

An optical study of amorphous $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ thin films using their transmission spectra

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Abstract

Optical constants (refractive index and extinction coefficient) have been studied for a - $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ ($x = 0, 2, 4, 6$) thin films using transmission spectra in the wavelength range 500–2500 nm. It is observed from optical transmission measurements that the optical energy gap (E_g) increases while the refractive index (n) and the extinction coefficient (k) decrease with the incorporation of Ge in the Se–Te system. The increase in the optical energy gap is interpreted by correlating the optical energy gap with the decrease in electronegativity and increase in the heat of atomization (H_s). The dispersion of the refractive index is discussed in terms of the single-oscillator Wemple–DiDomenico model.

1. Introduction

Chalcogenide glasses have attracted a great deal of attention because of their technical importance in various solid-state devices. These glasses are of tremendous interest because of their wide range of transparency in the far infrared region. Chalcogenide semiconducting alloys have found application not only due to their electrical and thermal properties but also due to their optical properties. Among the amorphous chalcogenide alloys, mostly selenium-based materials are preferred because of its unique property of reversible transformation, which makes these glasses useful as optical memory devices [1, 2]. Their various device applications like rectifiers, photocells, vidicon, xerography, switching and memory, etc. have made them attractive. Se is an excellent glass former, but pure Se has disadvantages such as short lifetime and low sensitivity. So certain additives are used to improve these properties. It has been found that substitution of Te by Se in Se–Te glasses breaks up the Se_8 ring structure and slightly increases the chain fraction but reduces the chain length [3]. Se and Te have the function of forming the network of the glass. Se–Te glassy alloys have gained much importance among chalcogenide glasses because of their high photosensitivity, greater hardness, high crystallization temperature and smaller ageing effect as compared with pure a -Se [4] and usefulness in practical applications [5].

The properties of chalcogenide semiconductors are usually affected by the addition of a third element. The addition of a third element creates compositional and configurational disorder in the material with respect to the binary alloys. Here we choose Ge as an additive to the Se–Te binary alloy because it produces stability and does change the optical properties of chalcogenide glassy semiconductors [6]. Ge also serves to increase the chemical and thermal durability of the glass. Ge-doped glasses have become an attractive material for fundamental research of their structure and properties [7–12]. A few data concerning the optical properties of Ge-additive in Se–Te alloys are available in the literature [6].

The optical energy gap (E_g), the refractive index (n) and the extinction coefficient (k) are the most significant parameters in amorphous semiconducting thin films. The optical behaviour of a material is utilized to determine its optical constant. Films are ideal specimens for reflectance and transmittance type measurements. Therefore, an accurate measurement of the optical constants is extremely important. The present paper aims to investigate the effect of Ge additive on the optical constants of thermally evaporated $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ thin films held at room temperature. Optical constants such as the refractive index, extinction coefficient and absorption coefficient (α) are calculated by the well-known Swanepoel method [13], using a transmission

spectrum in the UV–Vis–NIR region. Analysis of the absorption coefficient was also carried out to determine E_g and the nature of transitions. Also, by using the values of n , k and α , the real (ϵ_r) and imaginary (ϵ_i) parts of the dielectric constant and optical conductivity (σ) are calculated.

2. Experimental details

Glassy alloys of $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ ($x = 0, 2, 4, 6$) were prepared by the melt quenching technique. The sample under investigation was prepared from highly pure Se, Te and Ge (99.999%) elements. The constituents were weighed according to their atomic percentage and sealed in a quartz ampoule in vacuum of $\sim 10^{-5}$ mbar. The ampoules containing the material are heated to 1000°C and held at the highest temperature for 12 h. The ampoules were frequently rocked during heating to make the melt homogeneous. The quenching was done in ice-water. Quenched samples were obtained by breaking the quartz ampoules. The amorphous nature of these alloys was verified by x-ray diffraction (X-Pert PRO) as no prominent peak was observed in the spectra.

