Dependence of the optical gap GeO_x films ($0.21 \leq x \leq 1.95$) on their composition

© V.V. Lyamina[1], I.A. Azarov[1,2], T.V. Perevalov[2], P.V. Shvets[3], V.A. Volodin[1,2]

[1] Novosibirsk State University,
630090 Novosibirsk, Russia
[2] Rzhanov Institute of Semiconductor Physics, Siberian Branch of the Russian Academy of Sciences,
630090 Novosibirsk, Russia
[3] Scientific and Educational Center „Functional Nanomaterials", Immanuel Kant Baltic Federal University,
236041 Kaliningrad, Russia

E-mail: volodin@isp.nsc.ru

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The GeO_x films ($0.21 \leq x \leq 1.95$) were grown on fused silica substrates using pulsed laser deposition. Their composition was varied by changing the oxygen pressure during deposition and was determined from Rutherford backscattering data. Raman spectroscopy showed that films with a composition ($0.21 \leq x \leq 1.48$) contain amorphous germanium clusters. Spectral dependances of the real and imaginary parts of the refractive indices and film thickness were obtained from ellipsometry and transmission-reflection spectroscopy data. From these data, the dependence of the optical gap on the stoichiometric parameter x was determined. Experimental optical gap data were compared with data obtained from quantum chemical calculations; the calculated optical gap values exceed the measured ones..

Keywords: non-stoichiometric germanium oxide, transmission and reflection spectroscopy, absorption coefficient, Tauc model, optical gap, Raman scattering..

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1. Introduction

Thin oxide films play a critical role in optics and electronics. Germanium oxides have found their application among such thin-film materials. They are of interest as a dielectric material for the development of metal-insulator-semiconductor (MIS) structures, which are used, for example, in germanium-based field-effect transistors. Since germanium dioxide is not stable, to develop MDS transistors, films of non-stoichiometric germanium oxide GeO_x ($x < 2$) or GeO_xN_y (germanium oxynitride) are used [1]. Another application of GeO_x films is in memristors [2]. Besides, germanium oxides in the form of thin films are used as a coating that decreases light reflection in solar cells, thus improving their efficiency [3], and as anode layers in accumulator batteries [4]. Since germanium oxides have a good combination of mechanical and optical properties, they are also used to make lenses, waveguides, photodetectors and windows, transparent in the infrared range [5,6], and within multilayer interference filters [7,8]. In GeO_x films the effect of photoinduced change in the refraction index was found, which makes it possible to obtain holographic gratings on their basis [9]. However, the literature contains very scarce data on the dependence of the edge of the fundamental absorption of GeO_x films on their composition, only a paper by US researchers [10] and a paper by our group [11] are known. Therefore the presented paper is dedicated to filling this knowledge gap.

2. Method

Films of amorphous germanium oxide were obtained on substrates from fused (amorphous) quartz (silica) by the method of pulsed laser deposition (PLD). The original growth unit was used on the basis of SMART NanoTool PLD device (https://svta.com/systems/pulsed-laser-deposition-systems/).

The source of radiation was the fourth harmonic (266 nm) of the pulsed laser Nd:YAG, pulse duration was — 7 ns, frequency — 10 Hz, radiation density — ≈ 0.5 J/cm^2. A target for film deposition using PLD method was a pure germanium crystal, the substrate was not heated. The distance from the target to the substrate was 5.8 cm. The composition of the films was changed by variation of the oxygen pressure, which varied from 1 to 10 mTorr. The background vacuum was 10^{-7} Torr, therefore, the films were growing in the atmosphere of pure oxygen. The deposition time changed from 60 min (maximum oxygen pressure, deposition speed was higher) to 90 min (minimum oxygen pressure, deposition speed was lower).

The film thickness was controlled using the method of X-ray reflectometry — XRR. The XRR curves were obtained using the Bruker AXS D8 DISCOVER system with radiation of CuK_α (0.15406 nm) in the standard geometry $\theta-2\theta$. The Bruker LynxEye A17-B60 detector was turned to the point mode during measurements. The pitch was $2\theta = 0.002°$, and the data collection time — 3 s per point. The reflection data were analyzed using software with the open source code GenX 3 [12].

