Structural transformations in amorphous selenium as studied by the differential thermal analysis and exoelectron emission technique

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Abstract. The parameters (temperature, activation energy) of the surface and volume glass transition (retrification process) in amorphous selenium produced by rapid quenching of the liquid phase have been determined using the EEE and DTA techniques. EEE is a surface effect connected with structural transformations in the surface layer whereas the DTA measurements give the information about the transformations occurring in the volume of the sample. It has been found that the surface retrification of selenium occurs with activation energy smaller than the volume retrification, both observed in the first heating run. The value of activation energy for the volume retrification measured in the second DTA heating run is higher compared with that measured in the first heating run. Irradiation with X-rays accelerates both the surface and volume retrification of amorphous selenium.

1. Introduction

Amorphous semiconductors are the subject of intensive research effort spurred by both the scientific and technological interest. Owing to their unusual combination of various physical properties they are used or are considered as prospective materials in numerous advanced technological applications (microelectronics, optoelectronics, etc.) [1-3]. The applications are, however, limited by their thermodynamic instability. Amorphous semiconductors obtained by quenching from the liquid phase tend to change their structure in two subsequent processes: retrification (glass transition) and crystallization. Both of them are thermally activated processes causing distinct changes in physical properties.

In order to assess the thermal and temporal stability of glassy semiconductors one has to determine the activation energies for both the processes and transition temperatures determined at well defined heating rate. There is an additional complication stemming from the fact that structural transformations in the surface layer and in the volume of materials may occur at different temperatures and with different activation energies. In addition, all of these parameters depend on a variety of factors (quenching rate and temperature, irradiation, mechanical treatment, etc.).

In a series of papers [4-7] we demonstrated that the surface - sensitive exoelectron emission (EEE) in combination with conventional volume – sensitive techniques (differential thermal analysis – DTA, differential scanning calorimetry – DSC, thermomagnetometry, etc.) is a very useful tool in studies of the thermal and temporal stability of amorphous materials by permitting to determine the transition temperatures and activation energies for structural transformations on the surface and in the volume of various metallic and semiconducting glasses. Among others we already have investigated the crystallization kinetics of amorphous selenium, interesting, almost model, amorphous semiconductor and component of many interesting glassy semiconducting compounds obtained by
liquid quenching, vapor condensation and intensive ball milling. The effect of various factors (X-ray irradiation, quenching temperature, etc.) on the crystallization kinetics has been investigated, too.

The purpose of the present communication is to present the results of investigations of the volume and surface reorientation kinetics of liquid quenched amorphous selenium, as well as of the effect of X-ray irradiation on the temperature of both the volume- and surface reorientation.

2. Experimental conditions

All the samples used in the present study were prepared from metallic (grey) 5N purity, selenium supplied by POCh Gliwice. Nominally, the material should be fully crystalline, but control DTA measurements revealed the presence of a distinct amount of amorphous phase. The fully amorphous (black) selenium was produced by quenching a stream of liquid selenium, tempered at 570 K, in water at room temperature.

Prior to the measurements some of the amorphous selenium samples were irradiated with X-rays from a radiation generator SL201 with a Roentgen lamp GE 200/58 working at 141 kV and 5 mA.

Measurements of the temperature dependencies of the intensity of photostimulated exoelectron emission (EEE) were carried out by means of the arrangement described in [8]. An open air point counter with saturated ethanol quenching vapour was used for detecting the exoelectrons. The sample temperature, controlled using Ni-CrNi thermocouple with an accuracy of about 5 K, was changed at four constant heating rates (2, 5, 10 and 20 K/min). During the measurements the sample surface was irradiated with unfiltered radiation from a quartz lamp with a Q-400 burner.

The calorimetric investigations of the volume reorientation were performed at six heating rates (0.5, 1, 2, 5, 10 and 20 K/min) using the NETZSCH DSC 404/F differential calorimeter with E-type measuring head and high-density Al$_2$O$_3$ sample pans. An empty high-density Al$_2$O$_3$ crucible was used as the reference. All the EEE and DTA measurements were performed in ambient air.

