Effect of selenisation on the properties of antimony selenide thin films

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Abstract: Antimony Selenide (Sb\textsubscript{2}Se\textsubscript{3}) is an important photoconductive semiconductor and it has a band gap of 1.3 eV. It finds applications in solar selective and decorative coating, optical devices and thermoelectric cooling devices. In the present work, Sb\textsubscript{2}Se\textsubscript{3} thin film is prepared by Chemical Bath Deposition (CBD) technique. This method is most suitable for large area samples and it is very simple. Antimony chloride and sodium selenosulfate are used as precursors for the preparation of antimony selenide thin films. It was observed from XPS analysis that antimony oxide was also present as an impurity phase along with antimony selenide. In this work, selenisation is carried out in order to increase the selenium content in the pristine antimony selenide thin films. Selenisation was also done by the method of CBD. These samples were annealed at various temperatures and characterized structurally, morphologically and optically. It was observed that the inclusion of Se has lead to exclusion of oxygen from the surface layers of Antimony Selenide films. Se inclusion has also changed the morphology of Antimony selenide films drastically.

Key Words: Chemical Bath Deposition.

1. INTRODUCTION

Antimony chalcogenides (Sb\textsubscript{2}Ch\textsubscript{3}, Ch=O, S, Se, Te) with its high refractive index, photo-sensitivity, good electrical conductivity and transport properties have wide optoelectronic applications. Antimony selenide (Sb\textsubscript{2}Se\textsubscript{3}) is such a binary metal chalcogenide compound. It is has a band gap of 1–1.2 eV \cite{1} and absorption coefficient in the order of 10\textsuperscript{5} cm\textsuperscript{-1} at short wave length \cite{2}.The constituent elements Sb and Se are earth-abundant and low-cost. This makes the material a very promising absorber material for thin film photovoltaics\cite{3}. It finds applications as optical coatings in thermo photovoltaic devices and in fabrication of Hall Effect devices and cost effective solar cells. In the present work antimony selenide film is 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 and a non-pollutant method. It is most convenient method for large area deposition.

In order to improve the stoichiometry of the as-prepared antimony selenide film, selenium thin film is deposited over the antimony selenide thin films by CBD method. It is then annealed at various temperatures. Se inclusion changed the morphology of antimony selenide thin film significantly and lead to the exclusion of oxide impurity from as-prepared antimony selenide film. Band gap determination is done with the help of UV-Visible spectroscopy, structural characterization using the X-ray Diffraction technique, binding energy determination using XPS analysis and morphological and
chemical analysis is done using SEM and EDAX studies.

2. EXPERIMENTAL TECHNIQUE

Glass substrate was cleaned well with water and laboratory detergent and then ultrasonicated in acetone. Finally the substrate was dried in air.

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$_2$S$_2$O$_3$ were then added respectively. This solution is 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. Deposition was carried out undisturbed for 1hr at room temperature. Obtained films were uniform, reflective and adherent.

Formation of antimony selenide can be explained as follows. Antimony (III) chloride precipitates as oxochloride (SbOCl) in water. Strong ligands such as citrate, tartarate, triethanolamine and thio-sulfate form soluble complexes in SbCl$_3$ solution. It prevents the precipitation of basic salts in aqueous solutions. Sodium selenosulphate is used as a selenium precursor [6]. The formation of the Sb$_2$Se$_3$ film is based on slow release of Sb$^{3+}$ and Se$^2-$ in an aqueous ammonia medium leading to the condensation on the substrate. Citrate complexes with antimony giving Sb (III) (citrate) complex which reacts with Se$^2-$ ions to give Sb$_2$Se$_3$ film. Upon this antimony selenide film, Se film is deposited. Selenium deposition is initiated by adjusting the pH of 0.006M sodium selenosulphate solution to a value of 4.5. Deposition temperature is maintained at 10°C. Instead of continuous deposition for about 3 hours, Se deposition was done 3 times consecutively at 10°C, each of one hour duration. The samples are then annealed to about 100°C and 200°C for about one and a half hour. The samples were then characterized structurally, chemically, optically and morphologically.

3. RESULTS AND DISCUSSIONS

3.1 Structural Characterisation

![Figure 1. XRD Pattern of (a) pristine Sb$_2$Se$_3$ (b) pristine Se (c) Sb$_2$Se$_3$ with Se layer](image-url)
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$_2$Se$_3$ (PDF#651317). This pristine film shows peaks corresponding to (220), (330), (430), (060) and (061) planes respectively. XRD pattern of selenium film (figure 1(b)) obtained by the method of chemical bath deposition technique shows a prominent peak along (202) plane and comparison with JCPDS data PDF#24-0714 reveals monoclinic structure of Se. Figure 1 (c) shows the XRD pattern of stacked Sb$_2$Se$_3$ and Se films. In this all the peaks of both figure (a) and (b) are observed and peaks corresponding to Sb$_2$Se$_3$ became strong and more pronounced.

**Figure 2.** XRD patterns of stacked Sb$_2$Se$_3$ and Se layers. (a) as-deposited sample (b) sample annealed at 100°C (c) sample annealed at 200°C.

This stacked structure was annealed at different temperature and figure 2 shows the resulting XRD pattern. For samples annealed at 100°C and 200°C an additional peak has appeared at about 30°. This peak has correspondence with the antimony selenide peak (PDF#651317). Apart from the minor changes in certain orientations, there was no other significant observation.

