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SHORT COMMUNICATION

Preparation of $CdIn_2Se_4$ thin films by electrodeposition

E. A. DALCHIELE
Instituto de Física, Facultad de Ingeniería, Herrera y Reissig 565, C.C. 30, 11000 Montevideo, Uruguay

S. CATTARIN and M. M. MUSIANI
IPELP-CNR., Corso Stati Uniti 4, 35100 Padova, Italy

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1. Introduction

Cadmium indium selenide ($CdIn_2Se_4$) is a semiconducting ternary compound which belongs to the $A^{II}B_2^{III}X_4^{VI}$ family where A = Cd, Zn, Hg or Mg, B = Ga or In and X = S, Se or Te. The most common crystal structure of $CdIn_2Se_4$ is a tetragonal (actually pseudocubic) phase, α modification, in which each cation is tetrahedrally coordinated by four anions and each anion is in turn coordinated by two Cd ions, one In ion, and one vacancy [1–5]. Furthermore, the compound $CdIn_2Se_4$ may crystallize in other two different modifications which are usually referred to as β and γ and which only differ in their cation arrangement [5]. The energy bandgaps of the α-phase are 1.73 eV for the direct transition and 1.55 eV for the indirect transition [6–8].

Interest in compounds of the $A^{II}B_2^{III}X_4^{VI}$ type has increased greatly in the last decade due to their potential applications in nonlinear optics [5, 6]. Moreover, due to its high absorption coefficient in the visible α-$CdIn_2Se_4$ is promising in optoelectronic applications and solar cells [7, 8]. The photoelectrochemical properties of $CdIn_2Se_4$ single crystals were investigated [3, 7, 9, 10] showing that in the *n*-$CdIn_2Se_4$ aqueous polysulfide cell good quantum yields and output stability were obtained.

Although much research has been dedicated to bulk crystals [1–4, 6–12], little is published on thin films of $CdIn_2Se_4$ [3, 13]. Thin films of this material were obtained by vacuum evaporation [13] and by the slurry pasting technique [3]. Electrodeposition is simple and inexpensive [14–16], and may be an interesting alternative technique for the preparation of $CdIn_2Se_4$ thin films. Although the potential of this technique in preparing $CuInSe_2$ [17–20] and (CdGa)Se [21] films has already been demonstrated, there is no reference for electrodeposition of $CdIn_2Se_4$.

In this paper we report the preparation of $CdIn_2Se_4$ thin films by two different electrochemical approaches: (i) sequential electrodeposition of individual elemental layers, and (ii) direct alloy electrodeposition, that provides all constituents from the same electrolyte in a single step. After the electrodeposition processes, heat-treatments were carried out to produce reactions between the constituents and recrystallization.

2. Experimental details

Elemental layers and Cd + In + Se alloy films were cathodically deposited on Ti substrates in a two-compartment cell, with a double wall for temperature control. The Ti sheets with a surface area of about 2 cm^2 were first polished with graded emery paper and degreased with acetone, then etched in 10% HF for 3–5 s, rinsed with distilled water and dried in an air stream before use. The counterelectrode was a platinum wire. A saturated calomel electrode (SCE) was used as reference and all potentials are given vs SCE. Solutions were not stirred and were in contact with atmosphere. For better reproducibility 40 ml of fresh solution were used for each deposit.

Heat treatment of Cd + In + Se alloys and sequentially electroplated layers was accomplished in an evacuated and sealed glass ampoule at 400–480 °C for 1–5 h in the presence of Se powder. Scanning electron microscopy (SEM) pictures were taken on a Philips XL 40 LaB_6 apparatus. Quantitative standardless microanalyses were obtained using an energy dispersive X-ray analysis (EDX) PV 99 X-ray spectrometer equipped with a thin Be window. ZAF corrections (taking into account the factors of atomic number Z, absorption A, and fluorescence correction F) were made to quantitative measurements, taken with an accelerating voltage of 25 keV. Compositions were obtained as atomic fraction x of each element. X-ray diffractograms were obtained on a Philips PW3710 instrument (CuK_α radiation, 40 kV and 30 mA, narrow divergence slit of 1/6°).

