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Composition tunable memory and threshold switching in $Al_{20}As_xTe_{80-x}$ semiconducting glasses

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I-V studies indicate a composition dependent switching behavior (Memory or Threshold) in bulk $Al_{20}As_xTe_{80-x}$ glasses, which is determined by the coordination and composition of aluminum. Investigations on temperature and thickness dependence of switching and structural studies on switched samples suggest thermal and electronic mechanisms of switching for the memory and threshold samples, respectively. The present results also show that these samples have a wider composition range of threshold behavior with lower threshold voltages compared to other threshold samples.

I. INTRODUCTION

Many amorphous semiconductors, in particular, chalcogenide glasses, exhibit an abrupt change in electrical resistivity when subjected to sufficiently high electric fields.[1,2] The type of electrical switching in these materials can be memory or threshold and it depends on the local structural environment, thermal stability, and composition of the constituents. Memory switching involves local crystallization of the sample. The structure of memory switching chalcogenide glasses is usually characterized by long Te chains,[3] and atomic rearrangements are comparatively easier in memory materials. In threshold glasses, the structural cross-linking is generally higher, steric hindrances for structural reorganization are greater, and they usually have a larger energy barrier for crystallization. The threshold switching in chalcogenide glasses is known to be primarily electronic in nature, and the ON state is achieved when the charged defect states existing in these materials are filled by field injected charge carriers.[4] Many binary and ternary glassy systems such as Ge–Te, Si–Te, As–Te, Al–Te, Ge–As–Te, etc.[5–11] are found to exhibit memory switching over wide composition ranges. Only few quarternary systems, such as Si–Te–As–Ge (STAG),[2] exhibit threshold switching in thin film form. In these cases also, the threshold behavior is restricted to a narrow composition range and samples of other compositions are found to be of memory type. It is usually difficult to tune the composition of a bulk chalcogenide glass for the threshold behavior. In the present paper, we report composition tunable memory and threshold switching in ternary $Al_{20}As_xTe_{80-x}$ ($5 \leqslant x \leqslant 35$) glasses. The change in the switching type (memory/threshold) is found to be due to the changes in Al coordination with composition. Further, the dependence of switching on ambient temperature and on sample thickness indicates that the mechanisms of memory and threshold switching in these materials are primarily thermal and electronic, respectively.

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II. EXPERIMENTAL

Bulk Al–As–Te glasses belonging to the composition tie-line $Al_{20}As_xTe_{80-x}$ ($5 \leqslant x \leqslant 35$)[12] compositions were prepared from the pure (5N) elements by weighing the appropriate amounts of Al, As and Te to make 1 g of glass. Weighed elements were transferred into a quartz ampoule of 6 mm inner diameter, which was evacuated to a pressure of 10^{-5} Torr. The ampoules were maintained at this pressure for about 30 min, after which they were sealed under vacuum. The sealed tubes were heated to a temperature 850 °C in a rotating furnace and held at this temperature for 48 h to homogenize the melt. Subsequently, the ampoules were quenched in ice water + NaOH mixture. The quenched samples were confirmed to be amorphous by X-ray diffraction (XRD) and Differential Scanning Calorimetry (DSC). Virgin samples, without any annealing or post-preparative heat treatment, were used in the present study. No phase separation was detected in these samples, by scanning electron microscopy.

The I-V characteristics were studied using a PC based system developed in the laboratory.[13] Samples polished to different thicknesses (150–1200 μm) were placed in a special holder, between a point contact top electrode and a flat plate bottom electrode. A constant current was passed through the sample and the voltage developed across it was measured.

III. RESULTS AND DISCUSSION

A. The electrical switching characteristics of Al–As–Te glasses

The I-V characteristics of $Al_{20}As_xTe_{80-x}$ ($5 \leqslant x \leqslant 35$) glasses are shown in Fig. 1. It can be seen that to start

