Structural Characterization of $(Sb_{0.5}Bi_{0.5})_2S_3$ thin films by chemical deposition technique

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Abstract

A room temperature chemical bath deposition (CBD) method was developed to deposit $(Sb_{0.5}Bi_{0.5})_2S_3$ composite thin films. The preparative parameters such as concentration of bismuth ions, concentration of antimony ions, volume ratio of bismuth and antimony, complexing agent and deposition time were optimized to get good quality $(Sb_{0.5}Bi_{0.5})_2S_3$ composite thin film of terminal thickness 0.45µm. Occurrence of distinguish peaks in the diffractogram of the thin sample is suggestive of polycrystalline quality of the sample. Estimation of X-ray pattern data display that sample made up of orthorhombic crystal structure (JCPDS 17-0320, JCPDS-6-0474). Scanning electron microscopy (SEM) study for as-deposited films showed that Image shows a lot of rods. These rods were produced in tiny rope structure. The rods are randomly spread. EDAX pattern shows that composition of the films are Sb: 24.27 ,Bi: 29.54 and S:46.19 respectively.

Keywords: $(Sb_{0.5}Bi_{0.5})_2S_3$; Composite; Chemical bath deposition; Thin films.

Introduction

Semiconductor liquid junction solar cells have been attracting attention in the last few years, due to growing interest in solar energy conversion [1]. These cells are simple in construction and have an advantage that they can be used for both photovoltage and chemical energy conversion. In the field of energy conversion, semiconductor electrolyte interface may be used for photoelectrolysis, photocatalysis and photoelectrochemical power generation.The composites of Bi_2S_3 and Sb_2S_3 should have the band gaps in between their individual bandgaps, which will match with the maximum solar energy spectrum, and therefore it is possible to have a greater efficiency of the device to use in above stated applications. Some reports are available for such type of combinations for CdS–Cu_xS [2], PbS–Cu_xS [3] and Bi_2S_3–Cu_xS [4] by using chemical bath deposition (CBD) method.

Research done by Jones et al [5], and by Mendis and Durose [6], indicate that the optoelectronic properties of materials can be affected by the presences of these defects since the measurable optoelectronic parameters will be affected. Antimony sulphide belongs to the chalcogenides group and it has been reported to exhibit the orthorhombic crystal structure [7], and a n-type electrical conductivity [8-9]. The constituent materials (Sb and S) are abundant and more environmentally acceptable compared to the Cadmium-related materials used in the fabrication of some advanced thin film solar cells. Antimony sulphide can be grown using low-cost and effective deposition technique. Some research groups have deposited thin films of Sb_2S_3 for various applications using different techniques such as; thermal evaporation [10], spray pyrolysis [11-12], Radiofrequency sputtering [13] successive ionic layer adsorption and reaction-SILAR [14], electrodeposition [15], and dip method [16]. In the

literature, antimony sulphide has been used in several device applications such as; (i) target material for TV cameras [17-19], (ii) microwave devices [20], (iii) switching devices [21], (iv) decorative coatings[22], and in various optoelectronic applications [23-24].

Bismuth trisulphide in thin flm form is a particularly challenging material because of its midway band gap (Eg . 1.7 eV), absorption coefficient of the order of 10^4 to 10^5 cm^{-1}, reasonable conversion efficiency and stability together with low cost [25,26]. The electrical conductivity and photoconductivity of such flms have been observed to vary over a considerable range and it is generally agreed that these variations are associated with defect states in the material.

In the present investigation, we present simple CBD method in which composite thin film of $(Sb_{0.5}Bi_{0.5})_2S_3$ is formed by optimizing various preparative parameters stepwise such as concentration, volume of metal ions, complexing agent and time, to get good quality films.

