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Structural and electrical properties of the glassy semiconductor system Cu–As–Te

Part 1 *Electrical and switching aspects, and their correlation with the structure*

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A method has been developed for measuring electrical conductivity in bulk samples of glassy semiconductors, based on the procedure described by Valdes, which is used to determine the conductivity of the compositions $Cu_{0.05}As_{0.50}Te_{0.45}$ and $Cu_{0.15}As_{0.40}Te_{0.45}$. These experimental results are justified by the structural models corresponding to each of the compositions. The estimates of the number of bonds of each of the possible types, as well as their ionization energies, are used for this purpose. This analysis is preceded by the description of an electrical conduction model for this type of semiconductor material. Finally, the results obtained in the study of the properties of electrical switching are given.

1. Introduction

It is well known that chalcogenide glasses show switching effects, and the possibility of preparing optical memories [1, 2]. Nevertheless, these glasses are in many cases characterized by high resistivity values that impose limitations on their applications as well as measurements.

Copper has a marked influence on the electrical conductivity of selenides of arsenic [3]. For this reason, the analysis has been carried out on some compositions of the Cu–As–Te system, considering that the substitution of selenium by tellurium may be of advantage concerning the obtainment of more appropriate values of the characteristic parameters of the switching phenomenon.

One of the aims of this study is to attempt an explanation for the dependence of electrical resistivity on composition, on the basis of structural studies [4, 5], i.e. from the short-range order of these materials, and the analysis of the deviation of covalent coordination of the different elements, assuming this to be the coordination which fits the "octet" rule. The latter would allow us to establish the number of covalent bonds that exist between the different elements in the glass. This type of correlation, not frequently found in the literature, also permits the validity of the proposed structural model to be confirmed.

An analysis has been carried out of the switching properties of the compositions under study, correlating the values of the characteristic parameters with those found in other glassy chalcogenide compositions [6–8]. Thus, information on the nature of the switching phenomenon in bulk samples may be obtained.

2. Experimental procedure

The amorphous bulk material used in the experiments was prepared by the melt-quench method [6]. The same glassy ingot was used for obtaining X-ray diffraction intensities, and for electrical measurements. Part of the ingot was fragmented into pieces approximately 1 cm × 1 cm × 1 mm which were set in epoxy-type resin. The samples were polished with alumina powder (Al_2O_3) of different grain size, to attain a mirror-like surface. In the present study, the glassy compositions $Cu_{0.05}As_{0.50}Te_{0.45}$ (MI) and $Cu_{0.15}As_{0.40}Te_{0.45}$ (MII) were chosen to test the influence of copper content on electrical resistivity, and on the characteristic parameters of the switching phenomenon. Fig. 1 shows the region of glassy formation of the Cu–As–Te system [9], and the position within the system, of the two compositions under study. An electrode-holding device, described elsewhere [10], was used to carry out the electrical measurements corresponding to the study of switching properties. To measure electrical resistivity, a device consisting of four electrodes was built. This was constructed in a similar manner as the previous device, and the quality of electrical contact was ensured with gentle pressure by means of springs attached to the electrodes.

3. Electrical resistivity of glassy samples

The method used for measuring electrical resistivity is a variation of that proposed by Valdes [11, 12]. This permits measurements to be taken in samples having a wide variety of shapes. The basic model is shown in Fig. 2. Four sharp probes are placed on a flat surface of the material to be studied, direct current is passed through two electrodes (1 and 4) and floating potential is measured across two other electrodes (2 and 3). If the flat surface on which the probes rest is adequately large, and the sample of an appropriate size, the glassy

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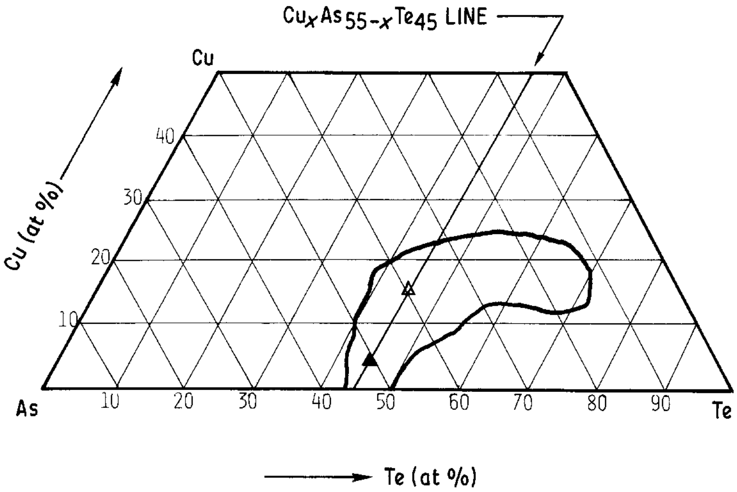

Figure 1 Glass formation region in the Cu–As–Te system.

semiconductor may be considered to have a semi-infinite volume.

