

# Antimony chalcogenide thin films: chemical bath deposition and formation of new materials by post deposition thermal processing

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Results of the deposition of thin films of sulfide and selenide of antimony from chemical baths containing  $\text{SbCl}_3$  and source of sulfide or selenide ions in presence of ligands forming soluble complexes with antimony will be presented. As prepared, the films are of poor crystallinity and show larger band gaps (eg., 2.2 eV in the case of  $\text{Sb}_2\text{S}_3$ ) than those reported for the material in bulk, due to quantum confinement arising from the very small crystallites. However, the films after annealing in nitrogen around 350 °C show well defined peaks in their x rays diffraction patterns. The paper will also deal with the formation of new thin film materials through annealing multilayer thin films involving the antimony chalcogenide films. This possibility opens up the fabrication of thin film semiconductors covering a wide range of structural, electrical and optical properties for large area photonic applications.

*Keywords:* Thin films, chemical bath deposition, new materials

## 1. Introduction

With an optical band gap in the range of 1.06 eV to 1.88 eV in crystals and in polycrystalline thin films with  $\text{V}_2\text{-VI}_3$  composition [1,2], the sulfides and selenides of antimony are potential absorber materials in devices for photovoltaic conversion of solar energy. The use of  $\text{Sb}_2\text{S}_3$  thin films in Schottky barrier solar cells of Pt-  $\text{Sb}_2\text{S}_3$  [3] and n-  $\text{Sb}_2\text{S}_3$  /p-Ge [4] structures with conversion efficiencies of 5.5 and 7.3 %, respectively, has been reported.

Chemical bath deposition (CBD) of different semiconductor thin films has been reported from our laboratory, as reviewed in a previous paper [5]. Annealing of multilayer thin films semiconductors like  $\text{Bi}_2\text{S}_3\text{-CuS}$  [6] and  $\text{Sb}_2\text{S}_3\text{-CuS}$  [7] has shown the formation of films of ternary composition,  $\text{Cu}_3\text{BiS}_3$  and  $\text{CuSbS}_4$ , respectively. We consider that the possibility of creating new materials through interfacial diffusion of atoms in chemically deposited multilayer stacks as demonstrated in  $\text{PbS-CuS}$ ,  $\text{ZnS-CuS}$  and  $\text{Bi}_2\text{S}_3\text{-CuS}$  films [6,8] is very high.

InSb is important for thermal infrared detection and as magnetoresistive element in position-sensitive or speed-sensitive sensors [9]. Plasma-assisted epitaxial growth [10] and electrodeposition [9] techniques have been reported for the deposition of thin films of InSb.  $\text{CuSbS}_2$  as a mineral is named chalcostibite [11, 12]. Chalcostibite is lead gray or black, has an orthorhombic structure, its average density is 4.87 g/cm<sup>3</sup>, its composition is 25.48 % of Cu, 48.81 % of Sb and 25.71 % of S and can be found in Wolfsberg in the Harz Mountains.

The aim of this work is to report our results about antimony sulfide and selenide thin films, respectively, by CBD and the formation of new compounds; in the case of InSb for the evaporation of In on the  $\text{Sb}_2\text{S}_3$  thin film and post deposition thermal annealing and in the case of  $\text{CuSbS}_2$  through annealing thin films of  $\text{Sb}_2\text{S}_3\text{-CuS}$ .

## 2. Experimental procedure

Antimony sulfide and antimony selenide thin films were deposited by chemical bath method. Microscope glass slides were used as substrates. These substrates were cleaned using commercial detergent and deionized water and dried in air. The bath for antimony sulfide was prepared in a 200 ml beaker as follows: 1.3 g of  $\text{SbCl}_3$  (Baker Analyzed Reagent) was dissolved in 5 ml of acetone. This was followed by the addition of 50 ml of 1 M  $\text{Na}_2\text{S}_2\text{O}_3$  (Reactive Analytic Monterrey) that was previously cooled to 10°C and 145 ml of cold deionized water and stirred well. The bath for antimony selenide was prepared in a 100 ml beaker as follows: 1 g of  $\text{SbCl}_3$  was dissolved in 37 ml of 1M sodium citrate, then was added 20 ml of ammonia and 24 ml of 0.4M  $\text{Na}_2\text{S}_2\text{O}_3$ , respectively. Water was added until complete 100 ml. The substrates were placed in the bath, vertically supported on the wall of the beaker. The antimony sulfide deposition was made at 10°C from 1 h until 4 h. At the end of deposition, glass slides covered with specularly reflective orange-yellow. The antimony selenide deposition was made at room temperature from 2 h until 5 h. All thin films were removed from the bath at the end of the deposition time, washed well with deionized water and dried.

