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Study of Linear and Non-Linear Optical Parameters of Zinc Selenide Thin Film

H. N. Desai*, J. M. Dhimmar*, B. P. Modi*
*(Department of Physics, Veer Narmad South Gujarat University, Surat-396 007, Gujarat, India)

ABSTRACT
Thin film of Zinc Selenide (ZnSe) was deposited onto transparent glass substrate by thermal evaporation technique. ZnSe thin film was characterized by UV-Visible spectrophotometer within the wavelength range of 310 nm-1080 nm. The Linear optical parameters (linear optical absorption, extinction coefficient, refractive index and complex dielectric constant) of ZnSe thin film were analyzed from absorption spectra. The optical band gap and Urbach energy were obtained by Tauc's equation. The volume and surface energy loss function of ZnSe thin film were obtained by complex dielectric constant. 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 polarizibility of ZnSe thin film was estimated by Clausius-Mossotti local field polarizibility. The non-linear optical parameters (non-linear susceptibility and non-linear refractive index) were estimated.
Keywords – linear optical absorption coefficient; Dispersion parameter; Wemple-DiDomenico model; single Sellmeier oscillator model; Clausius-Mossotti local field polarizibility; ZnSe thin film.

I. INTRODUCTION

II-VI semiconductor compound has promising materials for high performance optoelectronic devices, window layers in solar cells, protective and infrared coating because of its high iconicity, large band gap (between 1 eV-3 eV), luminescent, physical and chemical properties. Zinc Selenide (ZnSe) is one of the most attractive binary wide band gap semiconducting material which has potential applications for optoelectronic devices such as light emitting diodes (LEDs), Laser diodes, economical solar cell, transistors, photoelectrochemical (PEC) cell, detectors and sensors [1-7]. Also, ZnSe films are applicable for dielectric mirrors and filters in visible region because of its high refractive index and high transmittance [8, 9]. Crystalline ZnSe offer wide variety of possible application in nano electronic and nano photonics and as resonators in wave guide.

In present work, the linear optical parameters of ZnSe thin film have been evaluated from absorption spectra. As per author's information, first time the dispersion of refractive index and the non-linear optical parameters of thermally deposited ZnSe thin film were studied using semi empirical models.

II. EXPERIMENTAL PROCEDURE

A thin film of ZnSe was deposited onto transparent glass substrate using thermal evaporation technique at appropriate substrate temperature (485 K). A ZnSe powder (99.99% purity) was employed as a source material which is kept into molybdenum boat. The evaporation was performed in a vacuum environment ($5x10^{6}$ mbar) with the help of HINDHIV:15F6D coating unit. The transparent glass substrates were cleaned with ethanol and acetone in ultrasonic cleaner. The rate of deposition (2-5 Å/s) and film thickness (971 Å) was measured by Quartz crystal monitor.

The absorption, transmittance and reflectance spectra of ZnSe thin film were recorded using UV-Visible spectrophotometer (Cary-300, Varian, Australia) in the wavelength range of 310nm-1080nm at room temperature.

III. RESULTS AND DISCUSSION

The absorption, transmittance and reflectance spectra as a function of wavelength of ZnSe thin film are shown in Fig.1. The maximum value of transmittance is 94% in the visible region. The transmittance curve has interference pattern due to multiple interference between three interfaces (air and film, substrate and air, film and substrate) which shows that ZnSe thin film has good surface smoothness and good homogeneity [10].

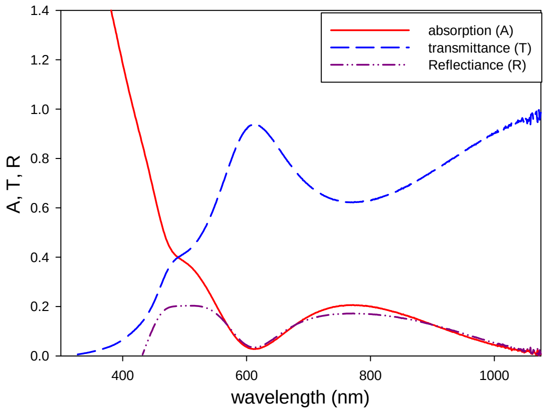

Fig.1 absorption, transmittance and reflectance spectra as a function of wavelength of ZnSe thin film.

