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OPTICAL PROPERTIES OF CHEMICAL BATH DEPOSITED $CuInS_2$ THIN FILMS WITH RARE DOPANT

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Abstract : $CuInS_2$ thin films with various rare earth dopant as well as flux added and undoped films were grown on cleaned glass substrates at 80^0C by chemical bath method. Transmittance and absorbance spectra of various films were recorded in the observable region between 300 nm to 900 nm. Optical constants such as E_g, k, n, ε_1 and ε_2 were estimated from these spectra. Except undoped film other film shows high transmittance (~ 60 - 82 %), low absorbance in the observable region (500 - 900 nm). The optical band gap energy was found to be in the range 2.19 –3.5 eV for undoped and rare earth doped films respectively.The value of α obtained in the observable range (300-700nm) is very high(~10^4) in all films. This high value indicates that synthesized films are of paramount interest for the fabrication of high absorptive layers of solar cells.

***Index Terms* - $CuInS_2$, Chemical bath, Observable region, Rare earth, Dopant.**

I. INTRODUCTION

The emerging trends involved in photovoltaic aims to forage for solutions that permits fabrication of high efficient photovoltaic devices at very reasonable price. The I-III-VI group materials well known as chalcopyrites such as $Cu(In,Ga)(S,Se)_2$ (CIGS) or (CIS) are semiconductors which proves as paramount compound of thin film industry which can bring revolutions to the photovoltaics in terms of supply of electrical power. Research on these materials can take the photovoltaic industry to the next level of success.This fascinating material has received noticeable attention due to its specific properties such as- (i) >20% efficiency in laboratory(ii) High adaptability for manufacturing(iii)Easily grown on any substrate. The remarkable energy conversion efficiency makes them one of the most important materials for thin-film photovoltaic industry. One of the most promising material for hetero-junction thin film solar cells is copper indium disulphide ($CuInS_2$). Direct band gap $CuInS_2$ (E_g = 1.5 eV) has been used as a light absorbent material together with different semiconductors such as copper indium disulfide/selenide ($CuInS_2/Se_2$–CIS/Se), and copper indium gallium sulfide/selenide ($Cu(In,Ga)S_2/Se_2$ (CIGS/Se), and technology is being developed to enhance efficiency by reducing costs and toxicity, etc. Theoretically efficiency about 20–25 % has been achieved but experimentally the value of this solar energy conversion efficiency is very less and it is ~13% [1]. In order to built opto-electronic devices; CIS thin films needs to have extensive optical characteristics. There are numerous methods or techniques for the deposition of $CuInS_2$ thin films. Two methods are there such as chemical methods and physical methods for growing the thin films. Chemical method includes chemical bath deposition (CBD) [2,3], electrodeposition [4,5], SILAR [6,7], spray pyrolysis [8,9] as well as physical method includes sputtering [10,11], molecular beam epitaxy [12,13], co-evaporation [14,15], chemical vapor deposition (CVD) [16,17]. Many researchers have attempted the deposition of CIS films by CBD and reported characteristic studies of these films [18,19,20], but very few papers are there where optical properties with rare earth dopant have been observed extensively. In this paper CBD method has been picked for deposition of $CuInS_2$ thin films as it is one of the easiest method as compared to other new and sophisticated methods. Here, we have reported a detailed study on the optical properties of various doped, undoped and flux added $CuInS_2$ thin films because by knowing the optical properties of these films we can explore many of their scientific, technological as well as industrial applications used in the field of optoelectronic devices particularly photovoltaic cells.