The elemental composition of the studied samples was determined using Rutherford backscattering spectrometry (RBS) on the Van de Graaff accelerator AN2500 (High Voltage Engineering Europa B.V.). The sample was irradiated with a beam $^4He^+$ with energy of 1.5 MeV. The angle between the beam and the normal line to the sample surface was 5°, the angle of emergence — 21°, the scattering angle — 160°. The beam current and the full accumulated charge were ~ 5 nA and 30 μC, accordingly. The experimental spectra were analyzed using software SIMNRA [13].

To analyze the presence of amorphous germanium clusters in the films, Raman scattering (RS) spectroscopy was used. The RS spectra were registered using spectrometer T64000 Horiba Jobin Yvon in the backscattering geometry at room temperature. The source of exciting radiation was a fiber laser with wavelength of 514.5 nm (Scientific Development and Production Center „Inversion-Fiber"). The spectral resolution was 2 cm^{-1}. The laser spot diameter was $\sim 30\,\mu$m, and the beam power was 1 mW, which did not cause noticeable local heating of the area under the laser spot and disproportioning of the films GeO_x in accordance with the reaction ($GeO_x \rightarrow (1 - x/2)Ge + x/2\,GeO_2$).

To register the transmission (T) and reflection (R) spectra, the paper used spectrophotometer Shimadzu UV-3600. The spectral resolution was 2 nm, the studied range — 190–2500 nm. To register the spectra of mirror reflection, a special attachment was used with the angle of light incidence to the normal line 5°. The reference mirror was a polished Si-plate. The measured spectrum was normalized by the reflection spectrum of the standard. To calculate the real and imaginary parts of the refraction index of films GeO_x and their thickness, the approximation of the measured transmission and reflection spectra was used with the calculated spectra, for this purpose special PC software was applied (the example of the software use was shown in paper [11]).

To find the thicknesses of GeO_x films, the real and imaginary parts of the refraction index, spectral ellipsometer ASEB-5 (Novosibirsk) was used. The spectral range was 250–900 nm, the resolution was 2 nm.

The calculations of the atomic and electronic structure GeO_x were conducted within the density functional theory (DFT) in the model of periodical cells, approximation of pseudopotentials with a plane-wave basis in the software package Quantum ESPRESSO. The model supercells GeO_x with $x = 0.75$, 1.0, 1.25, 1.5, 1.75, 2.0, were produced, the structure of which meets the model of the random bonding (RB). Structural relaxation calculations were performed using the exchange-correlation functional PBEsol, and the total density spectra of electronic states — with hybrid Heyd–Scuseria–Ernzerhof functional, which yields values E_g close to the experiment for GeO_2 (6.0 eV).

3. Results

The RBS spectra for the films with composition $GeO_{0.59}$ and $GeO_{1.72}$ are given in Figure 1. Ions with energy 1100–1250 keV are reflected from the germanium atoms, therefore, the higher the signal in this range relative to the substrate signal (600–800 keV), the lower the oxygen content is in the film. The film stoichiometry parameter was defined by adjusting the model spectrum to the experimental one. The model included a simple structure SiO_2/GeO_x, and the thickness of the film and the quantity of oxygen therein varied. The thickness was also additionally determined using XRR method by the Kiessig oscillation period (see insert in Figure 1).

RS spectra of films GeO_x and substrates from fused quartz are shown further in Figure 2. The substrate spectrum includes features related to oscillations of Si–O-bonds. This is a broad band from ~ 200 to 550 cm^{-1} and a small peak with the position of 495 cm^{-1}. The last peak in the literature is related to defects (five- and seven-member rings). You can see that the features related to the RS from the fused quartz substrate manifest themselves in the spectrum of only the most transparent film — $GeO_{1.95}$. In other films the signal from the substrate yields practically no contribution, therefore it was not subtracted from the spectrum of the samples.

The RS signal from the amorphous samples is determined by their effective density of oscillatory states. For the amorphous germanium it is a broad band with the maximum of 275–280 cm^{-1} [14]. From the figure you can see that these bands in the RS spectra start manifesting themselves for the composition $GeO_{1.48}$ and smaller x. This corresponds to the presence of exactly the amorphous germanium clusters in the films of such composition.

