Synthesis of Antimony Sulphoiodide by CVD and its Characterization

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Abstract

Antimony Sulphoiodide is most widely studied compound in group V-VI-VII family due to its large number of properties. Varoius methods of synthesis have been reported. We are the first to report synthesis of shiny SbSI crystals by the Chemical Vapor Deposition (CVD) technique using powder of Antimony, Sulphur and Iodine as the starting material. Needle shaped thin crystals of SbSI were found grown vertically on the walls of the quartz tube. Characterizations of the sample were done using different techniques such as powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX). The charcteristcs peaks in Raman scattering plots (0-500 cm^{-1}) match with the reported results. The compound exibits high resitivity at room temperature in the order of 10^7 Ω-cm and dielectric constant in the order of 10^3 measured at 1 KHz.

Keywords: *SbSI, CVD, XRD, SEM, EDAX*

Introduction

Synthesis of $A^V B^{VI} C^{VII}$ (Where A= Sb, Bi; B= S, Se, Te and C= I, Cl, Br) compounds has been achieved [2]. Antimony sulphoiodide (SbSI) is one of the ternary chalcogenide of this group having unique properties such as rare combination of strongly coupled photoconductive[1,2], semiconductive[1,11], pyroelectric[4,5], and ferroelectric[3] properties, which have been subjects of much interest. Furthermore the crystal exhibits large electro-optical and electro-mechanical properties too [6]. The SbSI compound crystallizes in the orthorhombic system with space group D^{16}_{2h} above 20 ^{o} C and with the space group C^9_{2v} at temperature below that[7]. Due to these properties it is an attractive and suitable material for thermal imaging [8, 9, 10-13], light modulator[8, 9,14], ferroelectric field effect transistor (FeFET) [15,16], gas sensors [17], piezoelectric elements used in certain types of electromechanical transducers [8,18, 19, 20], temperature auto stabilized nonlinear dielectric elements (TANDEL) [21,22], time-controlling devices [8,9,23] etc. The SbSI is taken into consideration as a valuable material for photonic crystals[24, 25].

Being a promising material with potential applications, SbSI was synthesized by many researchers in a variety of ways. For the first time SbSI was synthesized by Donges [26] in 1950. Since then a lot of techniques have been used to produce SbSI crystals. Nittsche et al.[2] employed the melt growth route with the Bridgman–Stockbarger technique to produce parallel bundles of fibrous crystals. Kern[6] and Belyaev et al. [27] have used vapor phase growth technique to produce millimeter

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size crystals in a vacuum between 360 ^{0}C and 410 ^{0}C. At the same time, hydrothermal growth method [28,29] has also been used to synthesize SbSI. Popolitov and Litvin[8] conducted experiments under hydrothermal conditions at 250–300 ^{0}C, and 400 – 600 **ata** from H_2S solution at pH 5–6. Rau and Rabenau[29] used a quartz ampoule with an external pressure of 2400 ata and a filling 9M HI solution at 250–490 ^{0}C. Nassau et al. [30] used a modified flux technique by using excess SbI_3 as the solvent and circum venting the inherent growth anisotropy to grow large SbSI crystals. Palaniappan et al.[31] obtained large column like crystals from vapor phase at lower temperature of 320 ^{0} C. Recently Nowak et al[33] adopted sonochemical method for the direct preparation of nano crystalline SbSI.
In most of the reports Sb_2S_3 and SbI_3[32] are used as the starting material to derive SbSI with the following chemical equation:

(i) $Sb_2S_3 + SbI_3 = 3SbSI$
(ii) $SbI_3 + 2Sb + 3S = 3SbSI$

Use of the elements Sb, S and I were avoided with a view that Sb, S and I unite exothermally generating a huge vapor pressure which may lead to explosion. In this paper we are, for the first time, reporting the synthesis of SbSI by Chemical Vapor Deposition (CVD)technique using Sb, S and I as the starting material with a simple chemical equation:

(iii) Sb + S + I = SbSI

Experimental Methods

Synthesis of the material

A CVD setup consisting of a high temperature furnace with temperature control unit, a quartz tube as the reaction chamber, Ar as the carrier gas and a suitable arrangement to control the gas flow was fabricated (Fig. 1).

