

Cyclic voltammetric and characterization studies of electrodeposited copper-indium for thin-film solar cell application

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Abstract. Copper-indium layers were grown on a carbon substrate by a one-step electrodeposition technique. Four deposition electrolytes were prepared: Two unitary electrolytes comprising of 300 mM copper (II) chloride and 700 mM trisodium citrate and 300 mM indium (III) chloride and 700 mM trisodium citrate; two binary electrolytes comprising of 300 mM copper (II) chloride, 300 mM indium (III) chloride and 700 mM trisodium citrate for deposition at potentials of -0.6 V and -0.9 V, respectively. The pH of the solution was left unaltered at 4.8. X-ray diffraction studies showed the produced copper indium layers had an amorphous structure. From the scanning electron microscopy studies, it was found that copper indium layers indicated a small grain size and grain shape was irregular. The structure was not compact. Energy dispersive spectroscopy showed presence of low percentages of copper and indium in all four samples and stoichiometric molar ratios of Cu:In of 1:1 can be achieved using deposition potentials between -0.6 to -0.9 V. SEM, EDS and XRD characterization helps in the identification of the reaction mechanism, the structure and morphology of the films deposited under different conditions. These characterization studies will assist in enhancing the efficiency of the thin-films deposited for maximum conversion of sunlight to electricity using this sustainable method. In this present study, an attempt has been made to obtain near stoichiometric films for higher efficiencies.

Introduction

The direct conversion of sunlight into electricity (photovoltaics) may be the most prevailing and potential alternative to the utilization of fossil fuels. Primary energy consumption decreased by 4.5% last year, which is the first decline since 2009. Nevertheless, alternative forms to fossil fuel are in dire need to protect the environment from global warming. Copper indium diselenide (CIS) and copper indium gallium diselenide (CIGS) are two of the most favorable absorber materials for low cost photovoltaics or thin film solar cells and extensive research is being conducted in the development of these thin film solar cells [1]–[4]. Copper indium diselenide has a I-III-VI₂ ternary chalcopyrite structure and possesses desirable physical properties such as a direct band gap at ~1 eV and a high absorption coefficient of greater than 10⁵ cm⁻¹ at photon energies above the band gap. CIS thin film of about 1 μm thickness absorbs 90% of the incident sunlight with photon energy greater than its band gap. The best CIGS solar cells have the following layer structure: Mo (1 μm) coated glass/CIGS absorber/CdS buffer layer/CdS-ZnO window layer/MgF₂ antireflection coating/Ni-Al alloy grid [5]. These qualities make it ideal for fabrication of high efficiency polycrystalline thin film photovoltaic devices [6]. Several techniques are present for the preparation of CIS thin films including co-evaporation [7], sputtering [8]–[10], spray pyrolysis [11]–[13], electrodeposition [1], [3], [14], molecular beam epitaxy [15], etc. The highest efficiency achieved for CIS thin-film solar cell is 23.35% reported by Solar Frontier in 2019 [16]. The

conductivity of this ternary semiconductor can be either n- or p-type which depends on the synthesis method and the composition of the constituent elements in the structure [17].

Several works have been published on chalcopyrite materials which have primarily used one-step electrodeposition process instead of physical vapor deposition because it allows achievement of low production cost, higher deposition speed and negligible waste of chemicals [18]. Owing to the reasoning that the co-electrodeposition process does not require very sophisticated equipment and is easy to use, this technique where the Cu-In-Ga-Se species are present in the same chemical bath is one of the suitable techniques to prepare low cost thin films [19]. PVD technique produces high quality films but is difficult to scale up. Co-electrodeposition process can be identified into two types: (1) where the elements involved have almost the same order of electrode potential, and (2) where the elements involved have different electrode potentials. In the cases where the elements involved have different electrode potentials, complexing agents such as trisodium citrate or EDTA can be utilized to reduce the difference in the deposition potentials.

Considerable amount of work has been done on the electrodeposition of CIS which includes a few studies devoted to the mechanism of CIS formation. Carbonnelle and Lamberts conducted an elementary study as well as the first step in understanding the mechanism of copper selenide electrodeposition to understanding the copper indium diselenide deposition from a ternary bath. Their results found that copper selenide is an intermediate or precursor for the formation of copper indium diselenide deposition [20].

The formation of the electrodeposited CIGS on the cathodic (working electrode) surface within an electrolysis cell typically depends on the pH level, redox (standard reduction) potential, deposition time, applied potential and the initial solution concentration along with some other factors [21]. In this paper, the final composition of the deposited film is determined using EDS analysis by studying the effects of initial concentrations of the electrolyte as well as the deposition potentials at which the reduction occurs. A detailed study through cyclic voltammetry, Energy Dispersive Spectroscopy, X-Ray Diffraction and Scanning Electron Microscopy is conducted in order to study the specific initial concentration of the electrolyte.

