Solution-Processed $CuSbS_2$ Thin Films for Solar Cell Application

A thesis submitted

in partial fulfillment 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 **"Solution-Processed $CuSbS_2$ Thin Films for Solar Cell Application"** submitted by **Isha, Roll No. 301604014**, in partial fulfilment of requirements for the award of the degree **M.Sc.** in **Physics** from the School of Physics and Materials Science, Thapar Institute of Engineering and Technology, Patiala is a record of candidate's own work carried out by her under my supervision and guidance. The matter embodied in this report has not been submitted in part or full to any other institute for award of any degree.

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Dedicated
To
My Family

Declaration

I hereby declare that the work been presented in this thesis report entitled "**Solution-Processed $CuSbS_2$ Thin Films for Solar Cell Application**" by me in partial fulfillment of the requirements for the award of degree of **Masters of Science** in **Physics** Thapar Institute of Engineering and Technology, Patiala is an authentic award record on my work carried out under the supervision of **Dr. Bhaskar Chandra Mohanty**, Associate Professor, School of Physics and Materials Science, Thapar Institute of Engineering and Technology, Patiala. The matter presented in this report has not been submitted in any other university/institute for award of master and science or any other degree.

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ABSTRACT

Ternary $CuSbS_2$ is an earth abundant and cost effective absorber material for solar cell application having optimum band gap value 1.52 eV and an absorption coefficient 10^4 Cm^{-1}. Thin films were grown on glass substrate using simple and cost effective Chemical Bath Deposition method. Copper chloride dihydrate ($CuCl_2.2H_2O$), antimony trichloride ($SbCl_3$) and thiourea ($NH_2.CS.NH_2$) were used as the ion sources of Cu, Sb and S respectively. Thin films were grown for 3 hour dip time and at room temperature. The effect of sulfurization temperature was studied. The properties of prepared thin films were investigated by XRD technique, Field emission scanning electron microscopy and UV-Visible spectrophotometer. The results indicated that prepared thin films sulfurized at 400 °C and 500 °C showed better crystallinity with a small amount of impurity as an unidentified phase.

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CHAPTER 1
INTRODUCTION

1.1 Thin films

Thin film is a layer of a material having thickness in the range of fractions of nanometers to several micrometers [1]. A common example of thin film is the household mirror which has a thin film coating of a metal on the back side of glass sheet to form a reflective interface. The behavior of thin films is different as compared to the bulk material from which they are made of. The properties of a bulk material mainly depend on the atoms present in the material. As the thickness of material is decreased, the ratio of atoms on surface to those in volume increases and thus, thin film properties will depend on surface atoms [2]. Thin films have found application in different fields such as in reflecting coatings, corrosion resistance, anti reflecting coatings, decoration, data storage, sensors, etc. In recent years, thin films in inorganic solar cells have drawn significant research interest. This work describes growth and characterization of $CuSbS_2$ thin films for potential solar cell application.

1.2 Thin film solar cells

Solar cell is a device which converts solar energy to electrical energy. It is pollution-free, noise-free, reliable, and works for a long time continuously. Thin film solar cells are second generation solar cells which are fabricated by depositing a thin layer of photovoltaic material on a substrate. Performance of a thin film solar cell is dependent on the choice of the optimum absorber layer material because both light absorption and the generation of the carriers take place in the absorber layer. Ideally, the bandgap is preferred to be slightly lower than the energy of the light we are trying to capture (sun light). This means that the light will excite electrons just into the conduction band. If the light energy is much higher than the bandgap value, it will still excite the electron from the valence band into the conduction band, but the electron will rapidly fall to the lower energy levels in the conduction band which leads to wastage of energy [3]. As can be seen from the **Fig. 1.1(a)** that most of the photons those reach earth's surface have energy in the range of 1 -1.5 eV. Ideally, 1.5 eV should be bandgap of the material to be used as an absorber layer in solar cells. **Fig. 1.1(b)** shows the graphical representation of efficiency of solar cells versus bandgap of absorber layer material used for solar cell. This figure indicates that the

material having bandgap value 1.5 eV have maximum efficiency. Therefore, (1.2-1.7 eV) bandgap semiconductors with high absorption coefficient are preferred for an absorber layer of thin film solar cell [4].

