# Semiconducting Thin Films of $CuSbS_2$

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***Abstract***
In this paper we present a method to produce polycrystalline $CuSbS_2$ thin ?lms through a solid-state reaction at 350 ºC and 400 ºC involving thin ?lm multilayer of $Sb_2S_3$ – CuS or $Cu_{2-x}Se$ by chemical bath deposition technique. The formation of the ternary compound was confirmed by X-ray di?raction (XRD). A direct optical band gap of approx. 1.57 eV and a p-type electrical conductivity of $10^{-3}$ $(\Omega \bullet cm)^{-1}$ were measured. These optoelectronic characteristics show perspective for the use of $CuSbS_2$ as a suitable absorber material in photovoltaic applications.

## 1. Introduction

Many authors have reported antimony sulphide ($Sb_2S_3$) thin films obtained by chemical deposition technique since early 1990's [1-4]. Chemical bath deposition (CBD) is a simple and low-cost method to produce thin films of different semiconductor compounds [5-6]. This method has been employed by some authors to synthesis ternary compounds of antimony chalcogenides involving heat treatments in air or nitrogen atmosphere [7-9]. Rodríguez *et al.* have reported the formation of $CuSbS_2$ by chemical bath with a p-type electrical conductivity of 0.03 $(\Omega \bullet cm)^{-1}$ and a direct optical band gap of 1.52 eV [7]. Subsequently, the same group reported the use of $CuSbS_2$ thin films in a p-i-n solar cell structure with an open circuit voltage of 345 mV [10]. Ezugwu *et al.* employed CBD technique to deposit directly $CuSbS_2$ with direct band gaps between 1.30 and 2.30 eV [11]. Its properties match with the requirement for the photovoltaic materials [12]. Manolache *et al.* have obtained this material by spray pyrolysis deposition with suitable characteristics for its application in photovoltaic devices [13]. Rabhi *et al.* have prepared polycrystalline $CuSbS_2$ using thermal evaporation method. The films showed direct band gaps at 1.3 and 1.79 eV after heat treatment at 200 °C in $N_2$ [14]. The growing effort to find absorber materials involving copper, is because of the p-type conductivity originating from copper deficiency, which can be utilized to produce p-type absorber films as an alternative to $Cu(In/Ga)(S/Se)_2$. An alternative to replace the $CuInS_2$ is $CuSbS_2$; which belongs to the same I-III-$VI_2$ group of semiconductor with the chalcopyrite structure, in which the ionic radius of indium and antimony are almost equal [7].

In this work, we present the formation of $CuSbS_2$ thin films of about 600 nm in thickness through the solid state reaction at 350-400 °C of chemically deposited thin films of $Sb_2S_3$–CuS or $Cu_{2-x}Se$.

## 2. Experimental details

### 2.1 $Sb_2S_3$ thin films

Thin films of $Sb_2S_3$ were deposited on clean microscope glass slides using a chemical bath deposition reported previously by Grozdanov [3] and modified later by Nair *et al.* as reported in reference [4]. The reaction solution was prepared by dissolving 650 g of $SbCl_3$ in 2.5 mL acetone and 25 mL 1 M $Na_2S_2O_3$. The bath was maintained at 1°C during 6 h. After this time an amorphous $Sb_2S_3$ thin film of 600 nm in thickness was obtained. The methodology of deposition has been explained in reference [15]. Heat treatment of these films in air at 200 °C during 15 min was necessary in order to give adhesion between the film and the glass substrate. Subsequently, a thin film of CuS was deposited on the preheated $Sb_2S_3$ films using the chemical bath reported previously in the reference [16] or chemical bath of $Cu_{2-x}Se$ using the composition reported in reference [17].