Materials and methods

Materials preparation

Copper (II) chloride (CuCl_2), indium (III) chloride (InCl_3) and trisodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) were all purchased from Sigma-Aldrich. All chemicals were used as received and deionized water was used for the deposition bath. A small circular carbon electrode with dimensions of 2 mm in diameter was used as the substrate. The electrodeposition was carried out potentiostatically in a three-electrode cell configuration. The reference electrode was silver/silver chloride electrode and the working and counter electrodes were made up of carbon. All substrates were cleaned with acetone and rinsed with deionized water, and subsequently dried. The electrolyte bath contained 100 ml deionized water and 300 mM copper (II) chloride, 300 mM indium (III) chloride and 700 mM trisodium citrate. The pH of the solution was 4.8. With the aim of checking the stability of the electrolyte solutions prepared, they were stored for at least 20 days at room temperature and pressure and their final stability at the end of 20 days was observed before usage. The pH of the electrolytes were not altered using any acidic agents such as hydrochloric acid or sulphuric acid.

Characterization

A Solartron ModuLab XM ECS potentiostat/galvanostat was used for the film depositions and cyclic voltammetry studies. The cyclic voltammograms were measured at a scan rate of 15 mV/s and were scanned only in the negative potential region. The cathodic potentials have been fixed at -0.6 V and -0.9 V for copper and indium deposition, respectively. The deposition time has been at

15 min. All film depositions and cyclic voltammogram measurements were performed in a stagnant bath at room temperature.

The surface morphology, chemical composition and crystalline properties of the electrodeposited films were characterized by scanning electron microscopy (SEM, Jeol JSM-6010PLUS/LA), energy dispersive X-ray spectroscopy and X-ray diffraction (XRD, X' Pert PRO MRD XL XRD system from Panalytical), respectively.

Results and discussion

The deposition solutions containing electrochemically active species Cu^{2+} and In^{3+} in the presence of trisodium citrate as a complexing agent are stable for a long time. Different potentials were employed to produce Cu-rich and Cu-poor deposition layers. Cu-rich layers were produced in a binary solution containing copper (II) chloride and indium (III) chloride along with trisodium citrate at a cathodic potential of -0.6 V and Cu-poor layers were produced at a cathodic potential of -0.9 V. Both the electrolytes for the electrochemical experiments at -0.6 V and -0.9 V have the same $[\text{Cu}^{2+}]/[\text{In}^{3+}]$ initial ratios. Electrodeposition was carried out without agitation. The chemical composition of the unitary deposits of copper and indium and binary deposit of copper-indium were analyzed by EDS. The results of the chemical compositional analysis of copper at -0.6 V, indium at -0.9 V and copper-indium layer at -0.6 V and -0.9 V are shown in table 1, 2, 3 and 4, respectively. One can observe the presence of copper, indium, sodium, chloride and oxygen atoms in the deposited layer. Apart from copper and indium, the other elements present are due to improper washing of the deposited layers.

Table 1 – Chemical composition of the synthesized layer of copper at -0.6V

Formula	mass%	Atom%
O	10.50	18.87
Na	32.71	40.94
Cl	40.35	32.75
Cu	16.44	7.44
Total	100.00	100.00

Table 2 – Chemical composition of the synthesized layer of indium at -0.9V

Formula	mass%	Atom%
O	52.12	67.91
Na	28.61	25.95
Cl	6.50	3.82
In	12.77	2.32
Total	100.00	100.00

Table 3 – Chemical composition of the synthesized layer of copper-indium at -0.6V

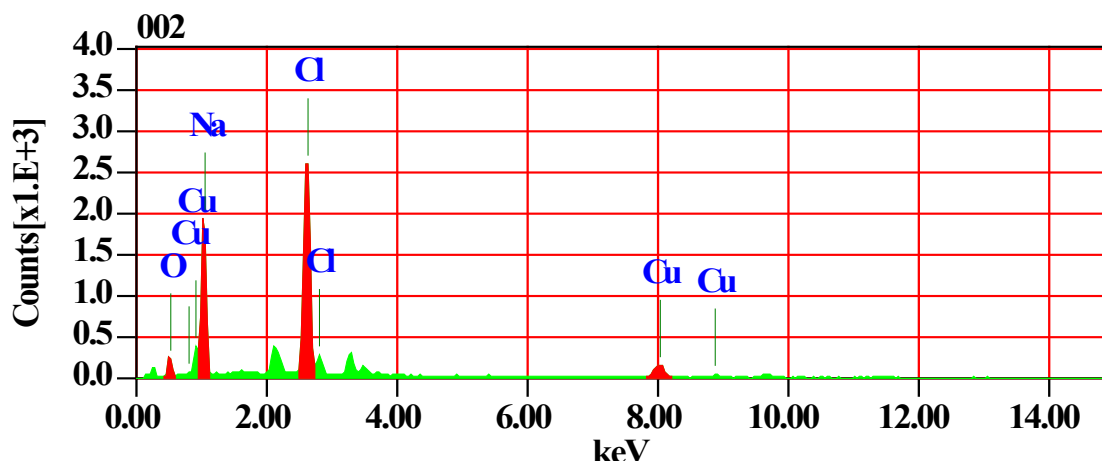
Formula	mass%	Atom%
O	30.27	49.45
Na	26.39	30.01
Cl	14.37	10.59
Cu	18.25	7.51
In	10.72	2.44
Total	100.00	100.00

