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Abstract: In2S3 thin films were deposited onto indium tin oxide coated glass substrates by Chemical Spray Pyrolysis method keeping the substrates at different temperature. The sprayed In2S3 thin films were characterized by X-Ray Diffraction and Raman spectroscopy for structural characterization and assessment of their crystal quality. Scanning Electron Microscopy and Atomic Force Microscopy were used for exploring the surface morphology and topography of thin films. The optical bandgap were determined through Optical transmission measurements. Indium sulfide phase exhibits a preferential orientation in the (0, 0, 12) crystallographic direction as confirmed by XRD analysis. Phonon vibration modes obtained by Raman spectroscopy also confirm the In2S3 phase of our samples. Surface morphology of film giving by Scanning Electron Microscopy reveals that films are free of defects and optical bandgap energy varied from 2.82 eV to 2.95 eV.

Dear Editor,

I'm submitting for your kind consideration to be published in Journal of Physics and Chemistry of Solids an original manuscript entitled

Spray pyrolysis of In_2S_3 thin films deposited at different temperatures

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This paper reports on synthesis and characterization of In_2S_3 thin films by the Spray Pyrolysis technique. In_2S_3 is a semiconductor material, which is gaining interest in photovoltaic applications. Spray Pyrolysis is a low cost deposition technique easily scalable and well suited for mass production. We have studied the structural and optical properties of In_2S_3 thin films deposited under different temperatures of the substrate for a fixed S/In ratio and as a result we are able to assess the optimal substrate temperature for obtaining the best quality In_2S_3 thin films.

This manuscript is the authors' original work and has not been published nor submitted simultaneously elsewhere. All authors have checked the manuscript and have agreed to the submission.

Yours sincerely,

Prof. Dr. Bernabé Marí

Chemical Spray Pyrolysis of β-In_2S_3 Thin Films Deposited at Different Temperatures

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Keywords: In_2S_3, Chemical Spray Pyrolysis, ITO, Raman Spectroscopy, AFM

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Abstract

In_2S_3 thin films were deposited onto indium tin oxide (ITO) coated glass substrates by Chemical Spray Pyrolysis method keeping the substrates at different temperatures. The sprayed In_2S_3 thin films were characterized by X-Ray Diffraction for the structure, Raman spectroscopy for thin films quality; Scanning Electron Microscopy and Atomic Force Microscopy were used for exploring the surface morphology and topography of thin films respectively. The optical band gap was determined through Optical transmission measurements. Indium sulfide phase exhibits a preferential orientation in the (0, 0, 12) crystallographic direction confirmed by XRD analysis. Phonon vibration modes obtained by Raman spectroscopy also confirm the In_2S_3 phase of our samples. Surface morphology of film giving by Scanning Electron Microscopy reveals that films are free of defects and optical band gap energy varied from 2.82eV to 2.95eV.

1. Introduction

The substitution of cadmium sulfide (CdS) using usually as buffer layer by another nontoxic and having better wider band gap in order to improve light transmission in the blue wavelength region is a challenge for researchers since a few decades. To answer this problem indium sulfide is a good candidate for its stability [1], band gap between 2.0 eV [2] to 2.8 eV [3], its transparency and photoconductivity behavior [4].

Chemical Spray Pyrolysis is a technique being considered in research to prepare thin and thick films, ceramic coatings, and powders [5]. It is chosen because it is economical, fast, no vacuum and simple to prepare thin film [6]. In addition it is suitable for industrial scale production.

Indium sulfide thin films has been deposited using various techniques like Successive Ionic Layer Adsorption and Reaction (SILAR) [7], Thermal Evaporation [8], Atomic Layer Deposition (ADL) [9], Chemical Bath Deposition (CBD) [10], Chemical Spray Pyrolysis (CSP) [11], Electrodeposition [12], etc. It is worth noting that the quality of films strongly depends on the growth technique.

In the literature the band gap of In_2S_3 varied between 2.0 to 3.7 eV depending of the deposition techniques used and assuming a direct band gap transition [13]. Copper indium gallium (di)selenide (CIGS) solar cells with In_2S_3 buffer layer co-evaporated from In and S powder have shown efficiencies of up to 12.4% [l4].

In this study we have deposited In_2S_3 thin films by Chemical Spray Pyrolysis (CSP) using a [S]/[In] molar ratio of 3 and using some amount of alcohol (5%) in aqueous solvent to reduce the surface tension of water. The [S]/[In] ratio of 3 was used to compensate the volatility of sulfur at the substrate temperature used in this work in order to achieve stoichiometric films. Several substrates temperature was used 250 °C, 277 °C, 300 °C and 330 °C and their effect on the crystalline structure, morphology and optical properties of sprayed In_2S_3 thin films were studied.

