Superlattices and Microstructures 75 (2014) 159–170

Contents lists available at ScienceDirect

Superlattices and Microstructures

journal homepage: www.elsevier.com/locate/superlattices

Physicals and electrochemical properties of $ZnIn_2S_4$ thin films grown by electrodeposition route

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ARTICLE INFO

Article history:
Received 24 July 2014
Accepted 25 July 2014
Available online 7 August 2014

Keywords:
$ZnIn_2S_4$
Thin film
Cyclic voltammetry
Effect of applied potential
Electrochemical impedance spectroscopy

ABSTRACT

We present a new work on the development of electrodeposition route for synthesis of ternary $ZnIn_2S_4$ alloy. These thin films were grown on (ITO)-coated glass substrate from acidic plating bath containing Zinc (II) Chloride ($ZnCl_2$), Indium Chloride ($InCl_3$) and sodium thiosulfate ($Na_2S_2O_3$) at room temperature. Prior to deposition, a cyclic voltammetry study was performed in binaries (Zn–S, In–S) and ternary ($ZnIn_2S_4$) systems. The influence of various deposition potentials on structural, morphological, optical, and electrical properties of samples was investigated. X-ray diffraction patterns of samples demonstrate the presence of major crystalline phase of $ZnIn_2S_4$ at an applied potential of −1050 mV versus Ag/AgCl. Energy band gap of samples determined from optical measurements has been estimated in the range of 1.90–2.50 eV. From atomic force microscopy (AFM) and scanning electron microscopy (SEM) analysis, it was found that surface morphology, grain size and roughness were strongly influenced by varying the deposition potentials. Electrochemical impedance spectroscopy data have been modeled using an equivalent circuit approach. Flat-band potential and free carrier concentration have been determined from Mott–Schottky plot and are estimated to be around −0.72 V and 1.46×10^{17} cm^{-3} respectively. The film was n-type semiconductor.

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http://dx.doi.org/10.1016/j.spmi.2014.07.039
0749-6036/

1. Introduction

Materials scientists have for some time been interested in compounds of ternary chalcogenide belonging to the AB_2X_4 (A: Zn, Cd, Hg, B: Al, Ga, In, X: S, Se, Te) class of semiconductors [1,2]. Physics of these compounds covers many areas of fundamental and technological interest [3–5]. As one of these compounds, $ZnIn_2S_4$ drew increasing attention due to its excellent optical and electrical properties [6,7]. $ZnIn_2S_4$ has a layered structure with a high chemical stability. This compound is an n-type semiconductor [8]. The band gap is within visible range, allowing it to be a promising candidate for ecofriendly, visible-light-driven photocatalyst [9,10]. $ZnIn_2S_4$ is also competent for multiple great potential applications such as thermoelectricity, photoconduction, charge storage [11,12]. Synthesis and functional property studies of semiconductors including $ZnIn_2S_4$ have been widely studied because the shape and size of these materials may exert a significant influence on their optoelectronic function and device performance, and sometimes induce more improved physical and chemical properties than their bulk counterparts. Up to now, several methods have been used to prepare $ZnIn_2S_4$ single crystals and thin films such as hydrothermal process [9,10,13,14], an oleylamine (OA)-assisted solvothermal method [15], a surfactant template technique [16], microwave-heating technique [11], thermal sulfidation [17], spray pyrolysis [18], chemical bath deposition [10], chemical synthesis [19], vapor-phase chemical transport method [20] and electrodeposition [21]. Among these methods, electrochemical techniques provide numerous advantages, including, low temperature processing, arbitrary substrate shapes, controlled film thickness, morphology, and potential low capital cost. It is an isothermal process mainly controlled by electrical parameters [22]. In addition, the electrochemical method is readily feasible given that the accurate control of the oxidation-state of group VI precursor is not required. Therefore, various electrochemical systems have been used for successful deposition of binary [23,24] and ternary [25–27] films. Electrodeposition of ternary and other higher multinary compounds containing more than two constituent elements is rather complex, owing to a large difference in deposition potential of the constituent elements, and due to the possibility of the formation of intermediate phases during electrodeposition.

To our knowledge, there have been no reports on electrodeposition mechanism of $ZnIn_2S_4$ thin films in the literature.

In the present work, thin films of $ZnIn_2S_4$ have been deposited on indium doped tin oxide (ITO)-coated conducting glass substrates using potentiostatic cathodic electrodeposition technique. In order to understand better the electrochemical behavior during the co-deposition of Zn, In, and S in acidic plating bath, a systematic cyclic voltammetric study was undertaken on a ITO-coated glass electrode. An attempt is made to optimize deposition potential in order to obtain high quality $ZnIn_2S_4$ thin films for their ultimate use in photovoltaic and photocatalytic activities. In addition, electrochemical behavior occurring in $ZnIn_2S_4$ electrode/Na_2SO_4 electrolyte solution interface is primarily investigated by electrochemical impedance spectroscopy (EIS) method.

2. Experimental

Cyclic voltammetry and electrodeposition experiments were performed using a potentiostat/galvanostat Autolab PGSTAT 30 (Eco Chemie B V) connected to a three-electrode cell (K0269A Faraday Cage, PAR) at room temperature (25 °C). In all electrochemical experiments, working electrode was an indium doped tin oxide (ITO)-coated glass substrate ($\rho \leqslant 5.0 \times 10^{-5}\ \Omega$ cm), reference electrode was an Ag/AgCl/3 M NaCl and platinum wire was used as a counter electrode. Before manipulation, all ITO-coated glass substrates were ultrasonically cleaned during 15 min with respectively acetone and iso-propanol and rinsed with deionized water. All precursors were dissolved in deionized water (i.e., >18 Mq) with 0.1 M KCl as supporting electrolyte. The pH of the solution was adjusted to 2–2.5 by adding drops of concentrated 1.0 M HCl in order to decrease the formation of metal complexes such as $In(OH)_3$. Electrolyte bath contains a mixture of 10^{-3} M $ZnCl_2$ (fluka chemika), 2×10^{-3} M $InCl_3$ (fluka chemika), and 4×10^{-3} M $Na_2S_2O_3$ (Fluka). Using cyclic voltammetry, the films were grown at various deposition potentials in the range varying from −900 mV to −1200 mV (vs. Ag/AgCl) for