SOME CONSIDERATIONS ON ELECTRICAL CONDUCTION AND THE SWITCHING PROCESS IN CHALCOGENIDE GLASSES

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Some electrical and switching properties characteristic of chalcogenide glassy semiconductors, obtained by the melt–quench method, were analyzed. A theoretical relationship was found between steady-state current increase and voltage, and was confirmed experimentally. The influence of temperature on ohmic resistance and threshold voltage was also researched. Lastly, a correlation between structural and electrical aspects was attempted, and the electrical resistivity values for the two glassy compositions studied were justified.

1. Introduction

It is a well-known fact that glassy semiconductors exhibit some interesting electrical properties, the most remarkable of which is the reversible switching effect [1–4]. The influence of the addition of metallic elements (Ag and Cu among others) on the physical properties of chalcogenide glasses has also been analyzed, and the subsequent increase in electrical conductivity was found to be advantageous for both the electrical characterization of these materials and their technological applications in the field of electronic devices [5].

In this paper, some electrical properties of the chalcogenide glassy alloy $As_{0.40}Se_{0.30}Te_{0.30}$ and the "metallic" chalcogenide glassy alloy $Cu_{0.15}As_{0.35}Se_{0.50}$ are analyzed. The electrode configuration used in this work is a double point contact on a surface (inter-electrode distance was approximately 1.1 mm). In this way, the previous study on the electrical properties of these semiconducting alloys [6,7] is completed. With this aim in mind, the relation between increase in steady-state current and applied voltage has been determined for $Cu_{0.15}As_{0.35}Se_{0.50}$. The influence of temperature on threshold voltage, V_{th}, and ohmic resistance, R_{Ω}, has also been studied for $As_{0.40}Se_{0.30}Te_{0.30}$. Finally, a justification of the values for electrical resistivity at room temperature has been attempted, based on the ionization energy of the different covalent bonds in the material.

2. Experimental

The bulk glasses studied were obtained using the usual melt–quench method [3]. The structural characterization of the material was done by X-ray diffraction and by differential scanning calorimetry (DSC), and the non-crystalline nature of the ingots was thus confirmed. The samples were prepared for carrying out the electrical measurements by embedding the fragments of the ingot in an epoxy-type resin, and polishing them until mirror-like surfaces were obtained.

The characteristics of the device used in these experiments are described elsewhere [8]. In order to carry out the measurements at different temperatures, the device was put into a cylindrical furnace, and its temperature was regulated by a temperature controller of $\pm 0.5\,^{\circ}C$ precision (Omron E5K). The temperature range studied for each composition is between room temperature and approximately 30 °C below the glass transition temperature. V_{th} was determined by the following criterion: threshold voltage is the first voltage that originates switching, when pulses of increasing amplitude, with a width of

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50 s and an interval of 10 min are applied. All measurements were carried out on virgin surfaces (in the dark and in air), and no trace of oxidation was found in the material.

3. Results and discussion

3.1. Relationship between increase in steady-state current and applied voltage

The $I(t=0)-V$ characteristics of $Cu_{0.15}As_{0.35}Se_{0.50}$ exhibit non-ohmic behaviour, the dependence of electrical resistance on voltage being of the type [6]

$$R(V)=R_{\Omega}\exp(-V/V_0)\,. \tag{1}$$

When a pulse is applied to a sample of these characteristics, current is increased as a result of Joule self-heating. Current increase, $\Delta I_{JH}(V,t)$, for voltage V at instant t, is given by the expression [3,6]

$$\Delta I_{JH}(V,t)=\Delta I_{JH}(V,\infty)[1-\exp(-t/\tau_{th})]\,, \tag{2}$$

τ_{th} being a time constant which characterizes the thermal process originated, and $\Delta I_{JH}(V,\infty)$ the steady-state current increase. Table 1 shows some of the experimental values of the current at the initial instant, $I(V,0)$, the steady-state Joule current increase, and the electrical conductance increase, $\Delta G_{JH}(V,\infty)$, which is a consequence of the temperature increase in the material, and which originates said current increase. The experimental results correspond to a temperature of 26°C.

Table 1
Some values of initial current, steady-state current increase and electrical conductance increase together with their corresponding voltages

Applied voltage V (V)	Initial current $I(V,0)$ (μA)	Current increase $\Delta I_{JH}(V,\infty)$ (μA)	Conductance increase $\Delta G_{JH}(V,\infty)$ (n℧)
110	6.63	0.76	6.9
120	7.51	1.12	9.2
140	10.21	1.62	11.6
150	11.79	1.91	12.7
160	13.23	2.42	15.1
200	17.83	4.48	22.4
220	22.04	6.15	28.0

