

Surface modification of electrodeposited p-CuInSe₂ thin films with selenium and ruthenium

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Changes in the surface composition of electrodeposited p-CuInSe₂ (CIS) thin films with electrodeposited selenium and ruthenium chemically adsorbed, improve the cathodic photocurrent response in sulphuric acid solution. The structural and chemical composition of the as-deposited and modified surface have been determined by X-ray diffraction and atomic absorption spectrometry before and after illumination. The estimates of the optical band gap have been analysed and discussed in terms of bulk modifications arising from the indium released, and its substitution by selenium or ruthenium.

1. Introduction

Electrodeposited thin film semiconductors are suitable candidates for photocatalysts in water electrolysis cells because they are formed by a low-cost process, and can be used for large-scale production [1–5]. The main difficulty in photoelectrochemical cells lies in the instability of these semiconductors in aqueous electrolyte solutions. However, modifications of the surface with some metallic and organic compounds lead to improvement of the stability of the semiconductor–solution interface. It has been suggested that adsorbed ions interact with the surface state located on the band gap of the material, creating new band edge positions by local bonding with the solid. The cathodic electrodeposition of p-CuInSe₂ (CIS) has been reported by a number of researchers, as one of the most promising materials for photoelectrochemical solar cells [6–8]. As a photocathode, the current obtained when the surface is illuminated is sometimes analysed in terms of hydrogen reduction reactions or surface degradation by charge carriers recombinations.

In this work, it was found that the electrodeposited selenium and ruthenium chemically adsorbed on the CIS surface improve the cathodic photocurrent in an acid medium. The chemical composition of the materials before and after illumination of the as-grown CIS and the modified surface were analysed by X-ray diffraction (XRD) and atomic adsorption spectroscopy. Variations in the energy gap were also determined and the results are discussed in terms of the material's stability.

2. Experimental procedure

Thin films of CuInSe₂ were prepared in an aqueous medium according to the procedure reported elsewhere

[9, 10], dissolving CuSO₄ (5 mM), In₂(SO₄)₃ (10 mM), SeO₂ (10 mM), K₂SO₄ (60 mM) and NaCit (60 mM). The pH of the solution was 1.7, adjusted with diluted H₂SO₄. The bath temperature was maintained at 37 °C, to avoid citrate ion decomposition. Thin oxide, and electrically conducting glass, obtained by spray pyrolysis in air [11], with a surface resistance of 50 Ω/□, was used as a working electrode. The working electrode was dipped to a depth of 1 cm into the solution, supported with a metallic holder.

Polarization curves were recorded at 2 mV s⁻¹, referring the potential to the saturated sulphate electrode (SSE). Under these conditions, thin films of p-CuInSe₂ were electrodeposited at -0.97 V versus SSE and characterized as previously reported [10]. The electrodeposition was carried out for 15 min under potentiostatic conditions in a stirred solution. The photodeposition of selenium was obtained by scanning the potential five-fold from -0.3 to -0.90 V versus SSE, in a 0.5 M SeO₂ solution, under illuminated conditions.

Chemical modification of the surface of the electrode with ruthenium was attained by immersing the CIS into 0.01 M RuCl₃ · 3H₂O in 0.1 M HNO₃ solution for approximately 20 min. A standard electrochemical (Schlumberger Mod 1286) apparatus was used for the current–potential measurement. A 1000 W xenon lamp was used as light source with an intensity of 45 mW cm⁻², eliminating ultraviolet radiation with a water filter.

Elemental analysis of the CuInSe₂, CuInSe_x and CuInSe_xRu_y was carried out by atomic absorption spectrometry (Perkin–Elmer Mod 2380). The analysis were performed in an air-acetylene flame with specific hollow cathode lamps, working at λ = 196.0, 303.9

and 324.8 nm for selenium, indium and copper, respectively. Standard solutions in a concentration range from 5–15 p.p.m. were used for calibration. Analysis of the elements was done on the solutions of the semiconductors dissolved in hot nitric acid for 5 min, then diluted with 5 ml doubly distilled water in a volumetric flask. The concentration values were obtained by direct reading. The molecular ratio between metals was calculated by dividing the concentration of each element by their atomic weight. The copper value was taken as the unit of the atomic ratio calculated. The band gap of the as-grown and modified material was evaluated from the transmission spectra obtained with a Cary 17D spectrophotometer. The XRD patterns were obtained with the CuK_α radiation of the XRD Shimadzu, model XD-3A.

