On Electronic Conduction in the Pre-switching Region of Glassy Semiconducting Alloys $As_{40}Se_{30}Te_{30}$ and $As_{20}Se_{50}Te_{30}$

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Abstract

The off-state direct current I–V characteristics for glassy alloys $As_{40}Se_{30}Te_{30}$ and $As_{20}Se_{50}Te_{30}$ at different temperatures were studied. For this study of electrical conduction properties, two kinds of electrode configurations were used: a double-point contact on one surface and a sandwich device. It was found that current flow can be space-charge limited, producing non-ohmic behaviour, which in turn reflects on the electrical switching effect that the materials exhibit. The influence of the selenium content on the electrical properties was also studied. The experimental results obtained were compared with those in the literature, and the differences justified by the method of material preparation. Lastly, the dependence of ohmic resistance on temperature was analyzed, and the characteristic behaviour of intrinsic semiconduction observed.

1. Introduction

During the past few years, a remarkable experimental effort has been made, aimed at characterizing the electrical properties of a large variety of chalcogenide glasses [1]. The main reasons for this attention is the discovery of reversible electrical switching, a phenomenon of great technological interest [2, 3]. However, in spite of the abundance of experimental results, there is still a demand for information on specific aspects of bulk samples of these materials, such as non-linear off-state I–V characteristics, which show the presence of very important electronic processes. Some of the basic processes are space-charge limited current [4] and field-assisted release of carriers from shallow trapping levels [5, 6].

The aim of this paper is to determine experimentally the direct current (d.c.) current–voltage characteristics, at different temperatures, of the glassy alloys $As_{40}Se_{30}Te_{30}$ and $As_{20}Se_{50}Te_{30}$. These are interpreted using an electronic conduction model. To carry out a more complete study, two types of electrode system were used: one consisting of two-point contacts the other of sandwich-type. The influence on electrical switching of the electronic effects which cause non-ohmic behaviour in the pre-switching region, and the effect of an increase in selenium content on electrical properties, were also studied.

2. Experimental procedure

The samples were prepared using the melt-quench method in a mixture of water and ice [7]. The glass ingot thus obtained was broken up, and the pieces were inlaid in epoxy-type resin. Afterwards, the samples were polished with 0.3 μm and 0.05μm alumina powder until mirror-like surfaces were obtained. Non-crystallinity was tested by X-ray diffraction. The well-defined peaks characteristic of crystalline materials were absent.

The glassy-forming region of the As–Se–Te system can be divided into two zones: one that does not crystallize with differential thermal analysis (DTA) and one that does [8]. The alloys studied are located in the crystallization zone, although they are very close to the limit between the zones. A characterization of the samples through calorimetry (DSC-2 Perkin-Elmer) was also carried out. Figure 1 shows, as an example, the thermogram for glassy alloy $As_{40}Se_{30}Te_{30}$. The heating rate was 1.25 °C min^{-1}, and 20 mg of powdered sample were used. The thermogram shows glass transition ($T_g \approx$ 125 °C), and also three exothermic crystallization peaks, the first two overlapping. Three endothermic peaks also appeared, and the first two of these overlapped.

Two electrode devices were used to obtain d.c. I–V characteristics. The characteristics of the one with two contact points are described elsewhere [9]. Its electrode material is tungsten, the distance between the points is about 3.0 mm, and the curva-

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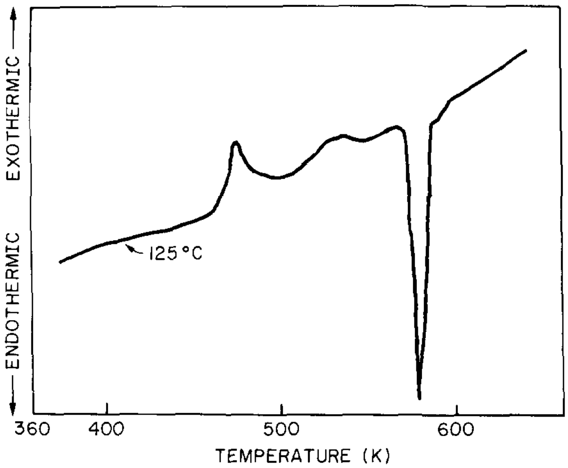


