FINAL REPORT

MINOR RESEARCH PROJECT

Financial Assistance No. 47-272/12(WRO) dated 25 FEB 2013

(UGC XI Plan)

"Preparation and Characterization of nano crystalline Tin Sulfide thin films by Spray Pyrolysis Technique"

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C O N T E N T S

DECLARATION AND CERTIFICATE

I hereby declare and certify that, the Minor Research Project entitled "Preparation and Characterization of nano crystalline Tin Sulfide thin films by Spray Pyrolysis Technique" Financial assistance No. 47-272/12(WRO) dated 25 FEB 2013 is a bonafide record of research work carried out by me during the year 2013- 2015. Further certify that the work presented in the report is original and carried out according to the plan in the proposal and guidelines of the University Grants Commission.

Date: **Principal Investigator**

Place: Peth Vadgaon

Forwarded through the Principal:

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Place: Peth Vadgaon

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Preparation and Characterization of nano crystalline Tin Sulfide thin films by Spray Pyrolysis Technique

1. Introduction:

World energy demand and CO_2 emissions will both increase by about 70% between 2000 and 2030 (1). Fossil fuels supplying 80 of all energy consumed worldwide are facing rapid resource depletion (2).The resource reserves of fossil fuels in the whole world in 2002 were projected in last 40 years for oil, 60 years for natural gas and 200 years for coal. Because of a growing demand for energy, combined with depletion of fossil resources, global warming and its associated climate change there is an urgent need for environmentally sustainable energy technologies. Renewable energy technologies which include photovoltaic, solar, thermal, wind turbines, hydropower wave and tidal power, biomass-derived liquid fuels and biomass fired electricity generation supply to dale only 14% of all energy consumed worldwide.

Advanced energy conversion and storage (ECS) devices (including fuel cells, photo electrochemical water splitting cells, solar cells, Li-ion batteries and super capacitors) are expected to play a major role in the development of sustainable technologies that alleviate the energy and environmental challenges we are currently facing. The successful utilization of ECS devices depends critically on synthesizing new nano materials with merits of low cost, high efficiency, and outstanding properties. Recent progress has demonstrated that nanostructure metal chalcogenides (MCs) are very promising candidates for efficient ECS systems based on their unique physical and chemical properties, such as conductivity, mechanical and thermal stability and cyclability(3).

In recent years metal chalcogenide thin layers have a number of applications in various fields of modern technologies, including coatings, interference filters, sensor, polarizer, thermoelectric cooling materials[4,5], narrow band filters, solar cells, photoconductors, IR detectors, waveguide coatings, magnetic and superconducting films, microelectronic devices and etc. [6]. Among many semiconducting metal chalcogenides,

tin sulfides have attracted extensive interest due to its photoconductivity properties for solar energy conversion due to report of high absorption coefficient [7]. SnS thin films have large optical absorption coefficient (>104 cm–1) and high photoelectric conversion efficiency (>24%) (8) for the fabrication of heterojunction solar cells. Tin sulphide belongs to groups IV–VI of compounds formed with tin as the cation and S as the anion. The constituent elements are nontoxic, cheap and abundant in nature leading to the development of devices that are environmentally safe and have public acceptability. SnS crystallizes in zinc blend with the lattice constant (a =0.5845 nm), orthorhombic with the lattice constants (a =0.385 nm, b =1.142 nm and c =0.438 nm), and herzenbergite crystal structure.

SnS is a very important optical semiconductor, which can exhibit both p-and n-type conduction depending on the mole concentration of tin and sulfur. SnS thin film has an energy band gap of about 1.3 eV between Si and GaAs and has potential applications in current controlled devices, sensor and laser devices, switching devices and photovoltaic devices (9). SnS films are highly suitable for many applications in a number of solid state devices, such as photovoltaic (10–13), photo electrochemical (PEC) (15), photoconductive cells (16), and intercalation battery systems (17). Like SnS, SnS_2 is also a semiconductor, with a larger band gap of 2.2–2.6 eV. The electronic nature and excellent structural properties of SnS_2 make it a possible candidate for use as the aperture in window-absorber solar cells, quantum well structures and the substrate for deposition of organic layers. (17-19).

1.1 Thin Film Deposition Techniques

The properties of a thin film essentially depend on the method of preparation. Several techniques have been developed for deposition of the desired thin films (20). The basic steps involved in the thin film formation are,

a) Production of materials to be deposited in atomic, molecular or ionic form.

b) Transport of materials thus created.

c) Deposition of film by nucleation and growth process.

