Effects of Dip-Time on the Optical and Solid State Properties of CdSe Thin Films Deposited By Chemical Bath Deposition (CBD) Technique

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ABSTRACT

Thin films of cadmium selenide (CdSe) were grown on glass substrates at room temperature using Chemical Bath Deposition (CBD) technique. The films were grown at various dip-times and characterized using Rutherford Back Scattering (RBS) spectroscopy for chemical composition. The analysis of the optical and solid state properties which include spectral absorbance, transmittance, reflectance, absorption and extinction coefficients, index of refraction, real and imaginary dielectric constants, optical conductivity and energy band gaps were done using the Avantes double beam spectrophotometer, model 2048, Ava soft 7.1 in the wavelength range of 320nm-900nm. The results show wide range of variations in these optical and solid state properties due to variation in dip-times thus providing various potential areas of applications in solar cells, window coatings, anti-reflection coatings in computer screen to reduce reflection.

Keywords: *Cadmium Selenide, Dip-Times, Band Gap, Characterized, Applications*.

1. INTRODUCTION

Cadmium Selenide (CdSe) is an interesting I1-VI binary semiconductor that has been extensively investigated because of its exceptional optoelectronic properties. It offers great potential for fabrication of solar cells, photodetectors, light-emitting diodes and high efficiency thin film transistors [1-3]. Band gaps in the range of 1.65eV-1.84eV have been reported by various authors [2, 4-6]. Recently, the techniques of thin film growth of this semiconductor has become of interest. Several researchers have prepared CdSe using several techniques such as electrodeposition [7], vacuum evaporation [1], spray pyrolysis [4], chemical bath deposition [6, 8-10]. Different preparation parameters such as concentration of metal ions, concentration of chalcogenide ions, deposition time, pH of resultant solution and temperature affect the properties of materials grown by chemical bath deposition technique. The current work reports the influence of varying deposition time on the optical and solid state properties of the films using chemical bath deposition method.

2. THEORETICAL CONSIDERATIONS

The absorption coefficient is related to the transmittance and thickness of the film by the expression [11-12]

$$\alpha = \frac{ln\left(\frac{1}{T}\right)}{t} \qquad (1)$$

The absorption coefficient dependence on the photon energy near the fundamental absorption edge [13-14] is given as follows:

$$\alpha h\nu = A(\alpha h\nu - Eg)^n \qquad (2)$$

Where hν is the energy of the photon, E_g is the band gap, n is the number which characterizes the optical processes, A is a constant.

n = ½ for allowed direct photon transitions and 3/2 for forbidden direct transitions. n = 2 for indirect and 3 if it is forbidden. Extrapolation of the straight line portion of $(\alpha h\nu)^2$ against hν to $(\alpha h\nu)^2 = 0$ yields the band gaps of the films.

For semiconductors and insulators, reflectance R and refractive index n are related by the expression [13, 15]

$$R = \frac{(n-1)^2}{(n+1)^2} \qquad (3)$$

Where $n = \frac{1 + R^{1/2}}{1 - R^{1/2}}$ (4)

The extinction coefficient k is related to the absorption coefficient by [14]

$$K = \frac{\alpha\lambda}{4\pi} \qquad (5)$$

Where λ is the wavelength of the electromagnetic waves

The complex dielectric constant is given by [13]

$$\mathcal{E} = \mathcal{E}_r + \mathcal{E}_i = (n + ik)^2 \qquad (6)$$

Where $\varepsilon_r = n^2 - k^2$ (7)

And $\varepsilon_i = 2nk$ (8)

The optical conductivity σ_{op} is given by [13, 16]

$$\sigma_{op} = \frac{\alpha nc}{4\pi} \qquad (9)$$

Where c = velocity of light in vacuum.

3. MATERIALS AND METHODS

Thin films of CdSe were deposited on glass substrates using chemical bath deposition method. The chemicals used were cadmium acetate as cadmium source, sodium selenosulphate as source of selenide ion, triethanolamine (TEA) as the complexing agent and ammonia solution for pH adjustment. The sodium selenosulphate solution was obtained by refluxing 8g of selenium powder mixed with 25g of anhydrous sodium sulfite in 200mls of distilled water at 90^0C for 6hrs [15,17]. This gave 0.4m of sodium selenosulphate solution. The glass substrates were previously degreased in acqua regia (3:1 mixture of conc. HCl and conc. HNO_3) for 48hrs, [15,18], cleaned in cold water with detergent, rinsed in distilled water and dried in air. The degreased substrates provide nucleation centres for the growth of the films thus giving highly adhesive and uniform films.

The principle underlying the deposition of CdSe as discussed by Chopra and Das [19] is based on the slow release of Cd^{2+} and Se^{2-} ions in basic solution and subsequent condensation of these ions on the substrate suitably mounted in the bath.

