

Influence of Deposition Time on Structural and Optical Properties of Chemically Deposited SnS Thin Films

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Abstract: Using chemical bath deposition (CBD) technique SnS thin films have been deposited at room temperature with different deposition times. The deposited films have been investigated through X-ray diffraction measurements to determine structural properties. The deposited SnS films found amorphous and polycrystalline with an orthorhombic herzenbergite structure. The grain size found to increase with deposition time. The surface morphology of the films has been examined using scanning electron microscopy (SEM). The chemical compositions of the films have been determined using energy dispersive analysis of x-rays (EDAX). The optical absorption spectra of the films in the wavelength range of 200-1200 nm have been investigated to determine the optical band gap and types of transitions involved in the absorption process. The direct allowed transitions found to be dominant and the corresponding band gap found to decrease with increase in deposition time. In order to evaluate the electrical parameters, thermoelectric power measurements have been performed. The films exhibited p-type electrical conductivity. A systematic study on the influence of deposition time on the properties of SnS thin films deposited by CBD at room temperature has been reported.

Keywords: Band gap, chemical bath deposition, lattice parameters, optical absorption, tin sulfide electron microscopy, X-ray diffractogram,

INTRODUCTION

The search for thin film materials for solar energy conversion and other related applications has been recently identified. Many efforts have been geared towards using metal chalcogenides as this class of materials had shown somewhat superior performance when compared to others. Among the important binary semiconductors of IV-VI group, the chalcogenides formed with Sn, especially SnS have attracted considerable attention in recent years. The lattice structure of SnS is closely related to the black phosphorous structure and can be considered either as a distortion of the NaCl structure or as a binary analog of the layered arsenic structure. The tin sulfide (SnS) is having orthorhombic crystal structure with eight atoms per unit cell. The cation (Sn) and anion (S) atoms form double layers made up of two planes of zigzag cation-anion chains perpendicular to the longest crystallographic axis. The double layers are stacked to each other through a weak van der Waals interaction whereas a relatively strong covalent bonding between the cation and anion atoms exists within the layers [1]. The compound SnS is a semiconductor with a band gap of 1.3 eV [2] and hence with the potential to become a versatile solar energy material. The high conversion efficiency obtainable from it in photovoltaic devices, according to Prince-Loferski diagrams and its acceptability from the point of view of cost, availability, toxicity and stability ascribe to SnS a unique position among the metal sulfides. The narrow band gap and the interesting structural properties of SnS satisfy most of the criterion to make them potential candidate in

photoelectrochemical solar cells, as solar absorbers in thin film solar cells, near infrared detectors, as photovoltaic materials and in other optoelectronic systems. The SnS films show both direct and indirect absorptions at room temperature. It exhibits p-type conduction and high absorption coefficient of the order of 10^4 to 10^5 cm^{-1} [3]. The most extensively studied thin film solar cells are based on CdTe and Cu(In,Ga)Se₂ (CIGS). However, there are concerns existing with respect to the use of Cd and In in this type of applications due to cost, toxicity, abundance and environmental issues. SnS is one of the promising materials for low cost thin film solar cell technology, due to its optimum energy gap, a high fundamental absorption coefficient, non toxicity and abundance.

For the deposition of thin films of SnS various methods like spray pyrolysis [4-10], electrodeposition [11-17], chemical vapor deposition [18-20], magnetron sputtering [21], successive ionic layer adsorption and reaction (SILAR) [22], vacuum evaporation [23-34], brush plating [35-36], microwave assisted chemical deposition [37] and chemical bath deposition (CBD) [38-53] have been employed. Among these methods CBD is relatively simple, more rapid and inexpensive method suitable for deposition on large substrates irrespective of the shape and morphology of substrates nearly at room temperature. Mainly, it is a technique for thin film deposition on a substrate from a diluted solution comprising of a source of metal, hydroxide and sulfide or selenide ions. In CBD control of reaction rate and pH of the bath is very necessary to deposit a good quality film. For this, use of appropriate buffer solutions in the bath has been seen many times [38-39]. Most of the CBD deposited SnS films used stannous chloride salt as a tin ion source and thioacetamide [38-39] or sodium thiosulphate pentahydrate [42,47] or sodium sulphate [54] as a sulphur

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ion source in the bath. To slowdown the immediate precipitation of the precursors in the bath buffer solutions are used. At the same time, increase in temperature increases the rate of reaction in the bath leading to an early deficit of the ions in the bath with may lead to a reverse reaction exhibiting pilling off of the deposited film. At low temperature the rate of reaction becomes low as compared to that at higher temperature which can be monitored and then optimized for better deposition of the film. Hence low temperature deposition of the film is interesting and challenging. Recently, the effect of deposition time on the properties of SnS thin films deposited by CBD using a buffer solution (ammonia/ammonium chloride) at 60 °C has been reported [38]. Such study on SnS thin films deposited at room temperature by CBD has not been found in literature survey. The temperature of the bath strongly influence the reaction mechanism and hence the formation of the film. Also at room temperature, the particle do not have enough kinetic energy and hence less probability to reach the substrate with a greater momentum to form a quick film. Under such condition the formation of SnS from the anion and cations preferably governs by the chemistry of the reactants only. In this context, a systematic study on the effect of deposition time on the structural and optical properties of SnS thin films at room temperature has been reported in the present work.

