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Photoelectrochemical response and characterization of p-$CuInSe_2$ electrodeposited with different citrate ion concentrations

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The photoelectrochemical response of electrodeposited p-$CuInSe_2$ thin films from sulfate bath and different citrate ion concentrations is reported. The best cathodic photoresponse was obtained with thin films deposited in 0.06 M sodium citrate. The film characteristics show a preferred orientation with $\langle 1\,1\,2 \rangle$ direction and sphalerite structure. Dark capacitance measurements in 0.5 M H_2SO_4 solution at 50 KHz showed a linear behaviour from which flat band potential, $V_{fb} \sim -0.275$ V versus saturated calomel electrode (SCE), and a doping level density, $N_A \sim 1.2\ 10^{16}\ cm^{-3}$, were determined.

1. Introduction

Cathodic electrodeposition of semiconducting materials in aqueous medium is an easy way of preparing a cheap and large area of polycrystalline semiconductors for various applications, in particular for the conversion of solar energy in photovoltaic or photoelectrochemical cells [1–3]. Polycrystalline thin films of $CuInSe_2$ have been reported as one of the most promising photovoltaic material for thin film solar cells [4–6]. Different electrochemical methods can be used for preparing these materials: selenization of electrodeposited copper–indium alloys, and cathodic electrodeposition from a single electrolyte containing copper, indium and selenium elements, using a complexing agent [7–10]. Citrate and tartrate ions are the most common complexing agents reported for the electrochemical deposition of $CuInSe_2$.

The aim of this work is to investigate the variation of the cathodic photoresponse in alkaline solution of p-$CuInSe_2$ thin films electrodeposited in different citrate ion concentrations. The electrochemical characterization, as well as the structure, flat band potential and carrier concentration of the electrodeposited material, are reported.

2. Experimental procedure

2.1. Electrodeposition of $CuInSe_2$ thin layers

Thin films of $CuInSe_2$ were prepared in aqueous medium according to the procedure reported in [10], dissolving $CuSO_4$ (5 mmol), $In_2(SO_4)_3$ (10 mmol), SeO_2 (10 mmol) at different sodium citrate concentrations (20–80 mmol). The pH of the solution was 1.7, and was adjusted with diluted H_2SO_4. The bath temperature was maintained at 37 °C.

2.2. Electrochemical setup and cell

A standard electrochemical (Schlumberger model 1286) setup was used for the current potential measurement and combined with a frequency response analyser (Schlumberger Model 1250) for the impedance measurements. The electrochemical depositions were carried out in a two compartment cell, each with a double wall for the temperature control bath and separated by a commercial N-324 nafion membrane. The working and reference electrodes were placed in one compartment and the counter electrode in the second half-cell. Photoelectrochemical studies were developed in a one compartment three electrode cell. A rotating nickel disc electrode ($A = 0.316\ cm^2$) and tin oxide deposited by spray pyrolysis onto glass substrates were used as working electrodes. A platinum grid was used as a counter electrode. Polarization curves were performed at $2\ mV\,s^{-1}$, referring the potential to the saturated sulfate electrode (SSE). The differential capacitance was measured, superimposed on an a.c. signal (10 mV peak-to-peak) to the linear voltage sweep. The photoelectrochemical activity was tested in 1 M KOH solution, using a platinum grid as the counter electrode and a saturated calomel electrode (SCE) as a reference. A 1000 W xenon arc lamp was used as the light source, with an intensity of $45\ mW\,cm^{-2}$.

2.3. Optical measurements

The band gap was evaluated from optical absorption measurements, corrected for SnO_2 substrates in the reference beam in the visible–near infrared region, obtained with a cary-17D spectrophotometer. The crystal structure was analysed with a Siemens X-ray diffractometer (XRD) using CuK_α radiation.

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3. Results and discussion

3.1. Electrodeposition of $CuInSe_2$

Polycrystalline thin films of $CuInSe_2$ electrodeposited from a chloride and sulfate bath were reported [10–12], fixing the concentration of the complexing agent. In order to obtain the same material for photoelectrochemical applications, the effect of citrate ion concentrations at a fixed pH and temperature of the bath were analysed. Fig. 1 shows the potentiodynamic response ($\Omega = 500$ r.p.m.) with nickel electrode at different citrate ion concentrations. The two peaks observed at -0.62 and -1.22 V versus SSE, are associated with the formation of Cu_2Se and Cu–In alloy, respectively [10]. Variations of the limiting current with the complexing ion concentrations are observed between -0.85 and -1.00 V versus SSE, corresponding to the range where the $CuInSe_2$ thin films are electrodeposited. The decrease of the limiting current as the complexing agent increases is associated with adsorption of the ions to the nickel's surface. The potential selected for the electrochemical deposition of $CuInSe_2$ was -0.970 V versus SSE for 15 min, and the electrodeposited sample was photoelectrochemically analysed.

