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Structural, electrical and optical studies on spray deposited Cadmium Sulphide and Copper Indium Disulphide thin films

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ABSTRACT

CdS and $CuInS_2$ thin films are deposited by spray pyrolysis technique. CdS thin films are deposited from the aqueous solution of cadmium chloride and thiourea with [Cd]/[S] ratio =1 on glass and ITO coated glass substrates at temperature of about 400^0C. $CuInS_2$ thin films are deposited on glass substrates at 350^oC from the aqueous solutions of copper chloride, indium chloride and thiourea with [Cu]/[In] ratio =1.1 and [Cu]/[In] ratio =1.25. The ratio of [S]/[Cu] = 3.5 in both the cases. X-ray diffraction shows that the films are polycrystalline in nature. The grain size and strain in the films are calculated from XRD. Surface morphology of the deposited films is observed by SEM. Hot probe method is used to determine the conductivity type of the films. Resistivity of the films is determined by van der Pauw method. Resistivity of all the films is in the order of 10^{-2} ohm-cm. Thickness and refractive index of the thin films is measured using an Ellipsometer. UV-Vis analysis is carried out to measure the energy gap of the films. The bandgap of 2.43eV and ~1.48eV is obtained for CdS and $CuInS_2$ thin films, respectively. The CdS film shows absorption coefficient (α) of about 2×10^4 cm^{-1} near the absorption edge. All the CdS films have transparency of about 70% in the wavelength range of 510nm – 800nm. The $CuInS_2$ films have absorption coefficient (α) in the order of 10^4 cm^{-1} in the visible and red region of the absorption spectra.

Keywords: Spray pyrolysis, CdS and $CuInS_2$ thin films, Electronic, Optical properties.

INTRODUCTION

The Cadmium sulphide (CdS) is a compound II-VI semiconductor which is a leading material for heterojunction thin film solar cells. The wide band gap (2.42 eV) and stability of CdS has been made it a favorable solar cell window material along with absorber semiconductors such as CdTe, and ternary I-III-VI semiconductors such as copper indium diselenide ($CuInSe_2$), copper indium gallium diselenide ($CuInGaSe_2$), Copper indium disulphide ($CuInS_2$) etc. The Copper indium disulphide has theoretically the highest conversion efficiency among the chalcopyrite based solar cells due to its direct band gap of 1.55 eV and high absorption coefficient ($10^5 cm^{-1}$) [1]. Various methods have been reported for the preparation of CdS and $CuInS_2$ thin films such as thermal evaporation, chemical bath deposition, sputtering, electrodeposition, chemical vapor deposition, close spaced sublimation, co-evaporation [2-10]. In this paper we report our study on CdS and $CuInS_2$ thin films deposited using homemade spray deposition unit. The films obtained are uniform and homogeneous. The films have low resistivity in the order of 10^{-2} Ω-cm, which can be used for the fabrication of photovoltaic devices [11].

MATERIALS AND METHODS

The schematic diagram of the spray deposition unit we used in this study is shown in the Fig.1. CdS thin films are obtained by spraying the solution containing 0.05M of $CdCl_2$ and 0.05M of thiourea ($(NH_2)_2CS$) with [Cd]/[S] ratio =1 on glass and ITO coated glass substrates maintained at a temperature of 400^0C [12]. The substrates are first ultrasonically cleaned, rinsed with acetone followed by a rinse with methanol and dried by flowing air. $CuInS_2$ thin films are deposited by spraying the solution containing 0.1M of $InCl_3$, $CuCl_2$, $(NH_2)_2CS$ with two different molar ratios of [Cu] and [In], [Cu]/[In] ratio =1.1 and [Cu]/[In] ratio = 1.25, with molar ratio of [S]/[Cu] = 3.5 in both the cases on the glass substrates kept at temperature of 350^0C [13]. The spray rate is kept at 5ml/minute. The structural properties of as grown thin films are characterized by X-ray powder diffractometer (Bruker AXS D8 Advance) using Cu Kα radiation (λ = 1.54178 Å). Full width half maximum (FWHM) and 2θ values of the peaks are used to calculate the grain size and strain in the films. Surface morphology of these films is studied using FESEM (Hitachi SU6600). Conductivity type of the films is determined by hot probe method. Resistivity of the films is measured by van der Pauw method using Keithley 236 source measure unit. Thickness and refractive index of the films are measured by an Ellipsometer (Holmarc opto mechatronics) using DPSS laser (532 nm) beam. Optical properties are obtained from UV-Vis (shimadzu 1800) absorption and transmittance spectra of the films.