Each technique has its own advantages and disadvantages. Therefore every time a new method is developed by overcoming disadvantages of previous methods. Thin film deposition techniques have been classified into two types,

Chemical deposition methods	**Physical deposition methods**
1. Spray pyrolysis	1. Thermal evaporation
2. Screen printing	2. Electron beam evaporation
3. Anodization	3. Activated reactive evaporation
4. Electrodeposition	4. Molecular beam epitaxy
5. Chemical vapour deposition	5. Sputtering
6. Chemical bath deposition	

1.1.1 Spray Pyrolysis Technique:

Spray Pyrolysis Technique is a potential deposition technique being used in research and industry to prepare thin and thick films of ceramic materials and powders. Unlike many other film deposition techniques, this technique is a very simple and cost-effective processing method (especially with regard to equipment and energy requirement) for depositing thin films over very large area. It offers an extremely easy way for preparing films of desired composition and stoichiometry. The method has been employed for the deposition of dense films, porous films, and for powder production. Even multilayered films can be easily prepared using this versatile technique. Spray pyrolysis has been used for several decades in the glass industry (21) and in solar cell production (22). Typical spray pyrolysis equipment consists of an atomizer, precursor solution, substrate heater, spray rate controller and temperature controller. A schematic of a typical spray pyrolysis unit set-up is as shown in Figure 1. The following atomizers are

usually used in spray pyrolysis technique: air blast (the liquid is exposed to a stream of air) (23), ultrasonic (ultrasonic frequencies produce the short wavelengths necessary for fine atomization. (24) and electrostatic (the liquid is exposed to a high electric field. (25)

Thin film deposition, using the spray pyrolysis technique involves spraying metal salt solution(s) onto a heated substrate. Droplets impact on the substrate surface, spread into a disk shaped structure and undergo thermal decomposition. Shape and size of the disk depends on the momentum and volume of the droplet, as well as the substrate temperature. Consequently, the film is usually composed of overlapping disks of metal salt whose film is required on the heated substrate.

Spray pyrolysis involves many processes occurring either simultaneously or sequentially. The most important of these are aerosol generation and transport, solvent evaporation, droplet impact with consecutive spreading and precursor decomposition. Deposition temperature is involved in all mentioned processes except in the aerosol generation. Consequently, the substrate surface temperature is the main parameter that determines the film morphology and properties. By increasing the temperature the film morphology can change from a cracked to a porous microstructure. In many studies, the deposition temperature was reported as the most important one in spray pyrolysis. Properties of deposited films can be varied and/or controlled by changing the deposition temperature.

2. Review of the Relevant Literature:

Ho Soonmin (26) prepared tin sulfide thin films using stannous chloride and sodium thiosulphate as precursor in presence of Ethylenediaminetetraacetic acid disodium salt-2-hydrate as complexing agent by the chemical bath deposition process at various pH and time The structure and morphology studied with the help of XRD and SEM. The film at pH 12 and time 3 hrs,have more thickness.

Santosh Kumar (27) deposited tin sulphide by spray pyrolysis using Stannous chloride and thiourea as as precursor solution. Polycrystalline nature of SnS film with orthorhombic crystal structure was investigated with XRD analysis.

M. R. Fadavieslam (28) studied effecct of deposition parameters on structural, optical, thermoelectrical and photoconductivity properties of tin sulphide deposited on glass substrate by spray pyrolysis method. Amorphous and polycrystalline structures observed for different parameters. The optical band gap was determined about 2.41-3.08 eV.

J.I. Onwuemeka (29) deposited tin sulphide by the chemical bath deposition process on glass substrate at room temperature for 3hrs. and 1hr. Optical properties characterised by double beam spectrophotometer showed band gap 1.98-2.01 eV for 3hrs.and 1.82-1.98 eV for 1 hr. deposition. EDXRF and Rutherford Back Scattering (RBC) showed thickness are 100nm for 3hrs. and 150nm for 1hr.

S. Polivtseva (30) grown tin sulphide film by spray pyrolysis technique using stannous chloride and thiourea as precursor in the ratio 1:1, 1:2, 1:4, 1:8 at temperture interval 200-410^{0}c in air. The structural, morphological and optical properties of tin sulphide was studied by XRD, SEM, EDAX and UV-VIS spectroscopy. More thickness and low band gap observed for thin film at molar ratio of Sn:S = 1:4 and 1:8.

B.G. Jeyaprakash (31) prepared tin sulfide thin films The optical band gap was 1.60eV.by spray pyrolysis techniques. Manifestation of nano SnS crystal was revealed by x-ray diffraction and scanning electron micro graph. VIS-NIR specor trophotometric showed the band gap lying in the range 1.30-1.40 eV.

C. Khelia (32) were grown crystals of β-SnS_2 by the spray pyrolysis technique using tin chloride and thiourea precursors at temperature 280^{0}C. The crystal characterization were carried out by means of scanning electron microscope, atomic force microscope and X-ray diffraction measurements.

