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Deposition Time induced Structural and Optical Properties of Lead Tin Sulphide Thin Films

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Abstract

Lead tin sulphide (Pb-Sn-S) thin films (TFs) were deposited on fluorine-doped tin oxide (FTO) substrates via the electrochemical deposition process using lead (II) nitrate [$Pb(NO_3)_2$], tin (II) chloride dehydrate [$SnCl_2.2H_2O$] and thiacetamide [C_2H_5NS] precursors as sources of lead (Pb), tin (Sn) and sulphur (S). The solution of all the compounds was harmonized with a stirrer (magnetic) at 300k. In this study, we reported on the improvements in the properties (structural and optical) of Pb-Sn-S TFs by varying the deposition time. We observed from X-ray diffractometer (XRD) that the prepared material is polycrystalline in nature. UV-Vis measurements were done for the optical characterizations and the band gap values were seen to be increasing from 1.52 to 1.54 eV with deposition time. In addition to this, the absorption coefficient and refractive index were also estimated and discussed.

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Keywords: Thin films, XRD, band gap, Pb-Sn-S, refractive index, absorption coefficient

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1. Introduction

Tin sulphide (SnS) is a potential material for the production of thin solar cells because of its high absorption coefficient ($\alpha \approx 10^4\ cm^{-1}$ near the fundamental edge), suitable band gap (E_g = 1.1–2.1 eV) and high hole mobility of 90 $cm^3\ V^{-1}\ S^{-1}$ [1-3]. SnS semiconductors could present p or n-type conductivity owing to the preparation conditions and doping materials, which allow the films to be used as an absorption layers in hetero-junction solar cells fabrication [1, 4, 5]. Theoretically, SnS thin films solar cells can be optimized such that a conversion efficiency of above 25 % can be reached [6]. SnS thin films has been prepared by several methods like thermal evaporation, spray pyrolysis, electron beam evaporation, SILAR, hot injection, aqueous solution, colloidal route, single solid approach, precipitation and electrochemical deposition (ECD) [5-7]. ECD technique was used to fabricate Pb-Sn-S thin films in this study. The method presents a simple route of depositing TFs due to its low cost of experimental system, uniformity of films thickness as well as its large area deposition at low temperature [8-10].

Recently, investigation into new photovoltaic materials with improved efficiency have assumed a considerable interest and researchers are investigating for understanding and engineering the properties of SnS TFs for photovoltaic application [5]. Doping with elements like lead has shown to enhance the structural as well as the optical properties of SnS TFs. The study presents the preparation of lead tin sulphide (Pb-Sn-S) thin films using

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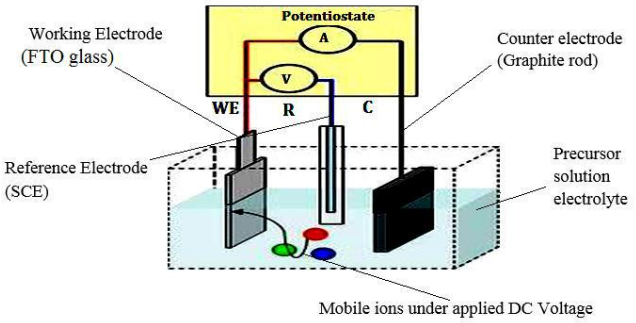

Figure 1. Schematic diagram of Pb-Sn-S deposition process

the electrochemical deposition technique. Our aim is to develop a better growth approach of new and non-toxic material for the production of low cost solar cells. Improvement in the properties of SnS TFs due to lead incorporation in SnS-system will enhance the device efficiency of the material. Particularly, this communication is concerned with the influenced of deposition duration on the properties (structural and optical) of Pb-Sn-S TFs via the electrochemical deposition technique which hitherto has not been studied using this route.

2. Materials and Method

Analytically graded chemical (Sigma-Aldrich) was used to deposit the Pb-Sn-S TFs. These chemicals include; lead (II) nitrate [$Pb(NO_3)_2$], tin (II) chloride dehydrate [$SnCl_2.2H_2O$] and thiacetamide [C_2H_5NS]. The electrochemical deposition bath system consist of a cationic precursor of 0.05 mol of Pb $(NO_3)_2$, 0.01 mol of $SnCl_2.2H_2O$ and an anionic (precursor) of 0.15 mol of C_2H_5NS mixed in distilled water. A stirrer (magnetic) was used to harmonize the reaction bath. Fluorine doped Tin Oxide (FTO) and carbons were employed as the cathode and anode electrodes respectively. The deposition using the electrochemical deposition method was achieved according to the scheme in Figure 1. The deposition were repeated for 20, 25, 30, 35 and 40 seconds and the samples were later coded as J0, J1, J2, J3, and J4 respectively.

