PRE-SWITCHING NON-LINEAR REGION AND DELAY TIME IN THE $Cu_{0.15}As_{0.35}Se_{0.50}$ SEMICONDUCTING GLASS

E. MÁRQUEZ, P. VILLARES and R. JIMÉNEZ-GARAY

Departamento de Física Fundamental, Facultad de Ciencias, Universidad de Cádiz,
Apartado 40, Puerto Real, Cádiz, Spain

Received 6 December 1985

The current–time and non-linear current–voltage characteristics in the $Cu_{0.15}As_{0.35}Se_{0.50}$ chalcogenide semiconductor glass are analyzed. From the measurements it is deduced that the electrical conductance varies according to $G_0 \exp(V/V_0)$. The role played by Joule heating in the switching phenomenon is investigated. Results obtained for the delay time are in agreement with solutions given by the thermal balance equation for the impulse breakdown limiting case.

1. Introduction

The last twenty years have seen the subject of amorphous semiconductors develop into a distinct field of solid-state electronics and physics [1]. Much of the initial impetus arose from the great interest provoked by electrical switching phenomena in chalcogenide glasses [2–4]. Generally, these are characterised by high resistivity values, which limit applications as well as measurements. However, the addition of copper to the amorphous materials can lead to significant changes in their conductivities [5–7].

Research in high-voltage electrical conductance is of considerable interest, since it can provide valuable information about the switching mechanism. However, the number of voltage-dependent electrical conductance measurements of the Cu–As–Se system published in the literature is limited.

The aim of the present study is to find the current–time characteristics, and the dependence between the electrical conductance and the applied voltage of $Cu_{0.15}As_{0.35}Se_{0.50}$ glass, using rectangular voltage pulses. The switching delay time t_D (period elapsed between the application of a voltage high enough to provoke switching and when this occurs) has been measured for several values of applied voltage. The excellent agreement between the solution of the thermal balance equation and the experimental results permits us to clarify the nature of the process.

2. Experimental

The amorphous bulk material used in the experiment was prepared by heating appropriate mixtures of the elements in vacuum-sealed fused-silica ampoules, for about 3 h at 950°C, and which were then air-quenched. The non-crystalline character was verified by X-ray diffraction experiments. Fragments of the ingot were inserted into an epoxy-type resin, and finished with 0.05 μm alumina polishing powder until a mirror-like surface was obtained.

An electrode-holding device described elsewhere [8] was used to carry out the electrical measurements, by means of which rectangular voltage pulses were applied to the sample under study. These pulses had a width of 50 s, and an interval of 10 min. This time span was considered sufficient for the sample to cool down. Delay time was measured by means of a memory oscilloscope (Trio, model MS-1650B) time base. All measurements were carried out on virgin surfaces in air at room temperature (299 K).

3. Results and discussion

3.1. Current–time characteristics

When a pulse is applied to a sample, the current rises from an initial value $I(V, 0)$ to reach a final

0 167-577x/86/$ 03.50 © Elsevier Science Publishers B.V.
(North-Holland Physics Publishing Division)

steady value $I(V, \infty)$ characteristic of the sample. The time dependence of the current is similar to that found in the literature for glass thin film [9]. The initial capacitive spike is very rapid, and the time dependence of the current is:

$$I(V, t) = I(V, 0) + \Delta I_{JH}(V, t) \tag{1}$$

and

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

where τ_{th} is a time constant which characterizes the thermal process taking place. Similar results have been described for other glassy alloys using the same disposition of the electrodes [3], although no information is given about the thermal process, or about the dependence of $\Delta I_{JH}(V, \infty)$ on the voltage. The value of $\Delta I_{JH}(V, t)$ was found to correspond to the internal heating undergone by the sample as a result of the current. The temperature increase in the conduction region calculated from the current increase, being the expected one for this kind of material [10]. Therefore, it seems reasonable to interpret $\Delta I_{JH}(V, t)$ as the Joule heating current component at the instant t.

Table 1 shows a set of results obtained. From the regression analysis it is deduced that the experimental values are correctly adjusted to the proposed functional model. Within the experimental limitations, it seems that the thermal time constant is independent of voltage. The value of $I(V, 0)$ was determined by extrapolating the functional model at the instant $t = 0$.