M.O. Abou-Helal (33) have been prepared thin films of tin sulfide (SnS_2) by the spray pyrolysis technique with the substrate temperature in the range of 300 - 400^{0}C in ambient atmosphere. X-ray diffraction measurements of polycrystalline tin sulfide (SnS_2) showed optical band gaps vary from 1.0 – 1.25 eV.

K.T. Ramkrushna Reddy (34) have been deposited thin film of tin sulfide using spray pyrolysis technique. The film formed between the temperature 300^{0}C and 360^{0}C

were polycrystalline, single phase and stiochiometric. These were p-type with an electrical resistivity of 30Ω and a net carrier concentration of $1.2 \times 10^{15} cm^{-3}$. These layers has a direct band gap of 1.32eV.

L. Amalraj (35) prepared tin disulfide by spray pyrolysis technique. X-ray diffraction analysis revealed the polycrystalline nature of the film with the hexagonal structure. The surface composition of the elements is analyzed with EDAX spectrum. The optical absorption and transmittance spectra have been recorded for this film in the wavelength range 380- 900nm. SnS_2 film shows band gap values of 2.17eV with indirect allowed and 1.82eV with indirect forbidden nature.

Robert W. Miles (36) has been thermally evaporated thin film of tin sulfide. For this film the film composition determined by energy dispersive X- ray analysis, phases are determined by X-ray diffraction, energy band gap is determined by transmittance and reflectance versus wavelength measurements, surface topology and topography is observed by scanning electron microscopy. Energy band gaps in the range 1.55- 1.7 eV were obtained for a film thickness of 0.8 micro meters.

3.Objectives

I propose to undertake extensive experimental work and related characterization studies on Spray deposited SnS thin films.

1. These thin films will be deposited by spray pyrolysis method.
2. Determine the thickness of the thin film.
3. Structural and Morphological study by XRD & SEM.
4. I-V characteristics study.

   After characterization of these thin films, optimized thin film will be used for testing solar cell by PEC.

4. Experimental Details:

4.1 Synthesis of Tin Sulphide:

Tin sulphide thin films were deposited on FTO and commercial glass substrate (75mm X 25 mm, thickness 1.35mm) by pneumatic chemical spray pyrolysis technique.

The glass substrates were cleaned by labolene at first and then by ultrasonic cleaning in ethanol followed by rinsing in distilled water. 2.256 gm of dihydrated stannous chloride (loba chemie, *India*) is dissolved in minimum quantity of concentrated hydrochloric acid and diluted to 100 ml. by double distilled water to form 0.1 M SnCl2. $2H_2O$ solution. 0.76 gm of thiourea is dissolved in double distilled water diluted to 100 ml. to form 0.1 M sodium thiosulphate solution. These two aqueous solutions were mixed together keeping the ratio [S] /[Sn] = 3 and pH = 2. This solution was sprayed on the substrates heated at 250 and 300^0c.

The ratio [S]/[Sn] is very crucial because if it is not well adjusted we get mostly SnO_2 instead of SnS_2 especially when the experiment is done in air with spray pyrolysis technique (37). The deposition parameters such as solution flow rate, nozzle to substrate distance and carrier gas flow rate were kept constant 8 ml/min., 25cm and 8 lit/min. respectively. The solution was stored in a volumetric reservoir at room temperature and connected to one side of the spray nozzle. The carrier gas, air was allowed to flow (8 lit./min.) through the pressure monitoring gauge, connected to other side of spray nozzle. The spray nozzle was moved in the x-y plane using the microprocessor controlled stepper motor system in order to achieve a uniform film coating. A resistive heater system is employed to alter the temperature of the substrate. The films prepared at substrate temperature 250^0C & 350^0C were highly adherent to the substrates and deep brown in colour.

4.2 Characterization Techniques

4.2.1 X-ray Diffraction studies (XRD):

Laue noted in 1912 that a scattered X-rays were believed to have wavelengths of the order of 10^{-8} cm, which is similar to interplanar distance of a crystal. Therefore the crystals could serve as grating for the diffraction of X-rays. X-ray diffraction also provides a convenient and practical means for the qualitative identification of crystalline compound (38).

A beam of X-ray incident on a plane at an angle 'θ' will be reflected making the same angle with the plane. The reflection is caused by the interaction of the electromagnetic radiation with the electron of the atoms at the lattice points. In order that the reflection is sufficiently intense, reflection from successive planes separated by the distance 'd' should be superimposed. This would require the path difference of the parallel beams from the source to the detector via the respective reflecting planes to be equal to an integral multiple of the wavelength of the radiation. The path difference due to two successive parallel planes 'd' is 2d sinθ. Hence,

$$n\lambda = 2d \sin\theta \qquad \text{----------1}$$

Where, n is a positive integer, λ is the wavelength of the X-rays used. This is Bragg's law of diffraction. By measuring the diffraction angle 'θ', it is possible to determine the corresponding interplanar distance 'd' [39]. In diffractrometer, a moving X-ray detector records the 2θ angle at which the beam is diffracted giving a characteristic diffraction pattern. This diffraction pattern acts as "fingerprint" of the material. This method is used for structure determination, determination of orientation, particle size, stress/strain determination, etc.