EXPERIMENTAL

Deposition of SnS Films

For the synthesis of SnS thin films using CBD, AR grade SnCl₂ 2H₂O and thioacetamide (TA) were used as Sn and S source respectively. The deposition bath was prepared first by mixing the 5 ml of 1M SnCl₂ 2H₂O with 10 ml of 3.75 M triethanolamine (TEA) (as supplied diluted to 50%) under a vigorous stirring. 2ml NH₃ was added drop-wise with constant stirring followed by addition of 5 ml of 1M TA. Finally distilled water added to make a total of 100 ml. The pH of the bath was kept 9.70 using ammonia. The solution was transferred to another thoroughly cleaned glass beaker with well cleaned amorphous glass substrate (76mm x 26mm x 1mm) placed inclined and rested on beaker wall. Before deposition process glass substrates were thoroughly cleaned using detergent, chromic acid and isopropyl alcohol in a systematic manner. The films were deposited at room temperature (27 °C) with deposition time of 24h, 48h and 72h. Each deposited film was sprayed with distilled water immediately after it was taken out of the beaker, allowed to dry and then kept in a desiccator to avoid any unwanted atmospheric effects.

Characterization of SnS thin Films

The X- ray diffractograms of the films were obtained using Philips Xpert MPD diffractometer employing CuK α radiation with $\lambda=0.15406$ nm in 2θ range from 20° to 70°. For surface morphology scanning electron microscopy (SEM) pictures were taken using computer controlled digital scanning electron microscope model Philips XL30 ESEM. The chemical compositions of the films were determined from the energy dispersive analysis of X-rays (EDAX) spectra obtained using the system attached with Philips XL30 ESEM. For the optical analysis, the optical spectra of the films were obtained using Perkin Elmer Lambda 19 UV-

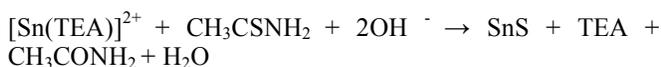
VIS-NIR spectrometer in the wavelength range 200 nm to 1200 nm. The Hall effect measurements were attempted on the films using Lakeshore 7504 Hall measurement set up system at room temperature. The thermoelectric power (TEP) measurements were carried out using the set-up available at and developed by Physics Department of S.P. University, Vallabh Vidyanagar, India.

RESULTS AND DISCUSSION

Mechanism of SnS Thin Film Deposition in CBD

Chemical bath deposition (CBD) refers to the deposition of films on a solid substrate from reaction occurring in a solution, almost always aqueous. Although CBD has been in use for long time involving quite simple reactions, the mechanism of the CBD process is often unclear. There are several mechanisms of CBD which can be divided into four fundamentally different types as; the simple ion-by-ion mechanism, simple cluster (hydroxide) mechanism, complex decomposition ion-by-ion mechanism and complex decomposition cluster mechanism as long as formation of metal chalcogenide films are concerned [44]. The first two mechanisms involve free chalcogen ion while the last two do not involve formation of free chalcogen ion. In simple ion-by-ion mechanism, first ions diffuse over the substrate which serve as a catalyst and facilitate the nucleation. The nucleation grows as a result of absorption of ions in the solution and nucleation of new crystals occurs. At further stage the crystals bonds with one another by the van der Waals forces forming a film. In simple cluster mechanism, hydroxide colloidal particles diffuse to substrate and adhere to it. These hydroxide colloidal particles adsorbed to substrate react with free ions in the solution resulting in displacement of hydroxide by the free ions. Such displacement reaction can occur both on the substrate and in the solution and continues until most of the hydroxide converts into sulfide. The primary particles occurring by reaction adhere to each other to make up an aggregated film on the substrate and other nonadsorbed particles also aggregate and precipitate out of the solution. In last two complex decomposition mechanisms, the complex (Sn-S-L, where L is ligand or part of the S forming species) decomposes to SnS on the substrate and to a greater or lesser extent also homogeneously in the solution. The SnS nuclei formed grow by adsorption and decomposition of more complex species until a film of aggregated crystal is formed in a similar manner as for the first two mechanisms.

