Structural and morphological studies of Sm doped and un-doped $CuInS_2$ nanocrystalline films with chalcopyrite-wurtzite polytypism structure

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This paper reports the synthesis of $CuInS_2$ nanocrystalline thin films on the glass substrate by using chemical bath deposition (CBD) method.$CuCl_2.2H_2O$ has been used as Cu source, $InCl_3$ as Indium (In) source and thiourea as sulphur source. TEA has been used as complexing agent. The film is doped with rare earth element Samarium.XRD studies show the existence of both chalcopyrite and wurtzite phases. The particle size calculated from XRD studies are in nano range (29-43nm). SEM micrographs show that the film surface is uniform and smooth. The band gaps of films are between (2.19eV and 2.35eV). EDX profile confirms the doping of rare earth element Sm.

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Keywords: $CuInS_2$, Thin films, CBD, XRD

1. Introduction

It is known that day by day the energy consumption rises and due to the conventional method of energy production there is a shortage of fossil fuels. This problem can be overcome by finding the alternative energy resources like photovoltaic devices. Chalcopyrite semiconductors $CuInS_2$ and $CuInSe_2$ are currently investigated for applications in photovoltaic, solar cells and LED devices [1]. $CuInS_2$ thin films exhibit many excellent physical and chemical properties such as high absorption coefficient of 10^5 cm^{-1} in the visible spectral range, high tolerance to the presence of defects, a direct band gap closes to 1.5eV, the optimum value for the photovoltaic conversion of solar energy, possibility to avoid n and p-type conductivity and high chemical stability [2]. The $CuInS_2$ compound exists in three polymorphic structures including chalcopyrite (CH), zinc blend (ZB) and wurtzite (WZ) structure. Moreover, polytypism of $CuInS_2$, the ability of a solid material to exist in more than one form or crystal structure have been synthesized in different reaction systems [3]. Further $CuInS_2$ is more environmental friendly material than those containing Se or Cd. There are various methods for the synthesis of $CuInS_2$ thin films such as co-evaporation [4], electrodeposition [5], sputtering [6], successive ionic layer absorption and reaction method [7], spray pyrolysis [8] and chemical bath deposition (CBD) [9]. The rare earth ions are well known to form efficient luminescent centres as they show distinct absorption and emission transitions within the $4f^N$ shell configuration.$CdCl_2$ has been used as flux which facilitates the incorporation of the rare earth ions into the lattice and helps in recrystallization [10]. This paper reports un-doped and Sm doped $CuInS_2$ nanocrystalline films with chalcopyrite-wurtzite polytypism structure deposited by simple chemical bath deposition (CBD) technique which is a low cost method, for producing uniform, adherent and reproducible films.

2. Experimental

In this paper $CuInS_2$ films were deposited on microscopic glass (24×75 mm) substrates by chemical bath deposition technique. Before using the glass substrates were cleaned several times by detergent. Then washed with acetone and deionised water. In a bath solution of $CuCl_2.2H_2O$ (0.1M), $InCl_3$ (0.1M), TEA and ammonia (25%) is taken. The colour of the solution was turbid. Sulphur source thiourea was then added to it. The solution was stirred for 10min. The cleaned glass slides were vertically dipped in a liquid bath. Here TEA works as a complexing agent and ammonia maintains the pH of the liquid bath. Now $CdCl_2$ (0.01 M) and Samarium (0.01M) were also added as an impurity to the solution. Addition of $CdCl_2$ in the solution is important as it is helpful for re-crystallization of the material and it behaves as a flux for the incorporation of samarium in the material. The pH of the solution bath was ~ 9.5. The bath temperature was kept constant at 80^0C.The deposition time was of 1 hour for all the films. After deposition films were taken out from the solution bath and washed thoroughly with deionised water and dried. The deposition occurs because of precipitation followed by condensation. The film thickness was measured by using gravimetric method assuming the film density same as that of the bulk (4.739 g/cm^3). The XRD patterns of $CuInS_2$ films have been recorded by using the XPERT-PRO PAN analytical X-ray

diffractometer with CuK_α radiation. For surface morphology studies of the film, scanning electron microscope (SEM) was used. For elemental study EDX has been recorded.The films were coated with gold-palladium alloy. Optical absorption spectra have been recorded by Elico SL210 double beam UV-VIS spectrophotometer.

