

Chapter 4**PROPERTIES OF INDIUM SULFIDE THIN FILMS PREPARED USING NITRATE BASED PRECURSOR SOLUTION****4.1 Introduction**

In recent years, there has been a significant increase in the research works on III-VI materials because they find great use in the electronic industry in optoelectronic or photovoltaic applications [1, 2]. Indium sulfide is a III-VI compound, which can be prepared using different chemical methods like organometallic chemical vapour deposition [3], chemical bath deposition, atomic layer epitaxy and chemical spray pyrolysis. Indium sulfate $\text{In}_2(\text{SO}_4)_3$, 80% hydrazine hydrate, thioacetamide, triethanolamine and ammonium chloride were used for the deposition of indium sulfide using chemical bath [4]. In atomic layer epitaxy In_2S_3 films were deposited using InCl_3 and H_2S as precursors [5]. In all the reports using spray pyrolysis, dealing with deposition of indium sulfide, indium chloride and thiourea were used as the precursor solutions and their structural, optical, photoelectrical and acoustic properties had been studied [6, 7, 8, 9].

In the previous chapter we described preparation of indium sulfide films using indium chloride as one of the precursor solutions. The properties of the films depend upon the precursor solution used for deposition. This chapter describes the effect of indium nitrate as one of the precursor solutions, on the properties of indium sulfide thin films. One of the advantages of indium nitrate is that it can be pyrolysed at relatively low temperature. Moreover there is no chance of inclusion of any impurities like chlorine in the film unlike the films prepared using indium chloride.

Our motivation behind the replacement of the precursor was to remove chlorine, which caused high enhancement of electrical resistivity of In_2S_3 films. At the same time we were interested in seeing whether we could get high photosensitivity and good crystallinity in these films prepared using nitrate precursor solution. Then it

will be a great achievement as one can control both electrical resistivity and photosensitivity as these are very important factors for solar cell fabrication. If this was found to be possible, we also aimed at optimizing the preparation condition so as to get the required values of these parameters for solar cell fabrication.

4.2 Experimental Details

β - In_2S_3 thin films were prepared using CSP technique with indium nitrate ($\text{In}(\text{NO}_3)_3$) and thiourea ($\text{CS}(\text{NH}_2)_2$) as precursor solutions. Indium nitrate was prepared by dissolving high purity (99.99%) indium in concentrated HNO_3 . Micro glass slides, having dimensions of $37 \times 12 \times 1.4 \text{ mm}^3$ were used as substrates. Indium to sulfur ratio was varied by varying molar concentrations of the precursor solutions. For this, the molarity of indium nitrate was kept at 0.025 M and that of thiourea was varied to have In/S ratios ranging from 2/1 to 2/8. The total volume of the solution sprayed was 400 ml and the rate of spray was 20 ml/min in all cases keeping the substrate at 300°C . Air was used as the carrier gas. These films were yellowish in colour. Samples having In/S ratio from 2/1 to 2/8 were named S1, S2, S3, S4, S5, S6 and S8 respectively. Samples were also prepared by varying indium concentration keeping sulfur concentration at 8 to get In/S ratio 1.2/8 and 2.5/8. These samples were named S12 and S25.

4.3 Results and Discussion

4.3.1 Effect of Variation of Sulfur Concentration

4.3.1.1 Structural Analysis

Structural analysis was done using X-Ray Diffraction (XRD) (Philips X'Pert-Pro. X-Ray Diffractometer having $\text{CuK}\alpha$; $\lambda=1.5405 \text{ \AA}$ radiation). In_2S_3 thin films prepared from indium nitrate showed an interesting property in the XRD analysis. Only the sample prepared using solution having In/S ratio 2/3 (S3) exhibited good crystalline property. This sample had five peaks corresponding to (103), (109), (220), (309) and (400) orientations [Fig.4.1].

On decreasing the sulfur concentration, the sample became amorphous (S1). But on increasing the sulfur concentration the sample showed a very small peak along the (103) plane. Further increase resulted in change of preferential orientation to (109) plane for the samples S6 and S8. Other than this, two peaks corresponding to (103) and (400) also appeared on increasing the sulfur concentration. The grain size of the film was calculated using the Debye-Scherrer formula $D = 0.9\lambda/\beta\cos\theta$, where D is the diameter of the crystallites forming the film, λ is the wavelength of CuK_α line, β is FWHM in radians and θ is the Bragg angle. It was found to be 28 nm for the sample S3 that reduced to 20.8 nm for S8.

Lattice constants a and c for the samples were calculated from the results of x-ray diffraction patterns using the (103) and (109) planes. For the sample S3, the values were found to be $a = b = 7.58 \text{ \AA}$, $c = 32.08 \text{ \AA}$. As the In/S ratio decreased, the lattice constants increased slightly (for the ratio 2/8 $a = b = 7.6 \text{ \AA}$, $c = 32.4 \text{ \AA}$) [7]. These values are comparable with those for $\beta\text{-In}_2\text{S}_3$ shown in JCPDS card (25-390).