The presence of the germanium clusters depends not only on the parameter of composition x, but also the model of non-stoichiometric amorphous oxide. There are two „extreme" cases — a random mixture model (RMM) and a random bonding model (RBM). In the first one the film GeO_x is a mixture of amorphous germanium and germanium dioxide, and the molar fraction of amorphous

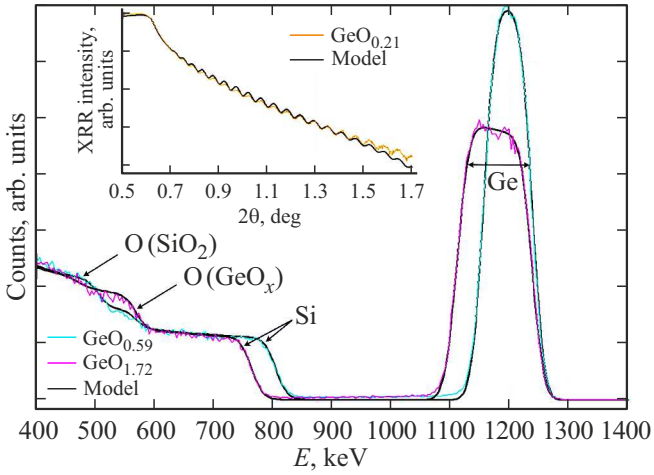


Figure 1. RBS spectra for the films GeO_x of various stoichiometry. The insert shows the XRR curve for the film $GeO_{0.21}$. The black curves are the modeling results.

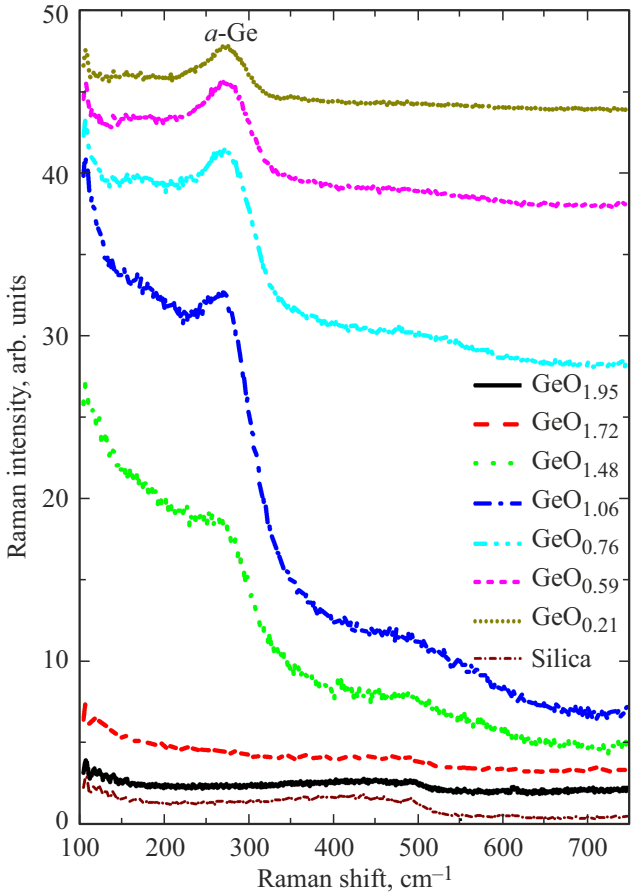


Figure 2. RS spectra of the studied samples.

germanium is $1 - x/2$. The second includes tetrahedrons $Ge{-}Ge_\nu O_{(4-\nu)}$ of all five possible types ($\nu = 0, 1, 2, 3$ and 4). The probability of presence of each type of tetrahedrons depends on the parameter of composition x [15]. Formally the germanium clusters are present in this case as well, even at x, tending towards 2. However, what is a germanium cluster? Is it two atoms of germanium, three, four or more? In our case a germanium cluster is an object, the electronic spectrum of which is close to the electron spectrum of amorphous germanium (with account of quantum-size effect). This is exactly the cluster that manifests itself in the RS spectra when excited with green light, since in this case the conditions of RS are close to resonant ones. The presence of such „big“ (according to our estimates, a hundred of atoms and more) clusters may depend on the method of film production, but mainly depends on the substrate temperature. At temperature of 400°C and higher, the disproportioning reaction follows, and the film structure tends towards the random mixture model. The fact that we do not see the presence of „big“ germanium clusters at parameter of composition $x = 1.72$ and more, tells us that our films in their structure are closer to the random bonding model.