Thin film samples were deposited by the vacuum evaporation technique (Hindivac 12A4D Model) onto thoroughly cleaned microscope glass substrates. A vacuum of the order of 10^{-5} mbar was maintained during the evaporation process. The films were kept inside the deposition chamber for 24 h to achieve a metastable equilibrium. The normal incidence transmission spectra (figure 1) in the transmission range 500–2500 nm of $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ ($x = 0, 2, 4, 6$) thin films were obtained by UV–Vis–NIR spectrophotometer (Perkin Elmer Lambda-750). All the measurements were performed at room temperature (300 K).

3. Results

3.1. Refractive index, film thickness, extinction coefficient and absorption coefficient

The optical behaviour of a material is generally utilized to determine its optical constants n and k . Films are ideal specimens for reflectance and transmittance type of measurements. The optical constants were calculated using Swanepoel’s method. This method has been used in glassy materials by various workers [14–16].

According to Swanepoel’s method, which is based on the idea of Manifacier [17], the envelope through the interference maxima and minima is drawn in the spectrum. The value of the refractive index of film in the spectral region of medium and weak absorption can be calculated by the expression

$$n = [N + (N^2 - s^2)^{1/2}]^{1/2}, \quad (1)$$

where

$$N = 2s \frac{T_M - T_m}{T_M T_m} + \frac{s^2 + 1}{2}, \quad (2)$$

where T_M and T_m are the transmission maximum and the corresponding minimum at a certain wavelength λ . The basic equation for interference fringes is given by

$$2nd = m_0\lambda. \quad (3)$$

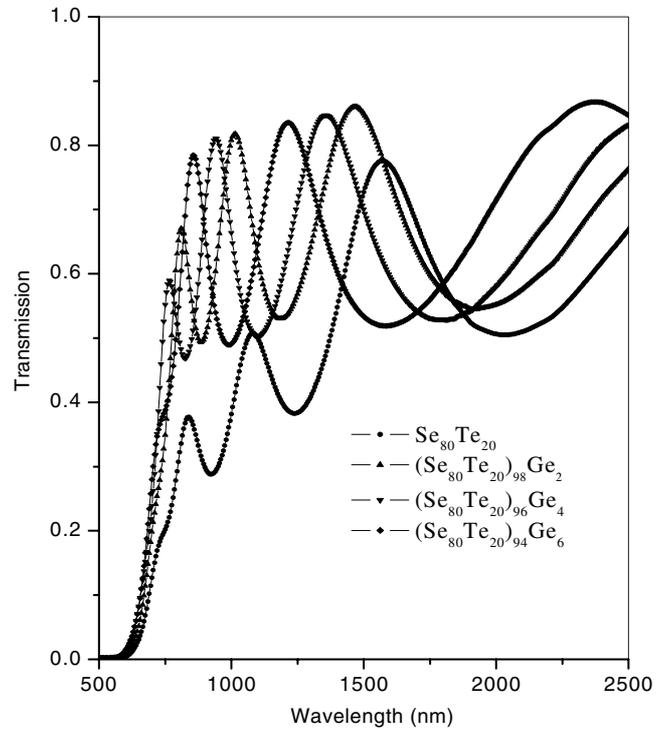


Figure 1. Transmission spectra of $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ ($x = 0, 2, 4, 6$) thin films.

Using this equation, the accuracy of the refractive index can be improved after calculating the thickness d . m_0 is an integer for maxima and a half integer for minima in the transmission spectra. If n_1 and n_2 are the refractive indices of two adjacent maxima and minima at wavelengths λ_1 and λ_2 , then the thickness of the film is given by the expression

$$d = \frac{\lambda_1\lambda_2}{2(\lambda_1n_2 - \lambda_2n_1)}. \quad (4)$$

The average value, \tilde{d}_1 , of d_1 can be used with n_1 to determine m_0 for the different maxima and minima using equation (3). By taking the exact integer or half integer values of m_0 , the accuracy of the film thickness can be increased significantly and d_2 , a new thickness (table 1), can be derived from equation (3) by using the values of n . Further using the accurate values of m_0 and d_2 , in equation (3), the final values of the refractive index n_2 are obtained. Now, n_2 can be fitted to the Cauchy dispersion relationship [18], $n_2 = (a + b/\lambda^2)$, which can then be used for extrapolation of the values of the refractive index to the shorter wavelength region.