Table 4 – Chemical composition of the synthesized layer of copper-indium at -0.9V

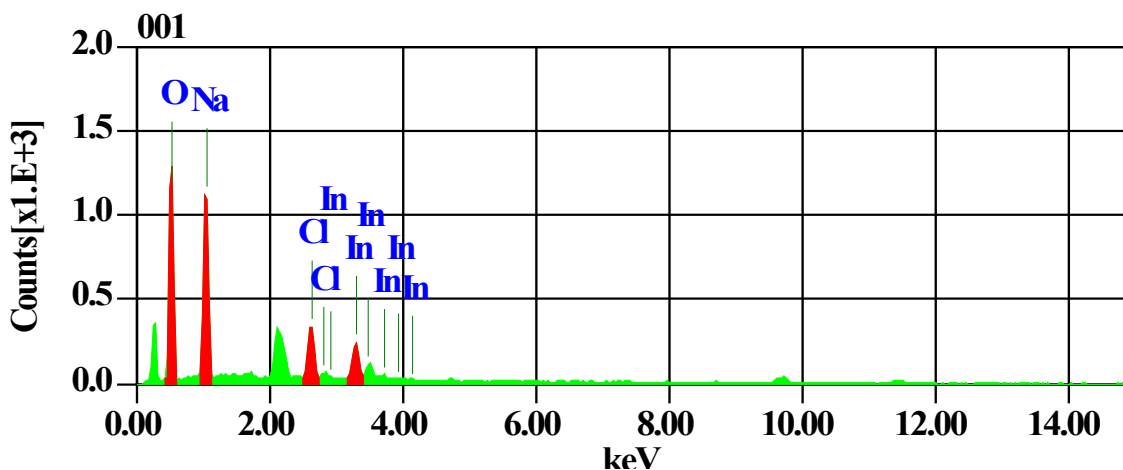
Formula	mass%	Atom%
O	29.27	50.13
Na	18.62	22.19
Cl	26.24	20.28
Cu	6.35	2.74
In	19.52	4.66
Total	100.00	100.00

Four cyclic voltammetric experiments were conducted: copper electrodeposition at -0.6 V, indium electrodeposition at -0.9 V, copper indium electrodeposition at -0.6 V and -0.9 V. The molar ratio of Cu:In at a deposition potential of -0.6V was found to be approximately 2:1. The molar ratio of Cu:In at a deposition potential of -0.9V was found to be approximately 1:3. Thus, to obtain stoichiometric molar ratio of Cu:In = 1:1, a deposition potential between -0.6 V and -0.9 V must be chosen. The atomic ratio for Cu:In at a deposition potential of -0.6 V was found to be 3:1 and at -0.9 V is approximately 3:2. Therefore, to obtain stoichiometric atomic ratio of Cu:In = 1:1, a more negative deposition potential should be selected. Figure 1 shows the EDS diagrams and indicates that the rates of Cu and In components obtained in this study are seen to be low which matches the data obtained from the compositional analysis.

(a)



(b)