Samples prepared using indium chloride also showed $\beta\text{-In}_2\text{S}_3$ phase with preferential orientation along the (220) plane. On increasing the sulfur concentration from 2/3 to 2/5, the intensity of the peak corresponding to this plane increased, but a further increase of sulfur concentration (2/8) resulted in the decrease of the peak intensity [10, 11]. There was no change in preferential orientation.

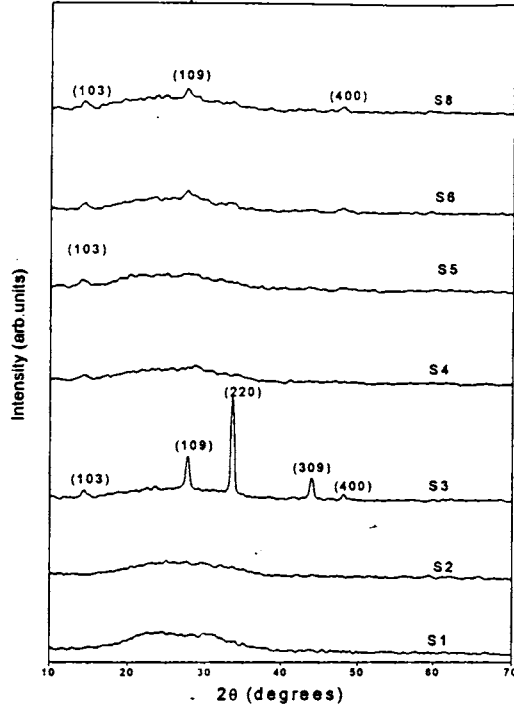


Fig. 4.1 XRD pattern of In_2S_3 samples, S1 to S8

4.3.1.2 Surface Morphology

Surface morphology was examined using Scanning Electron Microscopy (SEM). It revealed a dense structure and no cracks or voids were observed on the sample S3 [Fig.4.2a]. Fig.4.2 (b) show that granularity was lost on decreasing (S1) or on increasing (S4) [Fig. 4.3a] the sulfur concentration. The sample regained its granular structure [Fig.4.3b] when the ratio became 2/8 (S8). However the grain size was small even in this case. This was clearly observed in structural analysis (XRD) also [Fig.4.1].



(a)



(b)

Fig. 4.2 SEM micrographs of (a) S3 and (b) S1



(a)

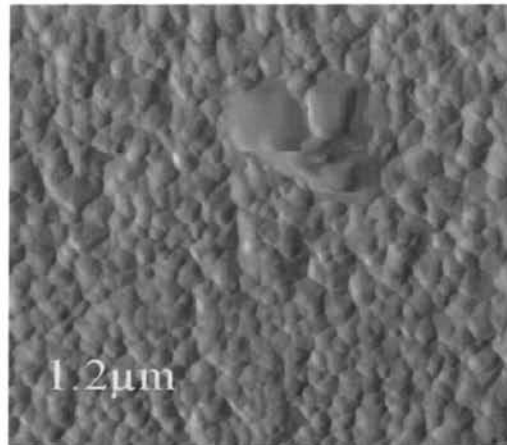


(b)

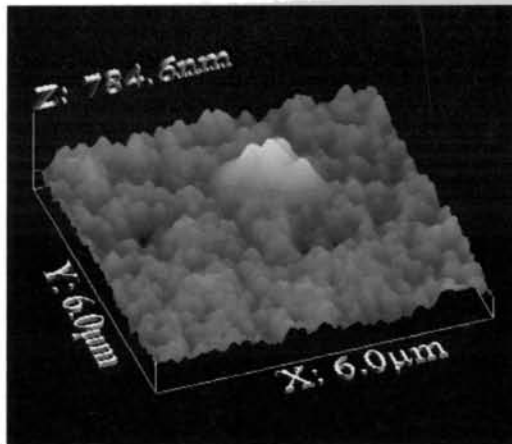
Fig. 4.3 Surface morphology of samples (a) S4 and (b) S8

4.3.1.3 AFM

Fig. 4.4 (a) and (b) depicts the AFM image (2D and 3D) of 6 micrometer square area of the sample S3. The sample was dense and grains were found to be uniform in size.



