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Synthesis and physical behaviour of In_2S_3 films

Abstract

In_2S_3 layers have been grown by close-spaced evaporation of pre-synthesized In_2S_3 powder from its constituent elements. The layers were deposited on glass substrates at temperatures in the range, 200–350 °C. The effect of substrate temperature on composition, structure, morphology, electrical and optical properties of the as-grown indium sulfide films has been studied. The synthesized powder exhibited cubic structure with a grain size of 63.92 nm and S/In ratio of 1.01. The films grown at 200 °C were amorphous in nature while its crystallinity increased with the increase of substrate temperature to 300 °C. The films exhibited pure tetragonal β-In_2S_3 phase at the substrate temperature of 350 °C. The surface morphological analysis revealed that the films grown at 300 °C had an average roughness of 1.43 nm. These films showed a S/In ratio of 0.98 and a lower electrical resistivity of 1.28×10^3 Ω cm. The optical band gap was found to be direct and the layers grown at 300 °C showed a higher optical transmittance of 78% and an energy band gap of 2.49 eV.

Keywords: In_2S_3 thin films; CSE technique; Structural and morphological properties; Optical properties

1. Introduction

In recent years, several semiconductor materials with wide band gap are being investigated for their potential applications in different opto-electronic devices [1]. This is mainly due to the fact that wide band gap semiconductor technology is less developed compared to that of silicon technology. Further, wide band gap materials and the corresponding devices are less reproducible and more expensive than silicon-based devices. Indium sulfide is one of the prominent wide band gap semiconductors, that has an attractive fundamental properties suitable for device applications, particularly for photovoltaic cells. In general In_2S_3 films crystallize in tetragonal structure with lattice parameters, $a = 7.619$ Å and $c = 32.329$ Å. Depending upon the growth temperature and pressure, In_2S_3 exists in three forms such as α, β and γ [2]. Among these structures, tetragonal β-In_2S_3 is the most stable form at room temperature and it crystallizes in defect spinel structure with high degree of vacancies [3]. Due to its high defect structure, β-In_2S_3 finds many applications in the preparation of red and green phosphors for television picture tubes, [4] dry cells, [5] and photochemical cells [6]. The electrical and optical properties of In_2S_3 indicated that it is an n-type semiconductor with a wide energy band gap of 2.5 eV and a high transmittance in the visible region. In addition, the constituents of this material are nontoxic. These characteristics made this material as one of the potential substitutes for CdS in Cu(In,Ga)Se_2-based solar cells. The production of large area solar cells would also require a controlled variation in the grain size and composition. The optical loss is another important issue for fabricating high-quality device with higher performance. The optical losses are due to the scattering of light by the grains and grain boundaries. Moreover, the surface roughness, microcracks and voids in the films that are induced during the deposition process would also induce optical losses [7]. During the last two decades, the experimental investigations on the structural, optical and electrical properties of β-In_2S_3 thin films obtained by different techniques were intensified [8–12]. But there were no detailed reports on the changes of structural, composition and morphological properties of In_2S_3 films induced by deposition temperature grown using thermal evaporation. This technique offers large possibilities to change the deposition conditions in order to obtain the better quality films with pre-determined structure and physical properties. However, in practice the substrate temperature can have significant influence on the crystalline structure, surface morphology, composition and other structure-derived properties. It is therefore important to study the effect of deposition temperature on the physical properties of In_2S_3 layers.

In this paper, we reported the effect of substrate temperature on the compositional, structure, morphological and electro-optical properties of In_2S_3 thin films deposited on corning glass substrates by close-spaced evaporation. The In_2S_3 powder used for deposition was synthesized in the laboratory from its constituent elements that seems to be quite economic. As the opto-electronic properties are highly sensitive to the ratio of In/S, one can easily control the elemental composition ratio in the grown layers. This technique is highly suitable for the growth of uniform layers with smooth surface.

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2. Experimental details

Thin films of In_2S_3 were prepared by close-spaced evaporation (CSE) technique using Hind Hi Vac Box Coater (model BC: 300). The schematic diagram and experimental arrangement for CSE technique was discussed elsewhere [13]. It is a novel and simple technique that is slightly different from the conventional thermal evaporation wherein the distance between the source and substrate is ~5 cm. The material to be evaporated is taken in a quartz bottle with a small opening of 2 mm in its neck, which is covered with quartz wool. The quartz bottle is then kept in a box type Mo-boat that is heated by resistive heating process.