The extinction coefficient (k) has been calculated using the relation

$$k = \frac{\alpha\lambda}{4\pi}, \quad (5)$$

where α is the absorption coefficient [13] and is given by

$$\alpha = \frac{1}{d} \ln \left(\frac{1}{x} \right), \quad (6)$$

where x is the absorbance and is calculated using [13].

The variations of the refractive index and the extinction coefficient with the wavelength are shown in figures 2 and 3.

Table 1. Values of thickness (d_2), refractive index (n), extinction coefficient (k), real part (ϵ_r), imaginary part (ϵ_i) of dielectric constant and optical conductivity (σ) are given at 800 nm for $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ ($x = 0, 2, 4, 6$) thin films.

x	d_2 (nm)	n	k	ϵ_r	ϵ_i	σ (s^{-1})
0	729	3.370	0.0660	11.355	0.445	8.34×10^{13}
2	731	3.243	0.02045	10.517	0.133	2.49×10^{13}
4	722	3.043	0.0183	9.2571	0.111	2.08×10^{13}
6	708	2.946	0.0179	8.6785	0.106	1.98×10^{13}

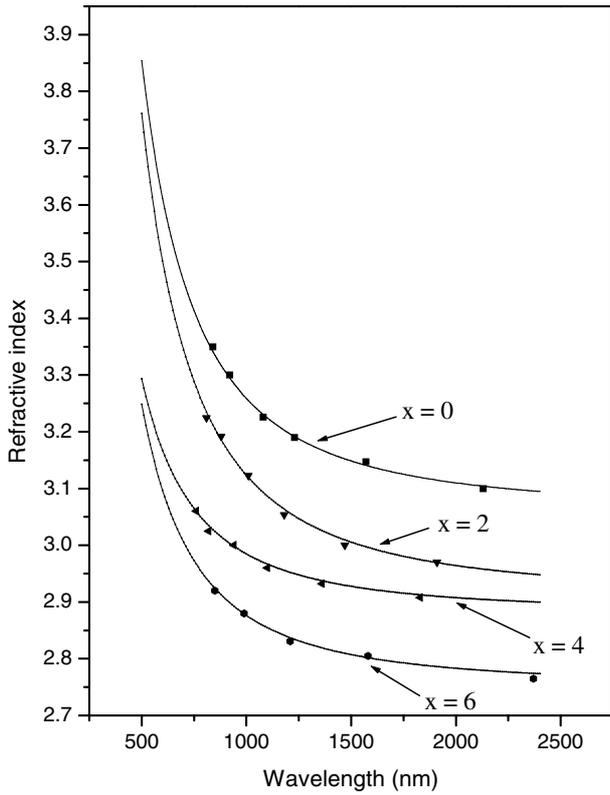


Figure 2. Plot of refractive index versus wavelength for $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ ($x = 0, 2, 4, 6$) thin film (values of n calculated at each extreme are represented as solid dots and in terms of Cauchy's fitting are shown as a line).

3.2. Dispersion energy, oscillator strength and static refractive index using Wemple–DiDomenico model

The data on dispersion of refractive index $n(\lambda)$ have been calculated using the single-effective-oscillator model proposed by Wemple and DiDomenico (WDD) [19]. They found that all the data can be described to an excellent approximation by the following expression:

$$n^2 = 1 + \frac{E_d E_o}{E_o^2 - (h\nu)^2}, \quad (7)$$

where E_o is the energy of the effective dispersion oscillator and E_d is the so-called dispersion energy, and it measures the average strength of interband optical transitions. E_o and E_d values can be calculated from the slope and the intercept on the vertical axis of the plot of $1/(n^2 - 1)$ versus $(h\nu)^2$ (figure 4). Table 2 collects the values of the dispersion parameters, the