3. Results and discussion

Fig. 1 shows the XRD of un-doped and Sm doped $CuInS_2$ films. The un-doped film consist of peaks of both chalcopyrite (CH) and wurtzite (WZ) phase of $CuInS_2$. The peaks at $2\theta = 27.8^0$ and 31.9^0 are of chalcopyrite $CuInS_2$ (JCPDS-98-065-6271) and at $2\theta = 27.8^0$ and 29.5^0 are of WZ $CuInS_2$. Also one peak at $2\theta = 22.4^0$ corresponds to $Cu_{1.8}S_1$. Peaks at $2\theta = 44.9^0$, 48.5^0 and 56.4^0 corresponds to In_1S_1 (JCPDS-98-008-1341). The Sm doped film also consists of both chalcopyrite and WZ phase. The peakscorresponding to WZ phaseoccurs at $2\theta = 26.44^0$, 29.58^0, 54.1^0 and 73.95^0(JCPDS-98-016-3489). The peaks at $2\theta = 31.86^0$ and 54.84^0 is of chalcopyrite phase (JCPDS-98-065-6271).Also peaks corresponding to copper sulfide (Cu_1S_1), digenite low ($Cu_{1.8}$ S_1) and copper indide (Cu_7In_3) appears. The reason for co-existence of both WZ and CH-$CuInS_2$ is due to TEA. TEA is the pivotal agent. It is a kind of versatile ligand that readily forms coordination compounds with almost all metal ions [11]. There is no peak observed corresponding to Sm. It means that doping element doesn't affect the polytypism structure of $CuInS_2$ film.

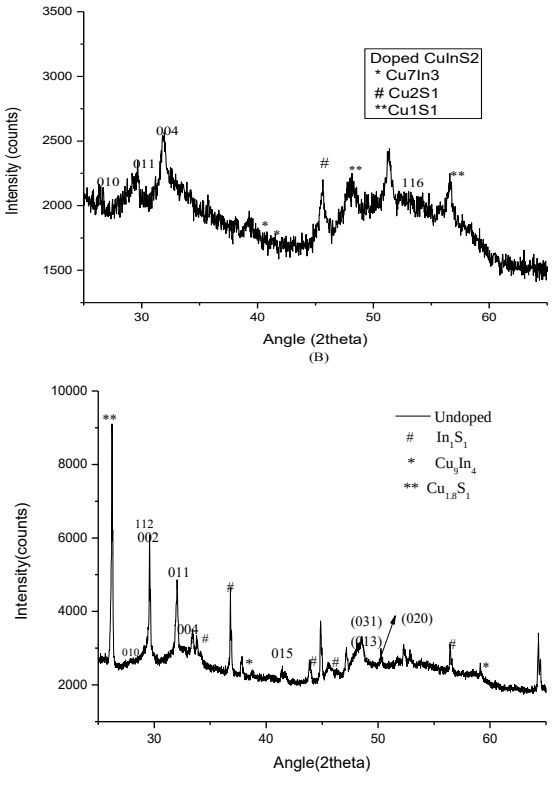


Fig. 1. XRD spectra of un-doped and Sm doped $CuInS_2$ thin films

The XRD data along with calculated and standard values of lattice constants are shown in Table 1. As mentioned above, films show combination of wurtzite and chalcopyrite phases and the values of lattice constants are quite close to reported values.

The particle size can be calculated by using the Debye-Scherer's formula [12]

$$D = \frac{0.94\lambda}{\beta_{1/2}\cos\theta} \quad (1)$$

where D is the particle size, λ is the X-ray wavelength used, $\beta_{1/2}$ is the full width at half maxima (FWHM) of the diffraction peak and θ is the diffraction angle. Broadening of several diffraction lines were observed. Fig. 2 shows broadening of $(010)_{wz}$,$(011)_{wz}$ and $(020)_{wz}$ peaks. Particle size calculated for $(010)_{wz}$,$(011)_{wz}$ and $(020)_{wz}$ peaks of un-doped and $CuInS_2$:$CdCl_2$,Sm films are: 39.48 nm, 39.7 nm, 43.12 nm and 29.6 nm and 37 nm, 32.39 nm respectively. Reduction in particle size confirms that films are nano sized. It is observed that doping of Sm causes disappearance of $(112)_{ch}$ plane. Also there is a reduction in the intensity of all lines except for $(020)_{wz}$ plane. Thus, it may be inferred that inclusion of Sm reduces the crystallinity of $CuInS_2$ films.

