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# A Novel $CuInS_2$/Polyaniline Base Heterojunction Solar Cell

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**Abstract** Copper indium disulfide ($CulnS_2$) has direct band-gap energy of about 1.5 eV and a large absorption coefficient, which are well suited to the photovoltaic conversion of solar energy. In this task a novel florin doped tin oxide (FTO)/$CuInS_2$/ polyaniline base/ZnO/FTO hetrojunction solar cell was fabricated. $CulnS_2$ thin films were electrodeposited onto fluorine doped tin oxide substrate by the electrodeposition technique. Current–voltage characteristic curves were measured under darkness and illumination. It found that Jsc, Voc, and η are $3.2x10^{-6}$ A/cm$^2$, 0.714 V and $1.92x10^{-3}$ % for FTO/$CuInS_2$/ZnO/ITO herterojunction solar cell while Jsc, Voc, and η are $3.25x10^{-6}$ A/cm$^2$, 0.724 V and $1.8x10^{-3}$ % for FTO/$CuInS_2$/polyaniline base ZnO/ITO herterojunction solar cell.

## 1. INTRODUCTION

Fossil fuels like coal, oil, natural gas and nuclear energy are considered the main sources for supplying the world with energy at the present time. While some uncertainties exist about the overall amount of these sources and how long they will be able to meet the growing demand, there cannot be any doubt that alternate sources of energy will be needed in a few decades. Not only are the sources limited, but the environmental impact of the present energy production also causes serious problems. At the moment mankind is only beginning to feel the consequences of global warming and atmospheric pollution. The most promising source of clean, safe, and abundant energy is the sun which made possible the life on earth itself. Photovoltaic devices (or simply solar cells) offer the direct conversion of sunlight into electricity [1-3]. Chalcopyrite semiconductors have attracted widespread attention for use in thin-film solar cells. Solar cell technologies using I-III-VI2 chalcopyrite semiconductors have made rapid progress in recent years. Conversion efficiencies for polycrystalline CIGS based solar cells have been significantly improved over recent years and the best cell have achieved at 19.9 % up to now.

However, among ternary chalcopyrite semiconductors, $CuInS_2$ may be the most promising material for photovoltaic applications due to the band gap energy of this material is about 1.5 eV, which matches the solar spectrum for energy conversion and a large absorption coefficient. Furthermore, since the material does not contain toxic Se atoms, this may have an advantage in comparison with the frequently studied $CuInSe_2$ and CIGS [1-3].

Various techniques such as molecular beam epitaxy, metalorganic chemical vapor deposition, physical vapor deposition, sputtering, e-beam thermal evaporation and electrodeposition have been reported for the preparation of $CuInS_2$ film [4-7]. Important advantages of electrodeposition are low equipment cost, high deposition speed, and negligible waste of chemicals, scalability and manufacturability of large area polycrystalline films. It is an isothermal process, mainly controlled by electrical parameters which can be adjusted to control film thickness, morphology and composition. In addition, toxic gaseous precursors are not involved as in chemical gas phase methods [8-10].

Currently, indium tin oxide (ITO) is the most commonly used anode in photovoltaic devices because of its high transparency (□90% at 550 nm), low resistivity, and relatively high work function (□4.8 eV). However, ITO-based anodes have several significant drawbacks such as high materials costs, an unstable work function, chemical instability, a high contact barrier for hole injection, and shortened device lifetimes. The results of many experiments in our lab of electrodeposition of $CuInS_2$ onto ITO substrate led us to conclude that ITO is unstable and its sheet resistance increases at low pH. Fluorine-doped $SnO_2$ (FTO) is a possible alternative substrate to ITO because $SnO_2$ films are inexpensive as well as chemically and thermally stable [11]. In addition, adhesion of $CuInS_2$ with FTO is better than ITO.

For many conjugated polymers, electron mobility is low; typically bellow $10^{-4}$ cm$^2$ s$^{-1}$. Enhancement of charge-carrier mobility can be accomplished by introducing organic-inorganic blends [12].

