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Electrical switching, local structure and thermal crystallization in Al-Te glasses

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ABSTRACT

Bulk Al_xTe_{100-x} glasses ($17 \leq x \leq 29$) prepared by melt quenching method are found to exhibit threshold switching. The local coordination of Al probed by MAS NMR indicates that Al resides in $^{[4]}$Al, $^{[5]}$Al and $^{[6]}$Al environments. With the addition of Al, there is an increase in C_3^+ defect centers which largely influences the switching properties of Al-Te glasses. The presence of higher coordinated Al crosslinks the network and the network becomes rigid. The switching voltage, glass transition and crystallization temperatures are found to increase with the increase of Al concentration. This indicates that the crosslinking and the rigidity of the structural network increases by the addition of Al. A memory switching material undergoes structural change between amorphous and crystalline states meaning a large structural reorganization. In a highly crosslinked rigid network, structural reorganization becomes difficult and hence results in threshold switching.

1. Introduction

The interest in chalcogenide glasses is growing as these glasses undergo a phase change between a high resistive amorphous (OFF) state and a low resistive crystalline (ON) state upon the application of a suitable current pulse [1]. They have been explored as one of the active components to overcome the limitation of the current semiconductor devices for high density data storage [2]. This switching of the chalcogenide glasses by electrical pulse is of two types; namely, (i) threshold (ii) memory [3–5]. Threshold switching device reverts back to its OFF state immediately upon the removal of the applied filed. It requires a minimum holding current (I_h) to remain in the ON state. A memory device remains in the ON state even after the complete removal of the applied field [6].

Threshold and memory switching is generally explained by electronic and thermal models respectively [1–3,5–8]. The electronic model is based on the defect states (C_3^+ and C_1^-) that are present in the mobility gap of the chalcogenide glasses. These defect states act as trap centers for charge carriers. The switching occurs after all the trap states are filled by the charge carriers [3,5]. On removing the current below $I_h (I < I_h)$, the device reverts to it high resistance OFF state [1,3–6]. In memory glass, due to Joule heating a high conducting crystalline filament formed between the electrodes. A high current pulse can locally melt the filament and reset the device to its OFF state [2,6,9]. Nucleation model also explains the memory switching based on the chemical stability of the amorphous phase against the crystalline phase [10,11].

Addition of metal atoms like Cu, Ag, Pb, Bi largely influences the thermal, electrical and optical properties of chalcogenide glasses [6,12–15]. Diffraction experiments find metal atoms in chalcogenide glasses are always in 4- fold coordination [16–18]. Formal valence shell (FVS) model also predicts 4-fold coordination for metal atoms in chalcogenide glasses [19]. This model allows a maximum of 4- fold coordination for each atom present in the network. This is possible when the lone-pair electrons of chalcogen atoms are formally transferred to the metal atoms [19]. By donating its lone-pair electrons, the local coordination of chalcogen atoms gradually increases from 2 to 4 [19,20]. This increases the crosslinking and the structural network becomes increasingly rigid. Among metal added chalcogenides glasses, Al-Te shows memory switching whereas Al-As-Te and Cu-As-Se glasses show both memory and threshold switching depending upon the concentration of metal atoms [6,14,15,21]. Observation of 4- and 6-fold coordinated Al in Al-Te and Al-As-Te glasses by NMR studies does not go well with the FVS model. The higher coordinated metal atoms greatly influences the network rigidity and the defect states, which inturn largely influences the electrical switching behaviour [14]. Usually, the higher coordinated atoms crosslinks the structural network and hence structural reorganization becomes

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difficult. To observe memory switching, a transition from amorphous/glass to crystalline phase should occur which essentially means a structural reorganization. So, in a highly crosslinked network, threshold switching is normally expected. The observation of memory switching in Al-Te, Al-As-Te and Cu-As-Se is surprising as these glasses are highly crosslinked.

The electrical switching in chalcogenide covalent glasses are closely related to the local structure and the amorphous to crystal transformation. Hence, thermal analysis is very important to understand the electrical switching phenomenon in chalcogenide glasses. For example, in $Cu_yAs_{40}Se_{60-y}$ glasses threshold switching is observed for $15 \leq y \leq 25$ and memory switching is observed for higher concentrations of Cu (x > 25) [6]. These glasses also show crystallization upon heating which means a structural reorganization as in the case of the memory switching glasses. The observed threshold switching was explained with the help of thermal studies as follows: A filament is formed at the time of switching in both threshold and memory glasses. The filament formation is by glass → melt → crystal/amorphous transition and not a by direct glass → crystal transition. This indicates that the material in the interelectrode region melts and solidify quickly at the time of switching [22,23]. The filament may phase separate into temporary (high resistive amorphous) and permanent (high conducting crystalline) regions. The ratio between crystalline to amorphous decides the switching type. A high viscous melt resists the nucleation and crystal growth. The growth of nuclei is sluggish in a high viscous melt (usually good glass formers) and hence, most of the nuclei will not achieve a stable critical size and disappear in the filament [10,11]. In this case, the ratio between crystalline to amorphous phases becomes less and the material exhibit threshold switching. In poor glass formers, the ratio can be high and hence the material exhibit memory switching.

