Original Research Article

STUDIES ON THE OPTICALDISPERSION PARAMETERS AND ELECTRONIC POLARIZABILITY OF CADMIUM SULPHIDE THIN FILM.

ABSTRACT

Thin film of Cadmium Sulphide (CdS) was deposited onto transparent glass substrate by chemical bath deposition technique. CdS thin film was characterized by UV-Visible spectrophotometer within the wavelength range of 280 nm – 920 nm using Single – Beam Helios Omega UV – VIS spectrophotometer. The optical parameters; extinction coefficient, refractive index and dielectric constant of CdS thin film were analyzed from absorption spectra. The optical band gap energy was obtained by Tauc's equation. The Dispersion parameters (dispersion energy, oscillation energy, moment of optical dispersion spectra, static dielectric constant and static refractive index) were calculated using theoretical Wemple-DiDomenico model. The oscillation strength, oscillator wavelength, high frequency dielectric constant and high frequency refractive index were calculated by single Sellmeier oscillator model. Also, Lattice dielectric constant, N/m* and plasma resonance frequency were obtained. The electronic polarizability of CdS thin film was estimated by Lorenz - Lorentz equation and Clausius Mossotti local field polarizability model.

Keywords: Dispersion parameter; Wemple-DiDomenico model; single Sellmeier oscillator model; Clausius-Mossotti local field polarizability; CdS thin film.

1. INTRODUCTION

The properties of Semiconductor materials are very important for determining their applicability in various fields. Moreover, in nanoscale some of the properties have been affected that made it differ from the bulk material especially the bandgap [1 – 4]. Since it is possible to adjust or tailor their electrical and optical properties especially when physical dimensions are reduced to a few nanometres which these properties depend upon, that makes them useful for application in optoelectronics, nonlinear optics and photoelectrochemical solar cell devices [1,4,5,6]. Dispersion parameters can be determined by parameterization of data. This is because these parameters depend on the dielectric functions of films and other corresponding function such as the bandgap, optical dispersion energies (E_o, E_d), dielectric constant $(\varepsilon,)$ ratio between the number of charge carriers and effective mass $\left(\frac{N}{M^*}\right)$ wavelength of the single oscillator λ, and plasma frequency ω_p. These parameters, especially the optical constants provide information about the microscopic characteristics of the material [7].

Chalcogenide semiconductors such as Cadmium Sulphide (CdS) have shown great usefulness and applicability in solar cells and optoelectronics such as linear and nonlinear optics, visible light diodes, and lasers [8,9]. This is because CdS has wide bandgap, low absorption loss, compact crystallographic cell structure and electronic affinity [10]. Moreso, CdS, is most widely used as a window layer in CdTe thin film solar cells and is a buffer layer in Copper Indium and Gallium Selenide (CIGS) thin film solar cells [11 – 15].

Several deposition techniques have been studied and employed in the fabrication of CdS thin films such as spin coating[16], Electro deposition ED [17], physical vapour deposition PVD[18], spray pyrolysis [19, 20, 21], Successive ionic layer adsorption and reaction SILAR [22], chemical precipitation [23], Sol - gel deposition [24, 25], Thermal evaporation[26, 27], and Chemical bath deposition CBD [2, 28, 29,30 31].

Among all these techniques for synthesizing CdS, CBD has been adjudged to be the simplest, does not require sophisticated and complex machine, does not require high temperature and it is very cheap. Chemical bath deposition of CdS consists of a chemical bath of a salt which contains Cadmium cations and anions of either sulphates, nitrates, chlorides or acetates [32]. The properties of CdS thin films obtained by CBD depends on the preparative parameters, hence several studies have been carried out to optimize such parameters such as; bath temperature, PH of bath content, concentration of different precursors and deposition time [33,34].

This paper reports the dispersion parameters of CdS thin films evaluated from the absorption spectra as a result of variation in deposition time in a chemical bath deposition technique. The accurate determination of these parameters is important not only to know the basic mechanisms but also the underlying phenomena and exploit and develop their interesting technological applications. The dispersion parameters considered are; dispersion energies (E_o, E_d),, dielectric constant $(\varepsilon,)$, the average values of oscillator strength (S), wavelength of single oscillator λ, and plasma frequency ω_p. Also considered was the electronic polarizability using the Lorenz - Lorentz equation and Clausius Mossotti local field model.