The chemical bath was formed by adding 2.5mls of 1m cadmium acetate into a 50ml beaker followed by 5mls of 7.4m triethanolamine and the mixture stirred, after which 2mls of 13.4m ammonia solution was added followed by 2mls of 0.4m sodium selenosulphate and finally 20mls of distilled water. The mixture was stirred for a few seconds and the resultant pH was 11. Previously cleaned glass slides were placed vertically into the chemical bath and were removed after dip-times of 8hrs, 12hrs and 16hrs; rinsed with distilled water and dried in air. The complexing agent helps to slow down the reaction since a thin film cannot be formed with fast precipitation. Preparation parameters are displayed in Table 1.

The chemical equation governing the reaction for the growth of CdSe films are:

Cadmium salt reacted with TEA to form complex Cd salt:

$$(CH_3COO)Cd.2H_2O + TEA \rightarrow [Cd(TEA)]^{2+} \qquad (10)$$

Hydrolysis of ammonia in water gives OH^- ions in solution according to the equation:

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \qquad (11)$$

Finally formation of CdSe thin films takes place via the chemical reaction:

$$[Cd(TEA)]^{2+} Na_2SeO_3 + 2OH^- \rightarrow CdSe + Na_2SO_4 + TEA + H_2O \qquad (12)$$

The films were characterized using Rutherford BackScattering Spectrometry (RBS) for the elemental composition, Avantes double beam spectrophotometer model 2048, Ava soft 7.1, for the Absorbance-

Transmittance-Reflectance (A-T-R) spectra and Veeco Dektak 150 stylus surface profiler for thickness measurement.

Table 1: Preparation parameters for Cadmium Selenide (CdSe) films.

Film samples	Deposition time (hrs)	Cadmium acetate		TEA		Na_2SeO_3		Ammonia soln		Vol. of H_2O (ml)
		Mol (M)	Vol. (ml)	Mol (M)	Vol. (ml)	Mol (M)	Vol. (ml)	Mol (M)	Vol. (ml)	
H_1	8	1	2.5	7.4	5	0.4	2	13.4	2	20
H_2	12	1	2.5	7.4	5	0.4	2	13.4	2	20
H_3	16	1	2.5	7.4	5	0.4	2	13.4	2	20

4. RESULTS AND DISCUSSION

The elemental composition of the sample was analyzed using Rutherford Backscattering Spectrometry (RBS). The average atomic percentage of Cd and Se is 52.94:4.06. The range of thickness of the films deposited is 0.460µm – 0.750µm. The result is shown in Fig.1 and Table.2

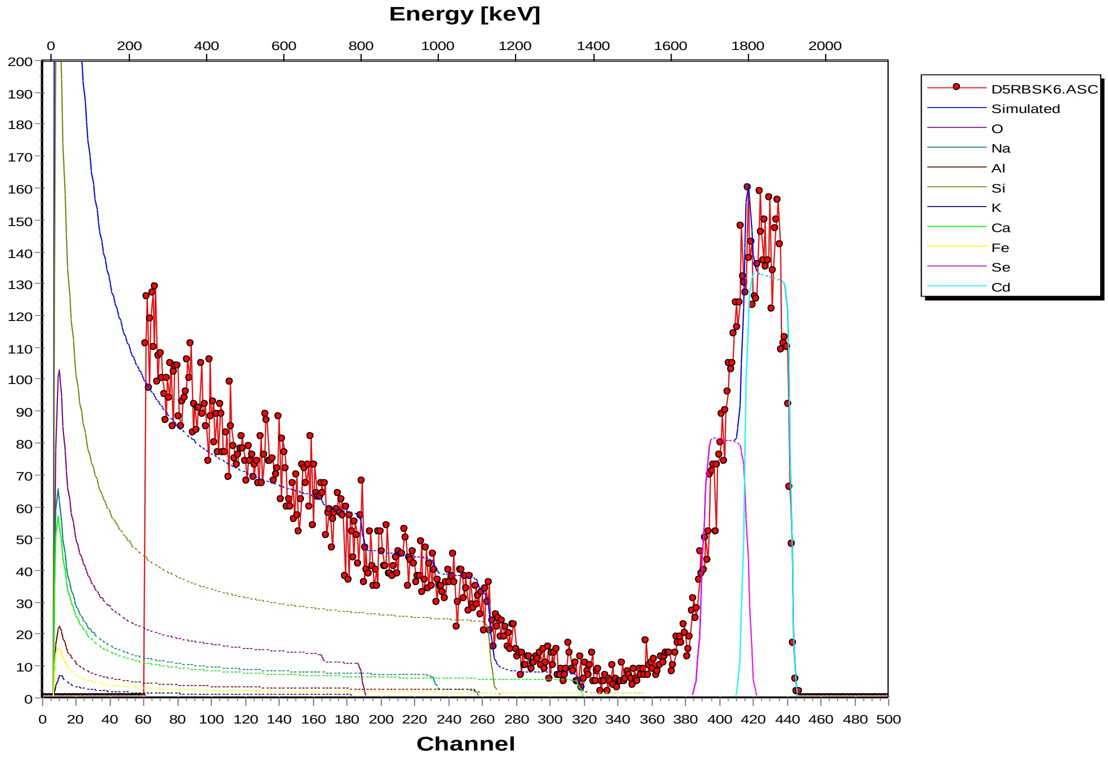

Fig 1: RBS analysis for CdSe thin films (sample H_1)

