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

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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 Cu$_{1.72}$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 a-CdS/CuInSe$_2$ solid state photovoltaic cells with 11% power conversion efficiency has been reported [5] while a photoelectrochemical cell formed with single crystal CuInSe$_2$/aqueous polyiodide showed 12% efficiency [6], and the one with polycrystalline a-CuInSe$_2$/aqueous polyiodide showed 5% 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$_2$Se) atmosphere at high temperatures. After annealing, polycrystalline p-type CuInSe$_2$ layers with > 10 µm grain size have been reported [13]; however toxicity of H$_2$Se was a serious setback 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$_2$ 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$^+$ 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 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 curve 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 Cu Kα 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 mM InCl$_3$ and 100 mM SeO$_3^2$-. 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 electrodeposited from the solution containing 100 mM CuCl$_2$ and 100 mM SeO$_3^2$-, 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$_3^2$- 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-In-Se layer 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 InCl₂-SeO₂ solutions respectively, on Ti and Mo substrates are shown in Figs. 1 (a) to 1 (c).

![Polarization curves for the following solutions](image)

- (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 surfact. The XRD pattern showed that these layers are polycrystalline in nature and contain different phases like In₅Se₆, In₅Se₇, 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°C - 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 In₅Se₆; 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 In₅Se₆. At 400°C, the composition corresponded to indium selenide and its XRD pattern is shown in Fig 2(a).

![XRD pattern of InSe layer after heating at 400°C](image)

![XRD pattern of Cu₁₇₅Se layer after heating at 500°C](image)
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 μm). The rough surface was removed, partly by etching the In-Se in Br₂/MeOH (2%). The SEM of etched InSe layer is given in Fig. 3(a).

The Cu-Se layers were dipped in Na₂S 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: Cu₄₇Se₇. The surface became rough after Na₂S dipping. The XRD showed the presence of Cu₂₋ₓSe and Se phases in the layers.

The ‘as-deposited’ layers heated to the range 250°C-500°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 Cu₁₋ₓSe and the surface became smooth with small grains. Fig. 3(b) shows SEM of Cu₁₋ₓSe layer. The XRD of Cu₁₋ₓSe layer demonstrated the presence of Cu₂₋ₓSe and Se phases and Fig 2 (b) that of Cu₁₋ₓSe.

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 μA/cm² 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-SeO₃ 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 H₂ 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 H₂ 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 μm) 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 Cu₁₋ₓSe 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 Cu₂₋ₓSe, Se and Cu.

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 CuInSe₂, Cu₂₋ₓSe, In-Se and Se. The SEM showed that the surface is rough and the Cu-In-Se layers were Cu-rich (Cu: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.

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$_{2}$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 nonhomogeneous 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.

**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 Cu$_{1.32}$Se respectively. The Cu-In-Se layers were formed by sequential deposition of Cu-Se on InSe or InSe on Cu$_{1.32}$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


## POLYPHENYLENE OXIDE COATING OVER MILD STEEL

As the electropolymerisation of phenolic compounds result in useful polyphenylene oxide type polymers, the following process has been developed employing catechol.

**Development of polyphenylene oxide coating over mild steel by electro-initiated polymerisation**

This polymer coating can be applied to automobile parts and also for electronic and electrical accessories.

This process consists of electrolysis of catechol in aqueous alkaline solution employing the mild steel as the anode and the same metal as the cathode. Prior to the electrolysis the mild steel plate or the m.s. part to be coated with the polymer film needs to be cleaned by sand blasting method. The coated mild steel part is then air dried and cured.

The process has been studied on a 10 litre capacity cell capable of obtaining PPO coating over 40cm² area m.s. plates.

### Raw materials

1. Catechol
2. Sodium hydroxide
3. Ethylene diamine
4. Trichloroethylene
5. Conc. hydrochloric acid

### Equipments

1. Rectifier
2. A rectangular PVC cell with electrical connections
3. FRP tanks
4. Sand blasting unit
5. Deionized water unit
6. Industrial oven
7. Thickness measuring tester

### Suggested economic unit

The suggested economic unit is 100 litre capacity cells, capable of giving a PPO coating of 10-15 micron thickness over 90,000 m.s. parts of size each 23cm x 13.5cm per 300 working days. It is estimated that the total investment required to put up such a unit will be Rs. 1.7 lakhs.

### Scope for sponsorship

Based on the above technology it will be quite attractive to take up the cheaper phenolic based raw materials to prepare polyphenylene oxide.

1. Number of essential oils contain thymol and carvacrol. The crude oils can be subjected to controlled electropolymerisation.
2. Multivalent phenol is normally a by-product in the low temperature carbonisation of lignite. This by-product is also a cheap raw material worth taking up.
3. CNS oil which contains anacardic acid and cardol, is yet another cheap source of phenolic matter which can be taken up for the preparation of polyphenylene oxide.
4. Crude petroleum is also a source of phenolic matter and can be used for the production of polyphenylene oxide.