

Chalcogenide glasses in optoelectronics

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1. Introduction

Professor B.T.Kolomiets was one of the authors of the discovery of electrical semiconductor properties of chalcogenide glasses. He developed a complex investigations of the structure and physical properties of a large group of chalcogenide glasses. He often underlined the importance of this class of materials for understanding of non-crystalline solids physics. Such appreciation can be found, for example, in one of the last of his summary papers "Chalcogenide glasses" written by him in 1981 on the occasion of the jubilee of Saint-Petersburg Physical-Technical Institute. In that paper the main attention was paid to describing the unique features of the glassy semiconductors, the the new phenomena, first theoretical notions and potentialities for practical applications were mentioned. Prof. Kolomiets was very reminiscent and noted in that article the contribution of Prof. A.F. Ioffe and Prof. N.A. Goriunova in the discovering of the new group of semiconductors — glassy semiconductors.

I am happy that my scientific activity began in the famous laboratory of Prof. B.T.Kolomiets in 1959 while the first researches of the chalcogenide glasses were developed, especially researches concerning optical, electrical, photoelectrical phenomena, etc. I remain very obliged to Prof. B.T.Kolomiets for the possibility to work in his laboratory and to deal with new class of non-crystalline semiconductors which became then materials of great interest in many laboratories of the world.

This is why it is a particular pleasure for me to contribute with a special article in honour of Professor B.T.Kolomiets ninetieth birthday. First of all, it is worthy to note what is the reason of interest for mentioning that class of materials. The main reason of interest of the scientific community to this class of materials was the fact that this class of glassy semiconductors successfully complements the properties of well known groups of crystalline semiconductors.

Really of an insignificant change of the composition or the content in the crystals is quite sufficient for achieving a sharp change of physical parameters, then chalcogenide glasses admit smooth change of properties even in cases of considerable changes of the composition or the strong alloy.

If many electronic processes in the crystals are controlled by the redistribution of charge carriers on the separate discrete local levels, then in the chalcogenide semiconductors a quasicontinuous distribution of localized states is discovered, which generates a great peculiarity of electronic processes, in particular, in the transport phenomenon, in optical and photoelectric processes.

For example, in the chalcogenide glass semiconductors the mobility of the charge carriers may differ from the mobility of crystals by million and more orders of magnitude.

If the crystals having hard crystal structures do not permit removing of atoms from their fixed position in the network, the chalcogenide glasses, as well as other disordered materials having a more labile structure, permit changing of the position of the neighbor atoms already on the insignificant energetic influence by means of optical and X-ray radiation or electron beam.

Comparing the properties of crystals and of glasses, the enumeration of these peculiarities of the chalcogenide glasses may be continued, but probably, even those mentioned above are quite sufficient for stressing the originality of the properties of chalcogenide glasses, allowing us to propose the above-mentioned class of materials for wide application.

We will confine ourselves to presenting only a short information concerning the peculiarities of energetical spectrum and its contribution to the photoinduced phenomena. Some results of application of this group of materials in optoelectronics will be also presented.

2. Peculiarities of the distribution of localized electron states

Authors [1–7] formulated a few of models of the distribution of localized states in noncrystalline solids. The key point of these models is the quasicontinuous distribution of localized states in forbidden gap which arised due to structural disorder in noncrystalline solids,

So, according to Gubanov [2] the absence of the further order in the distribution of atoms leads to the blurring of permitted zones edges and to the appearance of fluctuation levels. Cohen, Frizsche and Ovshinsky [3] have proposed the model of tail density of electron states which are spreaded in the forbidden zone. In dependence of the degree of order of the semiconductor the tail density of states are distributed near the edges of permitted zones or are spread deeply in the forbidden zone up to their mutual overlap. In the models by Mott and Davis [1] besides tails of permitted zones near the middle of forbidden zone the existence of rather narrow zone (~ 0.1 eV) of localized state is supposed. According to author [4] in vitreous semiconductors on the phone of monotone levels distribution zones with heightened state density can be observed. Marshall and Owen [5] localize the zones with heightened density of localized state both in the upper and lower half of the forbidden zone. It is

demonstrated by Bonch-Bruevich [6] that in the forbidden zone of the unregulating semiconductor the peaks of density of localized states are possible, conditioned by the presence on impurities or other defects, which with some assumption can be named as discrete localized levels. The nature of localized states in vitreous semiconductors is still not enough studied. In some works it is connected with the presence of defects. The first work of this kind is the article by Street and Mott [7] where the localized states are analyzed, being provoked by broken bonds. These states depending on the level of engaged condition of electron bonds correspond to the neutral, positive or negative charged centers.

