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Single oscillator energy and dispersion energy of uniform thin chalcogenide films from Cu–As–S–Se system

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Abstract

This paper presents some of the results obtained by using the modified envelope method, which takes substrate absorption into account. Samples investigated in this paper are the series of amorphous thin chalcogenide uniform films from system $Cu_x[As_2(S_{0.5}Se_{0.5})_3]_{100-x}$. Thin films were deposited under vacuum on glass substrates by thermal evaporation technique, from previously synthesized bulk samples. The dispersion of the refractive index is discussed in terms of the single oscillator model proposed by Wemple and DiDomenico. By using this model, i.e. by plotting $(n^2-1)^{-1}$ against $(\hbar\omega)^2$ and fitting a straight line, oscillator parameters, E_0 – the single oscillator energy and E_d – the dispersion energy, were directly determined.

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Keywords: Chalcogenides; Optical spectroscopy

1. Introduction

Some optical quantities, such as the optical band gap, refractive index, extinction coefficient as well as the thickness of the film can be determined by using the envelopes of the transmittance $T(\lambda)$ and/or a reflectance $R(\lambda)$ spectrum of the thin film deposited on a transparent substrate. Standard envelope method for determining the optical constants of thin film samples assumes that the glass substrate is absolutely transparent [1–6]. In practice, this is not the case and most glass substrates show significant absorption, whose neglecting can lead to the non-accurate values of determined optical parameters. The knowledge of accurate values of the wavelength dependent complex refractive index of thin solid films is very important, both from a fundamental and a technological viewpoint. Therefore, modified method based on analytical expressions derived for the transmission spectrum and its envelopes, taken at normal incidence of irradiation, for thin films, deposited onto a weakly absorbing substrate that takes substrate absorption into account, has been applied in this paper for calculation of presented parameters [7,8]. Once the dispersion of refraction index has been determined it can be fitted by the Wemple–DiDomenico relation [9,10]:

$$n^2(\hbar\omega) = 1 + \frac{E_0 E_d}{E_0^2 - (\hbar\omega)^2}, \tag{1}$$

where E_d obeys a simple empirical relationship

$$E_d = \beta N_c Z_a N_e (eV) \tag{2}$$

and N_c being the coordination number of the cation nearest-neighbour to the anion, Z_a the formal chemical valence of the anion, N_e the effective number of valence electrons

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per anion and $\beta = 0.37 \pm 0.04$ eV, for covalent crystalline and amorphous materials.

2. Experiment

The samples investigated in this paper were from $Cu_x[As_2(S_{0.5}Se_{0.5})_3]_{100-x}$ system for $x = 0$ at.%, 0.5 at.% and 1 at.%. Thin film samples were prepared from previously synthesized bulk samples which were synthesized in cascade regime from high purity elemental components (99.998%) and air quenched [11]. Bulk samples are then powdered and thin films were deposited under a vacuum of 10^{-5} Torr on glass substrates by thermal evaporation technique. The compositional and uniformity analyzes for the prepared thin films were done using a scanning electron microscope SEM-EDAX, Quanta 200. In order to suppress the crystallization, the substrate was cooled with a liquid nitrogen container. The temperature of the substrate holder was measured with a calibrated PT100 sensor embedded on the substrate holder. Substrates were standard glass microscope slides with thickness of $d = 1.00 \pm 0.05$ mm.

Transmission and reflection spectra of obtained samples and substrates were recorded by double-beam UV/VIS/NIR Perkin–Elmer spectrofotometer, model Lambda-19 and used for calculations of dispersion energies. The spectrophotometer was set with slit width of 1 nm. All optical measurements have been performed at room temperature (300 K). The envelope method applied for calculating the given parameters was taking into account the substrate absorption . First, the calculations of refractive index were carried and function $n(\lambda)$ has been plotted. Secondly, the dispersion of the refractive index is discussed in terms of the single oscillator model proposed by Wemple–DiDomenico and energies E_d and E_0 were calculated by plotting $1/(n^2 - 1)$ dependence on $(\hbar\omega)^2$. Obtained results enabled the estimation of n_0 – the refractive index extrapolated to $\lambda \to \infty$.

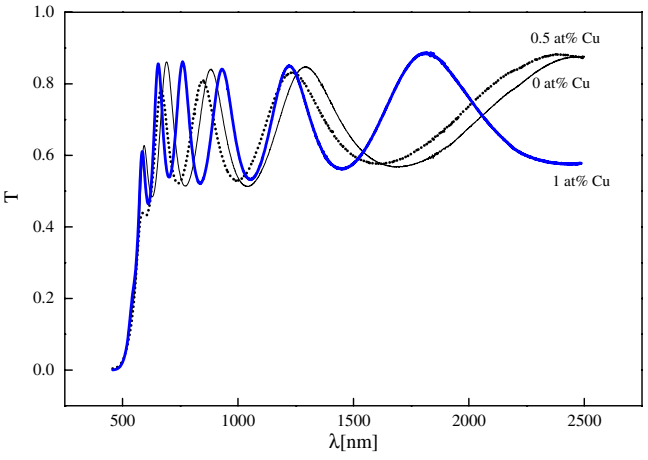

Fig. 1. Transmission spectra of amorphous thin films from $Cu_x[As_2(S_{0.5}Se_{0.5})_3]_{100-x}$ system.

