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Study on Antimony Chalcogenide thin films

Anu Kuruvilla[1, 2], Melda Francis[1, 2], Lakshmi M[2*]

[1, 2] Christ College, Irinjalakkuda, University of Calicut, Kerala, India

[2]Mercy College, Palakkad, University of Calicut, Kerala, India.

Abstract

Antimony sulphides and selenides are two important chalcogenide compounds that find application in the field of photovoltaics.Sb_2Se_3 is one such binary chalcogenide with bandgap of 1–1.2 eV and absorption coefficient in the order of 10^5 cm^{-1} at short wavelength.Sb_2S_3 is another similar chalcogenide with a bandgap in the range 1.7-2.3 eV. In this work, antimony sulphide and antimony selenide films were prepared by Chemical Bath Deposition (CBD) method. The prepared samples were characterized using UV-Visible spectroscopy, X-ray Diffraction technique, XPS analysis, SEM and EDAX studies.

Key words- Antimony Selenide thin film; Antimony sulphide thin film

Introduction

Antimony chalcogenides (Sb_2Ch_3, Ch=O, S, Se, Te) with its high refractive index, photo-sensitivity, good electrical conductivity and transport properties, have wide optoelectronic applications. Among the various antimony selenides, Sb_2Se_3 has a bandgap of 1–1.2eV and absorption coefficient in the order of 10^5 cm^{-1} at short wavelength [1, 2].This material is a very promising absorber material for thin film photovoltaics. It finds applications as optical coatings in thermophotovoltaic devices and in fabrication of Hall Effect devices and cost-effective solar cells. Sb_2S_3 has a bandgap in the range 1.7-2.3 eV and it serves as potential absorber for photovoltaic applications. This material is known for its high refractive index and well-defined quantum size effects [3]. The constituent elements of the above two compounds viz. Sb, S and Se are earth-abundant and are low-cost.

In the present work antimony sulphide and antimony selenide films were prepared by Chemical Bath Deposition (CBD) method. This method of thin film preparation is presently gaining considerable attention as it has proved to be a less expensive low temperature process. It is also a non-pollutant method. It is the most convenient method for large area deposition. Bandgap determination of the prepared samples was done with the help of UV-Visible spectroscopy, structural characterization using the X-ray Diffraction technique, compositional analysis using XPS and morphological and chemical analysis were done using SEM and EDAX studies.

Experimental Technique

The substrate used for thin film deposition was glass slide washed with laboratory detergent and ultrasonicated in acetone. Antimony selenide was prepared by dissolving 1 g of $SbCl_3$ in 37 ml of 1M sodium citrate solution. 20 ml of ammonium hydroxide and 24 ml of 0.4 M $Na_2S_2O_3$ were then added simultaneously. This solution was made up to 100 ml by adding water [4, 5].The solution will be clear and devoid of any precipitate at the beginning. Uniform thin film was formed on glass slides vertically supported on the walls of the beaker. The deposition was carried out undisturbed for 1hr at room temperature. Obtained films were uniform, reflective and adherent.

Antimony (III) chloride precipitates as oxochloride (SbOCl) in water. Strong ligands such as citrate, tartarate, triethanolamine and thio-sulfate

* *Corresponding author, E-mail: lakshmisethumadhavan@gmail.com*

form soluble complexes in $SbCl_3$ solution. This will prevent the precipitation of basic salts in aqueous solutions. Sodium selenosulphate is used as the selenium precursor [6].The formation of the Sb_2Se_3 film is based on the slow release of Sb^{3+} and Se^{2-} in an aqueous ammonia medium leading to the condensation on the substrate. Antimony Sb (III) complex reacts with Se^{2-} ions to give Sb_2Se_3 film.

The precursors used for the preparation of antimony sulphide thin film were antimony chloride and sodium thiosulfate. 0.5 M solution of antimony chloride was prepared in 10 ml acetone. 25 ml of 1 M solution of sodium thiosulfate was added to this solution under constant stirring. The resulting solution was made up to 100 ml by adding 65 ml of distilled water. In order to control the reaction rate, precooling of water and thiosulfate solution was done at 10˚C before mixing. Clean glass slides were placed vertically on the walls of the beaker containing this mixture. Room temperature deposition of the film for 1 hour resulted in the formation of orange-yellow Sb_2S_3 thin film. The substrate was removed from the bath and washed well with distilled water. The film was uniformly reflective, smooth and adherent to the substrate.

