

# Stationary and transient photocurrents in some amorphous Ge-As-Se thin films

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The stationary and transient characteristics of photoconductivity in thermally deposited amorphous  $\text{Ge}_{0.07}\text{As}_{0.07}\text{Se}_{0.86}$  thin films, with the theoretically calculated mean coordination number  $Z=2.21$ , are reported. Introduction of the metallic elements (Sn and Ge) in selenide and sulphide ( $\text{As}_2\text{S}_3$ ,  $\text{As}_2\text{Se}_3$ , As-S-Se) glasses, lead to the appearance of the tetrahedral structural units in the base glasses, which change the mean coordination number  $Z$ . These changes lead to non-monotonous changes of the electrical, optical and photoelectrical characteristics, depending on the glass composition. It was found that the dependence of the photocurrent on light intensity has a power-law behavior  $I_{ph} \sim F^\beta$  ( $1.0 \leq \beta \leq 0.5$ ), which is characteristic for the amorphous semiconductors with the exponential distribution of the localized states in the band gap  $E_g$ .

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## 1. Introduction

The Ge-As-Se and As-S-Se ternary glass systems actually attract a big attention due to their applications in IR optics, non-linear optics, photonics, optoelectronics, and as registration media for holography and e-beam lithography [1-5]. The physical properties of covalently-bonded glasses are determined by the mean coordination number  $Z$  (average number of the covalent bonds per atom) [5]. It is well known that the functionality of many photonic and optoelectronic devices is based on the intrinsic photoelectric effect. From this point of view, investigations of the stationary and transient characteristics of photoconductivity of the ternary amorphous thin films represent special interest. For the chalcogenide glasses, whose structure exhibits a quite high level of disorders, the incorporation of the impurity atoms is more easily accessible, and in many cases the metal additives can become electrically active by gaining or losing electrons.

According to the structural study of the  $\text{As}_x\text{Ge}_x\text{Se}_{1-2x}$  glasses [6-8] by X-ray diffraction, this ternary glass system may contain structural units the trigonal  $\text{AsSe}_{3/2}$  and tetrahedral  $\text{Ge}(\text{Se}_{1/2})_4$  structural units, which influence the physical properties. Recently it was demonstrated investigations of some photoelectrical properties of  $\text{As}_x\text{Ge}_x\text{Se}_{1-2x}$  and  $(\text{As}_4\text{S}_3\text{Se}_3)_{1-x}\text{Sn}_x$  amorphous thin films [9, 10].

In the present paper the experimental results on steady-state and transient photoconductivity of the amorphous  $\text{Ge}_{0.07}\text{As}_{0.07}\text{Se}_{0.86}$  thin films are reported. It was observed that the stationary and non-stationary Lux-ampere characteristics are described by the expression  $I_{ph} \sim F^\beta$ , where  $\beta$  takes the values  $1.0 \leq \beta \leq 0.5$ . The photocurrent relaxation in amorphous  $\text{Ge}_{0.07}\text{As}_{0.07}\text{Se}_{0.86}$  thin films was found to be consistent with the model of trap-controlled capture, exponentially distributed in the band gap, and of

recombination of non-equilibrium carriers. [11-13].

