Preparation and Studies of Electrodeposited CuSe Thin Films

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Abstract

Cathodic electrodeposition in the presence of sodium dodecyl-sulphate in aqueous solution was used to prepare CuSe thin film deposited on titanium substrates. The effect of deposition potential, concentration and deposition time were studied to determine the optimum condition for the electrodeposition process. The films were characterized by X-ray diffractometry. Scanning electron microscopy was used to study the morphology of the deposits. The photoresponse of the films prepared was analysed using linear sweep voltammetry in the presence of sodium thiosulphate.

Introduction

The use of renewable energy to meet the energy demands has been steadily increasing over the years. Solar energy seems to be the most attractive and promising alternative energy source for the future since it is environmentally benign, inexhaustible and available in amounts sufficient to cope with the needs of the present world requirements. Efforts have been made in finding new materials for energy conversion. Two important factors that should be considered in producing these materials are the band gap energy matching to the solar spectrum and the competitiveness of production cost.

Metal chalcogenides and their mixtures are attractive and useful systems for solar energy conversion studies by photoelectrochemical means [1-8]. Electrodeposition could be a cost-effective technology for the production of terrestrial photoelectrochemical (PEC) cells [9]. Thin-film photoelectrochemical technologies are being developed as a means of substantially reducing the cost of photoelectrochemical systems. The PEC cells technology seems ideal, as it requires no or very little maintenance and lubricants. Unlike the current electricity generators, it also involves no rotating parts. Furthermore, PEC, enable us to convert the daytime solar radiation energy and meantime store it as a chemical energy, so we can use it when we need it [10]. Thin-film modules are expected to be cheaper to manufacture owing to their reduced material costs, energy costs, handling costs and capital costs [11]. Reduction of cost for the thin film cells is achieved by minimization of the amount of material used, the possibility of inexpensive materials processing methods and the use of inexpensive mounting arrays [12]. The main advantage of thin film solar cells is their promise of being low cost, due to low cost production and the use of the relatively low cost materials.

We report here the preparation of CuSe thin films in the presence of sodium dodecyl-sulphate as a complexing agent through electrodeposition process.

Experimental

The deposition was carried out potentiostatically using an Eg&G Priceton Applied Research potentiostat driven by a software model 270 Electrochemical Analysis System. A conventional three-electrode cell is employed, where the reference electrode is a Ag/AgCl and Pt is the counter electrode. Titanium (Ti, 99.99%) was used as the working electrode. Sodium dodecyl-sulphate (SDS) was used as a complexing agent to chelate with Cu^{2+} to obtain Cu-SDS solution. The presence of complexing agent in aqueous solution was found to improve the lifetime of the deposition bath as well as the adhesion of the deposited film on the Ti substrate [14].

Electrodeposition was carried out on the cell containing the two solutions; Cu-SDS and Na_2SeO_3. The deposition bath consisted of 0.01 M Cu-SDS and 0.01 M Na_2SeO_3 solution. The experiment was performed at room temperature (27°C) under N_2 blanket with-

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out stirring. The pH was maintained at 2.5 using HCl. HCl was added to prevent the formation of hydroxyl species and insoluble compounds. The substrate and the counter electrode were polished prior to the insertion into the electrolyte cell. The surface of the working electrode that is not contact with in the electrolyte was sealed using PTFE tape.

The films were prepared at various deposition potentials, solution concentrations and deposition time. The deposited films were rinsed with distilled water and kept for further comparison and analysis. The films were characterized by X-ray diffraction (XRD). XRD analysis was performed using a Shimadzu XRD 6000 diffractometer for the 2θ range = 2–60° with Cu K_α radiation (λ = 1.5418 Å). Scanning electron microscopy (SEM) was performed on a JEOL JSM 6400 Scanning Microscope. Photo responsiveness of the samples was tested in 0.01 M $Na_2S_2O_3$ solution system, by running linear sweep voltammetry (LSV) between -0.30 to -1.00 V. An EG&G Princeton Applied Research potentiostat driven by a software model 270 Electrochemical Analysis System was used to control the LSV process and to monitor the current and voltage profiles. The photocurrent and darkcurrent of the PEC cells were recorded under dark and light illumination using a tungsten-halogen lamp (100 W). The dark and light illumination was done by chopping the light path manually.

