Study of antimony sulphide thin film grown from non-toxic solutions

A thesis submitted

in partial fulfilment of the requirement for

the award of the degree in

Master of Science

in

Physics

Submitted by:-

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CERTIFICATE

This is to certify that the report entitled **"Study of Antimony Sulphide Thin Films Grown from Non-Toxic Solutions"**, submitted by **Aarushi, Roll No. 301704001,** in partial fulfilment of requirements for the award of degree M.Sc. in Physics from School of Physics and Materials Science, Thapar Institute of Engineering and Technology, Patiala is a record of candidate own work carried out by her under my supervision and guidance. The work reported here has not been submitted, either in part or in full, for the award of any other degree in other institute or university.

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Dedicated

To

My Family

DECLARATION

I hereby declare that the thesis report entitled **"Study Of Antimony Sulphide Thin Films Grown From Non Toxic Solutions"** submitted by me in partial fulfilment of the requirements for the award of degree of **M.Sc**. in **Physics** from **School Of Physics And Materials Science** is a record of bonofide thesis report carried out by me under the supervision of **Dr. Bhaskar Chandra Mohanty,** Associate Professor, School of Physics and Materials Science, Thapar Institute of Engineering and Technology, Patiala. I further declare that work embodied in this report has not been and will not be submitted, either in part or in full, in any other institute or university for award of master and science or any other degree.

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ABSTRACT

Sb_2S_3 is an earth abundant and cost effective absorber material having an optical bandgap of 1.7 eV and a high absorption coefficient ~10^4 cm^{-1}. In this work, it is attempted to prepare these films by a simple, cost-effective non-toxic solution based method, such as spin coating. Antimony chloride, thiourea were used as precursor source for Sb and S, respectively and 2-methoxyethanol was used as solvent in the deposition process. The effect of drying temperature and post-deposition heat treatment temperature on the as-deposited films prepared at room temperature was studied. The phase, surface morphology and optical properties of the samples were investigated by X-ray diffraction, field emission scanning electron microscopy and UV-visible spectroscopy, respectively. When the as-deposited films were dried at 150 ˚C followed by sulfurization at 250 ˚C (less than the crystallization temperature of Sb_2S_3), $Sb_{9.5}S_{18}$ single phase was obtained. Samples grown at all other conditions were amorphous in nature as revealed by a broad hump in the XRD patterns.

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Chapter 1
INTRODUCTION

Over the years, an increase in the population has increased the energy demand. The conventional sources such as coal, petrol, fossil fuels have served the mankind so far. However, these sources of energy are getting depleted and won't last long. Furthermore, combustion of the fossil fuels results in the production of carbon dioxide as a by-product leading to global warming and environmental threat. Consequently, renewable sources like solar energy, wind energy, geothermal energy, which are clean and produce electricity without emission of any hazardous gasses, have drawn significant research attention.[1] Photovoltaics – a technology to directly convert solar energy to electricity – has become quite popular over last two decades.[2] The photovoltaic devices in the form of solar cells and solar panels absorb solar radiation and generate electricity in an eco-friendly manner.[3] The efficiency of the solar cells is strongly dependent on the absorber layers having large absorption capability. Silicon wafers and thin films of organic and inorganic materials have been used as absorber layer in solar cells.[4] Owing to the great progress in thin film fabrication and low material consumption, thin film absorber layers have been more recently widely studied for developing cost effective and efficient solar cells.

1.1 Solar cell

Solar cell is a p-n junction diode made from semiconductor materials, which converts solar energy into electrical energy as shown in **Fig. 1.1.**[5] In dark, the p-n junction is in thermal equilibrium. The equilibrium, however, is disturbed when sun light is made incident on it. The absorption of photons produces electron - hole pairs in the depletion region and significantly increase the density of electrons in the p-region and hole density in the n-region. The p and n layers are connected to a load by an external circuit to make electrons flow between two electrodes and to produce photocurrent.

The solar cell assembly is made up from many layers consisting an anti-reflecting layer, a buffer layer and an absorber layer. The performance of solar cells mainly depends on the type of absorber materials used. Si wafers are the first generation absorber material which produced high quality devices. The second and third generation solar cells are produced from thin films and polymers (organic), respectively. Among them, the thin film solar cells are proved to be

more durable, efficient and cost-effective. So, they are more likely to replace the conventional Si wafer based solar cells.

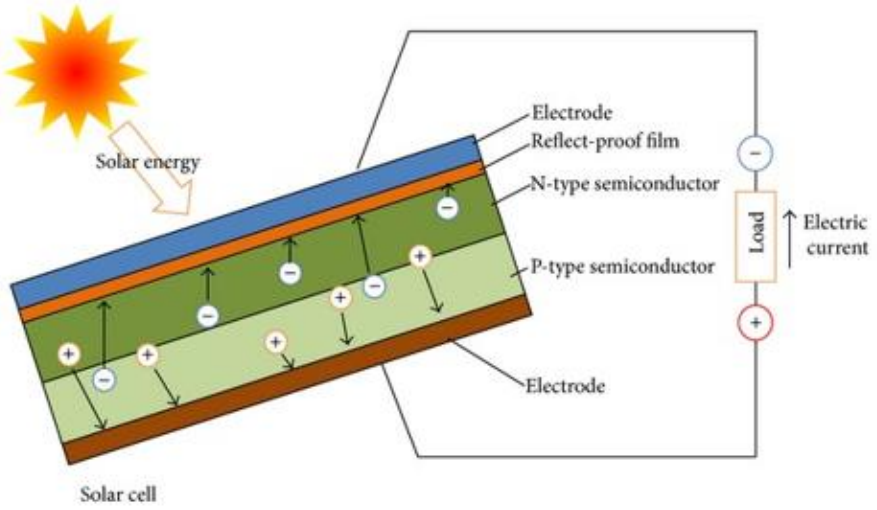


Figure 1.1: Schematic of a solar cell.[5]

The output can be increased by connecting several single cells in series or parallel forming a module. For example, if 20 cells having output of 0.5 V are connected in series, an output of 10 V can be produced from the module. Even the modules are interconnected to form a continuous solar array to increase the absorption area and hence the output voltage.

1.2 Thin film solar cells

Thin film solar cells are second generation solar cells having thickness in a few microns range.[6] Conventionally the thin film solar cell use inorganic semiconductors as the layers for fabricating the p-n junction. The highly efficient solar cells can be fabricated using materials having high absorption coefficient (10^4 – 10^5 cm^{-1}) with optimum thickness.[7] The optical bandgap of the absorber material should be less than the incident photon energy so that maximum absorbance of photons takes place in the upper valence band of the material. If the light energy is comparatively much higher than the bandgap value, the excited electron lifetime deficits and it makes transition to valence band rapidly resulting in energy losses as heat. **Figures 1.2a** shows the distribution of sunlight on the earth surface. As seen from the figure, the greatest value of the photons reaching surface is observed in wavelength range 500-700 nm, suggesting that an ideal absorber layer should have the bandgap in the range of 1-1.7 eV. **Figure 1.2b** shows the variation of reported cell efficiency with bandgap (i.e., of different absorber

materials), supporting the observation that the semiconductors with bandgap in 1-1.7 eV are the most efficient ones for use as absorber material in thin film solar cells.

