

X-ray diffraction and compositional studies of AgInS₂ thin films obtained by spray pyrolysis

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Received: 9 June 2007 / Accepted: 11 September 2008 / Published online: 16 October 2008
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Abstract Silver indium sulfide (AgInS₂) thin films have been prepared by the spray pyrolysis technique using silver acetate, indium acetate, and *N,N*-dimethylthiourea as precursor compounds. Depending on the film preparation conditions, AgInS₂ thin films are obtained which could be candidates to be used in photovoltaic devices. X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS) compositional studies were done on films formed at different substrate temperatures (T_s) and Ag:In:S ratios in the starting solutions. When Ag:In:S ratios are 1:1:1, 1:0.25:2, and 1:1:2, XRD patterns of the thin films indicated that the crystallographic structure is mainly chalcopyrite AgInS₂. An additional phase, acanthite Ag₂S, appeared when the depositions were done at low T_s . EDS analysis showed that AgInS₂ films near stoichiometric composition were obtained by using an atomic ratio of Ag:In:S = 1:1:2 in the starting solution and $T_s = 400$ °C.

Introduction

The I–III–VI₂ compounds are the ternary analogs of the II–VI compounds. AgInS₂ belongs to the I–III–VI₂

compounds, and it does exist in two ordered phases: chalcopyrite (tetragonal) and orthorhombic [1]. The orthorhombic modification of AgInS₂ (denoted here by o-AgInS₂) is pseudo-wurtzite, just as the chalcopyrite (tetragonal) structure (denoted here by ch-AgInS₂) is pseudo-zinc-blende [1]. The values for the unit cell dimensions of the tetragonal phase are $a = 5.8792$ and $c = 11.203$ Å; and those of the orthorhombic phase are $a = 7.001$, $b = 8.278$, and $c = 6.698$ Å [2]. AgInS₂ single crystals are generally considered to have the chalcopyrite structure at low temperatures, whereas their orthorhombic variation is a structure that has been synthesized only at higher temperatures, as described by Roth et al. [2]; they reported that the phase transition occurs at ~ 620 °C [2].

AgInS₂ thin films have considerable potential to be used as a photovoltaic absorber material, specially when it is mixed with CuInSe₂, as reported by Loferski et al. [3].

AgInS₂ single crystals have been prepared by several techniques, including: melting the constituent elements [2], directional freezing of melts [4], “Hot-Press” method [5], and vertical gradient freezing (VGF) method [6]. On the other hand, polycrystalline thin films of this material have been prepared by single-source thermal evaporation [7], hot wall epitaxy [8, 9], and spray pyrolysis [10–12]. At present, all the research work on AgInS₂ prepared by spray pyrolysis (SP) has been carried out by using silver chloride [10], silver nitrate [10], and silver acetate [10–12] as the silver source; indium chloride [10–12] as indium source; and thiourea [10–12] and *N,N*-dimethylthiourea as sulfur sources in the starting solutions. Gorska et al. [10] replaced thiourea by *N,N*-dimethylthiourea, and reported that all the properties of the films were essentially the same.

This work deals with the deposition and characterization of AgInS₂ thin films prepared using silver acetate, indium acetate, and *N,N*-dimethylthiourea as precursor compounds.

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We have used indium acetate instead of indium chloride as the indium source to deposit AgInS_2 by the SP technique to prevent the non-intentional doping with chlorine coming from the indium chloride. We are reporting the structural and chemical composition properties of the AgInS_2 thin films obtained using different deposition temperatures (T_s) and atomic ratios Ag:In:S in the starting solutions.