2. Experimental details

2.1. Films preparation

Indium sulfide (In_2S_3) thin films were deposited onto Indium Tin Oxide (ITO) coated glass substrate from an aqueous solution containing indium (III) chloride ($InCl_3$) (99.999 %), thiourea $CS(NH_2)_2$ (≥99%) and alcohol (5% in volume) to reduce the surface tension. The concentration of indium chloride was fixed at 0.026M and the [S]/[In] ratio was kept to 3. The substrate temperature was kept at 250 C, 277 °C, 300 °C and 330 °C, respectively by means of a PID

system with sensitivity of ±0.1 ºC. The volume sprayed was 5 mL at a spray rate of 1.5 mL/min. Air compressed was used as carrier gas at a pressure of 0.7 bar and the distance between the glass substrate and the nozzle was kept to 30 cm. ITO coated glass substrates were previously washed with HNO_3 and subsequently rinsed with water, ethanol and acetone.

Table I: Deposition parameters for preparation of In_2S_3 thin films by Chemical Spray Pyrolysis.

Spray solution volume	5 mL
Carrier gas pressure	0.7 bar
Spray deposition rate	1.5 mL/min
Nozzle-to-substrate distance	30cm
Substrate temperature (ºC)	250 - 277 - 300 -330

2.2. Films characterization

Structural properties were characterized by means of X-ray diffraction (XRD) measurement with a Rigaku Ultima IV diffractometer in Bragg-Bentano (Θ-2Θ) configuration and using CuKα radiation (1.5418Å). Phonon vibration properties were also characterized by Raman scattering measurements performed with LabRAM HR UV spectrometer coupled to a Peltier-cooled CCD camera with a spectral resolution of $3cm^{-1}$and using a 632.81nm laser excitation line. Morphology was characterized using JEOL-JSM6300 operating at 20keV and the Atomic Force Microscopy (AFM) study was carried out using Bruker Multimode 8 AFM Nanoscope V controller. Optical properties were monitored by transmittance using a Deuterium-Halogen lamp (DT-MINI-2-GS Micro park) in association with 500 mm Yvon-Jobin HR460 spectrophotometer using a back-thinned Si-CCD detector (Hamamatsu) optimized for the UV-VIS-Infrared range.

3. Results and discussion

3.1. X-Ray Diffraction (XRD) analysis

Figure 1 depicts the XRD spectra of In_2S_3 thin films deposited by spray pyrolysis at several substrate temperatures (250°C, 277°C, 300°C and 330°C). The X-ray diffraction patterns reveal the presence of In_2S_3 with ITO substrate peaks. The most intense XRD peaks corresponds to

crystallographic planes in the (0, 0, 12) direction, which means the thin films growth preferentially on the direction perpendicular to the sample's surface. Other diffraction peaks located at 14.343°, 27.638°, 44.113° and 48.080° and corresponding to crystallographic planes (1, 0, 3), (1, 0, 9), (1, 0, 15) and (2, 2, 12), respectively were also observed. Peaks labeled with * come from the polycrystalline ITO substrates. No peaks corresponding to oxide phases different than those come from the substrate are present, which means that the [S]/[In] ratio used avoids the formation of undesirable oxide phases. This statement is corroborated by the absence of any oxide related diffraction peak when the solution is sprayed onto glass substrate at the same temperature. The main peak (0, 0, 12) of our samples increased with substrate temperature up to Ts=300°C and decreased slightly at 330°C. Therefore sample labeled as S3 has the highest intensity and is better crystallized than the others.

The variation of grain size with substrate temperature was investigated using the Debye-Scherrer formula from (0, 0, 12) diffraction line:

$$D = K\lambda/\beta \cos\theta \qquad (1)$$

Where β is the Full Width at Half Maximum (FWHM), λ wavelength of X-ray whose value is 1.5418 Å (CuKα), K the Scherrer constant which generally depends on the crystallite shape and is close to 1 (K = 0.9 was used) and θ is the Bragg angle at the center of the peak. The crystallite size, D, obtained from this equation corresponds to the mean minimum dimension of a coherent diffraction domain. Values for crystallite size are shown in Table II (Column c). From Table II crystallite size increases with substrate temperature up to 300 °C and then decreases. Then, the best substrate temperature to deposited In_2S_3 onto ITO coated glass is 300 °C because it gave the best crystallinity with the biggest crystallite size. The intensity of the main (0, 0, 12) diffraction peak of our samples increased with the substrate temperature up to 300 °C and decreased slightly after.

The ratio between the (0, 0, 12) In_2S_3 peak and (4, 0, 0) ITO peak ranges from 32 to 80 when the substrate temperature increases from 250 to 330 ºC what means that the amount of crystallites with this preferential direction increases with the temperature of the substrate.

