On the growth and composition of conductive filaments on the surface of As–Se–Te bulk glassy semiconductors

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A memory (lock-on) phenomenon was observed in the semiconducting glasses belonging to the As–Se–Te system, and this phenomenon was studied through electrical, calorimetric, and x-ray diffraction methods. The structural characteristics were also correlated to the time it takes to reach the memory state. The growth process in composition $As_{0.40}Se_{0.30}Te_{0.30}$ exhibited a dependence on electrode polarity in such a way that it began at the positive electrode and finished at the negative one. The growth speed of the conductive filament was found to be approximately 22 μm s^{-1}. The crystalline nature of the lock-on filament was confirmed, and the peaks corresponding to the x-ray diffraction pattern of the surface of a sample of composition $As_{0.45}Se_{0.10}Te_{0.45}$, partially covered by filaments, correspond to monoclinic As_2Te_3. The memory effects found agree with those predicted through Ovshinsky's criterion, as the average coordination numbers for the noncrystalline structures of the alloys analyzed are 2.4 and 2.3, respectively.

I. INTRODUCTION

Electrical switching and memory (lock-on) phenomena in chalcogenide semiconducting glasses are a very important subject, from a scientific and technological point of view.[1–5] In the beginning of research on the memory phenomenon, Uttecht *et al.* observed the growth of a filament from the positive to the negative electrode, during the transition associated with the memory process, in the glasses of the As–Te–Ge system with a double point contact configuration.[6] Afterwards, Tanaka *et al.* discussed this process, using a simplified model based on the ionic behavior of the elements that constitute the switch-on plasma.[7] However, bibliographical information on the formation of lock-on filaments on the surfaces of samples belonging to other ternary chalcogenide glassy systems is scarce. A more complete characterization of the growth process of the filament associated to the memory effect is also necessary.

This paper describes an experimental study of the memory phenomenon in the As–Se–Te chalcogenide glassy system, with a coplanar point electrode configuration. With this aim in mind, two representative compositions of this system were studied: $As_{0.40}Se_{0.30}Te_{0.30}$ and $As_{0.45}Se_{0.10}Te_{0.45}$. The growth of the conductive filament was analyzed in detail in order to determine, among other magnitudes, its growth speed. Furthermore, a structural study was done through x-ray diffraction of the lock-on filament. Finally, the memory effects found were correlated to the short-range order structure of these glassy alloys.

II. EXPERIMENTAL PROCEDURE AND SOME SWITCHING CHARACTERISTICS

The As–Se–Te semiconducting glasses were prepared following the melt-quench procedure.[4] All the raw materials used were of a purity higher than 99.999%. The appropriate amounts of the elements were put into a fused quartz ampoule, which was evacuated to 10^{-5} Torr and sealed. This ampoule was put into a furnace at 650 °C for 72 h and was rotated at 1/3 rpm to assure homogenization. Finally, it was quenched in an ice-water bath.

The noncrystalline nature of the ingot was tested by x-ray diffraction (SIEMENS D500) and differential scanning calorimetric analysis (DSC-RIGAKU CN8059D2). The x-ray diffraction pattern did not exhibit the peaks characteristic of crystalline solids, and the DSC curve showed glass transition at temperature T_g and the exothermic reaction associated to the crystallization process at temperature T_0. Also, the value of electrical resistivity at room temperature, 1.8×10^7 Ω cm,[8] shows the glassy nature of the ingot. In order to obtain the bulk samples, the fragments of the ingot were embedded in an epoxy-type resin, and were later polished with alumina powder (Al_2O_3), grain size 0.3 and 0.05 μm. In this way, mirrorlike surfaces were obtained, which allowed both good electrical contact and a correct visualization of the post-switching transformations that take place on the sample surface.

The device with a double point contact electrode configuration, used for the application of electrical excitation to the samples, and which was designed and built

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in our laboratory, is described elsewhere.[9] Its basic feature is an electrode pressure regulation system, which allows adequate electrode-sample surface contact. When carrying out experiments at temperatures higher than room temperature, the device was put into a furnace whose temperature was regulated by a controller with ± 0.2 °C precision (OMRON E5K).