2.1. Characterization of thin films

The Pb-Sn-S films used for this study have good adherent with the FTO substrates. The XRD patterns of Pb-Sn-S TFs were observed using Advanced X-ray diffractometer (Bruker D8) operating with a wavelength of 1.5406$\dot{A}$ and, at a scanning range of 15 to 80^o. The UV-Visible optical measurements of Pb-Sn-S thin films were done using a UV-1800 Spectrophotometer in the range of 300 to 1000 nm at room temperature. The optical band gaps (Eg), absorption coefficient (α) as well as refractive index (n) were estimated from the optical data.

3. Results and Discussion

3.1. X-ray diffraction (XRD) studies

The XRD patterns of Pb-Sn-S TFs are shown in Figure 2. Although the deposition time is increased, the XRD spectra showed four similar main peaks at 21.70∘, 23.50°, 24.94° and 33.62°, which correspond to the diffraction peaks of (200), (201), (211) and (221). The presence of higher intensity peaks in the Pb-Sn-S films with narrower spectral widths indicated that the films are polycrystalline in nature [11, 12]. From the XRD patterns also, it is obvious that the Pb-Sn-S structures consist of mixtures of several phases including the orthorhombic Sn2S3 (JCPDS no 014-0619), hexagonal SnS2 (JCPDS no 023-0677) and cubic structure PbS thin films (JCPDS 01-0880). As known, the presence of secondary phases within the Pb-Sn-S system may have deteriorated the structural crystallization as well as the peaks patterns.

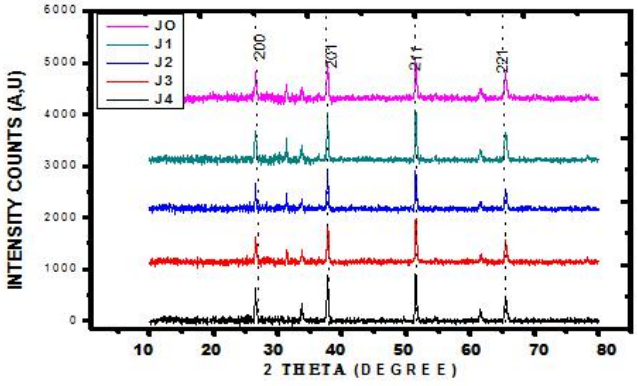

Figure 2. XRD patterns of the prepared PbSnS thin film

3.2. Optical studies

To ascertain the potentials of the electrochemical prepared Pb-Sn-S TFs for device fabrications, the absorbance was investigated in the spectra wavelength of 300 to 1000 nm. The absorbance A, was measured using the relation in equation(1) [13];

$$A = Log\left(\frac{1}{\mathrm{T}}\right) \tag{1}$$

Figure 3 shows the relationship between the optical absorbance and wavelength of Pb-Sn-S FTs. In the plot, it could be observed that the absorption was decreasing along the wavelength regions. As well from the figure, the absorbance decreases with deposition time. Such decrease in absorbance may be due to structural defects such as surface irregularity and defect density in the Pb-Sn-S system as a result of increase in deposition time [14], as indicated from the XRD measurement. The low absorbing nature of the films consequently indicates an improvement in the transmission [13]. The absorption coefficient (α) of the material was evaluated by means of the equation (2) [15];

$$\alpha = \frac{1}{t} ln\left(\frac{1}{\mathrm{T}}\right) \tag{2}$$

Table 1. Some optical properties of Pb-Sn-S TFs

Samples	Band gap (eV)	Absorption coefficient $(cm^{-1}) \times 10^4$	Refractive index (n)
JO	1.51	6.10	2.944
J1	1.52	15.0	2.939
J2	1.53	17.5	2.934
J3	1.54	13.2	2.929
J4	1.51	6.80	2.944

Equation (2) assumed a negligible reflectance while T and t are the respective transmittance and thickness of Pb-Sn-S films. The observed variation of the absorption coefficient with deposition time is shown in Table 1. It was observed that α increased from 6.1×10^4 to 17.5×10^4 cm^{-1} with deposition time of 30 seconds (Sample J2) and was decreased on further increase of deposition time. Also from the table, the magnitude of the absorption coefficient was found to be greater than the 10^4 cm^{-1} which makes Pb-Sn-S thin film a better alternative than GaAs and CdTe as absorber layers in photovoltaic applications [5,16]. The band gap (direct) was determined using the following relation in equation(3) [17];

