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Growth and characterization of tin sulphide thin films by chemical bath deposition using ethylene diamine tetra-acetic acid as the complexing agent

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ABSTRACT

Tin sulphide (SnS), a promising, non-toxic and low-cost solar cell absorber layer, is grown using Chemical Bath Deposition technique at room temperature. The effects of concentration of ethlene diamine tetra-acetic acid, the complexing agent in the starting solution, as well as thioacetamide, the source of sulphur, on the growth of tin sulphide films are investigated to obtain single phase SnS films. The films deposited under optimized conditions are found to be near-stoichiometric, single phase SnS with orthorhombic structure. The lattice parameters are found to be a = 0.428 nm, b = 1.141 nm and c = 0.396 nm. The direct optical band gap of these films is found to be 1.55 eV.

1. Introduction

There is an imperative need to develop low-cost solar cell absorber materials using non-toxic elements to achieve the objective of economically viable and environmentally beneficial solar cells. Crystalline Si solar cells, though relatively efficient, remain expensive due to the requirements of high crystallinity and thickness. Thin film heterojunction solar cells are being explored to reduce the cost. The semiconductor used as an absorber layer in heterojunction solar cell must have a direct optical band gap matching the solar spectrum, p-type electrical conductivity and long minority carrier life time. $CuInGaSe_2$ (CIGS) based thin film solar cells with a record efficiency of 20.3% [1] have been developed. However, the elements In and Ga in this compound are expensive and their long term availability is limited. Cu_2ZnSnS_4 (CZTS), $Cu_2ZnSnSe_4$ (CZTSe) and $Cu_2ZnSn(S,Se)_4$ (CZTSSe) are being investigated as alternate absorber materials to CIGS as these compounds contain elements which are non-toxic and abundant. CZTS, CZTSe, CZTSSe based solar cells with an efficiency of 8.4%, 3.6 % and 11.1% respectively have been reported [2–4]. Achieving stoichiometry is critical in these multinary materials. SnS, another p-type compound semiconductor, is a promising solar cell absorber material with its band gap (~1.3 eV) close to the ideal band gap (1.5 eV) for highest theoretical efficiency, p-type electrical conductivity and high optical absorption coefficient ($>10^4$ cm^{-1}). Its elements are non-toxic and abundant. Hence, intensive research efforts are needed through various approaches to come out with device quality SnS films. Further, SnS is used as a precursor layer for the growth of CZTS films [5]. SnS films have been grown by various techniques like vacuum evaporation [6], RF sputtering [7], spray pyrolysis [8–11], electrodeposition [12–15], chemical bath deposition (CBD) [16–20] etc. Among these, CBD is a simple and inexpensive technique well suited for large area deposition. Different complexing agents like triethanolamine [16,17], tartaric acid [18,19], and trisodium citrate [20] have been used in CBD technique to grow SnS films. The effects of triethanolmaine (TEA) and tin salt concentration in the bath on the growth of SnS films by CBD have been reported by us recently [21]. However, there are no reports on growth of SnS films using ethylene diamine tetra-acetic acid (EDTA) as the complexing agent. EDTA forms complexes with nearly all polyvalent metal ions. The structure of EDTA is such that the ligand formation ability is more in this hexaligand EDTA when compared to TEA which is a triligand [22]. Moreover EDTA is not as toxic as TEA. Hence we have chosen EDTA as the complexing agent in the present investigation. In this paper, we report the growth of SnS films using EDTA as the complexing agent in the CBD process and the effects of concentration of EDTA as well as thioacetamide in the starting solution on the structural and optical properties of the films grown.

2. Experimental details

The starting solution for the growth of tin sulphide films consists of 0.10 M of stannous chloride dissolved in 5 ml of acetone, ammonia solution (1.40 M), thioacetamide (0.10 M) and the complexing agent, EDTA. All the chemicals and reagents used are analar grade. In order to study the effect of EDTA concentration on the nature of tin sulphide films formed, experiments were conducted with different starting solutions having EDTA concentration in the range 0.05 M to 0.08 M while keeping the concentrations of other chemicals in the bath constant. The deposition was carried out at room temperature in a

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100 ml beaker into which ultrasonically cleaned soda-lime glass substrates (2.5 cm × 7.5 cm × 0.1 cm) were kept. After a deposition time of 3–4 hours, the substrates were removed from the bath, washed with distilled water and dried naturally.

The thickness of the films was determined from the mass of the film deposited obtained using a Mettler microbalance [Model AE 240] and the bulk density of tin sulphide. Spectral transmittance of the films was recorded in the wavelength range of 300–2500 nm using PerkinElmer Lambda 950 double beam spectrophotometer. X-ray diffraction (XRD) patterns of the films were recorded on SEIFERT computer controlled X-ray diffractometer (Model 3003TT) in θ–θ geometry using Cu K_α radiation (λ = 0.15406 nm). Raman spectra were recorded on Jobin Yuan confocal Raman spectrometer (Model Lab RAM HR 800 UV) using He – Ne laser (632.8 nm). The data acquisition time was 30 s. The microstructure was determined using Carl Zeiss scanning electron microscope (SEM) (Model EVO MA 15) operated at 20 kV. The elemental composition of the film was obtained using energy dispersive X- ray spectrometer (EDX)(Model INCA 250) attached to the above SEM and the data acquisition time kept was 2 min.