The reaction pathway for the formation of antimony sulfide film is as follows[3].The thiosulfate forms a very strong complex $Sb_2(S_2O_3)_3$ with antimony ion (Sb^{2+}), which hydrolyses to form Sb_2S_3.

$$Sb_2(S_2O_3)_3 + 3H^+ + 6e^- \rightarrow Sb_2S_3 + 3HSO_3^-$$

Results and discussions

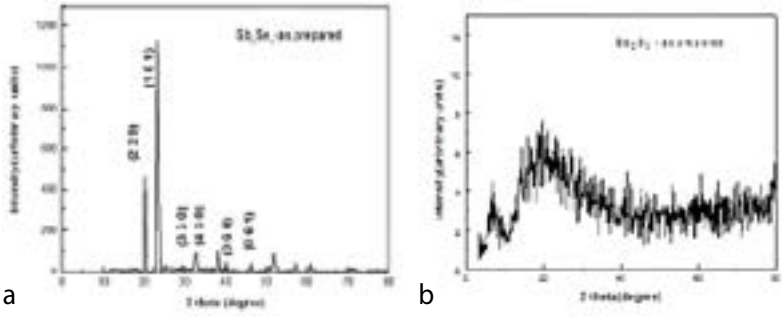
Structural CharacterisationXRD patterns were recorded using Cu Kα source of Rigaku D Max X-ray diffractometer. XRD pattern of as-prepared antimony selenide thin film is shown in figure 1(a). The obtained sample is polycrystalline with peak position matching with orthorhombic Sb_2Se_3 (PDF#651317).This pristine film shows peaks corresponding to (220), (101), (330), (430), (060) and (061) planes respectively. Figure1 (b) shows the XRD spectrum of pristine Sb_2S_3thin film and it suggests that the pristine sample is amorphous in nature.

Morphological Analysis

Morphology of the prepared samples was analyzed with SEM (Scanning Electron Microscope) model JEOL Model JSM - 6390LV. SEM images of pristine Sb_2Se_3 films are shown in figure 2(a). The films were found to be smooth, dense and without cracks. The image with a magnification of x5000 shows spherical structures uniformly distributed over the surface. The SEM image of Sb_2S_3 is shown in figure 2(b).The image shows that the grains are homogeneous and is spread throughout the surface. The grains are more or less uniform.

Chemical Characterisation

EDAX analysis as given in figure 3(a) of pristine Sb_2Se_3 film showed the presence of Sb and Se. The sensitivity of silicon and oxygen was found to be significant in the analysis. Sb to Se ratio was hence analyzed excluding the influence of the substrate. The expected ratio of antimony to selenium in Sb_2Se_3 is 2:3 or Se/Sb is 1.5. The Se/Sb the ratio obtained in the as-prepared thin film sample of Sb_2Se_3 is found to be only1.18.This suggests a



a b

Fig. 1. XRD pattern of pristine (a) Sb2Se3 thin film and (b) pristine Sb2S3 thin film.

Table 1. Elemental analysis of Sb2Se3.

