

ELECTROCHEMICAL SYNTHESIS AND CHARACTERISATIONS OF METAL CHALCOGENIDE THIN FILMS

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Introduction

Considerable efforts have been made in recent years in search for low cost materials for solar energy conversion. Among materials of great interest are polycrystalline metal chalcogenides. The materials may be electrosynthesised either anodically or cathodically from aqueous medium. This approach received enormous attention due to its simplicity and cost effectiveness (Morris and Vanderveen, 1992). In addition it has the advantages of being a low temperature and low material wastage process and having the possibility of using lower grade materials. The objective of this project was to locally develop and use electrochemical technique for synthesising semiconductor thin films. The focus was given to the materials, which has a relation to the local resource such as SnS and SnSe. However, other materials of global interest such as cadmium chalcogenides were also attempted. A variety of characterisation methods was used to study the properties of the materials including the structure, composition and photoelectrochemical characteristics.

Materials and Methods

The electrodeposition was normally carried out either on metal substrates or on conducting glass substrates such as indium tin oxide. An electrochemical cell with three electrodes was used as this facilitates the measurement of electrochemical potentials, which has significant effect on the deposition. Saturated calomel electrode (SCE) or Ag/AgCl electrode was used as the reference electrode, while platelet or spiral Pt (99.9%) as the counter electrode. Deposition was controlled by and EG&G Princeton Applied Research (PAR) Verstat driven by Model 270 Electrochemical Analysis System software. The electrodeposition baths were normally prepared from tin or metal salts depending on the materials to be deposited. Chalcogenides were incorporated into the bath from soluble chalcogen based salts or acids. Complexing agent namely, ethylenediaminetetraacetic acid (EDTA) was sometimes added as it was found to improve the deposit quality. All depositions were done using purified water from Mili-Q water purification system and the solutions were purge with N₂ gas prior and during the electrodeposition to avoid interference from dissolved oxygen.

Results and Discussion

Particular emphasis is given in this report on the results obtained from the study of SnS electrodeposition as significant amount of project time was allocated for this substance (Arniza Ghazali et al. 1998). Eventhough the nature of the study was quite similar to other substances the results obtained may vary. The prerequisite step in every electrodeposition study is cyclic voltammetry (CV) experiment, as this will determine the range of the potential to be employed. In the case of SnS, CV in the electrodeposition bath of this

substance showed cathodic current onset at -0.67 V which is associated with the reduction of Sn(II) into Sn. Thiosulfate ion was suspected to undergo decomposition in acidic medium forming colloidal sulphur. Thus the reduction of Sn(II) ion was followed by association of Sn⁰ and S⁰ to form SnS. The sample electrodeposited at -0.70 V appeared smooth and uniform with orange-brown colour indicating a near stoichiometry. The durability of the deposited films to peel test was manifested when they did not show tendency to peel off the substrate when subjected to a steady stream of distilled water. Photoactivity test was carried out using manually chopped white light to delineate the dark and the photocurrent. The photocurrent was obvious in the cathodic direction suggesting that holes are the majority carrier, which is indicative of p-type conduction. A sample prepared on ITO glass substrate was analysed for its band energy using Shimadzu UV-160A Spectrophotometer. The optical data, which were fitted into Stern equation, indicated indirect optical transition near the absorption edge. The Eg values obtained were around 0.9 to 1.1 eV. X-ray diffractometry with Cu K α radiation was performed on Philips PM 1730 diffractometer. Majority of the signals were found to overlap with the standard JCPDS data which strongly suggest that the deposit was SnS with the structure corresponding to the herzenbergite form of SnS. Microscopic examination using SEM JSM6400 JEOL Scanning Electron Microscope shows that the deposit is uniformly distributed over the whole substrate. Higher magnification image of the deposit shows that they were comprised of randomly oriented tetragonal structures with size spanning 0.5 - 1 μ m. EDAX (energy dispersive analysis of x-ray) confirmed the presence of Sn and S on the deposit. Both Sn_{K α} and S_{K α} peaks, which are almost of the same intensities, reflect near stoichiometric SnS deposit. Heat treatment may result in adverse effect on the morphology, composition, structure and photoactivity of the substance (Zulkarnain Zainal et al. 1998). Apart from SnS studies were also done on SnSe, CdSe and CdS.

Conclusions

The studies proved the ability of electrochemical method in synthesising chalcogen based semiconductor materials. The materials obtained are of acceptable properties and showed good photoactivity. Factors affecting the deposition can be controlled and deposition on a variety of conducting substrates are possible (Zulkarnain Zainal et al. 1997). Additives such as complexing agent and heat treatment may effect the properties of the deposit. However the effect may vary depending on the substances.

References

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