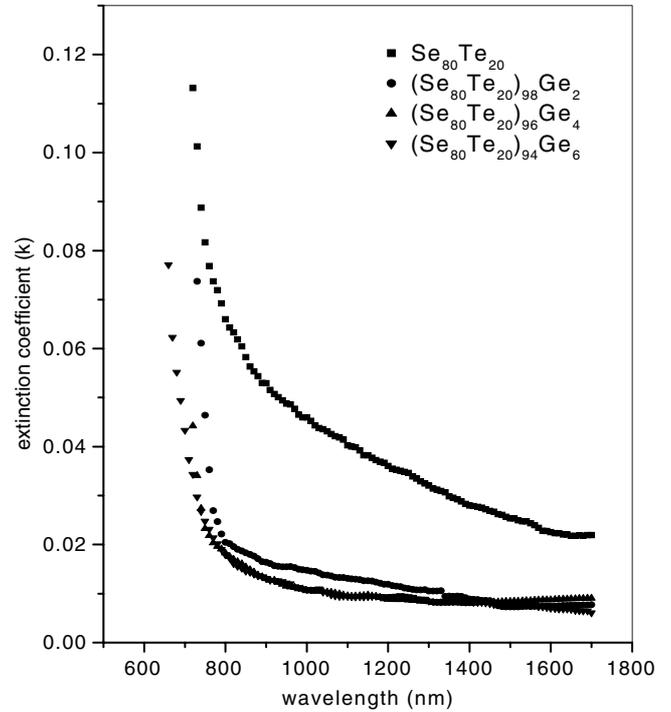


Figure 3. Plot of extinction coefficient versus wavelength for $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ thin films.

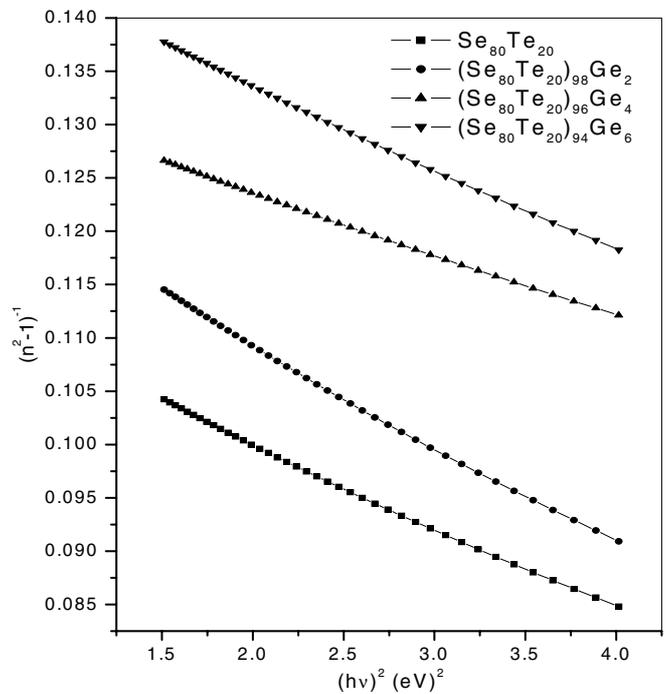


Figure 4. Plot of refractive index factor $(n^2 - 1)^{-1}$ versus $(h\nu)^2$ for $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ thin films.

static refractive index (n_o) and the high frequency dielectric constant $\epsilon_\infty = (n_o)^2$. The static refractive index is calculated from the relation

$$n_o^2 = \left(1 + \frac{E_d}{E_o}\right). \quad (8)$$

The values of the static refractive index are obtained by extrapolating equation (7) as $(h\nu) \rightarrow 0$.