**3.2: Morphological Analysis**
Morphology of the prepared samples were analysed with SEM (JEOL Model JSM - 6390LV Scanning Electron Microscope). SEM images of pristine Sb$_2$Se$_3$ films are shown in figure 3(a) and (b). 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. As the film growth proceeds by nucleation of clusters, it subsequently coagulates to cover the entire substrate surface showing a dense structure of islands uniformly distributed over the surface. This is visible in the image magnification at x15,000. Figure 3 (c) reveals the entirely different appearance of the selenium film. Inclusion of Se on to Sb$_2$Se$_3$ film has completely changed the morphology as seen in figure 3 (d) and 3(e). The structure shows irregularly shaped flakes spreading uniformly on the surface.

### 3.3. Chemical Analysis

EDAX analysis as in figure 4 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 analysed excluding the influence
of the substrate.

| Element | Line Type | Wt% | Atomic % |
|---------|-----------|-----|----------|
| Se      | L series  | 35.49 | 45.89   |
| Sb      | L series  | 64.51 | 54.11   |
| Total:  |           | 100  | 100      |

From Table 1 it is observed that the expected ratio of antimony to selenium is 2:3 or Se/Sb is 1.5. The Se/Sb ratio obtained in this thin film sample of \( \text{Sb}_2\text{Se}_3 \) is found to be only 1.18. This suggests lower concentration of Se than expected.

### 3.4. XPS Analysis

The XPS spectra of the films were obtained using Thermo Scientific K-Alpha X-Ray Photoelectron Spectrometer. The XPS survey as in figure 5 identifies the presence of Se and Sb binding energy peaks. Se binding energy is identified at 54.11 eV and 160.58 eV. These peaks correspond to Se 3d\(_{5/2}\) and Se 3P\(_{3/2}\) orbitals with the standard value of 54.64 eV and 161.4 eV respectively. The small peak at 229.47 eV has a correspondence with the 230.10 eV binding energy value of Se 3S. Similarly the peak at 529.57 eV corresponds with the Sb 3d\(_{5/2}\) orbital [7], though the presence of oxygen cannot be ruled out as the binding energy of oxygen usually overlaps with the binding energy of Sb. The peak at 766.4 eV corresponds to Sb 3P\(_{3/2}\) orbital (standard value 766.4 eV).

![Figure 5. XPS survey of selenised \( \text{Sb}_2\text{Se}_3 \) annealed at 100°C](image-url)

(a) ![Sb Surface](image-url)  
(b) ![Sb 10° c-axis](image-url)
As per figure 6 (c) which corresponds to the surface scan signal, only a single peak was identified for Se which corresponds to 54.26 eV. This corresponds to 3d$_{5/2}$ orbital of Se. The depth profile of Se in figure 6 (d) shows that this binding energy is seen only on the surface layers. As we go deeper into the sample from the surface, the selenium signal goes weak and moreover the chemical shift in binding energy value corresponding to 48.46 eV could not be identified with any of the reported values in references or standard values. Analysis of Sb orbital as per figure 6(a) shows the presence of binding energies 529.78 eV and 539.07 eV at the surface. This corresponds to the standard values of 529.34 eV and 538.73 eV of Sb 3d$_{5/2}$ and 3d$_{3/2}$ [7]. The 10$^{th}$ etch cycle of antimony as per figure 6(b) was found to consist of two merged peaks and hence it was deconvoluted to get the two peak position at 528.71 eV and 530.52 eV. The binding energy of 528.71 eV corresponds to Sb3d$_{5/2}$ of Sb$_2$Se$_3$ (reported value is 528.6 eV) [8] and the value 530.52 eV correspond to Sb 3d$_{3/2}$ of Sb$_2$O$_3$ (reported value is 530 eV) [8].

3.5: Optical Analysis
Optical studies were done using UV-Visible spectroscopy. With tauc relation a graph is plotted between \((\alpha h\nu)^2\) on y axis and \(h\nu\) on x axis\([9,10,11]\). Band gap determination of the sample as in figure 7 gives a direct band gap of 1.853 eV for as-prepared samples. Figure 8(a) and 8(b) gives a direct band gap of 1.14 eV and 1.13 eV for selenised samples annealed at 100°C and 200°C respectively.

Hall effect measurements confirmed p-type conductivity for the selenised samples annealed at both the temperatures.

4. CONCLUSION

This work studies the selenisation effect of antimony selenide thin film. XRD studies confirms that the selenisation of the samples has improved the quality of the as prepared antimony selenide film. Selenium has changed the morphology of the film. XPS analysis confirms the presence of Sb and Se binding energy peaks as in antimony selenide film. But the presence of oxygen throughout the sample suggested the impurity phase of antimony oxide. On annealing the as prepared antimony selenide with additional selenium layer helped in decreasing this impurity phase. The fact that this impurity phase could not be detected in XRD was another noticeable point and it may be due to the fact that this oxide impurity is amorphous in nature. Optical studies give a direct band gap of 1.85 eV for as-prepared samples. Direct band gap of 1.14 eV and 1.13 eV is obtained for selenised samples annealed at 100°C and 200°C respectively.

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