Synthesis and Characterisation of In_2S_3 Thin Films Deposited by Spray Pyrolysis Method

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Abstract
Indium sulphide has been extensively investigated as a component for different kind of photovoltaic devices (as buffer layer in thin film solar cells, as absorber layer in nanostructured solar cells, and also counter electrode in dye sensitised solar cells). In this work, the films were deposited on glass substrate using the spray pyrolysis method with substrate temperature varied as 210, 275, 340 and 405. Raman spectroscopy reveals peaks at 266, 306 and 323 cm^{-1} corresponding to ß-In_2S_3 in all the films. The transmittance in the visible range for all films show good transmittance reaching 80% and the band gap energy varies from 2.30 to 2.73 eV. Atomic force microscopy reveals that surface roughness decreased with increase in temperature.
Keywords; Thin film, Spray pyrolysis, Optoelectronics, Transmittance, Band gap, Surface Roughness.

1.0 Introduction
Indium sulphide (In_2S_3) thin films have attracted research interest due to their potential use in the manufacturing of optoelectronic devices. These films have wide band gap of 2.0 eV to 3.7 eV depending on the preparation method [1], and a high transmittance in the visible spectrum [2]. Therefore, they have been used as buffer layer in photovoltaic structures [3]. They also have been used as an absorber layer in nanostructured solar cells [4]. Indium sulphide films are relatively non-toxic and can be prepared by numerous dry and wet methods, such as thermal evaporation (PVD) [5], chemical bath deposition (CBD) [6], atomic layer deposition (ALD) [7], spray ion layer gas reaction (Spray-ILGAR) [8], spin coating [9], successive ionic layer adsorption and reaction (SILAR) [10], and chemical spray pyrolysis (CSP) [1]. However, films prepared by different methods also have different crystalline, electrical and optical properties [11]. The CSP method has been chosen in this work because the method is economical, requires short processing time, can be performed in atmospheric conditions and can prepare thin films using both pneumatic and ultrasonic spray modes [4]. The effect of growth temperature, solution composition and annealing temperature on the crystal structure, chemical composition and optical properties of In_2S_3 thin films prepared by CSP has been studied in previous works [2,3,]. It has been demonstrated by several studies that the main parameters influencing the properties of In_2S_3 films are the molar ratio of In and S sources (In/S) in the precursor solutions and the deposition temperature [2]. It has also been found that the In/S ratio in the spray solution has an effect on the crystal structure, the crystallite size [3,18], and the optical band gap of the In_2S_3 films [1]. For example, John *et al*. [2] have reported that the use of a sulphur-rich solution (In/S=2/8 instead of In/S=2/1) can decrease the optical band gap from2.81 to 2.64 eV. The growth temperature has been found to control the crystallite size and the crystal structure of In_2S_3 [3]. According to XPS, oxygen bonded to In has been found to be present in the films deposited at 340 °C with the In/S ratio of 1/2 in the spray solution [7]. When In_2S_3 films were deposited at temperatures below 300 °C using the In/S ratio of 2/8 [2], oxygen was present only on the film surface. Chlorine residues have been observed throughout the In_2S_3 films when they were grown at low temperatures using $InCl_3$ as In source [2]. To avoid chlorine contamination, the $InCl_3$ precursor has been replaced by $In(CH_3COO)_3$. [3] or $In(NO_3)_3$ [11], but amorphous films were obtained with a growth temperature of approximately 300 °C. Solvents such as water [2] or alcohols [3] and the CSP equipment may also have an effect on the properties of CSP-deposited In_2S_3 films.

Literatures have revealed nanostructured solar cell that included In_2S_3 as a buffer layer made by the CSP method [5]. In order to prepare an effective solar cell, it is important to know the properties of each layer in the solar cell structure. However, few studies have been done on the deposition of In_2S_3 films by pneumatic spray of aqueous $InCl_3$ and thiourea solutions [2], as we are using for the In_2S_3 buffer layer in the solar cell [5].

Therefore, the aim of this work was to study the effect of the substrate temperature and the molar ratio of precursors (In/S) in the spray solution on the phase and elemental composition, as well as on the structural and optical properties of In_2S_3 films deposited by CSP using aqueous spray solutions containing $InCl_3$ and $SC(NH_2)_2$ as precursor materials.