Glassy alloy $As_{0.40}Se_{0.30}Te_{0.30}$ at room temperature and with an interelectrode distance of approximately 1.2 mm, exhibited a very high Ohmic resistance, approximately 944 MΩ. To this resistance corresponds a threshold voltage, V_{th}, or lowest voltage at which switching occurs, of about 1.9 kV (evaluated according to the thermal model, which explains the switching effect generated in these bulk samples[10,11]). Bearing in mind the fact that, at voltages higher than 1.0 kV, there is an increased risk of disruptive discharge in the interelectrode environment, and that threshold voltage decreases with temperature, the experiments directed at the formation of lock- on filaments on the surfaces of the samples of composition $As_{0.40}Se_{0.30}Te_{0.30}$ have been carried out at a temperature of 58 °C. For alloy $As_{0.45}Se_{0.10}Te_{0.45}$, as its Ohmic resistance at room temperature is notably lower, 14 MΩ, it was not necessary to increase the temperature in order to reduce the threshold voltage. For a complete characterization of the growth process of the conductive filament, microphotographs were taken through scanning electron microscopy (SEM-HITACHI HHS-2R), at different stages of its formation process. All the experiments were carried out on virgin surfaces and in air.

III. RESULTS AND DISCUSSION

A. Growth speed of the conductive filament associated to the memory state

A voltage higher than V_{th} was applied to both samples under study, so after a certain time (delay time, t_D) the transition from the low electrical conductance state (OFF state) to the high electrical conductance state (ON state) took place.[4,11] This OFF–ON transition is accompanied by the formation of a molten path between the electrodes (switch-on path).[12,13]

For glassy alloy $As_{0.40}Se_{0.30}Te_{0.30}$ a switching voltage of 610 V was used, for which $t_D = 13.7$ s ($V_{th} = 550$ V, at a temperature of 58 °C). In the case of this alloy, if the high conduction state is maintained, at a certain instant one may observe the growth of a filament, which begins at the positive electrode and ends at the negative electrode. That is to say, the growth process of the filament depends on the polarity of the electrodes. During this process, interelectrode voltage decreases gradually, while the current is approximately constant (lock-on current, I_{LO}). The time that goes by from the instant switching takes place until the establishment of the memory state, that is, when the above-mentioned decrease in the interelectrode voltage stops, is called waiting time for lock on, t_w. Once the filament was formed, the composition at its axis was compared to that of the glassy matrix, through energy-dispersive analysis of x rays (EDAX technique). Figure 1 shows the spectrum of counts versus x-ray energy for each one of the zones (the left spectrum corresponds to the glassy matrix, and the one on the right corresponds to the lock-on filament). The composition of this filament, according to this analysis, is close to the stoichiometric compound As_2Te_3 (in order to evaluate the atomic concentration of the elements, a linear model was used). Table I summarizes some of the characteristics of the filament associated to the memory phenomenon for bulk sample $As_{0.40}Se_{0.30}Te_{0.30}$.

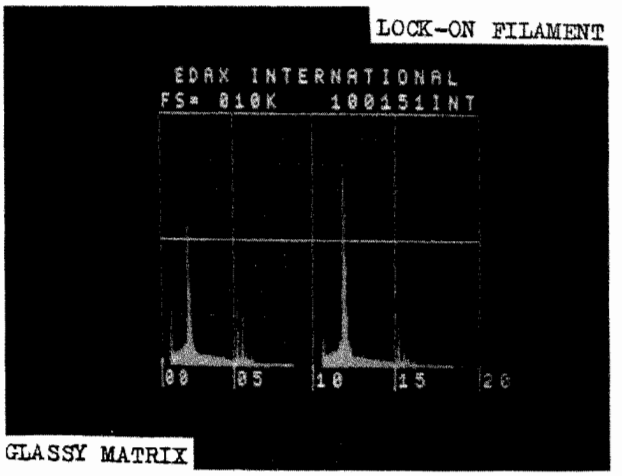

FIG. 1. Energy-dispersive x-ray analysis spectra of the glassy matrix and the center of the lock-on filament. The first peak of the spectrum belongs to the element Se (1.4 keV), the second corresponds to Te (3.8 keV) and the third is associated to As (10.5 keV).

The growth of the lock-on filament in composition $As_{0.40}Se_{030}Te_{030}$ is similar to the one observed in the glass samples of the As–Te–Ge system, with an As atomic concentration higher than 35%.[13] Therefore, it seems reasonable to assume that an electrolytic process takes place in the switch-on path, which originates the separation of the components, the same as in the high-As concentration region of the As–Te–Ge system. The electrical conductivity of the conductive filaments ob-

TABLE I. Some characteristics of the memory process for glassy composition $As_{0.40}Se_{0.30}Te_{0.30}$.