Multilayer structures consisting of electrochemically deposited n-types bulk $CuInSe_2$ and p-type polypyrrole have also been investigated for photovoltaic applications [13]. The aim of this work is to fabricate novel FTO /$CuInS_2$/ polyaniline base /ZnO/ITO heterojunctions solar cell. Polyaniline base can be played the role of CdS in this type of thin film solar cell. Current-voltage characteristic curves darkness and illumination have been measured for these types of solar cell.

## 2. EXPERIMENTAL WORK

**Materials**

$InCl_3.4H_2O$ was purchased from Aldrich. Copper acetate and sodium thiosulphate were obtained from Loba Chemie, India. Aniline (Loba Chemie, India) was purified by vacuum distillation before use and ammonium persulphate was purchased from Aldrich. The methanol, dimethylformamide (DMF) and diethyl ether solvents were bought from El-Gomhory Chemical Company (Egypt).

**Preparation of $CuInS_2$**

FTO with a sheet resistance equal to 50 Ω was prepared using spray pyrolysis techniques from a solution of tin chloride in methanol and glacial acetic acid was used as a precursor. Hydrofluoric acid (0.05 M) as a dopant was added to the precursor solution. The ratio of fluorine in the mixture was kept at 2.5% and the glass substrate temperature was 450 ºC.

$CuInS_2$ layers were prepared potentiostatically from one step using a plating bath of 0.1 M copper acetate, 0.1 M indium chloride and 0.1 M sodium thiosulphate. The pH of the solutions was adjusted with $H_2SO_4$ solution and using digital Solaron pH meter. A standard three-electrode cell was used; the working electrode was ITO substrate, the counter-electrode was Pt and a saturated calomel electrode (SCE) was used as a reference electrode. The electrodeposition was controlled using Gamry G750 Potentiostat/ Galvanostat with pilot integration controlled by PHE200 software. The electrodeposition thin film was annealed in a quartz tube putting in controllable tube furnace Hereaus for 30 min. in $N_2$ as an ambient at 400 $^0$C, then it was annealed for room temperature.

**Preparation of polyaniline base**

The preparation of chemical oxidative polymerization of aniline was carried out in an aqueous acidic solution using ammonium persulphate as oxidizing agent [14]. Emeraldine base (EB) was partially soluble in DMF (0.05 wt %). Thin layers of EB (15 drops) were deposited on the FTO/$CuInS_2$ by spin coating.

The thickness of this layer was determined using SEM to be 20 micron. The FTO/$CuInS_2$/EB was dried at 50 $^0$C for 30 min.

**ZnO preparation**

100 ml of methanol and based 0.14 M $LiOH.H_2O$ solution was first heated to 65 $^0$C, then 2.19 g of zinc acetate dehydrate was added. ZnO nanoparicles were formed in the solution whose color becomes clearer. This solution was filtered and washed with 50 ml double distilled water then dried in an oven at 60 $^0$C for 12 h. ZnO was suspension in double distilled water and casted on ITO and then dried at 80 $^0$C for 30 min.

**Fabrication of FTO/$CuInS_2$/polyaniline base /ZnO/ITO heterojunctions solar cell**

Two types of solar cell were fabricated in this work. The first is FTO/$CuInS_2$ stacked with ZnO/ITO and the second is FTO/$CuInS_2$/EB stacked with ZnO/ITO as shown in Fig 1.

