

Research Article

Electrodeposited CuInS₂ Using Dodecylbenzene Sulphonic Acid As a Suspending Agent for Thin Film Solar Cell

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CuInS₂ thin films were electrochemically deposited onto fluoride-doped tin oxide (FTO) substrate in presence of dodecylbenzene sulphonic acid to adjust pH of the solution and as a suspending agent for the sulfur. Cyclic voltammetry and chronoamperometry were carried out to determine the optimum pH. The composition, crystallinity, and optical properties of the compounds synthesized were studied by energy dispersive X-ray (EDX), X-ray diffraction, and UV-Visible spectra. It was found that the increasing of pH shifts the electrodeposited voltage toward more negative and lowers the deposition current. It was concluded that CuInS₂ with atomic stoichiometric ratio was prepared at pH equal to 1.5 and 150 ml of 0.1 M sodium thiosulphate, 5 ml of 0.1 M indium chloride, and 5 ml of 0.1 M copper chloride. The energy gaps were calculated to be 1.95 and 2.2 eV for CuInS₂ prepared at 1.5 and 2.5 of pH, respectively. It was found that J_{sc} , V_{oc} , and η are 1.02×10^{-4} A/cm², 0.52 V, and 1.3×10^{-2} %, respectively, for FTO/CuInS₂/ZnO/FTO heterojunction solar cell.

1. Introduction

CuInS₂ may be one of the most promising materials of ternary chalcopyrite semiconductors for photovoltaic applications due to the band gap energy of about 1.5 eV, which matches the solar spectrum for energy conversion and a large absorption coefficient. Furthermore, this material does not contain toxic elements in comparison with CuInSe₂ [1–4]. There are different methods for the preparation of CuInS₂ thin films, such as sputtering, chemical spray pyrolysis, chemical bath deposition, and electrochemical deposition [5–8]. The advantages of electrochemical deposition are low equipment cost, high deposition speed, 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 [9–14].

Berenguier and Lewerenz et al. fabricated photoelectrochemical solar cells consisting of CuInS₂ in V(II)/(III) redox electrolytes and the efficiency was equal to 2.4% for KCN etched samples and of 3.3% for the a mixed photoelectrochemical and electrochemical anodic conditioning treatment [11]. The highest conversion efficiencies achieved by one-step electrodeposited CuInS₂ absorber films without subsequent annealing under Se-containing atmospheres are those of Qiu et al. Their films were deposited from a single solution that contained ions and complexes of Cu, In, and Se. The films were postdeposition annealed and resulted in conversion efficiencies of 7% [15, 16].

Previously, we fabricated FTO/CuInS₂/polyaniline base/ZnO/FTO heterojunction solar cell and it was found that J_{sc} , V_{oc} , and η are 3.2×10^{-6} A/cm², 0.714 V, and 1.92×10^{-3} % for FTO/CuInS₂/ZnO/ITO heterojunction solar cell while J_{sc} , V_{oc} , and η are 3.25×10^{-6} A/cm², 0.724 V, and 1.8×10^{-3} % for FTO/CuInS₂/polyaniline base ZnO/ITO heterojunction solar cell [17, 18]. The problems of electrochemical deposition of

CuInS₂ film are the precipitation of the sulfur particles and increasing of the pH during the electrodeposition. The aim of this work is to use DBSA as a surfactant and suspending agent to prevent the precipitation of sulfur and to control the pH of the precursor solution. The optical, crystalline, and electrical properties of the prepared CuInS₂ compounds will be investigated.

2. Experimental Work

2.1. Materials. Indium Chloride (InCl₃) anhydrous is purchased from Alpha Chemika. Copper chloride (CuCl₂), acetic acid, sodium hydroxide (NaOH), zinc acetate dihydrate, and sodium thiosulphate (Na₂S₂O₃) were obtained from El Nasr pharmaceutical chemicals Co., Egypt. Methanol, dodecylbenzene sulphonic acid (DBSA) and hydrofluoric acid (HF) were obtained from Elgoumhouria Co. Egypt. Tin chloride (SnCl₂) was obtained from Prolabo Company, Paris, France.

