Kinetics of phase transitions in vitreous chalcogenide semiconductors $\text{As}_x\text{Se}_{100-x-y}\text{Bi}_y$ as studied by the differential thermal analysis and exoelectron emission methods

Cz Górecki$^1$ and T Górecki$^2$

$^1$Department of Physics, Opole University of Technology, 75 Ozimska str., 45-370 Opole, Poland
$^2$Institute of Physics, Opole University, 48 Oleska str., 45-052 Opole, Poland

E-mail: c.gorecki@po.opole.pl

Abstract. Kinetics of glass transition (retrification) in chalcogenide semiconductors $\text{As}_x\text{Se}_{100-x-y}\text{Bi}_y$ ($x = 20$ or $30$, and $y = 0$ and $1$) has been investigated by parallel differential thermal analysis (DTA) and exoelectron emission (EEE) measurements. EEE is a surface effect accompanying the structural transformations in the surface layer, whereas the DTA technique gives information about the transformations occurring in the volume of the sample. Temperature dependencies of the DTA signal and of the EEE intensity have been determined and the values of the activation energy for both the volume and the surface retrification have been determined by the Ozawa method for each of the four investigated materials. It has been found that addition of Bi into the vitreous $\text{As}_x\text{Se}_{100-x}$ glass changes distinctly the kinetics of both the surface and volume retrification. Addition of Bi causes a distinct decrease in the value of the activation energy for retrification process in both the surface layer and in the volume, i.e. reduces the thermal stability of investigated materials.

1. Introduction

Vitreous chalcogenide semiconductors remain to be a subject of intensive investigations because of unusual combination of their physical properties. The most stimulating factor for these studies steam from potential applications of these materials in numerous advanced technological applications (optoelectronics, microelectronics, etc.) [1]. These promising applications of chalcogenide glasses are, however, limited by the difficulties arising from their structural instability, resulting from the production process, in which the liquid phase is quenched to the ambient temperature [2]. The process of thermal ageing of the as-quenched material (e.g. long-lasting isothermal ageing at proper temperature) leads to the achievement of the metastable state characteristics of the overcooled liquid [1-5].

Amorphous materials tend to crystallize at a proper combination of temperature and time. The stability of the chalcogenide glasses may be characterized by the activation energies and temperatures of the thermally activated retrification and crystallization processes. There is an additional complicating factor caused by the fact, that the parameters determining the thermal stability of the volume and of the surface layer of amorphous materials may differ among themselves. About 20 years ago we elaborated a method [6] for determination of the thermal stability for both the surface and volume of amorphous materials by parallel measurements of the temperature dependencies of the DTA signal and the intensity of photostimulated EEE. This method has been already successfully applied in investigations of the kinetics of phase transformations in various chalcogenide glasses, including arsenic selenides [7-8] as well as in pure melt-quenched selenium [9].
Recently Golovchak and coworkers [10] reported on the effect of modification of the structure of arsenic selenide glasses by addition of bismuth. By analyzing the core-level XPS (X-ray photoelectron spectra) they have found that addition of Bi leads to formation of coordination defects and, with increasing concentration of Bi, to the formation of nanocrystallites in the vitreous matrix. The presence of such imperfections may lead to the lowering of potential barriers for structural transformations in investigated arsenic selenide glasses.

The purpose of the present study is to investigate the effect of Bi addition on the kinetics of the retrification process in the volume and in the surface layer of arsenic selenide glasses.

2. Experimental conditions

The investigated bulk chalcogenide glasses were prepared in Lviv Scientific Research Institute of Materials of SRC “Carat” by conventional melting of appropriate mixture of high purity (99,999%) precursors sealed in evacuated (~10^-3 Pa) quartz ampoules, followed by air quenching to room temperature. The amorphism of the obtained materials was checked by X-ray diffraction and IR transmission techniques.

Measurements of the temperature dependencies of photostimulated exoelectron emission (EEE) intensity were carried out by means of the arrangement described in [12]. An open point counter with saturated ethanol quenching vapour was used for detecting the exoelectrons. The sample temperature, controlled using a Ni-CrNi thermocouple with an accuracy of about 5 K, was changed at four constant heating rates (2, 5, 10 and 20 K/min). The sample surface was irradiated during the measurements by unfiltered radiation from a quartz lamp with a Q-400 burner.

