Ageing phenomena in thin amorphous As_xSe_{100-x} films

M. S. IOVU[*], I. A. VASILIEV, O. I. SHPOTYUK[a], E. P.COLOMEICO

Institute of Applied Physics, Academy of Sciences of Moldova, Str. Academiei 5, MD-2028 Chisinau, Republic of Moldova
[a]Scientific Research Company "Carat", 202 Stryjska str.202, 79031 Lviv, Ukraine

The quasi-static capacitance of amorphous $As_{10}Se_{90}$ thin films was studied in cycles of heating and cooling near the glass transition temperature T_g=343 K. Features in the capacitance behavior such as: non-exponential relaxation, non-Arrhenius character of time relaxations, hysteresis of temperature dependence, physical ageing - are revealed near this temperature. It was accepted, that the capacitance measurements allow finding the glass transition temperature T_g in amorphous $As_{10}Se_{90}$ thin films which is accompanied by freezing of some electric dipoles; these dipoles are forming from neighboring pairs of charged defects such as D^+ and D^-.

1. Introduction

Chalcogenide layers of $As_{10}Se_{90}$ represent an interesting alternative to $As_{40}Se_{60}$ layers with stoichiometric composition due to softness of amorphous network in Philips-Thorpe sense [1,2]. Such layers can be integrated with flexible substrate, which is important for their application in low-cost infrared cameras, in the optical fibers, solar cells, etc.

At the same time the physical ageing of chalcogenide layer associated with a slow structural relaxation toward the thermodynamic equilibrium limit these applications. Near the glass transition temperature T_g the ageing process emerges from bulk samples in Differential Scanning Calorimetric (DSC) studies well [3], but meets serious difficulties when thin layers are under investigations. For example, estimation of T_g in DSC mode depends on experimental conditions and has difference in dependence on layer thickness up to ten degrees of temperature [4].

Recently the method of dielectric spectroscopy has been successfully applied for detection of glass transition temperature T_g and studying of physical ageing in thin layers of polydimethyloxane and polycarbonate [4,5]. Earlier this method was applied to detection of phase transitions in glass-forming ferro-electrical SbSI [6] and even in liquid membranes [7,8]. The phenomenon of dielectric polarization is in a base of "dielectric" method for detection the glass transition temperature T_g: on low frequencies of applied electrical field it is determined by movement of weakly constrained polar molecular groups and dipoles. If, for example, the glass transition temperature T_g is reached by way of cooling the sample from above, polarization of dipoles will occur more and more slowly (because of growing viscosity of a material) until will take place their full freezing. Thus the value of permittivity on low frequency sharply decreases up to the values determined by electronic polarization [9].

In this article we shall give the detailed description of features of dielectric relaxation behavior in amorphous layers $As_{10}Se_{90}$ near the glass transition temperature T_g and we shall discuss distinctions which are observable in cycles of heating and cooling. Afterward we shall show result of definition T_g in layer As_2Se_{98} for comparison. In the end, - the effects of ageing and annealing of $As_{10}Se_{90}$ layer shall be presented.

2. Experimental

All experiments were carried out on the thin-film samples obtained by thermal evaporation in vacuum of an initial material of vitreous semiconductor onto the glass substrate. The samples had the sprayed upper and bottom (last between layer and substrate) aluminum contacts. The upper contact had 0.65 cm^2. The layer thickness of about 1 micron has been measured in the interference microscope. To make experiment at given temperature the sample was placed onto the copper plate, which could be warmed by the small electric furnace.

The temperature has been measured by the copper-constantan thermocouple and maintained within 0,05 degrees of temperature with the help of specially constructed auto-adjustment device. The quasi-static capacitance was measured on infra-low frequency ($f=2x10^{-2}$ Hz) by the application to the sample of the triangular voltage pulses. The amplitude of pulses did not exceed ~0,2 V. The electric current, which was received in such way, was amplified by the high-sensitive electrometric device and then was written down on X-Y recorder.

On the forward (or back) front of a pulse of a triangular voltage V(t), $0<t<T/2$, T=1/f this current comprises three components. The first or main component is the low-frequency capacitance current $\beta C_{LF}(t)$ (β=dV/dt), which changes when time is in progress; the

slow processes of molecular polarization determine it. The second component of a high-frequency capacitance current βC_{HF} is usually identified with geometrical capacitance of the sample and does not depend on time. The third component is a direct current $I_{d.c.}(t)$, which is associated with the ohmic resistance. That is, the measured current can be described by the formula:

$$I(t) = \beta C_{LF}(t) + \beta C_{HF} + I_{d.c.} \qquad (1)$$

In most cases the term βC_{HF} and/or $I_{d.c.}(t)$ could be defined directly from experimental curves using simple geometrical considerations. Hence the equation (1) gives a relaxation of low-frequency capacitance in real time.
As a rule this relaxation is non-exponential and can be described through the Kohlrausch-Williams-Watts function

$$C_{LF}(t) = C_{LF}(\infty)\left\{1 - \exp\left[-(t/\tau)^{\gamma}\right]\right\} \qquad (2)$$

Here τ is the decay time constant and γ is the parameter of non-exponential. Both parameters can be easily determined by adjustment of function (2) to the experimental data.

