Structural and optical properties of Pr doped CuInS$_2$ thin films synthesized by chemical bath deposition

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Abstract. The Pr doped CuInS$_2$ thin films have been prepared by chemically bath deposition technique at 80°C temperature. The semiconducting films are grown in bath containing aqueous solution of copper (II) chloride dihydrate, Indium (III) chloride, thiourea, TEA, ammonia (25%). Pr is used as the doping element. Chloride dehydrates is used for the copper ion source, Indium chloride for indium ion source and thiourea for sulphur ion source, TEA is a complexing agent and ammonia maintains the pH. The SEM Studies of Pr doped CuInS$_2$ films show that at lower volume polyhedral shaped particle appears on the surface. No voids are seen. But at higher volume of Pr; voids are seen on the surface. Particle looks like accumulated woolen balls or cubic like grains. Agglomeration of particle increases with volume and hence particle size also increases. In the XRD of prepared sample characteristic peaks of chalcopyrite phase appears between (24°- 80°) in all the films. Hall measurement shows that resistivity of Pr (6ml) doped film is very high. The conductivity of all doped films is higher than undoped film. In general, increased doping will leads to increased conductivity. In the Photoluminescence study the emission peak appears at wavelength 575nm, 550nm and 525nm wavelength. High transmittance, low reflectance found in the visible region in the entire prepared sample. The absorption peaks fall in the visible region. High Photocurrent is found, and in dark current study the linear behavior between voltage and current are seen. Quite good photosensitivity is observed in Pr doped CuInS$_2$ films.

1. Introduction
In 1953 Hahn and co-workers amalgamated a bunch of substances which reveal chalcopyrite structure with a composition of I−III−VI$_2$. In 1954, Goodman and Douglass showed the possibility of semiconductivity in such materials. Henceforth these substances are recognized 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$_2$ both presently probed in utilization in devices such as light emitting diodes, photovoltaic and solar cells etc. [1]. CuInS$_2$ thin films with chalcopyrite structure are having high scope as absorptive layers. Many exorbitant physical and chemical characteristics shown by CuInS$_2$ thin films like high value of coefficient of absorption $10^5$ cm$^{-1}$ within perceptible spectral range, more forbearance for occurrence of defects and a direct band gap of 1.5eV. Also in CuInS$_2$ the conversion efficiency of solar energy is most favorable to be used as photovoltaic devices, likelihood 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 [3]. For deposition of CuInS$_2$ thin film large number of techniques are there. For example; sol-gel [4], spray pyrolysis [5], d.c. magnetron sputtering [6], ILGAR [7], chemical bath deposition [8] etc. Various researchers have used chemical bath deposition (CBD) method for depositing different thin films. The reason is that it is the simplest method which requires only solution containers and mounting devices which make it economical. Large area processing is possible with this method. Also by varying the deposition time the thickness of the film can be controlled. With this method we can produce homogeneous, adherent and unbreakable films with good reproducibility. Therefore it is planned to synthesis films by CBD technique using appropriate fluxes, impurities and complexing agents to control reaction rate and hence to investigate the corresponding changes in structural and optical properties.

2. Experimental details

The solution of copper (II) chloride dihydrate [CuCl$_2$.2H$_2$O (0.5M)] and Indium (III) chloride [InCl$_3$ (0.5M)] were taken in a beaker. Both the solutions were mixed uniformly by stirring. Then triethanolamine (TEA) and ammonia (25%) were added into the beaker. Then sulphur source thiourea SC(NH$_2$)$_2$ was added to the solution. All AR grade 99.9% pure chemicals were used for preparing the solution. Stirring was done for 10 minutes in order to obtain uniform and adherent film. The cleaned microscopic glass substrates were dipped vertically into the solution. The beaker is then kept inside the liquid bath at 80$^\circ$C temperature for 1 hour. Definite volumes of 0.01M solutions of cadmium chloride (CdCl$_2$) and praseodymium nitrate [Pr(NO$_3$)$_3$] were added to the original solution to carry out sensitization and then the depositions were made. After 1 hour, the substrates were taken out and washed thoroughly with double distilled water and kept for drying at room temperature for 3-4 h. The synthesized films were homogeneous and well adhered to the substrate.