## 2. Methodology

The bulk chalcogenide glasses  $\text{Ge}_{0.07}\text{As}_{0.07}\text{Se}_{0.86}$  were synthesized from the elements of 6N purity (As, Se, Ge) by conventional melt quenching method. Thin film samples of thicknesses  $L \approx 2 \mu\text{m}$  were prepared by thermal evaporation in vacuum ( $P=10^{-5}$  Torr) using flash method, onto glass substrates held at temperature  $T_{substr}=100^\circ\text{C}$ . These samples have a sandwich configuration with two Al-electrodes, one of whom (top electrode) is transparent for the incident light. The dark conductivity  $\sigma_d$ , Lux-Ampere characteristics  $I_{ph} = f(F)$  and the spectral distribution of the stationary photocurrent  $I_{ph} = f(\lambda)$  were measured in the constant current conditions ( $j=2.8 \cdot 10^{-8} \div 2.8 \cdot 10^{-6}$  A/cm<sup>2</sup>) using the spectrophotometer SPM-2 (the dispersive element is Si prism) and the electrometrical amplifier U1-7, with the error less than  $\pm 1.0\%$ . The Lux-Ampere characteristics were investigated at the wavelength of the sample maximum photosensitivity ( $F \sim 10^{16}$ /cm<sup>2</sup>s at  $\lambda_{max}=560\text{nm}$ ). The light intensity was varied by the calibrated neutral filters. All experiments were performed at room temperature ( $T \approx 20^\circ\text{C}$ ). The photoconductivity transient experiments were performed at different wavelengths and light intensities. A photo-shutter was used to switch the light on/off. The experimental data was acquired in the digital form.

## 3. Results and discussion

Fig. 1 represents the normalized spectral distribution of the steady-state photocurrent for the Al-

$\text{Ge}_{0.07}\text{As}_{0.07}\text{Se}_{0.86}$ -Al thin film structure at positive (1) and negative (2) polarity of the applied voltage to the top Al illuminated electrode. It was observed that at positive polarity on the illuminated electrode the photocurrent is higher, and after reaching its maximum value, remain constant, while at negative polarity after maximum value the photocurrent decrease [10]. At the positive polarity at the illuminated electrode, the position of the maximum of the photocurrent is shifted to higher photon energy region. This can be explained both on the basis of contact phenomena between the interface of the metallic electrode and the amorphous film, as well as by the surface recombination processes. The different shape of these curves is caused by the contact phenomena between the interface of metallic electrode and the amorphous material and, as well as by the drift of the non-equilibrium carrier through the sample in the conditions of its multiple trapping on the localized states in the band gap of the disordered material. It was demonstrated that on the interface of the metallic electrode and of chalcogenide amorphous film contact is formed a potential barrier, the height of which depends on the nature of the metal and the amorphous material [14].

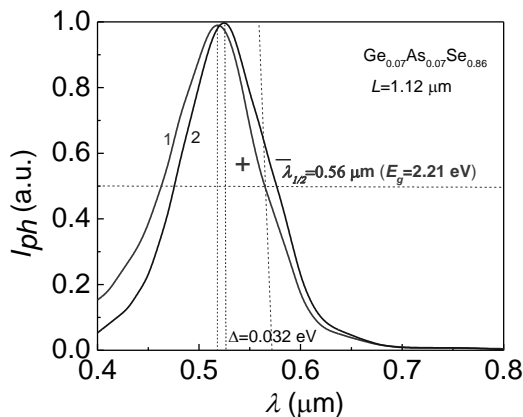


Fig. 1. Spectral distribution of the steady-state photocurrent for Al- $\text{Ge}_{0.07}\text{As}_{0.07}\text{Se}_{0.86}$ -Al thin film structure at positive (1) and negative (2) polarity of the applied voltage to the top Al illuminated electrode

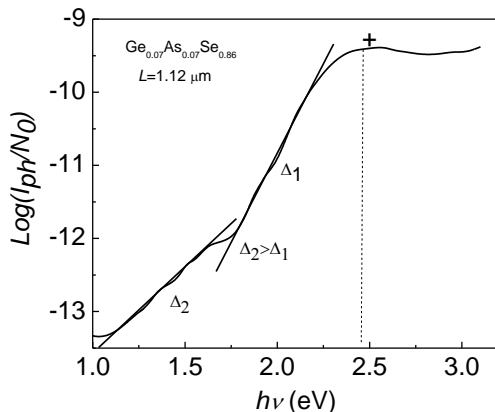


Fig. 2. Normalized spectrum of steady-state photocurrent for Al- $\text{Ge}_{0.07}\text{As}_{0.07}\text{Se}_{0.86}$ -Al thin film structure at positive polarity of the applied voltage to the top Al illuminated electrode

For estimation of the values of the band gap  $E_g$  both the spectra of the photocurrent and the Moss rule were used. According to this, the band gap corresponds to the value of the wavelength  $\lambda_{1/2} = \frac{1.24}{h\nu} = E_g^{ph}$  at which the photocurrent fall down to a half value from the maximum, as is shown in Fig. 1. The estimated value is  $E_g = 2.21$  eV.