Sprayed In_2S_3 films exhibit a preferential orientation following the (0, 0, 1) direction. In that direction the allowed diffraction peaks are (0, 0, 4), (0, 0, 8) and (0, 0, 12) and their relative intensities are 4, 3 and 50, respectively (JCPDS#25-390). Consequently the most intense diffraction peak takes place between (0, 0, 12) planes which are separated a distance of 2.694 Å.

As a comparison (0, 0, 4) planes are separated a distance of 8.090 Å and therefore longer-range order is required to observe its corresponding diffraction peak.

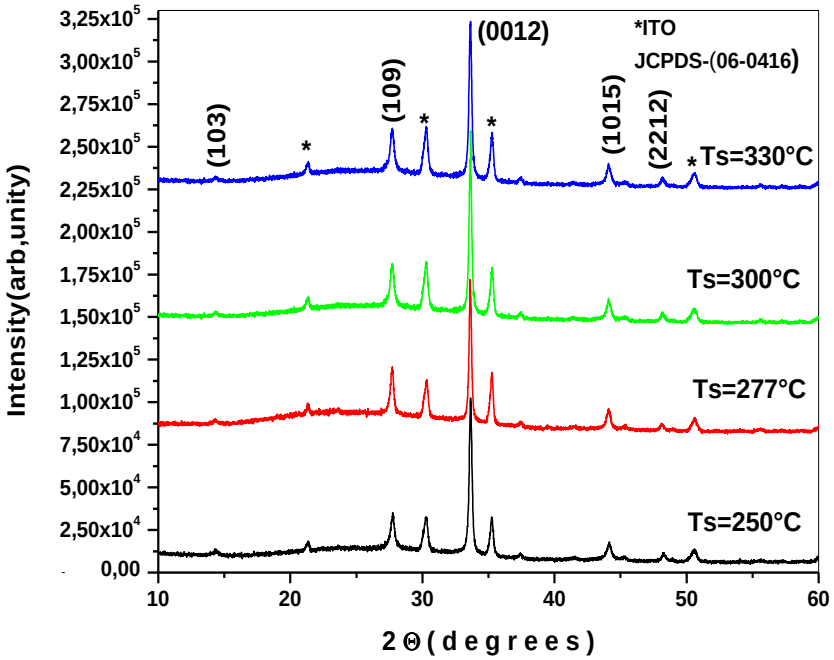

Figure 1. X-ray diffraction spectra for films deposited by Chemical Spray Pyrolysis at different substrate temperatures.

Table II: Grain size of samples obtained by Debye-Scherrer method from (0, 0, 12) main peak.

a	b	c	d	e	f
Sample ID	Substrate Temperature (ºC)	Crystallite Size (nm) from XRD	Surface Roughness (nm)	Grain size (nm) by AFM	Eg (eV)
S1	250	34.6	26.7	140.3	2.84
S2	277	41.5	8.68	126.8	2.82
S3	300	43.5	10.5	135.8	2.95
S4	330	37.8	10.6	117.6	2.88

3.2. Raman spectroscopy analysis

Raman spectroscopy is a powerful tool to analyze phase and structure of In_2S_3 thin films. According to Figure 2, modes obtained by Raman analysis confirms well know the β-In_2S_3 phase and structure of our samples with a main mode at 327 cm^{-1} corresponding to F_{2g}. Others modes belonging to β-phase and corresponding to A_{1g} at 251 $cm^{-1}$and E_g at 374 cm^{-1} are also observed. All samples are β-In_2S_3 thin films accordingly to the literature confirming the composition and the structure of our samples [15]. The β-In_2S_3 phase is known to be the most stable. It owns good characteristics among the other three phases in In_2S_3 (α-In_2S_3, γ-In_2S_3 and ε-In_2S_3) and only β-In_2S_3 phase commonly used in photovoltaic applications.

