Characterization of Tindisulphide Thin Film Using Chemical Spray Pyrolysis Technique

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Abstract- *Thin film of tin disulphide (SnS2) has been prepared on glass substrate by chemical spray pyrolysis technique using the precursor solutions of tin (IV) chloride and thiourea, which were atomized with compressed air as carrier gas. Thin layer of SnS2 has been grown at the temperature of 498 K. The structural properties have been determined by X-ray diffraction (XRD) and surface morphology studies. The optical properties of the deposited film was obtained using experimentally recorded transmission and reflectance spectral data as functions of the wavelength, in the range of 400– 900 nm. An analysis of the spectral absorption of the deposited film revealed optical direct band gap energy of 2.89 eV for SnS2 layer. Fourier transform infrared spectroscopy (FTIR) studies confirm the presence of Sn–S bonds in SnS2 film in the molecular structure.*

Keywords— thin film; diffraction; optical; transmittance; band gap;

I. INTRODUCTION

The electronic and optical properties of semiconductor materials are tunable varying their shapes and sizes [1-3]. The optical properties of semiconductors are often subdivided into those that are electronic and those that are lattice in nature. The electronic properties concern processes because of the technological importance of their practical applications [4].Metal chalcogenides thin films have been extensively studied due to their potential application in electronic, optical and superconducting devices [5,6].The different phases of tin sulfide compounds like SnS, SnS2, Sn2S3, Sn3S4, etc. due to the versatile coordinating characteristics of tin and sulfur [7-10]. Each preparation technique has its own characteristics merits and demerits in producing homogeneous and defect free thin film. Among them, spray pyrolysis method is principal to prepare tin disulphide thin film, which is low cost that can be used to deposit uniform coatings on large surface area [6].Thin films of SnS2 have been deposited using different techniques such as the vacuum evaporation [11], electro- deposition [12], electroless deposition [13,14], chemical melt growth [15], chemical vapour deposition (CVD) [16], plasma-enhanced CVD [17], spray pyrolysis [18,19]. Each preparation technique has its own characteristics merits and demerits in producing homogeneous and defect free thin film nano materials and new preparation methods are being evolved to produce controlled size and shape of desired morphology. Among them, spray pyrolysis method is principal to prepare tin disulphide thin film, which is low cost that can be used to deposit uniform coatings on large surface area [20]. The intention, it is reporting the characterization of SnS2 thin film using SnCl2 and thiourea as a starting material by a spray pyrolysis technique.

II. EXPERIMENTAL METHOD

The precursor solutions were mixed in the ratio 1:2 solution was stored in reservoir kept at NTP. The gas pressure monitoring gauge connected to the other side of the spray head. The spray head was allowed to move using the controlled stepper motor system in order to achieve a uniform coating of the film on the substrate. The molarities tin and thiourea solutions were mixed and sprayed on the substrate with an area of 75 x 25 mm2 at substrate temperature 498 K. The solution flow rate 3 ml/min, carrier gas flow rate of 0.6 kg/cm2 and nozzle to substrate distance of 25 cm. The golden yellow colour film is obtained with good adhesion. The structural studies of the films were examined using XPERT PRO diffractometer. The SEM photograph taken with JEOL JSM 5300 scanning microscope. The resistivity of the film was studied using four probe method and the band gap analysis was studied using UV-VIS NIR X ray spectrophotometer.

III. RESULTS AND DISCUSSION

The XRD profile of the spray pyrolysised SnS2 thin film on glass substrate at 498K is shown in Fig. 1. The corresponding XRD pattern exhibits a single prominent peak at 2θ position of 14.43˚. The peak is obtained due to the reflections from the miller planes having indices (002) which could be assigned hexagonal structure by comparing the JCPDS data no. 21 –1231 [21].

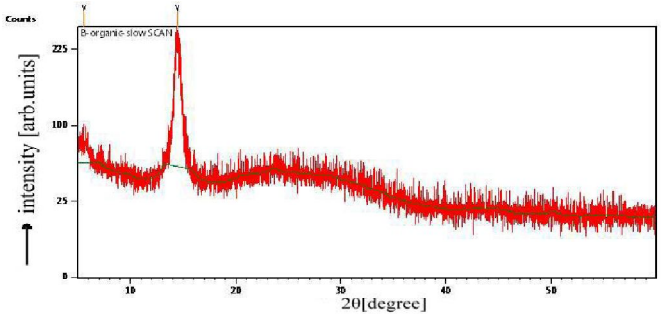

Fig 1 XRD pattern of SnS2 thin film at 498 K

The interplanar spacing of this peak is determined to be 6.13 Å, which is higher than the standard value (5.90 Å), which cannot be attributed to any other phases of tin and sulphur.The value of lattice parameter 'c' is determined to be 13.92 Å due to this hexagonal structure. It is found that the unit cell of this structure in the present study is elongated in c direction while comparing with the standard report of 11.80 Å. The elongated strain of 1.48×10-4 was calculated according to Basheer Ahamed et al. [22], which could be attributed to lower thermal energy deposition of this compound with relatively lower concentration solutions of SnCl4 precursor. Previous authors [23,24] also had observed strain in their SnS2 thin films prepared by SILAR and plasma – enhanced chemical vapour deposition methods respectively. From the full width at half maximum (FWHM) value of the peak obtained, the size of the tin disulphide crystallites was determined as 21.78 nm using Debye–Scherrer formula [25].