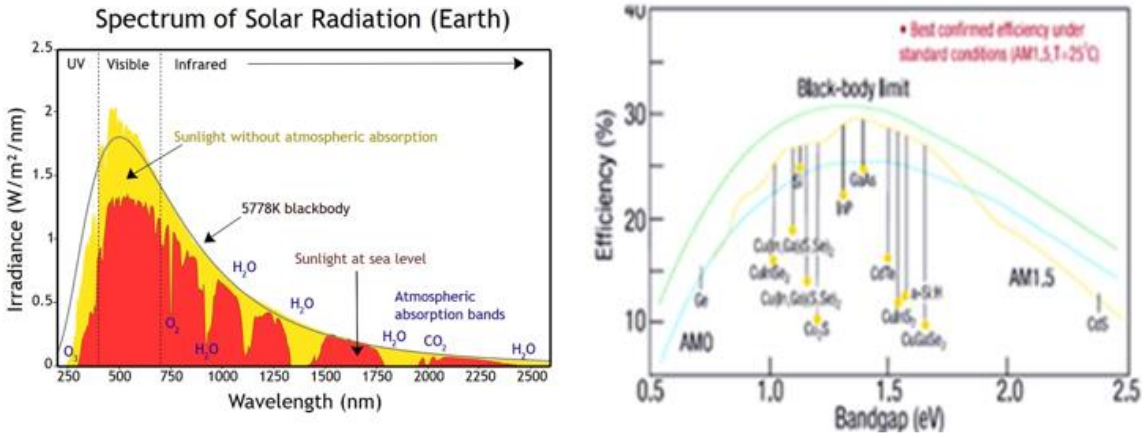


Figure 1.2: (a) Solar radiation spectrum recognized at the earth's surface (b) Reported cell efficiency variation with the bandgap of different absorber materials.[8]

1.2.1 Evolution of absorber material for thin film solar cell

Silicon based cells

Silicon is earth's abundant nontoxic element and absorbs broad range of light spectrum. The maximum efficiency reached 29% for commercially used crystalline silicon, 14-15% for amorphous silicon and nearly 20 % for multi crystalline silicon used in thin film solar cells. The life time of crystalline silicone solar cells is 25+ years.[9]

Cadmium telluride (CdTe)

CdTe is a p- type absorber material with bandgap value 1.5 eV, having high absorption coefficient and chemically stable. It is the second most commonly used solar cell in PV market. The growth in CdTe solar cell technology can be accounted by rise in efficiency from 10 to 20% in 30 years. [10]

$CuInSe_2$ (CIS) and $Cu(In_{1-x}Ga_x)Se_2$ (CIGS)

CIS is a ternary polycrystalline compound with high absorption coefficient (10^5 cm^{-1}). By replacing some of In by Ga i.e., $Cu(In_{1-x}Gax)Se_2$ the bandgap of the material can be modulated from 1.1 to 1.7 eV. The $Cu(In_{1-x}Gax)Se_2$ solar cells have yielded the highest efficiency of 22.8% which is comparable to crystalline silicon wafer based solar cells.[11]

Cu_2ZnSnS_4 (CZTS)

CZTS is a p-type I_2–II–IV–VI_4 quarternary semiconducting compound have bandgap value 1.5 eV and good optoelectronic properties which make it suitable candidate for absorber material. Its constituent elements are less toxic and earth's abundant. Till date the maximum PCE of 12.6% was reported for CZTS solar cell.[12]

Although the Si based solar cells have dominated the PV market, the fabrication process is still very complex and costly. On the other hand, due to the rare abundance of In, Ga and Te on surface and toxicity of Cd, the CIGS and CdTe technology is limited to a manufacturing capacity. The limitations with these materials provoke an increase in exploration. Now a days most research and studies are going for developing materials which are abundant on earth and eco-friendly. Metal chalcogenides have emerged as a better choice and these are based on sulfides, selenides and tellurides rather than oxides. Among them Sb_2S_3 a metal sulphide is more pronounced because of its good photovoltaic properties.[13]

Antimony sulphide (Sb_2S_3)

Sb_2S_3 is a group V-VI compound and has emerged as a promising absorber material with earth abundant constituent elements which are nontoxic. It has a high absorption coefficient (> $10^4 cm^{-1}$) with tuneable bandgap of 1.7-1.8 eV yielding maximum theoretical PCE of 40%.[13] **Figure 1.3** shows the comparison of natural abundance of different materials used in thin film solar cells. This work concerns growth of Sb_2S_3 thin films by a cost-competitive solution method.

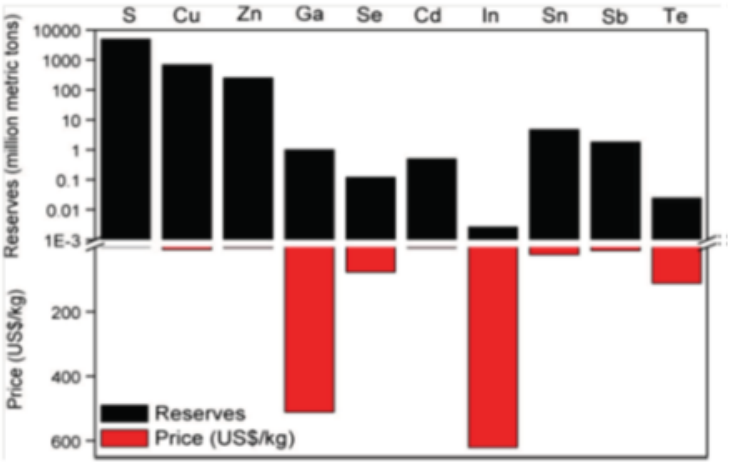


Figure 1.3: Comparison of natural abundance and price of different materials.[14]

1.3 Basic Properties of Sb_2S_3

1.3.1 Crystal structure

Sb_2S_3 crystallizes in orthorhombic space group (Pnma) as shown in **Fig. 1.4a.**[15] **Figure 1.4b** [16] shows the atomic arrangement along [010] direction. $(Sb_2S_3)_{2n}$ is the basic building block for Sb_2S_3 forming continuous chain. The two parallel chains are separated by Sb $5s^2$ orbital and linked by weak forces. Both Sb atoms are in +3 state where Sb1 atoms are covalently bonded to three S atoms (solid lines) forming a trigonal pyramidal geometry and Sb2 atoms are connected to three S atoms by covalent bonds and bonded to two S atoms by weak Vander wall forces (dashed lines) forming tetragonal geometry. The two chains are separated by red dashed lines shown in **Fig 1.4b**.

