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Research article

Synthesis and Optical Properties of Ternary Derivatives of Zn Doped CdS ($Zn_xCd_{1-x}S$) for Different Deposition Times with Different Compositions

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Abstract

$Zn_xCd_{1-x}S$ thin films are prepared by chemical bath deposition method. The optical properties of the films are investigated for different deposition times with different compositions. Optical characterization of prepared films was performed by UV-VIS Double Beam spectrophotometer Version 6.51. Optical characterization indicates that film deposited by CBD method shows that the value of the absorption edge shifted towards the shorter wavelength region and hence the direct band gap measurement shows that band gap of $Zn_xCd_{1-x}S$ changes with volume mixture ratio of Zn varies for 0,0.1, 0.2 ,0.3 ,0.4 and the band gap changes from 2.5eV to 2.57eV for 30 minutes deposition time, from 2.52eV to 2.9eV for 45 minutes deposition time and 2.6eV to 2.8eV for 60 minutes deposition time from CdS to $Zn_{0.4}Cd_{0.6}S$.This shows that the band gap of thin film totally dependent on chemical composition in bath solution. The optical conductivity of the film decreases with increasing Zn concentration which shows less absorbance or greater transmittance due to thickness of the film reduces. The extinction coefficient initially decreases then it increases due to variation in absorbance. The dielectric constant shows different shapes of curves for the real part of dielectric constant ϵ_r and the imaginary part of dielectric constant ϵ_i represents the absorption associated of radiation by free carriers.

Keywords: $Zn_xCd_{1-x}S$, optical transmission, deposition time, ternary derivates.

Introduction

A ternary derivative of CdS such as $Zn_xCd_{1-x}S$ is a promising material to decrease the optical absorption losses[1] and to enhance the response in the shorter wavelength region and wide bandwidth. The composition and the size dependence of the band gap are the most identified aspects in semiconductors[2]. The band gap increases either by changing composition or by reducing the particle size. The quantum confinement effect changes the physical and chemical properties of the materials[3]. In our study, preparation of $Zn_xCd_{1-x}S$ is based on chemical bath deposition method by changing composition and deposition time.

The control of the composition of $Zn_xCd_{1-x}S$ may lead to the development of ideal materials for short wavelength diode laser applications[4], promising materials for high density optical recording[5], photovoltaic applications[6] and for blue or even UV laser diodes, solar cells[7]. These applications are based on the structure of $Zn_xCd_{1-x}S$ which exhibit fundamental absorption edges that can varied from green to UV[8].

$Zn_xCd_{1-x}S$ is promising material for its use in various devices. A number of techniques e.g. chemical bath deposition[9-11], DC magneto sputtering[12] , sol-gel electrostatic deposition[13-14], solution growth[15], chemical vapour deposition[16], vacuum evaporation[17], screen printing[18], spray pyrolysis [19],molecular beam epitaxy[20], true liquid crystalline templating[21],etc. are used for preparation of CdS and $Zn_xCd_{1-x}S$ materials.

Experimental Details

$Zn_xCd_{1-x}S$ thin films were prepared from aqueous solution containing cadmium chloride (0.01M), zinc chloride (0.1M), thiourea (0.1M), 25% ammonia solution and triethanolamine (TEA). The pH of the solution was adjusted to be 10.8 by the addition of ammonium hydroxide solution. The chemical bath is prepared from 10ml of cation precursors (total volume of $CdCl_2$ + $ZnCl_2$ solutions) and 4ml (4% of the volume of the metal precursors) triethanolamine. The solution is stirred well and required amount of ammonia solution (25% of NH_3 solution) was added to get a pH value 10.8. After proper stirring the solution with homogenizer for 10 minutes at the rate of 125 revolutions per minute, 10 ml of thiourea is added into it and the reaction mixture was kept in a water bath at 80^0C. Three cleaned glass substrates were immersed vertically in the chemical bath and the deposition was carried out for 30 minutes, 45 minutes and 60 minutes respectively. After the deposition, the films were rinsed in distilled water and dried in open air at room temperature. $Zn_xCd_{1-x}S$ thin films were prepared for various volume mixture ratios (x) of the $ZnCl_2$ and $CdCl_2$ solutions. The volume mixture ratio of the cation precursors, 'x' can be represented as,

$$x = \frac{V_{Zn}}{V_{Zn} + V_{Cd}} \qquad (1)$$

V_{Zn} and V_{Cd} are the volumes of $ZnCl_2$ and $CdCl_2$ solutions.

The total volume ($V_{Zn} + V_{Cd}$) of the cation precursors is always kept as 10ml and the value of x was varied from x = 0 to 0.4 by mixing different volumes of the cadmium and zinc solutions.

The overall reaction of the CdZnS formation is

$$[Cd(NH_3)_4^{2+}] + [Zn(NH_3)_4^{2+}] + S^{2-} + NH_3 \rightarrow CdZnS + \text{Re}\,maining\ \ \text{Pr}\,oduct \qquad (2)$$

The deposition of the CdZnS thin films are based on the precipitation followed by condensation.

Results and Discussion

A. Optical Transmission Spectra

Optical quality of the film was investigated by UV-VIS Double Beam spectrophotometer Version 6.51 in the wavelength ranging from 200 to 1100 nm. The transmittance spectra of $Zn_xCd_{1-x}S$ thin film for x = 0, 0.1, 0.2, 0.3 and 0.4 deposited for 30 min, 45 min and 60 min is shown in FIG.1. It has been observed that the optical transmittance are nearly 80% , 85% , 90%, 95% and 100% for highest peak of transmission for 30 min depositions,70%, 80%,82% ,86% and 90% for 45 min depositions and 70%, 72%, 82%, 89% and 98% for 60 min depositions.

