



Optical and electrical characterization of AgInS₂ thin films deposited by spray pyrolysis

M. Calixto-Rodríguez^{a,*}, H. Martínez^a, M.E. Calixto^b, Y. Peña^c, Dalia Martínez-Escobar^d, A. Tiburcio-Silver^e, A. Sanchez-Juarez^d

^a Instituto de Ciencias Físicas-Universidad Nacional Autónoma de México, Apartado Postal 48-3, 62210, Cuernavaca, Morelos, México

^b Instituto de Física, Benemérita Universidad Autónoma de Puebla, Apartado Postal J-48, 72570, Puebla, Puebla, México

^c Facultad de Ciencias Químicas, Universidad Autónoma de Nuevo León, Pedro de Alba s/n, Ciudad Universitaria, 66451, San Nicolás de los Garza, Nuevo León, México

^d Centro de Investigación en Energía-Universidad Nacional Autónoma de México, 62580, Temixco, Morelos, México

^e Instituto Tecnológico de Toluca-SEP, Apartado Postal 20, 52176, Metepec 3, Estado de México, México

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ABSTRACT

Silver indium sulfide (AgInS₂) thin films have been prepared by spray pyrolysis (SP) technique using silver acetate, indium acetate, and N, N-dimethylthiourea as precursor compounds. Films were deposited onto glass substrates at different substrate temperatures (T_s) and Ag:In:S ratios in the starting solutions. Optical transmission and reflection as well as electrical measurements were performed in order to study the effect of deposition parameters on the optical and electrical properties of AgInS₂ thin films. X-ray diffraction measurements were used to identify the deposited compounds. It was found that different compounds such as AgInS₂, Ag₂S, In₂O₃, and In₂S₃ can be grown only by changing the Ag:In:S ratio in the starting solution and T_s . So that, by carefully selecting the deposition parameters, single phase AgInS₂ thin films can be easily grown. Thin films obtained using a molar ratio of Ag:In:S = 1:1:2 and T_s = 400 °C, have an optical band gap of 1.9 eV and n-type electrical conductivity with a value of $0.3 \Omega^{-1} \text{cm}^{-1}$ in the dark.

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1. Introduction

Ternary compounds of I-III-VI₂ groups are semiconductor materials used for optoelectronic and photovoltaic device applications [1,2]. AgInS₂ belongs to this group, and it can be grown into two ordered phases: chalcopyrite (tetragonal) and orthorhombic [3]. It has two direct band gaps for the tetragonal phase (1.86 and 2.02 eV [3]) and two for the orthorhombic phase (1.96 and 2.04 eV [4]). Because of these band gap values and its high absorption coefficient it can be used in solar cells [3,4]. Even though AgInS₂ shows n-type electrical conductivity [5], it can be doped with Sb [6] and Sn [7] atoms to change it to p-type conductivity. Electrical properties reported for AgInS₂ single crystals are: $\rho = 10 \Omega\text{-cm}$, $n = 4 \times 10^{15} \text{cm}^{-3}$, and $\mu = 150 \text{cm}^2/\text{V-s}$ [1].

Synthesis of AgInS₂ thin films is important for the preparation of quaternary and pentenary semiconductor materials. SP has been used to deposit AgInS₂ thin films [4,7–9]; however, all the research work has been carried out by using silver chloride [9], silver nitrate [9], and silver acetate [4,7–9] as the silver source; indium

chloride [4,7–9] as the indium source; N, N-dimethylthiourea [9], and thiourea [4,7–9] as the sulfur source in the starting solutions. In this work we used silver acetate, indium acetate and N, N-dimethylthiourea as the precursor compounds to prepare AgInS₂ polycrystalline thin films deposited by SP. By using indium acetate as the In source, incorporation of chlorine in the deposited films was avoided. Deposition parameters were optimized to obtain AgInS₂ thin films with suitable properties to be used in photovoltaic devices. Electrical and optical characterization results are presented and discussed.

2. Experimental details

Ag-In-S thin films were prepared by SP using solutions of silver acetate (0.025 M), indium acetate (0.025 M), and N, N-dimethylthiourea (0.025 M) as silver, indium, and sulfur sources, respectively. A detailed description on the preparation of AgInS₂ thin films can be found in our previous work [10]. We have used a pneumatic spray pyrolysis system to deposit AgInS₂ films. The following molar ratios in the starting solutions were used: Ag:In:S = 1:1:1, 1:0.25:2, and 1:1:2. Microscope glass slides from Corning with dimensions of $2.5 \times 2.5 \text{cm}$ were used as substrates. The deposition temperature, T_s , was varied from 250 to 450 °C while the deposition time was kept constant at 7 minutes. Air was

* Corresponding author. Tel.: +52 55 56227756; fax: +52 55 56227775.