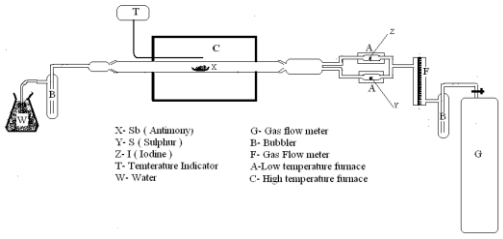

Fig-1 Schematic diagram of CVD setup used for synthesis of SbSI

Figure -2 Photograph of experimental setup used for the reaction

Known quantity of powered Sb was taken into a quartz boat and was placed inside the quartz tube, Sulphur and Iodine were placed in the two separate tubes of similar dimensions having separate openings, outside the high temperature zone of the furnace. The quartz tube had two inlet and one outlet openings and was inserted in high temperature zone of horizontal furnace. The two tubes were placed in two separate heating mantles (not shown in the figure – 1). To both the tubes Ar gas was supplied from one end; whereas the other end of both the tubes was connected to the quartz reaction tube. A flow meter was connected between the tubes and the gas cylinder to control the flow rate of the gas entering into the tubes. Along with the flow meter two bubblers were also introduced at the inlet and outlet of the quartz tube. The gas coming out of the reaction tube was immersed into a container filled with water.The actual experimental setup shown in the figure 2. Initially the quartz tube was flushed for 5 to 6 min with Ar, so that fully inert atmosphere is created in the reaction chamber. No gas flow was allowed there-after till the furnace attained 650 ^{0}C temperature. Then the heating mantles were switched ON, so that by the time

main furnace attains 650 ^{0}C, tubes containing Sulphur and Iodine attain the temperature little more than their meting points so that they produce the vapor of the S and I. These vapors were then carried to the quartz tube along with the flow of the Ar gas. The reaction time was standardized to 6 hrs. so that the whole amount of the S and I get transported to Sb chamber. The product was in the form of a large number of thin needle shaped SbSI crystals accumulated vertically on the walls of the quartz tube in the low temperature zone and a polycrstalline bulk in the boat. The crystals so obtained were regrounded and presses into pallets for further studies.

Characterization

The obtained needles were cleaned with CS_2 and CCl_4 and grinded to powder. SbSI crystals were characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX) and Raman scattering.

Electrical Propterties

Two probe setup was develped to find the reistance of the pallet in the temerature range of 40 ^{o}C to 250 ^{o}C. To menatin the inert atmosphre Ar gas was passed contineously through the chamber containing the sample. To find the dielectric constant, the SbSI pallet was sanwitched batween two parallel plates and its capcitance was measured at room temperature (30 ^{o}C). Aplab L-C-R meter was used to find the capacitance at 1 KHz.

Results and Discissions

Though the reaction amongst these three elements took place in the high temperature zone of the quartz tube, a large number of thin needles shaped SbSI crystals accumulated vertically on the walls of the quartz tube in the low temperature zone. Few agglomerated crystals were seen sticking on the wall of the tube (Fig-4). However, there was some residual material remaining in the boat too. The residue in the boat was found to be solidified form of Sb. The method is found suitable for the synthesis of SbSI and can be used to synthesise other group V-VI-VII elements but the yield of this method is as low as 29.25 % (Table-1). The loss in of the total weight of the constituent materials and the product with the outgoing vapors is observed. This is due to the high temperature and large reaction time with a significant flow rate of carrier gas to tarnsport the Sulfur and Iodine in the reaction Chamber containing Antimony.

