PHOTOCAPACITANCE RELAXATION AND RIGIDITY TRANSITION IN $Ge_xAs_xSe_{1-2x}$ AMORPHOUS FILMS

I. A. Vasiliev , M. S. Iovu, and E. P. Colomeiko
Institute of Applied Physics, Academy of Sciences of Moldova,
Academiei str. 5, Chisinau, MD-2028 Republic of Moldova

(Received 17 March 2011)

Abstract

The photocapacitance relaxation of $Ge_xAs_xSe_{1-2x}$ 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 dependences of the low-frequency dielectric permeability, decay time constant and the Kohlrausch parameter of nonexponentiality are deduced from these data. All parameters show two compositional thresholds, one situated near the $x_c(1)$=0.09, and the other 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 (P. Boolchand et al., Europhys. Lett., 52, p. 633, 2000).

1. Introduction

Chalcogenide vitreous semiconductors (ChVS), which were discovered in the early 1960s by B. T. Kolomiets and N. A. Goryunova, continue to draw attention due to unique optical, photoelectrical, structural properties, and the new physical phenomena, especially ChVS of Ge-As-Se system (which possess wide area of glass-forming) owing to novel applications in efficient optical femtosecond switches [1].

Glasses of the $Ge_xAs_xSe_{1-2x}$ system were investigated during last ten years by means of T-modulated differential-scanning calorimetric technique [2, 3], the Raman and neutron scattering methods [4], the Mossbauer spectroscopy and nuclear magnetic resonance [5]. This made it possible to determine flexible phases (free from mechanical stress) at $x<x_c(1)=0.09$, intermediate phases at $x_c(1)<x<x_c(2)=0.16$, and the stressed-rigid phases at $x>x_c(2)$.

Despite accumulated results, some questions remain open. First, the definition of an intermediate phase and a threshold of rigidity in thin films is not present clearly, because the majority of the listed above methods cannot be applied in this case. Second, the effects of the examined phase transitions onto optical, photoelectric and transport properties of materials are poorly studied; however, they are a source of additional information about the film structure near these transitions.

In the present paper, we have focused our attention on these problems, and amorphous films of $Ge_xAs_xSe_{1-2x}$ 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 and measurement technique

Thin-film samples for studies (thickness L~1 μm) were prepared by thermal evaporation in vacuum of the initial material of a given composition on a glass substrate heated up to a temperature of 100^0C. The samples had a "sandwich" type configuration with evaporated top (transparent) and bottom (between the chalcogenide film and the substrate) aluminum electrodes

(the effective area of electrode S ~ 0.65 cm^2).

The capacitance current (or otherwise, displacement current) was measured as the response to triangular voltage pulses, which was applied to the sample: $I_{dis.c.}=kC(t)$, $k=dV(t)/dt$ (frequency 2 x 10^{-2} Hz, amplitude ~ 0.2 V).

3. Results

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

One can see that the rate and form of the capacitance decay non-monotonously depend on

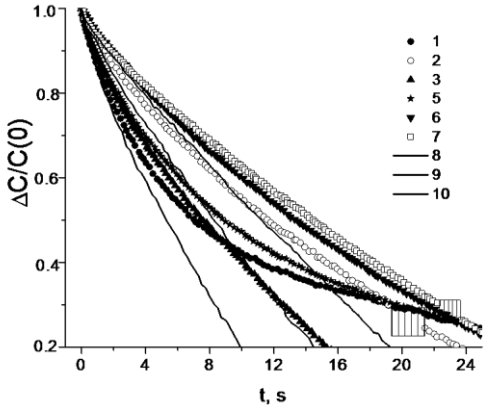

Fig. 1. Relaxation curves of the normalized photocapacitance for x = 0.05 (1), 0.07 (2), 0.09 (3), 0.14 (5), 0.16 (6), 0.18 (7), 0.20 (8), 0.25 (9), and 0.30 (10), at room temperature

