



Study on the Effect of Copper Doping on the Structural and Optical Properties of Cd_{0.7}Zn_{0.3}S Nanocrystalline Thin Films Prepared by Chemical Bath Deposition

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ABSTRACT

Cd_{0.7}Zn_{0.3}S thin films were deposited by the chemical bath deposition method on glass substrates from an aqueous solution that contains cadmium chloride, zinc chloride, and thiourea at 80 ± 5 °C. The effects of Cu doping on the structural and optical properties of Cd_{0.7}Zn_{0.3}S films were investigated. X-ray diffraction results showed that the grown Cd_{0.7}Zn_{0.3}S thin films were polycrystalline with a hexagonal structure. The particle size of Cd_{0.7}Zn_{0.3}S thin films varied between 7 and 2 nm. The absorption coefficient, optical bandgap value, extinction coefficient, refractive index, real and imaginary parts of the dielectric constant, as well as real and imaginary parts of the optical conductivity were calculated.

Keywords: CdZnS thin films; X-ray diffraction; Chemical bath deposition

1. INTRODUCTION

Group II–VI compounds can form ternary and quaternary alloys with a direct fundamental bandgap assignment over the entire alloy composition range and with high absorption coefficients. These alloys can be used as materials to fabricate heterojunction photovoltaic devices. Consequently, experimental and theoretical studies on the material and device properties of group II–VI compounds have intensified [1]. Cadmium zinc sulfide (CdZnS) thin films have been widely used as a wide bandgap window material in heterojunction solar cells and photoconductive devices. In solar cell systems, where CdS films have been demonstrated to be effective, replacing CdS with the higher bandgap ternary CdZnS has led to a decrease in window absorption losses. Thus, the short circuit current in a solar cell increased [2–5]. In recent years, the use of solar cell devices has gained increasing attention in the field of thin film semiconductors. CdZnS ternary compounds are also potentially useful as a window material to fabricate p–n junctions without lattice mismatch in devices based on quaternary materials such as CuIn_xGa_{1-x}Se₂ or CuIn(S_zSe_{1-z})₂ [6,7]. Films of Cd_xZn_{1-x}S nanostructures have wide potential applications in various optoelectronic nanodevices [8]. The CdZnS films have also become the subject of considerable interest because of the possibility of using these films in solar cells [9]. CdZnS thin films have been prepared by various techniques, which include evaporation, spray pyrolysis, chemical bath deposition (CBD), dip technique, electrodeposition, and metalorganic chemical vapor deposition. Among these various deposition techniques, chemical deposition yields stable, uniform, adherent, and hard films with good reproducibility by a relatively simpler process [1,10].

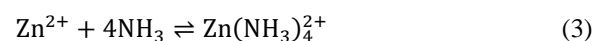
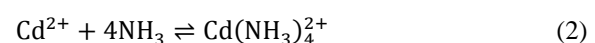
2. EXPERIMENTAL

Cd_{0.7}Zn_{0.3}S:Cu thin films were deposited on glass slides by using the CBD technique. A bath containing 0.1 M solutions

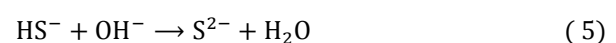
of copper nitrate, cadmium chloride, zinc chloride, and thiourea was developed. The pH of the solution was adjusted to 10 by adding NH₄OH. The glass slides were cleaned by using liquid detergent in an ultrasonic bath, dipped into a chromic acid bath for 2 h at room temperature, washed with distilled water and acetone, and dried. The glass substrates were immersed vertically in the reaction vessel, and the bath was set to a desired temperature. Deposition was carried out at 80 °C for 120 min, and the slides were left in the bath for 24 h at room temperature. The deposited films were then washed with distilled water and dried in air. The crystallinity phase and orientation of Cd_{0.7}Zn_{0.3}S:Cu films were determined by X-ray diffraction (XRD) by using a Philips PW 1840 instrument with a Cu-Kα target. A UV-VIS spectrophotometer (Jenway 6800) was used to measure the absorbance and transmittance of films in the wavelength (λ) range of 200 nm to 1100 nm. The optical parameters were calculated from these measurements. The reaction procedure for the formation of Cd_{1-x}Zn_xS can be described by the following steps [10].