Table 2: Composition of CdSe and substrate from RBS analysis

CdSe	Cd	Se	O	Si	Na	Fe	Al	Ca
H_1	52.94%	47.06%	-	-	-	-	-	-

Substrate	-	-	56.0%	28.0%	12.6%	0.52%	0.53%	1.83%

Fig. 2 shows the spectral absorbance of the films prepared at 300k. All the films exhibited maximum absorbance in the UV region. Films H_2 and H_3 which were deposited for 12hrs and 16hrs respectively have two pronounced absorbance peaks between 320nm-720nm with H_3 (16hrs) having the highest absorbance of 80.8% at 320nm. Film H_1 deposited for 8hrs has only one absorbance peak at 320nm and decreased in value throughout the VIS-NIR regions. From the spectra, absorbance increased with deposition time.

Fig. 3 shows the transmittance spectra in which samples with higher absorbance have lower transmittance values. Sample H_1 (8hrs) has highest transmittance of 69% in the NIR region. It compares well with the report of [20] which revealed a very small transmission below 400nm and high transmittance in VIS-NIR regions. All the films have poor transmittance 15%-21% in the UV region.

The reflectance spectra is shown in Fig. 4. Sample H_2 (12hrs) has peak reflectance of 22.18% at 900nm while H_3 (16hrs) has maximum reflectance of 20.33% in the VIS region. All the films showed relatively low reflectance less than 23% throughout the solar region. These results indicate that CdSe grown at different dip-times are potential good materials for different applications.

Sample H_1 (8hrs) with highest transmittance of 69% in the VIS-NIR regions and very low reflectance of 18% is a good material for thermal control window which is coatings for cold climates and anti-reflection coatings.

Sample H_2 (12hrs), H_3 (16hrs) with high absorbance throughout the UV-VIS-NIR regions of the electromagnetic spectrum could be used to form p-n junction solar cells with other suitable thin film materials for photovoltaic generation of electricity. They can also serve as good window layers for photocells.

Sample H_1 (8hrs) and H_2 (12hrs) with poor transmittance in the UV but moderately high transmittance in some portions of VIS and NIR regions and high absorbance values in the UV region make them good materials for screening off UV portion of the electromagnetic spectrum which is dangerous to human health as well as harmful to day old chicks that have not developed protective feathers. The films can be used to coat eye glasses for protection from sunburn caused by UV radiations. The films with high VIS-NIR transmittance can be used to coat poultry roofs and walls to ensure protection of day old chicks from UV radiation while chicks will derive warmth from the heating portion of the electromagnetic spectrum as well as admit VIS light in the house. They are also suitable as photosynthetic coatings for green houses.

The absorption coefficient increases with dip-time as shown in Fig. 5 and is higher at lower wavelengths. This is in line with the report of [1] on CdSe thin films deposited by vacuum evaporation. The average values for films H_1 (8hrs), H_2 (12hrs)and H_3 (16hrs) are 0.506 x 10^6m^1, 1.094 x 10^6m^{-1} and 1.183 x 10^6m^{-1} respectively. However, sample H_1 has the lowest absorption coefficient of about 0.387 X 10^6m^{-1}. The refractive index rose from minimum values in the UV region and was fairly constant in the VIS-NIR regions as shown in Fig. 6. Films deposited at 8hrs, 12hrs and 16hrs have average refractive indices of 2.39, 2.52, 2.47 and peak values of 2.64, 2.68, and 2.64 respectively. This falls within the range of values 2.0-2.7 reported by [21-22]. The refractive index of grown films is greater than 2.0 which make them good candidates for protective coatings in agriculture and architecture. The extinction coefficient increases with dip-time and also with wavelength in the VIS-NIR region as shown in Fig. 7. In general, all the films have lowest value of extinction coefficient in UV region films. H_1 (8hrs), H_2 (12hrs) and H_3 (16hrs) have peak values of 0.039, 0.063, and 0.095 respectively.

Figure 8 shows the plot of optical conductivity against wavelength. The average values of 2.84 x $10^{13}s^{-1}$ for H_1 (8hrs), 6.51 x $10^{13}s^{-1}$ for H_2 (12hrs) and 6.9 x$10^{13}s^{-1}$ for H_3 (16hrs) showed increase with dip-time.

The plots of ε_r Vs wavelength are displayed in Fig. 9. ε_r has maximum values that ranged between 6.94 and 7.26 with average values between 5.71 and 6.38.

Fig. 10 shows the imaginary dielectric constant that increased with dip-time in the VIS-NIR regions. All the films have lowest imaginary dielectric constant values in the UV region with average values between 0.108 and 0.287.

Optical band gaps of the grown films were estimated from $(\alpha h\nu)^2$ against $h\nu$ curves shown in Fig. 11, while the indirect band gap was estimated from Fig. 12.