2 Experimental details:

Deposition of $(Sb_{0.5}Bi_{0.5})_2S_3$ Thin Film

The deposition of typical $(Sb_{0.5}Bi_{0.5})_2S_3$ thin films samples was synthesized from a reaction mixture. The chemical substances have been used in the following manner: 5 mL (0.2M) Bismuth nitrate, 5 mL (0.2M) Antimony trichloride, 4 mL (1M) Glycine and 15 mL (0.2M) sodium thiosulphate was mixed in each bath. The overall quantity of the prepared solution to 50 mL by using double distilled water. The bath consists of reaction mixture became kept in ice bath at temperature 278 K. The pH of reactive mixture became observed 4.63. Glass slides as well as stainless steel strips were maintained vertically to some extent slanted in a reaction mixture. The temperature of the reactive mixture became permissible to increase very gradually to 298 K. The glass slides and stainless steel material were removed from the bath after four hour. When the deposition process completed, the substrates have been eliminated from the reactive mixture, rinsed with the help of distilled water. The samples were dried in atmosphere. the sample was deposited on both sides of glass.

3 Result and discussion

3.1 Growth Mechanism

The speed of preparation of sample is chiefly reliant upon supersaturation, pH, temperature of reactive mixture and components. The generation of sample on the template surface from the solution phase is a two stage procedure. Generation of nucleation centers in the solution and on the template is the primary stage, even as, growth is the another step. The growth procedure takes place by either cluster-by-cluster or ion-by-ion process. The cluster-by-cluster growth consequences in the thick, powdery and diffusely reflecting samples. The ion-via-ion growth outcome in the thin, uniform and adherent sample. When the ionic product of metal ions and chalcogen ion larger than the solubility product the generation of sample happen. At this circumstance, the solution becomes supersaturated. The ions come together to develop the metal chalcogenide nuclei on the

template. On one occasion metal chalcogenide is produced, it acts as a catalyst for the further synthesis of fresh segment of the metal chalcogenide preferentially.

Initially, at 278K reaction bath can be prepared by mixing $Bi(NO_3)_3$**,** $SbCl_3$ Glycine, sodium thiosulphate. No film or precipitate is formed at this time. The solution is clear. The metal ion ($Sb^{+3}$and Bi^{+3}) are in complexed state with glycine. As the temperature is low the kinetic energy is less which keeps away from solid formation. The liberation of cations via complexing group was thermally stimulating procedure[27]. As the temperature rise gradually to the 298 K, it consequences in disintegration of complexes. It results in the development of an alloy in thin film form.

$$M + \text{Glycine} \rightarrow [M(\text{Glycine})_3]^{+3} \quad (M=Sb^{+3}/Bi^{+3})$$

$$Na_2S_2O_3 \rightarrow 2Na^+ + S_2O_3^{-2}$$

$$6S_2O_3^{-2} \rightarrow 3S_4O_6^{-2} + 6e-$$

In acidic conditions $S_2O_3^{-3}$ may be disintegrates as follows

$$3S_2O_3^{-2} + 3H^+ \rightarrow 3HSO_3^- + 3S$$

$$3S + 6e^- \rightarrow 3S^{-2}$$

$$1\text{-}x\ (Sb^{+3}) + x\ (Bi^{+3}) + 3S^{-2} \rightarrow (Sb_{1-x}Bi_x)_2S_3$$

In dip technique, the ionic product must be larger compare to the solubility product; solid formation occurs and ions unite on the templates and in the solution to give nuclei followed by growth procedure. The solubility product of Sb_2S_3 is larger than that of Bi_2S_3 [Ksp $(Sb_2S_3)=10^{-93}$ and Ksp $(Bi_2S_3)=10^{-97}$]. As the temperature raise free Bi^{+3} ions are produced that merge with S^{2-} ion preferentially on the template than Sb^{+3} ions generating orange layer of Bi_2S_3. This layers act as a catalyst for further growth of the sample. The developed layer grows promote by adsorbing progressively Bi^{+3}, Sb^{+3} and S^{-2} ions to give ternary $(Sb_{0.5}Bi_{0.5})_2S_3$ film.

