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Electrochemical growth of CuInSe$_2$ thin film on different substrates from alkaline medium. Characterization of the films

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Abstract The simultaneous electrodeposition of the system Cu–In–Se was investigated. The study was carried out at pH 8.5 using diethylentriamine as complexing agent for the Cu^{+2} ion. The synthesis of CuInSe$_2$ semiconductor thin films was carried out by electrodeposition on different substrates [indium–tin oxide (ITO) on glass, aluminum and type 304 steel]. The simultaneous codeposition of the Cu, In, and Se was achieved by constant potential electrolysis technique in aqueous solutions containing the elements that conform this material. The deposits of CuInSe$_2$ were about 4 μm thick, which is thick enough for the photovoltaic effect to take place. The as-deposited films were characterized by atomic emission spectroscopy with inductive coupling plasm (AES-ICP) and scanning electronic microscopy (SEM). Annealed films were characterized X-ray diffraction, optical NIR spectroscopy, and photoelectrochemical studies The films were obtained with a well-defined composition, very close to the expected one. Homogeneous deposit with chalcopyrite structure was produced. A In$_2$O$_3$ phase was also observed. Annealing of the film improved the crystallinity of the films. Good photo response, an appropriate absorption coefficient, and a band gap of 1.09 eV were obtained.

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Introduction

The diselenide of indium copper (CuInSe$_2$), which is named CIS, is a ternary semiconductor from the I–III–IV2 groups. It belongs to the family of the chalcopyrite. In the last years, it has been an object of considerable interest [1–7] because of the use of this material in the production of optical and electronic devices, such as diodes, originators of laser beams, light detectors, photoelectrochemical and solar cells, etc. CuInSe$_2$ is a very important material, as it possesses an energy bandwidth of about 1.1 eV [2] and an absorption coefficient of 3×10^4 cm^{-1}; both values make it appropriate for the conversion of the solar energy. This is a direct-band semiconductor, and it can exhibit any of the two types of electric conductivity, n or p. These features make it a good candidate in the production of the above-mentioned electronic devices.

The study of CuInSe$_2$ polycrystalline films has stimulated the development of a huge variety of methods for their preparation. The electrodeposition method is probably the most appropriate and promising. This is due to its low cost, easiness, high efficiency, and stability of the product [3]. Electrochemical methods are suitable for growing large-area thin films economically, but compound deposition still suffers from many problems associated with the control of solution composition, deposition potentials, pH, and complexing agents. Triethanolamine and ammonia, citrate ions, citric acid, or thiocyanate as complexing agents have been used for the CuInSe$_2$ electrodeposition [8]. In this work, the
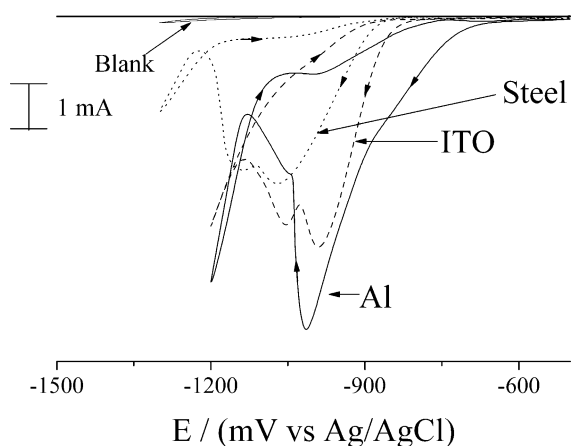
Fig. 1 Cyclic voltammograms of Al (*solid line*), ITO (*dashed line*), and type 304 steel (*pointed line*) electrodes, submerged in a 300-mM dietilentriamine/3 mM of $Cu(NO_3)_2$/3 mM $In(NO_3)_3$, and 5 mM SeO_2 (a), at pH 8.5. Scan rate was 20 mV s^{-1}

electrochemical growth of $CuInSe_2$ films is studied in alkaline medium. To avoid the formation of elemental Cu and In, dietilentriamine was used as complexing agent. Also, the influence of electrode material in the composition of the semiconductor was tested by using ITO on glass, aluminum, and type 304 steel as substrates. Optical and structural characterization of the films is also analyzed and reported.