The small peaks were observed in absorption spectra which exhibits that some defects state may be arise inside the band edge [11]. The value of reflectance spectra is lower than absorption and transmittance spectra which indicated that ZnSe thin film is applicable for window layer in solar cells. The optical absorption coefficient of ZnSe thin film is calculated by following relation [12];

$$\alpha = \frac{2.303 \times A}{t} \qquad (1)$$

Where A is absorption and t is film thickness.

Near the absorption edge, the direct optical band gap of ZnSe thin film can be obtained from Tauc's relation [12];

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \qquad (2)$$

Where A is energy independent constant, E_g is optical energy band gap of ZnSe thin film. The plot of $(\alpha h\upsilon)^2$ versus hυ (Tauc plot) of ZnSe thin film is shown in Fig.2. The Tauc plot of ZnSe thin film has linear nature in the strong absorption zone of the absorption spectra. The value of direct optical band of ZnSe thin film were determined by extrapolating the linear portion of Tauc plot to $(\alpha h\upsilon)^2 = 0$, which is listed in Table.1. The value of optical band gap is slightly different with standard value due to particle size and quantum confinement.

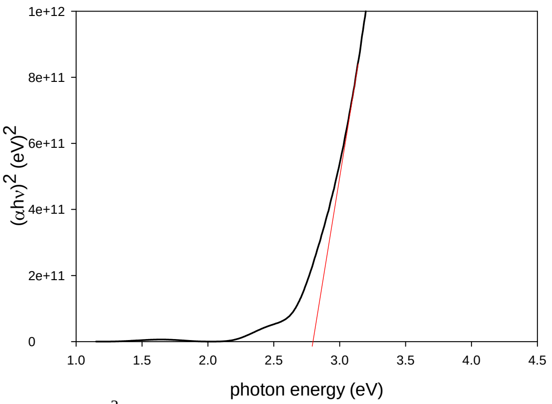

Fig.2 $(\alpha h\upsilon)^2$ versus photon energy (hυ) (Tauc plot) of ZnSe thin film.

In the Urbach Model, Urbach energy was determined the photon capture efficiency of ZnSe thin film. The width of localized states inside the optical band gap of the semiconducting thin films called Urbach energy. The Urbach energy was obtained by following relation [13];

$$\alpha = \alpha_0 e^{h\nu/\Delta} \qquad (3)$$

Where Δ is Urbach energy.

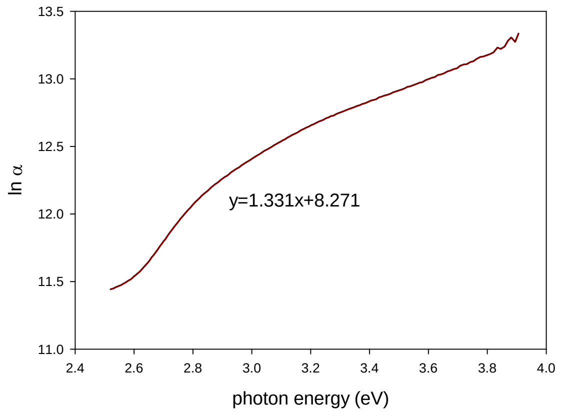

Fig.3 ln α versus photon energy (hυ) of ZnSe thin film.

The plot of ln α versus hυ of ZnSe thin film is shown in Fig.3. The Urbach energy is determined from inverse of slope. The value of Urbach energy is low in the range of meV which is represented that ZnSe thin film has lower density of localized defect states.