2. EXPERIMENTAL DETAILS

CdS thin film was prepared according to our previous work [5] by using ultrasonically cleaned glass substrate of size $(25.0x75.0x1.0)\,mm$. The major precursors for CdS are aqueous solutions from Cadmium acetate for Cadmium source and Thiourea for Sulphide source while Ammonium acetate was used as the complexing agent. All the chemicals used were of analytical grades. The bath consists of 30 ml of 0.264gdm^{-3} of Cadmium acetate, 15$ml\ of$ 0.158gdm^{-3} of ammonium hydroxide, 30 $ml\ of$ 0.153gdm^{-3} of Thiourea and 20$ml\ of$ 1.542gdm^{-3} of ammonium acetate which brought the volume of the content of the bath to 95ml. The temperature of the bath was maintained at 90℃ using 78HW-1 constant magnetic stirrer. The substrates were inserted vertically with the aid of a stand and clips. The deposition was allowed to take place at time intervals of (10, 30, and 50) minutes respectively after which the substrates were removed from the bath simultaneously and rinsed with de-ionized water and then annealed in an oven at a temperature of 400℃ for 60 minutes. we used the gravimetric method in calculating the thickness of the film grown in this work. This method is based on the direct determination of the mass deposited onto the glass substrate. The substrate was weighed before deposition and reweighed after deposition; the thickness was determined using relevant equation. The samples were characterized for optical properties using a single - beam UV-VIS Helios omega spectrophotometer by measuring the absorption of the samples within the wavelength range of (280 – 920) nm.

3. RESULTS AND DISCUSSION

3.1 **Optical Characterization**

Optical measurements of transmittance and absorbance of the films deposited at different deposition times are shown in figure 1 and 2. These measurements have been taken in the wavelength range of (280 – 920) nm. The transmittance was calculated using equation (2) [35,36]

$$T = \frac{1}{10^A} \tag{1,}$$

where A is absorbance as recorded from the spectrophotometer.

From equation (1) it can be understood that

$$A \log_{10} T \tag{2}$$

where A is absorbance

The coefficient of absorption (α) was calculated from the absorbance data using Beer Lamberts law [37] which relates the transmittance (T), absorbance (A) and thickness (d) of the film as shown in equation (3a, b)