3. Results and discussion

Fig. 1 shows a typical current–potential behaviour obtained on a nickel disc electrode ($A = 0.316 \text{ cm}^2$), turned at 500 r.p.m. Two peaks were observed at -0.62 and -1.22 V versus SSE, and were associated to the formation of Cu_2Se and Cu–In alloy, respectively [9]. A limiting current was observed between -0.85 and -1.00 V versus SSE, corresponding to the range where the polycrystalline CIS thin films were electrodeposited [10]. Thin films of CIS were electrodeposited on the conducting glass at a constant potential of -0.97 V versus SSE for 15 min.

The photoelectrochemical response obtained for CIS sample in 0.5 M sulphuric acid solution by sweeping the potential in a cathodic direction and illuminating, is shown in Fig. 2. A small photocurrent was observed in the working range from -0.40 to -0.80 V versus SSE with the bare surface; this may be generated by recombination processes due to the high density of the surface defects created by surface chemistry change or by reduction of the surface species of the electrodeposited layer [11]. However, the photoresponse was increased as the surface was modified with selenium (Fig. 2b) and then with ruthenium (Fig. 2c), respectively, due to the excess surface charge

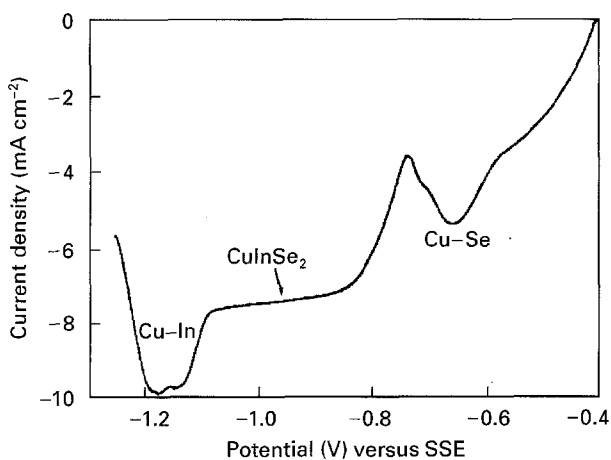


Figure 1 Current–potential characteristics for the CIS electrodeposition on a nickel electrode at $\text{pH} = 1.7$, 2 mVs^{-1} and 500 r.p.m. rotation rate.

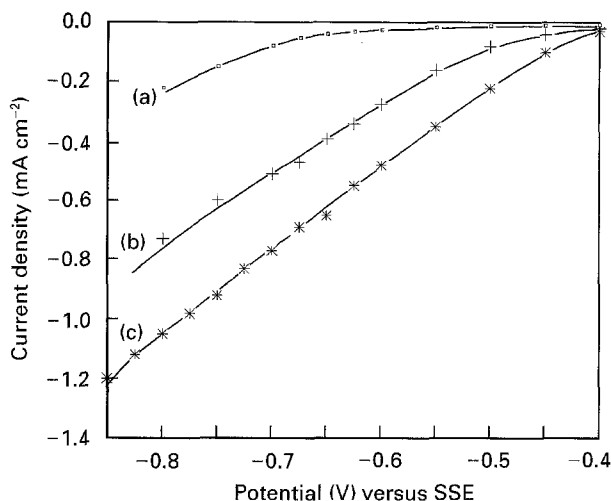


Figure 2 Photocurrent–potential behaviour under illumination of (a) as-deposited p-CuInSe₂, (b) p-CuInSe₂/Se and (c) CuInSe₂/Se/Ru in $0.5 \text{ M H}_2\text{SO}_4$. Light intensity = 45 mW cm^{-2} .

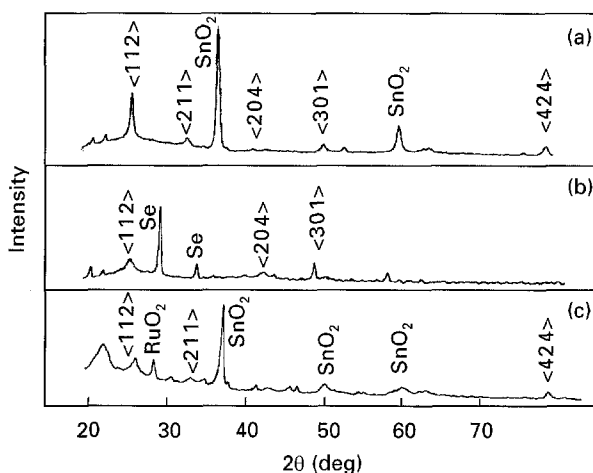


Figure 3 XRD spectra (CuK_α source) of (a) p-CuInSe₂, (b) p-CuInSe₂/Se, and (c) CuInSe₂/Se/Ru as-grown.

which induces transfer of photogenerated electrons by the reduction of dissolved protons into hydrogen [12].