3. Results and discussion

The XRD of CIS:Pr films with varying volume of praseodymium were shown in figures 1, 2 and 3. Film with Pr(4ml) consist of very few peaks of chalcopyrite structure. Peaks corresponding to (004) and (116/312) were observed. No peak corresponding to wurtzite phase was observed. Two additional peaks for (022) plane and (331) plane was observed for Cu$_{1.8}$S$_1$ and CuIn$_3$ respectively. Less number of peaks reveals poor crystallinity. Also less number of peaks means that the crystal is oriented in preferred direction. Similarly in the XRD of CIS film doped with Pr (6ml) there were only two main characteristic peak (112) and (004) for chalcopyrite phase appeared with less intensity. In addition to this; one peak corresponding to wurtzite phase (010) also appeared. Thus this film shows polytypic behavior. X-ray diffractograms of CIS:Pr(8ml) doped film consist of very high intense characteristic peaks (112),(121),(123), (116/312) and (134) corresponding to chalcopyrite phase (JCPDS-98-062-8051). No peak corresponding to wurtzite was appeared. Thus the synthesized film is highly crystalline in nature as more characteristic peaks were appeared with chalcopyrite structure. Additional peak corresponding to (022), (004) and (165) plane was observed for Cu$_{1.8}$S$_1$, Cu$_2$S$_1$ and In$_2$S$_1$ respectively. Thus the synthesized film was multiphase. At last we can conclude that doping of Pr affects the crystallinity of the sample and crystallinity increases with the increase of volume of doping element Pr.
Figure 1. X-ray diffractogram of Praseodymium (4ml) doped CuInS$_2$ film.

Figure 2. X-ray diffractogram of Praseodymium (4ml) doped CuInS$_2$ film.

In the dark current study the synthesized film is kept in dark region that means there is no light comes near to the prepared samples. The prepared thin films are good for conductivity. The concept of dark current in the semiconducting thin films is the movement of thermally excited charge carriers inside the material. Some of the charge carriers jump into the conduction band which is responsible for the conductivity. The dark current appears for limited voltage. We have observed the dark current appears in nano scale range.
It is clear from the figure that dark current varies linearly with applied voltage. This linear behavior shows that the electrode used is of ohmic type. In figure 4 rise and decay curves of Praseodymium (Pr) doped CuInS$_2$ films are shown. As volume of doping element increases the photo current also increases.

Figure 5 shows the rise and decay curves for CIS:Pr films with different concentration. The rise and decay curve looks identical in all the sample. When the radiation fall on the prepared thin film material the electron hole pair (photo carriers) becomes originate and those are responsible for the photocurrent.
In the present curves fast rise in the beginning followed by saturation. The increase in photocurrent is due to the generation of photo carriers. The slowly increasing part is when recombination becomes dominant. The decay part is in the form of exponential equation. The ratio of photocurrent to dark current is found to be the order of $10^3$ which is quite good. The mobility of charge carrier increases with increasing the volume of doping element and it is due to the inter gains barrier height is lowered. The production of photocurrent increases when the volume of Pr increases. Thus more charge carriers are generated by the rare earth element. The role of rare earth element is to provide a platform to the charge carriers to come in the conduction band so as to give the conductivity. Decay rates appeared to be slower in the reported films.

The lifetime of the charge carriers are calculated by using the relation

$$\tau = \Delta \sigma st / \tan \delta$$ (1)

where $\sigma$ is the static photocurrent and $\tan \delta$ is the slope of the initial state of the decay curve. The mobility is calculated by using the relation

$$G = \frac{\tau \mu V}{L^2}$$ (2)

Where $G$ is photoconductivity gain, $V$ is applied voltage between the electrodes and $L$ is the distance between electrodes.

![Figure 5. Rise and decay curve of various Praseodymium doped CuInS$_2$ film](image-url)
Table 1. Value of Dark current, Photocurrent, Life time, Mobility and Current gain of undoped and various Pr doped CuInS$_2$ thin films at V=15 volt.

| Sample          | $I_{dc}$ (μA) | $I_{pc}$ (μA) | Gain $\times 10^3$ | $\tau$ (in sec) | $\mu$ (cm$^2$V$^{-1}$s$^{-1}$) |
|-----------------|---------------|---------------|--------------------|------------------|-------------------------------|
| Undoped CIS     | 0.007         | 22.5          | 3.2                | 59.1             | 1.44                          |
| CIS: Pr(4ml)    | 0.005         | 31.5          | 5.7                | 209.0            | 0.72                          |
| CIS: Pr(6ml)    | 0.008         | 52.8          | 6.6                | 171.8            | 1.02                          |
| CIS: Pr(8ml)    | 0.007         | 44.1          | 6.3                | 72.9             | 2.30                          |