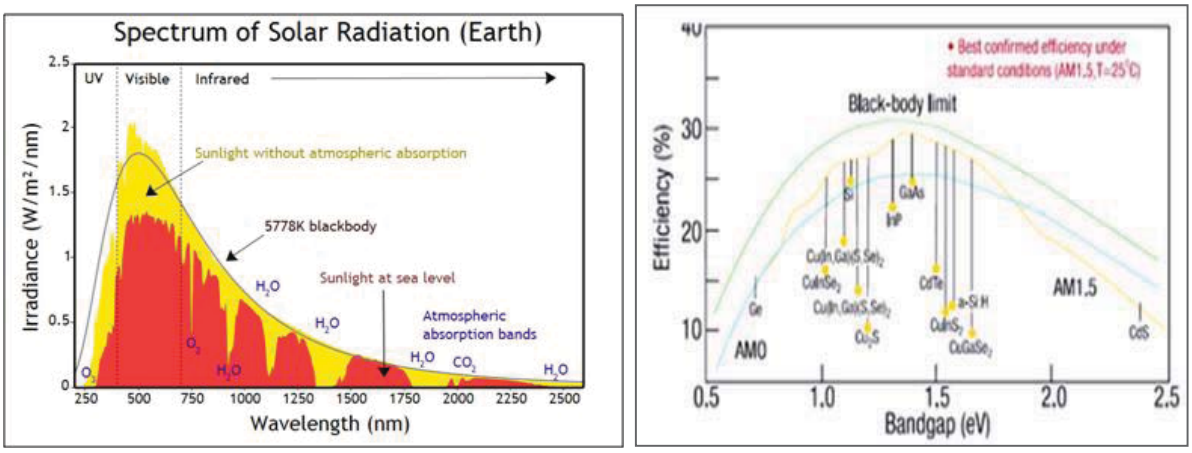

Figure 1.1: (a) Spectrum of solar radiation (b) efficiency versus bandgap of different absorber materials [5]

1.2.1 Various possible materials for absorber layer in thin film solar cells

Crystalline Si

Si is the earth abundant element. Crystalline Si solar cells are the most common solar cells available in world PV cell market. For single crystal cells, the laboratory Conversion efficiency is over 25% and for multicrystalline cells is over 20%. Industrially produced solar cells reached the conversion efficiency in the range from 18% to 22%. The life time of crystalline silicone solar cells is 25+ years [6].

CdTe

CdTe is a p-type absorber material with high absorption coefficient and bandgap of 1.45 eV. It is used in p-n hetrojunction solar cells as a p-layer such as CdTe/CdS solar cell. CdTe based solar cells are second most common solar cells in the photovoltaic technology market. Low cost manufacturing technology is used for manufacturing CdTe based solar cells. The main issue with this material is the high price and less abundance of Te and high toxicity of Cd. First

Solar has reported laboratory CdTe solar cell efficiency of 22.1% and average commercial module efficiency was recorded at 16.1% [7].

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

CIS is a ternary compound having p-type conductivity with high absorption coefficient (10^5 cm^{-1}). By replacing some of In by Ga, the bandgap of the material can be modulated from 1.1 to 1.7 eV. For an optimum value of Ga, higher open-circuit voltage (V_{oc}) has been obtained for CIGS based solar cells than CIS. The CIGS solar cells have yielded the highest efficiency of 22.8% which is comparable to crystalline silicon wafer based solar cells. The major issue with CIGS based solar cells is the increasing cost of In. For the fabrication of a 1 GW CIGS PV module about 31 tons of In is required [8].

Cu_2ZnSnS_4 (CZTS)

CZTS is a p-type I_2–II–IV–VI_4 quaternary compound obtained from iso-electronic substitution of In and Ga by Zn and Sn in CIGS. Apart from having earth abundant and less expensive constituents, CZTS has a bandgap of 1.5 eV and absorption coefficient better than 10^4 cm^{-1} [9]. Currently, the highest efficiency of 12.6% has been reported for CZTS based thin film solar cells [10].

$CuSbS_2$

In recent years $CuSbS_2$ has emerged as a promising absorber layer. It is more cost competitive than the popular $CuInSe_2$ because of the natural abundance of Sb compared to In. Fig 1.3 compares the natural abundance and price of $CuSbS_2$ and others. This work concerns growth of $CuSbS_2$ thin films by a cost-competitive solution method.

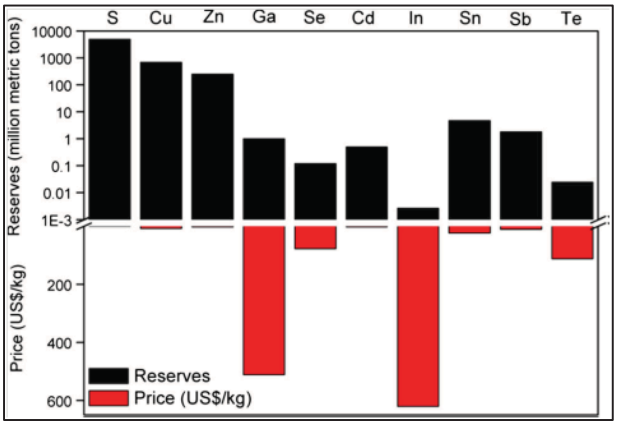

Figure 1.2: Comparison of natural abundance and price of different materials [11]

1.3 Properties of $CuSbS_2$

$CuSbS_2$ crystallize in orthorhombic structure. **Fig. 1.3** shows the crystal structure of $CuSbS_2$ with four formula units in one unit cell. A unit cell contains total sixteen atoms with four Cu, four Sb and eight S atoms. The Sb atoms (cation) are four-coordinated and Cu atoms are five-coordinated with respect to the S atoms (anion). This figure reveals that the structure is composed of the distorted square pyramidal SbS_5 units and the tetrahedral CuS_4 units.

