Structural Analysis And Activation Energy of Tin Disulphide Thin Film

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Abstract--*Tin disulphide (SnS2) in thin film form was deposited on glass substrate by chemical spray pyrolysis technique using the precursor solutions of $SnCl_2.2H_2O$ and n-n dimethyl thiourea at the molar concentration 0.3 M at the substrate temperature 473 K. Using the hot probe technique the type of conductivity is found to be n type. X ray diffraction revealed the polycrystalline nature with respect to the molar concentration. The preferential orientation growth of compound having (002) plane belongs to the hexagonal crystal structure. The size of the crystallite was determined using FWHM value of the Bragg peak and found to be 5.80 nm. The surface morphological and stoichiometric analysis has been determined of as prepared thin film and the activation energy of the film was 1.125 eV.*

Keywords-thin film; band gap; activation energy;hexagonal; crystallite;

I. INTRODUCTION

Tin forms a variety of sulfides SnS, SnS_2, Sn_2S_3, Sn3S4 and numerous polysulfide anions [1]. Due to their electrical and optical properties these binary compounds have a high potential into opto- electronic devices and photo conductive cells [2, 3]. Tin disulphide (SnS_2) is considered to be one of the most useful IV-VI group semiconducting tin chalcogenides, which has found applications in opto-electronic devices, a part of solar collectors, etc., SnS_2 was first synthesized some 200 years ago [4] and it is a layered semiconductor with CdI2 type structure composed of sheets of tin atoms sandwiched between two close-packed sheets of sulphur atoms. The optical band gap values of this film vary from 0.81 to 3.38 eV [5]. The typical direct band gap is about 2.9 eV and indirect energy band gap is 2.0 eV [6]. SnS2 thin films have large optical absorption coefficient (>104 cm-1) [10], wide band gap [6], n-type electrical conduction and possession of strong photo conducting behavior [6,8-10]. These characteristics make this compound suitable for a solar collecting material in a thin film solar cell [7]. In addition, the elemental constituents of this compound are non-toxic and abundant in nature. Thin film preparation techniques have been reported in various forms. These include chemical deposition [11,12], vacuum evaporation [13,14], chemical vapour transport [15], dip deposition [8] and chemical spray pyrolysis [7]. Every technique of thin film deposition has its own merits and demerits. Owing to simplicity and inexpensiveness, the chemical spray pyrolysis is a better method at a lower cost for the preparation of thin films with a large area and also for preparing pin hole free, homogeneous thin films with the required thickness. Previous authors at studied the formation of SnS2 monophase at lower thermal energy with lower concentration of precursor solutions of $SnCl_2.2H_2O$ and n-n dimethyl thiourea. The intention of this paper is to analyze the formation of SnS_2 thin film in the same precursors with higher thermal energy with lower concentration.

II. EXPERIMENTAL DETAILS

Tin disulphide film was prepared on microscopic glass substrate at the molar concentration 0.3 M at the substrate temperature 473 K using chemical spray pyrolysis technique. The precursor solutions of $SnCl_2.2H_2O$ with 0.1M and n-n dimethyl thiourea with 0.2M were dissolved separately in a solution containing deionised water and isoprophyl alcohol in proper ratio. A few drops of concentrated hydrochloric acid were added for complete dissolution. Equal volume of these two solutions were mixed together and sprayed on to microscopic glass substrate with dimension of 75x25 mm2. The substrate was cleaned with acetone, ethanol and deionised water. Film was deposited using microprocessor based spray unit, consists of substrate heater, temperature controller, dispenser container, spray nozzle, spray head and air compressor. The spray head was allowed to move in the X-Y plane using the microcontroller stepper motor in order to achieve a uniform coating on the substrate. A temperature controller has been employed for controlling the substrate temperature with an accuracy ± 5°C. Spray head and heater with substrates were kept inside a chamber provided with an exhaust fan for removing gaseous by-products and vapours of the solvent. For the preparation of fine quality film, various parameters such as nozzle to substrate distance at 20 cm, flow rate of air with 0.7 kg/cm2, solution flow rate at 2 ml/min etc. After deposition, the film

was allowed to cool slowly to room temperature, washed with distilled water and then dried. The structural characterization of deposited film was carried out by X-ray diffraction technique on JEOL JDX 803a diffractometer with monochromatic CuKα radiation, λ=1.5406 ^{6}. The XRD pattern was recorded in 2θ interval from 10° upto 80° with the step 0.05° at room temperature. The variation of DC electrical resistivity with respect to concentration was analyzed using Arhenious plot and the activation energy of the SnS2 thin film was found out.

