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**INVESTIGACIÓN** 

# Synthesis and characterization of In(O;OH)S/AgInS<sub>2</sub> interface heterojunction

Síntesis y caracterización de interfase de heterojuntura In(O;OH)S/AgInS,

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#### ABSTRACT

In this work, we presented some complementary studies for In(O,OH)S thin films deposited on AgInS<sub>2</sub> thin films to fabricate a new system absorbent-layer/ buffer-layer to be used in tandem and/or in one-junction solar cells. As showed in previous works carried out for us, AgInS<sub>2</sub> layers were grown by co-evaporation from metal precursors in a two-step process; and In(O,OH)S thin films were deposited by Chemical Bath deposition. X-ray diffraction measurements

indicated that  $AgInS_2$  thin film grown with chalcopyrite structure; and In(O,OH)S films grown with polycrystalline structure. The  $AgInS_2$  thin films presented p-type conductivity, and from transductance measurements it was found a high absorption coefficient (greater than  $10^4$  cm<sup>-1</sup>) and an energy band gap of 1.95 eV; and In(O,OH)S thin films presented Eg about 3.01 eV; morphological analysis indicated that under this synthesis conditions, In(O,OH)S thin films coated completely the  $AgInS_2$  absorber

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layer. Finally, the Avrami-Erofeev equation was used in this work to study In(O,OH)S thin film growth rate on AgInS<sub>2</sub> substrate. Results indicate that the developed system can be used in single-junction and multiple junction solar cells.

*Keywords:* absorber layer thin film, AgInS<sub>2,</sub> buffer layer, In(O,OH)S, optic window, solar cells.

#### RESUMEN

En este trabajo presentamos estudios complementarios de películas delgadas de In(O;OH)S depositadas sobre películas delgadas de AgInS<sub>2</sub> para fabricar un sistema capa absorbente/capa buffer utilizado en celdas solares tipo tándem o celdas de juntura simple. Como se demostró en trabajos anteriores realizados por los autores, las capas de AgInS<sub>2</sub> crecieron por coevaporación de los metales precursores en un proceso de dos etapas; y las películas delgadas de In(O:OH)S se depositaron por baño químico. Las medidas de rayos X indican que las películas de AgInS2 crecen con estructura tipo calcopirita y las de In(O:OH)S con estructura policristalina. Las películas de AgInS, presentan conductividad tipo P, y de las medidas de transductancia se encontró un coeficiente de absorción alto (mayor a 104 cm-1), y un gap de 1.95 eV; las películas de In(O:OH)S presentaron un gap de 3.01 eV; el análisis morfológico indica que bajo estas condiciones de síntesis, las películas de In(O:OH)S recubren completamente la capa absorbente de AgInS<sub>2</sub>. Finalmente, en este trabajo se aplicó la ecuación de Avrami-Erofeev para estudiar la tasa de crecimiento de las películas delgadas de In(O:OH)S sobre el substrato de AgInS<sub>2</sub>. Los resultados indican que el sistema desarrollado puede utilizarse en celdas solares de juntura simple o multijuntura.

**Palabras clave:** ventana óptica, AgInS2; In(O:OH)S, capa buffer, capa absorbente, película delgada, celdas solares.

# INTRODUCTION

The highest conversion efficiencies reported for thin film solar cells has reached over 20.8% (Green et al., 2014); this result was obtained for using CulnGaSe<sub>2</sub> (CIGS) as absorbent layer and Cadmiun Sulphide (CdS) as buffer layer. Other semiconducting compounds such as CuGaSe<sub>2</sub>, CuInS<sub>2</sub> have been used as absorbent layers; however, they have reported lower energy conversion efficiencies (Green et al., 2014, Wang et al., 2012, Goetzberger et al., 2003). It is well known in solar cell development technology that chalcopyrite type compounds from group I-III-VI, in periodic table have suitable properties to be used in single-junction and tandem solar cells because those compounds have shown direct gap. Nowadays, usage of Silver-Indium-Disulphide (AgInS<sub>2</sub>) as an alternative semiconductor material is expected to make a good solar cell absorber layer in multi-junction systems due to its large absorption coefficient and its band-gap energy (Eg) ranging from 1,87 to 2,03 eV (Albor *et al.*, 2007). Although, optimal Eg is around 1,45 eV and AgInS<sub>2</sub> has higher Eg values, its chalcopyrite structure and its lattice constant allows to form appropriate heterojunctions with semiconductors such as CdS and CuInSe<sub>2</sub>. The above mention argument justifies that AgInS<sub>2</sub> has possibly the required properties to be coupled successfully to grow CdS/AgInS<sub>2</sub>/CuGaSe<sub>2</sub> structures (Roth *et al.*, 1973; Loferski *et al.*, 1978).