Ammonia solution was added to the Cd and Zn salt solutions to form cadmium tetraamine ion [Cd(NH₃)₄²⁺] and zinc tetraamine ion [Zn(NH₃)₄²⁺], respectively, as follows:

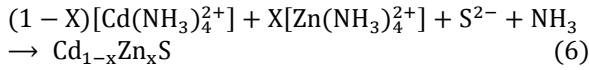


The sulfide ions are released because of the decomposition of thiourea in the alkaline medium, which is described by the following chemical reactions:





All three of these source ions combine in the reaction mixture, which leads to the formation of CdZnS.



3. RESULT AND DISCUSSION

1. X-ray diffractions

XRD measurements were carried out to study the crystal structure, particle size (PS), and crystalline quality of $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}:\text{Cu}$ thin films. The major peak located at 26.2972° is attributed to the (0 0 2) diffractive peak of $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}$. The subsequent peak is attributed to the scattering from (1 1 0) plane as shown in Fig. 1. After adding Cu to the compound, the diffraction peak shifted to a higher angle from 26.2972° to 26.7892° , as shown in Table 1. PS

was calculated from (0 0 2) and (1 1 0) by using the Scherrer formula [11].

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (7)$$

where $k=0.94$, λ is the X-ray wavelength, β is the full width at half maximum of the peak in radians, and θ is the Bragg angle. PS varied in the range of 2 nm to 7 nm. The variation of PS is not linear with composition. The lattice constants 'a' and 'c' for hexagonal phase of $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}:\text{Cu}$ thin films were calculated using the following equation [4].