We have applied many experimental methods to obtain the adequate distribution of localized states in the gap: thermostimulated currents, thermostimulated electrical depolarization, spectral distribution and kinetics of photoconductivity, transport phenomena, photoinduced absorption etc. [8].

On this basis of these experiments we have not only confirmed the quasicontinuous distribution of localized states in the gap with some portions of states with greater density but even were able to calculate in some energetical range the precise parameters of the energetical distribution.

For example, the parameters of energetical distribution of localized states $N(E)$ in As_2S_3 and As_2Se_3 thin films were studied by the method of electrophotography spectroscopy of deep levels. For a long period of time there was a discrepancy between data of the energetical distribution of localized states obtained from different experiments. So the transit time method [9] and photoinduced absorption method [10] indicate the exponential type of distribution of localized states. The other methods such as temperature dependence of photocurrent [11], photoluminescence [12], thermostimulated depolarization [13] indicate the presence of the groups of relative discrete levels. The mentioned discrepancy can be avoided in the case of electrophotography spectroscopy deep levels proposed by Abkowitz [14]. This method allows to determine the concentration of deep filled traps and their energetical distribution. As it was found by authors [15] the energetical distribution of traps in As_2Se_3 and As_2S_3 has the region of discrete levels in the range of 0.55–0.6 eV for As_2Se_3 and 0.75–0.80 eV for As_2S_3 , that confirms the data obtained in paper [11,13]. The full concentration of traps was in the range $(1 \div 5) \cdot 10^{16} \text{ cm}^{-3} \cdot \text{eV}^{-1}$.

Using the charging and discharging characteristics of metal–ChG–semiconductor–dielectric–semiconductor structure Me– As_2S_3 (As_2Se_3)– SiO_2 –Si the authors [16] determined that the energy distribution of the filled traps is quasicontinuous with the asymmetrical maximum in the energy field of 0.70–0.90 eV for As_2Se_3 and 0.85–0.15 eV for As_2S_3 [Fig. 1].

Studying the change with time of the transient capacitance of the space charge region at a Schottky barrier due to thermal relaxation of localized centers preliminary filled by a pulse of zero bias the authors [17] determined the density-of-states distribution in the upper half of the gap of As_2Se_3 in the interval of 0.35 eV above the Fermi level.

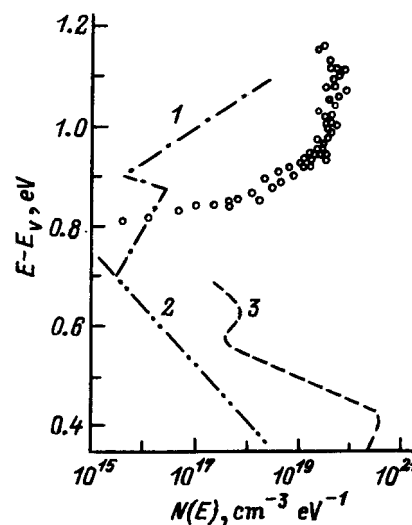


Figure 1. Sketch of the localized density-of-states distribution in the gap of $a\text{-As}_2\text{Se}_3$ according to the data of Ref. [9] (1), [D. Momroe, M.A. Kastner. Phys. Rev. B, **33**, 8881 (1986)] (2), [R.P. Barclay, J.M. Marshall, C. Main. J. Non-Cryst. Sol., **77 & 78**, 1269 (1985)] (3) and [10] (circles).

The data concerning the spectral distribution of localized states obtained by different authors are shown in Fig. 1. As it was shown the density-of-states has a broad maximum about $6 \cdot 10^{19} \text{ cm}^{-3} \cdot \text{eV}^{-1}$ at 1.15 eV, after which it sharply decays towards the middle of the gap to $10^{16} \text{ cm}^{-3} \cdot \text{eV}^{-1}$ [17]. The last mentioned concentration is confirmed by many previous papers.