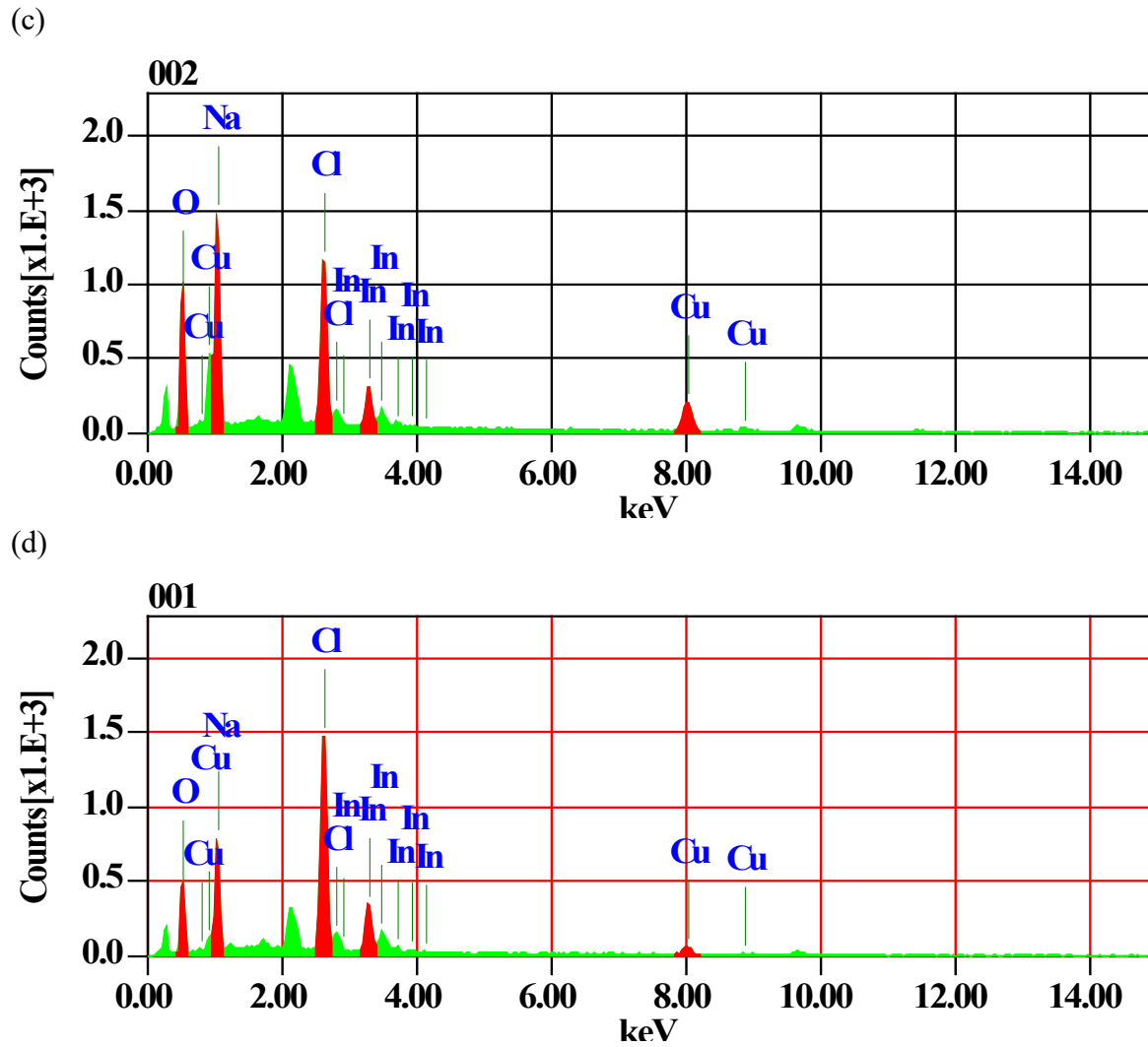


Fig. 1. EDS of the copper-indium layers.

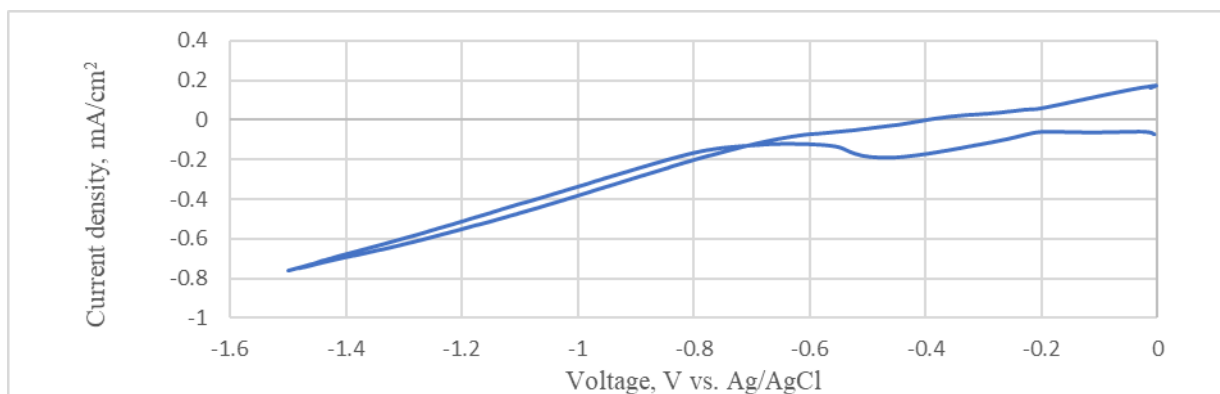


Fig. 2. 300 mM CuCl_2 + 300 mM InCl_3 without any complexing agent.

Fig. 2. shows no prominent peak for indium obtained in a binary solution of 300 mM copper (II) chloride and 300 mM indium (III) chloride without the usage of any complexing agents.