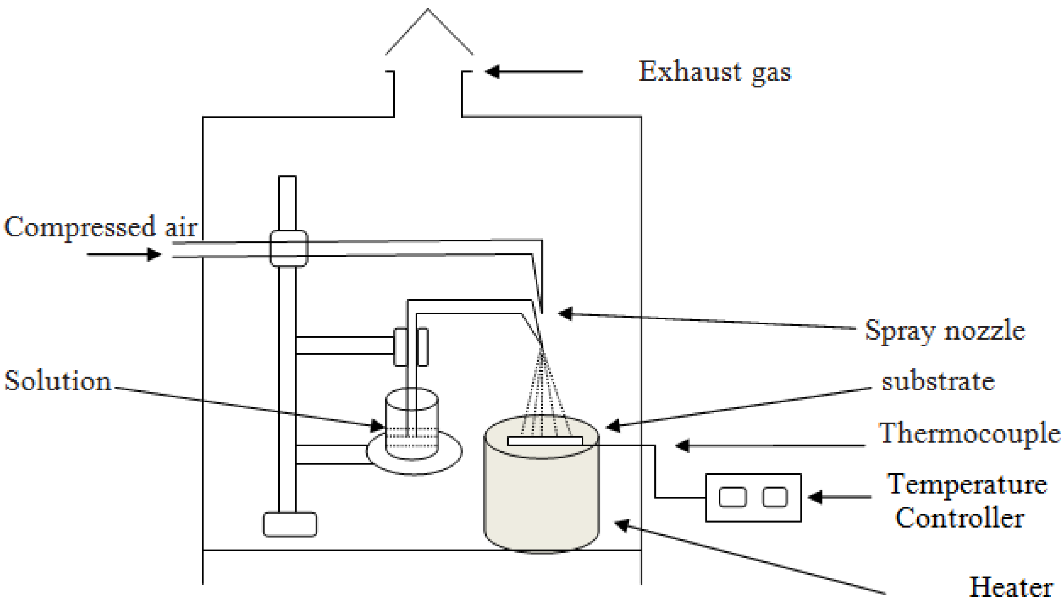

Fig.1 Schematic diagram of the spray deposition unit

RESULTS AND DISCUSSION

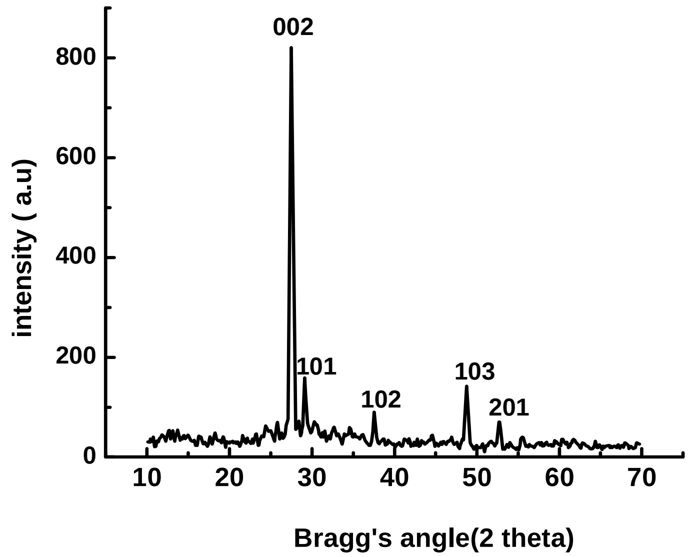

Fig. 2 (a) XRD spectra of CdS thin film on glass

3.1 Structural properties:
The structural properties of spray deposited CdS and $CuInS_2$ thin films have been investigated by X-ray diffraction techniques using CuK_α radiation. Fig. 2(a), Fig. 2(b), and Fig. 2(c) shows the X-ray diffraction pattern of CdS thin films on glass, ITO coated glass, and $CuInS_2$ thin films on glass substrates, respectively.