II. EXPERIMENTAL METHODS

$CuInS_2$ films doped with different rare earth elements were prepared on microscopic glass substrates of dimension 24mm×75mm by CBD method. Prior to use, substrates were rinsed many times by regular detergent. Then after cleaned with acetone and deionised water. In a beaker we have mixed solutions of $CuCl_2.2H_2O$ (0.1M), $InCl_3$ (0.1M), TEA and ammonia (25%) in an appropriate proportion.The colour of this mixed solution was turbid. Subsequently thiourea was added as a sulphur source to the same solution. With the help of magnetic stirrer stirring upto10min has been provided. The immaculate glass slides were vertically dipped into the liquid solution. TEA works as a complexing agent and ammonia maintains the pH of the liquid bath. The pH of the solution bath was ~ 9.5. The major role of complexing agent is uniform growth of thin films by reducing the quantity of free metal ions in the films. Now 0.01 M flux $CdCl_2$, 0.01M Samarium nitrate,0.01M Holmium nitrate and 0.01M Praseodymium nitrate were also added as an impurity to the solution for growing the doped films of $CuInS_2$. In presence of flux inclusion of rare earth dopants are more effective. Besides that it is helpful to increase the crystallinity. We have also grown films with only flux $CdCl_2$. The temperature of the liquid bath was 80^0C and it remains constant for all deposited films. Films were kept into the solution bath for 1 hour and then films were taken out from the solution bath and thoroughly washed with deionised water and dried at room temperature for 3-4 hours. The deposition is the consequence of precipitation followed by condensation. The slow reaction occurs between ions. Cu^+, In^+ and S^- ions are released from their complexes very slowly, according to the given steps [21].

$$CuCl_2+NH_3 \rightarrow [Cu\ (NH_3)_4]^{2+} \qquad (1)$$
$$InCl_3+TEA \rightarrow [In\ (TEA)]^{2+} \qquad (2)$$
$$CS(NH_2)_2+OH^- \rightarrow CH_2N_2+H_2O+HS^- \qquad (3)$$
$$HS^-+OH^- \rightarrow S^{2-}+H_2O \qquad (4)$$

The overall reaction is given here

$$[Cu\ (NH_3)_4]^{2+}+ [In\ (TEA)]^{2+}+S^{2-} \rightarrow CuInS_2+solution \qquad (5)$$

The film thickness was measured by using gravimetric method and by taking density same as that of the bulk (4.739 g/cm3). Optical absorption and transmission spectra have been recorded by Elico SL-210 double beam UV-VIS spectrophotometer in the ultraviolet (UV)/ visible region up to 900 nm.

III.RESULTS and DISCUSSIONS

Figure 1 shows the optical transmission spectra of undoped, flux added and different rare earth doped CIS thin films. $CdCl_2$ and rare earth doped film shows 60-82% transmission for wavelengths longer than 500 nm. The transmittance of Ho doped film is very high (>80%) in the visible range as compare to flux added and other rare earth doped films. The reason may be changes in the structure of the film and reduction of film thickness [19]. This feature increases the probability of such type of films to be used in solar cells. Wave-like pattern appears in transmission curves because of interference of films.

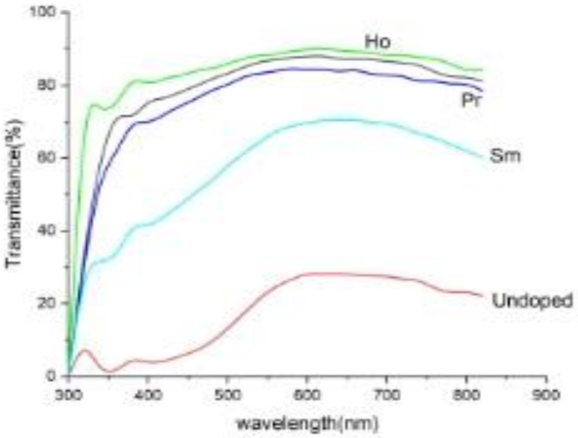

Figure 1. Transmittance spectra of various CIS films

The absorbance spectra of various $CuInS_2$ films are shown in figure 2. We can see clearly from the figure that initially absorption decreases in the visible region and again it starts increasing a little bit above 700nm. High absorption has been observed in undoped film (~1.4). All spectra appears to be shifted towards lower wavelength side as compare to that of bulk CIS whose band gap is 1.53eV at wavelength= 810nm. This Blue shift in absorption indicates decrease in particle size. The coefficient of absorption (α) has been calculated by using relation (6)

