

Photocapacitance relaxation and rigidity transition in $\text{Ge}_x\text{As}_x\text{Se}_{1-2x}$ amorphous films

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The photo-capacitance relaxation of amorphous $\text{Ge}_x\text{As}_x\text{Se}_{1-2x}$ thin films is investigated for $x=0.05, 0.07, 0.09, 0.14, 0.16, 0.18, 0.20, 0.25$ and 0.30 . Compositional dependencies of the low-frequency dielectric permeability, decay time constant and the Kohlrausch parameter of non-exponentially function are deduced from the experimental data. All parameters show two compositional thresholds, one situated near the $x_c(1)=0.09$, and another - near the $x_c(2)=0.16-0.18$. These phase transitions have been identified in the bulk samples by means of a differential-scanning calorimetric method [1].

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1. Introduction

Chalcogenide vitreous semiconductors (ChVS), which were discovered in the beginning of 60th in the last century by B.T. Kolomiets and N.A. Goryunova, up to the present, continue to draw attention due to the unique optical, photoelectrical, structural properties, new physical phenomena, and its potential applications in the modern photonics and optoelectronics [2-5].

Chalcogenide glasses based on the chalcogen elements S, Se and Te are attractive and widely investigated materials as they possess high optical transparency in the IR region. They have low phonon energy, high photosensitivity, easy fabrication and processing, and good chemical durability. The Ge-As-Se system has been extensively studied because of the fact that Ge, As and Se are the elements of the groups IV-VI, and it brings about the covalent character of the interaction between their atoms. This results in a broad glass formation region in Ge-As-Se system among other investigated three-component glassy systems. Chalcogenide glasses of Ge-As-Se system are characterized by high glass transition temperatures T_g , thermal stability, and high refractive index and transparency in the IR region [6-9].

Glasses of $\text{Ge}_x\text{As}_x\text{Se}_{1-2x}$ system were investigated during last ten years by the means of T-modulated differential-scanning calorimetric technique [1,6,7], by the Raman and neutron scattering methods [10,11], x-ray photoelectron spectroscopy [12], and by the Mössbauer spectroscopy and the nuclear magnetic resonance [13]. This has allowed to determine the flexible (free from mechanical stress) at $x < x_c(1)=0.09$, the intermediate - at $x_c(1) < x < x_c(2)=0.16$, and the stressed-rigid - at $x > x_c(2)$ phases. The synthesized $\text{Ge}_x\text{As}_x\text{Se}_{1-2x}$ glasses ($x=0.05 \div 0.30$) are from different above-mentioned phases,

and then we expect de dependence of the physical properties on glass composition.

Despite of accumulated results, some questions remain opened. First, the definition of an intermediate phase and a threshold of rigidity in thin films are not present clearly as the majority of the listed above methods cannot be applied in this case. Second, the effects of the examined phase transitions onto optical, photo-electric and transport properties of a material are poorly studied, however they are source of additional information about the film structure near these transitions. In the present paper we have focused our attention on these problems, and the amorphous films of $\text{Ge}_x\text{As}_x\text{Se}_{1-2x}$ were investigated in a wide range of compositions x (ranging from $x=0.05$ up to $x=0.30$) by a photocapacitance relaxation technique.

2. Samples preparation and experimental technique

The glassy samples of the $\text{Ge}_x\text{As}_x\text{Se}_{1-2x}$ glasses ($0.05 \leq x \leq 0.30$) were prepared by conventional melt quenching method. Elemental Arsenic (99.999 % purity), elemental Germanium (99.999 % purity), and elemental Selenium (99.999 % purity) were used as the starting materials. The mixture of high-purity precursors was melted in sealed evacuated quartz ampoules ($p=5 \cdot 10^{-6}$ Torr) placed in a rocking furnace. The total weight of the synthesized sample was 35 grams. The temperature of the quartz ampoule was slowly increased to 550 °C at the rate of 50 °C/hour and kept at this temperature during 24 hours for homogenization. Than the temperature was increased up to 980 °C at the rate 50 °C/hour and homogenized at this temperature during 72 hours, and then quenched in the regime of the disconnected furnace. Thin film samples of thickness $L=0.5 \div 4 \mu\text{m}$ were prepared by flash thermal