Experimental

The chronoamperometric and voltammetric experiments were carried out using a Potenciostat/Galvanostat EG&G Princeton Applied Research model 263, which was coupled to a PC. A single compartment cell (50 ml) was used. Indium–thin oxide (ITO) on glass, aluminum, and 304 steel were utilized as working electrodes, a platinum bar as counterelectrode, and saturated Ag/AgCl (KCl saturated) as reference electrode. All the electrolytic solutions were prepared with ultrapure water (18 MΩ) and the reagents were of analytic grade. The electrolytic medium was a mixture of 0.6 M nitric acid and 0.3 M dietilentriamine, the latter used as complexing agent. This medium contained 3 mM $Cu(NO_3)_2$, 3 mM $In(NO_3)_3$, and 5 mM SeO_2. The pH of the solutions was adjusted to 8.5, using HNO_3 and NaOH. The oxygen in the solutions was removed by bubbling argon gas for 5 min.

The cyclic voltammograms were recorded at 20 mV/s scan rate, in negative direction, at room temperature. Before each experiment, the aluminum and steel working electrodes were sanded with 240/400/600 silicon carbide material (carbonen) and polished with 0.3 μm alumina. Next, they were submerged in methylcetone to degrease them. Then, they were introduced in an ultrasonic bath for 5 min and, finally,

were dried with a soft cloth. The ITO glass electrode was degreased with methylketone before being used.

The films on different substrates were electrodeposited by constant potential electrolyses, in a cell of a single compartment and three electrodes. Solutions were not stirred during experiments. The applied potential was −1,100 mV for 1,800 s. The faraday yield was determined by assuming a molecular weight of 336.28 g/mole and 13 transferred electrons [9]. Film thicknesses were determined with a high-resolution vernier.

The amount of the chemical species and the film stoichiometry was determined by atomic emission spectroscopy with inductive coupling plasma (ICP-AES) using a Varian equipment, model Liberty sequential AX. Films were annealed in a quartz tube furnace (Thermolyne model F21125) under N_2 ambient, at 400 °C for ITO and 500 °C for Al and steel. Morphology of the film surfaces were observed by using a scanning electronic microscope, Hitachi model s-2500. The crystallinity of the films was studied by XRD using a diffractometer, Siemens model D5005. A spectrometer Cary 17I was used to perform optical transmission experiments. The photoelectrochemical behavior of the films was evaluated using the electrochemical system mentioned previously. A glass electrochemical cell with a quartz window and a 90-W Oriel 66056 tungsten lamp were utilized in these cases.
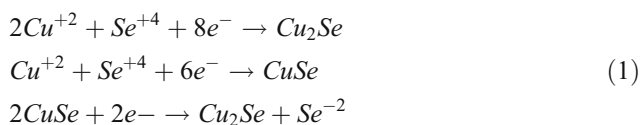
Results and discussion

Electrodeposition of $CuInSe_2$

At pH 8.5, Cu^{+2} and diethylenetriamine form a strong complex [10]. Diethylenetriamine complex formation displaces the copper reduction potential toward more negative values, bringing it near the deposition potential of the indium. Copper reduction to metallic copper during the process of formation of the semiconductor is avoided by this path.