Appearance of the filament	Thin and continuous
Composition of the filament	Close to As_2Te_3
Directional growth	Yes (+ → −)
Waiting time	Long

tained with different values of I_{LO} have turned out to be similar, the average value being 26 Ω^{-1} cm^{-1}.[8] This electrical conductivity value is about one order of magnitude lower than the one corresponding to crystalline compound As_2Te_3; this discrepancy can be explained by differences in composition.

In order to study the growth process of the lock-on filament in a more detailed manner, an experiment was carried out that consists of interrupting this growth at different stages. Electrical stimulation is suppressed, after being in the ON state for different periods of time. In this way one can quantitatively know the time evolution of the lock-on filament. Figure 2 shows some of the results of this experiment (the number of instants at which electrical stimulation was interrupted is 40). The instant at which electrical switching takes place has been established as $t = 0$. It may be observed in Fig. 2 that, from when the material switches until the growth begins, a considerable time goes by. Also, one may observe that the growth process takes place at a constant speed, $v_g \simeq 22\ \mu$m s^{-1}, i.e., it is a uniform process (the regression analysis correlation coefficient is 0.996). Also, the value of t_w deduced from the representation in Fig. 2, considering that the interelectrode distance is approximately 1.2 mm, is 67.3 s. The time in the ON state prior to growth is 13.4 s (20% of t_w). On the other hand, Fig. 3 shows, as an example, different SEM microphotographs of the interelectrode region at different instants. In them one may observe traces of the switch-on path, together with the conductive filament, and near the anode there is a dendritelike crystalline growth that may be attributed to the higher Te atomic concentration in this zone of the channel.[12]

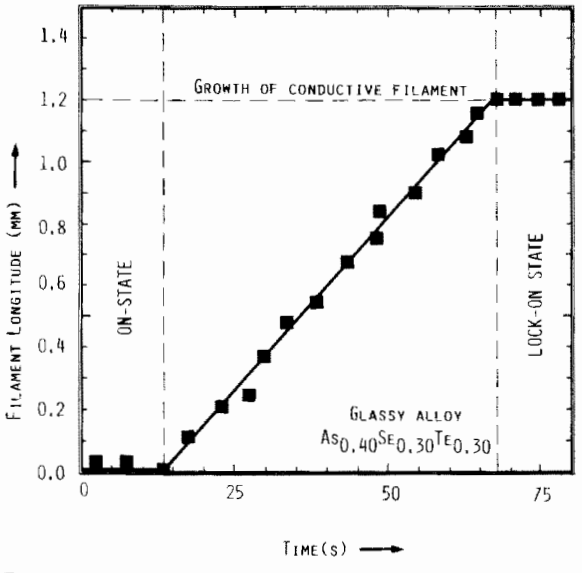

FIG. 2. Time evolution of the growth process of the conductive filament characteristic of the memory state (glassy alloy $As_{0.40}Se_{0.30}Te_{0.30}$).

The bibliography[14] quotes values for v_g between 10^{-2} cm s^{-1} and 10^2 cm s^{-1}, higher than the aforementioned value. Presumably, at least three factors can affect t_w: (1) The temperature of the filament compared to T_0; (2) the crystal growth rate at T_0; and (3) the change of composition on the growth interface, associated to electromigration.

As to the first of these factors, in glassy alloy $As_{0.40}Se_{0.30}Te_{0.30}$ it has been found that $T_0 = 274$ °C (glass transition temperature is 133 °C and the heating rate used is 20 °C/min), a value that may be considered as high.[7] As a first approximation one takes, as an indicating parameter of the crystallization rate, the temperature at which the exothermic transformation associated to crystallization in the DSC curve takes place, so the high value found for T_0 is a consequence of the low crystallization rate (this is characteristic of glassy alloys with a low Te content[7]). Furthermore, it has been observed that when the value of the lock-on current used in the formation process of the conductive filament increases, the value of t_w sensibly decreases. This fact may be a consequence of the probable temperature increase that takes place in the "active region" when the lock-on current increases (this could be verified by radiometry using an IR microscope). Table II shows some values of t_w and their corresponding I_{LO} values. As to the third factor, when the lock-on current varies, so presumably will the flow of electromigrating Te atoms. However, the lock-on filament area also depends on the I_{LO}, so the effect of the I_{LO} on the flux at the interface would have to be shown.

