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Local structure and electrical switching in chalcogenide glasses

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Bulk $Al_xAs_{40}Te_{60-x}$ and $Al_xAs_{40-x}Te_{60}$ glasses ($5 \leqslant x \leqslant 20$) are found to exhibit memory and threshold switching. ^{27}Al solid-state NMR measurements reveal that in both series of glasses, Al resides in tetrahedrally (fourfold) as well as octahedrally (sixfold) coordinated environments, with the fraction of fourfold coordinated Al atoms in the glasses decreasing with Al content. Fourfold coordinated Al atoms provide structural flexibility, and promote memory switching at low Al content ($x < 15$). At higher Al content, the growth in the fraction of sixfold coordinated atoms leads to increased network connectivity, which promotes threshold switching. [S0163-1829(98)02730-1]

I. INTRODUCTION

Amorphous chalcogenide semiconductors exhibit memory and threshold switching at high electric fields.[1,2] The structure of chalcogenide glasses exhibiting memory switching usually consists of long Te chains in which atomic rearrangements occur easily.[3] They possess high electrical conductance, which can result in large power dissipation. The application of a high electric field leads to crystallization of the glass and, as a result, the sample remains in the low resistance on state even after the removal of the field. In threshold materials, structural cross linking of chains is generally higher, leading to steric hindrances in which structural reorganization becomes more difficult. These materials have high thermal stability and a large energy barrier for crystallization. The conducting on state in Ovonic threshold switching materials is achieved primarily by excitation of lone-pair electrons of low ionization energy.[4] The original high impedance off state is recovered when the field is reduced.

There are many binary and ternary glassy systems such as Ge-Te, Si-Te, As-Te, Al-Te, As-Se-Te, Ge-As-Te, etc.,[5–11] which are found to exhibit memory switching over wide composition ranges. It is usually difficult to tune the composition of a chalcogenide glass for threshold behavior. The quartenary system Si-Te-As-Ge (Ref. 2) exhibits threshold switching. In these glasses, threshold behavior is restricted to a narrow composition range, and glasses of other compositions are found to be of memory type.

We have now achieved memory and threshold switching in a single ternary Al-As-Te glassy system by changing the glass composition. In the present work, we report on the crucial role played by the local structure in both types of switching in this ternary. The influence of thermal parameters on the switching behavior of these samples is also discussed.

II. EXPERIMENT

Bulk $Al_xAs_{40}Te_{60-x}$ ($5 \leqslant x \leqslant 20$) and $Al_xAs_{40-x}Te_{60}$ ($5 \leqslant x \leqslant 20$) glasses were prepared by conventional melt quenching. The samples were confirmed to be noncrystalline by x-ray diffraction. Differential scanning calorimetric (DSC) studies were undertaken in a Stanton-Redcroft DSC-1500 to establish glass transition temperatures (T_g) and crystallization temperatures (T_c). I-V characteristics of the glasses were recorded using a PC based system developed in the laboratory.[12] Polished samples of 0.20 mm thickness were placed in a special holder between a point-contact top electrode and a flat plate bottom electrode for the I-V measurements. A constant current was passed through the sample and the voltage developed across was measured.

Solid-state magic angle sample spinning (MASS) NMR (^{27}Al) spectra of the glasses were recorded with a Bruker DSX-300 spectrometer operating at 78.206 MHz. Al environments in the glassy state were correlated with switching behavior.

III. RESULTS AND DISCUSSION

A. The switching behavior of Al-As-Te glasses

Electrical switching studies on $Al_xAs_{40}Te_{60-x}$ ($5 \leqslant x \leqslant 20$) and $Al_xAs_{40-x}Te_{60}$ ($5 \leqslant x \leqslant 20$) glasses indicate that these samples exhibit a composition-dependent switching behavior. In both $Al_xAs_{40}Te_{60-x}$ and $Al_xAs_{40-x}Te_{60}$ series of glasses, samples at low Al content ($x < 20$) show memory switching, while those at higher Al content exhibit threshold switching (Figs. 1 and 2). For example, in Fig. 2, $Al_xAs_{40-x}Te_{60}$ glass at $x = 5$ shows a clear memory behavior; while the sample at $x = 10$ exhibits a tendency of threshold behavior before latching to the memory state. Samples at $x = 15$ and $x = 20$ exhibit stable threshold switching (Fig. 2). Al-As-Te glasses at higher Al content ($\geqslant 20$ at. % of Al) exhibit threshold switching, irrespective of the amount of As or Te.