evaporation in vacuum of the synthesized initial $\text{Ge}_x\text{As}_x\text{Se}_{1-2x}$ chalcogenide glasses onto glass substrates held at $T_{\text{subs}}=100$ °C. Table 1 reflects the synthesized compositions of chalcogenide glasses $\text{Ge}_x\text{As}_x\text{Se}_{1-2x}$, the mean coordination number $\langle r \rangle$, and the thickness L of amorphous deposited films. The samples had a configuration of type "sandwich", with evaporated top (transparent), and bottom (between a chalcogenide film and a substrate) aluminum electrodes (the effective area of electrode $S \sim 0.65$ cm²). The capacitance current (or otherwise, a displacement current) was measured as the response to a triangular voltage pulses, which was applied to the sample: $I_{\text{dis.c.}} = kC(t)$, $k = dV(t)/dt$ (frequency $\nu = 2 \times 10^2$ Hz, amplitude $U \sim 0.2$ V).

Table 1. The synthesized chalcogenide glasses $\text{Ge}_x\text{As}_x\text{Se}_{1-2x}$, the mean coordination number $\langle r \rangle$, and the thickness L of amorphous deposited films.

No.	Composition, $\text{Ge}_x\text{As}_x\text{Se}_{1-2x}$	$\langle r \rangle$	L (μm)
1	$\text{Ge}_{0.05}\text{As}_{0.05}\text{Se}_{0.90}$	2.15	0.511
2	$\text{Ge}_{0.07}\text{As}_{0.07}\text{Se}_{0.86}$	2.21	1.160
3	$\text{Ge}_{0.09}\text{As}_{0.09}\text{Se}_{0.82}$	2.27	2.550
4	$\text{Ge}_{0.11}\text{As}_{0.11}\text{Se}_{0.78}$	2.33	1.290
5	$\text{Ge}_{0.14}\text{As}_{0.14}\text{Se}_{0.72}$	2.42	1.150
7	$\text{Ge}_{0.18}\text{As}_{0.18}\text{Se}_{0.64}$	2.54	1.940
8	$\text{Ge}_{0.20}\text{As}_{0.20}\text{Se}_{0.60}$	2.60	1.980
9	$\text{Ge}_{0.25}\text{As}_{0.25}\text{Se}_{0.50}$	2.75	4.010
10	$\text{Ge}_{0.30}\text{As}_{0.30}\text{Se}_{0.40}$	2.90	0.910

3. Experimental results

Fig. 1 shows relaxation curves of the normalized capacitance obtained for all investigated compositions, at room temperature, in the conditions of continuous illumination by the "band-to-band" light. Energy of incident photon corresponded to a maximum of a photocurrent (or to a maximum of optical absorption) for each sample that provided equal conditions of measurement. Curves were normalized on value of a current in a point $t=T/2$, (T - period of the voltage pulses) corresponding to the beginning of capacitance decay, which in the further was accepted as zero.

It was established that the rate and the form of the capacitance decay non-monotonously depend on composition. So if for $x=0.07$ and $x=0.14$ (curves 1, 5) change of the capacitance current eventually occurs close to exponential law, for three last compositions (curves 8, 9 and 10) this change is nearer to linear dependence. This can indicate both on the greater value of the decay time constant, and the essential manifestation of the non-exponential character of relaxation. The obtained curves were processed by the equation:

$$C(t) - C_{\text{dark}} = C(0) \exp[-(t/\tau)^\beta] \quad (1)$$

It expresses the known Kohlrausch-Williams-Watt (KWW) empirical law for a dielectric relaxation. Here

C_{dark} term corresponds to the capacitance, measured in the darkness; the factor $C(0)$ is proportional to the maximal concentration of electric dipoles, induced by the light; τ - is a decay time constant and β - is Kohlrausch parameter of nonexponentiality, $0 < \beta < 1$. Parameters $C(0)$, β and τ (which were deduced from adjustment of Eq. (1) to experimental data) are presented on a Fig. 2, 3 and 4, in dependence on composition.