(a)



(b)

Fig. 4.4 AFM image of sample S3 (a) 2D and (b) 3D

4.3.1.4 EDAX Measurements

Concentration of sulfur was found to be low for samples S1 and S2 (~38%), but it exceeded 60% on increasing the sulfur concentration in solution. Atomic

concentrations of indium and sulfur were found to be almost equal for S3. This sample was found to be better in electrical conductivity ($232 \Omega\text{-cm}$) compared to S2, S4 and S5. Hence excess of indium indicated by EDAX analysis, might be occupying interstitial position. It had been reported that in relatively low resistive In_2S_3 , donor concentrations are high (In interstitials) [12]. Variation of atomic concentration with In/S ratios is given in Fig.4.5. Thus it was clear that the In/S ratio in the initial precursor solution determined the composition of the samples.

Concentration of sulfur in the sample never reached 60% when indium chloride was used to prepare the samples. Nevertheless an increase in the concentration of indium resulted in a corresponding increase in the concentration of chlorine in the sample. Stoichiometric films were obtained only when indium chloride was replaced by indium nitrate.

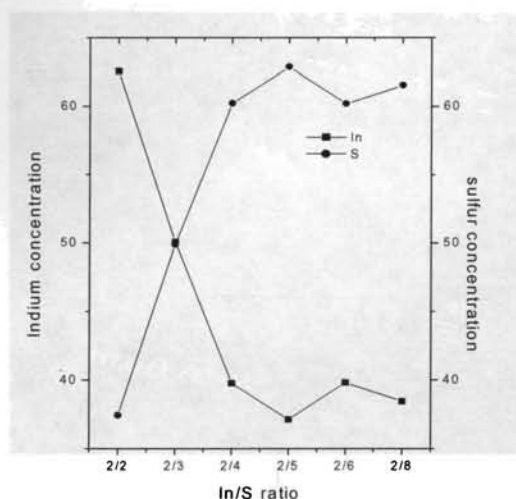


Fig.4.5 Variation of atomic concentration with In/S ratio

4.3.1.5 XPS Analysis

Depth profile of the sample S3 [Fig.4.6] showed that indium and sulfur were uniformly distributed throughout the depth of the sample. Binding energies of indium and sulfur clearly indicated the formation of indium sulfide. The values are compared in Table 4.1.

Table 4.1 Binding energies of indium and sulfur in indium sulfide

Element	Binding Energy (eV)
In3d _{5/2}	444.7
In3d _{3/2}	452.7
S2p	162

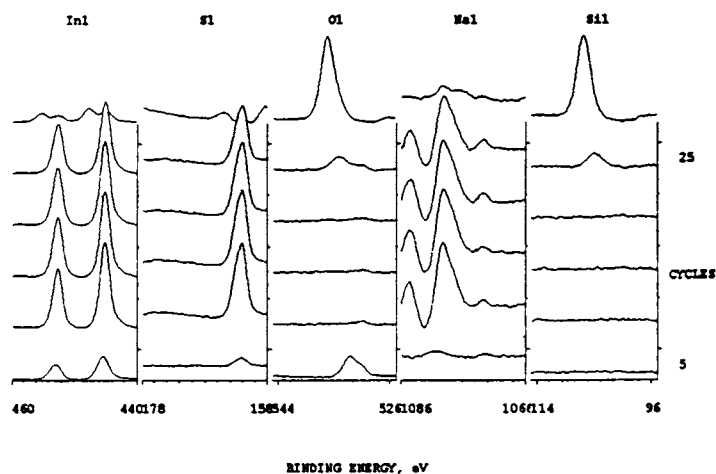
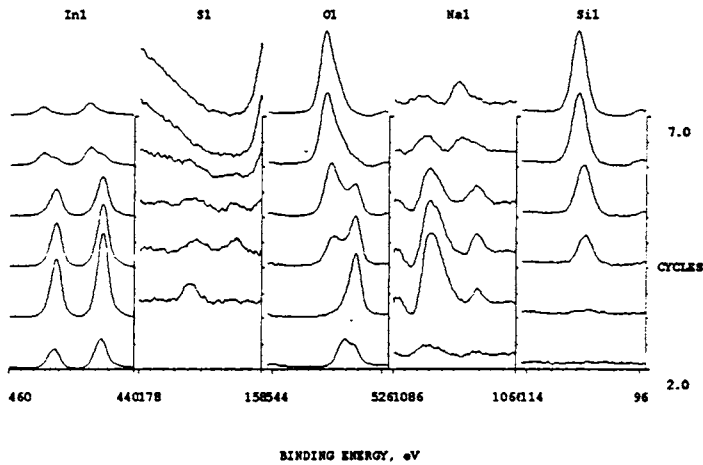


