ISSN: 0974-2115
www.jchps.com Journal of Chemical and Pharmaceutical Sciences

Structural and optical properties of spray pyrolysised tin disulphide thin film

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ABSTRACT

A thin film of tin disulphide has been prepared on glass substrate using the technique of chemical spray pyrolysis. The precursor solutions of $SnCl_2$ (0.04 M) and n-n dimethyl thiourea (0.08 M) were used to prepare the film at a substrate temperature of 398 K. The n type conductivity is found using hot probe method. The polycrystalline nature of the film with hexagonal structure (002) using X ray diffraction analysis. The surface of the film has been observed by using scanning electron microscope. A value of 2.22 x 10^{-7} mho/cm as the room temperature dark conductivity is determined using the four probe method. Activation energy of 0.47 eV is determined by arhenius plot. The absorption and transmittance spectrum have been plotted in the visible wavelength region. Direct allowed band gap value 2.78 eV and for indirect allowed 2.2 eV are observed respectively for this thin film.

KEY WORDS: tin disulphid, thin film, spray pyrolysis.

1. INTRODUCTION

Metal chalcogenides thin films have been extensively studied due to their potential application in electronic, optical and superconducting devices (Noguchi, 1994; Thangaraju, Kaliannan, 2000).The different phases of tin sulfide compounds like SnS, SnS_2, Sn_2S_3, Sn_3S_4, etc. due to the versatile coordinating characteristics of tin and sulfur (Jiang, 1998; Said, Lee,1973). 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 (Thangaraju, Kaliannan, 2000).Thin films of SnS_2 have been deposited using different techniques such as the vacuum evaporation (Noguchi, 1994), electro- deposition (Ghazali, 1998), electroless deposition chemical melt growth, chemical vapour deposition (CVD), plasma-enhanced CVD, spray pyrolysis (Jayachandran, 2001). 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. The intention, it is reporting the characterization of SnS_2 thin film using $SnCl_2$ and thiourea as a starting material by a spray pyrolysis technique.

2. EXPERIMENTAL SECTION

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 mm^2 at substrate temperature 398 K. The solution flow rate 3 ml/min, carrier gas flow rate of 0.7 kg/ cm^2 and nozzle to substrate distance of 24 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.

3. RESULT AND DISCUSSION

The X ray diffraction analysis of the film given in Fig 1.The spectra obtained in figure shows a predominant peak at the two theta position 14.60˚. The height of the peak is 369.58 counts. The d-spacing value obtained is 6.06 Å. The d-spacing value of 5.90* compared with the JCPDS data and the structure of the predominant peak of the film is hexagonal and the miller indices are (002). The lattice parameter of the film is c- value is 12.12 Å.

Sekar C. Ray (1999) also had obtained a single peak in their XRD pattern for their deposited SnS_2 thin film due to (001) plane reflection at $2\theta = 15.0^{\circ}$. The XRD pattern recorded by Thangaraju and Kaliannan (2000) for their 1μm thick SnS_2 thin film prepared by the same spray pyrolysis method with same starting material, also had a prominent Bragg peak with d-value 5.901 Å which was identified to be due to (002) plane reflection. From the XRD data, the size of the nanocrystal sample was calculated using Debye – Scherrer formula (Klug and Alexander, 1954). The particle size estimated was 5.33 nm. The SEM photograph of the film is shown in fig 2. It is found that the film becomes smoothened and also the grain size is very small.

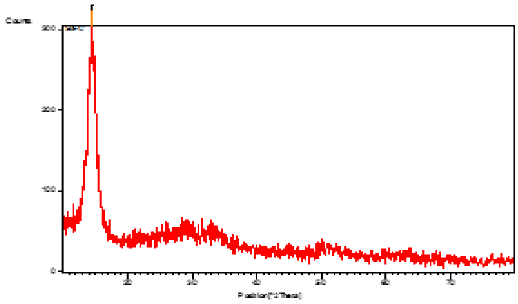

Figure.1. XRD pattern of the film prepared at 398 K

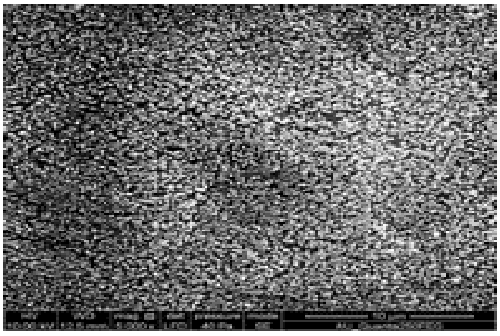

Figure.2. SEM image of SnS_2 thin film

The as prepared thin film exhibited n type semiconductor nature through the hot probe technique, which agrees well with the reported literatures (Said, Lee, 1973; Ortiz, 1996) .The DC electrical conductivity of SnS_2 single crystal reported by Domingo (1966) was that 10^{-7} mho/cm. Amalraj (2002) reported the value of room temperature DC electrical conductivity of the as prepared SnS_2 thin film is about 3.85 x 10^{-7} mho/cm. The value reported by Thangaraju and Kaliannan (2000) for their 1μm thick SnS_2 thin film was 2.5 x 10 $^{-4}$ mho/cm. This shows the semiconductor nature of the film which agrees with the present data. The activation energy of SnS_2 thin film can be calculated by the formula

$$\sigma = \sigma_0 \exp(-E_a/KT) \quad (1)$$

Where σ_0 is a pre-exponential factor and Ea is the activation energy. Both of which are determined by the best fit of the experimental data to equation(1).The arhenious plot is drawn as shown in fig 3 from which it can be predicted that the variation of conductivity of the SnS_2 film under study is being assisted by a single activation process with an activation energy of 0.47 eV.

