ISSN: 0974-2115
www.jchps.com Journal of Chemical and Pharmaceutical Sciences

Preparation and characterization of $CdIn_2S_4$ thin film grown by nebulized spray pyrolysis technique

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ABSTRACT

Nebulized spray pyrolysis is a simple and cost effective technique to deposit thin films. Cadmium Indium Sulfide ($CdIn_2S_4$) thin film has been deposited on amorphous glass substrate by this technique using the precursor solutions of AR grade $CdCl_2$, $InCl_3$ and thiourea salts at an optimized substrate temperature of 300˚C. The as prepared film was characterized by x-ray diffraction, optical transmittance, scanning electron microscope imaging, energy dispersive analysis by x-rays and electrical conductivity studies to find its suitability for solar cell applications. The x-ray diffraction analysis revealed that the as deposited film has a cubic structure with a preferential orientation of (111) miller planes. Spherical shaped grains were observed from the scanning electron microscopic imaging of the surface of the film. A direct band gap of 2.58 eV was estimated from the optical transmittance study. Energy dispersive analysis by x-rays showed almost nearly stoichiometric form of the film. The d.c electrical resistivity of the film was found to be 8.84 Ω.cm from four-probe technique. Carrier concentration and mobility of the same sample were found to be 7.36 x 10^{18} cm^{-3} and 66.2 cm^2/Vs from Hall Effect analysis.

KEY WORDS: $CdIn_2S_4$, band gap, resistivity, nebulized spray pyrolysis.

1. INTRODUCTION

Cadmium indium sulfide ($CdIn_2S_4$) is a semiconducting ternary chalcogenide, which belongs to the family of ternary compound A^{II}-B_2^{III}-C_4^{IV}. The ternary chalcogenide materials have been used to fabricate photo electro chemical solar cells due to their capability of solar energy conversion. $CdIn_2S_4$ has attained little attention as prospective materials for photoelectric chemical solar cells. Cadmium indium sulfide thin films have shown potential capability for applications in light emitting diodes (LED), optoelectronic devices, photo conductor and photo catalysis. A number of thin film deposition methods like spray pyrolysis, hydrothermal, successive ionic layer adsorption and reaction (SILAR), pulse electro deposition, electro deposition and hot wall epitaxy method have been reported for preparing $CdIn_2S_4$ thin films. Although physical techniques provide uniform and quality films, they are comparably expensive and high energy consuming. Nebulized spray pyrolysis is a versatile, inexpensive, time saving and efficient way of growing thin films at room atmosphere. This technique can be scalable to larger area deposition. An attempt is made to investigate the behavior of nebulized spray deposited n-$CdIn_2S_4$ thin film by perusing to properties of n-$CdIn_2S_4$ thin film. The structural, optical, morphological, elemental and electrical conductivity properties of $CdIn_2S_4$ thin film have been reported.

2. MATERIALS AND METHODS

The $CdIn_2S_4$ thin film was prepared by nebulized spray pyrolysis technique. Nebulizer is a sprayer mainly used for curing asthma patients by spraying medicine into the mouth. This technique used the same nebulizer unit to spray mist like particles of solution. A specially designed "Well" shaped oven was fabricated in our laboratory to prepare thin film samples. Well-cleaned and degreased glass substrate was kept inside an oven designed for this technique. High purity $CdCl_2$, $InCl_3.2H_2O$ and thiourea salts were dissolved separately in a solution containing deionized water and isopropyl alcohol in the ratio of 1:2:4 by volume. The molar concentration of $CdCl_2$, $InCl_3$ and thiourea solution was 0.1, 0.2 and 0.4M respectively. Equal volume of these three solutions were mixed and sprayed on to the glass substrate with an area of 7cm x 2.5cm. The substrate temperature was maintained at 300^{o}C. The flow rate of the solution was 1ml/min. The sample was kept on the substrate until it reached the room temperature after the deposition was over.

The structural properties of the film were analyzed by X-Pert Pro x-ray diffractometer (CuKα, λ=1.5404Å) and recorded in 2θ interval from 10^o to 80^o in steps of 0.05^o at room temperature. Surface morphological studies of $CdIn_2S_4$ film were examined with the Scanning electron microscope (SEM) photographs taken with GENISIS model. The surface elemental comparison of the film was made by energy dispersive analysis by x-rays (EDAX) attached to SEM instrument. Optical absorption spectrum was recorded in the wavelength range 300-1100 nm using Hitachy U3410 model double beam spectrophotometer. The electrical conducting properties were analyzed by Hall Effect measurement system by ECOPIA-HMS5000 model.