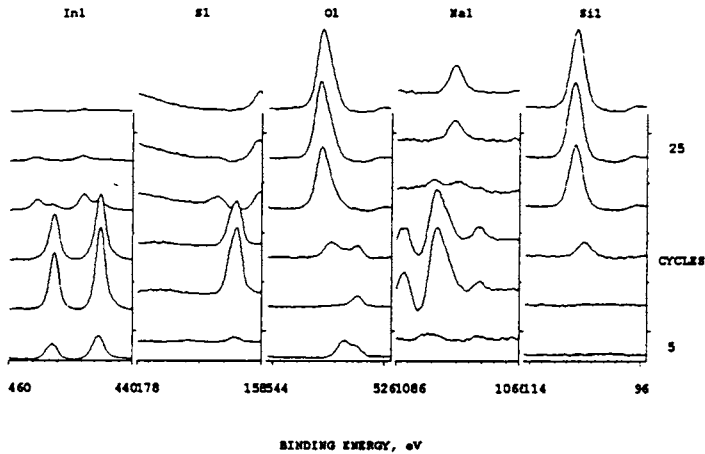
Fig. 4.6 XPS profile montage of sample S3

Oxygen was present only as a surface contaminant having binding energy 532 eV that corresponds to oxygen in the form of sulfate [13]. But sodium was present throughout the depth of the sample, which might be diffusing from the glass substrate, as the substrate was kept at high temperature (300° C). Moreover there was no sodium in any of the chemicals used for the preparation of the sample.

On decreasing the sulfur concentration (S1) [Fig.4.7] there was a shift in the binding energy of sulfur (170 eV), which corresponds, to that of sulfate. There was also oxygen present in the bulk of this sample with binding energy 530 eV. This corresponds to O1s in In_2O_3 . The sample S1 is suspected to be In_2O_3 eventhough we could not identify any In_2O_3 phase from XRD.



(a)



(b)

Fig. 4.7 XPS depth profile of samples (a) S1 and (b) S4

On increasing sulfur concentration (S4) the binding energies of indium and sulfur indicated the formation of indium sulfide, but the presence of In_2O_3 also was observed from the shift in the binding energy of oxygen in the bulk of the sample [Fig.4.7b]. BE of oxygen on the surface of the sample corresponds to that of surface contamination in the form of sulfate (532 eV). The sulfur atoms in sample S4 situated near film substrate interface or diffused into the substrate exhibited BE of 164 eV. This corresponds to that of elemental sulfur. These samples were amorphous, and there are earlier reports on amorphous nature of samples having excess sulfur [14].

On further increasing the sulfur concentration (S8), oxygen was found to be present only on the surface of the sample [Fig.4.8]. There was no In_2O_3 phase in samples S6 and S8. Presence of sodium in the bulk was observed for all the samples.

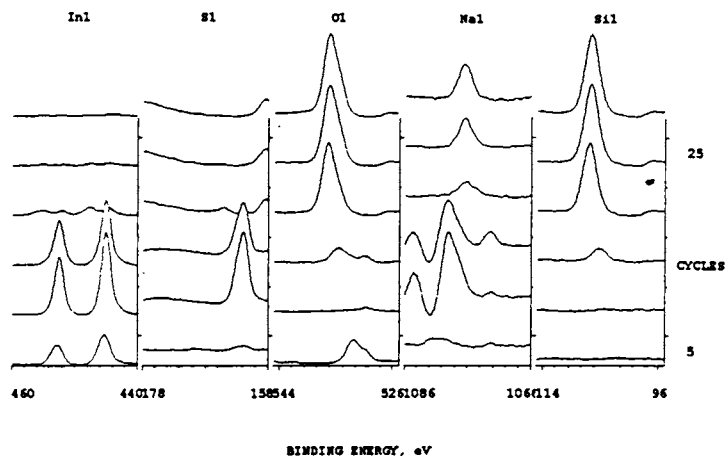


Fig. 4.8 Profile montage of sample S8

4.3.1.6 Optical Studies

From the plot of $(\alpha h\nu)^2$ vs $h\nu$ [Fig.4.9], a direct band gap of 2.66 eV was obtained for the sample S3. On decreasing sulfur concentration (S1) the band gap increased to 2.95 eV [Fig.4.10]. Increase in the band gap for smaller sulfur concentration could be ascribed both to the presence of secondary phases and to a more disordered structure. Incorporation of oxygen might be another reason for the widening of the band gap [14]. Band gap decreased to 2.73 eV on increasing the sulfur concentration (S8). Thus the band gap was found to vary with crystalline structure [Fig.4.1] of the sample.

Transmittance measurements were performed in the spectral range 400 nm to 1200 nm [Fig.4.11]. Sample S1 showed better transparency (might be due to the formation of In_2O_3 as observed from XPS). The band gap of this sample was also close to that of In_2O_3 [15].

