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Effect of Doping of Rare Earth Element Sm on $CuInS_2$ Films Synthesized by CBD Method and Characterization

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Abstract- This research paper is based on the synthesis of copper indium disulphide ($CuInS_2$) thin films by using inexpensive and simple chemical bath deposition (CBD) technique. Microscopic glass slides were used as substrates on which films were deposited. The effects of rare earth element Samarium(Sm) on the structural, morphological and optical properties were reported here by changing its volume. The band gap is ranging between 2.6eV to 3.2 eV. All film shows high absorption coefficient of $10^5 cm^{-1}$ which makes it suitable for photovoltaic cells. Maximum transmittance obtain is 70% in visible range and ~57-68% in near IR region for the film with 6ml volume of Sm. Chalcopyrite phase is observed from XRD in all films with different volume of rare earth. Film thickness changes with amount of Sm and ranges between 421.9nm to720 nm. EDX analysis confirms the doping of rare earth element. The resistivity of all films is in the range of $10^{-3}\Omega$-cm.

Index Terms - *CBD*1; *XRD*2; *SEM3*.

1. INTRODUCTION

In the present scenario when we are facing the crisis of fossil fuels, the whole human kind is looking into alternative sources of energy and what could be better than photovoltaic devices or solar cells. Thin films due to their interesting properties like less material requirement and better device performance have been used extensively in photovoltaic devices. Among different chalcopyrite material $CuInS_2$ emerges as the most promising material which can be used in photovoltaic devices because of its direct band gap energy of 1.53eV and high absorption coefficient of 10^5 cm^{-1}[1]. $CuInS_2$ thin films have been synthesized by using different methods such as chemical vapor deposition [2], electro deposition [3], spray pyrolysis [4], co evaporation [5], SILAR [6] and chemical bath deposition [7,8]. The chemical bath deposition (CBD) method is a simple and low cost method. Multi component films can also be prepared by this method. Thus we have selected this method in the present study for the synthesis of $CuInS_2$ thin films and to the best of our knowledge we are using for the first time $CuInS_2$ as a host material and studied the effect of rare earth element(Sm) by varying its volume.

2. RESEARCH METHOD

For thin film deposition substrate is required. Glass slides were taken as substrate. Before use glass slides were cleaned two to three times with detergent and thoroughly washed with deionised water. The glass slides were dried at room temperature. The cleaned glass slides were dipped vertically in a liquid bath containing $CuCl_2.2H_2O$ (0.5M), $InCl_3$ (0.5M) and thiourea as copper, indium and sulphur precursors. Then we have added TEA and ammonia (25%) in the liquid bath which can act as a complexing agent and maintain the pH of the liquid bath respectively. 0.01M $CdCl_2$ and 0.01M samarium nitrate were also added to the same solution. The solution was stirred for 10min to prepare homogeneous solution. The pH of the solution bath was 10. The bath temperature was maintained at 80^0C. The deposition time was of 1hr. After 60min of time films were removed from the solution bath and washed using deionised water and kept for dry. The deposition occurs because of precipitation followed by condensation. The film thickness were measured by using gravimetric method and found to be 720, 482.2 and 421.9 nm for Sm 4ml, 6ml and 8ml doped films respectively. PANalytical X-ray diffractometer with CuKα (1.540^0A) was used for XRD.Optical absorption spectrum was recorded by Elico SL 210 double beam UV-VIS spectrophotometer. SEM and EDX analysis were also recorded for the films.

3. RESULT AND DISCUSSION

3.1 Morphological study

SEM micrographs of $CuInS_2$:$CdCl_2$, Sm thin films at 30KX magnifications is shown in Fig.1 (a), (b) and (c). It is evident from the Fig that surface of the films are uniform, homogeneous, consisting of tiny particles. Particles are uniformly distributed on the surface of the film. Agglomerations are seen on the surface of the films with 4ml and 8ml Sm doping but comparatively few particles are secluded in the film with 6ml doping. The particle sizes are in nm range matching with XRD data. No voids are observed.