1) Phase Identification

Every crystalline substance has its own characteristic diffraction pattern which may be used for its identification. Standard patterns are given in the Powder Diffraction File (known as the JCPDS File or the ASTM File). Substances are indexed by any one of the two files. Mixture of substances may be identified provided that the component phases are available for comparison. The amount of a particular crystalline phase in a mixture may be determined by quantitative X-ray powder diffraction. It is a necessary to add internal standard which is a well-crystallized phase such as α-Al_2O_3. A line in the pattern of the phase of interest is selected and its intensity is compared with that of standard line (40).

2) Determination of accurate unit cell parameters

The position of the line in a pattern is governed by the value of the unit cell parameters. Unit cell parameters are used to deduce the shape and size of the unit cell.

Unit cell lattice parameters are normally determined by single crystal method. But accurate cell parameters may be obtained from powder pattern, provided Miller indices (hkl) and their positions have been accurately measured. Now a day several computer programs are available for determination of unit cell. Accurate unit cell parameters are particularly useful for measuring thermal expansion for studying the effects of composition on cell parameters, as well as for enabling complex powder patterns to be indexed.

3) Structure of Solids

The identification of the species from powder diffraction pattern is based upon the position of the lines and their relative intensities. The diffraction angle 2θ is determined by the spacing between a particular set of planes; with the help of the Bragg equation and the distance 'd' is calculated by known wavelength of source and the measured angle. XRD provides the data used for determination of crystal structure. The various types of crystal structure such as cubic, tetragonal, hexagonal, monoclinic etc. are easily interpreted.

4) Particle size measurement

Particle size measurement has a large range of useful applications. X-ray powder diffraction may be used to measure the average crystal size in a powdered sample, provided the average diameter is less than 2000 Å. The lines in a powder diffraction pattern are of finite breadth but if the particles are very small, the lines are broader than usual. The broadening increases with decreasing particle size. The crystallite size is determined by using full width at half maximum (FWHM). The average crystallite size is determined by Scherrer's formula

$$D = K\lambda / \beta\cos\theta \qquad \text{----------2}$$

Where, β is the broadening of diffraction line measured at FWHM in radians and D is particle size. λ is the wavelength of X-ray used. K is the constant related to the shape of the crystallites. It varies from 0.9 to 1.3. It is best approximated to a value of 0.9, when little is known about crystallite and shape. The FWHM become noticeable when D is near 1000 Å and become appreciable near 200 Å. If all the lines are broadened uniformly,

the crystals are more or less equidimensional in all directions. Any plane or planes, with smaller broadening denote an extension of the crystal is in the direction normal to the plane.

5) Intensity Studies

Intensity of X-ray reflections is important for two main reasons. Firstly, quantitative measurement of intensity is necessary to determine unknown crystal structure. Secondly, qualitative or semi quantitative intensity data is needed in using the powder diffraction method to characterize materials and especially in using the powder diffraction file to identify unknowns. Intensities depend on several factors such as polarization factor, structure factor, Lorentz factor, multiplicity, temperature factor, absorption factor, preferred orientation, excitation, etc.

4.2.2 Scanning Electron Microscopy (SEM):

SEM providing valuable information on particle size and shape of thin film materials under high magnification. The result obtained from optical microscopy provides information on submicrometer-sized particle, because of the depth of focus of SEM instruments. The resulting photographs have a definite three dimensional quality. Also the high resolution electron microscopy is capable of giving information on atomic scale by direct lattice imagining. The resolution of ~ 2Å has been achieved.

Electron microscope are of either transmission or reflection design. For studying transmission, the samples must be thinner than ~ 2000Å. This is because electrons interact with matter and are completely absorbed by thick particles. The scanning voltage is of the order of 1 Mega volt. When thicker sample is used, the beam is more penetrating as well as the amount of background scatter is reduced and higher resolution may be obtained.

The main reflection instrument is the SEM. It covers the magnification range between (~1μm) and upper practical working limit of transmission electron microscopy (~ 0.1μm), although SEM can be used to study structure over a much wider range, from 10^{-2} to 10^{2} μm.