While using CBD method, to deposit a good quality thin film on the substrate it is very important and essential that the reaction process in the bath leading to film formation must be sufficient slow enough. In the deposition process of SnS films when TEA was not used, the precipitation of solid elements like [Sn(OH)₂] occurs very rapidly in the solution and a proper film was not obtained on the substrate. In order to form a good quality film on the substrate, formation of such elements should be prevented and the rate of reaction must also be slowed down. To ensure these conditions TEA was used in the synthesis process as it acts as a good complexing agent with metal ions. The basic chemical reaction that leads to formation of SnS thin films is considered as follows [45].



The Sn^{2+} ion complexes with TEA initially to form $[\text{Sn}(\text{TEA})]^{2+}$ during the deposition preventing the rapid formation of solid materials like $[\text{Sn}(\text{OH})_2]$ and later this complex decomposes and releases Sn^{2+} ions to make bonds with S^{2-} ion present in the solution to form SnS.

During the deposition time the color of the solution in the bath was observed to change from initially milky white to light yellowish brown in couple of hours then to chocolate brown and with further increase in time to deep brown. The films obtained after deposition time of 24h were found to be light brown with yellowish transmission in daylight and reflecting multicolor whereas the films obtained after deposition time of 48h and 72h were found to be deep brown-blackish with deep reddish transmission and reflecting like mirror. The change in appearing color of the film is mainly attributed to the increase in thickness of the film with the increase in deposition time since Sn/S ratio is not much affected in the films as per the EDAX results. The SnS films of deep brown or chocolate color have been reported recently [10,39,55]. Very recently, color dependence of the SnS film on the film thickness has been reported revealing that color of SnS film changes from pale yellow to brown with increase in film thickness [56]. It should be noted that films deposited on the lower side of the substrate facing the bottom of the beaker only found well adherent and taken for studies while that on the upper side found to washed off easily with spray of distilled water.

Structural Analysis

The x-ray diffraction patterns of the films deposited at different deposition times of 24h, 48h and 72h at room temperature are shown in Fig. (1). For all films, the observed peaks have been analyzed and indexed using standard pattern for the mineral herzenbergite with orthorhombic structured SnS (JCPDS PDF Card # 39-0354). The analysis of the XRD pattern of film deposited after 24h indicates formation of a poorly crystalline film. Except for compounds that are commonly amorphous, CBD semiconductor films are rarely truly amorphous. Most of these films are classified as "amorphous" or "poorly crystalline" either on the basis of lack of any XRD peak or because the peak(s) are very broad [44] as it happens in this case also. The peaks observed in Fig. (1) at 2θ values of 26.34° , 31.88° and 42.80° were found to match with reflections from (120), (040) and (210) crystallographic planes of orthorhombic phase of SnS respectively. The peak seen at 26.34° is found also to contributing through reflections of maximum intensity from (110) plane of mineral cassiterite (SnO_2) (JCPDS PDF Card # 41-1445) from the glass substrate as observed earlier too [43].

The XRD patterns of films deposited after 48h and 72h shown in Fig. (1) exhibits sharp peaks at 2θ values of 31.48° and 31.42° respectively corresponding to (111) planes of orthorhombic structured SnS (PDF Card # 39-0354). There are some less intense peaks revealing good quality polycrystalline films with preferred orientation from (111) plane. In the XRD pattern of film with deposition time of 48h, a peak at 2θ values of 35.06° and in the XRD pattern of film with deposition time of 72h peak at 2θ values of 34.86°

are identifies as originating from (101) plane of Sn (PDF#18-1380). It should be noted that peaks corresponding to other phases of SnS (SnS_2 or Sn_2S_3) have not been found during the XRD analysis.