Results and Discussions

The electrodeposition process was carried out at different potentials, -0.30, -0.40, -0.50, -0.60 and -0.70 V *vs.* Ag/AgCl. The XRD pattern of films prepared at -0.40, -0.50 and -0.60 V show two peaks attributed to the formation of CuSe as shown in Fig. 1. For the film prepared at -0.30V, there is only one peak at 2θ = 53.2° corresponding to interplanar distance of 1.71 Å, which is in good agreement with the JCPDS value (File No: 27-0185). The film deposited at potentials -0.40, -0.50 and -0.60 V showed two peaks at 2θ = 40.7° and 53.3° corresponding to interplanar distances of 2.21 Å and 1.71 Å, respectively, which matches the correlating theoretical values of 2.21 Å and 1.71 Å. As the deposition potential was increased to more negative value (-0.70 V) only one peak at 2θ = 53.3° corresponding to interplanar distance of 1.71 Å could be observed.

The SEM micrographs (Fig. 2) of the film deposited at -0.30 V shows incomplete material deposition. The surface of the substrate was not covered
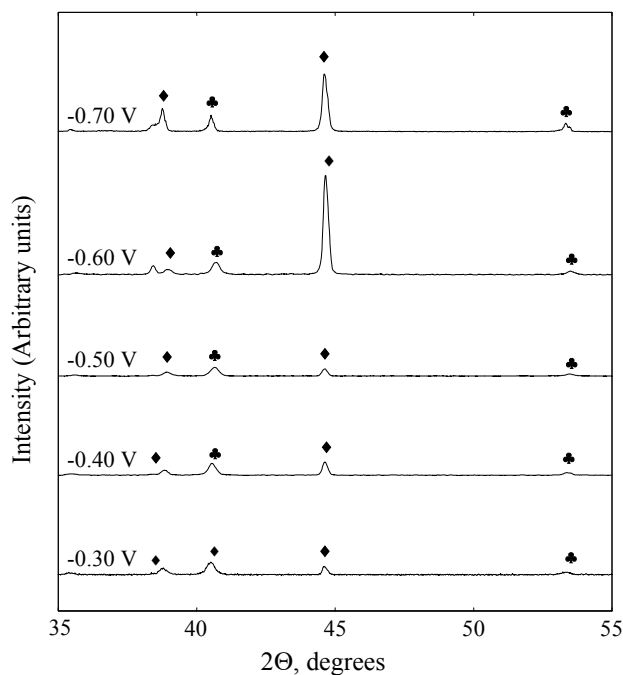

Fig. 1. XRD patterns of samples prepared at different potentials, Ti(♦), CuSe(♣).

completely. As the deposition potential was increased to -0.400 V, the surface of the substrate was covered almost completely. However the size of the grains were rather small (< 2 μm). The size of the grains increased to more than 2.5 μm as the potential was increased to -0.50 V. The surface of the substrate was completely covered as the potential was increased to -0.60 V. The size of the grains were rather uniform. The film failed to form effectively at -0.700 V as seen form the SEM micrographs.

Figure 3 shows the photoresponse of the deposited films in contact with 0.01 M $Na_2S_2O_3$ solution. The graph shows the resulted change in the current when the samples, employed as a cathode in the electrochemical cell, have been illuminated intermittently. This current change with the illumination confirms that the films posses semiconducting behaviour. The fact that the photocurrent occur on the negative (cathode) potential indicates that the films prepared are of *p*-type (positive) and they can be deployed as photocathode in the PECs application to facilitate a reduction reaction of the electroactive species in the solution.