3. Optical properties

3.1. Photoinduced absorption on the basis of electron processes

As it was mentioned above disorder in noncrystalline solids causes a quasicontinuous distribution of localized states in the forbidden gap. While the ChG samples are excited by the light with the energy of $h\nu > E_g$ nonequilibrium carriers appearing in the free bands are very quickly captured by the localized states and participate in the photoinduced absorption at the energies of $E < E_g$ (Fig. 2).

As it was approved by many experiments, the characteristic time of the photoinduced processes can be in a wide range of values from $\sim 10^{-12}$ to 10^3 s.

The longlived photoinduced processes are connected with the change of the physicochemical properties of the ChG and are termed in scientific literature as photostructural transformations. As a rule, the photostructural transformations are observed in this glass films and they are accompanied by a shift of the absorption edge to the lower energy, by the decrease of the steepness of the edge and by the change of the observed a dynamic reversible change of the optical parameters [8].

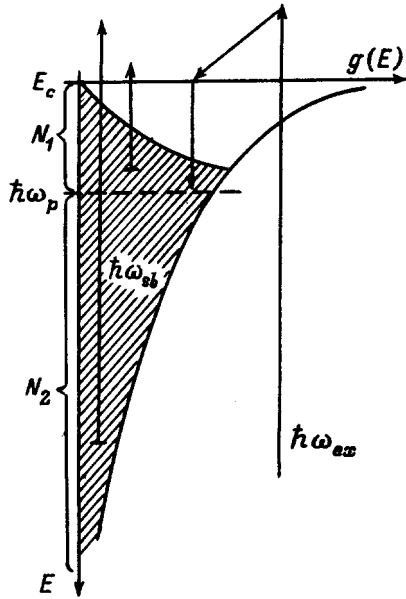


Figure 2. The steady-state excess carrier distribution in the exponential tail of localized states.

The use of fibre samples rather than thin film or bulk samples enabled us to observe better the small changes in midgap optical absorption at low intensity of exciting light because of the longer optical path of probing light in the fibre.

The probing light with photon energy $h\nu < E_g$ from the mid gap energy range was launched into the input face of the fibre. At the output of the fibre the intensity of probing light transmitted through the fibre was measured. When illuminating the fibre lateral surface with continuous bandgap light the intensity of probing light at the output of the fibre decreases from its initial value (in the dark) I_0 to a new one I . The photoinduced absorption coefficient $\Delta\alpha$ is determined as follows: $\Delta\alpha = L^{-1} \ln(I_0/I)$, where L is the length of the illuminated segment of the fibre. It should be noted that the intensity of the probing light in PA measurements was chosen to be so weak that it did not cause any significant change in the PA coefficient.

The main feature of the PA in our experiments is a full restoration of the minimal optical transmittance after secession of illumination. The restoration rate depends on the illumination conditions and the glass composition. The spectral distribution of the PA coefficient measured in the energy range of probing light 0.6–1.9 eV is presented in Fig. 3.

We note the exponential character of the $\Delta\alpha(h\nu)$ dependence for a rather large energy range. Illumination of the fibre at a lower temperature (77 K) leads to a significant increase of PA with respect to room temperature illumination [18].

The intensity dependence of the PA coefficient exhibits a power-law behaviour $\Delta\alpha \sim P_{\text{exc}}^n$ when the intensity of the exciting light (P_{exc}) is varied by about four orders

of magnitude ($10^{-6} - 10^{-2} \text{ W/cm}^2$) (Fig. 4). The value of n changes with probing light photon energy in the range 0.3–0.5.

Experimental results can be interpreted in terms of the model with carriers multiple trapping in localized states (Fig. 2), distributed continuously in the gap [18]. Illumination of the fibre with bandgap light leads to excitation of non-bonding electron states and injection of excess carriers into the conduction band. Shortly after excitation the electrons are captured by the tail states proportionally to their density, since the capture coefficient is supposed to be the same for different values of trap energy E . The appearance of excess carriers on the localized states in the gap leads to an additional absorption of probing light in a wide energy range $h\nu < E_g$.