In SEM, electrons from the electron gun are focused to a small spot, (50 to 100 Å in diameter) on the surface of the sample. The electron beam is scanned over the sample. Both X-ray and secondary electrons emitted by the sample are used to build up an image of the sample surface and is displayed on a screen. A limitation with SEM instruments is in its lower limit resolution. The average grain size was obtained by using Contrell's method. This method relates the number of intercepts of grain boundary per unit length 'P_L' and is given by;

$$P_L = (n/2\pi r)\, M \qquad \text{----------3.}$$

Where, n is the total number of intercepts, r is the radius of curvature, M is the magnification used. Using P_L, the grain size 'L' was determined by using the following relation;

$$L = [1/(P_L)^{1/2}] \qquad \text{----------4.}$$

5. RESULTS AND DISCUSSION

5.1 X Ray Diffraction Study:

The X ray diffraction graph for thin films of tin sulfide deposited by spray pyrolysis technique at substrate temperature 250^0C & 350^0C are as shown in fig.2 The films were found to be granular with orthorhombic structure and matches well with the standard patterns. The peaks are observed at $2\theta = 28.759^0$ (021), 31.906^0 (400) plane of orthorhombic phases of SnS. The peaks from the XRD patterns were indexed by using standard card of orthorhombic SnS (JCPDS card no. 331375, 010984,752115).

5.2 Scanning Electron Microscopy:

The surface morphology of SnS thin films deposited by spray pyrolysis technique at temperature 250^0C & 350^0C are shown in figure 3. Surface morphological studies of the SnS thin films have been carried out using Scanning Electron Microscopy. The SnS

films have a granular morphology with good surface coverage the grain size at temperature 350^0C is 55nm and at temperature 250^0C is 40nm. As temperature increases, the grain size increases which is superior material for solar cell efficiency.

The thickness of the SnS film was calculated using a weight-difference method, i.e. the relation t = m/(ρ-A) where, m is the mass of the film deposited on the substrate in g, 'A' the surface area of the film in cm^2 and 'ρ' is the density of deposited material. The thickness of the SnS film was 630 nm at substrate temperature 250^0c and 710 nm at substrate temperature 350^0c.

5.3 Photo electrochemical characterization:

To study the charge transfer mechanism occurring across the semiconductor electrolyte interface, the electrical characterization of the PEC cell was tested. I-V, characteristics in dark, measurement of built-in-potential and power output characteristics under illumination were studied. A wire wound potentiometer was used to vary the voltage across the junction and current flowing through the junction was measured with a current meter. Photo electrochemical activities were studied under 30 mW/cm^2 light illumination. The illumination intensity was measured with Meco Lux meter.

Current-Voltage (I-V) characteristics of the PEC cell n-SnS / 0.1M H_2SO_4 / C have been studied at 303 K. The dark voltage and dark current were found to develop. The polarity of this dark voltage was negative towards the semiconductor electrode. The dark voltage is developed due to difference between the two half cell potential of a cell [23];

$$E = E_{SnS} - E_{carbon} \qquad \text{----------5}$$

Where, E_{SnS} ,E_{carbon} are the half cell potential of photoelectrode and counter electrode respectively. Half cell potential is developed when the electrode is directly in contact with the electrolyte. But,

$$E_{SnS} > E_{carbon} \qquad \text{----------6}$$

After illumination of the junction, the magnitude of voltage varies with change in polarity towards the thin film. The sign of this photovoltage gives the conductivity type

of SnS photoelectrode. This indicates that SnS is a n- & p-type conductor. The current-voltage characteristics are shown in Fig. 5.

The photovoltaic power output characteristics of SnS thin films are recorded under 30mW/cm^2 illumination intensity. The calculations show that the fill factor is 49.97% and conversion efficiency is 6.24% for SnS thin films.

6. CONCLUSION

In conclusion nanocrysraline tin sulphide thin films have been deposited on glass substrate and FTO by simple spray pyrolysis technique. The scanning electron microscopy investigates SnS films have granular morphology and tightly bonded well formed dense network without pin hole. These grains are oriented uniformly with nearly equal size. As temperature increases, the grain size increases which is superior material for solar cell efficiency. Thickness of film increases as the substrate temperature increases. The X-ray diffraction study shows that SnS films with orthorhombic structure and crystalinity increases with increase in temperature. The tin sulphide thin films deposited on FTO shows the fill factor is 49.97% and conversion efficiency is 6.24%.

