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Phase Transformation from In_2S_3 to $CuInS_2$ using Ultrasonic Spray Pyrolysis

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Abstract:

In this work systematic conversion of In_2S_3 into $CuInS_2$ was studied using ultrasonic spray pyrolysis (USP) system. The ternary compound group of I-III-VI is important for solar cell because In_2S_3 acts as a buffer layer, while $CuInS_2$ acts as an absorber layer in solar cell. $CuInS_2$ thin films were synthesized by adding certain amounts of copper salt in the solution containing 0.06 M indium chloride and 0.36 M thiourea. In the absence of copper, the above solution forms In_2S_3. The copper salt added solution was ultrasonically sprayed on a glass substrate kept at 350 ^oC. For synthesis of n-type and p-type $CuInS_2$, copper chloride with concentrations of 0.04 M and 0.06 M was added, respectively, in the solution containing indium chloride and thiourea. These films were characterized by X-ray diffraction (XRD), Raman spectroscopy, UV-Vis spectrophotometer, Hall effect measurement, etc.

Keywords: In_2S_3, $CuInS_2$, Ultrasonic spray pyrolysis, Phase transformation.

Introduction:

Solar energy has become a crucial aspect due to depletion in fossil fuels. Hence, from last two decades researchers have focused on harvesting solar energy using photovoltaic cells[1]. Initially, solar cells were made of CIS i.e. $CuIn(S,Se)_2$ as an absorber layer and CdS as a window layer[2]. However, CdS is toxic and hence now-a-days eco-friendly solar cells are preferred [3]. From amongst the various metal chalcogenides, In_2S_3 is stable at room temperature, is environmental friendly and thus seems to be a better candidate for buffer layer. In_2S_3 is an n-type semiconductor having a wide band gap in the range of 2 to 3.5 eV and also used for applications like photo sensor [4, 5].

Copper indium disulphide ($CuInS_2$) is a material which is very useful in solar cell as an absorber layer due to its absorption co-efficient and direct band gap of 1.5 eV, which covers a considerable part of solar spectrum reaching earth. $CuInS_2$ is obtained in both n-type and p-type forms [6, 7].

Several deposition methods like chemical vapor deposition, radio-frequency (RF) sputtering, atomic layer epitaxy, chemical bath deposition (CBD), spray pyrolysis, etc. have been adopted to synthesize $CuInS_2$ as well as In_2S_3 thin films previously [8-10]. Among these, spray pyrolysis is a low cost, easy and large area deposition method [11, 12]. Ultrasonic spray pyrolysis (USP) is an advanced version of spray pyrolysis. High frequency is applied to nozzle, which converts precursor solution into tiny droplets of few microns size[13]. Due to uniform spray over entire substrate, very thin and compact films can be achieved [14, 15]. Hence, in this work we selected USP method to deposit thin films.

In this work, first we deposited In_2S_3 thin films. On addition of various concentrations of copper in In_2S_3 precursor solutions, $CuInS_2$ thin films were also systematically deposited for, indium rich and for equal concentrations of copper and indium.

Experimental:

Indium chloride ($InCl_3$) and thiourea ($CS(NH_2)_2$) both purchased from Sigma Aldrich (99.99 %) were used as initial precursors for synthesis of In_2S_3 thin films. To prepare In_2S_3 thin films, indium to sulphur ratio was kept as 1: 6 by keeping molarities of 0.06 and 0.36 M, respectively[16]. To prepare a homogeneous solution, the solution was stirred for 15 minutes using magnetic stirrer at 500 revolutions per minute (rpm). USP system comprised of *Sono-Tek* nozzle and 120 kHz frequency generator with syringe pump for precise control of solution sprayed on glass substrate. Cleaning of glass substrate is important to avoid defects or impurity in thin films. Therefore, glass substrates (dimensions: 75 x 25 x 1 mm) were cleaned by washing with detergent solution and then keeping in piranha solution for few hours. After acidic cleaning the glass substrates were ultrasonically cleaned in an ultrasonic bath using distilled water. Nozzle to substrate distance was kept 25 cm. Compressor was used to supply air and a valve was used to maintain a constant air flow rate of 6 L/min. Solution flow rate was controlled by syringe pump and was fixed as 60 mL/hr. In_2S_3 thin films were deposited on glass substrates pre-heated up to 350 ^oC. To prepare $CuInS_2$ thin films the above process and parameters were kept constant and copper chloride was added to the solution of indium chloride and thiourea. Two different concentrations viz. 0.04 and 0.06 M of copper chloride were used to obtain $CuInS_2$ thin films.