In order to theoretically find a relationship between steady-state current increase and applied voltage, the steady-state thermal balance equation was taken first (it is assumed that the sample is heated in a uniform manner)

$$VI(V,\infty)=K_{th}(T-T_a)\,, \tag{3}$$

K_{th} being the thermal conductance of the system, and T_a the ambient temperature. The relation between electrical conductance and temperature, characteristic of this type of material, has also been taken into account (this relationship is analyzed in the next section)

$$G(V,T)=G_a(V)\exp\left[\frac{\Delta E_{\sigma}}{k_B}\left(\frac{1}{T_a}-\frac{1}{T}\right)\right]\,; \tag{4}$$

here ΔE_{σ} is the activation energy for the electrical conduction process, k_B is the Boltzmann constant and G_a is the electrical conductance at ambient temperature. Also, according to eq. (1),

$$G_a(V)=G_{\Omega}(T_a)\exp(V/V_0)\,.$$

From what is left for the deduction of the relationship between $\Delta I_{JH}(V,\infty)$ and V, only the dependence of electrical conductance on temperature is considered (the experimental results analyzed correspond to applied voltages lower than V_0). From eq. (4), the expression for the increase in current may be deduced, as a function of temperature in the sample

$$\Delta I_{JH}(V,T)=I(V,T_a)\left\{\exp\left[\frac{\Delta E_{\sigma}}{k_B}\left(\frac{1}{T_a}-\frac{1}{T}\right)\right]-1\right\}\,. \tag{5}$$

By solving this equation in temperature, and introducing it into expression (3), one obtains the transcendent equation

$$K_{th}\left(\frac{x_a}{x_a-\ln\alpha}-1\right)=\frac{V^2G_a}{T_a}\alpha\,, \tag{6}$$

in which $\alpha=1+\Delta I_{JH}(V,\infty)/VG_a$ and $x_a=\Delta E_{\sigma}/k_BT_a$. If one introduces the functions

$$F_1(V,\Delta I_{JH})=\frac{x_a}{x_a-\ln\alpha}$$

and

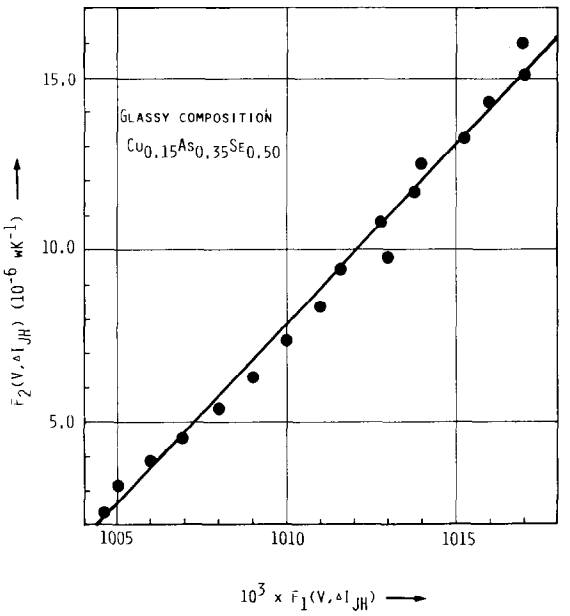

Fig. 1. $F_1(V,\Delta I_{JH})$ versus $F_2(V,\Delta I_{JH})$ (the values correspond to a temperature of 26°C).

$$F_2(V,\Delta I_{JH}) = \frac{V^2 G_a}{T_a}\alpha ,$$

eq. (6) changes to

$$K_{th}(F_1(V,\Delta I_{JH}) - 1) = F_2(V,\Delta I_{JH}) . \quad (7)$$

Fig. 1 represents $F_1(V,\Delta I_{JH})$ versus $F_2(V,\Delta I_{JH})$. It shows good agreement between the experimental results and functional model (7) (the correlation coefficient corresponding to the regression analysis is 0.995). For the evaluation of F_1 and F_2 it has been taken into account that the ohmic resistance at 26°C is 14 MΩ. From a regression analysis, one deduces that $K_{th} = 1.0$ mW K^{-1}. The agreement of the experimental values with eq. (7) confirms that current increase is a consequence of Joule self-heating associated to electrical excitation.

3.2. Influence of temperature on ohmic resistance and threshold voltage

3.2.1. R_Ω versus T

Fig. 2 shows the values of ohmic resistance at different temperatures, on a semilogarithmic scale, for $As_{0.40}Se_{0.30}Te_{0.30}$. The relationship which fits the

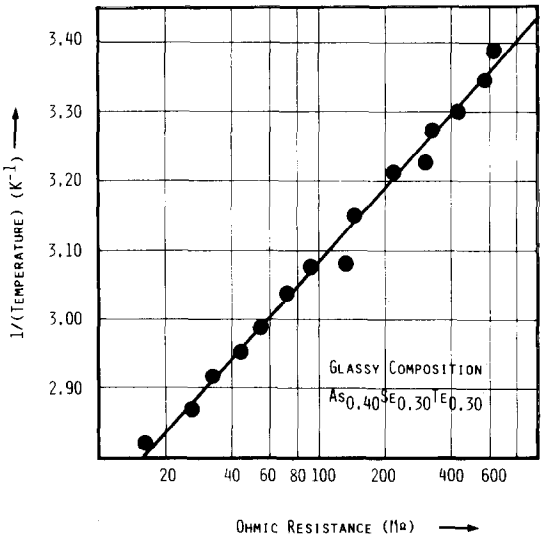

Fig. 2. Ohmic resistance versus inverse temperature (semilogarithmic scale).