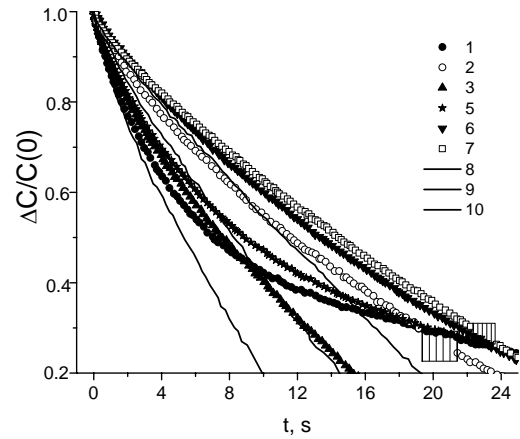


Fig. 1. Relaxation curves of the normalized photocapacitance for amorphous $\text{Ge}_x\text{As}_x\text{Se}_{1-2x}$ films at room temperature: $x=0.05-1$, $0.07-2$, $0.09-3$, $0.014-5$, $0.016-6$, $0.018-7$, $0.020-8$, $0.025-9$, $0.030-10$.

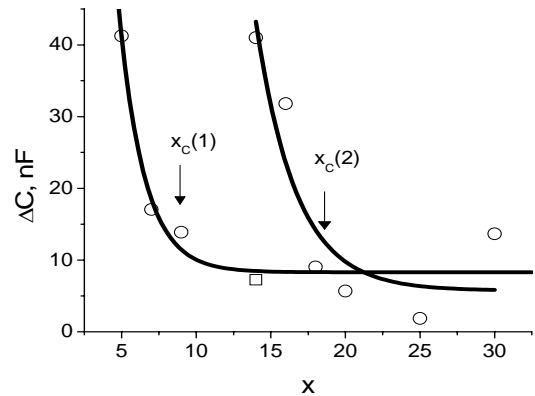


Fig. 2. Compositional dependence of photocapacitance $\Delta C = C(0) - C_{\text{dark}}$ for amorphous $\text{Ge}_x\text{As}_x\text{Se}_{1-2x}$ films. Continuous lines are guide on eye.

Fig. 2 shows the compositional dependence of photocapacitance $\Delta C = C(0) - C_{\text{dark}}$ which is related to the dielectric strength $\Delta\epsilon$ ($C = \epsilon_0 \Delta\epsilon S/L$) induced by illumination. It is seen that in the region of floppy mode and inside the region of an intermediate phase the value of photocapacitance decrease with increasing x near the threshold $x_c(1)=0.09$ for the first region, and $x_c(2)=0.18$ for the second one. In the region of $x > 0.18$ the value of photocapacitance is less than capacitance C_{dark} , measured in darkness.

We suggest that such behavior of the photocapacitance in the region of floppy mode and in the

region of an intermediate phase is caused by dipoles of different nature as the value of the photocalpacitance in the second region exceeds the change of the photocalpacitance extrapolated to this region from the first one. Is worthy the fact that the value of the photocalpacitance near to both thresholds is small and is of the same order as the capacitance C_{dark} . It evidences both the increase of rigidity and reduction of concentration of the non-equilibrium defects near the both thresholds. Clearly that the both tendencies are interdependent because the increase in average coordination number in the region of floppy mode and an intermediate phase *by definition* reflects reduction of concentration of the coordination defects participating in formation of a dipole.

4. Model of the dielectric relaxation

In the defect diffusion model [14,15] it is suppose that the electric field is applied to the medium containing polar molecules (or their groups) for some time, and that the direction of their dipole moments remain "frozen" after cessation of the field. Moreover, it is suppose that the medium contains mobile defects, which achieve the site with the frozen dipole and cause a relaxation of medium up to such degree, that the dipole can be reoriented by any way. If diffusion of defects towards a dipole is made as the random walk continuous in time, then function of a relaxation has the exponential form:

$$\varphi(t) = \exp[-cS(t)] \tag{2}$$

where c is a relative concentration of mobile defects; $S(t)$ - is a number of the individual sites, which the defect visits in time t .