The transmittance of the fabricated films increases due to the incorporation of decrease in thickness of film, which allowed the optical band gap (Eg) to be determined. From the spectrograph the absorption edge of sample found to occur in the range 450-550 nm the optical band gap Eg can be estimated from tauc's plot

$$\alpha h\nu = A(h\nu - E_g)^n \tag{3}$$

Where E_g is the band gap corresponding to particular transition occurring in film, α is absorption coefficient, A is a constant, υ is transition frequency and the exponent n characterizes the nature of band transition. n is 1/2 for direct band gap materials. The graph between hυ vs. $(\alpha h\upsilon)^2$ plotted for deposition times of 30 min, 45 min and 60 min respectively. The extrapolation of straight line to $(\alpha h\upsilon)^2 = 0$ axis gives the value of energy band gap of CdS thin film. The band gap of thin films observed to be for 30 min, 45 min and 60min respectively.

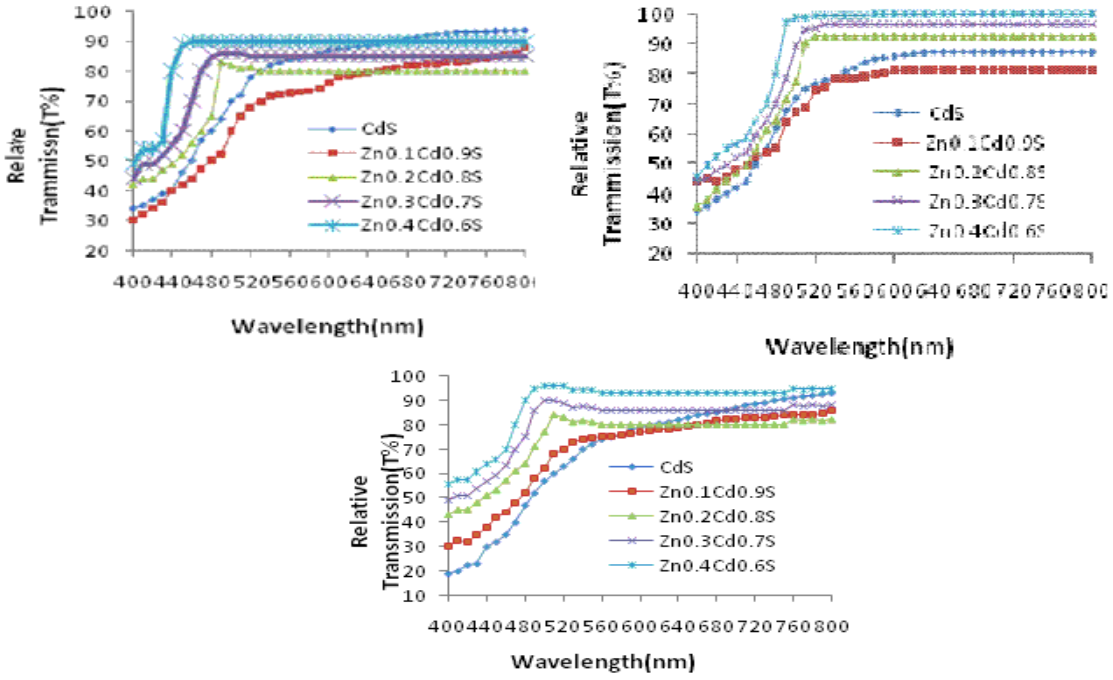

FIG.1. Transmittance of films for 30min, 45 min and 60 min depositions

The value of the absorption coefficient α can be determined by

$$\alpha = -\frac{\log_e T}{t} \tag{4}$$

Where T is the transmittance in % and t is the film thickness which is determine by taking the difference of masses of substrate before and after deposition.

It is observed from the FIG.2 that the transmittance decreases as Zn content decreases and the values of the absorption edge shifts towards shorter wavelengths with increasing Zn content. The direct allowed optical band gap Eg is estimated from the plots of $(\alpha\lambda\nu)^2$ versus (hν) shown in Table.1 for 30 min, 45 min, 60 min depositions. The variation of Eg with x can be calculated theoretically from the following quadratic equation:

$$E_g(x) = E_g(0) + 0.7x + 0.5x^2 \tag{5}$$

Where Eg(0) is the band gap energy of CdS.

