

ELECTRODEPOSITION OF SEMICONDUCTOR LAYERS OF In-Se, Cu-Se and Cu-In-Se

C D LOKHANDE

Central Electrochemical Research Institute, Karaikudi-623 006

The semiconducting layers of indium-selenide (In-Se), copper-selenide (Cu-Se) and copper-indium-selenide (Cu-In-Se) have been electrodeposited under d.c. conditions. As deposited, In-Se and Cu-Se layers were selenium rich. Heat treatment resulted in the formation of In-Se and $\text{Cu}_{1.72}\text{-Se}$ compounds.

Cu-In-Se layers have been prepared by three routes; by sequential electrodeposition of In-Se layer on Cu-Se; vice versa; and direct electrodeposition of Cu-In-Se layers. All these layers were found to be Cu-rich and polycrystalline in nature.

Key words: Electrodeposition, indium selenide, copper selenide, copper indium selenide

INTRODUCTION

Copper-indium-diselenide (CuInSe_2) is a direct band gap semiconductor with a band gap energy equal to 1.1 eV. The primary interest in it has been in their applications in photovoltaic cells due to excellent optical and transparent properties [1-4]. A reasonable stability of CuInSe_2 , both in the single crystal and in thin film forms has made it one of the promising candidates for photovoltaic energy conversion. A thin film n-CdS/p-CuInSe₂ solid state photovoltaic cells with 11% power conversion efficiency has been reported [5] while a photoelectrochemical cell formed with single crystal n-CuInSe₂/aqueous polyiodide electrolyte had 12% efficiency [6], and the one with polycrystalline n-CuInSe₂/aqueous polyiodide showed 6% efficiency [7].

The approaches developed can be broadly classified under the single step and two step preparation of CuInSe_2 thin layers. A variety of single step techniques, namely, R.F. sputtering, spraying, vacuum deposition and electrodeposition have been worked out for thin CuInSe_2 layers [8-11]. Similarly, there are reports on two step deposition [12-17]. In such an approach, Cu-In alloys were either vacuum evaporated or electrodeposited and subsequent selenization has been carried out by chemical, electrochemical conversion or by annealing in hydrogen selenide (H_2Se) atmosphere at high temperatures. After annealing, polycrystalline p-type CuInSe_2 layers with $> 10 \mu\text{m}$ grain size have been reported [13]; however toxicity of H_2Se was a serious set back for such a process.

In the present work one of the components of CuInSe_2 , namely, Cu-Se of In-Se is electrodeposited on titanium (Ti) and molybdenum (Mo) substrates and sequentially the remaining component is electroplated over it. The resultant films are annealed at high temperature to form a CuInSe layer. The scanning electron microscope (SEM), X-ray diffraction (XRD), Energy Dispersive Spectroscopy (EDS) techniques have been employed for the characterization of such films. The Cu-In-Se layers were also electrodeposited from a ternary bath containing Cu^+ , In^{+3} and HSeO_3^- ions.

EXPERIMENTAL

All layers were applied by electrodeposition with d.c. under potentiostatic conditions. Three electrode system was employed and the potentials were with respect to saturated calomel

electrode (SCE). The distance between cathode and platinum auxiliary electrode was 1.0 cm. The solutions were prepared in double distilled water. The substrates were polished, degreased and washed with a detergent. The back side of the substrate was covered with adhesive tape. All solutions were unstirred and the layers were deposited at ambient temperature (26°C). After deposition, the substrates were washed with distilled water and dried.

The polarisation curves were recorded with a Wenking-83 programmer and Omnigraph recorder-100. The scan rate was 10 mV/sec. The XRD data were obtained using a Philips diffractometer with $\text{Cu K}\alpha$ radiation. The scanning electron photomicrographs and semiquantitative analyses were obtained with Philips SEM-505 model equipped with Northan Tracer.

Deposition of In-Se layers

The In-Se layers were deposited from the solution containing 100 μM InCl_3 and 100 mM SeO_2 . The pH of the bath was 1.2. The layers were deposited on Mo and Ti substrates. The potential was -1000 mV (vs SCE) with a current of 20 mA/cm^2 during the deposition period of 10 mins.