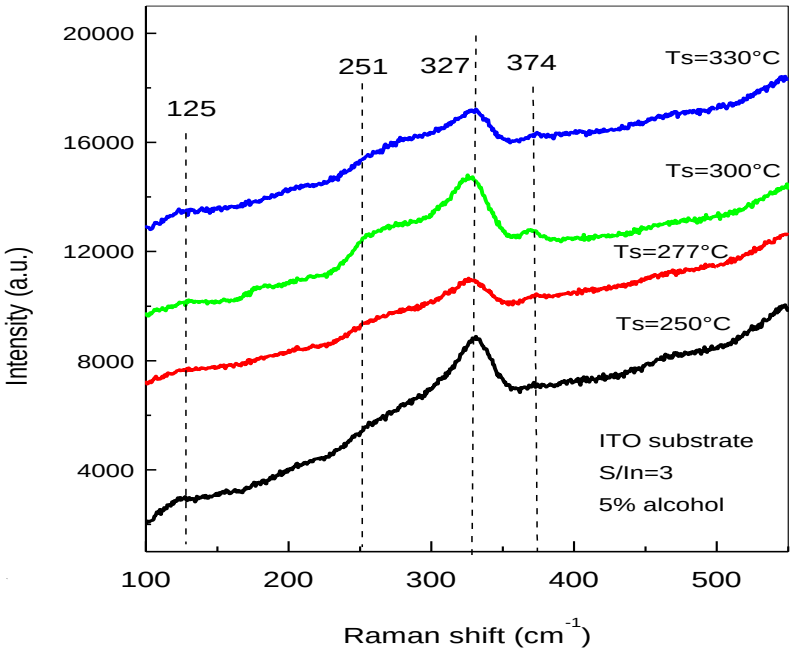

Figure 2. Raman spectra of samples deposited by Chemical Spray Pyrolysis at different substrate temperature

3.3. Scanning Electron Microscopy (SEM) analysis

Figure 3 shows SEM micrographs of In_2S_3/ITO prepared with different substrate temperature. As be seen in this figure all samples were pinhole and cracks free. Films are well covered, compact and homogeneous which is good for photovoltaic application. According to SEM images the most uniform surface sample seems to be reached for sample S4 following by sample S3 which are good characteristic for thin film used in solar cell applications.

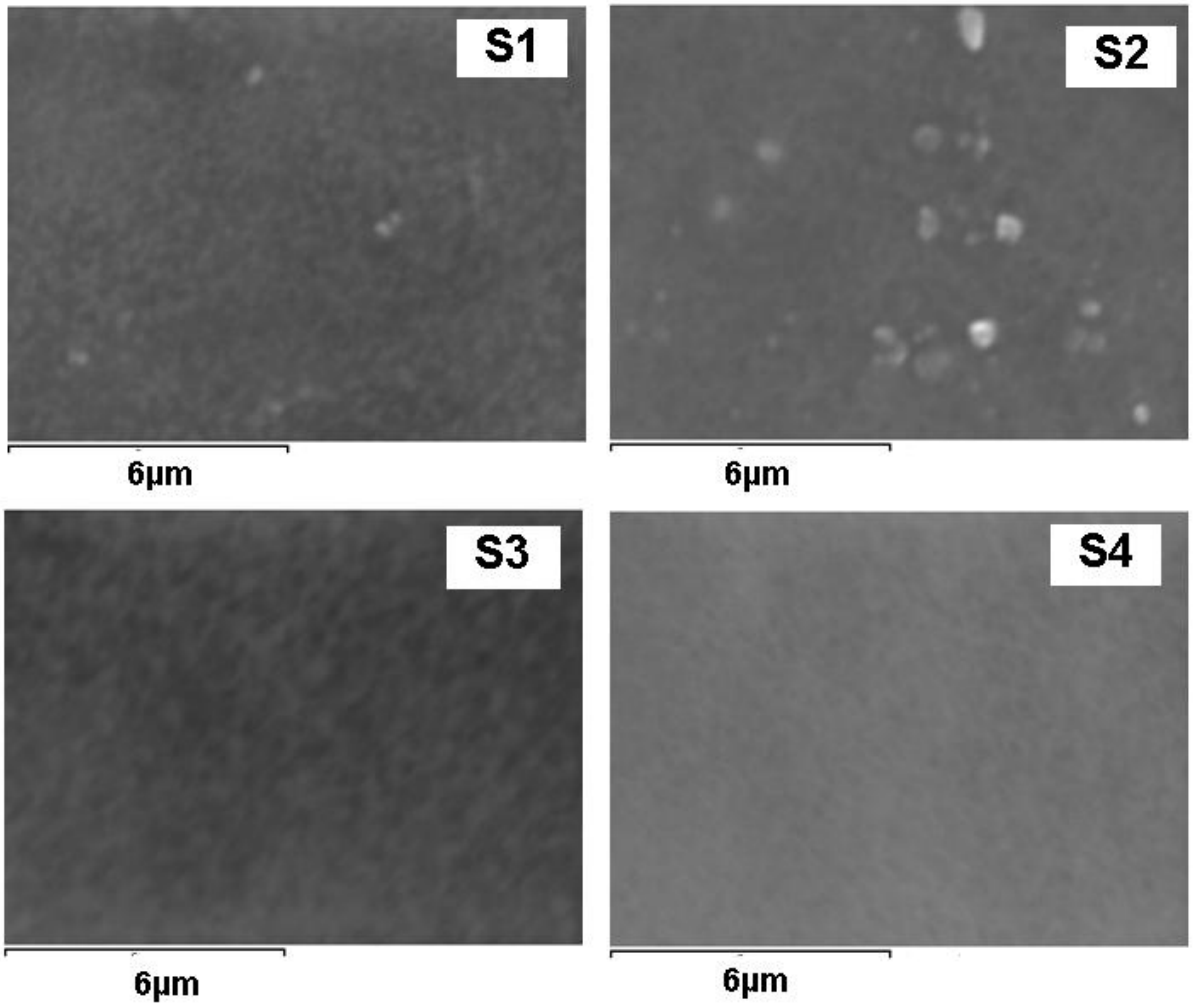

Figure 3.SEM images of samples deposited by Chemical Spray Pyrolysis at different substrate temperatures.