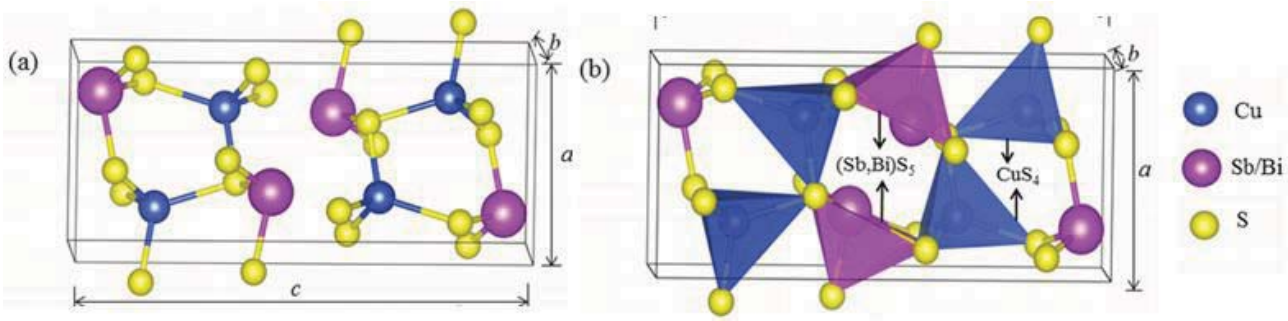

Fig 1.3: Crystal structure of $CuSbS_2$ showing (a) normal view and (b) polyhedral view of unit cell. [12]

As Cu exists in Cu^+ state in $CuSbS_2$ and Cu 3d state is present on the top of the valence band which means in the conduction band we do not find any copper state indicated in the graph of $CuSbS_2$ between density of states and $E\text{-}E_f$ as shown in **Fig. 1.4** Therefore, upon photo excitation Cu^+ changes to Cu^{2+} which may have influence for hole transport in $CusbS_2$ [13].

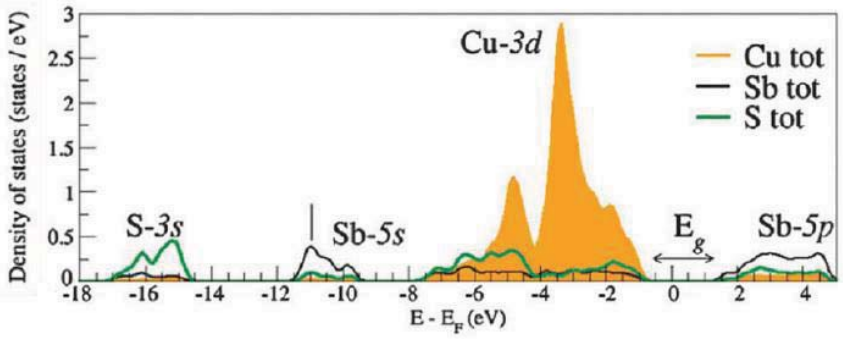

Figure 1.4: Orbital-projected density of states for $CuSbS_2$ [12].

$CuSbS_2$ thin films show bandgap value of 1.52 eV with high absorption coefficient (greater than 10^4 Cm^{-1}) [14].

1.4 Literature review on $CuSbS_2$ thin films

In 2001, Rodrıguez-Lazcano et al. deposited sequentially Sb_2S_3 and CuS thin film on clean glass slides using chemical bath deposition method (CBD). The analysis of XRD results showed that the $CuSbS_2$ is formed only if film is annealed at 350 and 400 °C. Using the optical transmittance and reflectance spectra the optical bandgap has determined to be 1.52 eV. Also, the photocurrent response results showed p-type conductivity of the material [15]. In 2005, the same group prepared photovoltaic structure (n) CdS: In-(i) Sb_2S_3-(p) $CuSbS_2$ using the $CuSbS_2$ films prepared from annealing of sequential stacks of Sb_2S_3 and CuS films at 350-400°C in nitrogen atmosphere. The devices had J_{sc}=0.18 mA/cm^2 and V_{oc}=345 mV [16].

In 2007, Duta et al. prepared $CuSbS_2$ film by using spray pyrolysis deposition technique by varying both substrate temperature and precursor weight ratio. From XRD analysis, they observed that by increasing amount of antimony and fixing the amount of sulfur and copper, the crystalline size is increasing from 49.68 nm to 88.31 nm. Also pinhole free $CuSbS_2$ film is obtained from precursor having higher amount of antimony than precursor having low amount of antimony [17].

In 2010 Ezema et al. have grown $CuSbS_2$ thin film using the CBD method first by a lower dip time followed by the second deposition for higher dip time. They studied the influence of dip time on the optical and structural properties of prepared thin film. XRD analysis showed

the better crystallization of films prepared for higher dip time. They observed that transmittance was low for film prepared at higher dip time because thickness is increasing with increase in deposition time [18].