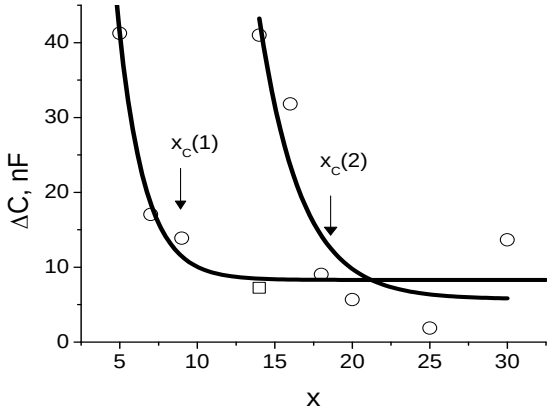

Fig. 2. Compositional dependence of photocapacitance $\Delta C=C(0)-C_{dark}$ for amorphous $Ge_xAs_xSe_{1-2x}$. Continuous lines are guide on eye

composition. So, if for x = 0.07 and 0.14 (curves *1, 5*) the change in the capacitance current eventually occurs close to an exponential law, for three last compositions (curves *8, 9*, and *10*) this change is nearer to a linear dependence. This can indicate both 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

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

Eq. (1) expresses the known Kohlrausch-Williams-Watt (KWW) empirical law for a dielectric relaxation. Here the C_{dark} term corresponds to the capacitance measured in the dark; 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) versus composition are presented in Figs. 2-4.

Figure 2 shows the compositional dependence of photocapacitance $\Delta C=C(0)-C_{dark}$ which is related to the dielectric strength $\Delta\varepsilon$ ($C=\varepsilon_0\Delta\varepsilon S/d$) induced by illumination. It is evident that, in the

region of floppy mode and inside the region of an intermediate phase, the value of photocapacitance decreases 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 the dark.

We think that this behavior of the photocapacitance in the region of the floppy mode and in the region of the intermediate phase is caused by dipoles of different nature, because the value of the photocapacitance in the second region exceeds the change of the photocapacitance extrapolated to this region from the first one.

It is worthy of note that the value of the photocapacitance near both thresholds is small and is of the same order as the capacitance C_{dark}.

It evidences both the increase in rigidity and the reduction in the concentration of the nonequilibrium defects near the two thresholds. It is clear that both tendencies are interdependent, because the increase in average coordination number in the region of the floppy mode and the intermediate phase *by definition* reflects the reduction in the concentration of the coordination defects participating in the formation of a dipole.

4. Dielectric relaxation model

In the defect diffusion model [6, 7], it is assumed 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 remains "frozen" after the cessation of the field. Moreover, it is assumed that the medium contains mobile defects, which achieve the site with the frozen dipole and cause the relaxation of the medium up to such a degree that the dipole can be reorientated by any way.

If the diffusion of defects towards a dipole occurs as the random walk continuous in time, then the relaxation function has the exponential form:

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

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

For homogeneous distribution of traps $S(t) \sim t^{1/2}$ at $d = 1$ or $S(t) \sim t$ at $d = 3$, d is dimensionality [6]. Thus, the relaxation function has the fractional-exponential form in one-dimensionality ($\beta = 1/2$), and it is pure exponential in three-dimensionality ($\beta = 1$).

In fact, the problem of searching the function of relaxation $\varphi(t)$ was reduced to the well-known problem of traps [8]. In this problem the particle (defect) performs a random walk on the lattice and instantly dies after collisions with a trap (dipole); then probability of survival $\varphi(t)$ is the aim of searching.

The examined model suggests some important generalizations. *First*, it is clear that, in case of nonuniform distribution of the traps, the traveling particle (walker) cannot possess collisions with traps for a long period of time, if it gets in a significantly *greater* region which is free from them. These regions are rare; however, it is they that restrict the relaxation on long times. The calculations presented in [8] show that, in this case,

$\varphi(t) \sim \exp(-\text{const} \times t^{\beta})$, where

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

We see 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 increase in the heterogeneity of the medium near the rigidity transition. Obtained

values of β ~ 0.65 in the region of the stressed-rigid phase within the limits of experimental error coincide with the value of β=3/5 (d=3). For molecular glasses, which are mainly organized by the covalent bonds between atoms [9], this directly corresponds to Eq. (3).

For comparison, we presented in Fig. 3 the relaxation data for the elastic stress, which were obtained in [10] for glasses of the $Ge_xAs_ySe_{1-x-y}$ system also. It is noteworthy that these values of β well coincide with our data for the range of coordination number <r> = 2.2-2.6.

The second generalization of the defect diffusion model has been made in [7] 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 a wide dispersion of relaxation times with an infinite average value. In the case of $d = 3$, this directly leads to the function:

$$S(t) \sim \begin{cases} t, \text{ for } < t > \text{ limited}, \\ t^{\beta}, 0 < \beta < 1, \text{ for } < t > \to \infty, \end{cases} \tag{4}$$

and the KWW law of relaxation.

