Chemical Spray Pyrolysis pure and Transition Metal doped Structural, Morphological and Optical properties of SnS Thin Films

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Abstract— Cadmium doped tin sulfide (SnS) is a promising low cost photovoltaic material for its direct optical band gap (~ 1.4 eV). In this report cadmium doped tin sulfide thin films were prepared by chemical spray Pyrolysis method. The precursor solution cadmium chloride, tin chloride and thiourea are dissolved in de-ionized water. All the deposited films are characterized by different technique such as structural, morphological and optical properties have been studied. The XRD pattern the films are polycrystalline in nature and orthorhombic structure. The average particle size decreased with increasing transition metal doping concentration. SEM image reveals the cornflake shape. The FTIR spectrum used to confirm the functional group of 569 cm^{-1} Sn-S bond. The optical transmission spectra of transition metal doped SnS thin films the average transmission- 60% in the visible region, the doping level increase the optical band gap values also increased from 1.4- 1.7 eV. PL spectra of all samples exhibited a broad emission in the visible range.

Keywords— Sulfide, Transition Metal, XRD, Cornflake shape, Band gap.

I. INTRODUCTION

In recent years the metal sulfides have been attracted in the field of photovoltaic and super capacitor applications. The thin films are widely used in fabrication of photovoltaic devices. Tin Sulfide (SnS) belongs to group IV-VI semiconductor with orthorhombic crystal structure. It's low cost, abundant and non toxic material [1]. During the last decades thin film solar cells have attracted. Materials containing post-transition metals with an ns^2 electronic configuration (e.g. Pb^{2+}, Sn^{2+}, Ge^{2+}, Sb^{3+} and Bi^{3+}) are attracting significant recent attention for their ability as solar absorbers [2]. Recently tin sulfide (SnS) thin films have emerged as alternative absorber layers and promising material for low coast thin films solar cells technology. The direct band gap is 1.3 and 1.5 eV [3]. Tin sulfide is a binary semiconductor with wide range of applications and optoelectronic devices [4]. In recent years, tin chalcogenide compounds such as SnS^2, SnS_2 have role in fabrication of photovoltaic devices. Tin mono sulfide (SnS) is very promising material for the optoelectronic devices and direct band gap around 1.35 eV [5]. In tin sulfide thin films, loferski theoretically proved that a maximum efficiency of 25% is achievable for this material [6]. Due to optimum band gap, high absorption coefficient and p-type conductivity, SnS results to be a suitable candidate for absorber layer in thin film solar cells whereas SnS2 for window layer because of

the wider band gap and n-type conductivity [7]. The SnS thin films can be prepared by several methods such as Spray Pyrolysis technique [8-11], Successive Ionic Layer Absorption and Reaction Method (SILAR) [12], Magnetron Sputtering [13], Chemical Bath Deposition [14], Pulsed Laser Irradiation [15], Spin Coating [16].

Among these methods Spray Pyrolysis technique is simple, low cost, and large area coatings. The coated films are well crystalline and homogeneous deposits with thickness. Some metal elements such as Bi, Sb, Ag, Cu, Cd, and In were doped into SnS films to improve the properties [17]. There are very few result are available in the Cd doped SnO_2 thin films by different deposition techniques for the optoelectronics and transparent electrodes [18-19]. But no result in the Cd doped SnS thin films by chemical Spray Pyrolysis technique, so we tried to investigate the cadmium doped SnS thin films by the spray Pyrolysis technique.

In this present work, we have introduced an excellent Spray Pyrolysis technique. The SnS thin films have been deposited on micro class substrates. The structural, surface morphological and optical properties of the films have been investigated as a function of the films.

II. MATERIALS AND METHODS

Tin Chloride (Sncl$_2$·5H$_2$O), Thiourea ((NH2)2CS) and Cadmium Chloride (CdCl$_2$.5H$_2$O) is purchased from Merck, India and de-ionized water was used throughout the reaction process.

Preparation of Transition metal doped Tin Sulfide Thin Films

Pure and transition metal doped Tin sulfide (SnS) thin films have been deposited on the micro class substrate with different doping level of cadmium using chemical Spray Pyrolysis technique. The precursor solution is prepared using Sncl$_2$·5H$_2$O and thiourea ((NH$_2$)$_2$CS) both solutions were mixed and diluted with 40 ml de-ionized water with constant stirring for one hour. Well cleaned glass substrate of dimension 75 x 25 mm^2 dimensions at the substrate distance 30 cm. Cadmium was doped with Tin Sulfide (SnS) thin films using CdCl$_2$ (5 at%, 10 at%) as the doping source. The prepared solution was sprayed onto ultrasonically cleaned glass substrates kept at 250°C. Films prepared by this method have uniform thickness and well adherent with the substrate. The Optimum thermal/ spray Pyrolysis deposition condition for the preparation of Cd doped SnS thin films are listed in Table 1.