Table 1
Physical parameters corresponding to the time dependence of the current

Applied voltage V(V)	Thermal constant τ_{th} (s)	Initial current $I(V, 0)$ (μA)	Current increase $\Delta I_{JH}(V, \infty)$ (μA)
110	9.6	6.63	0.76
120	10.0	7.51	1.12
140	9.5	10.21	1.62
150	9.6	11.79	1.91
160	9.6	13.23	2.42
200	9.7	17.83	4.48
220	9.5	22.04	6.15

Fig. 1 represents $[I(V, \infty) - I(V, t)]/\Delta I_{th}(V, \infty)$ versus t on a semilogarithmic scale. It is clear from fig. 1 that the thermal time constant remains approximately invariable. A correlation coefficient of 0.9872 was obtained for the straight line of fig. 1, a value of 9.6 s being calculated for τ_{th}.

3.2. *Dependence of the current on the applied voltage*

The following relation between $I(V, 0)$ and V was found:

$$I(V, 0) = I_0(V/V_0) \exp(V/V_0), \tag{3}$$

from which an expression for conductance may be obtained:

$$G(V) = G_0 \exp(V/V_0), \tag{4}$$

where $G_0 = I_0/V_0$; i.e. the conductance becomes superohmic at high voltages. Therefore, as usual in the current–voltage characteristics for amorphous semiconductors [11], the linear region at low voltage is followed by a non-linear region, fig. 2, before normal S-type switching occurs (conventionally observed switching from the high to low resistance state). Fig. 3 shows the normalized experimental values on a semilogarithmic scale, as well as the regression line, with a correlation coefficient of 0.9966. Also, the values of the parameters V_0 and I_0 found were: $I_0 = 8.25$ μA, $V_0 = 223$ V and $V_0/I_0 = 27$ MΩ, the last value corresponding to that of weak field resistance. By means of another independent experimental procedure (multimeter Thurlby, model 1905a) the ohmic resistance was determined. This value was approximately the same as before, thus confirming the validity of the functional dependence (4). The current–voltage characteristics for the $Cu_{0.10}As_{0.30}Se_{0.60}$ specimen, with sandwich-type electrode configuration, unlike the present case, show linear behaviour up to a voltage value close to the threshold voltage [7].

3.3. *Delay time of the switching*

Measurements of delay time were analyzed in terms of a thermal model, based on the thermal balance equation. If the duration of the change from the off to the on state is short compared to the thermal time constant, then the thermal balance equation describes adiabatic heating. According to this approxi-

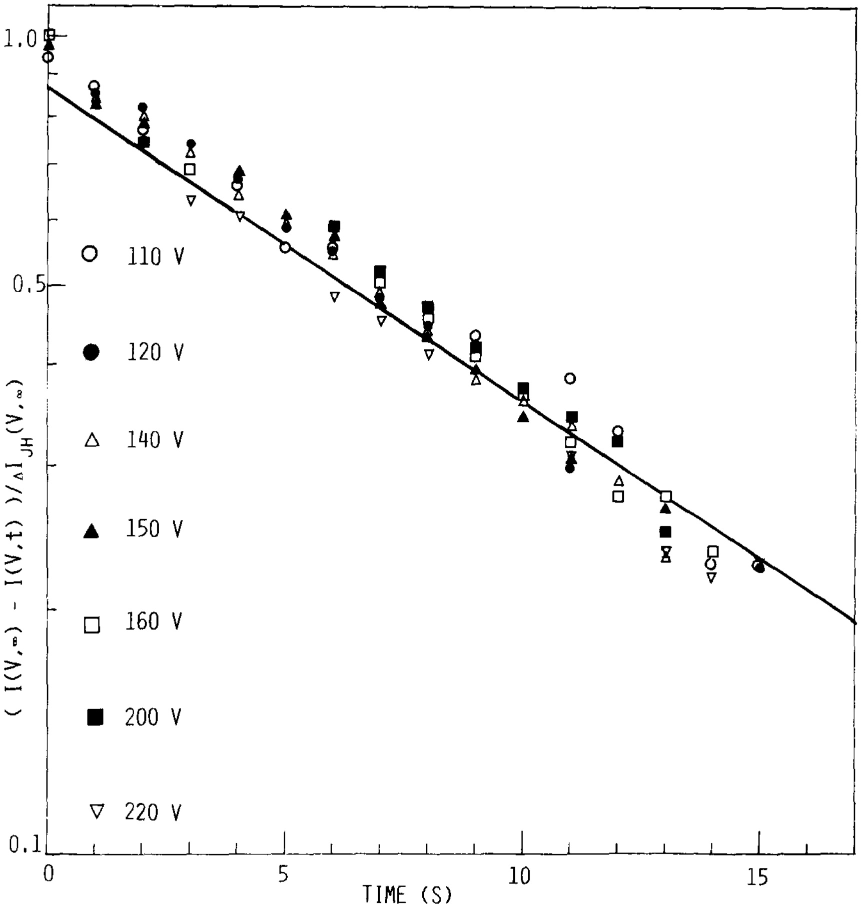

Fig. 1. Semi-logarithmic plot of $[I(V,\infty) - I(V,t)]/\Delta I_{JH}(V,\infty)$ versus t for the different applied voltages

