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OPTICAL PROPERTIES OF AMORPHOUS $Se_{94}Te_6$ AND $Se_{91}Te_9$ THIN FILMS DEPOSITED BY THERMAL EVAPORATION

SUSHIL KUMAR*, M. A. MAJEED KHAN[a]
Department of Physics, Chaudhary Devi Lal University, Sirsa, 125055, India
[a]King Abdullah Institute for Nanotechnology, King Saud University, Riyadh, 11451, Saudi Arabia

The optical properties of Se-Te thin films deposited on glass substrates by vacuum evaporation technique were studied. The amorphous nature of thin films was detected by X-ray diffraction. The optical properties of thin films have been studied in the wavelength range 200–800 nm. The mechanism of optical absorption follows the allowed 'non-direct electronic transition' model proposed by Tauc. It was found that the optical band gap E_g decreases while the width of localized states (Urbach energy) E_c increases as Te content increases.

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1. Introduction

Semiconducting glasses, namely chalcogenide glasses, contain one or more chalcogen elements (group VI elements S, Se, Te) as alloy elements. They behave as semiconductors, or more precisely, they exhibit amorphous semiconductor behaviour with band gap energies from 1 to 3 eV. Since chalcogenide glasses have unique properties such as high refractive indices and transparency in IR region, they are excellent materials to be used in photonic applications [1-3]. Glassy alloys of Se-Te system based on Se have become materials of considerable commercial, scientific and technological importance. They are widely used in many fields as optical recording media because of their excellent laser writer sensitivity, xerography and electrographic applications such as photoreceptors in photocopying and laser printing, infrared spectroscopy and laser fiber techniques [4-5]. Se-Te alloys have greater hardness, higher crystallization temperature, and lower ageing effect as compared to amorphous Se [6]. It was found that the substitution of Se by Te in Se–Te glasses breaks up Se_8 ring structure, increases the chain fraction and reduces the chain structure [7]. Attempts have been made to produce stable glasses which have good photosensitive properties and can easily be doped to be n- or p-type semiconductors.

The present work deals with the determination of the optical band gap, the absorption coefficient, the refractive index and the extinction coefficient of Se-Te thin films of thickness about 200 nm by analyzing the apsorption spectra in the UV-visible region.

2. Experimental details

The bulk samples of amorphous $Se_{94}Te_6$ and $Se_{91}Te_9$ were prepared by melt-quenching technique. Materials (99.999 % purity) were weighed (6 gm) according to their atomic percentage and then filled them into quartz ampoules (length ~ 12 cm, internal diameter ~ 0.8 cm). The ampoules were sealed after evacuation to a pressure of 1.3×10^{-4} Pa. The sealed ampoules were kept inside a furnace where the temperature was increased upto 900 ^{o}C at the heating rate of 3 ^{o}C/min. The ampoules were heated at 900 ^{o}C for 10 h; during the melt process these ampoules

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*Corresponding author: sushil_phys@rediffmail.com were agitated frequently in order to intermix the constituents and to ensure the homogenization of the melt. Quenching was done in ice cold water. The amorphous nature of the samples has been confirmed by X-ray patterns recorded by X-ray diffractometer (Figs. not shown here).

Thin films of a-Se-Te system were deposited on clean glass substrates (size ~ 2 x 2 cm^2) by vacuum evaporation technique keeping substrate at room temperature and base pressure of 1.3 x 10^{-4} Pa using a molybdenum boat. The glass substrates were first washed with soap solution, then ultrasonically cleaned by trichloroethylene followed by a dip in acetone. Finally, the substrates were cleaned with double distilled water and then dried in an oven at about 110 °C. The evaporation rate as well as the film thickness were controlled using a quartz crystal monitor. The thickness of the films was ~ 200 nm. The films were kept inside the deposition chamber for 24 h to attain thermodynamic equilibrium as suggested by Abkowitz [8] in chalcogenide glasses. The deposition parameters and ambient conditions were kept same for all the samples so that a comparison of results could be made for different samples. The optical absorbance of films was measured in the spectral range 200–800 nm using double beam spectrophotometer (Hitachi U 3400) and a reference glass substrate was placed in the path of one beam.

3. Results and discussion

Optical measurements provide the most important means of determining the band structures of semiconductors. The optical absorbance spectra of the thin films of $Se_{94}Te_6$ and $Se_{91}Te_9$ semiconductor chalcogenides were recorded at room temperature by spectrophotometer. The absorption coefficient has been measured in high and intermediate absorption region, not in the weak absorption region. The values of absorption coefficient (α) are calculated using the well-known relation

$$\alpha = \frac{1}{d} ln \frac{1}{x} \tag{1}$$

where x is the absorbance and d is the thickness.

The obtained values of absorption coefficient as a function of wavelength for as-deposited films are shown in Fig. 1. Fig. 2 shows that the absorption edge can be divided into two regions, namely Urbach region and Tauc region.