The upper value corresponds to the current when the sample was illuminated (photocurrent), while the lower value corresponds to the dark current, when the light was interrupted by chopping. The photocurrent output, in mA, for the films prepared from potential -0.30 to -0.50 V show almost similar response.
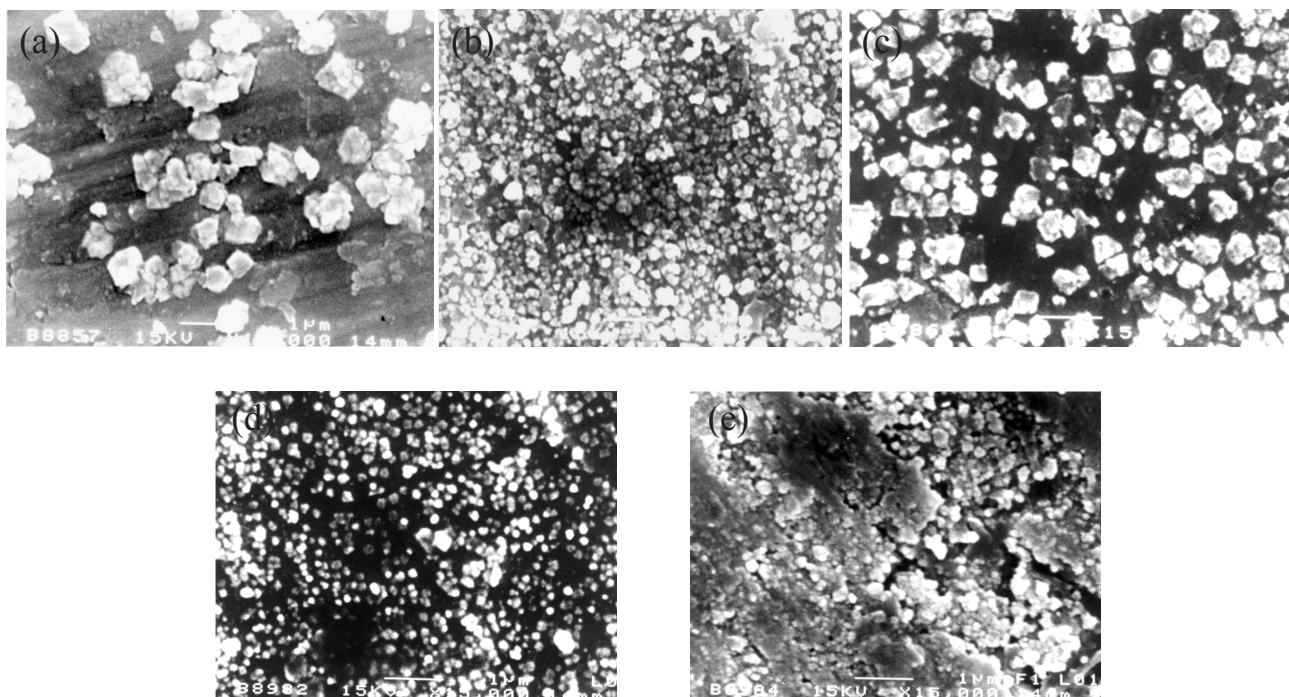
Fig. 2. SEM micrographs of films prepared at various potential: (a) − 0.300 V; (b) − 0.400 V; (c) − 0.500 V; (d) − 0.600 V and (e) -0.700 V.
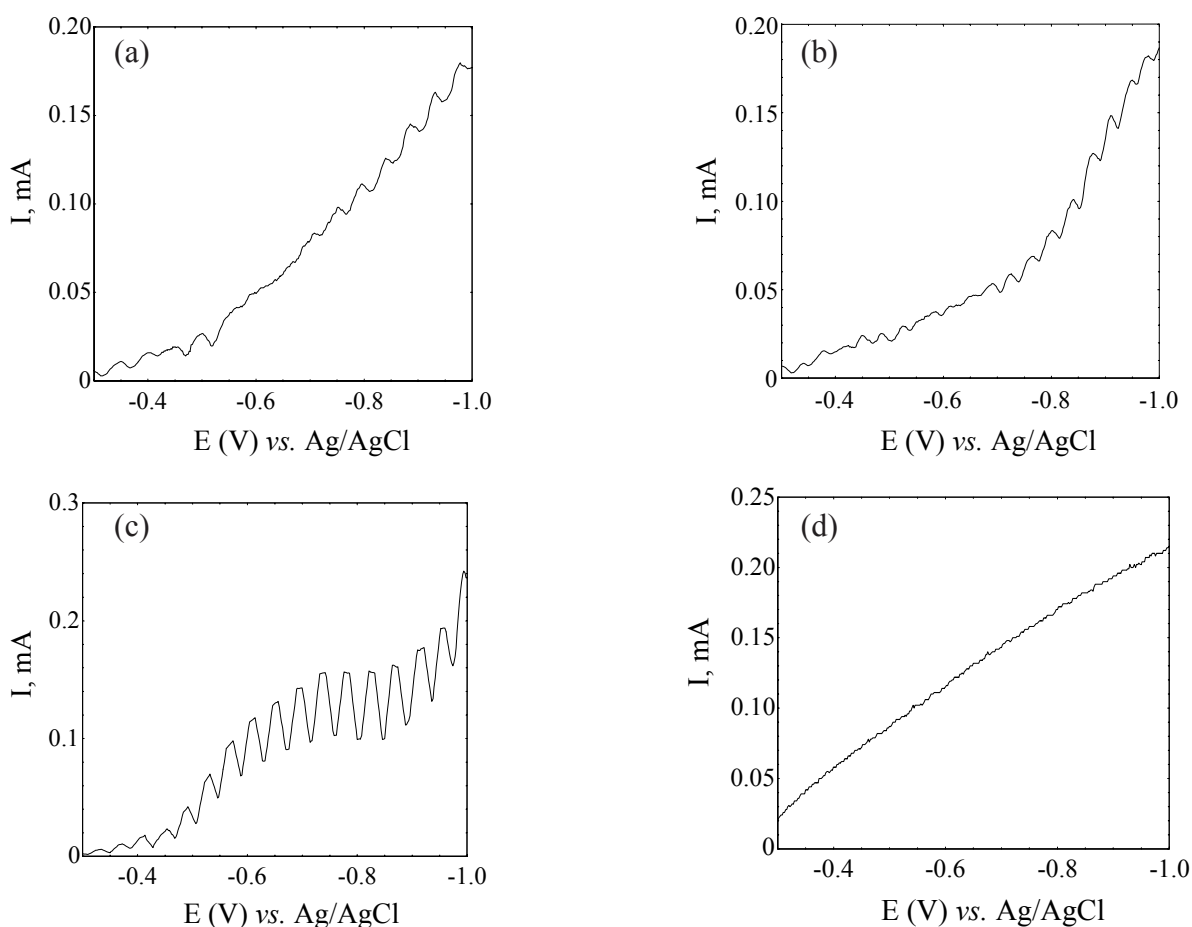

