

Optical properties of Ge–As–S thin films

I.D.Tolmachov, A.V.Stronski

V.Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, 41 Nauki Ave., Kyiv, Ukraine

Received October 11, 2008

Thin Ge-As-S films have been prepared by thermal vacuum evaporation. Optical parameters and thickness values of the films have been calculated basing on transmission spectra. The dispersion dependences of the refractive index have been shown to be described well by the single oscillator model. The optical band gap width has been determined using the Tauc dependence. The non-linear optical properties of the films have been estimated basing on the data obtained.

Методом термического вакуумного испарения получены тонкие пленки состава Ge-As-S. Из спектров пропускания рассчитаны толщины пленок и оптические постоянные. Показано, что дисперсионные зависимости показателя преломления хорошо описываются одноосцилляторной моделью. С помощью зависимости Тауца определена ширина оптической запрещенной зоны. На основании полученных данных проведена оценка нелинейных оптических свойств пленок.

Highly non-linear optical materials attract the attention because of their potential application in telecommunication systems as ultra-fast optical switchers (10^{-15} s), frequency converters, electrooptical modulators, etc. Chalcogenide glasses are materials of good prospects in this area of application due to high optical nonlinearity and transparency in visible and near IR spectral regions. Third order non-linear optical susceptibility $\chi^{(3)}$ of chalcogenide glasses exceeds by more than two orders of magnitude that of silica glass [1]. Therefore, study of optical properties of these materials is of great interest.

To predict non-linear optical properties basing on linear ones, semi-empirical relationships proposed in [2–4] can be used. The present work is concerned with the study of optical properties of Ge-As-S thin films and estimation of non-linear characteristics thereof. Photostructural transformations in the films under investigation were also studied.

The glasses of $\text{As}_{12.6}\text{Ge}_{23.8}\text{S}_{63.6}$ composition were prepared by conventional melt-quenching technique. Thin films were prepared by thermal vacuum evaporation onto

a glass substrate being at room temperature. A planetary system was used to provide the film thickness homogeneity. Some samples were exposed to halogen lamp radiation or natural light up to saturation of photostructural changes. The transmission spectra of the films were measured at room temperature in the 0.4–2.5 μm range. The Swanepoel method [5] was used to evaluate optical constants, refractive index n and the film thickness d .

In Fig. 1, typical $n(\lambda)$ curves for unexposed and exposed films are shown. The solid line shows extrapolation result of the values obtained by the function $n(\lambda) = a/\lambda^2 + c$. The wavelength dependences of refractive index are well described by single oscillator model [6]:

$$n^2 - 1 = \frac{E_d E_0}{E_0^2 - E^2}, \quad (1)$$

where E_0 is the single oscillator energy; E_d , dispersion energy; E , the photon energy. E_0 defines the position of effective oscillator connected with average energy gap; the dis-

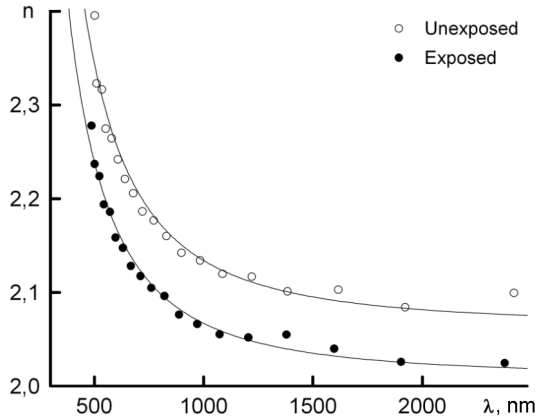


Fig. 1. Refractive index dispersion curves.

persion energy E_d characterizes the strength of interband transitions. The expression (1) was applied successfully to analyze the dispersion data for more than hundred different materials: covalent, ionic, crystalline, and amorphous [6]. To obtain E_0 and E_d , we have plotted equation

$$(n^2 - 1)^{-1} = f(E^2) \quad (2)$$

at the points corresponding to the spectrum extremes and then performed least squares fitting to a straight line (see Fig. 2). The points corresponding to maximum photon energy are seen to drop out of the linear dependence, therefore, they were excluded from consideration when evaluating the E_d and E_0 parameters.

