CuOH formed from the reaction of Cu^{2+} ions with OH-ion is immediately dehydrated and formed layer of Cu_2O.

In the electrodeposition process by providing a fixed current, a Galvanostate arrangement is performed on the potentiostat tool. At electrodeposition Cu_2O is carried out at a constant current of -0.1 mA for 1200 s.

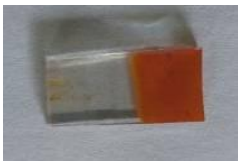


Fig.3 The synthesis of Cu_2O

Figure III.3 shows the synthesis of layers of yellowish-red Cu2O. The electrodeposition process of Cu_2O synthesis yields a layer of 4.4 mg.

b.Elektrodeposition of ZnO

Zn $(CH_3COO)_2$ as the source of Zn and which will be reduced is O from bubbling process, KNO_3 as electrolyte and NaOH for pH regulator to obtain an environment with pH 8.

Treatment of air bubbling and heating aims to increase the concentration of dissolved oxygen in the solution so that the possibility of the formation of hydroxide ions on the FTO glass can be greater. The 70 ° C heating also aims to dehydrate the Zn $(OH)_2$ formed after Zn^{2+} ions and OH-reacting ions to form ZnO on the FTO glass.

The reaction occurring at the time of ZnO electrodeposition is as follows:

Cathode : $Zn^{2+} + ½O_2 + 2e^- \rightarrow ZnO$

Anode : $H_2O \rightarrow 2H^+ + ½O_2 + 2e^-$ All : $Zn^{2+} + H_2O \rightarrow ZnO + 2H^+$

In the electrodeposition process by providing a fixed current, a Galvanostatic arrangement is performed on the potentiostat tool. In Cu_2O electrodeposition is performed at a fixed current of -2 mA for 1200 s

Fig.4 The synthesis of Cu_2O-ZnO/FTO

Figure III.4 shows the result of the synthesis of a layer of ZnO compound before it is calcined white and after calcined in grayish white. The electrodeposition process of ZnO synthesis yields a layer of 5 mg.

Characterization with XRD

Characterization with X-ray diffraction (PanAlytical) was performed to determine qualitatively the presence of ZnO and Cu2O in thin layer electrodes that have been synthesized on fluor doped thin oxide (FTO) media. The process of analysis with X-ray diffraction instrument (PanAlytical) to the sample was performed at the diffraction angle range (2θ) 30.00o- 80.00o with CuKα1 radiation (λ = 1,54060Å), 400 kV and 300 mA. The X-ray diffraction results in the sample are given in Figure IV.5 compared to the d spacing values of the crystalline peaks present in the spectra with standard peaks of Cu_2O and ZnO based on the RRUFF standard