CdS is typical buffer compound used in chalcopyrite solar cells; however, CdS compounds are considered hazardous materials to environment (Toxic Lethal Value: 50µg/m<sup>3</sup>) and, therefore, other less-toxic suitable compounds are being researched to substitute the CdS buffer layer based on two main arguments (Sankapal *et al.*, 2004; Lee *et al.*, 2012): (1) The expected environmental risks arising from implementation of synthesis CdS thin film by CBD process in a CIGS module production line requires additional safety regulation (McEvoy *et al.*, 2013).

(2) The possibility to improve the light transmission in the blue wavelength region for using a material with a wider band gap than CdS (McEvoy *et al.*, 2013; Arredondo *et al.*, 2012).

Alternative buffer layers to CdS films have been assessed to fabricate Cd-free devices to improve photocurrent generation. Buffer layers composed by ZnS deposited by CBD and Atomic Layer Deposition (ALD) have shown high potential to be used as a buffer material (Naghavi et al., 2006; Ennaoui et al., 2005); system Zn(O,OH)S/ZnO reported efficiencies above 18% in CIGS based cells (Contreras et al., 2003). Buffer layers in chalcopyrite based solar cells constituted by In<sub>2</sub>S<sub>3</sub>, In<sub>2</sub>Se<sub>3</sub>, ZnSe and (Zn, In) Se, have shown positive results as alternative buffer layer (Hariskos et al., 2005). Moreover, properties such as stability, band gap energy (2,5-3,0 eV), photoconductor behavior and high transmittance (75-85%) in the visible range, make In(O,OH)S thin films an option to substitute CdS as buffer layer (Barreau *et al.*, 1995).

Different chemical and physical methods have been reported in the literature for AglnS<sub>2</sub> thin films deposition; however, best results have been obtained with AglnS<sub>2</sub> thin films obtained by physical methods (Yoshinory *et al.*, 1995; Ueno *et al.*, 1990; Sharma, 1995); for In(O,OH)S thin films, the CBD synthesis offers a low-cost option as it does not required high tech instrumentation, and chemicals are easily available, along this method uses low temperature deposition; it helps to avoid oxidation and corrosion substrates (Bhattacharya *et al.*, 2005).

This research articles focuses on the study of the characteristics of In(O,OH)S/AgInS, interface

heterojunction to be implemented on solar cells (single-junction or tandem cells). AgInS<sub>2</sub> thin films were deposited by co-evaporation method in a two-step process; and In(O,OH)S thin films were deposited by CBD method.

#### MATERIALS AND METHODS

#### AgInS, thin film preparation

AgInS, thin films were prepared by co-evaporation from metallic precursor species on glass substrate on an evaporation chamber connected to a vacuum system with pressures around 10<sup>-5</sup> Torr, two tungsten crucibles (to evaporate Ag and In respectively), a tantalum effusion cell to evaporate sulfur, and a thickness monitor (Maxtec TM-400) with a quartz crystal to measure the evaporated elements flux. The substrate temperature was controlled with a programmable PID controller (Eurotherm 900C); figure 1 shows general scheme of physical deposition system. AgInS<sub>2</sub> thin films deposition was accomplished in two stages. An In<sub>s</sub>, layer is grown in the first stage by means of simultaneous evaporation of In and S, keeping the substrate temperature at 300° C. The In flux and S evaporation temperature were kept at 2.5 Å/s and 135°C respectively during the whole stage.