In this context, the present study concentrates on the electrical switching behaviour of Al_xTe_{100-x} ($17 \leq x \leq 29$) glasses and its direct relation with the local structure changes around Al atoms. The local structure studied by ^{27}Al MAS NMR reveals 4-, 5- and 6-fold coordination for Al in Al_xTe_{100-x} glasses. This is the first observation of 5-fold coordinated Al atoms in non-oxide chalcogenide glasses. In a recent report 5- fold coordinated Al is observed in crystallline Al-Te-Sb samples and the corresponding amorphous films show only 4- and 6- fold coordination [24]. Earlier NMR studies on Al_xTe_{100-x}($17 \leq x \leq 29$) glasses also show only 4- and 6-fold coordination for Al and these glasses were reported to exhbit memory switching [25]. In the present studies, Al_xTe_{100-x} glasses are found to exhibit threshold switching for an applied current of 3 mA. These findings are understood on the basis of the local structure changes and the changes in the defect states in Al_xTe_{100-x} glasses.

2. Experimental methods

Bulk Al_xTe_{100-x} glasses ($17 \leq x \leq 29$) were prepared by normal melt quenching method. Appropriate amounts of high purity elements (99.999%) taken in a quartz ampoule were sealed under a vacuum better than 10^{-5} Torr. The sealed ampoules were loaded into a resistive furnace. The temperature of the furnace was increased to 900 °C at a rate of 100 °C/h. The ampoule was continuously rotated to ensure the homogenization of the melt. After 48 h, the melt was quenched in NaOH + ice + water bath. The amorphous nature of the samples was confirmed by X-ray diffraction(XRD). A PerkinElmer differential scanning calorimeter (DSC 8000) was used to measure the thermal properties at a scan rate of 10 °C/min. About 15 mg of sample was taken in a crimped aluminium pan. An empty crimped aluminium pan was used as the reference. The prepared glass samples were thermally treated under a vacuum ~10^{-5} Torr in two ways: (i) annealed at their respective crystallization temperatures (T_c) for 2 h; (ii) heated to its melting temperatures (T_m) and quenched in water at room temperature. Electrical switching studies were carried out using a Keithley Sourcemeter (Model: 2410) interfaced with a PC controlled by Lab VIEW 8.5 (National Instruments) [26]. Samples thinned down to a thickness of ~0.30 mm were placed between a flat plate bottom electrode and a point contact top electrode using a spring loading mechanism. Both the electrodes were made of brass. A controlled current was passed through the sample and the corresponding voltage developed across the sample was measured. ^{27}Al MAS-NMR was performed on powdered samples spinning at 10 KHz under a high magnetic field of 9.4 T in Joel ECX – 400 MHz NMR spectrometer.

Results and discussion

I–V characteristics of Al_xTe_{100-x} bulk glasses ($17 \leq x \leq 29$) are shown in Fig. 1. Initially, current and voltage follow a linear path. At a critical voltage called threshold voltage (V_{Th}) the I–V curve deviates from the linear behaviour and follows a negative differential resistance region [1,5,8] leading to the ON state. When the current is reduced to zero, the Al_xTe_{10-x} glasses switches back to its initial high resistive (OFF) state indicating a threshold switching character. Earlier report shows memory switching for Al_xTe_{100-x} glasses [21]. This observed change in switching type can be attributed to changes in the sample preparation conditions and varied experimental conditions.

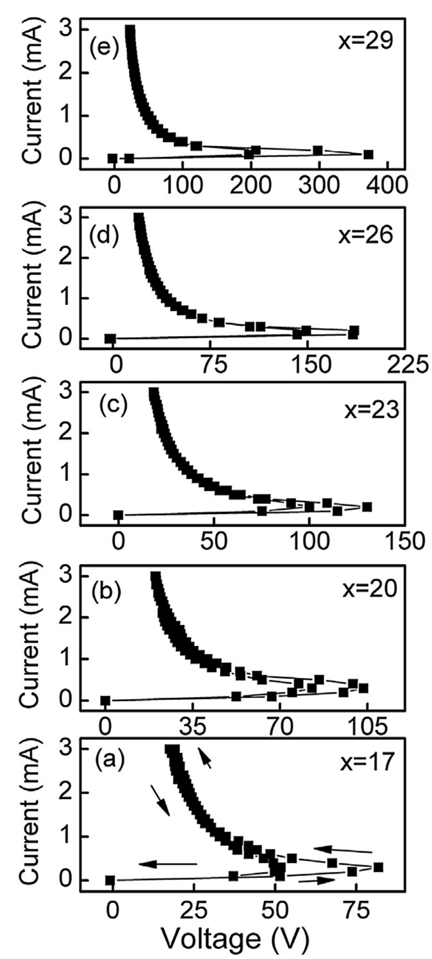

Fig. 1. I–V of representative compositions in Al_xTe_{100-x} glasses showing threshold switching behaviour.