The direct band gap, E_g was determined by extrapolating the straight portion to the energy axis at $(\alpha h\nu)^2 = 0$. It was found to be 1.73eV-1.83eV as shown in Table 3. This falls within the range of values reported by [20] (1.70eV-1.80eV), [23] (1.45eV-1.98eV) for chemically deposited CdSe, [24] (1.77eV-1.92eV) for electron beam evaporated and [7] (1.82eV) for electrodeposited CdSe. The indirect band gap was found to be between 1.47eV and 1.62eV.

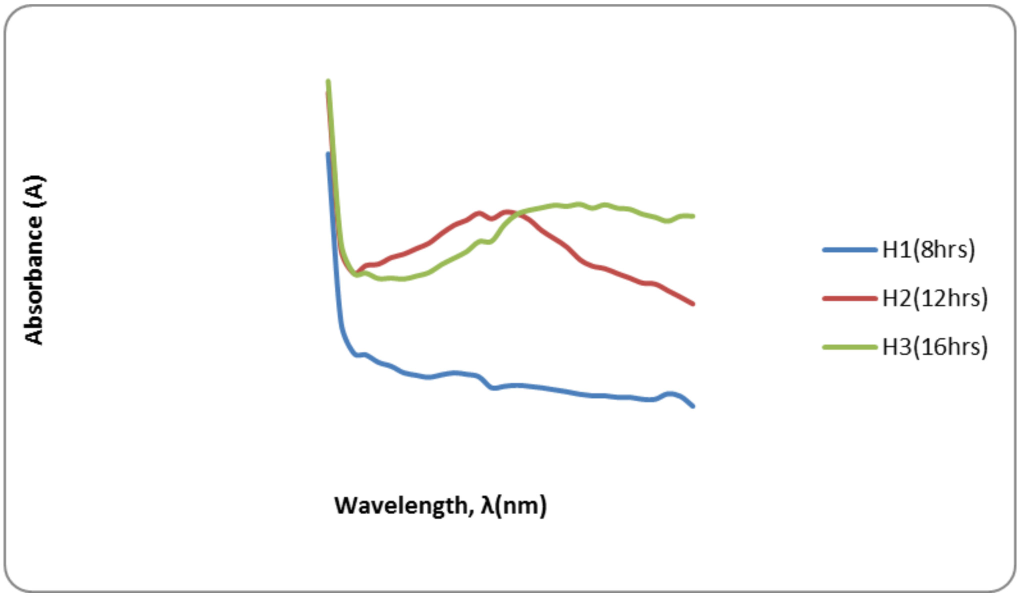

Fig 2: Absorbance as a function of wavelength for CdSe films deposited at different dip-times.

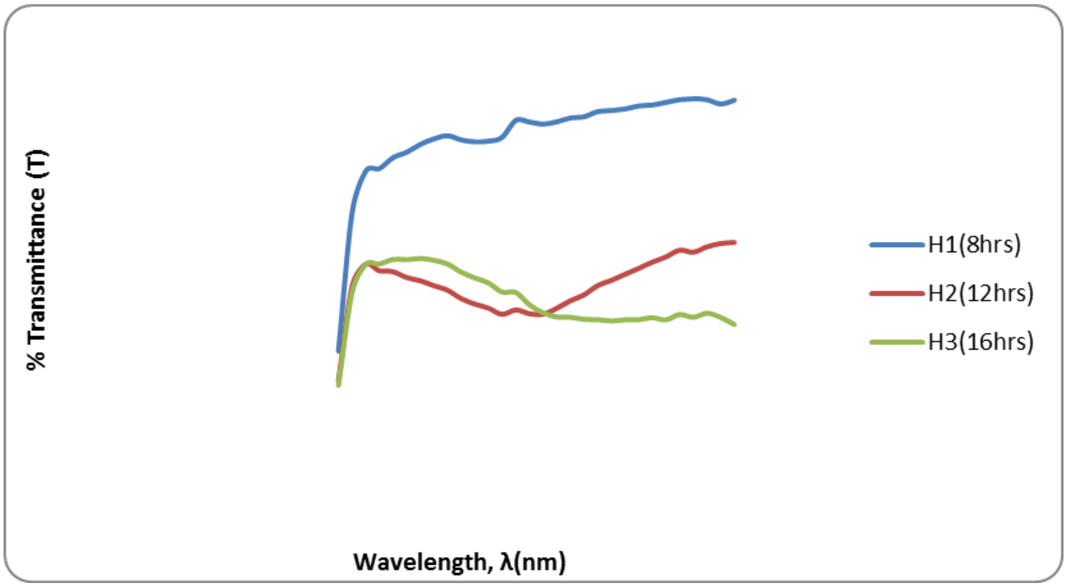

Fig 3: Transmittance as a function of wavelength for CdSe films deposited at different dip-times.