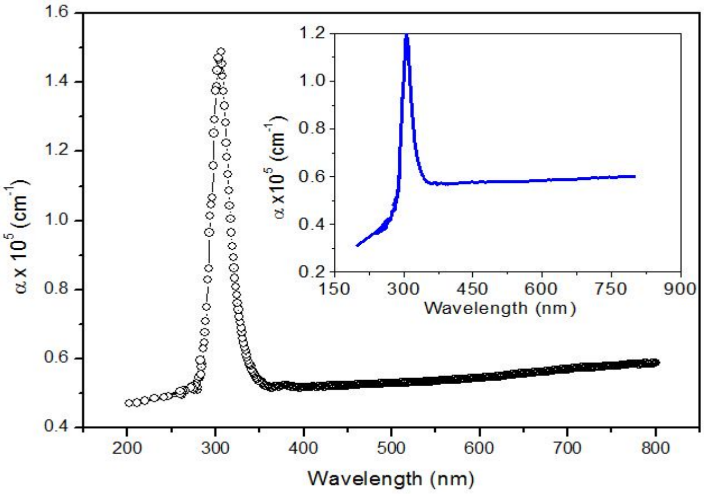

Fig.1. The variation of absorption coefficient (α) as a function of wavelength (λ) for $Se_{94}Te_6$ thin film and inset shows for $Se_{91}Te_9$ thin film.

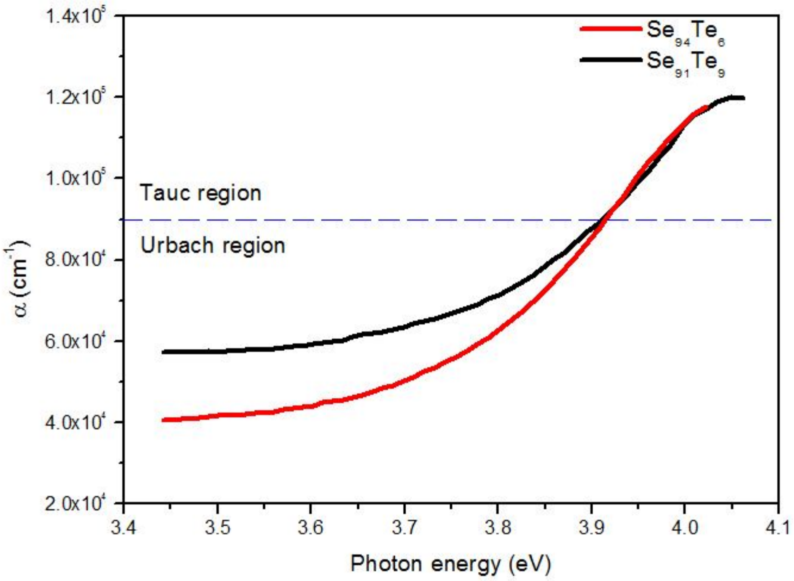

Fig. 2. The variation of absorption coefficient (α) as a function of photon energy (hν) shows Tauc and Urbach region for $Se_{94}Te_6$ and $Se_{91}Te_9$ thin film.

In the low absorption region ($\alpha \leq 10^4$ cm^{-1}), the absorption coefficient shows an exponential
dependence on photon energy (hν), and obeys the Urbach relation [10]

$$\alpha = \alpha_o \exp\left(\frac{h\nu}{E_c}\right) \tag{2}$$

where α_o is a constant and E_c is the Urbach energy interpreted as the width of band tails of localized states in the band gap region and in general represents the degree of disorder in an amorphous semiconductor [11]. The plots of Urbach, Eq. (2), for $Se_{94}Te_6$ and $Se_{91}Te_9$ amorphous thin films are presented in Figs. 3(b)&4(b) and the obtained fitting parameters E_c and α_0 are given in Table 1.

Table 1. Fitting parameters obtained using Tauc and Urbach model.

Sample	Tauc			Urbach	
	A	E_g	m	α_o	E_c
$Se_{94}Te_6$	$2.27x10^5$	2.63	1.35	4927.82	1.65
$Se_{91}Te_9$	$1.26x10^5$	2.51	1.31	15643.88	2.69

In the high absorption region (where $\alpha \geq 10^4$ cm^{-1}), involving interband optical transitions between valence and conduction bands, the absorption coefficient data as a function of wavelength, which follows the non-direct electronic transition model proposed by Tauc [9], given by the equation

$$(ah\nu)^m = A(h\nu - E_g) \tag{3}$$

where hν, E_g and A represent the photon energy, the optical band gap and band tailing parameter respectively. In the above equation *m*= 2 and 1/2 in the case of allowed direct and indirect optical transitions respectively; while *m* = 2/3 and 1/3 in the case of forbidden direct and indirect optical transitions respectively. The plots of Tauc, Eq. (3), for $Se_{94}Te_6$ and $Se_{91}Te_9$ chalcogenide films are shown in Fig. 3 (a) & 4 (a) and the obtained fitting parameters E_g, m, A are given in Table 1. It has been found that the optical band gap decreases with increasing Te content. This variation of E_g as a function of Te content may be interpreted as tellurium-based glasses contain short chains, while selenium-based glasses contain a mixture of chains and Se_8 rings. An introduction of Te decreases the Se ring concentration with an increase in long Se–Te polymeric chains and mixed rings [12], which makes the system more rigid. However, at higher concentration of Te, the possibility of Te–Te bonding may also exits.