$$T = e^{\alpha d} \tag{3a}$$

So that

$$\alpha = 2.303 \frac{A}{d} \tag{3b}$$

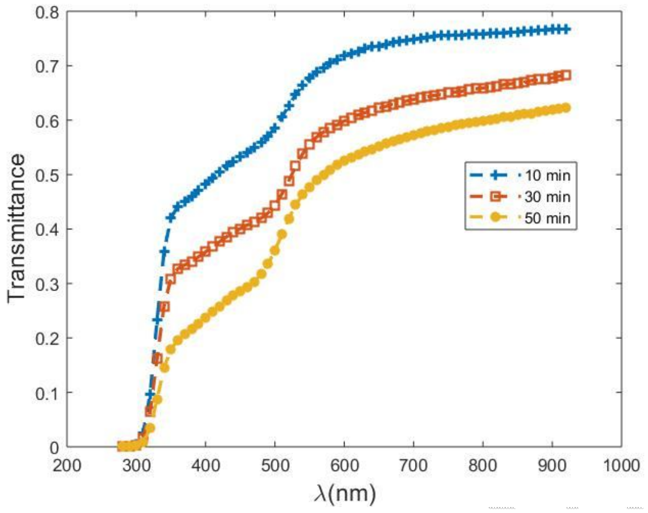

Fig. 1. Variation of Transmittance with the wavelength

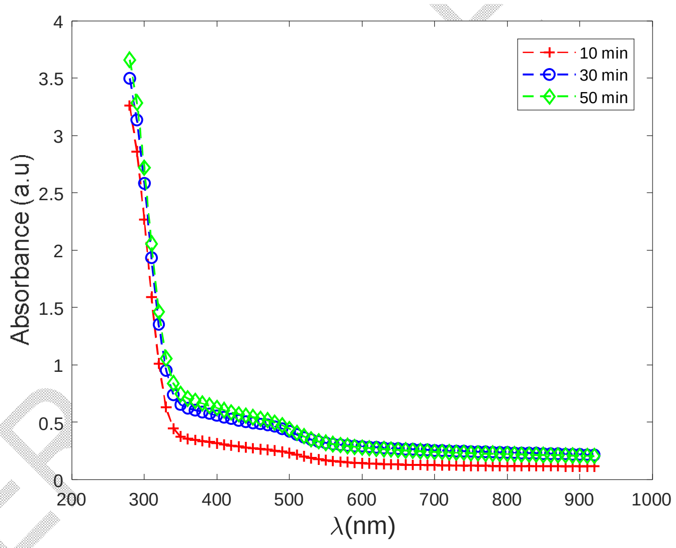

Fig. 2. Variation of absorbance with the wavelength

3.2.1 Optical energy gap.

The optical bandgap of CdS was obtained from the Absorbance data using the Tauc's relation [38] as shown in equation (4).

$$(\alpha h\nu) = A\left(h\nu - E_g\right)^m \qquad 4$$

Where A is a constant called the band tailing parameter, E_g is the bandgap corresponding to a particular transition occurring in the film, ν is the transition frequency, h is the planks constant given by $6.63x10^{-34}m^2kgs^{-1}$, The value of m which is the characteristic nature of the band could be $\frac{1}{2},\frac{3}{2}$, 2, or 3 depending on the nature of the electronics transition responsible for absorption, $m = \frac{1}{2}$ for direct band gap semiconductors. An extrapolation of the linear region of the plot of $(\alpha h\upsilon)^2$ vs $h\upsilon$ gives the value of optical band gap E_g. *[39]*

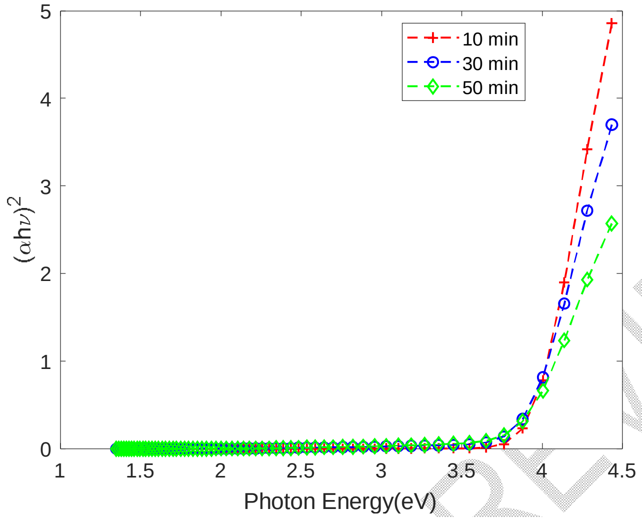

Fig. 3. Plot of $(\alpha h\upsilon)^2$ vs $(h\upsilon)$ of CdS thin film of different deposition time

Figure 3 shows the bandgap energy values of the CdS thin films with different deposition times of 10, 30, and 50 minutes and is listed in table 1.

3.2.2. Refractive index analysis;

One of the distinctive and essential property of an optical material is its refractive index n. This is because it is one of the major factors to be considered in selecting materials used for fabricating optical devices or for optical applications. Therefore, it is essential to understand the refractive index of a material since many optical phenomena are dependent on its value. The refractive index η is closely related to both electronic polarization of ions and the local field inside the optical materials [40]. The refractive index η was determined using equation (5) [41, 42]

$$\eta = \frac{1+\sqrt{R}}{1-\sqrt{R}} \tag{5}$$

where R is the reflectance of the film.

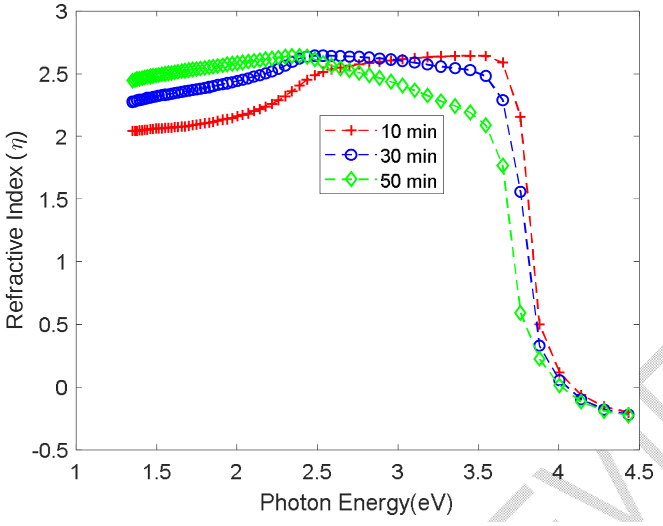

Fig. 4. Plot of $Refractive\ Index$ (η) vs $(h\nu)$ of CdS thin film of different deposition time