E-mail address: manuela@fis.unam.mx (M. Calixto-Rodríguez).

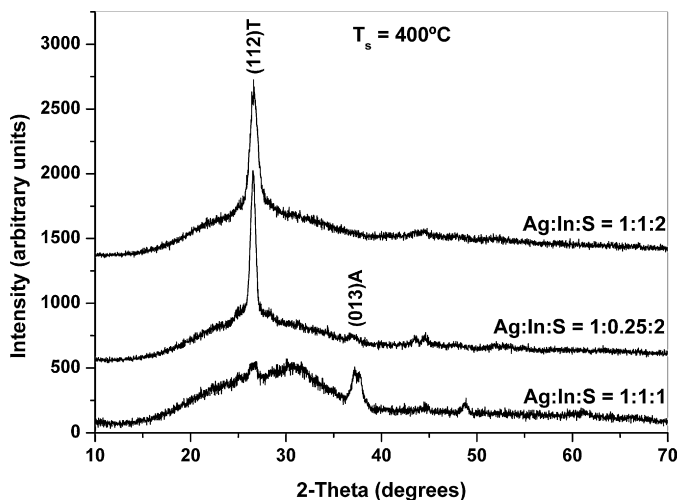


Fig. 1. XRD patterns for films deposited at $T_s = 400^\circ\text{C}$, and different molar ratios of Ag:In:S. "A" corresponds to Ag_2S (acanthite), and "T" to AgInS_2 (chalcopyrite).

used as the carrier gas at a pressure of 4 bar with a flow rate of 10 l/min, and the solution flow rate was 5 ml/min.

X-ray diffraction (XRD) measurements were performed by using a Rigaku D-Max diffractometer with $\text{Cu-K}\alpha$ (wavelength, $\lambda = 1.5406 \text{ \AA}$) radiation. The chemical composition of the AgInS_2 thin films was determined by energy dispersive X-ray spectroscopy (EDS) using an Oxford Instruments system attached to the scanning electron microscope (SEM). Optical transmission at normal incidence, $T(\lambda)$, and reflection, $R(\lambda)$, of deposited thin films were measured with a Shimadzu model 3101PC double-beam spectrophotometer. The absorption coefficient (α) was calculated from $T(\lambda)$ and $R(\lambda)$ measurements, and the optical band gap (E_g) was obtained from its relationship with the photon energy ($h\nu$). Thickness of deposited thin films was measured using an Alpha Step model 100 from Tencor Instruments. Electrical conductivity values for AgInS_2 films were obtained from I-V measurements made by using two silver electrodes (10 mm long, with a separation of 1.5 mm between them) deposited by thermal evaporation. The conductivity type was determined by the "hot point probe" technique [11].

3. Results and discussion

3.1. Structural characterization and chemical composition analysis

Ag:In:S molar ratio and substrate temperature T_s are the main parameters which allow to control the composition of the AgInS_2 films in the SP technique. Fig. 1 shows the X-ray diffraction patterns for representative films deposited at $T_s = 400^\circ\text{C}$ by using different Ag:In:S molar ratios: 1:1:1; 1:0.25:2, and 1:1:2. Films with the lowest indium content in the starting solution apparently had the best crystalline quality with a crystallite size of 16 nm, however here we have to take into account the change and mixture of phases present in the growing films, which may be contributing to the sharpening of the main peak, according to the XRD results previously reported [10]. Films deposited using molar ratios of Ag:In:S = 1:0.25:2 and

