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Pr doped copper indium sulphide thin films synthesized by chemical bath deposition method

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Abstract: Work on Proseodymium (Pr) doped copper indium sulphide $CuInS_2$ (CIS) thin film grown by using very economical chemical bath deposition method is reported here. Bath temperature was kept constant at 80^0C. The main aim of this work was to synthesize a good photosensitive semiconducting film for use in photovoltaic devices like solar cells. The SEM images showed that the synthesized film is non-uniform and densely packed with few cracks on the surface. X-ray diffractogram confirmed chalcopyrite and wurtzite phase of $CuInS_2$. Absorption peaks were blue shifted, which may be due to decrease in particle size. It was found that initially transmittance is low in UV region, but increases in visible region. Higher transmittance of 84.4% was obtained between 580-660nm. Thus this film can be used in solar cells. Reflectance is low in the synthesized film showing that the film is anti reflection substance. The Pr doped film possesses larger band gap of 2.3 eV as compared to bulk film of $CuInS_2$, which is due to reduced particle size. Refractive index and extinction coefficient calculated at 820 nm are 1.95 and 0.016 respectively. Pr doped $CuInS_2$ film is quite good photosensitive material.

Keywords: Reflectance; Semiconducting films; TEA; Transmittance

1. Introduction

Chalcopyrite is a copper iron sulfide mineral having chemical formula $CuFeS_2$. In 1954, Goodman and Douglass showed the possibility of semi conductivity in these materials. Thereafter these materials are known as chalcopyrite type semiconductors. Since last two decades, ternary chalcopyrite materials have drawn attention of the researchers worldwide due to their electro-optical properties, which make them to be used to develop photovoltaic system as an alternative energy source. Out of different chalcopyrite semiconductors $CuInS_2$ and $CuInSe_2$ are currently investigated for applications in photovoltaic, solar cells and LED devices [1]. It is known that thin film solar cells are having many advantages than silicon-based solar cells; such as lightweight, low cost, flexible and could be used on the curved surfaces of many buildings and instruments. This makes this as a main and promising development direction of future solar energy application. $CuInS_2$ thin films with chalcopyrite structure are having high absorptive layers. $CuInS_2$ 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]. Further $CuInS_2$ is more environmental friendly material than those containing Se or Cd. Thin films due to their interesting properties like less material requirement and better device performance have been used extensively in photovoltaic devices. Various methods for the synthesis of $CuInS_2$ thin film have been reported including reactive radio frequency magnetron sputtering [3], co-evaporation [4], ion layer gas reaction [5], spray pyrolysis [6] and chemical bath deposition [7,8]. The chemical bath deposition (CBD) method is somewhat simple, inexpensive and highly reproducible technique. By CBD method, the dimensions of the crystallites can be assorted controlling deposition parameters like pH, reaction time, temperature and presence of impurities in the solution [9]. CBD is a method of growing thin film of certain materials on a substrate immersed in an aqueous bath containing appropriate reagents at temperatures ranging from room temperature to 100^0C.Therefore it is intended to synthesize films by CBD technique using appropriate impurities and complexing agents to control reaction rate and to investigate the corresponding changes in structural and optical properties.

2. Experimental

Rare earth element Pr doped $CuInS_2$ thin film was synthesized from a solution of highly pure and analytical reagent grade of $CuCl_2.2H_2O$(99%), $InCl_3$(99%) and thiourea(99.8%) in an alkaline solution of ammonia and double distilled water. Microscopic glass slides were used as substrates. Substrates were cleaned many times in double distilled water, HCl and acetone ultrasonically. The glass slides were kept vertically in a solution bath. For the deposition of CIS:Pr films; 10ml solution of copper chloride{$CuCl_2.2H_2O$(0.1 M)}, 10 ml of Indium chloride{$InCl_3$(0.1M)}, 2ml of triethylamine (TEA),20ml of thiourea (0.1M) were taken in a beaker in which 10ml of ammonia was added for the maintaining pH of the solution. Then 0.001 M of Pr impurity was added with 8ml concentration to the basic solution of $CuInS_2$. Film deposition was the consequence of precipitation followed by condensation on glass substrates. Thin films were prepared at 80^0C for 1 hour. The prepared films were homogeneous, well adhered to the glass substrate.