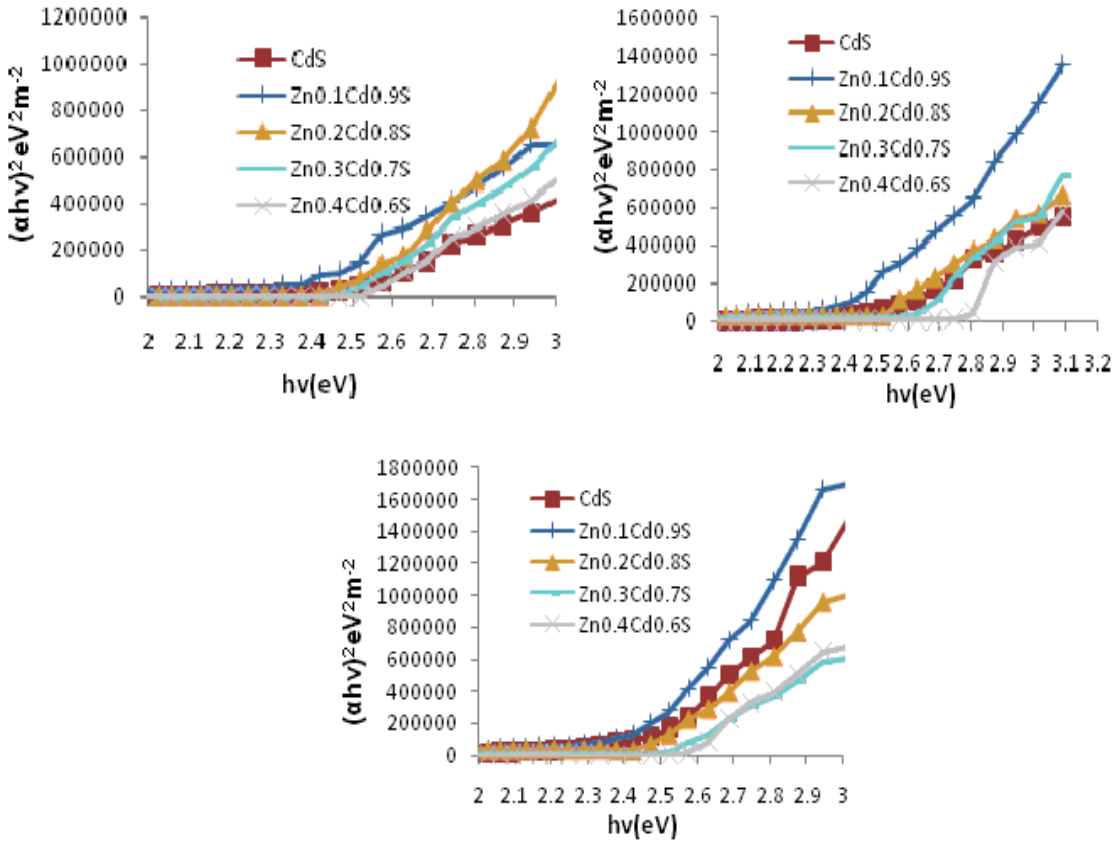

FIG. 2. Energy band gap for 30 min, 45 min and 60 min depositions.

TABLE I. Deposition Parameter and Results of Band Gap Calculations

Deposition Time	Composition	Band Gap, Eg(eV) from Tauc's Relation	Band Gap from Quadratic Equation	Error Ratio
30 Minutes	CdS	2.5eV	2.5eV	0.040
	Zn0.1Cd0.9S	2.4eV	2.475eV	0.030
	Zn0.2Cd0.8S	2.55eV	2.434eV	0.048
	Zn0.3Cd0.7S	2.56eV	2.655eV	0.036
	Zn0.4Cd0.6S	2.57eV	2.76eV	0.069
45 Minutes	CdS	2.52eV	2.57eV	0.050
	Zn0.1Cd0.9S	2.56eV	2.475eV	0.034
	Zn0.2Cd0.8S	2.60eV	2.434eV	0.068
	Zn0.3Cd0.7S	2.70eV	2.655eV	0.017
	Zn0.4Cd0.6S	2.90eV	2.76eV	0.051
60 Minutes	CdS	2.60eV	2.6eV	0.083
	Zn0.1Cd0.9S	2.65eV	2.475eV	0.071
	Zn0.2Cd0.8S	2.70eV	2.434eV	0.109
	Zn0.3Cd0.7S	2.75eV	2.655eV	0.036
	Zn0.4Cd0.6S	2.80eV	2.76eV	0.014

The variation of E_g with x is linear as shown in FIG.3 and in well agreement with results [15]. Kwok *et al.* [22] reported similar empirical formula for $Zn_xCd_{1-x}S$ microcrystalline material.

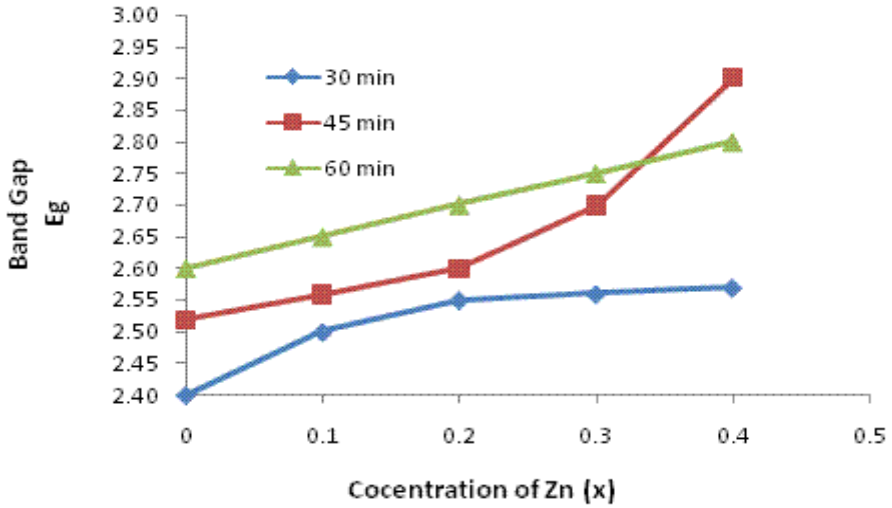

FIG.3. Concentration of Zn Vs Band Gap for 30 min, 45 min and 60 min.

B. Optical Absorption Spectra

The absorption spectra of the thin film $Zn_xCd_{1-x}S$ having different thickness for 30 min, 45 min and 60 min deposition, shown in FIG.4.