This analysis of the lock-on filament growth rate versus glass composition shows that, in order to obtain physical insight on the relationship between t_w and other properties of the glassy system, it is necessary to carry out new experiments that would allow a quantitative discussion of the three factors mentioned.

B. Structure and composition of the conductive filament

The surface of a bulk sample was covered with conductive filaments, in order to confirm its crystalline structure and, if possible, to determine its composition. Glassy alloy $As_{0.45}Se_{0.10}Te_{0.45}$ was used for this experiment, and the formation of filaments was done at a switching voltage of 350 V, which corresponds to $t_D = 1.1$ s ($V_{th} = 193$ V, at room temperature). Waiting time is considerably shorter for this alloy, due to its higher Te concentration. This fact is exhibited in its corresponding DSC curve (heating rate 20 °C/min), which shows that glass transition temperature is 122 °C and that the temperature that corresponds to the crystallization process is 192 °C.

On the other hand, when one tries to form lock-on

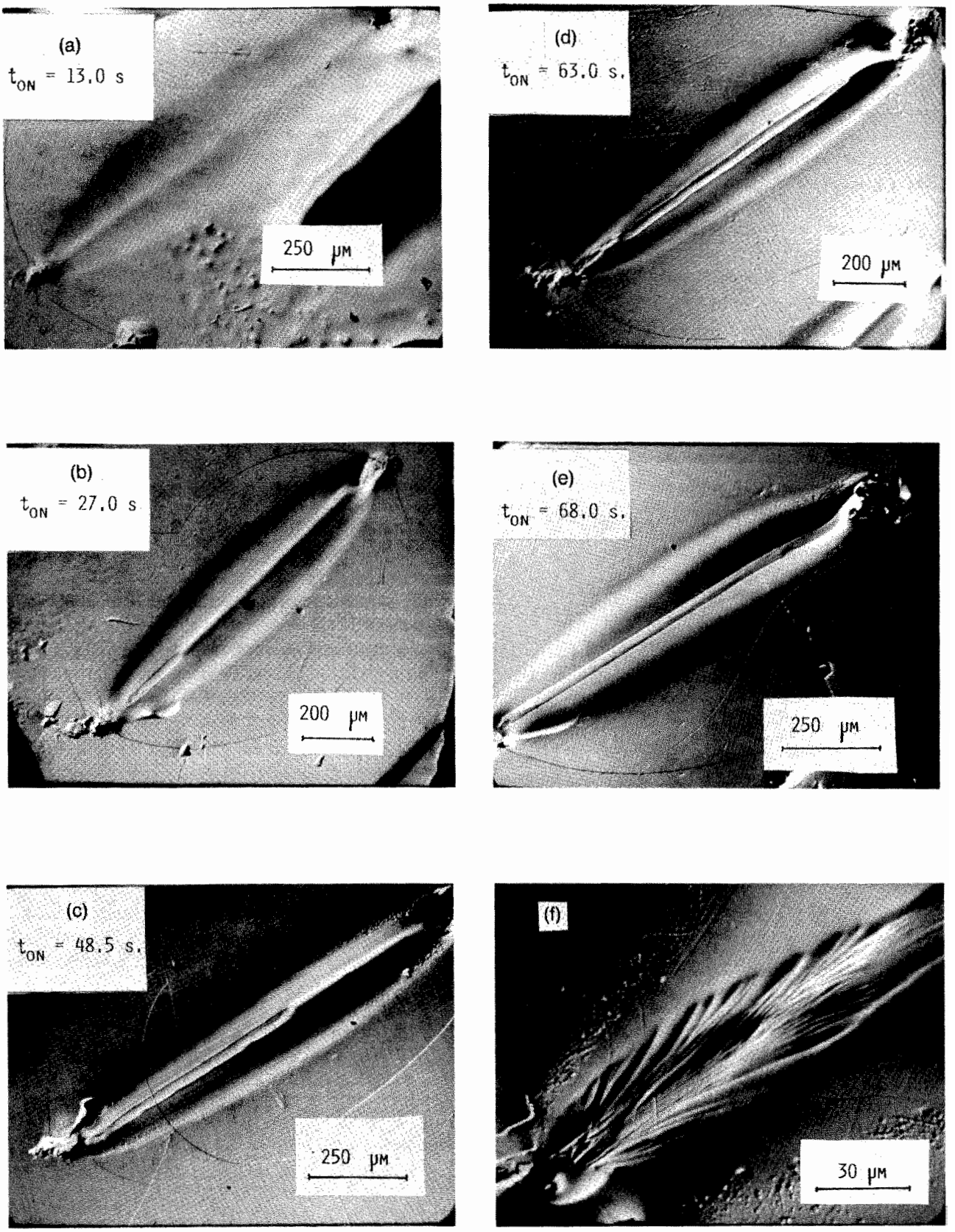

FIG. 3. Scanning electron microscopy microphotographs of the interelectrode zone at different stages of the memory process. Each one of the microphotographs shows the corresponding instant.