3. Results and discussion

The DTA curve for as quenched selenium sample registered at the heating rate of 20 K/min in the temperature range extending over the broad temperature range (RT – 550 K) including the melting transition, is presented in Fig. 1. Three thermal effects are clearly visible on this thermogram: a weak low-temperature endotherm (320-330 K) connected with the reorientation process, the product of which is relaxed glassy selenium with structure corresponding to that of overcooled liquid phase and a distinct exotherm (370-430 K) corresponding to the crystallization of glassy selenium. With further rising the temperature, the product of this process (crystalline grey selenium) melts, which is manifested by an intensive endotherm (490-520 K). The temperature dependencies of EEE intensity.
registered at the same heating rate displayed maxima more or less coinciding with the three structural transformations observed on the DTA curve.

In the present study we concentrated on the retrification process. For this purpose, at each of the five heating rates the DTA curves for each sample were registered in two subsequent heating runs. In the first heating run the as-quenched sample was heated at a chosen heating rate up to 355 K. Next, each of the samples was cooled down to the room temperature at a constant cooling rate of 1 K/min. After reaching the room temperature, the second heating run was started with the heating rate the same as in the first heating run. All this procedure was realized without removing the sample and the measuring head from the furnace of the DSC apparatus.

In EEE measurements only one heating run was possible, because our measuring set does not allow for cooling of the sample at a controlled, constant cooling rate.

A comparison of the DTA traces and temperature dependencies of the EEE intensity, registered at different heating rates is presented on Fig. 2. As it is seen, all the DTA and EEE curves display extrema in the temperature range corresponding to the retrification of investigated material. The positions of the EEE maxima, corresponding to the surface retrification are systematically shifted towards higher temperatures as compared with corresponding DTA endotherms revealing the volume retrification. The volume retrification temperatures registered in the second DTA run are systematically lower than those observed in the first heating run (see DTA curves 2 and 2 II on Fig. 2 and data points for DTA in Fig. 3). With increasing the heating rate, both the DTA and EEE extrema systematically shift towards higher temperature. The last effect is typical of thermally activated processes and allows for determination of the value of activation energy.

The activation energies for the volume- and surface retrification processes observed in the DTA and EEE experiments, correspondingly, have been determined by the method proposed by Ozawa [9]. For this purpose the so called Ozawa’s plots \( \ln \nu = f(1/T) \) (Fig. 3) were constructed, where \( T \) denotes the transition temperature determined at the heating rate \( \nu \). For DTA data, \( T \) has been determined from the deflection point of endotherm from the base line. In the case of EEE, \( T \) corresponds to the position of the maximum of the EEE curve on the temperature scale. As it is seen

![Figure 2](image-url)
from Fig. 3, the data points for surface retrification (EEE) and for volume retrification (DTA) observed in two subsequent heating runs (lines I and II), are located along straight lines. The slopes of these lines multiplied by the Boltzmann’s constant give the values of activation energies, indicated in Fig. 3.

![Ozawa’s plots](image)

**Figure 3.** Ozawa’s plots for the surface (EEE) and volume (DTA) retrification temperatures. I and II denote the volume retrification temperatures determined in the first and the second heating run, correspondingly.

As it is seen, the value of activation energy for the surface retrification (EEE measurements) is more than two times higher than that for the volume retrification (DTA experiments). Moreover, the activation energy for volume retrification observed in the first heating run is distinctly lower than that in the second heating run. This is manifestation of the effect of the thermal history of the sample on the retrification kinetics.

![Effect of irradiation time](image)

**Figure 4.** Effect of the irradiation time (dose) on the surface (EEE) and volume (DTA) retrification temperature of as-quenched amorphous selenium.

Figure 4 represents the results of the investigation of the effect of X-ray irradiation on the retrification temperature, determined from the DTA and EEE measurements on as-quenched selenium, performed in the first heating run at the same constant heating rate of 20 K/min. As it is seen, with
increasing the irradiation time (dose) the temperatures of both the surface (EEE) and volume (DTA) retrification systematically shift toward lower value, with a tendency to stabilize at the level of about 315 K for prolonged irradiation time. This observation confirms the effect of irradiation on the stability of the structure of investigated material, observed also for other amorphous materials. The effect of X-ray irradiation on the retrification kinetics deserves further, more detailed studies, which are in progress.

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