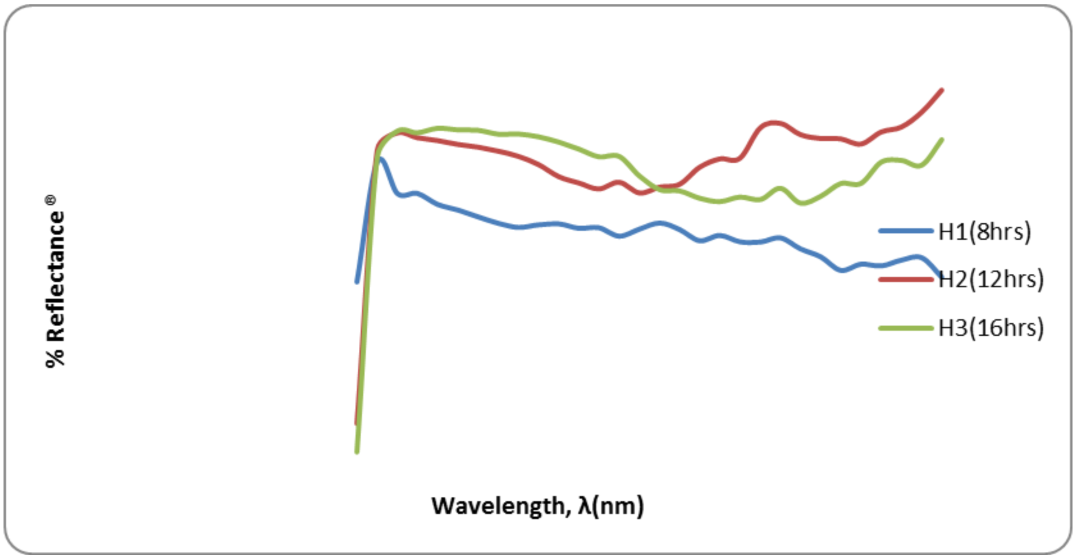

Fig 4: Reflectance as a function of wavelength for CdSe films deposited at different dip-times.

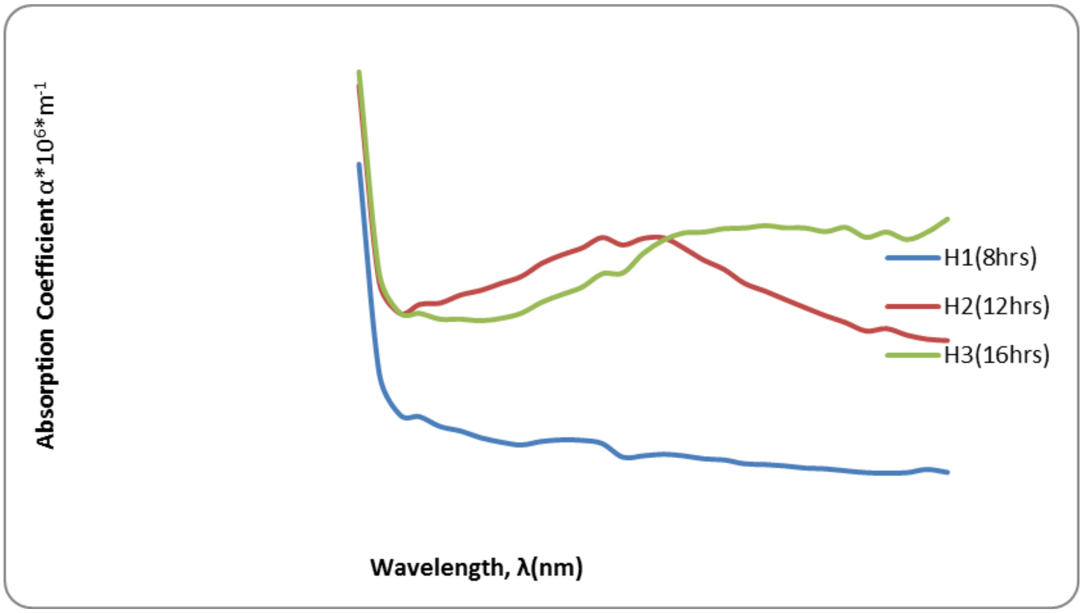

Figure 5: Absorption coefficient α as a function of wavelength λ for CdSe films deposited at different dip-times.