Consecutively, on the second stage,  $AgInS_2$ is formed by evaporating Ag (in a chamber filled with sulfur) over a layer of previously grown  $In_xS_y$ (first stage); substrate temperature and Ag flux were 400-600°C and approx. 3 Å/s respectively.  $AgInS_2$ films were exposed to a post-deposition thermal annealing in S environment during approx. 1 hour, in order to improve its chemical composition.



**Figure 1.** General scheme of physical deposition system using for AgInS, thin films deposition

Source: The authors.

# In(O,OH)S thin film preparation

In(O,OH)S layers were deposited using a solution prepared with thioacetamide (Scharlau) (TA) and indium chloride (InCl<sub>3</sub>) as sources of S<sup>2-</sup> and In<sup>3+</sup> ions respectively; InCl<sub>3</sub> was prepared in our laboratory using metallic In (99,9%) and HCl 36% (99.9% Merck). Acetic Acid (99,9% Merck) and Sodium Citrate (Riedel-de Haën) (Cit) were used as complexing agents of In<sup>3+</sup> ions. Two substrates were used to grow In(O,OH)S layers: soda lime glass coated with Indium Tin Oxide (ITO) and AgInS<sub>2</sub> deposited on soda lime glass; specific experimental conditions are described on Vallejo *et al.* (2010). The chemical reaction of the film preparation is presented in equation 1, as follows:

 $[In(AcO)_{4-x}HCit_X]_{(ac)} + CH_3SCNH_{2ac} + H_3O^- \Leftrightarrow \qquad (1)$ 

 $[In(O,OH)S]_{film} + NH_4^{+} + AcOH + H_3Cit$ 

### Analytical methods

Optical, structural and morphological properties of AgInS<sub>2</sub> and In(O,OH)S thin films were studied through transmittance, XRD and AFM measurements carried out with a VIS–IR Oriel spectrophotometer, a Shimadzu 6000 diffractometer with Cu-K<sub>a</sub> radiation ( $\lambda = 0,15418$  nm) source over the diffraction angle 20 between 20° and 80° and PSI AFM microscope with a scanned area (2 µm×2 µm). Film thickness was determined using a Veeco Dektak 150 surface profiler. AgInS<sub>2</sub> conductivity was determined by means of thermoelectric power measurements.

# **RESULTS AND DISCUSSION**

### In(O,OH)S thin film growth on AgInS<sub>2</sub> layers

CBD process kinetics for In(O,OH)S thin film growth on  $AglnS_2$  layers and ITO substrates are presented on figure 2. Results obtained from the trials tend to follow a sigmoidal trend, typical from autocatalytic reactions (O'Brien *et al.*, 1998). Such behavior can be described by means of the Avrami-Erofeev equation (2).

$$\alpha = 1 - \exp\left(-kt^n\right) \tag{2}$$

Where  $\alpha$  is the fractional decomposition; *t* the time; *k* is a rate constant, and *n* the Avrami exponent which determines the nucleation and growth mode. The equation expresses the rate of formation of the nuclei, in the event when completely random nucleation occurs (Zhai *et al.*, 1007). During the growth process of In(O,OH)S thin film, 3 phases were identified: (1) induction time (start-up of the nucleation process), (2) an initial linear phase, and (3) final saturation phase (figure 2a). Induction time depends mainly on solution temperature, reagents concentration and substrate composition. During the second phase, film thickness increases exponentially with the time, while on the last phase growth

rate decreases as reagents concentration decay; normal behaviour of CBD process. Furthermore, it was observed that substrate composition can influence the growth rate of the In(O,OH)S. Kinetic rates are faster when AgInS, was used as substrate than ITO. CBD growth process is affected by the surface kinetic processes (Froment et al., 1995). Determination of site availability for the formation of nuclei depends on composition and morphology of substrate, particularly the presence of defects as vacancies and interstitials (Ag, In, S) which can facilitate the presence of those sites (Arredondo et al., 2010). If we considered that buffer thin film formation is based on the nucleus generation and succeeding growth (assuming constant temperature during the process), the Avrami-Erofeev equation (3) can be used to calculate the kinetic reaction parameters on different substrates (Zhai, 2007):

$$Ln[-Ln(1-\alpha)] = Ln k + n Ln(t)$$
(3)