3.4. Atomic Force Microscopy (AFM) analysis

AFM is a technique to analyze surface topography of a film. It gives the grain size, structure and surface roughness of a thin film. AFM micrographs reveal well adhering films to ITO substrate with small grain size for sample elaborated at Ts=330 °C and Ts=277 °C. The roughness of sample giving by Ra indicates that sample deposited at low substrate temperature (250 °C) is rougher than others and that fact can be explained through the aggregation of small grains to form irregular big ones with grain boundaries. Table II (columns d, e) displays the Roughness of the surfaces and the grain size as measured by AFM, respectively.

AFM micrographs revealed that sample S1 has a topography different to others and has the highest roughness and big grain size. The biggest grain size obtained by sample S1 deposited at 250ºC may be related to the lower diffusion of atoms on the substrates due to their lower thermal energy. Otherwise sample S3 deposited at 300 ºC seems to possess the best characteristics, low roughness and high grain size.

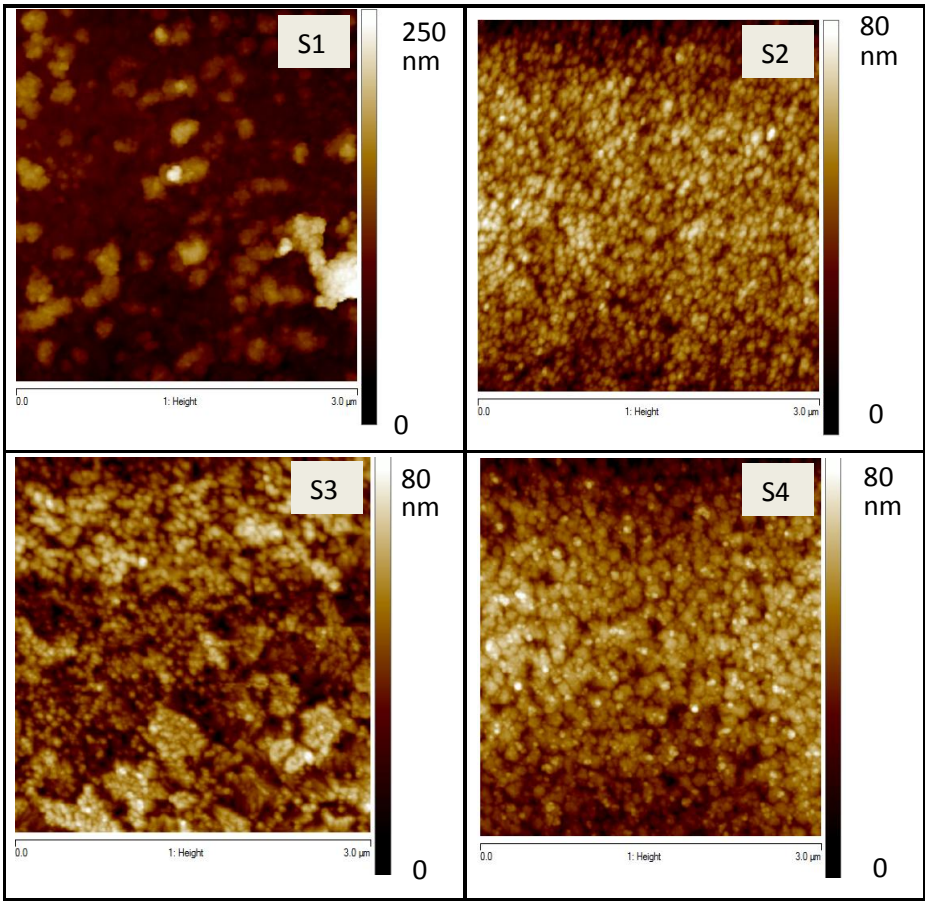

Figure 4. AFM micrographs of samples deposited by Chemical Spray Pyrolysis at different substrate temperatures.

3.5. Optical analysis

The optical transmittance of In_2S_3 deposited by Chemical Spray Pyrolysis onto ITO coated glass is displayed in Figure 5. There is no significant change in optical transmittance of our films as substrate temperature is increased from 250 °C to 330 °C. The transmittance increases from 50% to 70% when the substrate temperature increases from 250 °C to 300 °C and then decreases at 330 °C. Therefore, the highest transmittance was obtained at 300 °C substrate temperature.