You can note that the RS spectra of some films show a background that is growing in the area of low frequencies. Possibly, it is related to a boson peak, which is often present in the RS spectra of glass-like materials [16]. You can see that the background growing in the area of low frequencies is observed for the films GeO_x „of the average“ composition ($0.76 \le x \le 1.48$). The reason for that is still unclear and may serve as the subject of further studies.

For all films, the spectral dependences of ellipsometric angles Δ and Ψ were obtained. Then the inverse problem of ellipsometry was solved as follows. In the single-film model, the values of angles Δ and Ψ were calculated, and by variation of parameters, they were adjusted to the values obtained from the experiment. The parameters were the thickness of the film, and to produce the real and imaginary parts of the refraction index and thickness of the films GeO_x the Lorentz–Lorenz formula was used. Then the absorption coefficient α was defined based on the wavelength. The results are shown in Figure 3. You can see that the lower the oxygen content is in the film, the less transparent it is.

The transmission (T) and reflection (R) spectra of all films, and also the substrates were measured and presented in Figure 4, *a* and *b*. You can see that the quartz substrate was transparent to the wavelength ≈ 250 nm. The transmission and reflection spectra showed maxima and minima related to light interference in the films. The presence of interference does not allow to precisely detect the edge of absorption in the films GeO_x. For the quantitative analysis of absorption and refraction indices, the transmission and reflection spectra of films GeO_x were approximated using the above software. The example of approximation of the experimental transmission and reflection spectra of films GeO_x may be found in papers [11,17]. Thus, the modeling was used to determine the parameters of refraction (n) and absorption (k), and also thickness of the films so that the experimental and calculated spectra of transmission and reflection coincided. As a result, the spectral dependences of optical constants n and k were obtained. The dependence of the extinction coefficient (k) on the wavelength (λ) may be used to calculate the spectral dependence of the

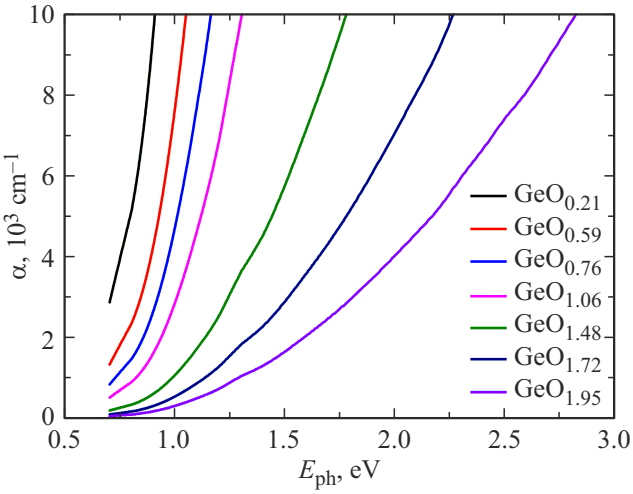


Figure 3. Dependence of absorption coefficient on photon energy obtained from spectral ellipsometry data.