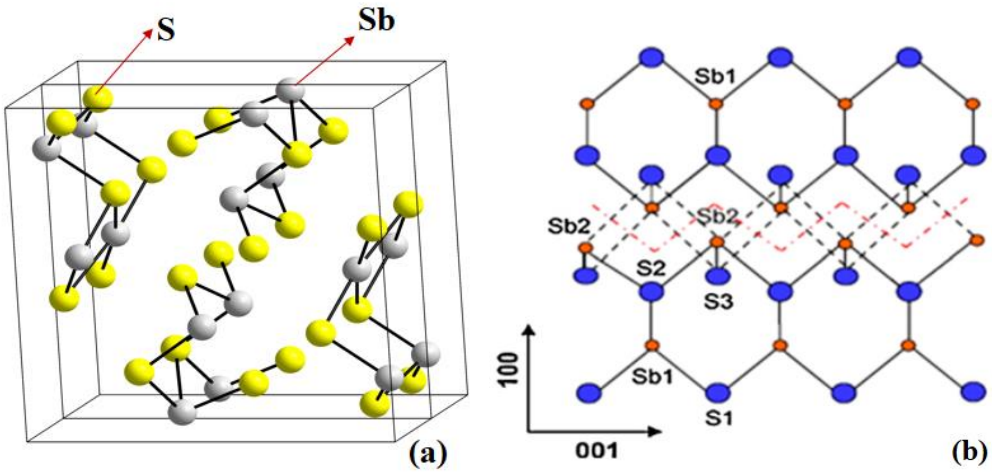


Figure 1.4: a) Crystal structure of Sb_2S_3 b) Atomic arrangement of Sb_2S_3 along [010] direction.

1.3.2 Electronic Properties

Sb_2S_3 has multivalley electronic structure in which electron density in upper valence band is mostly filled by Sb 5p, 5s and partly by S 3p orbitals whereas Sb 5p with little addition of S 3p orbitals forming lower conduction band. As shown in **Fig. 1.5** the maxima and minima of crystal orbitals of Sb and S occur at same momentum state, hence Sb_2S_3 is a direct semiconductor. The optical bandgap is found to be 1.76 eV. The presence of nonbonding electrons in valence band of Sb makes Sb_2S_3 favourable for electrical conductivity of 0.2×10^{-6} $(ohm\ cm)^{-1}$and optical absorption coefficient of 10^4- 10^5 cm^{-1}. [13, 16]

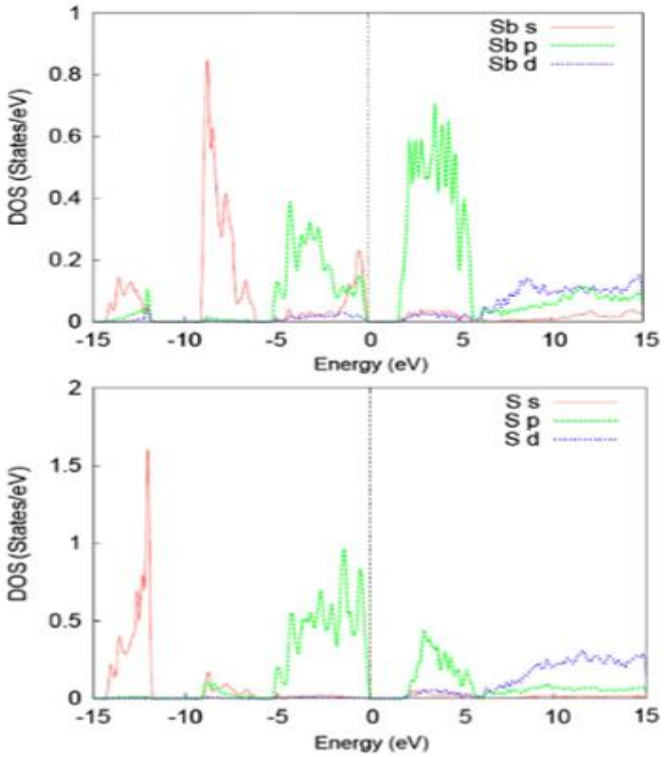


Figure 1.5: Angular momentum distribution of density of states in Sb_2S_3. [17]

1.4 Literature review on Sb_2S_3 thin film

In literature, one can find a number of methods used for the fabrication of Sb_2S_3 thin films. The non-vacuum processes especially the ones based on solutions are considered to be very attractive for mass production. The solution based methods don't require large capital investments as the vacuum based techniques do. Furthermore, process steps are simple and cost effective. In this view, this work aims at preparing Sb_2S_3 thin films by a solution method. In the followings, a brief literature review in the Sb_2S_3 thin films prepared by the solution methods is given.

In 1992, Savadogo et al. prepared Sb_2S_3 thin film from chemical bath deposition (CBD).[18] By optimizing the process conditions, they observed that grain size increased from 0.12 to 0.82 µm when annealed at 300˚C for 1h in N_2 atmosphere. They observed that Sb_2S_3 had an indirect bandgap of 1.86 eV, which was decreased to 1.74 eV with an incorporation of Silicotungstic acid during reaction which has led to the photoconversion efficiency (PCE) of 3.9%.[18] In 1993, the same group prepared n- Sb_2S_3 chemically under similar conditions at 350˚C which showed a reduced bandgap of 1.72 eV. An increased PCE from 3.9 to 5.19% was observed.[19]

In 2001, Salem et al. studied the effect of deposition time on film prepared by CBD at low temperature. The XRD results showed that as-deposited film is amorphous in nature. With increase in deposition time from 0.5 to 2.0 h the particle size increased from 20 to 100 nm. Furthermore, the grains became less ordered, inhomogeneous and rough resulting in shifting of the absorption edge to slightly longer wavelength.[20]

In 2002, Lokhande et al. prepared Sb_2S_3 film from solutions by the CBD method on the glass substrates using tartaric acid as a complexing agent. The deposition took place at low temperature (~6˚C). The XRD results confirmed the formation of orthorhombic crystal structure having grain size about 4-5 nm. The grains were randomly oriented and not periodically arranged over the surface.[21]

In 2010, Meherzi et al. prepared Sb_2S_3 thin film from CBD and studied the effect of temperature and deposition time on morphology of the films. From transmission and reflection spectra bandgap value determined to be 2.24 eV for the solution with compositional ratio 0.85 of Sb/S.[22]