Deposition of Cu-Se layers

The Cu-Se layers were deposited from the solution containing 100 mM CuCl and 100 mM SeO_2 , at a pH of 1.4. The substrates were Mo and Ti. Cathodic potential was -400 mV (vs SCE) and the current density was 20 mA/cm^2 during the deposition period of 2 min.

Deposition of Cu-In-Se layers

The Cu-In-Se layers were deposited by three different methods by (i) sequential deposition of In-Se over Cu-Se (ii) sequential deposition of Cu-Se over In-Se and (iii) direct deposition of Cu-In-Se layer from a ternary alloy bath.

Sequential deposition of In-Se over Cu-Se layer

The Cu-Se layers were electrodeposited on the Ti substrates as described earlier, and dipped into a bath containing 100 mM InCl_3 and 100 mM SeO_2 solutions and In-Se layers were electrodeposited at -1000 mV (vs SCE), at a current density of 22 mA/cm^2 for a period of 5 mins.

Sequential deposition of Cu-Se over In-Se layer

The In-Se layers on Mo substrates were electrodeposited as described earlier. These layers were dipped in a bath, containing 100 mM CuCl and 100 mM SeO₂ solutions, and Cu-Se plating was carried out for 2 mins at -500 mV (vs SCE) at 10 mA/cm² current density.

Direct deposition of Cu-In-Se layer from a ternary alloy bath

Cu-In-Se layers were electroplated from ternary alloy bath containing 50 mM InCl₃, 50 mM CuCl and 50 mM SeO₂ solutions on Ti and Mo substrates. The plating potential was -800 mV (vs SCE) at a current density of 9.0 mA/cm².

RESULTS AND DISCUSSION

In-Se layers

The polarization curves for the reduction of indium, selenium and indium selenide from InCl₃, SeO₂ and InCl₃-SeO₂ solutions respectively, on Ti and Mo substrates are shown in Figs. 1 (a) to 1 (c).

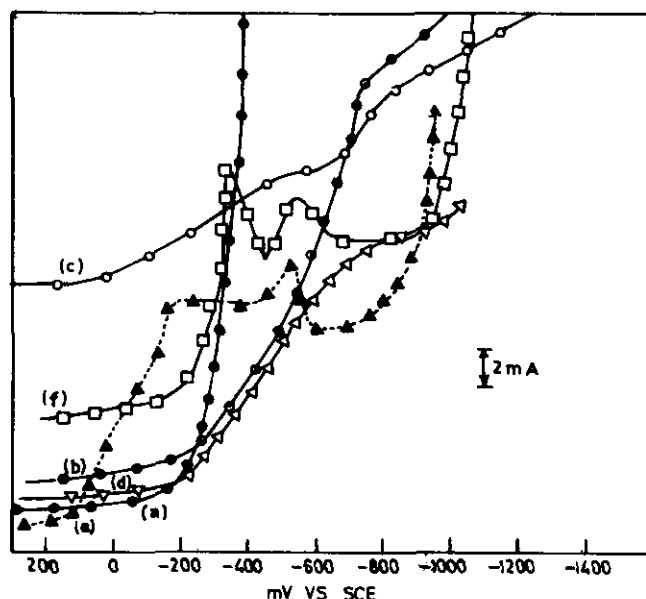


Fig. 1: Polarization curves for the following solutions

- (a) 100 mM InCl₃ (b) 100 mM SeO₂
 (c) 100 mM InCl₃ + 100 mM SeO₂ (d) 100 mM CuCl
 (e) 100 mM CuCl + 100 mM SeO₂
 (f) 50 mM CuCl + 50 mM InCl₃ + 50 mM SeO₂
 The scan rate is 10 mV/sec

On molybdenum, indium reduction started at -200 mV (vs SCE) followed by large amount of H₂ evolution. Selenium reduction started at -200 mV. However, the In-Se reduction started at -400 mV, followed by a limiting current and subsequently a large current at -700 mV due to H₂ evolution. In the case of titanium substrate, reduction of indium, selenium and indium-selenide started at more negative cathodic potentials than at Mo

substrate. Addition of NaCl, and Na₂SO₄ as the supporting electrolytes for above solutions, did not change reduction potentials for the In-Se system.