In 2014, Yang et al, deposited a $CuSbs_2$ thin film on FTO substrate using Hydrazine solution with the help of spin coating technique. To produce a film of 1 μm thickness after depositing film with spin coater, film was dried at 100°C for 10 minutes and annealed at 250°C for 3 minutes. This process was repeated for 4 times to produce the film of desired thickness. At the end, they concluded that $CuSbS_2$ thin film is indeed a very suitable absorber material for photovoltaic applications [19].

In 2014, Thiruvenkadam et al. studied the effect of substrate temperature on the prepared $CuSbS_2$ thin films deposited by spray pyrolysis deposition method. They observed that how structural, morphological and optical properties like bandgap values of prepared films changes with change in substrate temperature. GIXRD results showed that films prepared at all substrate temperature were impure phase. Raman spectra analysis confirmed the presence of $CuSbS_2$ phase but also presence of Cu_2S phase as an impurity. The bandgap value of prepared films was found between 1.35-1.50 eV which is very close to bandgap value required for a solar cell absorber layer which indicated that $CuSbS_2$ thin films are suitable absorber layer for solar cells [20].

In 2015, Choi et al, deposited a thin film of $CuSbS_2$ on FTO substrate using Copper-antimony-thiourea solution by repeated cycles of spin coating and thermal decomposition at 200°C temperatures. After preparing thin film it was annealed at 300°C to 500°C temperatures. XRD analysis showed the formation of $CuSbS_2$ phase with an impurity phase Sb_2S_3 for the thin films annealed at 300°C. They also studied that the number of repeated cycles also influences the amount of $CuSbS_2$ thin film on substrate [21].

In 2016, Shaji et al, prepared a thin film of $CuSbS_2$ using spray pyrolysis deposition method. During deposition substrate temperature was kept at 200°C and by changing the precursor composition. They prepared the samples by changing S/Cu ratio. XRD analysis confirmed the presence of $CuSbS_2$ phase and a secondary phase Cu_2S in all prepared films. XPS results showed the presence of all components. Optical properties like bandgap value and conductivity was observed as 1.45eV and p-type conductivity respectively [22].

In 2016, Vijila et al, studied the effect Cu Concentration on the Structural and Optical properties of $CuSbS_2$ thin films prepared by CBD method. XRD results showed that pure $CuSbS_2$ phase was not observed. As the Concentration of Cu was increasing in thin film, formation of secondary phases Cu_3SbS_3 and $Cu_{12}Sb_4S_{13}$ was decreasing. Surface morphology of films was also improving by increasing Cu concentration may be due to the fact that by increasing cu concentration smaller grains were grouping together to form larger grains or may be due to the diffusion of Cu at higher concentration. The increase in Cu concentration leads to the increase in thickness and bandgap value of deposited films from 176nm to 194nm and 1.7eV to 2.4eV respectively [23].

In 2018, Michael et al, prepared CuS thin film on a glass substrate with CBD method at 70°C and then a layer of Sb_2S_3 on the CuS film at 4-10°C. In order to prepare $CuSbS_2$ thin film Sb_2S_3/CuS bilayer was thermally annealed at various temperatures. They observed that by increasing annealing temperature the film crystallinity was also increasing but formation of secondary phase was also increasing. At the end, they concluded that $CuSbS_2$ thin film is a suitable absorber layer for thin film solar cell with band gap value 1.58 eV [24].

1.5 Motivation and Objective

The brief literature presented above indicates that $CuSbS_2$ thin films have been prepared in multiple process steps with limited success. It is of interest to prepare the films via a simple solution process such as CBD using common salts in a single step and at reasonably low temperature. In view of this, the main objective of the present work is to grow $CuSbS_2$ thin films with simple, less expensive and non-toxic chemical bath deposition method and study the effects of different post-sulfurization conditions on various properties of the resulting films.

CHAPTER 2
EXPERIMENTAL TECHNIQUES

In this chapter, experimental technique used for the growth of the films and their characterization techniques are presented. Section 2.1 gives a brief description of sample preparation and section 2.2 gives details of the characterization techniques used for studying film properties.

2.1 Growth of $CuSbS_2$ thin films

Among various techniques used for the synthesis of thin films, the solution based processes have assumed much importance due to easy control of process parameters, low capital cost and their ability to deposit uniform films on large area substrates. For sulfide thin films, CBD method has emerged as the most popular one over recent years. **Fig. 2.1** shows a schematic diagram of the CBD method.