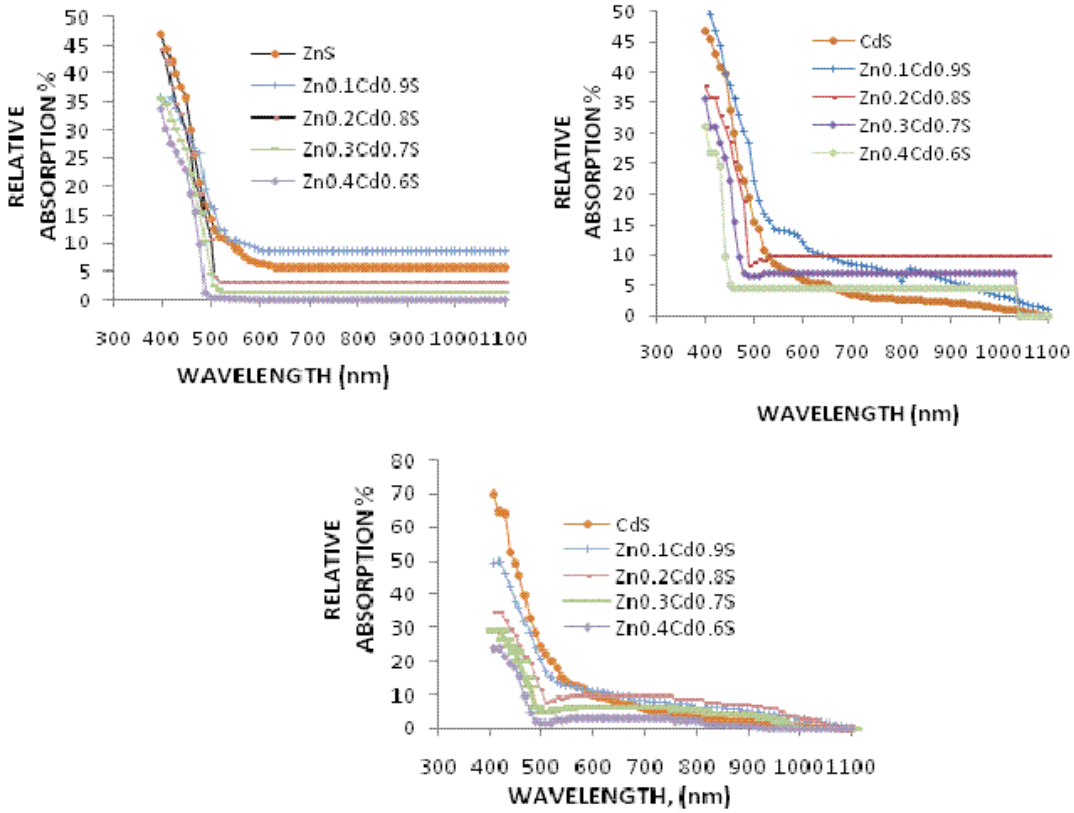

FIG. 4. Absorption Spectra of thin films for 30 min, 45 min and 60 min.

It is observed that the absorption decreases as the deposition time as well as concentration of Zn increases and maximum absorption peak shifts towards the lower wavelength with increasing Zn concentration. This shows that the film thickness decreases as the Zn concentration as well as deposition time increases.

Using the fundamental relation of photon transmission and absorbance, the absorption is given by Beer-Lambert law

$$A = -\log\frac{I}{I_0} = -\log\frac{T}{100} \tag{6}$$

T is the transmittance of light.

C. Optical Refection Spectra

The reflectance of the film has been found by using relationship

$$R + T + A = 1 or R = 1 - (T + A) \tag{7}$$

R= reflectance, T=transmittance and A= absorbance.

The reflectance of the film decreases with the increase in concentration of Zn as well as increase in deposition time. The reflectance is high in near infrared and visible region shown in FIG.5.