The normalized spectra of steady-state photocurrent to the number of incident photons  $N_0$  ( $\text{Log}(I_{ph}/N_0)$ ) for the Al- $\text{Ge}_{0.07}\text{As}_{0.07}\text{Se}_{0.86}$ -Al thin film structure at positive polarity of the applied voltage to the top Al-illuminated electrode are represented in the Fig. 2. It is well known that in chalcogenide glasses the absorption edge is broader than in crystalline analogues. This is caused by a broad energy distribution of the electronic states in the band gap due to disorders and different kind of defects. The absorption edge in the high absorption region ( $\alpha > 10^4 \text{ cm}^{-1}$ ) is described by a quadratic function:

$$\alpha \propto \frac{1}{h\nu} (h\nu - E_g)^2, \quad (1)$$

And when it is plotted in the Tauc coordinates  $(\alpha h\nu)^{1/2}$  vs.  $(h\nu)$ , it gives the value of the optical band gap  $E_g$ , which is determined as the energy difference between the onsets of the exponential tails of the allowed energy bands [15]. The photocurrent spectrum represented in the Fig. 2 and describes the absorption coefficient of the respective amorphous films. In the Urbach edge region ( $\alpha \approx 1 \div 10^3 \text{ cm}^{-1}$ ) the absorption coefficient spectra depend exponentially on the photon energy:

$$\alpha \propto \exp\left(\frac{h\nu}{\Delta_1}\right), \quad (2)$$

where  $\Delta_1$  is the parameter, which characterizes the distribution of the localized states in the band gap. In addition, the  $\Delta_1$  value for amorphous  $\text{As}_2\text{S}_3$  found earlier is  $\Delta_1 = 0.056$  eV, whereas for  $\text{As}_2\text{S}_3$  doped with Dy and Sm  $\Delta_1$  is found to be somewhat higher [15]. In our case for the amorphous  $\text{Ge}_{0.07}\text{As}_{0.07}\text{Se}_{0.86}$  thin film, the value of  $\Delta_1$ , estimated from the spectra represented in Fig.2 is  $\Delta_1 = 0.083$  eV.

The absorption coefficient spectrum, in the region of weak absorption ( $\alpha < 1 \text{ cm}^{-1}$ ), depends strongly on the conditions of the sample preparation, composition and impurities, and is also described by an exponential dependence:

$$\alpha \propto \exp\left(\frac{h\nu}{\Delta_2}\right), \quad (3)$$

In this case we have such a relation  $\Delta_2 > \Delta_1$ . The value of  $\Delta_2$  for vitreous  $\text{As}_2\text{S}_3$  was found to be  $\Delta_2 \approx 0.31$  eV, and doping of vitreous  $\text{As}_2\text{S}_3$  with metal impurities affect drastically the parameter  $\Delta_2$ . In our case for the amorphous  $\text{Ge}_{0.07}\text{As}_{0.07}\text{Se}_{0.86}$  thin film, the value of  $\Delta_2$ , estimated from the spectra represented in Fig. 2, was found to be  $\Delta_2 = 0.196$  eV. The nature of the weak absorption tail in chalcogenide glasses spectra remains to be investigated. This weak absorption may be attributed to the additional

states created by defects and/or impurities, or to the increase of the average amplitude of the internal electric fields produced by the introduction of the additional charged centers.