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8. FIGURES

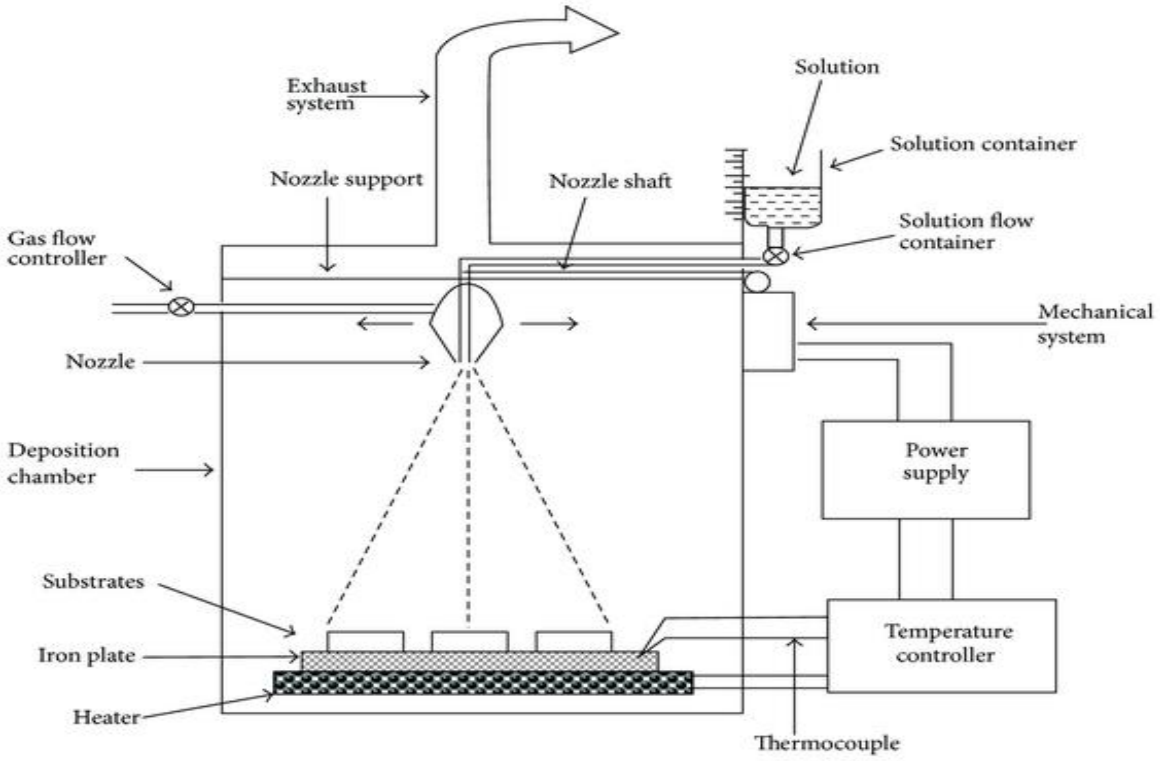

Fig.1 Spray Pyrolysis Unit

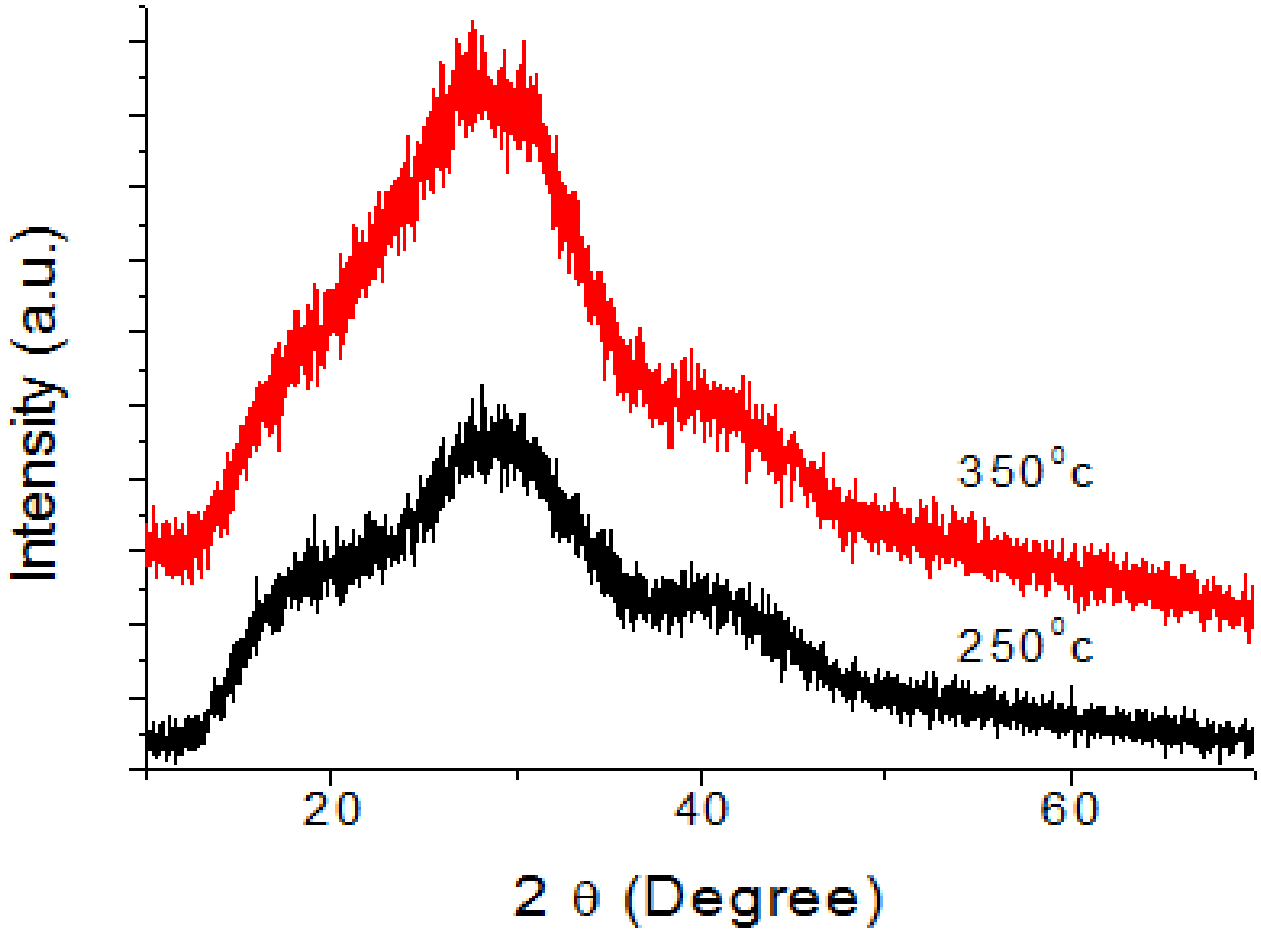

