

ELECTRICAL CONDUCTION IN $\text{As}_2\text{Te}_{2.8}\text{Si}_{3.2}$ BULK TERNARY GLASS

M. Leonovici

Department of Solid State Physics, Faculty of Physics, University of Bucharest,
POB MG. 5, Bucharest-Magurele, Romania

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1. Introduction

Chalcogenide glassy semiconductors have specific characteristics that can be applied to devices. They show a continuous change of various properties with the change in chemical composition. They are easily prepared in large size as homogeneous glasses. They are not attacked by moisture, organic solvents and some strong acids and are well wetted by various metals [1].

Since switching phenomena were observed in several vitreous semiconductors [2], the electrical properties of chalcogenide glasses have attracted much attention. Some attempts have been made to explain the switching properties of chalcogenide glasses on the basis of thermally induced structural transformations [3].

On the other hand, in all glasses, conditions may occur in which the self-generated Joule heat exceeds the capacity of the system to dissipate it. The current increases with the temperature, which leads to more Joule self-heating and the consequent thermal runaway. Chalcogenide glassy semiconductors have large negative temperature coefficients of electrical resistivity and low thermal conductivity, so thermal runaway must always be considered as a possible breakdown mechanism in high electrical fields. Even if it is not the dominant mechanism which gives rise to the switching process, thermal effects are likely to be present and their influence must be understood [4].

Generally speaking bulk samples have been studied less than thin amorphous films. The bulk alloy $\text{As}_4\text{Se}_3\text{S}_3$ has been systematically characterized in terms of the runaway process [4]. The relationship between low-voltage ohmic resistance and temperature has been carefully investigated.

The structure and properties of ternary glasses are less understood. Recently, several studies on thin binary chalcogenide films doped by metals have been carried out [5, 6]. The As-Te glasses allied with silicon or germanium are important because the interaction between very different components results in local chemical environments at variance with those of the crystalline compounds, in addition to the topological disorder.

In this paper we have studied the electrical conduction properties of a typical glass from the system As-Te-Si. A large domain of glass formation characterizes the system. The glass temperature, T_g , decreases with the increase of the tellurium content and increase with the increase of the silicon content. The investigated composition is situated not very far from the glassy composition with the highest softening temperature: $\text{As}_2\text{Te}_4\text{Si}_4$.

2. Experimental

The preparation of the glasses followed the standard procedure described in the literature. The proper amount of the starting materials (As of 5n purity, Te of 4n purity and Si of 5n purity) was sealed in a quartz ampoule under vacuum (10^{-6} Torr). The ampoule was heated in a furnace up to 950°C for 24 h. After melting and homogenization the content of the ampoule was quenched in water. The aspect of the fracture and, also, the optical microscopy investigation has shown that the ingots are

in the vitreous state. The non-crystalline state of the ingot has been checked, also, by X-ray diffraction analysis in a TUR M62 diffractometer provided with Ni target and proportional counter.

The samples intended for electrical measurements were sawn from the ingots and polished with alumina powder and diamond paste. Evaporated aluminum films were employed as electrodes and found to make ohmic contact with the samples. The size of a typical parallelepiped sample was $7 \times 6 \times 2 \text{ mm}^3$. The electrical measurements were performed in dark, in the temperature range 14–389 °C, in normal atmosphere. The temperature was controlled to within $\pm 0.5 \text{ }^\circ\text{C}$. The direct current conductivity was measured by the conventional method using a dc Keithley electrometer.

3. Results and discussion

The first electrical conduction measurement was made in the range 14–132 °C, running a virgin sample forth and back down to 62.5 °C. Fig. 1 shows the results. It is remarkable the region from 14 to 44 °C, where the plot does not exhibit a perfect linearity. Moreover, at the end of this low temperature interval one observes a step in the conductivity curve (at $\sim 3.18 \text{ K}^{-1}$). The behaviour of the electrical conductivity in this region is probably due to the influence of the water adsorbed on the sample surface. The conductivity curve in the region 44–132 °C shows a nearly perfect linearity. When the temperature decreases no hysteresis is observed.

From the slope of the Arrhenius graph we have determined an activation energy for conduction of 0.756 eV. This value corresponds to half of the width of the mobility gap of the glass.

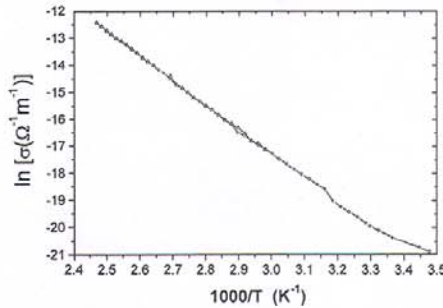


Fig. 1 Arrhenius plot of the electrical conductivity of a vitreous sample of composition $\text{As}_2\text{Te}_{2.8}\text{Si}_{3.2}$ in the temperature range: 14–132 °C.
ooooo heating regime $\Delta\Delta\Delta\Delta$ cooling regime.

Further, we have measured another sample, cut from a different ingot, from the room temperature up to 345 °C. The results are shown in Fig. 2. A surprising deviation from linearity was observed in the high temperature part of the plot starting from 175 °C. We have ascribed the peculiar behaviour to an irreversible transformation in the glass due to a phase change in the glassy state.