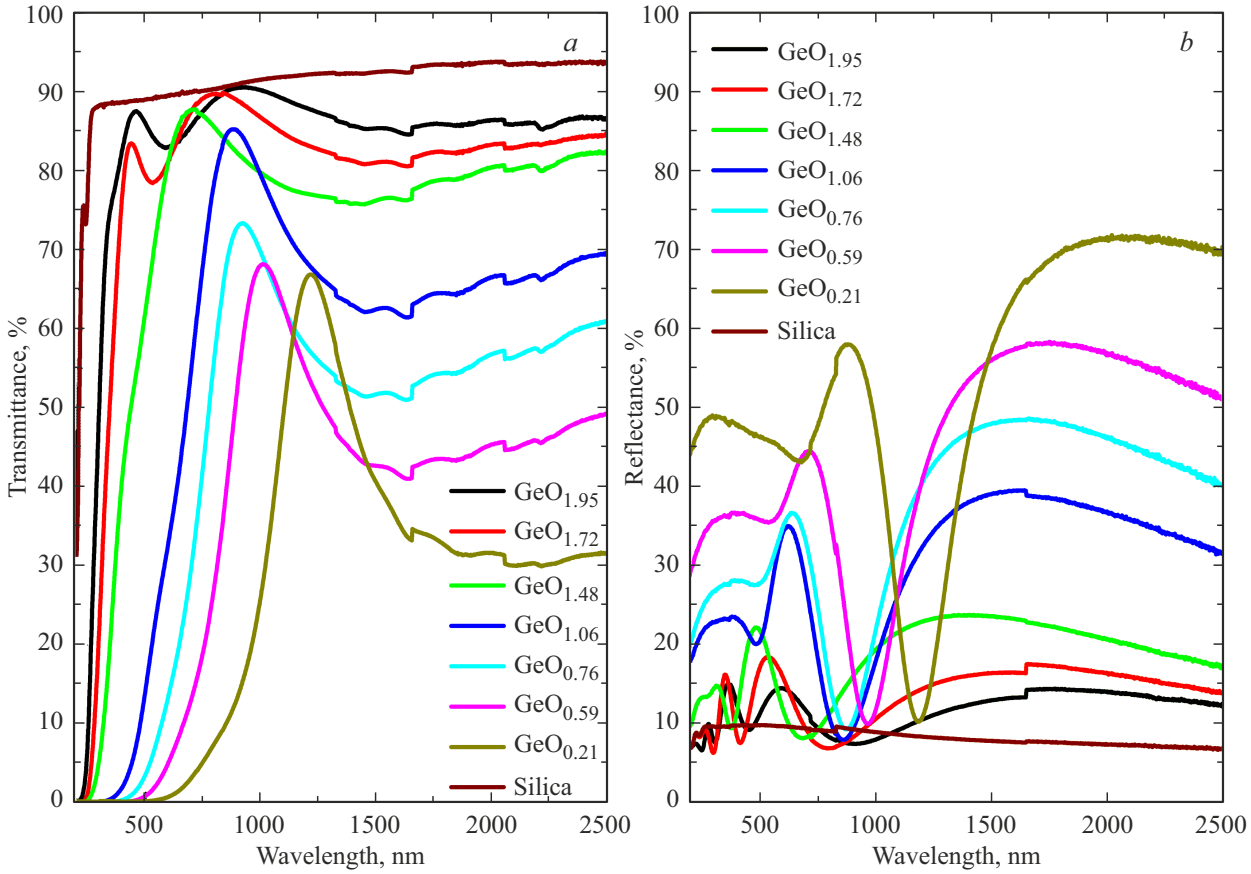


Figure 4. Transmission (a) and reflection (b) spectra of studied samples.

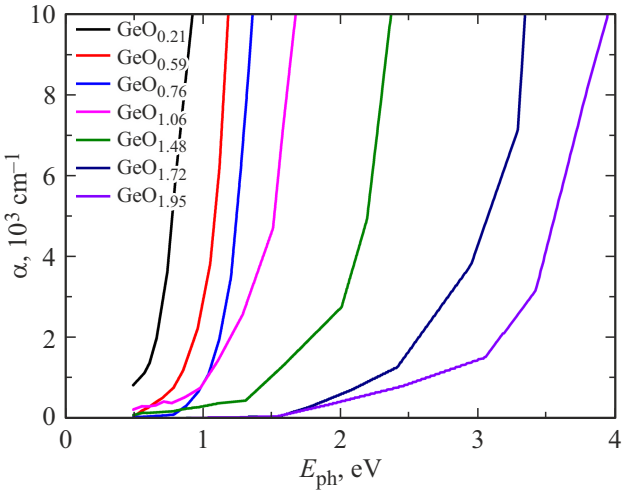


Figure 5. Dependence of absorption coefficient GeO_x on photon energy using modeling data from transmission and reflection spectra.

absorption coefficient (α — in cm^{-1}) using the formula $\alpha = \frac{4\pi \cdot 10^7}{\lambda(\text{nm})} \cdot k$.