It was demonstrated that all investigated amorphous  $\text{Ge}_x\text{As}_x\text{Se}_{1-2x}$  thin films have a light sensibility with the magnification of the photocurrent about  $k_{ph} \sim 100$ , and the dependence of optical parameters on the film composition is different for *floppy*, *intermediate* and *stressed-rigid* phases, determined from the experiments of the photocapacitance relaxation [16]. Experiments of high-resolution X-ray diffraction demonstrated that the topology of  $\text{Ge}_x\text{As}_x\text{Se}_{1-2x}$  glasses evolves with increase cation concentration ( $x$ ) in the network, consisting of the separate  $\text{GeSe}_{4/2}$  tetrahedra and  $\text{AsSe}_{3/2}$  pyramids interconnected via Se chains, towards the formation of the structural fragments based on Ge-As, As-As and Ge-Ge bonds [6].

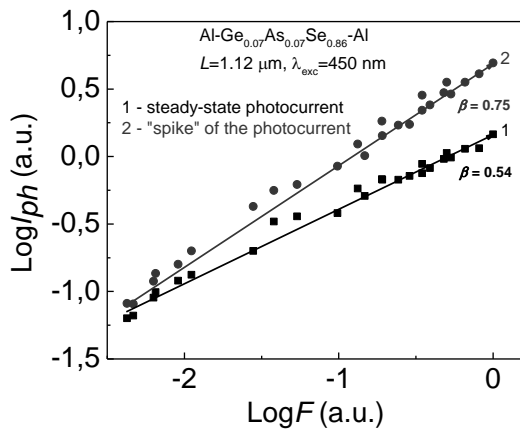


Fig. 3. Dependence of the photocurrent for amorphous  $\text{Ge}_{0.07}\text{As}_{0.07}\text{Se}_{0.86}$  thin films on the light intensity  $\text{Log}I_{ph}=\text{Log}F$

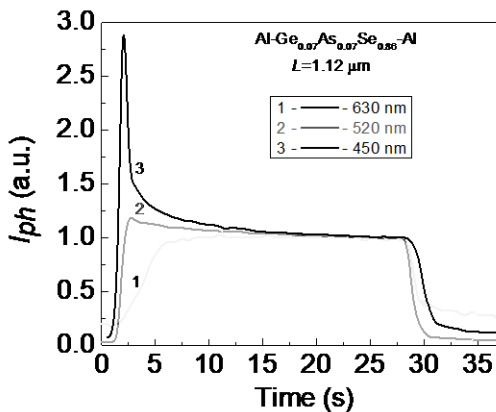


Fig. 4. Photocurrent relaxation curves for amorphous  $\text{Ge}_{0.07}\text{As}_{0.07}\text{Se}_{0.86}$  thin films at different wavelengths  $\lambda$  (nm): 1-630; 2-520; 3-450

Fig. 3 represents the dependence of the steady-state photocurrent (curve 1) and the maximum of the photocurrent, so-called "spike" (curve 2), on the light intensity  $I_{ph}=f(F)$  for the amorphous  $\text{Al-Ge}_{0.07}\text{As}_{0.07}\text{Se}_{0.86}$ -Al thin film. It was established that this dependency is

non-linear, and in the case of the exponential distribution of localized states in the band gap, is described by the expression  $I_{ph} \sim F^\beta$ , where  $\beta$  (power index) takes the values  $0.5 \leq \beta = \frac{T^*}{T+T^*} \leq 1.0$ , where  $T^*$  - is the parameter of the localized states distribution [18, 19]. In our case the calculated parameter  $T^*$  for the amorphous  $\text{Ge}_{0.07}\text{As}_{0.07}\text{Se}_{0.86}$  thin films is  $T^*=950$  K. This parameter is expressed through the parameter  $\Delta_I=kT^*$ , determined from the spectral distribution of the photocurrent (Fig. 2), gives the value  $\Delta_I=0.082$  eV, and is in a good agreement with that determined from the photocurrent spectra (Fig. 2).