The band gap energy for In_2S_3 thin films were obtained from optical transmission data plotting $(Ahν)^2$ versus hν at various temperatures where A is the absorbance and hν is the photon energy. The calculated optical band gaps for every sample appear in Table II (column f). The observed trend is the higher the substrate temperature the higher the optical bandgap.

The optical bandgap values obtained for sprayed In_2S_3 films (between 2.82 and 2.95 eV) are higher than the optical bandgap for pure β-In_2S_3 (2.10 eV [16]). This increase in the optical bandgap of our films can be due to the presence of oxygen in the lattice and, in this case, according to data extracted from the reference 16 we deduce that our sprayed In_2S_3 films would contain between 12-14% of oxygen. Further, the increase of the bandgap energy can also be assigned to other causes apart from the presence of oxygen. According to literature, the excess of sulphur [17] as well as the small size of crystallites' size [18] can also be at the origin of higher optical bandgaps. However, we believe that the main reason for higher bangaps is related to oxygen content due to diffusion from ITO/glass substrates. In fact, when In_2S_3 films are sprayed onto glass substrates on similar temperature and [S]/[In] ratio conditions the diffusion of oxygen is very low and consequently the bandgap of In_2S_3 films is also lower [19].

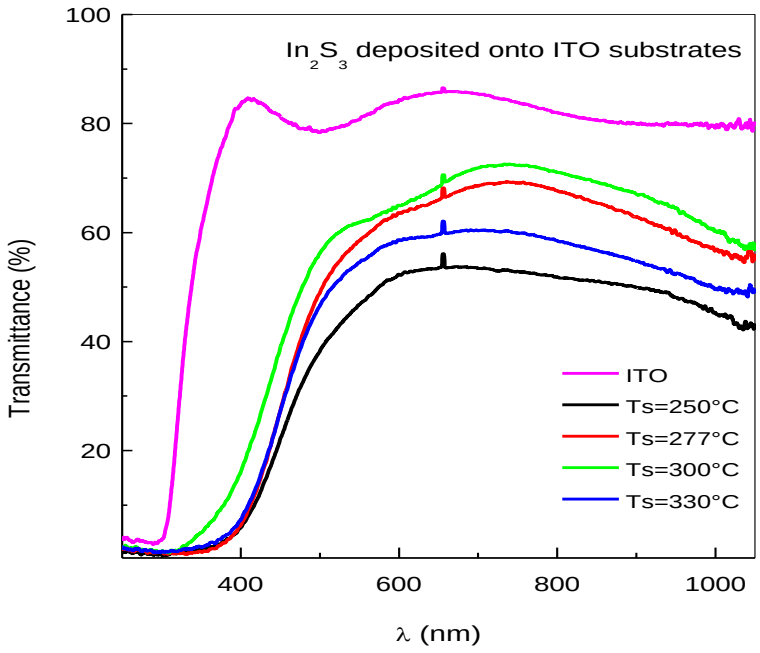

Figure 5.Transmittance spectra of samples at different substrate temperatures.

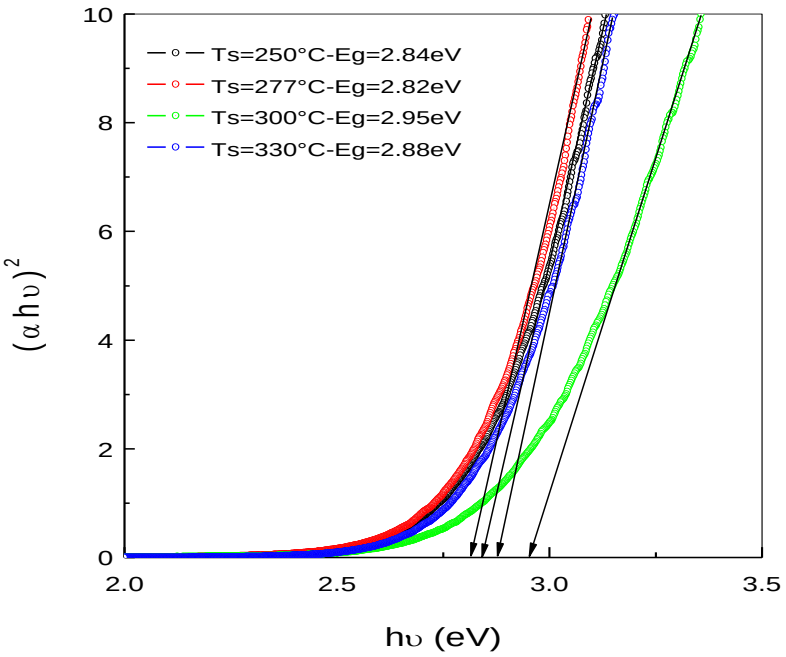

Figure 6. Band gap variation of thin films at different substrate temperatures.