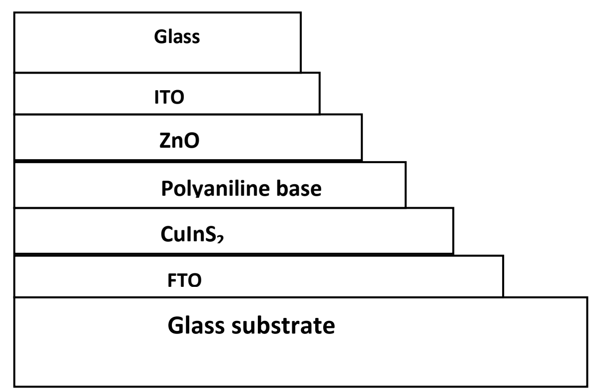


Fig. 1 Structure of FTO/CuInS2/EB stacked with ZnO/ITO

**Current-voltage measurements**

The current-voltage characteristics were measured by both darkness and illumination (direct sun) using computerized Keithley 2635A source meter. The level of illumination of tungsten halogen lamp was calibrated using Solarex standard solar cell.

## 3. RESULTS and DISCUSSION

**Electrodeposition of $CuInS_2$**

From our previous work, it was concluded that the optimum preparation condition of $CuInS_2$ are 150 ml of sodium thiosulphate and pH 1 at -1 V. Fig. 2 indicates the chronoamperometry curve of electrodeposited $CuInS_2$ at -1.0 V from solution containing 5 ml of 0.1 M copper acetate, 5 ml of 0.1 M indium chloride and 150 ml of sodium thiosulphate at pH 1 for 1 h.

The chronoamperogram shows a sharp initial current maximum, which relates to the charge of the electrical double layer or capacitive contribution at the film/solution interface. After this maximum current, the current plateau regions occur and slightly increase with time.

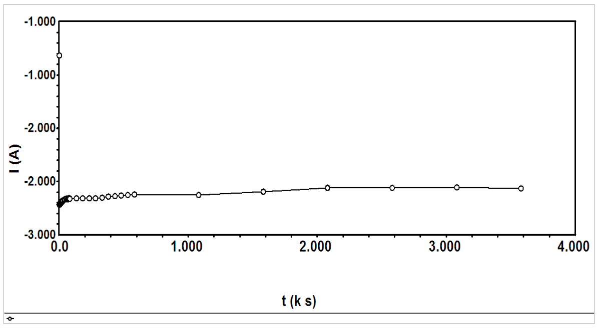


Fig. 2 Electrodeposited of $CuInS_2$ at -1.0 V from solution containing 5 ml of 0.1 M copper acetate, 5 ml of 0.1 M indium chloride and 150 ml of sodium thiosulphate at pH 1 for 1 h.

**Current-voltage curves**

Fig. 3 shows the I-V characteristic curves of FTO/$CuInS_2$/ZnO/ITO herterojunction solar cell under darkness and illumination. The I-V curves can be separated into two distinct regions: i) at reverse bias and at forward bias up to approximately 0.9 V, the characteristic is nearly symmetrical and is governed by a “leakage” current through the shunt resistance; ii) at bias corresponding to flat-band conditions, the injection starts and the exponential region can be distinguished [15]. Under illumination, the heterojunction solar cell can be described by the following equation [15-16].

$$J = J_0 [exp(q(V - JR_s)/ nkT)-1] - J_L \qquad (1)$$

where $J_0$ is the saturation current, Rs is the series resistance, n is the ideality factor, k is Boltzman constant, T is the temperature and $J_L$ is the photogenerated current density, $J=J_L \approx J_{SC}$ at V=0 V.

The photovoltaic cell characteristics, i.e., open circuit voltage ($V_{OC}$), short circuit current density ($J_{SC}$), fill factor (FF) and energy conversion efficiency (η), and were performed under illumination (0.1 W/cm$^2$) as shown in Table (1). It was found that Jsc, Voc, and η are 3.2x10-6 A/cm2, 0.714 V and 1.92x10-3 % for FTO/CuInS2/ZnO/ITO herterojunction solar cell.

It was found that the efficiency of FTO/$CuInS_2$/polyaniline base/ZnO/ITO herterojunction solar cell could be decreased maybe due to mismatch between polyaniline base and $CuInS_2$.