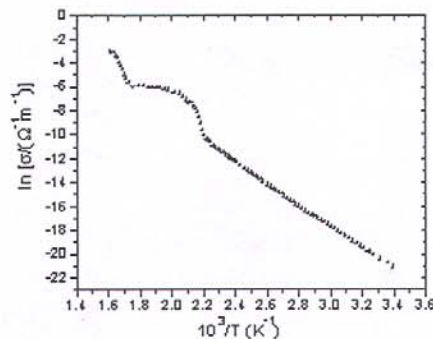


Fig. 2 The Arrhenius plot of the $\text{As}_2\text{Te}_{2.8}\text{Si}_{3.2}$ glassy sample for the temperature range 21–345 °C.

An other experiment consisted in the measurements performed on an other glassy sample (virgin) starting from the temperature of 125 °C and ending at 389 °C. Fig. 3 shows the results. The large anomaly in the conductivity curve is reproduced although with a broader extension towards high temperatures.

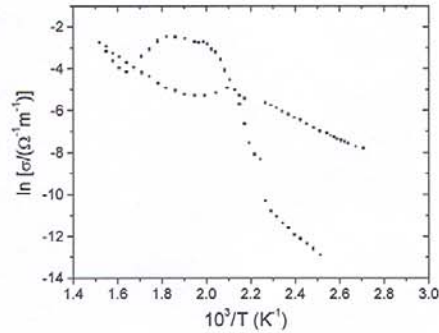


Fig. 3 The Arrhenius plot of the $As_2Te_{2.8}Si_{3.2}$ glass in the temperature range 125 – 389 °C.

We note that the differential thermal analysis of the same material has evidenced for a heating rate of 10 K/min an endothermic peak at 382 °C (for some samples the position of the peak was recorded at 366 or 378 °C) which can be ascribed to a phase transformation in the vitreous state. As shown by Platakis [7] the bulk As_2Te_3 phase melts at 374 ± 1 °C. This temperature is situated in the vicinity of the endothermic peak experimentally observed and this fact speaks in favour of the existence of a phase separated As_2Te_3 in the ternary sample. We remark that Asokan and Gopal [8] has shown that in the system Si-Te, the glassy composition $Si_{10}Te_{90}$ melts at 383 °C. This fact leads us to the suggestion that the silicon-tellurium alloy together with As_2Te_3 might be both responsible for the endothermic peak at 382 °C.

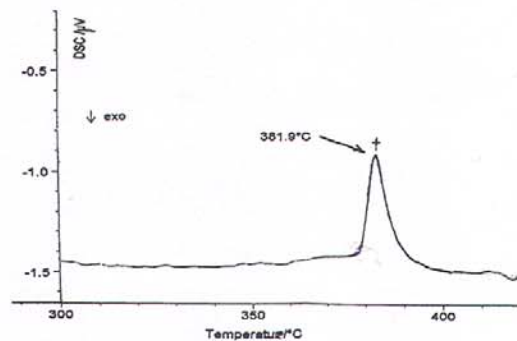


Fig. 4 The differential thermal analysis (DTA) curve for the heating regime of a sample of glassy $As_2Te_{2.8}Si_{3.2}$.

After reaching the maximum temperature the sample was slowly cooled and the measurements were continued down to 95 °C. The most interesting feature was the complete change of the conductivity curve. It becomes nearly linear, the bump in the curve nearly disappeared. At the end of the measurement the conductivity of the sample are five order of magnitude larger than for the initial measurement. This result has been interpreted as the consequence of an irreversible transformation related to the changes in the amorphous phase (or phases) of the sample. Nevertheless,

the differential thermal analysis of the investigated glass has shown that the T_g temperature is situated at 443 °C. Therefore, no important transformation in the sample can be supposed. The X-ray diffraction patterns taken after heating and cooling have shown that the sample preserved the vitreous state and no crystalline phases were formed. Therefore we are forced to suppose that the change in conductivity is due to the changes of the microphases which are present in the virgin samples. These microphases are probably based on tellurium. The difference between the position of the conductivity anomaly and the DTA endothermic peak can be due to the rate of heating. During the electrical conductivity measurements the temperature variation was much slower: only 1 K/min. In this case the transformation evidenced by the DTA peak should be produced at a lower temperature, so that the possibility to correlate this peak with conductivity anomaly becomes more realistical.

5. Conclusions

DC electrical conductivity of vitreous $As_2Te_{2.8}Si_{3.2}$ has been investigated. Up to 132 °C the glass is remarkably stable. A large bump in conductivity was observed in the range 175-370 °C. At the end of this temperature range, a small endothermic peak has been observed on the DTA curves. When the heating overcomes the position of the conductivity anomaly during cooling the conductivity maintains values that are higher than those obtained in the heating regime. At room temperature the conductivity is five order of magnitude larger than the initial conductivity. The peculiar behaviour of the electrical conductivity with the temperature demonstrates the possible existence of an irreversible change in the bulk glassy samples at the level of the glassy microphases separation.

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