Element	Atomic %
Se	45.89
Sb	54.11
Total:	100

Table 2. Elemental analysis of Sb2S3

Element	Atomic %
Sb	56.09
S	43.91
Total:	100

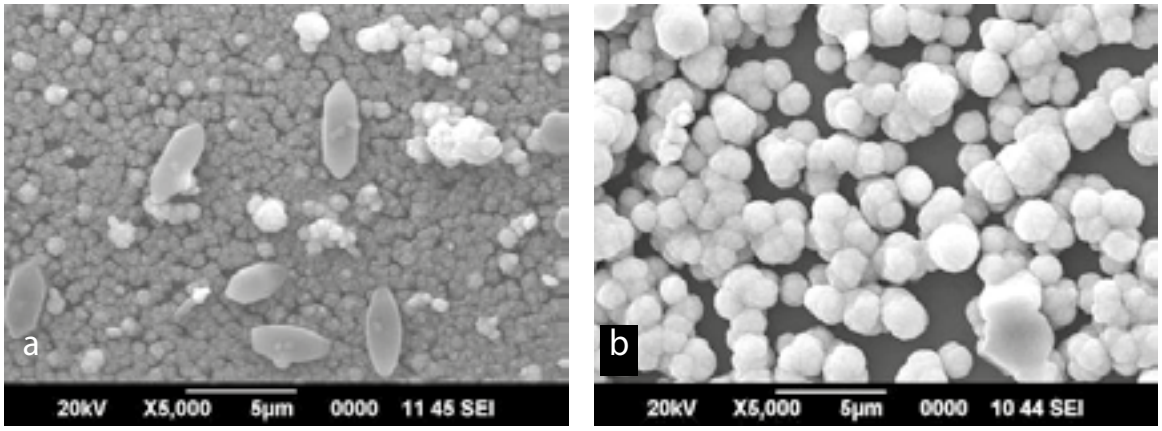


Fig. 2. SEM image of pristine (a) pristine Sb2Se3 thin film and (b) pristine Sb2S3 thin film.

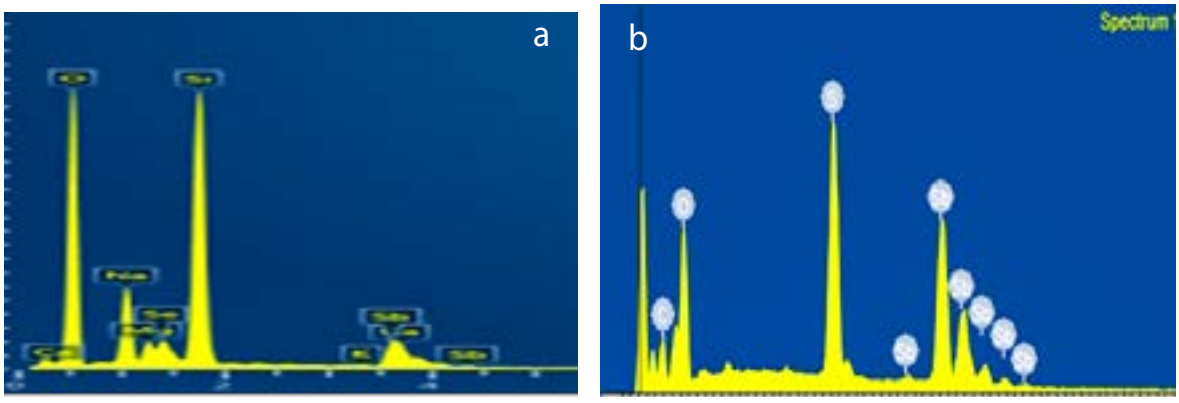


Fig. 3. EDAX image of (a) pristine Sb2Se3 film and (b) pristine Sb2S3

lesser concentration of Se than expected.

Elemental Characterisation of Sb_2S_3 thin film by EDAX analysis is illustrated in figure 3(b). The result shows the presence of Sb and S in the sample. While the expected stoichiometry of S/Sb in antimony sulphide film is 1.5, the obtained ratio was 1.28.

XPS Analysis

The XPS survey of pristine Sb_2Se_3 is shown in figure 4(a).The survey identifies the binding energies corresponding to Sb $3P_{3/2}$ orbital of antimony along with Sb $3d_{5/2}$ and Sb $3d_{3/2}$ orbitals of Sb_2Se_3. Selenium binding energy corresponding to Se $3d_{5/2}$ and Se $3P_{3/2}$ is also identified. The XPS survey of