2.2. Preparation of CuInS₂ onto FTO Substrate. CuInS₂ was electrochemically deposited onto FTO substrate. FTO with a sheet resistance equal to 40 Ω/□ was prepared using a spray technique by adding 22.5 g methanol, 2.5 g acetic acid, and 1.0 g tin chloride and then mixing these solutions together in ultrasonic bath. One drop of HF was added to the previous solution and spraying the final solution onto the glass substrate at temperature 400°C. CuInS₂ layers were prepared electrochemically in one step from 0.1 M copper chloride, 0.1 M indium chloride, and 0.1 M sodium thiosulphate. The pH of the solution was adjusted with dodecylbenzene sulphonic acid (DBSA) using digital Solaron pH meter. A standard three-electrode cell was used; the working electrode was FTO substrate, the counter-electrode was Pt sheet, and the saturated calomel electrode (SCE) was used as a reference electrode. The electrochemical deposition process was controlled by Gamry G750 potentiostat/galvanostat device with pilot integration controlled by PHE200 software. Cyclic voltammetry and chronoamperometry were carried out under different conditions, such as pH, In, Cu, and S ions concentrations. The electrodeposited thin films were annealed in a silica tube placed in a controllable tube furnace for 30 minute in N₂ as an ambient at 400°C.

2.3. Fabrication of FTO/CuInS₂/ZnO/FTO Heterojunction Solar Cell. ZnO NPs powder was prepared as follows: 100 mL of a methanol-based 0.1 M NaOH solution was first heated to 65°C and 2.19 g of zinc acetate dihydrate was then added under constant stirring till a transparent solution formed and 50 mL distilled water was added to precipitate the ZnO NPs powder. The resulting powder was washed with double distilled water then dried in an oven at 200°C for 3 hrs. The ZnO powder was grounded in a porcelain mortar in a small amount of double distilled water. FTO substrate was cleaned in acetone and methanol in ultrasonic bath. The ZnO electrode was prepared by spreading of ZnO colloidal onto FTO. The electrode was sintered for 30 min at 250°C an atmospheric ambient. The heterojunction solar cell was fabricated by sandwich of both FTO/CuInS₂ and ZnO/FTO.

2.4. Thin Film Characterization. Transmission spectra of the electrodeposited thin films onto FTO were obtained using Evolution 200 spectrophotometer in the range of 300–900 nm. X-ray diffraction (XRD) scans were carried out using Shimadzu-7000 diffractometer at room temperature in the range of Bragg angle (2θ) from 5 to 90°. The XRD characterization was done using a Cu Kα radiation (k = 1.54 Å). Atomic compositions were obtained by JEOL JSM6360LA. Current-voltage characteristics were measured both in the darkness and under illumination using a computerized Keithley 2635A source meter. The level of illumination of tungsten halogen lamp was calibrated using a Solarex standard solar cell.

3. Results and Discussion

3.1. Cyclic Voltammetry and Chronoamperometry Studies. Figure 1 shows the cyclic voltammetry of solution containing 5 mL of 0.1 M CuCl₂, 5 mL of 0.1 M InCl₃, and 150 mL of Na₂S₂O₃ at different pHs with 25 mV/s scan rate. In cathodic one-step electrochemical deposition of compound semiconductor thin films, the simultaneous reduction of all the constituent ions at the same potential in suitable proportions is necessary in order to achieve the desired film composition. Acidic solutions are used because the reduction of thiosulphate ions is facilitated. Acidity of solution or pH was adjusted to the required value by adding DBSA to prevent the precipitation of the sulfur element. Colloidal sulfur is consumed to form sulfide through the electrochemical deposition. It is observed that pH has a great affect on the adhesion and compositions of CuInS₂ films. From CVs shown in Figure 1, it is noted that the increasing of pH shifts the electrodeposited voltage to more negative. The formed films were thin and adherent to the substrate. In addition, the decreasing of pH increases the deposition current. The sulfur element precipitates at pH lower than 1.5 and the formation of CuInS₂ thin films will be difficult.