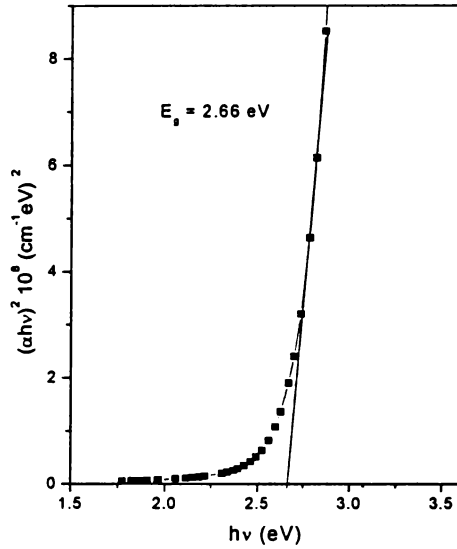


Fig. 4.9 $(\alpha h\nu)^2$ vs $h\nu$ plot of sample S3

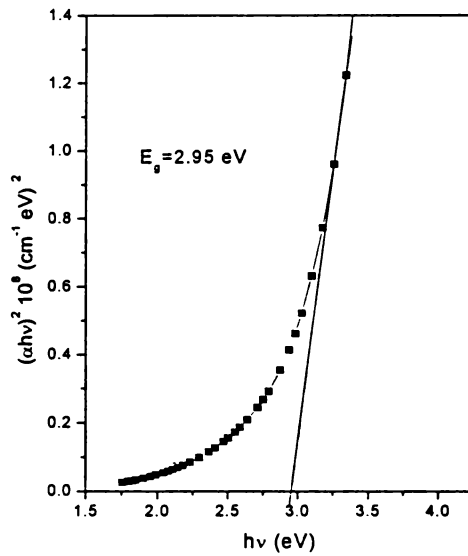


Fig.4.10 Band gap of sample S1

Refractive index was calculated using the envelope method from transmission spectra for samples S3 and S8. The value was found to vary in the range 1.57 to 1.77 with wavelength [Fig. 4.12]. Increase in the value of refractive index with the concentration of sulfur in the film might be due to diminishing crystallinity [16]. For sample S3, variation of extinction coefficient with wavelength is shown in Fig. 4.13.

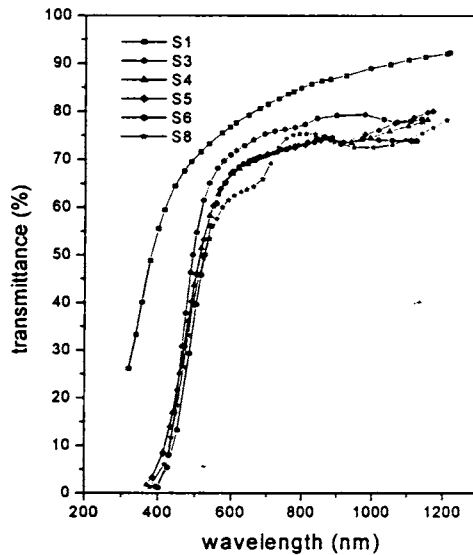


Fig. 4.11 Variation of transmittance with In/S ratio

When indium chloride was used as the precursor solution, band gap was found to be almost the same (2.67 eV) for the sample S3. It increased to 2.81 eV on decreasing the sulfur concentration (S1) and reduced to 2.64 eV on increasing the same in that case [10]. Here also widening of the band gap on reducing the sulfur concentration might be due to presence of oxygen in the sample. But In_2O_3 phase was not detected either from XRD or from XPS.