TABLE II. Memory process waiting times together with their corresponding lock-on currents.

I_{LO} (mA)	t_w (s)
1.0	102.3
1.5	96.3
2.0	94.9
2.5	81.8
3.5	67.3
4.5	48.3

filaments on a surface, if there is already one near the zone where one wants to generate a new filament, it produces a change in the lines of the applied electric field. This is due to the presence on this surface of a region with higher electrical conductivity (approximately 8 orders of magnitude higher than the glass matrix). Therefore, the new lock-on filament is formed through the perpendicular line in relation to the one that already exists. Figure 4 shows the surface partially covered with lock-on filaments (which take up about 40% of the sample surface), and one may observe the above-mentioned influence of the conductive filaments formed.

Figure 5 shows the x-ray diffraction pattern of the surface of glass sample $As_{0.45}Se_{0.10}Te_{0.45}$ covered with lock-on filaments. The broad peaks typical of amorphous materials, over which nine crystalline peaks are superimposed, may be observed. The d spacing for these peaks is shown in Table III, together with the ones that correspond to monoclinic As_2Te_3 (ASTM files). Figure 5 also shows the Miller indices associated to the different crystalline peaks found. Therefore, it seems reasonable to admit the presence of the crystalline compound As_2Te_3 in the lock-on filament. Similar results have been found in the identification of the composition of the lock-on filaments formed on As–Te–Ge glasses, which belong to the high-As region.[13]

From the experimental results noted in these two sections, one may infer that the memory phenomenon observed in the bulk samples of the As–Se–Te glassy semiconducting system is due to a thermally-induced glass–crystal structural transformation (Joule self-heating). Furthermore, the results are compatible with the growth model based on the electromigration of the ionized elements within the switch-on path. According to this growth model, the Te atoms are negatively ionized in the switch-on plasma, so they move towards the anode through the electric field, whereas the As and Se atoms are positively ionized and move towards the cathode (the ionized atoms can readily diffuse in the high-

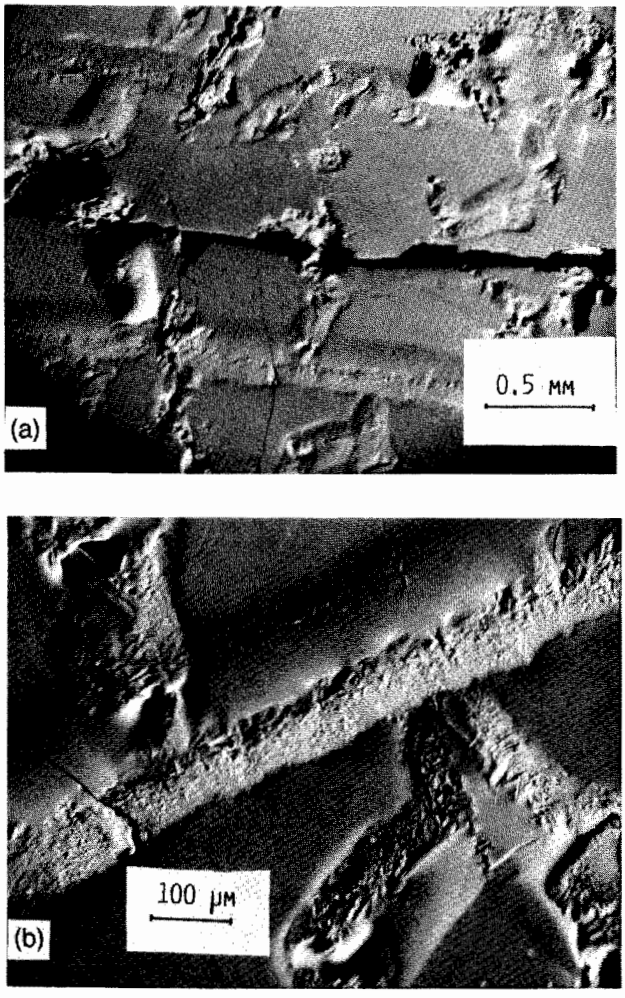

FIG. 4. Scanning electron microscopy microphotographs of the surface of a bulk sample of composition $As_{0.45}Se_{0.10}Te_{0.45}$, partially covered with conductive filaments (approximately 40%).