In 2014, Choi et al. prepared Sb_2S_3 by CBD and studied the effect on surface morphology by spin coated thioacetamide. They observed that structure of Sb_2S_3 remained same, rather than the impurity phase Sb_2O_3 formed on the surface. Sb_2O_3 was reduced drastically after TA treatment which enhanced the PCE from 5.5 to 7.1% with J_{sc} of 16.1 mA cm^{-2}, V_{oc} of 711.0 mV and FF of 65%.[23]

In 2015, Choi et al. prepared Sb_2S_3 thin film by single step spin coating technique to reduce the drawbacks in film prepared from CBD and studied the effect of controlled compositional ratio of Sb / S in DMF used as solvent. From the FESEM images they observed that 5 spin coating cycles with 1:1.8 molar ratio yielded homogeneous films which can be used as absorber layer. They reported efficiency of 6.4% with V_{oc} of 595.5 mV and J_{sc} of 16.1 $mAcm^{-2}$ when the spin coated film is thermally decomposed at 200˚C in inert atmosphere.[24]

In 2016, Gil et al. prepared Sb_2S_3 thin film using the spin coating technique and studied the film morphology by varying solvent volume, compositional ratio and spin coating cycles. The electrical and photovoltaic properties of Sb_2S_3 were directly related to the compositional ratio. From surface and cross-sectional SEM images, they observed that the solution of volume 20 ml with 1:1 precursor weight ratio and 3 spin cycles yielded thick and uniform film in comparison to the CBD method.[25]

In 2016, Raptis et al. prepared Sb_2S_3 thin film from two methods, i.e., spin coating and CBD. They prepared film with 1: 2 molar ratio of $SbCl_3$: thiourea (TU) and reported that spin coating is the better technique due to ease in handling during the processes. The Sb_2S_3 films

were found to be very light sensitive and had high absorption coefficient with PCE of 3.5%. It was also seen that film annealed in inert atmosphere had less impurities.[26]

In 2017, Sung et al. compared the photovoltaic properties of Sb_2S_3 film prepared from CBD and spin coating techniques. Irregular grains were seen in SEM images of the films prepared by the CBD while smooth grain surface were seen in the spin coated Sb_2S_3 films. The X-ray photoelectron spectroscopy (XPS) confirmed the formation of antimony oxide during CBD while only a single peak was seen in spin coated Sb_2S_3 with higher compositional ratio of $SbCl_3$: TU, confirming the purity of film deposited. Along with this TU/$SbCl_3$ of 2.0 showed the 3.8% of efficiency.[27]

In 2018, Kaienburg et al. compared the Sb_2S_3 film prepared using two different sulphur sources (thiourea and butyldithiocarbamic acid) under different process conditions. From the SEM images they observed that film should be annealed at 265- 300˚C to get pinhole-free crystalline Sb_2S_3 thin films. A PCE of 4.16% is found with Sb-TU and about 5% with Sb-BDC precursor solutions, with max V_{oc} = 611 mv and J_{sc} = 15.2 mA cm^{-2}.[28]

In 2018, Tang et al. synthesized Sb_2S_3 absorber layer from spin coating technique with doping of $ZnCl_2$. They reported that uniform and homogeneous film with PCE of 5.15% can be deposited with compositional ratio 1:3 ($SbCl_3$: TU) and suitable annealing temperature to form crystalline Sb_2S_3 is 270˚C. With 4.8% doping of $ZnCl_2$ increases the efficiency of film from 5.15% to 5.6 - 6.35% with J_{sc} of 16.4 mA cm^{-2}.[29]

In 2018, Li et al. prepared Sb_2S_3 film from spin coating technique using Sb_2O_3, 3-mercaptopropionic acid, and ammonia as precursors due to their low cost and less toxicity. For the uniform crystal growth and to reduce the unwanted reactions to take place at room temperature, the film was processed in nitrogen glove. The carbon free solar cell was formed with maximum PCE of 5.57% at 270˚C.[30]

In 2019, Zheng et al. studied the effect of annealing temperature on the optical properties and morphology of spin coated Sb_2S_3 films. They observed that the increase in annealing temperature from 200 to 300˚C increased particle size from 85 to 115 nm, which had an intense peak at (200) as confirmed by XRD. Optical properties were also improved at reaching temperature 300˚C. A PCE of 1.91% at 300˚C was obtained.[31]

In 2019, Alimoradi synthesized Sb_2S_3 thin films by spray pyrolysis on two different substrates. It is observed that with increase in substrate temperature Sb_2S_3 changes from amorphous to crystalline phase with decrease in optical transmittance. Bandgap was reduced from 1.75 to 1.68 eV when the film is grown on glass substrates rather on fluorine doped tin oxide (FTO) coated substrates.[32]

1.5 Motivation and objective

The brief literature presented above indicates that Sb_2S_3 thin films have been prepared by solution methods with fair success. It is of interest to prepare the films via a simple spin coating using common salts in a single step and at reasonably low temperature. In view of this, the main objective is to synthesize Sb_2S_3 thin films with simple, less expensive and non-toxic spin coating method and study the effects of deposition parameters on the properties of the resulting films.

Chapter – 2

EXPERIMENTAL DETAILS

In this chapter, the experimental process used for the growth of Sb_2S_3 thin films is presented followed by a brief description of different techniques used to characterize the samples.

2.1 Experimental techniques used for the growth of Sb_2S_3 thin film

Among various vacuum and non-vacuum based techniques, solution based techniques are preferred due to low capital investment and better/easier process control. Both CBD and spin coating methods belong to the family of solution processed techniques. Ultrathin Sb_2S_3 layer can be synthesized by CBD as it is based on simple chemical reaction between $SbCl_3$ and $Na_2S_2O_3$ in an aqueous solution; however the formation of antimony oxide, sulphate or hydroxide cannot be neglected.[27] Moreover, this technique requires precise control of substrate temperature which limit the process reproducibility. In the present study, to overcome the drawbacks in CBD method, the films are synthesized by the spin coating method, as it is cheap and easy, and yields films with suitable optical bandgap, surface morphology, carrier concentration and electrical properties.