Thin films of indium were deposited on the  $\text{Sb}_2\text{S}_3$  thin films by thermal evaporation of 20-60 mg of 99.999% In (Alfa Products) in a high-vacuum coating unit after attaining a residual pressure of 10<sup>-6</sup> mbar. Since the films of indium are very soft, step thickness measurement was not possible. Thus the thickness of In film deposited on the slides was estimated gravimetrically; approximately 0.075 μm of In film was deposited on an  $\text{Sb}_2\text{S}_3$  coated substrate for an indium source of 20 mg. The  $\text{Sb}_2\text{S}_3\text{-In}$  films were annealed for 1 h each in a vacuum oven (T. M. Vacuum Products Inc., New Jersey) in 50 m Torr of nitrogen. Thin films of copper sulfide were deposited on antimony sulfide.

The deposition bath for copper sulfide was prepared by the sequential addition of 10 ml of 0.5 M  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,

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8 ml of 50 % triethanolamine, 8 ml of 30 % NH<sub>4</sub>OH, 10 ml of 1M NaOH, 6 ml of 1 M thiourea and 58 ml of deionized water to a 100 ml beaker. Glass substrates coated with antimony sulfide thin films were placed in the copper sulfide bath. The deposition were made at room temperature during 2 h. The Sb<sub>2</sub>S<sub>3</sub>-CuS films were annealed for 1 h each in a vacuum oven in 100 mTorr of nitrogen.

**3. Characterization**

X-ray diffraction (XRD) patterns were recorded using Cu-K<sub>α</sub> radiation on a Siemens D-500 diffractometer. The optical transmittance (T%) and the near-normal specular reflectance (R%) of the films were recorded on a Shimadzu UV-3101PC UV-VIS-NIR scanning spectrophotometer with air and a front aluminized mirror, respectively, as references. For the electrical measurements, silver paint electrodes were printed on the samples in a coplanar configuration. The dark- and the photo- currents were recorded on a computerized system using a Keithley 619 electrometer and a Keithley 230 programmable voltage source. Photocurrent response measurements were made under 300 W/m<sup>2</sup> intensity of illumination from a tungsten-halogen lamp. The thickness of the films were measured using an Alpha Step 100 unit

**4. Results and discussion**

Figure 1 shows the thickness of the films obtained at different time of deposition for antimony sulfide and selenide, respectively. The Sb<sub>2</sub>Se<sub>3</sub> samples obtain a major saturation thickness than the Sb<sub>2</sub>S<sub>3</sub> samples, whereas the last ones have a small nucleation time. In the Sb<sub>2</sub>Se<sub>3</sub> case the quantity of ammonia controls the velocity of the reaction.

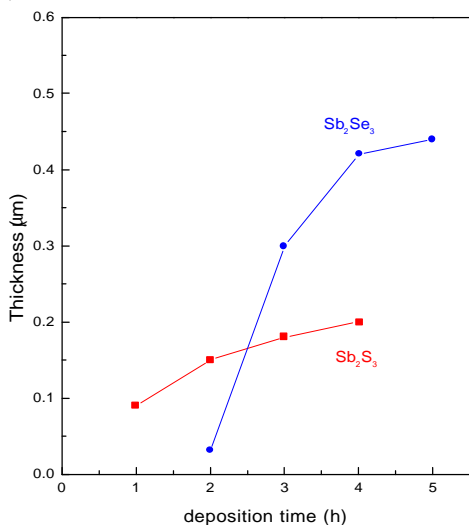


Fig 1.- Thickness versus deposition time for the Sb<sub>2</sub>S<sub>3</sub> and Sb<sub>2</sub>Se<sub>3</sub> samples.

Figure 2 gives the optical transmittance spectra of Sb<sub>2</sub>S<sub>3</sub> and Sb<sub>2</sub>Se<sub>3</sub> samples before and after thermal annealing.