As deposited, In-Se layers were 2-3 μm thick, well adherent to the substrate and reddish in colour. The semi-quantitative analyses showed that the films were selenium-rich; with Mo substrate, selenium content was 82-84 atomic % and with Ti substrate, it was 90-92 atomic %. As deposited, layers had smooth surface. The XRD pattern showed that these layers are polycrystalline in nature and contain different phases like In₆Se₇, In₂Se₃, Se and In. The layers on Ti substrates were not sufficiently thick and contained more selenium, hence further characterizations were restricted to the In-Se layers deposited on Mo substrates.

Attempts have been made to deposit In-Se layers at high temperatures (60°C - 70°C) and with low current densities (2-3 mA/cm²), however, these parameters resulted in the formation of a black selenium layer containing 2 atomic % indium. At high temperatures, Mo reacted with SeO₂ solution and MoSe₂ was formed.

Addition of surfactants like cetyltrimethyl ammonium bromide (CTAB), or Triton X 100 did not change the film composition; however, the films turned black; were thin and nonadherent to the substrate. Similarly, addition of the supporting electrolytes like Na₂SO₄ and NaCl resulted in an increase in current due to more of hydrogen evolution.

In order to take out excess selenium from 'as deposited' films, initially, the layers were dipped in 1M Na₂S solution for 5-10 seconds. This treatment resulted in In:Se becoming 2:3; but the surface became rough and nonhomogenous.

The In-Se layers were heated at high temperatures, ranging from 200° - 400°C in a hydrogen atmosphere. Below 250°C, InSe layers turned black; however, the composition and morphology did not change. Above 250°C, excess selenium from In-Se layer reacts with H₂ and results in H₂Se. At 250°C, In-Se layer corresponded to In₂Se₃; however, XRD showed the presence of In-Se and Se phases. Heating In-Se layer at 300°C, resulted in the formation of a mixture of three phases of In₂Se₃. At 400°C, the composition corresponded to indium selenide and its XRD pattern is shown in Fig 2(a).

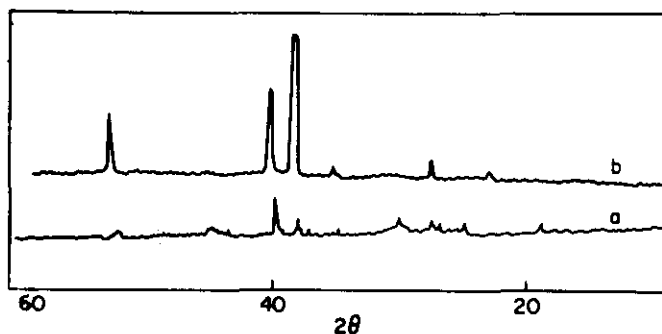


Fig. 2 (a): XRD pattern of InSe layer after heating at 400°C
 Fig. 2 (b): XRD pattern of Cu_{1.72}Se layer after heating at 500°C.

The morphology of In-Se was altered after heat treatments; the film surface was rough with a continuous underneath layer of fine grains ($0.5 \mu\text{m}$). The rough surface was removed, partly by etching the In-Se in Br_2/MeOH (2%). The SEM of etched InSe layer is given in Fig. 3(a).