2.1.1 Spin coating process

Spin coating is a much widely used technique to produce uniform thin film of the order of micrometres and nanometres due to its simplicity and low cost. The two main stages in process that affects the final thickness of film most are the stability of the fluid flow and the evaporation process. In the process, an excess amount of solution is dispensed on the centre of a substrate, which is then rotated at a high speed (typically around 3000 rpm) about an axis perpendicular to the coating area in order to spread the fluid (**Fig. 2.1**). The centrifugal force causes the solution to spread equally on the substrate. Subsequently, the sample is dried to remove the excess solvent through evaporation.[33]

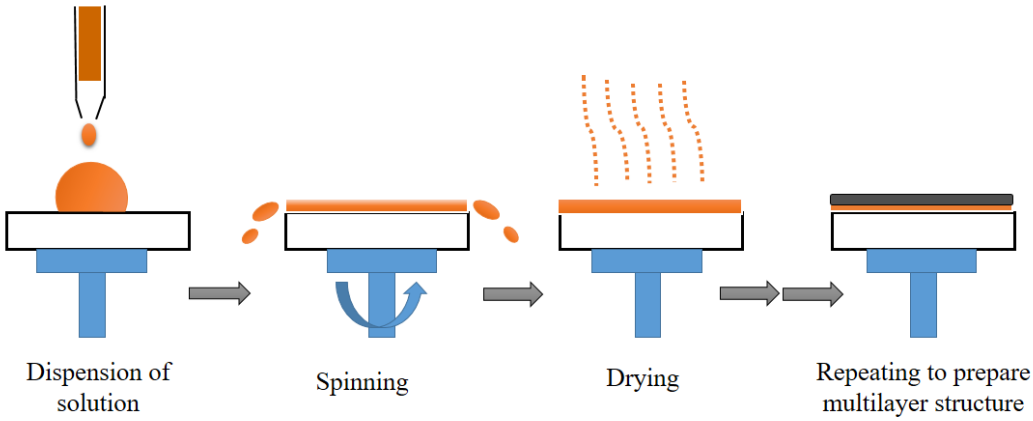


Figure 2.1: Process description of spin coating unit.

The whole coating process is divided into four stages: dispense of solution, spin up, spin off (fluid flow) and evaporation of solvent.

Dispersion of solution: Static dispense and Dynamic dispense are the two common mode of dispense of the solution on to the substrate.

- In static dispense, bigger puddle is dropped at the centre depending on the size of the substrate to coat on the full perimeter.
- Dynamic dispense is a process in which solution is dropped on rotating substrate at slow speed, causing less wastage of solution, will results into spreading the sol over the substrate.

Spin up:

In the spin up process, the substrate is accelerated to its final rotational speed in order to get desired thickness. Due to the rotational motion of substrate, centrifugal force acts on the particles and they get dispersed in order to form uniform film.

Spin off:

This is the third stage in which fluid thinning takes place to increase the viscosity of sample, to cease the flow of fluid. Due to constant rotation, the fluid spread outward increase thickness of deposition more than at centre. Thinning takes until enough solvent is removed, this is more beneficial with volatile solvents.

Evaporation process:

After the spin off stage, once the flow of fluid is ceased the next step is to drying the film to final thinning. Due to evaporation there is loss in solvent, leads in formation of thin film on the substrate. The solvents with fast evaporation rate leads to more viscous solution as flow of solution become slower and concentration increases.

This whole process including four stages, is repeated several time to achieve the desired thickness of film. In general, higher spin speed and longer spin time creates thinner film.

2.1.2 Synthesis of the films

2-methoxyethanol was used as solvent, while antimony chloride and thiourea used as Sb and S source respectively (shown in Fig. 2.2a and b). The Sb-solution was prepared by dissolving 650 mg of $SbCl_3$ in 10 ml of 2-methoxyethanol by continuous stirring for 30 min. After the complete dissolution, thiourea (TU) was added to the Sb-solution in Sb/S molar ratio of 1: 2, and the solution were stirred again for 30 min at room temperature. After the complete dissolution of TU in Sb-solution, the yellowish precursor solution was obtained. **Figure 2.2** shows the photographs of the chemicals used, prepared Sb stock solution and solution after mixing TU in Sb solution.

Glass substrates (25 mm × 25 mm) were sequentially cleaned by ultrasonically in ethanol and isopropyl acetone. The thin film samples were prepared by coating the precursor solution onto glass substrate at 1400 rpm for 1 min by an in-house built spin coater. After every coating the samples were air dried at 130- 150˚C for 3 min, then were sulfurized at 250- 450˚C in furnace for 15 min in Ar atmosphere. **Figure 2.3** shows photographs of film after 3 different stages. **Figure 2.4** shows photograph of tabular furnace used for sulfurization.

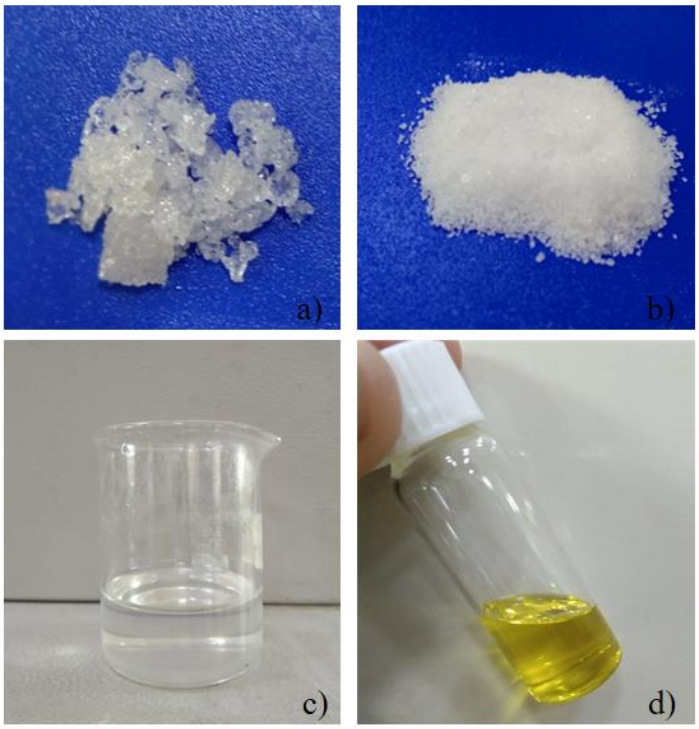


Figure 2.2: (a) Antimony trichloride powder (b) Thiourea powder (c) Antimony trichloride in 2-methoxyethanol (d) resulting Sb-TU solution after addition of TU.