Fig. 2 XRD Pattern of SnS deposited by Spray Pyrolysis Technique

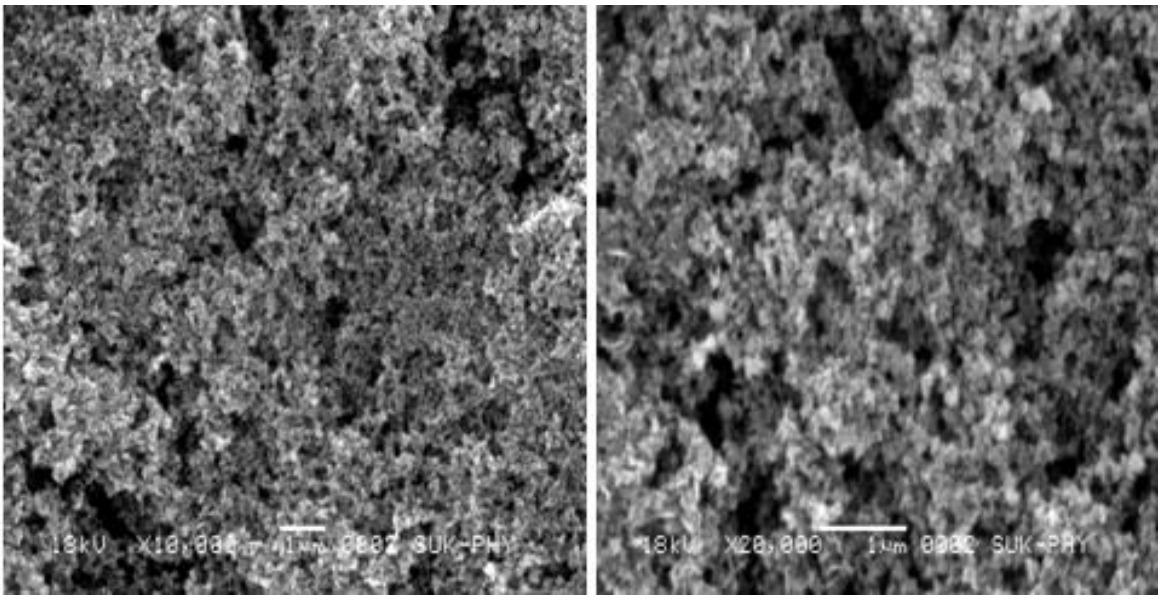

Fig.3 SEM images of SnS deposited by spray pyrolysis at 250^0c.