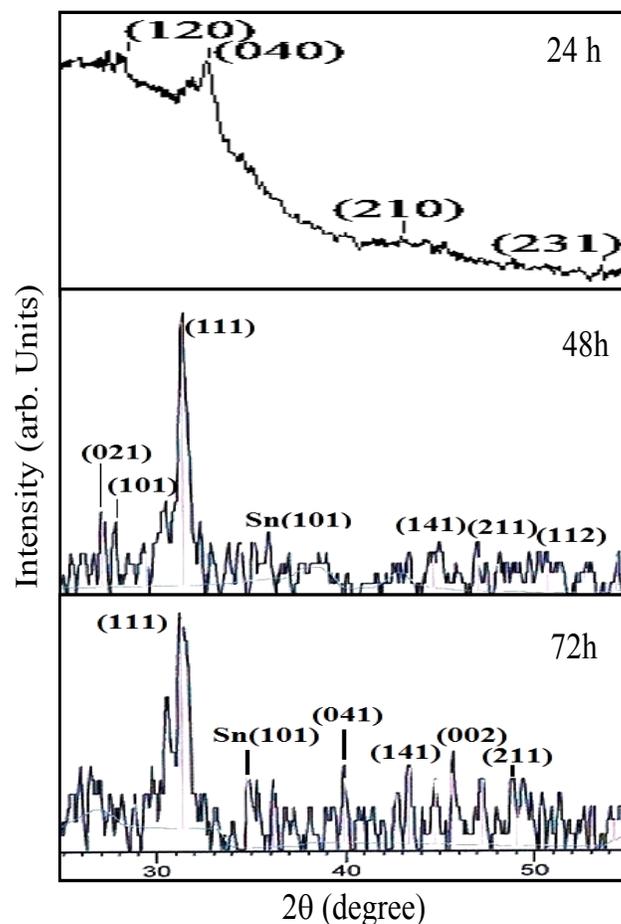


Fig. (1). XRD spectra of SnS films deposited using CBD with different deposition times.

The lattice parameters of the deposited films have been calculated from the observed values of $2\theta^0$ and using d -values (interplaner spacing) for the orthorhombic structure, which is given by [57]:

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (1)$$

where (hkl) are the Miller Indices of the plane concerned and a , b and c are lattice parameters. The values of lattice parameters so obtained are shown in Table 1. The values of the lattice parameters have been found in good agreement when compared with the standard values taken from JCPDS Card # 39-0354. The crystallite or grain sizes were estimated using the Scherrer's formula [57]:

$$D = \frac{0.9\lambda}{\beta_c \cos\theta} \quad (2)$$

where D is the crystallite size, λ is the wavelength of the $\text{CuK}\alpha$ radiation, β_c is the experimentally observed diffraction peak width at half maximum intensity (FWHM) and θ is the

Bragg angle. The values of the crystallite size determined using above relation are 13.06 nm, 26.9 nm and 27.05 nm for the films with deposition time of 24h, 48h and 72h respectively. When compared to XRD patterns of bulk SnS, the XRD patterns of the deposited films show the broadening of the peaks. Such effects are mainly arising due to small crystalline size and strain. Both crystalline size and strain effects are interconnected in the line broadening of the peaks which makes it difficult to separate. Williamson-Hall technique [58] is one of the many methods for the evaluation and separation of size and strain parameters from the occurring line broadening. In this method which is adopted in present work, grain size D and strain ε are related as

$$\frac{\beta_c \cos \theta}{\lambda} = \frac{1}{D} + \varepsilon \left(\frac{\sin \theta}{\lambda} \right) \quad (3)$$

where β_c is the instrumental effect corrected full width at half maximum of the peak measured, θ is the diffraction angle and λ is the wavelength of X-ray. The slope of the plot between $\beta_c \cos \theta / \lambda$ and $\sin \theta / \lambda$ (Williamson –Hall plot) gives micro strain ε and the inverse of intercept on y axis gives average grain size value. The variation of grain size and strain of SnS films deposited at room temperature at different deposition time are shown in Fig. (2). The results of the Williamson –Hall plots shown in Table 1 indicates that grain size increased from 12.65 nm to 28.57 nm as the deposition time increased from 24h to 72h. These values are in good agreement with those obtained from Scherrer formula as shown in Table 1. It is obvious to expect that with increase in deposition more ions released from the reaction contribute to the film formation process leading to an increase in grain size until deficit of either Sn or S ion occurs in the bath solution. Also, with increase in deposition time from 24h to 42h strain value decreased from 43×10^{-4} to 3.6×10^{-4} . Similar behavior has been observed on SnS films deposited with spray pyrolysis at increasing substrate temperature [5]. However, with further increase in deposition time to 72h strain value found to increase to 28×10^{-4} but still decreased from that for film with deposition time of 24h. This may seem to be plausible due to sufficient time available for growth of defects as the films remains in the bath for a longer time.

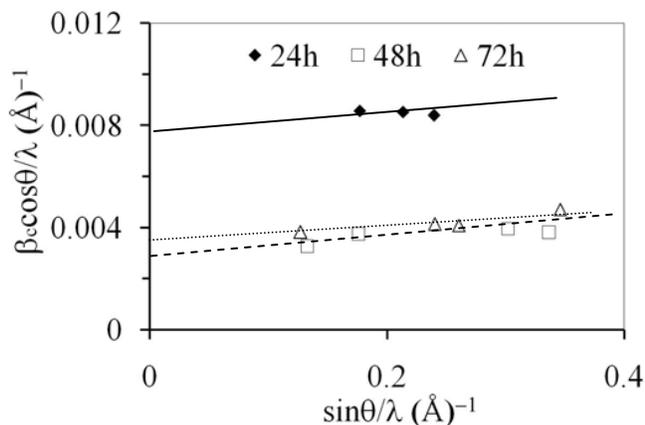


Fig. (2). Williamson-Hall Plots of SnS films with different deposition times.

