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Structural and optical characterization of indium and gallium indium sulfide films prepared by modulated flux deposition

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Indium and gallium indium sulfide thin films were deposited on soda-lime glass substrates at 350 °C, in a wide range of sulfur delivery conditions, by Modulated Flux Deposition (MFD). Indium sulfide films were highly crystalline β-In_2S_3 (tetragonal) with $E_g = 2.68$ eV. Depending on the availability of sulfur, gallium indium-poor sulfide films consisted on metal-rich hexagonal β-GaS layers or stoichiometric amorphous films with $E_g = 3.0–3.3$ eV. Finally, gallium indium-rich sulfide films formed a mixture of β-In_2S_3 and β-GaS that became near amorphous as more sulfur was supplied; a bandgap energy of $E_g = 2.44$ eV was found.

1 Introduction

Nowadays, there are a variety of chemical routes to obtain III–VI materials. Thin films of these semiconductors attract a broad interest due to their optoelectronic and energy potential applications. Currently, polycrystalline In_2S_3 thin films are widely investigated as an attractive substitute for the CdS buffer layer in Cu(In,Ga)$(S,Se)_2$ (CIGS) solar cells [1–3]. This material can be obtained by a good number of dry and wet methods [4–10].

Polycrystalline GaS films are a possible substitute for CdS in GaS/CdTe heterojunction solar cells [11]; moreover, it might be applied to CIGS and GaAs solar cells. Also, GaS films become effective surface passivation layers in GaAs-based optoelectronic devices [12–14]. Gallium sulfide films (GaS and Ga_2S_3) are usually obtained by single-source metal-organic chemical vapor deposition (MO-CVD) [15, 16]. Some studies have been done in vacuum thermal evaporation [17] and radio-frequency reactive magnetron sputtering [18]. However, despite indium sulfide films may be easily attained by chemical bath deposition (CBD), the literature does not mention any success on gallium sulfide film deposition from aqueous solutions, which has the handicap of the extensive hydrolysis undergone by gallium (III) salts [19].

The bandgap energy of In_2S_3 thin films may be shifted with regard to the bulk In_2S_3 value ($E_g = 2.0$ eV) [15] in a certain degree, due to a variety of effects (quantum size effect, sulfur deficiency, oxygen and sodium doping), up to a maximum value of 2.8 eV [8]. In contrast, hexagonal β-GaS and monoclinic α-Ga_2S_3 are reported to have direct bandgaps of 3.05 eV and 3.42 eV, respectively [15]. As gallium sulfides exhibit wider bandgap energies than indium sesquisulfide, it might be possible to develop Ga–In–S films with improved properties for optoelectronic and photovoltaic applications. Kim et al. have reported $In_{2-x}Ga_xS_3$ films prepared by spray pyrolysis at 350 °C [20]. Starting from crystalline

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β-In_2S_3 films, the gradual addition of gallium reduced their crystallinity. Amorphous films were obtained above $x = 0.6$, the minimum reported E_g being 2.0 eV. Amorphous films corresponding to $InGaS_3$ had a bandgap energy $E_g = 2.3$ eV.

Compared to indium sulfide, there is still little research in gallium and gallium-indium sulfide films. Previous investigations on the In–S system reported the formation of tetragonal β-In_2S_3 thin films by Modulated Flux Deposition (MFD) [21]. However, there is not any available information about Ga–S and Ga–In–S thin films prepared by this method yet. This work is focused on the effect of sulfur on the crystallinity and optical properties of Ga–In–S films with different metal atomic ratios. The deposition parameters have been adjusted in order to achieve films within a range of thickness (around 100 nm) that provides a high transmission and wide bandgap energies.

2 Experimental

This vacuum thin film deposition technique, named Modulated Flux Deposition (MFD), has been described in detail elsewhere [22]. Various evaporation sources, which are focused on different points of the chamber, operate at the same time while the substrate follows a cyclical circular path, so the vapors from the different metal sources condense alternatively on the heated substrate within a reactive chalcogen atmosphere.

Three series of samples were prepared: indium sulfide films (named set A), using a pure indium evaporation source; gallium indium-poor sulfide films (set B), heating a 90 at% Ga – 10 at% In alloy in another evaporation source; and finally gallium indium sulfide films (set C), with an intermediate Ga/In atomic ratio, using both metal evaporation sources.