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad (8)$$

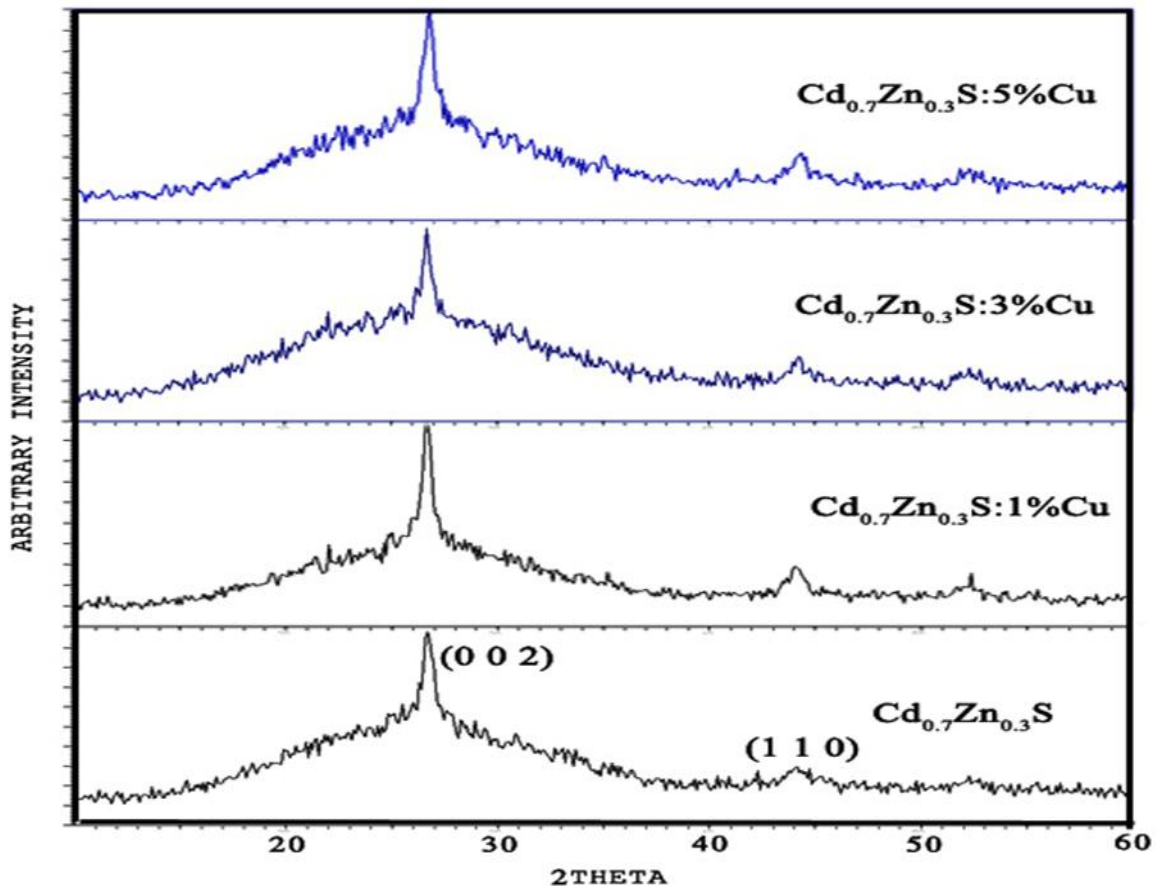


Fig 1: XRD Pattern of Thin Films prepared

**Table 1: Structural Parameters for the Prepared Thin Films**

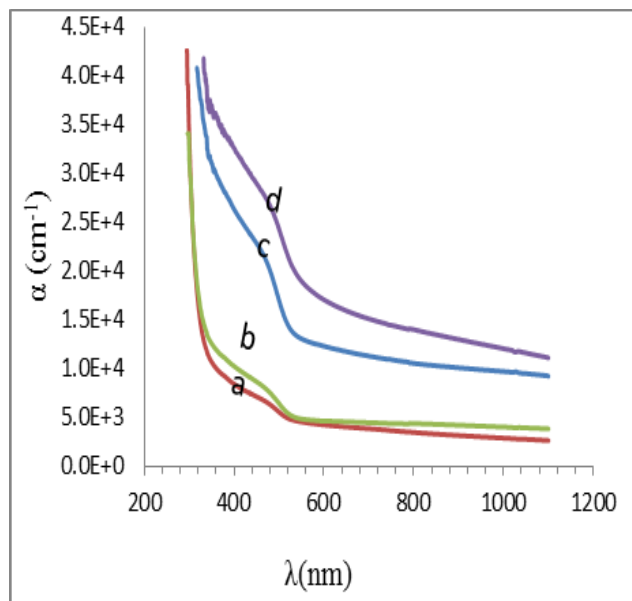
No.	Sample	2Theta	hkl	P.S. (nm)	d (Å)	a (Å)	c (Å)
1	Cd _{0.7} Zn _{0.3} S	26.2972	0 0 2	3	3.38627	4.092	6.77254
2	Cd _{0.7} Zn _{0.3} S:1% Cu	26.3826	0 0 2	2	3.37550	4.09572	6.751
3	Cd _{0.7} Zn _{0.3} S:3% Cu	26.6808	0 0 2	7	3.33845	4.10458	6.6769
4	Cd _{0.7} Zn _{0.3} S:5% Cu	26.7892	0 0 2	5	3.32519	4.09174	6.65038

The value of lattice constants 'a' and 'c' varies with the composition from 4.092 Å to 4.10458 Å and 6.65038 Å to 6.77254 Å, respectively. The change in lattice constant values and the grain sizes with the Cu ratio are given in Table 1.

2. OPTICAL CHARACTERIZATIONS

The absorption coefficient (α) was directly obtained from the absorbance against λ values by using the relation [12].

$$\alpha = \frac{2.303A}{t} \quad (9)$$

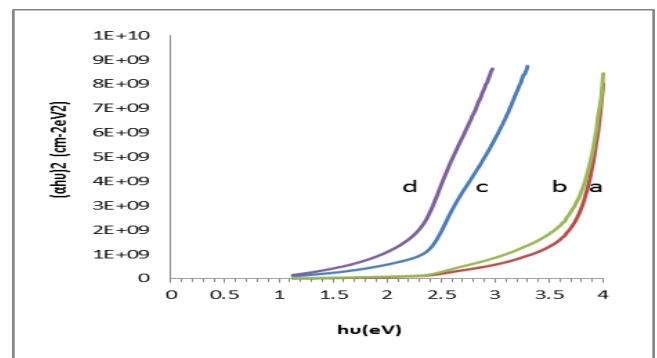
**Fig.(2) the variation of α with λ for thin films prepared**(a) Cd_{0.7}Zn_{0.3}S, (b) Cd_{0.7}Zn_{0.3}S:1%Cu,(c) Cd_{0.7}Zn_{0.3}S:3% Cu, (d) Cd_{0.7}Zn_{0.3}S:5% Cu**Table 2: Optical Bandgap for the Prepared Thin Films**