Table-1 *Percentage yield of CVD method in the synthesis of SbSI*

Sample no.	Mass of Sb	Mass of S	Mass of I	Mass of Sb+S+I	Mass of produced SbSI	Yield (%)
					residue + needles	
L-1	1 gm	1.0 gm	1.0 gm	3 gm	0.960 gm	32.00
L-2	1.0 gm	1.0 gm	1.5 gm	3.5 gm	0.820 gm	23.43
L-3	1.0 gm	1.0 gm	2.0 gm	4.0 gm	0.990 gm	14.75
L-4	1.0 gm	1.5 gm	1.0 gm	3.5 gm	0.830 gm	23.71
L-5	1.0 gm	1.5 gm	1.5 gm	4.0 gm	0.980 gm	24.50
L-6	1.0 gm	1.5 gm	2.0 gm	4.5 gm	1.040 gm	22.22
L-7	3.0 gm	4.0 gm	2.0 gm	9.0 gm	2.970 gm	33.00
L-8	3.0 gm	4.0 gm	3.0 gm	10 gm	2.380 gm	23.80

L-9	7.5 gm	10.0 gm	10.0 gm	27.5 gm	6.050 gm	22.00
L-11	3.0 gm	2.0 gm	3.0 gm	8 gm	2.720 gm	34.00
L-12	3.0 gm	2.0 gm	4.0 gm	9 gm	2.690 gm	29.89
L-13	4.0 gm	3.0 gm	2.0 gm	9 gm	3.100 gm	34.44
L-14	4.0 gm	3.0 gm	3.0 gm	10 gm	3.410 gm	34.10
L-15	4.0 gm	3.0 gm	4.0 gm	11 gm	3.730 gm	33.91
L-16	4.0 gm	4.0 gm	2.0 gm	10 gm	4.200 gm	42.00
L-18	4.0 gm	4.0 gm	4.0 gm	12 gm	4.200 gm	35.00
Average Percentage yield = 29.25 %						

XRD Analysis

The XRD pattern of the reaction product (Fig. 3) shows well defined, sharp peaks indicating high purity and well crystallized structure. All the diffraction peaks can be indexed to be a pure orthorhombic phase for SbSI with the cell constants a= 8.516 ^{0}A, b =10.124 ^{0}A, c = 4.122 ^{0}A. The identification was done using the PCW computer program. In each XRD pattern, the reflections can be indexed to those of the corresponding pure phases, and all the lattice parameters are very close to the reported data[34]. The intensities and positions of the peaks are in good agreement with literature values for SbSI[34]

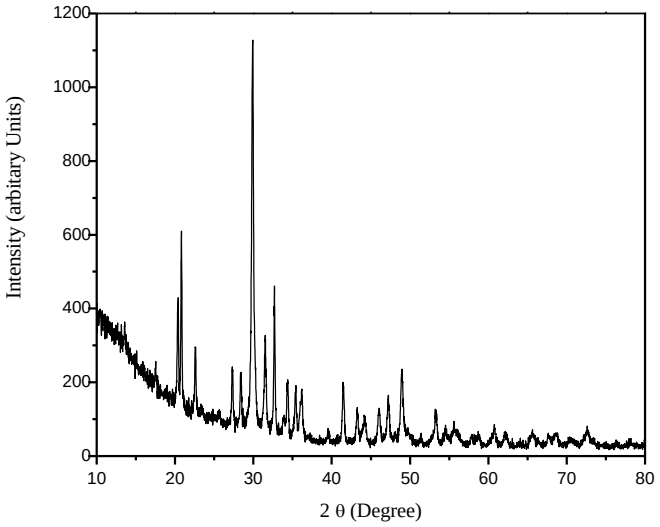

Figure-3*. XRD of SbSI at room temperature*

Energy Dispersive X (EDAX)

The characteristic EDAX peaks for antimony, sulfur and iodide were observed and confirmed with an elemental atomic percentage of 29.53: 31.00: 39.47 for Sb, S and I averaged over the SbSI. So, it indicates within the experimental error a Stoichiometric SbSI.

SEM Analysis

The photograph (Fig.-4 and 5) and the SEM images (Fig.-6 and 7) of the sample reveal its predominant needle like morphology.