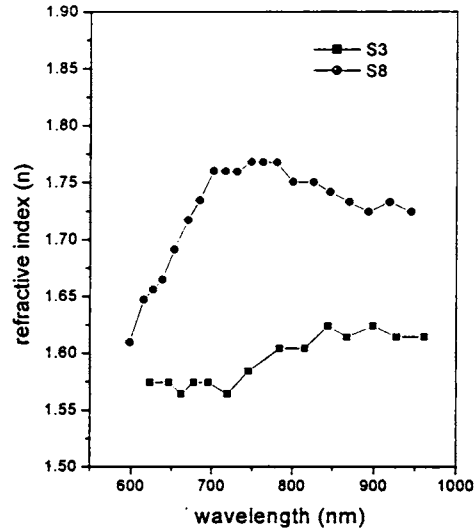


Fig. 4.12 Variation in refractive index with wavelength for samples S3 and S8

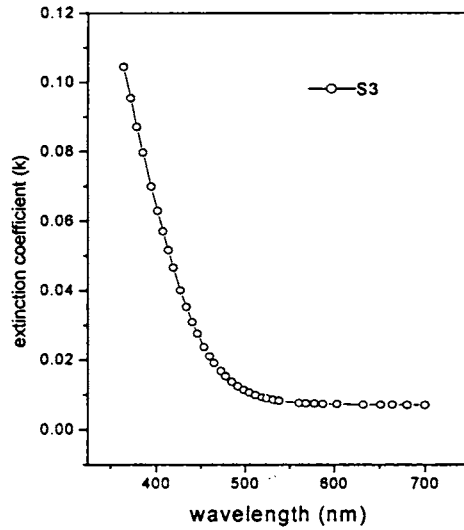


Fig. 4.13 Extinction coefficient with wavelength for sample S3

4.3.1.7 Resistivity and Photosensitivity

Resistivity of the sample S1 was found to be $9.6 \Omega\text{-cm}$, which was very low when compared with that of samples having higher sulfur concentration, indicating the presence of mainly In_2O_3 . But it was observed that small quantity of In_2O_3 phase in In_2S_3 films decreased the conductivity very much. This was true for samples S2 and S4 ($\rho = 1.8 \times 10^4 \Omega\text{-cm}$) in which In_2O_3 phase was found to exist along with In_2S_3 from XPS profile montage [17]. On increasing the sulfur concentration (S8) the sample showed maximum conductivity ($\rho = 59.4 \Omega\text{-cm}$). This was actually against the expectation as we feel that increase in sulfur concentration might decrease electrical conductivity as observed in the case of chloride samples. This might be because of the slightly better stoichiometry and the change of preferential orientation to the (109) plane [as per JCPDS data (25-390) this is the maximum intensity peak for $\beta\text{-In}_2\text{S}_3$]. Fig. 4.14 depicts the variation of resistivity with sulfur concentration.

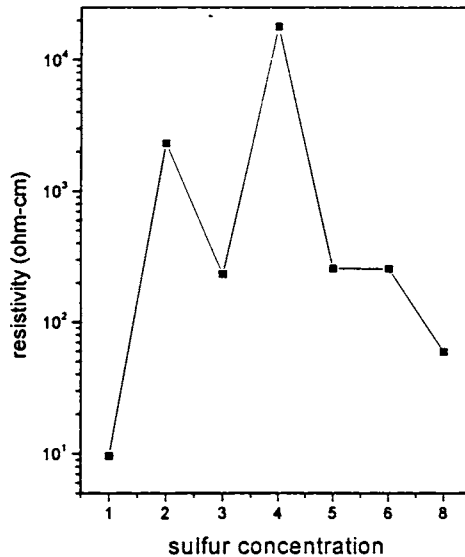


Fig. 4.14 Variation of resistivity with sulfur concentration

Fig.4.15 shows the variation of the photosensitivity with In/S ratio. Sample S4 showed maximum photosensitivity. High resistivity of samples S2 and S4 indicated a reduction in the number of majority carriers. So, probably the minority carriers, surviving to contribute to photoconductivity for these two samples might be more, indicating high photosensitivity.

However photosensitivity was low for samples prepared using nitrate based precursor solution when compared to that prepared using chloride based precursor solution. We suspect that the chlorine present in the sample, prepared using indium chloride, might be the reason for the decrease in dark conductivity (and hence increase in photosensitivity) of those samples [10].

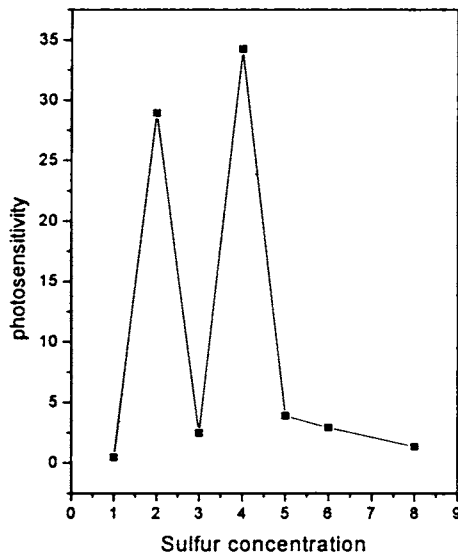


Fig. 4.15 Variation in photosensitivity with In/S ratio

4.3.2 Effect of Variation of Indium Concentration

The concentration of indium in the solution was varied by keeping the sulfur concentration at 8. For this the molarity of thiourea was kept at 0.1 M and that of indium nitrate was varied.

4.3.2.1 Structural Analysis

Four peaks were observed in the XRD spectra corresponding to the planes (103), (109), (220) and (400) with preferential orientation along the (109) plane for sample S25 [Fig. 4.16c].