XRD patterns of CIS and modified materials are shown in Fig. 3. In addition to all peaks of the SnO_2 substrate on which the as-grown films were deposited, Fig. 3a corresponds to CIS with a chalcopyrite structure [7–9], with a preferred orientation in the $\langle 112 \rangle$ plane (JPCDS card 23–209); this was also observed by Pottier and Maurin [9]; the width of the peaks shows the formation of large crystals of CIS. However, the non-linearity of the background shows the formation of an important quantity of amorphous material. Fig. 3b depicts the CIS coated with selenium; here the height of the CIS peak decreases and two new peaks appear at $2\theta = 30.6^\circ$ and 35.1° ; these peaks correspond to metallic selenium (JPCDS cards 27601 and 27602). The CIS_xRu (Fig. 3c) shows a broad peak at $2\theta = 22.2^\circ$ which has not yet been identified; the other peak at $2\theta = 28.75^\circ$ corresponds to RuO_2 . The selenium metal peak disappears. XRD patterns of all samples obtained after illumination are shown in Fig. 4. Fig. 4a and b show similar spectra to Fig. 3a and b, indicating that the structures were not modified

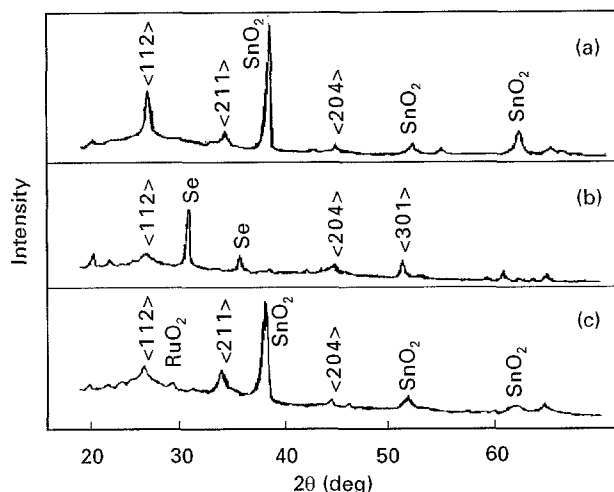


Figure 4 XRD spectra (CuK α source) of (a) p-CuInSe $_2$, (b) p-CuInSe $_2$ /Se, and (c) CuInSe $_2$ /Se/Ru after illumination.

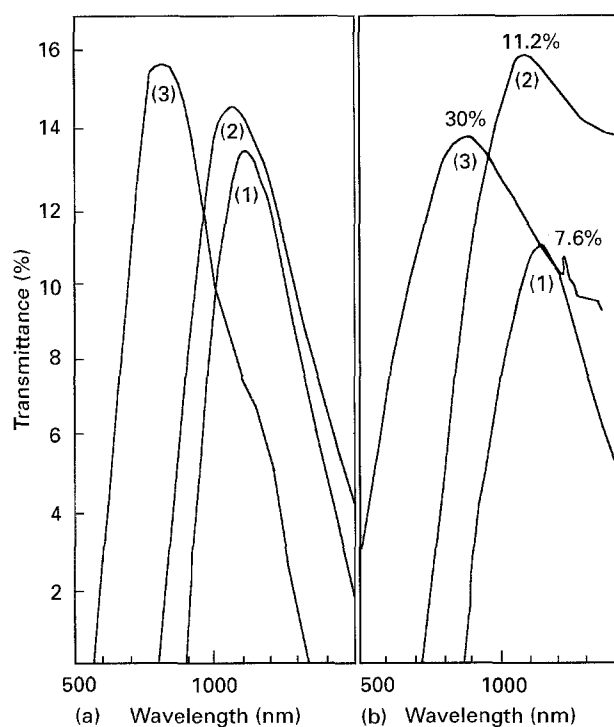


Figure 5 Transmittance spectra of the semiconductors, (a) before and (b) after illumination. 1, CIS, 2, CIS/Se; 3, CIS/Se/RuO $_2$.

during illumination, whereas the CIS $_x$ Ru peak at $2\theta = 28.75^\circ$, corresponding to RuO $_2$, decreases; the peak which was not identified at $2\theta = 22.2^\circ$, disappears.