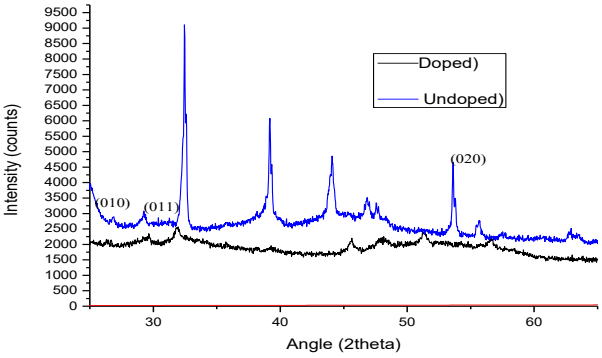


Fig. 2. Broadening of diffraction lines (lying within the 2θ range (25°–56°)

SEM micrographs (Fig. 3) show the morphological features of un-doped and doped $CuInS_2$ films.The surface of both the film appears to be uniform and smooth at 10 kx and 20 kx magnification. The surface consists of large number of nano sized grains. The grain sizes in undoped and doped films are 100 nm and 67 nm respectively. Thus grain size decreases with dopant (Sm). This is may be due to the nature of the dopant which plays an important role in the formation of the solid product on the substrate [13]. In Fig. 4 EDX of doped $CuInS_2$ film is shown. It confirms the formation of $CuInS_2$film with presence of rare earth element. In Fig. 5 absorbance and transmittance spectra of un-doped and Sm doped $CuInS_2$ thin films in the range 300-1100 nm are shown. The un-doped film shows good absorbance in visible range but transmittance is very low (13%). Absorbance of doped film increases above 700 nm

which may be due to hyperchromic effect. But it is interesting to observe that the transmittance of the film deposited with Sm is showing higher transmittance of about 70%. The sharp increase of transmittance in the absorption range of the dopedfilm may be attributed to decrease in thickness.

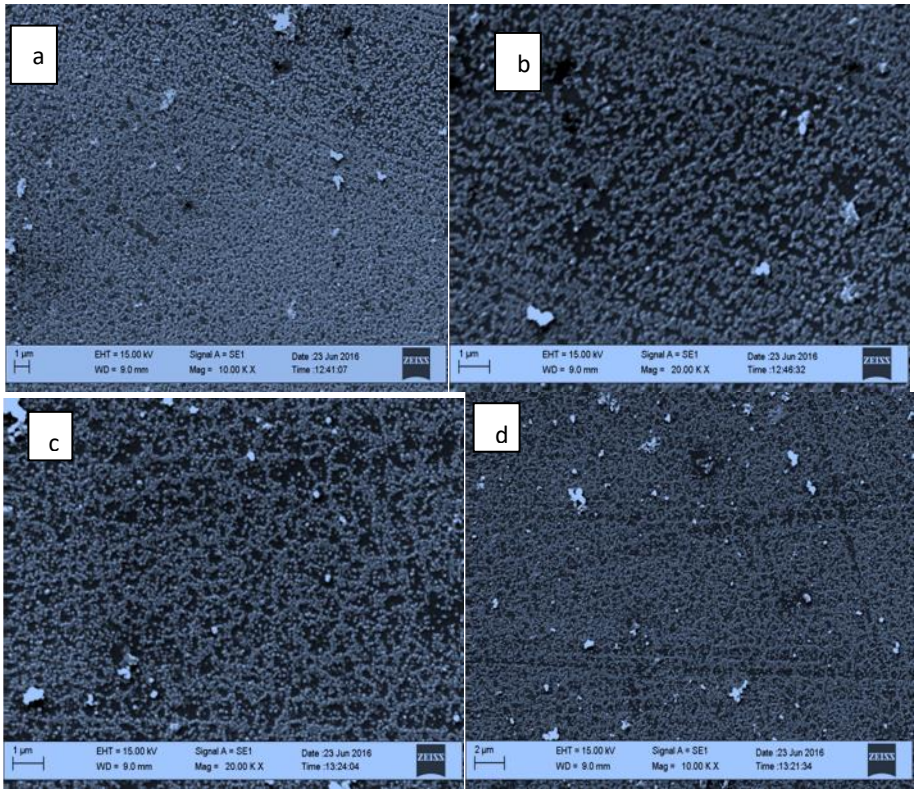


Fig. 3. SEM micrographs of $CuInS_2$ films (a,b) Un-doped film (c,d) Doped film

Table 1. XRD data of un-doped and Sm doped $CuInS_2$ film (deposition time =1hr at 80^0C)