Using the data of modeling of the spectra T and R, knowing the values of the imaginary part of the refraction index, the curve was built for the dependence of the absorption coefficient on photon energy (Figure 5). The curve looks „broken“, since the software did the adjustment using points, and the values between the points were interpolated with linear dependence.

These data were further used to calculate the edge of absorption (optical band gap) using the Tauc model [18]. The method consists in the following. Since the amorphous materials contain no translational symmetry and do not conserve quasimomentum, the optical transitions are possible from the energy state occupied by the electron to the non-occupied energy state, and only the energy conservation law must be met. The imaginary part of dielectric permittivity in the amorphous material is proportionate to the following expression:

$$\epsilon_2(\omega) \propto \frac{1}{\omega^2} \int g_c(E) \cdot g_v(\hbar\omega - E) dE, \qquad (1)$$

where g_c and g_v — densities of states in the conduction band and in the valence band, accordingly. For further simplification, it can be assumed that near the edges of zones $g_c(E) \sim E^{1/2}$ and $g_v(E) \sim E^{1/2}$, as in crystalline materials. This means that the energy is counted from the edge of the corresponding zone, i. e. $g_c(E) \propto \sqrt{E - E_c}$ and $g_v(E) \propto \sqrt{E_v - E}$, where E_c and E_v — are energies of

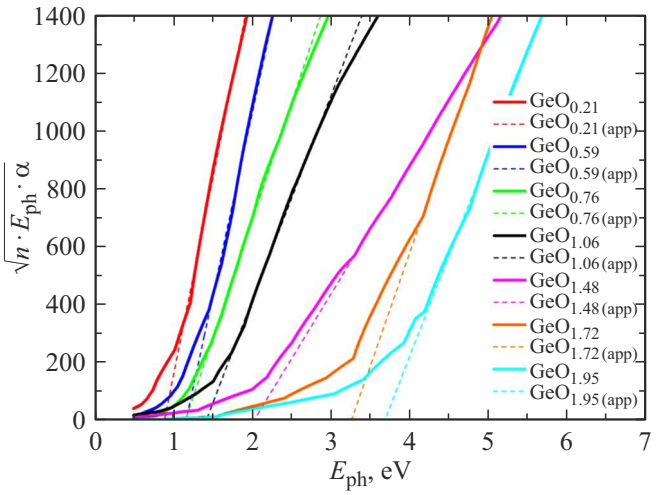


Figure 6. Approximation in Tauc coordinates for all films GeO_x.

the conduction band and valence band. In this case the convolution product (1) will be

$$\int_{E_g}^{\hbar\omega} \sqrt{E - E_g} \cdot \sqrt{\hbar\omega - E} dE, \qquad (2)$$

$E_g = E_c - E_v$ — width of the band gap. After integral calculation, we get:

$$\epsilon_2(\omega) \propto \frac{(\hbar\omega - e_g)^2}{\omega^2}.$$

Connection between the absorption coefficient $\alpha(\omega)$ and imaginary part of dielectric permittivity:

$$\alpha(\omega) = \frac{\omega}{n(\omega)c} \epsilon_2(\omega), \qquad (3)$$

where n — refraction index (real part). Having substituted $\epsilon_2(\omega)$ in (3), we get

$$\alpha(\omega) \propto \frac{(\hbar\omega - E_g)^2}{n(\omega)c\omega}. \qquad (4)$$

Let us take the square root and multiply both parts by $\hbar\omega$:

$$\sqrt{\alpha(\omega) \cdot n(\omega) \cdot \hbar\omega} \propto (\hbar\omega - E_g). \qquad (5)$$

Thus, formula (5) describes the Tauc model. It is convenient because the value of the expression in the left part of the formula (5) „is rectified“ depending on the photon energy.

Figure 6 shows the results for the absorption coefficients of all studied films built in the Tauc coordinates. You can see that the absorption edge moves towards the „blue“ spectral region as the oxygen content increases. Besides, Figure 6 also shows the presence of so called Urbach „tails“. This is always observed in case of orderless solid bodies.