III. RESULT AND DISCUSSIONS

The XRD profile of the spray pyrolysised SnS2 thin film on glass substrate at 0.3 M is shown in fig 1.The corresponding XRD pattern exhibits a single prominent peak at 2θ position of 14.32°.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. 89 –3198 [16]. The interplanar spacing of this peak is determined to be 6.17 Å due to this hexagonal structure which is higher than the standard value 5.90 Å which cannot be attributed to the any other phases tin and sulphur. 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 similar elongated strain was calculated according to the previous author [17]. Previous authors [18,19] had reported strain in SnS2 thin films prepared by SILAR and plasma enhanced chemical vapour deposition methods respectively.
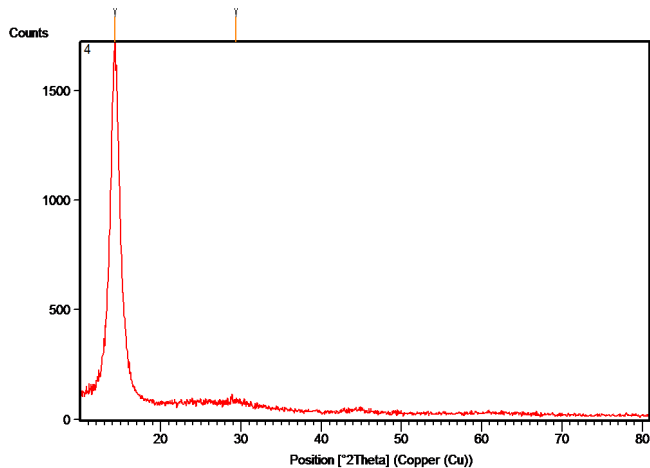

Fig 1: XRD Pattern of thin film at concentration 0.3 M

From the XRD data, the crystallite size of the compound formed as a thin film by chemical spray technique corresponding to the prominent peak was calculated. If the wavelength of X-ray (λ), Full width half maximum (β) and (θ) values are known, then crystallite size of the compound was found to be 5.80 nm using Debye–Scherrer formula [20],

strain 5.971x 10-3 m and dislocation density 2.9671 x 1016 nm-2 spray pyrolysis SnS2 thin film corresponding to the crystallite grown in (0 0 2) direction.

The SEM Photograph was taken with a magnification no of 5000 x for the chemical spray pyrolysis SnS2 thin film deposited with a concentration 0.3 M. The average crystallite size is found to be 0.25 μm in 0.3M sample. The picture shows needle shaped formation of different crystallites. This may be attributed to the greater number of secondary electrons being emitted from the surfaces of the sample when the electron beam is focused on a smaller area to get higher magnification.
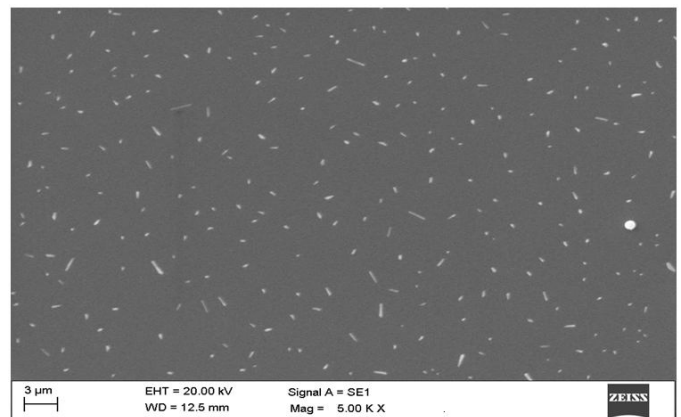