The optical transmittance spectra of the film is shown in fig 4.The transmittance T can be expressed as

$$T = (1-R^2) \exp(-\alpha d) \quad (2)$$

Where R is the reflectivity coefficient, α is the absorption coefficient and d is the thickness of the sample. In the high photon energy region, the energy dependence of the absorption coefficient, $\alpha \geq 10^4$ cm^{-1}, suggests the occurrence of a direct optical transition .The high absorption region is investigated for the evidence of direct or Indirect allowed transitions. The direct-allowed transition depends on photon energy is given by the relation.

$$(\alpha h\nu) \propto (h\nu - E_g)^n \text{ ------------ } \quad (3)$$

Where E_g is the direct transition band gap and n = ½ for a direct-allowed transition.

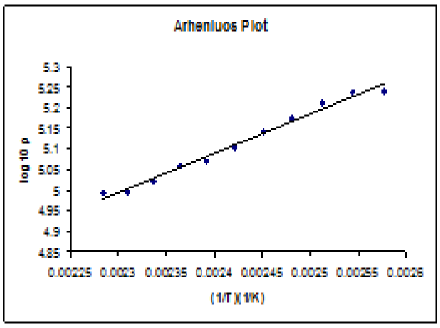

Figure.3. Variation of electrical conductivity of SnS_2 thin film

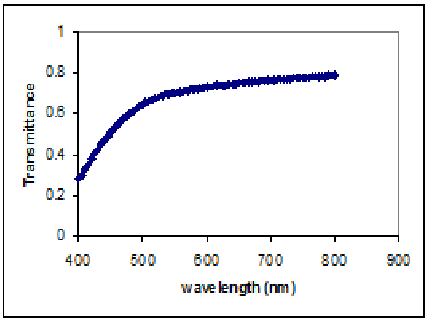

Figure.4. Transmittance of function of wavelength of SnS_2 film.

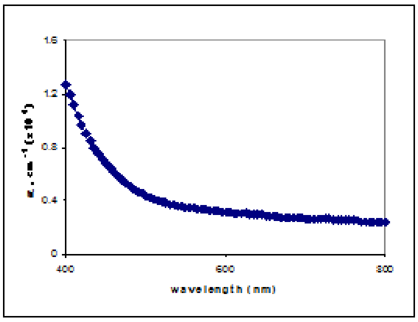

Figure.5. Absorption coefficient α versus wavelength for SnS_2 film

The band gap estimation of SnS_2 thin films achieved by plotting $(\alpha h\nu)^2$ as a function of (hν) , as shown in fig 6.The plot yields a straight line which indicates a good fit, extrapolation of the straight line to $(\alpha h\nu)^2$ = 0 gives the band gap of 2.8 eV for the substrate temperature of 398 K, which is evidence(Domingo, 1966) for direct allowed transitions. Similarly the films achieved by plotting $(\alpha h\nu)^{1/2}$ as a function of (hν) , as shown in fig.7, which gives the band gap of 2.2 eV, which is evidence (Amalraj, 2002) for indirect allowed transitions. Optical band gap measurements on SnS_2 single crystal (Greenaway and Nitsche, 1965; Said, Lee, 1973) and thin film (Ortiz, 1996; Jayachandran, 2001) have been reported by previous workers and they have observed another indirect allowed transition at 2.31 eV.

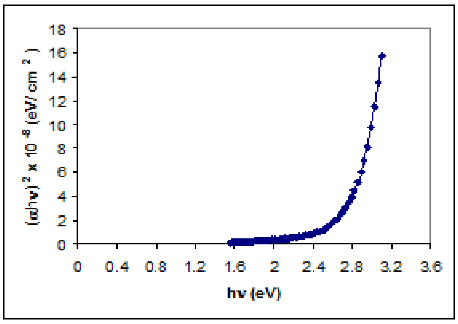

Figure.6. A typical plot of ($\alpha h\nu)^2$ against (hν) for SnS_2 thin film.

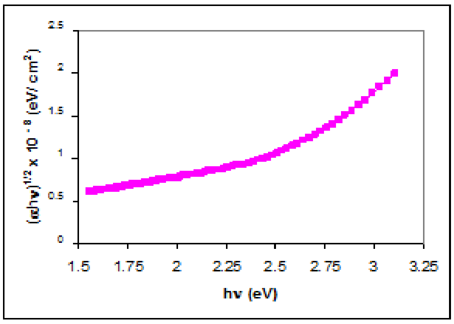

Figure.7. A typical plot of ($\alpha h\nu)^{1/2}$ against (hν) for SnS_2 thin film.

4. CONCLUSION

A thin film of SnS_2 has been deposited by spray pyrolysis method using tin chloride and thiourea alcoholic solution at 398 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 2.8 eV and indirect allowed band gap of 2.2 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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