The fact that the dependence of photoinduced absorption has a power law character following the square-root function confirms that carriers excited in the process of photoabsorption as well as carriers participating in photoconductivity recombine according to bimolecular mechanism. As it was shown in paper [19] this can be used for determining the magnitude of bimolecular coefficient from photoinduced absorption data and to calculate on this basis the magnitude of drift mobility. It is very important in the case of highly resistivity semiconductors as As_2S_3 and As_2Se_3 glasses.

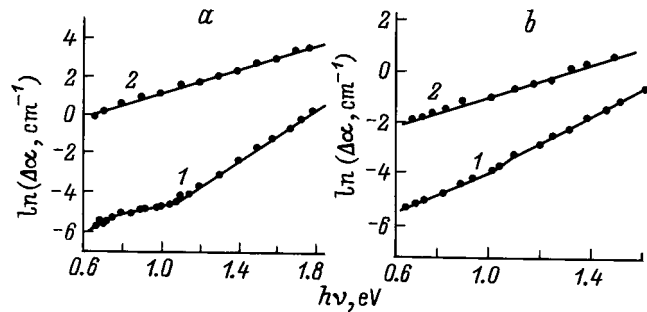


Figure 3. Spectral distribution of PA steady-state-coefficient $\Delta\alpha$ in As_2S_3 (a) and As-S-Se (b) fibres after irradiation with Ar-laser light ($\lambda_{\text{exc}} = 0.46 - 0.52 \mu\text{m}$). The intensity of exciting light $P_{\text{exc}} = 10 \text{ mW/cm}^2$, 1 — 300 K, 2 — 77 K.

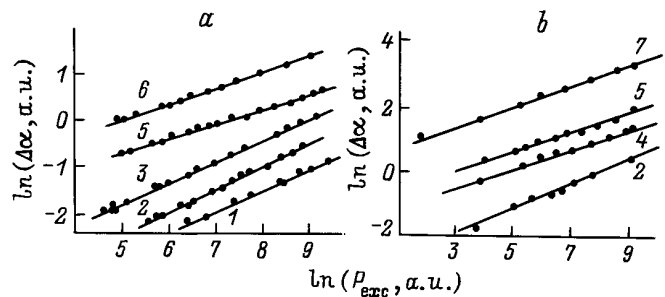


Figure 4. Intensity dependence of the PA steady-state-coefficient in As_2S_3 (a) and As-S-Se (b) fibres at room temperature for various probing light photon energies eV: 1 — 0.7, 2 — 0.8, 3 — 0.95, 4 — 0.98, 5 — 1.08, 6 — 1.2, 7 — 1.3. The wavelength of exciting light $\lambda_{\text{exc}} = 0.35 - 0.75 \mu\text{m}$.

3.2. Photoinduced absorption on the basis of phase change

There exist ChG which have two or more distinct atomic structural states characterized by different amounts of disorder [20]. In the opinion of authors [20] an energy barrier separates the structural states thereby providing the temporal stability required by a memory device. The change of atomic configuration can be realized by exposure to a laser beam, electron beam or electrical field. By the way, laser beam can be used not only for recording but also for erasing and rewriting processes each of these processes being going on at the different levels of intensity of the beam. Selecting the compositions of the ChG it is possible to produce transformation between amorphous and crystalline structural states. An example of such materials can be materials from the pseudobinary system GeTe and Sb_2Te_3 [20]. The phase change materials were successfully used for optical memory disks with 650 Mbyte capacity and the next product to be introduced will be 2.6 Gbyte DVD-RAM disk [20].

Studying the process of Ag-migration in Ag-As(Ge)-S(Se) glasses the author [21] proposed the mechanism of photo- and electron-induced chemical modifications. As it was shown light illumination and electron beams accelerated at low voltages can induce Ag-gathering effects. The mechanism is assumed to be caused by interval electric fields built up by photoexcited carriers and by electrons [22].

Studying the physico-mechanical and structural modifications induced by UV — light in $Ge_xAs_{40-x}S_{60}$ amorphous films the authors [23] observed that irradiation is accompanied with significant release of sulphur which leads to a giant film contraction.