The calorimetric investigations of the volume retrification were performed at five heating rates (1, 2, 5, 10 and 20 K/min) using the NETZSCH DSC 404/3/F differential calorimeter with E-type thermocouple using an empty crucible made of high density Al₂O₃ as references.

All the EEE and DTA measurements were performed in air atmosphere under ambient pressure.

3. Results and discussion

Temperature dependencies of the intensity of photostimulated exoelectron emission and of the DTA signal were measured at different heating rates. The shape of the registered termograms and of the temperature dependencies of the EEE intensity for all the samples is very similar. All of them display single peaks corresponding to the retrification in the volume (DTA) or in the surface layer of investigated samples. The positions of these peaks, and their intensities for different chemical composition are different and depend on the heating rate.

As an example, on Fig. 1 the temperature dependencies of the EEE intensity and of the DTA signal for As₂₉Se₇₀Bi₁, measured at different heating rates, are presented. The temperature dependencies of the intensity of exoelectron emission presented in Fig. 1 display a maximum coinciding with the endothermal effect occurring on the DTA curves. The temperatures of these anomalies occurring on both the EEE and DTA curves systematically increase with increasing the heating rate. The process responsible for the effects displayed by the EEE (surface sensitive method) and DTA (volume sensitive method) is the retrification process occurring in the surface layer and in the volume of investigated sample, correspondingly. The temperature of the anomalies occurring on the DTA and EEE curves presented in Fig. 1 systematically shift toward higher values with increasing the heating rate. This confirms that the process responsible for the occurrence of these anomalies (retrification) is a thermally activated process.

Measurements of the temperature dependencies of EEE intensity at four different heating rates, and the DTA curves at five heating rates, enabled the determination of the activation energy for the retrification process on the surface and in the volume of the samples, responsible for the occurrence of the maxima on the EEE and DTA curves, correspondingly. Activation energy was determined using the well-known Ozawa relation [11]:

$$\ln V = A – E/kT$$
where \( V \) is the heating rate, \( A \) – constant, \( E \) – activation energy, \( k \) – Boltzmann’s constant and \( T \) – transformation temperature.

![Graph showing temperature dependencies of EEE intensity and DTA signal](image)

**Figure 1.** Temperature dependencies of the intensity of photostimulated exoelectron emission (EEE) and DTA signal for As\(_{30}\)Se\(_{70}\)Bi\(_1\) glass. Parameter – heating rate in K/min.

The dependencies of the transformation (retrification) temperatures \( T \), determined from the temperature dependencies of the EEE intensity and DTA signal, on the heating rate \( V \), represented in the Ozawa coordinates \( \ln V = f(1/T) \) - so called Ozawa plots for As\(_{30}\)Se\(_{70}\) and As\(_{29}\)Se\(_{70}\)Bi\(_1\) samples are shown on Fig. 2. The retrification temperature \( T \) has been determined from the position of the maximum on the EEE curves [12], and as the deflection point (from the base line) on the DTA curves [13]. The shapes of the Ozawa’s plots for the second pair of investigated glasses (As\(_{30}\)Se\(_{70}\) and As\(_{29}\)Se\(_{70}\)Bi\(_1\)) differs from those shown in Fig. 1 only by their slope.

**Figure 2.** Ozawa’s plots for the surface (EEE) and volume (DTA) retrification temperatures of As\(_{30}\)Se\(_{70}\) and As\(_{29}\)Se\(_{70}\)Bi\(_1\) glasses.

Activation energy of the retrification process is a parameter characterizing well the thermal stability of amorphous materials. The values of the activation energy for the retrification process in the
surface layer and in the volume of four investigated materials determined in present study on the basis of systematic EEE and DTA investigations by Ozawa method are collected in Table 1.