The layers were prepared by evaporating In_2S_3 powder synthesized by direct mixing of 5N pure individual elements according to their weight percentages and heated together in an evacuated quartz ampoule at a temperature of 900 °C for 24 h. The ampoule temperature was initially raised at a rate of 25 °C/h upto 500 °C and then increased by 100 °C/h. After the synthesis, the melt was cooled down to room temperature at a rate of 50 °C/h. The ampoule was continuously kept under rotation and rocking during the course of heating and cooling in order to ensure the homogeneity of the molten mixture. Ultrasonically cleaned Corning 7059 glass slides were used as substrates for depositing In_2S_3 films. The films were deposited at different substrate temperatures that vary in the range, 200–350 °C. The rate of deposition and thickness of the experimental films were determined using the quartz crystal thickness monitor (model QTM-101). The as-grown layers were characterized by studying the composition, structure, morphology, electrical and optical properties. The crystallinity of In_2S_3 films was measured using a Siefert X-ray diffractometer with Cu Kα radiation source (λ = 1.542 Å). The morphological properties of the films were evaluated using Zeiss EVO 50 scanning electron microscope (SEM) as well as Vecco atomic force microscope. The elemental composition of the layers was studied using VG Microtech ESCA2000 energy dispersive X-ray analysis (EDAX). The electrical characterization was done by four-probe method using evaporated silver as electrodes.

3. Results and discussion

Fig. 1(a) shows the X-ray diffractogram of the synthesized In_2S_3 powder, which shows the (4 4 0) plane as the predominant orientation along with other reflections that correspond to the cubic β-In_2S_3 phase (JCPDS no.32-0456). However, there might be some other phases of In_2S_3 present in the films in addition to β-In_2S_3 in the amorphous state that could not be identified by the X-ray diffraction analysis. The chemical composition of bulk In_2S_3 synthesized from the individual elements was found to be In = 49.75 at.% and S = 50.25 at.% that gives an S/In ratio of 1.01, and the corresponding EDAX spectrum is shown in Fig. 1(b). The crystallite size and lattice constant of the bulk material were found to be 63.92 nm and 10.774 Å, respectively. The visual observation of as-grown In_2S_3 layers was pinhole-free, uniform and dark red in color. These layers were well adherent to the substrate surface. The thickness of the layers was approximately ~0.3 μm and did not change significantly with substrate temperature.

3.1. Compositional analysis

Chemical composition of In_2S_3 films deposited at different substrate temperatures was evaluated using EDAX analysis. Fig. 2(a) shows the EDAX spectrum of In_2S_3 layers deposited at T_s = 300 °C. The variation of S/In ratio with substrate temperature is shown in Fig. 2(b). It could be observed that the films deposited at $T_s < 300$ °C were sulfur-rich, whereas the films deposited at $T_s > 300$ °C were indium-rich. It can also be observed that at T_s = 300 °C the In and S peaks are of equally height with approximately equal area and the average atomic ratio of S/In was found to be 0.98. This analysis revealed that the deposition temperature had a significant influence on the stoichiometry of the grown layers. The deviation of stoichiometry at lower temperatures might be due to the slight decomposition of the starting material during the evaporation or due to the difference in the vapour pressures of the constituent elements of the compound. A large deficit of sulfur content in the films was noticed when the substrate temperature, $T_s \geq 350$ °C. This could be due to the re-evaporation of sulfur from the substrate surface prior to the formation of In_2S_3 that

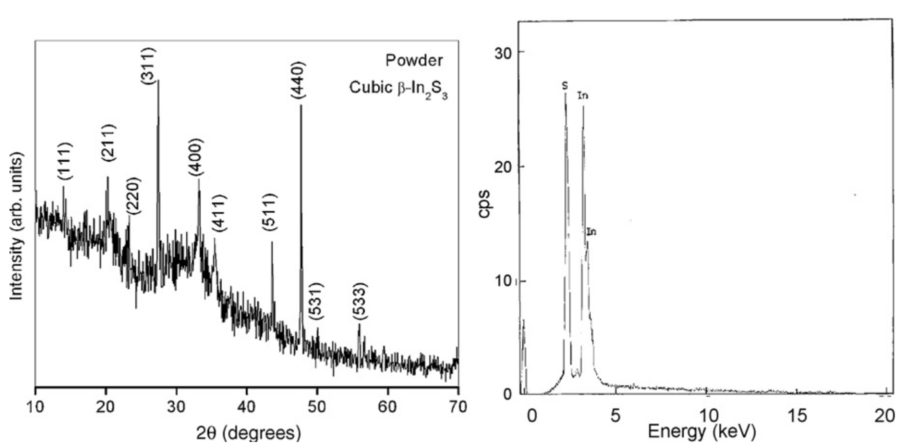

Fig. 1. (a) X-ray diffraction spectrum and (b) EDAX spectrum of synthesized In_2S_3 powder.