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CHARACTERIZATION OF MICROWAVE ASSISTED CHEMICALLY DEPOSITED SnS THIN FILM

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Tin sulfide thin films were prepared on glass substrate by microwave assisted chemical solution deposition technique. The deposition was carried out in the range of microwave power output from 160 to 720 watts. X-ray diffraction pattern, surface micrograph and visible - near infra red spectra of the film has been analyzed and reported in this paper.

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1. Introduction

In recent years metal chalcogenides are used as sensor, polarizers and thermoelectric cooling materials [1,2]. Among many semiconducting metal chalcogenides, tin sulfides have attracted extensive interest due to its photoconductivity properties for solar energy conversion. Tin sulfide exists in variety of phases such as SnS, Sn_2S_3, Sn_3S_4 and SnS_2 due to bonding characteristics of tin and sulfur [3]. Also it has both p and n-type conduction with a direct band gap of 1.3eV and an indirect bandgap of 1.0eV [4, 5]. Several methods such as Electrodeposition [6], SILAR [7], Spray pyrolysis [8, 9] and Co-evaporation [10] have been studied for preparing tin sulfide thin film. For the past few years thin film nanomaterials based devices are fabricated due to its unique physical and chemical property which differs from its bulk and enhancing device performance. There are numerous methods of preparing thin film nanomaterials. These methods can be broadly classified into Vapour deposition and Solution deposition method. Each method has its own characteristics merits and demerits in producing homogeneous and defect free thin film nanomaterials. For which new preparation methods are being evolved to produce controlled size and shape of desired morphology. Recently the use of microwave in solution method has been introduced as an efficient tool for preparing high purity, controlled size and shape to yield nanomaterials [11, 12]. Further this method does not require vacuum condition and hence leads to cost effective method than vapour deposition where it is necessary one. The basis of microwave is that it provides homogenous heating on the precursor materials which leads more rapid and simultaneous nucleation to form nanomaterials than the conventional heating method. In the present work the effect of microwave output power towards the x-ray diffraction, optical energy band gap and surface morphology of the films on glass substrate was studied.

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2. Experimental

All the reagents used in the work are of analytical grade without further purification. To prepare tin sulfide thin film a precursor solution is prepared by dissolving the salts of Stannous Chloride ($SnCl_2.2H_2O$) of 0.01M and Thiourea ($CS(NH_2)_2$) of 0.01M in Ethylene glycol of 15ml. Few drops (~0.5ml) of concentrated HCl is added to get clear solution. Finally 35ml of deionised water is added to the above solution. The as prepared solution is stirred at room temperature for about 15 min under constant stirring of about 600 rpm using magnetic stirrer and transferred into the specially designed glass vessel with refluxing unit to be placed in the slightly modified domestic microwave oven shown in figure (1). The unit is operating at a frequency of 2.45GHz and maximum power output of 800W with nine power level control facility from 80 to 800W in step of 10% from the minimum level.

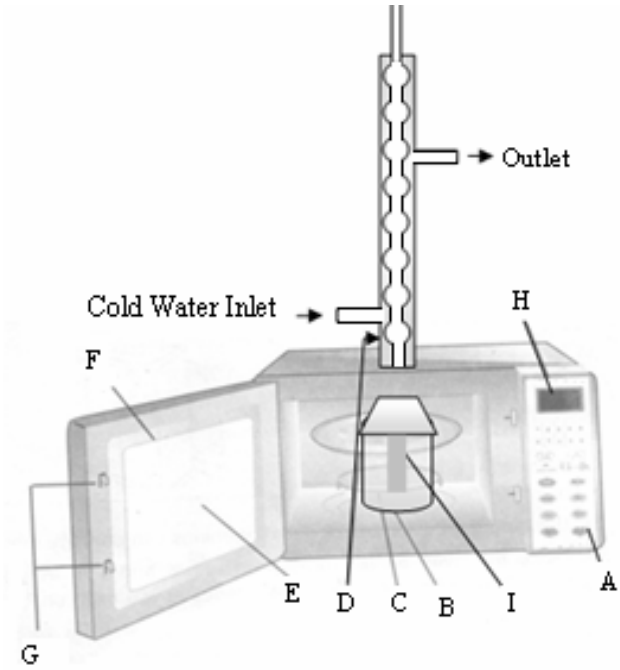


Fig – 1. Modified domestic microwave oven for preparation of SnS thin film

A) Power and time Control Panel
B) Thick walled glass beaker
C) Magnetic stirrer assembly
D) Refluxing condenser unit
E) Observations window
F) Door assembly
G) Safety interlock system
H) Display Unit
I) Substrate