The resistivity is computed [11, 12] as

$$\varrho = \left(\frac{V}{I}\right) 2\pi \Bigg/ \left(\frac{1}{r_{21}} + \frac{1}{r_{43}} - \frac{1}{r_{31}} - \frac{1}{r_{42}}\right) \qquad (1)$$

where V is potential difference, I is current and r_{ij} is the distance between probes i and j. Equation 1 was deduced by taking into account that the floating potential V_f at a distance r from an electrode carrying a current I in a material of resistivity ϱ is given by

$$V_f = \frac{\varrho I}{2\pi r} \qquad (2)$$

In Fig. 3 are shown the current and potential difference values, on log–log scales, between electrodes 2 and 3 for the two compositions studied. From these experimental values, together with the interelectrode distances, the electrical resistivity is determined. The results are $4.0 \times 10^2\,\Omega\,m$ for Composition MI and $9.3\,\Omega\,m$ for Composition MII (the experiments having been carried out at 20° C and in air). As expected, the effect of increasing the copper content is to reduce the resistivity at room temperature (in the present case by nearly two orders of magnitude). Given that (depending on the composition) the conductivity of glassy semiconductors varies within a wide range, from 1 to $10^{-6}\,\Omega^{-1}\,m^{-1}$ [13], both compositions may be classified as high-conductivity glasses.

4. Correlation between electrical conduction and structure

In an attempt to extract more information from the structural models, the chemical bonds present in each alloy have been considered which, together with their ionization energies, may justify the electrical resistivity values found.

4.1. Ionization energy of chemical bonds

During the redistribution of thermal vibrational energy, the valence bonds (v) absorb energy ε_i from time to time with transition of one of the two bond electrons to a local excited orbit. This gives rise to a weaker single-electron bond, which may be regarded as a vacant site or hole (h) with an effective positive charge. Thus, a two-electron v-bond is converted into

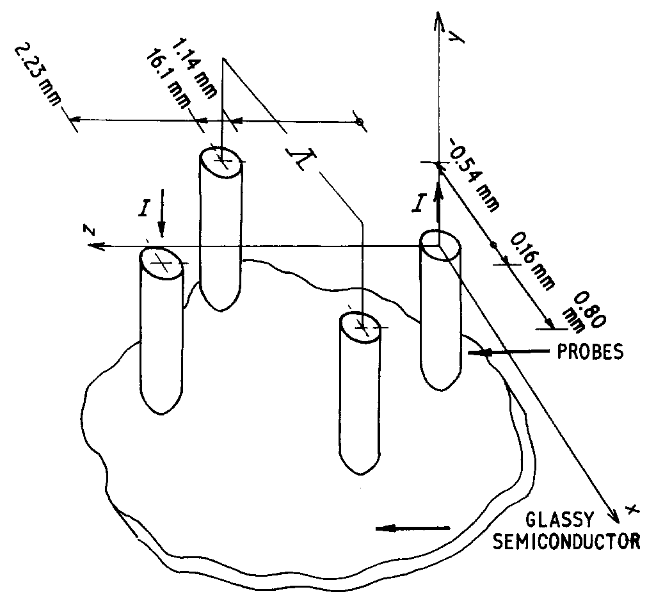

Figure 2 Model for the four-probe electrical resistivity measurements.