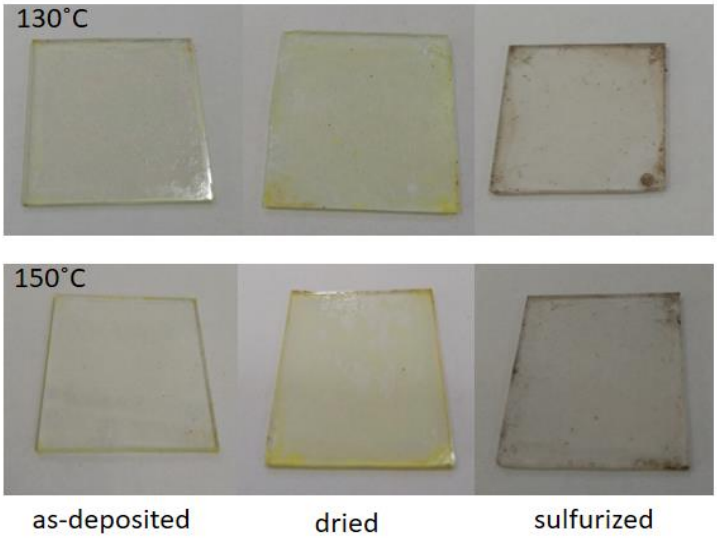
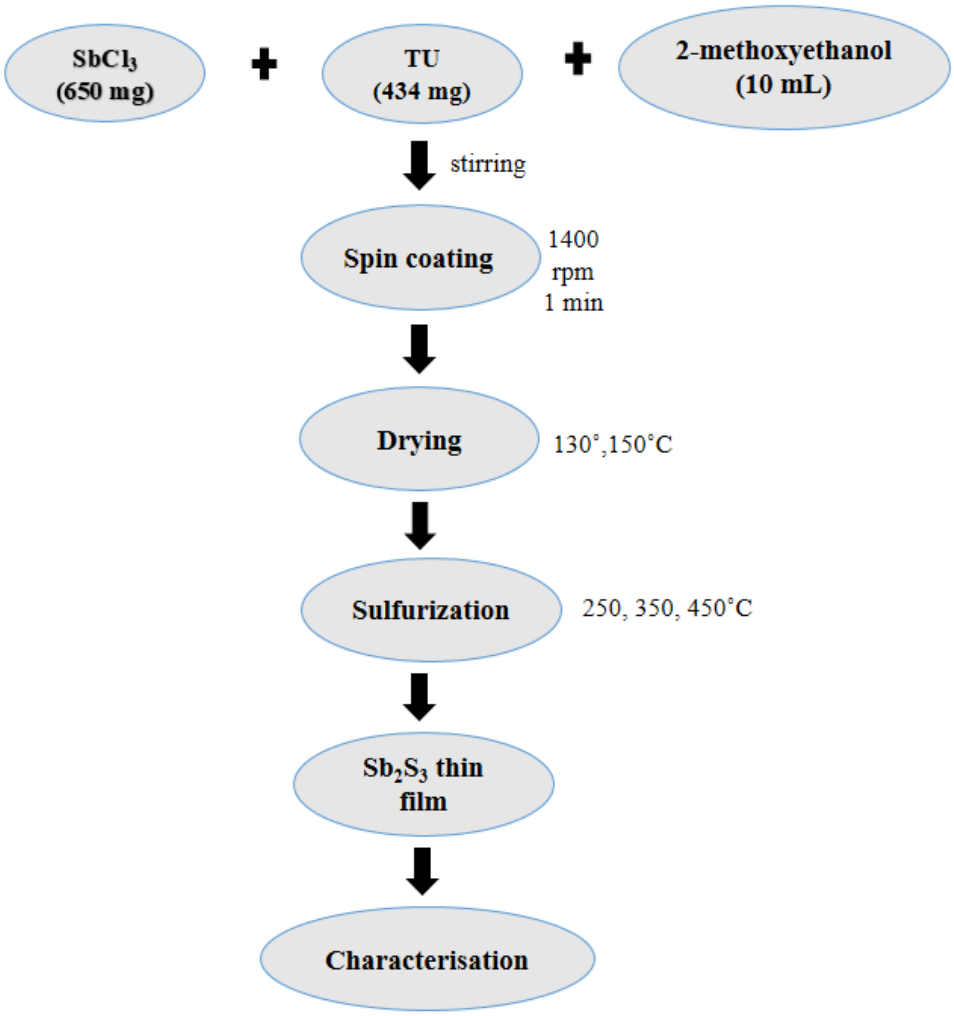


Figure 2.3: Photograph of deposited Sb_2S_3 thin films. Two sets of samples with drying temperature of 130 and 150 °C were prepared.

Figure 2.4: Tabular furnace used for sulfurization

Process flow chart for preparation of Sb_2S_3 thin film



2.2 Characterization methods

X-ray diffraction was carried out in Shimadzu XRD-6000, to study the phase formation and crystal structure of the deposited films using Cu kα radiation (λ = 1.5416 Å). Field emission scanning electron microscope (FE-SEM) system (Hitachi-PU) was operated at an accelerating voltage of 5.0 kV, and was used to study the morphology of exposed sample to determine the structure, grain growth and thickness of the deposited film. UV-visible spectra of samples were recorded using Shimadzu UV-2600 spectrophotometer in wavelength range 250 to 1400 nm. Transmission and reflection spectra are recorded to study the effect of substrate temperature.

Chapter -3
RESULTS AND DISCUSSION

3.1 XRD studies

A representative XRD pattern of a spin-coated film on glass substrates, dried at 150 °C and heat treated at 250˚C in inert atmosphere for 15 min is shown in **Fig. 3.1.** Several peaks can be observed in the pattern indicating the polycrystalline nature of the sample. In the pattern, the observed five peaks at 11.45, 17.15, 22.92, 26.53 and 28.76˚ are identified with (111), (202), (-222), (400), and (-224) planes of monoclinic $Sb_{9.8}S_{15}$ phase, [34] as referenced to the JCPDS file: 01-077-2467. Absence of any peak corresponding to the oxides or elemental Sb/S suggests the phase pure nature of the samples. It is, however, not clear the reason of the stoichiometric deviation from the intended Sb_2S_3.

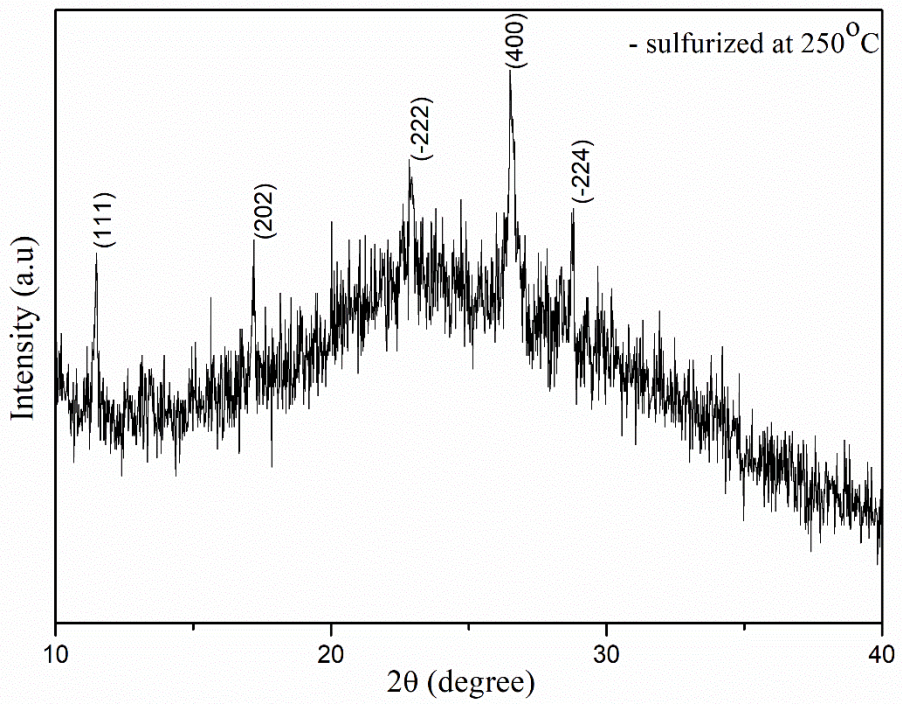


Figure 3.1: XRD pattern of the thin film deposited by spin coating method with sulfurization temperature 250˚C.