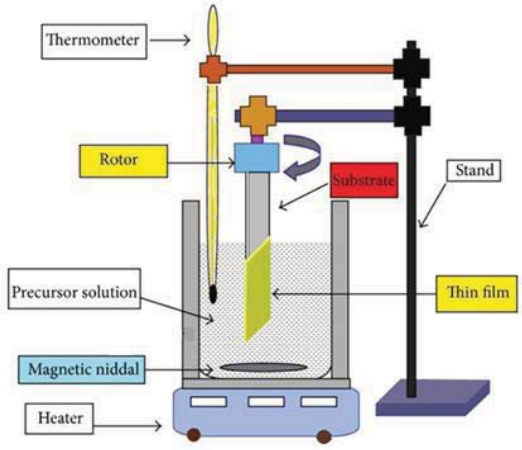

Figure 2.1: Schematic diagram of the CBD method

In this work, CBD technique was used to prepare the $CuSbS_2$ thin films. Copper chloride dihydrate ($CuCl_2.2H_2O$), antimony trichloride ($SbCl_3$) and thiourea ($NH_2.CS.NH_2$) were used as sources of Cu, Sb and S, respectively. Stock solutions of 40 ml of 0.24M antimony trichloride in isopropyl alcohol and 40ml of 0.2M copper chloride dihydrate in methoxyethanol were separately prepared. After adding antimony trichloride to isopropyl alcohol, the solution was continuously magnetically stirred for 30 minutes to prepare a transparent stock solution. Copper stock solution was prepared by adding copper chloride dihydrate to methoxyethanol and stirring

continuously for 10 minutes. **Fig. 2.2** shows the photographs of prepared Cu and Sb stock solutions and the solution after missing both stock solutions.

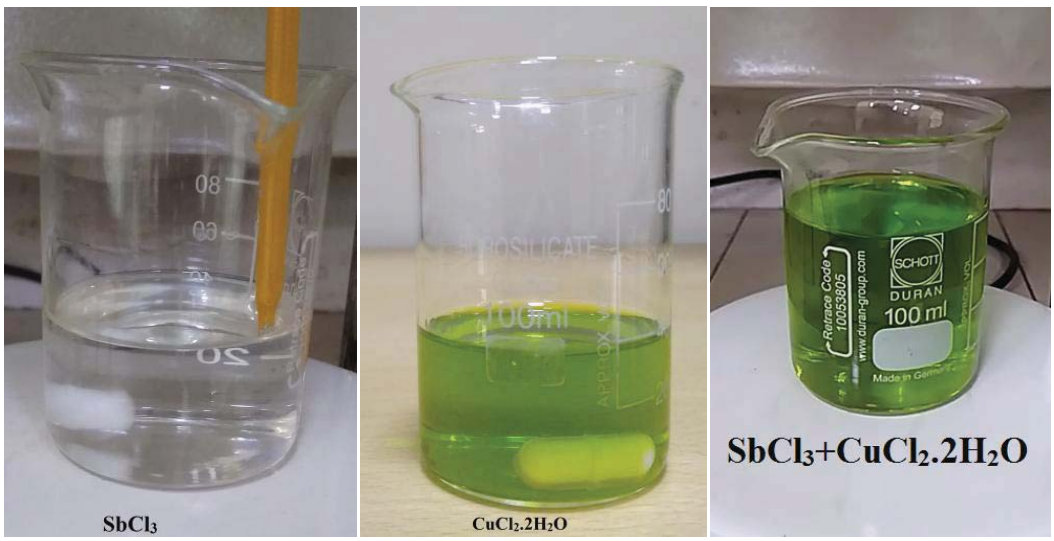

Figure 2.2: Photographs of stock solutions of antimony trichloride and copper chloride dihydrate and solution obtained after mixing both stock solutions.

Glass slides were used as a substrate for the deposition of the thin films. Firstly, glass slides were cleaned ultrasonically with acetone followed by DI water, for 5 minutes each. Finally, the glass slides were cleaned with isopropyl alcohol. The cleaned glass slides were vertically kept in the solution which was obtained after mixing both stock solutions. After inserting cleaned glass slides, thiourea was added in the solution with constant stirring of solution (0.5M). Stirring of the solution was carried out at room temperature and 700 RPM for the entire deposition process. For measuring the temperature of solution a thermometer was dipped in the solution for whole process of deposition. Dip time was fixed to 3 hours for each sample. Only one glass slide was used during each deposition process. After adding thiourea in solution, the colour of the solution changes immediately to black colour. With increase in deposition time colour of solution changed to yellow colour. **Fig. 2.3** shows the photographs of bath solution showing changes in colour with time after adding thiourea in the mixture of stock solutions.

Figure 2.3: The color of bath solution changes with time after adding thiourea in the mixture of both stock solutions.

After 3 hours deposition time, the glass slide was removed from solution and air dried at 130 °C temperature for 5 minutes in hot air oven. **Fig. 2.4** shows photograph of the as-prepared films after air drying. Following air drying step, a high temperature anneal in argon and sulfur atmosphere was performed which is also called sulfurization. **Fig. 2.5** shows the photograph of tubular furnace used in this work for Sulfurization process.