We wish to emphasize this advantage of a method. It is known the work [10], for example, in which (with the aim of estimation of parameter γ in a rubber) authors have been used the Fourier-transform method to obtain the imaginary part of dielectric permittivity $\varepsilon''(\omega)$ as function of time. Only after that stretched exponential function has been used in this work [11].

3. Results and discussions

(i) Non-exponential relaxations

We have been used the results of measurement of glass transition temperature T_g for bulk sample of As$_{10}$Se$_{90}$ [3,12], and we have chosen a range of temperature for capacitance measurements in amorphous layers of this material in order to guarantee passage through the point T_g, even if it differs from the published value.

Measurements of capacitance were carried out in the cycles of heating and cooling the sample. For this purpose the sample was shielded from external electromagnetic interference and daylight illumination and then gradually (step by step) it was heated up to the top border of the chosen range of temperature. After that we gave start to process of its gradual (also step by step) cooling. The relaxation of the capacitance was recorded on each step of process of heating or cooling the sample, after the given temperature was established.

The example of sequence of a capacitance relaxations curves, obtained during heating of amorphous layer As$_{10}$Se$_{90}$ in the range of low temperatures (T<T_g, curves 1-3), in transition range (T~T_g, curves 8-10) and in the range

of the increased temperatures (T>T_g, curves 15-17), is demonstrated on Fig. 1.

Already from qualitative comparison of presented curves it seems that in the range of low temperatures in a relaxation current the component of high-frequency capacitance βC_{HF} is dominates. In the range of temperatures T>T_g this component is negligible in comparison with the main component of a capacitance current $\beta C_{LF}(t)$.

In the range of intermediate temperatures, on a background of current $\beta C_{LF}(t)$ (that apparent after beginning of relaxation), the component of a direct current $I_{d.c.}$ also is well visible. This last component can be determined as asymptote of the general relaxation curve in a limit of indefinitely long times.

Parameters of relaxation curves, such as $C_{LF}(\infty)$, $I_{d.c.}$, τ, and γ were defined by adjustment of function (2) to the experimental points. The results of this fitting are shown in Fig. 1 by solid lines. The similar picture of changes in the capacitance relaxation curves was observed and at a stage of cooling of the sample. Fig. 2(a) shows dependences of saturation capacitance $C_{LF}(\infty)$ from temperature, which were obtained from a relaxation curves (similar to curves of Fig. 1) during heating (curve 1) and cooling (curve 2) of a sample.

From the Fig. 2 it seems that up to 320 K (that is, in the range of low temperatures), the essential change of the saturation capacitance do not occur. Further the increase of capacitance is observed. It takes place in the wide range of intermediate temperatures (from 320 up to 360 K) and finish with saturation in the range of the highest temperatures.

The subsequent cooling of a sample does not lead to essential change of saturation capacitance in the range of low and the intermediate temperatures. However, it accompanied by appreciable narrowing of the transitional range of the temperature, and by abrupt change of the capacitance, which now occurs in an interval of temperatures from 340 up to 350 K.

These distinctions are visible on curves of Fig. 2(b), which were obtained by differentiation of corresponding dependences of the saturation capacitance presented in Fig. 2(a).

Here intensity of peak of the derivative function $dC_{LF}(T)/dT$ increases almost twice and the half-width of this peak decreases about three times, at transition from a curve 1 (findings at heating the sample) to a curve 2 (finding at its cooling). Nevertheless the position of the peak of derivative function does not vary and is near T=345 K.

The described change of capacitance in a vicinity of the glass transition temperature T_g is accompanied by increase in the conductivity also: its maximum (Fig. 2(c), curve 2) coincides with the beginning of abrupt increase in capacitance near the T=343 K. It corresponds to the data, which were described earlier for polymeric films and obtained from the dielectric measurement [4,9].

Recently similar dependence of conductivity near the glass transition temperature T_g in glass-forming glycerol has been obtained with the help of unique measurements

of low-frequency noise. Fluctuations of polarization were found out as current noise with a maximum on the temperature dependence, rigidly connected with the glass transition [13].