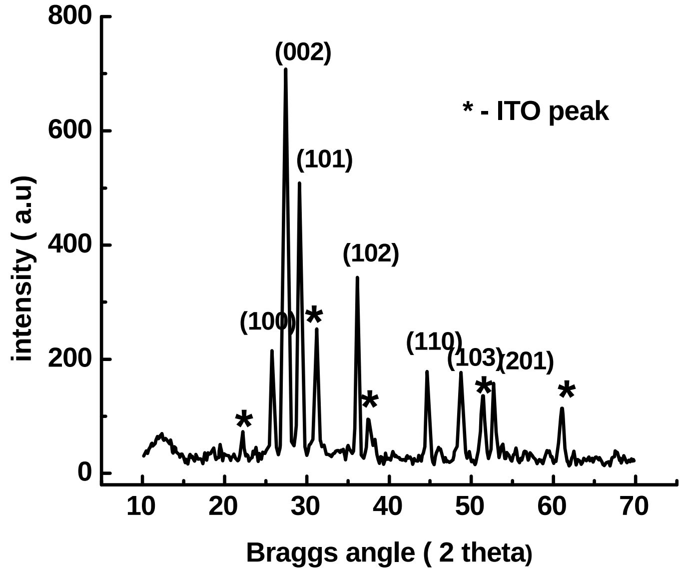

Fig. 2(b) XRD spectra of CdS thin film on ITO coated glass

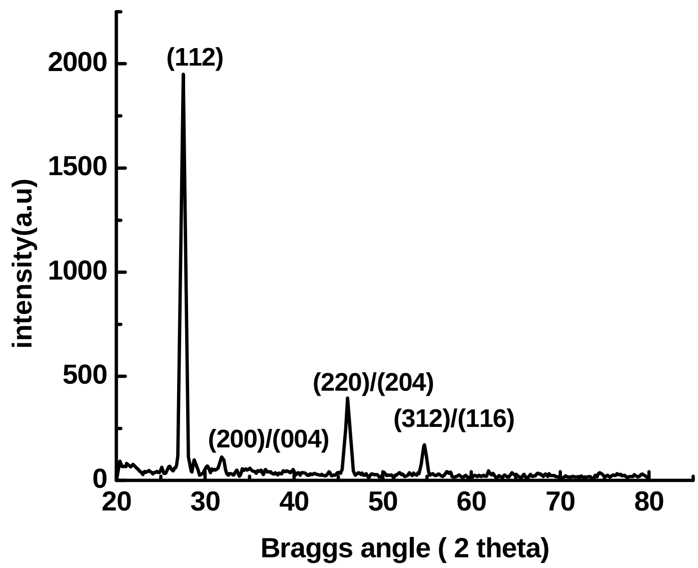

Fig.2(c) XRD spectra of $CuInS_2$ thin film on glass

rom the XRD pattern it is observed that the films are polycrystalline in nature. CdS thin film shows hexagonal structure and $CuInS_2$ thin film shows tetragonal chalcopyrite crystal structure [7, 14]. Prominent peaks are (002) and (112) in CdS and $CuInS_2$ thin films, respectively. The crystallite size is estimated from FWHM of these peaks using the Scherer's formula [15].

$$D = \frac{k\lambda}{\beta \cos\theta}$$

Where, D is the crystallite size, k is a constant taken to be 0.94 [16], β is the full width at half maximum (FWHM) and λ is the wave length of the x-rays. The obtained grain size values are listed in the Table. 1. Strain in the films are calculated from FWHM of prominent peaks using the relation

$$\varepsilon = \frac{\beta \cos\theta}{4}$$

The strain in the films is in the order of 10^{-3} and is listed in the Table. 1. These values are in good agreement with the earlier reported values [17].

Table. 1 Grain size and strain in the CdS and $CuInS_2$ thin films

Sample	Grain size (D) nm	Strain (ε) x 10^{-3}
CdS on glass	33.5	4.55
CdS on ITO coated glass	22.36	6.8
$CuInS_2$ on glass	22.59	6.73

3.2 Surface morphology:

Fig. 3(a) and 3(b) shows the SEM images of surface of the CdS thin films on glass substrates. The growth of the films is found to be uniform, dense and well covered to the glass substrate.