3.2.3 Extinction coefficient

The extinction coefficient k is determined using equation (6) [41, 42]

$$K = \frac{\alpha\lambda}{4\pi} \qquad 6$$

where α is the absorption coefficient and λ is the wavelength of the incident beam. The extinction coefficient also known as the absorption index is so important in determining several optical measurements that are related to the absorption of light waves in the medium and dielectric constant [43]. The extinction coefficient k spectra as a function of incident waves is shown in fig 5.

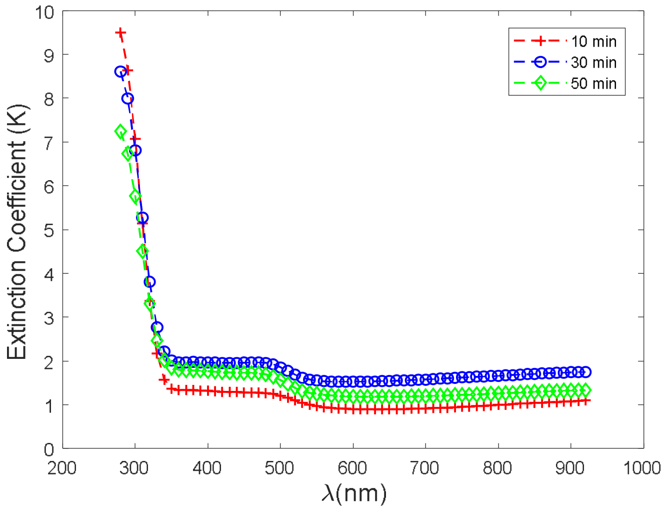

Fig. 5. Plot of $Extinction\ Coefficient$ (K) vs $Wavelength\ \lambda(nm)$ of CdS thin film for different deposition time

The figure shows that the extinction coefficient decreases with increase in the incident waves.

3.2.4 Dielectric constant analysis

The fundamental electron excitation spectra of CdS thin film are described with complex dielectric constant ε^*. The real part of dielectric constant ε_r is related with the property of slowing down the speed of light in materials as well as dispersion of electromagnetic waves that travels within the material whereas the imaginary part of the dielectric constant ε_i provides a measure of the disruptive rate of the wave in the material, meaning that it is responsible for the energy absorption from electric field due to dipole motion [44, 45]. The values of real and imaginary part of the dielectric constant were obtained using equation (7 a, & b) [46] and shown in figure 6and 7.

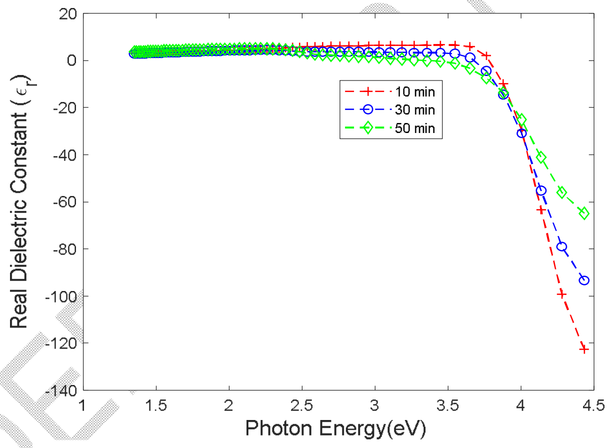

Fig. 6. Plot of $Real\ Dielectric\ Constant\ (\varepsilon_r)$ vs $Photon\ energy\ (eV)$ of CdS thin film of different deposition time