To form thin film, glass substrate is first boiled in chromic acid of 0.1M at 80°C for one hour. It is then rinsed with deionised water for several times and kept in nitric acid for 2 days in a closed beaker and then rinsed several times with deionised water. This process of cleaning the substrate is to create nucleation site on the glass substrate [13] where the growth of thin film begins. This freshly activated glass substrate is immersed vertically in the above precursor solution kept in the microwave unit. Initially the power level is set at 80W (10% of max. power level) and irradiated to one minute without stirring. Then power level is fixed at 160W (20% of max. power level) and irradiated to 5 minutes with vigorous stirring. After about 15 minutes, the substrate is removed and cleaned with deionised water for further characterization. The initial irradiation at low power level is to warm up the substrate for better adhesiveness. Similarly samples were prepared at 400W and 720W power level without changing other parameters.

X-ray diffraction (XRD) studies were carried out using PANalytical X-ray diffractometer (Model X'per PRO). Ni-filtered CuKα radiation (λ = 1.5148Å) was employed with generator setting of 30mA and 40kV. Continuous scanning was applied with a scanning speed of 10°/min. A range of 2θ from 20° to 80° was scanned from a fixed slit type, so that all possible diffraction peaks could be detected. X-ray line broadening technique is adopted to determine grain size of the film. Surface morphology of the films was investigated by using HITACHI Scanning Electron Microscope (Model S-3000H) with an accelerating potential of 18 kV. Prior to imaging, the films were sputtered with thin gold film to enhance the emission of secondary electron for better imaging.

Optical absorbance and transmission measurements for the film were carried out using computer controlled single beam Elico Spectrophotometer (Model SL159) with uncoated glass as reference. The experimental accuracy for absorbance is ± 0.005 Abs and of wavelength is ±0.5nm.

3. Results and discussion

It is observed that microwave power and the solvent ethylene glycol decide the adhesiveness and morphology of the film. At high microwave power ethylene glycol absorb maximum microwave radiation [12] due to its high dielectric constant (e = 39). This makes the precursor excessive heating at short time resulting powder formation in the solution rather than film on glass substrate with poor adhesive.

3.1. X-ray diffraction Studies

Figure (2) shows the XRD pattern of obtained tin sulfide film at different microwave power. It is seen that as power level increased the peaks intensity found to decreases due to lesser deposition. This can be confirmed from the obtained film thickness as shown in figure (3) where the film thickness found to decreases as microwave power increased. All reflections can be indexed to pure orthorhombic SnS phase as compared with standard JCPDS card no. 39-354 with no impurities peaks such as elemental tin, sulfur and other tin sulphide phases, indicating the formation of single phase SnS. Also it is observed that there is small shift in 2 theta value of the prominent peak from its standard value indicating strain in the materials. This strain arises because of faster growth of film at higher power level. X ray line broadening technique is adopted to determine the grain size of the films utilizing Scherrer equation [14].

$$D = \frac{k\lambda}{\beta \cos\theta} \tag{1}$$

Where D is the grain size, θ is the diffraction angle, K is the shape factor and is equal to 0.9, λ is the wavelength of x-ray and β the full width at half maximum of prominent peaks in radian. From figure (3) it is seen that the calculated grain size found to increase as microwave power increases.