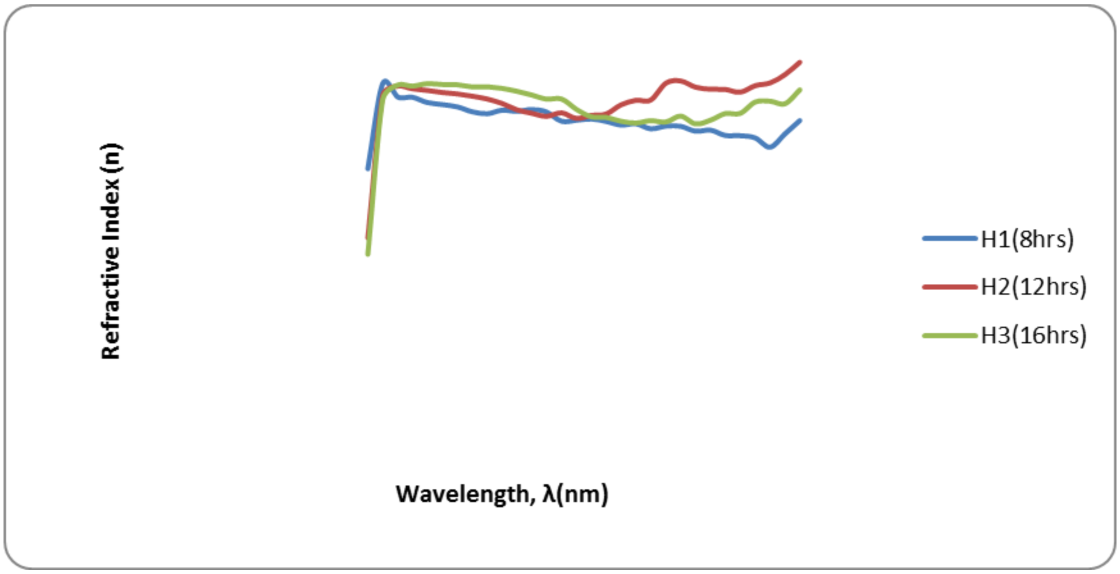

Figure 6: Refractive index n as a function of wavelength λ for CdSe films deposited at different dip-times.

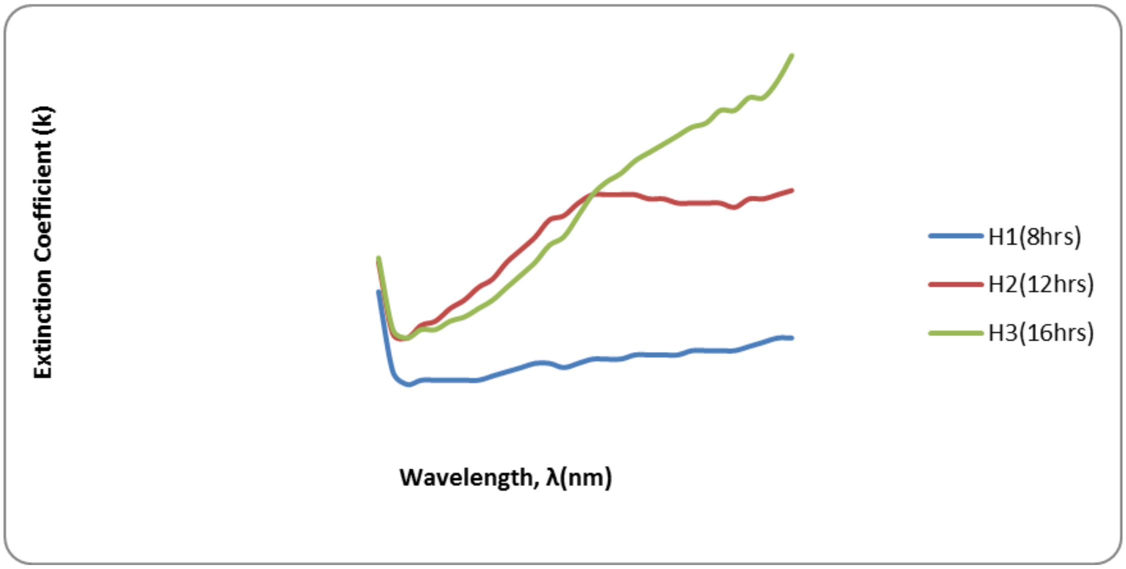

Figure 7: Extinction coefficient k as a function of wavelength for CdSe films deposited at different dip-times.