In addition, Fermi level at the interface of the polyaniline base and CuInS2 interface is not as low as would be anticipated for “bulk” polyaniline base, thus leading to reduced values of built in potential [17]. The interfaces also maybe play a very critical role in charge extraction and electric-field distribution. Interfacial dipoles, defects, and traps can create barriers for carrier extraction leading to this lower in the efficiency. The Jsc, Voc, and η are $3.25x10^{-6}$ A/cm$^2$, 0.724 V and $1.8x10^{-3}$ % for FTO/$CuInS_2$/polyaniline base ZnO/ITO herterojunction solar cell.

Table. 1 Characteristic electronic parameters of herterojunction solar cells

| Herterojunction solar cells / Solar cell Parameters | FTO/$CuInS_2$/ ZnO/ITO | FTO/$CuInS_2$ /EB/ZnO/ITO |
|---|---|---|
| **Voc (V)** | 0.714 | 0.724 |
| **Jsc (A/cm$^2$)** | $3.2x10^{-6}$ | $3.25x10^{-6}$ |
| **Vm(V)** | 0.306 | 0.25 |
| **Jm(A/cm$^2$)** | 2.17 x10$^-$ | $2.42x10^{-6}$ |
| **FF** | 0.29 | 0.297 |
| **η %** | 1.92x10 | $1.8x10^{-3}$ |

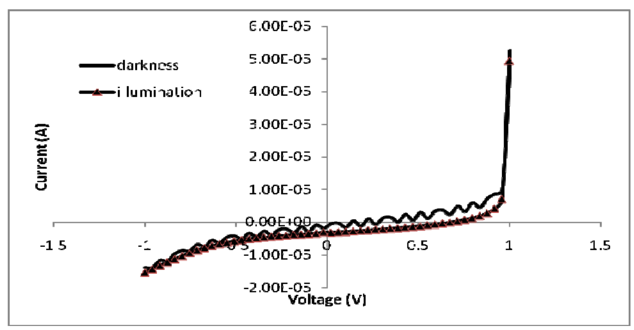


Fig. 3 I-V characteristic curves of FTO/$CuInS_2$/ZnO/ITO herterojunction solar cell under darkness and illumination.

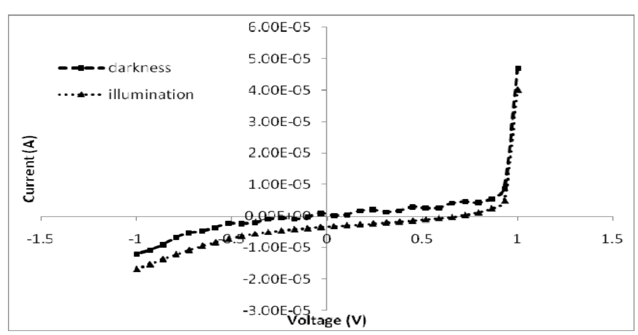


Fig. 4 I-V characteristic curves of FTO/$CuInS_2$/polyaniline base/ZnO/ITO herterojunction solar cell under darkness and illumination..

## 4. CONCLUSION

It was successfully fabricated a novel FTO/$CuInS_2$/ polyaniline base/ZnO/FTO hetrojunction solar cell was fabricated. $CulnS_2$ thin films were electrodeposited onto fluorine doped tin oxide substrate by the electrodeposition technique at -1 V. It was found that Jsc, Voc, and η are $3.2x10^{-6}$ A/cm$^2$, 0.714 V and $1.92x10^{-3}$ % for FTO/$CuInS_2$/ZnO/ITO herterojunction solar cell while Jsc, Voc, and η are $3.25x10^{-6}$ A/cm$^2$, 0.724 V and $1.8x10^{-3}$ % for FTO/$CuInS_2$/polyaniline base ZnO/ITO herterojunction solar cell.

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## REFERENCES

[1] Y. Akaki, S. Nakamura, K. Nomoto, T. Yoshitake, K. Yoshino, *Effect of annealing for $CuInS_2$ thin films prepared from Cu-rich ternary compound, Phys. Status Solidi C 6*, pp. 1030-1033, 2009.