Experimental transmission spectra of the as-deposited film of CIS, with electrodeposited selenium and adsorbed ruthenium are shown in Fig. 5a, these spectra were obtained before illumination. Fig. 5b shows the transmission spectra of different semiconductors after illumination; at the top of each peak, the corresponding transmission percentage is given. There were no changes in the wavelength of the maximum transmission spectra for the samples before and after illumination. The transmission bands of as-deposited CIS/Se were slightly modified. However, when the CIS/Se was treated with ruthenium, the transmission

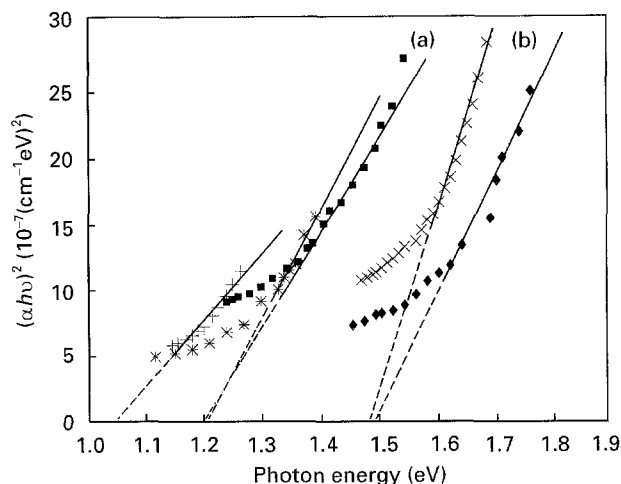


Figure 6 Estimation of the band gap energy from the plot of $(\alpha h\nu)^2$ against photon energy for the semiconductors (a) before and (b) after illumination. (a) (+) p-CIS, (*) p-CIS $_x$, (■) p-CIS $_x$, (×) p-CIS $_x$ Ru $_y$, (◆) p-CIS $_x$ Ru $_y$.

TABLE I Energy band gap and chemical composition of p-CuInSe $_2$ and modified semiconductors

Material	E_g (eV)	Chemical composition after illumination
CuInSe $_2$	1.0	CuIn $_{0.33}$ Se $_{1.55}$
CuInSe $_x$	1.2	CuIn $_{0.33}$ Se $_{1.5.86}$
CuInSe $_x$ Ru $_y$	1.5	CuIn $_{0.11}$ Se $_{1.55}$ /RuO $_2$

spectrum was also modified and the maximum was shifted towards the visible region. Similar behaviour was also maintained after illumination. The transmission spectra of Fig. 5a were slightly increased with the modification of the CIS. However, after illumination (Fig. 5b), this effect was more remarkable owing to the degradation of material by release of indium (Fig. 5b, 2) and ruthenium (Fig. 5b, 3). These effects were accomplished by the CIS dissolution, as confirmed by XRD and atomic absorption measurements. The transmission spectra were analysed using the model of direct dipolar transitions between parabolic bands [13]. Fig. 6 shows the plot of $(\alpha h\nu)^2$ against the photon energy ($h\nu$) to estimate the variation in the optical band gap, E_g , on the naked and modified surfaces. It has been reported previously that $E_g = 1.04$ eV with naked CIS [10, 14]. Table I summarizes the E_g values estimated from Fig. 6. As can be seen, the E_g values were maintained when the CIS/electrolyte and CIS/Se/electrolyte interfaces were illuminated. The E_g value of CIS/Se/Ru is understandable in terms of ruthenium incorporation into the CIS lattice creating another less crystallized material, as observed from the XRD patterns (Figs 3c and 4c).

The chemical composition obtained by atomic absorption spectrometry reported in Table I after illumination of the semiconductors, shows evidence that the kinetics of the reduction reaction occur simultaneously with those of material degradation, related to indium released from the materials.

4. Conclusion

It has been shown that the effect of a thin film of p-CuInSe₂ modified by both electrodeposited selenium and adsorbed ruthenium, induces an excess surface charge which enhances the cathodic photocurrent in a sulphuric acid solution. This effect is probably related to the formation of novel materials due to the indium release and substitution by selenium or ruthenium. This is confirmed by the band gap variation of the modified semiconductor.

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