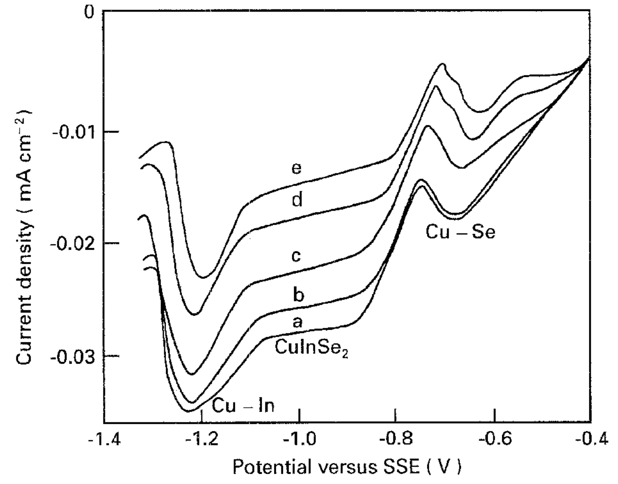

Figure 1 Current–potential curves for Cu–In–Se electrodeposition on a nickel electrode with different citrate ion concentrations: (a) 0.02, (b) 0.04, (c) 0.05, (d) 0.06 and (e) 0.07 mol l^{-1}, respectively. Rotation rates were 500 r.p.m.

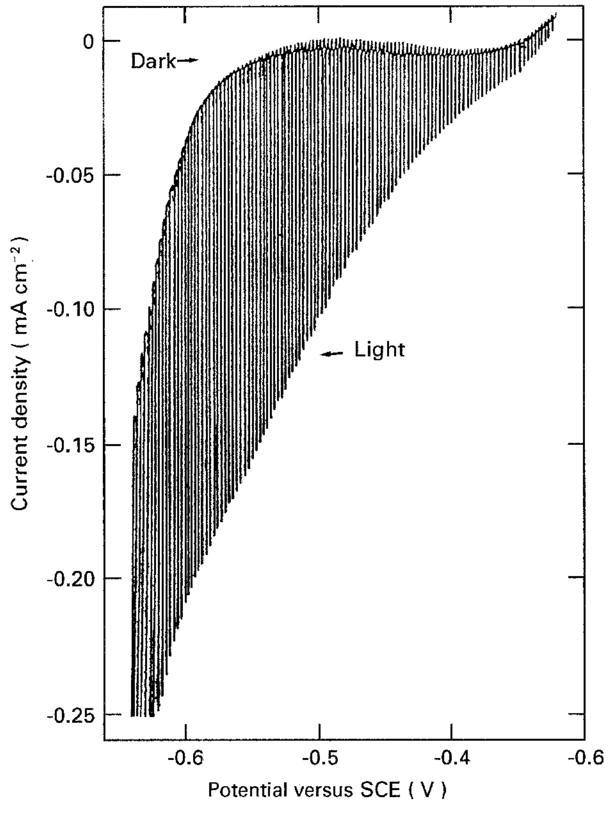

Figure 2 Photocurrent–potential curve under chopped light of the electrodeposited p-$CuInSe_2$–1 M KOH interface. The light intensity was 40 mW cm^{-2}.

3.2. Photoelectrochemical response

$CuInSe_2$ electrodeposited on nickel substrates were tested for photoelectrochemical response in a 1 M KOH solution. In this case, a saturated calomel electrode (SCE) was used as the reference electrode. The cathodic photoresponse of the thin film electrodeposited from a solution containing 0.02 M citrate ion concentration is depicted in Fig. 2. This

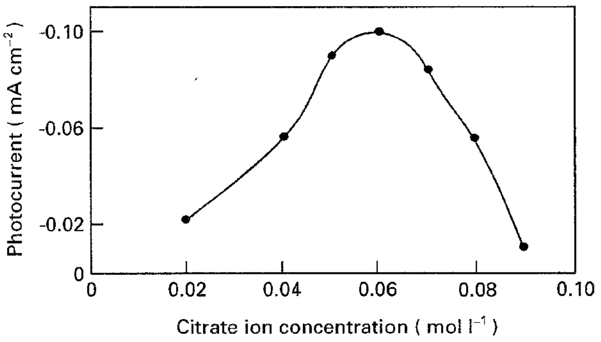

Figure 3 Dependence of the photocurrent of electrodeposited p-$CuInSe_2$ as a function of citrate ion concentration.