From the absorption and reflectance spectra, the extinction coefficient (k) and refractive index (n) of ZnSe thin film was determined using following formulae [14, 15];

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

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}} \qquad (5)$$

Where R is reflectance and λ is wavelength of incident beam.

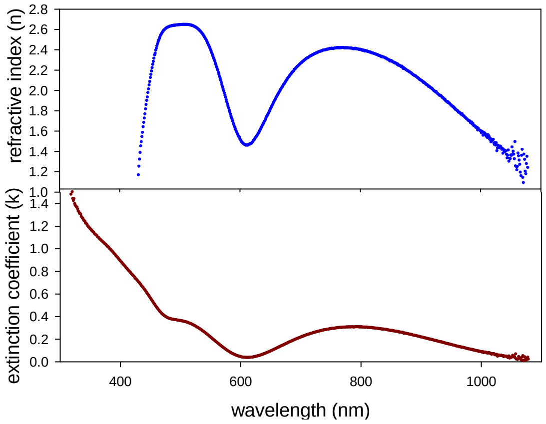

Fig. 4 refractive index and extinction coefficient versus wavelength of ZnSe thin film.

The refractive index and extinction coefficient as a function of wavelength is shown in Fig.4. The value of extinction coefficient is low over the entire spectral range which is indicated that ZnSe thin film has highly transparent and good surface smoothness [12].

The fundamental electron excitation spectra of ZnSe thin film are described with complex dielectric constant. The real part of dielectric constant is related with the property of slowing down the speed of light in the materials. Whereas, the imaginary part of dielectric constant is related with absorb energy from electric field due to dipole motion [12, 16]. The value of real and imaginary part of dielectric constant was obtained from following formula;

$$\varepsilon_1 = n^2 - k^2 \quad (6)$$

$$\varepsilon_2 = 2nk \quad (7)$$

Where ε_1 and ε_2 are real and imaginary part of dielectric constant.

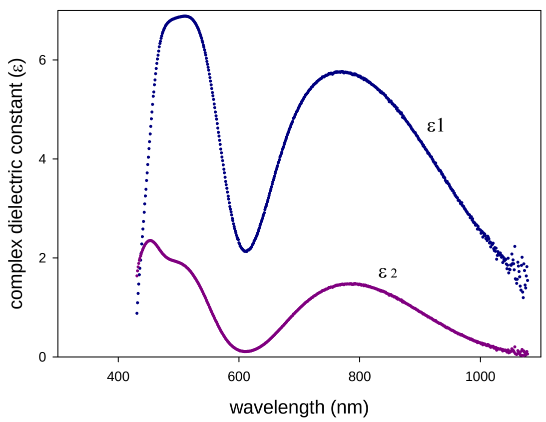

Fig.5 complex dielectric constant versus wavelength of ZnSe thin film.

The plot of dielectric constant as a function of wavelength is shown in Fig.5 which shows that value of ε_1 is higher than the value of ε_2.

The surface and volume energy loss functions are directly related with characteristic energy loss of electrons which travelling through bulk and surface of material respectively.

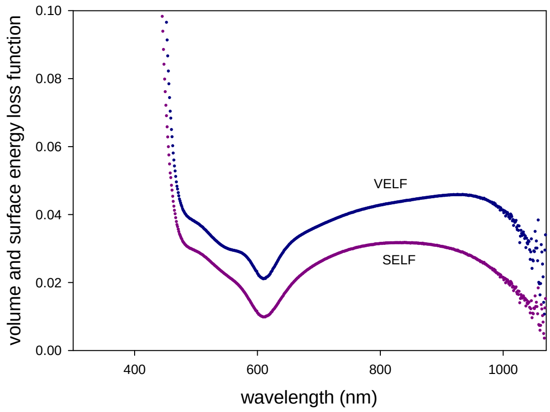

Fig.6 volume and surface energy loss function versus wavelength of ZnSe thin film.