The SEM photograph with a magnification of 80k is recorded on the SnS2 thin film is shown in Fig 2.It reveals that the average size of grains is 55 nm. Agglomeration of grain is not uniform throughout the film. As a result, grains with different dimensions are seen on the surface. It was understood that several particles were not perfect sphere. In the study of particle morphology it was understood that it is diffusion drying after crust shell formation in spray pyrolysis plays an important role.

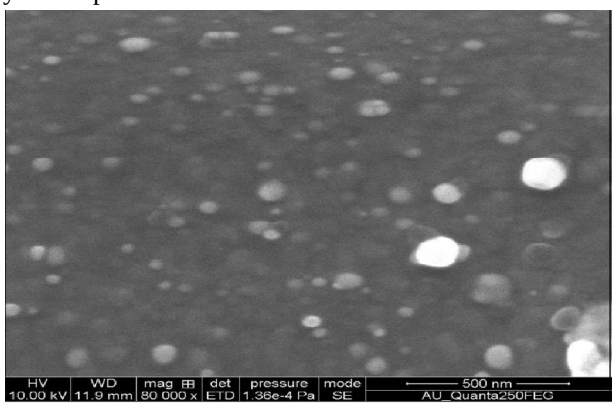

Fig 2 Scanning electron micrograph of SnS2 thin film at 498K

The crust thus formed will result into fragment particles while it reaches the hot substrate, resulting in irregular shape [26].The EDAX spectrum of the SnS2 thin film was recorded in the binding energy range 0–20 keV as shown in Fig 3. It is found that atomic tin and sulphur are present almost in stoichiometric ratio and is 38:62 percent, which is in agreement with Amalraj et.al [27]. This shows that a very little excess of tin is observed which may be due to the un reacted tin in the sample. Previous author [28] also had reported the nearly similar result of tin and of sulfur.

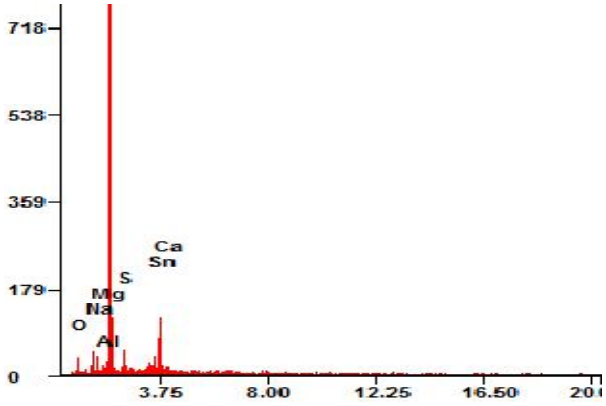

Fig 3 EDAX spectrum of the SnS2 thin film

To study the optical properties of the deposited thin film, the optical absorption spectra is recorded in the wavelength range 400–900 nm using the double beam spectrometer shown in fig 4. It shows the film has high absorption in the range of ultraviolet and the absorption coefficient reduces rapidly with the increase in the wavelength, when the wavelength is at 400- 700 nm and the absorption is very smaller becomes zero near the wavelength of nearly 800 nm. Hence the optical transmittance (T) with respect to wavelength of spray pyrolysised SnS2 thin film at 498 K, which is observed that, was a considerable transmittance of 85 % (fig 5)