3. Results and discussion

3.1. *Sequentially electrodeposited Se–Cd and Se–Cd–In layers*

Precursors were prepared by sequentially plating the elements in the order Se–Cd–In over titanium substrates. The electrodeposition of metallic gray-black selenium was carried out galvanostatically (2 mA cm^{-2}) from aqueous 3 M SeO_2 bath. To avoid the formation of nonconducting red amorphous selenium a plating temperature of 80 °C was chosen [22, 23]. Cadmium layers were electrodeposited galvanostatically (30 mA cm^{-2}) over Se layers from a bath that contained 0.5 M CdO, 0.3 M HBF_4, 0.2 M H_3BO_3, adjusting the pH to 5 with NH_4OH. The fluoborate bath is known to yield smooth and homogeneous cadmium deposits [24]. The fairly high pH was chosen since at low pH Ti corrosion was observed, presumably due to HF produced by the equilibrium $BF_4^- + H_2O \longleftrightarrow BF_3(OH)^- + HF$ [25].

The indium films were potentiostatically electrodeposited at −0.95 V vs SCE, from a bath containing 0.1 M $In_2(SO_4)_3$, 0.5 M Na_2SO_4, at pH 2 adjusted with sulfuric acid. All samples were prepared with a stoichiometry Se : Cd : In = 4 : 1 : 2; the amount of deposited metal was controlled by coulometric measurements and checked by weighing the deposits.

3.1.1. Se–Cd layers. As can be seen in Fig. 1(a), the X-ray diffraction of an electrodeposited Se–Cd layer annealed at 480 °C for 5 h in the presence of Se shows peak that can be ascribed to the hexagonal wurtzite structure of CdSe. The diffraction peaks are intense and narrow, indicating good crystallinity of the sample film, with relative intensities that are close to those of the relevant JCPDS card [26]. <?tlsb=-0.1mm>Calculation of the cell parameters gives a value of $a = 427$ pm and $c = 702$ pm, close to literature values ($a = 430$ pm and $c = 702$ pm [27]). A minor amount of a second phase is observed, with peaks at $2\theta = 32.8°$ and $2\theta = 51.6°$, well matching the positions of the major peaks of $TiSe_2$ [28].

The deposits consist of nodules uniformly covering a smooth and dense film, as revealed by SEM studies.

3.1.2. Se–Cd–In layers. Figure 2(a) shows a typical X-ray diffraction pattern of a sample consisting of sequentially electrodeposited layers of Se, Cd and In (with a composition before heat treatment: Cd : In : Se = 1 : 2.0 : 4.3 and a thickness of about 3 μm) annealed for 5 h at 480 °C, in the presence of selenium. The spectrum shows sharp diffraction peaks due to polycrystalline $CdIn_2Se_4$ and minor peaks due to CdSe, unreacted elemental Se and In, and Ti substrate. The peak positions match the JCPDS pattern [29], see Fig. 2(b), but in our sample a strong (1 1 1) preferred orientation is observed. This result was already observed in the literature for both vacuum evaporated thin films and powder $CdIn_2Se_4$ samples [13]; for instance in the latter case the reported relative intensities are 100% (1 1 1), 50% (2 0 2) and 30% (1 1 3).

The cubic lattice parameter of the $CdIn_2Se_4$ films was determined by least-squares refinement of the seven most intense reflections and found to be 577 pm, slightly below the literature value of 581.5 pm [2, 4]. Hence, sequential electrodeposition of Se–Cd–In