B. The composition dependence of switching voltages of Al-As-Te glasses

Figure 3 shows the variation of the switching voltages in $Al_xAs_{40-x}Te_{60}$ and $Al_xAs_{40}Te_{60-x}$ glasses with Al content. Switching voltages for both memory and threshold Al-As-Te glasses increase with the aluminum content of the glasses. The presence of sixfold coordinated aluminum in the network apparently promotes network connectivity of these glasses, and leads to increased switching voltages.[13] A similar increase in switching voltages with Al content was observed[8] in binary Al-Te glasses.

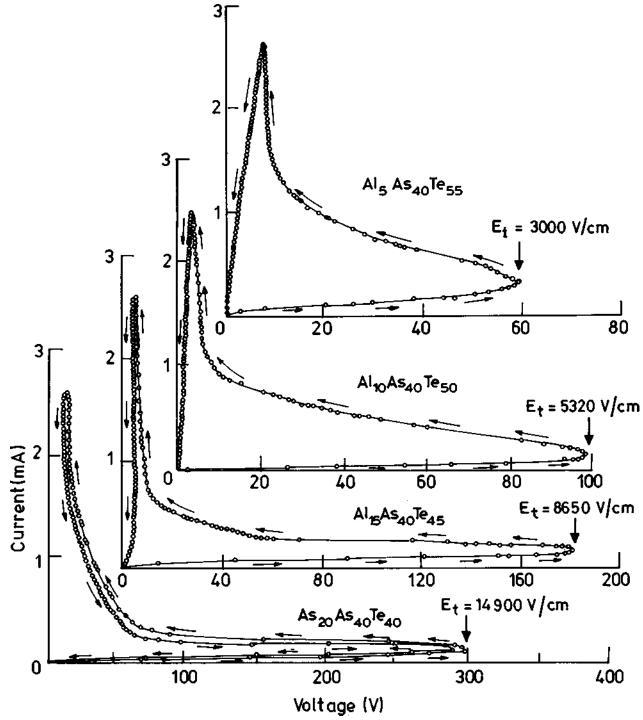

FIG. 1. Composition-dependent current-voltage characteristics of $Al_xAs_{40}Te_{60-x}$ $(5\leq x\leq 20)$ glasses.

It is interesting to note here that the electrical resistivity of both $Al_xAs_{40}Te_{60-x}$ and $Al_xAs_{40-x}Te_{60}$ $(5\leq x\leq 20)$ glasses increase with the increase in Al content. Earlier papers[14] indicated a direct correlation between switching voltages and sample resistivity in a variety of chalcogenide glasses. In this sense, the composition dependence of switching voltages and electrical resistivity of Al-As-Te glasses are consistent.

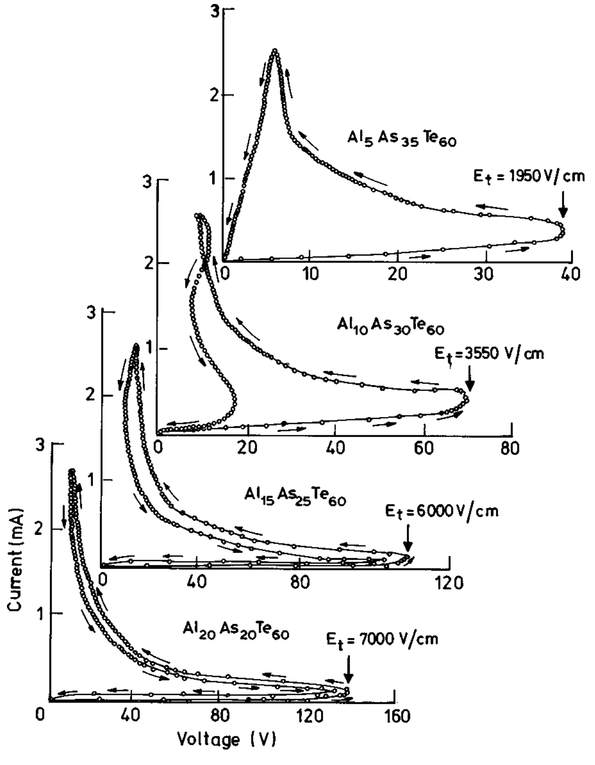

FIG. 2. Composition-dependent current-voltage characteristics of $Al_xAs_{40-x}Te_{60}$ $(5\leq x\leq 20)$ glasses.