Fig. 1. Thermogram for glassy alloy $As_{40}Se_{30}Te_{30}$ (heating rate was 1.25 °C min^{-1}).

ture radius of the electrode tip is approximately 20 μm. In the sandwich-type device, the electrode material is silver paste, and the glass sample is 1.9 mm thick. Rectangular voltage pulses, of increasing amplitude and width 60 s, were used (power supply, HP6521A). After electrical stimulation, the sample was allowed to cool, to recover its initial resistance. An electrometer (Keithley model 602) was used to measure the current. In the experiments with the device with point contacts, at different temperatures, a furnace was adapted to it, with a temperature controller (OMRON E 5K) with an accuracy of ± 0.2 °C. To measure temperature, a chromel–alumel thermocouple was used. For the sandwich device, the thermocouple was located in the sample holder of the calorimeter, so temperature regulation was carried out precisely by the controller of this apparatus. Through this unusual use of the calorimeter, it was possible to measure the heat emitted by the device when the current passed through the sample.

3. Results and discussion

3.1. D.C. I–V characteristics at different temperatures

To determine accurately the current at $t=0$ (the instant at which electrical stimulation is applied), the values of the current at different instants, during electrical stimulation, were adjusted to the phenomenological time dependence characteristic of this type of material [10]

$$I(t, V; T) = I(0, V; T) + \Delta I_{\mathrm{JH}}(\infty, V; T)\left(1 - \exp\left(\frac{-t}{\zeta_{\mathrm{th}}}\right)\right) \quad (1)$$

where ζ_{th} is a time constant which characterizes the thermal process that takes place and $\Delta I_{\mathrm{JH}}(\infty, V; T)$ is the current increase resulting from the Joule effect, in the steady state, for voltage V and temperature T. In this way, by taking $t=0$ in this functional model, the initial current, with applied voltage V and temperature T, $I(0, V; T)$, is determined. By this procedure, Joule self-heating and the effects derived from an increase in the temperature of the sample are avoided. So the electronic effects existing in high-field electrical conduction, which cause non-ohmic behaviour in the pre-switching region, can be isolated [7, 10].

Figure 2 shows the off-state I–V characteristics at different temperatures for alloys $As_{40}Se_{30}Te_{30}$ and $As_{20}Se_{50}Te_{30}$. In the interest of clarity, only a few of the temperatures studied are shown. The voltage range analyzed is limited, obviously, by the threshold voltage or minimum voltage at which switching is generated, and the highest voltage applied was, in all cases, below 1 kV, since that is the maximum for the power supply used.

