Effects of Copper Doping on Chalcogenide (Cadmium Sulfide) Thin Films by Chemical Bath Deposition Method

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Abstract— Chalcogenide cadmium sulfide (CdS), with various concentrations of Cu^{2+} (0.1, 0.2, 1 and 2M) - doped CdS thin films have been successfully synthesized by a chemical bath deposition (CBD) method. The synthesized thin films were characterized by UV–Visible absorption (UV–Vis), X-ray diffraction (XRD) and photoluminescence (PL) spectroscopy. The absorption peaks of the synthesized films were noticeably blue / red-shifted from the bulk material depends on the different Cu^{2+} molar concentration. The bandgap value of the films decreases within the Cu^{2+} concentration. The XRD analysis confirmed the formation of polycrystalline in nature for all samples. The average size of the particles ranged from 9.55 nm to 129nm. The decrease of luminescence intensity at the higher Cu^{2+} concentrations and Particles with increased Cu^{2+} concentrations had a red shift in their PL emission spectra.

Key words: thin films, CBD method, optical properties, structural properties .

I. Introduction

Cadmium sulfide is an n-type semiconductor material that has been used widely in many applications, including photo resistance sensors, energy conversional devices, light emitting diodes, laser materials and nonlinear optical devices [1-5].

Doping process, it has the ability to change the entire properties of the semiconducting material. Copper impurity, which can change the CdS semiconducting material from n to p type [6-7]. Merging of Cu decreases the direct bandgap due to increase of Cu^{2+} concentration in the films and also improves its photoelectrical properties [8].

Direct energy band gap may be reduced because of Cu^{2+} ions can replace either substitutional or interstitial Cd^{2+} ions in the CdS lattice [9]. Here we report the results on CdS:Cu which is quite interesting. Anomalous changes are seen in optical and structural measurements at different doping levels of Cu^{2+} ions in the chemical solution.

II. Experimental Procedure

To prepare Cu^{2+}doped CdS thin films, the following chemicals $3CdSO_4.8H_2O$, CuSO4.5H2O, CH_4N_2S, and NH_4OH were used. All steps of synthesis process were performed at room temperature. Aqueous solution 0.1M of cadmium sulphide ($CdSO_4.5H_2O$), thiourea (CH_4N_2S) was taken as the precursor for CdS thin films, $CuSO_4 \cdot 2H_2O$ was used for Cu doping. The pH value of the mixed solution was adjusted by ammonium hydroxide solution into the solution drop by drop. The products colour changed from yellow to brownish yellow with increase of dopant from 0.1 to 2M. The prepared CdS: Cu samples were characterized by UV-Vis spectroscopy, XRD and PL and techniques. Fig.1 shows flow chart for synthesis of Cu doped CdS thin films.

Fig.1: Flow chart of synthesis of Cu doped CdS thin films.

III. Results and Discussion

A. *Optical properties:*

In Fig.2 absorption spectra of CdS:Cu thin films with different molar concentration of Cu were compared. As depicted, the exitonic peak has a red shift when the doping percentage increases from 0.1 to 2M. Many authors reported that, the additional peaks are obtained at lower energy. This is attributed by the presence of energy levels within the forbidden gap due to copper as different type impurities. It is confirmed from decreasing bandgap of the films [10].

Red shifted absorption edge are indicates that the particle size is increased when the dopent concentration increased; it was confirmed by SEM images.

Absorbance of the films decreases with concentration of Cd^{2+}/Cu^{2+} ion or may be thickness of the films [11]. The absorption spectra of the samples are very strong and show long absorption tails due to light scattering at high concentration of nanoparticles. The crystalline nature improvement of the films has an important effect on the enhancement of the optical transmittance.

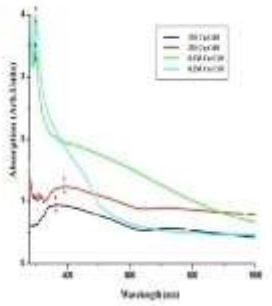


Fig. 2: Absorption spectra of CdS:Cu thin filmsfor differnet Cu molar concentrations.

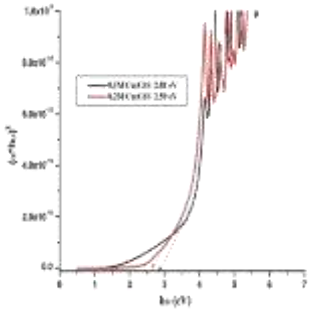
B. Bandgap:

The absorption, which corresponds to electron excitation from the valence band to conduction band, can be used to determine the nature and value of the optical bandgap. Reduction of bandgap is occurred in doped semiconductors and as a result of mutual exchange and coulomb interactions between the added free electrons in the conduction band and electron-impurity scattering [12].