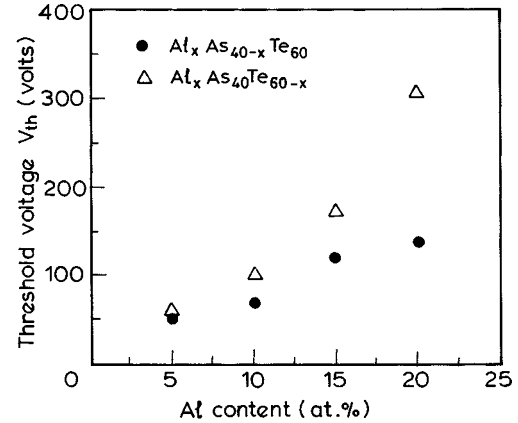

FIG. 3. Variation of switching voltages (V_{th}) with Al content for $Al_xAs_{40}Te_{60-x}$ and $Al_xAs_{40-x}Te_{60}$ $(5\leq x\leq 20)$ glasses.

C. Memory and threshold switching in Al-As-Te samples

Figures 1 and 2 show that Al-As-Te glasses at low Al content exhibit memory behavior while samples at larger Al content show threshold switching. It is known that structural cross linking, weaker bonds, and more lone-pair interactions favor memory switching in chalcogenide glasses.[4] Also, the thermal stability of samples play a crucial role in the memory switching. The present study indicates that the change in the switching behavior of Al-As-Te samples is influenced by structural cross linking (decided by the coordination of Al) and thermal effects, as seen below.

1. Aluminum coordination and switching behavior of Al based chalcogenide glasses

In the glassy state, Al is known to reside in three different structural environments, having fourfold, fivefold, and sixfold coordinations, respectively.[15,16] The present MASS NMR experiments indicate that in the Al-As-Te system, only fourfold and sixfold coordinated Al atoms are present. Figures 4 and 5 show the MASS NMR spectra of $Al_xAs_{40}Te_{60-x}$ and $Al_xAs_{40-x}Te_{60}$ glasses $(10\leq x\leq 20)$, which indicate the presence of fourfold and sixfold coordinated Al atoms. Here, it is convenient to define two quantities, f_4 and f_6, the percent fraction of fourfold and sixfold coordinated Al atoms, in relation to the total Al content of the glasses,

$$f_4=\mathrm{Al}(4)\times 100/[\mathrm{Al}(4)+\mathrm{Al}(6)],$$

$$f_6=\mathrm{Al}(6)\times 100/[\mathrm{Al}(4)+\mathrm{Al}(6)].$$

In both series of glasses ($Al_xAs_{40}Te_{60-x}$ and $Al_xAs_{40-x}Te_{60}$), Al alloying lowers the fraction f_4. For example, in the $Al_xAs_{40}Te_{60-x}$ ternary, f_4 decreases from 18% to 10% as x increases from 10% to 20% (Fig. 4, inset). While in the $Al_xAs_{40-x}Te_{60}$ ternary, f_4 shows a modest decrease from 11.1% to 9.1% as x increases from 10% to 20% (Fig. 5, inset).