$$\varepsilon_r = \eta^2 - k^2 \qquad 7a$$

and

$$\varepsilon_i = 2\eta k \qquad 7\ b$$

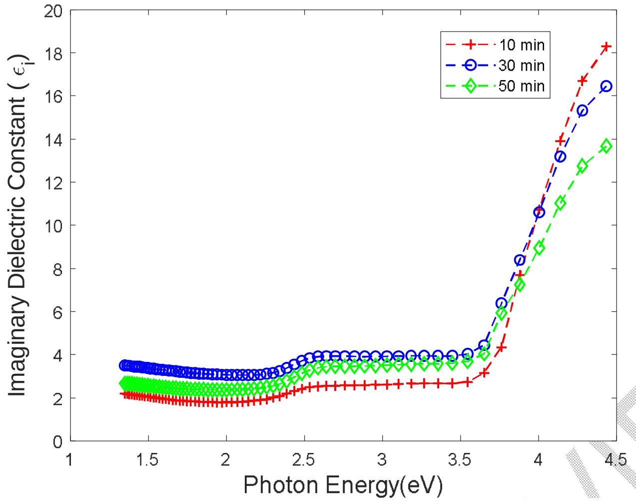

Fig. 7. Plot of $Imaginary\ Dielectric\ Constant\ (\varepsilon_i)$ vs $Photon\ energy\ (eV)$ of CdS thin film of different deposition time

3.2.5 Dispersion energy parameters

In optical communication and designing devices, the dispersion of the refractive index is very important. The spectral dispersion is obtained from the Wemple DiDomenico model given in equation (8).[47]

$$\eta^2 - 1 = \frac{E_d E_o}{E_o^2 (h\nu)^2} \qquad 8$$

where E_d is dispersion energy and is related to the strength of the inter band optical transition. E_o is the oscillator energy which gives the quantitative information on the overall band structure of the CdS thin film. By plotting $\frac{1}{n^2-1}$ against the square of the photon energy $(h\nu)^2$ as shown in figure 8a. The values of $E_d$and E_o are calculated from the slope $(E_0 E_d)^{-1}$ and intercept $\left({E_0}/{E_d}\right)$ on the vertical axis as extracted from the linear fit of each of the deposited sample is given in table 1. From the values of E_d and E_o, the static refractive index (η_o) and static dielectric constant(ε_o) are calculated using equation (9) [47].

$$\varepsilon_o = \eta_o{}^2 = 1 + \frac{E_d}{E_o} \qquad 9$$

The moments of optical dispersion spectra m_{-1} and m_{-3} are evaluated from equation (10a) and (10b)

$$E_o{}^2 = \frac{M_{-1}}{M_{-3}} \qquad 10a$$

And the values of η_o, ε_o, M_{-1} and M_{-3} are listed in table 1.

$$E_d{}^2 = \frac{M_{-1}^3}{M_{-3}} \qquad \text{10b.}$$

The Wemple–Didomenico formula can be modified to find the static optical index of refraction at infinite wavelength [48, 49,50] in the form of

$$\frac{\eta_\infty^2-1}{\eta^2-1} = 1-\left(\frac{\lambda_0}{\lambda}\right)^2 \qquad \text{11a}$$

By plotting $\frac{1}{n^2-1}$ against λ^{-2} of CdS as shown in figure 8b, the high frequency refractive index (η_∞) was calculated from the intercept extracted from the linear fit of each of the deposited sample whereas $\eta_\infty^2 = \varepsilon_\infty$ and were also listed in table 1.

TABLE 1. OPTICAL AND DISPERSION PARAMETERS OF CdS THIN FILMS

$Time$	10 min	30 min	50 min
E_g	3.78 eV	3.72 eV	3.70 eV
E_d	13.16 eV	27.64 eV	20.98 eV
E_o	4.44 eV	4.25 eV	1.48 eV
η_o	1.99	2.75	3.90
ε_o	3.96	7.58	15.18
M_{-1}	2.96	6.50	14.18
M_{-3}	0.1502 eV^2	0.36 eV^2	6.47 eV^2
S_0	3.795×10^{-5}	7.62×10^{-5}	2.02×10^{-5}
λ_o	279.30 nm	292.22 nm	838.50 nm
η_∞	1.72	2.74	3.90
ε_∞	2.96	7.51	15.18
ε_L	7.02	5.99	5.30
$\frac{N}{M^*}$	$1.62 \times 10^{41} kg^{-1}m^{-3}$	$2.31 \times 10^{41} kg^{-1}m^{-3}$	$5.8 \times 10^{41} kg^{-1}m^{-3}$
ω_p	$1.25 \times 10^6 Hz$	$8.18 \times 10^5\ Hz$	$1.30 \times 10^6\ Hz$
α_p	$9.27 \times 10^{-33} Fm^2$	$7.90 \times 10^{-33} Fm^2$	$1.01 \times 10^{-33} Fm^2$