Characterization Techniques

As deposited thin films showed uniform coverage over entire surface with high adhesion. In_2S_3 films were yellow in color whereas, the addition of copper changed the color of films to little brownish. As deposited films were characterized by various characterization techniques like X-ray diffraction (XRD), Raman spectroscopy, UV-Vis spectrophotometer, Hall effect measurement, etc. X-ray diffraction pattern for structural confirmation were recorded using a Bruker D8 advance diffractometer using Cu kα (λ = 1.5406 Å). RAMAN (Renishaw) spectrophotometer was used to study Raman spectroscopy with laser of 532 nm. The optical absorbance of thin films was measured with a JASCO-6 UV-Vis spectrophotometer, the nature of as deposited thin films was determined by Hall effect measurement.

X-ray Diffraction (XRD)

Figure 1(a) shows XRD pattern of as deposited In_2S_3 thin film. The films exhibited well crystalline nature. Diffraction peaks of the films were found at 14.3, 27.6, 28.8, 33.3,43.2, 47.7 and 59.7 2-theta degrees corresponding to the reflections from (103), (213), (206), (220), (309), (400) and (012) crystal planes. These peaks showed good agreement with JCPDS card no. 511160 of the tetragonal β-In_2S_3 phase formation.

Figure 1(b) and figure 1(c) showed XRD patterns, when copper to indium ratio was 0.04 and 0.06 M i.e. indium rich was named as C1 thin film and equal ratio of copper and indium named as C2 respectively. Figure 1(b) shows just formation of $CuInS_2$ phase from In_2S_3 and figure 1(c) shows pure phase formation of tetragonal $CuInS_2$ which was in accordance of JCPDS

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(27-0159). As deposited films of $CuInS_2$ showed prominent peak orientation at 27.9° (112) while Other peaks were observed at 32.4 (200), 46.4 (220) and 55.1° (312) . All thin films obtained were well crystalline in nature.

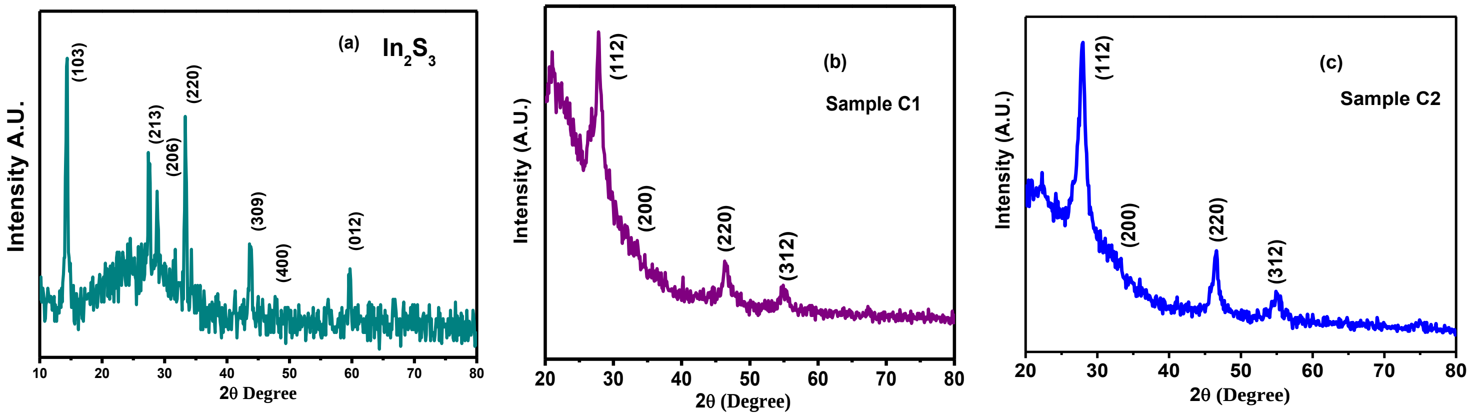

Fig. 1 (a-c) shows XRD of In_2S_3, n-type and p-type $CuInS_2$ respectively

Raman Spectroscopy

Raman spectrophotometer is a device which works on the vibrational modes of a crystal phase and it also gives the confirmation of phase. Figure 2 (a-b) shows Raman spectroscopy for as deposited thin films of In_2S_3 and typical Raman spectroscopy of $CuInS_2$, respectively. Figure 3 shows Raman spectroscopy for In_2S_3 thin film. At 245 and 305 cm^{-1} the prominent modes which confirm the β-In_2S_3 phase are attributed to the vibrations of octahedral and tetrahedral nature, respectively. For $CuInS_2$ thin films, vibrational mode A^1 was observed at 296 cm^{-1} as a prominent peak and at 345 cm^{-1} E^1_{LO} was observed as a shoulder peak. No other phase like Cu_xS were observed.