The Sb<sub>2</sub>S<sub>3</sub> thin films show higher transmission. The thermal annealing of the samples produced a notable shift in the transmittance curve toward the longer wavelength side of the curve, indicating a decrease in the optical band gap.

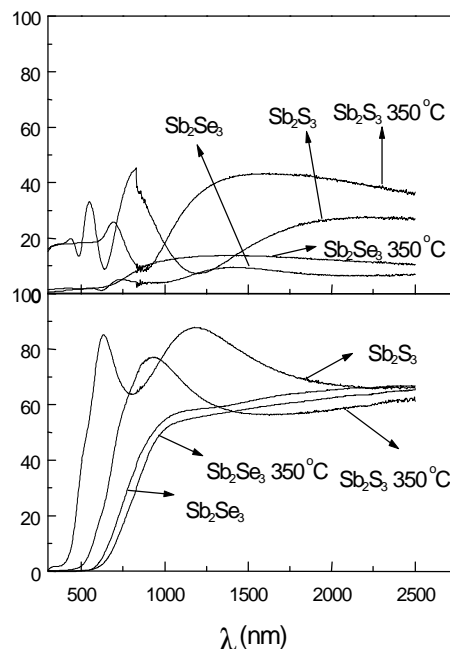


Fig 2.- Optical transmittance spectra for the as prepared and annealed Sb<sub>2</sub>S<sub>3</sub> and Sb<sub>2</sub>Se<sub>3</sub> samples.

The optical absorption coefficients (α) of the materials were determined from the T% and R% values: α = (1/d) ln [(T%-R%)/T%], where d is the film thickness. Values of α<sup>2</sup> for Sb<sub>2</sub>S<sub>3</sub> annealed at 350 °C and α<sup>1/2</sup> for Sb<sub>2</sub>Se<sub>3</sub> annealed at 400 °C, respectively are plotted against photon energy hv in Fig. 3. The as-prepared Sb<sub>2</sub>S<sub>3</sub> sample shows a direct band gap of 2.43 eV which is higher than that of the annealed sample, 1.78 eV, due to quantum confinement in the nanocrystalline sample [3]. The same behavior is observed for the Sb<sub>2</sub>Se<sub>3</sub> samples. As grown Sb<sub>2</sub>Se<sub>3</sub> thin films have a band gap of 1.71 eV which is higher than that of the annealed sample, 1.21 eV, which is in agreement with the 1.11 eV reported.

As prepared, the films of Sb<sub>2</sub>S<sub>3</sub> and Sb<sub>2</sub>Se<sub>3</sub> show high electrical resistance, approximately 10<sup>7</sup> Ω cm. The results of photoconductivity measurements for both type of samples as grown and annealing are given in Fig. 4. The as grown Sb<sub>2</sub>Se<sub>3</sub> are more photosensitivity than the as grown Sb<sub>2</sub>S<sub>3</sub> thin film. The samples annealed are more photosensitivity, due, probability to an enhanced in the grain size.

Figure 5 gives the XRD patterns of Sb<sub>2</sub>S<sub>3</sub>-In films after annealing at 300°C in nitrogen for 1 h. The XRD patterns of the annealed samples of Sb<sub>2</sub>S<sub>3</sub>-In films show peaks that match with the peaks due to reflections from the (111), (220) and (311) planes of cubic InSb (JCPDS 6-0208). This suggests that annealing the multilayer films of Sb<sub>2</sub>S<sub>3</sub>-In results in the reaction in solid state between Sb<sub>2</sub>S<sub>3</sub> and In

leading to the formation of an InSb film. A little quantity of In<sub>2</sub>O<sub>3</sub> is still present, but we can remove by etching in HCl. In the low energy region the data may be extrapolated to indicate a direct band gap of less than 0.3 eV, as is showing in Fig. 6. This is higher than the reported band gap value of 0.17 eV, possibly due to the very small crystallites. The order of magnitude of the absorption coefficient is in agreement with the reported values for this material [ref 4, p.751].