No.	Sample	E _g (eV)
1	Cd _{0.7} Zn _{0.3} S	3.8
2	Cd _{0.7} Zn _{0.3} S:1% Cu	3.75
3	Cd _{0.7} Zn _{0.3} S:3% Cu	2.4
4	Cd _{0.7} Zn _{0.3} S:5% Cu	2.1

The variation of α as a function of λ for polycrystalline Cd_{0.7}Zn_{0.3}S:Cu thin films is shown in Fig. 2. The results indicate that α decrease with increasing λ for all prepared thin films. The optical bandgap energy of the products can be determined from the following equation [13].

$$\alpha h\nu = A(h\nu - E_g)^n \quad (10)$$

where A is constant, E_g is the optical bandgap of the material, and n assumes values of 1/2, 2, 3/2, and 3 for allowed direct, allowed indirect, forbidden direct, and forbidden indirect transitions, respectively. For allowed direct transition, n = 1/2. α is in the order of 10⁴ cm⁻¹ for all compositions, which supports the direct bandgap nature of the semiconductor [14]. The curves of $(\alpha h\nu)^2$ versus $h\nu$ were plotted and are shown in Fig. 3. The optical bandgap of pure Cd_{0.7}Zn_{0.3}S is 3.8 eV and continuously decreases to 2.1 eV for Cd_{0.7}Zn_{0.3}S:5% Cu, as shown in Table 2.

**Fig (3) the optical energy gap (E_g) value for thin films prepared (a) Cd_{0.7}Zn_{0.3}S, (b) Cd_{0.7}Zn_{0.3}S:1%Cu, (c) Cd_{0.7}Zn_{0.3}S:3% Cu, (d) Cd_{0.7}Zn_{0.3}S:5% Cu**



The extinction coefficient, k , is a measure of the fraction of light lost because of scattering and absorption per unit distance in the participating medium. k was calculated using the following equation [15].

$$k = \frac{a\lambda}{4\pi} \quad (11)$$

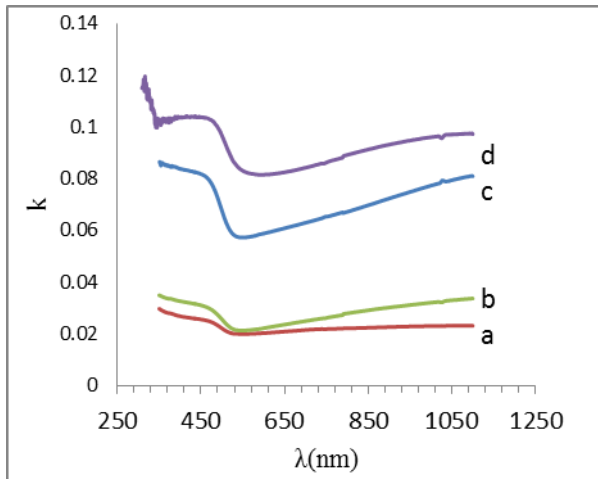


Fig.(4) The variation of k with λ for thin films prepared (a) $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}$, (b) $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}:1\%\text{Cu}$, (c) $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}:3\%\text{Cu}$, (d) $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}:5\%\text{Cu}$

Fig. 4 shows the spectral dependence of k for $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}:\text{Cu}$ thin films. k decreases with increasing λ , but increases with increasing Cu concentration in the thin films.

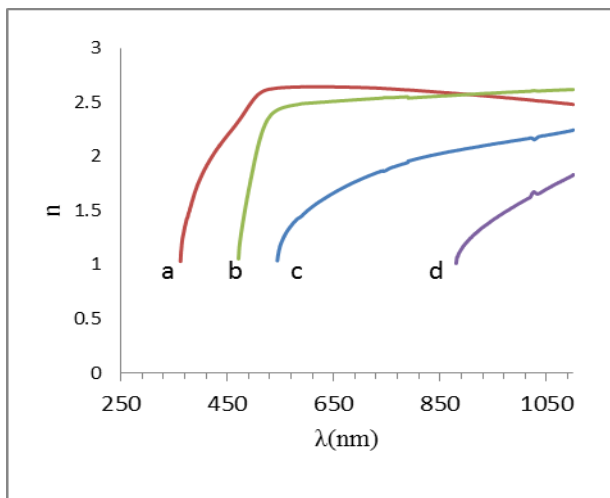


Fig.(5) The variation of n with λ for thin films prepared (a) $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}$, (b) $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}:1\%\text{Cu}$, (c) $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}:3\%\text{Cu}$, (d) $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}:5\%\text{Cu}$