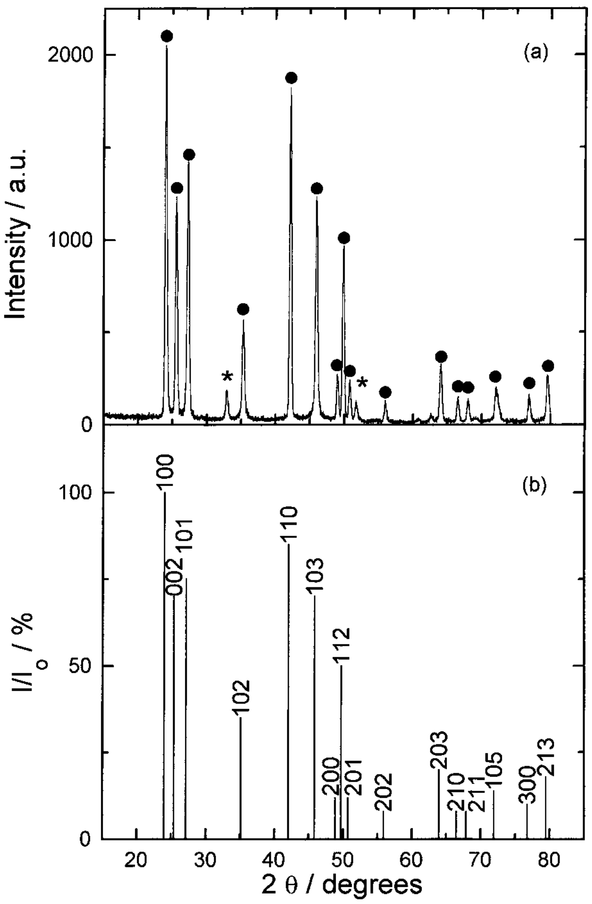

Fig. 1. (a) XRD pattern of a Se–Cd bi-layer after 5 h annealing at 480 °C in the presence of Se vapour. (●) CdSe, (*) possibly $TiSe_2$ [28]; (b) JCPDS pattern of the hexagonal CdSe compound [26].

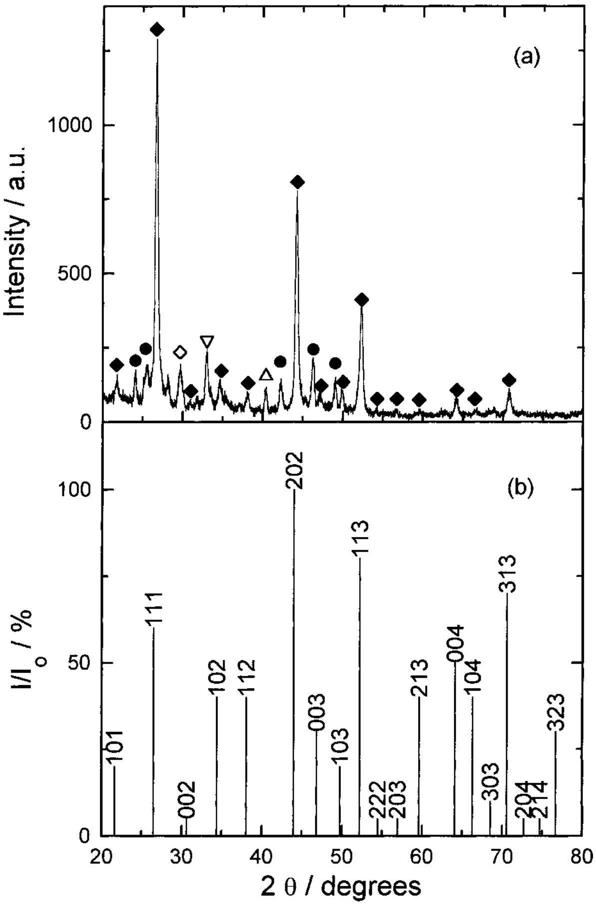

Fig. 2. (a) XRD pattern of a Se–Cd–In electrodeposited sequential layer, after 5 h annealing at 480 °C in the presence of Se powder (◆) $CdIn_2Se_4$, (●) CdSe, (◇) Se, (▽) In and (△) Ti. (b) JCPDS pattern of the α-$CdIn_2Se_4$ [29].

produced smooth and dense films, with good adherence to Ti substrate, and no detachment occurred during annealing. Scanning electron microscopy revealed a compact morphology, with large grains.