The electrochemical behavior of the Cu–In–Se system was studied by cyclic voltammetry on different substrates (ITO, aluminum, and type 304 steel), at pH 8.5. The deposition potential for ternary $CuInSe_2$ semiconducting material was determined from experimental results. Figure 1 shows the voltammetric response during the electrodeposition of the semiconductor on these materials, which were immersed in solutions containing $Cu(NO_3)_2$ 3 mM, In $(NO_3)_3$ 33 mM, and SeO_2 5 mM. At pH 8.5, Se^{+4} is present in solution as SeO^{-2}, according to Pourbaix diagrams [11]. Two cathodic peaks are observed for ITO and steel electrodes; in the case of aluminum, a cathodic peak and a shoulder are observed. This voltammetric behavior has been previously reported for CIS formation on Mo,
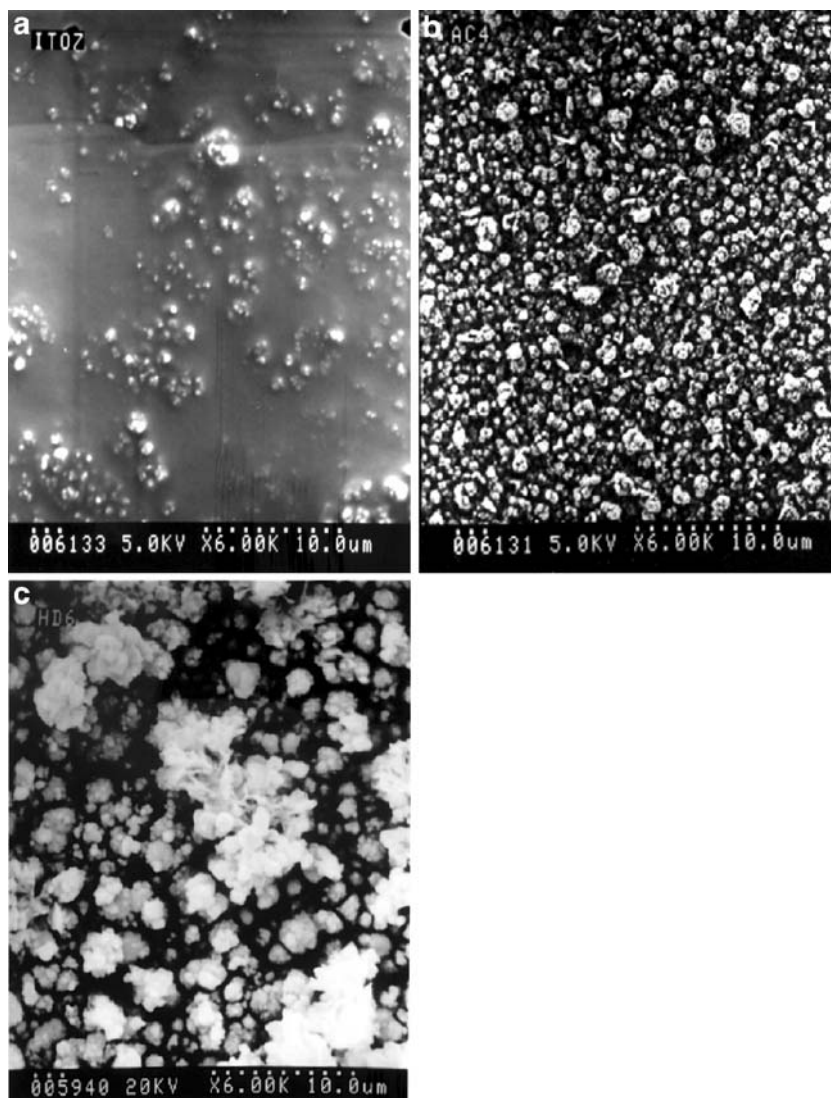
Fig. 2 SEM micrographs from electrodeposited CuInSe$_2$ film on **a** ITO, **b** Type 304 Steel, and **c** Al

graphite, and Au electrodes in acid media [12, 14–16]. A reaction mechanism has been proposed [5, 6], the main reactions being:

$$2Cu^{+2} + Se^{+4} + 8e^- \rightarrow Cu_2Se$$
$$Cu^{+2} + Se^{+4} + 6e^- \rightarrow CuSe \qquad (1)$$
$$2CuSe + 2e- \rightarrow Cu_2Se + Se^{-2}$$

$$2In^{+3} + 3Se^{-2} \rightarrow In_2Se_3$$
$$Cu_2Se + In_2Se_3 \rightarrow 2CuInSe_2 \qquad (2)$$

In our case, the CIS deposition potential is shifted to more negative potential due to the pH value and the presence of diethylentriamine complexing agent. It is also observed that the electrochemical behavior of the system Cu–In–Se is not strongly affected by the nature of the used substrate; only a small difference in the cathodic current was observed probably as a result of the differences in roughness factor for the different used materials. A small negative shift in the deposition potential on 304 steel was also observed.