On the other hand, heat treatment at higher temperature (i.e., 350 and 450 °C) yielded non-crystalline/amorphous nature of the film, as evidenced from a broad hump in the XRD patterns (shown in **Fig. 3.2**). Reportedly, the lower and upper limit for the crystallization temperature of

Sb_2S_3 is 250 and 300˚C.[28] Thus, due to the heating of films at temperature 350, 450˚C higher than the crystallization temperature, thin film evaporates from the glass substrate, no such peaks of Sb_2S_3 is observed in XRD pattern.

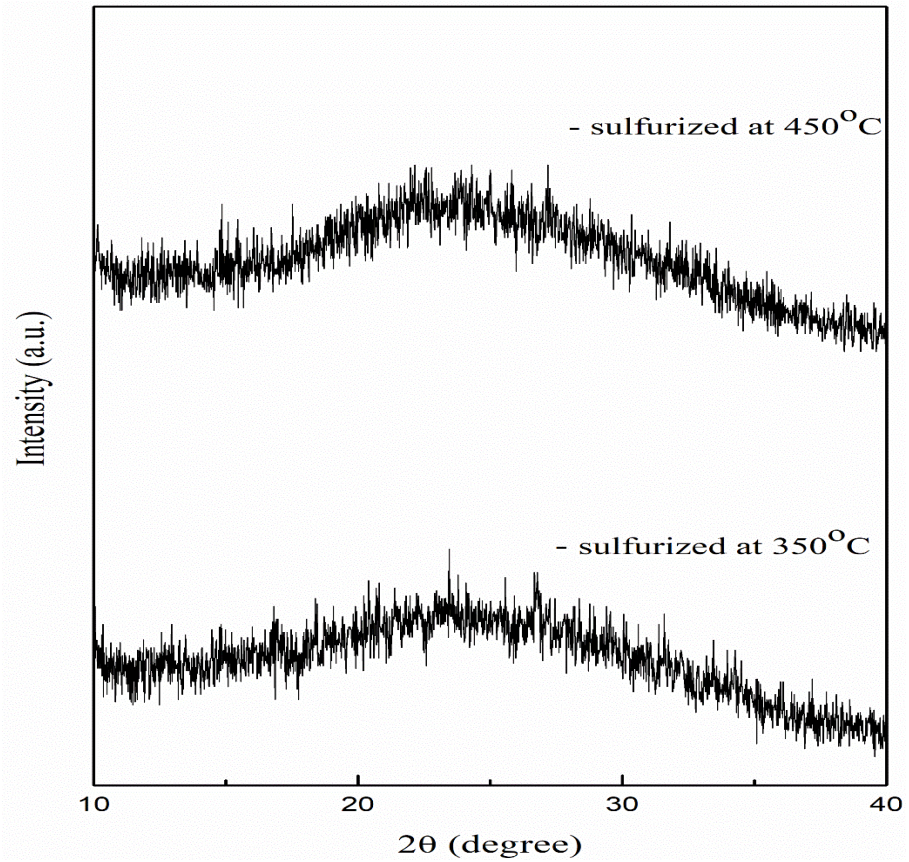


Figure 3.2: XRD pattern obtained from films sulfurized at 350 and 450˚C.

3.2 FESEM studies

The morphology of prepared thin film is studied by FESEM. **Figures 3.3a** and **b** show the surface features of the spin coated films dried at 130 and 150 °C followed by heat treatment at 450 °C. For the film dried at 150˚C, the topographic image revealed the presence of scattered particles on the surface, which may be of Sb_2O_3, as many had reported earlier.[35] As the drying temperature was changed, the morphology of the film changed appreciably. Top view **(Fig. 3.3b)** of the film dried at 130˚C showed considerably uniform, and well distributed compact fine particles with a few pinholes. The cross-sectional view of film at 130˚C in Fig. 3.3c displayed the arrangement of grains with high lucidity.

The presence of scattered particles as defects may be attributed to the ongoing decomposition reaction during evaporation at high temperature which causes formation of oxide particles on surface leaving sulphur vacancy.[36]

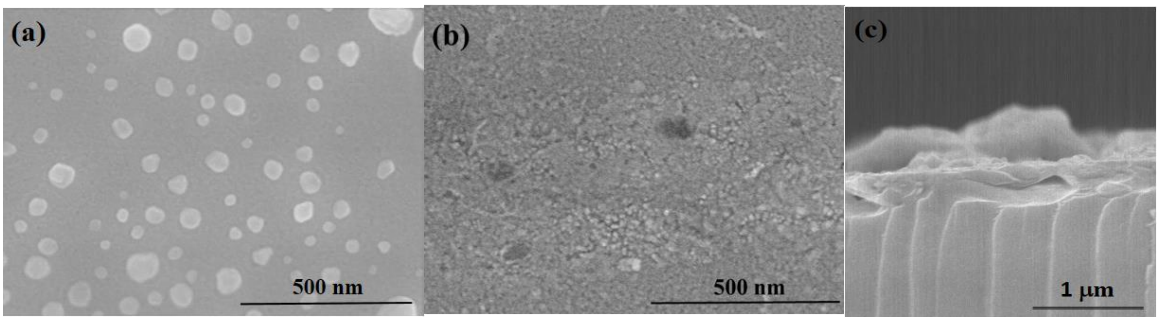


Figure 3.3: FESEM of the deposited Sb_2S_3 thin film at 450˚C (a) top view of spin coating film thermally decomposed at 150˚C, (b) at 130˚C and (c) cross section image of film dried at 130˚C.

3.3 Optical studies

The optical properties of Sb_2S_3 thin film are studied from the transmittance and reflectance spectra in the wavelength range 250-1400 nm. The typical transmittance and reflectance spectra of the films dried at 130 and 150 C followed by heat treatment at different temperatures are shown in **Fig. 3.4.** For the samples prepared at a drying temperature of 130˚C, an average percentage transmission and reflectance is 80 and 10% respectively was observed. On the other hand, drying at 150˚C, both transmittance and reflectance marginally increased to 86 and 12%, respectively. This increase in values is possibly due to the increased transparency in film and also to the presence of loosely bounded particles on the surface of the film which allows maximum UV-visible light to transmit through it.