3.2. Interpretation of off-state non-linear I–V characteristics

The above results fit the functional dependence

$$I(0, V; T) = G_{\Omega}(T)\, V \exp\left[\frac{V}{V_0(T)}\right] \quad (2)$$

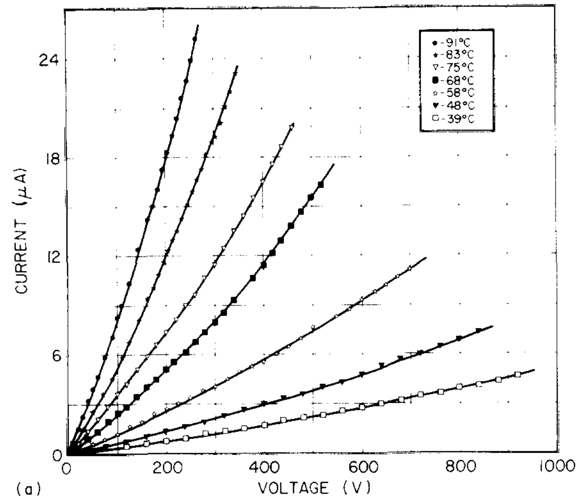
which can be rewritten as

$$G(V, T) = G_{\Omega}(T) \exp\left[\frac{V}{V_0(T)}\right] \quad (3)$$

where G is the electrical conductance, G_{Ω} is the ohmic conductance and V_0 is a parameter which depends on temperature. For both alloys, and at all temperatures, regression analysis gave a correlation coefficient superior to 0.99, which shows a high degree of reliability. Equation (3) may correspond to the single-carrier space-charge limited current flow (SCLC) model, with a Fermi level in a uniform trap distribution [11], and the model corresponding to field-assisted carrier release from shallow trapping levels. In this last mechanism, at sufficiently intermediate voltages, the electrical conductance expression is of the type [6]

$$G(V, T) = G_{\Omega}(T) \frac{\sinh(reV/k_{\mathrm{B}}TL)}{(reV/k_{\mathrm{B}}TL)} \quad (4)$$

where r is the effective radius of the trapping centre, k_{B} is the Boltzmann constant, e is the electronic



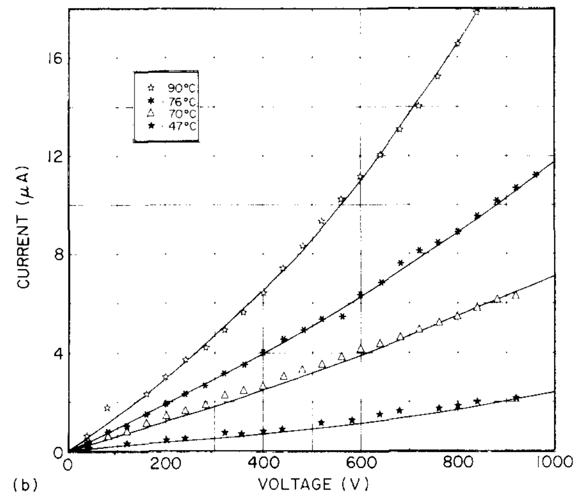


Fig. 2. Current–voltage characteristics at different temperatures, in a double-point contact configuration for: (a) alloy $As_{40}Se_{30}Te_{30}$; (b) alloy $As_{20}Se_{50}Te_{30}$.

charge and L is the interelectrode distance. This expression, at sufficiently high voltages, and considering a square-well-type trapping centre, becomes eqn. (3) [6]. In this conduction mechanism, the expression of V_0 is

$$V_0 = \frac{k_B TL}{a(T)e} \tag{5}$$

in which $a(T)$ is the temperature-dependent activation distance, and eqn. (3) is valid for voltage values higher than parameter V_0. (According to this mechanism, transition to ohmic behaviour takes place at voltages $V \lesssim V_0$.) However, the values of V_0 determined by adjusting the experimental data to eqn. (3) are remarkably higher than the applied voltages, which is inconsistent with the necessary conditions for the application of eqn. (3).