3. RESULTS AND DISCUSSION

The X-ray diffraction pattern of the nebulized spray pyrolysised $CdIn_2S_4$ thin film on amorphous glass substrate is shown in Fig. 1. The obtained Bragg peaks of the film found at 2θ = 14.15, 23.27, 27.34, 28.51, 33.14, 43.41, 47.58, 59.03, 66.40 and 76.05 correspond to the reflection from (111), (220), (311), (222), (400), (511), (440), (444), (731), (751) crystallographic planes. The prominent Bragg reflection occurring at 2θ = 14.15 along with other peaks confirms the polycrystalline nature of the film and inter planar distance (d) corresponding to this peak is 6.2542Å. Besides, the d-spacing values of other weak peaks were also observed and tabulated as in Table-1. These values can be indexed with a strong preferred orientation along (111) direction in the standard JCPDS data cards 27-0060 and 31-0229. Horiba (1979) also had obtained cubic structured $CdIn_2S_4$ thin film with (111) preferable orientation by vacuum deposited $CdIn_2S_4$ thin film. The lattice parameter found in the present study is a=10.83 Å whereas the reported value is a= 10.84 Å.

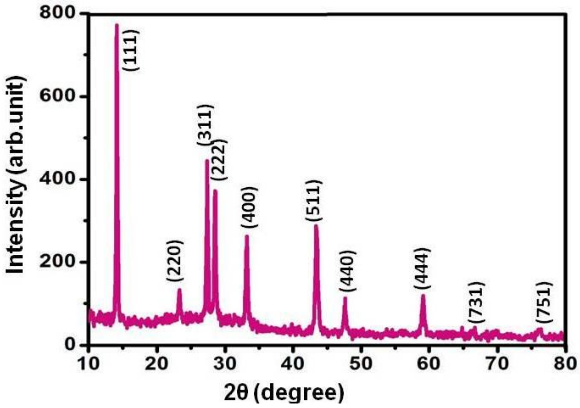

Fig.1.X-ray diffraction pattern of $CdIn_2S_4$ thin film

The average crystalline size (D) of the film is estimated by the Debye's Scherrer equation.

$$D = k\lambda/\beta\cos\theta, \quad \text{(Equation.1)}$$

Where k is the constant, λ is wavelength of x-ray, β is full width at half maximum (FWHM) of the diffracted peak. The number of crystallites per unit area (N) of the samples found using the relation $N=t/D^3$, Where D is the grain size and t is the thickness of the film. The thickness for all the samples was obtained in the range of 515 nm by using stylus profilo meter. The strain (ε) of the film was determined using the formula $\varepsilon_s=\beta\cos\theta/4$. The dislocation density (δ) of the film was determined using the equation $\delta=1/D^2$ lines/unit area.

Table.1.Comparison of d-values and relative intensities with standard data

Observed		JCPDS	
d values (Å)	I/I_0	d values (Å)	(hkl)
6.2542	100	6.2600	111
3.8202	-	3.8300	220
3.2592	-	3.2640	311
3.1280	-	3.1310	222
2.7005	-	2.7040	400
2.0828	-	2.0820	511
1.9096	-	1.9110	440
1.5635	-	1.5620	444
1.4068	-	1.4090	731
1.2505	-	1.2490	751

However, the amount of defects in a crystal could be found by measuring δ value and the corresponding result confirmed that $CdIn_2S_4$ thin film with good crystallanity was formed with fewer amounts of defects. This might be attributed due to the technique used in this work. The average crystalline size of $CdIn_2S_4$ thin film was found to be 53.56 nm. The crystallization levels of the film were good due to their less amount of dislocation density (δ) and lower strain (ε_s) values, which represent the amount of defect in the film. The average dislocation density of the film was calculated as 2.8 x 10^{14} lines/ m^2. The strain of the film was found to be $7x10^{-4}$. The number of crystallites formed by the same sample was calculated to be 2.92 $x10^{15}m^2$.

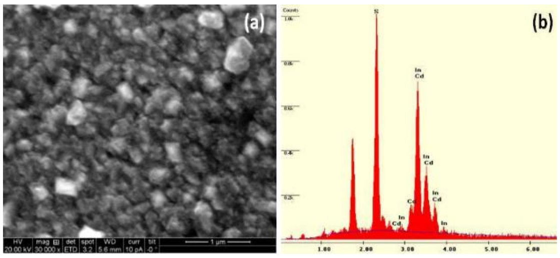

Fig. 2. (a) SEM Photograph and (b) EDAX spectrum of $CdIn_2S_4$ thin film

The scanning electron microscope is an expedient and versatile tool to study the surface morphology of the film. The surface morphology of nebulized spray deposited $CdIn_2S_4$ thin film was studied and analyzed by SEM photograph as shown in Fig. 2(a). The microscope study revealed that uniform distribution of numerous nano sized spherical grains well covered with substrate without any voids, cracks and pinholes. Overgrown grains were observed in some region of the film. The average size of the crystallites was 50-100 nm.

The EDAX spectrum of the $CdIn_2S_4$ film was recorded in the binding energy region of 1.0-7.0 eV as shown in Fig. 2(b). The peaks observed in the spectrum shows the presence of Cd, In and S in the film. The atomic percentage of cadmium, indium and sulfur elements were observed as 12.95%: 34.52%: 52.53%. The deficiency of sulfur might be attributed due to oxidation process happened at deposition temperature. In addition, deficiency of cadmium was also found in the sample.