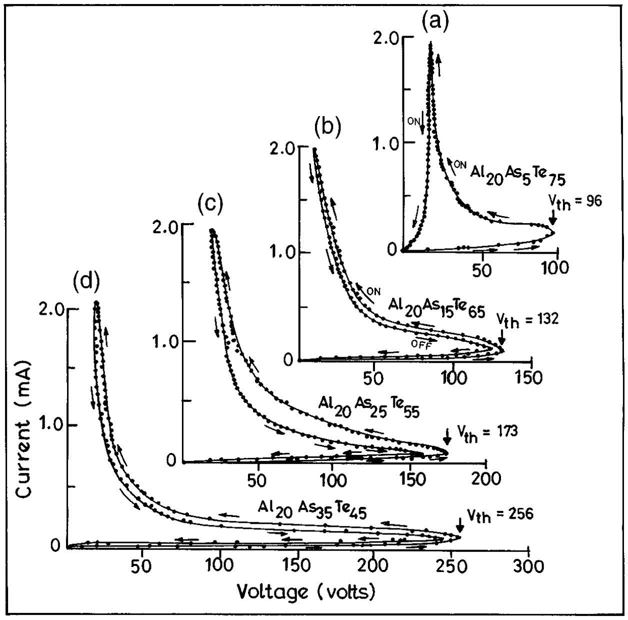

FIG. 1. The current-voltage characteristics of $Al_{20}As_xTe_{80-x}$ ($5 \leqslant x \leqslant 35$; thickness $d = 180$ μm) glasses. Here, $Al_{20}As_5Te_{75}$ is memory type (a) and other compositions show the threshold behavior (b–d). The arrows indicate the onward and return path of the characteristic, and V_{th} indicates the switching voltage.

with, samples exhibit ohmic behavior (high resistance OFF state). Around a critical voltage V_c (corresponding to a critical current I_c), the characteristics become nonlinear. At V_c, the samples exhibit switching to the low resistance ON state. It is found that $Al_{20}As_5Te_{75}$ glasses exhibit memory switching and the samples get locked into the ON state even if the current is reduced to zero [Fig. 1(a)]. Al–As–Te glasses of higher As content ($x > 5$), on the other hand, are found to exhibit threshold type switching. These samples revert back to the OFF state, on reducing the current [Figs. 1(b)–1(d)].

B. The composition dependence of switching voltages and change in the switching behavior of Al–As–Te glasses

Figure 2 shows the variation of the switching voltages (V_{th}) of $Al_{20}As_xTe_{80-x}$ ($0 \leqslant x \leqslant 35$) glasses with the concentration of As, which indicates that the switching voltages of both memory and threshold glasses increase with the increase in arsenic proportion. In Al–Te and As–Te glasses also, an increase in the switching voltages has been observed with the increase in the amount of As and Al,[6,7] due to an increase in the network connectivity of these glasses.[14]

The present results indicate that Al–Al–Te glasses of higher As concentrations (above 5 at.%), exhibit threshold switching. The change in the switching behavior at higher As proportions seems to be intimately connected with the local environment of constituent

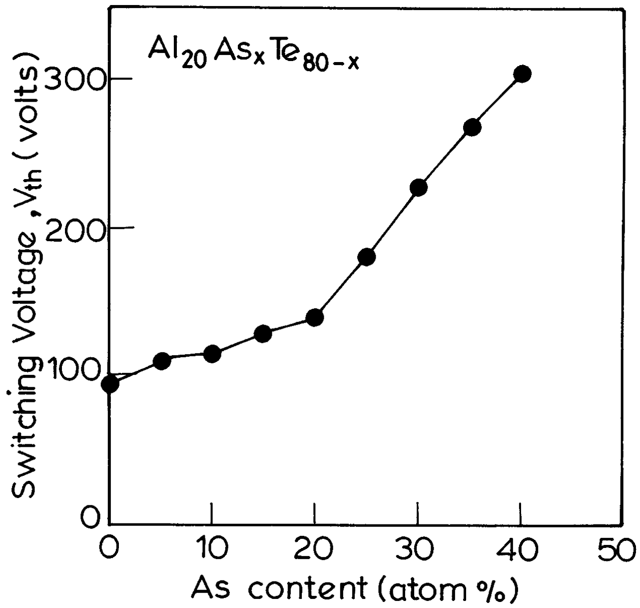

FIG. 2. The compositional dependence of switching voltages of Al_{20}-As_xTe_{80-x} ($5 \leqslant x \leqslant 40$) glasses.

atoms. MASS NMR studies[15] on ^{27}Al indicate that in $Al_{20}As_xTe_{80-x}$ ($5 \leqslant x \leqslant 35$) glasses, Al has two different coordination environments, namely 4-fold and 6-fold, respectively. At lower As concentrations (5 at.% of As), the ratio between 4-fold and 6-fold coordinated Al atoms is around 50%. With increasing x, the number of 4-fold coordinated Al decreases and it becomes zero around 25 at.% of As. It is clear that in compositions which exhibit threshold switching, Al is predominantly 6-fold coordinated. The increase in the coordination of Al can lead to a higher connectivity of the glass. Consequently, in samples with higher structural connectivity, memory switching becomes difficult and threshold behavior is more favorable.