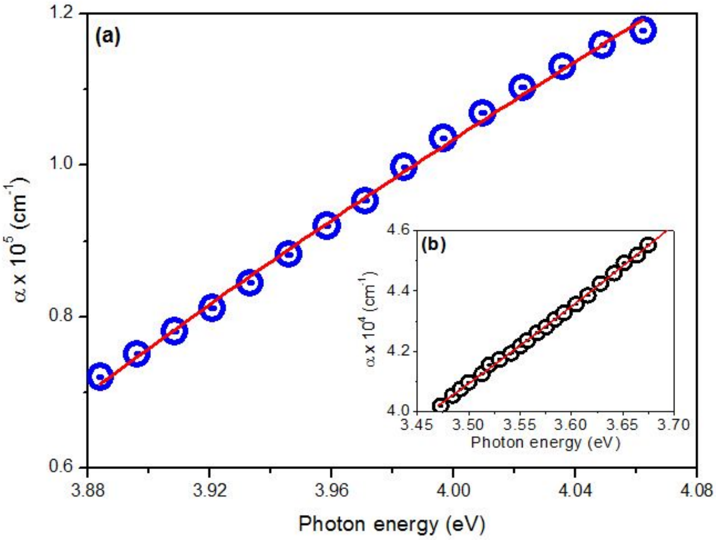

Fig. 3. The absorption coefficient (α) versus photon energy (hν) for $Se_{94}Te_6$ film. The circles represent the observed α and solid lines represent calculated α from: (a) Tauc model, (b) Urbach model.

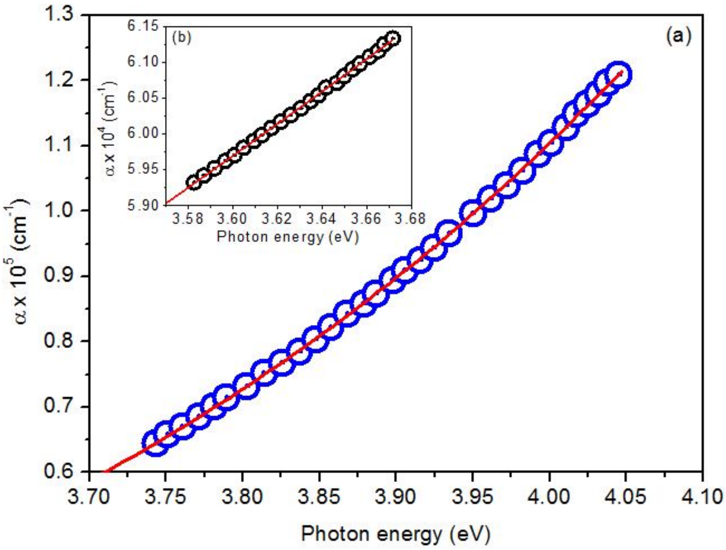

Fig. 4. The absorption coefficient (α) versus photon energy (hν) for $Se_{91}Te_9$ film. The circles represent the observed α and solid lines represent calculated α from: (a) Tauc model, (b) Urbach model.

Further, the optical band gap is strongly dependent on the fractional concentration of Te atoms. This may be due to the tendency of Te atoms to form chemical disordering and to create localized states in the band gap. According to Mott and Davis [13] the width of localized states near the mobility edge depends on the degree of disorder and defects present in the amorphous structure. Such defects are formed due to unsaturated bonds which produce localized states in the band gap. The presence of a high concentration of localized states in thin films is responsible for low optical band gap. Therefore, the addition of Te increases the concentration of localized states in the Se–Te alloy leading to the decrease in the band gap. The electronegativities of Se and Te are 2.55 and 2.1 respectively. According to these values, it is noticed that Te is less electronegative than Se, so the substitution of Se by Te may raise the energy of some lone-pair states and hence broaden the valence band. This will give rise to additional absorption over a wider range of energy leading to band tailing and hence shrinking of the band gap.

4. Conclusion

In conclusion, the optical characterization of $Se_{94}Te_6$ and $Se_{91}Te_9$ compositions of thermally evaporated amorphous semiconducting films has been carried out, using the absorbance spectra at normal incidence. X-ray analysis predicts the amorphous nature of prepared films. Optical band gap is indirect in nature and decreases with the increase of Te content in a-Se thin films. The change in optical parameters with Te incorporation in a-Se is explained on the basis of Mott and Davis model.

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