The local structure seems to play a major role in the composition-dependent switching behavior of Al-As-Te glasses. In both $Al_xAs_{40}Te_{60-x}$ and $Al_xAs_{40-x}Te_{60}$ series of

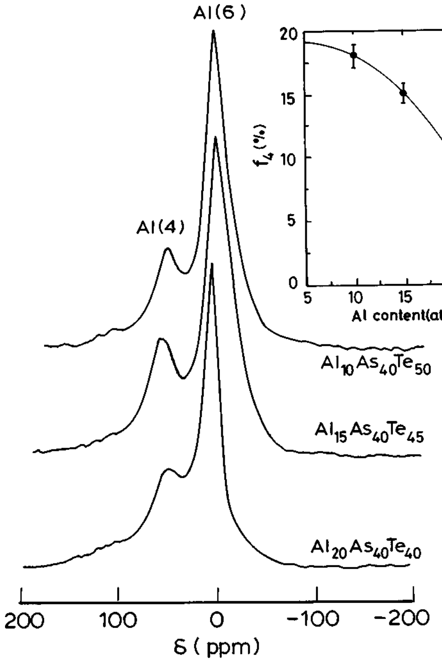

FIG. 4. Compositional dependence of the 76.206 MHz ^{27}Al-MASS NMR spectrum of $Al_xAs_{40}Te_{60-x}$ $(10 \leqslant x \leqslant 20)$ glasses. The chemical shifts near 0 and 60 ppm are assigned octahedral and tetrahedral coordinations, respectively. Inset shows the composition dependence of the % fraction of fourfold (f_4) coordinated Al atoms; $f_4 = \mathrm{Al(4)} \times 100/[\mathrm{Al(4)}+\mathrm{Al(6)}]$.

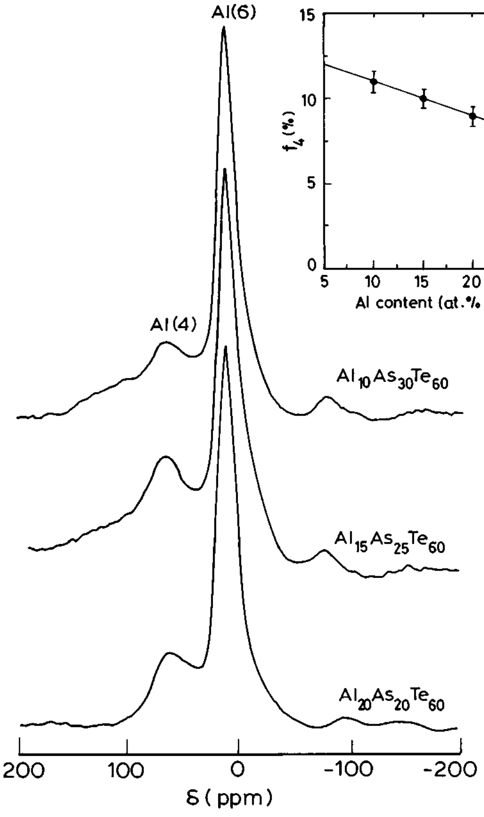

FIG. 5. ^{27}Al-MASS NMR spectrum of $Al_xAs_{40-x}Te_{60}$ $(10 \leqslant x \leqslant 20)$ glasses. Inset shows the composition dependence of the % fraction of fourfold (f_4) coordinated Al atoms; $f_4 = \mathrm{Al(4)} \times 100/[\mathrm{Al(4)}+\mathrm{Al(6)}]$.

TABLE I. Variation V_{th}, T_g, T_c, $T_c - T_g$, and ρ of $Al_xAs_{40-x}Te_{60}$ $(0 \leqslant x \leqslant 20)$ glasses.

x	V_{th}	T_g (°C)	T_c (°C)	$T_c - T_g$ (°C)	ρ (Ω cm)
0	48	110	182	72	2.12×10^4
5	54	125	215	90	8.54×10^4
10	71	137	244	107	5.45×10^5
15	120	149	280	131	7.54×10^6
20	140	166	336	170	3.60×10^7

glasses, at higher Al content $(x > 15)$, f_6 is greater than f_4. The presence of larger numbers of sixfold coordinated Al atoms results in increased structural cross linking in Al-As-Te samples. In samples with high network connectivity, structural reorganization required for memory switching becomes difficult, and threshold behavior is favored. On the other hand, in Al-As-Te glasses with low Al content, fourfold coordinated Al atoms promote structural flexibility. Network structural reorganization is easier, and such glasses exhibit memory switching.