The surface and volume energy is obtained from complex dielectric constant [17].

$$SELF = \frac{\varepsilon_2}{(\varepsilon_1 + 1)^2 + \varepsilon_2^2} \quad (8)$$

$$VELF = \frac{\varepsilon_2}{\varepsilon_1^2 + \varepsilon_2^2} \quad (9)$$

The plot of volume and surface energy loss function of ZnSe as a function of wavelength is shown in Fig.6. The value of SELF is lower than VELF.

The dissipation factor of ZnSe thin film can be obtained from following formula [18];

$$\text{Dissipation factor} = \frac{\varepsilon_2}{\varepsilon_1} \quad (10)$$

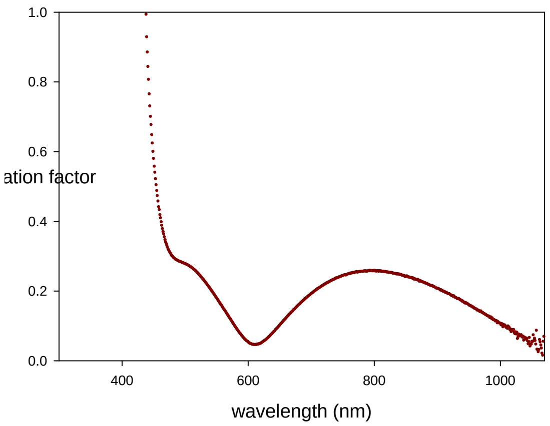

Fig. 7 dissipation factor versus wavelength of ZnSe thin film.

The plot of dissipation factor as a function of wavelength is shown in Fig.7. The value of dissipation factor is low which indicated that Se thin film has good homogeneity.

The dispersion of refractive index is plays important role in optical communication and designing devices for spectral dispersion which is obtained from Wemple-DiDomenico model. The dispersion energy (E_d) and oscillator energy (E_o) can be expressed by following relation [19];

$$n^2 - 1 = \frac{E_d E_o}{E_o^2 - (h\nu)^2} \qquad (11)$$

Where E_d is dispersion energy which related with strength of the inter band optical transition. Also, E_d is depending on charge distribution within each unit cell, coordinate number and the chemical valency. E_o is oscillator energy which gives quantative information on the overall band structure of the material. The plot of $(n^2-1)^{-1}$ versus $(h\upsilon)^2$ for ZnSe thin film is plotted in Fig.8 (a). The value of E_d and E_o are calculated from the slope and intercept on vertical axis and are given in Table.1. Using the obtained value of E_d and E_o, static (zero frequency) refractive index (n_0) and static dielectric constant (ε_0) are calculated from following formula [20];

$$\varepsilon_0 = n_0^2 = 1 + \frac{E_d}{E_o} \qquad (12)$$

Also, the moments of optical dispersion spectra (M_{-1} and M_{-3}) are determined by following formula [20];

$$E_o^2 = \frac{M_{-1}}{M_{-3}} \qquad (13)$$

$$E_d^2 = \frac{M_{-1}^3}{M_{-3}} \qquad (14)$$

The value of n_0, ε_0, M_{-1} and M_{-3} are listed in Table.1.

From single Sellmeier oscillator model, the oscillator strength and oscillator wavelength of ZnSe thin film can be analyzed by following relation [20];

$$n^2 - 1 = \frac{S_o \lambda_o^2}{1 - (\lambda_o / \lambda)^2} \qquad (15)$$

Where λ is incident photon wavelength, S_o is oscillator strength and λ_o is oscillator wavelength. The plot of $(n^2-1)^{-1}$ versus λ^{-2} of ZnSe thin film is shown in Fig.8 (b). The value of S_o and λ_o are obtained from slope and intercept on vertical axis. The value of high frequency refractive index (n_∞) and high frequency dielectric constant (ε_∞) can be calculated from the intercept the linear portion of curve at $(n^2-1)^{-1}$ axis.