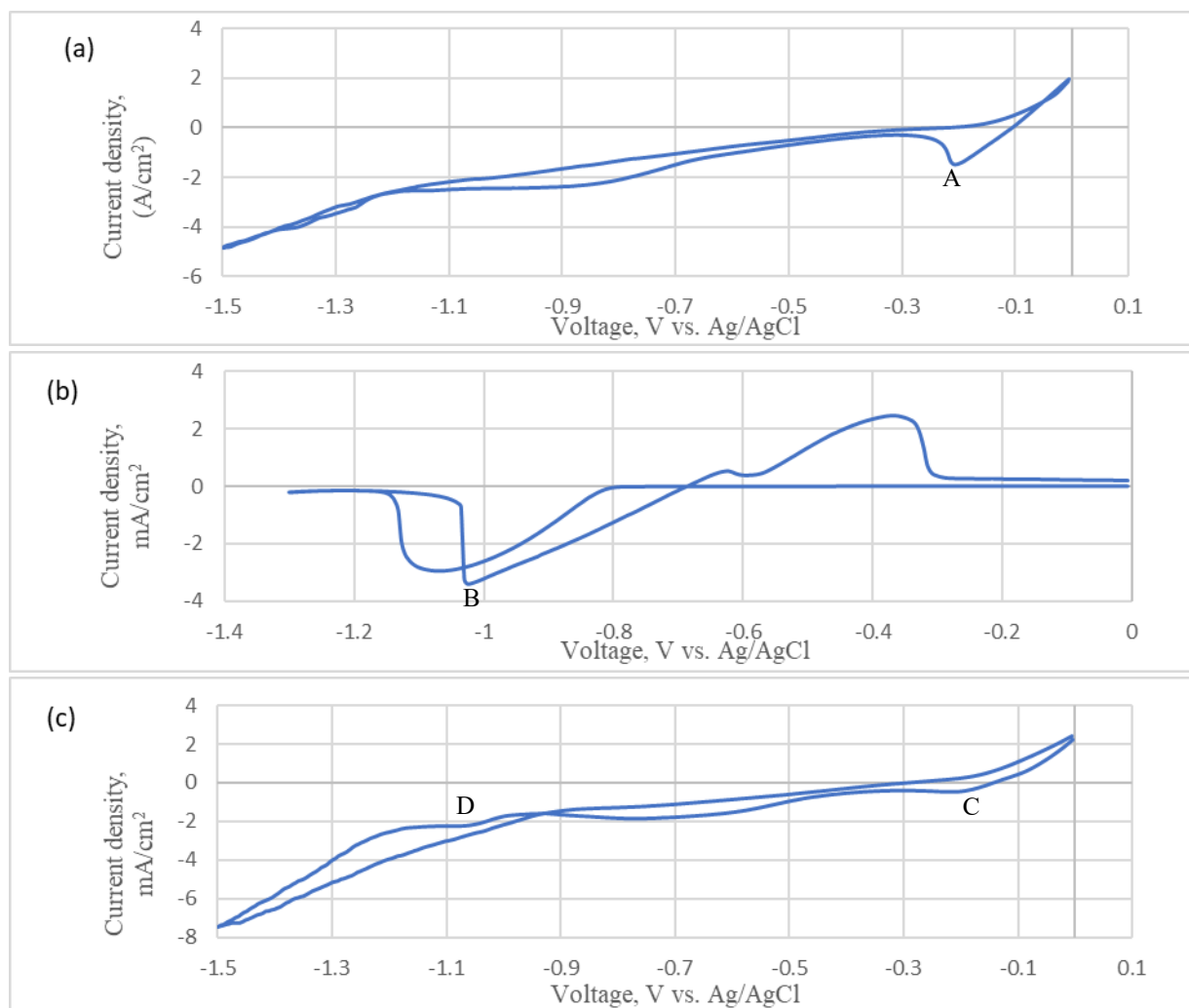


Fig. 3. Cyclic voltammograms of a Carbon electrode in (a) 300 mM CuCl_2 + 700 mM Trisodium Citrate, (b) 300 mM InCl_3 + 700 mM Trisodium Citrate and (c) 300 mM CuCl_2 + 300 mM InCl_3 + 700 mM Trisodium Citrate.