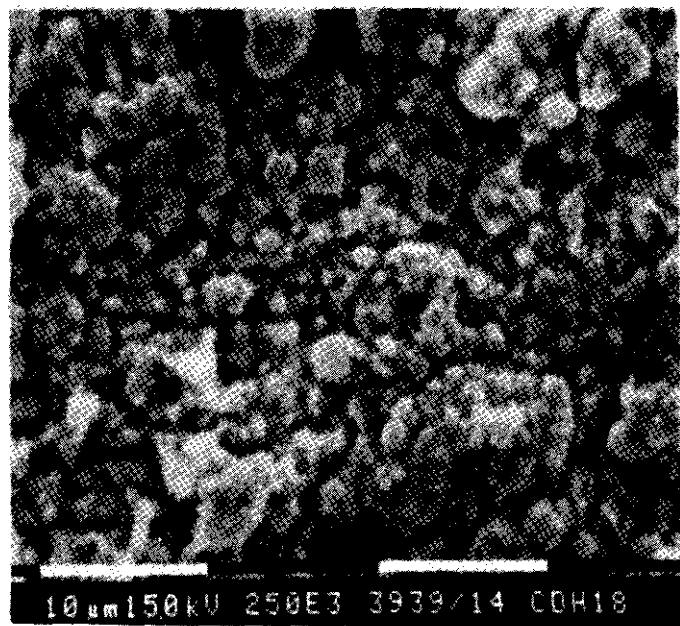


Fig. 3 (a): Scanning electron micrograph of In-Se layers X 2500, after etching in Br_2/MeOH

InSe layers were semiconducting in nature and were photoactive with n-type response in a polyiodide solution. The short circuit photocurrent was of the order of $70 \mu\text{A}/\text{cm}^2$ and open circuit photovoltage was of the order of 200 mV; however, no further attention was paid for the characterisation with (photo) electrochemical techniques.

Cu-Se layers

The polarization curves for the reduction of copper and copper-selenide from CuCl and CuCl-SeO_2 solutions respectively at the Ti substrate are shown in Fig. 1(d) and 1(e). Copper reduction started at -200 mV followed by a large current due to H_2 evolution at Ti electrode. In the case of Cu-Se, a reduction started at 0 mV followed by two peaks, one at ~ 300 mV and another at -640 mV, corresponding to the reduction of CuSe and Se respectively. A large current due to H_2 evolution was observed after -1000 mV. The nature of the polarisation curves for Mo substrates was similar to those on Ti electrode.

Cu-Se layers became thick ($2-3 \mu\text{m}$) in 2 mins. of deposition period. The layers were dark gray in appearance and well adherent. Their deposition on Mo substrate needed higher cathodic (-600 mV) potential and longer deposition time than on Ti substrate and further, the layers were non-uniform, porous and rough in appearance.

'As-deposited' layers of Cu-Se on Ti were analysed for their composition and morphology. They corresponded to $\text{Cu}_{1.1}\text{Se}$ and

were more homogenous. Scanning electron microscope showed that the surface contained needle like structure with the same composition as the layers. From the XRD study it was concluded that the Cu-Se layers were polycrystalline in nature and contained different phases of Cu_{2-x}Se , Se and Cu.

The Cu-Se layers were dipped in Na_2S solution for 5-10 seconds in order to take out the free selenium. The colour was changed to violet-gray. From the semiquantitative analyses, it was noticed that the layers had the composition: $\text{Cu}_{1.78}\text{Se}$. The surface became rough after Na_2S dipping. The XRD showed the presence of Cu_{2-x}Se and Se phases in the layers.

The 'as-deposited' layers heated to the range $250^\circ-500^\circ\text{C}$ in hydrogen atmosphere showed interesting behaviour. Below 300°C the composition of the layer and morphology were not changed significantly. At 500°C , the composition corresponded to $\text{Cu}_{1.72}\text{Se}$ and the surface became smooth with small grains. Fig. 3 (b) shows SEM of $\text{Cu}_{1.72}\text{Se}$ layer. The XRD of $\text{Cu}_{1.72}\text{Se}$ layer demonstrated the presence of Cu_{2-x}Se and Se phases and Fig 2 (b) that of $\text{Cu}_{1.72}\text{Se}$.



Fig. 3 (b): Scanning electron micrographs of $\text{Cu}_{1.72}\text{Se}$ layer after heat treatment X 1490

Cu-In-Se layers

Cu-Se on InSe

The surface of 'as-deposited' layers looked violet and well adherent to InSe layer. The XRD showed that the 'as-deposited' layers were polycrystalline in nature with the presence of different phases of CuInSe_2 , Cu_{2-x}Se , In-Se and Se. The SEM showed that the surface is rough and the Cu-In-Se layers were Cu-rich ($\text{Cu}:\text{In} = 1.44$).

After heating these Cu-In-Se layers at 400°C, in argon atmosphere, different phases of In-Se and Se have disappeared and the grain size was not changed significantly. The films were still Cu-rich (Cu:In = 1.30). The XRD and morphology of such layers are shown in Fig. 4(a) and 5(a) respectively.