While the temperatures of evaporation of the metal sources remained constant, a broad interval of temperature was used for the sulfur source ($130\ °C < T_S < 210\ °C$). The samples were deposited on soda-lime glass (SLG) substrates which rotated at 30 r.p.m. and were hold at the same maximum temperature ($T_{Subst} = 350\ °C$). The base pressure was around 5×10^{-5} Pa.

The structure of the samples was analyzed by X-ray diffraction (XRD) using a Phillips X'Pert apparatus with nickel-filtered Cu $K_{\alpha 1}$ radiation. Optical properties were determined by measuring transmittance and reflectance at normal incidence, from 300 nm to 1500 nm, with a Perkin–Elmer Lambda 9 UV/VIS/NIR spectrophotometer. The thickness of the films was determined by means of a DEKTAK 3030 surface profilometer. The chemical composition was determined by Energy Dispersive X-ray analysis (EDX) using a Hitachi S-2500 Scaning Electron Microscope (SEM); Corning 7059 glass substrates were used for this purpose, in order to avoid the detection interferences of sodium from SLG substrates.

The absorption coefficient (α) of the films was calculated using their transmittance T, reflectance R and thickness d from Eq. (1):

$$e^{-\alpha d} = \frac{\sqrt{\left(\frac{(1-R)^4}{T^2} + 4R^2\right)} - \frac{(1-R)^2}{T}}{2R^2} . \tag{1}$$

3 Results and discussion

As an overview, Fig. 1a shows the variation of the chalcogen/metal atomic ratio as a function of the sulfur source temperature (T_S) for the three mentioned groups of films. From this graph, some preliminary conclusions can be drawn.

Indium sulfide layers (curve A) reached a constant S/In ratio, attributable to In_2S_3, at intermediate values of T_S, while it appears that lower and higher T_S values provided a deficiency and an excess of sulfur, respectively. Regarding to gallium indium-poor sulfide films (curve B), the S/(Ga + In) ratio increased as T_S was risen until a nearly constant value corresponding to GaS was reached. Finally, gallium indium sulfide films (curve C), which were sulfur deficient at low T_S values, reached chalcogen/metal

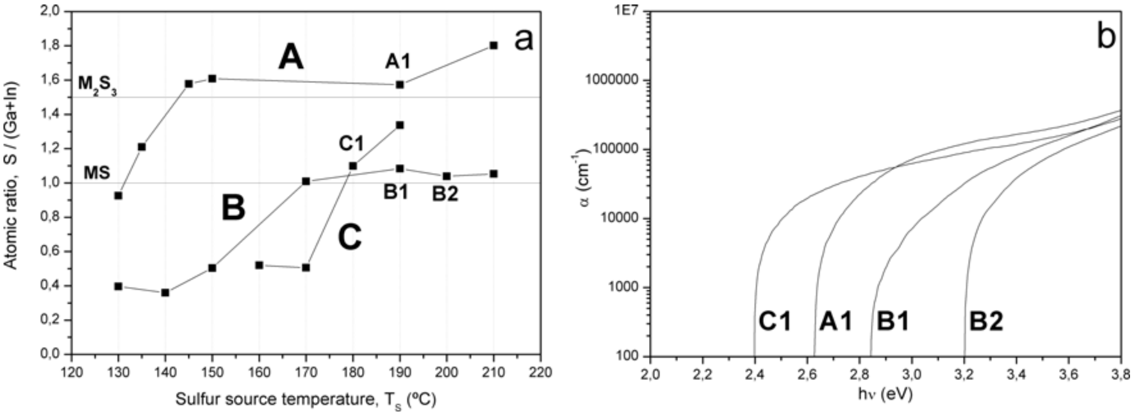

Fig. 1 a) Variation of the chalcogen/metal atomic ratio with respect to the sulfur source temperature within the sets of films A–C. b) Absorption coefficient (α) of high-transmission sulfide layers selected from the sets of films A–C.

atomic ratios between M_2S_3 and MS as T_S was increased; therefore, it might be interpreted as the formation of a mixture of the two proposed sulfides (In_2S_3 and GaS).