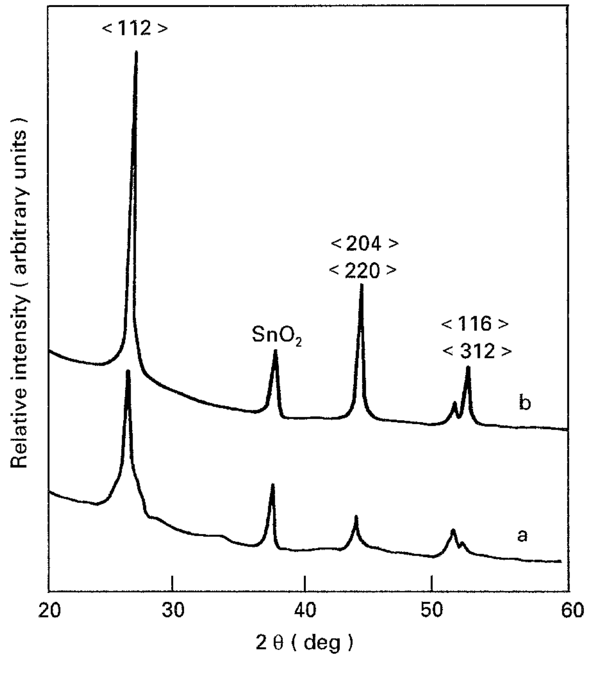

Figure 4 X-ray diffraction patterns of electrodeposited film with 0.06 M ion citrate: (a) as-deposited at -0.970 V versus SSE and (b) annealed at 320 °C.

photoresponse is characteristic of a semiconducting material with p-type conductivity. The onset of the photocurrent was around − 0.320 V and increased with the potential scan, without arriving at a saturated value. The variation of the photocurrent for samples electrodeposited with different citrate ion concentrations is shown in Fig. 3, with a photocurrent value obtained at − 0.550 V versus SCE. The best photoresponses were obtained with samples electrodeposited with 0.06 M sodium citrate. Samples of $CuInSe_2$ electrodeposited on nickel substrates and annealed at 320 °C showed almost the same photoresponse. However, for samples electrodeposited on SnO_2 substrates and annealed under the same conditions, the photoresponse decreased, due perhaps to the high resistivity of the substrate.

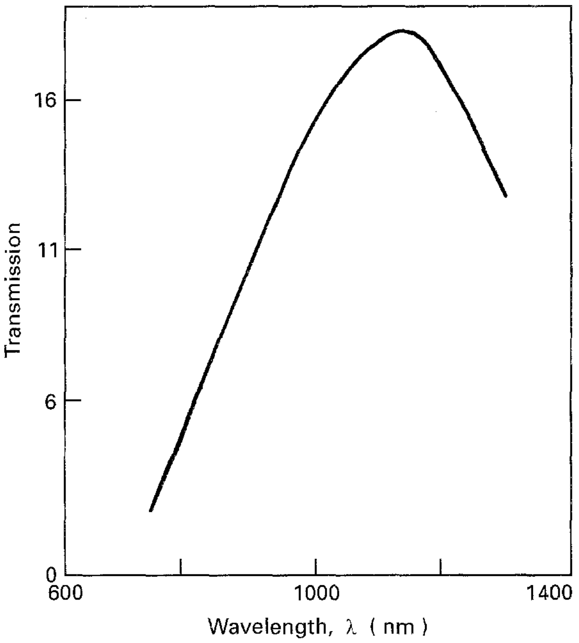

Figure 5 Transmission spectrum of as-electrodeposited p-$CuInSe_2$ film in the conditions of Fig. 4.

3.3. Structural characterization

The structure of electrodeposited p-$CuInSe_2$ with the best photoresponse was analysed using XRD. The X-ray spectra of the as-deposited sample is shown in Fig. 4. The XRD peaks were identified and have been marked in the figure. The XRD data indicated that the as-deposited samples and those annealed at 320 °C showed the same structure, with enlarged grain size in annealed samples. The three main diffraction peaks (⟨1 1 2⟩, ⟨2 0 4, 2 2 0⟩ and ⟨3 1 2, 1 1 6⟩) are displayed. The ⟨1 1 2⟩ peak increased significantly compared to the other two doublets, indicating a preferred structural orientation in the ⟨1 1 2⟩ plane. Pern *et al.* [12] have pointed out that thin film $CuInSe_2$ with these characteristics has a sphalerite structure.