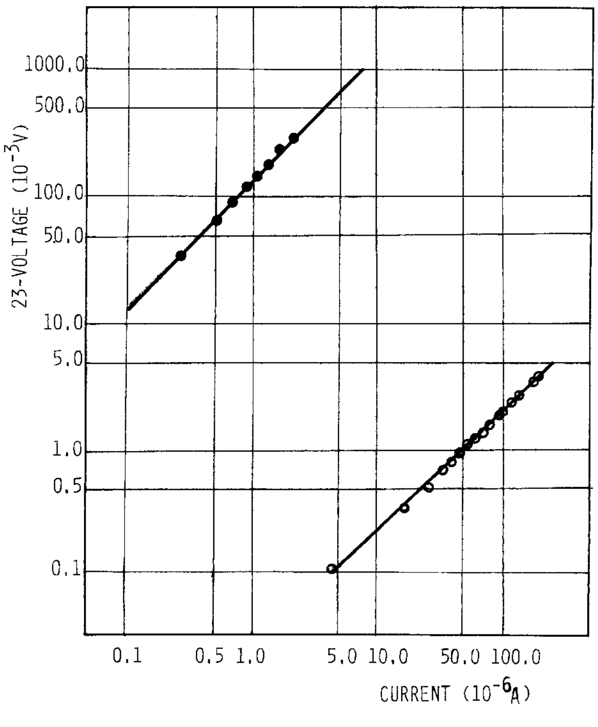

Figure 3 Plot on log–log scales of current against potential difference between electrodes 2 and 3: (●) MI, (○) MII.

a single-electron h-bond and an electron in an excited orbit, or v → h + e.

The excited electron and the hole, overcoming the now slight activation barrier ε_a, are displaced in different directions and ionization of the electron-pair bond is thereby complete. The excited electron stops briefly at the individual links between atoms (ev), held back by weak polarization forces. When an excited electron meets a hole, they may recombine. Accordingly, the equation for the equilibrium reversible reaction of ionization of an electron-pair bond may be written as

$$2\mathrm{v} + \varepsilon_i \rightleftharpoons \mathrm{h} + \mathrm{ev}$$

The ionization constant of the electron-pair bond may be represented in the form

$$\frac{n_h n_e}{n_v^2} = K = \frac{Q_h Q_e}{Q_v^2} \exp\left(-\frac{\varepsilon_i}{k_B T}\right) \qquad (3)$$

where n_h, n_e and n_v are the concentrations and Q_h, Q_e and Q_v the sum of the states of holes, excited electrons and electron-pair valence bonds, respectively; k_B is Boltzmann's constant and T the absolute temperature.

In the case of intrinsic conduction, as in the present situation [14], we have

$$n_h = n_e = n_i \ll n_v$$

In addition, the sum of the states Q_v of the electron-pair in the initial normal state is unity. The sum of the states Q_e of the electron at the excited interatomic orbit is two, as is the sum of the states Q_h of the electron remaining in the normal state. Equation 3 can therefore be rewritten in the form

$$n_i = 2n_v \exp\left(-\frac{\varepsilon_i}{2k_B T}\right)$$

where n_v is the number of covalent bonds.

This equation has been proposed by Myuller [14] when analysing the nature of the electrical conduction of the covalently bonded polymeric selenium chain (successive pairs of atoms are linked by homopolar electron-pair bonds). Thus, the influence of temperature, concentration of covalent bonds and ionization energy in the process of charge-carrier generation is shown in a quantitative manner.

The influence of the increase of copper content on resistivity has been analysed, using Equation 3 as a first approximation. For this, the ionization energies of the different covalent bonds must be known (Table I), so that together with their corresponding concentrations, the contribution of each type of bond to the process of electrical conduction may be evaluated.

TABLE I Ionization energies of the different bond types; all data appear in Borisova [13], and some of them have been confirmed by Minami *et al.* [15]

Bond type	Ionization energy (eV)
Cu–Cu	< 0.2
Cu–As	< 1.2
Cu–Te	< 0.9
As–As	1.2
As–Te	0.9
Te–Te	0.9

4.2. Contributions of bonds and consequences of radial distribution functions

The structural models of compositions MI and MII [16] permit an estimation of the bonds between the different elements present in the alloys, as shown in Table II. This table, besides giving the bonds present in 100 atoms, also shows the percentages of such bonds with regards to total bond number. In Composition MI, the total number of bonds in 100 atoms according to the model is 118, while for Composition MII it is 134, as a result of the increase in copper content, whose most probable coordination is 4 [17].

When studying bond contributions, these should be separated into two groups for the sake of convenience. One of these groups is made up by the Cu–Cu, Cu–As and Cu–Te bonds, the remaining bonds making up the other group. When the copper content is increased by 10%, the total number of bonds belonging to the first group increases by 26%, giving rise to a notable increase in the number of carriers, as all these bonds are easily ionized. On the other hand, the number of As–Te bonds is reduced by 9%, and that of Te–Te bonds is similar in both compositions. Given that both these bond types are of low ionization energy, their effect is contrary to that produced by bonds belonging to the copper group. Nevertheless, the net balance of the latter is unfavourable, so that when the copper content in the alloy is increased, so is the number of charge carriers, giving place to an increase in electrical conductivity, as shown experimentally. As–As bonds were not considered in this analysis, their possible ionization being hindered by their higher ionization energy in comparison to the other bonds.