The temperature dependence of conductivity, which is observed during heating of a sample (curve 1) also, differs from a case corresponding to its cooling (curve 2). An extended plateau in the range of intermediate temperatures (instead maximum) is observed. The maximum of

conductivity (or an imaginary part of dielectric permittivity also) usually are associates with random movement of molecular chains and dipoles in an amorphous phase, which accompanies the process of a structural relaxation and glass transition.

Other interpretation [4] assumes increase in a relative fraction of a crystal phase in an amorphous layer and increase in conductivity owing to growing structural ordering of a material.
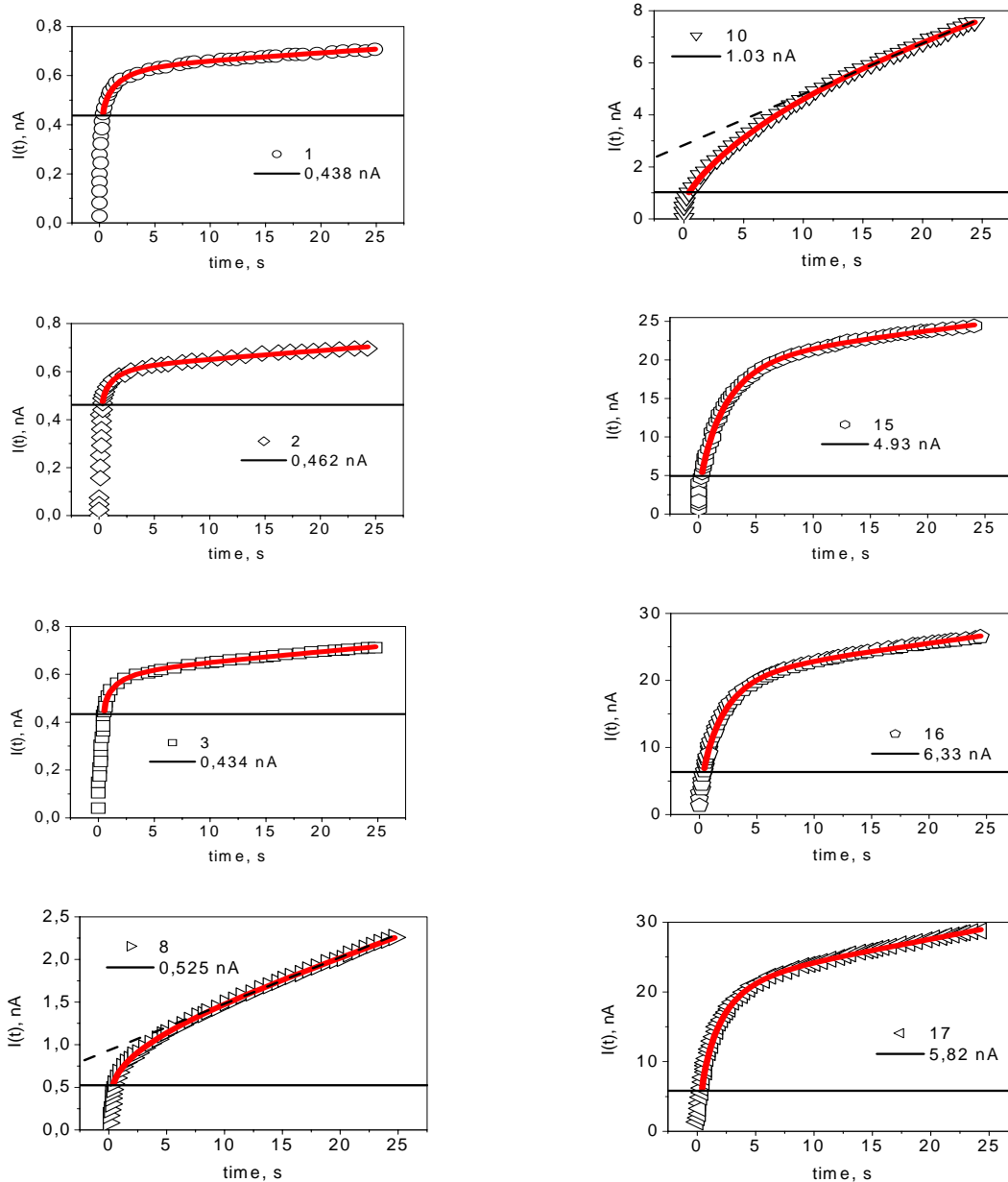

Fig. 1. Sequence of a relaxation curves for amorphous layer of As$_{10}$Se$_{90}$, which have been written on X-Y recorder as the response to a pulse of a triangular voltage with amplitude of about 0.2 V (f=2x10^{-2} Hz). Curves are obtained at a stage of heating a sample from 18.4 (curve 1) up to 102.9 ^{0}C (curve 17); For curves 2, 3, 8, 9, 10, 15 and 16 temperature of a sample was 19.9, 25.1, 54.9, 60.6, 65.8, 92.1 and 97.3 ^{0}C, respectively. Solid lines represent adjustment of function (1) to experimental points.