In this generalization of the model, the transform from the exponential relaxation to the fractional-exponential one can be explained by changes in the pattern of the relaxation time distribution. For exponential distribution of activation energies E: $g(E) \sim \exp(E/k_BT_0)$, T_0 is the 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 wider distribution of g(E) in these regions (by *greater* values of T_0).

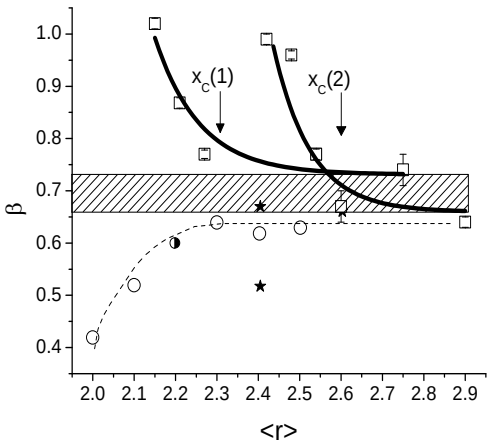

Fig. 3. Kohlrausch parameter β vs. average coordination number <r>. The various segments of behavior are shown by continuous lines. Experimental data from [10] (circles) are also presented.

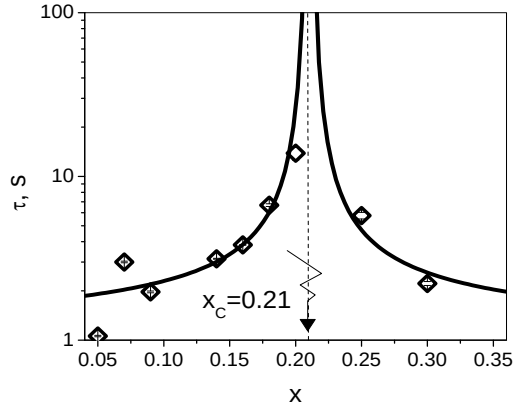

Fig. 4. Dependence of the decay time τ vs. x (points), and the model curve (solid line), which was obtained by the adjustment of the modified equation (5) to experimental data.

The following *third* generalization is basic for understanding the compositional dependence of a relaxation time. In the original formulation of the model [7], it was assumed that the aggregation of defects and their correlation in the range of temperatures $T > T_C$ (T_C is the 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 the form

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

Here τ_1 is pre-exponential factor, which depends on defect concentration, $B_1=BT_C^s$, $B=-L^3\ln(1-c)/\beta d_0^3$, L is parameter of defect correlation length: $\xi(T)=L[T_C/(T-T_C)]^s$, 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: τ_1~2.2±0.015 s; B=0.07±0.001; x_C=0.21±0.0002. It seems that the reasonable value of ratio L/d_0~3 can be obtained already at concentration of defects c~0.0015.

5. Summary

The central result of our studies is detection of three various segments in behavior of a dielectric relaxation of $Ge_xAs_xSe_{1-2x}$ 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 $x>xc(2)$ =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 parameterβ, 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 [2,4].

Acknowledgments

The authors are grateful to STCU Project no. 3745 for the financial support of this work.

References

[1] A. Zakery and S.R. Elliott, Optical nonlinearities in chalcogenide glasses and their applications. Springer Publisher, 2007, 199 p.
[2] Y. Wang, P. Boolchand, and M. Micoulaut, Europhys. Lett., 52, 633, (2000).
[3] T. Qu, D.G. Georgiev, P. Boolchand, and M. Micoulaut, Mat. Res. Soc. Symp. Proc., 754, CC8.-1.1 (2003)
[4] M.F. Thorpe, D.J. Jacobs, M.V. Chubynsky, and J.C. Phillips, J. Non-Crystall. Solids 266-269, 859, (2000).
[5] R. Mullmann, B.D. Mosel, and H. Eckert, Phys. Chem. Chem. Phys., 1, 2543, (1999).
[6] M.F. Shlesinger and E.W. Montroll, Proc. Natl. Acad. Sci. USA, 81, 1280, (1984).
[7] J.T. Bendler and M.F. Shlesinger, J. Stat. Phys., 53, 531, (1988).
[8] R. Rammal, Phys. Lett., 102 A, 117, (1984).
[9] J.C. Phillips, Phys. Rev. B, 73, 104206, (2006).
[10] R.Bohmer and C.A. Angell, Phys. Rev. B, 45, 10091 (1992).