The lattice dielectric constant (ε_L) of ZnSe thin film can be calculated by following formula [21];

$$n^2 = \varepsilon_L - \left[\frac{e^2}{4\pi c^2 \varepsilon_0}\frac{N}{m^*}\right]\lambda^2 \qquad (16)$$

$$n^2 = \varepsilon_L - \left(\frac{\omega_p^2}{4\pi c^2}\right)\lambda^2 \qquad (17)$$

Where e is charge of electron, c is velocity of light, ε_o is permittivity of vacuum, N/m^* is ratio of number of free charge carriers and effective mass of electrons and ω_p is plasma resonance frequency which is referred as material change from metallic to dielectric response. The plot of n^2 versus λ^2 of ZnSe thin film is shown in Fig.8 (c). Using the slope and intercept of the curve, the value of ε_L, N/m^* and ω_p are obtained and are listed in Table.1.

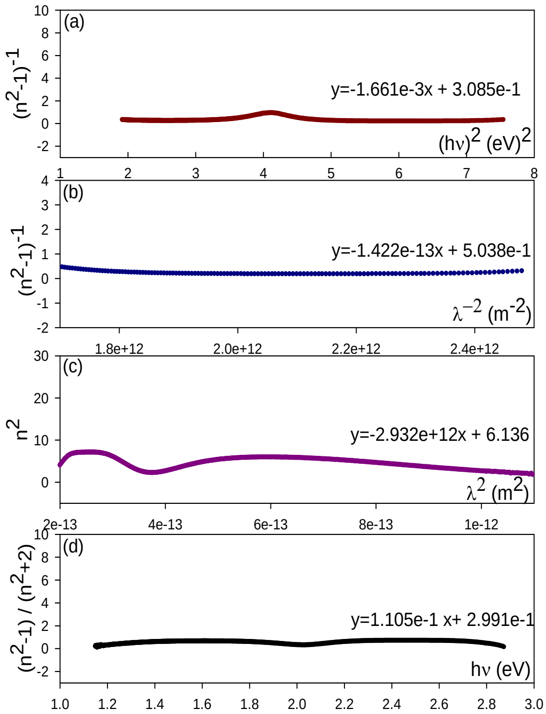

Fig. 8 (a) $(n^2-1)^{-1}$ versus $(h\upsilon)^2$ (b) $(n^2-1)^{-1}$ versus λ^{-2} (c) n^2 versus λ^2 (d) $(n^2-1)/(n^2+2)$ versus $h\upsilon$ of ZnSe thin film.

The electronic polarizability (α_p) of ZnSe thin film is calculated by following formula;

$$\left(\frac{n^2 - 1}{n^2 + 2}\right) = \frac{N_A \rho}{3\varepsilon_0 M}\alpha_p \qquad (18)$$

This equation is known as Clausius-Mossotti equation [22]. Where n is refractive index, N_A is Avogadro’s number, M is molar mass of bulk Se and ρ is density of bulk ZnSe. The plot of $(n^2-1)/(n^2+2)$ versus $h\upsilon$ of ZnSe thin film is shown in Fig.8 (d). The intercept of plot on vertical axis gives the value of α_p and is listed in Table.1.

The non-linear optical parameters are useful for the frequency conversion and optical switching devices [23]. The third order optical non-linear susceptibility gives the information about the strength of chemical bonds between the molecules of ZnSe thin film. In long wavelength limit ($h\upsilon \rightarrow 0$), the nonlinear optical parameters ($\chi^{(3)}$) are calculated from linear optical susceptibility ($\chi^{(1)}$) [24].