[2] S. Nakamura, A. Yamamoto, *Preparation of $CulnS_2$ films with sufficient sulfur content and excellent morphology by one-step electrodeposition, Solar Energy Materials and Solar Cells*, vol. 49,pp. 415-421,1997.

[3] A. V. Mudryi, A. V. Ivanyukovich, M. V. Yakushev, R. Martin, A. Saad, *Magnetic field effect on free and bound excitons in chalcopyrite $CuInS_2$, Journal of Applied Spectroscopy*,vol 74. 2007.

[4] N.B. Chaure, J. Young, A.P. Samantilleke, I.M. Dharmadasa, *Electrodeposition of p–i–n type $CuInSe_2$ multilayers for photovoltaic applications, Solar Energy Materials & Solar Cells* , vol 81.pp.125-133, 2004.

[5] A. Mere, O. Kijatkina, H. Rebane, J. Krustok, M. Krunks, *Electrical properties of sprayed $CuInS_2$ films for solar cells, Journal of Physics and Chemistry of Solids,* vol 64,pp.2025-2029,2003.

[6] M. Ortega-LoÂpez, A. Morales-Acevedo, *Characterization of $CuInS_2$ thin films for solar cells prepared by spray pyrolysis, Thin Solid Films* , vol 330. pp. 96-101, 1998.

[7] T. T. John, M. Mathew, C. S. Kartha, K.P. Vijayakumar, T. Abe, Y. Kashiwab, *$CuInS_2$/$In_2S_3$ thin film solar cell using spray pyrolysis technique having 9.5% efficiency, Solar Energy Materials & Solar Cells* , vol 89.pp 27-36,2005.

[8] A.M. Martinez, L.G. Arriaga, A.M. Fernandez, U. Cano, *Band edges determination of $CuInS_2$ thin films prepared by electrodeposition, Materials Chemistry and Physics* ,vol 88.pp 417-420, 2004.

[9] B.Berenguier, H.J. Lewerenz, *Efficient solar energy conversion with electrochemically conditioned $CuInS_2$ thin film absorber layers, Electrochemistry Communications* , vol 8.pp 165-169, 2006.

[10] R. Cayzac, F. Boulch, M. Bendahan, M. Pasquinelli, P. Knauth, *Preparation and optical absorption of electrodeposited or sputtered, dense or porous nanocrystalline $CuInS_2$ thin films, C. R. Chimie xx*, pp 1-7 ,2008.

[11] H. Kim, G.P. Kushto, R.C.Y. Auyeung, *Optimization of F-Doping $SnO_2$ Electrodes for Organic Photovoltaic Devices, Appl. Phys. A,* vol 93.pp 521-526,2008

[12] S. Bereznev, J. Kois, E. Mellikove, A. Opik, D. Meissner, *17th European photovoltaic solar energy conf. Munch*, October, 2001.

[13] E. Arici, N. S. Sariciftci, D. Meissner, *Hybrid solar cells based on nanoparticles of $CuInS_2$ in organic matrices, Adv. Funct. Mat, vol.* 13, pp 165-171, 2003.

[14] Sh. Ebrahim, *Fabrication of Schottky diode based on Zn electrode and polyaniline doped with 2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt, J. Polym. Res*.vol 16, pp 481, 2009.

[15] K. Kawano, N. Ito, T. Nishimori, *J. Sakai*, *Open circuit voltage of stacked bulk heterojunction organic solar cells, Appl. Phys. Lett. vol 88, pp* 073514, 2006.

[16] A.M. Martinez, A.M. Fernandez, L.G. Arriaga, U. Cano, *Preparation and characterization of Cu–In–S thin films by electrodeposition, Materials Chemistry and Physics*, vol 95 , pp 270-274, 2006.

[17] B. Xu, J. Choi, P. A. Dowben, *deposited polyaniline thin films on gold J. Vac. Sci. Technol. A 20* , pp 741 , 2002.