The smaller the supersaturation, the metal chalcogenide formation is sluggish. At lower pH, the amount of Bi^{+3} ions diminish so that the ionic product of ions become fewer than solubility product of Bi_2S_3, as an outcome the creation Bi_2S_3 is not likely. The nucleation is not found out within the first 55 minutes and therefore the procedure necessitates an induction period for the nucleation on templates. These propose the ion-via-ion growth system as opposed to cluster-by-cluster. The current analysis specifies that homogenous samples were prepared at 300 min. The thickness became determined every 60 min and plotted against time as indicated in Fig. 1.From the figure, the thickness changes linearly with time, however exceeding 300 minute.

The amount of the reactive group diminishes and consequences in reduce in thickness. The entire thin sample have been homogenous well adherent to the templates. Growth kinetics for the preparation of usual $(Sb_{0.5}Bi_{0.5})_2S_3$ films is shown in Fig.1. The figure indicates that, in early steps of growth the deposition changes linearly with deposition time and then reduce subsequent to typical time. At higher temperature the speed of liberates of metal and sulphide ions are more rapidly, so solid formation happens rather than film synthesis.

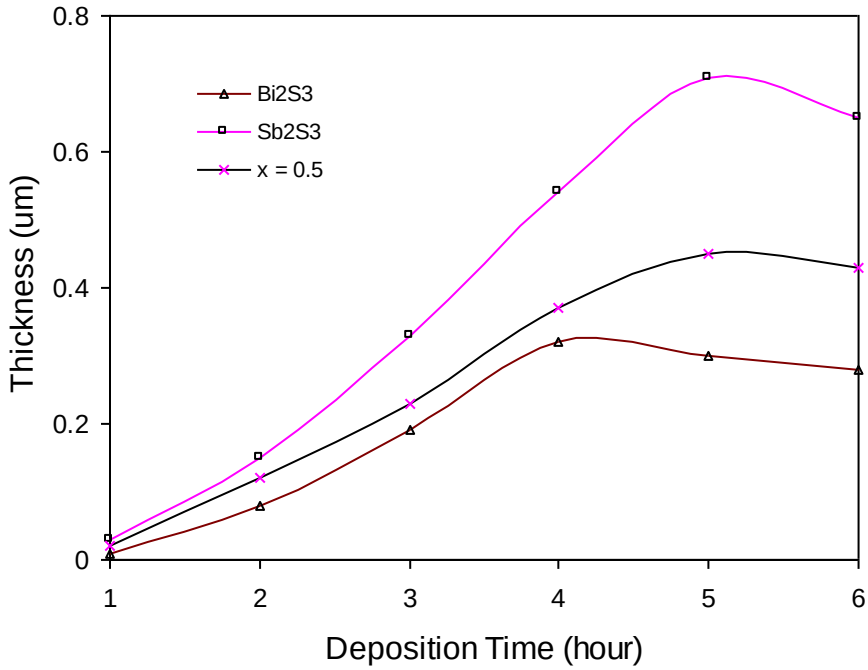

Diagram.1: Plot of thickness against deposition time for Bi_2S_3, Sb_2S_3 and x = 0.5 thin films

3.2 Thickness Measurement

Terminal thickness of the film has been determined by weight difference consideration technique via using equation.

$$t = m/\sigma A \text{----------} [1]$$

Where m-mass of the material coated on the template, A-Area of coated sample and σ is the density of prepared sample. (Sb_2S_3=4.64g/cm^{-3}, Bi_2S_3 =6.78g/cm^{-3}) Thickness was measured every one hour.[28-30] The behavior of thickness verses deposition time for Sb_2S_3 and Bi_2S_3 thin film shown in diagram : 1 The sample thickness increase with dipping time, but after certain time the growth development increase the maximum and afterwards simply smaller thickness may be obtained. This is primarily because of decreasing in amount of the free ions with reaction period in addition to dissolve of the sample in the reactive mixture. Similarly thickness was calculated each 5^{0}C rise and plotted with deposition temperature as indicated in diagram: 2 The plot