The refractive index (n) is one of the fundamental properties of an optical material because of its close relationship to the electronic polarization of ions and the local field inside materials. Evaluation of the refractive indices of optical materials is considerably important for applications in integrated optic devices, such as switches, filters, and modulation, among others, in which n is a key parameter for the device design [16]. The value of n for thin films can be calculated from their reflectance and transmittance spectra by using simple approximations [15].

$$n = \frac{1+R}{1-R} + \left[\frac{4R}{(1-R)^2} - K^2 \right]^{\frac{1}{2}} \quad (12)$$

The calculated n values of $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}:\text{Cu}$ thin films are shown in Fig. 5. As shown in Fig. 5, n increases as λ increases. The highest value of n is at the shortest λ of 490 nm (strong absorption region) for $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}$ and $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}:1\%\text{Cu}$ thin films. This result is due to the resonance effect between the incident electromagnetic radiation and the electron polarization, which leads to electron coupling in films to the oscillating electric field [16]. The following relationships were used to calculate the values of the real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric constant for the prepared thin films [15].

$$\epsilon_1 = n^2 - k^2 \quad (13)$$

$$\epsilon_2 = 2nk \quad (14)$$

The values of ϵ_1 and ϵ_2 parts of the dielectric constant of the prepared thin films are shown as functions of λ in Figs. 6 and 7. Both the ϵ_1 and ϵ_2 parts of the dielectric constant increase with increasing λ for all samples of thin films prepared.

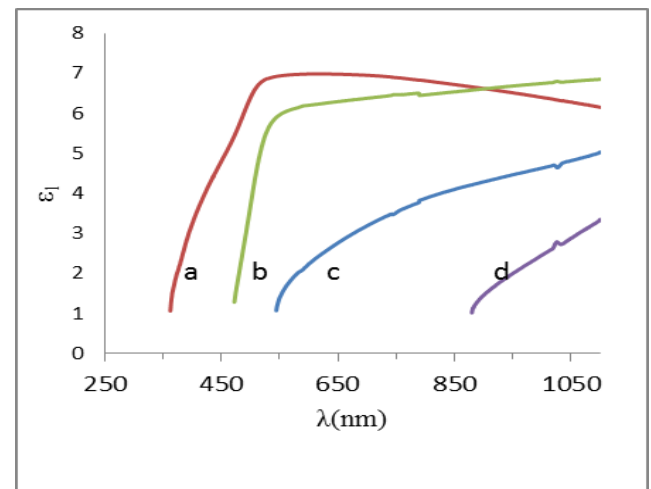


Fig.(6) The variation of ϵ_1 with λ for thin films prepared (a) $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}$, (b) $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}:1\%\text{Cu}$, (c) $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}:3\%\text{Cu}$, (d) $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}:5\%\text{Cu}$

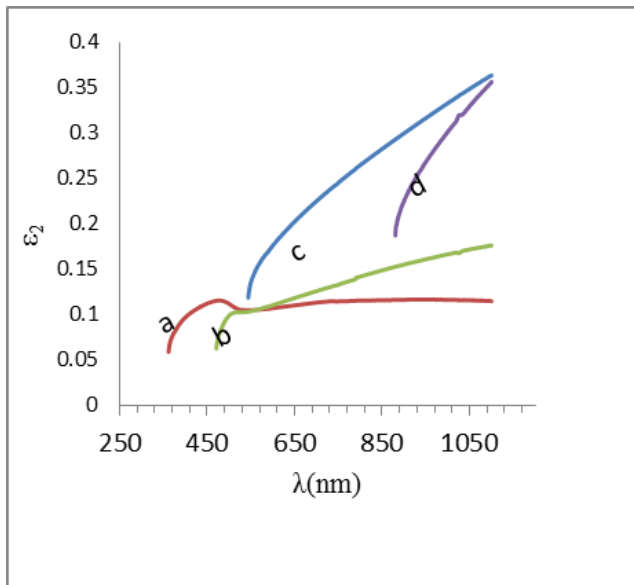


Fig.(7) The variation of ϵ_2 with λ for thin films prepared (a) $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}$, (b) $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}:1\%\text{Cu}$, (c) $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}:3\%\text{Cu}$, (d) $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}:5\%\text{Cu}$