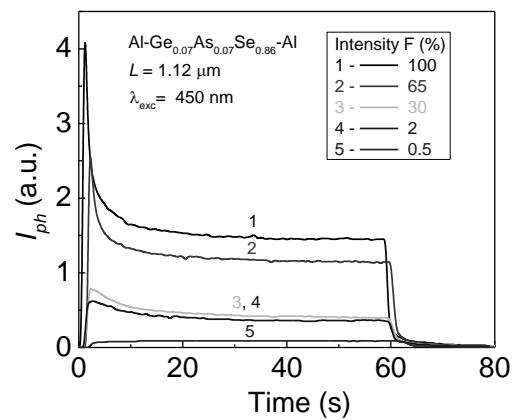


Fig. 5. Photocurrent relaxation curves for amorphous  $\text{Ge}_{0.07}\text{As}_{0.07}\text{Se}_{0.86}$  thin films at different light intensities  $F$  (%): 1-100; 2-65; 3-30; 4-2; 5-0.5

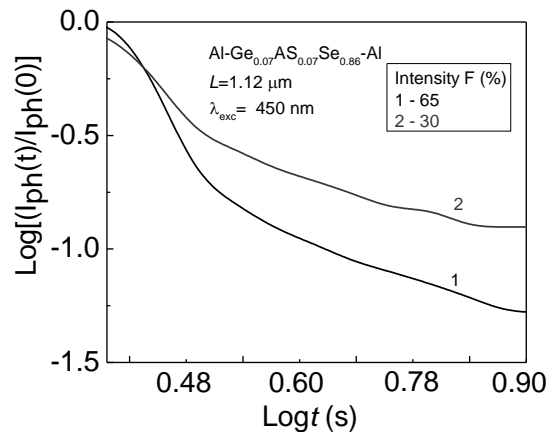


Fig. 6. Time dependence of the normalized photocurrent  $\text{Log}[I_{ph}(t)/I_{ph}(0)]$  vs  $\text{Log}t$  for amorphous  $\text{Ge}_{0.07}\text{As}_{0.07}\text{Se}_{0.86}$  thin films at two light intensities  $F$  (%): 1-65; 2-30

In the Fig. 4 the photocurrent relaxation curves for the amorphous  $\text{Ge}_{0.07}\text{As}_{0.07}\text{Se}_{0.86}$  thin films at different wavelengths  $\lambda$  are illustrated. With the increasing of the photon energy  $h\nu$  (decrease the wavelength  $\lambda$ ) the photocurrent reaches the stationary value passing through the maximum. Fig. 5 represents the photoconductivity

relaxation curves for amorphous  $\text{Ge}_{0.07}\text{As}_{0.07}\text{Se}_{0.86}$  thin films at different light intensities  $F$ . It was observed that at low light intensities the steady-state values of the photocurrent reach the stationary state without passing through the maximum (curve 5). At higher intensities of the relaxation curves we observe a “spike”, after that the photocurrent relaxes to its stationary values (curves 1-4). With an increase in the light intensity, the amplitude of the “spike” also increases.

Photoconductivity relaxation in amorphous chalcogenides is satisfactorily interpreted within the framework of the model of multiple trapping in the band gap states, quasi-continuously distributed in the mobility gap of the amorphous semiconductor [13, 19, 20]. Application of this model allows for better understanding of some other non-equilibrium processes specific only for the chalcogenide glassy semiconductors, such as dispersive transport and induced optical absorption, including the transients between steady states. The analysis of these processes leads to the conclusion about the exponential form of the energy distribution  $N(E)$  of the localized state density, in such form:

$$N(E) = (N_t/kT^*) \exp(-E/kT^*), \quad (4)$$

where  $N_t$  is the total gap-state density.

By using standard simplifying assumptions, the relation between the states density  $N(E)$  and absorption spectrum  $\alpha(h\nu)$ , the (4) takes the form:

$$N(E_c - h\nu) = M[d\alpha/d(h\nu)], \quad (5)$$

where  $M \approx 10^{17} \text{ cm}^{-2}$ .