Using the single Sellmeier oscillator model, [43] equation (11b), the oscillator strength and oscillator wavelength of CdS thin film were evaluated and listed in table 1.

$$\eta^2 - 1 = \frac{S_o\lambda_o^2}{1-\left(\frac{\lambda_o}{\lambda}\right)^2} \qquad \text{11b}$$

Where λ is incident wavelength, S_0 is oscillator strength and λ_0 is oscillator wavelength. By plotting $\frac{1}{n^2-1}$ against λ^{-2} of CdS as shown in figure 8b. The values of S_o and λ_o are obtained from the slope and intercept extracted from the linear plot of all the deposited samples.

The lattice dielectric constant (ε_L) of CdS thin film is also calculated from equation (12) [51].

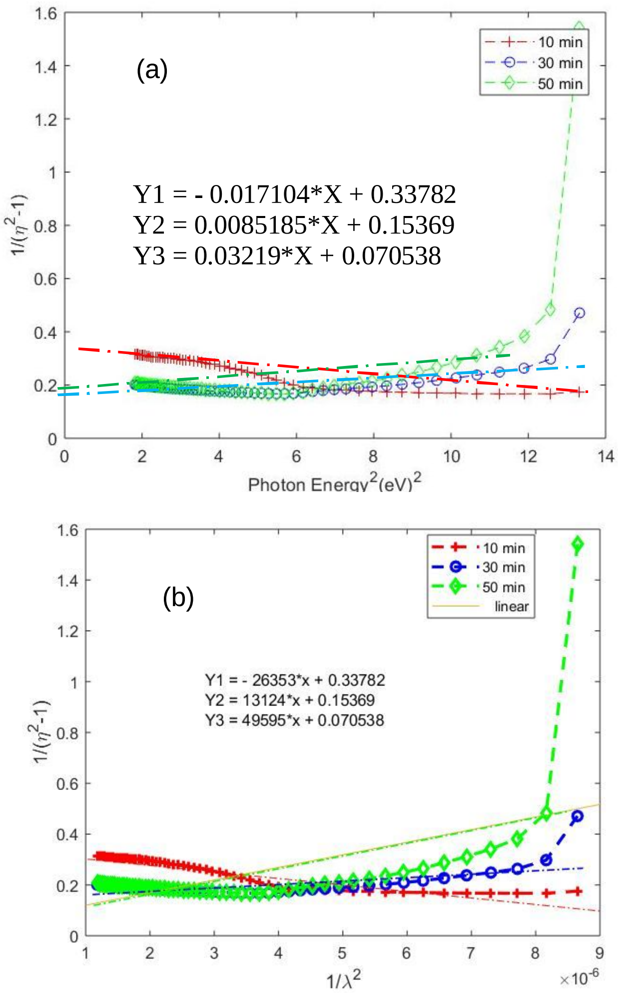

Fig 8 (a) $\frac{1}{\eta^2-1}$ $Versus\ hv^2$ $(b)\frac{1}{\eta^2-1}$ $Versus$ $\frac{1}{\lambda^2}$

$$\eta^2 = \varepsilon_L - \left[\frac{e^2}{4\pi c^2 \varepsilon_o}\frac{N}{M^*}\right]\lambda^2 \qquad 12$$

where e is the charge of electron, c is the speed of light, ε_0 is the permittivity of free space, $\frac{N}{M^*}$ is the ratio of number of free charge carriers and effective mass of electrons. Also, the plasma resonance frequency ω_p which is referred to as the material change from metallic to dielectric can be evaluated from the curve n^2 versus λ^2 using equation (13) [43].

