Effect of annealing on structural and optical properties of SnS$_2$ thin films grown by thermal evaporation and post sulphur annealing technique

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Abstract. Recently, two-dimensional layered semiconductors caught attention due to their tuneable thickness dependent properties and its optoelectronic device applications. This paper reports the effect of annealing temperature and annealing duration on structural, compositional and optical properties of tin disulphide thin films (SnS$_2$) fabricated using a bi- stage process. The process involves thermal evaporation of metallic tin precursor films and post sulphur annealing process in a non-vacuum furnace. The annealing temperatures ranged from 300 $^\circ$C to 500 $^\circ$C while annealing time varied from 0.5 to 3 hours. The annealing at 300$^\circ$C improved the crystallinity of SnS$_2$ thin films. Raman analysis showed a prominent peak at 207 cm$^{-1}$, while at higher temperatures nanocrystalline SnS$_2$ phase is observed. Optical bandgap got reduced as annealing temperature increased and at 300$^\circ$C, the bandgap was 2.7 eV. The above obtained properties of SnS$_2$ opens a pathway for using these films for potential applications.

1. Introduction

Recent studies in the field of flexible optoelectronic and display devices throws light to an innovative class of semiconductors, commonly called as two dimensional (2D) materials. Notable geometrical structure and mechanical properties exhibited by these materials makes them suitable for a wide range of applications in nanoelectronics industry. Since 2004, graphene, the monolayer of graphite, has been the most studied 2D material. The ability of graphene to form atomic sheets with attractive optical, electrical and mechanical properties caught the attention of scientists [1,2]. However, the absence of bandgap and low switching ratios made graphene less suitable for applications in optoelectronic devices. In this scenario, it became a necessity to find semiconductors which possess appreciable bandgap with magnificent electrical and mechanical properties. The demand for new class of 2D materials paved the path for development of other layered materials especially layered metal dichalcogenides (LMCs) [3]. LMC have been identified as a promising group of semiconductors due to possibility of processed in reduced dimension while maintaining appreciably better charge transport. It is observed that layered
materials have better electrostatic control when the dimensionality of the material scales down to atomic thickness[4]. This property is utilized in bendable and wearable electronics which marks its superiority over other organic compounds [5]. Studies suggests that layered metal chalcogenides satisfies the criteria of both the tunable bandgaps as well as better electrical properties [6]. Their peculiarities adopt them in optoelectronic and flexible display device applications.

Two-dimensional materials generally possess strong intra layer covalent bond while the weak Van der Waals bond binds the inter layers enabling the isolation of bulk to single layers [4]. Even though MoS$_2$ takes the dominant position of being the first 2D semiconductor [7] which shows a transition from indirect bandgap in bulk to direct bandgap as it becomes monolayer [8], LMC also opens a novel field of semiconductors which has wider bandgap. SnS$_2$ falls to this class of materials which is basically a non-transition dichalcogenides semiconductor. It is a representative of layered metal sulphides with a bandgap of 2.75 eV [9], which is larger than most of the transition metal dichalcogenides (TMDCs). The wider bandgap has an added advantage on suppressing the short channel effects in field effect transistor (FETs). SnS$_2$ is isostructural with hexagonal cadmium iodide (CdI$_2$) crystal. S-Sn-S forms a stack of triple layer which are bonded together by strong covalent forces and the adjacent triple layers are coupled together by means of weak Van der Waals interactions [10]. This structure enables the peeling out of bulk crystal into different layers. SnS$_2$ poses high absorption coefficient (>10$^4$ cm$^{-1}$) in the visible region [11]. Importance of tin sulphide compounds is that basically they are nontoxic compounds and are abundantly available [12]. Novel fabrication methods for the preparation of SnS$_2$ with good quality and better properties caught the interest of many researchers. Tin disulfide thin films can be obtained by various methods like successive ionic layer adsorption and reaction (SILAR) [13], spray pyrolysis [14], thermal vacuum evaporation [15], plasma-enhanced chemical vapour deposition (PECVD) [16], dip coating [17] etc., each one with its advantages and disadvantages. Recently, SnS$_2$ has proven as an attractive material for its potential applications as a light absorber layer for dye sensitized solar cells, gas sensing and energy storage applications [18,19].