Table.1: Optimum thermal / spray Pyrolysis deposition conditions for the preparation of pure and transition metal doped SnS Thin Films

Precursor molar concentration	0.1M
Cadmium concentration	0 %, 5% and 10%
Solvent volume	40 ml
Substrate temperature	250°C
Substrate to nozzle distance	25cm
Spray angle	45^0
Spray interval	10 min

X-ray diffraction (XRD) analysis was performed on X-ray diffractometer (PAN analytical X-Pert PRO) operated at 40 kV and 30 mA. The pattern was recorded by Cu-Kα radiation with of 1.54056 Å. Scanning rate of 2°/min and a sample interval of 0.02° were employed in the 2θ range from 10° to 80° for the determination of crystallinity, purity and crystallite size of the Thin Films. The average grain size of the Cd doped SnS Thin Films calculated using Scherrer formula $D = 0.89\lambda / \beta \cos\theta$. Where, d is diffraction angle, constant value of (k) =0.89, λ- wavelength and β is the FWHM (full width half maximum) of consistent peak, θ = Bragg's reflection angle. Size and surface morphology of Cd doped SnS Thin Films was examined by JEOL JSM 6390 Scanning Electron Microscope (SEM) instrument operated at an accelerating voltage at 15Kv. Elemental analysis was carried out by Energy Dispersive (X-ray) EDAX analysis, the particles were dried on a carbon coated copper grid and performed on SEM instrument with thermos EDAX attachment. The FTIR analysis of the thin films was performed by Perkin Elmer make Model Spectrum RX1

(Range 4000 cm^{-1}- 400 cm^{-1}) using KBr compressed pellet method. The optical studies were carried out by Perkin Elmer Lambda 35 UV-VIS-NIR double beam spectrophotometer for a wavelength range of 300nm to 1100nm. Photoluminescence was observed from the Varian carry eclipse PL spectrograph.

III. RESULTS AND DISCUSSION

Structural Analysis

Figure.1 shows the X-ray diffraction pattern of pure and transition metal doped SnS Thin Films with different doping concentrations. The diffraction peaks are observed at the deposited films like 2θ value of 32.5º, 35.5º, 38.9º, 46.2º, 48.8º, 61.5º, 66.5º and 68.8º are corresponding to the crystal planes of (021), (011), (111), (311), (411), (201), (301) and (240) respectively. The preferential orientation along the sharp peaks at (111) planes good agreement with the standard JCPDS card no- (75-2115) with the standard orthorhombic crystal structure. It indicates the maximum number of crystallites have appear in the (111) plane direction. In addition to that small shift is observed for the peaks (021),(011) and (311) for all the deposited films. The observed marginal shift is attributed to presence of strain between a substrate and the deposited films [5]. The doping molar concentration of the films produces a considerable decrease in crystalline, because of the dopant concentration should be increased. The average crystalline size of the transition metal doped SnS coated films is around 27 to 55 nm. The structural parameters such as average crystalline size (D), dislocation density (ε), micro strain (δ), and Lattice Distortion (LD) of the films are calculated using the relations [20].
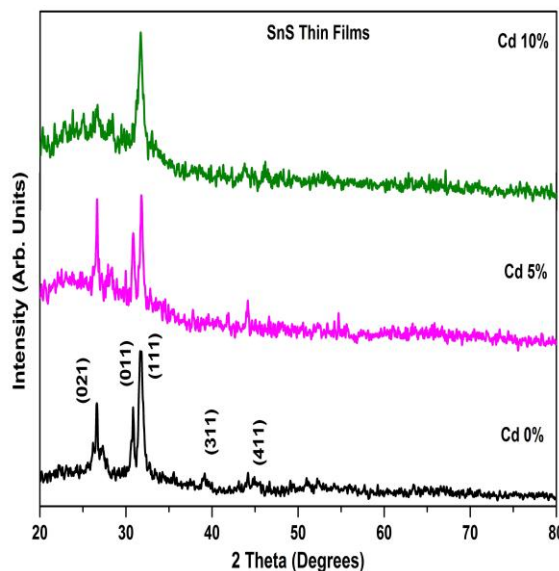

Fig. 1 XRD patterns of pure and transition metal doped SnS thin films with different doping concentrations.