Plotting  $Ln[-Ln (1-\alpha)]$  vs Ln (t), the reaction constant (k) and the Avrami exponent (n) can be obtained from the slope and the intercept of the lineal fitting respectively. Figure 2b indicates that substrate type affects growing rate of In(O,OH)S thin films; n value found indicates that both types of substrate consist of the same In(O,OH)S crystals nucleation mechanism because its values are approximately the same (table 1). However, unlike n, k value changes significantly when substrate type varies; this value doubles when AgInS<sub>2</sub> absorbent layer is used, indicating that the growth process occurs at a greater rate on AgInS, than Soda Lime. This phenomenon can be attributed to different nucleation mechanism or the number of sites is different for the generation of nuclei. As a consequence of similar *n* values in both substrates, nucleation pathway has the same trend, and therefore, AgInS, presents a greater number of sites for nuclei generation than ITO substrate for In(O,OH) S crystals growing; results explained based on their composition and surface topography (in agreement with reports on Zn(O,OH)S and In(O,OH)S

thin films deposition on CulnS<sub>2</sub> layers) (Zhai *et al.,* 2007; Vallejo *et al.,* 2010).

**Table 1.** Growth kinetics parameters of In(O,OH)S thin films synthesized on different type substrates by CBD

Substrate	K* <b>1000</b>	п
AIS	7,5	1,36
ITO	3,0	1,41

Source: The authors.



**Figure 2.** (a) In(O,OH)S growth rate variation on time synthesis and substrate type. (b)  $Ln[-Ln (1-\alpha)]$  vs Ln (t) curve with different substrates type

Source: The authors

### Structural characterization





Source: The authors.

#### AgInS, thin films

Figure 3 shows XRD spectra of AgInS, films deposited by co-evaporation; results were analyzed based on the data reported in the JCPDS database for these types of compounds, and performing theoretical simulation of the XRD pattern with PowderCell package. Rietveld method was used for simulation of tetragonal AgInS, phase; geometry Bragg-Brentano with March-Dollase model was used to find the preferential orientation, and it was found to be (112). The function Pseudo-Voigt 1 was used; the number of iterations was 550 and the final  $\varphi$  factor (shi factor) was 1,5. The described procedure was fundamental to identify the phases present in the samples with a high degree of confidence. It was found that AgInS<sub>2</sub> had grown with tetragonal structure. Seven peaks were observed: the highest was observed at  $2\theta=26,68^{\circ}$  corresponding to preferential plane growing (112); other peaks were identified as follows:  $2\theta = 30, 4^{\circ}$  to plane (200);  $2\theta=31,96^{\circ}$  to plane (004);  $2\theta=43,55^{\circ}$  to

plane (220);  $2\theta$ =46,62° to plane (204);  $2\theta$ =51,80° to plane (312) and  $2\theta$ =55,02° to plane (224). These results are in agreement with JCPDS No. 251330. The lattice parameters determined from the X-ray diffraction spectra for AgInS<sub>2</sub> films grown with chalcopyrite type tetragonal structure are: *a* = 5,8980Å and *b* = 11,1935Å. These results indicate that AgInS<sub>2</sub> layer fulfils structural requirements to be used as absorbent layer in thin film solar cells.



**Figure 4.** (a) XRD pattern AgInS<sub>2</sub> thin films deposited by co-evaporation; and XRD pattern of In(O,OH)S thin films deposited by CBD on (b) AgInS<sub>2</sub> and (c) ITO substrates (ITO signal were deleted)

#### Source: The authors

#### In(O,OH),S thin films

Figure 4 shows XRD pattern corresponding to In(O,OH)S thin films deposited on ITO and AgInS<sub>2</sub> substrates. Due to its small thickness, crystallinity

of In(O,OH)S thin films were very poor; XRD patterns demonstrate that In(O,OH)S layers are polycrystalline. Samples deposited on ITO present just three reflections: the first two at  $2\theta$ =33,7° and at  $2\theta$ =34,1°, which corresponds to (001) and (200) planes of Indium Oxide Hydroxide (InOOH) (JCPDS # 17-0549), and the third reflection at  $2\theta$ =48,37° associated to (2212) plane from tetragonal β-In<sub>2</sub>S<sub>3</sub> phase (JCPDS #25-0390).