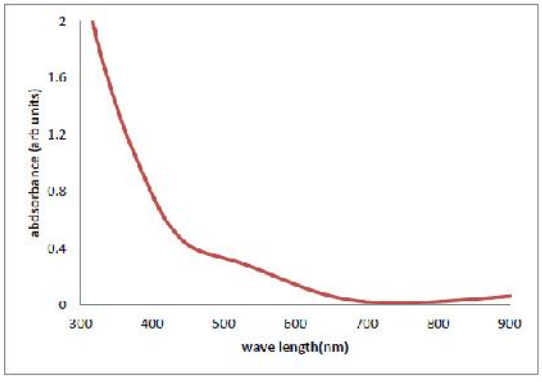

Fig 4 optical absorption spectrum of SnS2 thin film at 498K

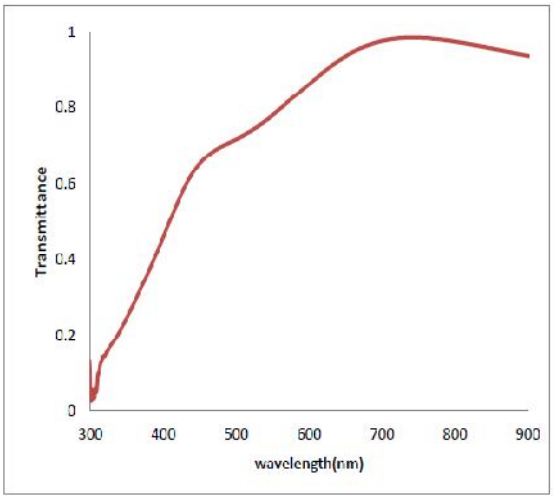

Fig 5 optical transmission spectrum of SnS2 thin film at 498K

To determine the energy band gap Eg, and the type of optical transition responsible for this intense optical absorption, and the absorption spectrum was analyzed using the equation for the near-edge absorption.

$$(\alpha h\nu)\, n = A\,(h\nu - Eg)$$

where, A is a constant and n characterizes the transition process. We can see n = 2 for direct allowed transitions.The best fit of the (αhν) 2 versus hν and its extrapolation to (αhν) 2=0 given a band gap of 2.89 eV for this thin film. Previous worker Domingo et.al [29] reported the wide optical direct band gap of tin disulfide thin film as 2.88 eV with good agreement of as deposited film.

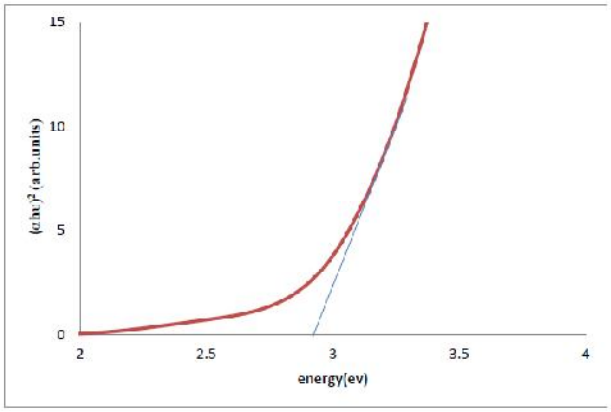

Fig 6.Direct band gap of optimized SnS2 thin film

The direct allowed band gap value have been reported by [30] (2.44 eV) and [31] (2.6 eV). In the present study, even though the above such band gap in the ultraviolet region could not be observed due to glass substrate, a higher band gap of 2.80 eV at the substrate temperature 498 K with direct transition obtained here can be attributed to the nano crystallite formation of SnS2, which is evident from XRD spectrum.

The type of conductivity of SnS2 thin film prepared in the present study show n- type electrical conductivity, which agrees well with the reported literatures [29- 31].FTIR spectrum of tin disulfide particles are prepared by nebulized spray pyrolysis technique prepared at 498K is presented in Fig. 7. It shows SnS characteristic vibration bands at 2350 cm–1 and 930 cm–1 attributed to the hydroxyl groups and SnS groups. The observed wave for a SnS2 molecule is nearly equal to the reference wave number 2350 cm-1 which stretching mode vibration is similar to the previous worker [32]. These peaks are ascribed to the stretching vibration of Sn–S bonds, indicating the formation of SnS2 film. The results of FTIR analysis are in good agreement with XRD results.

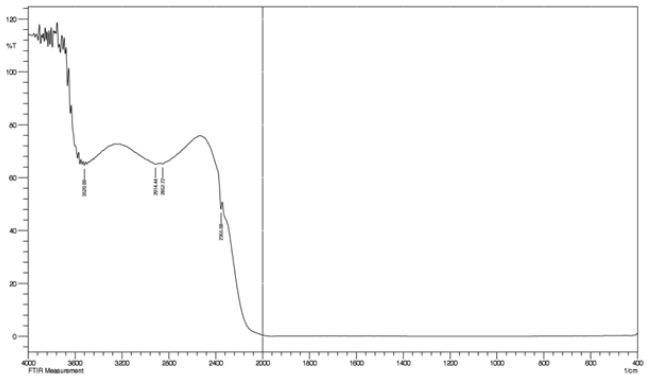

Fig 7. FTIR spectrum of tindisulfide thin film

IV. CONCLUSION

A thin film of SnS2 has been deposited by spray pyrolysis method using tin chloride and thiourea alcoholic solution at 498 K. The optical absorbance spectra have been recorded for the film in the visible wavelength range. The thin film shows direct optical allowed band gap of 2.89 eV, which agrees the reported values. From the above experimental results on the film, it can be concluded that the materials are potential candidates for thin film solar cell and photo detector devices.

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