Thicknesses of films obtained using various methods

Sample	Thicknesses of films, nm		
	XRR	Ellipsometry	Modeling T and R
$GeO_{1.95}$	248 ± 2	252 ± 15	260 ± 15
$GeO_{1.72}$	220 ± 2	215 ± 12	220 ± 12
$GeO_{1.48}$	172 ± 2	170 ± 9	172 ± 8
$GeO_{1.06}$	165 ± 1	169 ± 7	173 ± 7
$GeO_{0.76}$	142 ± 1	148 ± 5	147 ± 5
$GeO_{0.59}$	140 ± 1	147 ± 6	137 ± 4
$GeO_{0.21}$	136 ± 1	133 ± 3	133 ± 3

Besides, in addition to the XRR data, the thicknesses of the films were defined from the analysis of the spectral ellipsometry and transmission and reflection spectroscopy data, the results are given in the table.

The values of the fundamental edge of absorption were obtained using various methods: from the Tauc model, from the data of spectral ellipsometry and transmission and reflection spectroscopy. Besides, there is also a simplified method to determine the edge of absorption. Often the edge of absorption is assumed to be the value of photon energy, at which the absorption coefficient α is 10^4 cm^{-1} [19]. The values of the absorption coefficient α were also defined from the data of spectral ellipsometry and transmission and reflection spectroscopy. Figure 7 shows the values of the absorption edge obtained using all four methods.

In agreement with the experimental data, the monotonic growth of values E_g calculated ab initio is observed as the parameter x increases (Figure 7). The calculated data consistently overestimate values E_g, which may be explained by using the model of infinite perfect crystal in the calculations.

You can see that the experimental dependence of the absorption edge produced from the transmission and reflection spectroscopy data by simplified method ($\alpha = 10^4$ cm^{-1},

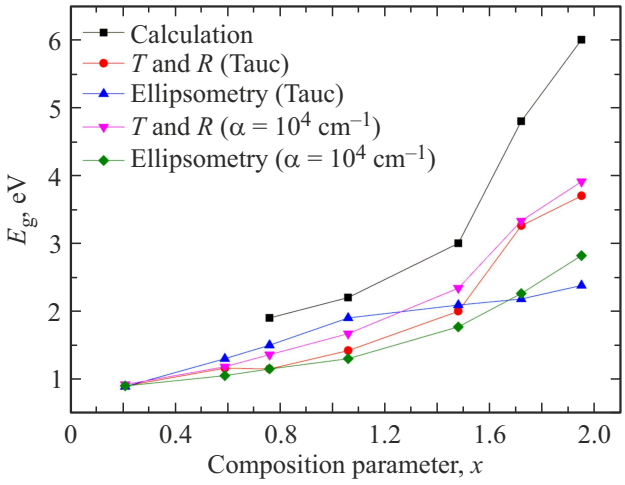


Figure 7. Dependence of absorption edge on quantity of oxygen in GeO_x, the data were obtained using four different methods. Black line with small squares — calculated data.

pink curve, triangles with the top down in Figure 7), follows the calculations well, only the values of the calculations are overestimated. The biggest error is in sample with $x = 1.95$, since in the Shimadzu UV-3600 spectrometer in the UV-range the sensitivity decreases, and the noise increases. Thus, for the quick estimate of the absorption edge you can apply a simplified method. However, to analyze the Urbach „tails“ it is important to use the Tauc model.

4. Conclusion

The transmission and reflection spectra of films GeO_x ($0 < x < 2$) were studied in the range of wavelengths from 190 to 2500 nm. The presence of the germanium clusters was detected in the films with composition of $x \leq 1.48$. The values of refraction and absorption indices (n and k) were obtained for each film using computer modeling of transmission and reflection spectra. The thicknesses of the films were compared using three methods: XRR, ellipsometry and modeling of transmission and reflection spectra. The optical absorption edges were calculated for the films of various composition in Tauc coordinates. The dependence of the optical width of the band gap on the stoichiometric composition of films GeO_x developed by the pulsed laser deposition method was obtained. It was found that the increase in the oxygen concentration within the film led to increase in its optical transparency, which is accompanied with the shift in the edge of the absorption band towards shorter wavelengths. The obtained data in general agree with the theory and may be used in optical applications.

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Conflict of interest

The authors state that they have no conflict of interest.