3. Results and discussion

3.1. Deposition mechanism

When the ionic product $[Sn^{2+}]$ $[S^{2-}]$ in the bath exceeds the solubility product (Ksp) of SnS (Ksp = 1×10^{-26} at 25 °C), SnS precipitation takes place. In order to avoid instantaneous precipitation and achieve the desired film formation, usually one or two complexing agents are added. In this investigation, only one complexing agent, namely EDTA was used. $SnCl_2$ and thioaceatamide [TA] were used as the sources of tin and sulphur respectively. The metal ion forms a complex with the ligand EDTA and the complex ions slowly release free metal ions in a controlled way. These metal ions react with S^{2-} arising out of hydrolysis of thioacetamide forming SnS. The actual reaction mechanism is very complex and the simplified equation representing the growth of SnS using EDTA as the complexing agent is given by

$$[Sn(EDTA)]^{2+} + CH_3CSNH_2 + 2OH^- \rightleftarrows SnS + EDTA + CH_3CONH_2 + H_2O$$

Fig. 1 shows the variation of SnS film thickness with deposition time grown at room temperature. Initially, the film growth is negligible due to long incubation period required for the nucleation to occur. The films in the initial stage were found to be non-uniform. With increase in the deposition time, film thickness increased almost linearly up to a deposition time of ~200 min, beyond which it saturates. The terminal thickness attained is about 525 nm. In CBD process, the films can grow by ion-by-ion process or by hydroxide cluster mechanism or by complex decomposition of colloidal compound [23]. The initial longer incubation period and longer deposition times suggests that the growth mechanism in this case is not by ion-by-ion mechanism. Colloidal formation was not observed in the bath and hence the formation of SnS films through the mechanism of complex decomposition of colloidal compound is unlikely. Hence the growth of SnS with EDTA as the complexing agent might be due to hydroxide cluster mechanism. The growth depends on the composition of the bath, the complexing agents used, bath temperature, pH etc.

3.2. Effect of EDTA concentration on the growth and properties of SnS thin films

3.2.1. Growth dependence on EDTA concentration

Fig. 2 shows the variation of film thickness with the concentration of EDTA. When the EDTA concentration in the bath is low, complexation being weak, homogeneous precipitation of SnS occurs in the bath without any film formation. As the EDTA concentration increases, the complexation is better. Thus homogeneous precipitation of SnS in the bath decreases and the film growth improves with increase in the EDTA concentration in the bath. This explains the increase of terminal thickness with increase in EDTA concentration up to 0.07 M. With further increase in EDTA concentration, the availability of free Sn^{2+} ions in the bath reduces due to strong complexation with EDTA. Thus, due to the less availability of free Sn^{2+} ions in the bath, the film thickness decreases with increase of EDTA beyond 0.07 M.

3.2.2. Structural characterization

3.2.2.1. X-ray diffraction studies. Fig. 3 shows the XRD patterns of tin sulphide films deposited from different baths each with a different concentration of EDTA. Films deposited from a bath with [EDTA] = 0.05 M are polycrystalline SnS with Sn_2S_3 as the secondary phase. The intensity of the peak corresponding to Sn_2S_3 phase decreased in the diffraction pattern of the films obtained from a bath with [EDTA] = 0.06 M.

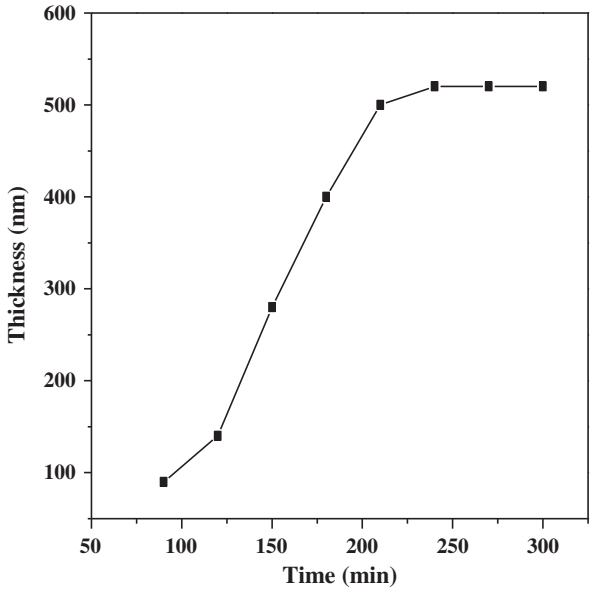

Fig. 1. Variation of film thickness with deposition time for films grown from a bath containing [$SnCl_2$] = 0.10 M, [TA] = 0.10 M, [NH_3] = 1.40 M & [EDTA] = 0.07 M.

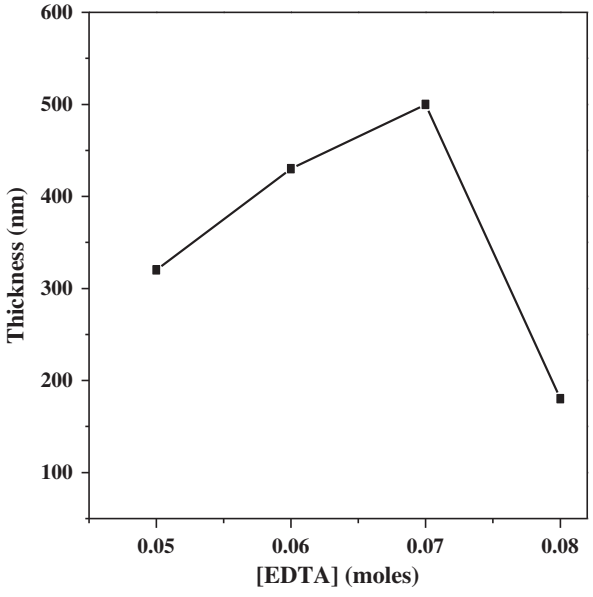

Fig. 2. Variation of film thickness with concentration of EDTA for films grown from a bath containing [$SnCl_2$] = 0.10 M, [TA] = 0.10 M & [NH_3] = 1.40 M.