Fig: 2 SEM image of SnS2 thin film at 0.3M

The EDAX spectrum of the SnS2 film was recorded in the binding energy region of 0 -14 keV as shown in fig 3. It is found that tin and sulfur are present this thin film and is observed as tin 58.48% & sulfur 41.52 % respectively, which is in agreement with previous author [7]. This shows that a very little excess of tin is observed which may be due to the unreacted tin in the sample.
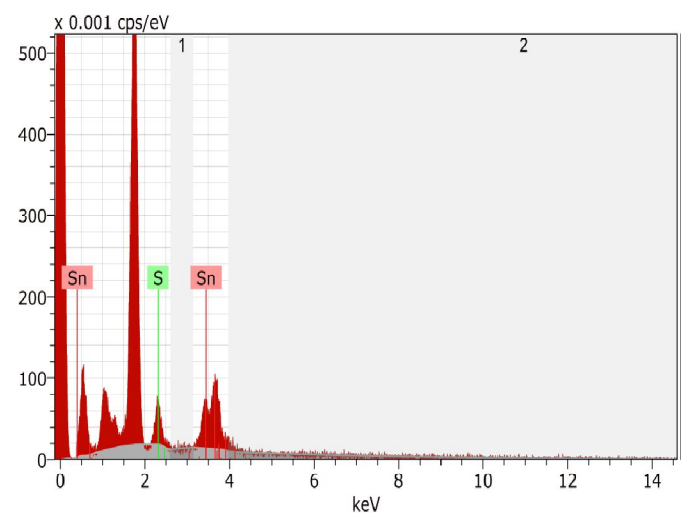

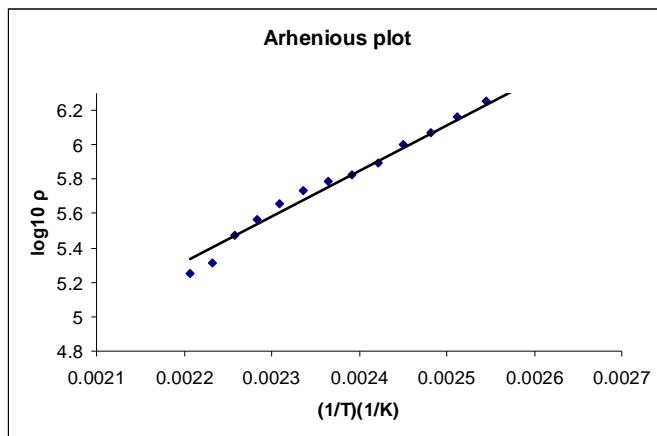Fig 3 EDAX Spectrum of SnS2 thin film at 0.3M

Fig 4 Arhenious plot of tin disulphide thin film

The variation of resistivity of the as prepared film with respect to temperature was determined. A decrease in the resistivity is found as the temperature of the sample is increased which predicts the n – type semiconductor nature of the SnS2 thin film deposited in the present study. The activation energy of the thin film can be calculated by the formula

$$\rho = \rho_o \exp Ea / KT$$

where ρ_o is pre-exponential factor and Ea is the activation energy. Both of which are determined by the best fit of the experimental data to the above equation. The Arhenious plot is drawn with the experimental data as shown in fig 4 at the molar concentration 0.3 M, which it can be predicted that the variation of resistivity of this SnS_2 thin film is being assisted by a single activation process which is determined by the best fit of the experimental data to the equation. The activation energy of the SnS_2 thin film for the molar concentration 0.3 M is obtained as 1.125 eV. Previous authors [7, 21] also had reported the same the activation energy of tin disulphide thin film at ambient temperature at the substrate temperature 458 K for the SnS_2 thin film prepared by the same method $SnCl_4.5H_2O$ as one of the precursors.

IV. CONCLUSION

The golden yellow colored thin film of tin disulphide was deposited onto glass substrate at the molar concentration 0.3M. X ray diffraction analysis, surface morphological , stoichiometric and activation energy of this film were determined. From the above experimental results, it can be inferred that SnS2 thin film with nano crystallites can be deposited with spray pyrolysis method using the precursors which could be a potential candidate for opto electronic thin film devices.

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