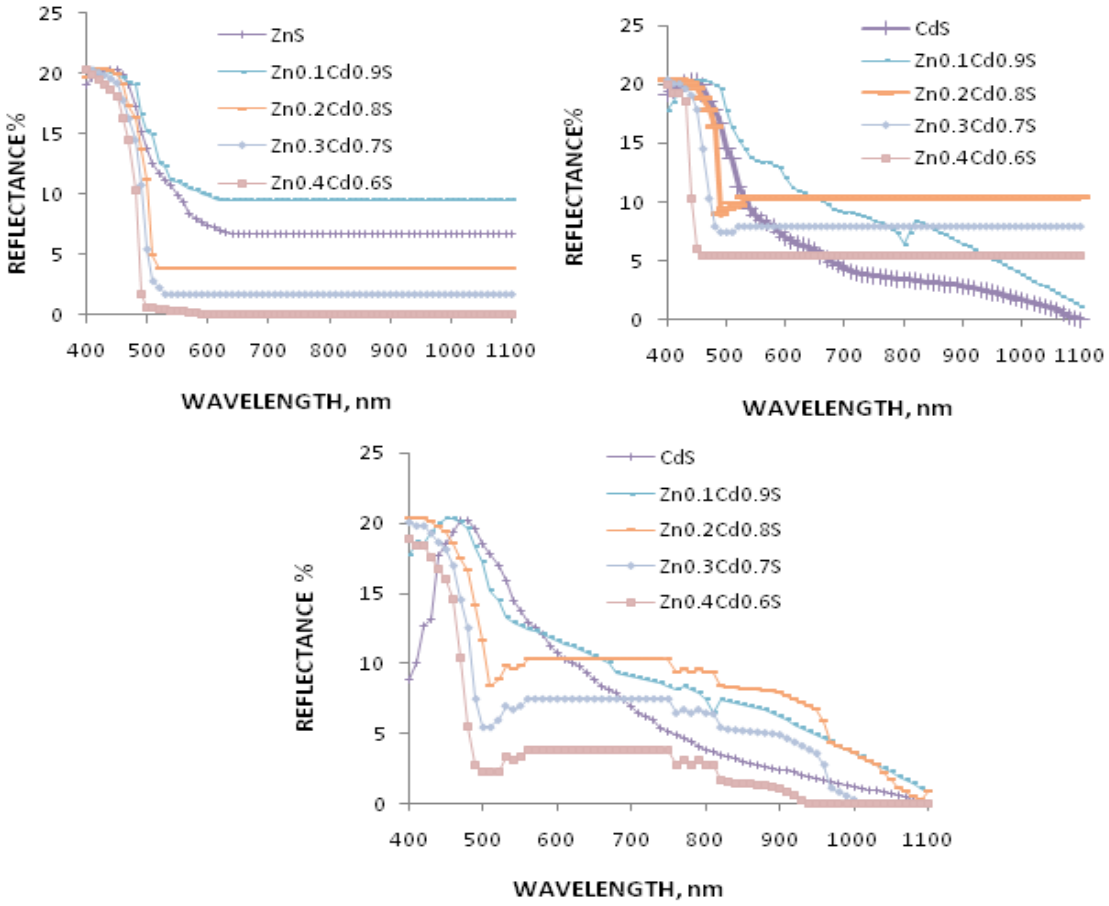

FIG. 5. Reflectance Spectra of thin films for 30 min, 45 min and 60 min.

A similar behavior is reported by S. Y. Kim [24] for TiO_2 thin films prepared using electron beam evaporation and is claimed to be due to interference of the light transmitted through the thin film and the substrate. These variations have been observed to increase with film thickness.

D. Refractive Index

The refractive of the film has been calculated by knowing reflectance that can be determine by formula:

$$R = \frac{(n-1)^2}{(n+1)^2}, \tag{8}$$

Where R is the normal reflectance.

Using this relation refractive index n can be determined by the formula:

$$n = \frac{(R)^{1/2} - 1}{(R)^{1/2} + 1} \tag{9}$$

FIG.6 shows the variation in the refractive index with the incident photon energy.

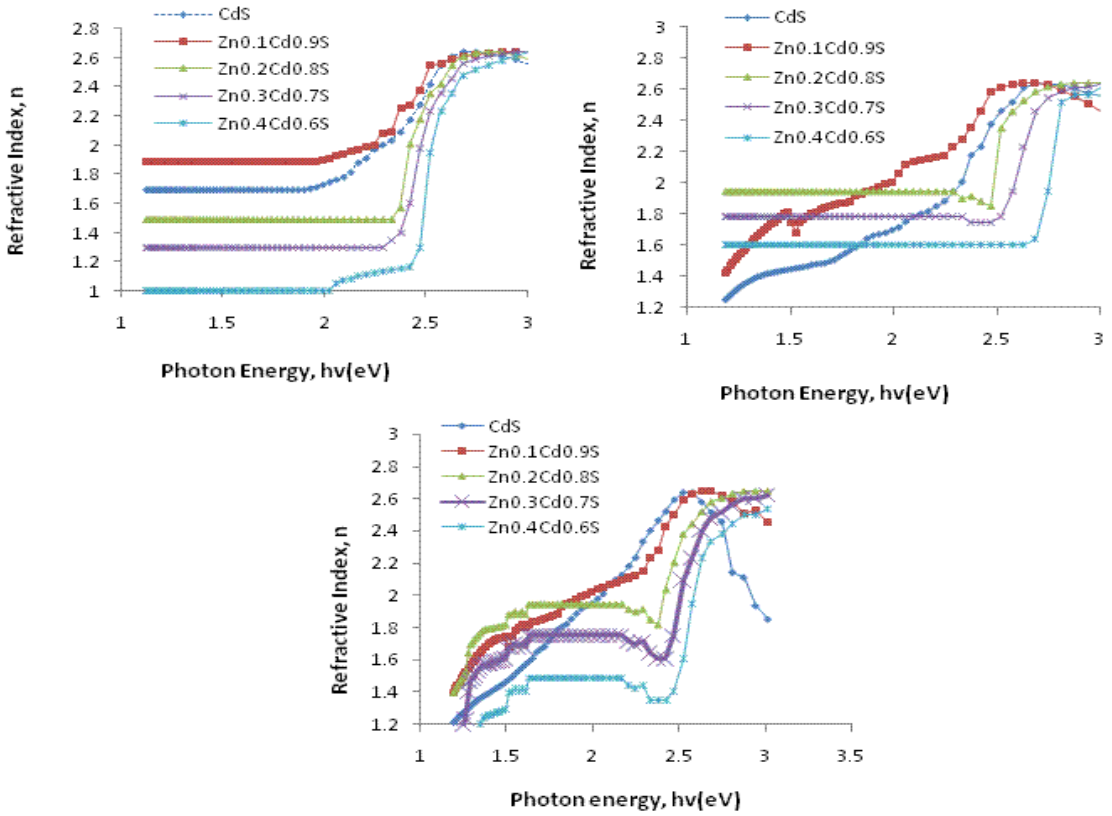

FIG. 6. Refractive Index of thin films for 30 min, 45 min and 60 min.

As the reflectance of the film decreases and becomes a constant, the refractive index of the film becomes constant up to 2eV photon energy and then increases. The refractive index of the film also decrease with respect to increase in Zn concentration shows that film becomes thin as increasing the Zn concentration. The increase in the film thickness results in the over all increase in the refractive index. This increase is due to the over all increase in the reflectance with the film thickness. The peak value of the refractive index for the ZnS thin films of various thickness vary in the range of 2.3eV to 3eV which is in good agreement with the value 2.62 reported by I. C. Ndukwe [23].