d values (in ^{0}A)		Relative intensities		hkl	Lattice constant(in^{0}A)	
Obs.	Reported	Obs.	Reported		Obs.	Reported
$CuInS_2$ film(Un-doped)						
3.40	3.38	100	75	$(010)_{wz}CuInS_2$	a = 3.92	a = 3.90
3.02	2.99	55.7	100	$(011)_{wz}$ $CuInS_2$	c = 6.6	c= 6.42
1.70	1.69	2	8	$(020)_{wz}CuInS_2$	a = 3.93	a= 3.90
3.19	3.19	11.9	100	$(112)_{ch}CuInS_2$	c =11.10	c = 11.12
2.79	2.77	46.9	5.7	$(004)_{ch}$ $CuInS_2$	a = 11.18	c = 11.12
$CuInS_2$:$CdCl_2$,Sm						
3.37	3.38	7.40	75	$(010)_{wz}CuInS_2$	a = 3.88	a = 3.90
3.01	2.99	16.1	100	$(011)_{wz}$ $CuInS_2$	c = 6.59	c= 6.42
2.80	2.77	27.82	5.7	$(004)_{ch}$ $CuInS_2$	c = 11.2	c = 11.12
1.69	1.69	5.95	8	$(020)_{wz}CuInS_2$	a =3.90	a = 3.90
1.28	1.27	3	5.2	$(120)_{wz}$ $CuInS_2$	a = 3.91	a = 3.90
1.67	1.67	4.63	13.1	$(116)_{ch}$ $CuInS_2$	c = 11.10	c = 11.12

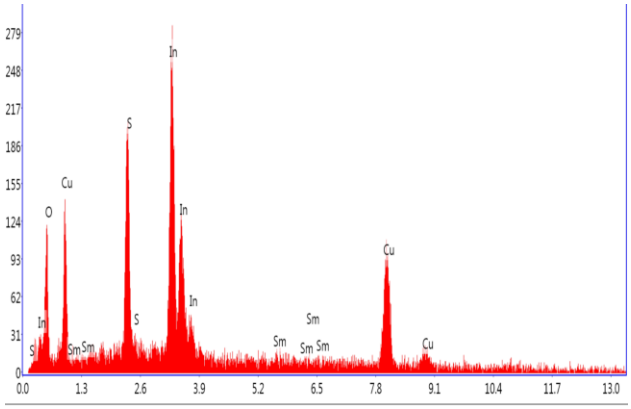


Fig. 4. EDX profile of doped $CuInS_2$ film

For direct band gap materials, the absorption coefficient (α) can be given by [14]

$$\alpha = \frac{c(h\nu - Eg)^{1/2}}{h\nu} \qquad (2)$$

where c is a constant. A graph between $(\alpha h\nu)^2$ and (hν) is plotted in Fig. 5. The extrapolation of this graph will give the band gap. The band gaps of the undoped and doped films are 2.19 eV and 2.35 eV respectively which is higher than bulk $CuInS_2$ (1.5eV). This is due to smaller particle size which shows nanostructure. Also doping of Sm increases the band gap. This is attributed to non-crystallinity and non-stoichiometry of the film [15].

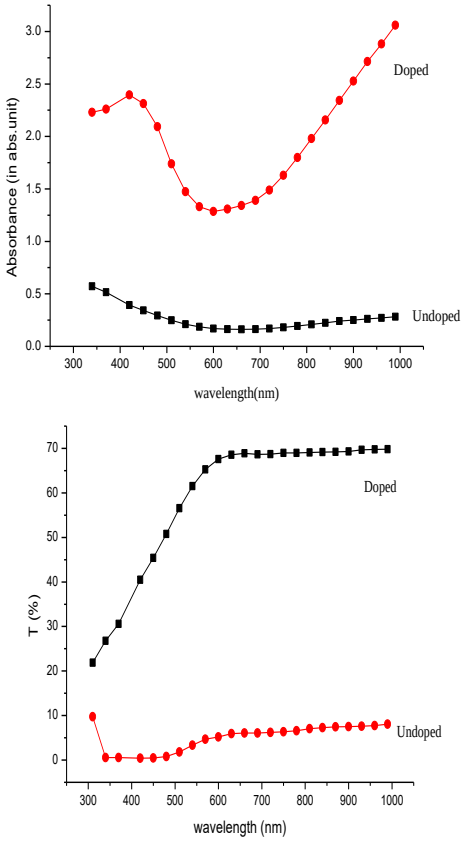
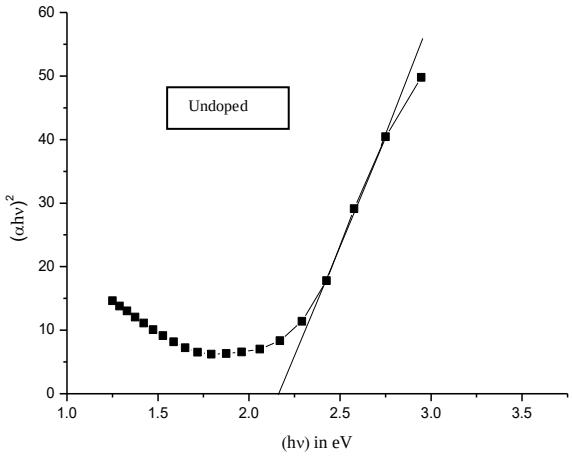