3.3. Electric controlled photoinduced absorption

The change of the surface relief by means of mechanical residual deformations under the simultaneous action of the illumination and applied electric field was established by authors [24-26], using the thin film structure Me-ChG-Me. The nature of the electrostimulated and photoinduced surface microdeformations is explained by a sharp increase of the density of the photocurrent in the illuminated portions of the specimen and a strong heating of the ChG up to a T_g temperature. As a result, the viscous forces in the illuminated portions are relaxed under the actions of the electrostatic forces of the conductor the optical properties of the structure are changed. So, we obtain the effect of optical image recording which is manifested through changing of transmittance and reflectance. It is important to note that when an interference picture is projected on the surface of the sample the deformation grains lie strongly along the illuminated bands giving the possibility to record holographic information. When the illumination of the structure is more intense to develop the deformations, it is necessary to apply an electric field with less intensity. In this case, the value of the recording light intensity is

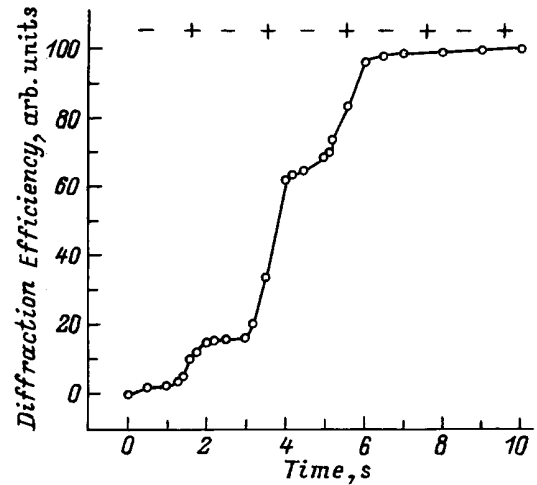


Figure 5. The kinetics of diffraction efficiency of the microholograms recorded in the Al-In₂S₃/As₂Se₃-Al heterostructure when a series of negative and positive ("—" and "+") voltage pulses is applied.

a photographic characteristic of the recording structure. It was shown that recording process strongly correlates with photoconductivity its kinetics, dependence of spectrum or light intensity. This allowed authors [26] to utilize heterostructures Me-In₂S₃(In₂Se₃)/As₂Se₃-Al as recording medium which had better photoconductivity parameters and consequently better photographic characteristics. On the basis of the mentioned phenomenon and heterostructures the new photographic process was proposed as well as new materials for its realization. The diffraction efficiency growth of the elementary holograms recorded on the Me-In₂S₃/As₂Se₃-Al when negative and positive voltage impulses are applied is shown in Fig. 5.

3.4. Optical hysteresis and nonlinear absorption laser pulses in ChG

The interest to the study of the nonlinear propagation peculiarities of the laser radiation in noncrystalline semiconductors is determined not only by the new fundamental physical mechanisms in these materials, which can appear in the strong fields of the laser pumping, but also by a wide spectrum of possible applications in the optoelectronic devices and photonic switching. The promising effects are the optical bistability and optical hysteresis, on the basis of which it is possible to make up fast-acting, all-optical switching and logical elements (see, for example [8] and the references given there).

Thin-film samples of chalcogenide glass semiconductors As-S, As-Se, Ge-Se, As-S-Ge and others (0.2–5.0 μm thickness) have been obtained by the vacuum thermal sputtering method. It was shown that when the input light pulse (with $h\nu \geq E_g$) intensity was relatively low the transmission of the thin ChG films decreased according to

the usual exponential law with the corresponding linear light absorption coefficient for the given wavelength. However, on increasing the incident light intensity over some threshold values (I_0) leads to a nonlinear character of the light transmission by the ChG films [11]. The characteristic value of the threshold light intensity depends on the ChG film composition, wavelength of excitation, temperature and the laser pulse duration.

As a result of the nonlinear light absorption a change of time profile of the laser pulses is observed which leads to a hysteresis-line dependence of the output light intensity of the corresponding value of the input intensity.

Nonlinear absorption in chalcogenide glasses was observed even in femtosecond range that is due to either intraband or interband transitions [27].

