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Changes in the electrical conductivity of amorphous semiconductors

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Abstract

The changes in the electrical conductivity occurring in chalcogenide amorphous semiconductors, from the system GeSeTe, have been studied. This study includes the determination of $I-V$ characteristics, the electrical conductivity and its relationship with temperature, and, finally, the ageing of samples started by annealing and by thermal switching due to Joule self-heating. To complete the analysis, the possible structural modifications which could have been produced during the experiments have been verified by means of X-ray diffraction.

Keywords: Amorphous semiconductors; Electrical conductivity; Thermal switching

1. Introduction

Chalcogenide glassy semiconductors have been a topic of great interest for materials science researchers over the past 25 years, since the discovery of their switching properties by Ovshinsky, back in the late 1960s [1]. Nevertheless, some aspects relating to their transport properties are still not well established. Among these aspects, the problem of the electrical conduction mechanism is, in all probability, the one that has received the most attention during these years. Several theoretical models have been proposed [2] to explain the electrical properties of chalcogenide glasses, but some features of these glasses remain unsolved. The effect of the evolution of the glassy structure from the initial disordered lattice to a more ordered one, as in a forced ageing process, is one of the typical aspects studied.

2. Experimental

The samples studied here have the nominal composition $Ge_3Se_3Te_4$. Results from the literature [3] show that, among others, the electrical conductivity at ambient temperature is $\sigma \approx 10^{-9}$ $(\Omega \cdot \mathrm{cm})^{-1}$, with a glass transition temperature $T_g = 228$ °C. These values have been well confirmed by our own work.

The bulk samples were obtained by mixing their elements (99.99% purity), which were then introduced into a quartz tube, of 6 mm internal diameter, subjected to vacuum (10^{-3} torr) and sealed. The mixtures were heated up to 1000 °C, inside a rotary furnace, for 48 h. Finally, they were taken out of the furnace and quenched in water to ambient temperature. Their amorphicity was verified by the usual procedures (X-ray diffraction (XRD) and differential scanning calorimetry). The ingots obtained after quenching were cut into thin slices, and the samples for electrical measurements were sandwiched between two copper disks adhered with colloidal graphite.

For the study of the d.c. characteristics, an experimental technique was implemented, consisting of a sensing fixed resistor in series with the sample, with a nominal value lower than 0.1% of the sample resistance. The values of the current were then easily obtained by the voltage drop at this resistor, measured with a digital oscilloscope (Trio), when a pulse of 90 ms to 60 s was applied to the circuit. A voltage source (HP-6521A)

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was used for this purpose, with a maximum voltage of 1000 V and a maximum current of 20 mA. Both instruments were controlled, via GPIB interface, by means of a software application designed to synchronize the measurement of the current with the application of the voltage, and obtain the value of the initial current. This technique avoids the effect of Joule self-heating when the current is measured. After the application of the pulse, for those currents and temperatures for which such self-heating effects are appreciable, the sample resistance was subsequently checked by applying a low voltage pulse.

The control of the temperature of the furnace was carried out with a temperature controller (OMRON E5AX) and a Pt100 sensor. The voltage applied to the furnace was 75 V, and with this experimental system, the temperature of the furnace was stabilized with a deviation of lower than ± 0.1 °C.

Finally, the effects of forced ageing, started by thermal annealing of the samples at 120 °C over a period of seven days, as well as that started by several stages of thermal switching, were checked. The thermal switching experiments were carried out by limiting the current to avoid an increase in the internal temperature much over T_g. Additionally, the possible structural changes were checked during the experiments.

3. Results

The d.c. measurements show a linear behaviour of current versus voltage ($I = G(T) \cdot V$), for the entire range under study. Fig. 1 shows these results combining the current, the voltage and the temperature of the experiment. As expected, the conductance shows here an exponential relationship with temperature (Arrhenius-type behaviour):

$$G(T) = G_0 \exp\left[-\frac{\Delta E}{k_B T}\right] \tag{1}$$

where G_0 is the pre-exponential factor, ΔE is the activation energy and k_B is the Boltzmann constant. The experimental data can also be related to the expression proposed by Male [3], which can be approximated by

$$G(T) = G_a \exp\left[\frac{\Delta E}{k_B}\left(\frac{1}{T} - \frac{1}{T_a}\right)\right] \approx G_a \exp\left[\frac{T - T_a}{T_0}\right] \tag{2}$$

where $G_a = G(t = 0, T_a)$ represents the conductance at the initial or working temperature, and T_0 is a fitting parameter, which has been evaluated to be, for the samples under study, between 16 and 23 °C, in line with those shown by previous work [4]. By means of this equation, it is possible to evaluate the average increase in temperature and to define the current limit corresponding to temperatures below the glass transition.