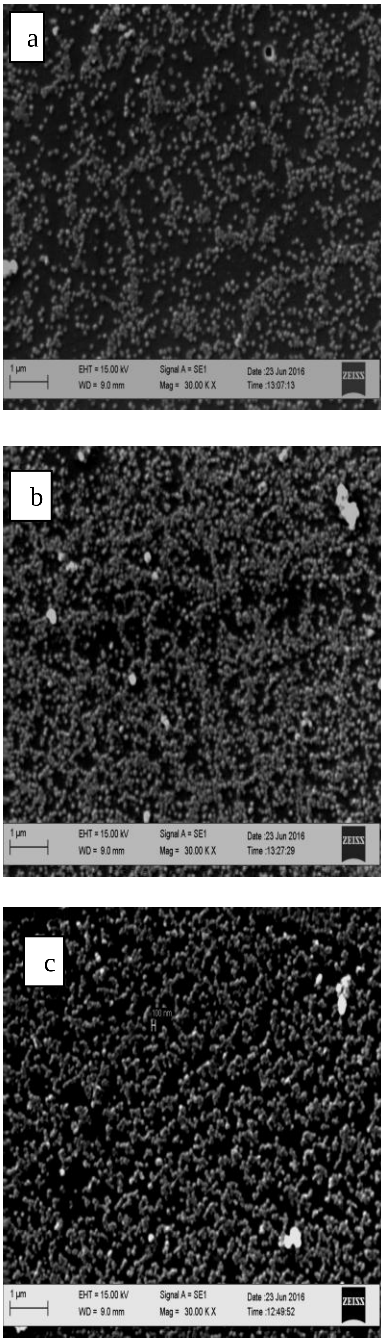


Fig. 1.SEM micrograph of $CuInS_2$:$CdCl_2$, Sm films; (a)4ml,(b)6ml,(c)8ml

3.2 Crystallographic study

In order to study the crystallography of the obtained films X-ray diffractograms were recorded by using PANalytical X-ray diffractometer with CuKα (1.540^0A).Fig 2(a),(b)and(c) are depicting the X-ray diffractograms of $CuInS_2$ thin films with Sm (4ml,6ml ,8ml) doping respectively. The film with Sm(4ml) consist of peaks of plane (004),(121) and (136)of chalcopyrite phase marked in green (JCPDS-98-002-6271) with additional peaks of (111) and (022) marked in blue of $Cu_{1.8}S_1$(JCPDS-98-004-2710) and (220) plane marked in navy blue of $Cu_{11}In_9$(JCPDS-98-018-0115). In the film with Sm(6ml)chalcopyrite phase is confirmed with peaks of plane (112),(004),(015),(134) and (136). Also additional peaks corresponding to plane (110) marked in yellow of Cu_1S_1 (JCPDS-98-006-7581) appears with high intensity.But film of $CuInS_2$ with 8ml of Sm is having peaks of (112), (004) and (116)/(312) and (136) of chalcopyrite phase and peaks of $CuIn_3$ (JCPDS-98-062-7992) marked in red. Also one peak corresponding to plane (021) of Cu_1S_1 (JCPDS-98-062-8808) and (022) of $Cu_{11}In_9$ (JCPDS-98-018-0115) appears. Thus all the films are showing secondary phase with Sm doping.. No peaks corresponding to Sm is obtained.

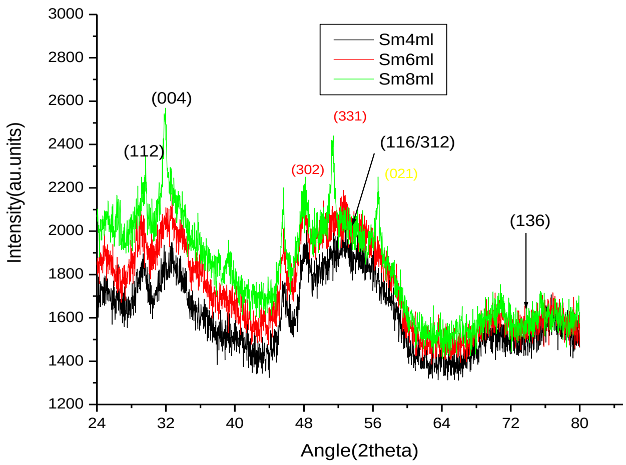


Fig.2. XRD of $CuInS_2$:$CdCl_2$, Sm thin films

By using Scherer's formula [9]

$$D = \frac{0.9\,\lambda}{\beta\cos\theta} \qquad \text{----------------------} \quad (1)$$