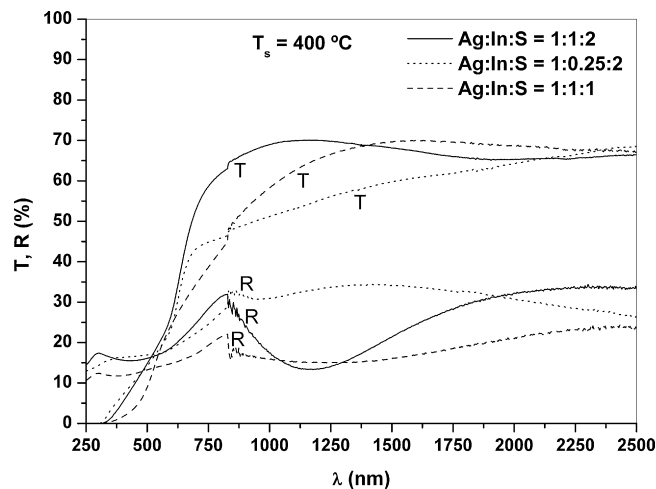


Fig. 2. $T(\lambda)$ and $R(\lambda)$ spectra for films deposited at $T_s = 400^\circ\text{C}$, and different molar ratios of Ag:In:S.

1:1:2 showed a preferential growth orientation along the (112) direction, with the peak located at $2\theta = 26.5^\circ$ associated to the chalcopyrite (tetragonal) phase of AgInS_2 compound (JCPDS 25-1330). Thin films deposited using a molar ratio of Ag:In:S = 1:1:1 are formed by two compounds: one identified as Ag_2S with a diffraction peak at $2\theta = 37.2^\circ$ (JCPDS 14-0072), and the other one as AgInS_2 with a diffraction peak at $2\theta = 26.6^\circ$ (JCPDS 25-1330).

Table 1 shows the chemical composition results for films prepared at $T_s = 400^\circ\text{C}$ using molar ratios of: Ag:In:S = 1:1:1, 1:0.25:2, and 1:1:2 in the starting solutions. According to these values, films prepared using a molar ratio of Ag:In:S = 1:1:2 have a nearly stoichiometric composition.

3.2. Optical characterization

Optical transmission and reflection spectra measurements were recorded in the 250 – 2500 nm range. Fig. 2 shows $T(\lambda)$ and $R(\lambda)$ responses for samples deposited at $T_s = 400^\circ\text{C}$ using molar ratios in the starting solutions of Ag:In:S = 1:1:1, 1:0.25:2, and 1:1:2, respectively. As we can see, transmission spectra responses are different for films deposited at various molar ratios as expected. Although it may be possible that secondary phases like indium oxide/indium sulfide in amorphous state contribute to the observed response, considering that films were grown using air as carrier gas. It is also observed that films deposited using a molar ratio of Ag:In:S = 1:1:2 have the highest transmission response in the 650 – 1360 nm range.

The absorption coefficient (α) was calculated using $T(\lambda)$ and $R(\lambda)$ data and the well known expression, for direct optical transitions [12,13], given by

$$\alpha h\nu = A(h\nu - E_g)^r \quad (1)$$

where A is a constant, and E_g is the optical band gap. In this equation $r = 1/2$ for direct allowed optical transitions and $3/2$ for the direct forbidden ones. The band-gap value can be obtained from the best linear approximation in the $(\alpha h\nu)^{1/r}$ vs. $h\nu$ plot and its extrapolation to $(\alpha h\nu)^{1/r} = 0$. Fig. 3 shows (a) the $(\alpha h\nu)^{2/3}$ vs. $h\nu$ plot for a film deposited at $T_s = 400^\circ\text{C}$ using a molar ratio in the

Table 1
Chemical composition of AgInS_2 thin films deposited at $T_s = 400^\circ\text{C}$, and different molar ratios of Ag:In:S.

Molar ratio	Ag content (at.%)	In content (at.%)	S content (at.%)
[Ag]:[In]:[S] = 1:1:1	29.2	45.4	25.4
[Ag]:[In]:[S] = 1:0.25:2	29.9	15.9	54.2
[Ag]:[In]:[S] = 1:1:2	23.8	25.9	50.3