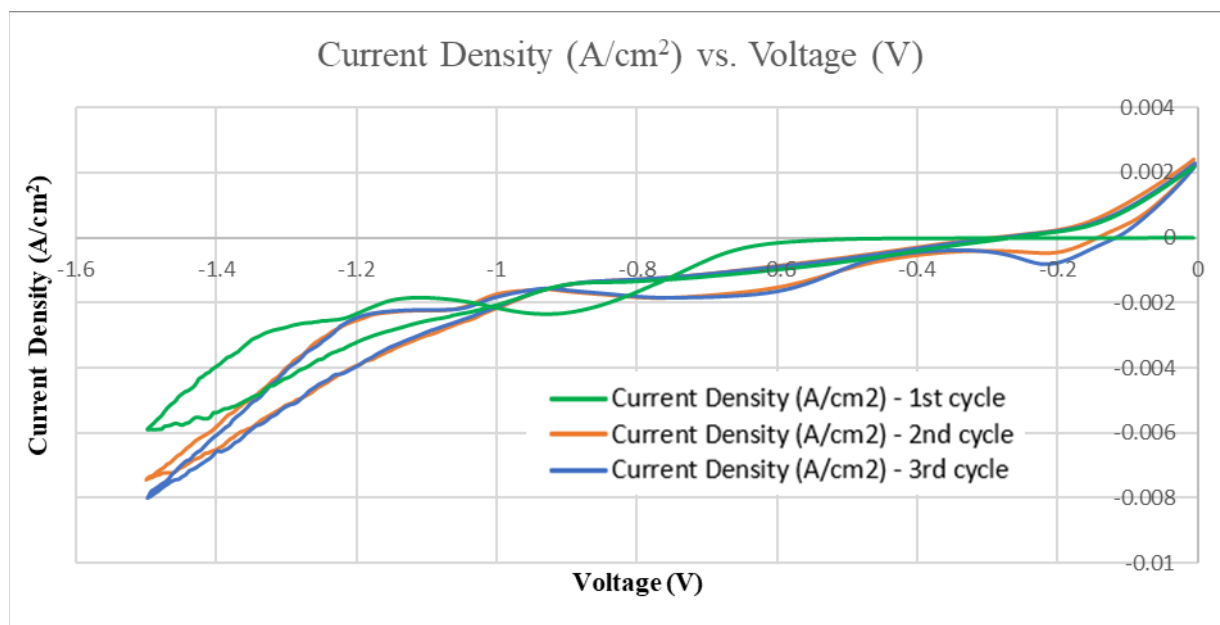
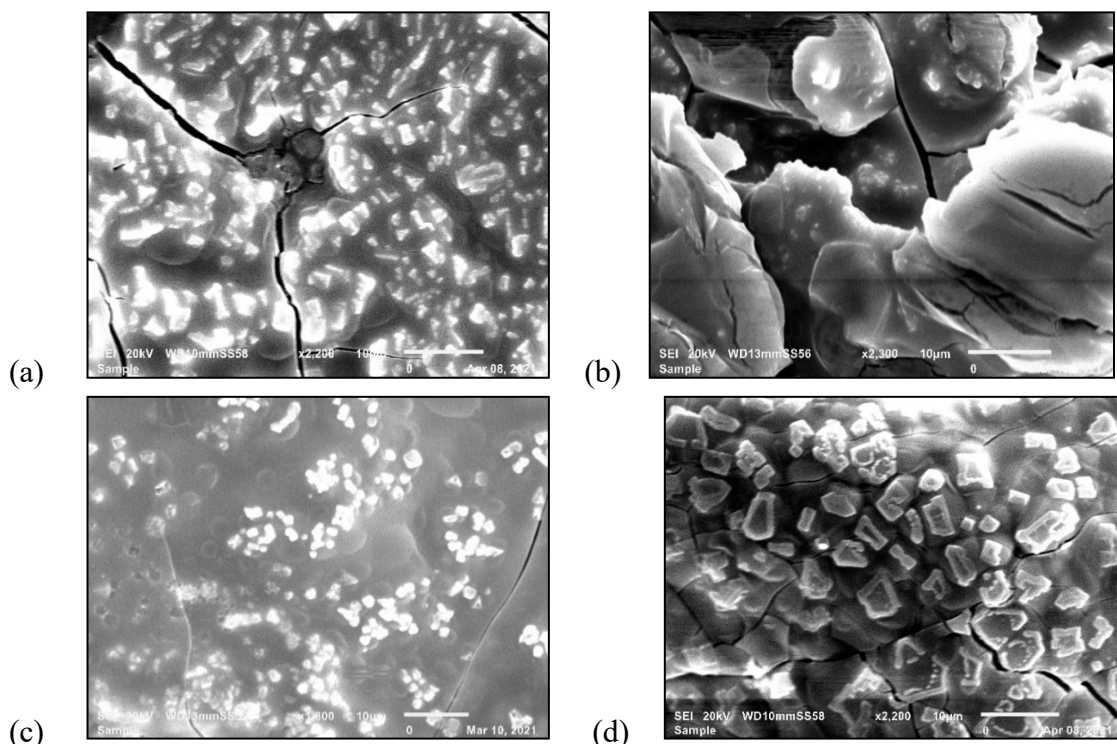


Fig. 4. Three cycles of cyclic voltammograms for binary solution of copper (II) chloride + indium (III) chloride and trisodium citrate.

On juxtaposing the successive cyclic voltammograms, slight differences are observed in the three cycles. As observed in Figure 4, for the third successive cycle, no copper peak is observed whereas an indium peak is observed but it seems to appear shifted to more negative deposition potential. Not much difference in the peaks is observed for the first and second cycles. The explanation for this could be that some copper is not oxidized back into copper ions and some nucleation sites are left covered on the carbon electrode by copper which reduces the number of nucleation sites available for copper reduction. This is known as the surface effect.