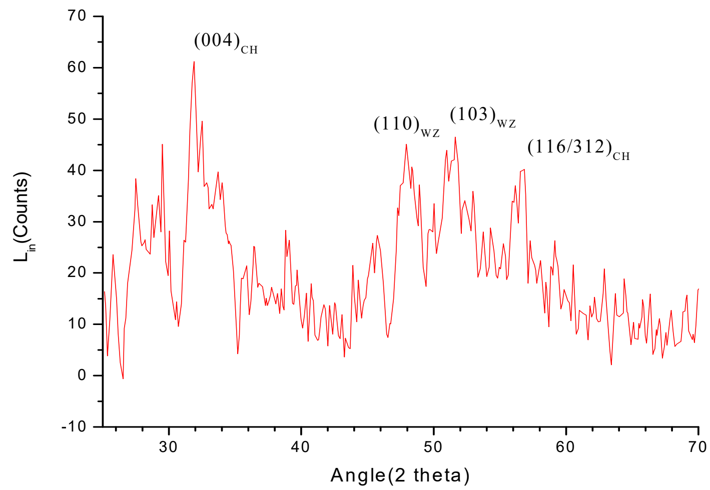


Fig .1 XRD of CIS:Pr doped thin film

3. Results and discussion

3.1. Structural Study

The X-ray diffraction patterns of the CIS films doped with Pr prepared on glass substrates is shown in Fig. 1. It is found that the film consists of peaks corresponding to chalcopyrite and wurtzite phase of $CuInS_2$. This is called polytypism. No peaks corresponding to Pr is observed which shows that doping of rare earth element does not change the structure. The relationship between grain size and line broadening can be described by Scherrer's formula –

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

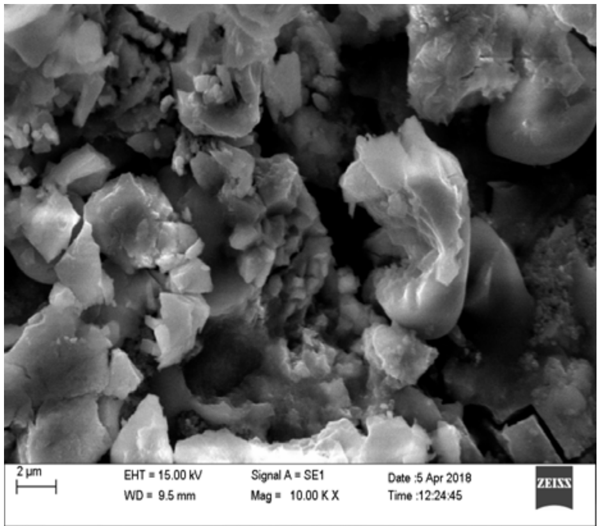
where λ represents the wavelength of X-ray light, β, and θ are the full width at half maximum (FWHM) of a peak, and the Bragg's angle respectively. The grain size 'D', the strain value 'ε' and the dislocation density 'δ' is calculated corresponding to the prominent peak $(004)_{CH}$. These values are summarized in Table 1.

3.2 Surface Study

The surface morphology of $CuInS_2$: Pr thin film was analyzed using scanning electron microscopy technique at 10KX and 50KX magnification and shown in Fig.2. It is clear from the SEM images that the film is non uniform, densely packed and have few very small pinholes or cracks. The synthesized film is highly agglomerated.

3.3 Optical Study

In Fig.3 absorption spectra is shown. The absorbance spectrum shows a sharp increase in absorption at wavelength near to the absorption edge. The absorption peaks are blue shifted in Pr doped CIS films as compared to that of the bulk CIS (band gap = 1.53eV, λ_{max}= 810nm). The reason of blue shift in absorption is due to decrease in particle size in comparison to the bulk material. With decreasing size of the particle, binding energy of exciton increases because of the increasing columbic overlap enforced by spatial localization of the wave functions [10].



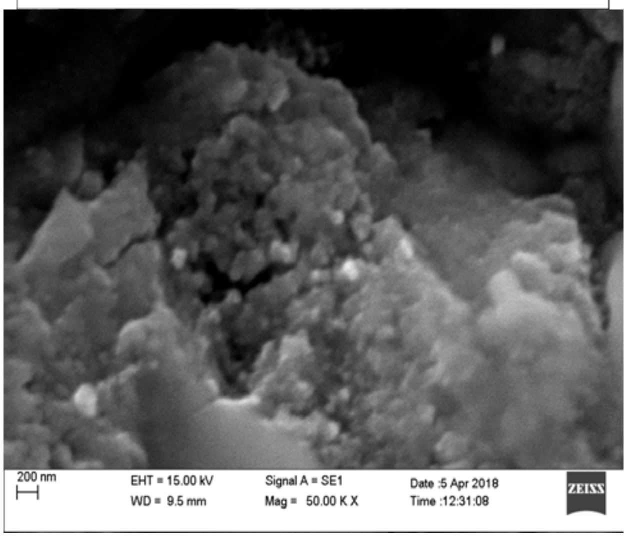


Fig.2 SEM images of CIS:Pr doped thin film

In Fig.4 transmittance spectra is shown in the wavelength range 320-900nm. The film has 84.4% transmittance between 580-660nm. Thus it is having good scope to be used in solar cells. The band gap energy (Eg) and absorption coefficient (α) of the synthesized film is determined from the absorption data. The absorption coefficient (α) can be calculated by

$$\alpha = \frac{c\,(h\upsilon - Eg)^{1/2}}{h\upsilon} \quad \text{--------------------- (2)}$$

where c is a constant. The value of absorption coefficient obtained is 10^5 cm^{-1} in the visible region. The high value of absorption coefficient opens a door for the production of high absorptive layers of solar cell. In order to get the value of band gap a graph is plotted between $(\alpha h\nu)^2$ and photon energy (hν) in Fig.5. As $CuInS_2$ is a direct band gap material, the extrapolation will give the value of band gap. The band gap obtained for Pr doped film is 2.3eV. The band gap of undoped CIS film obtained is 2.19eV as discussed in earlier paper [11]. The larger band gap is due to decreasing particle size. The levels corresponding to valence band are shifted to lower energy side but levels of conduction band are shifted to higher energy side. Using the hyperbolic band model, we have studied the optical properties of synthesized $CuInS_2$ thin film. Average particle size has been calculated by using equation [12].