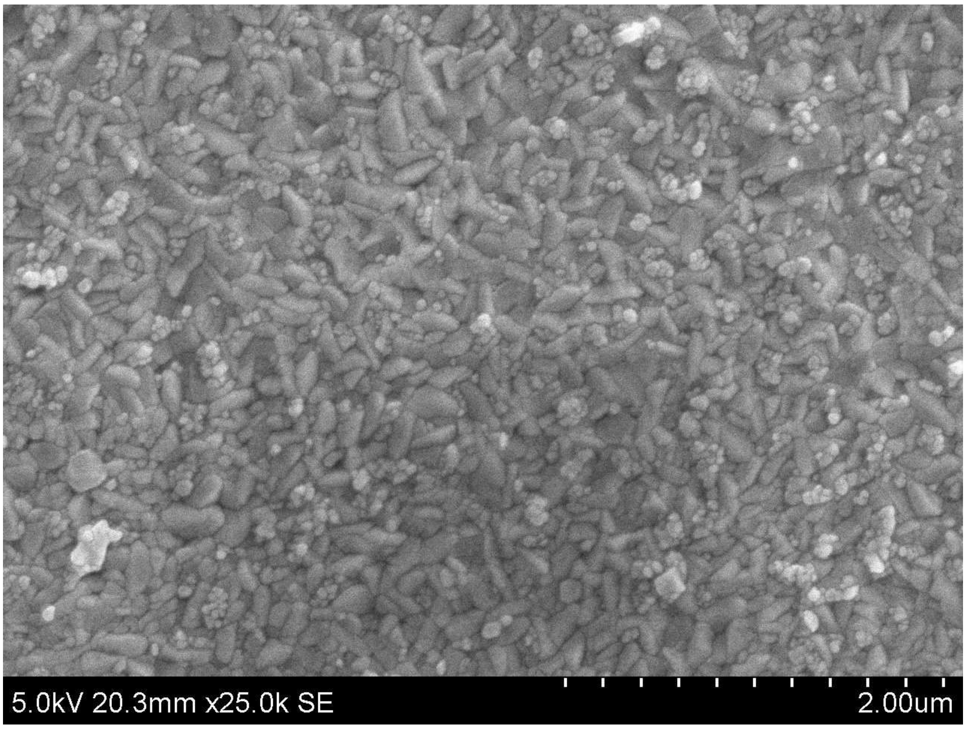

Fig. 3(a) SEM images of CdS thin film of thickness 249 nm

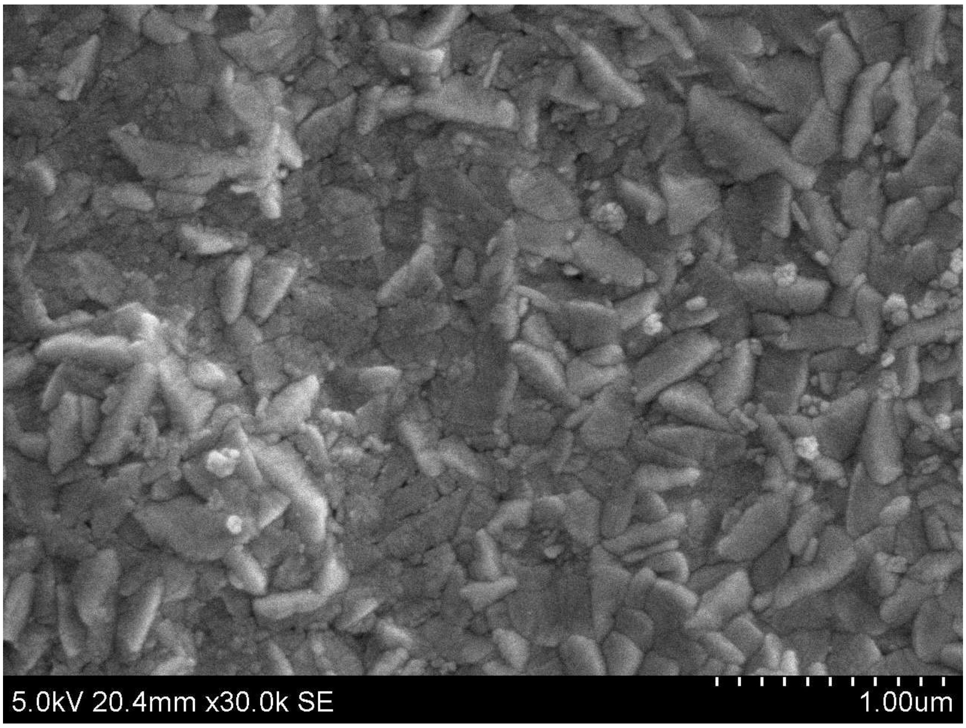

Fig. 3(b) SEM images of CdS thin film of thickness 260 nm

Fig. 4(a), 4(b), 4(c) and 4(d) show the SEM images of $CuInS_2$ thin films with different precursor molar ratio. From these images it is observed that the films are dense and uniform. It is interesting to see that the certain regions of $CuInS_2$ thin films grown with molar ratio of [Cu]/[In] =1.1 and [S]/[Cu] = 3.5 shows the formation of rod-like nanostructures, shown in Fig. 4(b) and 4(c). Further work is underway in optimisation of the growth of the nanostructures of $CuInS_2$ by spray pyrolysis.