3.4. Optical characterization

A transmission spectrum of $CuInSe_2$ thin film electrodeposited on SnO_2 substrate at − 0.970 V SSE, from the sulfate bath containing 0.06 M sodium citrate, is shown in Fig. 5. The maximum of the curve is observed at 1150 nm in the visible–near infrared zone. From this spectrum, the band gap of the semiconducting material has been determined, using the model of direct dipolar transition between parabolic bands [13]. A plot of $(\alpha h\nu)^2$ against $h\nu$ is shown

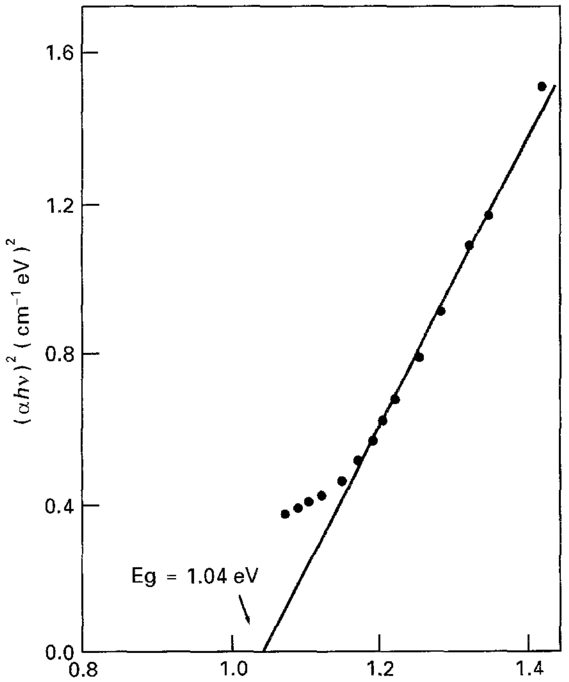

Figure 6 Determination of band gap energy from a plot of $(\alpha h\nu)^2$ against $Eh\nu$ for as-deposited p-$CuInSe_2$.

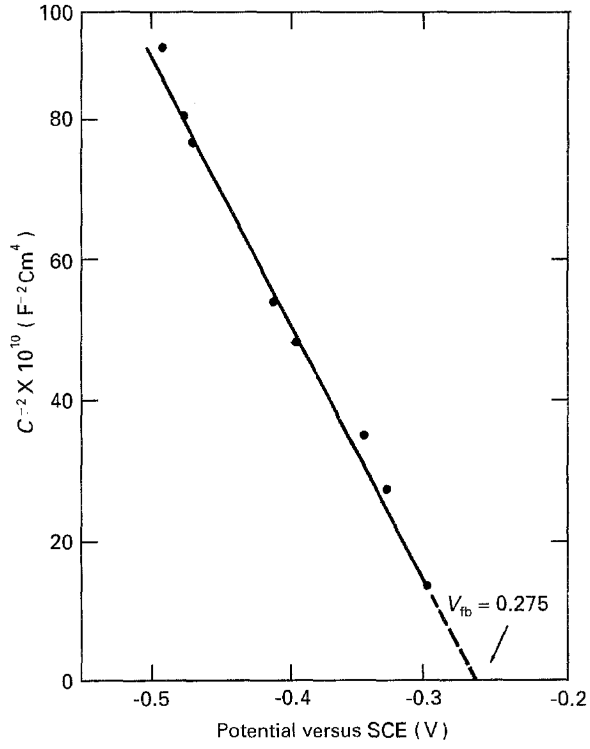

Figure 7 Mott–Schottky plot for a p-$CuInSe_2$ thin film in 0.5 M H_2SO_4.

in Fig. 6, from which an Eg of 1.04 eV, was evaluated. This value is in agreement with previously reported values for polycrystalline $CuInSe_2$ thin films [5, 10].

3.5. Energetic characterization

Dark differential capacitance was measured as a function of an applied voltage for $CuInSe_2$ thin films in 0.5 M H_2SO_4. The relation between the capacitance and the voltage for p-type semiconducting materials is described by the Mott–Schottky equation [14]

$$\frac{1}{C^2} = \frac{2}{\varepsilon_0 \varepsilon e N_A A^2}\left(- V + V_{fb} - \frac{kt}{e}\right) \quad (1)$$

where C is the capacitance of the space charge layer, V the applied voltage, ε_0 the permittivity, A the surface area, e the elementary charge and the other quantities have their usual meanings. A plot of C^{-2} against the applied potential is depicted in Fig. 7. The flat band potential, $V_{fb} = -0.275$ V versus SCE, was determined by extrapolation to $C^{-2} = 0$ and a doping level, $N_A \sim 1.2 \times 10^{16}\,\mathrm{cm}^{-3}$ was obtained from the slope of the Mott–Schottky plot, assuming a dielectric constant value, ε, as ten [15].

4. Conclusions

The effect of citrate ion concentration has been analysed in the photoresponse of p-$CuInSe_2$ electrodeposited at -0.970 V versus SSE. The best photocurrents were obtained with thin films electrodeposited with 0.06 M sodium citrate. The XRD data for as-deposited samples and annealed at 320 °C showed a polycrystalline material with preferential crystallographic orientation in the $\langle 1\,1\,2 \rangle$ direction and sphalerite structrue. From optical and electrical characterizations, values of 1.04 eV for Eg and $V_{fb} = -0.275$ V versus SCE, were obtained. These values are in agreement with those reported for p-$CuInSe_2$ thin films.

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