Particle sizes were calculated for (004) plane. The obtained value of particle size, strain and dislocation density calculated by using formulae is tabulated in Table 1. It is clear from the X-ray diffractograms that as the volume of Sm increases the intensity of main characteristic peak (112), (004) also increases. The value of dislocation density is minimum for the film *$CuInS_2$:$CdCl_2$,Sm(4ml)*and thus the particle size is large. Thus we can infer that this sample is more crystalline as compare to other samples [10]. There is a slight variation in the observed and standard d values which shows that the synthesized film is nonstoichiometric [11].

Table1. The value of β, D, ε and δ corresponding to (004) plane of $CuInS_2$:$CdCl_2$,Sm films

Sample	FWHM (β)	Particle Size(D)	Strain (ε)	Dislocation density(δ)
$CuInS_2$:$CdCl_2$,Sm(4ml)	0.3744	22.39nm	0.0056	1.99×10^{15}
$CuInS_2$:$CdCl_2$,Sm(6ml)	0.3744	22.10nm	0.0056	2.04×10^{15}
$CuInS_2$:$CdCl_2$,Sm(8ml)	0.4992	16.86nm	0.0076	3.51×10^{15}

The thickness of the film increases with the increase in particle size [12].

3.3 Energy dispersive X-ray study (EDX)

In order to get qualitative idea about composition of elements EDX is an important technique. In Fig.3 EDX of $CuInS_2$:$CdCl_2$,Sm(6ml)film is shown.

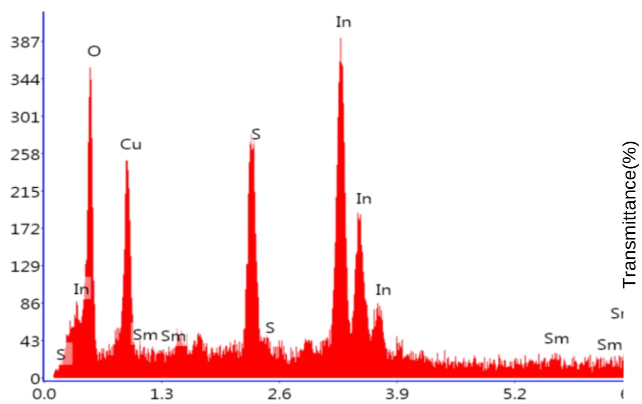


Fig.3.EDX of Sm doped $CuInS_2$ film

It shows peaks of Cu, I and S along with Sm. Thus doping of rare earth element is confirmed.

The EDX data of *$CuInS_2$:$CdCl_2$,Sm (6ml)& $CuInS_2$:$CdCl_2$,Sm(8ml)* are given in Table.2.

Table2. Elemental composition of Sm doped films by EDX

Films	Parameter	Element				
		Cu	In	S	Sm	O
$CuInS_2$:$CdCl_2$,Sm(6ml)	Weight%	34.02	36.77	10.41	2.49	16.30
	Atomic%	24.17	14.45	14.65	.75	45.99
$CuInS_2$:$CdCl_2$,Sm(8ml)	Weight%	22.67	34.52	9.13	4.06	29.62
	Atomic%	12.65	10.66	10.10	0.96	65.64

3.4 Optical study

Optical transmission and absorption spectra recorded in the wavelength range 500-800nm of doped and undoped films are represented in fig.4 and fig.5.