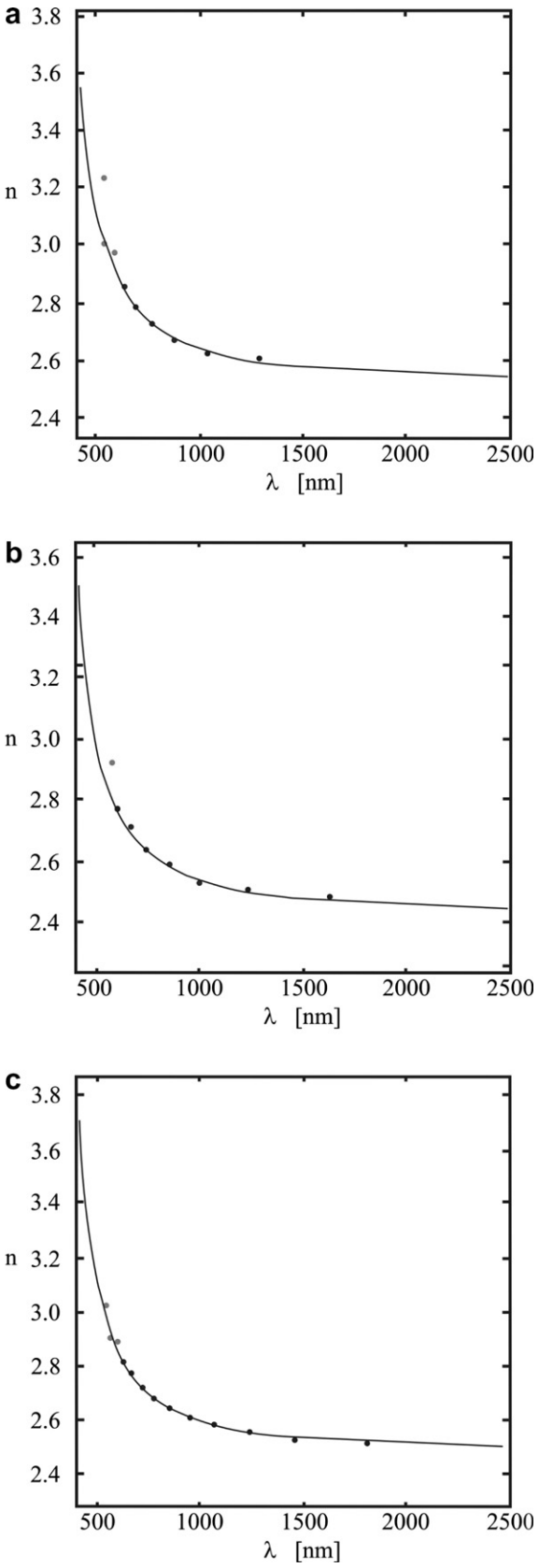

Fig. 2. Refractive index dispersion of amorphous thin films from $Cu_x[As_2(S_{0.5}Se_{0.5})_3]_{100-x}$ system for: (a) $x = 0$ at.%, (b) 0.5 at.% and (c) 1 at.%.