Experimental

AgInS_2 thin films were prepared by SP using solutions of silver acetate, indium acetate, and *N,N*-dimethylthiourea as silver, indium, and sulfur sources, respectively. In a previous study [13] we have used the same indium and sulfur sources to prepare In_2S_3 thin films. In this work, silver and indium acetates were dissolved separately in deionized water at 60 °C by stirring continuously during 30 min; it was necessary to add some acetic acid, in order to obtain precipitate-free solutions (pH = 3). For the silver acetate solution, 5 ml of acetic acid for each 100 ml of solution was sufficient to avoid precipitates, whereas for the indium solution 26 ml of acetic acid for each 100 ml of solution should be added to obtain precipitate-free solutions. *N,N*-dimethylthiourea was dissolved in ethyl alcohol at ambient temperature by stirring continuously for 10 min. The starting solutions to be sprayed were prepared by mixing the appropriate amount of each solution. The following atomic ratios in the starting solutions were used: Ag:In:S = 1:1:1 (molar concentrations of 0.025 M of indium acetate, 0.025 M of silver acetate, and 0.025 M of *N,N*-dimethylthiourea); Ag:In:S = 1:0.25:2 (molar concentrations of 6.25×10^{-3} M of indium acetate, 0.025 M of silver acetate, and 0.05 M of *N,N*-dimethylthiourea); and Ag:In:S = 1:1:2 (molar concentrations of 0.025 M of indium acetate, 0.025 M of silver acetate, and 0.05 M of *N,N*-dimethylthiourea). Microscope glass slides from Corning with dimensions of $2.5 \times 2.5 \text{ cm}^2$ were used as substrates. The substrates were cleaned using standard procedures.

The spray pyrolysis setup is described elsewhere [14]. Air at a pressure of 4 bar was used as carrier gas. The gas and solution flow rates were kept constant at 10 l/min and 5 ml/min, respectively. The substrate-to-nozzle distance was 30 cm. The substrates were heated using a molten tin bath. The temperature was measured by having a K-type thermocouple in contact with the tin bath. The tin bath temperature was varied from 250 to 450 °C in steps of 50 °C. The deposition time was selected to be 7 min.

The X-ray diffraction measurements were performed by X-ray diffraction (XRD) using a Rigaku D-Max diffractometer with Cu-K_α (wavelength, $\lambda = 1.5406 \text{ \AA}$) radiation. The average dimensions of the crystallite sizes were

determined by the Scherrer formulae. The chemical composition of the thin films was determined by the energy dispersive X-ray spectroscopy (EDS) using an Oxford Instruments system attached to the scanning electron microscope (SEM).

Results and discussion

The AgInS_2 films prepared throughout this study were reddish brown in transmitted daylight and pinhole free. Samples were prepared using T_s from 250 °C to 450 °C.

X-ray diffraction studies

Figure 1 shows the XRD patterns of Ag–In–S samples prepared at T_s in the range of 250–450 °C using an atomic ratio in the starting solution of Ag:In:S = 1:1:1.

In this figure there are no diffraction peaks for $T_s = 250 \text{ °C}$. This may indicate that the deposited material is either amorphous or the crystallite sizes are very small. At substrate temperatures below 400 °C only two minor peak intensities associated to the (013) and $(\bar{1}03)$ directions of Ag_2S [JCPDS 14-0072] start becoming relevant. At $T_s = 400 \text{ °C}$ also some peaks associated to the (012), (014), and (015) directions of the same Ag_2S are present, and two peaks that can be associated to the (112) and (204) directions of ch-AgInS_2 [JCPDS 25-1330] can also be seen. At the highest substrate temperature used (450 °C), even if traces of Ag_2S are still present, the intensity of the (200)