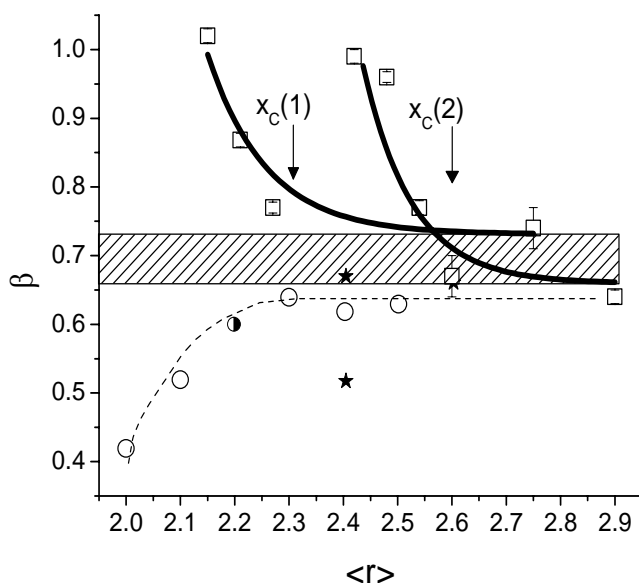


Fig. 3. Kohlrausch parameter β vs. average coordination number $\langle r \rangle$ of $Ge_xAs_xSe_{1-2x}$ glassy system. The various segments of behavior are shown by continuous lines. Experimental data from [16] (circles) are also presented.

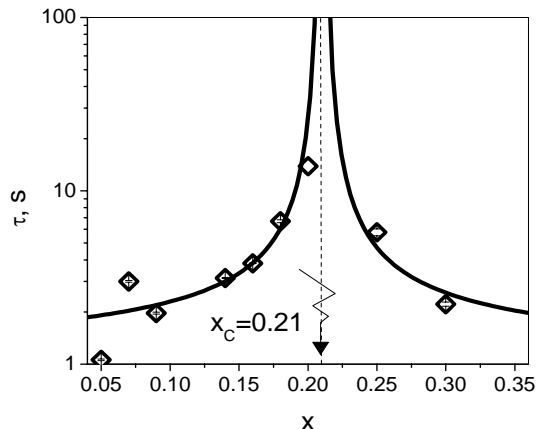


Fig. 4. Dependence of the decay time τ vs. composition x for amorphous $Ge_xAs_xSe_{1-2x}$ films (points), and the model curve (solid line), which was obtained by adjustment of the modified equation (5) to experimental data.

For homogeneous distribution of traps $S(t) \sim t^{1/2}$ when $d=1$ or $S(t) \sim t$ when $d=3$, d - is dimensionality [14]. Thus, function of a relaxation has the fractional-exponential form in one-dimensionality ($\beta=1/2$) and it is pure exponential in three-dimensionality ($\beta=1$). In essence, the problem of searching the function of relaxation $\varphi(t)$ was reduced to the well-known problem of traps [17]. In this problem the particle (defect) performs a random walk on a lattice and instantly dies after collisions with a trap (dipole); then probability of survival $\varphi(t)$ is the aim of searching.

The examined model supposes some important generalizations. *First*, it is clearly that in case of non-uniform distribution of the traps, the traveling particle (walker) can not possess collision with traps the long period of time, if will get in essential *greater* region, which is free from them. These regions are rare, but just they restrict the relaxation on long times. Calculations presented in work [17] shows, that in this case $\varphi(t) \sim \exp(-const \times t^\beta)$, were

$$\beta = \frac{d}{d+2} \tag{3}$$

We observe that at $d=3$, $\beta=3/5$ and $\varphi(t)$ is the fractional-exponential function of time. Thus the transform of the Debye (pure exponential) relaxation to the fractional-exponential can be explained as the increasing of heterogeneity of medium near the rigidity transition. Obtained values of $\beta \sim 0.65$ in the region of the stressed-rigid phase within the limits of an experimental error coincide with the value of $\beta=3/5$ ($d=3$). For molecular glasses, which are mainly organized by the covalent bonds between atoms [18], this directly corresponds to Eq. (3).

For comparison we have presented on Fig. 3 the relaxation data for the elastic stress, which were obtained in [16] for glasses of $Ge_xAs_ySe_{1-x-y}$ system also. It is noteworthy, that these values of β well coincide with our data for the range of coordination number $\langle r \rangle = 2.2 \div 2.6$.