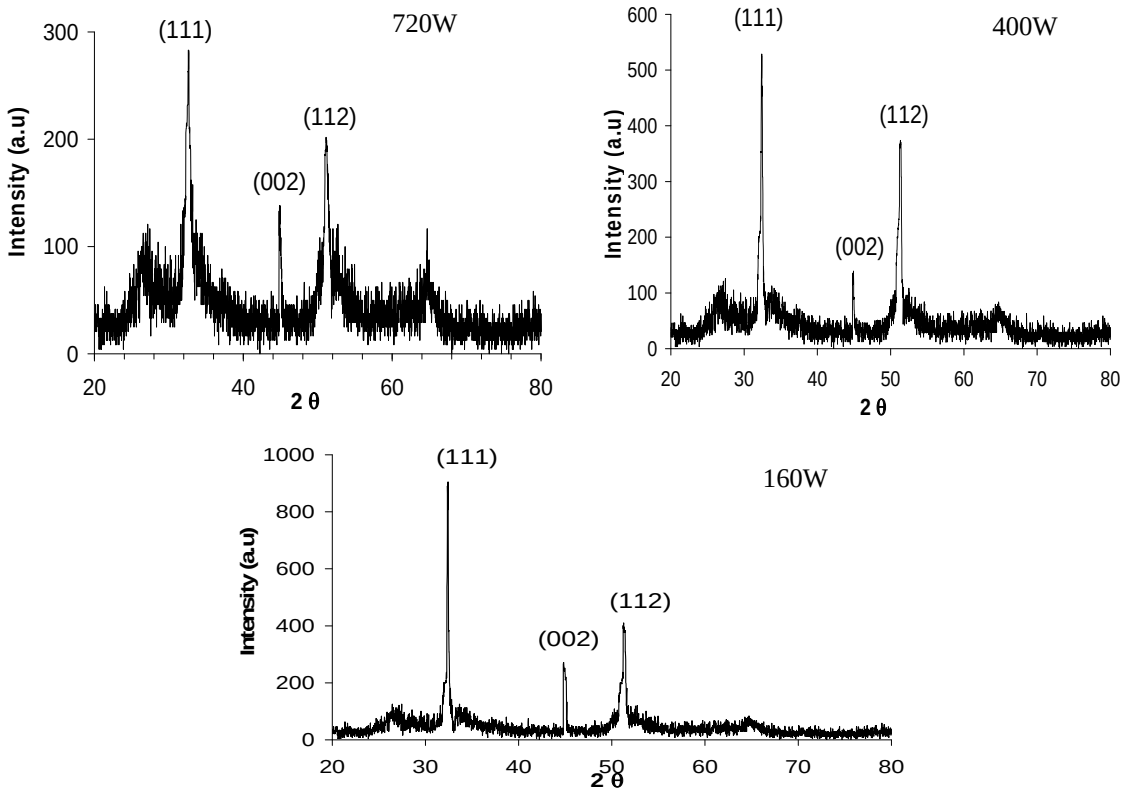


Fig – 2. XRD pattern of SnS thin film prepared at different microwave power

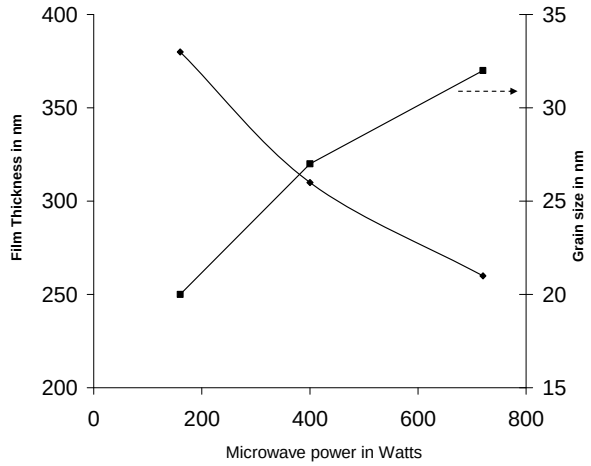
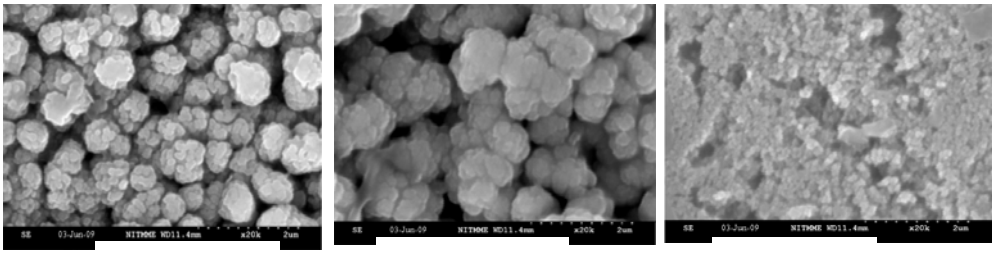


Fig. 3. Variation of film thickness and grain size as the function of micro wave power

3.2. Surface morphology studies

Figure 4(a-c) shows the surface micrograph of film prepared at different microwave power. The film prepared at microwave power of 160W has spherical grains. Each grain consists of cluster of particles. This structure repeats throughout the materials with closely packed to each other indicating good adhesiveness of film with the substrate. The grains size is found to be 20 nm which is comparable with that calculated value from x-ray diffraction studies. Film prepared at 400W has grain size higher than that prepared at low microwave power as shown in figure 4b. This is due to coalescence of two or more grains at higher microwave power. Film prepared at microwave power 720W shows discontinuous in nature with missing of spherical grain type structure. This is believed that at high microwave power too fast reaction on the substrate results in stress and leads to powdery, porous and less adhesive of film which is observed visually. In the present work the concentration of precursor is fixed. However further work can be done to study the variation of concentration effect on the morphology of film.