The average crystalline size was estimated by Debye-Scherer's relation as

$$D = \frac{k\lambda}{\beta Cos\theta}$$ ------------ (2)

Where the constant 'k' is the shape factor = 0.94, 'λ' is wavelength of X-rays (1.5406 ÅCuK$_\alpha$) 'θ' is the Bragg's angle and 'β' is FWHM. The value of dislocation density was calculated using the relation

$$\delta = \frac{1}{D^2}$$ ------------ (3)

The lattice strain (ε) was calculated using the relation

$$\varepsilon = \frac{\beta Cos\theta}{4}$$ ------------- (4)

The lattice distortion (LD) is calculated using the relation such as [21]

$$L.D = \frac{\beta}{4\tan\theta}$$ ------------ (6)

The micro structural parameters of pure and transition metal doped tin sulfide films is listed in table 2.

Table – 2: Micro - structural parameters

Cd Doping Level	Crystallite Size (D) × 10^{-9} m	Dislocation density δ × (10^{16} lines/m)	Micro Strain ε × (10^{-3} Lines^{-2} m^{-4})	Lattice Distortion (LD) × (10^{-3})
0%	55.87	0.3203	0.9972	2.2792
5%	33.58	0.88661	1.67140	3.7667
10%	27.977	0.78271	2.0156	4.536

The doping concentration increases (5%, 10%), then crystalline size also decreased. Otherwise the micro strain, dislocation density, lattice distortion and stacking fault probability increased.

Morphological and Compositional Analysis:
Fig. 2(a)-(b) shows the SEM micrographs of pure and transition metal doped tin sulfide thin films with the different doping concentrations. The SEM images around 200 nm magnifications. The surface morphology is remarkable consequence on the performance of the thin films. All the deposited films are homogeneous and polycrystalline in nature. The transition metal doped tin sulfide thin films are formed by cornflake like particles, homogeneous, with uniform surface and good adhesion to substrates. Substrates are well covered and no pinholes are observed [22]. The average particle size is around 20±5 nm.
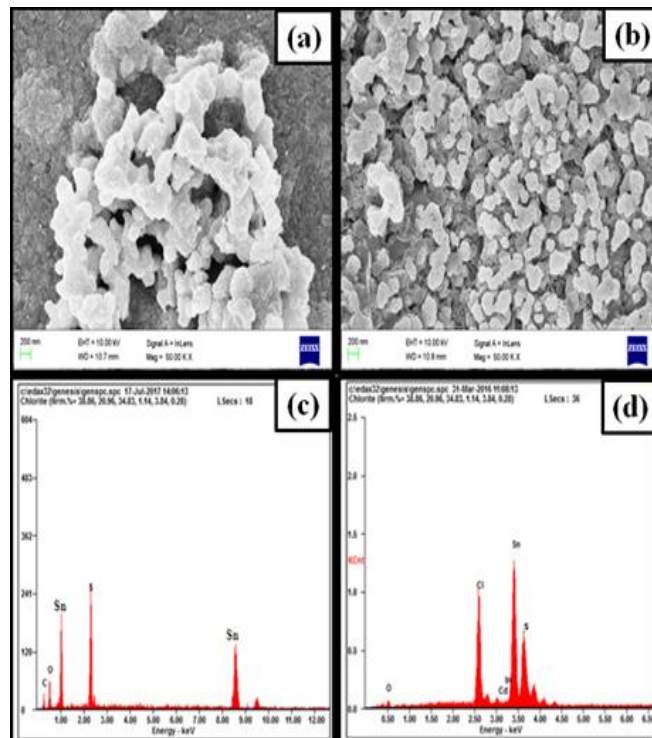

Fig. 2: (a)-(b) & (c)-(d) SEM and EDAX Spectrum of pure and 2% Cd doped SnS thin films.

In Fig. 2(c)-(d) we have announced a historic EDX spectrum of pure and transition metal doped SnS thin films. As we can see, Sn, S and Cd elements are presents in the film composition along with C, O and Cl. O and C may originate from methanol and thiourea [3].