Fig. 3. Comparison of the photoresponse of the sample prepared at various potentials: (a) − 0.300 V; (b) − 0.500 V; (c) − 0.600 V and (d) − 0.700 V.

The film deposited at -0.60 V shows the highest photoresponse. The film deposited at -0.70 V shows very low photoresponse compared to the other films.

From the results obtained, we can conclude that the potential -0.600 V as the optimum condition to deposit CuSe films using this experimental set-up. The following experiment was carried out to determine the suitable solution concentration to prepare CuSe films. Various concentration of Na_2SeO_3 (0.001 M, 0.0025 M and 0.005 M) with a fixed concentration of 0.010 M of Cu-SDS was used. The deposition was carried out for 45 minutes at the deposition potential of -0.60 V (vs. Ag/AgCl). XRD pattern of the deposited sample of 0.001 M Na_2SeO_3 (Fig. 4) showed two peaks at 2θ = 40.4° and 53.3° corresponding to interplanar distances of 2.22 and 1.71 Å which are in good agreement with the JCPDS values of 2.21 and 1.71 Å. Two peaks corresponding to interplanar distance of 2.22 Å and 1.71 Å were also observed for the film prepared from 0.0025 and 0.005 M Na_2SeO_3. However, the intensity of the peaks attributable to CuSe decreased at this concentration (0.005 M Na_2SeO_3).

Figure 5 show the SEM micrographs of the film prepared using 0.001 M Na_2SeO_3 which shows the formation of grains that completely covers the surface of the substrate. The size of the grains are almost similar to one another varying from 2−3 μm.
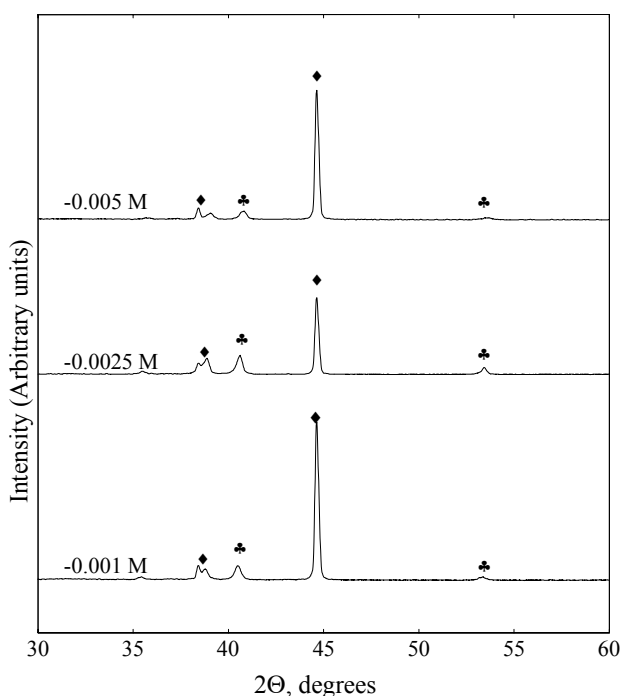
As the concentration was increased the formation of the grains are uneven and the grains are not distributed evenly over the surface of the substrate.

Effect of time towards the deposition process was also studied. The deposition was performed by varying deposition time ranging from 15 to 45 minutes using 0.01 M of Cu-SDS and 0.001 M Na_2SeO_3. The XRD pattern (Fig. 6) for the sample deposited for 15 minutes shows two peaks belong to CuSe at 2θ = 40.6° and 53.3° corresponding to interplanar distance of 2.22 Å and 1.71 Å. Two peaks at 2θ = 40.4° and 53.2° was also detected for samples prepared at 30 and 45 minutes, corresponding to interplanar distances of 2.22 and 1.71 Å respectively, which are in good agreement with the JCPDS value of 2.21 and 1.71 Å.
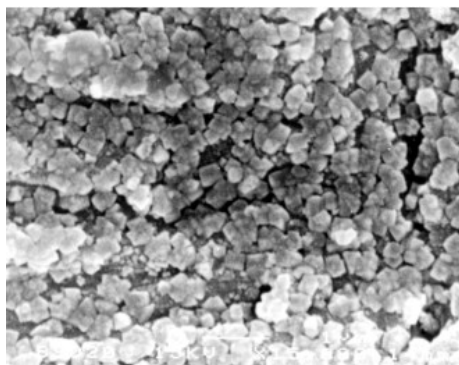