Thus, the presumable glass transition in amorphous layer $As_{10}Se_{90}$ is accompanied by a characteristic temperature hysteresis. It result in discrepancy of a temperature trace of capacitance curve at heating and cooling of a sample and has anomaly in point T~345 K, near the glass transition temperature of vitreous $As_{10}Se_{90}$. This hysteresis is caused by processes of a slow relaxation of non-equilibrium polarization toward the equilibrium curve. The relaxation time increases with lowering of temperature: near the temperatures which have difference with T_g more than 20 K, the capacitance changes becomes not observable in time scales of our experiment. However, in the range of temperatures near T_g a relaxation time is not so long, and simultaneously to cooling there is a movement downwards to equilibrium curve. For this reason a backward curve passes below, and even can cross a line of equilibrium curve.

(ii) Non-Arrhenius character of decay time constant

Glass transition in the majority of glass-forming materials is accompanied by process of a structural relaxation known from literature as a cooperative α-relaxation [14,15]. In dielectric measurements this process shows some universal features such as: (a) the deviation from Debye law of complex dielectric permittivity, (b) the non-Arrenius form of the temperature dependence of relaxation time. This, last is often analyzed by the empirical Vogel-Fulcher-Tamman (VFT) law (see [16], for example):

$$\tau = \tau_0 \exp\left[A / \left(T - T_0 \right) \right] \quad (3)$$

Here τ_0 is the pre-exponential factor, A is the constant and T_0 ($<T_g$) is the characteristic temperature at which a relaxation time aspires to infinity.

Apparently already close to T_0 the relaxation time achieves the upper border of times registered in our experiment. It is equal to the width of forward front of the triangular voltage pulse acting on a sample, that is to say $\tau=\tau_{max}$=25 s. It is close to the 100 s, usually accepted as a standard level for definition the temperature T_g from dielectric measurements [9].

Temperature dependence of a relaxation time for amorphous layer of $As_{10}Se_{90}$ is presented on figure 3(a). For comparison the dependence of τ vs. T for amorphous layer As_2Se_{98} is depicted on figure 3(b) also. Solid lines are result of the best adjustment of the function described by the equation (3) to experimental points. Parameters τ_0, A and T_0, which were obtained as a result of this fitting for both curves, are presented in the Table 1.

The non-Arrhenius character of the decay time constant, such as is shown in figure 3 (a) and 3 (б) (for samples $As_{10}Se_{90}$ и As_2Se_{98}, accordingly) it is convenient to characterize by a parameter of fragility $m=\log_{10}\tau(T)/d(T_g/T)\big|_{T=T_g}$ [17] or:

$$m = A T_g \log_{10} e / (T_g - T_0)^2 . \quad (4)$$

Here e is the base of natural logarithm. Really, at such definition of the parameter m, it characterizes a steepness of a curve $\log_{10}\tau$ versus T_g/T near T_g, which is more, when more the deviation from Arrhenius law. In this context the classification of glasses on strong and fragile has been proposed [17,18].

According to this classification a glass with m=16 are strong. Only a few glasses have parameter of fragility less than 25. Glycerol is an intermediate material with m=50. Amorphous As_2Se_3 has m=40 and is an intermediate material also. The most fragile glass-forming material is decalyn (m=150). As it follows from Table 1, on this scale of parameters m the sample of $As_{10}Se_{90}$ and As_2Se_{98} investigated by us also occupy the intermediate position.
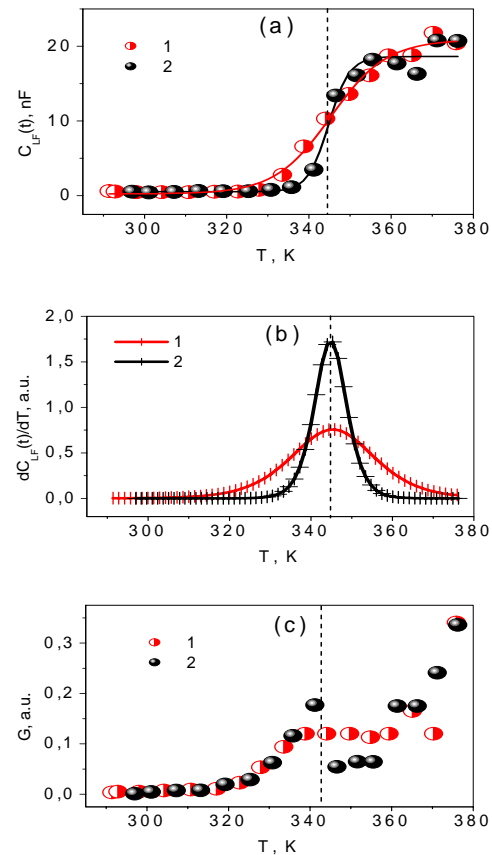