It should also be noted that the bond length of As–As is much smaller than that of Te–Te. Therefore, free rotation of molecules becomes difficult at higher arsenic concentration because of the higher energy barrier to rotation. It is likely that the formation of arsenic "pair locks" at higher arsenic content[16] also contributes to the change in switching type.

C. Temperature dependence of switching of Al–As–Te glasses

Figure 3 shows the I-V characteristics of $Al_{20}As_5$-Te_{75} memory glass at different temperatures, and the inset in Fig. 3 gives the variation with temperature of the switching voltages V_{th}. It can be seen from Fig. 3 that the I-V characteristic becomes broader and the switching becomes more sluggish in $Al_{20}As_5Te_{75}$ memory samples at high temperatures. Also, the switching voltages are found to decrease with an increase in temperature. As

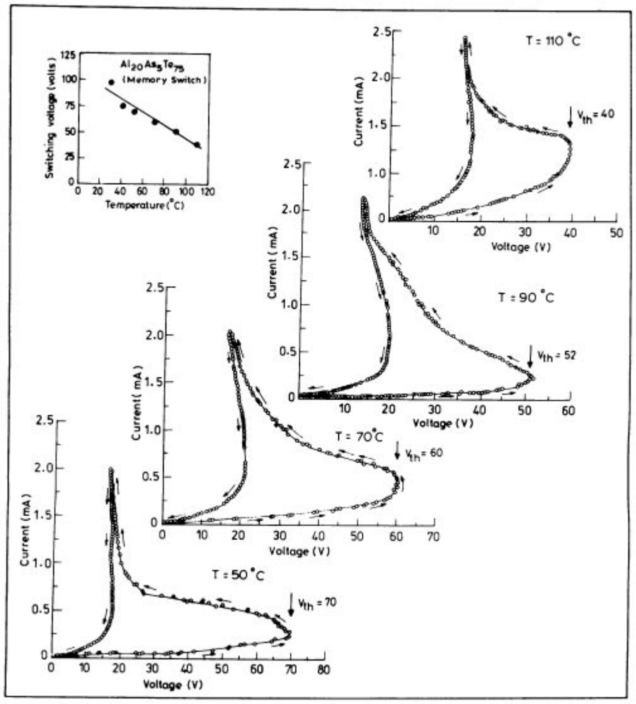

FIG. 3. The current-voltage characteristics of a representative memory glass ($Al_{20}As_5Te_{75}$) at different temperatures. The inset in the figure shows temperature dependence of switching voltages (V_{th}).