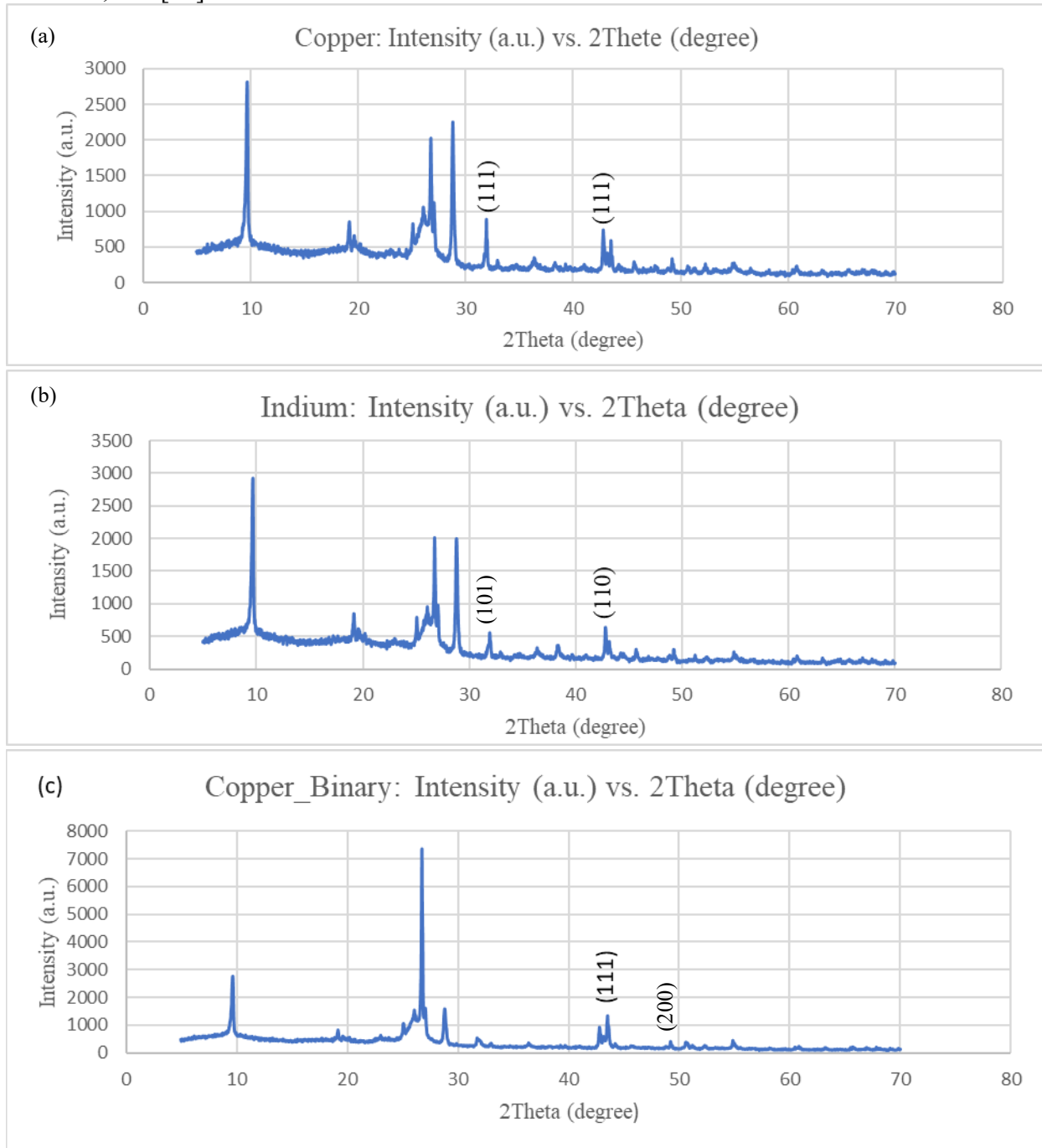
The charge transfer reaction corresponding to the peaks A and B in Figure 3 (a) and (b) at -0.2 V and -1 V potentials respectively must be related to the electrodeposition of copper and indium respectively. Cathodic peaks C and D are attributed to copper and indium electrodeposition in the binary electrolyte. These plots are for unitary solutions of copper (II) chloride and indium (III) chloride containing trisodium citrate as the complexing agent. For binary solution, respective peaks for copper and indium were found at -0.2 V and -1 V as well. For Figure 3 (a), (b) and (c), the voltammogram shows a badly defined hump at -0.8 V, -0.6 V and -0.6 V, respectively which might be attributed to the hydrogen evolution reaction. On juxtaposing Figures 2 and 3 which are cyclic voltammograms for the electrolytes in the absence and presence of the complexing agent, respectively, obtained in similar conditions, a negative shift in the peak potential of the respective element is observed by a degree of 0.2 V. This seems to suggest that some kind of complexation between the citrate anion and copper (II) and indium (III) cation occurs.