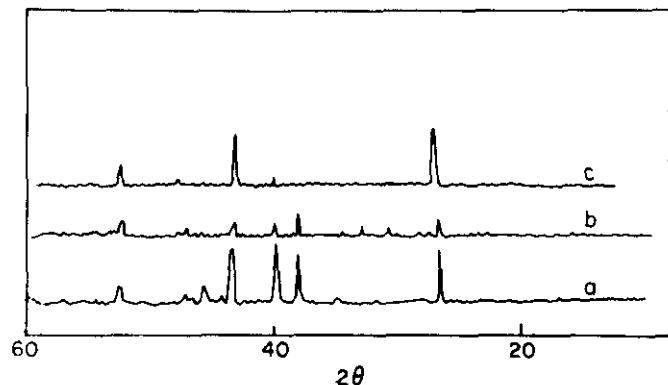


Fig. 4: XRD patterns of

- (a) Cu-In-Se prepared by sequential deposition of Cu-Se on In-Se
- (b) Cu-In-Se prepared by sequential deposition of In-Se on $\text{Cu}_{1.72}\text{Se}$ and
- (c) Cu-In-Se prepared by direct deposition

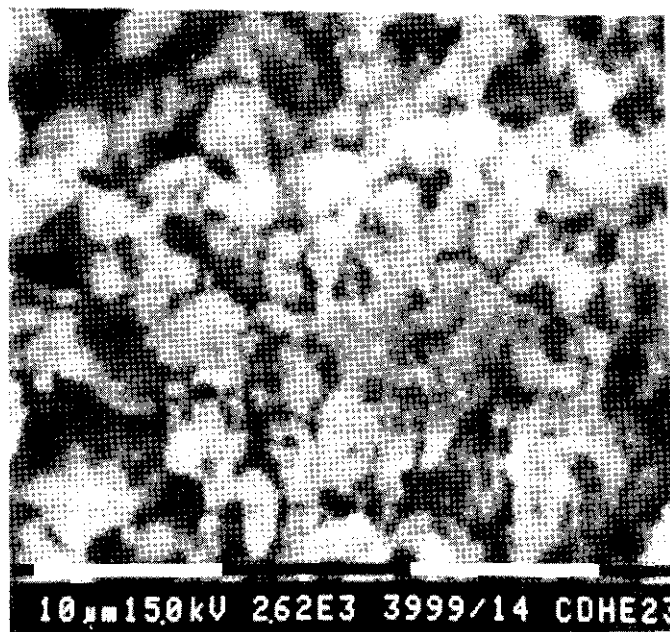


Fig. 5(a): Scanning electron micrograph of Cu-In-Se prepared by sequential deposition of Cu-Se on In-Se X 2620

In-Se on $\text{Cu}_{1.72}\text{Se}$

'As-deposited' layers were reddish in colour, uniform and adherent to the $\text{Cu}_{1.72}\text{Se}$ layer. The layers were Cu-rich (Cu:In = 1.32).

After heating at 400°C, layers became black in colour, but still Cu-rich (Cu:In = 1.25) and smooth. The XRD showed that the layers were polycrystalline in nature and contain Cu_{2-x}Se and CuInSe_2 phases Fig. 4(b).

Direct deposition of Cu-In-Se layers

The polarization curve for reduction of Cu-In-Se is shown in Fig. 1(f). 'As-deposited' Cu-In-Se layers were black in colour, thin, rough and less adherent. The layers were Cu-rich (Cu:In = 1.48) and nonhomogenous in composition. The grain size was typically 2.3 μm but loosely packed. The XRD showed that the layers were polycrystalline in nature and contained mixed phases of CuInSe_2 , Cu_{2-x}Se and In-Se.

On heating to 500°C, in argon atmosphere the Cu:In ratio was changed to 1.33. The XRD showed the presence of CuInSe_2 and Cu_{2-x}Se phases. The layers were homogenous with average grain size of 2.3 μm. Fig 4(c) and 5(b) show XRD and SEM of such layers.