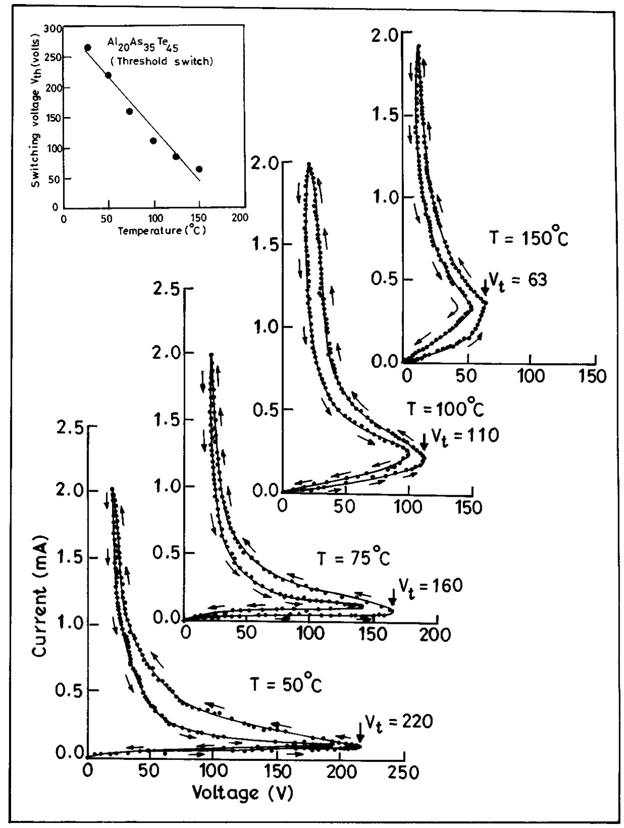

FIG. 4. The current-voltage characteristics of a representative threshold glass ($Al_{20}As_{35}Te_{45}$) at different temperatures. The inset in the figure shows temperature dependence of switching voltages (V_{th}).

mentioned earlier, memory switching in chalcogenide glasses involves the formation of a conducting crystalline channel in the material.[17–20] Therefore, decrease of switching voltages of memory materials can be expected, as the energy barriers for crystallization are reduced at higher temperatures.

Figure 4 shows the I-V characteristic of a representative $Al_{20}As_{35}Te_{45}$ threshold sample at different temperatures. The behavior is similar for other threshold switching Al–As–Te samples at room temperature. It can be seen from Fig. 4 that there is no appreciable broadening in the I-V characteristic with temperature as compared to the memory materials. However, there is a considerable decrease in switching voltages with temperature (Fig. 4, inset).

The electrical properties of chalcogenide glasses are controlled by positively and negatively charged defect states existing in the material (C_3^+ and C_1^-), known as valence alternation pairs. Here, C represents the chalcogen and the subscript and superscript denote the coordination and the charge state, respectively. The threshold switching in these materials occurs when these charged trapping centers are filled by field-injected charge carriers.[4,21] It has been recently pointed by Kolobov that the thermal conversion of the charged defect states results in the conversion of C_3^+ centers into C_1^0 and C_1^- centers into C_1^0 centers, with a creation of a free hole and an electron, respectively.[22] While the conversion at the C_3^+ site involves structural modification and is irreversible, the initial state may be restored at the C_1^- center during recombination. Nevertheless, there is a reduction in the trapping centers at higher temperatures due to the above thermal excitation of the defect states, which accounts for the decrease in the switching voltages of the threshold samples with temperature. As mentioned earlier, in spite of this decrease in V_{th} there is no appreciable thermal degradation of the I-V characteristics of the threshold Al–As–Te samples.

D. Thickness dependence of switching voltages of Al–As–Te glasses

1. Memory samples

Figure 5(a) shows the variation of switching voltage with thickness (in the range 150–1000 μm) for the $Al_{20}As_5Te_{75}$ memory sample, which indicates that the switching voltage has a $d^{1/2}$ dependence with the sample thickness. As mentioned earlier, the memory switching in chalcogenide glasses is basically thermal in origin.[20] The detailed treatment of steady-state thermal breakdown of dielectrics has been done a long time ago considering a slab of homogeneous dielectric of thickness d and of large area with electrodes so thin so