Figure 1b compares the absorption coefficient (α) of the most representative layers of these sets, namely those that had chalcogen/metal atomic ratios higher than 1 and the highest transmission spectra. Here, the selected gallium indium sulfide film (named C1) showed the shortest bandgap. In comparison, the absorption edge of the indium sulfide film (named A1) was slightly shifted towards higher energies. Finally, both selected gallium indium-poor sulfide films (named B1 and B2) exhibited the widest bandgaps.

Assuming these semiconductor compounds to have a direct interband transition, their optical bandgap energies (E_g) were calculated by plotting $(\alpha h\nu)^2$ versus $h\nu$ and making a linear interpolation near the absorption edge region. Hence, the estimated values of E_g were the following: 2.44 eV (sample C1), 2.68 eV (A1), 2.97 and 3.30 eV (B1 and B2).

Next, each individual group of samples will be discussed in detail.

3.1 Indium sulfide films

Firstly, a set of indium sulfide layers was prepared at different T_S values. It is worth noting that these In–S films (Fig. 2a) had quite more intense diffraction lines than the two remaining sets of films, as it will be shown in Sections 3.2 and 3.3.

According to Fig. 2a, all the samples had a tetragonal β-In_2S_3 structure (JCPDS 25-0390) and exhibited a strong (103) orientation, as observed in previous investigations [21]. Together with Fig. 1a, we can observe that the tetragonal structure was retained even in largely sulfur-deficient samples, despite it might be expected from their stoichiometries the appearance of indium-richer phases (monoclinic In_6S_7, orthorhombic InS). The FWHM values of the (103) peak confirm that the layer obtained at the lowest value of T_S (130 °C) had a certain degree of crystallinity, that it became sharply enhanced as T_S was increased up to $T_S = 190$ °C (sample A1 in Fig. 1a and b), and that it decreased partially in the sulfur-richest layer prepared at $T_S = 210$ °C.

Regarding to the optical properties, their transmission spectra are shown in Fig. 2b. The sample obtained at $T_S = 130$ °C, which was the least crystalline of them, exhibited a rather low transmission. In contrast, the increase on the sulfur temperature made the remaining samples to reach transmission maxima higher than 80%.

In summary, β-In_2S_3 MFD-films achieved a high transmission and a good crystallinity as soon as a minimal amount of sulfur was available.

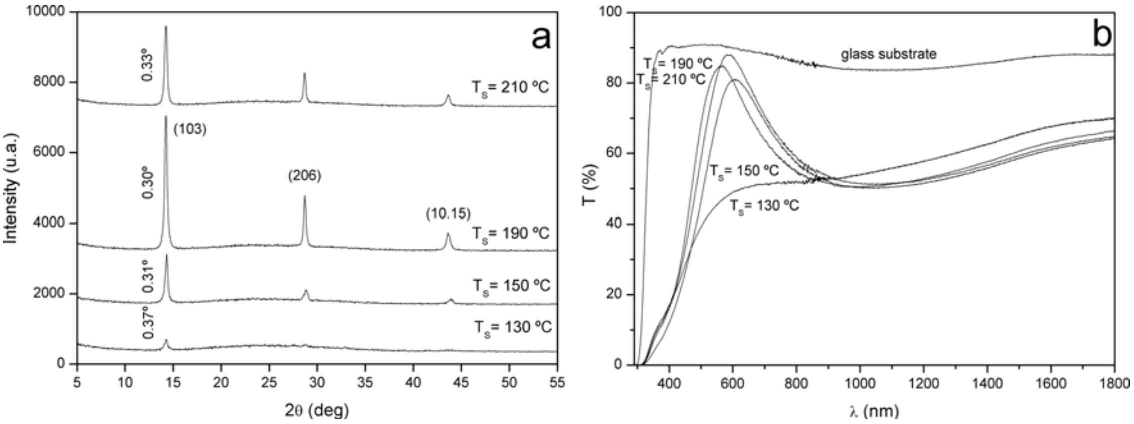

Fig. 2 a) Diffraction patterns and b) transmission spectra of In–S films obtained at different sulfur source temperatures. The vertical notations indicate the FWHM values of the (103) peak.