FTIR Analysis:
In the FTIR studies is used to find the molecules and functional groups presence in the deposited thin films. The FTIR spectrum of pure and transition metal doped SnS thin films are shown in figure 3. The FTIR spectrum of observed that the peaks located at (3271) (2954) (926) (615) (569) (458) cm^{-1} respectively. A small absorption peak is observed at 569 and 686 cm^{-1} are possibly due to the stretching vibrations of Sn-S [12]. A broad band appears at 3250–3500 cm^{-1}, which is due to OH stretching vibration. Strong and sharp bands appear in the spectrum at 615, 1000–1200 and 2354 cm^{-1}, which are due to the characteristics peaks of SnS [23].
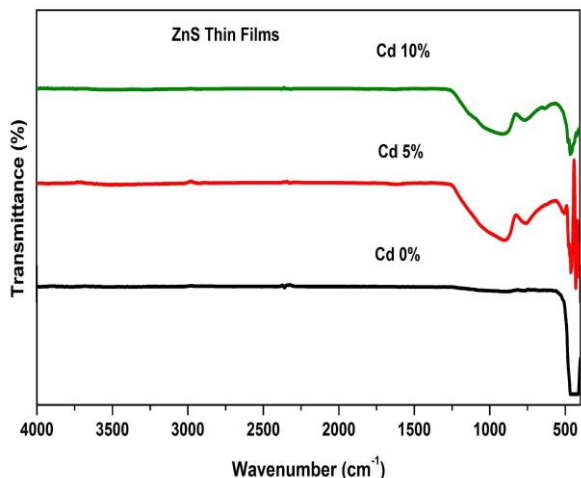
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Fig. 3: FTIR spectrum of pure and transition metal doped SnS thin films.
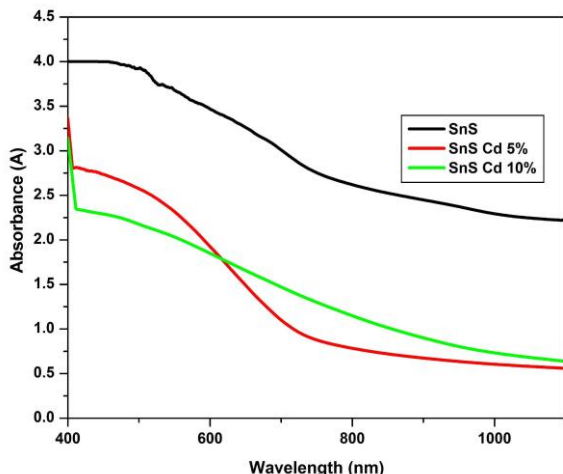
Optical properties

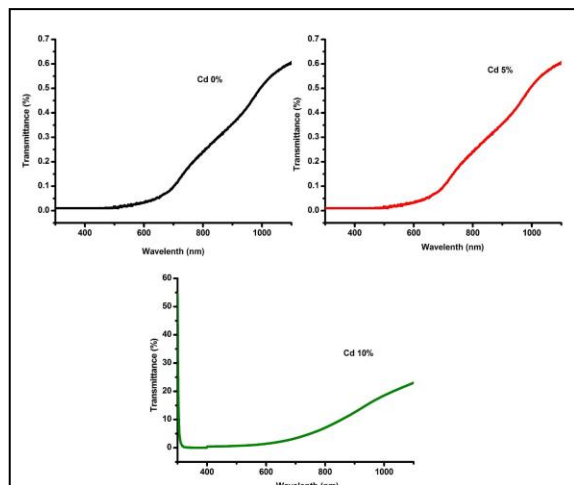Fig. 5: UV-Vis absorption spectra

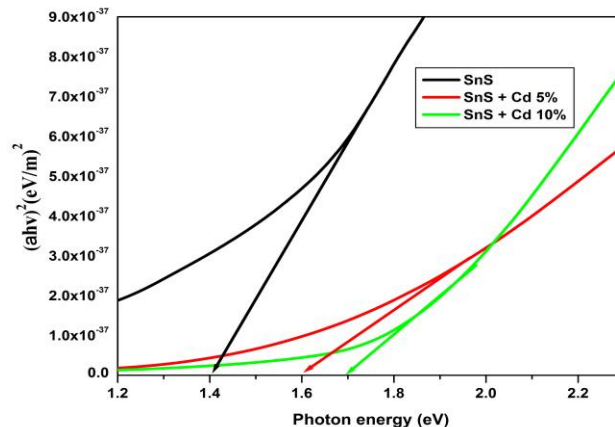Fig. 5: UV-Vis transmission spectra.