Table 1. Activation energies for the volume and surface retrification of investigated chalcogenide glasses as determined from the DTA and EEE measurements.

| Composition       | Surface retrification | Volume retrification |
|-------------------|-----------------------|----------------------|
| As$_{20}$Se$_{80}$ | 1,10                  | 1,61                 |
| As$_{19}$Se$_{80}$Bi$_{1}$ | 0,83               | 1,56                 |
| As$_{30}$Se$_{70}$ | 1,28                  | 1,62                 |
| As$_{29}$Se$_{70}$Bi$_{1}$ | 0,67               | 1,38                 |

The data collected in Table 1 permit to conclude that:
1. The activation energy for both the surface and the volume retrification of arsenic selenide glasses increases with increasing the arsenic content. This agrees well with the results of our previous studies [7,8].
2. Admixture of bismuth causes a distinct lowering of the activation energy for retrification of arsenic selenide glasses. This effect is most probably caused by formation of coordination defects and even mixed As$_2$Se$_3$ – Bi$_2$Se$_3$ nanocrystallites, observed in [10].
3. The combination of the EEE and DTA methods would be very useful and efficient in investigations of the crystallization kinetics of structural transformations and of the thermal stability of chalcogenide glasses.
Further studies are in progress.

4. Acknowledgments
The authors are very grateful to Prof. O. Shpotyuk and Dr R. Golovchak for kind donation of the samples of investigated materials.

References

[1] Saiter J M 2001 Physical ageing in chalcogenide glass J. Optoelect. Adv. Mat., 3 685-694
[2] Ohta T, Birukawa M, Yamada N and Hirao K 2002 Optical phase change and magneto-optical recording J. Magn. and Magn. Mater. 242-245 108-115
[3] Golovchak R, Górecki Cz, Kozdraś A and Shpotyuk O 2006 Physical ageing effects in vitreous arsenic selenides Sol. State Commun. 137 67-69
[4] Golovchak R, Shpotyuk O, Shpotyuk M, Górecki Cz and Kozdraś A 2005 Ageing effects in As$_{10}$Se$_{90}$ chalcogenide glasses induced by γ-irradiation Ukr. J. Phys. 50 690-693
[5] Wagner T, Kasap S O and Petkow K 1997 Temperature-modulated differential scanning calorimetry studies of the structure of bulk and thin film Ge$_x$As$_{1-x}$S$_{60}$ chalcogenide glasses J. Mat. Sci. 32 5889-5893
[6] Górecki Cz, Górecki T and Michno Z 1987 Thermal stability of the Fe$_{10-x}$Ni$_x$Cr$_{20}$ metallic glasses as studied by the EEE and DTA methods Acta Phys. Polon. A72 157-160 Thermal stability of the Ni$_{85}$Si$_{15}$B$_{22}$ metallic glasses as studied by the EEE and DTA methods Acta Phys. Polon. A72 161-163
[7] Górecki Cz, Górecki T, Golovchak R Żurawska A and Wacke S 2005 Kinetics of phase transitions in semiconducting amorphous chalcogenides As$_{100-x}$Se$_x$ as studied by differential thermal analysis and exoelectron emission techniques Visnyk Lviv Univ. 38 399-403
[8] Górecki Cz, Górecki T, Kozdraś A and Golovchak R. 2007 Kinetics of phase transitions in vitreous chalcogenide semiconductors As$_{100-x}$Se$_x$ as studied by differential thermal analysis (DTA) and exoelectron emission (EEE) methods Visnyk Lviv Univ. 40 254-260
[9] Górecki Cz and Górecki T 2007 Structural transformations in amorphous selenium as studied by the differential thermal analysis and exoelectron emission technique J. of Phys. 79 1-5
[10] Golovchak R, Shpotyuk O, Kovalskiy A, Miller A C, Cech J and Jain H 2008 Coordination
defects in bismuth-modified arsenic selenide glasses; High-resolution x-ray photoelectron spectroscopy measurements Phys. Rev. B 77 172201 1-4

[11] Ozawa T 1970 Kinetics of non-isothermal crystallization of amorphous materials J. Thermal Anal. 2 301-312

[12] Sujak B and Górecki T 1973 Egzoemisja elektronów podczas przemian fazowych i reakcji w ciałach stałych Wiadomości Chemiczne 37 361-384

[13] Schultze D 1974 Termiczna Analiza Różnicowa (PWN Warszawa)