*Fig. 5. SEM micrographs of (a) copper deposits at -0.6 V (*2200), (b) indium deposits at -0.9 V (*2300), (c) copper-indium deposits at -0.6 V (*1800) and (d) copper-indium deposits at -0.9 V (*2200).*

High resolution scanning electron microscopy micrographs were recorded to investigate electrodeposited films of copper, indium and copper-indium. The copper films deposited at room temperature consisted mainly of grains with diameter varying about 2-4 μm as seen in Figure 5 (a). A few rods are also observed with the mean length 5 μm randomly oriented. Grains shape and size is irregular. SEM for copper film deposited at -0.6 V show crystallite structure compared to cauliflower-like structure produced in literature which could be a result of not washing the deposits after electrodeposition. Similar grain sizes and structure have been reported in literature. As can be seen from the surface morphology, the film deposit is not crack-free. Indium particles seem to be bigger than copper particles with their average size being 20 μm as compared to copper average particle size being around 2 μm as seen in Figure 5 (b). For indium, literature has reported densely packed particles whereas those shown in Figure 5 (c) are more compact. Shape and size of the particles is more irregular. In literature, grains had more regular circular shape [22]. The surface morphology of the Indium deposit also shows cracks on the surface. SEM depicted in Figure 5 (c) indicates smaller grain size when compared to copper alone. Again it seems that the particles are in the initial stages of nucleation. The small grains is irregular in shape and size. The size ranged from 1 to 3 μm . The surface morphology examination from the $\times 900$ magnification shows a lot of cracks on the surface. Having cracks on the surface is not recommended and needs to be corrected by altering the deposition conditions such as deposition time, pH, concentration of electrolytes and potential. Figure 24 (a) and (b) indicates large indium particles as compared to copper deposition in the previous case. From the SEM morphology diagrams in figure 24 (c) and (d), it can be observed that copper and indium suppress each other's formation. Grain size and shape is irregular, and the average size is 5 μm . Similar to the previous SEMs for the different deposits, cracks are observed on the surface. From literature, these cracks could be avoided by improving the process

conditions of the bath such as pH, deposition time, deposition voltage, bath composition, bath additives, etc. [21].



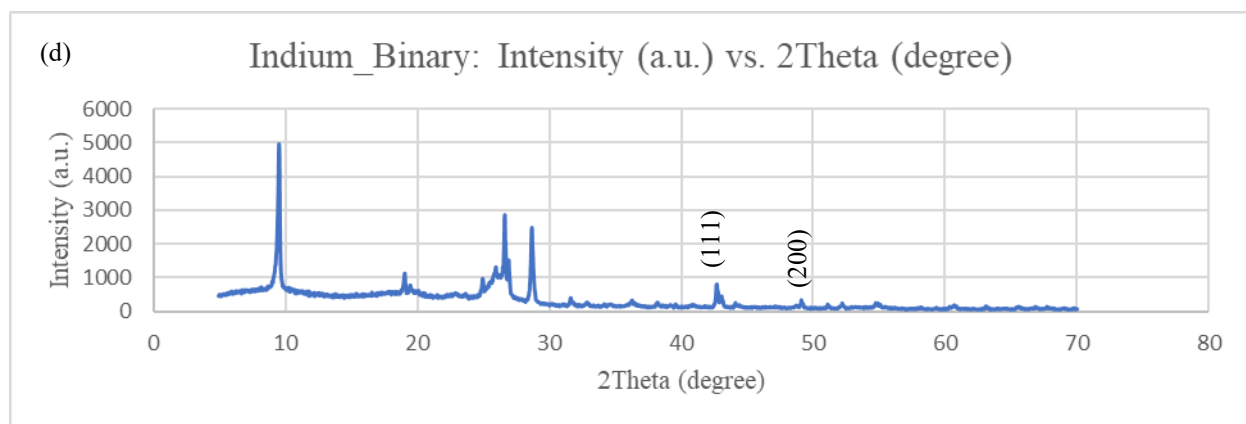


Fig. 6. X-ray diffraction patterns of the copper-indium layers at different deposition potentials.

Figure 6 depicts the X-ray diffractograms of the four deposited layers. XRD figures indicate a more amorphous structure. Figure 6 (c) and (d) show the presence of copper-indium at 2theta of 49° at a preferential plane of (200) to the growth of copper-indium. The XRD diffraction patterns cannot be compared with the JCPDS database owing to the small amount of the substance present in the deposited layer analyzed.

Conclusion

The study reports non-vacuum and easy production of copper indium layers by the co-deposition method. In this paper, the electrodeposition process for the fabrication of copper-indium has been studied which includes cyclic voltammetry, X-ray diffraction, scanning electron microscopy and energy dispersive X-ray spectroscopy. Results can be used in further studies to determine the structure, morphology and reaction mechanism of the films deposited. It can be concluded that best results are obtained at a deposition potential of -0.8 V by comparing the results of the cyclic voltammograms for the binary solutions at -0.6 V and -0.9 V. SEM characterization studies showed cracks on the surface for all four samples and irregular grain shape and size between 2 - 20 μm . X-ray diffraction studies indicate the presence of copper-indium at 2theta of 49° at a preferential plane of (200) to the growth of copper indium. EDS studies indicate a relatively low amount of copper and indium and that a 1:1 ratio of Cu:In will be obtained at approximately -0.8 V. This study is a good elementary study which can be used to determine which composition of the final deposited layer give maximum conversion efficiency.

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