References

[1] P. Bhatt, K. Chaudhuri, S. Kothari, A. Nainani, S. Lodha. Appl. Phys. Lett., **103**, 172107 (2013). DOI: 10.1063/1.4826142
[2] A.V. Shaposhnikov, T.V. Perevalov, V.A. Gritsenko, C.H. Cheng, A. Chin. Appl. Phys. Lett., **100**, 243506 (2012). DOI: 10.1063/1.4729589
[3] V.G. Dyskin, M.U. Dzhanklych. Appl. Solar Energy, **57**, 252 (2021). DOI: 10.3103/S0003701X2103004X
[4] D. Lv, M.L. Gordin, R. Yi, T. Xu, J. Song, Y.-B. Jiang, D. Choi, D. Wang. Adv. Funct. Mater., **24** (8), 1059 (2013). DOI: 10.1002/adfm.201301882
[5] A. Choudhury, A. Dalal, S.M. Manohar Dhar Dwivedi, A. Ghosh, N. Halder, S. Das, A. Mondal. Mater. Res. Bull., **142**, 111397 (2021). DOI: 10.1016/j.materresbull.2021.111397
[6] A. Chiasera, C. Macchi, S. Mariazzi, S. Valligatla, L. Lunelli, C. Pederzolli, D.N. Rao, A. Somoza, R.S. Brusa, M. Ferrari. Opt. Mater. Express, **3** (9), 1561 (2013). DOI: 10.1364/OME.3.001561
[7] V.F. Zinchenko, V.P. Sobol, I.R. Magunov, O.V. Mozgova. Vopr. Khim. Khim. Tekhnol., **6**, 29 (2018). DOI: 10.32434/0321-4095-2018-121-6-29-33
[8] K.S. Eloyan, V.A. Volodin, M. Vergnat. Sci. Lett., **4**, 94 (2015).
[9] F.A. Nazarenkov, N.A. Rastrenenko. Opt. i spektr., **46** (5), 1013 (1979) (in Russian).
[10] N.R. Murphy, J.T. Grant, L. Sun, J.G. Jones, R. Jakubiak, V. Shutthanandan, C.V. Ramana. Optical Mater., **36**, 1177 (2014).
[11] K.N. Astankova, N.A. Kislukhin, A.D. Samus, A.A. Matsynin, S.V. Komogortsev, I.A. Azarov, V.A. Volodin. FTT, **68** (2), 269 (2026) (in Russian). DOI: 10.61011/FTT.2026.02.62716.8833
[12] A. Glavic, M. Björck. J. Appl. Crystallogr., **55**, 1063 (2022). DOI: 10.1107/S1600576722006653
[13] M. Mayer. AIP Conf. Proc., **475**, 541 (1999). DOI: 10.1063/1.59188
[14] M. Wihl, M. Cardona, J. Tauc. J. Non-Cryst. Sol., **8–10**, 172 (1972). DOI: 10.1016/0022-3093(72)90132-9
[15] K.N. Astankova, V.A. Volodin, I.A. Azarov. FTP, **54** (12), 1296 (2020) (in Russian). DOI: 10.21883/FTP.2020.12.50228.9508a
[16] J. Schroeder, W. Wu, J.L. Apkarian, M. Lee, L.-G. Hwa, C.T. Moynihan. J. Non-Cryst. Sol., **349**, 88 (2004). DOI: 10.1016/j.jnoncrysol.2004.08.265
[17] G. Hamoud, A. Samus, A. Matsynin, S. Komogortsev, V. Zhandun, I. Prosvirin, K. Astankova, I. Azarov, P. Geydt, I. Milekhin, V. Volodin. Thin Sol. Films, **836**, 140869 (2026). DOI: 10.1016/j.tsf.2026.140869
[18] J. Tauc. Mater. Res. Bull., **3**, 37 (1968). DOI: 10.1016/0025-5408(68)90023-8
[19] T.V. Perevalov, V.A. Volodin, G.N. Kamaev, G.K. Krivyakin, V.A. Gritsenko, I.P. Prosvirin. J. Non-Cryst. Sol., **529**, 119796 (2020). DOI: 10.1016/j.jnoncrysol.2019.119796

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