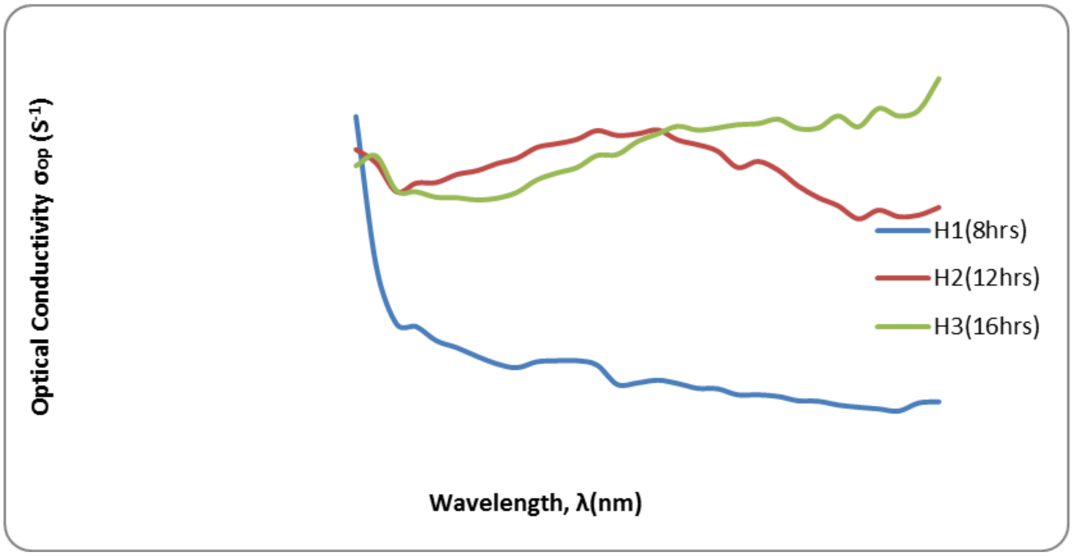

Figure 8: Optical conductivity σ_{op} as a function of wavelength λ for CdSe films deposited at different dip-times.

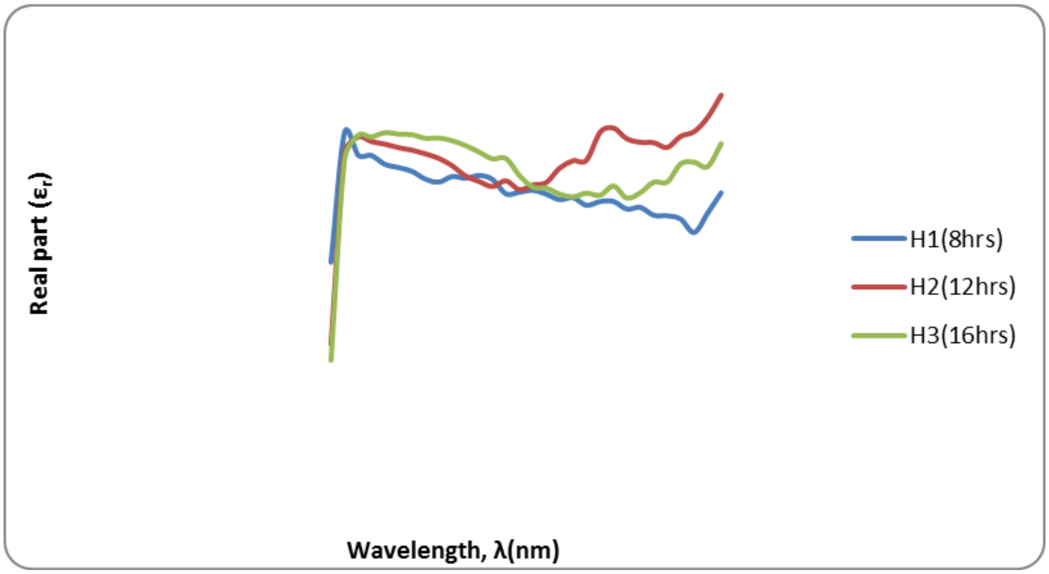

Figure 9: Real part of dielectric ε_r as a function of wavelength λ for CdSe films deposited at different dip-times.

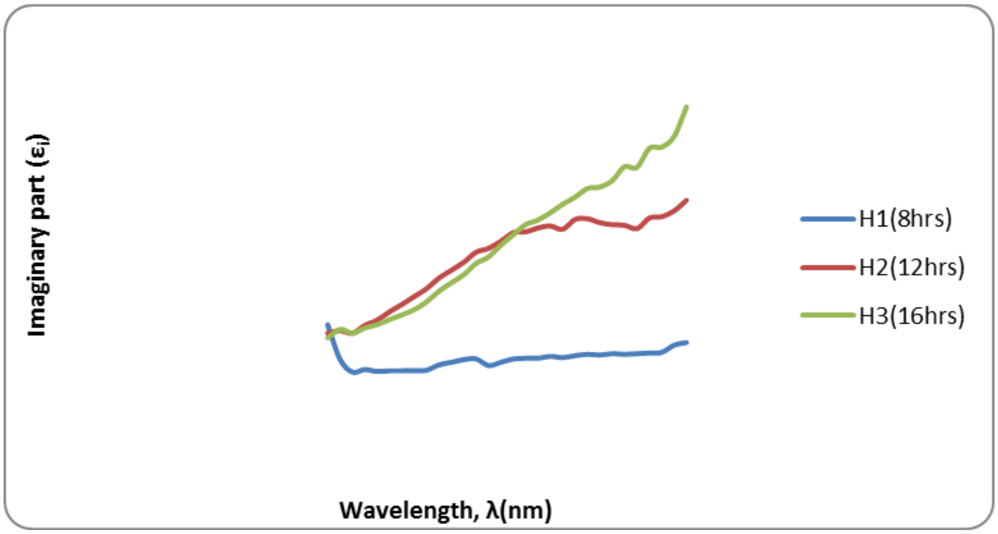

Figure 10: Imaginary part Ɛi as a function of wavelength λ for CdSe films deposited at different dip-times.