In this context, it is also interesting to compare switching behavior and Al coordination in Al-Te and Al-As-Te glasses. In Al_xTe_{100-x} glasses $(17 \leqslant x \leqslant 30)$, Al is found to be both tetrahedrally and octahedrally coordinated, with the fractions f_4 and f_6 being almost equal at all x compositions.[17] Al_xTe_{100-x} glasses at all compositions exhibit memory switching[8] only. This result confirms that a larger fraction of the sixfold coordination of Al is required for threshold switching in Al based glasses.

2. The thermal stability and electrical switching of Al-As-Te, As-Te, and Al-Te glasses

In addition to the local structure, thermal properties are also found to play a role in the switching behavior of Al-As-Te samples. Table I summarizes the glass transition and crystallization temperatures of representative $Al_xAs_{40-x}Te_{60}$ glasses, obtained by DSC. It can be seen from Table I that the glass transition temperatures of Al-As-Te samples increase with the Al content, in a fashion parallel to the switching voltages. Earlier papers[8,18,19] also indicate a direct relationship between switching voltages and glass transition temperatures in chalcogenide glasses.

Furthermore, we note that for memory switching to occur, crystallization temperatures of glasses are generally low. The crystallization temperatures increase linearly with Al content, and for the threshold sample $(Al_{20}As_{20}Te_{60})$, it is about 100 °C higher than that for memory materials.[20] Further, the separation between the crystallization and glass transition temperatures of $Al_xAs_{40-x}Te_{60}$ glasses $(T_c - T_g)$, which is indicative of the stability of the glass against devitrification, increases with x (Fig. 6). Such an increase in the thermal stability of Al-As-Te glasses at higher Al content also contributes to the memory-threshold change observed in the switching behavior.

As mentioned earlier, Al-Te and As-Te glasses exhibit only memory switching in the entire composition range of glass formation.[7,8] Al-As-Te glasses, on the other hand, exhibit memory or threshold behavior depending on the composition. In this context, it is interesting to compare the ther-

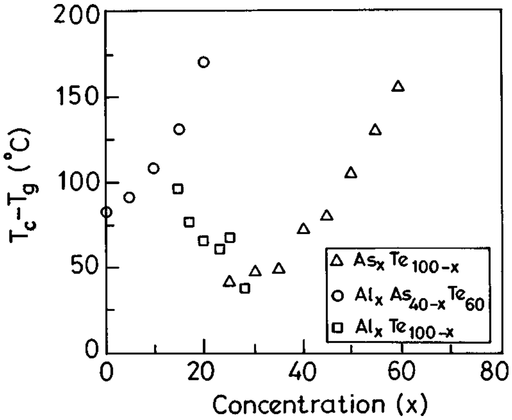

FIG. 6. Variation of thermal stability ($T_c - T_g$) with composition for Al-As-Te, Al-Te, and As-Te glasses.

mal stability of As-Te, Al-Te, and Al-As-Te samples. The thermal stability of Al-Te glasses decreases with Al content, in spite of the increase in T_g due to the decrease in T_c (Ref. 21) (Fig. 6). The decrease in thermal stability also contributes to the memory switching exhibited by Al-Te glasses at higher Al concentrations, in addition to the coordination effects discussed earlier. Figure 6 also shows the composition dependence of thermal stability of As-Te glasses. It can be seen that the thermal stability of As_xTe_{100-x} glasses, unlike the Al_xTe_{100-x} samples, increases with composition (x). The memory switching observed in these glasses may arise due to the lower coordination of the constituents.

IV. CONCLUSIONS

Bulk $Al_xAs_{40}Te_{60-x}$ and $Al_xAs_{40-x}Te_{60}$ glasses ($5 \leqslant x \leqslant 20$) are found to exhibit a change in the electrical switching behavior (memory to threshold) as a function of Al concentration. MASS NMR studies indicate that, in these samples, Al resides in tetrahedral [Al(4)] as well as octahedral [Al(6)] coordination environments. The fraction of fourfold coordinated Al atoms decreases with the increase in Al content in both series of glasses. The larger fraction of sixfold coordinated Al atoms at higher Al content leads to an increased structural connectivity that is less favorable for structural reorganization. Consequently, these samples show threshold behavior. The comparatively larger fraction of fourfold coordinated Al provides the structural flexibility required for memory switching at lower Al concentrations. The composition-dependent memory-threshold change is also consistent with the variation with composition of the thermal properties of Al-As-Te glasses.

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