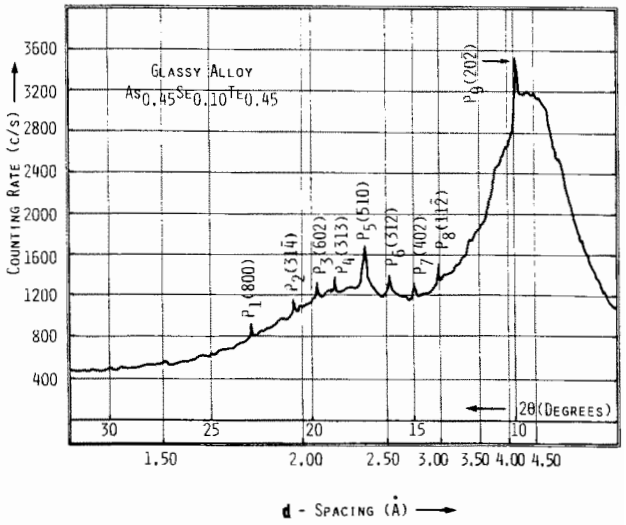

FIG. 5. X-ray diffraction pattern of the conductive filaments growing on the surface of the glass sample $As_{0.45}Se_{0.10}Te_{0.45}$ (radiation $K\alpha$ Mo was used).

TABLE III. The d spacings of the lock-on filaments induced on the surfaces of alloy $As_{0.45}Se_{0.10}Te_{0.45}$ and crystalline compound As_2Te_3. The d spacings of the crystalline compound As_2Te_3, which are close to those belonging to the filaments, are underlined.

Filaments corresponding to glassy alloy $As_{0.45}Se_{0.10}Te_{0.45}$ (Å)	Crystalline compound As_2Te_3 (Å)
4.18	4.19
2.97	3.61
2.80	3.25
2.52	3.00
2.35	2.87
2.16	2.76
2.07	2.53
1.96	2.32
1.78	2.26
	2.21
	2.17
	2.07
	2.00
	1.97
	1.83
	1.81
	1.78

temperature molten region between the electrodes). In this way, the composition differences found between the glass matrix and the lock-on filament can be explained.

C. Correlation between memory effects and short-range order

In order to try to justify the memory effects in the As–Se–Te system, through its short-range order structure, the atomic radial distribution function (RDF) obtained by x-ray diffraction has been used.[15] The area enclosed under the first RDF peak of the glassy alloy represents the average number of atoms, C, which surround a reference atom; i.e., the average coordination number for the glassy structure. Furthermore, the position of the first RDF maximum, r, establishes the average interatomic distance for the glassy structure. Therefore, both parameters characterize the short-range order of the glassy material.

In Table IV the values for C and r in both of the compositions analyzed are indicated, together with their corresponding errors.[16,17] On the other hand, Ovshinsky's criterion allows one to classify the different types of amorphous materials, to be used in making switching devices, into two categories, unistable or threshold and bistable or memory, depending on whether the average coordination number of the structure is near 2.9 atoms or 2.4 atoms, respectively.[3] According to this criterion, both compositions should exhibit memory-type behavior, and the confirmation found reaffirms the accuracy of this criterion. Furthermore, another consequence, which may be inferred, is that, in the glassy composition with a higher Te content, the crystallization process must be quicker because C, as has been noted, has a lower value.

TABLE IV. Main RDF characteristics of the glassy compositions under study.