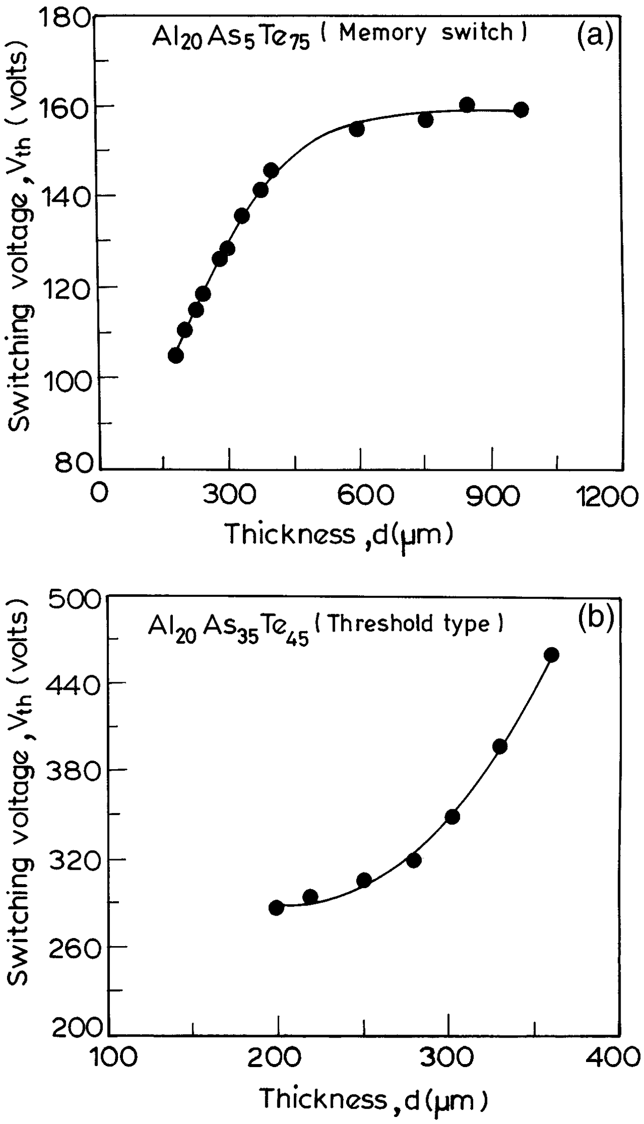

FIG. 5. (a) The thickness (d) dependence of switching voltages of a $Al_{20}As_5Te_{75}$ memory sample. The points represent the experimental data and the line shows the fit to $d^{1/2}$. (b) The thickness (d) dependence of switching voltages of a $Al_{20}As_{35}Te_{45}$ threshold sample. The points represents the experimental data and the line shows the fit to d^2.

as to constitute no thermal impediment to the ambient medium.[23] Here, the thermal conductivity of the material (κ), as well as a constant external thermal conductivity (λ) which quantifies the heat lost by the dielectric through the electrode surface, are important. If $\lambda d \leqslant 2\ \kappa$, the dielectric behaves as a thermally thick slab and it is said to be thermally thin if $\lambda d \leqslant 2\ \kappa$. In the first case, the temperature drop within the material is greater than the temperature drop at the boundary and there is a nonuniform temperature distribution within the sample. In the second case, the temperature drop at the boundary is higher due to the larger heat loss at the electrodes and a more uniform temperature distribution occurs within the sample; V_{th} has a dependence of the type $V_{th} \propto d^{1/2}$ for a thermally thin slab and $V_{th} \propto d$ for a thermally thick slab.[23]

It can be appreciated from the above that in electrical switching with thermal origin, either a linear or square-root dependence of switching voltages with sample thickness can be observed, depending on the parameters λ (determined by the electrode geometry and electrode material) and κ (decided by the sample). For example, in Al–Te–Ge (0.5–2.5 μm),[24] Ge–As–Se (0.2–1.4 μm),[25] As–Se (0.1–1.2 μm),[26] and Se (0.1–1 μm)[27] amorphous semiconductor memory switches, V_{th} is found to vary linearly with thickness d. However, memory switching Ge–As–Te (0.1–10 μm)[28] and Ge–Te (0.2–1 μm)[29] samples show a square-root dependence of switching voltages with the device thickness. It is interesting to note from the present investigations that the switching voltages of bulk, Al–As–Te memory glasses (150–1000 μm thickness) vary with thickness as $d^{1/2}$ [Fig. 5(a)]. As mentioned earlier, a point contact electrode geometry is used in the present experiments, which is likely to reduce the heat dissipation through the electrodes. Consequently, a $d^{1/2}$ dependence is seen. Further, concentration of electric stresses at electrodes is also known to give rise to a square-root dependence of thermal breakdown voltages on sample thickness.[30] The nonuniform field distribution associated with the point-contact geometry can also contribute to the observed square-root dependence.

2. Threshold samples

There are several models, proposed by Lucas,[31] Henisch *et al.*,[32] and others, to understand the electronic processes involved in the threshold switching of chalcogenide glasses. One feature that is generally applicable to the electronic models based on carrier injection at electrodes is that the switching voltage is a function of the square of the sample thickness.[33] In literature, there are no data available for the thickness dependence of bulk chalcogenide threshold switches. However, thin film threshold samples of Si–Te–As–Ge (0.1–5 μm)[34] and (0.5–2.5 μm)[24] are found to show a linear dependence of V_{th} with d. It is also found that in these samples, a higher sample thickness leads to a sublinear dependence, owing to an additional thermal contribution.[35]

