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EFFECT OF γ-RAY ACCELERATION OF PHYSICAL AGEING IN VITREOUS $As_{10}Se_{90}$

M. Shpotyuk

Lviv Polytechnic National University, 12, Bandera str., UA-79013, Lviv, UKRAINE

ABSTRACT

Effect of γ-ray acceleration of physical ageing in 20-years aged chalcogenide vitreous semiconductor $As_{10}Se_{90}$ was studied by differential scanning calorimetry method. The glass transition temperature T_g and endothermic peak area A in the region of glass-to-supercooled liquid phase transition was shown to be changed after the period of additional natural storage of γ-irradiated samples.

INTRODUCTION

Chalcogenide vitreous semiconductors (ChVS) [1-3] owing to their unique physicochemical properties are the perspective materials for application in modern optoelectronics [4-6]. However, the wide implementation of ChVS is limited by their structural metastability – the common feature of all disordered solids originated from preparation conditions (melt quenching procedure, for example). It means that ChVS are always obtained in thermodynamically non-equilibrium state tending with time towards thermodynamic equilibrium of supercooled liquid. It is obvious, that physicochemical properties and, consequently, the exploitation characteristics of ChVS-based devices should be changed during such transition [7]. This phenomenon, called physical ageing, was shown to be strongly dependent on the chemical composition of ChVS.

In view of P. Boolchand [8] the value of physical ageing in certain ChVS system is determined by the average coordination number z defined as average number of covalent chemical bonds per one atom of glass formula unit. Due to this parameter the glass forming region of ChVS could be divided into three parts, two of them, which glass compositions are more or less sensitive to the physical ageing, being called *"floppy"* (chalcogen-enriched compositions with small z) and *"stressed rigid"* (chalcogen-deficit compositions with large z) regions respectively. It was shown that relaxation processes in ChVS from second region needs much more time than in ChVS from the first one. These two regions are separated by a so-called thermally reversing window – the compositional range where no ageing effects are expected.

The analogous to physical ageing effect can be produced by external factors, such as photo- or γ-irradiation [9, 10]. It was shown, in part, that γ-irradiation led to the acceleration of physical ageing in as-prepared vitreous Se [10].

However, the influence of γ-irradiation on ChVS with completely saturated natural physical ageing is not investigated.

The aim of present investigations is to study the effect of γ-irradiation on the physical ageing in 20-years aged $As_{10}Se_{90}$ as typical representative of floppy ChVS [8].

EXPERIMENTAL

The investigated $As_{10}Se_{90}$ ChVS was chosen owing to a relatively high value of glass transition temperature T_g in comparison to vitreous Se, ensuring the weak rate of thermal erasing of γ-induced changes during the radiation treatment and next storage at natural conditions.

The experimental $As_{10}Se_{90}$ samples were synthesized by quenching from the melt of the mixture of initial As and Se (purity 99.999 %) chemical elements. All samples were stored under natural conditions during 20 years before our experiments.

One part of these samples was γ-irradiated at room temperature by γ-quanta of Co^{60} sources to the absorbed dose of 2.05 MGy. The other part of the samples was kept at the same thermal conditions but without radiation.

The differential scanning calorimetry (DSC) measurements were performed on NETSCH 404/4 microcalorimeter, pre-calibrated with a set of standard elements (In, Sn, Zn and Al), with 1 K/min heating rate. DSC-reflexes of γ-irradiated $As_{10}Se_{90}$ samples were obtained through 2 days, 1 month and 1 year periods after γ-irradiation. The non-irradiated $As_{10}Se_{90}$ ChVS were measured just before γ-irradiation and simultaneously with γ-irradiated samples.

The glass transition temperature T_g was estimated in the cross-point of tangents at the beginning of glass-supercooled liquid phase transition (a so-called "*onset*" T_g value) [2]. The maximum error of T_g determination did not exceed ±0.3 K (including accuracy of the equipment).

RESULTS AND DISCUSSION

The DSC-reflexes of non-irradiated $As_{10}Se_{90}$ ChVS were not changed essentially during the whole period of investigations (Fig. 1, solid curve). So, we can conclude that process of physical ageing in $As_{10}Se_{90}$ samples is almost completed after 20 years of natural storage or is very slow to be recorded experimentally.

The DSC-reflexes of γ-irradiated $As_{10}Se_{90}$ ChVS, recorded 2 days after γ-irradiation were not differed essentially from those of non-irradiated ones, the difference being compared with the accuracy of DSC measurements (Table 1).

However, 1 month of additional natural storage after γ-irradiation lead to the measurable increase of T_g and A values (Fig.1, dash curve, Table 1) testifying in the favor of γ-induced effect in $As_{10}Se_{90}$ ChVS. This increase is not significant achieving 1.7 K (0.5 %) for T_g and 0.08 J·K/g·s (7.8 %) for A. In spite of small values we can consider these changes as natural physical ageing activated by γ-irradiation. To check this hypothesis the DSC-reflexes of γ-irradiated samples were recorded through 1 year of natural storage.

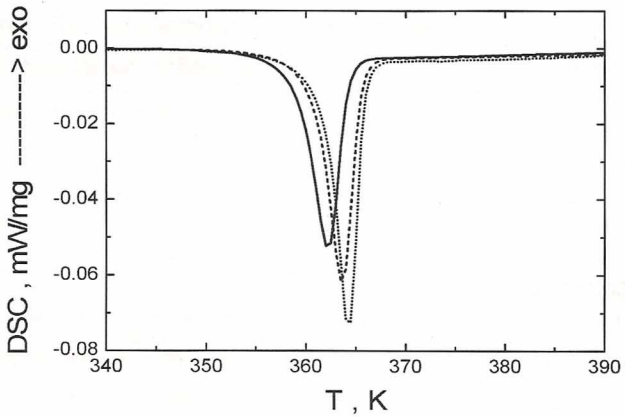

Figure 1. DSC-reflexes of $As_{10}Se_{90}$ ChVS: before and just after γ-irradiation (solid), after 1 month (dash) and 1 year (dot) of additional natural storage of γ-irradiated samples.

Table 1. Changes in glass transition parameters for $As_{10}Se_{90}$ ChVS caused by γ-irradiation and additional natural physical ageing.

Prehistory	T_g, K	A, J·K/g·s
20 years	358.9	1.03
20 years+ γ-irradiation	359.1	1.05
20 years + γ-irradiation + 1 month	360.6	1.11
20 years + γ-irradiation + 1 year	361.7	1.21

As it is shown in Fig. 1 (dot curve) the γ-modified ChVS structure relaxes during this period of time towards thermodynamic equilibrium of supercooled liquid giving an evidence for γ-accelerated physical ageing in $As_{10}Se_{90}$ ChVS. This effect is revealed through the increase in T_g and A values (Table 1).

Totally, the γ-activated physical ageing in 20-years aged $As_{10}Se_{90}$ ChVS is characterized by 2.8 K (0.8 %) increase in T_g and 0.18 J·K/g·s (17.5 %) increase in A values.

CONCLUSION

It was shown that very slow relaxation process of physical ageing in 20-years aged $As_{10}Se_{90}$ ChVS can be accelerated by γ-irradiation. The γ-irradiated samples kept at natural conditions for a 1 year reveal an increase in glass transition temperature and endothermic peak area in the vicinity of glass transition giving the evidence for natural physical ageing in γ-modified glass networks even after a very long period of natural storage.

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