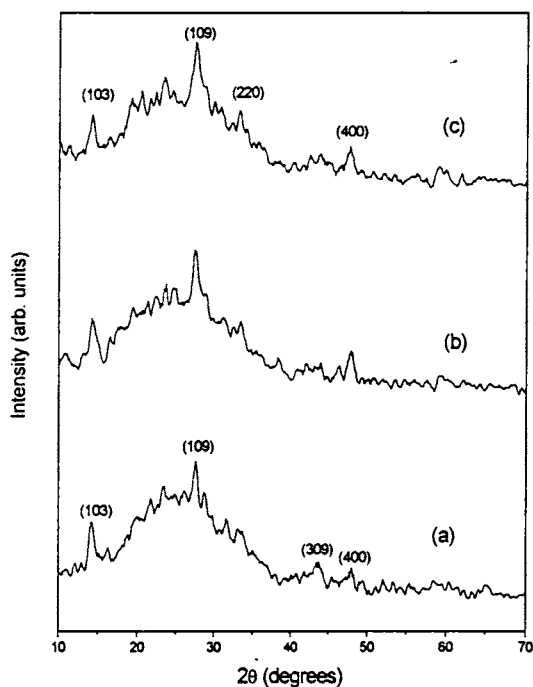


Fig.4.16 XRD spectra of (a) S12 (b) S8 and (c) S25 samples

The intensity of preferentially oriented (109) plane increased on increasing the indium concentration (S12 to S25). The small peak corresponding to the (309) plane disappeared in the case of sample S25, while that corresponding to (400) plane gained intensity. In the case of samples prepared using indium chloride as one of the precursor solutions, all these samples showed preferential orientation along (220) plane.

4.3.2.2 Optical Studies

Band gap varied from 2.77 eV for sample S12 to 2.67 eV for sample S25. The wavelength dependence of absorbance on these samples is shown in Fig. 4.17. The decrease in band gap might be due to the improvement in crystalline structure of the samples on increasing indium concentration. Transmittance spectrum of the samples in the wavelength range 350-1400 nm is shown in Fig. 4.18.

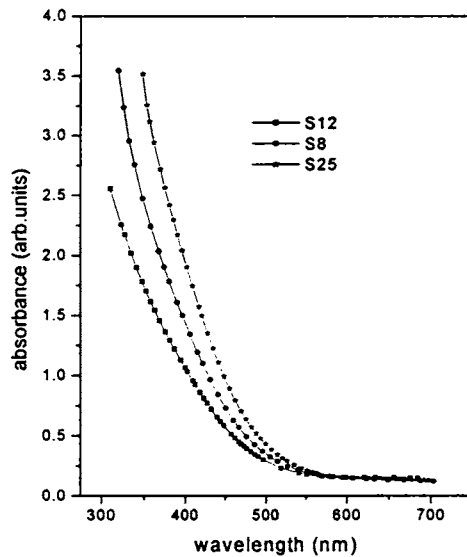


Fig. 4.17 Wavelength dependence of absorbance for samples S12, S8 and S25

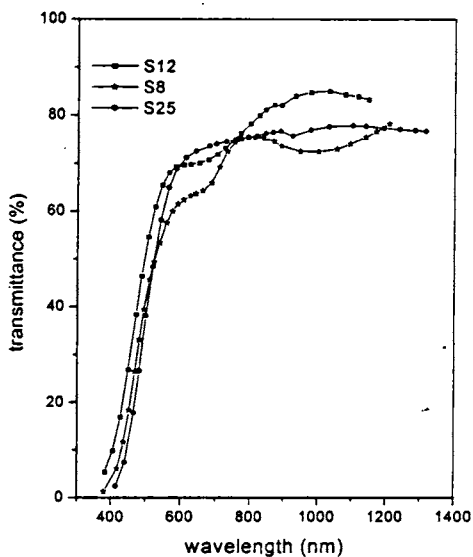


Fig. 4.18 Transmittance spectra of samples S12, S8 and S25

4.3.2.3 Photosensitivity Measurements

Photosensitivity of the samples decreased on increasing the indium concentration. Among the three samples S12, S8 and S25, the sample S12 showed maximum sensitivity. But the value was found to be much less than those samples prepared using chloride based precursor solution. Variation of photosensitivity is given in Fig. 4.19.

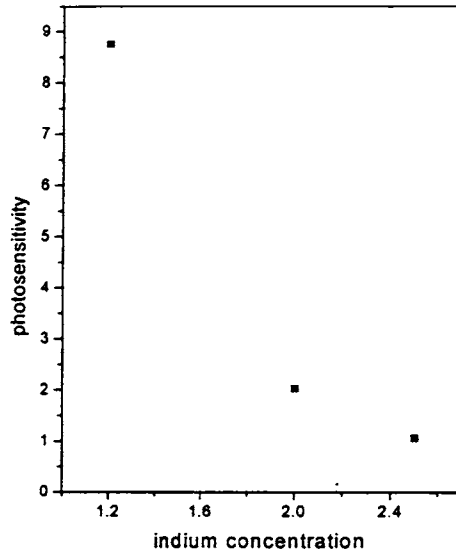


Fig. 4.19 Variation in photosensitivity: S12, S8 and S25

4.4 Conclusion

Indium nitrate, instead of indium chloride, could be used as the precursor solution for preparing β - In_2S_3 thin films using CSP technique. Interestingly only the sample having In/S ratio 2/3 in the solution showed good crystallinity with band gap 2.66 eV, while chloride samples showed better crystallinity on increasing the sulfur concentration. We could get better control over stoichiometry of the films by varying In/S ratio taken in the solution, using nitrate-based precursor. Concentration of sulfur exceeded 60% on increasing sulfur concentration in the solution. Moreover presence of chlorine in the sample could be avoided using indium nitrate as precursor. When indium chloride was used, increasing concentration of indium resulted in a corresponding increase in chlorine also. Because of this the In/S ratio in the film was found not to follow the variation of In/S ratio in the solution. Another important point worth mentioning here is the variation of electrical conductivity with increase of