(a) 160W (b) 400W (c) 720W

Fig. 4. SEM micrograph of SnS thin film prepared at different microwave power

3.3. Optical Studies

Optical absorption measurements were carried out in the wavelength region 380 to 1100nm. Figure (5) shows optical transmittance of film prepared at 160W. It indicates a smooth increase and almost saturate at 600nm to 85% of transmittance. This smooth increase is due to high crystalline nature of the prepared film. Also it is observed the transmittance of film shown in table (1) increases as microwave power increased. This is due to lesser absorbance of film due to reduce in film thickness. The absorption coefficient α is calculated from Lamberts law (α= (2.303 A) / t) .Where ‘A ‘is optical absorbance and ‘t’ is the film thickness which is obtained from the cross sectional view of SEM image and is found to be 380nm which is shown as an insert in the transmission spectra. Optical band gap E_g and absorption coefficient is related as

$$(\alpha h\nu)^{1/p} = A(h\nu - E_g) \qquad (2)$$

Where A is a constant, exponent p is the transition probability. For p = ½ the transition is direct and allowed, p=2 indirect and allowed and p =3/2 for direct forbidden. To determine direct allowed band gap a graph between $(\alpha h\nu)^2$ and $h\nu$ is plotted and is shown in figure (6). The straight portion of the graph is extrapolated to energy axis to give Eg value. It is found to be 1.35eV which agrees with the reported value [4]. Also it is seen from table (1) the energy band gap found to increases as microwave power decreases. This is due to quantum size effect [15].

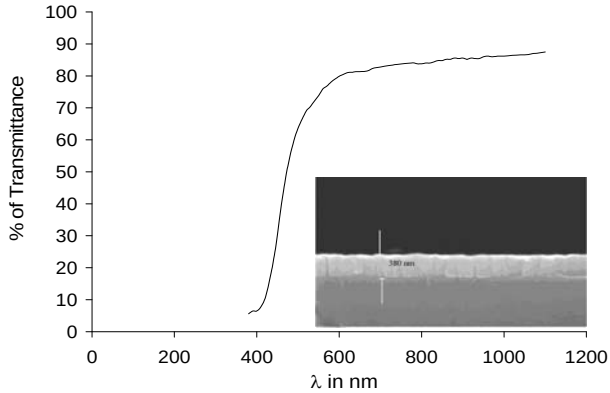


Fig. 5. Transmittance spectra of SnS thin film prepared at 160W. The insert shows cross sectional SEM view of film prepared at 160W

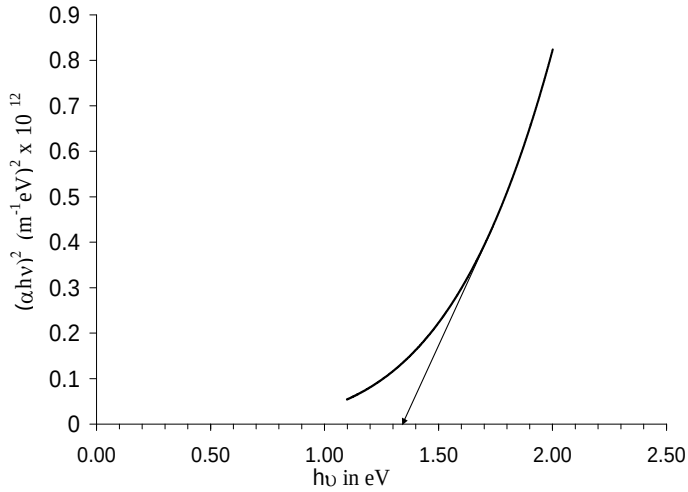


Fig. 6. Energy band gap plot of SnS film prepared at 160W

Table 1. Film thickness, grain size, band gap and % of Transmission of SnS films prepared at different microwave power

Microwave power (watts)	**Film thickness (nm)**	**Grain size (nm)**	**Band gap (eV)**	**% T at 650 nm**	**Film nature**
160	380	20	1.40	83.0	Uniform and adherent
400	310	27	1.35	85.4	Not Uniform but adherent
720	260	32	1.30	87.6	Powdery and less adherent

4. Conclusion

In summary, microwave irradiated chemical solution deposition method was used to prepare tin sulfide thin film on glass substrate from the precursor solution containing salts of stannuous chloride and thiourea with solvent of ethylene glycol. X-ray diffraction pattern indicates the formation of single phase SnS crystalline material. SEM study shows that the film has spherical shape grains and closely packed together. Optical studies reveal that the film has direct allowed transition with band gap of 1.35eV. It is concluded that to obtain uniform well adherent of spherical grain crystalline SnS film the microwave power must be fixed to 160W and irradiated to 5 minutes.

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