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Effect of precursor concentration on physical properties of nebulized spray deposited In_2S_3 thin films

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ABSTRACT

The present work investigates the effect of precursor concentration (m_c) on the structural, optical, morphological and electrical conductivity properties of In_2S_3 thin films grown on amorphous glass substrates by nebulized spray pyrolysis (NSP) technique. The mixed phase of cubic and tetragonal structure of In_2S_3 thin films at higher concentration has been observed by X-ray diffraction pattern. The reduced strain by increasing the precursor concentration increased the average crystallite from 17.8 to 28.9 nm. The energy dispersive analysis by X-ray (EDAX) studies confirmed the presence of In and S. The transmittance, optical direct band gap energy, Urbach energy and skin depth of In_2S_3 films have been analyzed by optical absorption spectra. The better conductivity and mobility noticed at m_c = 0.15 M are explained by carrier concentration and crystallite. Better optical and electrical conductivity behaviour of In_2S_3 thin film sample proposes for effective solar cell fabrication.

1. Introduction

Despite the fact that the highest efficiency of chalcopyrite ($CuFeS_2$) based solar cells is accomplished with CdS absorbing material [1,2], there are various reasons to replace the deposition method as well as the materials. The high absorption coefficient (10^5 cm^{-1}) and comparatively low energy band (2.4 eV) of cadmium sulphide (CdS) bound the spectral response of the device in the wavelength in the low region (<520 nm). In order to get the better of this restriction, buffer layer materials with lower absorption coefficient and/or higher energy band gap are needed. The III–VI semiconductors, In_2S_3, have been the promising materials during the past two decades due to its potential use in the semiconductor device fabrications with ordered vacancies in the III-sub lattice. The involvement in this material is stimulated owing to its applications in optoelectronic devices as a buffer layer in photovoltaic structures [3–5] and as an absorber layer in nanostructured solar cells [6,7]. Moreover, an essential research goal in processing photovoltaic devices is the substitution of n-type CdS layers in polycrystalline heterojunction thin film solar cells. In_2S_3 has benefited increasing involvement in solar cell technology since it has been identified as a desirable alternative to cadmium sulphide (CdS) buffer layer in thin film solar cells. Indium sulphide is an n-type semiconductor presenting in three forms: a defect cubic β-structure under adjacent conditions; a defect spinel β-In_2S_3 formed at 693 K and β-In_2S_3 formed at 1013 K [8–10]. Also, β-In_2S_3 is the constant phase of In_2S_3 from room temperature to 693 K and it forms in a defect spinal lattice with a high degree of vacancies, ordering tetrahedral cation sites [11].

The deposition of In_2S_3 thin films has been explored by distinct techniques such as physical vapour deposition [12], chemical bath deposition (CBD) [13–16], successive ionic layer absorption and reaction (SILAR) [17], spin coating [18] and spray pyrolysis [2,19–21]. Among these methods, even though the physical techniques deposit high quality and uniform thin films, they are comparably overpriced and extremely energy consuming. Nebulized spray technique (NSP) is a versatile, cost-effective, simple, time-saving and efficient way of depositing thin films at room atmosphere. This technique can be ascendable to large area deposition. NSP technique has been widely used to deposit binary, ternary and chalcogenide thin films [22–27]. In the present investigation, the binary In_2S_3 thin films have been deposited on the micro glass substrate by NSP technique for different precursor concentrations (m_c) from 0.05 M to 0.15 M. Structural, optical, morphological, elemental and electrical conductivity properties of nebulized spray deposited In_2S_3 thin films have been reported.

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Nomenclature and units

D	crystallite (nm)
λ	wavelength of X-ray (Å)
d	lattice spacing (Å)
θ	Bragg's angle (deg)
ε	lattice strain
T	transmittance (%)
$h\vartheta$	photon energy (eV)
E_g	optical band gap (eV)
E_u	Urbach energy (eV)
ρ	resistivity (Ω cm)
μ	mobility (cm/V s)
N	carrier concentration (cm^{-1})

2. Experimental technique

2.1. Mechanism of a nebulizer

Fig. 1 depicts a schematic diagram of a simple nebulizer which is also named as "atomizer". The nebulizer is attached by tubing to a compressor that efforts compressed air or oxygen to flow at high velocity to a precursor solution to change it into an aerosol, which is then sprayed on the glass substrate through the "L" glass tube which has small tapering at the substrate side to transfer the tiny droplets of precursor solution.