According to the voltammetric results, films were electrodeposited on different electrodes at a constant potential of −1,100 mV. After 30 min of electrodeposition, adherent thin dark-gray films were obtained on the working electrode surface. The working electrode was extracted from the cell and copiously washed with ultra-pure water.

Chemical composition of the films

The whole as-deposited films were dissolved in HNO$_3$ and then analyzed by ICP-AES technique. The average com-
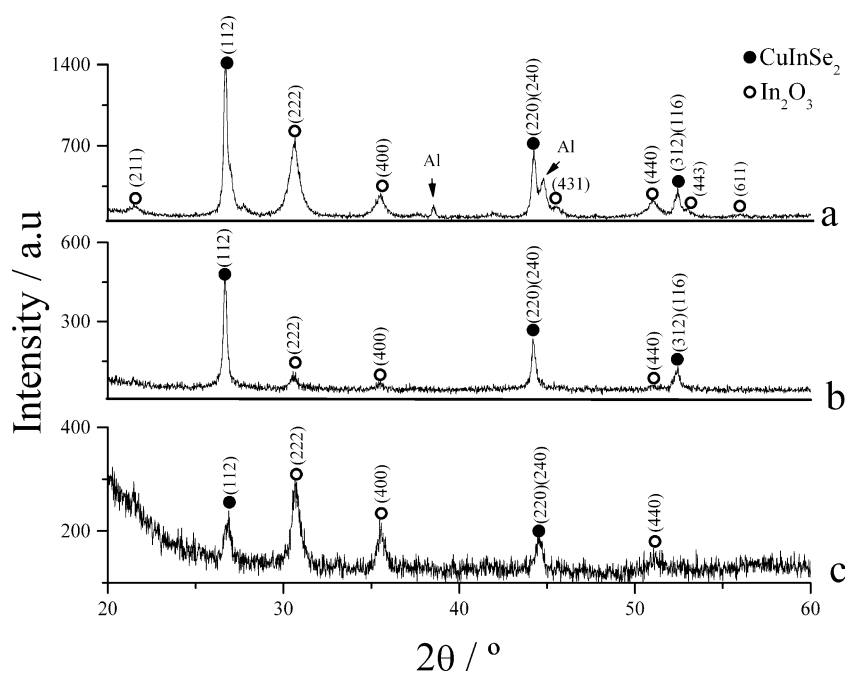
Fig. 3 X-ray diffraction patterns of annealed electrodeposited CIS film on **a** Al, **b** ITO glass, and **c** 304 steel

position of the films in all substrates, allows us to estimate an empirical formula as: $Cu_{2.40}In_{1.00}Se_{3.40}$. According to these results, the stoichiometry obtained from the electrodeposited films could be related to $CuInSe_2$ species, with an excess of CuSe. At the same time, this technique allows us to quantify the amount of the Cu–In–Se deposited on each film. Assuming 13 transferred electrons, a 97% faradaic yield was reached.

Scanning electronic microscopy (SEM) experiments

The analyses of the surface morphology of the as-deposited films were carried out by scanning electronic microscopy. Figure 2a shows the typical morphology of a $CuInSe_2$-prepared film on ITO. A uniform deposit with a compact surface can be observed. Figure 2b shows the SEM micrograph of $CuInSe_2$ film, which was synthesized on steel substrate. It is possible to observe a deposit with a well-defined structure. This structure exhibits multinuclei with uniform size and is cauliflower-shaped. This is a more compact film, in comparison with those deposits obtained from acid media [12, 14, 15]. The prepared $CuInSe_2$ films on aluminum show particles of great size with a more remarkable cauliflower appearance; micrograph is shown in Fig. 2c. Obviously, the difference in morphology can be ascribed to the difference of the substrates nature.