In this paper, we report a simple and cost-effective approach to prepare tin disulphide (SnS$_2$) thin films on glass substrates by thermal evaporation of tin powders as precursor followed by post sulphur annealing process. The influence of annealing temperature and annealing time on crystal structure, chemical composition and optical properties of the films has been examined.

2. Experimental Details

2.1 Growth of SnS$_2$ thin films

Glass substrates were cleaned by sequential ultrasonication for ten minutes each in acetone, isopropyl alcohol and distilled water. Metallic tin (Sn) precursor films were thermally evaporated using tin powders (99.995 % purity) in a vacuum system at a constant current of 40 A. The weight of tin precursor was varied from 0.08 g to 0.2 g. The coating time varied from 2 minutes to 8 minutes as the weight of tin precursor changed. The deposition was followed by annealing of the evaporated tin thin films in the presence of sulfur in a non-vacuum tubular furnace of 8 cm length. During annealing, the sulfur atmosphere was maintained by means of sulfur powder kept inside the tubular furnace. Both ends of the furnace were sealed with ceramic blocks and N$_2$ carrier gas was introduced into the tube using stainless steel pipes. The rate of N$_2$ gas flowing through the furnace was controlled by a needle valve. Sulfur powder (99.95% purity) was kept in alumina crucible at a distance of 10 cm to 20 cm from the center near the carrier gas inlet end of the furnace. Figure 1 represents the schematic diagram of annealing set up. The thermally evaporated tin thin films were kept at two different positions inside the furnace. The samples were loaded on top of alumina boat to elevate the sample to a certain height. The samples were placed at the centre of the furnace. When the furnace attained required temperature, it was held constant for required duration. The temperatures chosen ranged from 300 °C to 500 °C and duration of annealing varied from 0.5 to 5 hours. After the required annealing time was achieved, the samples were cooled slowly by leaving them overnight in the furnace. There was excess sulfur left in the boat.
after the annealing process is completed. Following the sulfurization, thin films were analyzed using different characterization techniques.

Figure 1. Schematic diagram of post sulfur annealing setup.

2.2 Characterization techniques
XRD data was measured using PANalytical (Aeris Research) system with Cu Kα radiation (λ = 1.540598 Å). The absorption was measured by UV-Vis spectrophotometer (Perkin Elmer Uv/Vis Lambda 365 double beam spectrophotometer) in the wavelength range of 190 - 1100 nm, and their optical bandgaps were estimated from the absorbance data. Raman analysis of the samples was done using Raman spectrometer (HORIBA JOBIN YVON Lab RAM HR) with Argon ion laser (514.5 nm) having a spectral resolution of 0.3 – 1 cm⁻¹.

3. Results and Discussions
Processing temperature of 2D materials is crucial for different device applications. Low temperature processing is fairly recommended for the sensors and transistor applications, especially on flexible substrates. We deposited SnS₂ films at comparatively low temperature and post sulfur annealing treatment was done to improve the phase purity as well as crystallinity of SnS₂ thin films.

3.1 Structural Characterizations

Figure 2. (a) Diffraction patterns of samples annealed at various temperatures for one hour at centre of the furnace. (b) Diffraction patterns of samples, kept at the centre of the furnace at 300°C for different durations.

3.1.1 X-Ray Diffraction Analysis. Figure 2(a) shows the diffraction patterns of the films grown at different annealing temperatures. The tin disulfide films exhibited hexagonal structure similar to that of the mineral Berndtite. The diffraction patterns were indexed using ICDD file no 023-0677 [20]. The strongest peak at annealing temperature 300 °C indicates that the SnS₂ film is preferentially oriented along the (101) plane. Gedi et al [21] reported similar results and many other research groups also supports this result [22]. The integral intensity ratio of SnS₂ to SnS obtained from XRD patterns is
greater than unity for sample annealed at 300 °C for 1 hour. As the annealing temperature increased, mixed phases were formed along with SnS$_2$ phase which is in accordance with the results reported by Reddy et al [23]. Reports reveal that as the annealing temperature increases, Sn loss occurs in tin sulfide films. This is attributed mainly to the volatile nature of tin phase and hence they get decomposed according to the reaction mentioned below. [24]