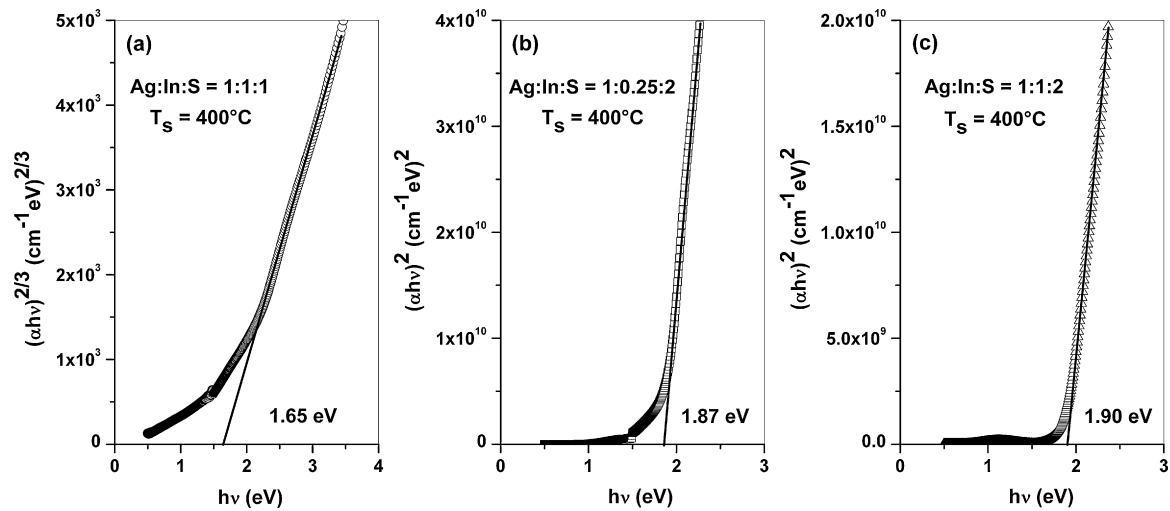


Fig. 3. $(\alpha h\nu)^{1/r}$ vs. $h\nu$ plots for films deposited at $T_s = 400^\circ\text{C}$, and different molar ratios of Ag:In:S.

Table 2

Band gap values for AgInS₂ thin films.

Substrate temperature ($^\circ\text{C}$)	Ag:In:S = 1:1:1 Optical band-gap, E_g (eV)	Ag:In:S = 1:0.25:2 Optical band-gap, E_g (eV)	Ag:In:S = 1:1:2 Optical band-gap, E_g (eV)
300	1.66	1.90	1.94
350	1.66	1.89	1.90
400	1.65	1.87	1.90
450	2.47	1.85	2.25

starting solution of Ag:In:S = 1:1:1; (b) and (c) are the $(\alpha h\nu)^2$ vs. $h\nu$ plots for films deposited at $T_s = 400^\circ\text{C}$ using molar ratios in the starting solutions of Ag:In:S = 1:0.25:2, and 1:1:2, respectively.

Table 2 shows the band-gap values for films deposited at different T_s using molar ratios of Ag:In:S = 1:1:1; 1:0.25:2; and 1:1:2. According to this table, the band gap values obtained for films deposited at T_s in the 300–400 $^\circ\text{C}$ range using a molar ratio in the starting solution of Ag:In:S = 1:1:1 may correspond to the presence of a mixture of phases as previously reported [10], AgInS₂ (ch) and Ag₂S (acanthite), which have reported band gap values of 1.86 eV [3] and 0.9 eV [14], respectively. The highest band gap value obtained for films deposited at $T_s = 450^\circ\text{C}$ (2.47 eV) corresponds to a mixture of AgInS₂ (ch) and In₂O₃ (cubic) phases, since indium oxide has a wide band gap in the 3–4 eV range [15]. On the other hand, films deposited using a molar ratio of Ag:In:S = 1:0.25:2 consist on a mixture of AgInS₂ (ch) and Ag₂S (acanthite) phases in the whole temperature range of 300 to 450 $^\circ\text{C}$. It was found that films deposited at $T_s = 400^\circ\text{C}$ have a 1.87 eV band gap value, which is in agreement with the E_g value reported for the tetragonal phase of the AgInS₂ compound [3]. And finally, films deposited using a molar ratio of Ag:In:S = 1:1:2 consist of a mixture of AgInS₂ (ch), AgInS₂ (o), Ag₂S (acanthite), and In₂S₃ (tetragonal) phases. Films deposited at $T_s = 300^\circ\text{C}$ consist mainly of AgInS₂ (ch), AgInS₂ (o), and Ag₂S. These films have a band gap value of 1.94 eV, which is very close to that reported for AgInS₂ (o) of 1.96 eV [4]. Films deposited at T_s in the 350–400 $^\circ\text{C}$ range are mainly formed by both phases of AgInS₂ (chalcopyrite and orthorhombic), the band gap value obtained for

these films is 1.90 eV. Films deposited at $T_s = 450^\circ\text{C}$ consist of a mixture of the AgInS₂ (ch), AgInS₂ (o), and In₂S₃ phases. The band gap value obtained (2.25 eV) is higher than that obtained for films deposited at $T_s < 450^\circ\text{C}$. This value corresponds to the wide energy gap reported for indium sulfide, which is in the 2.0–2.45 eV range [16,17]. In a previous work [18] we have reported the formation of In₂S₃ thin films at $T_s = 450^\circ\text{C}$, with a band gap value greater than 2.0 eV.