XRD analysis

The thin films were characterized by XRD on the different substrates, with and without annealing. The XRD patterns

of the $CuInSe_2$ samples were registered in the interval from 20 to 60° in 2θ, with a path width of 0.02° and a counting time of 20 s/step. Experimental details have been published elsewhere [13]. Pattern was examined using the PDF-ICDD Database [14].

As-deposited films were amorphous in all cases. Figure 3 shows a typical XRD pattern for a CIS-annealed film on: a) Al, b) ITO glass, and c) 304 steel. A series of characteristic peaks are identified, such as (112), (220), (204), (312), and (116). These peaks correspond to the chalcopyrite phase of the $CuInSe_2$ [15–17]. Additionally, other diffraction peaks are observed, which are ascribed to In_2O_3, which could be formed during thermal treatment. Considerable amounts of In_2O_3 could be formed during the annealing of the film deposited on Al and 304 steel at 500 °C; this can occur by reacting with surface oxides of the substrate and/or with residual oxygen present in N_2 gas. XRD patterns of CIS film on ITO show a minor amount of In_2O_3; in this case, the annealing temperature was 400 °C and the oxide formation is less favoured.

The X-ray patterns of $CuInSe_2$ do not show any preferred orientation. The intensities of the reflections (112), (204), (220), (116), and (312) in the X-ray pattern confirm a statistical distribution of crystallites (ICSD #73351, ICDD-PDF 81-1936). No Cu_2Se peaks were observed in the XRD patterns of the CIS films, probably due to the fact that the diffraction peaks of the Cu_2Se are quite close to some peaks of the CIS chalcopyrite phase [17]. On the other hand, Cu_2Se may also be present as an amorphous phase. Contrary to the results from other authors [15], the annealing of the film in N_2 atmosphere
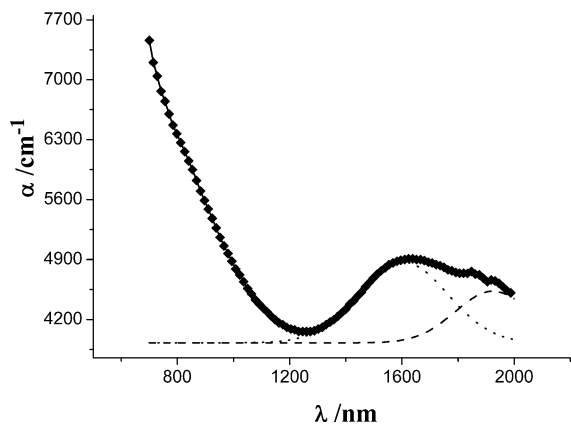
Fig. 4 Typical absorption spectrum for CuInSe$_2$ film deposited on ITO

avoided CuO and SeO$_2$ formation as decomposition products from CIS. In addition, neither elemental Cu nor Se was formed in the electrodeposition process due to the shifting of the deposition potential of these elements by the influence of complexing agent and the pH of the solution.