$$2SnS_2 \rightarrow Sn_2S_3 + S \quad (1)$$

$$Sn_2S_3 \rightarrow 2SnS + S \quad (2)$$

Figure 2(b) shows the diffraction patterns of the films grown at 300°C for different duration of annealing time. 30 minutes annealing resulted films with mixed composition which changes to dominant SnS$_2$ phase when the annealing time increased to one-hour duration. But as the annealing time was further increased to higher span, presence of the mixed phases again increased. The formation of SnS was noted as the annealing time increased and it is mainly due to re-evaporation of sulfur from the films. Since the furnace used for annealing was a non-vacuum system, the samples contained presence of SnO phase also. Thus, for samples which were annealed beyond 300 °C, the presence of SnS and SnO phases were detected. It has been reported that increase in sulfurization temperature favors the reaction of Sn and S phases to form SnS [25]. Even if excess sulfur is present in the furnace, annealing at temperatures higher than 350 °C could lead to high sulfur deficiency in the layers. The presence of mixed phases in the x ray diffraction patterns indicate that the post annealing process done in the furnace could not sulfurize the tin samples completely. Even if the ambient atmosphere of sulfur was provided inside the tubular furnace, the presence of oxygen added the oxide impurity along with the sulphide phases. Raman result also supports the formation of traces of other tin sulphide phases at higher annealing temperatures. In order to know more about the sub phases, Raman spectroscopy was also done.

3.1.2 W-H plot Analysis. Figure 3 shows the W-H plot analysis. Crystallinity variation in the film is manifested through the broadening of diffraction peaks. Peak width analysis helps to calculate the crystallite size and lattice strain. There are many reasons for strains in a crystal. Studies show that stress arises at the walls of grains and also during sintering or annealing treatments [26]. Lattice strain and crystallite size affects the peak width as well as the intensity and results in shifting of 20 values. Crystallite size is usually calculated using Debye Scherrer formula, while the strain is calculated using Williamson formula. Hence by finding the FWHM of diffraction peaks from the x-ray diffraction, crystallite size and strain of the film can be evaluated. The Bragg peak breadth has a combined contribution from instrument and sample dependent effects.

![Figure 3. W-H plot for different annealing time.](image)

In Williamson-Hall method, line broadening $\beta_D$ of a Bragg reflection $(h k l)$ originating from the small crystallite size follows Scherrer equation $\beta_D = \frac{0.94\lambda}{D \cos \theta_{hkl}}$. Here $\lambda$ is the X-ray wavelength, $\theta$ is the Bragg
angle and D is the effective crystallite size normal to the reflecting planes. Also, the strain induced broadening $\beta_\varepsilon$ is given by the Williamson formula as

$$\beta_\varepsilon = 4\varepsilon \tan \theta_{hkl}.$$ 

Here $\varepsilon$ is the root mean square value of the macrostrain. Assuming that the particle size and strain contributions to line broadening are independent of each other, the observed line breadth is calculated by adding the Scherrer equation and Williamson equation.

$$\beta_{hkl} = \beta_D + \beta_\varepsilon$$ (3)

$$\beta_{hkl} = \frac{0.94 \lambda}{D \cos \theta} + 4\varepsilon \tan \theta$$ (4)

On re-arranging the equation (4),

$$\beta_{hkl} \cos \theta = \frac{k\lambda}{D} + 4\varepsilon \sin \theta$$ (5)

$\beta \cos \theta$ was plotted with respect to $4\sin \theta$ for the peaks of SnS$_2$ annealed at different durations. Strain is obtained from slope and particle size is calculated from y-intercept of the fitted line. From the graph, strain obtained is $1.5 \times 10^{-2}$ and studies show that positive slope is mainly due to tensile strain [27]. The average particle size calculated from the y-intercept of W-H plot is found to be around 68 nm.

Figure 4: (a) Raman analysis of samples annealed at different temperatures for 1 hour. (b) Raman analysis of samples annealed at 300 $^\circ$C for different durations