Fig. 2. The dependences of saturation capacitance $C_{LF}(\infty)$ (a), its derivative functions (b) and conductivity (c), obtained during heating (curves 1) and cooling (curves 2) of sample $As_{10}Se_{90}$ from the relaxation curves (see text for details).

For comparison we shall note only, that an amorphous films, investigated recently in [19], in overwhelming number of cases show m=25 and the small deviation from Arrhenius law (of decay time constant).

Most of glass-forming materials have the index of fragility m that correlates with the parameter of non-exponentiality γ. According to [17] the fragile materials have small values γ, while strong (with small m) have γ~1.

The value of parameter m, which was calculated for our samples from equations (4) are presented in

Table 1. It seems that it is surprisingly close to the value known for amorphous selenium. We think, that this is a very important observation, because as first, it confirms the non-Arrhenius form of the relaxation time vs. temperature dependence. Second, - emphasizes connection between features of a capacitance relaxation that are found out in our experiment and the phenomenon of the glass transition.
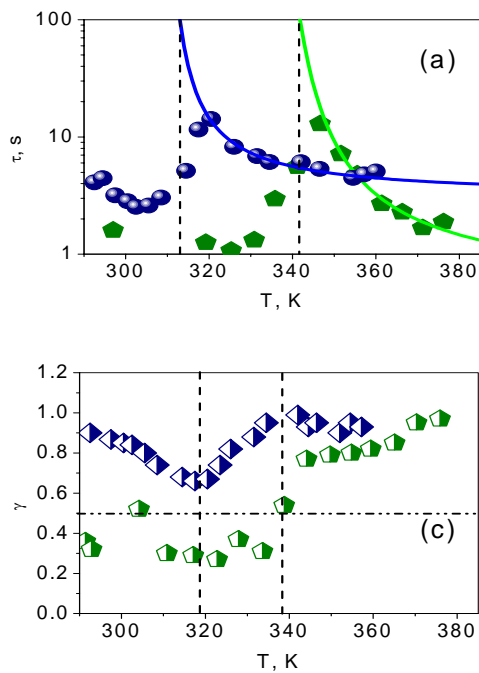

Fig. 3. The dependences of a decay time constant τ and an index γ versus T for sample As$_2$Se$_{98}$ (on the left) and As$_{10}$Se$_{90}$ (on the right). Solid lines in figures above show extrapolation of function VFT to a standard level "100 s", for definition of temperature T$_g$ (as it follows from dotted line). Solid lines below are guide by an eye.

As it has been argued in [20], an experimental value of γ(T$_g$) in the range of T<T$_g$ can be understood through the equation:

$$\gamma\left(T_g\right) = d/(d+2).\qquad(5)$$

The idea of these arguments originates from the known electronic and/or molecular interaction in presence of short-range forces: only dimensionality d has the natural value (usually d=3 and γ(T$_g$) =3/5).

In presence of strong correlation causing by long-range Coulomb potential the value d must be replaced with d/2, (in this case the g value is 3/7).

For molecular systems the range of this interaction depends on type of material.

In organic material (for example, such as glycerin) the interaction between molecules is defined by short-range forces. But in polymer (in which there are no strong hydrogen bonds) the intra-chained relaxation is governed by long-range Coulomb potential.

For example, in amorphous selenium, which is characterized by chained structure, γ(T$_g$) =0,43. In Se-As-Ge this parameter is about 0,6 (such as 0.61 in glycerin). It immediately follows from the equation (5) for d=3.

As it seems from figure 3(b) in the range of T <T$_g$ the value γ(T$_g$) of As$_{10}$Se$_{90}$ and As$_2$Se$_{98}$ differ one from another.

If for the first sample these values oscillate near to 0,4, for the second sample it is nearby 0,6. Both values can be obtained by means of the equation (5).

In the range of elevated temperatures T>T$_g$, γ=1. This corresponds to a case of independently cooperating molecular units with the simple form of exponential dependence.