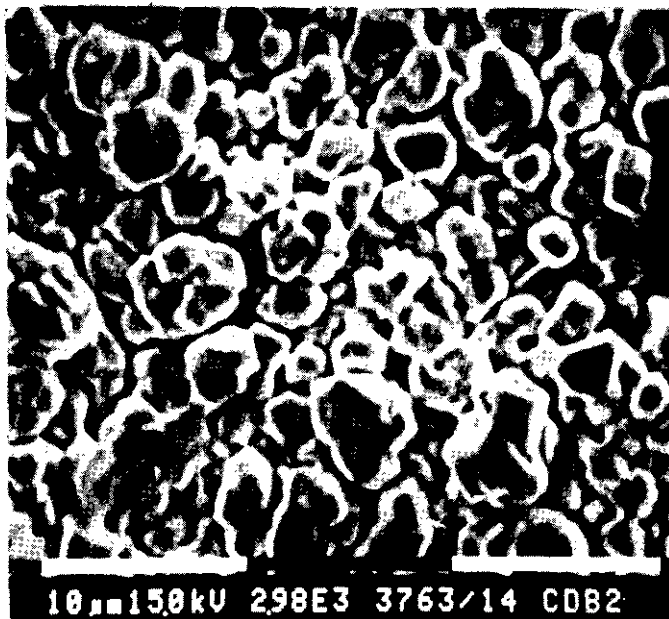


Fig. 5(b): Scanning electron micrograph of Cu-In-Se prepared by direct deposition X 2900

CONCLUSIONS

A cathodic electrodeposition technique has been employed for the deposition of different forms of In-Se, Cu-Se and Cu-In-Se layers on Ti and Mo substrates. 'As-deposited' In-Se and Cu-Se layers are selenium-rich but H_2 heat treatment at high temperature changed film composition to InSe and $\text{Cu}_{1.72}\text{Se}$ respectively. The Cu-In-Se layers were formed by sequential deposition of Cu-Se on InSe or InSe on $\text{Cu}_{1.72}\text{Se}$ and direct deposition of Cu-In-Se from ternary alloy bath. Irrespective of deposition methods, electrodeposited Cu-In-Se layers were Cu-rich.

REFERENCES

1. R Noufi, R Axton, C Herrington and S K Deb, *Appl Phys Lett*, **45** (1984) 668
2. R Janam and O N Srivastava, *Solar Ener Mater*, **11** (1985) 409
3. M Verela, J L Morenza, J Esteve and J M Codina, *J Phys D Appl Phys*, **17** (1984) 2423
4. R M Hermann and L Fabick, *J Crystal Growth*, **61** (1983) 658
5. R R Potter and J R Sites, *Appl Phys Lett*, **41** (1983) 843
6. S Menezes, *Appl Phys Lett*, **45** (1984) 148
7. D Hanemann and S Szot, *Appl Phys Lett*, **46** (1985) 778
8. M Gorska, R Bealieu, J J Loferski and B Rossler, *Solar Ener Mater*, **1** (1979) 313
9. G Slaviati and D Seuret, *Thin Solid Films*, **104** (1983) L-75
10. J Parkes, R D Tomlinson and M J Hampshire, *Solid State Electronics*, **16** (1973) 773
11. R N Bhattacharya, *J Electrochem Soc*, **130** (1983) 2040
12. G Hodes, T Engelhard, D Cahen L L Kazmerski and C R Herrington *Thin Solid Films*, **128** (1985) 93
13. T L Chu, S S Chu, S C Lin and J Yue, *J Electrochem Soc*, **131** (1984) 2182
14. G Hodes, D Cahen and C D Lokhande, *Ternary adamantine materials for low cost solar cells*, Quarterly. tech. report Nov. 1985 – Jan. 1986 Project No. IL-5-04132-1 SERI-USA
15. G Hodes, D Cahen and C D Lokhande, *Ternary adamantine materials for low cost solar cells*, Annual report Nov. 1984 - Oct. 1985 Project No IL-5 04132-1 SERI, USA
16. Annual report of Solid State Photovoltaic Research Branch: F.Y. 1984, April 1985 SERI - USA page 90
17. C D Lokhande and G Hodes, *Solar cells* (in press)