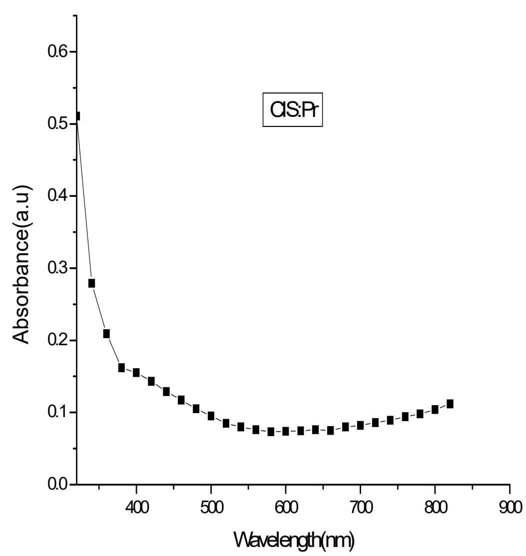
$$E^2{}_{gn} = [E^2{}_{gb} + \frac{2\hbar^2}{m{*}R^2}\ E_{gb}\ \pi 2] \quad \text{--------------- (3)}$$

where m* is the effective mass of the electron, E_{gn} and E_{gb} are the band gap of nano and bulk sample. The calculated value is 1.25nm. The refractive index and extinction coefficient of the film has been calculated for λ=820 nm by the formula [13]

$$n = \frac{(1+R)}{(1-R)} + \sqrt{\frac{4R}{(1-R)^2}} - k^2 \quad \text{------------------------- (4)}$$

$$K = \frac{\propto\lambda}{4\pi} \quad \text{----------------- (5)}$$

and listed in Table.3



3. **Fig.3 Absorbance spectra of CIS:Pr doped film**

Conclusions

The film of $CuInS_2$ with rare earth element Proseodymium (Pr) has been synthesized successfully by chemical bath deposition method on the microscopic glass slides. The synthesized film is having wurtzite structure with multiphase. The morphology of the synthesized film is non uniform, densely packed with few cracks. Agglomeration of particles could be viewed clearly in SEM images. The transmittance of the deposited film is high

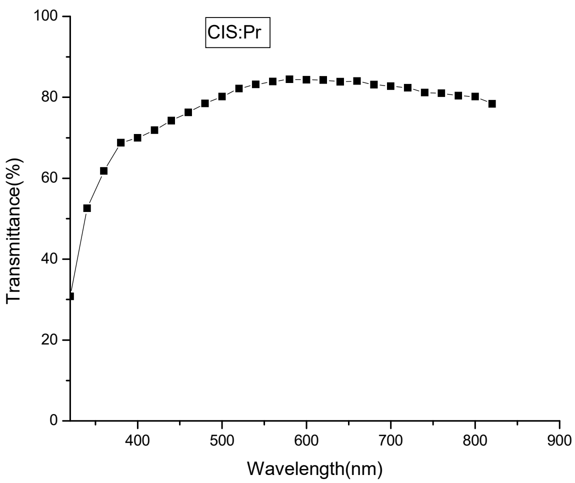


Fig.4 Transmittance spectra of CIS:Pr doped film

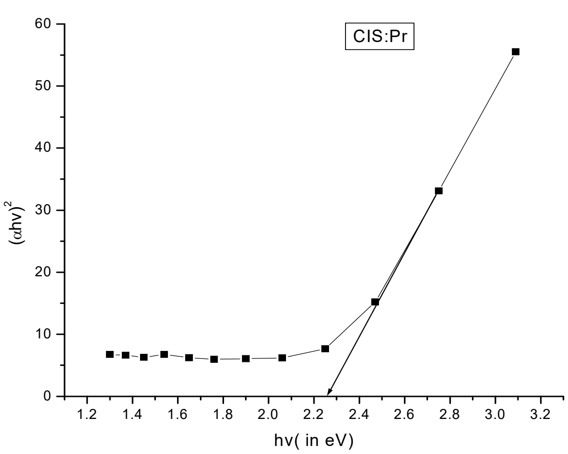


Fig.5 Plot between $(\alpha h\nu)^2$ and hν

~84.4% between 580-660nm. Thus this material has good scope to be used in solar cells. The absorbance spectrum shows a steep increase in absorption at wavelength near to the absorption edge. The absorption peaks are blue shifted. This blue shift in absorption is due to decrease in particle size in comparison to the bulk material. The band gap of the film obtained is 2.3eV.

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