Correlation is established between the molecular units, when the temperature decreases.

In this case the value γ will drop until T will reach T$_g$.

Here γ(T) reaches the constant value, which is defined by effective dimensionality of d/2.

Table 1. The VFT function parameters obtained as a result of fitting procedure for amorphous layers of A$_{10}$Se$_{90}$, As$_2$Se$_{98}$, and fragility parameters m. Last parameter was evaluated in accordance with the formulas (4). For comparison the parameter m for vitreous bulk materials Se from [17] are presented also.

	τ_0 (s)	A (K)	T_0 (K)	T_g (K)	$\gamma(T_g)$	m
As$_2$Se$_3$				376	0.41	40
As$_{10}$Se$_{90}$	0,47	54.4	331.6	341.8	0.4	77.9
As$_2$Se$_{98}$	3.93	10.1	312.6	315.5	0.6	162
Se				313	0,43	87

If we shall assume that fragments of selenium chains play the leading role in the polarization of a material then these values can be consequence of a known rule for the glass-forming polymers [21]: the more molecular weight of a chain, the is more fragility of a material. Besides, the reduction of relative density of As atoms, which are playing a link role between chains of Se (like a some bridge), with transition from As$_2$Se$_3$ to As$_2$Se$_{98}$ and Se also leads to some increase in fragility of a film.
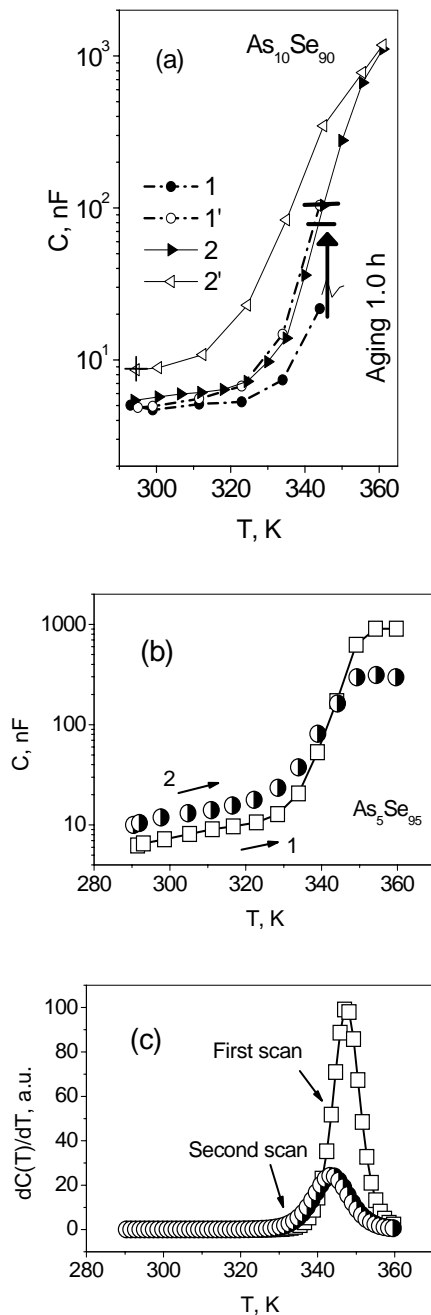
Fig. 4 (a). The capacitance changes, which have been written down for sample $As_{10}Se_{90}$ for two successive heating and cooling cycles (curves 1, and 2, accordingly). The arrow directed vertically upwards, shows the change of capacitance under annealing $(T_{a1}=344\ K)$ during 1 hour. (b) and (c) show the capacitance changes C(T) in dependence on temperature and its derivative function dC(T)/dT for sample As_5Se_{95}. Curves 1 and 2 were obtained after the first and second scan of actual temperature area.

We want to note the large values of the pre-exponential factor τ_0, which were determined in our

measurement. It suggests that polarization of an amorphous layer (in the limits of high temperatures) is determined by slow processes such as diffusion of atoms and defects through the charged double layer on interface with contact. Thickness of this layer has an order of magnitude as the length of screening L_D. Then, characteristic time-of-flight of atoms through this layer, in the limits of high temperatures, can be appreciated as

$$\tau_D \sim 2L_D^2/D_0. \qquad (6)$$

Here D_0 is the pre-exponential factor for diffusion coefficient.

As show estimations, when the typical value of D_0 is about 10^{-9} cm^{2}s^{-1} [22] and L_D is 0,1μm, the characteristic diffusion time constant τ_D is about 0.1 s, which coincides with the values of τ_0 listed in Table 1. When defects are vacancies (nano- and microvoids, for example) it will be in agreement with the formal notions of dielectric polarization. According to this interpretation, "the free volume" is necessary in order the molecular groups and dipoles could be reoriented in response to the applied voltage pulse.