### 2.2 CuS thin film

Thin films of CuS were deposited on the $Sb_2S_3$ thin films using a reaction solution containing 10 mL of 0.5 M $CuCl_2$, 8 mL of triethanolamine (TEA) 50%, 8 mL of 15 M ammonia (aq.), 10 mL of 1 M NaOH, 6 mL of 1 M thiourea and distilled water to complete a volume of 100 mL. During one hour at 30 °C, a CuS thin film of ~ 120 nm in thickness was deposited on the $Sb_2S_3$ films. The preheated $Sb_2S_3$ films were placed in the CuS bath after 30 min of the bath preparation, in order to avoid the peeling of the $Sb_2S_3$ films due to the ammonia contained in the CuS bath. Temperature of the bath was maintained at 30 ºC. Samples were removed from this bath after 1 h, 2 h and 3 h, rinsed in distilled water and dried in air at room temperature.

### 2.3 $Cu_{2-x}Se$ thin film

The thin films of $Cu_{2-x}Se$ were deposited on $Sb_2S_3$ thin films using reaction solution containing 10 mL of 0.5 M $CuSO_4$, 1.5 mL of ammonia (aq.) 15 M, 12 mL 0.4 M $Na_2SeSO_3$ solution and distilled water to complete 100 mL volume bath. Substrates with $Sb_2S_3$ thin film previously deposited were placed in the $Cu_{2-x}Se$ bath 30 min after preparation. The chemical bath was maintained at 30 °C during 1 h, 2 h and 3 h. Samples were taken out from the bath each hour, rinsed in distilled water and dried in air at room temperature.

### 2.4 Characterization

X-ray diffraction (XRD) patterns were recorded using a Rigaku D-Max 2000 diffractometer using Cu-K$\alpha$ ($\lambda$= 1.5406 Å) radiation in the glazing incidence mode (1.5°). The optical transmittance and specular reflectance spectra were measured using a Shimadzu 3100 PC spectrophotometer in the wavelength range of 250 – 2500 nm. Photocurrent responses of the films were obtained using tungsten–halogen radiation and a computerized measurement system using a Keithley 230 programmable voltage source and a Keithley 619 multimeter. Thickness of the films was measured using Alpha Step 100 (Tencor, CA).

## 3. Results and discussion

### 3.1 X-Ray Diffraction

Figure 1 shows the XRD patterns of $Sb_2S_3$ (600 nm) – CuS (120 nm) annealed at 350 °C (figure 1a) and annealed at 400 °C (figure 1b) in $N_2$ at 40 Pa during 1 h. We observed that for the sample heated at 350 °C, the majority of the diffraction peaks correspond to the XRD pattern of $Sb_2S_3$ (PDF 42-1393). In the case of the sample heated at 400 °C, the peaks correspond to the pattern given for $CuSbS_2$ (PDF 44-1417). From figure 1a and 1b we may note that the conversion of $Sb_2S_3$–CuS film to $CuSbS_2$ begins at 350 °C, but a near complete conversion takes place when the films are annealed at 400 °C as reported by Rodríguez *et al.* [10]. The stoichiometric calculations of these films were obtained from the mass densities and mass formula of the individual layers as suggest in reference [10].

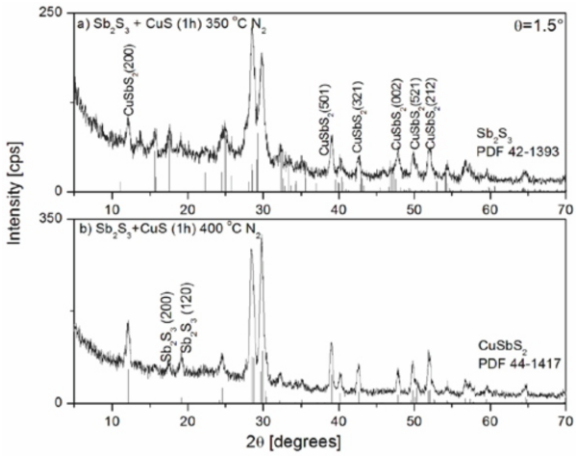


**Figure 1.** XRD patterns of $Sb_2S_3$ (600 nm) – CuS (120 nm): a) annealed at 350 °C in $N_2$ at 40 Pa for 1 h and b) annealed at 400 °C in $N_2$ at 40 Pa for 1 h.