$$\alpha= \frac{c(\hbar - E_g)^{1/2}}{\hbar} \qquad (6)$$

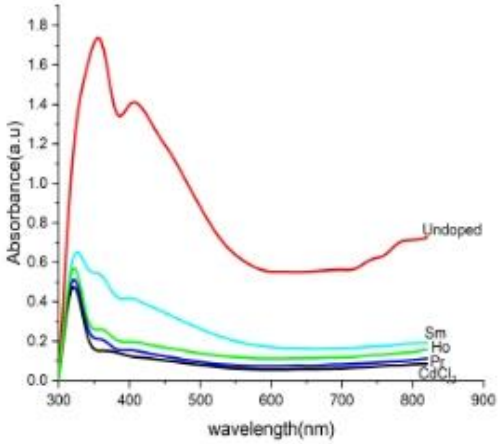

Figure 2. Absorbance spectra of various CIS films

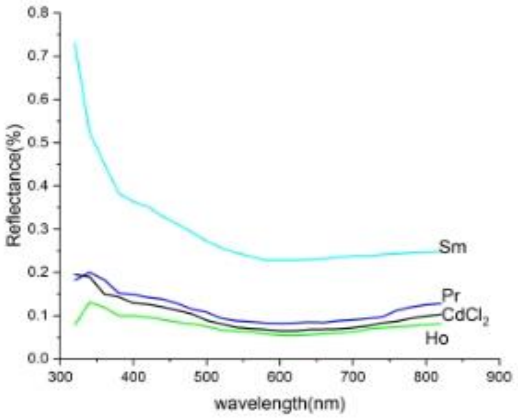

Figure 3. Reflectance spectra of various CIS films

In figure 3 reflectance spectra of different $CuInS_2$ films are presented. All graph shows the same tendency. As wavelength increases the value of reflectance decreases in the observable region(300-700nm). The value of α obtained in the observable range is very high in all doped films. This high value indicates that grown films are of paramount interest for the fabrication of high absorptive layers of solar cells.The optical band gap was evaluated by the Tauc method; the optical absorbance region defined according to the following equation [22]

$$(\alpha \hbar)^{1/n} = A(h\nu - E_g) \tag{7}$$

Here A is a constant, E_g is bandgap and n is a constant which denominate the type of transition. We can find the type of transition by plotting a graph between $(\alpha h\nu)^2$ and $h\nu$ as shown in figure 4.