(iii) Ageing phenomena, memory, rejuvenation

The first introduction about influence of annealing on dielectric properties of $As_{10}Se_{90}$ sample follows from comparison of curves 1 (1') and 2 (2') on figure 4 (a). The curve 1 has been recorded for a sample, which has been stored about one year in darkness, near the room temperature on air (that is, in usual conditions) and was not measured before. After the temperature was increased to T_{a1}=344 K the sample was annealed at this temperature within one hour and then was cooled (a curve 1'). As well as in the cases described in the previous section, change of temperature was carried out gradually (step by step) and measurement of a capacitance relaxation was carried out on each of these steps after the temperature was established.

After end of the first cycle the sample was again heated up, but already to higher temperature T_{a2}, and after that the process of his cooling (up to room temperature) was started again. At this room temperature the sample was maintained 15 hours, however the appreciable change of the capacitance has not been revealed.

Some of the important features of a capacitance relaxation follow from comparison of curves on figure 4(a). The first feature consists in the appreciable (about fourfold) increase in capacitance as result of annealing at T_{a1}. The second is the memory effect to which frequently refer in the literature [23,24]. For example, at reheating a sample, the change of capacitance follows the path of a curve 1, on which the previous change of capacitance (that caused by experimental circumstances) has occurred as though the sample remembered the prehistory.

As it follows from figure 4(a), the capacitance does not decrease, but increases during annealing. Besides, the capacitance rejuvenations is not observed after the

annealing and cooling of sample. Such behavior of electrical capacitance can be associated with contraction of the film and reduction of its thickness. This explanation is supported by two experimental observations:

(1) The capacitance of non-annealed $As_{10}Se_{90}$ layer is small and low-frequency relaxation current component (typical for polarization of molecular dipoles) disappear.

(2) Band near 252 cm^{-1} is dominates in the Raman spectra of amorphous $As_{10}Se_{90}$ layer, according to closed rings $(Se)_8$ also well. Such rings do not give the contribution to polarization of the sample, but can easily be packed into dense structure at annealing [26].

We have repeated experiment for sample As_5Se_{95}, in a simple mode. Fig. 4(b) shows the curves of the capacitance change, which were obtained in the first and second scan of temperature from 290 up to 370 K (curves 1 and 2, accordingly). As it seems, at the low temperatures the curve (2) goes above a curve 1, as well as should be in case the sample remembers the prehistory.

We want to note that the dependence of a derivative function dC(T)/dT (figure 4(c)) shows a features similar to what have been obtained in the calorimetric explorations for thermal capacitance of bulk samples near the temperature T_g. Really, the peak with the large intensity corresponding to a sample, which has experienced ageing, at least, within one year in usual conditions, was moved towards the higher temperatures in comparison with peak of smaller intensity. It conform to the picture described in work [3] if to assume, that at heating a sample in the first scan up to temperature $T>T_g$, and its subsequent cooling up to room temperature, the process of a samples rejuvenation takes place. At the same time, absence of any appreciable change of capacitance after storage of sample about 15 hours near the room temperature (marked above on Fig. 4 (a)) confirms its long-term, or even irreversible ageing.

4. Conclusions

The dielectric properties of the $As_{10}Se_{90}$, As_2Se_{98} and As_5Se_{95} thin amorphous layers have been investigated in the cycles of heating and cooling, near the glass transition temperature. The obtained results clearly show, that the method of dielectric relaxation spectroscopy (anyway, in variant which has been proposed in our investigations) can be used for studying the glass transition in these samples. In particular it allows defining the temperature T_g in thin (~ 1 μm) layers of amorphous semiconductors "in-situ". Evaluated T_g=343 K (for $As_{10}Se_{90}$), and T_g=315 K (for As_2Se_{98}) are in the good consent with the data that were reported in the literature.

As a result, it was found that the dielectric relaxation in region $T>T_g$ can be expressed through the KWW-function.

The validity of VFT empirical equation for the relaxation time dependence from temperature has been shown. This dependence allows to assume, that such important parameters of the glassy materials, as

temperature T_0 ($T_0<T_g$) and parameter of fragility m can be extracted from these studies.

The found values of parameter m for studied samples of $As_{10}Se_{90}$ and As_2Se_{98} (at temperature T_g) allows classifying our materials as fragile.

The effect of the annealing and prehistory for $As_{10}Se_{98}$ sample (in process of physical ageing) also has been shown.