Figure 2 indicates the chronoamperometry curves at –1.0 V of a solution containing 5 mL of 0.1 M copper chloride, 5 mL of 0.1 M indium chloride, and 150 mL of sodium thiosulphate at different pHs. This confirms that the decreasing of pH leads to the increasing of electrodeposition cathodic current. At pH equal to 1.5, the chronoamperograms show 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.

3.2. XRD and EDX Studies. The CuInS₂ compound films obtained onto FTO/glass substrate show a good uniformity and adherence, yellow to brown color that converts to dark brown after heat treatments at 400°C in nitrogen atmosphere for 30 min. Figure 3 shows XRD patterns of films grown onto FTO at –1.0 V from solution containing 5 mL of 0.1 M copper chloride, 5 mL of 0.1 M indium chloride, and 150 mL of sodium thiosulphate at different pHs. According to the standard JCPDS cards, one set corresponds to the tetragonal structure of CuInS₂ and the other corresponds to the

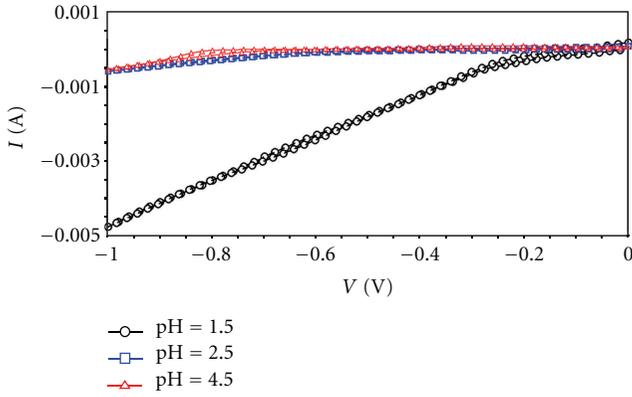


FIGURE 1: Cyclic voltammograms of solution containing 5 mL of 0.1 M CuCl_2 , 5 mL of 0.1 M InCl_3 , and 150 mL of 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ at different pHs with 25 mV/s scan rate.

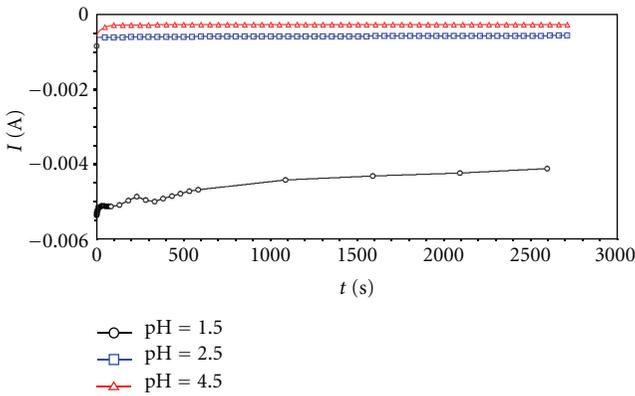


FIGURE 2: Chronoamperometry curves of the formation of Cu-In-S compounds from solution containing 5 mL of 0.1 M CuCl_2 , 5 mL of 0.1 M InCl_3 , and 150 mL of 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ at -1.0 V at different pHs.

FTO substrate. A series of characteristic peaks indicate the formation of a tetragonal cell of CuInS_2 compound at 26.11° , 27.41° , 37.3° , and 46° [19]. These peaks are well defined and more intense at pH equal to 1.5. The planes (112), (222), (220), and (312) in CuInS_2 compound correspond to the following Bragg angles 26.11° , 27.41° , 37.3° , and 46° , respectively. The XRD signals intensity from the CuInS_2 compound phases increases with the decreasing pH and at pH equal to 1.5 the films are strongly oriented along the (222) plane. It is concluded that the electrochemical deposition process proposed gives rise to the formation of CuInS_2 the compound, without requiring the second H_2S annealing step.