The states density  $N$ , calculated from the differentiation of the  $\alpha(h\nu)$ , and represented in the photoconductivity spectra (Fig. 2), gives the value  $N \approx 5 \cdot 10^{17} \text{ cm}^{-3} \text{ eV}^{-1}$ , that it is in a good agreement with the obtained one for the vitreous  $\text{As}_2\text{S}_3$  [15]. The absorption coefficient  $\alpha(h\nu)$  is determined by the optical transitions from the filled localized states to the free states in the conduction band; the dipole matrix element of the transition does not depend on the excitation energy; the distribution of delocalized states is approximated by a step function.

The theoretical consideration of the photocurrent relaxation in the frame of the multiple trapping model with energy states, exponentially distributed in band gap, allows revealing several definite time domains in curves of transient photocurrent. Each of these domains corresponds to a power dependence of photocurrent upon time, and are determined by capture of free carriers in traps or by their recombination in monomolecular (MR) or bimolecular (BR) regimes.

The absence of a “spike” in the increasing sections of the photocurrent in amorphous  $\text{Ge}_{0.07}\text{As}_{0.07}\text{Se}_{0.86}$  thin films at low light intensities indicates, that capture of non-equilibrium carriers is intensified, since the generation of the photocurrent is balanced by capture and non recombination. Contrary, at higher light intensities the presence of “spike” in the rise portions of the photocurrent

indicates that the rate of bimolecular recombination (BR) process is higher than that the capture rate one.

In the Fig.6 is shown the time dependence of the decay portions of the normalized photocurrent  $I_{ph}(t)/I_{ph}(0)$  for amorphous  $\text{Ge}_{0.07}\text{As}_{0.07}\text{Se}_{0.86}$  thin films measured at two light intensities  $F$  (%): 1-65; 2-30. The photocurrent decay rate sharply increases with raise of the light intensity. The non-equilibrium relaxation of the photocurrent is typical for the majority of amorphous semiconductors, and is usually attributed to the wide spectrum of the localized states in a mobility gap [13, 20]. For the amorphous  $\text{As}_2\text{S}_3$  and  $\text{As}_2\text{S}_3:\text{Pr}$  films it was shown that after switching light off, the photocurrent decay occurs, initially due to the capture of non-equilibrium charge carriers by band tail of localized states, and later on, due to their recombination.

It was established that the experimental data can be approximated by stretched exponential function, which describes the multiple-trapping relaxation of the exponential distribution of the states with the temperature characteristic  $T^*$  larger, than the experimental temperature one. These suggestions are also valid in our case, for the amorphous  $\text{Ge}_{0.07}\text{As}_{0.07}\text{Se}_{0.86}$  thin films with the characteristic temperature  $T^* = 950 \text{ K}$ , obtained from the Lux-Ampere characteristics (Fig. 2).

#### 4. Summary

It was presented and discussed the experimental results on steady-state photoconductivity of the amorphous  $\text{Ge}_{0.07}\text{As}_{0.07}\text{Se}_{0.86}$  thin films. It was shown that the spectral distribution of the stationary photoconductivity depends on polarity of the applied voltage to the illuminated electrode. The experimental results are interpreted taking into account the contact phenomena between metal and amorphous semiconductor and the drift of non-equilibrium carriers through the sample. It was found that the dependence of the photocurrent on light intensity has a power-law behavior  $I_{ph} \sim F^\beta$  ( $1.0 \leq \beta \leq 0.5$ ), which is characteristic for the amorphous semiconductors with the exponential distribution of the localized states in the band gap  $E_g$ . At the photon energies  $h\nu \geq E_g$  and high light intensities, the rise portion of the relaxation curves of the photocurrent has a “spike”, which is quenched at higher wavelengths and low light intensities. The photocurrent relaxation in the amorphous  $\text{Ge}_{0.07}\text{As}_{0.07}\text{Se}_{0.86}$  thin films was found to be consistent with the model of trap-controlled capture, exponentially distributed traps in the band gap, and of recombination of the non-equilibrium carriers.