Table 2. Values of heat of atomization (H_s), oscillator energy (E_o), dispersion energy (E_d), static refractive index (n_o), high frequency dielectric constant (ϵ_∞), optical energy gap (E_g) and electronegativity (χ) for $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ ($x = 0, 2, 4, 6$) thin films.

x	H_s (kcal g ⁻¹ atom ⁻¹)	E_o (eV)	E_d (eV)	n_o	ϵ_∞	E_g (eV)	χ
0	48.72	3.02	31.13	3.363	11.308	1.41	2.46
2	49.5	3.17	30.23	3.247	10.543	1.51	2.45
4	50.3	3.22	28.66	3.147	9.901	1.56	2.44
6	51.19	3.68	27.59	2.91	8.497	1.61	2.43

Furthermore, there is a simple empirical relationship by WDD which relates the dispersion energy E_d to the other physical parameters of the material, $E_d = \beta N_c Z_a N_e$, where N_c is the effective co-ordination number, Z_a is the formal chemical valency of the anion, N_e is the effective number of valence electron per anion and β is a constant ($\beta = 0.26 \pm 0.03$ eV for ionic material and $\beta = 0.37 \pm 0.04$ eV for covalent and amorphous material).

3.3. Optical energy gap, optical conductivity and dielectric properties

The optical absorption spectrum is the most productive tool for developing the energy band diagram. The absorption coefficient of an amorphous semiconductor in the high absorption region ($\alpha \geq 10^4$ cm⁻¹) can be calculated by using Tauc's relation [20]

$$\alpha h\nu = B(h\nu - E_g)^m, \quad (9)$$

where B is a constant, E_g is the optical energy gap of the material and m determines the type of transition ($m = 1/2$ for the direct transition and $m = 2$ for the indirect allowed transition). Figure 5 plots $(\alpha h\nu)^{0.5}$ versus $(h\nu)$. The values of the optical energy gap (E_g) obtained for indirect allowed transition for $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ thin films by making $(\alpha h\nu)^{0.5} \rightarrow 0$ are given in table 2.

The complex dielectric constant is a fundamental intrinsic material property. The real (ϵ_r) and imaginary (ϵ_i) parts of the dielectric constant of thin films were also calculated by using the value of n and k in the following relations [21]:

$$\epsilon_r = n^2 - k^2 \quad (10)$$

$$\epsilon_i = 2nk. \quad (11)$$

It is evident from table 1 that the values of ϵ_r and ϵ_i decrease on incorporating Ge into the Se-Te system. The optical conductivity is determined using the relation [22]

$$\sigma = \frac{\alpha n c}{4\pi}, \quad (12)$$

where c is the velocity of light. The values of n , k and σ are given in table 1.

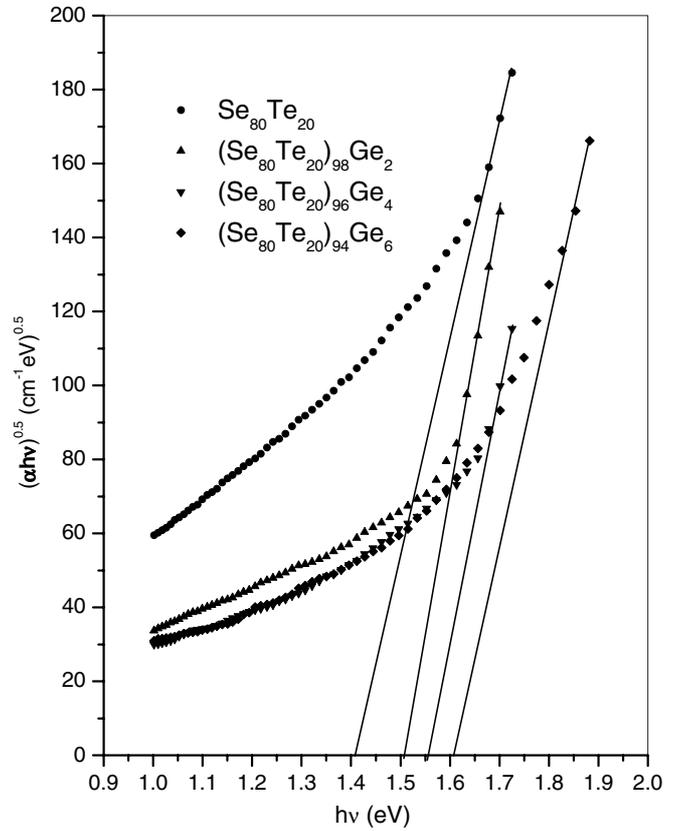


Figure 5. Plot of $(\alpha h\nu)^{0.5}$ versus $(h\nu)$ for $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ thin films.