4. Conclusion

Beta Indium sulfide (β-In_2S_3) thin films were deposited onto ITO covered glass substrate by Chemical Spray Pyrolysis method. Films obtained shows good crystallinity with a main peak along (0, 0, 12) direction perpendicular to substrate surface and without presence of other secondary phases. β-In_2S_3 phase and tetragonal structure are also confirmed by Raman spectroscopy analysis with the main mode located at 327 cm^{-1}. All samples are well covered and no crack neither pinhole in the surfaces is observed. The most uniform samples are S4 and S3 as revealed by SEM analysis and confirmed by AFM micrographs. The highest roughness is reached for samples deposited at Ts=250 °C and then the roughness decreases with the temperature. A transmittance higher than 70% and a band gap of 2.95 eV is obtained for samples deposited at Ts=300°C. So, finally the best substrate temperature of the ITO coated glass substrate to deposit β-In_2S_3 on it with optimal characteristics by Chemical Spray Pyrolysis was 300 °C.

Acknowledgments

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Highlights

1. ß-In_2S_3 thin films were synthetized by Spray Pyrolysis.
2. Solutions with S/In=3 were sprayed onto ITO substrates at different temperatures.
3. Optical bandgap values (2.82-2.95 eV) suggest O content about 12-14%.

Ref: PCS-D-14-00213R1 Response to reviewers' comments

Reviewers' comments:

Reviewer #1: Report on the manuscript: "Spray pyrolysis of In2S3 thin films deposited at different temperatures."

Today, CdS is used as n-type buffer layer in photovoltaic cells based on CIGS. The technique used to deposit this buffer layer is the chemical bath deposition. This technique induces a bottleneck in the industrial process used to make solar panels. Therefore it is of interest to look for a new buffer layer. In2S3-xOx is one of them. Therefore the present study deserves interest. However it needs some improvement before publication. The technique used by the authors is the spray pyrolysis in room air. It is well known that, when these experimental conditions are used there is some oxygen contamination of the film. In the present case it has been shown that the presence of oxygen is positive since it allows increasing the band gap of the In2S3. However in the present study, there is not no study nor discussion of the oxygen contamination. It is necessary since the bang gap of In2S3-xOx depends strongly on the value of x, while the band gap of pure In2S3 is only 2 eV, which is too small to use it as buffer layer in solar cells [evolution of the band structure of b-In2S3-x03x buffer layer with its oxygen content, N. Barreau et al. J. Appl. Phys. 93 (2003)16] 5456]. Therefore in order to give an accurate discussion of the optical properties of their films, the authors must discuss their results as a function of oxygen present in their films.

We agree with the referee that the bandgaps of our films can also be due to the presence of oxygen in the lattice and according to data extracted from the reference provided by the referee [N. Barreau et al. J. Appl. Phys. 93 (2003) 5456] we deduce that our In_2S_3 films would contain between 12-14% of oxygen.

However, according to literature, the increase of the bandgap energy can also be due to other causes and not only to the presence of oxygen. The excess of sulphur [W. T. Kim, C. D. Kim. Optical energy gaps of β-In_2S_3 thin films grown by spray pyrolysis Journal Applied Physics, 1986, 60(7): 2631-2634.], as well as the small size of crystallites' size [T. Yoshida, K. Yamaguchi, H. Toyoda, K. Akao, J. Sugiura and H. Minoura, Proc. Of Electrochem. Soc, Electrochemical Society, Pennington, NJ97-20 (1997)37] can also be at the origin of higher optical band gaps. Unfortunately, with our available facilities we are not able to determine the precise composition of films because the presence of ITO substrates impedes the right determination of both In and O

through EDS.

This discussion has been included into the manuscript.

Moreover some others improvements are needed:

-In formulae (1), "beta"is such that beta = (beta(exp)2-beta(o)2)1/2, with (beta(exp) experimental FWHM) and beta(o) FWHM due to the apparatus itself.

In the value of β in equation (1) the contribution of the apparatus has been taken into account, so β=β(experimental)-β(apparatus).

-Bottom p 7, the explanation proposed for the decrease of the roughness when the deposition temperature increase (grain size increases) is not convincing! Usually, larger are the grain higher is the roughness! It is well known that amorphous films are smoother than polycrystalline films.

The reason is that films grown at low temperature (250°C) shows aggregations of small grains to form irregular big ones with grains boundaries.

Reviewer #2:
In this manuscript, author developed a method to deposit β- In2S3 film on ITO thin film with preferential growth direction along (0, 0, 12). The work is new and the data presented is clear. I believe this manuscript should be published in Journal of Physics and Chemistry of Solid. There is couple of questions:

1. In the XRD data shown in this manuscript, the (0, 0, 12) peak is predominating, which is a new phenomenon. Could author give some explanation? I wonder how the intensity of the (0,0,12) peak change with the temperature. Please use the ITO peak intensity as a reference.