The values derived for the electrical conductivity at different voltages, fit to an equation of the form

$$\sigma(T, V_i) = \sigma_0(V_i) \exp\left[-\frac{\Delta E}{k_B T}\right] \tag{3}$$

show a slight variation in the pre-exponential factor σ_0 with this variable (Fig. 2), although this effect could be due to a certain degree of covariance induced by the fitting method.

3.1. *Modification of* I–V *characteristics by ageing or thermal breakdown*

The $I-V$ characteristics of the samples were modified during the experiments due, fundamentally, to two types of processes: accelerated ageing by thermal annealing at temperatures below the glass transition, and

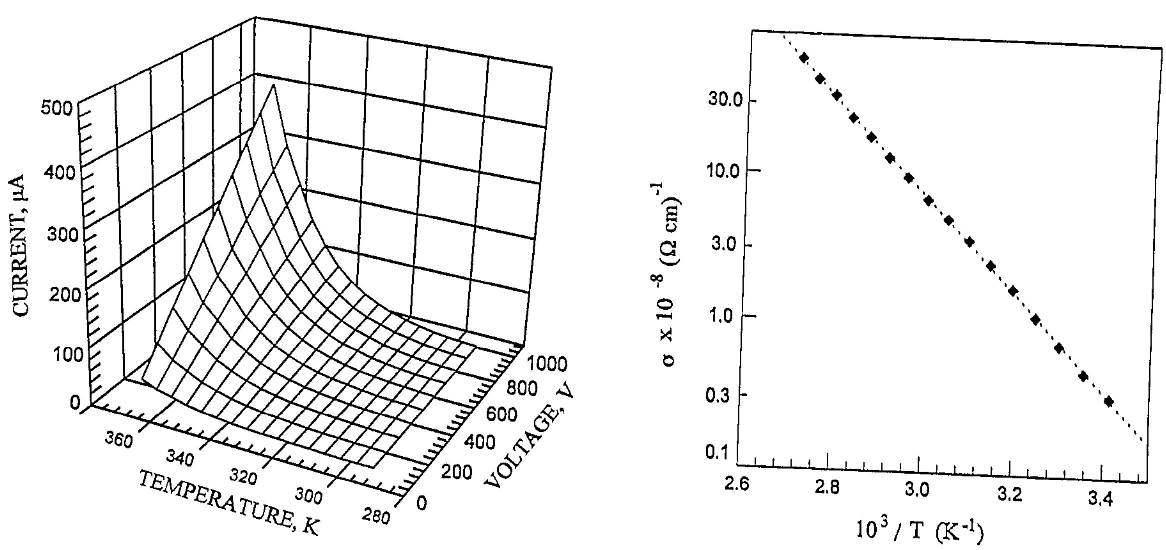

Fig. 1. $I-V-T$ characteristics and variation of conductivity with temperature in the initial state of glassy alloy $Ge_3Se_3Te_4$ (sandwich electrode configuration).

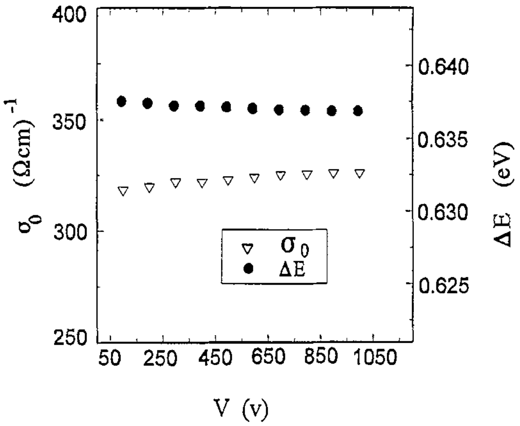

Fig. 2. Parameters σ_0 and ΔE calculated for different applied voltages, according to Eq. (3).

a stronger change started during the application of (moderately) high voltages pulses by thermal breakdown. The ageing process can be carried out maintaining the sample at these high temperatures over a period of days or even weeks.

Thus, the $I-V$ characteristics were measured before and after seven days of being subjected to a temperature of 120 °C. The left graph in Fig. 3 shows the observed variation of $I-V$ characteristics, before and after the process. The difference between the parameters due to the ageing has been considered for two cases, yielding a factor of 0.4 between the current measured at all temperatures, or in other words, an increase in conductance of 2.5 times. In this thermal process, the linear dependence of current on voltage was not altered, nor the relationship of electrical conductivity with the inverse of temperature, nor the parameter ΔE. Nevertheless, σ_0 suffered an increase of an order of magnitude, from 744 to 10 000 $(\Omega \cdot cm)^{-1}$.