Surface Morphology

The surface morphology of the films deposited at room temperature with different deposition times are shown in Fig. (3). The SEM images show homogeneous surfaces of the films free from any pinhole or cracks with presence of large spherical crystallites surrounded with small crystallites. The

Table 1. Results of XRD Analysis of SnS Films Deposited with Different Deposition Times

Dep. Time (h)	Lattice Parameter			Grain Size		Strain $\times 10^{-4}$
	(Å)			(nm)		
	a	b	c	Scherrer Formula	W-H Plot	
24	4.38	11.20	3.99	13.06	12.65	43
48	4.28	11.29	3.90	26.9	26.31	3.6
72	4.32	11.13	3.97	27.05	28.57	28
	4.33 ^a	11.19 ^a	3.98 ^a			

^aJCPDS PDF # 39-0354.

SEM images indicate that with increase in deposition time the number of crystallites increases leading to formation of more homogeneous film. The presence of more number of small grains as compared to larger ones can be attributed due to deposition at room temperature at which ions in the bath generally do not possess enough mobility to form a grain with larger size. The Fig. (3c) is the SEM image of the film deposited after 72 hour. In CBD, after a sufficient time when reaction of formation of SnS from the respective ions in the bath is saturated the reverse reaction starts which leads to pilling off of the films from the substrate. This effect can be seen just in its initial state to occur in Fig. (3c) in some directions.

EDAX Analysis

Fig. (4) shows the EDAX spectrum of the film with deposition time of 72h. The EDAX analysis of the films with deposition time of 24h, 48h and 72h exhibited atomic ratio of Sn/S of ~ 0.99, 1.19 and 1.18 respectively. This has been indicating that deposited films are almost stoichiometric. It is evident that films with deposition time of 48h and 72h has presence of small excess amount of tin. This may be due to the fact that at longer deposition time the release of Sn ion is not counterbalanced by availability of S ions in the bath as concentration of S ions in the bath had been utilized fully. The results of XRD analysis of the corresponding films justify the presence of Sn. The Na, Mg, Si, O and Ca elemental peaks have resulted due to the elements in glass substrates and distilled water.

Optical Analysis

The optical absorption technique was employed to determine the values of band gap and type of optical transitions involved in the absorption process in the films. The absorption spectra of the films obtained in the

wavelength range of 200-1200 nm are shown in Fig. (5). The absorption edges have been found broad and pronounced around 800 nm for film with deposition time of 24h and around 850 nm for films with that of 48h and 72h. It can be seen from the Fig. (5) that absorption edge tends to be sharpening as the deposition time of the film increases. This can be attributed to the increase in thickness of the films with increase in deposition time.

The optical band gaps E_g of the films were evaluated using the relation [59]:

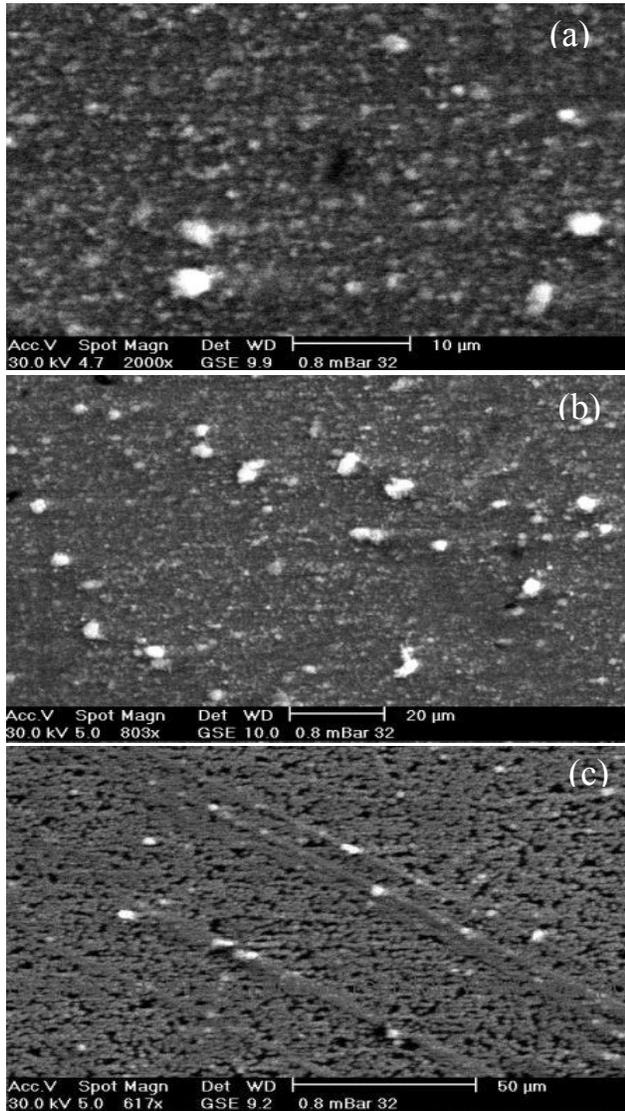


Fig. (3). SEM images of SnS films deposited by CBD at deposition time of (a) 24h (b) 48h and (c) 72h.

$$\alpha h\nu = A(h\nu - E_g)^n \tag{4}$$

where A is the parameter that depends on the transition probability, α is the absorption coefficient and n is the index that has value equal to 1/2 for the direct allowed transitions, 2 for the indirect allowed transitions, 3/2 for direct forbidden transitions and 3 for indirect forbidden transitions. The SnS thin films prepared by CBD has exhibited both direct [10,15, 38-39,41-42,47-48,50-51] as well as indirect [11,38-

39,45,49,51] transitions. However to investigate the types of optical transitions involved with the value of corresponding optical band gap, the spectral variations of $(\alpha h\nu)^{1/2}$, $(\alpha h\nu)^2$, $(\alpha h\nu)^{2/3}$ and $(\alpha h\nu)^{1/3}$ were plotted as a function of photon energy $h\nu$ as shown in Fig. (6) for the SnS films deposited with different deposition times. The value of intercept on the x-axis obtained by extrapolation of the straight-line portion of the curve at $\alpha = 0$ has been used to estimate the optical band gap of the corresponding film [11,13, 38-40,42,47,49,51]. Also to determine optical band gap many researchers [40] use the Tauc-relation [60] which is consistent with equation (1).

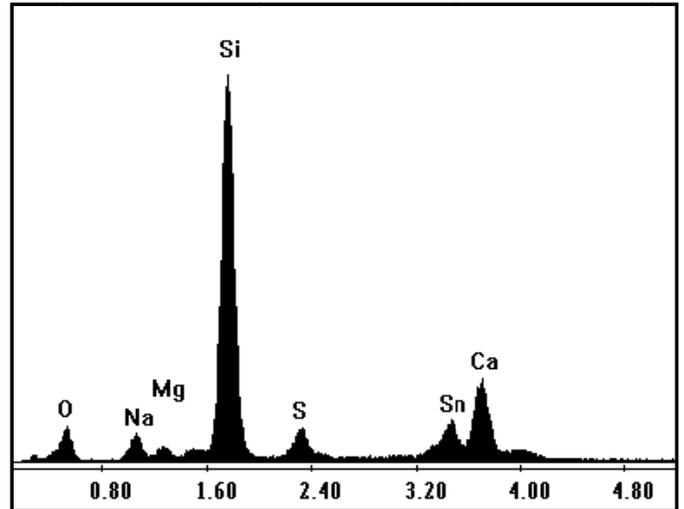


Fig. (4). EDAX spectrum of SnS film deposited by CBD with deposition time of 72h.

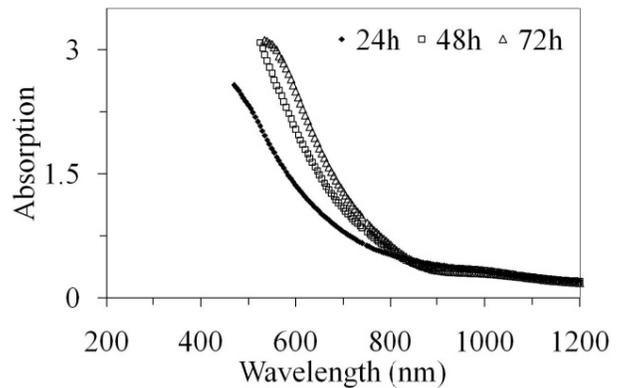


Fig. (5). Optical absorption spectra of SnS thin films deposited by CBD with different deposition times.

Fig. (6) show that for the deposited films the straight line portion best fits for allowed direct transitions with lesser probability for other transitions. However, the variations of band gap values with deposition time for the deposited films are shown in Fig. (7) for all types of transitions.