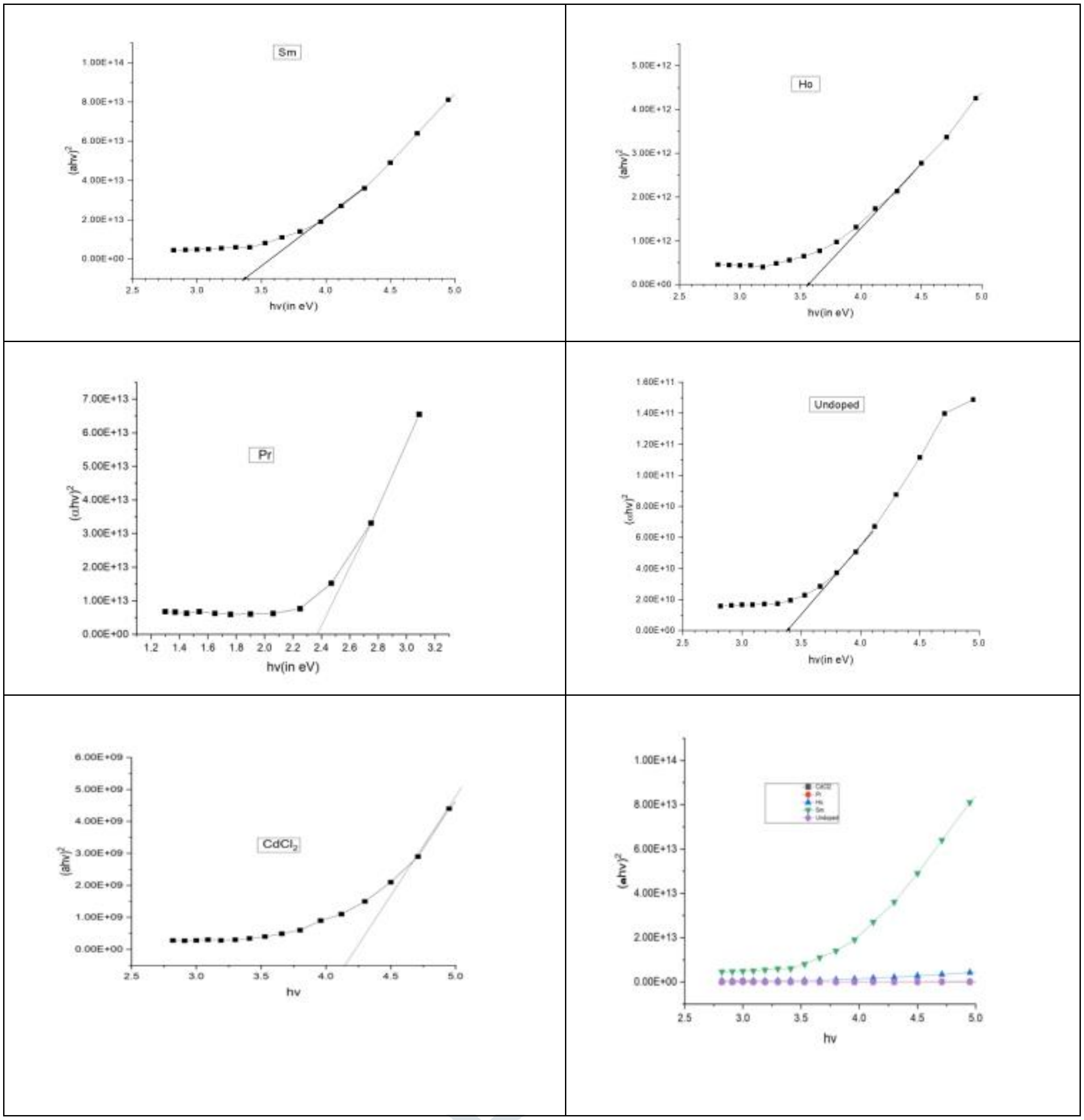

Figure 4. Tauc's Plot of various CIS films

The transition is a direct transition because the graph is linear. For an allowed direct transition the value of n=1/2. The extrapolation of Tauc's plot will provide the band gap of $CuInS_2$ thin films[23,24,25]. The band gap of undoped and rare earth doped CIS thin films are in the range 2.19 – 3.5 eV and is tabulated in the Table.1. The band gaps are relatively higher than band gap of bulk CIS (1.5eV). Band gap increases for rare earth doped and $CdCl_2$ added films as compared to undoped films.This increase in optical band gap may be ascribed to the the secondary phase which could have increased the density of localized states in the band gap.

We have calculated refractive index of deposited films to get information about film density, speed of light and cavities in the films. The refractive index (n) has been calculated by using relation (8)

$$n = \frac{1+R}{1-R} + \left[\frac{4R}{(1-R)^2} - k^2\right]^{1/2} \qquad (8)$$

Here R is reflectivity. Figure 6 represents the changes in the values of n with the wavelength (λ). It is observed that n decreases with increasing value of λ upto 550 nanometre and then the value of n increases. The value of n is dependable on material polarization. As polarization increases velocity of light decreases and consequently n changes. Polarization is depending on crystalline and grain size. Optimum value of n is obtained for Sm doped CIS film and this is equal to 2.6.

Average particle size has been calculated by using equation (9)

$$E^2_{gn} = E^2_{gb} + \frac{2\hbar^2}{m*+R^2} E_{gb}\pi^2 \qquad (9)$$

here m* = effective mass of the electron, E_{gn} & E_{gb} are optical band gap of nano crystalline and bulk sample. The calculated particle size is in nm range.

In order to compute the light loss due to scattering and absorption per unit volume of penetrating medium the extinction coefficient has been calculated by using the following relation [26]

$$k = \frac{\alpha\lambda}{4\pi} \qquad (10)$$

where λ is the wavelength of light. A graph for k vs. λ is shown in figure 5. From this graph we can see that behavior of extinction coefficient (k) is not systematic. In almost all the films the value of k decreases with increasing of λ till 550nm.This verifies that with increasing wavelength there is a decrease in loss of light by scattering as well as by absorbance.