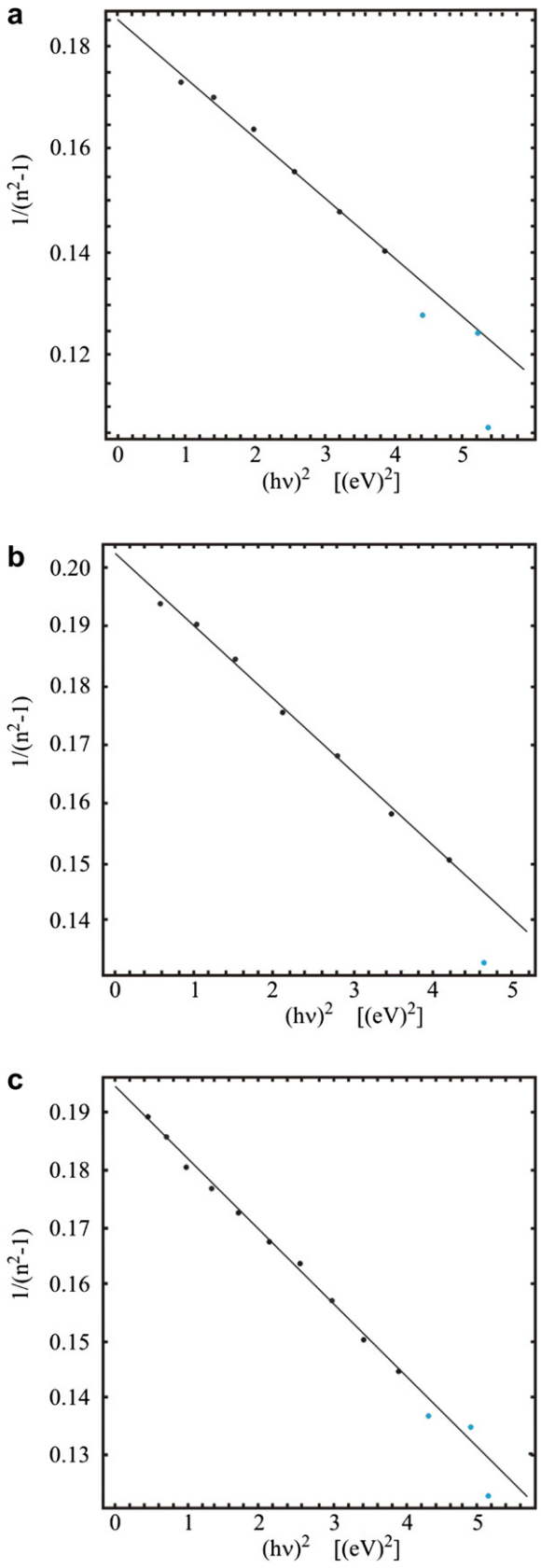

Fig. 3. Dependence of $1/(n^2-1)$ on $(\hbar\omega)^2$ of amorphous thin films from $Cu_x[As_2(S_{0.5}Se_{0.5})_3]_{100-x}$ system for: (a) $x = 0$ at.%, (b) 0.5 at.% and (c) 1 at.%.

3. Results

Fig. 1 shows transmission spectra of amorphous thin films from $Cu_x[As_2(S_{0.5}Se_{0.5})_3]_{100-x}$ system. The obtained spectra covered spectral region from 400 to 2500 nm. These spectra were used for applying the envelope method and further for calculations of the refractive indexes n, absorption coefficients α, and the average thickness $\bar{d}$.

Obtained $n(\lambda)$ functions are plotted and shown in Fig. 2.

4. Discussion

The lack of shrinking in the amplitude of the interference fringes of the transmission spectra presented in Fig. 1 indicated that all investigated thin film samples were uniform in thickness, which is the very important characteristic for many applications [12]. Uniformity was also checked together with the homogeneity by SEM method.

Refractive index dispersion enabled the analysis according to the Wemple–DiDomenico single oscillator model and calculation of E_0 – the single oscillator energy and E_d – the dispersion energy from dependence of $1/(n^2-1)$ on $(\hbar\omega)^2$ (Fig. 3).

Values of E_0 – the single oscillator energy, E_d – the dispersion energy, static refractive index n_0 and effective coordination number of the cation nearest-neighbour – N_c are given in Table 1. Extrapolated parts of refractive index dispersion along with static refractive index are calculated according to the Wemple–DiDomenico single oscillator model and shown in Fig. 2.

Values of the single oscillator energy are from 3.92 to 4.03 eV and the dispersion energy from 19.92 to 21.7 eV depending on particular sample. Static refractive index values are in the range of 2.438–2.530.

According to the empirical Eq. (2) effective coordination numbers of the cation nearest-neighbour to the anion were determined. Other parameters in Eq. (2) were assummed to be constant.

Considering the mainly covalent character of the bonds in alloys from investigated system and their chemical composition, constant from Eq. (2) have the folowing values:

$Z_a = 2$, $N_e = (40\times5 + 60\times6)/60 = 28/3$ and $\beta = 0.37 \pm 0.04$ eV. Obtained values for N_c for all investigated samples are shown in Table 1.

5. Conclusions

In this paper, optical-dispersion data were analyzed using the Wemple–Di Domenico single oscillator model. Calculated values of relevant optical parameters were obtained from transmission and reflection spectra using the envelope method and taking the substrate absorption into account.

Knowing that in arsenic–sulphur glass matrix copper can be introduced only in small amounts, in investigated four-component system $Cu_x[As_2(S_{0.5}Se_{0.5})_3]_{100-x}$ type copper content also has to be small ($x \leqslant 1$ at.%). Taking this

Table 1
Characteristic parameters of investigated thin amorphous films

Composition	E_0 (eV)	E_d (eV)	n_0	N_c
$As_2(S_{0.5}Se_{0.5})_3$	4.02 ± 0.09	21.7 ± 0.5	2.530 ± 0.007	3.1 ± 0.3
$Cu_{0.5}[As_2(S_{0.5}Se_{0.5})_3]_{99.5}$	4.03 ± 0.06	19.92 ± 0.28	2.438 ± 0.004	2.9 ± 0.3
$Cu_1[As_2(S_{0.5}Se_{0.5})_3]_{99}$	3.92 ± 0.04	20.18 ± 0.20	2.479 ± 0.003	2.9 ± 0.3

E_0 – the single oscillator energy, E_d – the dispersion energy, n_0 – static refractive index, and N_c – effective coordination number of the cation nearest-neighbour.

into consideration the significant influence of copper on determined values of E_0 – the single oscillator energy, E_d – the dispersion energy, static refractive index n_0 and effective coordination number of the cation nearest-neighbour – N_c was not expected and has not been observed.

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