$$\chi^{(1)} = \frac{n_0^2 - 1}{4\pi} \quad (19)$$

$$\chi^{(3)} = A[\chi^{(1)}]^4 \quad (20)$$

Where, A is constant (1.7 x 10^{-10} esu).
The non-linear optical refractive index of ZnSe thin film can be determined by following semi-empirical relation [25];

$$n_2 \approx \frac{B}{E_g^4} \quad (21)$$

Where B is constant (1.26 x 10^{-9} esu eV^4).
The linear and non-linear optical parameters of ZnSe thin film are listed in Table.1

Linear Optical Parameters			
E_g	2.79 eV	n_∞	1.73
Δ	746.32 meV	ε_∞	2.98
E_d	44.17 eV	ε_L	6.14
E_o	13.62 eV	N/m^*	1.15 x 10^{57} kg^{-1} m^{-3}
n_0	2.06	ω_p	1.82 x 10^{15} Hz
ε_0	4.24	α_p	3.61 x 10^{-40} Fm^2
M_{-1}	3.24	**Non-linear Optical Parameters**	
M_{-3}	0.017 eV^2	$\chi^{(1)}$	0.26
S_o	7.03 x 10^{12} m^{-2}	$\chi^{(3)}$	0.78 x 10^{-12} esu
λ_o	531.72 nm	n_2	2.079 x 10^{-11}

Table.1 linear and non-linear optical parameters of ZnSe thin film

IV. CONCLUSION

Zinc Selenide (ZnSe) thin film was deposited by thermal evaporation technique on transparent glass substrates. The ZnSe thin film has high transmittance and low reflectance entire electromagnetic spectral range which justifies that ZnSe thin film is transparent and homogeneity. Hence, it is applicable as window layers in solar cell. The value of optical band gap is 2.79 eV. Urbach energy has been calculated which indicated that the ZnSe thin film has low density of defect state. The dielectric constant has been evaluated from linear refractive index and extinction coefficient. The dispersion parameters (E_d, E_o, moment of optical spectra, S_o, λ_o, N/m*, ω_p and α_p), dielectric constants (ε_0, ε_∞ and ε_L) and linear refractive index (n_0, n_∞ and n_L) have been calculated form Wemple-DiDomenico model and single Sellmeier oscillator model. The electronic polarizibility of ZnSe thin film has been obtained by Clausius-Mossotti local field polarizibility. The non-linear optical parameters ($\chi^{(1)}$, $\chi^{(3)}$ and n_2) have been obtained from semi empirical relation.

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REFERENCES

[1] G. I. Rusu, V. Ciupina, M. E. Popa, G. Prodan, G. G. Rusu, C. Baban, Microstructural Characterization and Optical properties of ZnSe thin films, *J. of nanocrystalline solids 352*, 2006, 1525- 1528.
[2] P. A. Chate, D. J. Sathe, P. P. Hankare, Growth and Characteristics Zn-Se-S thin layers by dip method, *J. of alloys and compounds 509*, 2011, 9425- 9427.
[3] S. A. Mohamad, M. H. Ali, Z. A. Ibrahim, A. K. Arof, *Mater. Sci. Forum 517*, 2006, 278- 208.
[4] A. Manzoli, M. C. Santos, S. A. S. Machaolo, Voltammetric and nanogravimetric study of ZnSe electrodeposition from an acid bath containing Zn (II) and Se (VI), *Thin Solid Films 515*, 2007, 6860- 6866.
[5] S. Venkatachalam, D. Mangalaraj, Sa. K. Narayandass, K. Kim, J. Yi, Structure, Optical and Electrical properties of ZnSe thin films, *Physica B 358*, 2005, 27- 35.
[6] A. Sennaroglu, U. Demirdas, N. Vermeulen, H. Ottevaere, H. Thienpont, Chromium-doped zinc Selenide gain media: from synthesis to pulsed mid-infrared laser operation, *Opto. Commun. 268*, 2006, 115- 120.
[7] H. N. Desai, J. M. Dhimmar, B. P. Modi, Study of Physical Characteristics of Zinc Selenide Thin Film, *International Journal of Engineering Research & Technology 4(5)*, 2015, 1132-1136.
[8] C. Cruz-Vazquez, F. Rocho Alonzo, S. Burruel Ibarra, M. Barboza Flores, R. Bernal, M. Inoue, A new chemical bath deposition method for fabricating ZnS, $Zn(OH)_2$ and ZnO thin film and optical and structural characterization of these materials, *Appl. Phys. A 79*, 2004, 1941-1945.
[9] H. R. Dobler, *Appl. Opto. 28*, 1989, 2698- 2701.
[10] Jeewan Sharma, Deepshikha, S. K Tripathi., Optical and Electric Properties of ZnSe Thin Film: Vacuum annealing, *Romania Reports in Physics 66(4)*, 2013, 1002-1011.
[11] H. N. Desai, J. M. Dhimmar, B. P. Modi, Preparation and Characterization of thermally