Using the curve, the values of ε_L, $\frac{N}{M^*}$ and ω_p were obtained and listed also in table 1

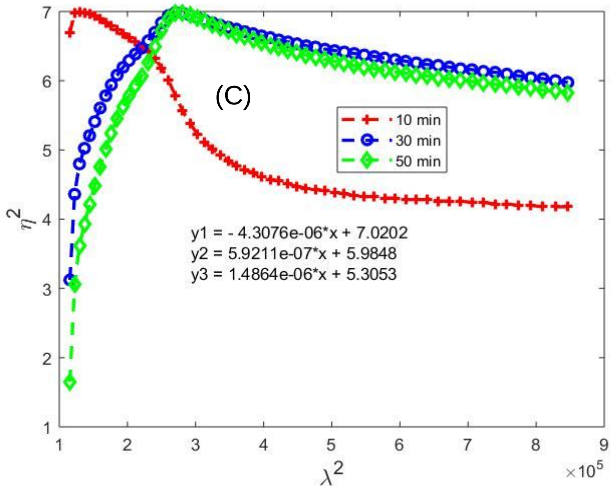

Fig 8 (c) η^2 $Versus$ λ^2

3.2.6 Electronic polarizability

The electronic polarizability (α_p) gives the degree of the electronic response to the application of an electromagnetic field on the electron clouds [44]. The polarizability (α_p) of CdS thin film can be evaluated using Lorenz - Lorentz equation and Clausius Mossotti local field model [51, 52] as shown in equation (14).

$$\left(\frac{\eta^2-1}{\eta^2+2}\right) = \frac{N_A \rho}{3\varepsilon_o M}\alpha_p \qquad 14$$

where η is the refractive index, N_A is the Avogadro's number M is the molar mass of bulk CdS and ρ is the density of bulk CdS. Therefore, the plot of $\frac{n^2-1}{n^2+2}$ against $h\nu$ of CdS thin film is shown in figure 8(d). The intercept of plot on the vertical ais gives the value of α_p and listed in table 1, as extracted from the linear plot of the deposited samples.

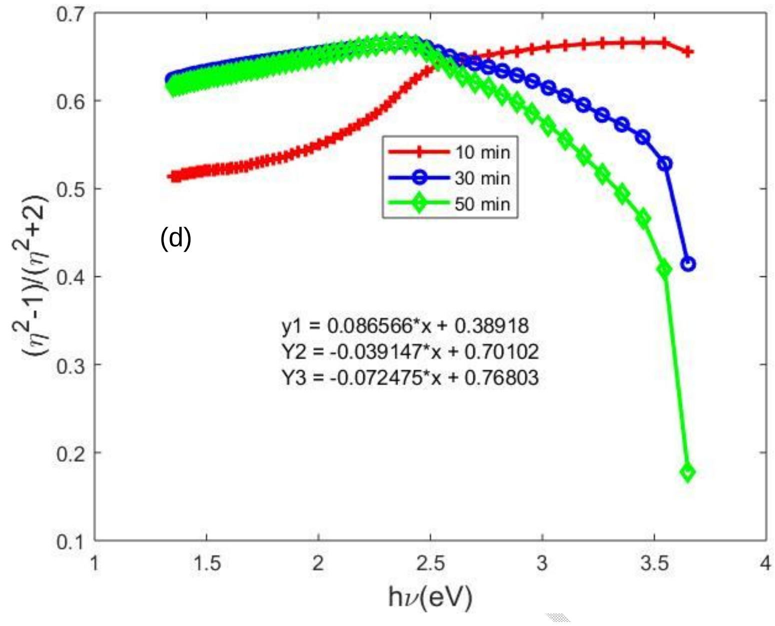

Fig 8 (d) $\frac{\eta^2-1}{\eta^2+2}$ $Versus\ hv\ (eV)$

4.0 Conclusion

Cadmium Sulphide (CdS) thin film was deposited by chemical bath deposition technique on a transparent glass substrate. The CdS thin film has a very high transmittance through the entire electromagnetic spectral range which justify it as a good material for optoelectronic devices and solar cells. The dielectric constant was evaluated from the linear refractive index and extinction coefficient. The dispersion parameters (E_d, E_0, $moment\ of\ optical\ spectra\ S_0$, λ_0, $\frac{N}{M^*}$, ω_p, and α_p,) dielectric constants ($\eta_0, \eta_\infty, and\ E_L$) have been evaluated using Wemple DiDomenico model and single Sellmeier oscillator model. The electronic polarizability of CdS thin film was evaluated using Clausius - Mossotti local field polarizability model.

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