On the other hand, samples deposited on AgInS<sub>2</sub> presented one reflection at  $2\theta = 25,7^{\circ}$  which corresponds to (110) plane of Indium Oxide Hydroxide (InOOH) (JCPDS # 17-0549). Under reaction conditions, it is possible that during CBD process, a mixture of  $In_2S_3$ ,  $In(OH)_3$  and  $In_2O_3$  can be obtained (Larina et al., 2003); however, results reported by other authors on In<sub>2</sub>S<sub>2</sub> thin films structure deposited by CBD, suggesting a mixture of the cubic a and b In<sub>2</sub>S<sub>3</sub> phases (Lokhande et al., 1999; Bayon et al., 2000). The presence of Indium oxide hydroxide and another phases of In<sub>2</sub>S<sub>3</sub> such as g and e have been also reported (Larina et al., 2003, Bayon et al., 2000). Results indicate that buffer layer films deposited on ITO and AgInS, exhibit polycrystalline structure and might contain a mixture of  $In_2S_3$  and In(O,OH) phases.

This phenomenon can be explained due to its hydrodynamic of reaction medium because in our case a co-precipitation of another species is possible; due to final composition of buffer layer synthesized by CBD (where different chemical phases are mixed), is common named this material as In(O,OH)S. Along with this, In(O,OH)S thin films deposited by CBD were polycrystalline on both ITO and AgInS, substrates. These results are important because they indicate that the recipe used allows to obtain polycrystalline thin film independently on the substrate used. To photovoltaic application, it is necessary to obtain a correct junction with electric contact on top cell (ZnO commonly used) for electrical transport and, In(O,OH)S thin films were polycrystalline on AgInS<sub>2</sub> substrates, this enhance the junction to electric contact.

# **Optical characterization**

AgInS<sub>2</sub> and In(O,OH)S thin films were characterized through spectral transmittance measurements; optical properties of In(O,OH), S were determined from transmission measurements in the range of 300–1000 nm. Figure 5 shows typical transmission spectra of AgInS<sub>2</sub> and In(O,OH)S films. In(O,OH)S films deposited on AgInS<sub>2</sub> substrate were homogeneous with adequate substrate adherence. In(O,OH) S thin film showed optical transmission of 80-90% in the visible range. High transparency in the visible region indicates absence of adsorbed powdery colloids formed by homogeneous reaction during the film growth. A sharp absorption edge is observed in the visible region, indicating relatively good crystallinity and low defect density near the band edge (Gracia et al., 2005). For AgInS, thin films, it is observed that transmittance spectra have a sharp absorption edge in the visible region.

Based on the optical transmission measurements, the square of absorption coefficient ( $\dot{\alpha}^2$ ) is plotted as a function of photon energy (hv). Figure 6 shows results of n vs. I, a vs. I and  $(\alpha hn)^2$ vs. hn for AgInS<sub>2</sub> substrates and buffer layers. Those results were determined based on (Gracia et al., 2005). Figure 6 shows that AgInS, films have an absorption coefficient a greater than 10<sup>4</sup> cm<sup>-1</sup> and an optical gap Eg of 1,93 eV. These results indicate that AgInS, thin films have suitable properties for using them as absorber layers in two junction tandem solar cells. In(O,OH)S band gap (3,01eV) was greater than  $In_2S_3$  bulk band gap (2,4-2,7eV) (Asenjo et al., 2007; Sandoval-Paz et al., 2005); this shift may be due to the CBD technique. The E of In(O,OH)S depends on the film's stoichiometry, and it can be found between 2,0 eV and 3,7 eV for In<sub>2</sub>S<sub>3</sub> and In<sub>2</sub>O<sub>3</sub> respectively (Bayon et al., 1998). This result is in agreement with the E<sub>a</sub> reported for In(O,OH)S thin films obtained by CBD (Larina et al., 2003; Huang et al., 2001; Yousfi et al., 2000).