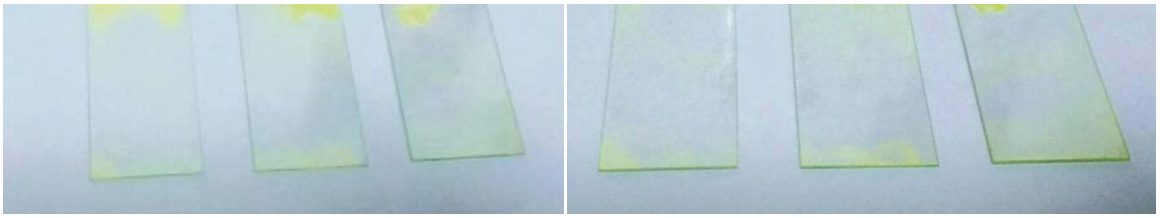

Figure 2.4: Photograph of prepared $CuSbS_2$ thin films

Figure 2.5: Photograph of tubular furnace used for sulfurization process.

2.2 Characterization techniques

Crystal structure and phase purity of the samples were determined from the analyses of the X-ray diffraction (XRD) patterns. Cu k_α characteristic X-rays (λ = 1.54 Å) were used and the diffraction patterns were recorded in a Bruker D-8 advance diffractometer.

Surface microstructure of the films was investigated using field emission scanning electron microscopy (FESEM). In this work FESEM measurements were carried out on samples using Hitachi field emission scanning electron microscope. The operating voltage used for this measurement was 5.0 KV.

Optical properties, namely transmittance and the reflectance were studied using UV-Visible spectroscopy. In this work optical transmittance and reflectance spectra is recorded using Shimadzu UV-2600 UV-Visible spectrophotometer in wavelength range 300 nm to 1400 nm.

CHAPTER 3

Results and discussion

In this chapter, the details of results obtained after using characterization techniques (as described in chapter 2) for samples prepared via the CBD method and sulfurized at different temperatures ranging from 250 to 500 °C with steps of 50 °C are presented. A brief discussion of results is also presented in this chapter.

3.1 XRD analysis

Figure 3.1 shows typical XRD patterns of the samples sulfurized at different temperatures as described in the experimental section (chapter 2). For the sample sulfurized at 250 °C, only one diffraction peak at ~26.3° is observed which is corresponded to (-202) plane of Cu_3SbS_3 phase (JCPDS No. 01-083-0563) of Cu-Sb-S system. As the sulfurization temperature is increased to 300 °C, peak at 26.3° disappeared and six new peaks appeared. The peaks at about 15.6° and 17.5° correspond to (-111) and (102) plane of Cu_3SbS_3 phase. The other four diffraction peaks namely at 24.9°, 28.7°, 32.2° and 35.5° are identified with various peaks of $CuSbS_2$ phase (JCPDS No. 44-1417) suggesting partial conversion to $CuSbS_2$ phase from the Cu_3SbS_3 phase. When the sulfurization temperature is further increased to 350 °C, one peak corresponding to (220) plane of $CuSbS_2$ phase at 32.2° disappeared and two new peaks at 11.1 and 22.3° corresponding to (110) and (220) plane of Sb_2S_3 phase (JCPDS No. 042-1393) appeared. Interestingly, the intensity of the other peaks significantly increased. With further increase in the sulfurization temperature to 400 °C, the peaks of the Cu_3SbS_3 and Sb_2S_3 disappeared and three diffraction peaks (at 19.3°, 28.7°, 29.2°) corresponding to $CuSbS_2$ phase were observed. A diffraction peak at ~9.7° was observed which could not be identified with any of the possible chemical entities. There was no change in the pattern except increase in intensity of the peaks when the films were sulfurized at higher temperature of 450 and 500 °C.

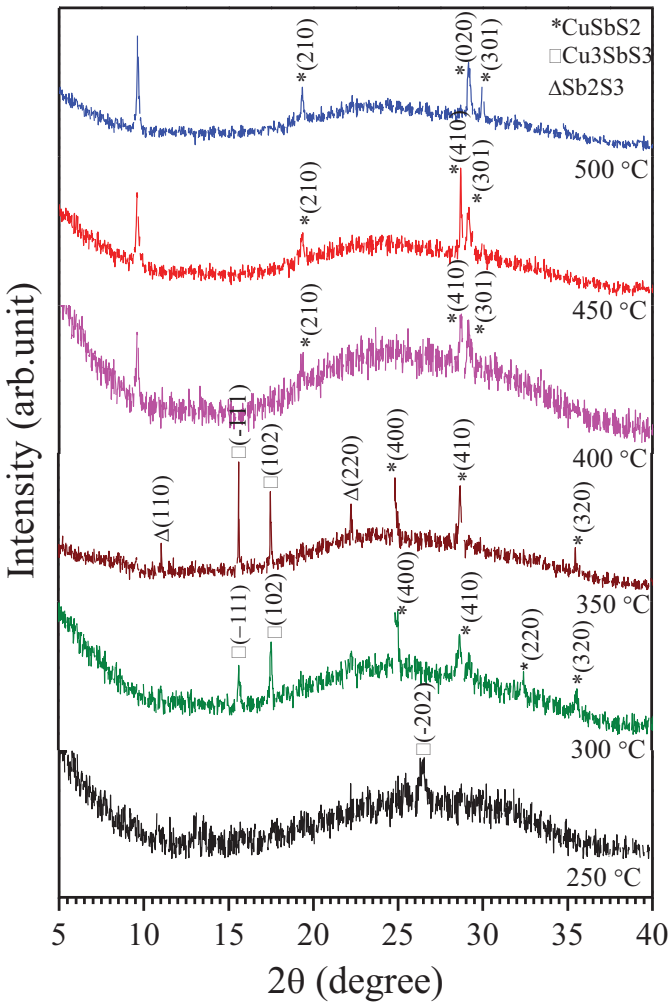

Figure 3.1: XRD patterns of thin films deposited on glass substrate and sulfurized at different temperatures

