

Electrodeposition and Characterization of CuInS₂ Thin Films Used in Aprotic Electrochemical Photovoltaic Cells

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INTRODUCTION

Electrochemical photovoltaic cells (EPC) are based on a junction between a semiconductor and an electrolyte containing one redox couple; an auxiliary electrode completes the device. If the semiconductor and electrolyte Fermi levels are different and well suited, a built-in potential will develop at their interface and the device will exhibit rectification in the dark and produce a photocurrent and a photovoltage under proper illumination. Low-band gap n-type semiconductors, such as Si, CdS and CdSe, are unstable under sustained illumination in aqueous media. The use of a non-aqueous electrolyte may eliminate the photocorrosion process due to its larger electrochemical stability window and low solvation energy for the ions that compose the semiconductor materials. Recently, we reported the characterization of an all solid-state EPC based on the junction between a polycrystalline n-CdSe electrode and a polymer electrolyte (1). The cell CdSe | modified PEO₁₂-CsT/0.1T₂ | ITO, where POE stands for poly(ethylene oxide), T⁻ for 5-mercapto-1-methyltetrazolate ion, T₂ for the disulfide, and ITO for indium tin oxide conducting glass, demonstrated very stable photocurrents and photovoltages when it was illuminated with a tungsten-halogen lamp. The attractive features of this redox couple include good solubility and ionic conductivity in several aprotic liquid solvents and polymers, high anodic potential (0.52 V vs NHE), low cost and low toxicity. In order to improve the EPC energy conversion efficiency, particularly at room temperature, the T⁻/T₂ redox couple was dissolved in a mixture of DMF and DMSO, and incorporated in poly(vinylidene fluoride), PVdF, to produce a gel electrolyte (2). On the other hand, the ternary semiconductor CuInS₂ possesses several advantages over CdSe, namely a bandgap energy (1.5 eV) that closely match the visible part of the solar spectrum, a higher absorption coefficient (10⁵ cm⁻¹) and a lower toxicity. The main objectives of this work are to prepare CuInS₂ thin films by electrodeposition on a Ti substrate, to optimize the preparation parameters and to characterize the deposited films.

EXPERIMENTAL

The cathodic deposition bath consisted in an aqueous solution containing 400 mM Na₂S₂O₃·5H₂O, 6-14 mM CuSO₄ and 3-7 mM In₂(SO₄)₃. The pH was adjusted to 2 with an aqueous tartaric acid solution (1 M) and then to 1.5 with an aqueous sulphuric acid solution (0.9 M). The working electrode was a 1.7 cm² Ti foil (0.127 mm thick), whereas the auxiliary electrode consisted in a 9.0 cm² Pt foil (0.1 mm thick). The Ti foil was previously degreased in CH₂Cl₂, washed in nanopure water, dipped for 30 s in sulfochromic acid, and rinsed once again in nanopure water. A Solartron 1287 Electrochemical Interface was used to set the Ti potential to -0.9 V vs Ag/AgCl. The deposition time was 60 min and the solution was stirred. The electrodes were then

annealed for 1 h in a N₂ atmosphere at a selected temperature (350-500°C) in a triple zone oven (Lindberg 59744). X-ray diffraction patterns of CuInS₂ films were obtained using a Siemens D-5000 instrument with a Co-K_{α1} radiation (λ=1.789Å). Surface morphology of the electrodes was examined with a scanning electron microscope (Hitachi, model S-2300) and surface composition was assessed through semi-quantitative EDAX analysis. Finally, the type of semiconductivity was determined using cyclic voltammetry in the dark (two electrodes system: Ti and Pt) at slow scan rate (1 mV s⁻¹) in the following non-aqueous electrolyte: 1.37 M CsT, 0.13 M T₂ in a mixture of DMSO (40%) and DMF (60%).

RESULTS AND DISCUSSION

X-ray diffractograms of CuInS₂ films prepared by electrodeposition from a solution with a Cu:In ratio of 8:12 revealed the formation of the tetragonal CuInS₂ crystalline phase. For example, peaks observed at 2θ = 32.485° and 54.367°, associated respectively to the (112) and (204) planes, are present and highly intense. The (004) and (312) planes were also observed. It has been shown that annealing is necessary to obtain highly crystalline deposits, and that the optimal temperature is 450°C. At lower temperatures (350-400°C), the crystallinity is low and at 500°C an In₂O₃ phase, ascribed to the partial oxidation of CuInS₂, is detected. Varying the Cu:In ratio in the deposition solution influences the percentage of crystallinity of the samples and the percentage of CuInS₂ in the deposited material. These parameters are very low at a ratio of 6:14 (49% of crystallinity and 55% of CuInS₂), and are maximal at a ratio of 8:12 (74% and 93%, respectively).

Scanning electron microscopy shows that the CuInS₂ films obtained using the optimal preparation parameters are highly porous, which will favorize high photocurrents when used in a EPC. EDAX analysis indicates that the total Cu content in the deposited film increases with the concentration of CuSO₄ in the deposition solution up to a ratio of 12:8, and then decreases when the ratio is 14:6. The total In content in the film decreases when the concentration of In₂(SO₄)₃ in the solution is decreased with a minimum at a ratio of 12:8. The total S content seems to follow the same trend than the In content. It is interesting to note that the film prepared from a deposition solution with a ratio Cu:In of 14:6 showed a CuIn₅S₈ phase in the X-ray diffractogram (excess of In and S).

Cyclic voltammograms of a CuInS₂ thin film electrode, prepared from a solution containing the optimal Cu:In ratio (8:12), was carried out in the dark. The current-voltage curve of the cell CuInS₂ | DMSO (40%)/DMF(60%)/1.3 M CsT/0.13 M T₂ | Pt demonstrates that the semiconductor/electrolyte interface exhibits a rectifying behavior with a cathodic current (direct) much greater than the anodic current (reverse), which is typical of a Schottky junction formed between a n-type semiconducting material and an electrolyte.

REFERENCES

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2. I. Renard, M.Sc. Thesis, Université du Québec à Montréal, Montréal (1997).

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