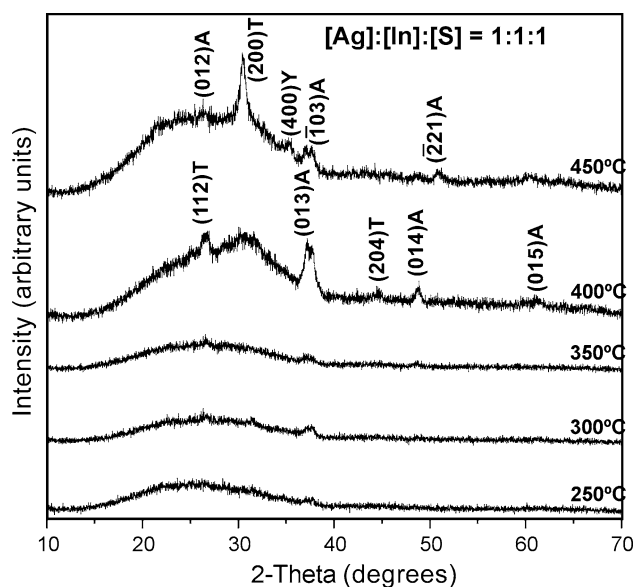


Fig. 1 XRD patterns for samples prepared at different T_s using an atomic ratio in the starting solution of Ag:In:S = 1:1:1. “A” corresponds to Ag_2S (acanthite), “T” to the tetragonal variation of the AgInS_2 (chalcopyrite) and “Y” to In_2O_3 (cubic)

peak associated with a reflection of ch-AgInS₂ [JCPDS 25-1330] is predominant, besides another minor intensity associated to cubic In₂O₃ [JCPDS 06-0416]. This could mean that such a temperature is the upper limit before an oxidation of the film may occur. Gorska et al. [10] and Ortega-López et al. [12] report also the presence of this traces, even when they used N₂ as the carrier gas. Thus, the use of N₂ instead of air as carrier gas could not avoid the oxidation of indium during the deposition process, specially when films are deposited at high T_s .

Using the Scherrer's formulae without any correction, the average crystallite sizes were estimated to be 13.4 and 24.5 nm, for films grown at $T_s = 400$ °C and $T_s = 450$ °C, respectively. The lattice parameters were also calculated for films grown at $T_s = 400$ °C and $T_s = 450$ °C. As at $T_s = 400$ °C our films are mainly Ag₂S [JCPDS 14-0072], we obtained the following lattice parameters: $a_0 = 3.8282$, $b_0 = 7.0665$ and $c_0 = 7.8189$ Å. At $T_s = 450$ °C we have ch-AgInS₂ [JCPDS 25-1330] as a main compound, and the calculated lattice parameters are: $a_0 = 5.8790$ and $c_0 = 12.6091$ Å. In this last case we have, thus, a chalcopyrite AgInS₂ lattice with an opened structure in the c_0 direction (from reference [JCPDS 25-1330], the standard for c_0 is equal to 11.203 Å). A possible reason for this behavior is proposed in the section "Compositional analysis."

Next, we dropped the atomic concentration of indium in the starting solution to have an atomic ratio of Ag:In:S = 1:0.25:2. Figure 2 shows the XRD patterns for samples prepared at T_s in the range of 300–450 °C. The diffraction pattern of the film prepared at $T_s = 300$ °C showed peaks on the (110), ($\bar{1}$ 12), ($\bar{1}$ 21), ($\bar{1}$ 03), (200), and

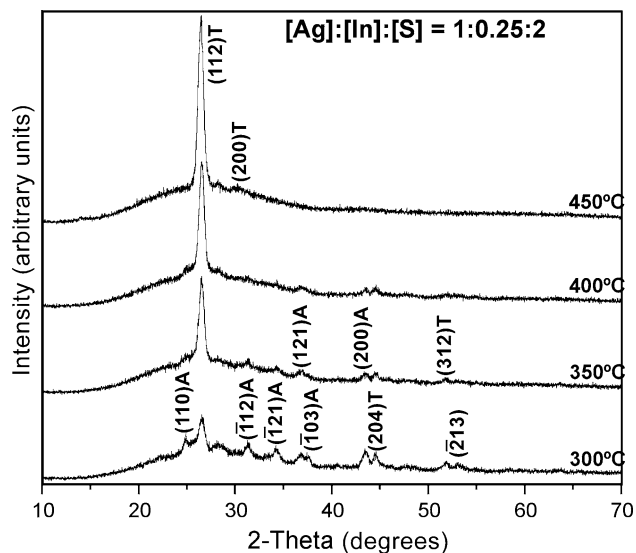


Fig. 2 XRD patterns for samples prepared at different T_s using an atomic ratio in the starting solution of Ag:In:S = 1:0.25:2. "A" corresponds to Ag₂S (acanthite) and "T" to the tetragonal variation of the AgInS₂ (chalcopyrite)