There is a notable dissolution of the $Sb_2S_3$ films during the deposition of the subsequently CuS layer. This was confirmed by the thickness measurements of the as-prepared $Sb_2S_3$ (300 nm) thin films and the final thickness after the CuS deposition. In table 1 these measurements are given. However, the thin film of CuS grew quickly on the $Sb_2S_3$ films heated at 200 °C in air during 15 min. Also we found that the $Sb_2S_3$ losses can be avoided if a chemical bath of $Cu_{2-x}Se$ is used instead of the CuS bath. The thickness measurements of the as - prepared films of $Sb_2S_3$ after the $Cu_{2-x}Se$ deposition are also given in table 1.

**Table 1.** Final thickness measurements of the as-prepared stack films of $Sb_2S_3$-CuS and $Sb_2S_3$+$Cu_{2-x}Se$.

| Duration (h) | Thickness $Sb_2S_3$+CuS (nm) | Thickness $Sb_2S_3$+$Cu_{2-x}Se$ (nm) |
|---|---|---|
| 0.5 | 205 | 340 |
| 1.0 | 300 | 350 |
| 1.5 | 304 | 420 |
| 2.0 | 305 | 520 |

Figure 2 shows the XRD patterns of the $Sb_2S_3$ (300 nm) + $Cu_{2-x}Se$ (100 nm) layers after heat treatment in: a) $N_2$ atmosphere at 350 ºC during 1h. b) 350 °C in air during 5 min and c) 400 °C in air during 5 min. In these systems we found ternary compounds of $Cu_3SbS_3$ and $Cu_3SbSe_3$ for the sample heated in $N_2$ at 350 °C during 1 h, due to the excess of copper in the samples. A rapid thermal treatment in air during 5 min was made in order to avoid the losses of sulfur or selenium, as well as, to do the heat treatment easier for large area applications. The formation of a solid solution is expected from figure 2a, 2b and 2c because the position of the XRD peaks are between the peaks for $Cu_3SbS_3$ - $Cu_3SbSe_3$ and $Cu_3SbS_4$ - $Cu_3SbSe_4$ due to the presence of selenium in the reaction solution for the deposition of $Cu_{2-x}Se$.

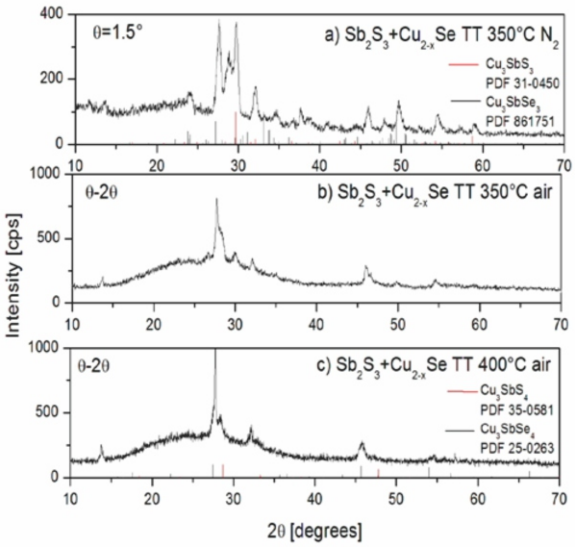


**Figure 2.** XRD patterns of the films $Sb_2S_3$ (300 nm) + $Cu_{2-x}Se$ (100 nm) after heat treatment in: a) $N_2$ at 350 °C and 40 Pa during 1h b) 350 °C in air during 5 min and c) 400 °C in air during 5 min.