The modification of $I-V$ characteristics is substantial indeed, not only in the values of fitting parameters, but also on the dependence shown, when the samples are subjected to temperatures over the glass transition, as a consequence of Joule self-heating phenomena studied here [5]. This is the case, analyzed on the sample M14 with a sandwich electrode configuration, when it is subjected to several processes of thermal breakdown controlled by current limit (Fig. 4), for which a maximum temperature increase was allowed, according to the dependence of the conductance on the temperature previously evaluated.

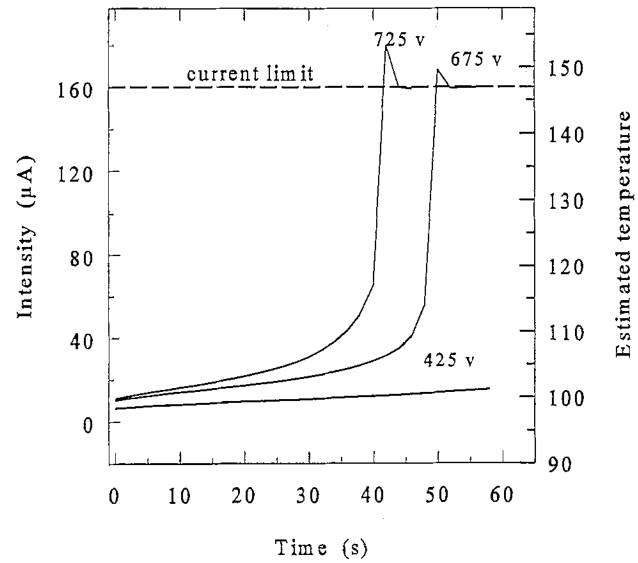

Fig. 4. Switching processes carried out with limited current. Temperature on the right axis was estimated from Eq. (2).

As Fig. 5 shows, the relationship between current and voltage, after the switching process to which the samples were subjected, becomes exponential following the model of conduction for intense fields with a uniform distribution of trap levels [6,7]. According to this model, an increase in current is allowed due to the effect of screening produced by the carriers, which are

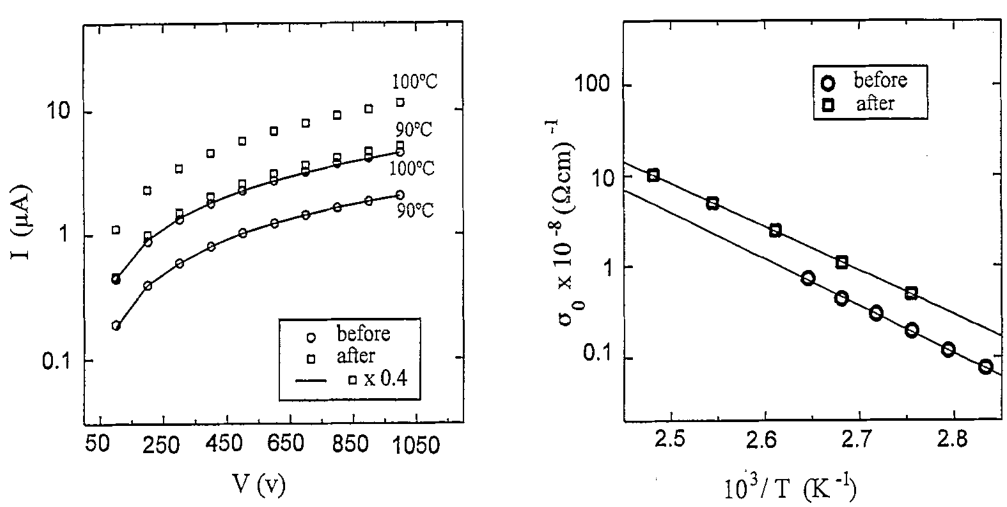

Fig. 3. Change in $I-V$ characteristics and in the pre-exponential factor of Eq. (3), for the compound $Ge_3Se_3Te_4$, produced by forced ageing of the sample under 120 °C.