4. Devices based on ChG

On the basis of function of many devices lies ChG, which can change their electrophysical and optical parameters under applying of electrical field, exposition by light, electron beam, X-irradiation, etc. At the same they manifest resistance to nuclear radiation. Besides that, ChG could be obtained using very simple technologies and in many cases (but not in all cases) they do not need very high purity. It allows to produce industrially electrical switches, xerographic and thermoplastic media, photoresistant and holographic media, optical filters, optical fibers, optical sensors, thin films waveguides, nonlinear elements, etc.

In 60s a great attention was paid to threshold switching elements which were able under the pulse of voltage to pass from state with a very high resistivity in the state with low resistivity [20].

The industrial technology was put by R.S.Ovshinsky who named his optimized element as ovonic threshold switching [20].

The process of switching carries out in the very short time less than 10 nanoseconds.

A great success was the utilization of ChG thin films as target of vidicon image tube (for TV camera).

Another successful application has been the use of ChG thin films in photocopying electrophotography machines. Thin films of Se, As_2Se_3 and other materials store the charge distribution produced by the image projected onto it. The image presented by charge distribution is transferred to paper using electrostatic method [8].

Observed photoinduced phenomena in ChG allowed to apply these materials as recording media for registration of the optical information using ChG thin films heterostructures, photothermoplastic structures, thin waveguides and fibers.

The Me-Chalcogenide glassy semiconductor–dielectric–semiconductor ChDS (Me– As_2S_3 – SiO_2 –Si) structure allow the writing and readout processes of the optical images with high resolution [8]. The structure make the positive and negative images possible. The device works in regimes both

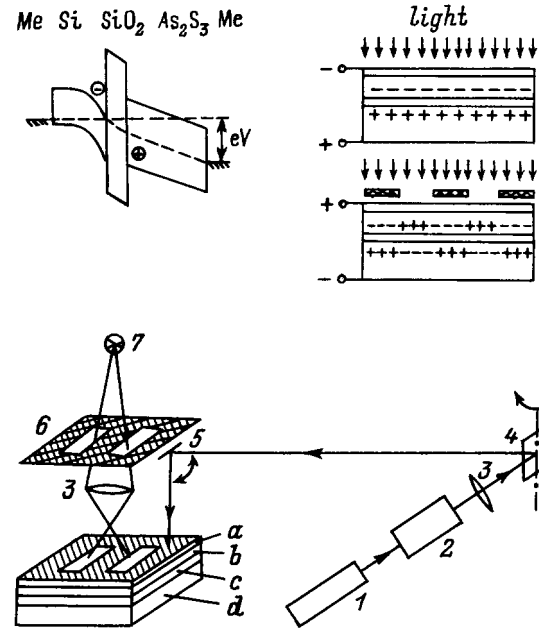


Figure 6. The schematic energy-band diagram of Me–ChDS structure during the positive charge writing process and the scheme of writing and readout of image. 1 — He–Ne-laser ($0.6328 \mu\text{m}$); 2 — modulator, 3 — condensers; 4, 5 — the galvanometer mirrors; 6 — the mask (object); 7 — source of illumination; 8 — Me–ChDS structure: a — semitransparent Al electrode, b — As_2S_3 layer, c — SiO_2 layer, d — Si.

accumulation of the small signal and real time. The space functional separation of the recording and readout allows to carry out undestroyed repetition readout of the image and other operations (Fig. 6).

Photoinduced phenomena in chalcogenide glass fibers were utilized in order to propose a novel type of variable fiber-optic attenuator [8]. It can be used in visible and near infrared range of spectrum for continuous change of light intensity in fiber optic circuits. If the lateral surface of chalcogenide glass fiber is illuminated by light with photoenergy near the glass bandgap a strong decrease of fiber-attenuating light at the output and of the fiber occurs changing the optical signal from its initial value I_0 (in the dark) to a new one:

$$I = I_0 \exp(\Delta\alpha L),$$

where L is the length of illuminated segment of the fiber and $\Delta\alpha$ is the photoabsorption coefficient. The proposed fiber-optic attenuator provides the attenuation in the range 0–20 dB in the 0.8 – $1.8 \mu\text{m}$ wavelength range.

Chalcogenide glasses thin films are promising materials for the integrated optic devices—such as lenses, gratings, optical filters, multiplexors and demultiplexors optical scanners and printer heads, multiple-output logical elements. etc. [8].

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