experimental results ($r = 0.991$) is of the Arrhenius type (characteristic of thermally activated processes)

$$R_\Omega(T) = R_0 \exp(\Delta E_\sigma / k_B T) . \quad (8)$$

The values of R_0 and ΔE_σ are 0.22 Ω and 0.56 eV respectively. According to eq. (8), one establishes that the electrical behaviour of $As_{0.40}Se_{0.30}Te_{0.30}$ at low voltages (at which it obeys Ohm's law) is characteristic of intrinsic semiconduction. Therefore, electrical conduction is due basically to the excited carriers, which are in the non-localized or extended states belonging to the conduction band of the glassy semiconductor [9]. From the value obtained for the activation energy, one deduces that the width of the mobility gap is 1.12 eV.

3.2.2. V_{th} versus T

The experimental values of threshold voltage at different temperatures have been found to fit the functional model

$$V_{th}(T) = C_1 \exp[C_2(T_g - T)] , \quad (9)$$

where C_1 and C_2 are two parameters, and T_g the glass transition temperature for the semiconducting alloy. The value of T_g for $As_{0.40}Se_{0.30}Te_{0.30}$ is approximately 133°C (deduced from the DSC curve). Fig. 3 shows the results obtained by measuring the

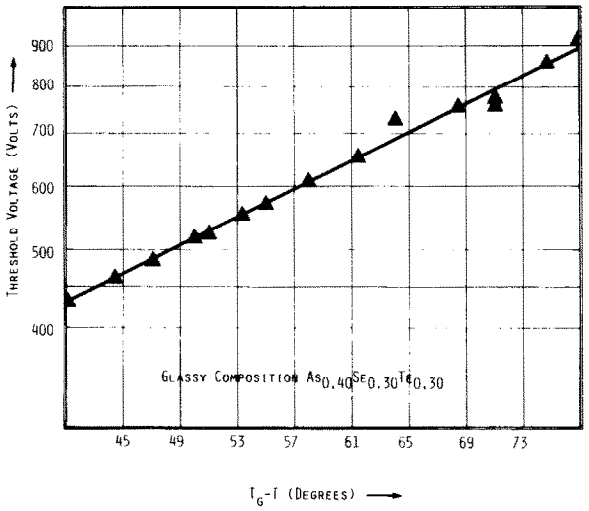

Fig. 3. Threshold voltage versus the difference between glass transition temperature and ambient temperature (semilogarithmic scale).

threshold voltage at different temperatures, for $As_{0.40}Se_{0.30}Te_{0.30}$. V_{th} versus $T_g - T$ is represented on a semilogarithmic scale. From a regression analysis one obtains $C_2 = 0.023\ K^{-1}$ ($r = 0.992$). This value is similar to that found for other chalcogenide glassy systems, when the double point contact electrode configuration is used for electrical stimulation [10,11]. Therefore, this result may be a general characteristic of this kind of material. Also, the relationship mentioned in this paper between V_{th} and T is verified in those cases where an explanation of a basically thermal nature is proposed for switching (positive feedback mechanism) [3]. On the other hand, relationship (9) is of great interest for manufacturing switching devices based on these materials, as it allows one to predict in a simple way the dependence of threshold voltage on temperature.

3.3. Correlation between glassy structure and electrical conduction

The addition of Cu to glasses of the As–Se binary system reduces electrical resistivity remarkably (the values at room temperature are $2.5 \times 10^{12}\ \Omega$ cm [12] for As_2Se_3 and $7.9 \times 10^5\ \Omega$ cm for $Cu_{0.15}As_{0.35}Se_{0.50}$ [13]). This is explained by the formation of Cu–As and Cu–Se covalent bonds, which have a lower ionization energy (< 1.7 eV and < 1.2 eV, respectively) than the As–Se (1.7 eV) and Se–Se bonds (2.1 eV) [12]. Electrical resistivity at room temperature for $As_{0.40}Se_{0.30}Te_{0.30}$ is $1.8 \times 10^7\ \Omega$ cm [14]. In this composition, the type of covalent bond which contributes most to the carrier generation process is the As–Te bond (0.9 eV), which has the lowest ionization energy of those present in the alloy.

In order to justify the fact that the electrical conductivity at room temperature for $Cu_{0.15}As_{0.35}Se_{0.50}$ is higher than that of $As_{0.40}Se_{0.30}Te_{0.30}$, the number of bonds in 100-atom samples of each of the alloys has been determined. Assuming 3-coordination for As and 4-coordination for Cu [15], and considering the hypothesis of equiprobability of the different types of covalent bonds, the result, according to ref. [16], is that there are 30 Cu–Se type and 21 Cu–As type bonds, while there are only 36 As–Te type bonds. Therefore, the larger number of Cu–X bonds (X = As, Se), compared to the number of As–Te bonds, can explain the higher electrical conductivity of the chalcogenide–metallic alloy.

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