3.2 Surface morphology analysis

Figure 3.2 shows the FESEM images of samples sulfurized at different temperatures 300 (a-b), 400 (c-d) and 500 °C (e-f). FESEM image of thin film sulfurized at 300 °C shows bimodal particles covering the sample surface. There were large size irregular shaped particles as well as small sized nearly spherical shaped particles on the surface of thin film. FESEM image of $CuSbS_2$ thin film sulfurized at 400 °C (Figs. 3.2c and d) shows rod shaped particles on the surface of the films. Rod shaped $CuSbS_2$ grains are also observed for the sample prepared via spray pyrolysis deposition method [25]. When the sulfurization temperature is increased to 500 °C, there is a change in morphology of the thin film surface which is indicated in **Fig. 3.2 (e, f)**.

It is observed that some large spherical grains are formed on the surface of thin film, which indicates the better crystallinity.

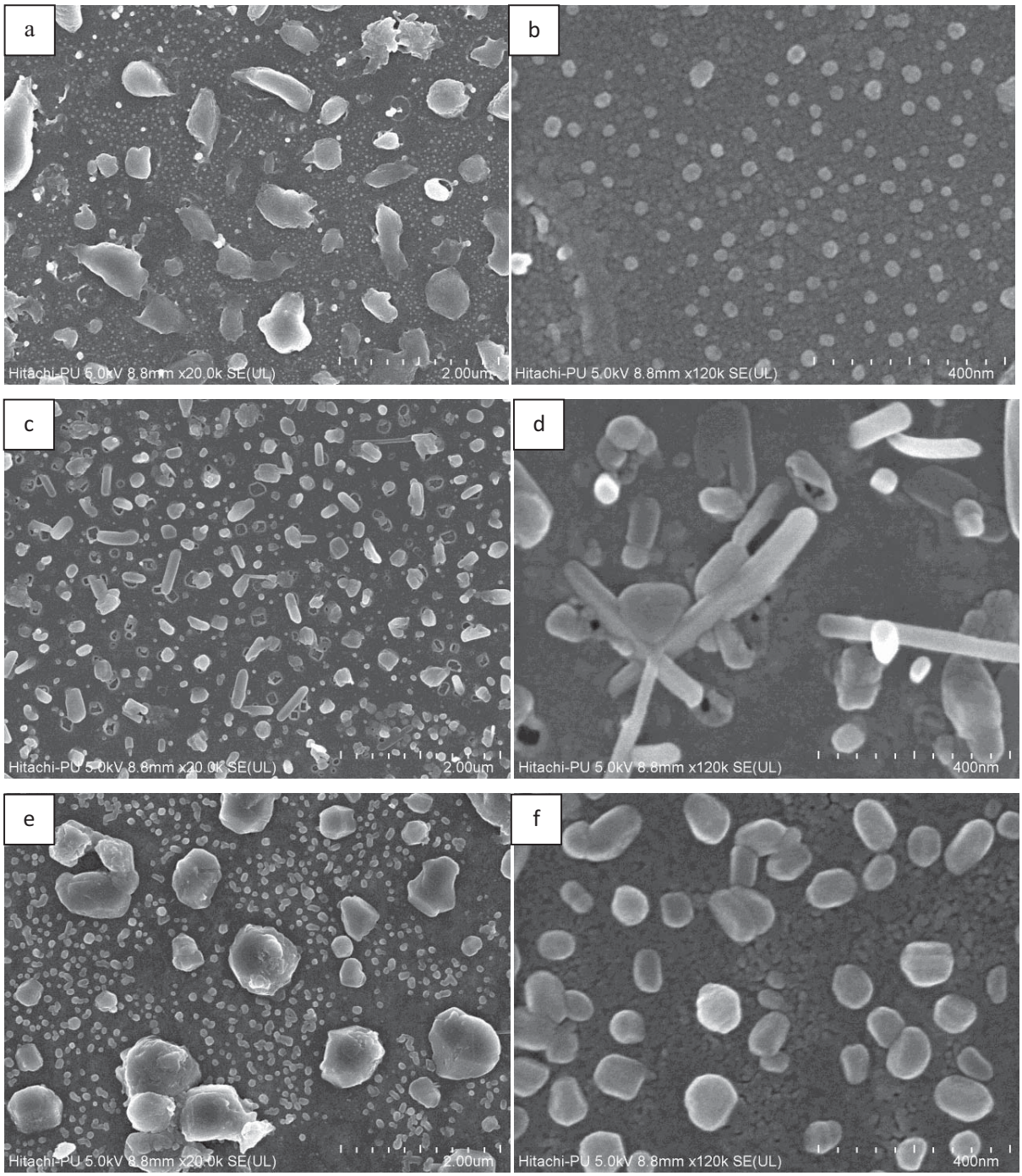

Figure 3.2: FESEM images of the samples sulfurized at different temperatures: (a, b) 300 °C, (c, d) 400 °C, (e, f) 500 °C