In the radial distribution functions (RDFs) of each composition [16], it is seen that the first neighbour peak becomes bigger as the copper content increases. The average coordination numbers of the alloys are 2.44 for MI and 2.86 for MII, this being a consequence of the coordination number of copper. Likewise, there is no distinct peak associated with copper bonding, since appropriate Cu–As and Cu–Te distances are about the same as the As–Te distance. This is confirmed by the structural models [16], which show that all average bonding distances are close to 0.26 nm. Therefore, the band gap is reduced (its value for Composition MI is approximately 1.0 eV, while for Composition MII it is approximately 0.4 eV [13]), since the average coordination number is increased, which may be a reason for the increase in conductivity. Similar

TABLE II Bond numbers corresponding to each type which appears in the alloys

Bond	Composition MI	Composition MII
Cu–Cu	1 (1%)	2 (1%)
Cu–As	13 (11%)	39 (29%)
Cu–Te	6 (5%)	17 (13%)
As–As	38 (32%)	23 (17%)
As–Te	45 (38%)	39 (29%)
Te–Te	15 (13%)	14 (10%)

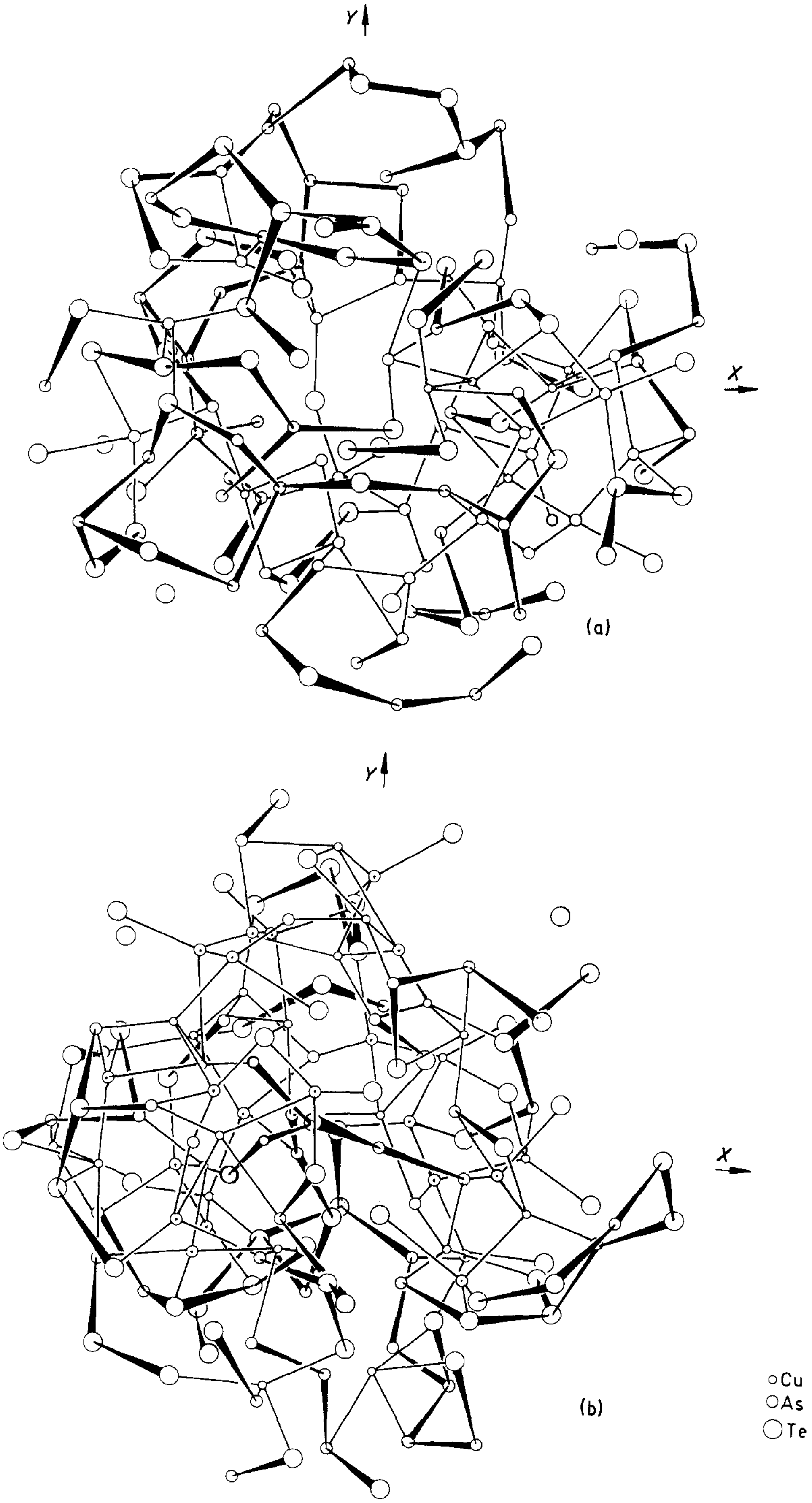

Figure 4 Spatial representations of structural models of glassy compositions (a) $Cu_{0.05}As_{0.50}Te_{0.45}$ and (b) $Cu_{0.15}As_{0.40}Te_{0.45}$.

results have been reported by Liang *et al.* [18] in the case of $Cu_x(As_{0.4}Se_{0.6})_{100-x}$ amorphous alloys.

This is illustrated in Fig. 4, where the spatial representations of the structural models of Compositions MI and MII are shown. Composition MII, having a higher coordination number than MI, has a greater amount of crosslinks, which give rise to greater structural rigidity and stability. Consequently, the glass transition temperature T_g of Composition MII is higher than that of Composition MI (Table III).