Table 1 shows the results of EDX of the electrochemical deposited films at -1.0 V at different pHs from solution containing 5 mL of 0.1 M copper chloride, 5 mL of 0.1 M InCl_3 , and 150 mL of 0.1 M sodium thiosulphate. It is observed that the increasing of pH leads to a decrease in the amount of sulfur in the CuInS_2 compound and deviate from the stoichiometric ratio. It is noted that the sample

prepared at pH equal to 1.5 has the atomic composition near the conventional composition or stoichiometric compound. According to these results, the stoichiometry obtained from the electrochemical deposited films could be related to CuInS_2 species.

3.3. Optical Spectra. Annealed CuInS_2 compound films electrochemically deposited at -1 V onto FTO glass substrate were used to determine the band gap energy at room temperature. The optical transmission spectra of the films at different pHs from the solution containing 5 mL of 0.1 M copper chloride, 5 mL of 0.1 M indium chloride, and 150 mL of sodium thiosulphate were recorded in the interval of 300–900 nm as shown in Figure 4. It is noted that the transmittance level was lowered in the visible range and increased in the infrared region. This is maybe due to the presence of other phases of CuInS_2 as was shown in the XRD patterns. In addition, the transmittance level decreases with the decrease of pH. Transmittance (T) was normalized with respect to film thickness ($d = 1 \mu\text{m}$) by the following equation [14, 20]:

$$\alpha = \frac{-(\ln T)}{d}, \quad (1)$$

where α is the absorption coefficient. The absorption coefficient for direct gap material is given by [20]:

$$\alpha h \nu = B(h\nu - E_g)^{1/2}, \quad (2)$$

where $h\nu$ is the photon energy, h is the Planck constant, E_g is the optical band gap, and B is the constant which is different for different transitions. Inset of Figure 4 shows $\alpha h\nu$ as a function of $h\nu$ for these films. A linear region is observed from values of $h\nu$ higher than about 1.5 eV. The energy gaps were determined by extrapolation to the photon energy axis and the values of energy gaps were found to be 1.95, 2.2, and 2.26 eV for CuInS_2 prepared at pH 1.5, 2.5, and 4.5, respectively. This result confirmed the presence of other phases with the main CuInS_2 phase.

3.4. Current-Voltage Characteristic of FTO/ CuInS_2 /ZnO/FTO Heterojunction.

Figure 5 shows the J - V characteristic curves of FTO/ CuInS_2 /ZnO/FTO structure under darkness and illumination. Under darkness the device behaves like a diode showing excellent junction properties. The J - V curves can be separated into three distinct regions: (i) at reverse bias and at forward bias up to approximately 0.75 V, the characteristic is nearly symmetrical and is governed by a “leakage” current through the high shunt resistance; (ii) at bias corresponding to flat-band conditions, the injection starts, and the exponential region can be distinguished; (iii) at saturation due to series resistance that is observed at higher bias [21].

The different electronic parameters of the solar cell such as J_{sc} , V_{oc} , and efficiency can be calculated from J - V curves under illumination (0.09 W/cm^2).