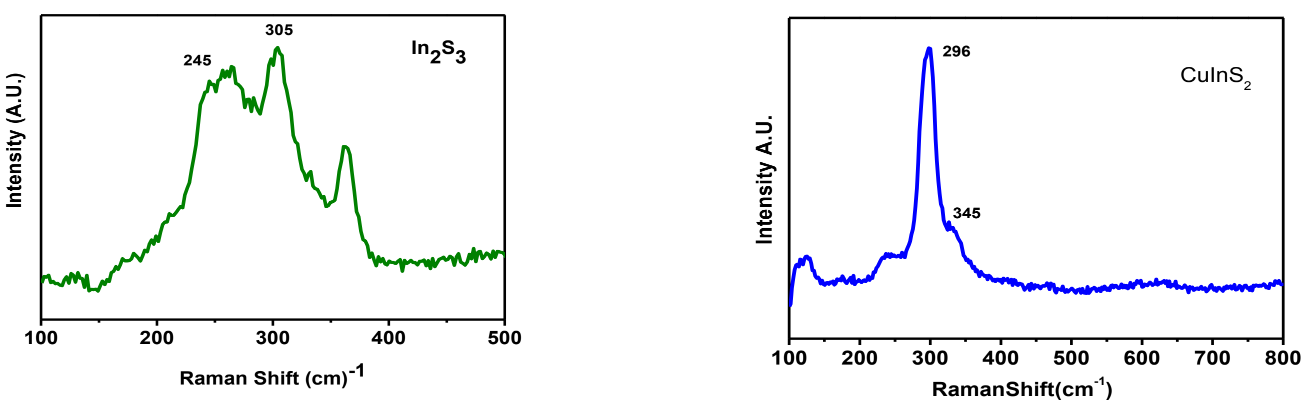

Figure 2 . Raman spectroscopy of In_2S_3 and typical $CuInS_2$ thin films

UV – VIS spectroscopy

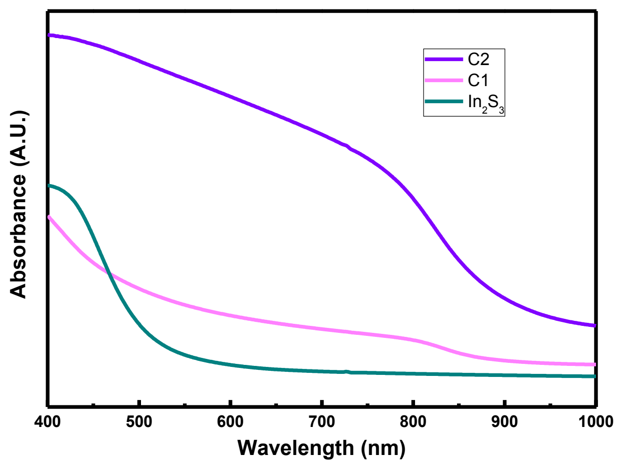

Figure 3 shows UV-VIS spectrum for In_2S_3 and $CuInS_2$ thin films

Figure 3 shows depicts absorbance spectra of C1, C2 and In_2S_3 samples. Absorption edge of the In_2S_3 is blue shifted than C2 and C1 sample which is in accordance with their band gap vaules[17-19]. Moreover absorbance of the C2 film was found to be increased that C1 which may be due to increase in the absorbing species like thickness[20].

Hall effect

The semiconducting properties of the $CuInS_2$ films were analyzed by using Hall measurement[21] which was shown in Table 1. Hall coefficient of C1 sample showed n-type whereas C2 sample showed p-type behavior. Moreover, charge carrier mobility of the C2 is more than C1 sample which is useful for solar cell application.

Table 1: Hall measurement parameters obtained for $CuInS_2$ film Hall parameter Value

Parameter	***C1***	***C2***
Bulk concentration (/ cm^3)	-3.635E+12	1.023E+14
Charge carrier mobility (cm^2/Vs)	2.974E+1	3.682E+1
Hall coefficient (cm^3 / C)	-1.717E+6	6.099E+4
Conductivity (1/ W cm)	1.732E-5	6.037E-4
Sheet concentration (cm^2)	-1.818E+8	5.117E+9

Conclusion

In_2S_3 and $CuInS_2$ thin films were successfully deposited using ultrasonic spray pyrolysis method. Well crystalline, thin, compact and uniform converge over entire substrate gives rise to tetragonal phase of In_2S_3 and $CuInS_2$ thin films. Indium rich or copper deficient film gives rise to n-type $CuInS_2$, whereas, equal ratio of copper and indium gives formation of p-type $CuInS_2$ thin films. These p-type $CuInS_2$ thin films can be used as absorber layer in solar cells.

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