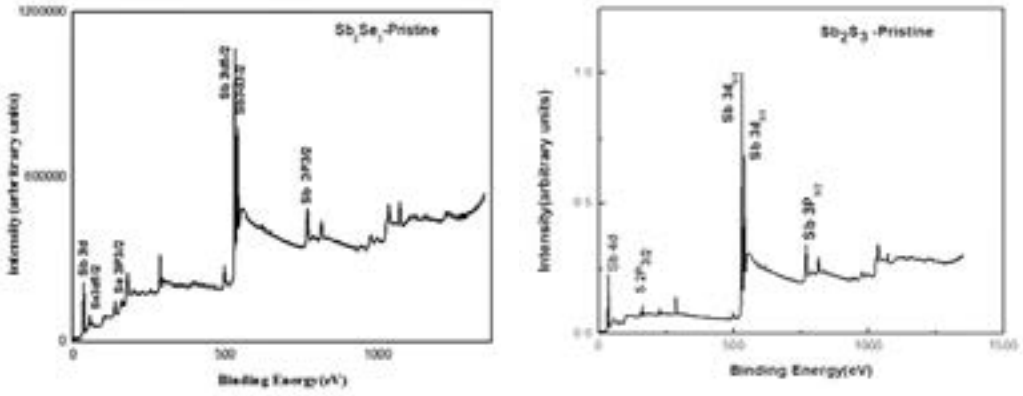


Fig. 4. The XPS survey of (a) pristine Sb_2Se_3 (b) pristine Sb_2S_3

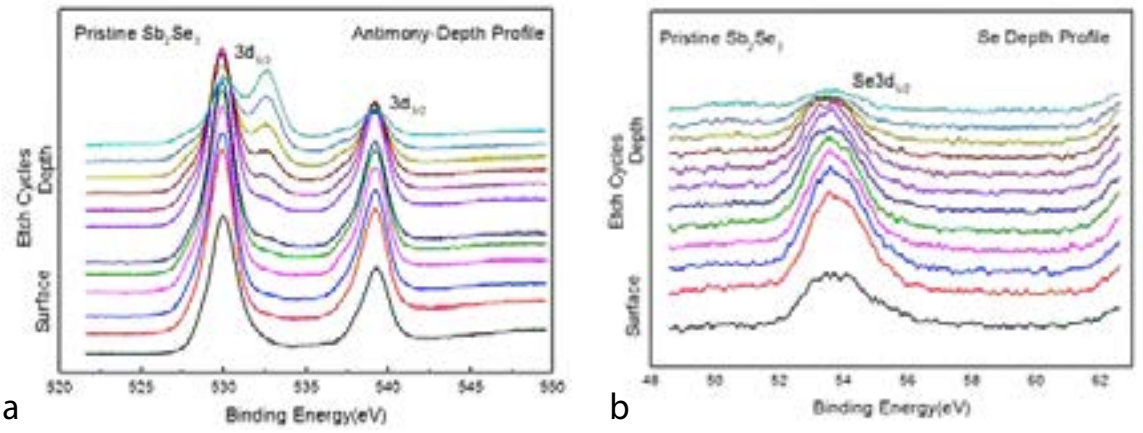


Fig. 5. (a) Depth profile of Sb in pristine Sb2Se3 (b) Depth profile of Se in pristine Sb2Se3.

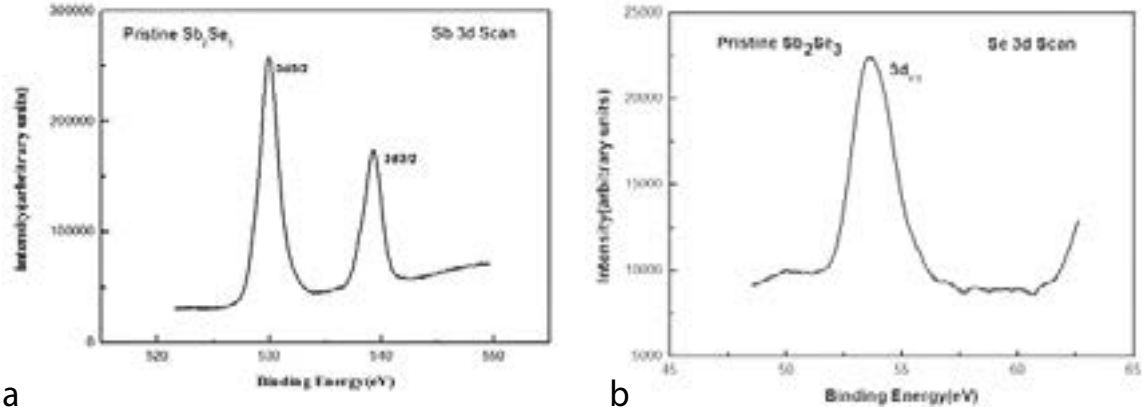


Fig. 6. (a) Sb 3d Scan of pristine Sb2Se3 (b) Se 3d Scan of pristine Sb2Se3.