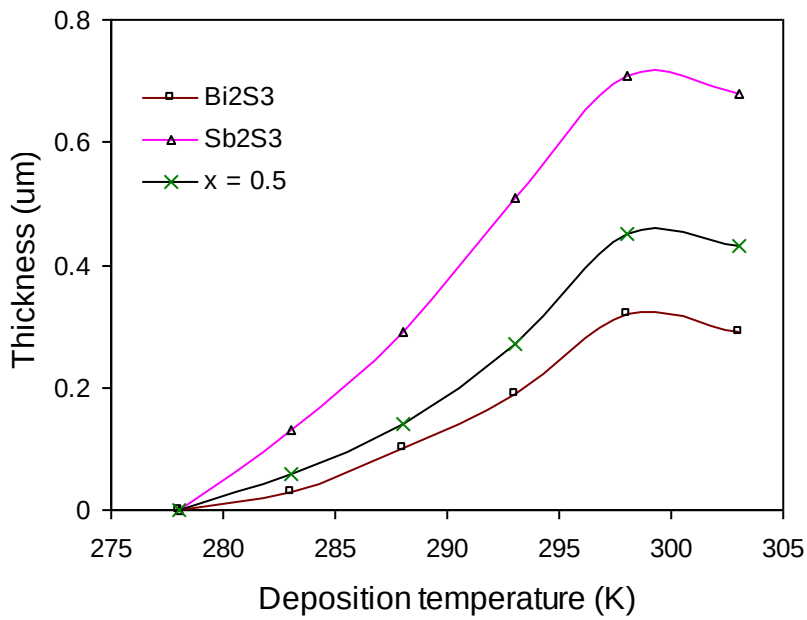

Diagram. 2: Plot of thickness against deposition temperature for Bi_2S_3, Sb_2S_3 and x = 0.5 thin films

indicates that in initial portion of formation of sample changes linearly with preparation temperature. The rate of formation of free antimony, bismuth and sulphide ions is more rapidly; therefore precipitation takes place instead of film formation. The maximum thickness was observed to be 0.71 and 0.32 µm for Sb_2S_3 and Bi_2S_3 thin film respectively. The deposition of Sb_2S_3 is found to be faster than that of Bi_2S_3 material. The variation of thickness is enlisted in table :1.

Table: 1 Thickness and Composition

Composition	Sb	Bi	S	Thickness (µm)
Sb_2S_3	46.22	-----	53.78	0.71
$(Sb_{0.5}Bi_{0.5})_2S_3$	24.27	29.54	46.19	0.45
Bi_2S_3	-------	47.16	52.84	0.32

3.3 X-ray diffractogram

X-ray diffractogram of $(Sb_{0.5}Bi_{0.5})_2S_3$ samples synthesized on non-conducting templates is presented in diagram: 3 Occurrence of distinguish peaks in the diffractogram of the thin sample is suggestive of polycrystalline quality of the sample. Estimation of X-ray pattern data display that sample made up of orthorhombic crystal structure (JCPDS 17-0320, JCPDS-6-0474).

The investigation of spectrum suggests that the pseudo binary thin sample is belonging to orthorhombic structure. The diffused background is due to amorphous templates as well as some amorphous phase there in $(Sb_{0.5}Bi_{0.5})_2S_3$ samples.