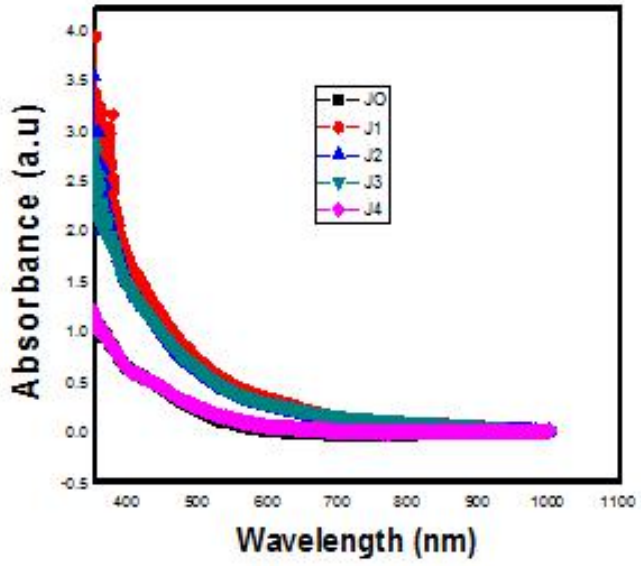

Figure 3. Absorbance against wavelength of the prepared PbSnS thin films

$$(\alpha hv)^2 = k\,(hv - Eg) \tag{3}$$

where hv is the photon energy, α is the absorption coefficient, k is a proportionality constant, and Eg is the optical band gap. A plot of the square of absorption coefficient against photon energy gives a curve illustrated in Figure 4. Since the prepared Pb-Sn-S films is a direct semiconducting material [2], extrapolating the linear portion of Figure 4 to the x-axis at x = 0 gives the band gap energy (Eg). The band gap obtained was seen to be between 1.52 – 1.54 eV as indicated in Table 1. Also from the table, the band gap energy values were observed to be increasing with increase in deposition time. Generally, band gap energy in semiconducting materials are mostly influenced by their structural defects, crystallinity, impurities, grain sizes as well as grain boundary disorders [18].

Consequently, the observed increase in band gap energy in Pb-Sn-S samples can be explained in terms of the effect of impurities in their lattice system as indicated from the XRD studies. Sebastian et al. [2] have reported a band gap range of 1.60 to 1.90 eV for lead doped tin sulphide (SnS:Pb) TFs grown by varying lead concentration using Nebulized spray pyrolysis (NSP) technique. Orimi et al. [19] estimated an optical band gap of 1.63 to 1.80 eV for Pb1-xSnxS nano-powder using chemical precipitate technique. Our obtained values are relatively lower than these values which could be the direct effect of the electrochemical deposition method employed in the preparation of this film.

The refractive index (n) is an essential property of optical materials. It is closely related to the electronic polarization of ions as well as the local field within the optical materials [20]. Many optoelectronic devices such as switches, modulators, filters, waveguides, solar cells and detectors are based on refractive index [21]. Generally, the n of Pb-Sn-S TFs is related to the optical band gaps. Moreover, the refractive index of the prepared Pb-Sn-S films was estimated using the proposed relation by Herve and Vandamme, given in equation (3) [21, 22]

$$n = \left[1 + \left(\frac{A}{Eg\ +\ B}\right)^2\right]^{\frac{1}{2}} \tag{4}$$

where Eg is the band gap, A (13.6 eV), and B (3.4 eV) are constants. The estimated values of the refractive index are indicated in Table 1. The results indicated that the n values of Pb-Sn-S TFs decreased from 2.944 to 2.929 with enhance deposition time. The range of the refractive indices of the material indicate that Pb-Sn-S film is a ternary material whose properties falls between the binary constituents of PbS (1.8 – 6.0) [23] and SnS (3.5 – 5.5) [4], and compares favorable well with values in literature.

4. Conclusion

Thin films of Pb-Sn-S have been prepared by the electrochemical deposition method and the structural and optical properties were investigated as function of the deposition time. The XRD measurements indicated a polycrystalline film with no much difference in their crystallinity as deposition time increases. The increased deposition time resulted in the variation of the

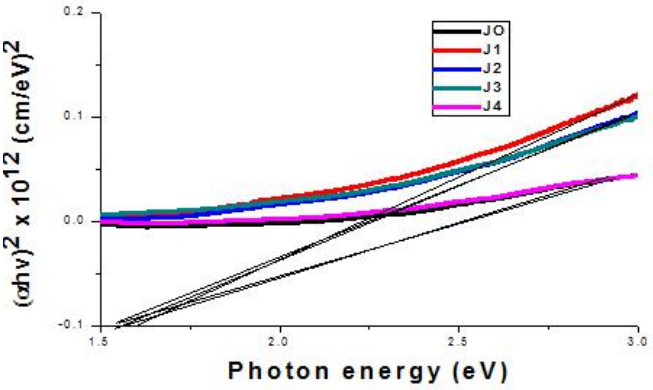

Figure 4. Square of absorption coefficient and photon energy for Pb-Sn-S TFs

absorption coefficient and band gap from 6.1×10^4 to 17.5×10^4 cm^{-1} and 1.51 to 1.54 eV respectively. The refractive index was observed to decrease with deposition time except for sample J4, and obeyed the Harve and Vandamme model. The high absorption coefficient obtained for the material suggests that the prepared Pb-Sn-S would create good absorbing properties in solar cell fabrications.

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