3.2 Gallium indium-poor sulfide films

Secondly, a series of gallium sulfide films with a low content of indium was prepared. In contrast to the moderate influence of sulfur on the structural and optical properties of indium sulfide layers, the availability of sulfur played a critical role in these samples.

At low T_S values (130 °C and 150 °C), the diffraction patterns indicated the formation of hexagonal gallium monosulfide (β-GaS) (JCPDS 84-499), which is a layered compound with the atomic layers parallel to the (001) crystallographic plane. As only diffraction from (00*n*) planes was observed in these polycrystalline films, it is clear that the atomic layers had a parallel orientation with respect to the surface of the substrate. This preferential orientation was also observed in GaS films prepared by a sputtering method [18]. The increase on T_S from 130 °C to 190 °C, corresponding to the incorporation of a larger amount of sulfur into the film, reduced the intensity of the diffraction lines gradually, until amorphous films were obtained (Fig. 3a). Further increase on sulfur temperature (T_S = 200 °C) provided an amorphous sample as well.

From an optical point of view (Fig. 3b), the polycrystalline sulfur-poorest film (T_S = 130 °C) exhibited a really low transmission spectra. It may seem that the optical behavior of the films changed at T_S = 190 °C. Thus, an amorphous structure and a high transmission were reached at the same time. More-

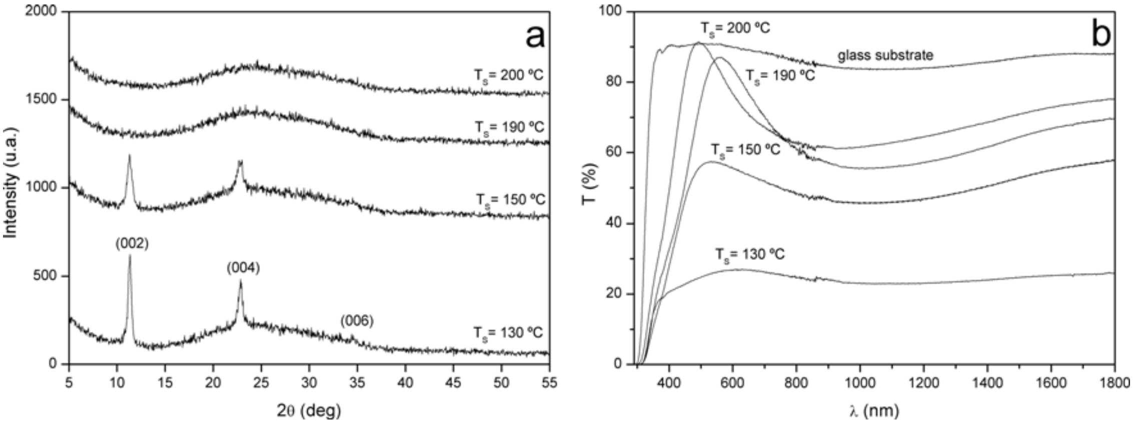

Fig. 3 a) Diffraction patterns and b) transmission spectra of gallium indium-poor sulfide films deposited at different sulfur source temperatures.

over, the additional increase on T_S provided an upper maximum of transmission as well as a shift of the absorption edge towards higher energies. In Fig. 1a and b, these amorphous layers prepared at T_S = 190 °C and 200 °C are named B1 and B2, respectively.

It remains to elucidate if the small content of indium of these films played a significant role in their properties, or if they are essentially inherent to the gallium sulfide material obtained by this technique. In this sense, some investigation focused on the preparation of pure GaS films at the same substrate temperature is under way.

3.3 Gallium indium-rich sulfide films

Eventually, a collection of films was deposited using both metal evaporation sources, in order to obtain films with significant amounts of gallium and indium.

In Fig. 4a, films deposited at low sulfur temperatures (160 °C and 170 °C), having a clear chalcogen deficiency according to Fig. 1a, showed diffraction lines corresponding to the sulfides (001)-oriented β-GaS and (103)-oriented β-In_2S_3. On increasing the sulfur temperature (180 °C and 190 °C), which provided layers with chalcogen/metal ratios between MS and M_2S_3, the diffraction lines decreased and near amorphous films were obtained.