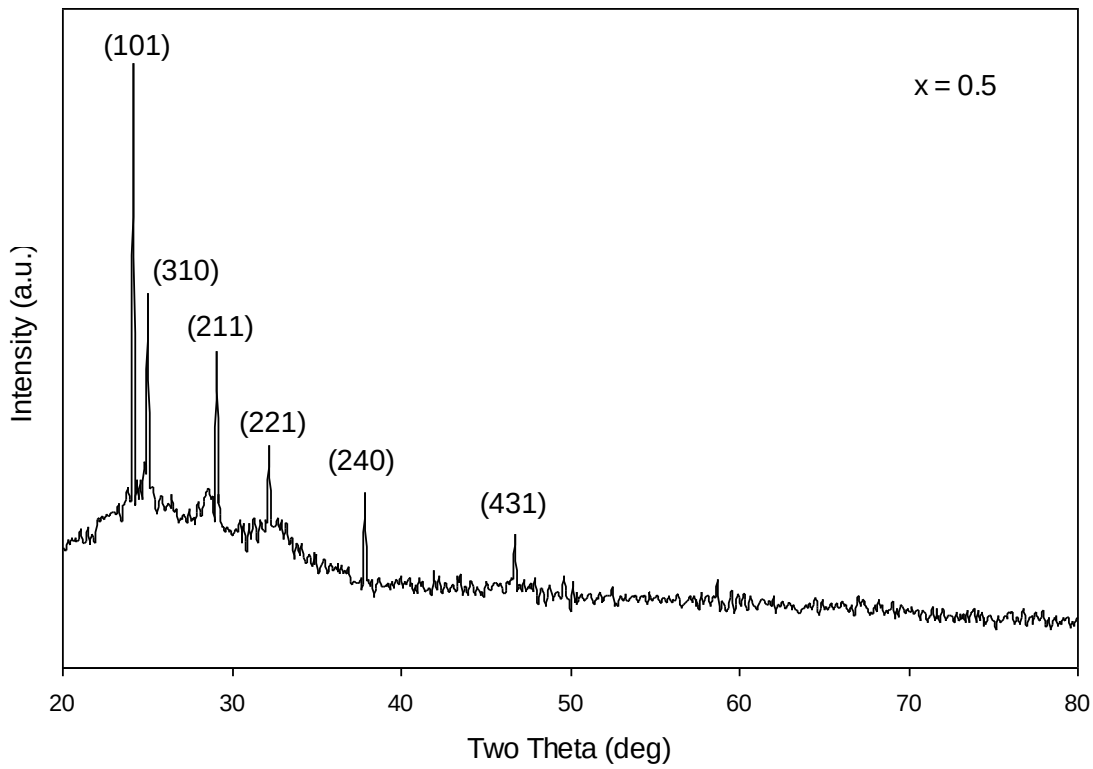

Diagram 3: X-ray diffractrogram of $(Sb_{0.5}Bi_{0.5})_2S_3$ sample.

Planes of elemental antimony, bismuth or sulphur were not found out and as a consequence it is indicated that the thin sample prepared in single phase. The strong and prominent reflection peaks suggesting that the thin films had been well crystallized. The $(Sb_{0.5}Bi_{0.5})_2S_3$ samples are recommend the utmost reflection along with (101) plane. The peak height of plane (101) go up significantly greater than another peaks (310) (211) (221) (240) and (431) suggesting a reasonably favored structure reflection in the (101) plane. The methods that observe the amount of the preferential orientation parameter 'f' for a observed peak related to remaining peaks in thin samples became applied.

In reference to such method the preferential orientation parameter 'f' (101) of the (101) plane for the $(Sb_{0.5}Bi_{0.5})_2S_3$ samples has been estimated via the path of comparing the fraction of (101) peak height with the sum of intensities of the whole planes have been determined for the $(Sb_{0.5}Bi_{0.5})_2S_3$ samples. f(101) = 0.3305, f(310) = 0.2051, f(211) = 0.1731, f(221) = 0.1215, f(240) = 0.0963, f(431) = 0.0732.

The various lattice factor have been measured apply of the subsequent relation.

$$(1/d^2) = (h^2/a^2+k^2/b^2+l^2/c^2) \text{-------} [2]$$

The lattice constant was determined to be a = 11.322, b = 10.433 and c = 3.889 Å The volume of single unit can be estimated via applying equation.[31]

$$V= abc \text{----------} [3]$$

The volume of single unit became found out to be 459.37 $(Å)^3$ The particle dimension is also measured applying the diffraction plane broaden of the peak (101) via applying

Equation.[32]

$$D = 0.9\lambda / \beta\cos\theta \text{----------} [4]$$

The particle dimension becomes measured to be 467.03 Å. The microstrain available in the thin sample was estimated by applying relation [33]

$$\varepsilon = \beta\cos\theta/4 \text{---------} [5]$$

The magnitude of microstrain obtained was 7.421 x 10^{-4}. Dislocation density is calculated applying the relation[34]

$$\varepsilon = \beta\cos\theta/4 \text{---------} [6]$$

The magnitude was found to be 4.584 x 10^{14} m^{-2}.