The value of indirect allowed band gap found to be not much influenced by deposition time as it decreased fractionally from 1.18 eV to 1.14 eV. The values are in the agreement with those reported for SnS films prepared by CBD [11,38-39,49]. With increase in deposition time the direct forbidden band gap found to decrease from 1.44 eV to 1.32 eV. These values are in the range observed earlier [43]

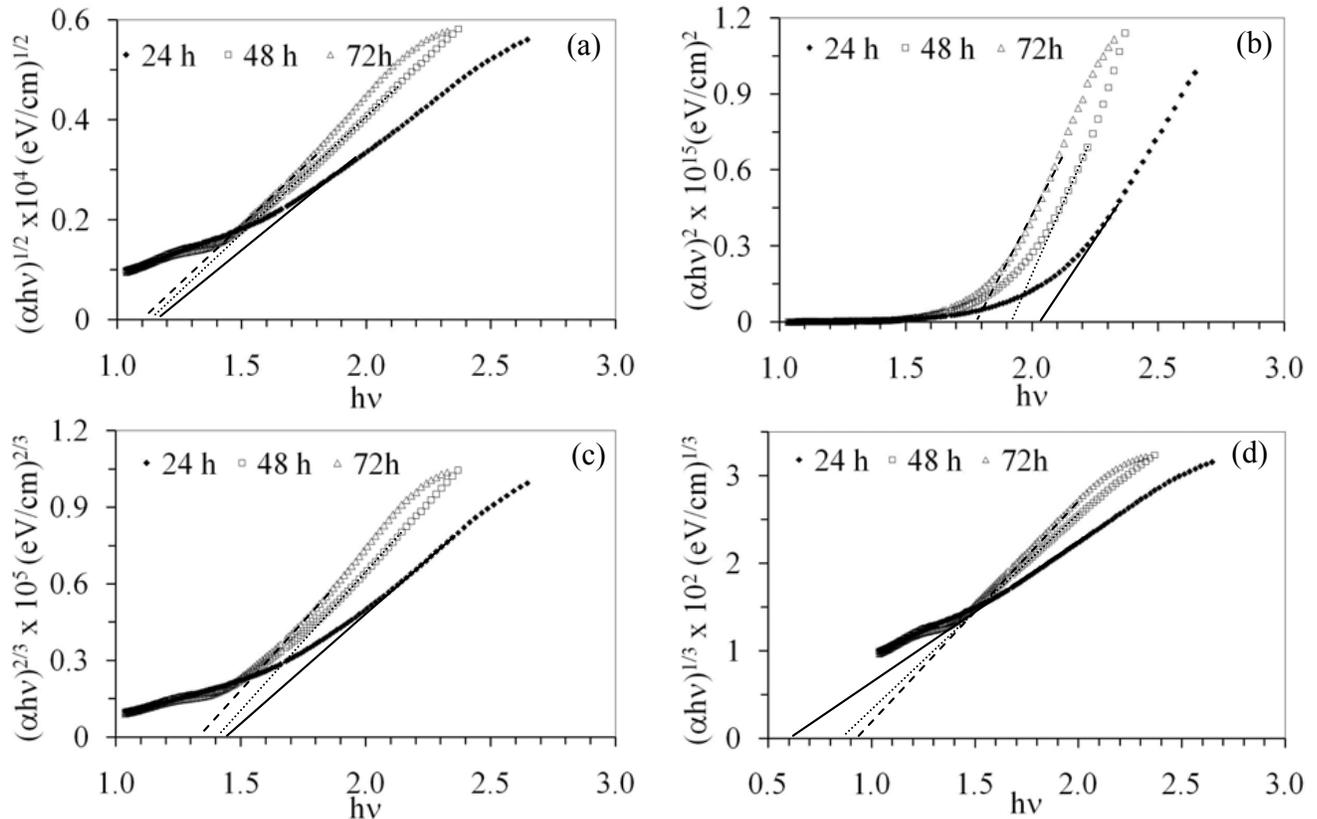


Fig. (6). Spectral variations of (a) $(\alpha hv)^{1/2}$, (b) $(\alpha hv)^2$, (c) $(\alpha hv)^{2/3}$ and (d) $(\alpha hv)^{1/3}$ with $h\nu$ for the SnS films deposited with different deposition times.

but higher than those observed by other researchers [11,49,52] for SnS films deposited by CBD. The direct forbidden gap of the order of 1.7 eV have been reported for SnS films prepared by CBD with orthorhombic [49] and zinc blende structures [11,40,46] and also for SnS films prepared by successive ionic layer adsorption and reaction (SILAR) method [61]. The nature of the variations of $(\alpha hv)^{1/3}$ as a function of photon energy ($h\nu$) as shown in Fig. (6d) indicates that indirect forbidden transitions are less probable in films under investigations. However, indirect forbidden band gap estimated to increase from 0.6 eV to 0.82 eV.