It has been observed that the plots of $(\alpha h\upsilon)^2$ versus $h\upsilon$ are linear over a wide range of photon energies indicating the direct type of transition as in Fig. 3(a & b). Form the spectra the bandgap values are shrinking from 2.92eV to 1.76eV in different molar concentration of Cu^{2+} ions. The decrease in the bandgap with concentration was due to the increase of the crystalline size [13] and it is well known that as the lattice parameter increases the optical bandgap decreases [14].

C. Optical conductivity:

The optical conductivity against photon energy graph is presented in Fig.4 (a&b). The optical conductivity of the specimens vary with photon energy in similar manner, increasing sharply from various values of $7.4043*10^4 s^{-1}$ at 4.13eV for 0.2M Cu concentration CdS films, $7.440*10^4 s^{-1}$ at 4.14eV for 0.1M Cu concentration CdS films, $4.736x10^1 s^{-1}$ at 3.2eV for 1M Cu concentration CdS films and $3.51*10^1 s^{-1}$ at 3.6eV for 2M Cu concentration CdS films and various maximum values are obtained. After this, fluctuations were observed. From the graph, it is clearly depicted that the optical conductivity is decreased in high copper content.



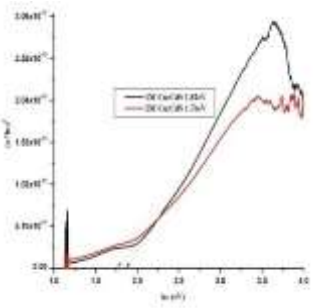


Fig. 3: (a &b), Relation between $(\alpha h\gamma)2$ and $h\gamma$ for CdS:Cu filmsfor differnet Cu molar concentrations.

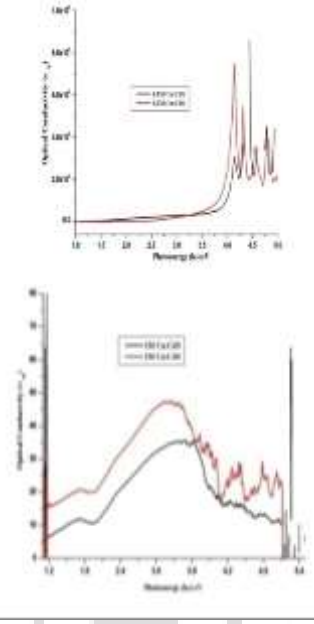


Fig. 4: (a&b), Optical conductivity against photon energy for CdS:Cu thin filmsfor differnet Cu molar concentrations.

D. Photoluminescence:

Fig.5 (a&b) shows that, the photoluminescence "PL" spectra of Cu doped CdS films for different Cu molar concentrations. The PL spectrum of 0.1M, 0.2M , 1M and 2M Cu doped CdS thin films shows the multiple emission peaks at blue emission 417nm (2.97eV),459nm (2.70eV) and 485nm (2.55eV) for low (0.1M ,0.2M) mole Cu doped CdS films and green emission at 493nm (2.51eV), 505nm (2.45eV) and 521 nm (2.38eV) for high (1M, 2M) mole Cu doped CdS films.

PL spectrum is shown in the range of 2.18eV – 2.54eV, which is close to the band edge of CdS, are called "green" bands and luminescence was observed around 2.5eV and 2.9eV typically referred as "blue" bands.

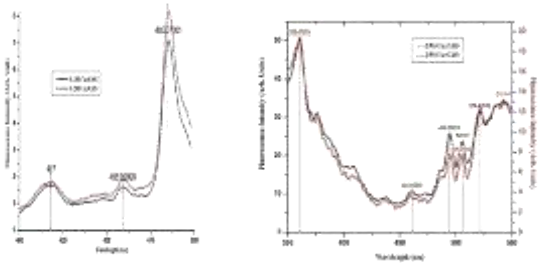


Fig. 5: (a&b) PL spectra of CdS:Cu films for different Cu molar concentrations.

The PL spectrum of the sample CdS:Cu except a blue band and green band emission for different Cu2+ ions Fig. As shown in Fig. 5 the PL intensity increased as the Cu concentration increased from 0.1M to 2M. Intensity of the green band is greater than that of the blue band. As increasing the concentration of Cu, the intensity of the blue band decreases while the intensity of the green band increases and reaches maximum at Cu2+ ions = 2M. This depicts those Cu2+ ions which are substituted in the positions of Cd2+ ions or vacancies of Cd in CdS crystal planes.