To show case the effect of doping element on morphology of the film; SEM images of the CuInS$_2$ films were taken. Figure 6 is the SEM micrograph of CIS: Pr (4ml) film at magnifications 2.5KX and 5KX. The surface of the film is non uniform with polyhedral shaped particles on the surface. The film is amorphous in nature. No voids are seen. But at higher volume (6ml) of Pr voids are seen on the surface (Figure 7). More agglomeration of particles is seen. Particle looks like accumulated woolen balls or cubic like grains. Film morphology shows kind of Pin holes or cracks with 8ml volume of Pr (Figure 8). Agglomeration of particle increases with volume and hence particle size also increases. The grain size calculated for undoped film was 123nm and for doped film (Pr) was 100nm. Thus we can infer that grain size decreases with doping which confirms that films were nano sized.

The study of optical properties of CuInS$_2$ thin films is having special implication in the field of science, technology and industry for developing new optical devices. Optical absorption study provides useful information which is helpful to analyze band gap of thin film which are directly related to particle size. As we know that band gap of thin films is important for designing the photovoltaic cells. In figure 9 the absorption spectra of undoped film at various temperature is shown. In figure 10 absorption spectra of Pr doped films are shown. When volume of doping element increases the spectra is red shifted towards higher wavelength side. The band gap energy ($E_g$) & absorption coefficient ($\alpha$) of synthesized CuInS$_2$ film is calculated from the absorption statistics. The coefficient of absorption ($\alpha$) can be computed by using relation [9].

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

Figure 6. SEM of CIS: Pr (4ml) at magnifications 2.5KX and 5KX.
The value of absorption coefficient in all the films is found to be in the range of ten to the power five in the observable range (400-700nm). High coefficient of absorption clearly indicates that synthesized films are important for the fabrication of high absorptive layers of solar cell. For calculating band gap of films; a graph is plotted between \((\alpha h\nu)^2\) and \((h\nu)\) known as Tauc’s plot. The extrapolation of nonlinear curve between \((\alpha h\nu)^2\) and \((h\nu)\) will lead to the value of \(E_g\) of \(\text{CuInS}_2\) thin films[10,11,12]. Using the hyperbolic band model the optical properties of \(\text{CuInS}_2\) thin film was studied. Average particle size has been calculated by using equation (4).

\[
E_g^2_{\text{gn}} = [E_g^2_{\text{gb}} + \frac{2\hbar^2}{m^*R^2} E_g \pi^2]
\]  

(4)

where \(m^*\) = effective mass of the electron, \(E_{\text{gn}}\) & \(E_{\text{gb}}\) are optical band gap of nano crystalline and bulk sample. The particle size is in nm range. Tauc’s plot for Pr doped films is shown in figure 1. In all undoped and rare earth doped \(\text{CuInS}_2\) thin films transmission spectra are recorded between 300-900nm.
ranges shown in figure 12. In Pr (6ml) CuInS\textsubscript{2} thin films very high value of transmittance ~90\% is obtained in the visible range. Thus these materials are having good scope to be used in solar cells.

**Figure 9.** Absorption Spectra of Undoped CuInS\textsubscript{2} films at various temperatures.

**Figure 10.** Absorption Spectra of various Praseodymium doped CuInS\textsubscript{2} film.
Hall measurement is the significant technique to get the concentration of charge carrier, mobility and resistivity of a sample which is conductive. In figure 13 and figure 14 graph between Hall voltage and current for 6ml and 8ml doped films are shown. It is clear that as volume of Pr increases then resistivity decreases. It was found that the mobility reduces with the increasing volume of doping element. The reason may be the increased grain size. The resistivity of CIS: CdCl₂, Pr (6ml) is very high. The conductivity of all doped films is higher than undoped film. In general, increased doping will leads to increased conductivity. The reason is higher value of carrier concentration.