The second generalization of the defect diffusion model has been made in [15] and touches the mechanism of diffusion. It is known, that the jumps of defects interlink with overcoming of the activation barriers. Then the smooth distribution of the activation barriers can generate wide dispersion of relaxation times, with infinite average value. In the case of $d=3$ this directly leads to the function:

$$S(t) \sim \begin{cases} t, & \text{for } \langle t \rangle \text{ limited,} \\ t^\beta, & 0 < \beta < 1, \text{ for } \langle t \rangle \rightarrow \infty, \end{cases} \quad (4)$$

and the KWW law of relaxation.

In this generalization of the model, transform from the exponential relaxation to the fractional-exponential one can be explained by changes in character of the relaxation times distribution. For exponential distribution of activation energies E : $g(E) \sim \exp(-E/k_B T_0)$, T_0 - is parameter, k_B - is the Boltzmann constant, $\beta = T/T_0 < 1$. Therefore, its variations with the transition to the intermediate and stressed-rigid phases (Fig. 3) can be explained by a more wide distribution of $g(E)$ in these regions (by great values of T_0).

The following third generalization is basic for understanding the compositional dependence of a relaxation time. In the original formulation of model [15] it has been assumed that the aggregation of defects and their correlation in the range of temperatures $T > T_C$ (T_C is a critical temperature at which concentration of mobile defects falls to zero) can be described through the theory of critical fluctuations. This theory leads to the generalized Vogel-Fulcher-Tammann law of a kind

$$\tau = \tau_1 \exp \left[\frac{B_1}{(T - T_C)^s} \right] \quad (5)$$

Here τ_1 is pre-exponential factor, which depends on defect concentration, $B_1 = B T_C^s$, $B = -Q^3 \ln(1-c) / \beta d_0^3$, Q is parameter of defect correlation length: $\xi(T) = Q [T_C / (T - T_C)]^s$, d_0 - is lattice spacing, $s = d\gamma/2$ and γ is equal to unit in a limit of an average field. From formal reasons clear, that the rigidity transition at $x = x_C(2)$ should be described by the similar equation, if to make substitution: $x \rightarrow T$, $x_C(2) \rightarrow T_C$. Fig. 4 shows the compositional dependence of the relaxation time τ . It follows the curve traced according to the modified equation (5). The following set of parameters was obtained: $\tau_1 \sim 2.2 \pm 0.015$ s; $B = 0.07 \pm 0.001$; $x_C = 0.21 \pm 0.0002$. It seems that the reasonable value of ratio $Q/d_0 \sim 3$ can be obtained already at concentration of defects $c \sim 0.0015$.

Fig. 5 represents the distribution of the investigated compositions in the three distinguished phases: mechanically floppy (free from mechanical stress at $x < x_C(1) = 0.09$), intermediate - at $x_C(1) < x < x_C(2) = 0.16$, and stressed-rigid - at $x > x_C(2) > 0.18$ phases.

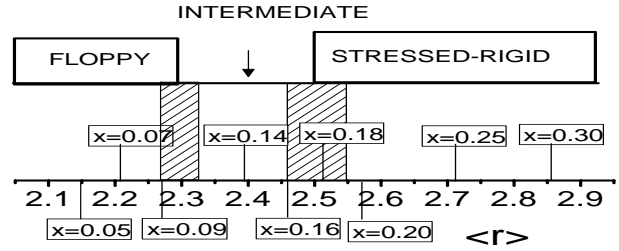


Fig. 5. The diagram of the investigated compositions (x) on an axis of average coordination number $\langle r \rangle$ in glasses $\text{Ge}_x\text{As}_x\text{Se}_{1-2x}$.

The arrow shows Phillips-Thorpe threshold. The thresholds $x_C(1)$ and $x_C(2)$, which were reported by some authors [1,6,10] are shown by dashed regions.

5. Conclusions

The central result of our studies is detection of three various segments in behavior of a dielectric relaxation of $\text{Ge}_x\text{As}_x\text{Se}_{1-2x}$ amorphous films, which coincide with known elastic phases of this ternary: the flexible phase at $x < x_C(1) = 0.09$, stressed-rigid phase at $x > x_C(2) = 0.18$, and intermediate phase at $x_C(1) < x < x_C(2)$. The result appears from the analysis of compositional dependence of photocapacitance ΔC , of Kohlrausch parameter β , of decay time τ (Fig. 2, 3 and 4). Both threshold $x_C(1)$ and $x_C(2)$, are in a good agreement with the reported results [1,10].

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