The complex optical conductivity ($\sigma^* = \sigma_1(\lambda) + i\sigma_2(\lambda)$) σ_1) and imaginary (σ_2) parts of the optical conductivity as a function of λ are shown in Fig. 8 (a, b). These figures show that optical conductivity increases with increasing λ . This result suggests that the increase in optical conductivity is due to the excitation of electrons by the photon energy.

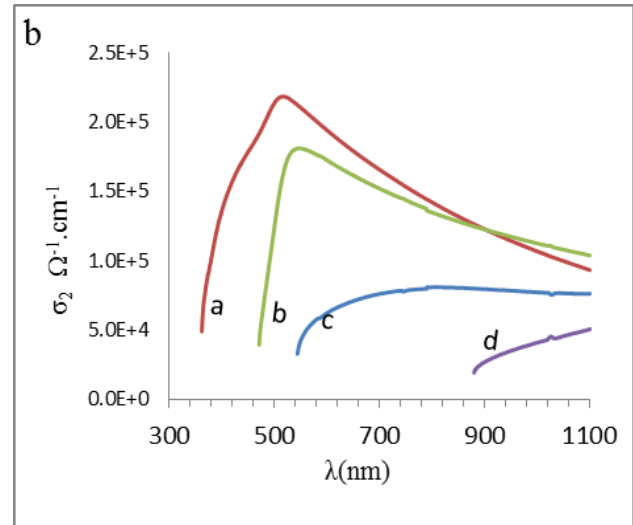
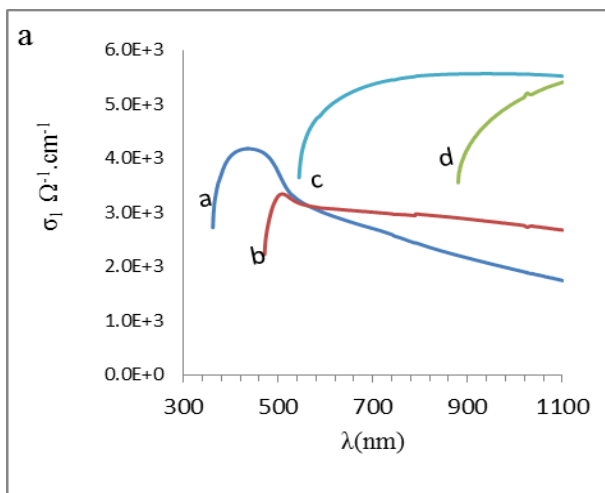


Fig.(8) The variation of real (a) and imaginary (b) σ with λ is related to the complex dielectric constant ($\epsilon^* = \epsilon_1(\lambda) + i\epsilon_2(\lambda)$) by the relation [8,17].

$$\sigma_1 = \omega \epsilon_2 \epsilon_0 \tag{15}$$

$$\sigma_2 = \omega \epsilon_1 \epsilon_0 \tag{16}$$

where ϵ_0 is the free space dielectric constant and ω is the incident light frequency. The real (for thin films prepared (a) $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}$, (b) $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}:1\%\text{Cu}$, (c) $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}:3\%\text{Cu}$, (d) $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}:5\%\text{Cu}$).

3. CONCLUSIONS

We have shown that $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}:\text{Cu}$ thin films can be formed on glass substrates by the CBD technique. The structural and optical dispersion parameters were studied for $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}:\text{Cu}$ thin films. XRD results indicate that $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}:\text{Cu}$ thin films are in the polycrystalline form with a hexagonal structure. The energy bandgaps of the $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}:\text{Cu}$ samples obtained using optical absorption spectra vary between 2.1 eV and 3.8 eV. Such films are advantageous for solar cell applications because of their wide optical bandgap.

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