3.1.3 Raman Analysis. Raman spectroscopy is a versatile experimental tool to analyse the 2D material structural properties which mainly includes identification of crystal polytype. Smith et.al reported the Raman spectra of different polytypes of SnS$_2$ [28]. Figure 4(a) is the Raman spectra of SnS$_2$ films annealed at different temperatures for a span of one hour. SnS$_2$ has two vibration modes named as $E_g$ which is doubly degenerate and $A_{1g}$ which is singly degenerate active mode. In $A_{1g}$ active mode, the two sulfur atoms get displaced out of phase parallel to c-axis with respect to each other keeping the Sn atom stationary while $E_g$ mode arises due to the in-plane vibration mode of S-Sn-S of 2H SnS$_2$ [29]. Reports assign the peak at 311.5 cm$^{-1}$ to the $A_{1g}$ phonon mode of 2D SnS$_2$ crystals (30). According to the group theory analysis given by Lucovsky et al. [31], 311.5 cm$^{-1}$ peak corresponds to the $A_{1g}$ mode of nanocrystalline SnS$_2$ while $E_g$ phonon mode at 207 cm$^{-1}$ corresponds to bulk SnS$_2$ crystals. The dominance of $E_g$ peak over the $A_{1g}$ peak indicates that the bulk SnS$_2$ crystals are formed. It is reported that there is a disappearance of $E_g$ peak due to the formation of nanocrystals of SnS$_2$ [29]. Here, as the annealing temperature increased, the $E_g$ peak corresponding to 207 cm$^{-1}$ disappeared while $A_{1g}$ peak corresponding to 311.5 cm$^{-1}$ peak appeared. Raman analysis also suggests the presence of traces of SnO and SnS which supports the results obtained from XRD. Figure 4(b) shows the Raman spectra of samples annealed at different durations at annealing temperature of 300$^\circ$C. The spectra show bands at 109 cm$^{-1}$, 163 cm$^{-1}$ and 207 cm$^{-1}$. Raman shift peaks at 109 cm$^{-1}$, 163 cm$^{-1}$ and 207.2 cm$^{-1}$ has been identified as SnO ($B_{1g}$ mode), SnS ($B_{2g}$ mode) and SnS$_2$ ($E_{2g}$ mode) respectively (28). The peak at 207 cm$^{-1}$ confirms the formation of SnS$_2$ compound at 300$^\circ$C for a duration of one hour [32].
3.2 Optical Studies.
The optical properties of the films were studied from the transmittance spectra of the films recorded in the wavelength range 190-1100 nm. The absorption coefficient $\alpha$ and optical bandgap $E_g$ are related by the Tauc relation (33): $\left(\alpha \nu\right)^m = A_n(\nu - E_g)$ [6]

where: $A_n$ is an energy independent constant, the exponent $m$ depends on the nature of the transition type. $m = 2$ for a direct allowed transition and $m = \frac{1}{2}$ is for an indirect allowed transition. The direct bandgap $E_g$ of the samples can be obtained by extrapolating the straight-line portion of the $(\alpha \nu)^2$ vs $\nu$ plot to the energy axis which is shown in the figure 5a. The bandgap is found to be decreasing as the annealing temperature increased which is due to the change in the stoichiometry of the deposited films [34]. The variation of bandgap with annealing temperature is shown in figure 5b. The variation in the bandgap with the increase in the annealing temperature is showing a gradual decrease. This nature of optical bandgap is due to the change in the stoichiometry of thin films. XRD and Raman results confirmed the formation of mixed phases as the temperature increased. This trend is manifested in optical studies also through gradual lowering of bandgap.

4. Conclusion
Tin disulfide thin films have been prepared by physical evaporation of Sn powder and by post sulfur annealing at various temperatures from 300 °C up to 500 °C. XRD results confirmed the formation of SnS$_2$ thin films at 300 °C with hexagonal structure. As the annealing temperature increased, the formation of mixed phases was noted in XRD results. Raman studies of annealing time variation showed SnS$_2$ phase along with traces of SnS and SnO. But as the annealing temperature increased, the absence of $E_g$ peak points to the formation of SnS$_2$ nanocrystals. The W-H plot was analysed and strain is obtained from the slope of the graph. Strain is found to be 1.5 $\times$ 10$^{-2}$ and average particle size obtained from the W-H plot is 68 nm. The SnS$_2$ films showed direct bandgap which was found to vary in the range 2.7 eV to 2.3 eV gradually as the annealing temperature increased. This variation in the bandgap is due to the formation of mixed phases. Also, as the annealing temperature increased, there is a tendency for the formation of SnS$_2$ nanocrystals. From the experimental results, it can be concluded that SnS$_2$ can be opted for the fabrication of channel layer in nano electronic and optoelectronic devices.
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