We hope, that the method of a dielectric relaxation will find one more important field for the application also. Still we think, already known features of the complex dynamical processes near the glass transition will find the confirmation in studying of classical glassy-like materials, such as chalchogenide semiconductors.

References

[1] M. F. Thorpe, D. J. Jacobs, M. V. Chubinsky. J. C. Philips, J. Non-Cryst. Solids, **266-269**, 859 (2000).

[2] R. Golovchak, H. Jain, O. Shpotyuk, A. Kozdras, A. Saiter and J.-M. Saiter, Phys. Rev. B **78**, 014202(1)-(6) (2008).

[3] R. Ya. Golovchak, Cz. Gorecki, A. Kozdras, O. I. Shpotyuk, Sol. St. Commun. **137**, 67 (2006).

[4] P. D'Angelo, M. Barra, M. Nicodemi, A, Cassinese, Journ. of Appl. Phys. **101**, 044910(1)-(5) (2007).

[5] D. Cangialosi, M. Wübbenhorst, J. Groenewold, E. Mendes, S. J. Picken, Journ. of Non-Cryst. Solids pp. 1-6 (2005).

[6] A. A. Babaev, I. K. Kamilov, C. N. Kallaev, S. B. Sultanov, A. A. Amirova, A. M. Dzhabrailov, J. Optoelectron. Adv. Mater. **5**, 791 (2003).

[7] V. F. Antonov, A. A. Anosov, V. P. Norik, E. A. Korepanova, E. Y. Smirnova, Eur. Biophys. J., **32**, 55 (2003).

[8] N. Nakashima, K. Yamashita, T. Jorobata, K. Tanaka, K. Nakano, M. Takagi, Analytical Sciences, **2**, 589 (1986).

[9] A. Scönhals, "Dielectric properties of amorphous polymers" in "Dielectric spectroscopy of polymeric materials"; J. P. Runt, J. J. Fitzgerald (Ed's); American Chemical Society, Washington, DC, 1997.

[10] P. Janic, M. Paluch, J. Ziolo, W. Sulkowski, L. Nikiel, Low-frequency dielectric relaxation in rubber, Phys. Rev. E **64**, 042502(1)-(4) (2001).

[11] Note: $\varepsilon''(\omega)$ is the main measurable quantity in the dielectric spectroscopy.

[12] A. Saiter, J.-M. Saiter, R. Golovchak, M. Shpotyuk, O. Shpotyuk, J. Phys.: Condens. Matter. **21**, 075105(1)-(7) (2009).

[13] N. E. Israeloff, Phys. Rev. B **53**, R1191(3)-(6) (1996-II).

[14] J. C. Dyre, Rev. of Mod. Phys., **78**, 953-972 (2006).

[15] P. G. Debenedetti and F. H. Stillinger, Nature, **410**, 259-267 (2001).

[16] M. A. Miller, M. Jimenez-Ruiz, F. J. Bermejo, N. O. Birge, Phys. Rev. B **57**, R139(77)-(80) (1998-II).

[17] L.-M. Wang, C. A. Angell, R. Richert, The Journ. Of Chem. Phys., **125**, 074505(1)-(8) (2006).

[18] C. A. Angell, Proc. Natl. Acad. Sci. USA, **92**, 6675-6682, Colloquium Paper (1995).

[19] A. L. M. Smits, M. Wubbenhorst, P. H. Kruiskamp, J. J. G. van Soest, J. F. G. Vliegenthart, J. van Turnhout, J. Phys. Chem. B **105**, 5630 (2001).

[20] J. C. Phillips, Phys. Rev. B **52**, R863(7)-(9) (19995-II).

[21] I.-S. Park, K. Saruta, S. Kojima, Journ. of the Phys. Soc. of Japan, **67**, 4131 (1998).

[22] F. Faupel, W. Frank, M.-P. Macht, H. Mehrer, V. Naundorf, K. Rätzke, H. R. Schober, S. K. Sharma, H. Teichler, Rev. of Mod. Phys. **75**, 237 (2003).

[23] L. Bellon, S. Ciliberto, C. Laroche, Europhys. Lett. **51**, 551 (2000).

[24] K. Fukao, H. Koizumi, Glassy dynamics in thin films of polystyrene, arXiv:0801.0795v1 [cond-mat. Soft] 5 Jan 2008, pp. 1-7.

[25] P. Lunkenheimer, R. When, U. Schneider, A. Loidl, Phys. Rev. Lett. **95**, 055702(1)-(4) (2005).

[26] M. S. Iovu, E. I. Kamitsos, C. P. E. Varsamis, P. Boolchand, M. Popescu, Chalcogenide Letters **2**, 21 (2005).

_____

[*]Corresponding author: miovu@asm.md