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Effect of different S/In ratio of In_2S_3 films prepared by chemical spray pyrolysis method

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Abstract

In_2S_3 thin films were prepared using chemical spray pyrolysis technique. An aqueous solution of $InCl_3$ and $CS(NH_2)_2$ was sprayed on to glass substrates and kept at 300 °C, using air as a carrier gas. Stoichiometry of the films was varied by adjusting the molarity of the spray solution. Structure and properties of films with different S/In ratios have been investigated. Raman spectroscopy present bands at 302 and 329 cm^{-1} indicating the presence of the β-phase in all the films. Optical transmittance of films is over 80% in the visible region and its energy band gap decreases from 2.7 to 2.67 ev. PL emission in the wavelength range 300–800 nm was recorded.

Keywords: Thin films, In_2S_3, Spray pyrolysis, S/In ratios, PL spectroscopy

1. Introduction:

Indium sulfide (In_2S_3) is a (III_VI) promising semiconductor material for optoelectronic, photovoltaic and photo electrochemical solar cell applications due to its stability, transparency, wider band gap energy and photo conducting behavior [1,2]. In_2S_3 exhibits different polymorphic structures such as α, β and γ depending on the processing parameters [3].The β-In_2S_3 phase was found to be the stable crystalline phase of indium sulfide at room temperature with tetragonal structure [4]. It is a nontoxic material of n-type semiconductor with an energy band gap of 2.0-2.8 eV [5], and having a high transmittance in the visible part of the spectrum. In general, the physical properties of the grown thin films strongly depend on the deposition technique, deposition parameters and the film thickness [6]. Thin films of this material have been successfully synthesized using numerous techniques like close space evaporation [7], thermal evaporation [8], [9], chemical bath deposition [10,11], physical vapor deposition [12] and spray pyrolysis [13,14].

In the present work, we study the Effect of different S/In ratio on properties of In_2S_3 films prepared by a low cost simple spray pyrolysis method.

2. Experimental details:

Aqueous solution of indium chloride ($InCl_3$) and thiourea ($CS(NH_2)_2$) were used to deposit the binary In-S film. The substrate temperature is maintained at 300℃ and The concentration of indium chloride was fixed at 0.03 mol/l with [S]/[In] ratio from 1.25 to 1.75. The glass substrates (25mm×25mm×1mm) were cleaned with HNO_3, alcohol, acetone, and distilled water for 30 minutes respectively. Compressed air was used as the carrier gas where the gas pressure was fixed at 2.5 bar. The starting solutions were sprayed on glass substrates, with a solution flow-rate of 1 mL/min, and a nozzle to substrate distance of 25 cm. The deposition time was fixed at 15 min. The deposited thin films were characterized structurally, optically and electrically using, Raman spectroscopy, UV-visible spectroscopy and Photoluminescence spectroscopy.

3. Results and discussion

3.1. Raman spectroscopy

The Raman spectra of as-prepared In_2S_3 films with different S/In ratios are shown in Fig.1. The films showed the β_In_2S_3 phase comparable with the ref [15]. The intensity of the two peaks corresponding respectively to 302 and 329 cm^{-1} positions increased first and then decreased. The film with S/In =1.25 ratio do not have a good crystallinity, because the sulfur concentration is low. This crystallinity increases significantly with the S/In ratio from 1.25 to 1.5. But it has a slightly decreasing trend when S/In ratio increases from 1.5 to 1.75. The effects of variation of sulfur concentration on the properties of CSP grown films were investigated by Kim et al [3].