evaporated Selenium Thin Film, *Proc. National Conference on Recent Advances in Engineering for Sustainability, India,* 2005, 15ASH20.

[12] K. S. Usha, R. Sivakumar, C. Sanjeeviraja, Optical constant and dispersion energy of NiO thin films prepared by radio frequency magneto sputtering technique, *J. of Appl. Phys. 114*, 2013, 123501-10.

[13] F. Urbach, The long-wavelength edge of photographic sensitivity and of the electronic absorption of solids, *Physical Review 92(5)*, 1953, 1324.

[14] Z. Z. You, G. J. Hua, Electrical, Optical and microstructure properties of transparent conducting GZO thin films deposited by magnetron sputtering, *J. Alloys and Compounds 530*, 2012, 11-17.

[15] M. S. Aziz, H. M. El-Mallah, Electrical and Optical Properties of azo dye, *Indian J. Pure Appl. Phys. 47*, 2009, 530-534.

[16] P. Sharma, V. Sharma, S. C. Katyal, Variation of Optical constant in $Ge_{10}Se_{60}Te_{30}$ thin film, *Chalcogenide Letters 3*, 2006, 73-79.

[17] Wug Dong park, Optical constant and Dispersion parameters of CdS Thin Film prepared by Chemical Bath Deposition, *Transactions on Electrical and Electronic Materials 13(4)*, 2012, 196-199.

[18] J. I. Ponkova, *Optical Processes in semiconductors* (Dover Publications, new York, 1975).

[19] E. Marquez, J. B. Ramirez-Malo,P. Villares, R. Jimenez-Garay, R. Swanepoel, Optical Characterization of wedge-shaped Thin Films of amorphous Arsenic Trisuphide based only on their shrunk transmission spectra, *Thin Solid Films 254*, 1995, 83.

[20] S. H. Wemple, M. Jr. DiDomenico, Behavior of the electronic dielectric in covalent and ionic materials, *Phys. Rev. B 3*, 1971, 1338-1351.

[21] T. S. Moss, G. J. Burell, E. Ellis, Semiconductor Opto-Electronic, (Butterworths, London, 1973).

[22] M. A. M. El-Morsy, H. H. Wahba, Determination of the optical Properties of a bent Optical Fiber by Using an automatic Fringe Pattern Analysis, *J. of Korean Physical Society 59(5)*, 2011, 3080-3085.

[23] Rashmi chauhan, Amitkumar Srivastava, Arvind Tripathi, Krishnakant Srivastava, Linear and nonlinear optical changes in amorphous As_2Se_3 thin film upon UV exposure, *Progress in Natural Science: Materials International 21*, 2011, 205-210.

[24] H. Ticha, L. Tichy, Semiempirical relation between non-linear susceptibility (refractive index), linear refractive index and optical gap and its application to amorphous chalcogenides, *J. Optoelectron. Adv. Mater. 4(2)*, 2002, 381-386.

[25] C. C. Wang, Empirical relation between the linear and the third order nonlinear optical susceptibilities, *Phys. Rev. B 2(6)*, 1970, 2045-2048.