The straight line portions of the curves in Fig. (6b) indicate that direct allowed transitions are dominant in the deposited SnS films. The direct band gap decreased from 2.03 eV to 1.79 eV with increase in deposition time. These values are higher than those reported earlier [37,39,41-42,47,50-51] but are within the range as observed in SnS films deposited by CBD [38] at room temperature and SnS films deposited by thermal evaporation [23-24]. The increase in deposition time improves the crystallinity as well as enhances the film thickness with growth of crystallites of larger size till enough Sn and S ions exist in the solution to support the growth mechanism of the film to continue. This mainly affects the optical absorption which eventually affects the optical band gap of the film. The analysis of the XRD patterns of the films showed a better crystallinity and increase in grain size in the films with increase in deposition time. The difference in crystalline structure of the films deposited at room temperature as compared to those mostly prepared at increased temperature may be the reason for

higher values of the direct band gap. It should be noted that presence of other phases of tin sulfide i.e. SnS₂ ($E_g = 2.44$ eV) and Sn₂S₃ ($E_g = 2.0$ eV) is not found in the deposited films. So the decrease in band gap in these films with increase in deposition time can be attributed mainly to increase in both the grain size and the film thickness with increase in deposition time. For SnS thin films, decrease in band gap with increase in film thickness has been observed several times for films deposited at near room temperature [23-24,38,62]. Use of SnS thin films with the band gap of the order of 1.7 eV as absorber layer deposited by CBD have been reported recently [43]. The CBD films are often nanocrystalline and the most apparent effect of very small crystal size is the increasing band gap due to size quantization. This effect is quite visible to eye if the band gap is in the visible region of the spectrum. The optical spectroscopy is fast and simple pointer to crystal size, since band gap-size correlations have been made for a number of colloids and films [44]. Also with decrease in deposition time the film thickness also decreases. Since thinner film thickness results in larger transmission in the shorter wavelength, the absorption edge shifts to shorter wavelength, thereby leading to larger band gap as seen in this study too.

CONCLUSIONS

Using CBD amorphous and polycrystalline thin films of SnS are deposited at room temperature without using a buffer solution. The influence of different deposition times on thin films of SnS deposited using CBD at room temperature has been studied first time. The XRD analysis of

the films indicates that films deposited at 24h are poorly crystalline (almost amorphous) and the films deposited at 48h and 74h are polycrystalline with orthorhombic SnS structure. The XRD analysis indicates that increase in deposition time has improved the crystallinity of the films. The average grain size is found to increase from ~13 nm to ~28nm with increase in deposition time with film color changes from light yellowish brown to deep chocolate brown. The SEM images show that deposited films are

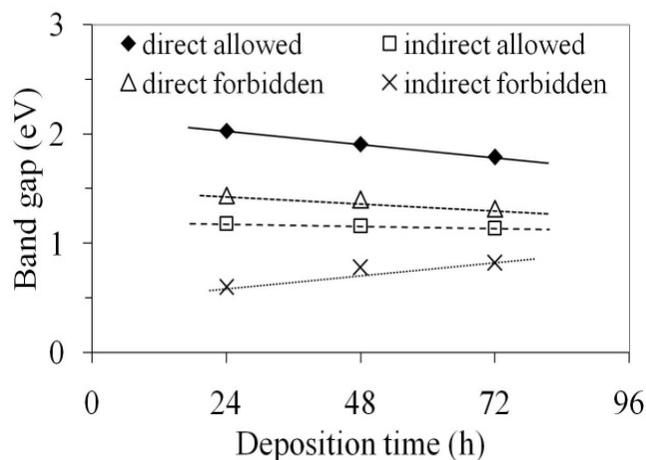


Fig. (7). The variations of band gap with deposition time.

homogeneous and free from any pinholes or cracks with increase in number of crystallites with increase in deposition time. The EDAX report show atomic ration of Sn/S in the range from 0.99 to 1.19 suggesting that films deposited are almost stoichiometric. The optical absorption spectra of the films show that direct allowed transitions are dominant in the films. The allowed direct band gap is found to decrease from 2.03 eV to 1.79 eV with increase in deposition time and is mainly attributed to increase in film thickness with increase deposition time. The higher values of the band gap are attributed to small grain size and to the room temperature deposition as other phases of SnS are not found in the film. The SnS films deposited by CBD with the values of band gap obtained are suitable for absorber layers in solar cells. Work is in progress to investigate in detail the electrical properties of the films. The crystalline and optical property of the films seems to be influenced by the deposition time. The SnS films suitable for photovoltaic structures can be prepared using a cheap, safe simple CBD technique at room temperature.

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CONFLICT OF INTEREST

None declared.

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