3.3. Electrical characterization

Table 3 resumes the electrical conductivities for films deposited using the molar ratios of Ag:In:S = 1:1:1, 1:0.25:2, and 1:1:2. For films prepared from solutions with a molar ratio of Ag:In:S = 1:1:1 and deposited at T_s in the 300–450 $^\circ\text{C}$ range, the electrical conductivity increases up to six orders of magnitude. This might be attributed to an improvement of the films crystalline quality with the increase in T_s , but as we mentioned before this is unlikely if we take into account the change and mixture of phases present in the growing films, that may be contributing to the sharpening of the main peak, according to the XRD results previously reported [10]. Results obtained from the “hot point probe” technique have shown that films deposited at $T_s \geq 400^\circ\text{C}$ are n-type. Low values of the electrical conductivity for films deposited at $T_s < 400^\circ\text{C}$ did not allow the use of the same technique to evaluate the conductivity type. For films obtained from solutions with a molar ratio of Ag:In:S = 1:0.25:2 and deposited at T_s in the

Table 3

Electrical conductivities for AgInS₂ thin films.

Substrate temperature ($^\circ\text{C}$)	Ag:In:S = 1:1:1 Electrical Conductivity (Ωcm) ⁻¹	Ag:In:S = 1:0.25:2 Electrical Conductivity (Ωcm) ⁻¹	Ag:In:S = 1:1:2 Electrical Conductivity (Ωcm) ⁻¹
300	5.5×10^{-6}	3.5×10^{-5}	3.4×10^{-5}
350	3.0×10^{-3}	1.6×10^{-5}	1.7×10^{-2}
400	1.17	1.1×10^{-5}	3.0×10^{-1}
450	6.85	8.9×10^{-2}	1.01

300–450 °C range, the electrical conductivity increased by three orders of magnitude. Due to their low values, it was not possible to determine the conductivity type in these films by the ‘hot point probe’ technique. For films prepared from solutions having a molar ratio of Ag:In:S = 1:1:2 and deposited at T_s in the 300–450 °C range, the electrical conductivity increased by five orders of magnitude. Films deposited at $T_s \geq 400$ °C are n-type. It was not possible to determine the conductivity type for films obtained at $T_s < 400$ °C.

4. Conclusions

We have reported the results of the optical and electrical characterizations of AgInS₂ thin films deposited by SP using indium acetate instead of indium chloride as the In source. The molar ratio Ag:In:S and T_s can be varied to obtain thin films with chalcopyrite structure of the AgInS₂ compound with nearly stoichiometric composition. The conditions to achieve this is by using a molar ratio of Ag:In:S = 1:1:2 and $T_s = 400$ °C. Band gap and electrical conductivity values obtained for deposited films changed due to variations in the molar ratio Ag:In:S in the starting solutions, and in T_s . For films deposited using a molar ratio of Ag:In:S = 1:1:1, the electrical conductivity varies from 10^{-6} to $6.8 \Omega^{-1} \text{ cm}^{-1}$ with the increase in T_s . The electrical conductivity varies from 10^{-5} to $10^{-2} \Omega^{-1} \text{ cm}^{-1}$ for films deposited using a molar ratio of Ag:In:S = 1:0.25:2. And for films deposited using a molar ratio of Ag:In:S = 1:1:2, the electrical conductivity varies from 10^{-5} to $1.0 \Omega^{-1} \text{ cm}^{-1}$. In all cases E_g values of deposited films depend on the mixture of phases present in the films. Band gap and electrical conductivity values obtained for films with nearly stoichiometric composition were 1.90 eV and $0.3 \Omega^{-1} \text{ cm}^{-1}$, respectively. In conclusion, using the economic and simple spray pyrolysis technique we can obtain AgInS₂ thin films with physical properties suitable to be used in photovoltaic structures.

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