Analysis by optical absorption spectroscopy

Annealed films deposited on ITO glass substrate were used to determine the CIS band gap energy at room temperature. The absorption spectra were recorded in the interval of 500–2,000 nm. The variation of the absorption coefficient as a function of the wavelength (λ) is shown in Fig. 4. A wide absorption band is observed in the interval (1,300–2,000 nm), which is attributed to the sum of the absorption bands from all the possible phases present in the films. Individual bands are obtained by Gaussian deconvolution. The observed bands could be related to CuInSe$_2$ (dotted line) and In$_2$O$_3$ and an excess of Cu$_2$Se (broken line).
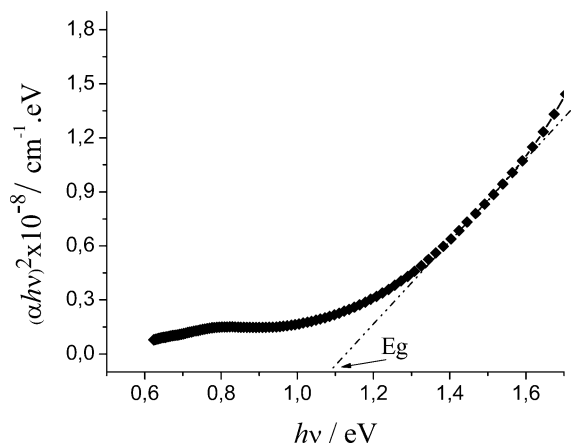
Fig. 5 Graphic representation of $(\alpha h\nu)^2$ vs $h\nu$ for CuInSe$_2$ thin film deposited on ITO, for E_g determination
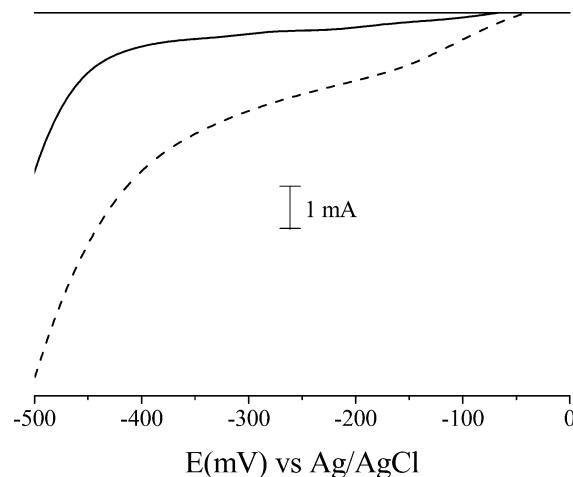
Fig. 6 Lineal scanning voltammograms of a CIS film electrodeposited on aluminum electrode. Film underwent thermal treatment at 500 °C for 20 min; *solid line* recorded without illumination, *broken line* recorded under illumination. Scan rate: 10 mV/s. Medium was 500 mM of K$_2$SO$_4$ at pH 4.5. Light intensity was 90 W

According to the Tauc relation [11, 12, 15], the absorption coefficient for direct gap material is given by

$$\alpha = B\left[h\nu - E_g.\right]^{1/2} \Big/ h\nu,$$

where $h\nu$ is the photon energy, E_g is the band gap energy, and B is the constant, which is different for different transitions.

Figure 5 is the graphic representation of $\alpha h\nu$ as a function of $h\nu$ for a CuInSe2 film, which was prepared in basic medium. A lineal region is observed from values of $h\nu$ higher than 1.2 eV. The E_g was determined by extrapolation from the photon energy axis; a value of 1.14 eV was calculated. This value is very similar to those reported in the literature [12, 19], which is in the interval from 1.04 to 1.21 eV.

Photoelectrochemical experiments

The electrochemical responses of thermally treated CIS films were analyzed in a 500 mM Na$_2$SO$_4$ solution at pH 4.5. Figure 6 shows the typical lineal voltammetry from a CIS thin film, under N$_2$ inert atmosphere, the observed current is ascribed to H$^+$ reduction. A considerable increment in the current was observed when the sample was illuminated; this behavior was more or less the same in all substrates, only small differences were found in the current increments for CIS deposited on different substrates, being the current increments in the substrate order ITO>Al>Steel. This, clearly, is related to the film composition after annealing. Obtained CIS thin films show a cathodic photoelectrochemical behavior, which is characteristic of p-type semiconductors [18].

Conclusions

The CIS thin films could be grown under potentiostatic condition from aqueous solution containing Cu^{2+}, In^{3+}, Se (IV) species in basic media, combined with the use of dietilentriamine as complexing agent. The analysis of the films revealed the stoichiometric formula $Cu_{2.40}In_{1.00}Se_{3.40}$ that corresponds to $CuInSe_2$ species with an excess of CuSe, the formation of the chalcopyrite structure in the CIS films. An additional phase attributed to the In_2O_3 is also detected. An E_g of 1.09 eV was determined, which becomes a p-type semiconductor, an appropriate material for photovoltaic applications.

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