### 3.2 Optical Properties

The optical transmittance T (%) and specular reflectance R (%) spectra of the films of approximately 600 nm in thickness obtained from $Sb_2S_3$-CuS heated in $N_2$ at 350 °C and 400 °C and from $Sb_2S_3$-$Cu_{2-x}Se$ of 400 nm in thickness heated in $N_2$ at 350 °C were recorded to evaluate the absorption coefficient ($\alpha$) of the films considering multiple reflections [18]:

$$\alpha = \frac{1}{d}\ln\left[\frac{(1-R)^2+\sqrt{(1-R)^4+(2RT)^2}}{2T}\right]$$

The optical band gap of the material was obtained from the intercepts of plots of $(\alpha h\nu)^2$ or $(\alpha h\nu)^{2/3}$ versus photon energy ($h\nu$), depending on whether the optical transitions are allowed or forbidden transitions.

The values of $(\alpha h\nu)^n$ vs. $h\nu$ of: a) $Sb_2S_3$+CuS annealed in $N_2$ at 350 °C, b) $Sb_2S_3$+CuS annealed in $N_2$ at 400 °C and c) $Sb_2S_3$+$Cu_{2-x}Se$ annealed in $N_2$ at 350 °C are showed in figure 3.

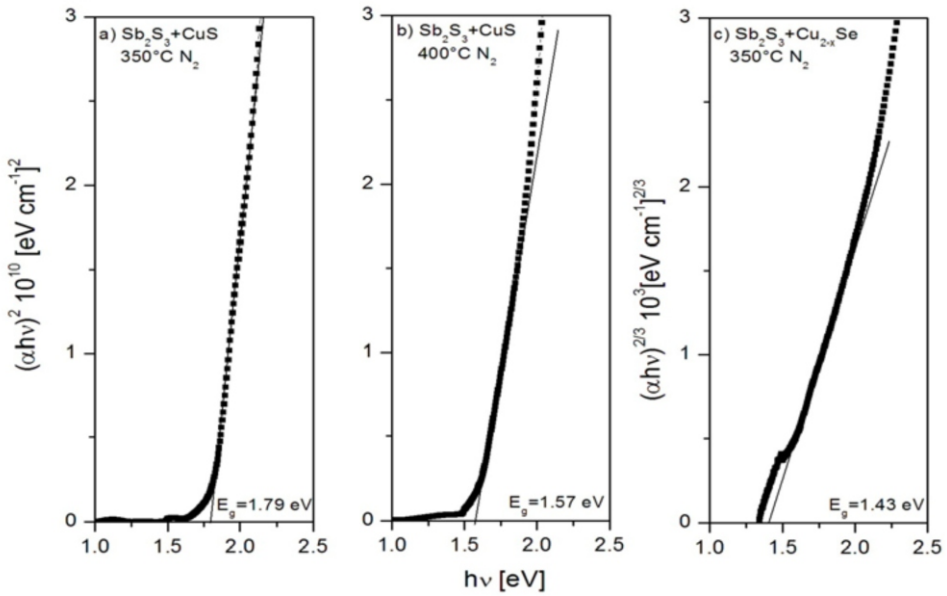


**Figure 3.** Plots of $(\alpha h\nu)^n$ vs. $h\nu$ of: a) $Sb_2S_3$+CuS annealed in $N_2$ at 350 °C, b) $Sb_2S_3$+CuS annealed in $N_2$ at 400 °C and c) $Sb_2S_3$+$Cu_{2-x}Se$ annealed in $N_2$ at 350 °C.

A straight line was observed in the plot of $(\alpha h\nu)^2$ vs. $h\nu$ for the samples showed in figure 3a and 3b which indicates the presence of a direct optical band gap.

To obtain the value of $E_g$, an extrapolation of the plot to the photon energy axis was made. For the sample annealed at 350 °C (figure 3c) $E_g$ equals to 1.79 eV. This value corresponds to that reported for crystalline $Sb_2S_3$ [19] as observed in the XRD patterns showed in figure 1a. For the sample annealed at 400 °C the energy gap is located in 1.57 eV, which corresponds to that value reported for $CuSbS_2$ suggesting a total conversion of the stack films [10].