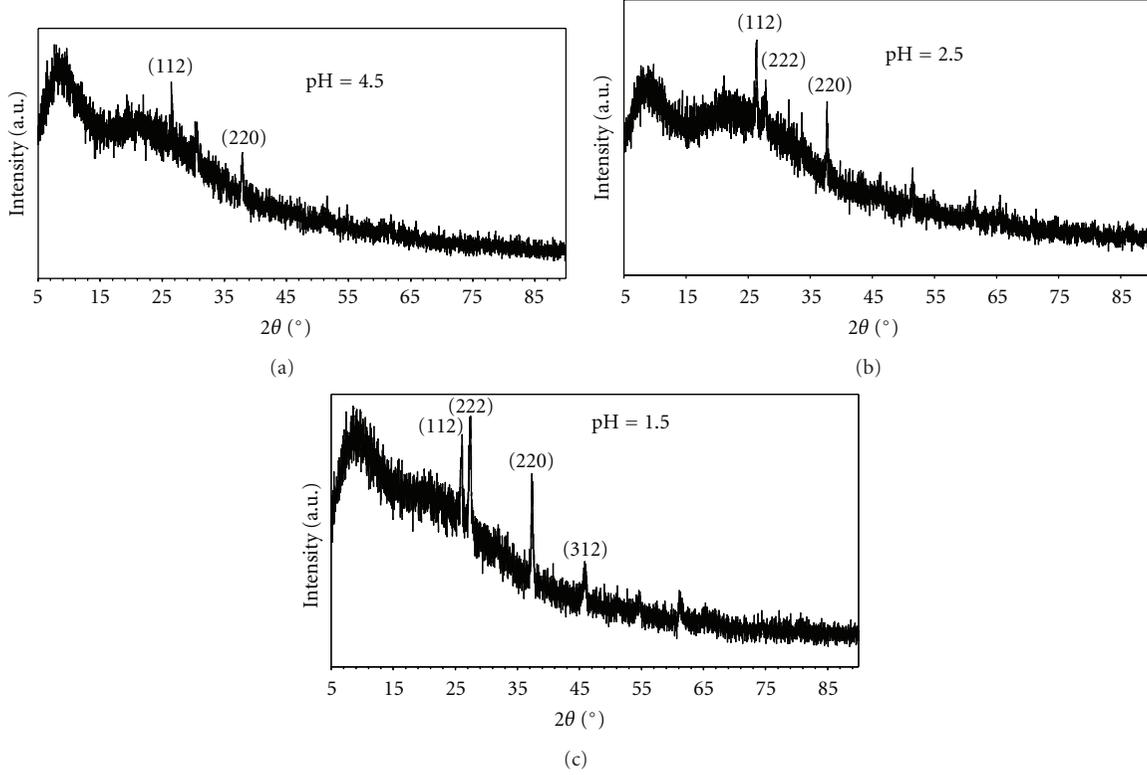


FIGURE 3: XRD patterns of CuInS_2 compounds electrochemical deposited at -1.0 V from solution containing 5 mL of 0.1 M copper chloride, 5 mL of 0.1 M indium chloride, and 150 mL of sodium thiosulphate at different pHs.

TABLE 1: Atomic compositions obtained for the electrochemical deposited films at -1.0 V at different pHs from a solution containing 5 mL 0.1 M of copper chloride, 5 mL 0.1 of M InCl_3 , and 150 mL of 0.1 M sodium thiosulphate.

pH	% of element		
	Cu	In	S
4.5	32	14	54
2.5	38	15	47
1.5	26	23	51

The efficiency η and fill factor FF have been calculated from the J - V curves according to [22]:

$$\text{FF} = \frac{V_m J_m}{V_{oc} J_{sc}}, \quad (3)$$

$$\eta = \text{FF} \frac{V_{oc} J_{sc}}{P_{\text{light}}}, \quad (4)$$

where V_m , J_m are voltage and current density at the maximum power point, respectively, and P_{light} is the illumination intensity in units of power/area. It is found that J_{sc} , V_{oc} , and η are 1.02×10^{-4} A/cm 2 , 0.52 V, and $1.3 \times 10^{-2}\%$, respectively for FTO/ CuInS_2 /ZnO/FTO heterojunction solar cell. The illuminated heterojunction solar cells have low efficiencies and fill factors due to the high series resistance. The violation of the superposition of light and dark characteristics is also observed, which is known as crossover. This shift relates to

the deep level acceptor states, which are present either in the absorber layer or at the interface. This crossover, which reduces FF, may be attributed to the surface recombination of electrons at back contact. The back contact barrier serves as a secondary parasitic diode connected in series but with opposite polarity to the main photocurrent-generating diode. Such a barrier has a distinct signature: a reduced FF along with the so-called crossover of the J - V curve.