2.0 Methodology

In_2S_3 thin films were deposited on the glass substrates using chemical spray pyrolysis technique. Aqueous solution, containing Indium chloride (0.03 M) and thiourea (0.3 M), was sprayed at the rate of 6 ml/min onto the glass substrate (20 x 20 x 1.1mm^3). The substrate temperatures were varied as follows; 210, 275, 340 and 405^{o}C using compressed air (pressure-1.5 bar) as the carrier gas. At the substrate surface, the spray droplets vaporised leaving dry precipitate which instantly decomposed to form thin layer of In_2S_3. On completing the deposition process, the films were annealed for 30 minutes at the substrate temperature. Here the concentration of thiourea was made larger than the stoichiometric requirement to compensate for the loss of sulphur that may have occurred during pyrolysis.

The film samples were subjected to evaporation temperature of 160 ^{o}C for twenty minutes. Then finally the films were annealed at 100^{o}C for one hour. The film thickness was determined to 60 nm.

The deposited buffer layer films were investigated by studying the composition, structural, optical and electrical properties.

3.0 Results and Discussion

3.1 Raman Spectroscopy

The Raman scattering strongly depends not only on the nature of the investigated system, but also on the crystallographic form and crystallinity of the compound. Raman spectroscopy is a non destructive and a relatively fast experimental technique to determine the phase and the quality of the deposited films. As can be seen in Figure 1, the Raman modes located in the energy region 250-350 cm^{-1} had broad and low-intensity peaks due to the nanocrystalline nature of the sprayed films. Modes observed at 266, 306 and 323 cm^{-1} positions correspond to ß-In_2S_3 in all the films [10, 11].

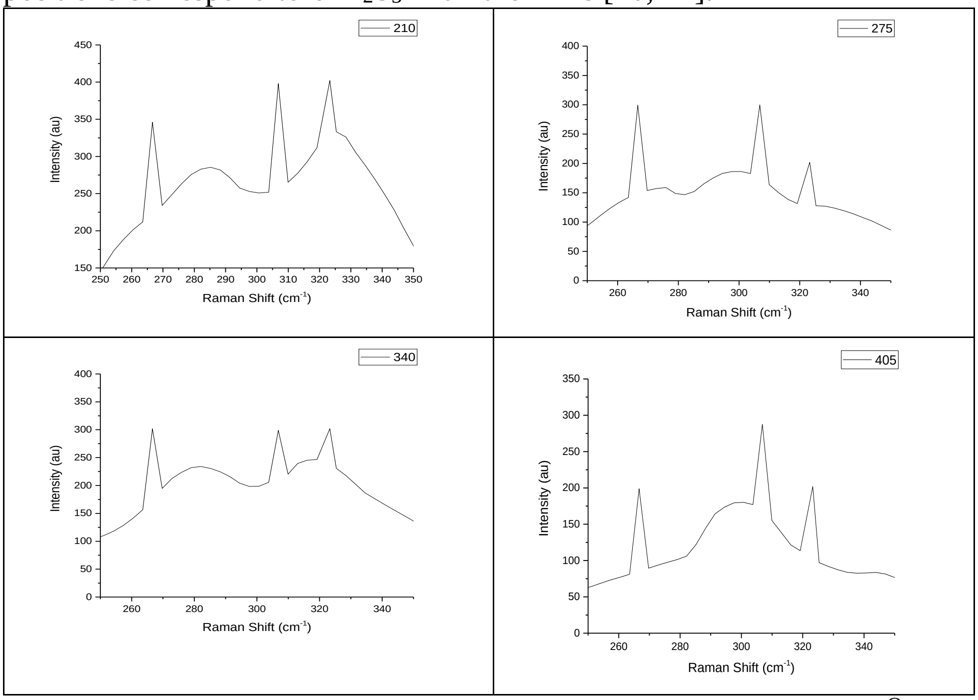


Figure 1: Raman spectra for In_2S_3 for substrate temperature 210-405 ^{O}C

3.2 Optical Transmittance

Optical transmission measurements in the wavelength range 300-800 nm in order to investigate the effect of substrate temperature on the optical performances of the In_2S_3 thin films for solar cell window layer is shown in Figure 2.