E. Structural properties:

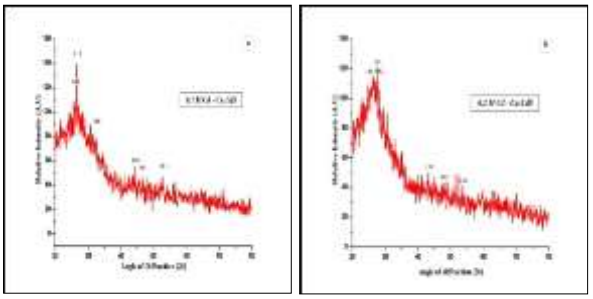
The XRD patterns of the Cu doped CdS in different Cu concentrations are depicted in Fig. 6 (a, b, c & d). The diffraction prominent peaks were existed at angle of 2θ = 26.0˚, 26.5˚, 39.2˚, 44.0˚, 46.2˚corresponding to the planes of (002), (002/111), (220), (220) and (311) for CdS:Cu films for 0.1 M of Cu^{2+} ions concentration. The peak at 2θ = 26.5˚ corresponds either to the (002) hexagonal or to the (111) cubic planes [15, 16].

The diffraction prominent peaks were existed at angle of 2θ = 26.6˚, 27. 4˚, 43.6˚, 47.9˚corresponding to the planes of (111/002), (111), (110) and (103) for CdS:Cu films for 0.2 M of Cu^{2+} ions concentration. The peak at 2θ = 26.6˚ corresponds either to the (002) hexagonal or to the (111) cubic planes [17-19]. The peak at 2θ = 26.6˚ corresponds either to the cubic (111) or to the hexagonal (002) planes.

The diffraction prominent peaks were existed at angle of 2θ = 26.4˚, 30.2˚, 51.5˚, corresponding to the planes of (002/111), (200), (220/311) for CdS:Cu films for 1 M of Cu^{2+} ions concentration. The peak at 2θ = 26.4˚ corresponds either to the (002) hexagonal or to the (111) cubic planes. And the intense peak of 2θ = 33˚ is related with (111) planes of CdO cubic structure.

The diffraction prominent peaks were existed at angle of 2θ = 24.8˚, 28.5˚, 30.2˚, 30.5˚, 43.5˚, corresponding to the planes of (100), (101), (200), (200) and (110) for CdS:Cu films for 2 M of Cu^{2+} ions concentration. And the intense peak of 2θ = 33˚ is related with (111) planes of CdO cubic structure [20].

From XRD analysis, it is confirmed that the copper concentration increases the crystallite property of the films [9]. Because $CuSO_4$ crystals acts as small nucleation centres and if the concentration of Cu^{2+} ions increases, the solution become denser and the crystalline size in the film also increases.



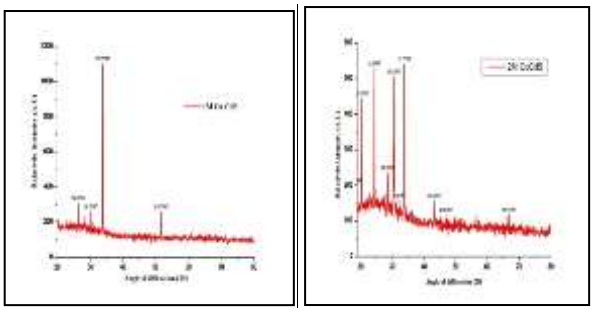


Fig. 6: (a, b, c & d), XRD patterns of Cu doped CdS films for different Cu molar concentrations.

The broad background is due to the amorphous glass substrate and also possibly due to some amorphous phase in the thin films [9]. The grain size of the films was calculated by using Scherrer equation [21].

$$\mathbf{D} = \frac{\mathbf{0.\ 94\lambda}}{\mathbf{\beta Cos(\theta)}} \qquad (1.\ 1)$$

where λ is the wavelength of the X-ray used (1.540Å), β is the full-width at half-maximum (FWHM) of the peak which has maximum intensity and θ is the Braggs angle. The grain size was found to be ranged from 9.55nm to 129 nm.

IV. Conclusion

Cu doped CdS thin films have been synthesized successfully and their crystalline sizes lie in the range of 9.5nm~ 129nm. The absorption edge is red shifted with respects Cu doped CdS that indicate the increase of particle size and Cu^{2+} ions concentration which can improved the crystalline size which have inferred by UV, XRD and SEM. XRD analysis of the sample indicated CdS:Cu thin films to be polycrystalline nature (mixture of two phases namely hexagonal and cubic). The bandgap and optical conductivity of the films are decreased in high copper content. Hence such synthesized CdS:Cu thin films have a great potential to be used in photonic device fabrication

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