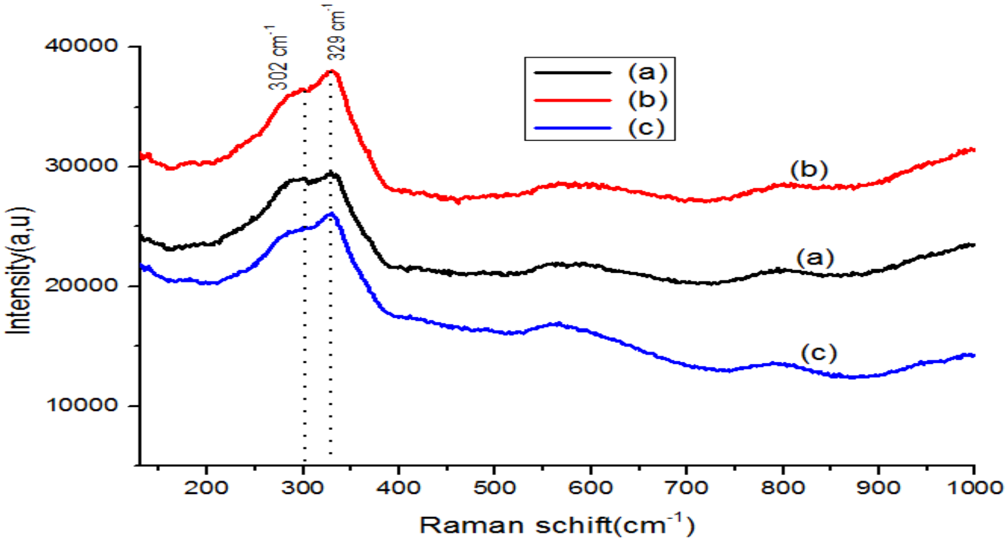

Figure 1: Raman analysis of In_2S_3 thin film prepared at various S/In ratios, (a) =1.25, (b) =1.5 and, (c) =1.75

3.2. Transmission

In Figure 2 the optical transmittance spectra of In_2S_3 films with different S/In ratio are compared. All films have strong visible transmission up to 80% with no significant change according to the S/In ratio. There is then a "visible window" of transmission that is an attractive of this material for photovoltaic applications.

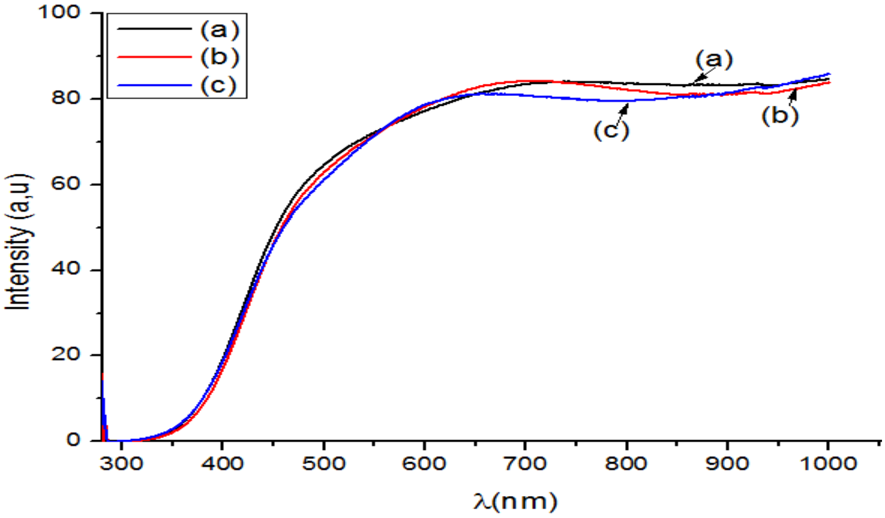

Figure 2: Transmission spectra of In_2S_3 films with various S/In ratios.

Figure 3 shows the $(Ahυ)^2$ plots for the In_2S_3 films with different S/In ratios. The values of energy gap Eg of the samples of In_2S_3 were obtained by extrapolating the linear part of the curves to the zero absorption. The results show that the energy band gap decreases slightly from 2.7 to 2.67 eV when the S/In ratio increases from 1.25 to 1.75. Otto and al observed that the films deposited in the temperature range of 205–320 °C with different In/S molar ratios in the spray solution indicated only minor differences in optical band gap values [16]. Teny and al reported the band gap for In/S ratio 2/3 for indium sulfide thin films prepared using chloride based precursor solutions [17]. The variation of Eg is due to the change of defect densities [18]. Obviously, the degree of crystallinity plays a very important role in the variation of the optical band gap of In_2S_3 films. The appropriate S/In ratio leads to the larger optical band gap.