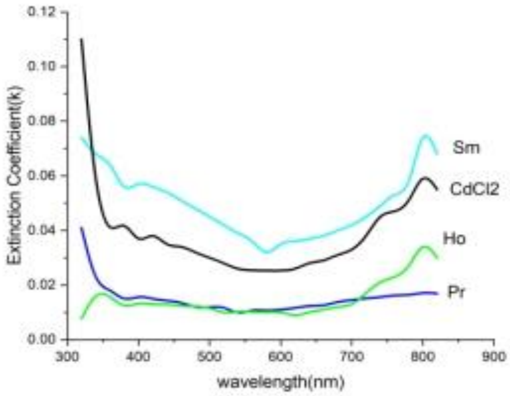

Figure 5. Extinction coefficient vs wavelength graph

Real and imaginary parts of dielectric constants were determined using the following equations [27]

$$\varepsilon_1 = n^2 - k^2 \qquad (11)$$

$$\varepsilon_2 = 2nk \qquad (12)$$

Figure 7 and figure 8 represents the variation of (ε_1) and (ε_2) with wavelength which are real and imaginary dielectric constants respectively. It is clearly evident from figure 7 that the three curves corresponding to CIS:Sm, CIS:Pr and CIS:$CdCl_2$ intersects at a maximum value of 6.4 at wavelength 350nm.The real part of dielectric constant provides information about the polarizability of matter. From figure 8 we can see that behavior of ε_2 is similar to that of k.

Sample	(n)	(k)	(ε_1)	(ε_2)	(E_g)	(α)	D(nm)
Undoped	2.38	0.001	5.66	0.0057	2.19eV	$0.27\times10^3 cm^{-1}$	19.8nm
CIS:Sm	2.22	0.036	4.92	0.15	3.3 eV	$1\times10^4 cm^{-1}$	16.86nm
CIS:Ho	1.79	0.068	3.47	0.23	3.5eV	$0.32\times10^4 cm^{-1}$	11.29nm
CIS:Pr	1.95	0.016	3.96	0.21	2.39eV	$0.83\times10^4 cm^{-1}$	13.82nm
CIS:$CdCl_2$	1.62	0.072	3.35	0.31	4.1eV	$0.26\times10^4 cm^{-1}$	11.15nm

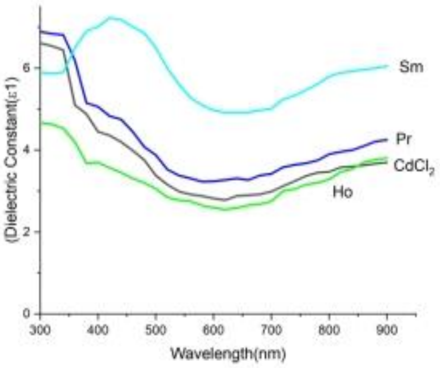

Figure 7. Real Dielectric constant vs wavelength

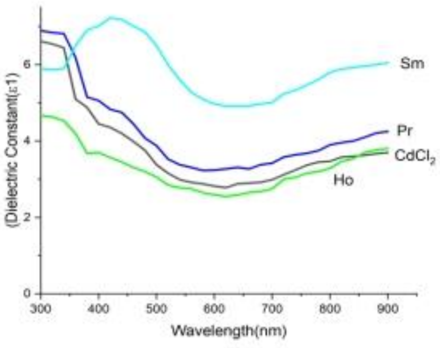

Figure 8. Imaginary Dielectric constant vs wavelength

Table : 1 Value of band gap, refractive index (n), coefficient of extinction (k), real & imaginary dielectric constants(ε_1,ε_2) and absorption coefficient for undoped and doped $CuInS_2$ thin films at λ=820nm

IV. CONCLUSIONS

Various doped, undoped and flux added thin films of $CuInS_2$(CIS) has been grown successfully by chemical method in a liquid bath and studied comprehensively using optical measurements. Transmittance and absorption spectra has been studied to know about how much light is being transmitted and absorbed by the grown films and also to know about optical band gap energy. Despite of this K, n, ε_1 and ε_2 were also calculated for various thin films of CIS and their variation with wavelength of light were also studied. $CdCl_2$ and rare earth doped film shows 60-82% transmission for wavelengths longer than 500 nm. The transmittance of undoped film is very less(<35%) in the visible range as compare to flux added and rare earth doped films. Absorbance is high in the observable region from ~ 500nm to 900nm. Due to these properties the grown films specially the rare earth doped CIS films are best suited for opto-electronic devices, particularly as absorbent material in photovoltaic cells. All grown film shows a direct transition in the range 2.19–3.5 eV.

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