sulfur concentration in the sample. Unlike in the case of samples prepared from chloride precursor, here conductivity increased considerably for samples having In/S ratio 2/6 and 2/8. This might be due to the structural changes for these samples as revealed by XRD or due to carriers released from defects. Thus indium nitrate proved to be a good precursor for preparing In_2S_3 films. However, there was considerable decrease in photosensitivity for In_2S_3 prepared using indium nitrate. Maximum photosensitivity was obtained for the sample having In/S ratio 2/4 (34.23) among nitrate based samples, while it was for 1.2/8 (949.97) in chloride-based samples. But this sample had very high sheet resistance ($>2000 \text{ M}\Omega/\square$) when compared with nitrate sample having In/S ratio 2/4 ($99 \text{ M}\Omega/\square$). Nitrate based samples were found to be more conducting compared to chloride samples. Presence of chlorine might be the reason for the high resistivity of chloride-based samples. But because of the low photosensitivity of nitrate samples, it may not be as good as chloride samples for fabricating solar cells.

References

- [1] A. R. Barron *Adv. Mater. Opt. Electro.* **5** (1995) 245
- [2] M. Amlouk, M. A. Ben Said, N. Kamoun, S. Belgacem, N. Brunet and D. Barjon
Jpn. J. Appl. Phys. **38** (1999) 26
- [3] R. Nomura, K. Konishi and H. Matsuda *Thin Solid Films* **198** (1990) 339
- [4] C. D. Lokhande, A. Ennaoui, P. S. Patil, M. Giersig, K. Diesner, M. Muller and H. Tributsch *Thin Solid Films* **340** (1999) 18
- [5] T. Asikainen, M. Ritala and M. Leskelä *Appl. Surf. Sci.* **82/83** (1994) 122
- [6] N. Kamoun, S. Belgacem, M. Amlouk, R. Bennaceur, J. Bonnet, F. Touhari, M. Nouaoura and L. Lassabatere *J. Appl. Phys.* **89(5)** (2001) 2766
- [7] W. T. Kim and C. D. Kim *J. Appl. Phys.* **60(7)** (1986) 2631
- [8] L. Bhira, H. Essaidi, S. Belgacem, G. Couturier, J. Salardenne, N. Barreaux and J. C. Bernède *Phys. Stat. Sol. (a)* **181** (2000) 427
- [9] M. Amlouk, M. A. Ben Said, N. Kamoun, S. Belgacem, N. Brunet and D. Barjon
Jpn. J. Appl. Phys. **38** (1999) 26.
- [10] Teny Theresa John, S. Bini, Y. Kashiwaba, T. Abe, Y. Yasuhiro, C. Sudha Kartha and K. P. Vijayakumar *Semicond. Sci. Technol.* **18** (2003) 491
- [11] Teny Theresa John, S. Bini, C. Sudha Kartha, K. P. Vijayakumar, T. Abe and Y. Kashiwaba *Proc. International Symposium on Recent Advances in Inorganic Materials (RAIM-2002)* Mumbai, India (2002) 106
- [12] R. S. Becker, T. Zheng, J. Elton and M. Saeki *Sol. Energy. Mater.* **13** (1986) 97
- [13] Teny Theresa John, K. P. Vijayakumar, C. Sudha Kartha, T. Abe and Y. Kashiwaba *Proc. World Conference on Photovoltaic Energy Conversion (WCPEC-3)* Osaka, Japan (2003) 1P-C3-24
- [14] N. Barreau, J. C. Bernède, H. El Maliki, S. Marsillac, X. Castel and J. Pinel *Solid State Commun.* **122** (2002) 445
- [15] K. Hara, K. Sayama and H. Arakawa *Sol. Energy Mater. Sol. Cells* **62** (2000) 441

- [16] N. Kamoun, R. Bennaceur, M. Amlouk, S. Belgacem, N. Mikli, J. M. Frigerio and M. L. Theye *Phys. Stat. Sol. (a)* **169** (1998) 97
- [17] Teny Theresa John, C. Sudha Kartha, K. P. Vijayakumar, T. Abe and Y. Kashiwaba *Appl. Surf. Sci.* (under revision)