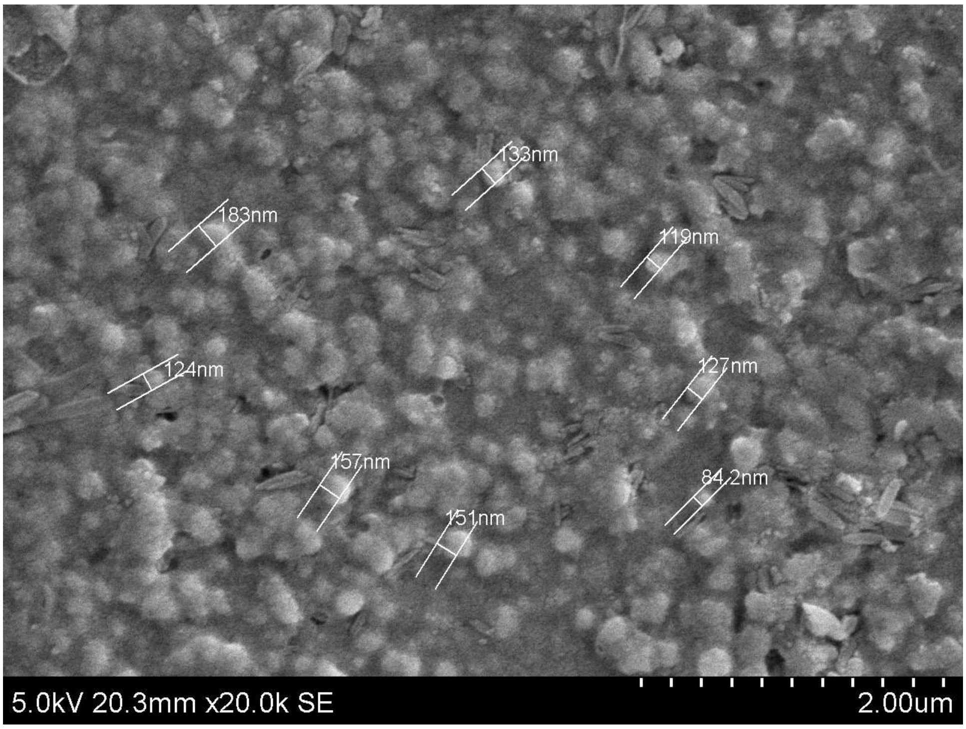

Fig. 4(a) SEM image of $CuInS_2$ thin film with [Cu] / [In] ratio =1.1

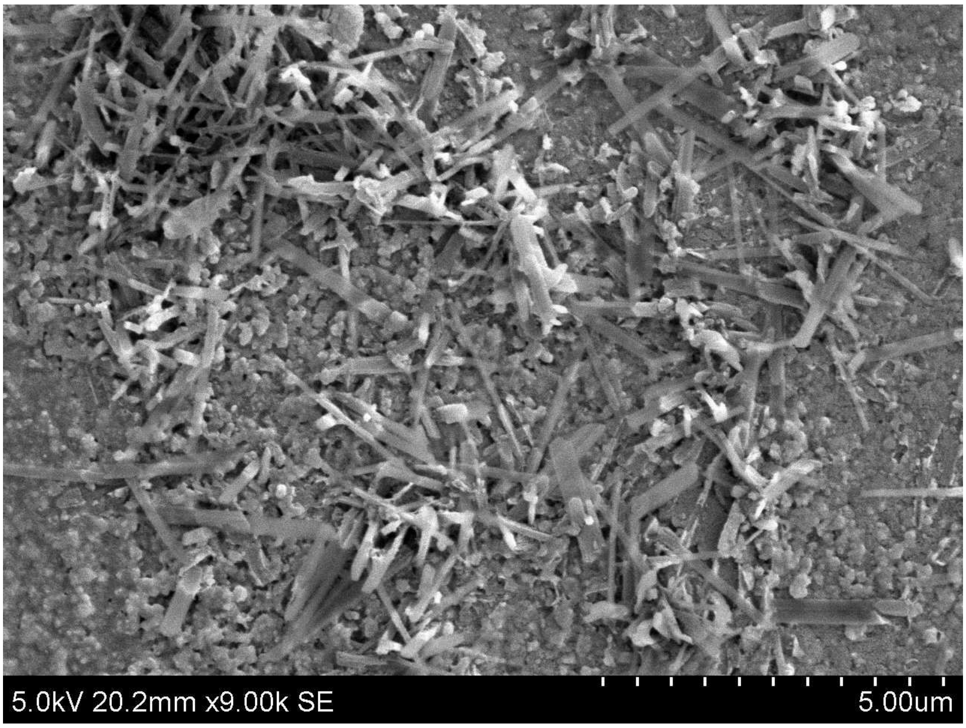

Fig. 4(b) SEM image of $CuInS_2$ thin film with [Cu] / [In] ratio =1.1

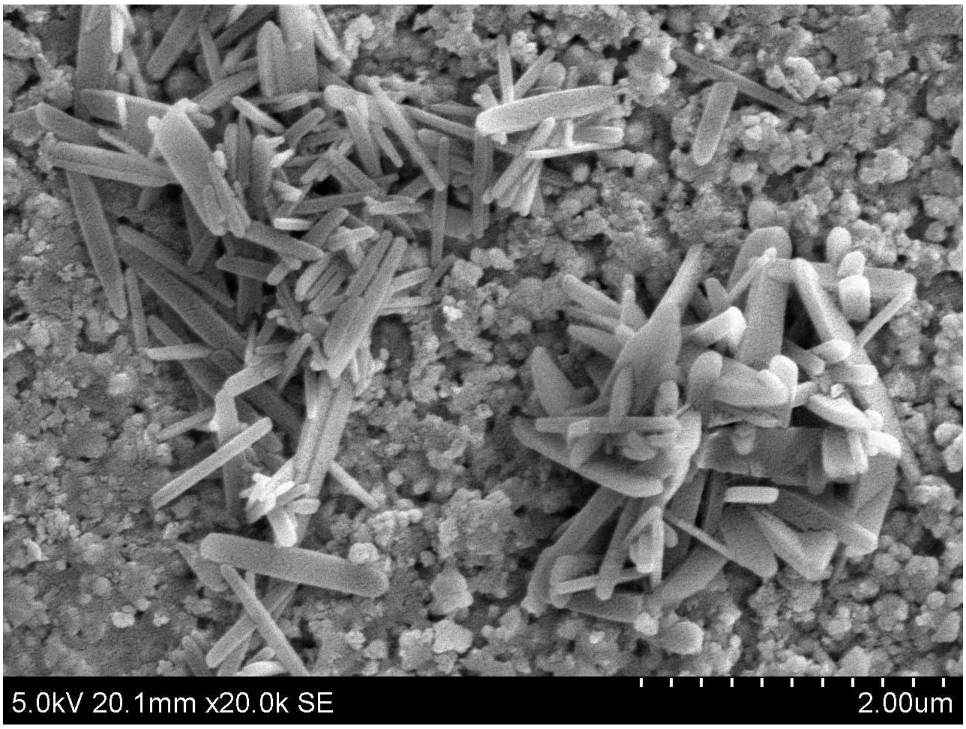

Fig. 4(c) SEM image of $CuInS_2$ thin film with [Cu] / [In] ratio =1.1

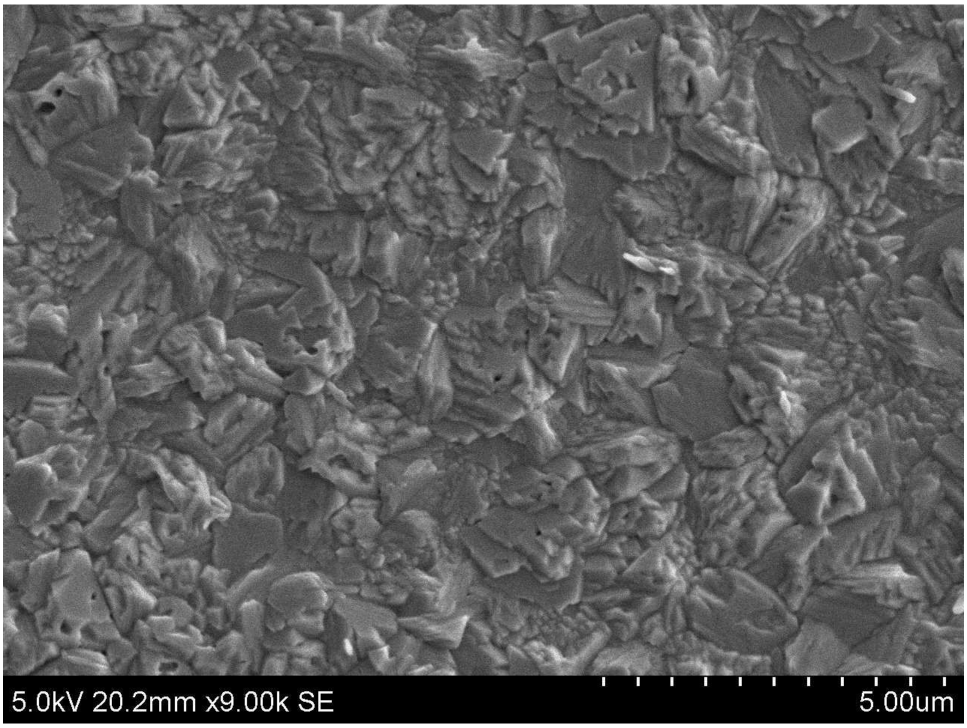

Fig. 4(d) SEM image of $CuInS_2$ thin film with [Cu] / [In] ratio =1.25

3.3 Optical properties:
Refractive index and thickness of the films are obtained using an Ellipsometer. Thickness of the films is in the range of 240nm to 275nm. Refractive index decreases with increase in thickness of the film. We obtained an average refractive index of 2.6 and 2.7 for CdS and $CuInS_2$ thin films, respectively.