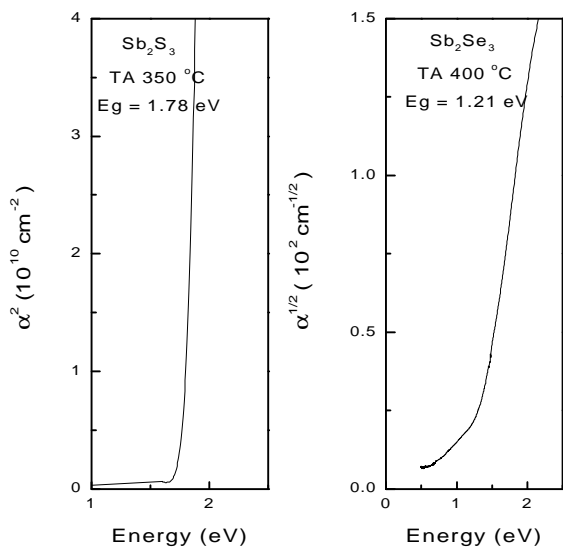


Fig 3.- Values of  $\alpha^2$  for Sb<sub>2</sub>S<sub>3</sub> annealed at 350 °C and  $\alpha^{1/2}$  for Sb<sub>2</sub>Se<sub>3</sub> annealed at 400 °C, respectively plotted against photon energy.

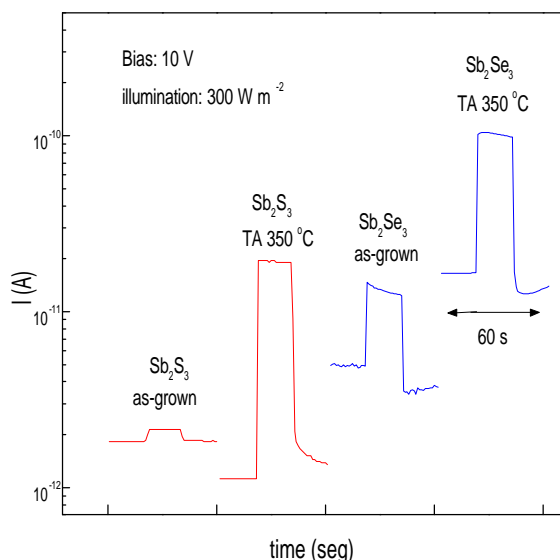


Fig 4.- Photocurrent response curves for the as prepared and annealed Sb<sub>2</sub>S<sub>3</sub> and Sb<sub>2</sub>Se<sub>3</sub> samples. Bias: 10 V. Illumination 300 W m<sup>-2</sup>.

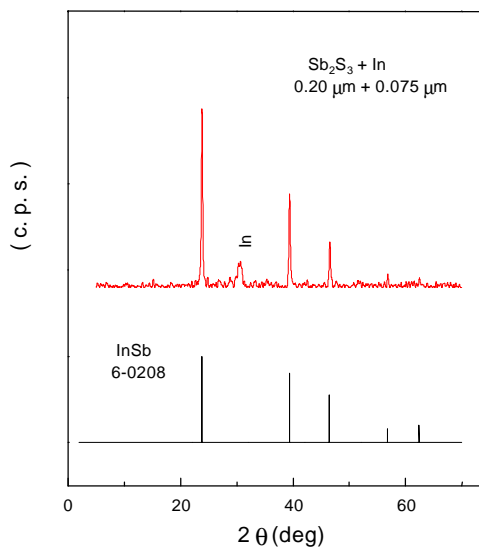


Fig 5. XRD spectra of InSb sample.

The thickness of the two participating films could be varied in such a way that the molar ratio of Sb<sub>2</sub>S<sub>3</sub>:In is nearly 1:2 as required for the stoichiometric reaction, Sb<sub>2</sub>S<sub>3</sub> + 2In → 2InSb + 3S↑. Typically, for a 0.2 μm film of Sb<sub>2</sub>S<sub>3</sub> (mass density, 4.1 g/cm<sup>3</sup>, molecular mass 339.7 g/mol), 0.076 μm of In (mass density, 7.3 g/cm<sup>3</sup>, atomic mass 114.8 g/mol) is required for complete conversion

A current of 5x10<sup>-3</sup> A observed at a bias of 10 V in the InSb-In<sub>2</sub>O<sub>3</sub> film indicates a sheet resistance of 2x10<sup>3</sup> Ω/square. This is due to the conductive In<sub>2</sub>O<sub>3-x</sub> layer formed on the surface during the annealing, indicated in the XRD patterns in Fig. 5. The conclusion that this layer is located at the top is based on the observation of the decrease in the current by six orders of magnitude during etching the film in dilute HCl. The optical transmittance spectra (not shown) shows that the etching does not significantly affect the curves, indicating that the absorber layer is left almost intact during the process.