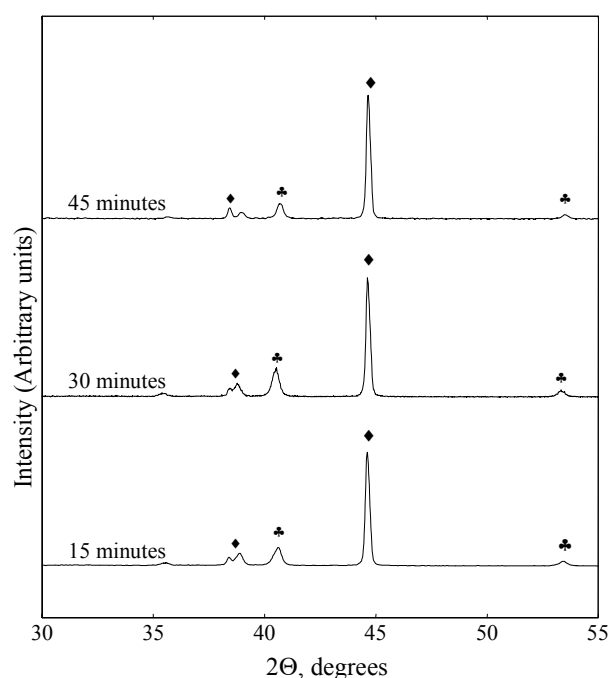Fig. 5. SEM micrographs of film prepared using 0.001 M Na_2SeO_3 and 0.01 M Cu-SDS.

Fig. 4. XRD patterns of samples prepared at different Na_2SeO_3 concentrations: Ti (♦), CuSe(♣).

Fig. 6. XRD patterns of samples prepared at different deposition period. Ti(♦), CuSe(♣).

The SEM micrographs (Fig. 7) show the growth of the grains at various deposition time. The film deposited for 15 min shows incomplete coverage over the surface of the substrate. Hairline cracks could be observed on the surface of the film. The grain size is relatively small compared to the grains obtained for samples deposited for 45 min. The SEM micrograph of the film deposited at 30 min show complete substrate coverage and formation of small grains of similar sizes.
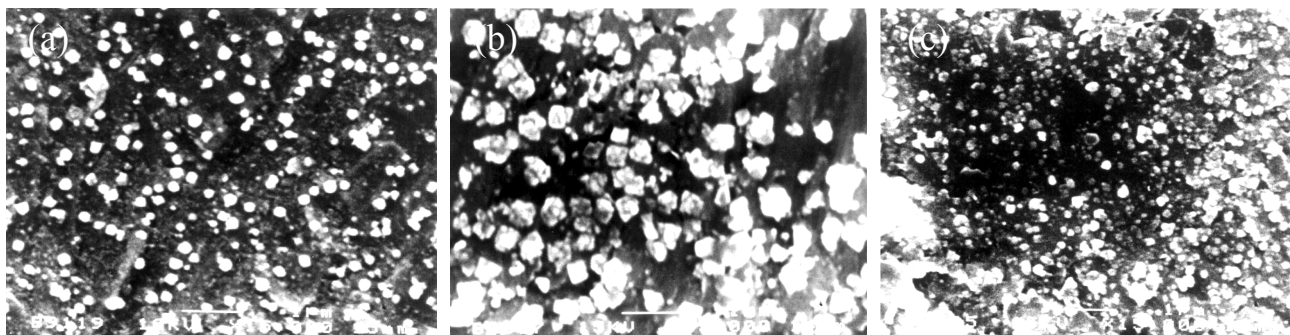

Fig. 7. SEM micrographs of films prepared at various deposition time (a) 15 min (b) 30 min (c) 45 min.

Conclusion

The optimum potential to deposit CuSe thin film was found to be at –0.60V. Deposition for 45 minutes in the presence of 0.001 M $Na_2Se_2O_3$ and 0.01 M Cu-SDS proved to be the optimum concentration and optimum time to deposit CuSe thin films.

Acknowledgements

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