Composition	r(Å)	C(atoms)
$As_{0.40}Se_{0.30}Te_{0.30}$	2.50 ± 0.01	2.40 ± 0.10
$As_{0.45}Se_{0.10}Te_{0.45}$	2.65 ± 0.01	2.30 ± 0.10

Figure 6 shows a space representation of the struc-

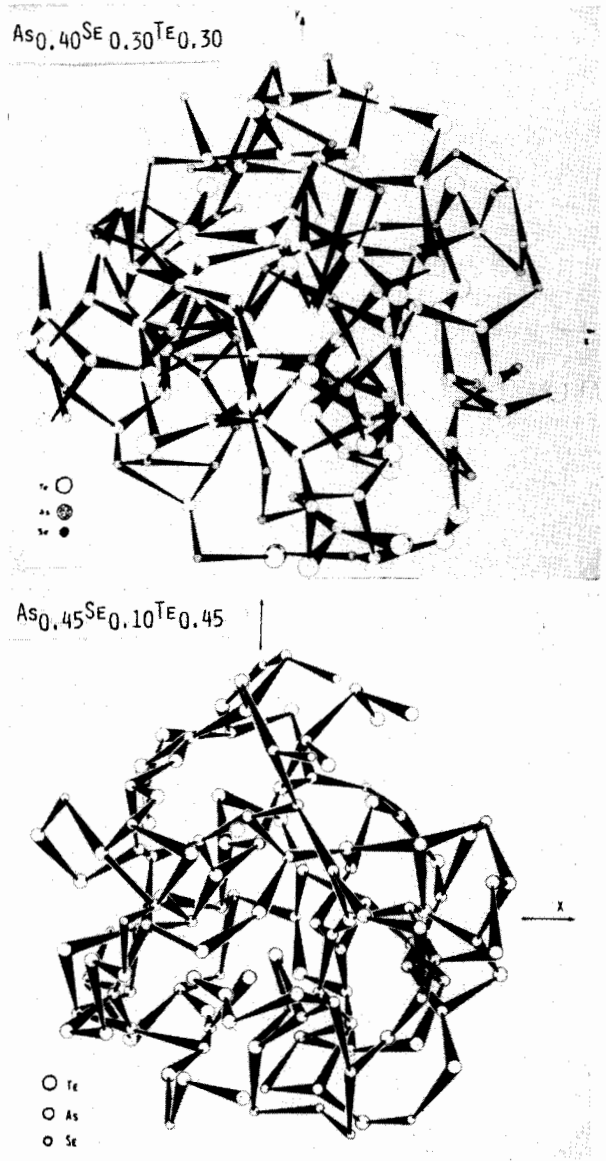

FIG. 6. Space representation of the short-range order structure models of glassy semiconducting alloys $As_{0.40}Se_{0.30}Te_{0.30}$ and $As_{0.45}Se_{0.10}Te_{0.45}$.

tural models of the compositions under study. These have been computationally generated, following the well-known Metropolis–Monte Carlo method (all the aspects related to this short-range order structural model generation method have been published elsewhere[15]). Unlike threshold-type materials,[3] these materials do not have a great number of cross links, and their bond strengths are lower (for example, the one corresponding to the As–Se bond, 40 kcal mol^{-1}, which is lower than the ones for Ge–Ge and Si–Si bonds, 45 and 53.2 kcal mol^{-1}, respectively, typical of threshold materials). Because of these characteristics, the crystallization process barrier can be overcome, through the internal energy elevation produced by the Joule self-heating associated to electrical conduction. One may also observe in Fig. 6 that the position of the atoms in both glassy compositions originates a flexible, elastic structure. This agrees with what is deduced from the low values of T_g in both compositions (the value of T_g is a simple indicator of the structural stability degree of the glass). Furthermore, by comparing both structures, one observes a greater number of Te chains in the structure of composition $As_{0.45}Se_{0.10}Te_{0.45}$, which explains its lower average coordination. Also, its structure is less compact, as may be deduced from the parameters characteristic of short-range order.

IV. CONCLUSIONS

In the preceding section, the memory phenomenon in the As–Se–Te glassy semiconducting system, using the double point contact electrode configuration on a surface, has been microscopically analyzed, bearing structural characteristics in mind. It has been shown that the low average coordination in the short-range order structures of the glassy alloys under study, and the existence of weak bonds, may be responsible for the formation of memory filaments on the surfaces of the bulk samples. Also, it is reasonable to consider that the time previous to the growth of the lock-on filament may be due to the electromigration and nucleation processes, which in the present case have turned out to be slow. In short, the results found suggest that the lock-on phenomenon is based on the crystallization of the material due to air cooling from the super-cooled liquid state, which is formed between the electrodes by switch-on action. Finally, the interesting electrical characteristics of the As–Se–Te glassy system allow one to hope for their possible use within the electronic field, as ROM (read only memory) and RMM (read mostly memory)-type devices.[13]

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