E. Optical Conductivity

The conductivity of the film can be determine by using relation

$$\sigma = \frac{\alpha nc}{4\pi} \tag{10}$$

Where c is the velocity of light n is the refractive index and α is the absorption coefficient.

FIG.7 shows the variation of optical conductivity with the incident photon energy. The increased optical conductivity at high photon energies is due to high absorbance of $Zn_xCd_{1-x}S$ film in that region.

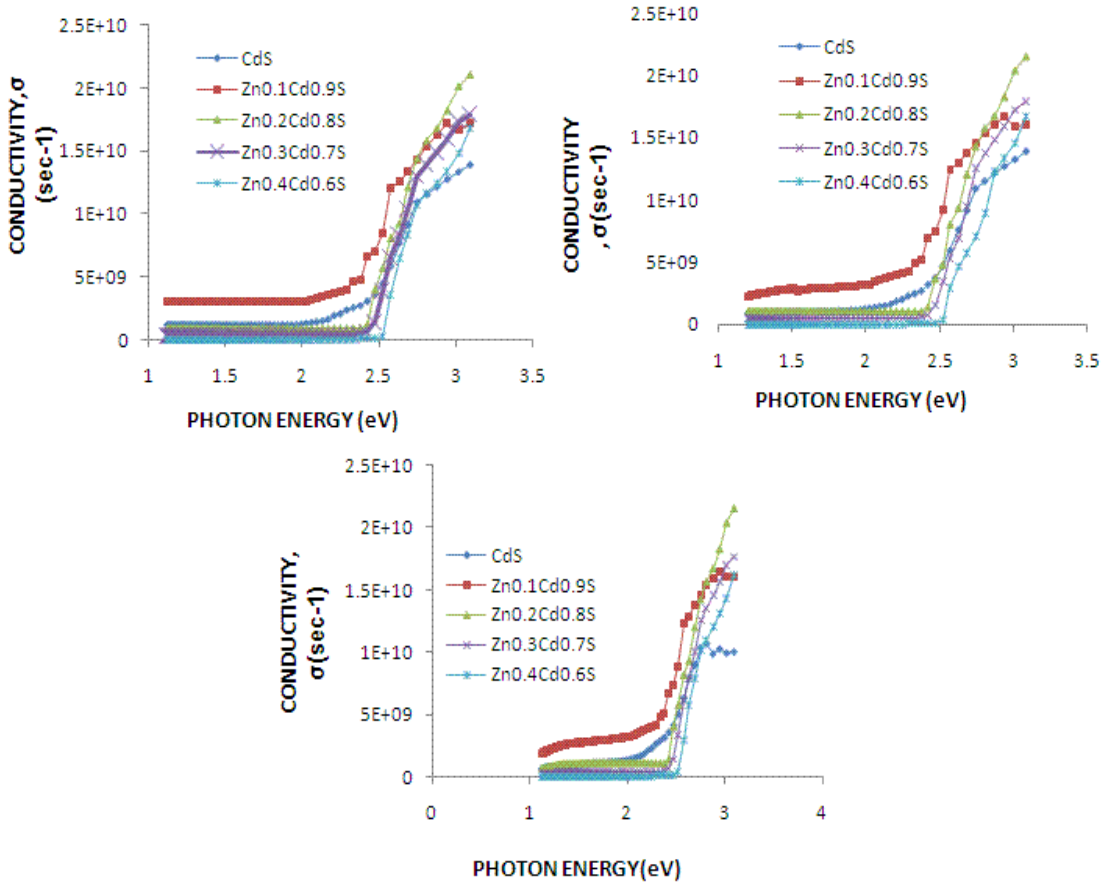

FIG. 7. Optical Conductivity of thin films for 30 min, 45 min and 60 min.

The conductivity is constant up to 2.3eV of photon energy after that it increases with increase in photon energy. This shows that when the absorption of photon by film increases conductivity will also increases. The conductivity of the films decreases with increase in Zn concentration which shows that absorption decreases and transmittance increases as the film becomes thin with increase in Zn concentration.

F. Extinction Coefficient

The extinction coefficient can be determine by using the relation,

$$k = \frac{\alpha\lambda}{4\pi} \tag{11}$$

λ is the wavelength of light.

FIG.8 shows the change in extinction coefficient with the photon energy. The extinction coefficient initially decreases from 1.1 to 2.3eV of photon energy after that it increases due to variation in absorbance. The increased optical conductivity at high photon energies is due to the high absorbance of ZnS thin films in that region.