Figure 6 gives the XRD patterns of CuSbS<sub>2</sub> sample. Upon annealing the Sb<sub>2</sub>S<sub>3</sub> (0.22 μm) + CuS (0.07 μm) at 400 °C during ½h in a 100 mT nitrogen atmosphere, the conversion to CuSbS<sub>2</sub> is observed. Well defined peaks matching with the (002), (102), (004), (111), (013), (015), (106)/(212), (213), (020), (215), (311) and (122)/(304) planes of the orthorhombic chalcocite are observed. The relative intensity ratios of the standard CuSbS<sub>2</sub> is very nearly followed in the CuSbS<sub>2</sub> thin film produced, thus, no notable preferential orientation is present in these films. The thickness of the two films could be varied in such a way that the molar ratio of Sb<sub>2</sub>S<sub>3</sub>:CuS is nearly 1:2 as required for the stoichiometric reaction: Sb<sub>2</sub>S<sub>3</sub>+2CuS→2CuSbS<sub>2</sub>+S↑. Typically, for 0.2 μm film of Sb<sub>2</sub>S<sub>3</sub> (mass density of 4.1 g/cm<sup>3</sup> and molar mass of 339.7 g/mol), 0.1 μm of CuS (mass density of 4.6 g/cm<sup>3</sup> and molar mass of 95.61 g/mol) is required for the complete

formation. This is mostly satisfied in the case of annealed  $Sb_2S_3$  (0.20  $\mu m$ ) +  $CuS$  (0.08  $\mu m$ ) film, leading the nearly total conversion. Values of  $\alpha^2$  are plotted against photon energy  $h\nu$  in Fig. 7. A band gap of 1.53 eV was calculated from the optical absorption, as was described above.

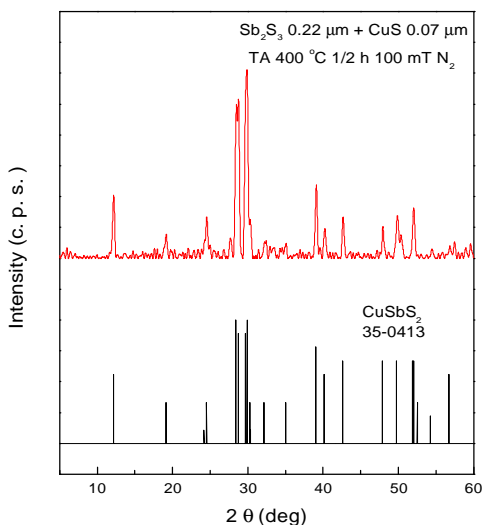


Fig 6. XRD spectra of  $CuSbS_2$  sample.

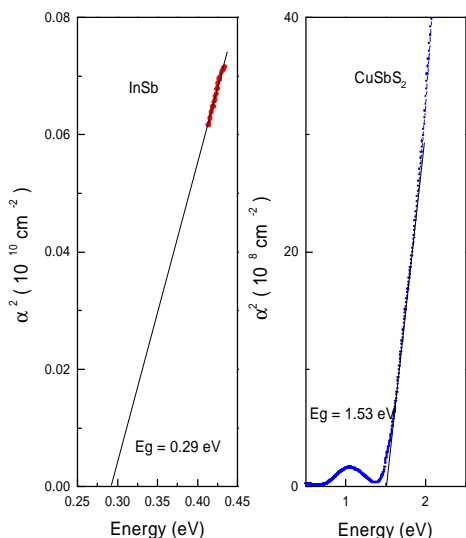


Fig 7.- Squares of the optical absorption coefficients plotted against photon energy for the  $InSb$  and  $CuSbS_2$  samples.

### 5. Conclusions

In this paper we present a chemical bath deposition method to obtain thin films of antimony sulfide and selenide, respectively.  $InSb$  was obtained by the evaporation of  $In$  on thin films of  $Sb_2S_3$  and post deposition thermal annealing. The possibility to obtain ternary

compounds, like  $CuSbS_2$ , using CBD and post deposition thermal annealing is shown.

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