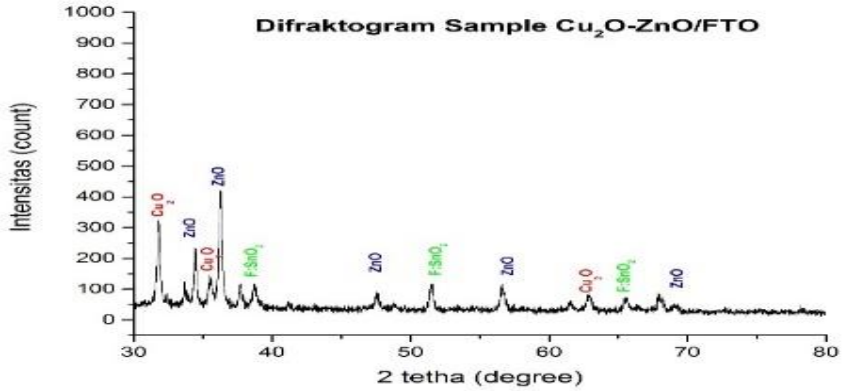


Fig.5 Difractogram of Cu_2O/ZnO

The results of X-ray diffraction analysis were compared with RRUFF data of RRUFF no. R050419 for standard ZnO and RRUFF no. R050384 for Cu_2O standards. In the sample difractogram two-step electrodeposition results at 2θ of 31.79°; 36.28 ° and 61.58 peak is almost coinciding with Cu_2O standard at 2θ 32.62 °; 36.19 ° and 61,41 ° with the difference of 0.82 respectively; 0.08; 0.17. At a value of 2θ 34.42 °; 47,52 °; 56.63 ° almost coincides with ZnO standard peak at 2θ at 34.35 °; 47,66 °; 56.67 ° with difference of 0.05; 0.14 and 0.04 indicate that ZnO is present in thin layer electrodes of synthesis but in a low quantity. This indicates that there exists a thin layer electrode Cu_2O-ZnO / FTO with a high enough quantity. The presence of SnO_2: F compounds is shown in peak 38,72 °; 51,42 °; 65.48 ° which coincides with 38.24 °; 51.77 °; 65.99 ° with difference of 0,48; 0.34; 0.51 which has a low intensity

The average crystal size can be calculated using the Debye-Scherrer equation. The crystallinity change can be proved by the FWHM value (Full Width at Half Maximum) of the X-ray diffraction peak. FWHM values can be obtained from XRD analysis results. The value is used to calculate the size of the crystal grains of Cu_2O and ZnO.

Table 1 FWHM value and grain size of Cu_2O-ZnO crystals

Metal Oxide	2θ	θ	FWHM	D
ZnO	34,4°	17,20 °	0,15	57,69
	56,63 °	28,31 °	0,40	23,47
	47,52 °	23,76 °	0,23	38,71
Cu_2O	31,79 °	15,89 °	0,16	51,56
	36,28 °	18,14 °	0,26	32,63
	61,58 °	30,79 °	0,40	24,06

Table1 shows the FWHM value and the size of the crystal grains of the ZnO-Cu_2O / FTO sample the lower the FWHM value, the crystallinity and the grain size increases. This corresponds to the Debye-Scherrer equation that the FWHM and grain size of the crystal are inversely proportional. Good crystal quality is characterized by small FWHM values and large grain size. The greater the FWHM value indicates that the crystal lattice becomes less homogeneous and the crystal arrangement is irregular. The average size of crystal grains of Cu_2O was 36.09 nm while ZnO was 39.96 nm.

***Photocurrent* Test**

After the synthesis of the Cu_2O-ZnO / FTO thin layer, the test was performed to determine that the material had been semiconductor by coupling the thin layer of FTO glass as the working electrode, Pt as the counter electrode and Ag / AgCl as the reference electrode. The test is performed with chop irradiation.

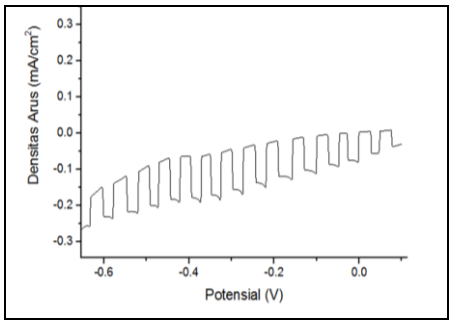


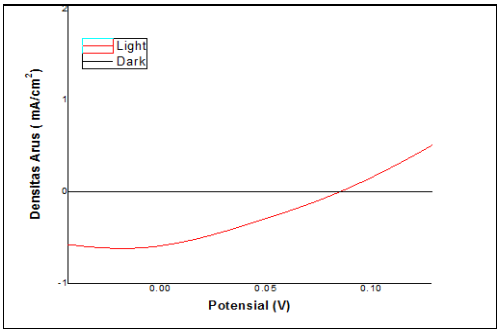
Fig.6 Curve of *Photocurrent*

Determination of photocurrent test with chop irradiation was done to know that the synthesized thin layer has been semiconductor. This test uses sodium sulfate solution at pH 9 by conditioning using 0.1 M NaOH simulated by irradiation using lamps with 100 mWatt / cm^2 power using a potentiostat tool with a linear sweep voltammetry command with an initial potential setting of 0.1 volts and an end potential of -1 , 4 volts. In the irradiation test is done on off for 10 seconds once . Obtained a J-V photocurrent curve with chop irradiation as follows