The optical band gap E_g was determined using the Tauc law, $(\alpha\hbar\omega)^{1/2} = f(E)$. In Fig. 3, the energy dependence of $(\alpha E)^{1/2}$ parameter is plotted, where the linear section in the high photon energy region corresponds to the Tauc law. The E_g value corresponds to the point where the straight line intersects with abscissa axis. In Fig. 4, the absorption coefficient (in logarithmic scale) vs the incident photon energy is plotted. The almost linear region where the absorption coefficient ranges from $2 \cdot 10^2$ to $5 \cdot 10^3 \text{ cm}^{-1}$ meets the Urbach law:

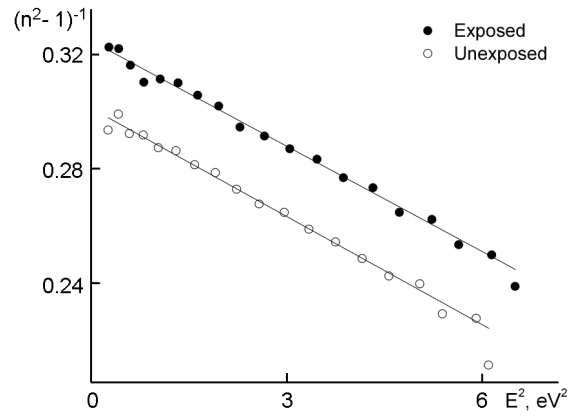


Fig. 2. Evaluation of oscillator parameters.

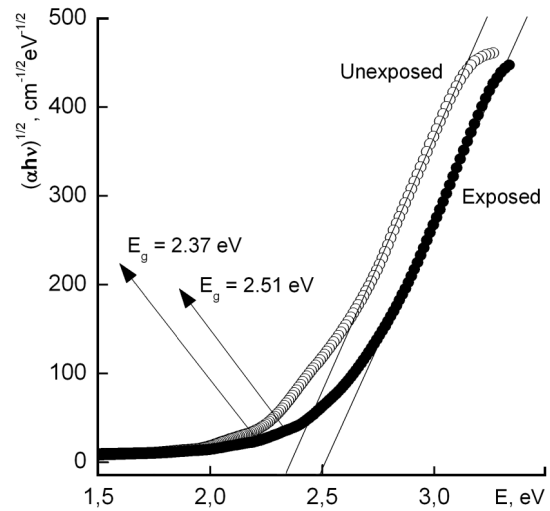


Fig. 3. Tauc plots.

$$\alpha(E) = \alpha_0 \exp\left(\frac{E}{E_c}\right). \quad (3)$$

In Table 1, the film optical parameters determined from transmission spectra are presented (n_0 is refractive index in the limit $E \rightarrow 0$). It is seen from the Table that E_0 scales well with the optical band gap ($E_0 \approx 2 \cdot E_g$). The Ge-As-S glasses contain covalent chemical bonds besides of the homopolar ones. Structural fragments of different dimensionality can co-exist simultaneously within the covalent-bonded network of such topologically disordered glasses or

Table 1. Films parameters obtained from transmission spectra

Film	d , nm	E_d , eV	E_0 , eV	E_g , eV	E_c , eV	n_0
Unexposed	1150	16.1	4.9	2.37	0.15	2.07
Exposed	1167	15.8	5.1	2.51	0.15	2.02

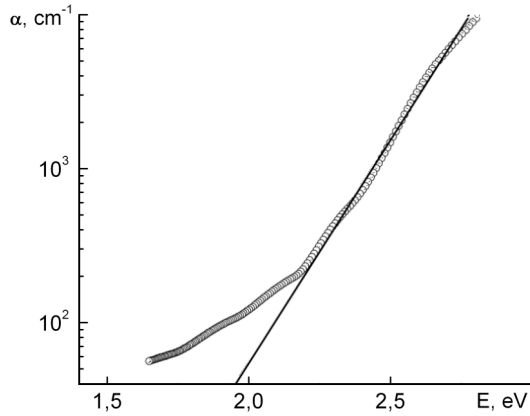


Fig. 4. Urbach's absorption tale.

films. Freshly deposited Ge-As-S films contain the same main structural units as in the respective bulk glasses as well as some non-stoichiometric molecular fragments forming As-enriched and/or Ge-enriched nanophases. The density of such fragments in fresh films is higher than in the glasses (and in well-annealed films), thus indicating a higher disorder degree therein. It is seen from Table 1 that illumination of fresh films results in increased E_g value, i.e. in photo-bleaching. The photoinduced structural transformations and structural rearrangement cause some increase of the film thickness (by about 1–2 %). The presence of the photostructural changes makes it possible to use such films in information recording and photolithography.