In both cases the straight line indicates the presence of a direct band gap. For the sample $Sb_2S_3$+$Cu_{2-x}Se$ (figure 3c) the straight line can be seen in the plot of $(\alpha h\nu)^{2/3}$ vs. $h\nu$ which suggests the presence of a direct band gap with forbidden transitions with $E_g$ = 1.43 eV as expected for this material due to the presence of selenium in the film.

### 3.3 Electrical properties

The photocurrent response of the $CuSbS_2$ thin films obtained from: a) $Sb_2S_3$+CuS annealed at 350 °C and b) $Sb_2S_3$+CuS annealed at 400 °C in $N_2$ are given in figure 4. A bias, 10 V has been applied in each case. The electrical conductivity of the films in the dark is in the range of $10^{-3}$ $(\Omega \bullet cm)^{-1}$.

Upon illumination, there is an increase in the conductivity by almost an order of magnitude, but the films annealed at temperature 400 °C have more conductivity. P-type conductivity was confirmed by the hot-probe method.

The photo-response of the samples obtained by annealing of the $Sb_2S_3$+$Cu_{2-x}Se$ was negligible, hence this response is omitted in figure 4, and the formation of $CuSbS_2$ was observed only in the samples with heat treatment of $Sb_2S_3$+CuS thin films. The very small effect of illumination in these samples is similar to those presented in degenerate semiconductors materials.

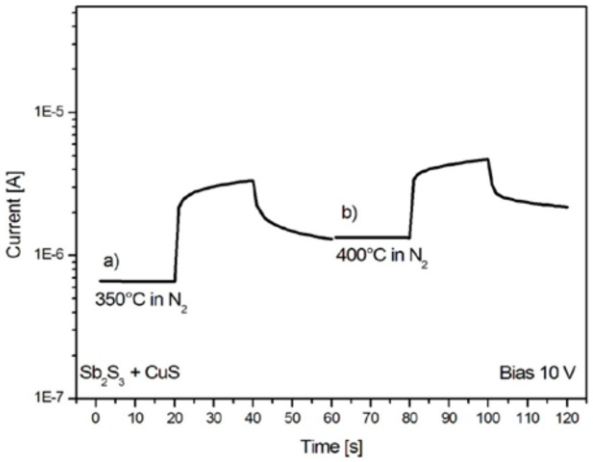


**Figure 4**. Photocurrent response of: a) $Sb_2S_3$+CuS annealed at 350 °C and b) $Sb_2S_3$+CuS annealed at 400 °C in $N_2$.

## 4. Conclusions

Thin films of $SbS_2$ were deposited by chemical bath deposition technique on glass substrates. It has been demonstrated that the obtained films must be annealed in vacuum at temperature of 400 °C for an almost total conversion. For the films of $Sb_2S_3$+CuS annealed at 400 °C, an optical direct band gap was observed at 1.57 eV which correspond to the reported for $CuSbS_2$. For the films heated at 350°C the energy band gap was observed at 1.79 eV which corresponds to $Sb_2S_3$. For the films obtained by annealing of $Sb_2S_3$+$Cu_{2-x}Se$ a direct band gap was observed at 1.43 eV, however, involves forbidden transitions. The p-type conductivity of the samples was confirmed by the hot-probe measurements. Dark conductivity in the order of $10^{-3}$ $(\Omega \bullet cm)^{-1}$ for $CuSbS_2$ thin films matches well with previous reports for this material, but no effect of illumination was observed in the samples with $Cu_{2-x}Se$.

T he dissolution of $Sb_2S_3$ thin film in the CuS bath was avoided by pre-heating the $Sb_2S_3$ films in air during 15 min before the deposition of CuS or by using a chemical bath of $Cu_{2-x}Se$, which was demonstrated by the thickness measurements of the films. The optical and electrical properties of the thin films presented here show its suitable characteristics for application in photovoltaic devices. Further work on the optimization on the film thickness in the stack films of $Sb_2S_3$ - $Cu_{2-x}Se$ and heat treatments are necessary to produce $CuSbSe_2$.

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