($\bar{2}$ 13) directions corresponding to Ag₂S [JCPDS 14-0072] and peaks corresponding to (112), (204), and (312) directions of ch-AgInS₂ [JCPDS 25-1330]. At $T_s > 300$ °C, the XRD patterns are characterized by the presence of the strong intensity associated with the (112) reflection of ch-AgInS₂ [JCPDS 25-1330], and only minor presence of other reflections associated with Ag₂S [JCPDS 14-0072] in the lower part of this temperature range. These results are in agreement with those reported by Ortega-López et al. [15]. They found also that, in samples prepared using indium chloride instead of indium acetate, and starting solutions less indium-rich, a strong reflection located at $2\theta \approx 26.6^\circ$, associated to the (112) direction of ch-AgInS₂ [JCPDS 25-1330] was predominant in samples prepared at T_s in the range of 350–400 °C.

The average crystallite size was estimated for films grown at $T_s \geq 350$ °C, and was found that it increased with deposition temperature from 14.1 to 16.8 nm, as calculated by using the Scherrer's formulae without any correction. Also, lattice parameters have been calculated for these films, and the results are reported in Table 1.

From these results, it becomes apparent that some stress is present in our films, with an anisotropic deformation of the lattice. However, as changes in lattice parameters are not too significant, we could not expect a strong influence of these changes on the electrical transport properties of our films. These studies are in due course.

Finally, we kept the same atomic content for silver and indium and increased the atomic content of sulfur, using an atomic composition in the starting solution of Ag:In:S = 1:1:2 that is the same than that required for an stoichiometric AgInS₂. Figure 3 shows the XRD patterns for samples prepared at T_s in the range of 300–450 °C. The diffraction pattern of the thin film prepared at 300 °C showed a mixture of phases: peaks on ($\bar{1}$ 01), (110), (023), and (040) directions of Ag₂S [JCPDS 14-0072]; peaks on the (112) and (204) directions associated with reflections of ch-AgInS₂ [JCPDS 25-1330]; and some strange presence of a reflection that seems to be associated to the (121) direction of o-AgInS₂ [JCPDS 25-1328].

Like in the past case, where we used an atomic ratio in the starting solution of Ag:In:S = 1:0.25:2, again the patterns of

Table 1 Lattice parameters in AgInS₂ films prepared at $T_s \geq 350$ °C using an atomic ratio in the starting solution of Ag:In:S = 1:0.25:2

T_s (°C)	Chalcopyrite AgInS ₂	
	a_0 (Å) [reference: 5.8792 Å]	c_0 (Å) [reference: 11.203 Å]
350	5.8659	11.3948
400	5.8732	11.3912
450	5.9000	11.3208