3.4 scanning electron Microscopy

The scanning electron image of the $(Sb_{0.5}Bi_{0.5})_2S_3$ samples prepared on the non conducting material was studied (Diagram 4). Image shows a lot of rods. These rods were produced in tiny rope structure. The rods are randomly spread, however their size and shape are rather consistent. These rods fused with each other. They well covered the glass substrate. No spherical grains were observed.

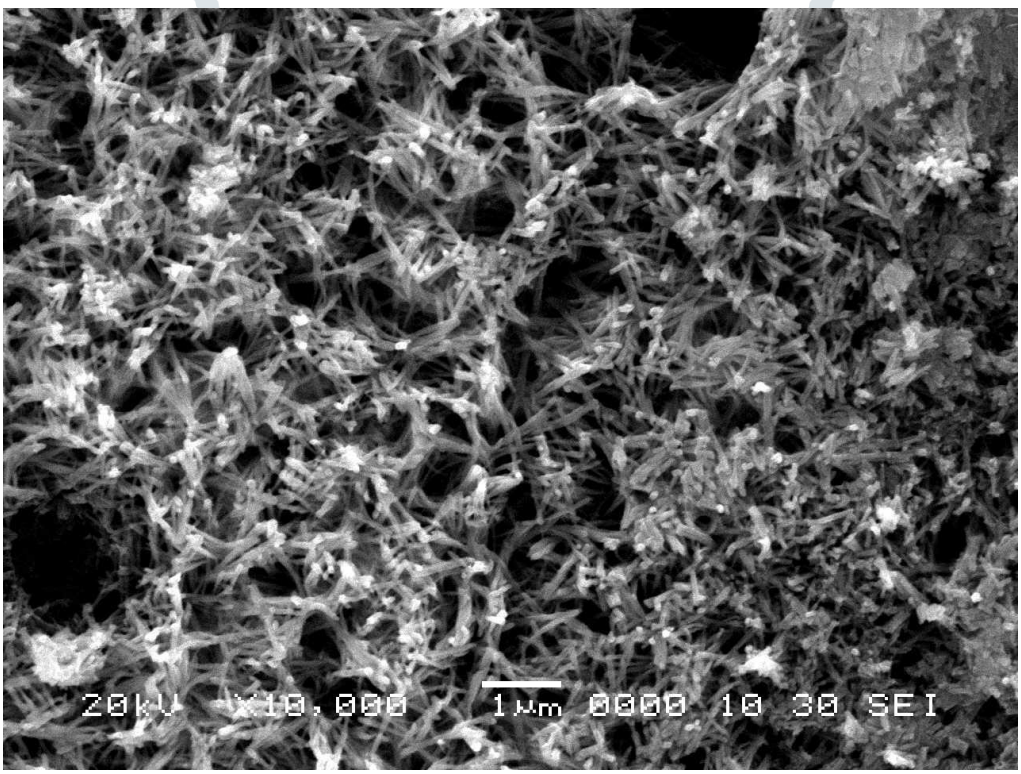

Diagram 4: Scanning electron image of $(Sb_{0.5}Bi_{0.5})_2S_3$ thin films.

3.5 Compositional Studay

Compositional analysis is too significant for estimating stoichiometry of grow thin film. Consequently compositional analysis makes available valuable information regarding the material property. Elemental properties of the sample was carried out using the energy dispersive method for $(Sb_{0.5}Bi_{0.5})_2S_3$ to find out the components in the sample. Diagram: 5 shows EDAX pattern of $(Sb_{0.5}Bi_{0.5})_2S_3$ thin film samples. The elemental investigation became take place only for antimony, bismuth and sulphur. The amount of Bismuth entered in the

lattice of Sb_2S_3 was determined. There is no other impurity in the film. The composition of the films are Sb:24.27,Bi:29.54 and S:46.19 respectively.