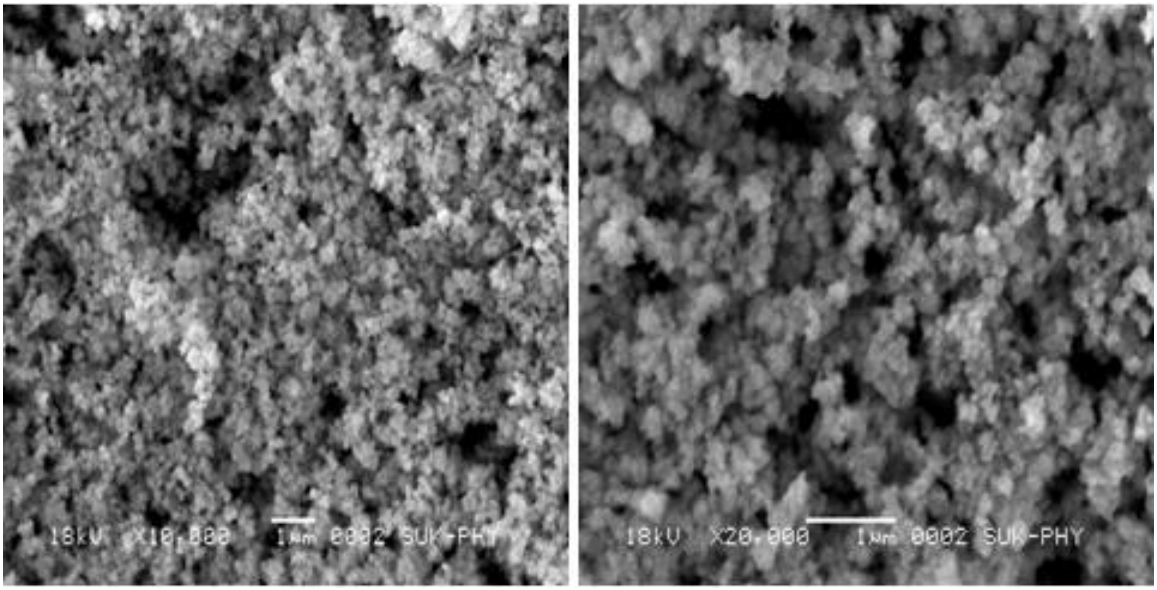

Fig.4 SEM images of SnS deposited by spray pyrolysis at 350^0c.

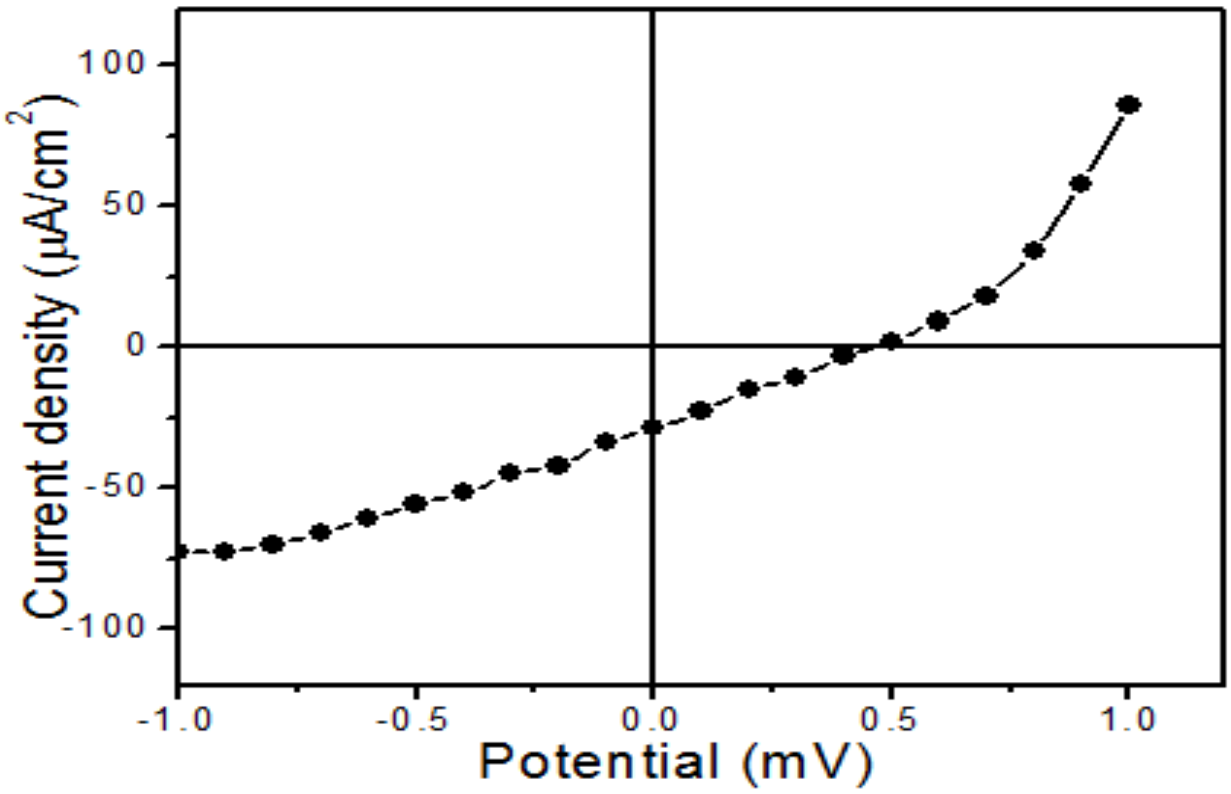

Fig. 5 I-V characteristic of SnS thin film in 0.1M H_2SO_4 at room temperature