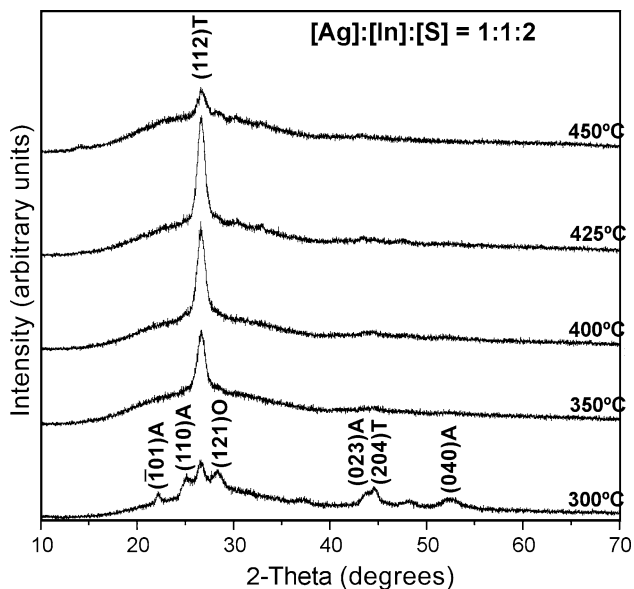


Fig. 3 XRD patterns for samples prepared at different T_s using an atomic ratio in the starting solution of Ag:In:S = 1:1:2. “A” corresponds to Ag_2S (acanthite), “O” to the orthorhombic variation of the $AgInS_2$ compound and “T” to its tetragonal (chalcopyrite) structure

films obtained at $T_s > 300\text{ }^\circ\text{C}$ are characterized by the presence of the strong intensity of the (112) peak associated with the reflection of the tetragonal structure of $AgInS_2$. Gorska et al. [10] report they have obtained only the orthorhombic phase of the $AgInS_2$ for the same atomic ratio in the solution. This could be ascribed to the different starting compounds they used (chlorides and nitrates as the silver and indium sources). The average crystallite size was estimated and was found that it increases with deposition temperature, being 67 Å for $T_s = 300\text{ }^\circ\text{C}$, 73 Å for $T_s = 350\text{ }^\circ\text{C}$, 76 Å for $T_s = 400\text{ }^\circ\text{C}$, and 83 Å for $T_s = 425\text{ }^\circ\text{C}$.

According to our XRD measurements, $AgInS_2$ and Ag_2S exist in all the films deposited at $T_s = 300\text{ }^\circ\text{C}$, regardless of the atomic ratio in the starting solution. For $T_s > 300\text{ }^\circ\text{C}$ the diffraction peaks of Ag_2S are strongly reduced and the tetragonal variation of the $AgInS_2$ becomes the main phase. This suggests that at this substrate temperature range our films are mainly composed of ch- $AgInS_2$. It can be seen in Figs. 2 and 3 that as the substrate temperature is increased, the (112) peak of $AgInS_2$ becomes bigger and sharper, indicating an improvement of the film crystalline quality.

Compositional analysis

Table 2 shows the chemical composition results in at% for films prepared at $T_s \geq 400\text{ }^\circ\text{C}$ using an atomic ratio in the starting solution of Ag:In:S = 1:1:1, where the $AgInS_2$ is already present.

From this chemical compositional analysis, it is evident that our films are anion deficient, where the indium content

Table 2 Chemical composition of $AgInS_2$ films prepared at $T_s \geq 400\text{ }^\circ\text{C}$ using an atomic ratio in the starting solution of Ag:In:S = 1:1:1

Substrate temperature, T_s ($^\circ\text{C}$)	Ag content (at%)	In content (at%)	S content (at%)	Ag/S	In/S
400	29.2	45.4	25.4	1.1471	1.7853
450	25.6	54.1	20.3	1.2653	2.6749

is always higher than silver and sulfur content. At $T_s = 400\text{ }^\circ\text{C}$, indium excess may be located as segregated atoms in grain boundaries, as neither significant clusters of metallic indium, nor indium compounds other than minor quantities of $AgInS_2$ were found in our structural studies, and there is no significant changes on the lattice parameters compared to those given in reference [JCPDS 14-0072]. At $T_s = 450\text{ }^\circ\text{C}$, there is still more indium excess. Indium seems to start becoming oxidized, as revealed by the XRD studies. This could explain some of the higher indium contents at this temperature. Also, given the low energy needed for the Ag–S bonding, we can expect that as the temperature increases, the indium excess available will be bonded to the oxygen always present from the carrier gas. In addition, may be some of this indium excess could be located as interstitial atoms, being the origin in the increase on the c_o direction already reported in the section “X-ray diffraction studies.” As for the structural studies, this non-stoichiometry will surely have its effects on the electrical and optical properties of the films. If our assumptions on the indium excess are correct, we could expect a significant increase on the electrical conductivity of our films. These studies are in progress and will be presented in a forthcoming paper.