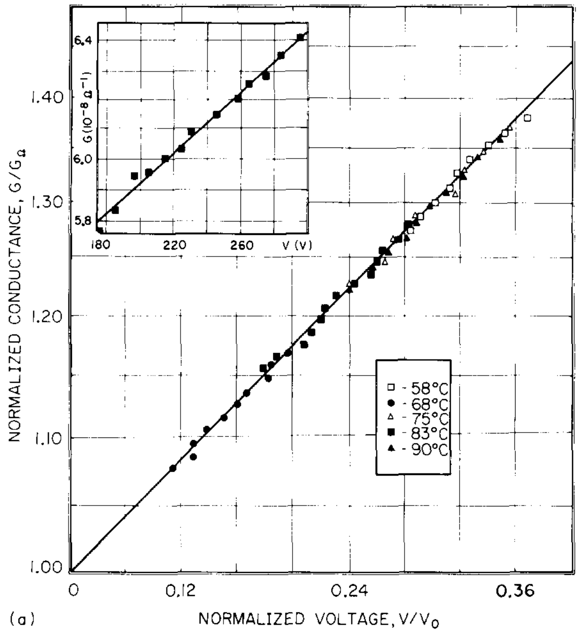
On the other hand, when the experimental values are adjusted to eqn. (4), the fit is worse than that found for the functional dependence of eqn. (3); *i.e.* the electrical conductance expression corresponding to the conduction model associated with carrier release from shallow traps at intermediate voltages is not valid either. Besides, returning to eqn. (5), as the experimentally-found dependence between V_0 and T is linear, the existence of an activation length dependent on temperature, as predicted by the carrier release model, would not be possible in these conditions. However, this experimentally-determined V_0–T dependence agrees with that for the SCLC model. Also, the value of $a(T)$ determined through the experimental results corresponding to the present work is approximately 178 Å, and this is much higher than those quoted in the literature (the highest is 40 Å, and corresponds to the lowest of the temperatures, $T \approx 60$ K, as $a(T)$ decreases when temperature increases) [6]. Another interesting case, within the carrier release mechanism from shallow traps, is the coulombic centre, whose behaviour at high voltages is the familiar Poole–Frenkel effect. The dependence between electrical conductance and voltage is, in this effect

$$G(V, T) = G_\Omega(T)\exp\left(\frac{\beta V^{1/2}}{k_B TL^{1/2}}\right) \tag{6}$$

in which β is a parameter which depends on the dielectric constant of the material. As in eqn. (4), the adjustment of the experimental data to the functional form of eqn. (6) is inferior to that found for eqn. (3). As a consequence of this analysis, the experimental results will be discussed in terms of the SCLC conduction model, as the evidence presented allows hope for the validity of this model for the glassy alloys under study.

Figure 3(a) shows, on a semi-log scale, the normalized experimental values for alloy $As_{40}Se_{30}Te_{30}$ using point contacts, *i.e.* representing $G(V, T)/G_\Omega$ *vs.* $V/V_0(T)$, so all points are adjusted to the same line. The same figure shows the non-normalized results for a temperature of 83 °C. Figure 3(b) shows the normalized values for alloy $As_{20}Se_{50}Te_{30}$, and the non-normalized values for a temperature of 90 °C. As in the double-point configuration, the experimental values for the sandwich configuration fit the functional dependence of eqn. (2); *i.e.* the SCLC electrical conduction model may also be valid. The distribution of the localized states in the pseudo-gap is not, therefore, of the exponential type proposed by Hulls and McMillan for bulk samples of binary glasses obtained from the

As-Se-Te system [12]. Moreover, their experiments also showed that when copper or silver were used, there was no ohmic contact (there is no charge reserve, in the semiconductor-electrode interface, that could be injected into the appropriate band by applying an electric field), whereas there was with gold. In the present work, silver was observed to make good electrical contact, as non-linear current-voltage characteristics were found (these constitute experimental proof of the existence of ohmic contact, if we admit that the SCLC conduction process can take place).



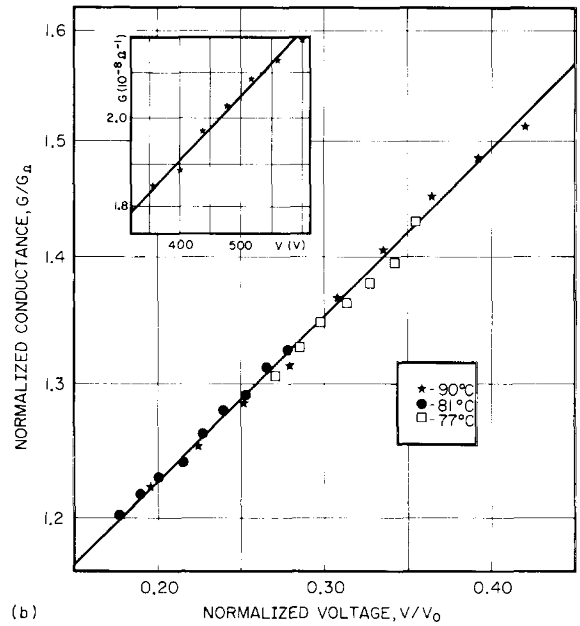


Fig. 3. Normalized electrical conductance G/G_Ω, *vs.* normalized voltage V/V_0 at different temperatures for: (a) alloy $As_{40}Se_{30}Te_{30}$; (b) alloy $As_{20}Se_{50}Te_{30}$.