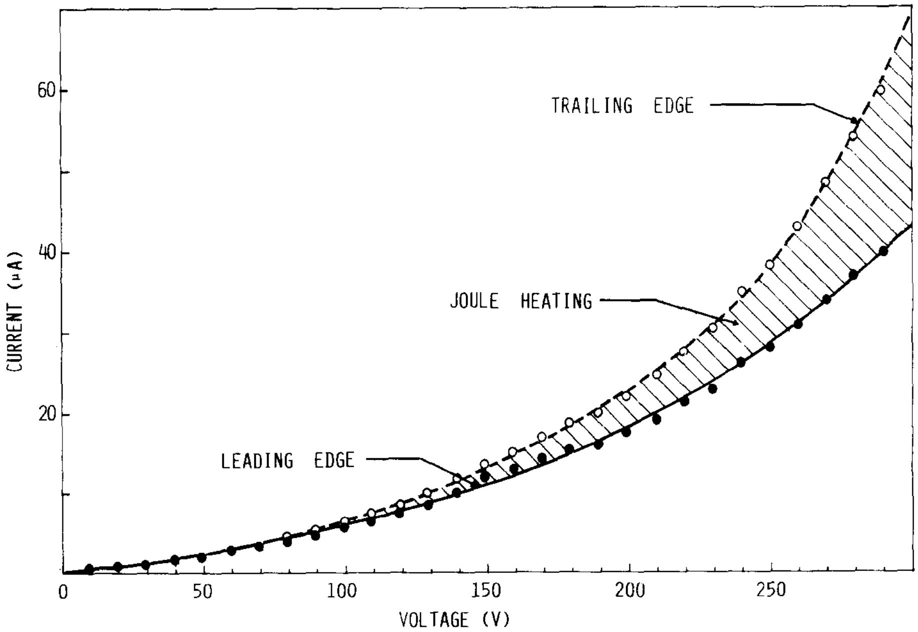

Fig. 2. I–V characteristics in the high-resistance state for sample under study at 299 K.

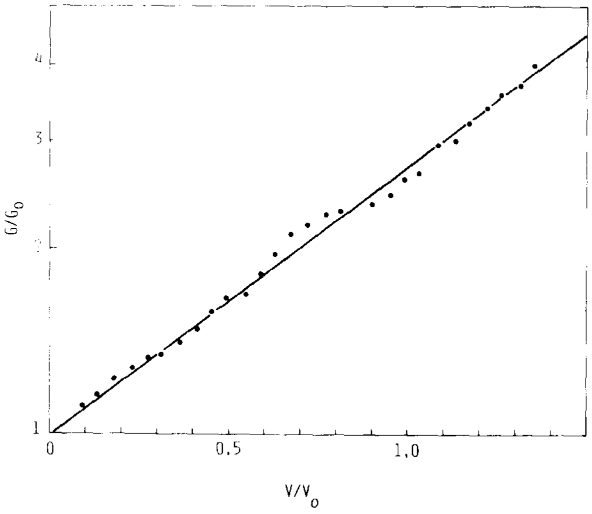

Fig. 3. Normalized conductance in the off-state versus applied voltage at room temperature (299 K).

mate solution, the relation between t_D and V in the case of a square-wave voltage pulse is given as follows [12],

$$t_D = CLk_B T_0^2 R(T_0) S / V^2 \Delta E. \quad (5)$$

Here, ΔE is the ohmic activation energy, k_B the Boltzmann constant, T_0 the ambient temperature, $R(T_0)$ the resistance at ambient temperature, C the specific heat per volume, L the electrode separation and S the total cross-sectional area.

Fig. 4a shows a good linearity for the relation between V and $1/t_D^{1/2}$, the correlation coefficient being 0.9986. This result indicates that

$$t_D = k/(V - V_{th})^2, \quad (6)$$

where k is a constant and V_{th} is the threshold voltage corresponding to $t_D = \infty$. Similar results are found in the literature [13], for the same electrode configuration as the one used in this study but with a different glassy system. In the case of thin films of chalcogenide glasses, Ovshinsky reported that t_D is proportional to $\exp(-V/V_1)$ [2]. The present data plotted on a semi-logarithmic scale in fig. 4b showed deviation from a straight line.