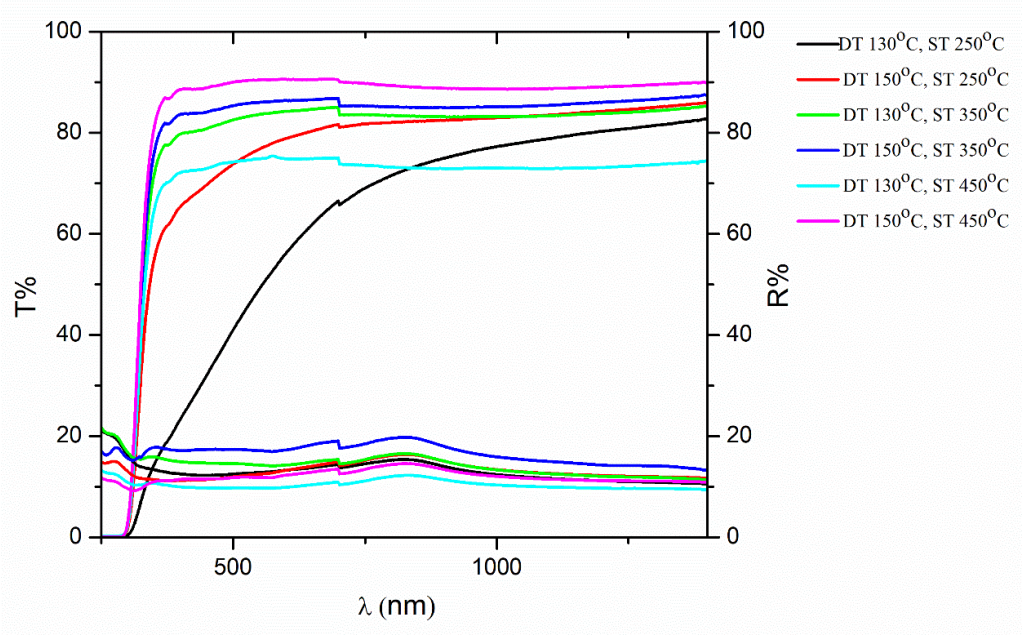


Figure 3.4: Spectra of %T and %R of Sb_2S_3 film grown on glass substrate at different deposition atmosphere. DT stands for drying temperature, while ST stands for sulfurization (post-deposition heat treatment) temperature.

The optical bandgap of the films is estimated from the Tauc formula which relates the absorption coefficient with the bandgap of the material. The Tauc formula is given as $(\alpha h\nu)^n = B(h\nu - E_g)$, where, α is the absorption coefficient at frequency ν, E_g is the optical bandgap of the material to be determined, n is index no. whose value varies as 2, 1/2, 1/3 depending on the type of allowed transition of electron and B is a constant.[37]

A graph $(\alpha h\nu)^2$ vs. $h\nu$ is plotted and bandgap is find by extending the Tauc plot to the energy axis i.e. to zero absorption axis ($\alpha = 0$) and in the present case n = 2 is chosen to characterizes a fine linear fit [38] shown in **Fig.3.5**.

The Tauc plot implies that the film deposited at 150˚C followed by sulfurization at 250 ˚C yielded a bandgap of 3.71 eV. For other samples, since the absorption edge of the thin films is lower than that for the bare glass substrates, analysis of the Tauc plot is not useful. Hence, it is not possible to estimate the bandgap of the samples from the given transmittance and reflectance spectra.

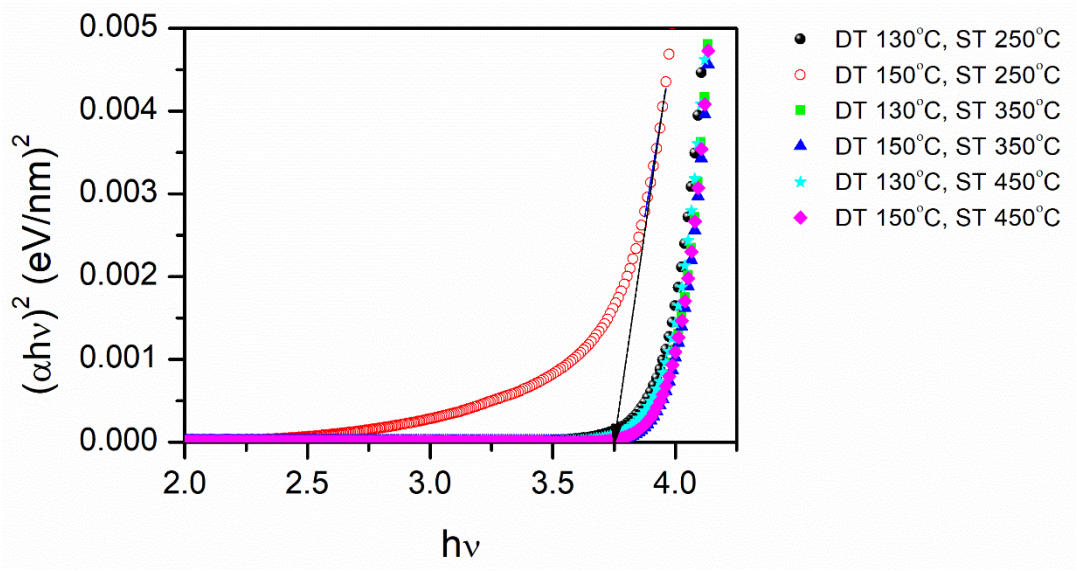


Figure 3.5: Plot of $(\alpha h\nu)^2$ vs. $h\nu$ represent UV-visible absorption spectra for Sb_2S_3 thin film under different conditions. DT stands for drying temperature, while ST stands for sulfurization (post-deposition heat treatment) temperature.

Chapter-4
CONCLUSION

It was attempted to prepare Sb_2S_3 thin films from the spin coating technique from a non-toxic solution on glass substrates. After spin coating, the samples were dried at 130 and 150 °C followed by a post-deposition heat treatment at various temperatures ranging from 250 to 450 °C. The structure, morphology and optical properties of films were characterized using XRD, FESEM and UV-visible spectroscopy, respectively. It was found that the properties of the films is strongly dependent on both drying and post-deposition heat treatment temperatures. When the as-deposited films were dried at 150˚C followed by sulfurization at 250 ˚C (less than the crystallization temperature of Sb_2S_3), $Sb_{9.5}S_{18}$ single phase was obtained. Samples grown at all other conditions were amorphous in nature as revealed by a broad hump in the XRD patterns. The FESEM results revealed the presence of Sb_2O_3 particles on the sample surface for the film deposited at 150˚C while a uniform and well distributed grains were present at 130˚C with a few pinholes. The film grown by drying at 150˚C and sulfurized at 250 ˚C showed an optical bandgap of 3.71 eV, which is larger than the reported value.

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