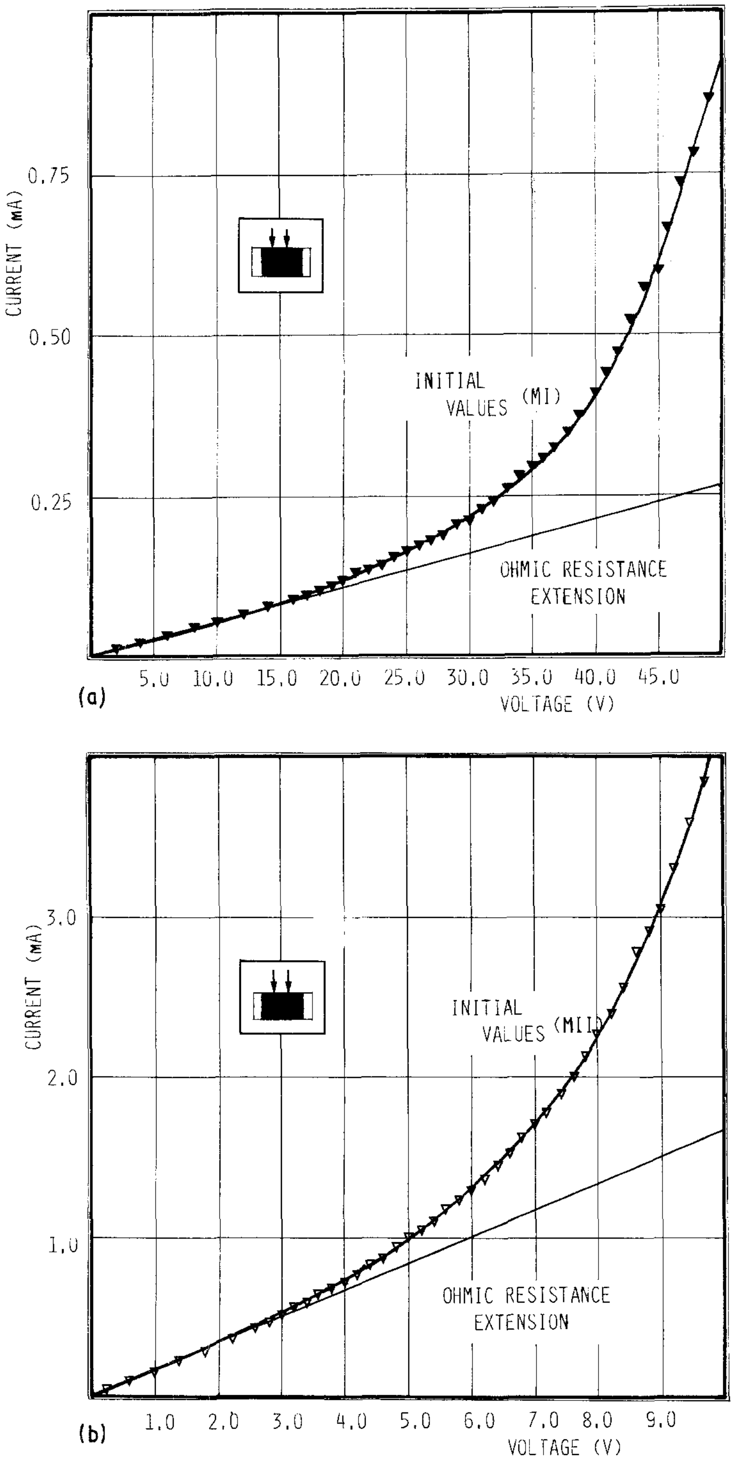

Figure 5 Room-temperature d.c. $I-V$ characteristics for bulk specimens (a) $Cu_{0.05}As_{0.50}Te_{0.45}$ and (b) $Cu_{0.15}As_{0.40}Te_{0.45}$.

5. Current–voltage characteristics in off-state and switching properties

Typical room-temperature d.c. $I-V$ characteristics in the off-state or high-resistance state of Compositions MI and MII are shown in Fig. 5. The current represented corresponds to the instant $t = 0$, to avoid introducing effects associated with self-heating of the sample, i.e. only those processes of electronic nature are present. To obtain the initial current, the values of the current corresponding to different instants are adjusted by the functional model [6]

$$I(t) = I(0) + \Delta I_{JH}\left[1 - \exp\left(\frac{-t}{\tau_{th}}\right)\right] \quad (4)$$

where τ_{th} is a time constant which characterizes the thermal process taking place, and ΔI_{JH} is the increase in the current as a consequence of Joule heating. The reason behind such extrapolation is that it is not possible to measure with certainty the current at the initial instant.

At low fields the characteristics were found to be ohmic. On increasing the potential difference across the sample the characteristics become non-linear, indi-

TABLE III Threshold voltage and d.c. resistance measurements, together with the minimal initial power of switching and glass transition temperature

Property	Composition MI	Composition MII
V_{th} (V)	40	9
R (Ω)	188×10^3	4×10^3
P_{th} (W)	8.5×10^{-3}	20.3×10^{-3}
T_g (°C)	~ 129	~ 159

cating that the electrical resistivity depends on the applied voltage [19].

The threshold voltage V_{th} of both compositions was measured with two point contacts having a separation of 2.5 mm. Rectangular voltage pulses with a width of 50 sec and an interval of 10 min were applied. The time span was considered sufficient for the sample to cool down. All measurements were carried out on virgin surfaces.

The threshold voltages obtained for each composition are listed in Table III, with the corresponding resistance in the off-state and the minimal initial switching power $P_{th} = V_{th}^2/R$. Each threshold voltage was measured an appropriate number of times and over different samples of the same composition, thus obtaining good reliability.