In contrast to the previous collection of gallium sulfide films (Section 3.2), whose low content of indium did not allow the formation of β-In_2S_3, this set of samples with a significant amount of indium showed some In_2S_3 diffraction peaks. However, under no circumstances they became intense, as it could be expected taking into account the excellent crystallinity observed in the In–S binary system (Section 3.1).

According to Fig. 4b, the samples obtained at low T_S values (160 °C and 170 °C) exhibited a moderate transmission. The maximum transmission was achieved by the sample prepared at T_S = 180 °C (named C1 in Fig. 1a and b), having a stoichiometry near to MS (Fig. 1a). Also, the transmission decreased for the film prepared at T_S = 190 °C, whose chalcogen/metal ratio (also between MS and M_2S_3) was higher.

Therefore, it has not been observed the formation of any ternary compound. On the contrary, it appears that a kind of competition for sulfur was established between gallium and indium at low T_S values, resulting in a mixture of both binary sulfides. Even more, it would seem that the gallium played an interfering role on the indium sesquisulfide formation and, as a consequence, it reduced its crystallinity markedly. In any case, as T_S was increased, both polycrystalline compounds tended to form an amorphous mixed sulfide.

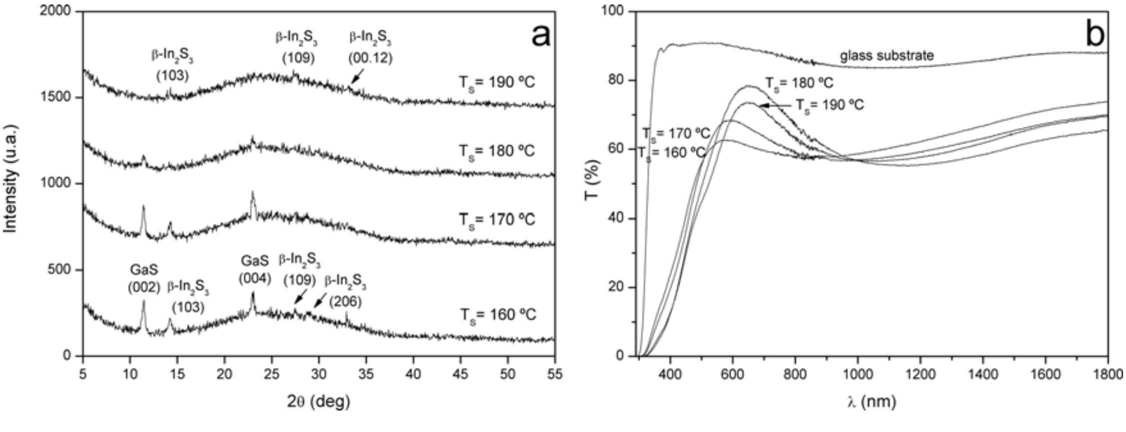

Fig. 4 a) Diffraction patterns and b) transmission spectra of gallium indium-rich sulfide films obtained at different sulfur source temperatures.

4 Conclusions

Indium sulfide thin films were deposited on glass substrates at 350 °C by Modulated Flux Deposition (MFD). Good-quality tetragonal β-In$_2$S$_3$ films with (103) orientation and $E_{\mathrm{g}} = 2.68$ eV were easily obtained. As soon as a minimal amount of sulfur was delivered, their crystallinity as well as their transmission enhanced strongly. However, gallium sulfide films with a low content of indium had a more complex behavior, the availability of sulfur being critical. A low delivery of sulfur provided (001)-oriented hexagonal β-GaS films, but it was associated to a gallium excess that provided low transmission films. Larger amounts of sulfur formed amorphous films with transmission maxima higher than indium sulfide layers; their estimated bandgap energy values (E_{g}) varied between 3.0 eV and 3.3 eV. Finally, gallium indium sulfide films were prepared; X-ray diffraction did not show any ternary compound, but a mixture of β-GaS and β-In$_2$S$_3$ was formed. When the sulfur content was increased, the mixture of crystalline sulfides tended to form an amorphous mixed sulfide with a higher transmission; the bandgap energy was $E_{\mathrm{g}} = 2.44$ eV, slightly lower than for the indium sulfide films.

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