The dependence of parameter V_0 on temperature, for alloy $As_{40}Se_{30}Te_{30}$, is shown in Fig. 4. It may be noted that there is a linear relationship between both parameters in the temperature range studied (between room temperature and approximately 30 °C below glass transition temperature, to prevent the self-heating associated with electrical stimulation from giving way to exceeding temperature T_g). The relationship between V_0 and T in the case of single-carrier SCLC, in a semiconductor whose distribution of localized states in the mobility gap is uniform, is of the type [11, 13]

$$V_0 = eN_t k_B T \frac{L^2}{\varepsilon} \tag{7}$$

where N_t is the density of the traps and ε is the dielectric constant. From the slope of the line represented in Fig. 4, whose value is 5.05 V K^{-1}, and bearing in mind that $\varepsilon = 17.7$ (CGS units) [14], $N_t = 7.2 \times 10^{14}$ eV^{-1} cm^{-3}. This density is similar to the value found by Hulls and McMillan for thin films of the glass $Se_{80}Te_{20}$ [12]. However, the density of the traps might be underestimated; as the values for V_0 are so high and the voltages applied are below 1 kV, the non-ohmic effects are not very relevant, so might be somewhat masked by experimental errors. Furthermore, the simplifying hypotheses in the deduction of eqn. (2) may have contributed to the underestimation of N_t [15]. Parameter V_0 was independent of the selenium content, a fact which results in similar trap densities for both alloys. Work by Owen and Robertson [13] includes

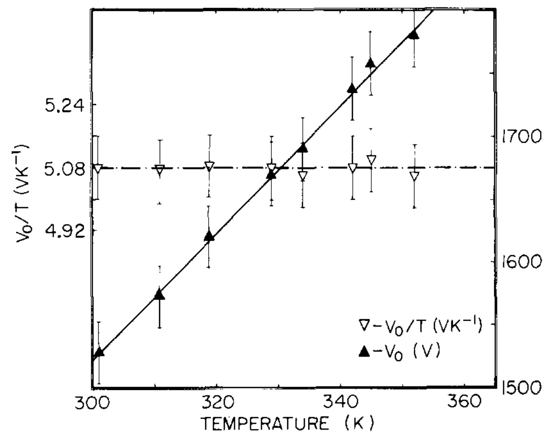


Fig. 4. Dependence of parameter V_0 on temperature for alloy $As_{40}Se_{30}Te_{30}$ in a sandwich configuration.

a figure similar to Fig. 4, which was originally considered evidence in favour of the SCLC model; however, misgivings arose as to its applicability, since the line does not intersect zero, as it should do according to eqn. (7). This is not true for the alloys studied, in which intersection with the V_0 axis is practically null, and so verifies the relationship between V_0 and T for the above-mentioned model within the temperature range under study.

3.3. Other considerations on electrical conduction and its influence on the switching process

The relationship between ohmic resistance R_Ω and temperature was also studied. Figure 5 shows the experimental results for glassy alloy $As_{40}Se_{30}Te_{30}$ with a sandwich configuration. The functional dependence which the experimental values fit is characteristic of intrinsic semiconduction

$$R_\Omega(T) = R_0 \exp\left(\frac{\Delta E}{k_B T}\right) \tag{8}$$

where ΔE is the activation energy for the process of electrical conduction. The value found for ΔE is 0.67 eV, slightly higher than determined by other procedures [16]; this is a consequence of the difficulties in the study of non-ohmic effects. Furthermore, by taking the value of R_0, the area of the cross-section and the thickness of the sample, a value for σ_0 close to $10^3\ \Omega^{-1}\ cm^{-1}$ is obtained. According to Mott and Davis [17], this means that electrical conduction, in the low-voltage off-state region, arises from the transition of carriers to extended states, generated by thermal excitation.