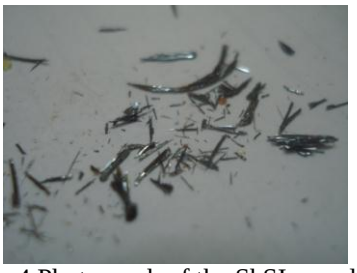

Fig-4 Photograph of the SbSI samples

Fig-5 Photograph of the SbSI single crystal

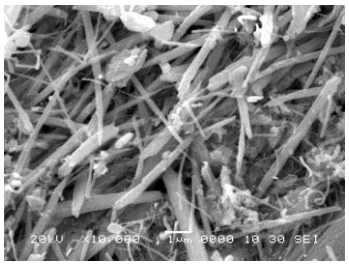

Fig-6 SEM image of SbSI crystals

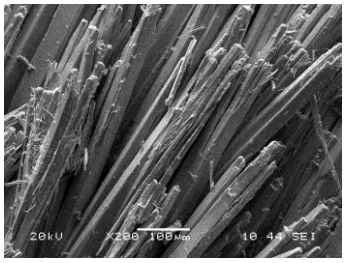

Fig-7 SEM image of SbSI poly crystalline bulk

Raman Scattering Data

The Raman spectra of powdered SbSI observed at room temperature matches with the reported data [35]. The reported Raman shift was in the range of 40- 200 cm^{-1} where as the Raman spectra shown in fig-8 ranges from 0 to 500 cm^{-1} with characteristics peaks at 70, 81, 90, 118 , 151, 226 and 331 cm^{-1}. Therefore we are reporting additional peaks in the range of 200 to 500 cm^{-1}.

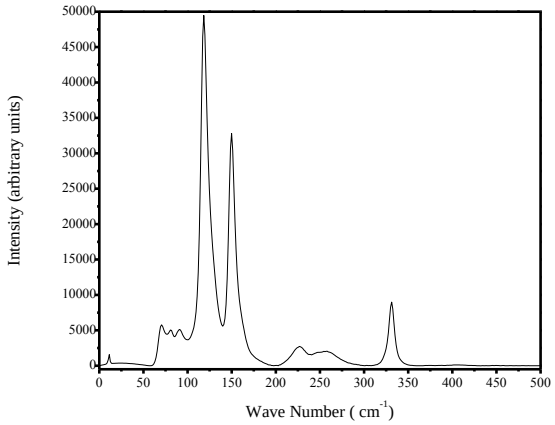

Fig-8 *Raman Spectrum of SbSI*

The observations made shows that the CVD method can be a novel method to prepare fine needles of SbSI, but it does not seem to be suitable for fabricating big single crystals.
It seems that SbSI belongs to the family of many solid materials [33] that naturally grow into polycrystalline structure and this habit is determined by the highly anisotropic bonding in the crystallographic structure. The observed rod type morphology of the product is possibly due to the inherent chain type structure and growth habit of SbSI.

Resistivity and Dielectric Constant

The Resistance vs Temperature measuremts indicate semiconducting behaviour shown by the material (fig-9). The electrical resitivity of the sample was calculated to be 5 x 10^7 Ω-*cm* whereas the dielectric constant was found to 10232 at 30 ^{o} C.

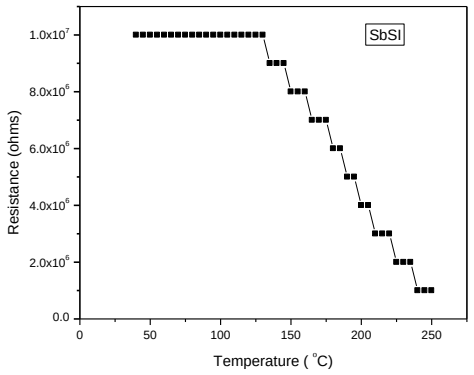

Fig-9 *Resistance varisation of SbSI with Temparature*

Conclusion

The compound was prepared essentially quantitatively from the constituents (the elements: antimony, sulphur and iodine) using Chemical Vapor Deposition. Characterization of the SbSI was confirmed using various different techniques, such as powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX). The charcteristcs peaks in Raman scattering plots (0-500 cm^{-1}) match with the reported results. The compound exibits high resitivity at room temperature in the order of 10^7 Ω-cm and dielectric constant in the order of 10^3 measured at 1 KHz.The chemical Vapor deposition method can be a novel method to prepare fine needles of SbSI, but it does not seem to be suitable for big single crystals. The loss of the constituent materials with the outgoing vapors is also observed with the measurement of the total weight the constituent materials and the product. This method can be a suitable method for the development of uniform thin films of SbSI as seen on the walls the quartz tube.

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