Eq. (6) approximates eq. (5) in the limiting case of the impulse thermal breakdown, i.e. when the applied voltage is much greater than the threshold voltage. Therefore, the result of the simple analysis based on a thermal mechanism is consistent with the observed delay time–voltage characteristics.

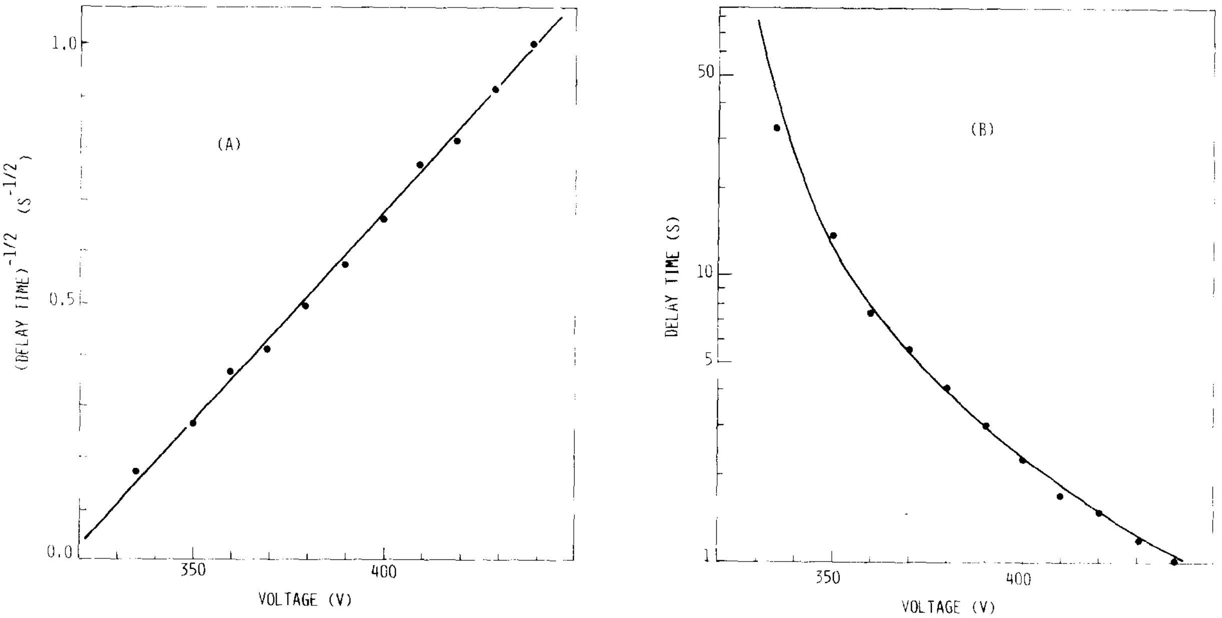

Fig. 4. (a) Linear relationship between applied voltage and the inverse square-root of delay time. (b) Semilogarithmic plot of delay time against applied voltage.

Acknowledgement

The authors wish to express their gratitude to Miss Paloma Peers and Professor M. Milla for helpful suggestions for the English version of the manuscript.

References

[1] S.R. Ovshinsky, J. Non-Cryst. Solids 73 (1985) 395.

[2] S.R. Ovshinsky, Phys. Rev. Letters 21 (1968) 1450.

[3] E. Márquez, P. Villares and R. Jiménez-Garay, J. Non-Cryst. Solids 74 (1985) 195.

[4] E. Márquez, P. Villares and R. Jiménez-Garay, Mat. Letters 3 (1985) 503.

[5] Y. Asahara and T. Izumitani, Japan. J. Appl. Phys. 11 (1972) 109.

[6] Y. Asahara and T. Izumitani, J. Non-Cryst. Solids 11 (1972) 97.

[7] M.M. Haifz, M.M. Ibrahim, M. Dongol and F.H. Hammad, J. Appl. Phys. 54 (1983) 1950.

[8] E. Márquez, L. Esquivias, P. Villares and R. Jiménez-Garay, Rev. Sci. Instr. 56 (1985) 1262.

[9] J.M. Robertson and A.E. Owen, J. Non-Cryst. Solids 8–10 (1972) 439.

[10] F.M. Collins, J. Non-Cryst. Solids 2 (1970) 496.

[11] J.E. Hall, J. Non-Cryst. Solids 2 (1970) 125.

[12] T. Takeda and G. Nogami, J. Non-Cryst. Solids 51 (1982) 11.

[13] M. Sugi, M. Kikuchi, S. Iizima and K. Tanaka, Solid State Commun. 7 (1969) 1805.