Fig. 5. Absorbance and transmission spectra of doped and un-doped $CuInS_2$ films



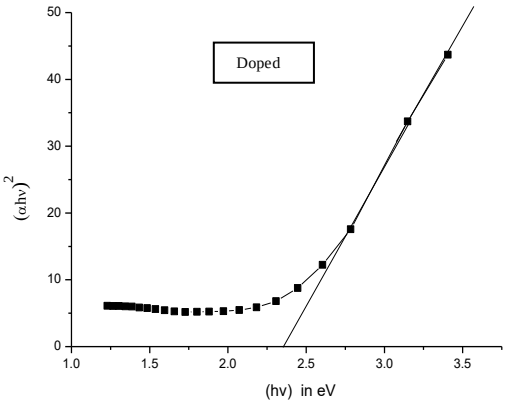


Fig. 6. Plot of $(\alpha h\nu)^2$ and $(h\nu)$ of un-doped and doped $CuInS_2$ thin films

4. Conclusions

The undoped and Sm doped nanocrystalline $CuInS_2$ films were prepared with polytypism structure by chemical deposition technique. SEM studies on pure and Sm doped $CuInS_2$ film shows nano size grains. Also the surface of the film is uniform. XRD studies show existence of both wurtzite and chalcopyrite phases in both thesystems. In doped film increase in FWHM is observed suggesting a further reduction in particle size. The sharp increase of transmittance in the absorption range of the doped film shows that particle size decreases. The increase in band gap in comparison to bulk $CuInS_2$ shows formation of nanostructure.

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References

[1] N. Suriyanarayanan, C. Mahendran, Archives of Physics Research **3,** 54 (2012).

[2] M. Ben Rabeh, N. Chaglabow, M. Kanzari, Chalcogenide Letters **6,** 155 (2009).
[3] Y. Vahidshad, M. N. Tahir, S. M. Mirkazemi, A. I. Zad, G. W. Tremel, Appl. Phys. A **122,** 187 (2016).
[4] M. Ben Rabeh, N. Chaglabou, M. Kanzari, B. Rezig, Phys. Procedia **2**, 745 (2009).
[5] K. W. Cheng, W. H.Chiang, J. Electroanal. Chem. **661,** 57 (2011).
[6] Y. B. He, A. Polity, H. R. Alves, I. O. Sterreicher, W. Kriegseis, D. Pfisterer, B. K. Meyer, M. Hardt, Thin Solid Films **62**, 403 (2002).
[7] Y. Shi, Z. Jin, C. Li, H. An, J. Qiu, Appl. Surf. Sci. **252,** 3737 (2006).
[8] T. John, T. Sebastian, C. S. Kartha, K. P. Vijaya Kumar, T. Abe, Y. Kashiwaba, Physica B**388,** 1 (2007).
[9] F. Cui, L. Wan, Z. Xi, Y. Sun, D. Yang, J. Mater. Sci. Mater. Electron. **20**, 609 (2009).
[10] S. Bhusan, P. Sandhya, Fizika A**18,** 141 (2009).
[11] X. Sheng, L. Wang, L. Yeping, Y. Deren, Sheng, Nanoscale Research Letters **6,** 562 (2011).
[12] L. Jinsong, J. Cao, Z. Li, G. Ji, S. Deng, M. Zheng, J. Mat. Sci. **42,** 1054 (2007).
[13] E. Garskaite, G. Ting Pan, Y. C. K. Thomas, H. S. Tung, A. Kareiva, Solar Energy **86**, 2584 (2012).
[14] A. L. Dawer, P. K. Shihodia, J. Chouhan, G. Kumar, A. Mathur, Mat. Sci. Lett. **9**, 547 (1990).
[15] M. D. Mahanubhav, L. A. Patil, P. S. Sonawane, R. H. Bari, V. R. Patil, Sensors & Transducers Journal **73,** 826 (2006).

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