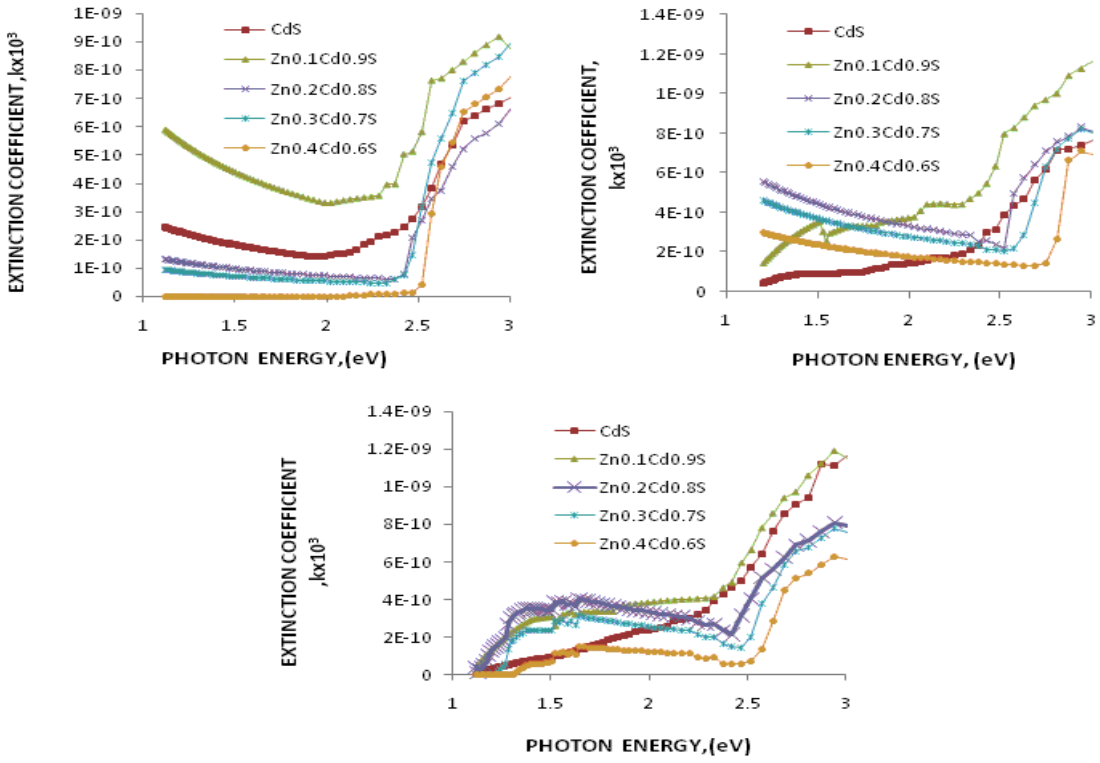

FIG.8. Extinction Coefficient of thin films for 30 min, 45 min and 60 min.

G. Dielectric Constant

The real and the imaginary parts of the dielectric constant can be determined by using the relation:

$$\varepsilon_c = \varepsilon_r + \varepsilon_i = (n+ik)^2 = n^2 - k^2 + 2nik \qquad (12)$$

Where ϵ_r is the real part of the normal dielectric constant which is given by

$$\varepsilon_r = (n^2 - k^2) \qquad (13)$$

FIG.9 shows the variation of real dielectric constant with photon energy, hv for 30 min, 45 min and 60 min respectively.

Different shapes of curves due to different effective thickness of the film for the real part of dielectric constant has been observed. The range of variation of dielectric constant is in agreement with the observations of I. C. Ndukwe [23].

The imaginary part of dielectric constant $\varepsilon_i = 2nk$, represents the absorption associated of radiation by free carriers. FIG. 10 shows the variation of imaginary dielectric constant with photon energy, hv for 30 min, 45 min and 60 min respectively.