4. Discussion

From figures 2 and 3, it is clear that both the refractive index and the extinction coefficient decrease with an increase in the wavelength for films under investigation. The decrease in the refractive index and the extinction coefficient with the increase in wavelength may be correlated with the increase in the transmittance and decrease in the absorption coefficient. The decrease in the value of the refractive index with wavelength shows the normal dispersion behaviour of the material. Dispersion of the refractive index, in terms of the WDD model, throws valuable light on the structure of the material, through the value of E_d , the oscillator strength. Table 2 shows a smooth decrease in E_d with increasing Ge content. The single-oscillator energy, E_o , is considered an average energy gap. E_o is therefore related to the average molar bond energy of the different bonds present in the material. Thus, the increase observed in E_o (table 2) is due to larger bond energy of the Ge-Se bonds (2.12 eV), in comparison with that of Se-Te bonds (1.76 eV) and Se-Se bonds (1.91 eV) [23]. The decrease in the extinction coefficient with an increase in the wavelength shows that the fraction of light lost due to scattering and absorbance decreases. The variation of both ϵ_r and ϵ_i dielectric constants with wavelength follows the same trend as that of n and k . From table 2 it is revealed that with increasing Ge content the optical gap increases. The value of E_g for the $\text{Se}_{80}\text{Te}_{20}$ system is found to be 1.41 eV, which is almost comparable to the

values obtained by other researchers for the same composition [24, 25]. The increase in E_g with the increase in Ge content can also be related to the calculated values of the average heat of atomization H_s [26]. The average heat of atomization for the compound $A_\alpha B_\beta C_\gamma$ is a direct measure of the cohesive energy and thus of the average bond strength, and is defined as

$$H_s = \frac{(\alpha H_s^A + \beta H_s^B + \gamma H_s^C)}{\alpha + \beta + \gamma}. \quad (13)$$

The heat of atomization for Ge, Se and Te elements are 90, 49.4 and 46 Kcal $g^{-1} \text{atom}^{-1}$ [23]. The calculated values of H_s for the investigated material are listed in table 2. The obtained data show that H_s increases with increasing Ge content, i.e. average bond strength of the compound increases. A similar behaviour has been obtained by Fayek *et al* [6] for the Se–Te–Ge system. The increase in the optical energy gap could also be explained on the basis of electronegativity. Pauling [27] defines the electronegativity of an atom as the power to attract an electron to itself in a molecule. When the two atoms which differ in their electronegativity value combine to form an alloy, the element of higher electronegativity attracts an electron pair more towards itself and behaves as an anion whereas the other element behaves as a cation. Using Sanderson's principle [28] of equalization of electronegativity, χ between Se–Te and Se–Te–Ge alloys has been calculated for different elements. The calculated values are given in table 2. When the electronegativity difference is large, it is expected that the probability of defects formation will be more. It has been observed that χ decreases with increasing Ge content. The correlation of the electron affinity with the optical energy gap [29] was considered by various workers. According to Mulliken [30], the electronegativity is the average of the ionization potential and the electron affinity. It is difficult to assign an electron affinity value for a semiconducting alloy, e.g. $(\text{Se}_{80}\text{Te}_{20})_{100-x}\text{Ge}_x$ system. Thus, it will be appropriate to correlate the electronegativity with the optical energy gap. In the present system, we observe that the optical energy gap increases with decreasing electronegativity of a sample.