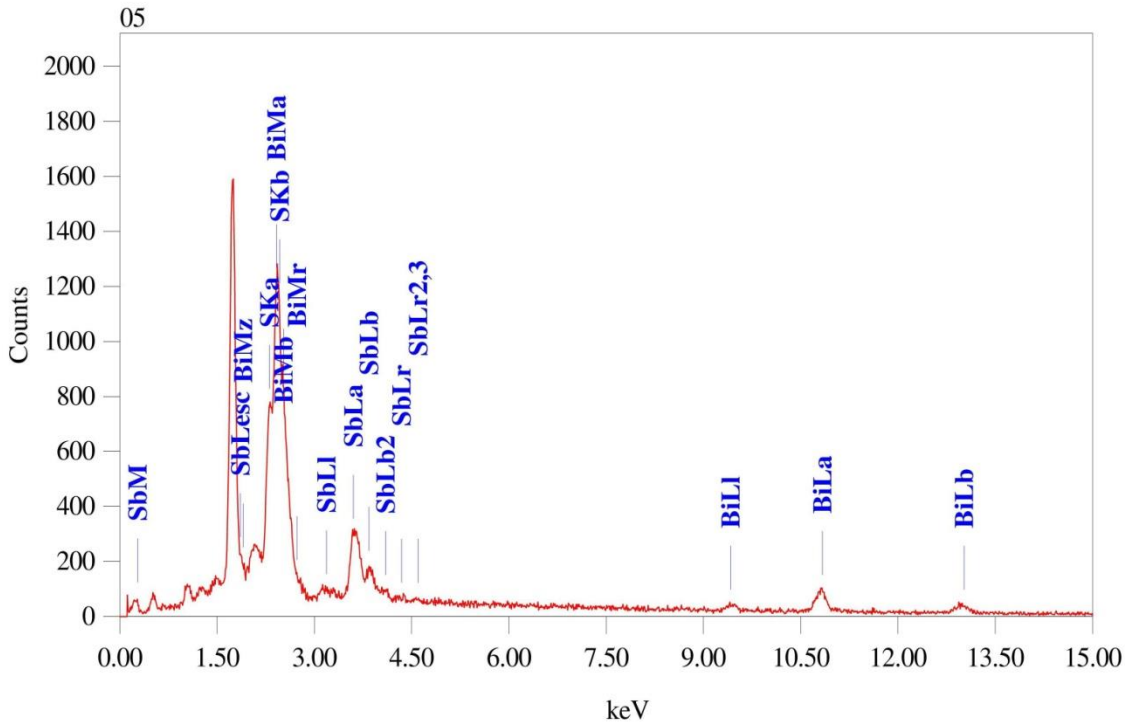

Diagram 5: EDAX pattern of $(Sb_{0.5}Bi_{0.5})_2S_3$ sample

Conclusion

1) The sample thickness increase with dipping time, but after certain time the growth development increase the maximum and afterwards simply smaller thickness may be obtained.

2) The diffractogram of the thin sample is suggestive of polycrystalline quality of the sample.

Estimation of X-ray pattern data display that sample made up of orthorhombic crystal structure.

3) The lattice constant was determined to be a = 11.322, b = 10.433 and c = 3.889 Å.

4) The particle dimension becomes measured to be 467.03 Å.

5) The magnitude of microstrain obtained was 7.421×10^{-4}.

6) The dislocation density was found to be 4.584×10^{14} m^{-2}.

7) SEM shows a lot of rods. These rods were produced in tiny rope structure .The rods are

Randomly spread.

7) The composition of the films are Sb:24.27,Bi:29.54 and S:46.19 respectively.

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