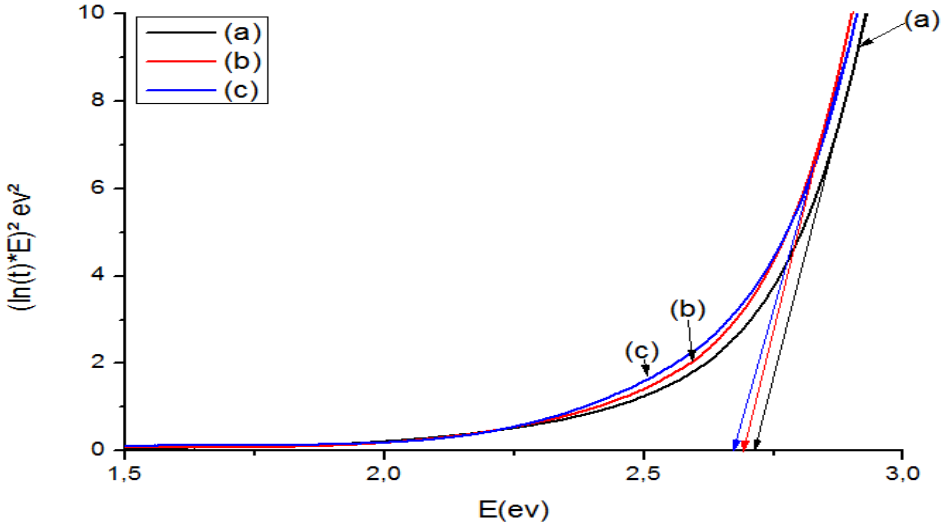

Figure 3: Plot of $(Ah\upsilon)^2$ versus hυ of sample (a), sample (b) and sample (c)

Table 1: the values of energy gap as a function of S/In ratio

Samples	S/In ratios (mol/l)	Gap Energy (eV)
(a)	1.25	2.7
(b)	1.5	2.69
(c)	1.75	2.67

3.2. PL spectroscopy

PL spectroscopy is an attempt that has been made to characterize the defect levels in the thin films by varying the stoichiometry. PL is a non-contact, non-destructive probe, which is highly selective and sensitive to the defect chemistry of the subject [19]. The PL spectrum of In_2S_3 consists of two emission bands : a green emission (Band A) and the red emission (Band B), The green emission is due to the transition between donors created by vacancies of sulfur (V_s) and acceptors due to vacancies of indium (V_{In}). The red emission arises as a transition from indium interstitial (In_i) donors to oxygen in vacancy of sulfur (OV_s) acceptors [20]. In_2S_3 is a material where two thirds of the lattice sites are vacant by birth itself [21]. When indium is diffused into In_2S_3, it occupies the vacant cationic sites focusing mainly on the green emission in the PL spectrum of figure 4.

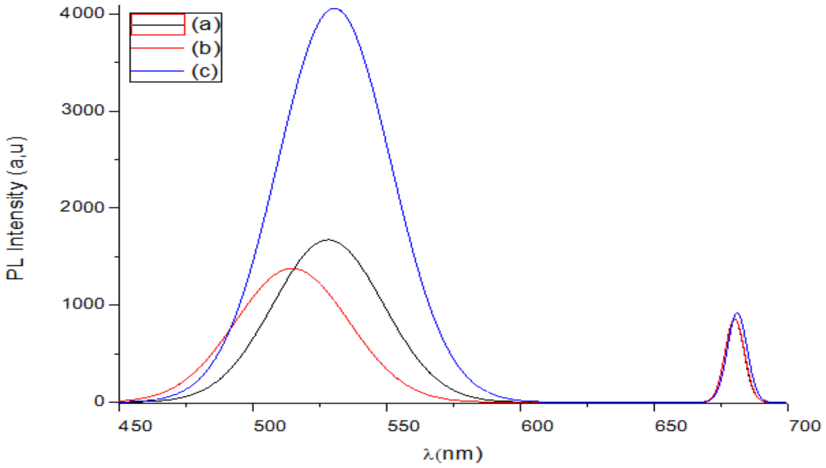

Figure 4: Photoluminescence spectra of In_2S_3 thin Films with different S/In ratios (a) 1.25, (b) 1.5, and (c) 1.75mol/l.

In sample (c) the highest emission peaks were at 529 nm (green emission), and 680 nm (red emission). In the case of sample (b), the higher energy emission was shifted to 514 nm. Again, for the sample (c), the PL emission intensity was stronger (along with a broadening of the rising edge of the 529 nm peak toward the higher energy side) which proved the presence of higher defect concentration. The intensity of the red emission was low (compared to green emission) [22].

Conclusion

The effect of S/In ratio on the formation of In_2S_3 thin films was investigated. S/In ratios have significant effects on the structure and the properties of films. Raman spectroscopy presents bands at 302 and 329 cm^{-1} indicating the presence of the β-phase in all the films. Optical transmittance of films is over 80% in the visible region and its energy band gap decreases slightly from 2.7 to 2.67 eV when the S/In ratio increases from 1.25 to 1.75 mol/l. The room temperature PL spectra of the In_2S_3 thin film from different S/In ratios, with an excitation wavelength of 325nm showed that there were two emissions around (514-529 nm) and 680 nm.

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