5. Conclusion

The optical transmission spectra of a -($\text{Se}_{80}\text{Te}_{20}$) $_{100-x}\text{Ge}_x$ ($x = 0, 2, 4, 6$) thin films have been measured in the wavelength range 500–2500 nm by a spectrophotometer. The optical absorption measurements on a -($\text{Se}_{80}\text{Te}_{20}$) $_{100-x}\text{Ge}_x$ films indicate that the absorption mechanism is due to indirect transition. The increase in the optical energy gap with the incorporation of Ge in the Se–Te alloy has been explained on the basis of heat of atomization and electronegativity. The refractive index and extinction coefficient are found to decrease while the real and imaginary parts of the dielectric constants

and optical conductivity increase with an increase in photon energy.

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References

- [1] Seddon A B *et al* 2006 *J. Non-Cryst. Solids* **352** 2515
- [2] Shaaban E R, Kaid M A, El Sayed Moustafa and Adel A 2008 *J. Phys. D: Appl. Phys.* **41** 125301
- [3] Sharma P and Katyal S C 2008 *J. Non-Cryst. Solids* **354** 3836
- [4] Kasap S O, Wagner T, Aiyah V, Krylouk O, Berkirov A and Tichy L 1999 *J. Mater. Sci.* **34** 3779
- [5] Moharram A H 2001 *Thin Solid Films* **392** 34
- [6] Fayek S A, El-Ocker M and Hassanien A S 2001 *Mater. Chem. Phys.* **70** 231
- [7] Maged A F, Sanad A M, El-Fouly M F and Amin G A M 1998 *J. Mater. Sci.* **13** 1128
- [8] Ganesan R, Madhusoodanan K N, Srinivasan A, Sangunni K S and Gopal E S R 1999 *Phys. Status Solidi* **212** 223
- [9] Sharma P and Katyal S C 2007 *Mater. Lett.* **61** 4516
- [10] Othman A A, Aly K A and Abousehly A M 2007 *Thin Solid Films* **515** 3507
- [11] Haruvi-Busnach I, Dror J and Croitoru N 1996 *J. Mater. Sci.* **5** 1215
- [12] Atyia H E and Bekheet A E 2008 *Phys. B: Condens. Matter* **403** 3130
- [13] Swanepoel R 1983 *J. Phys. E: Sci. Instrum.* **16** 1214
- [14] Nenkov M R and Pencheva T G 2008 *Eur. Phys. J. Appl. Phys.* **42** 219
- [15] Marquez E, Bernal-Oliva A M, Gonzaliz-Leal J M, Rrieto-Allon R and Wagner T 2006 *J. Phys D: Appl. Phys.* **39** 1793
- [16] Sharma P and Katyal S C 2008 *Mater. Chem. Phys.* at press doi:10.1016/j.matchemphys.2008.07.035
- [17] Manifer J C, Gasiot J and Fillard J P 1976 *J. Phys E: Sci. Instrum.* **9** 1002
- [18] Moss T S 1959 *Optical Properties of Semiconductors* (London: Butterworth)
- [19] Wemple S H and DiDomenico M 1971 *Phys. Rev. B* **3** 1338
- [20] Tauc J 1970 *The Optical Properties of Solids* (Amsterdam: North-Holland)
- [21] Wakkad M M, Shoker E K H and Mohamed S H 2000 *J. Non-Cryst. Solids* **265** 157
- [22] Pankove J I 1975 *Optical Processes in Semiconductors* (New York: Dover) p 91
- [23] Sharma P and Katyal S C 2007 *J. Optoelectron. Adv. Mater.* **9** 1994
- [24] Suri N, Bindra K S and Thangraj R 2006 *J. Phys: Condens. Matter* **18** 9129
- [25] Amin G A M 2007 *Opt. Mater.* **29** 562
- [26] Yamaguchi M 1985 *Phil. Mag.* **B 51** 651
- [27] Pauling L 1932 *J. Am. Chem. Soc.* **54** 3570
- [28] Sanderson R T 1971 *Inorganic Chemistry* PUT (New Delhi: Affiliated East–West Press)
- [29] Koffeyberg F P 1992 *J. Phys. Chem. Solids* **53** 1285
- [30] Mulliken R S 1984 *J. Chem. Phys.* **2** 782