3.2. *Electrodeposition and characterization of Cd + In + Se alloys*

3.2.1. Effect of deposition parameters on film composition. Two solution compositions were used, containing: (a) 5 mM SeO_2, 5 mM $CdSO_4$, 50 mM $In_2(SO_4)_3$ and 0.5 M Na_2SO_4, with a concentration ratio $r = [Se(IV)]_{sol}/[Cd(II)]_{sol} = 1$ and (b) 10 mM SeO_2, 5 mM $CdSO_4$, 50 mM $In_2(SO_4)_3$ and 0.5 M Na_2SO_4 with $r = 2$. The pH of the solutions was adjusted to 2.0 with sulfuric acid. The deposition potential was varied from −0.700 to −1.000 (V vs SCE). The electrodeposition charge was fixed to ~15 C cm^{-2} so that the thickness of the films was about 1 μm for our substrates (~2 cm^2). All depositions were carried out at 50 °C.

After deposition the Cd + In + Se alloys were analysed by EDX. Typical composition–potential data are shown in Fig. 3 for a series of thin films deposited from baths containing the same amount of In(III) ions and two different r values. In both cases, as the deposition potential was made more negative the In atomic fraction in the alloy increased and that of Se decreased, as expected from thermodynamic reduction potentials [30]:

$$Cd^{2+} + 2e^- \longrightarrow Cd \qquad E^\circ = -0.402\,V \text{ vs NHE}$$

$$In^{3+} + 3e^- \longrightarrow In \qquad E^\circ = -0.342\,V \text{ vs NHE}$$

$$H_2SeO_3 + 4H^+ + 4e^- \longrightarrow Se + 3H_2O \qquad E^\circ = 0.740\,V \text{ vs NHE}$$

On the same basis an increase of the atomic fraction of Cd would be expected for depositions carried out at more negative potentials; it is not observed, possibly due to transport limitations in a solution with a low Cd^{2+} concentration.

As can be seen in Fig. 3(a), the cadmium atomic fraction of films deposited from a solution with $r = 1$ is always higher than the stoichiometric amount of Cd in the $CdIn_2Se_4$ compound, indicated by the dashed line. So, to achieve the correct composition, r was increased. For $r = 2$ alloys close to the stoichiometric composition were obtained in the potential range from −0.900 to −0.950 V (Fig. 3(b)). In this range, current densities were around 15 mA cm^{-2}, for an estimated deposition rate of about 0.46 μm min^{-1}.

The percentage current efficiencies, QE, were calculated from deposit weight and composition according to the following formula:

$$QE = \frac{100\,WF}{Q} \times \frac{\Sigma_i x_i n_i}{\Sigma_i x_i w_i} = \frac{100\,WF}{Q} \times \frac{(2x_{Cd} + 3x_{In} + 4x_{Se})}{(x_{Cd}w_{Cd} + x_{In}w_{In} + x_{Se}w_{Se})}$$

where W is the electrodeposited mass; F is the faraday charge; Q is the transferred charge; x_i is the atomic fraction of the element i; n_i is the number of electrons necessary to deposit an atom of that element from solution; w_i is the relevant atomic mass. Current efficiencies close to 100% were obtained for both solutions. This proves that hydrogen evolution was of minor importance, in spite of the negative deposition potentials, probably due to the inhibiting action of SeO_2.