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## References

- [1] Z. Tang, V. S. Shiryaev, D. Furniss, L. Sojka, S. Sujecki, T. M. Benson, A. B. Seddon, M. F. Churbanov, *Optical Materials Express* **5**(8), 1722 (2015).
- [2] I. Blonskyi, V. Kadan, O. Shpotyuk, M. Iovu, P. Korenyuk, I. Dmitruk, *Applied Physics B***104**, 951 (2011).
- [3] A. V. Stronski, M. Vlcek, S. A. Kostyukevych, V. M. Tomchuk, E. V. Kostyukevych, S. V. Svechnikov, A. A. Kudreavtsev, N. L. Moskalenko, A. A. Koptuykh, *Semiconductor Physics, Quantum Electronics & Optoelectronics* **5**(3), 284 (2002).
- [4] M. Reinfelde, J. Teteris, *J. Optoelectron. Adv. M.* **13**(11-12), 1531 (2011).
- [5] M. S. Iovu, S. A. Sergheev, O. V. Iaseniuc, *Optoelectron. Adv. Mat.* **12**(7-8), 377 (2018).
- [6] R. Golovchak, O. Shpotyuk, M. Iovu, A. Kovalskiy, H. Jain, *J. of Non-Crystalline Solids* **357**(19-20), 3454 (2011).
- [7] M. S. Iovu, O. V. Iaseniuc, D. Dinescu, M. Enachescu, *Proc. SPIE 10010, Advanced Topics in Optoelectronics, Microelectronics, and Nanotechnologies VIII*. M. Vladescu, R. Tamas, I. Cristea (Eds.), December 14, 2016. Conference "Advanced Topics in Optoelectronics, Microelectronics, and Nanotechnologies VIII", Constanta, Romania, August 25, 1001000 (2016).
- [8] O. V. Iaseniuc, M. Enachescu, D. Dinescu, M. S. Iovu, S. A. Sergheev, *J. Optoelectron. Adv. M.* **18**(1-2), 34 (2016).
- [9] O. Iaseniuc, M. Iovu, *Rom. J. Phys.* **62**(9-10), 609 (2017).
- [10] O. Iaseniuc, M. Iovu, *Rom. Rep. Phys.* **69**(3), 505-1-505-11 (2017).
- [11] M. S. Iovu, S. D. Shutov, V. I. Arkhipov, G. J. Adriaenssens, *Rom. Rep. Phys.* **51**(3-4), 297 (1999).
- [12] M. S. Iovu, S. D. Shutov, V. I. Arkhipov, G. J. Adriaenssens, *J. of Non-Crystalline Solids* **299-302**, Part 2, 1008 (2002).
- [13] V. I. Arkhipov, M. S. Iovu, A. I. Rudenko, S. D. Shutov, *Solid State Commun.* **62**(5), 339 (1987).
- [14] M. A. Iovu, M. S. Iovu, S. D. Shutov, *JTF Letters* **4**, 1246 (1978).
- [15] M. S. Iovu, S. D. Shutov, A. M. Andriesh, E. I. Kamitsos, C. P. E. Varsamis, D. Furniss, A. B. Seddon, M. Popescu, *J. Optoelectron. Adv. M.* **3**(2), 443 (2001).
- [16] I. A. Vasiliev, M. S. Iovu, E. P. Colomeico, *Moldavian Journal of the Physical Sciences* **10**(2), 5 (2011).
- [17] A. Rose, „Concepts in photoconductivity and allied problems”, Interscience Publishers, New York-London, 168 (1963).
- [18] M. Popescu, A. Andriesh, V. Ciumas, M. Iovu, S. Sutov, D. Tiuleanu, „Physics of chalcogenide glasses”, Ed. Bucharest – I.E.P. Stiinta, Chisinau, 486 (1996).
- [19] V. I. Arkhipov, M. S. Iovu, A. I. Rudenko, S. D. Shutov, *Sov. Phys. Semicond.* **19**(1), 101 (1985).
- [20] M. S. Iovu, I. A. Vasiliev, E. P. Colomeico, E. V. Emelianovna, V. I. Arkhipov, G. J. Adriaenssens, *J. Phys: Condens. Matter.* **16**(17), 2949 (2004).

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