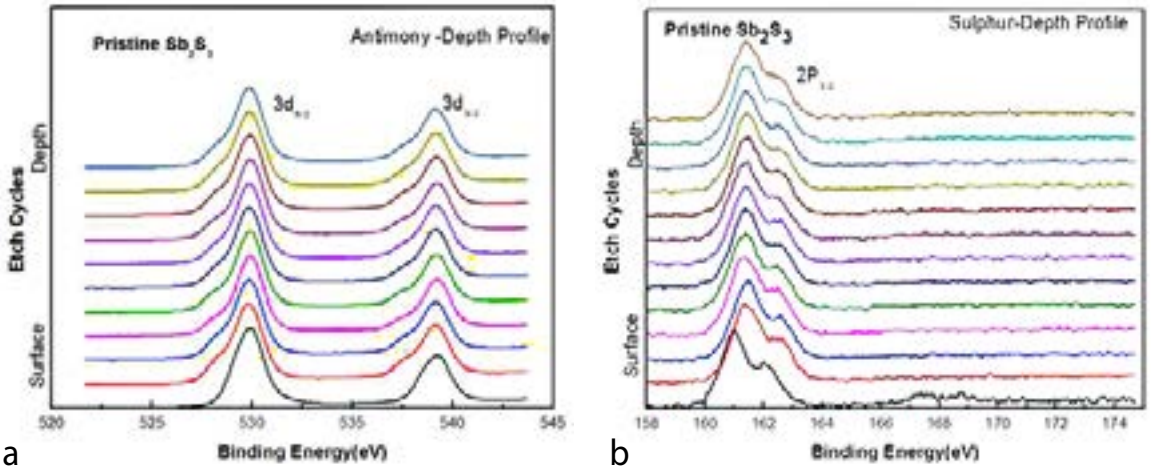


Fig. 7. (a) Depth profile of Sb, pristine Sb2S3film (b) Depth profile of S, pristine Sb2S3 film

pristine Sb2S3 is given in figure 4(b).The survey identifies the binding energies corresponding to Sb 3P3/2 orbital along with Sb 3d5/2 and Sb 3d3/2 orbitals of Sb2S3. The sulphur binding energy corresponding to 2P3/2 orbital is also identified for this compound.

Figure 5(a) and 5(b) shows the depth profile of Sb and Se in pristine Sb2Se3 thin film. Distribution of the elements is found to be uniform throughout the sample.

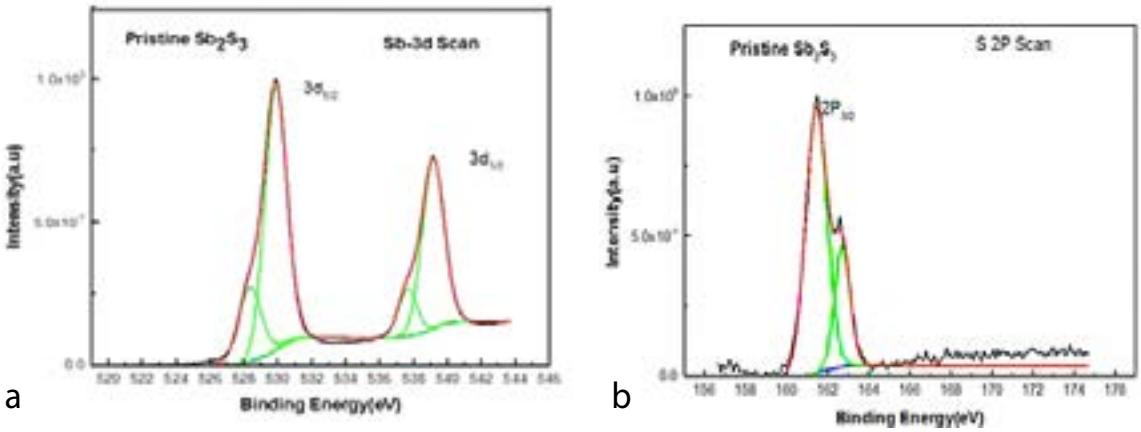


Fig. 8. (a) Sb 3d Scan of pristine Sb2S3 film (b) S 2P Scan of pristine Sb2S3 film