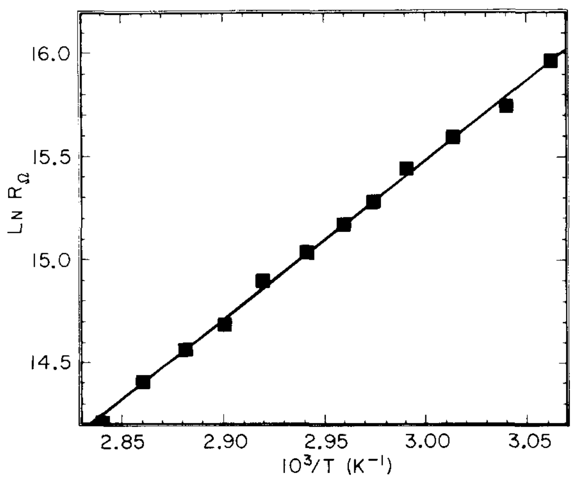


Fig. 5. Semi-logarithmic scale representation of ohmic resistance *vs.* temperature inverse for alloy $As_{40}Se_{30}Te_{30}$.

The reduction in the selenium content of the alloy reduced electrical resistance. This can be explained by the appreciable increase in the number of As–As and As–Te bonds found through structural analysis of these glassy alloys [18, 19]. These bonds are easily ionized (ionization energy is 1.2 eV and 0.9 eV respectively [8]) and so contribute considerably to the generation of charge carriers. The total number of bonds in the glass is related to the mean co-ordination number of the structure, which is 2.4 ± 0.1 for alloy $As_{40}Se_{30}Te_{30}$ and 2.1 ± 0.1 for alloy $As_{20}Se_{50}Te_{30}$, which means that when the selenium content is increased, the total number of bonds decreases.

One important consequence of the electrical behaviour found is that the nature of the switching phenomenon in the alloys studied has an electronic contribution, as the non-linear I–V characteristics show. That is to say, although the switching process in these bulk samples is of a basically thermal origin (Joule self-heating and the inability to evacuate heat are mainly responsible) [7], the existence of non-ohmic effects implies that the phenomenon may be explained by the electrothermal theory [20]. This model predicts a lower threshold voltage than that corresponding to the strictly thermal theory, as electrical power in the presence of non-ohmic effects, $(V^2/R_\Omega(T))\exp(V/V_0)$, is higher than ohmic electrical power, $V^2/R_\Omega(T)$.

4. Conclusions

Regression analyses show that all the results are reliable and constitute data which may shed light on the electronic processes in this type of non-crystalline solid. It has also been shown that the experimental results obey some of the relationships predicted for the SCLC model. However, to confirm the validity of the proposed conduction model, it would be desirable to analyze the dependence on the thickness of parameter V_0. (According to the SCLC process, the relationship ought to be of the type $V_0 \propto L^2$.) The value for N_t found from the V_0 expression (eqn. (6)) is reasonable, constituting additional evidence in favour of the choice of electronic process carried out. The differences found between the results obtained in the present work and those found by Hulls and McMillan [12] can be explained by the differences in the method of preparation of the glasses, and especially by the quenching process. The reason for this is the considerable interdependence between the distribution of localized states and the method of synthesis. Furthermore, SCLC research has proved ideal for studying the distribution of localized states in the mobility gap of amorphous semiconductors. The results presented in this work suggest immediate technological application of these materials in varistor-type electronic devices, owing to their non-ohmic behaviour and simple manufacturing process.

Acknowledgments

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