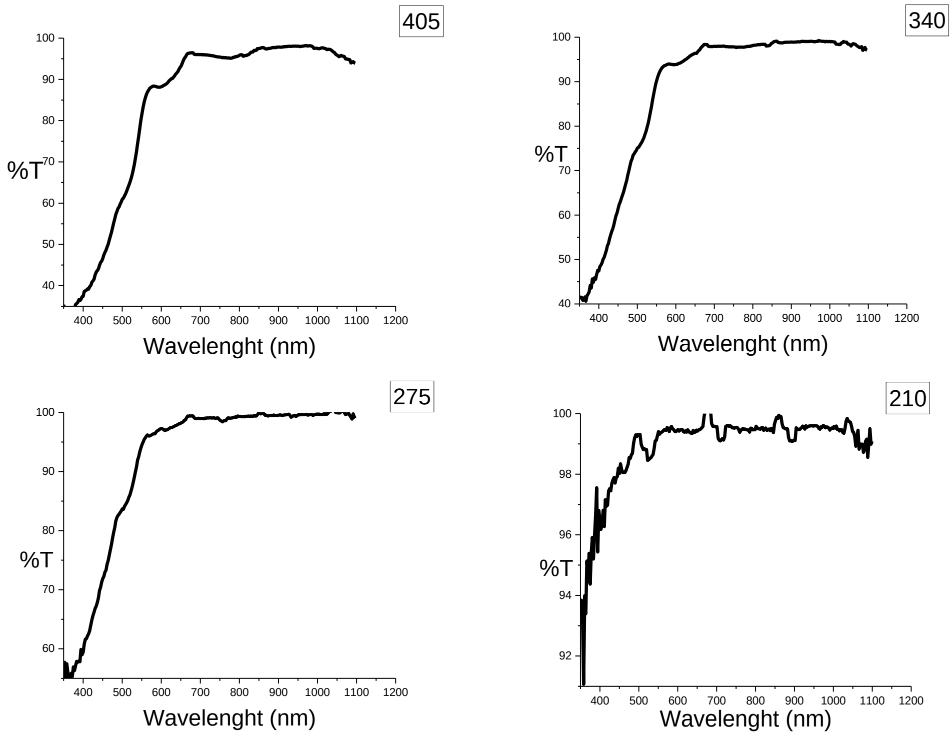
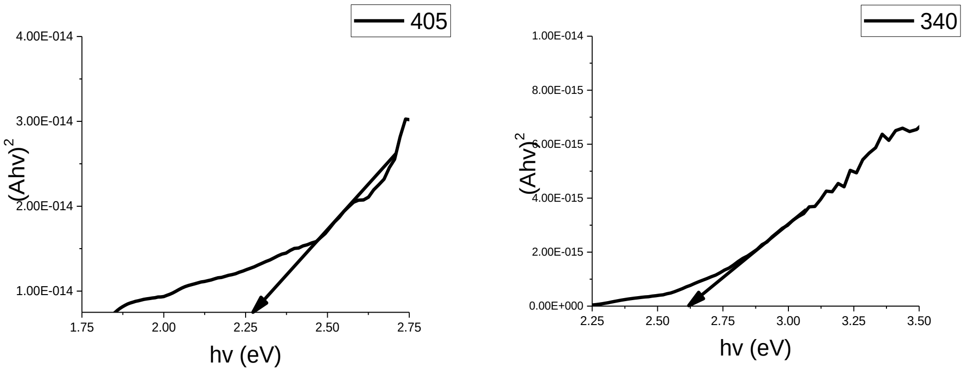


Figure 2: Transmittance spectra for In_2S_3 thin films for substrate temperatures 210-405 ^{O}C

All films show good transmittance reaching 80% in the visible region. In order to determine the optical band gap, (αhv versus hv) graphs were plotted in Figure 3. Optical band gap was determined from this plot for all films by the linear fit in the straight portion of the graph [11]. The value of the gap energy varies from 2.30 to 2.73 eV. But it is remarkable that this variation is not linear with the substrate temperature.