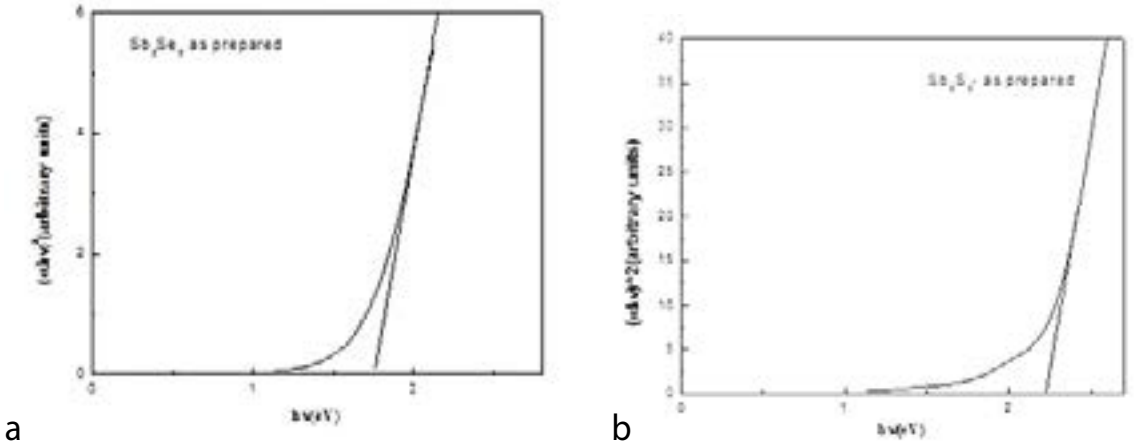


Fig. 9. Bandgap analysis of (a) pristine Sb2Se3 (b) pristine Sb2S3.

Analysis of Sb binding energy in Sb_2Se_3sample(figure 6(a)) gives binding energy values of 529.9eV and 539.2eV in the third etch cycle .This corresponds with the standard binding energy values of Sb $3d_{5/2}$(529.3eV)and Sb$3d_{3/2}$orbital of Sb_2Se_3(538.7eV). Se binding energy value identified at 53.7eV (figure 6(b)) matches with the Se $3d_{5/2}$ orbital of Sb_2Se_3.

Figure 7(a) and 7(b) shows the depth profile of Sb and S in pristine Sb_2S_3 thin film. Distribution of the elements is found to be uniform throughout the sample.

Analysis of the third etch cycle (figure 8 (a)) of Sb binding energy reveals that $3d_{5/2}$ and $3d_{3/2}$ peaks of antimony is a result of the superposition of two peaks. Deconvolution of $3d_{5/2}$ peak gives binding energies values at 528.31eV and 529.85eV respectively. In this 528.31eV matches with Sb $3d_{5/2}$of elemental antimony (standard value 528.25eV) while 529.85eV corresponds to Sb $3d_{5/2}$ orbital of Sb_2S_3 (standard value 529.7eV). Deconvolution of $3d_{3/2}$ peak gives binding energy values at 537.62eV and 539.13eV.The smaller peak at 537.62eV matches with Sb$3d_{3/2}$ corresponding to elemental antimony (standard value 538eV). Second peak at 539.13eV matches with Sb$3d_{3/2}$ of Sb_2S_3 (standard value 539.10eV).This result confirms the formation of antimony trisulphide phase along with traces of elemental antimony.

Deconvoluted peaks corresponding to sulphur binding energy in the third etch cycle (figure 8(b)) is obtained at 161.43eV and162.69eV.The first peak corresponds to $2P_{3/2}$ binding energy of Sb_2S_3 (standard value 161.20eV).The second peak corresponds to $2P_{3/2}$of elemental sulphur whose standard value is at 162.35eV.Thus the detailed analysis of

antimony and sulphur confirms the formation of Sb_2S_3 even though traces of the elemental form is also incorporated.

Optical Properties

The optical bandgap of the pristine sample is determined from the Tauc plot. (αhυ)^2 is plotted against energy value hυ and extrapolation of the linear portion of the graph to the x-axis gives the bandgap value [7, 8, and 9].Bandgap determination of the sample as in figure (9a) gives a direct bandgap of 1.853 eV for as-prepared Sb_2Se_3 samples. The pristine Sb_2S_3in figure (9 b) showed a direct bandgap of 2.23 eV.

Conclusion

Sb_2Se_3 and Sb_2S_3 thin films could be prepared by CBD method. The XRD analysis confirmed the polycrystalline nature of Sb_2Se_3 and amorphous nature of Sb_2S_3. EDX results revealed the overall stoichiometry of these films. Optical analysis showed a direct bandgap of 1.853eV and 2.23eV for Sb_2Se_3 and Sb_2S_3 films respectively. The binding energy analysis using XPS also confirmed the formation of antimony selenide and antimony sulphide thin film. Thus CBD proves to be a less expensive and less-pollutant method for the preparation of antimony chalcogenide films.

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