Figure 5(b) shows the thickness dependence of switching voltages of a representative $Al_{20}As_{35}Te_{45}$ threshold sample. The behavior is similar for other threshold switching Al–As–Te samples investigated. It can be seen from Fig. 5(b) that the switching voltages of the threshold Al–As–Te samples vary as d^2 in the thickness range 140–300 μm, which indicates that the threshold switching in these glasses is primarily electronic in nature.[19]

E. X-ray and electron microscopic analysis of memory and threshold materials

Figure 6 shows the x-ray diffraction (XRD) pattern of the switched portion of representative memory and threshold switching Al–As–Te glasses. The diffraction pattern of the memory material recovered after the first switching cycle shows that the material is crystalline [Fig. 6(a)]. The crystalline phase formed primarily corresponds to As_2Te_3, in spite of the appreciable amount of Al in the virgin glass [Fig. 6(a)]. It is known that the temperature of the conducting filament rises to 600 °C and above during switching,[36,37] which is sufficient to locally melt the material (M.P. of the $Al_{20}As_5Te_{75}$ glasses being of the order 400 °C). In memory materials, the molten conducting channel solidifies into the crystalline state. As the bond energies of As–Te, Al–Te, and Te–Te bonds are 78, 64, and 63 kcal/mol, respectively,[38] the formation of As–Te bonds from the melt is more favorable than the formation of Al–Te and Te–Te bonds. Hence, the crystallizing channel formed is essentially As_2Te_3, and it can be concluded that the excess Al is redistributed in the surrounding amorphous matrix.

The threshold switching Al–As–Te samples remain amorphous even after many switching cycles. Figure 6(b) shows the XRD pattern of representative $Al_{20}As_{35}Te_{45}$ threshold sample recovered after 25 switching cycles, which confirms that there is no crystallization of the material.

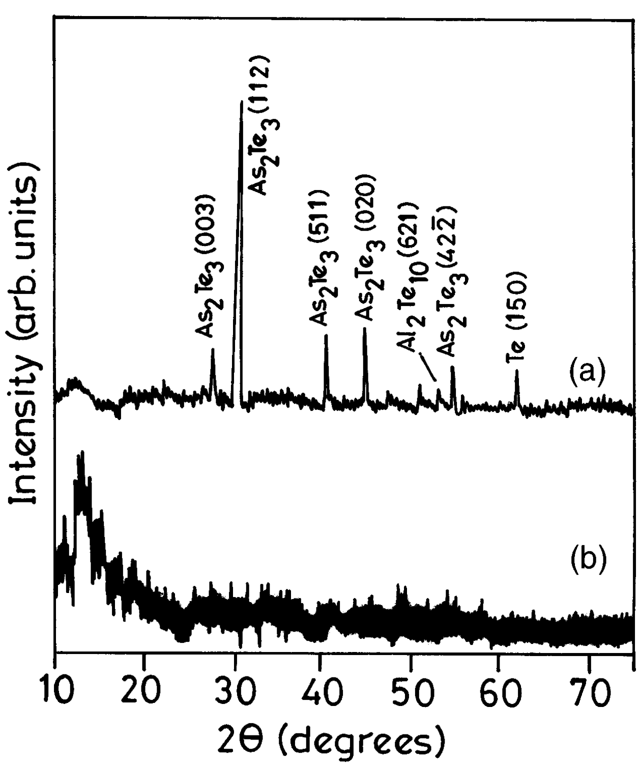

FIG. 6. (a) XRD pattern of the switched portion of memory material ($Al_{20}As_5Te_{75}$). (b) XRD pattern of the switched portion of threshold material ($Al_{20}As_{35}Te_{45}$) recovered after 25 switching cycles.

IV. CONCLUSIONS

Bulk, melt-quenched Al–As–Te glasses are found to exhibit memory or threshold switching, depending on the composition. The memory-threshold change in the switching behavior is found to be intimately connected with the coordination of Al and the formation of As–As pair locks. The temperature and thickness dependence of switching voltages and structural investigations suggest the thermal mechanism of switching for memory materials. Further, the threshold switching in Al–As–Te glasses is found to be primarily electronic.

The present studies also indicate that Al–As–Te glasses have a wider composition range of threshold behavior (15–40 at.% of As) and lower threshold voltages (95–300 V for 200 μm thickness) compared to other threshold switching samples (400–500 V for 100 μm thickness).

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