**Figure 11.** Graph between $(\alpha h\nu)^2$ and $(h\nu)$ of various Praseodymium doped CuInS₂ films.

**Figure 12.** Transmittance spectrum of various Praseodymium doped CuInS₂ film.
Table 2. Peak position, band gap and particle size of undoped and Pr doped CuInS₂ thin films

| Sample              | Peak Position | Optical band gap (eV) | Emission Band energy (eV) | Particle Size (nm) |
|---------------------|---------------|-----------------------|--------------------------|--------------------|
| Undoped CIS        | 580nm         | 2.19eV                | 2.12eV                   | 16.71nm            |
| CIS: Pr(4ml)       | 575nm         | 2.54eV                | 2.16eV                   | 13.51nm            |
| CIS: Pr(6ml)       | 550nm         | 2.48eV                | 2.25eV                   | 13.93nm            |
| CIS: Pr(8ml)       | 525nm         | 2.38eV                | 2.36eV                   | 14.72nm            |

Figure 13. Graph between Hall voltage and current for CIS: Pr (6ml) doped film.

Table 3. Hall measurement results of various undoped and doped CuInS₂ thin films.

| Sample                | V_H/I_H (Ω) | R_H (cm³/c) | Type of carriers | Concentration of charge carrier [cm⁻³] | σ at RT (Ω-cm⁻¹) | Hall mobility [cm²/Vs] | ρ[Ω·cm] |
|-----------------------|-------------|-------------|------------------|----------------------------------------|-----------------|------------------------|--------|
| CIS at 80°C           | 140         | 89.74       | Holes            | 6.9×10¹⁶                                | 0.016           | 1.44                   | 62.5   |
| CIS: CdCl₃,Pr(6ml)    | 200         | 102         | Holes            | 6.1×10¹⁶                                | 0.008           | 0.88                   | 125    |
| CIS: CdCl₃,Pr(8ml)    | 266         | 134.6       | Holes            | 4.6×10¹⁶                                | 0.017           | 2.30                   | 58.8   |

Room temperature (RT) photoluminescence emission spectrum of CuInS₂ films are taken by exciting the samples at a wavelength of 450 nm. PL spectra were recorded between 400-800 nm. In figure15 PL
emission spectrum of various Praseodymiums doped CuInS\textsubscript{2} film is shown. Blue shift occurs in the film which is may be due to quantum confinement appearing as a result of modified surface to volume ratio. Quantum size effect or confinement effects are followed by quantization of electronic energy levels that is molecule like energy levels even in the crystals and not exhibiting distinct band type structure. The emission in this case is evident of such structure in the prepared film. Such band edge luminescence can be caused by the recombination of excitons and or shallowly trapped electron–hole pairs.

![Graph between Hall voltage and current for CIS: Pr (8ml) doped film](image)

**Figure 14.** Graph between Hall voltage and current for CIS: Pr (8ml) doped film

The peak sharpness in terms of intensity increases by increasing amount of rare earth doping element. The emission peak appears at wavelength 575nm, 550nm and 525nm in 4ml, 6ml and 8ml doped Pr films. Band gap of doped films are higher than undoped film. The observation shows that when amount of doping element increases the band gap also increases. This result is expected at higher volume because coalescence of particle is there. The particle size falls in nm range. In Table 2 peak position, band gaps and particle size of undoped and Pr doped CuInS\textsubscript{2} films are given. Higher luminescent intensities were observed in nano range particles than bulk material. The reason may be due to more defect states and high value of surface to volume ratio. This will make availability of more carriers for photoluminescence.
4. Conclusions
The Pr doped CuInS$_2$ thin films have been prepared successfully by chemically bath deposition technique at 80°C temperature. The SEM Studies show that at lower volume polyhedral shaped particle appears on the surface. No voids are seen. But at higher volume of Pr; voids are seen on the surface. Agglomeration of particle increases with volume and hence particle size also increases. In the XRD of prepared sample characteristic peaks of chalcopyrite phase appears between (24° - 80°) in all the films. High transmittance, low reflectance found in the visible region in the entire prepared sample. The absorption peaks fall in the visible region. High Photoconductive gain of $10^3$ is found. Quite good photosensitivity is observed in Pr doped CuInS$_2$ films. We have observed that the dark current study show linear behavior and plot a curve between resistance and the voltage which is also found in linear manner in doped and undoped film. Hall measurement shows that all the films are of p-type. The conductivity of all doped films is higher than undoped film.

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