Table 3 shows the chemical composition results in at% for films prepared at $T_s \geq 350\text{ }^\circ\text{C}$, where the $AgInS_2$ is the predominant phase, using an atomic ratio in the starting solution of Ag:In:S = 1:0.25:2. At $T_s = 350\text{ }^\circ\text{C}$ the Ag/S ratio was the highest, with high silver excess. This could explain the formation of Ag_2S at this temperature. At $T_s = 400\text{ }^\circ\text{C}$ the Ag/S ratio was near stoichiometry. Looking at the indium content, we note that while the In/S

Table 3 Chemical composition of $AgInS_2$ films prepared at $T_s \geq 350\text{ }^\circ\text{C}$ using an atomic ratio in the starting solution of Ag:In:S = 1:0.25:2

Substrate temperature, T_s ($^\circ\text{C}$)	Ag content (at%)	In content (at%)	S content (at%)	Ag/S	In/S
350	39.9	12.3	47.8	0.8355	0.2576
400	29.9	15.9	54.2	0.5505	0.2933
450	21.6	16.5	61.9	0.3481	0.2666

Table 4 Chemical composition of AgInS₂ films prepared at $T_s \geq 350$ °C using an atomic ratio in the starting solution of Ag:In:S = 1:1:2

Substrate temperature, T_s (°C)	Ag content (at%)	In content (at%)	S content (at%)	Ag/S	In/S
350	19.3	36.4	44.3	0.4340	0.8218
400	23.8	25.9	50.3	0.4722	0.5143
425	12.1	30.0	57.9	0.2089	0.5191
450	14.9	22.9	62.2	0.2406	0.3676

ratio was almost constant, all of this films are indium poor. This behavior may be explained by the low indium at% ratio in the starting solution used in this case. Thus, the best composition so far for the AgInS₂ thin films was for the film prepared at $T_s = 400$ °C. According to XRD studies, by using this at% ratios in the starting solution we have grown silver indium sulfide films, although, the EDS analysis indicates that the stoichiometric composition of AgInS₂ has not been achieved. In order to obtain AgInS₂ thin films near stoichiometry we would require an increase in the at% concentration of indium in the solution, keeping the same at% concentrations of silver and sulfur.

Table 4 shows the chemical composition results in at% for films prepared at different T_s , using an atomic ratio in the starting solution of Ag:In:S = 1:1:2. According to this table, by using a stoichiometric at% ratio in the starting solution and doing the depositions at $T_s = 400$ °C, we were able to grow AgInS₂ near to the stoichiometric composition.

Conclusions

AgInS₂ thin films have been prepared by the spray pyrolysis technique using silver acetate, indium acetate, and *N,N*-dimethylthiourea as the precursor compounds. XRD results revealed that Ag₂S (acanthite) is formed in all the films deposited at $T_s = 300$ °C, regardless of the molar ratios of Ag:In:S used in the starting solution. Using molar ratios of Ag:In:S = 1:0.25:2 and 1:1:2 at $T_s > 300$ °C the phase Ag₂S almost disappears and the phase AgInS₂

(chalcopyrite) becomes the predominant one. We were able to grow films with stoichiometric composition of AgInS₂ by using a molar ratio of Ag:In:S = 1:1:2 in the starting solution and $T_s = 400$ °C.

Acknowledgements The authors would like to thank Dra. Hilda Esperanza Esparza Ponce (CIMAV-Chihuahua) for EDS analysis, M.C. Ma. Luisa Ramón for XRD analysis, and Ing. J. Ortega-Cruz for technical assistance in the electrical measurements. The authors are grateful to DGAPA-UNAM (project IN 111506) for the financial support.

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