The non-linear optical properties were estimated by two different ways basing on linear ones calculated from the transmission spectra. In [3], to estimate the non-linear properties of chalcogenide glasses, a generalized Miller rule was used which establishes relation between linear optical susceptibility, $\chi^{(1)}$, and third order non-linear optical susceptibility, $\chi^{(3)}$. According to this rule,

$$\chi^{(3)} \cong A(\chi^{(1)})^4. \quad (4)$$

Here A is a constant. Its value for chalcogenides appears to be $A = 1.7 \cdot 10^{-10}$ and so the $\chi^{(3)}$ value is obtained in esu. We

compared the estimated and experimentally measured values and achieved a satisfactory agreement within one order of magnitude.

It was proposed in [4] to use a classical anharmonic oscillator model to establish correlation between $\chi^{(3)}$ and E_g :

$$\chi^{(3)} \cong B \frac{1}{E_g^6} \left[1 - \left(\frac{h\nu}{E_g} \right)^2 \right]^{-4}, \quad (5)$$

where $h\nu$ is photon energy,

$B = 2.846 \cdot 10^{-16}$ esu·(eV)⁶ is a constant. Values of n_2 and E_g were measured independently for silica glasses, some oxides and chalcogenides and plotted in the form of function

$$n_2 = f \left(\frac{1}{E_g^6} \left[1 - \left(\frac{h\nu}{E_g} \right)^2 \right]^{-4} \right), \quad (6)$$

representing the results obtained by authors of the work as well as literature data. All the values were fitted well by a straight line.

In Table 2, estimations of n_2 and $\chi^{(3)}$ are obtained using formulas (8) and (9) for unexposed and exposed films. The results coincide within an order of magnitude but the values obtained using generalized Miller rule exceed by about 50 % those obtained basing on the anharmonic oscillator model. The non-linear optical parameters of studied films are more than two orders of magnitude higher than those of silica glass. The high values of non-linear optical parameters show that such media are of good promise for the use in optical switching, frequency converters, electrooptical modulators and optical signal processing devices.

References

1. J.M.Harbold, F.O.Ilday et al., *IEEE Photonics Techn. Lett.*, **14**, 822 (2002).
2. K.Petkov, P.J.S.Ewen, *J. Non-Crystal Solids*, **249**, 150 (1999).
3. H.Ticha, L.Tichy, *J. Optoelectron. and Advanced Mater.*, **4**, 381 (2002).
4. J.S.Sanghera, C.M.Florea, L.B.Shaw et al., *J. Non-Crystal. Solids*, **354**, 462 (2008).
5. R.Swanepoel, *J. Phys. E: Sci. Instrum.*, **16**, 1214 (1983).
6. S.H.Wemple, *Phys. Rev. B*, **7**, 3767(1973).

Table 2. Estimated non-linear properties of films

Film	$\chi^{(3)}$, 10^{-12} esu		n_2 , 10^{-11} esu	
	Miller's rule	Anharmonic oscillator	Miller's rule	Anharmonic oscillator
Unexposed	0.78	0.44	1.43	0.81
Exposed	0.63	0.30	1.17	0.56

Оптичні властивості тонких плівок Ge–As–S

І.Д.Толмачов, О.В.Стронський

Методом термічного вакуумного випаровування отримано тонкі плівки складу Ge-As-S. Із спектрів пропускання розраховані оптичні сталі та товщини плівок. Показано, що дисперсійні залежності показника заломлення добре описуються одноосциляторною моделлю. За допомогою залежності Тауца визначено ширину оптичної забороненої зони. На основі отриманих даних проведено оцінку нелінійних оптичних властивостей плівок.