We appreciate the comment of the referee. The ratio between the (0 0 12) In_2S_3 peak and (4 0 0) ITO peak ranges from 32 to 80 when the substrate temperature increases from 250 to 330 ºC what means that the amount of crystallites with this preferential direction increases with the temperature of the substrate.

Sprayed In_2S_3 films exhibit a preferential orientation following the (0 0 1) direction. In that direction the allowed diffraction peaks are (0 0 4), (0 0 8) and (0 0 12) and their relative intensities are 4, 3 and 50, respectively (JCPDS#25-390). Consequently is not strange to observe the main diffraction peak takes place between (0 0 12) planes which are separated a

distance of 2.694 A. As a comparison (0 0 4) planes are separated a distance of 8.090 A and therefore longer-range order is required to observe its corresponding diffraction peak.

In Table II, the S3 sample has biggest Crystallite and Grain size, smallest Roughness, and widest band gap, which is somehow inconsistent with the optical transition theory and previous experiment result. Because in the tens to hundreds nanometers grain size range, the smaller grain size means bigger quantum confinement and optical transition energy.

Yes, we agree with the reviewer. If quantum confinement effects exits lower crystallite size should result in higher bandgaps. However, the presence of oxygen produces the same effect. In this case we believe that the increase of bandgap is more probably related to higher oxygen content that quantum confinement. Unfortunately we have not enough data to distinguish both effects.

2. In this paper, 300 ℃ is a turning point for most physical parameter. Comparing with previous work, it is a very low turn temperature point.

According to our results the substrate temperature about 300 °C provides the best In_2S_3 thin films regarding both crystallinity and stoichiometry. After optimization of the deposited parameters in a previous work **[T. Sall et al.; J. Semiconductors 35 (6) 2014],** we decided to use 330 °C as the highest temperature in order to avoid oxygen diffusion from ITO substrates and sulfur loss that alters the right stoichiometry.

3. Does author consider the side effect caused by element diffusion between ITO and In3S2 films?

Yes, this question has been already addressed in the revised manuscript. Through the analysis of the optical bandgap of our sprayed In_2S_3 samples we conclude that our sprayed In_2S_3 films contain between 12-14 % of oxygen. We believe that diffusion between ITO and In_2S_3 films is the responsible of the oxygen content because when the samples are sprayed over glass substrates on similar conditions the bandgap is lower which means less content of oxygen.

Reviewer #3: In the manuscript, In2S3 films are deposited at different temperatures are characterized by XRD, Raman Spectroscopy, SEM, AFM and optical transmission. The paper needs some queries to be answered and corrections to be made. After that it may be accepted for publication

1. Why (S)/(In) ratio was taken as 3. How do authors know that

with this ratio pure In2S3 films will be formed?

The optimization of parameters such as (S)/(In) ratio were made in previous papers [T. Sall et al.; J. Semiconductors 35 (6) 2014] and revealed that the [S]/[In]=3 gives In_2S_3 films with good stoichiometry.

2. Why K=0.9 in Scherrer equation was used?

The value of K in Scherrer's formula depends of the grains shape and the value K=0.9 is used for grains with spherical form.

3. Why the crystallite sizes calculated from Scherrer eq. are different from that of AFM analysis?

Scherrer equation gives the size or crystallites while AFM gives grains' size. However, one grain (as seen by AFM) can contain several crystallites (as detected by XRD).

4. In2S3 crystallites have four phases; their names may be mentioned at page 6 line 7.

The four phases of In_2S_3 are: α-In_2S_3 (cubic), β-In_2S_3 (tetragonal), γ-In_2S_3 (hexagonal) and ε-In_2S_3 (rhombohedral) [H. Okamoto, Phase Diagrams of Indium Alloys and Their Engineering Applications, Indium Corporation of America, Utica, N.Y., and Materials Information Soc., Materials Park, Ohio, 1992]. This information has been included into the manuscript.

5. There are many grammatical mistakes. Few of them are mentioned below for corrections: Addressed

* Elaborated word in the manuscript may be replaced with deposited or grown.
* Introduction -Line 3 to 5 .The sentence should be rewritten.
* Line 8–´has elaborated` may be replaced with´´ thin films have been deposited´´
* Page 4 line 5 ´´No peaks corresponding---``- sentence is not clear.
* Page 4 line 8 dissolution may be replaced with solution.
* Page 4 line 11´´ then`` may be deleted.
* Page 9 line 6 ´´lower quantity`` may be replaced with ´´small numbers``

All grammatical mistakes have been corrected.