In CBD process the co-precipitation of another species is common; in our case,  $In(OH)_3$ and  $In_2O_3$  can be presented in a buffer layer; these compounds could shift the band gap to blue energies; this phenomenon is very favorable because blue response in solar cells enhance system performance. Furthermore, figures 5 and 6 showed that In(O,OH)S thin films presented better optical properties than CdS thin films; this properties allow to use In(O,OH)S thin films as buffer layer on solar cells. Along, differences in band gaps materials are favorable to heterojunction; high band gap values for In(O,OH)S (3,01eV) guarantee that sun radiation on visible range will not be absorbed on the buffer layer but it will be absorbed on AgInS<sub>2</sub> (greater than 10<sup>4</sup> cm<sup>-1</sup>); this system present typical characteristics to be used in single-junction solar cells and as top cell in a tandem solar cell system.



**Figure 5.** Optical transmission spectra of as-grown AgInS<sub>2</sub> thin films (1µm thickness), and as-grown In(O,OH)S (100nm thickness)

Source: The authors



**Figure 6.** Plot of  $(\alpha hv)^2$  vs hv for: (a) as-grown AgInS<sub>2</sub> and (b) as-grown In(O,OH)S

Source: The authors

**Table 2.** Grain size average and roughness valuesderived from images displayed in figure 6

Grain size (nm)	Roughness R <sub>ms</sub> (nm)
50	2,1
80	2,8
	Grain size (nm) 50 80

Source: The authors

#### Morphological characterization

Figure 7 shows AFM images of In(O,OH)S thin films deposited by CBD over  $AgInS_2$  layer. The  $AgInS_2$ -substrate AFM image shows columnar crystals, typical for  $AgInS_2$  (1µm thickness) with tetragonal structure; it also shows the effect of In(O,OH)S morphology on thin film thickness; it is clearly seen from AFM images that grain size of In(O,OH)S particles are smaller than grain size of  $AgInS_2$ particles (240 nm).

After 15 minutes buffer deposition has started, grain particles of different sizes are distributed randomly throughout the substrate without any crack (figure 7); along, In(O,OH)S thin films grain size and  $R_{ms}$  roughness increases significantly when the film thickness increases (table 2). At the initial stage of deposition, many nucleation centers are present on the substrate, and small crystallites are produced; for short time deposition intervals, films with small crystallites are not able to grow into bigger ones, whereas for thicker films the crystallinity of the film crystallites grew bigger. It can also be seen in figure 7 that after 30 minutes of CBD process is possible to cover completely and uniformly the AgInS<sub>2</sub> surface. It is a very important requirement for thin films as buffer layer.



**Figure 7.** Atomic force micrographs of In(O,OH)S thin films deposited on  $AgInS_2$  with different deposition times.

Source: The authors.

# CONCLUSIONS

By using a system composed of In(O,OH)S/AgInS<sub>2</sub> (buffer/absorbent), it was found that In(O,OH)S buffer layers growth on AgInS<sub>2</sub> substrates were uniform, adherent and specular. It also presented good macroscopic properties. Furthermore, kinetic studies on deposition of In(O,OH)S over AgInS, indicated a growth rate variation on the substrate type used. Nucleation process model indicates a significant faster process on AgInS, than ITO substrates, explained by the differences in composition and topography of the surface substrates. XRD analysis showed that buffer layer films deposited on ITO and CGS exhibited polycrystalline structure with a possible mixture of In<sub>2</sub>S<sub>3</sub> and In(OOH) phases; additionally, it was found that AgInS<sub>2</sub> has grown with tetragonal structure at plane (112) as preferential plane. Optical, structural and morphological characterization of the system indicate that In(O,OH)S/AgInS<sub>2</sub> layers obtained can be used in single-junction and multiple-junction solar cells.

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