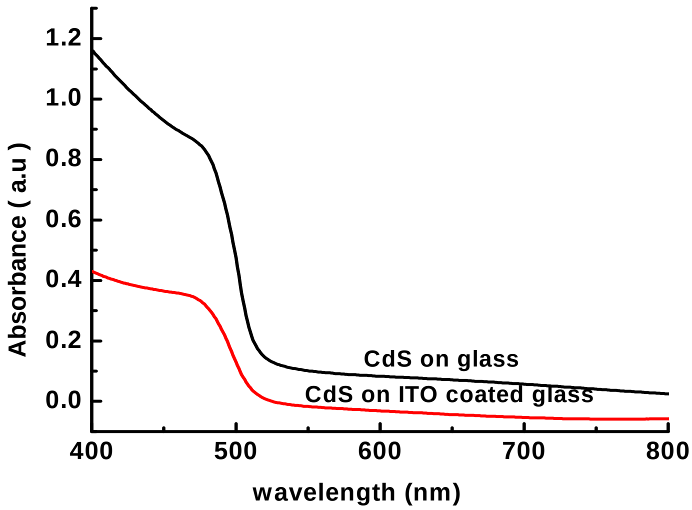

Fig. 5(a) Absorbance spectra of CdS on glass and CdS on ITO coated glass

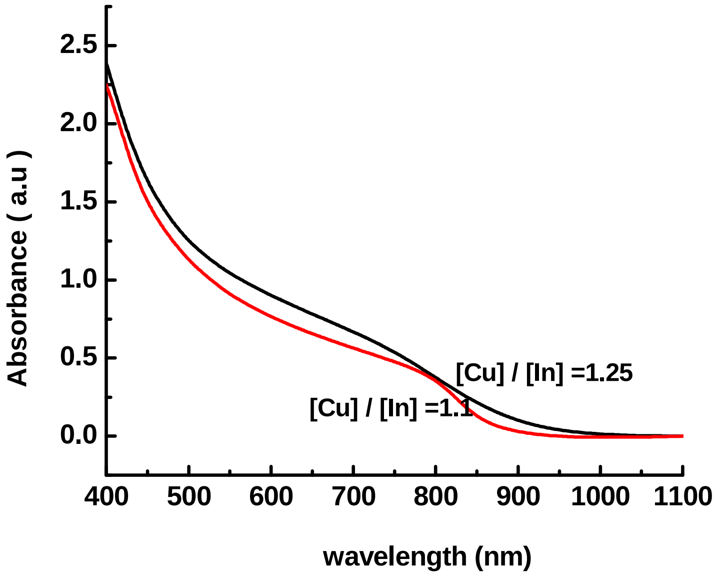

Fig. 5(b) Absorbance spectra of $CuInS_2$ with [Cu] / [In] =1.1 and [Cu] / [In] =1.25

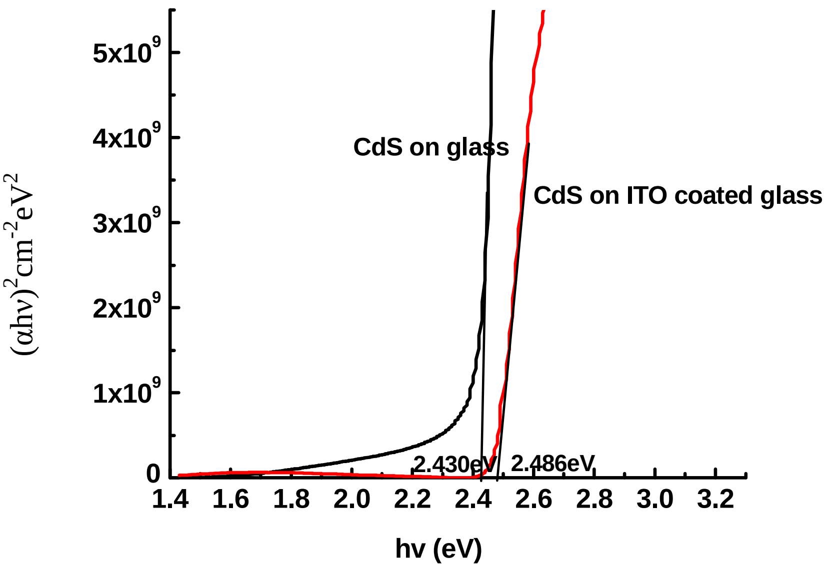

Fig. 6(a) hυ Vs. $(\alpha h\upsilon)^2$ graph of CdS on glass and ITO coated glass

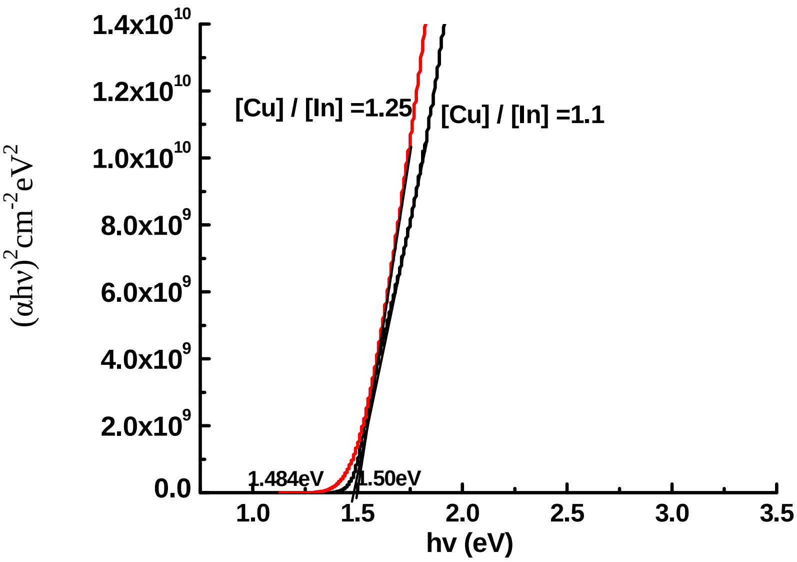

Fig. 6 (b) hυ Vs. $(\alpha h\upsilon)^2$ graph of $CuInS_2$ with [Cu] / [In] =1.1 and [Cu] / [In] =1.25