The comparison of these results with those reported in other glassy alloys [6, 19] shows that the threshold power of Composition MI is very close to those described earlier, while that of Composition MII is different. This may possibly be explained by the different activation energy. The role played by electrical power in this process suggests that thermal effects will be dominant in the observed switching process [20]. It was also observed that after electrical excitation, when the current is turned off, the sample resistance rises slowly during several seconds until the initial value is recovered, showing a hot-conduction state.

Some authors have found a phenomenological relation between room-temperature threshold voltage and glass transition temperature in thin-film [21] and bulk samples [22]. The relation for the latter is of the following type:

$$V_{th} = C_1 \exp(C_2 T_g) \tag{5}$$

parameter C_1 being dependent only on the glassy system, i.e. independent of the atomic percentages of each of the elements, and C_2 being a constant. Contrary to what is deduced from Equation 5, Composition MI presents a higher threshold voltage than MII (in spite of having a lower glass transition temperature). This may be justified, as in the case of electrical power, by the difference existing between the activation energies of the two compositions, which does not occur in the glassy systems where Equation 5 is valid.

The results presented indicate that the mechanisms responsible for the observed switching process are similar to the electrothermal model proposed by Owen *et al.* [23]. The glassy semiconductors of the Cu–As–Te system analysed offer the technological advantage of presenting reversible switching phenomena, with threshold voltage values lower than those obtained in other glassy compositions, with the same electrode configuration (in many of them of approximately several hundred volts, as they have higher electrical resistance). For this reason, and because of their hardness, permitting an easier preparation process, both compositions MI and MII are suitable for device purposes.

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