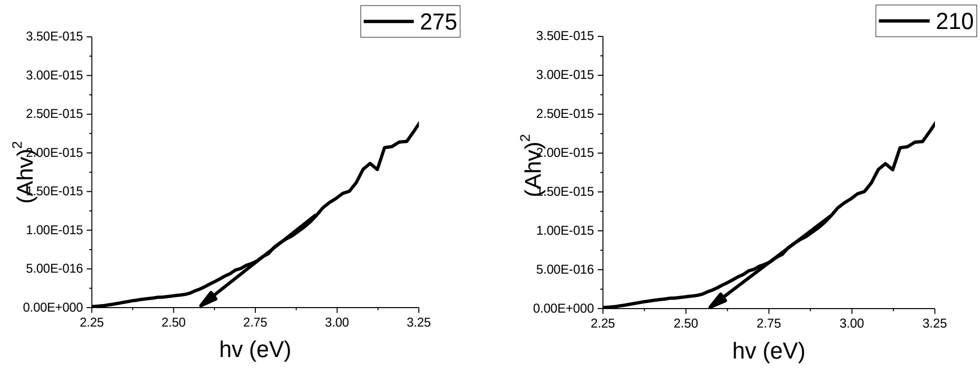
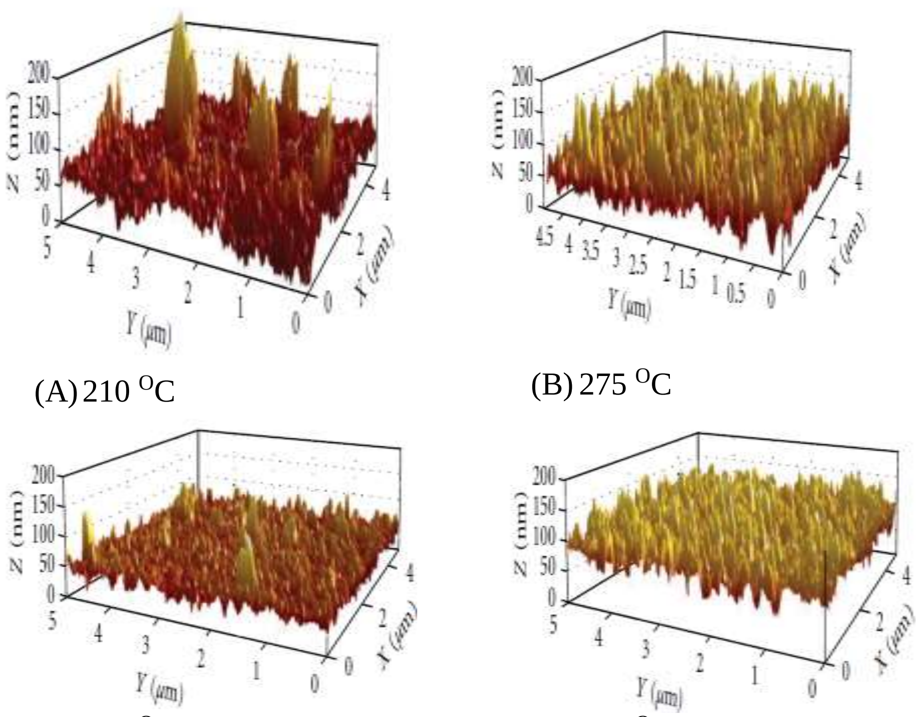


Figure 3: Band gap energy spectrum for In_2S_3 thin films

3.3 Morphology Characterisation

Morphological characterisation of the In_2S_3 films was performed by Atomic force microscope (AFM). The roughness of the deposited films shows a strong dependence with the substrate temperature while detectable changes at different substrate temperature were not detected. This shows that a mass transport if it occurs is limited to short-range diffusion. Films deposited at lower temperatures show a relatively large roughness characterised by asperities which were dispersed in dimensions.

By increasing the substrate deposition temperature, the roughness and the size dispersion of the grains constituting the In_2S_3 films decrease continuously reaching a minimum around 340 ^{O}C. At this temperature, the trend is inverted and the films deposited at higher substrate temperature show again an increase in the roughness as a consequence of the formation of larger crystalline agglomerates.



(A) 210 ^{O}C (B) 275 ^{O}C

(C) 340 ^{O}C (D) 405 ^{O}C

Figure 4; AFM images for In_2S_3 thin films

Conclusion

This study shows that β-In_2S_3 films could be successfully deposited by spray pyrolysis method while varying the substrate temperature range of 210–405 ^{O}C. Results obtained from Raman spectroscopy, UV-vis spectroscopy and Atomic force microscopy (AFM) indicates that all films displayed desirable properties for its use in photovoltaic applications.

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