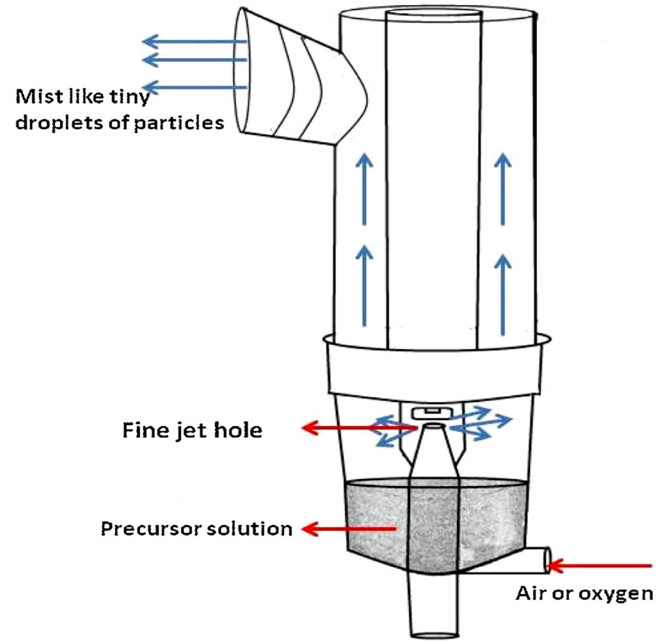

Fig. 1. Schematic diagram of the simple nebulizer.

2.2. Materials and methods

For the preparation of In_2S_3 thin films, high purity chemicals (>99% purity) such as indium chloride (In_2Cl_3) (Sigma–Aldrich) and thiourea (CS $(NH_2)_2$) (GR E Merck) were used as precursors without further purification. The precursors $InCl_3$ and CS $(NH_2)_2$ were used as source materials of In^{2+} and S^{2-} ions respectively. Micro glass slides have been used as substrates to deposit In_2S_3 thin films. Substrate cleaning leads to a major role in the thin film deposition. The contamination on the surface of the substrate may create nucleation sites alleviating the growth, which results in non-uniform film growth. Hence, the micro glass substrate of dimension 7.5 cm × 2.5 cm × 0.25 cm was first water washed well with soap detergent. The washed glass slides were kept in hot chromic acid for an hour to remove grease or oil presented during the manufacturing process of glass plates. After that, they were rinsed with acetone and double distilled water before the deposition of the films. In this work, the In_2S_3 thin films were deposited with different precursor concentrations from 0.05 M to 0.15 M. The substrate temperature was constrained by an iron-constantan type thermocouple and kept constant as its optimized value of 300 °C. The oxygen carrier gas flow rate was maintained at 1 kg/cm^2 corresponding to an average pressure solution rate of 5 ml per 20 min. The schematic diagram of an experimental set-up of NSP technique is shown in Fig. 2. The precursor solution was held in the nebulizer unit, which is connected to an air compressor. The compressed air is transported by tubing and stimulates the precursor solution through an "L" glass tube. The mist-like tiny droplets of particles were carried from the glass tube to deposit onto the glass substrate kept in the uniform hot zone of the furnace. After deposition, the films were allowed to cool at room temperature and then preserved them in desiccators.

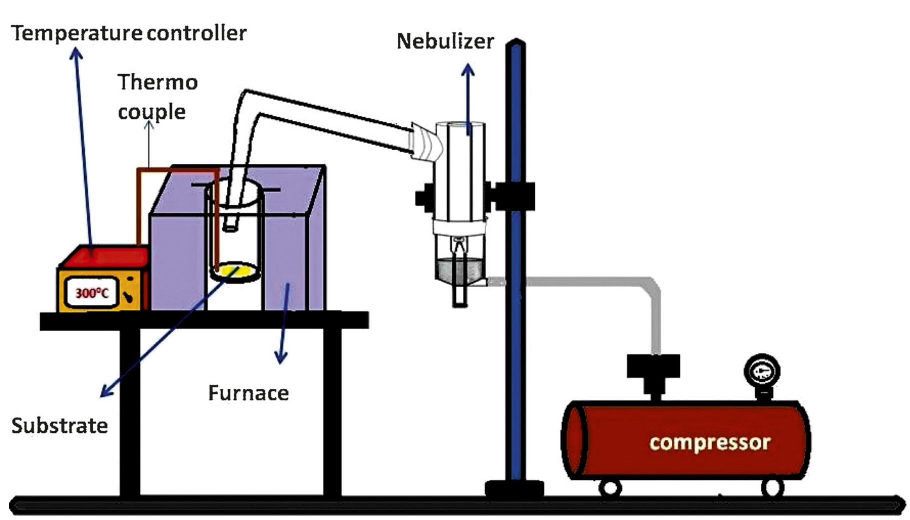

Fig. 2. Experimental set-up of nebulized spray pyrolysis technique.