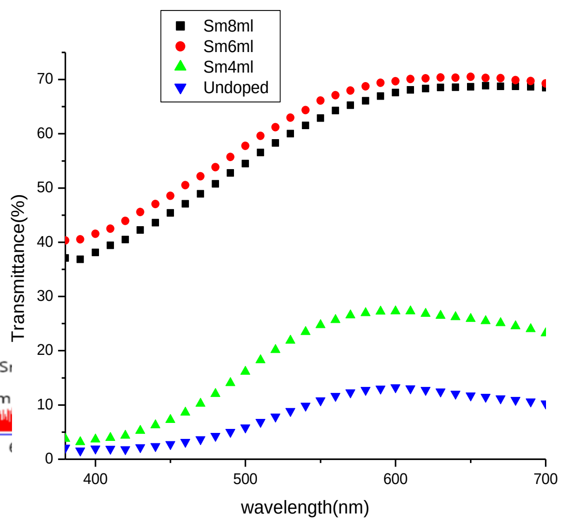


Fig. 4.Transmisson spectra of undoped and $CuInS_2$: $CdCl_2$,Sm films

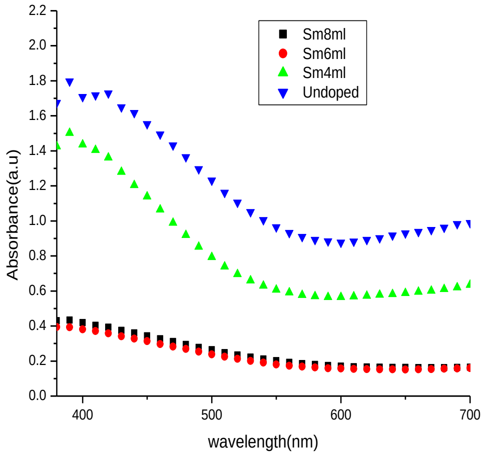


Fig.5. Absorption spectra of undoped and $CuInS_2$: $CdCl_2$,Sm film

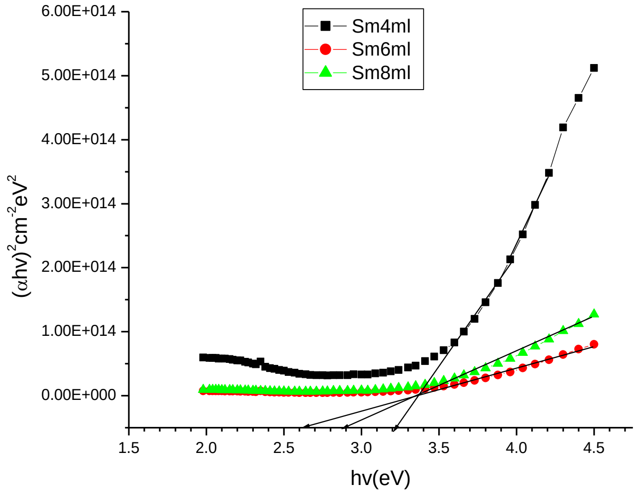
Spectra of undoped and $CuInS_2$:$CdCl_2$, Sm films
The transmittance of the undoped $CuInS_2$ film is < 10% but as the volume of rare earth element (Samarium) increases it also increases. The highest value of transmittance is 70% obtained for $CuInS_2$:$CdCl_2$,Sm(6ml) film in the visible range and ~57-68% in the near IR region. All the film shows absorption in the visible range.

The absorption coefficient has been calculated by using the formula

$$\alpha = \frac{2.303A}{t} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where A is the absorbance and t is the thickness of the synthesized film. All film shows high absorption coefficient of $10^5 cm^{-1}$. This behavior makes the $CuInS_2$:$CdCl_2$,Sm films suitable for photovoltaic cells. The absorption coefficient of *$CuInS_2$:$CdCl_2$,Sm(4ml)* doped film is high as compare to other films. In order to get the value of band gap energy a graph has been plotted between $(\alpha h\nu)^2$ and hv.

This is called Tauc's plot shown in Fig.6.



The band gap is ranging between 2.6eV to 3.2 eV. The obtained band gap is quite high than the single crystal $CuInS_2$ of 1.55eV. The reason may be the deviation from stoichiometry which produces defect states and hence increases the band gap. The XRD result also affirms the same.

4. CONCLUSION

The film of $CuInS_2$ has been synthesized successfully by the inexpensive chemical bath deposition technique. SEM image shows that the surfaces of film are uniform and homogeneous with tiny particles**.** X-ray diffractograms confirms the chalcopyrite phase of films. Slight variation is observed in the observed and standard d value which shows that the synthesized film is nonstoichiometric. Transmittance of the film increases with doping of rare earth element Samarium. The highest value of transmittance is 70% obtained for $CuInS_2$:$CdCl_2$,Sm (6ml) film in the visible range. The highest value of band gap ranging between 2.6eV to 3.2 eV exhibits the nonstoichiometric nature of the film. The film doped with 4ml Sm is more crystalline with high absorption coefficient.

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