The optical absorption data of $CdIn_2S_4$ film deposited by nebulized spray pyrolysis technique had been used to evaluate the nature of transition, absorption coefficient and band gap energy involved. The optical absorption spectrum of $CdIn_2S_4$ predicts that this compound absorbs fewer amounts of photons in the higher wavelength region corresponding to the wavelength range 580 nm to 1100nm. Multiple interference effect was predominant in this region due to the low absorption of photon energy. Strong photo absorption was observed in the ultra violet region. The variation of absorption coefficient with wavelength was plotted as shown in Fig.3(a). It is observed that the absorption coefficient decreases exponentially as the wavelength increases from 300-1100 nm.

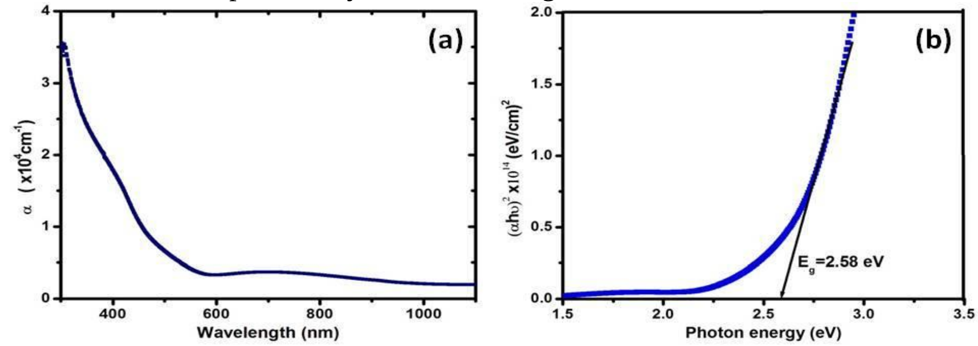

Fig. 3. (a) α versus wavelength and (b) $(\alpha h\upsilon)^2$ versus photon energy of $CdIn_2S_4$ thin film deposited by nebulized spray pyrolysis technique

The absorption coefficient (α) is determined using the given equation

$$\alpha = -\frac{1}{t} \times ln\left(\frac{1}{T}\right) \quad \text{(Equation.2)}$$

Where T is the transmittance and t is film thickness. The optical band gap (E_g) can be determined by the absorption coefficient (α) and photon energy (h υ) by the equation

$$(\alpha\, h\, \upsilon) = A\,(h\upsilon - E_g)^p \quad \text{(Equation.3)}$$

Where A is constant, h is plank's constant, p has ½, 2, 3/2 (or) 3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect transition respectively, υ is the frequency of transmitted light and E_g is optical band gap.

The absorption coefficient is of the order of 10^4 cm^{-1} and n=1/2 supports the direct band gap nature of $CdIn_2S_4$ semiconductor for allowed direct transition. Fig. 3(b) shows a plot between $(\alpha h\upsilon)^2$ and photon energy. The band gap value was determined by extrapolating of the linear region on x-axis. The band gap value of $CdIn_2S_4$ thin film was found to be 2.58eV. Wei Zhang et al [10] had reported the similar band gap value of $CdIn_2S_4$ thin film prepared by hydrothermal method.

The as prepared $CdIn_2S_4$ film exhibited n-type semiconductor nature through Hall Effect measuring instrument showing negative hall coefficient value. This is in good agreement with the reported literature. Very few authors had evaluated the electrical conductivity of cadmium indium sulfide thin films. However nebulized spray deposited film shows least electrical resistivity 8.84 Ω cm. The mobility of the film was found to be 66.2 cm^2/Vs, which helps the transition of electron in the valence band to conduction band easier. Baek (2004) had reported Hall mobility and carrier density of $CdIn_2S_4$ epilayer at 293K such as 219 cm^2/Vs and $9.01x10^{16} cm^{-3}$. The bulk carrier concentration of the as prepared $CdIn_2S_4$ thin film sample was found to be 7.36×10^{18} cm^{-3} that is comparably higher than the reported one. The nebulized spray deposited $CdIn_2S_4$ thin film has shown that a wide band gap material having high conductivity can draw the possible usage of this material in solar cell applications.

4. CONCLUSION

In this study, we showed that $CdIn_2S_4$ film could be successfully deposited by simple and low cost nebulized spray pyrolysis technique. X-ray diffraction studies resulted in film with preferred orientation along the (111) plane with cubic structure. The film obtained in this condition showed the band gap value of 2.58 eV around direct transition, which confirms to the literature data. Spherical nano shaped grains were observed from scanning electron microscope analysis. EDAX studies showed that the elements are in good stoichiometric ratio. The electrical conductivity studies were observed with low resistivity and high bulk carrier concentration. Hence, the film prepared in this technique can play an important role in solar cell applications.

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