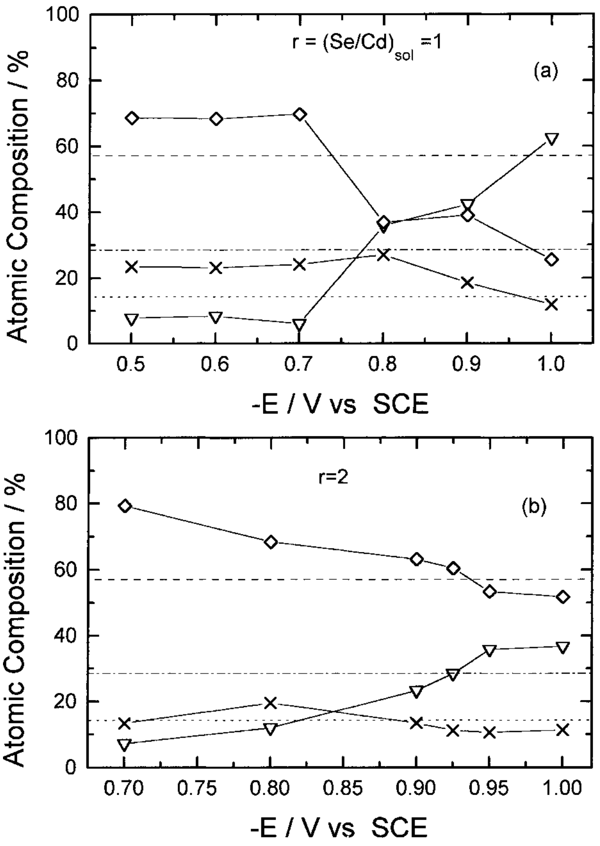

Fig. 3. Effect of potential on composition of Cd + In + Se alloys deposited onto Ti substrates from solutions with different r ratios (see text): (a) 5 mM SeO_2, 5 mM $CdSO_4$, 50 mM $In_2(SO_4)_3$, 0.5 M Na_2SO_4, $r = 1$; (b) 10 mM SeO_2, 5 mM $CdSO_4$, 50 mM $In_2(SO_4)_3$, 0.5 M Na_2SO_4, $r = 2$. Key: (◇) Se, (▽) In and (×) Cd. Theoretical composition of the $CdIn_2Se_4$ phase is shown by dashed lines: (– – –) Se, (———) In and (- - - -) Cd.

3.2.2. Morphology of the deposits and X-ray diffraction study. Both before and after thermal annealing the Cd + In + Se alloys appeared to SEM investigations as consisting of crystallites 1–2 μm in size, forming a noncompact deposit with a rough surface.

As deposited Cd + In + Se alloy films with compositions near the stoichiometry were analysed by X-ray diffraction to assess the formation of crystalline phases. Typical diffraction patterns of as-grown films electrodeposited at −0.900 to −0.950 V from a solution with $r = 2$, were characterized by broad scattering peaks with maxima at $2\theta \simeq 25°$ and $2\theta \simeq 47°$, and other peaks corresponding to unreacted metallic indium; these features showed that these samples were mainly amorphous in nature.

Although, in principle, preparation of $CdIn_2Se_4$ should be also possible by annealing Se deficient alloys in the presence of Se vapours, only alloys with $Cd:In:Se \simeq 1:2:4$ were submitted to annealing. After heat-treatment of the films at 480 °C for 5 h in vacuum (with Se added in the chamber), the diffraction pattern showed the formation of α-$CdIn_2Se_4$ and β-In_2Se_3 phases, with some residual metallic indium. When samples of similar composition were annealed at 400 °C in the absence of Se, there was no extensive formation of the ternary phase, and mainly formation of CdSe was observed. Loss of part of the volatile Se was possibly the cause of this result.

The XRD spectra of annealed alloys showed that the mixing of Cd, In and Se on an atomic scale, which was expected to favour formation of chemically homogenous films, did not produce better material than that obtained by sequential deposition.

4. Conclusions

Hexagonal CdSe films of good crystallinity have been obtained by annealing an electrodeposited Se–Cd bilayer at 480 °C in the presence of Se. $CdIn_2Se_4$ polycrystalline thin films were obtained by the sequential electrodeposition–annealing process.

Cd + In + Se alloy of correct stoichiometry were obtained by one-step electrodeposition and converted to $CdIn_2Se_4$ by heat treatment at 480 °C in the presence of Se. Some secondary phases were detected.

Sequential electrodeposition allowed the choice of both optimal deposition potentials and solution compositions for each deposited element, so that better morphologies were obtained compared with alloy electrodeposition.

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