3.3 Optical properties of the films

Figure 3.3 shows the typical optical reflectance (R) and transmittance (T) spectra of the thin films sulfurized at different temperatures and glass, in the wavelength range of 300 to 1400 nm. The average transmittance and reflectance of sample sulfurized at 250 °C is 66.87% and 11.61% respectively. As the sulfurization temperature is increased to 300 °C, average transmittance and reflectance becomes 60.09% and 19.39% respectively. For the sample sulfurized at 350 °C, average transmittance and reflectance are 55.58% and 19.13% respectively. With further increase in sulfurization temperature to 450 °C, average transmittance and reflectance becomes 63.23% and 19.12% respectively. Similarly if the sulfurization temperature is increased to 500 °C average transmittance and reflectance are 66.87% and 21.10% respectively. Transmittance of all the samples is less than transmittance of glass and reflectance of all the samples is greater than reflectance of glass.

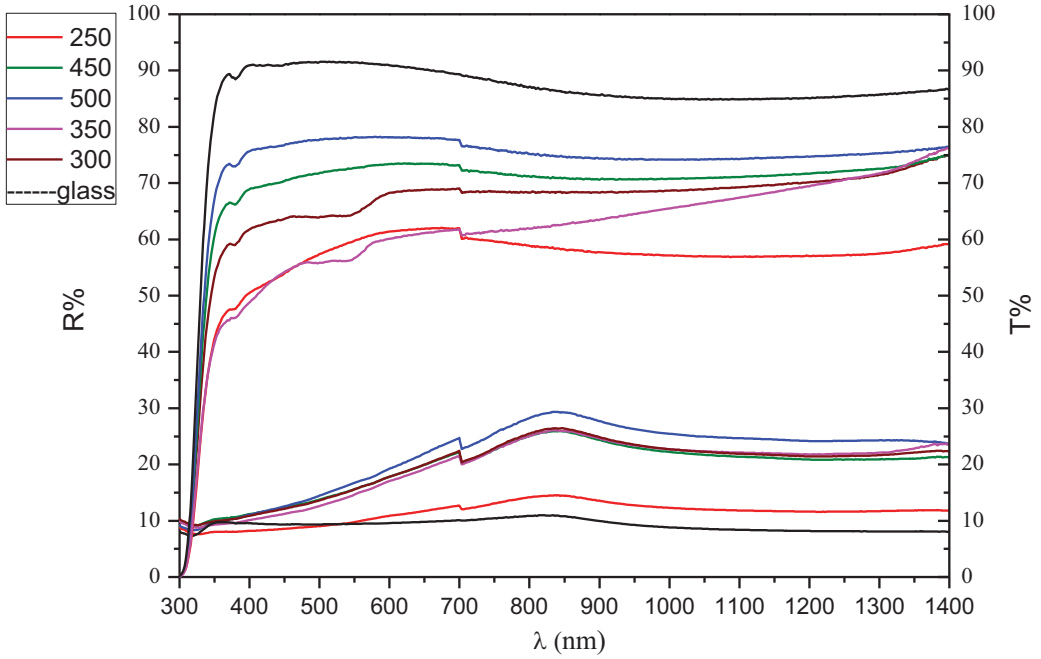

Figure 3.3: Spectrum of %T and %R of the samples sulfurized at different temperatures and glass.

CHAPTER 4

Conclusion

Thin films were prepared on a glass substrate by the simple and less expensive CBD method using common salts of copper chloride, antimony chloride and thiourea. The deposition was done for three hour dip time and at room temperature. The structural, morphological and optical properties of prepared thin films were studied using XRD, FESEM and UV-Visible spectroscopy, respectively. The sulfurization temperature has a large effect on the phase formation of as prepared thin films. With increase in sulfurization temperature, the phase structure is changed from Cu_3SbS_3 to $CuSbS_2$ phase along with an unidentified phase formation. The FESEM results suggest that surface morphology of samples sulfurized at different temperatures also changes. With increase in sulfurization temperature transmittance of samples was found to increase. It is summarized that the prepared thin films sulfurized at 400 °C to 500 °C are predominately crystalline chalcostibite copper antimony sulfide ($CuSbS_2$) with minor contamination of an unidentified phase. Before integrating in a solar cell, further experiments are required to ascertain the origin of the unidentified phase and steps should be taken for the removal of the same.

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