Fig. 6: UV-Vis Tauc plate

The optical transmission spectra of pure and transition metal doped SnS deposited thin films at different doping percentage of wavelength range from 200 – 1200 nm. The average transmission 60% in the visible region, but the doping level increase the optical transmittance value increased is show in figure 4. The doping level increase the maximum transparency of the deposited film is acquired. The absorption spectra of pure and transition metal doped SnS thin films deposited on the micro class substrate with different doping percentages were studied in the wavelength range 500-1200 nm. The optical band gap values for these films were evaluated using the Tauc plots (**Fig. 5.**) The nature of the transition involved (direct or indirect) during the absorption process was determined by studying the dependence of the absorption coefficient A, on photon energy hγ as calculated using the relation as [24].

$$\alpha h v = A(h v - E_g)^n \underline{\hspace{4cm}} \quad (5)$$

Where A is the constant, E_g is the band gap energy, hy is the photon energy, the plots of $(\alpha h y)^2$ versus hy for different substrate temperatures are shown in the Fig. 6. The direct band gap energy of pure 1.3 eV which is in good agreement with the value reported in the literature [25]. It was seen that the direct band gap values increased from 1.4 – 1.7 eV with increased in doping molar concentrations. Optical band gap values of pure and Transition metal doped Tin Sulfide thin films are shown in Table - 3**.** This is a way of achieving band gap tuning in semiconductor materials and hence the development of new thin films for efficient photovoltaic application. As that doping percentage increased, the sharp absorption edge was formed because the grain size increased has they became more crystalline [26].

Table - 3. Optical band gap values

Film	Direct Energy Band Gap (eV)
Pure SnS	1.4
5% Cd Doped SnS	1.6
10% Cd Doped SnS	1.7

Photoluminescence Analysis:

Fig 7 shows the photoluminescence spectra of pure and transition metal doped SnS thin films with different Cd percentage (5 %, 10 %) variations. The broad peak entered between 470 – 540 nm at an excitation wavelength is 550 nm. The yellow and red bands are associated with the point defects and surface states, respectively. On the other hand, the origins of green and orange bands are due to the atoms or excitonic transitions and the I_{Cd} - V_{Cd} complex defects, respectively [27].
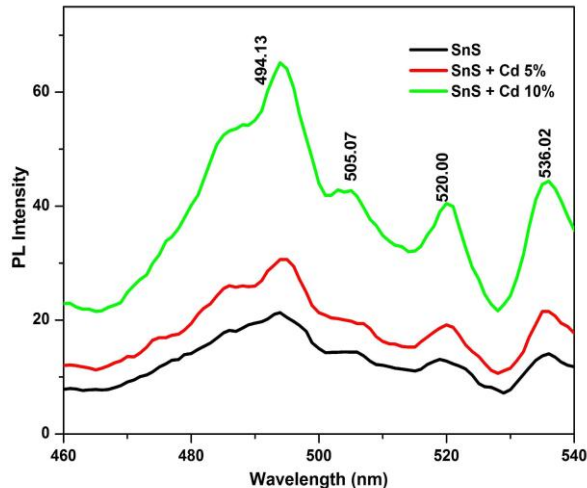

Fig. 7: photoluminescence spectra

In the XRD measurement in which the intensity of (111) planes predominant peak has increase in the 10 at. %. The strong band-edge emission around 495 nm the emission peak improved because of doping Cd level. Ac-cording to quantum confinement theory, the energy band gap of a semiconductor depends on the crystal size; its value will increase with a decrease in crystal size from our XRD pattern [28]. In the possible reason transition metal doped Tin Sulfide deposited films the doping molar concentrations increases up to 10 at.% the band-edge emission peak shifted the higher wavelength region.

IV. CONCLUSION

Effect of transition metal doped on structural, morphological and optical properties of Tin Sulfide thin films deposited by chemical spray Pyrolysis technique have been investigated. The XRD pattern shows that all the deposited films have polycrystalline in nature the preferential orientation along the sharp peaks at (111) plane as the preferred orientation orthorhombic crystal structure. The Cadmium doping the crystalline size also decreased from 55- 27 nm. SEM study reveals that the films are uniform, dense and cornflake shape. FTIR shows the strong and weak bands associated with deposited films. The transmittance value in the visible region was found to be 60% and optical band gap value is increased

from 1.4 -1.7 eV. In the PL spectra the broad peak entered between 470 – 540 nm at an excitation wavelength is 550 nm.

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