4. Conclusion

CuInS_2 thin films were successfully electrodeposited in presence of dodecylbenzene sulphonic acid to adjust pH of the solution and as a suspending agent for the sulfur element onto fluoride doped tin oxide (FTO) substrate. It was found that the increasing of pH shifts the electrodeposited voltage toward more negative and lowers the deposition current. It was concluded that CuInS_2 with an atomic stoichiometric

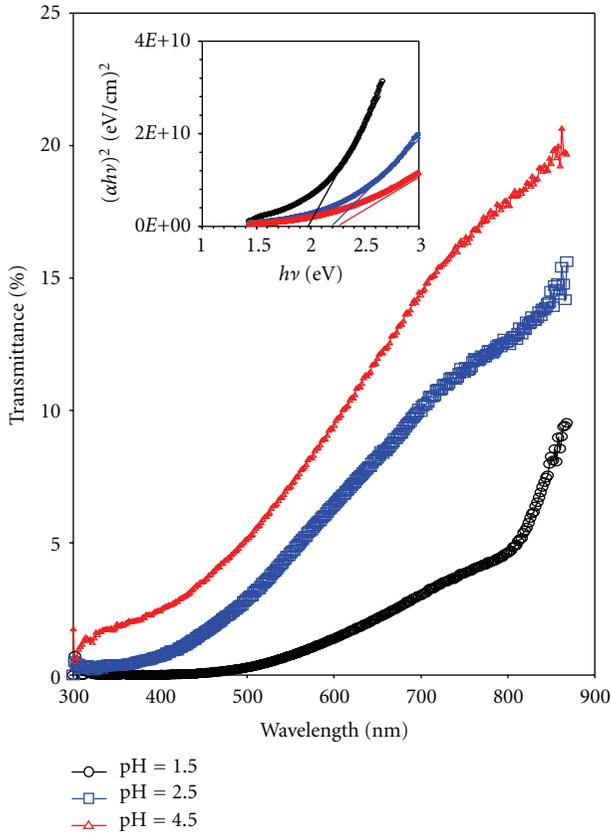


FIGURE 4: UV-visible of CuInS_2 films electrochemical deposited at -1.0 V from solution containing 5 mL of 0.1 M copper chloride, 5 mL of 0.1 M InCl_3 , and 150 mL of 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ at different pHs inset: band gap estimation.

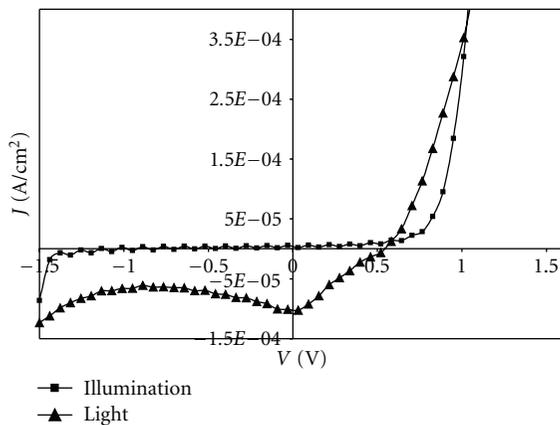


FIGURE 5: Current-voltage characteristic curves of $\text{FTO}/\text{CuInS}_2/\text{ZnO}/\text{FTO}$ heterojunction under dark and illumination.

ratio was prepared at pH equal to 1.5 and 150 mL of 0.1 M sodium thiosulphate, 5 mL of 0.1 M indium chloride, and 5 mL of 0.1 M copper chloride. It was found that J_{sc} , V_{oc} , and η are 1.02×10^{-4} A/cm², 0.52 V, and $1.3 \times 10^{-2}\%$, respectively for $\text{FTO}/\text{CuInS}_2/\text{ZnO}/\text{FTO}$ heterojunction solar cell.

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