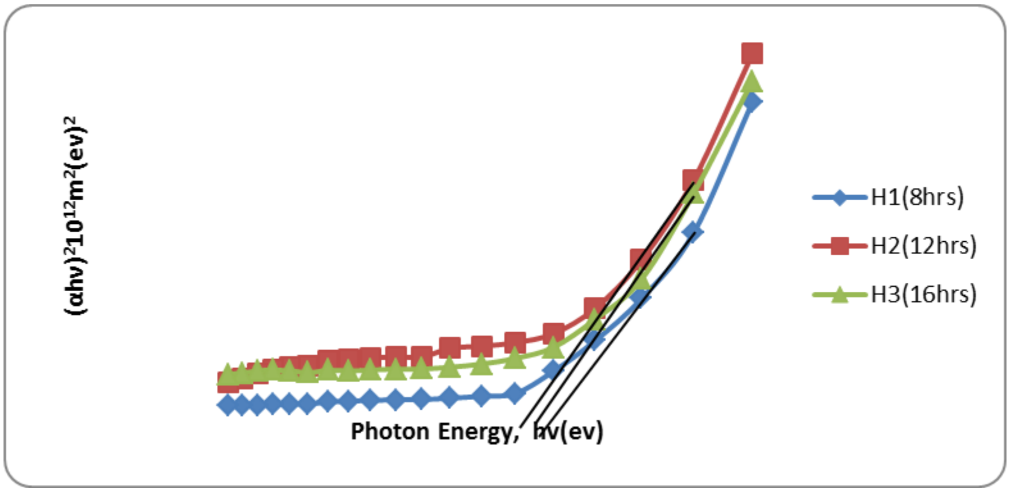

Figure 11: Plot of $(\alpha h\nu)^2$ vs hν for CdSe films deposited at different dip-times.

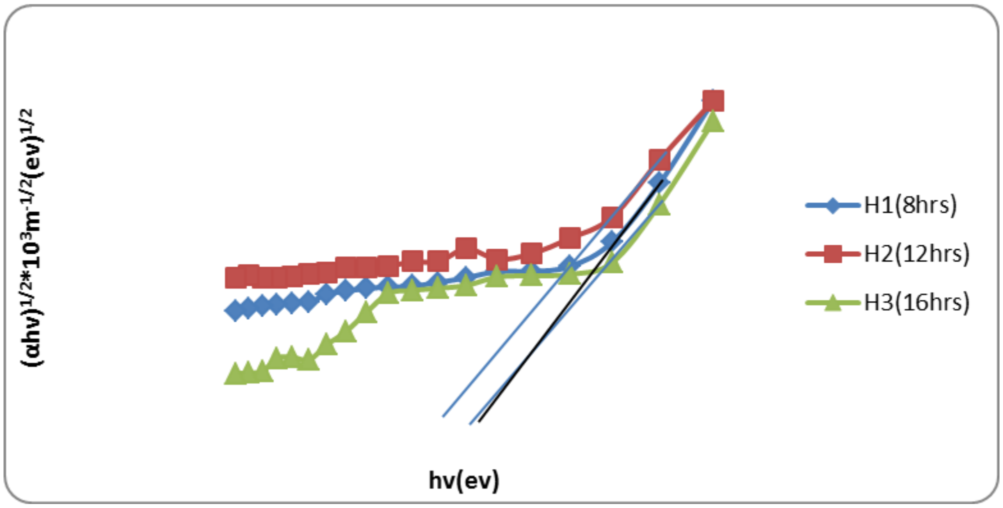

Figure 12: Plot of $(\alpha h\nu)^{1/2}$ vs hν for CdSe films deposited at different dip-times.

Table 3: Variation of Optical and Solid State properties of CdSe thin films with dip-time and thickness at 300k.

Sample	Dip-time (hrs)	Peak α x $10^6 m^{-1}$	Peak n	Peak k	Peak σ_{op} x $10^{13} s^{-1}$	Peak ε_r	Peak ε_i	E_g (eV)	Thickness t (µm)
H_1	8	1.52	2.64	0.039	7.49	6.95	0.133	1.83	0.460
H_2	12	1.81	2.68	0.063	7.64	7.26	0.349	1.73	0.630
H_3	16	1.86	2.64	0.095	8.19	6.94	0.491	1.78	0.750

CONCLUSION

The effect of dip-time on chemical bath deposited CdSe thin films has been studied. It was found that the optical and solid state properties of the grown films are functions of dip-times. Absorbance increased with dip-time while transmittance was shown to be the inverse. Some films were found to absorb highly in the UV-VIS-NIR regions and transmit in the VIS-NIR regions. Film thickness varied from 0.460µm-0.750µm and the energy gap, E_g, varied between 1.73eV and 1.83eV while indirect energy gap varied between 1.47eV and 1.62eV. All the films showed low reflectance of less than 23% throughout the solar region. Some of the films could be used as thermal window coatings for cold climate, anti-reflection coatings in computer screen to reduce reflection while others could find application in solar cell technology, poultry protection and coating of eye glasses against UV radiation.

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