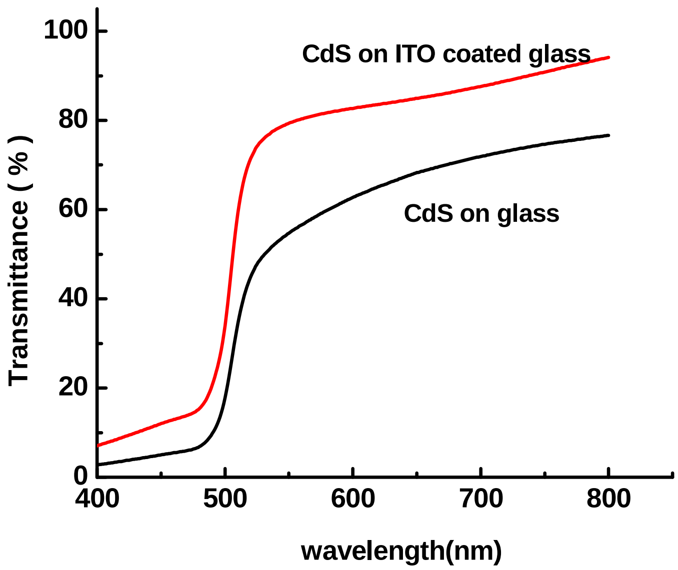

Fig. 7 Transmittance spectra of CdS on glass, ITO coated glass

The optical absorbance spectra of CdS thin films on glass, ITO coated glass and $CuInS_2$ thin films on glass with different precursor molar ratio are shown in Fig. 5(a) and 5(b).The optical band gap can be estimated by using the relation [15]

$$\alpha h\upsilon = A\,(h\upsilon - E_g)^n$$

Where E_g is the band gap of the thin film material, A is a constant, υ is transition frequency and the exponent n characterizes the nature of band transition, n = ½ for direct band gap semiconductor material. The graph between hυ vs. $(\alpha h\upsilon)^2$ plotted and shown in Fig 6(a) and 6(b). The extrapolation of linear region of the graph to $(\alpha h\upsilon)^2 = 0$ axis gives the value of energy band gap of thin film materials. The energy gap and absorption coefficient of the films are given in the Table 2. CdS films have transparency greater than 70% in the wavelength range 500nm to 800nm, shown in Fig. 7. These transparency values of the films are ideal for solar cell window materials [18]. Hence these films can be used for fabrication of $CdS/CuInS_2$ heterojunction solar cells.

Table.2 Energy gap and absorption coefficient values of CdS and $CuInS_2$ thin films

sample	Energy gap (eV)	Absorption coefficient (10^4 cm^{-1})
CdS on glass	2.43	1.7
CdS on ITO coated glass	2.453	4.7
$CuInS_2$ with [Cu] / [In] =1.1	1.482	1.65
$CuInS_2$ with [Cu] / [In] =1.25	1.494	2.41

3.4 Electrical properties:

Conductivity type of the films is determined using hot probe method. All the CdS thin films show n -type conductivity and $CuInS_2$ thin films show p-type conductivity. P-type conductivity of $CuInS_2$ thin films indicates that these films are of copper rich [19]. Therefore we can use these p-$CuInS_2$ thin films as absorber layer with CdS as n-type window layer in n-CdS/p-$CuInS_2$ heterojunction solar cells. Sheet resistivity of the films is measured using van der Pauw method. The obtained values are given in the Table. 3. These values are in agreed with the earlier reported values [11, 20].

Table. 3 Thickness and resistivity values of CdS and $CuInS_2$ thin films

sample	Energy gap (eV)	Absorption coefficient (10^4 cm^{-1})
CdS on glass	2.43	1.7
CdS on ITO coated glass	2.486	4.7
$CuInS_2$ with [Cu] / [In] =1.1	1.484	1.65
$CuInS_2$ with [Cu] / [In] =1.25	1.50	2.58

Resistivity of the films decreases with increase of the film thickness in both CdS and $CuInS_2$ thin films.

CONCLUSION

Thin films of CdS and $CuInS_2$ are obtained by chemical spray deposition method. The grown films are polycrystalline in nature. Surface morphology is studied from FESEM. Energy gap and absorption coefficient of the films are obtained from UV-Vis spectral analysis. The energy gap value is obtained as 2.43eV and 1.48eV for CdS and $CuInS_2$ thin films, respectively. $CuInS_2$ has absorption coefficient in the order of 10^4 cm^{-1} and CdS thin films has transmittance greater than 70% in the visible region of the solar spectrum. Conductivity type and the resistivity values of the films meet the requirements of p-n junction solar cell materials.

Acknowledgements

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