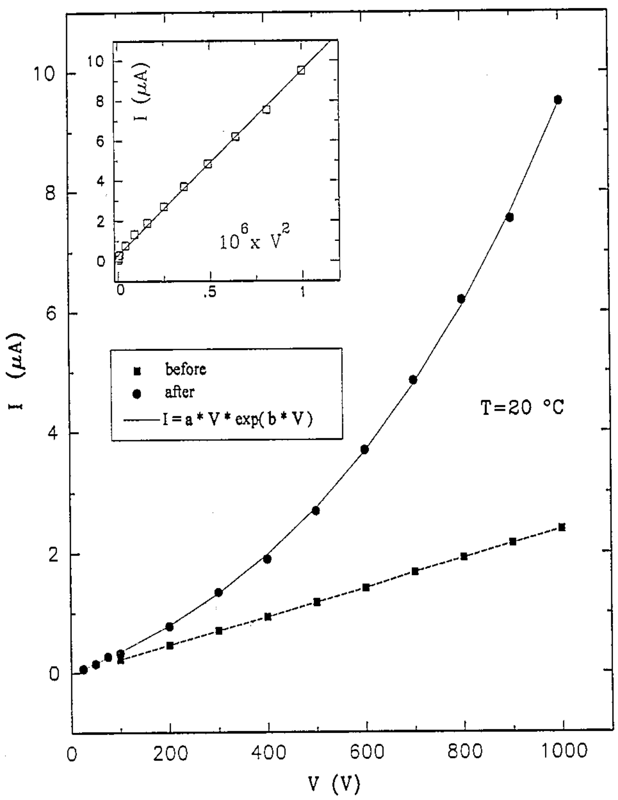

Fig. 5. $I-V$ and $I-V^2$ characteristics of the sample before and after the thermal switching.

subjected to a higher number of recombinations than in the pre-switching state. The relationship between current and voltage should be then described by [8]

$$I = G_0 V \exp(V/V_0)$$

Nevertheless, a quadratic dependence cannot be rejected from the analysis of our results, as the one shown in the inset of Fig. 5, although, in this case, the values for low voltage do not fit to this model.

From the analysis, it is easy to deduce that the glassy alloys at high temperatures give way to an increase in the number of localized states, which causes, at first, an increase in the electrical conductivity without any change in the activation energy. For higher temperatures, the appearance of surface or deep traps causes an irreversible change in the $I-V$ characteristics, which fit to the theoretical models of current limited by spatial charge studied here.

The X-ray diffractograms, shown in Fig. 6, confirm that the material continues to be amorphous after the process is carried out, and the slight differences could be attributed to slight structural modifications. In fact, the movement of the second peak towards higher angles means that the material tends to a more ordered structure.

4. Conclusions

It has been shown that the effects of thermal and electrothermal annealing on the electrical properties of the glassy chalcogenide semiconductor $Ge_3Se_3Te_4$ are quite different. When the samples are subjected to forced ageing at 120 °C over seven days, the only change that appears is in the value of the pre-exponential factor of the conductivity, which increases approximately one order of magnitude. This change makes the sample conductivity increase of the same order. On the other hand, when a switching pulse is applied to the samples, in such a way that the glass transition temperature is over, the electrical behaviour of samples is drastically changed. The dependence of current on applied voltage changes from a linear to an

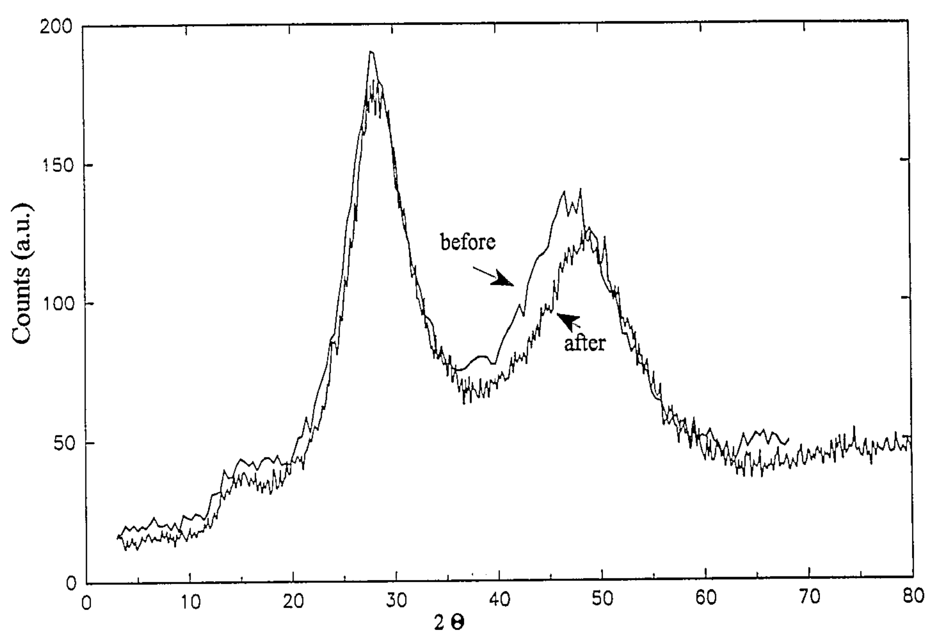

Fig. 6. X-ray diffractograms for the sample under study before and after the electrothermal annealing.

exponential function. This change can be explained by the conduction model of space charge limited current. Since the XRD patterns before and after the experiment are quite similar, it should be supposed that the switching pulse only makes the amorphous sample acquire a more ordered, but still amorphous, structure.

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