Figure 6 shows that the thin layer has characterized as a semiconductor material. Where the semiconductor material has a small forbidden (Eg) width. With such a small distance, this material requires only less energy to allow the electrons to transition. This is indicated when the thin layer is initiated with the light (on) then the current will rise but when in a state not being given off (off) the current will decrease. Given these events indicate that the thin layer electrode undergoes a photovoltaic process only when there is a photon source to generate electrical energy. The current density generated when without illumination is the residual current in the circuit which is still readable by the potentiostat tool.

Solar Cell Application

After making sure that the material is semiconductor then J-V characteristic is then performed for the performance of solar cell by coupling FTO as working electrode (cathode) as well as alloy between opponent electrode and comparative electrode as anode. The synthesized thin layer is coupled with contact attachment in the form of a carbon paste that serves for the lighter current. The test was performed with two treatments in the initial potential range of -0.3 volts to 1.5 volts using linear sweep voltammetry program. The first treatment was initiated by a light beam with a power of 100mWatt / cm^2 in the initial potential range until the final potential. And the second treatment is done without giving the light from the initial potential to the final potential as well. From the curve obtained can be determined some performance of solar cells. The J-V curve can be seen in the following figure.



FigI. 7 Curve of J-V Cu_2O-ZnO

The determination of solar cell performance was done by measuring the J-V characteristic by irradiation of lamp with 100 mWatt / cm^2 with active glass area of 0.5 cm^2 and obtained some parameters such as Voc, Jsc VMpp and JMpp so that efficiency value can be obtained. Voc is the maximum voltage of solar cell current density 0 and obtained value of 0.083 V. Jsc is the maximum current density when the voltage of the solar cell has a value of 0 and obtained a value of -0.6239 mA / cm2. The multiplication of V and J produces power. The max power curve is square. Graphically, the maximum peak and square power that has the largest area and point of tangency between the square with this curve is called VMpp and JMpp. Value of VMpp obtained by 0,0028 V and JMpp of -0.3762 mA / cm2..

The performance of solar cells can be known the efficiency value of solar cells. Based on the measurement of these parameters obtained an efficiency value of 0.01% which means that only 0.01% solar

energy can be converted into electrical energy.

In this case, the principle of a solar cell is a p-n junction semiconductor material. Zinc Oxide (ZnO) is a n-type semiconductor that has a band gap of 3.4 eV so that ZnO can be activated by UV radiation with a wavelength of 388 nm UV light. Cu2O is a p-type semiconductor that has a 2.1 eV band gap so it can be activated by visible light radiation with a wavelength of 591 nm. The irradiation is done with a solar simulator with a power of 100 mWatt / cm^2 where the light is a simulator of sunlight so that the ray is a collection of visible light and UV rays. When the rays are about semiconductors there will be absorbed energy and the energy being passed on. The amount of energy corresponding to the band gap is to be absorbed. This energy will be used for electron transitions and electrons out of their atomic bonds where the electrons are not supplied to the wires but to the electrolyte solution of sodium sulfate so that the voltage can be detected by the opposing electrode and the current flowing is detected by the comparative electrode so that the J-V curve will appear at the potentiostat.

IV. Conclusion

The Cu_2O-ZnO / FTO thin layer electrode has been successfully synthesized via a two-step electrodeposition using an application stream for Cu_2O of -0.1 mA at pH 12 whereas ZnO at an application current of -2 mA with pH 8 with 361 nm Cu_2O grain size and ZnO 39.9 nm. Solar cells efficiency is 0.01%.

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