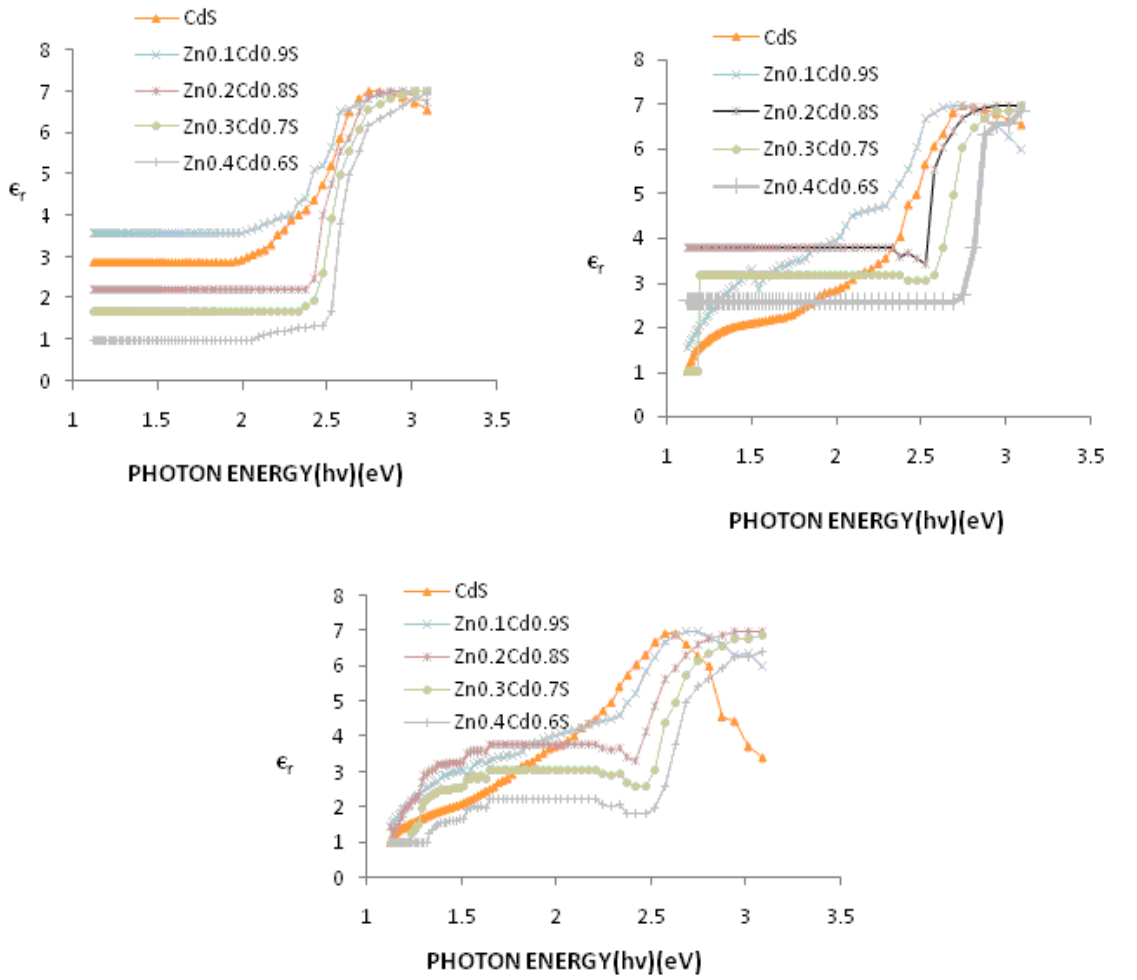

FIG. 9. Real Dielectric Constant of thin films for 30 min, 45 min and 60 min.

Conclusions

$Zn_xCd_{1-x}S$ film deposited on glass substrate by chemical bath deposition for x=0 to 0.4 for 30 min, 45 min., 60 min. The band gap of the film varies from 2.5eV to 2.57eV for 30 min deposition time, from 2.52eV to 2.9eV for 45 min deposition time and 2.6eV to 2.8eV for 60 min deposition time from CdS to $Zn_{0.4}Cd_{0.6}S$. The transmittance increases, absorbance as well as reflectance decreases as the Zn concentration increase. The conductivity decrease shows that the film becomes thin due to increase in Zn concentration. The extension coefficient initially decreases from 1.1eV to 2.3eV of photon energy after that it increases due to variation in absorbance.

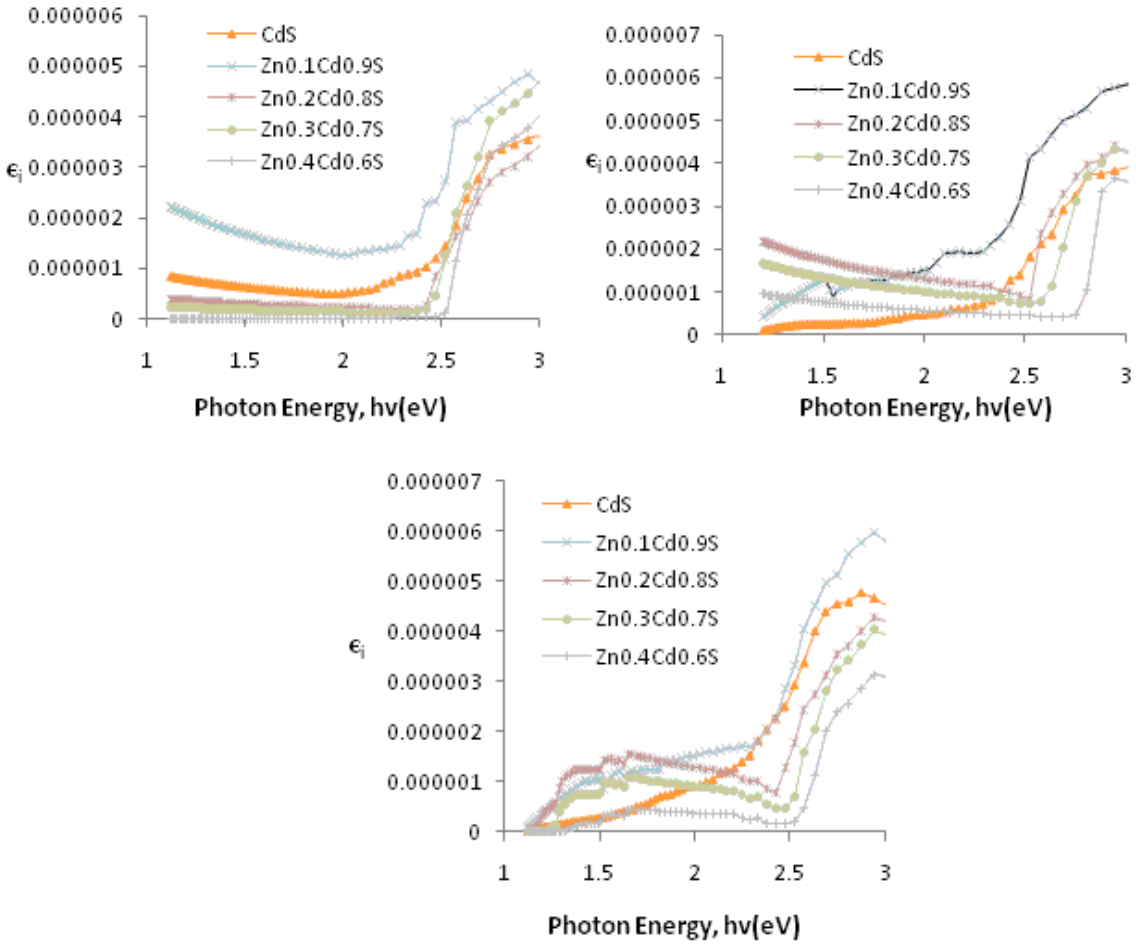

FIG. 10. Imaginary Dielectric Constant of thin films for 30 min, 45 min and 60 min.

The dielectric constant shows different shapes of curves due to different effective thickness of the film for the real part of dielectric constant ϵ_r and the imaginary part of dielectric constant ϵ_i represents the absorption associated of radiation by free carriers.

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