

## ELECTRICAL SWITCHING IN CHALCOGENIDE GLASSES- SOME NEWER INSIGHTS

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The recent studies on the switching behavior of several chalcogenide semiconductors indicate that there exists a close relation between the electrical switching and structural effects in these materials; the two network topological Thresholds, namely the Rigidity Percolation and the Chemical Threshold are found to influence considerably the composition dependence of the switching voltages/fields of many memory and threshold switching glasses. Further, changes in the coordination of constituent atoms are found to effect a change in the switching behavior (memory to threshold). Also, an interesting relation has been established between the type of switching exhibited and the thermal diffusivity of the material.

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### 1. Introduction

Electrical switching in chalcogenide glasses has been discovered by Ovshinsky nearly about three decades ago [1]. Though the promised applications in information storage or power control have not been fully realized, electrical switching has remained to be one of the fascinating properties of these materials.

The relation between switching parameters and other properties of chalcogenide glasses has been a topic of intense investigations for long time. Several investigations have been directed towards understanding the relation between the switching voltages and glass transition temperature [2,3], crystallization temperature [4], electrical resistivity [5], ambient temperature and conductivity activation energy [6], etc., of glassy chalcogenides. In the recent times, considerable attention has been given to understand the influence of the two network topological thresholds, namely the Rigidity Percolation Threshold (RPT) and Chemical Threshold (CT) respectively, on the switching behavior of chalcogenide glasses [7-9]. Rigidity Percolation deals with network connectivity and at the rigidity percolation threshold an equilibrium is established in a chalcogenide network glass, between the degrees of freedom per atom and the number of constraints acting on it [10-13]. For a network with purely covalent bonding, the rigidity percolation occurs at a mean coordination number  $\langle r_c \rangle = 2.4$  [10-13]. If medium range order is taken into account in the constraint balance equation, the percolation threshold may shift to higher  $\langle r \rangle$  values [14]. It has also been recently pointed out that in certain glassy systems, the Rigidity Percolation may be spread over a range of composition around the mean-field threshold of  $\langle r_c \rangle = 2.4$  [15,16]. The Chemical Threshold (CT) is usually taken to be the critical composition at which the chemical ordering is maximized in a chalcogenide network glass, with the bonding being fully heteropolar [17]. The stoichiometric glass, which is energetically closest to the crystalline state, is also considered to be a Chemical Threshold in a glassy system.

In this paper, an effort is made to summarize the effect of RPT and CT in the composition dependence of switching fields of a variety of chalcogenide glasses. Further, the role played by the coordination of the constituents, thermal diffusivity, etc. in determining the type of switching exhibited by the sample is discussed.

### 2. Experimental

Bulk, semiconducting chalcogenide glasses have been prepared by vacuum-sealed melt quenching method. Appropriate quantities of high purity constituent elements were sealed in an evacuated quartz ampoule (at  $10^{-5}$  Torr) and slowly heated in a horizontal rotary furnace. The ampoules were maintained at 1000 °C and rotated continuously for about 24 hours at 10 RPM to ensure the homogeneity of the melt. The ampoules are subsequently quenched in a bath of ice water and NaOH mixture to get bulk glassy samples. The amorphous nature of the quenched samples was confirmed by X-ray diffraction. The electrical switching studies are undertaken in an IBM PC controlled system developed in the

laboratory [18]. Samples polished to the required thickness are mounted in a holder made of brass, in between a flat plate top electrode and a point contact electrode using a spring loading mechanism. A constant current is passed through the sample and the voltage developed across the sample is measured.

### 3. Results and discussion

#### i) Effect of topological thresholds on switching voltages

Fig. 1(a) shows the I-V characteristics of  $\text{Ge}_{20}\text{Te}_{80}$  and  $\text{Ge}_{23}\text{Te}_{77}$  glasses from the series  $\text{Ge}_x\text{Te}_{100-x}$  ( $15 \leq x < 25$ ). They indicate that these samples exhibit memory switching. The switching voltages of  $\text{Ge}_x\text{Te}_{100-x}$  glasses lie in the range 4-11 kV/cm.

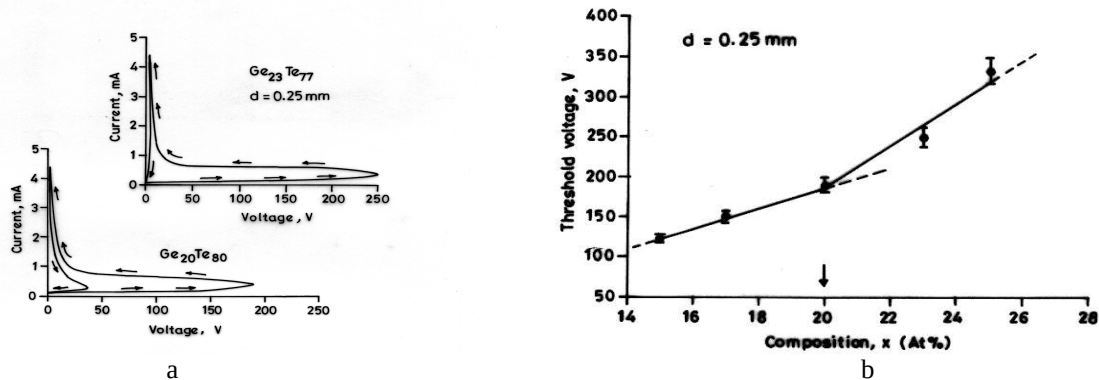


Fig. 1. a) I-V characteristics of  $\text{Ge}_{20}\text{Te}_{80}$  and  $\text{Ge}_{23}\text{Te}_{77}$  glasses, b) Composition dependence of switching voltages of  $\text{Ge}_x\text{Te}_{100-x}$  glasses.

The variation of switching voltages with the composition of  $\text{Ge}_x\text{Te}_{100-x}$  glasses is presented in Fig. 1(b), which shows that the switching voltages of  $\text{Ge}_x\text{Te}_{100-x}$  samples increase with Ge content (x) in the composition range  $15 \leq x < 20$ . At the composition  $x = 20$ , there is a sharp change in slope (lower to higher) in the composition dependence of switching voltage. It has been identified long back that the composition  $x = 20$  in the  $\text{Ge}_x\text{Te}_{100-x}$  system corresponds to its percolation threshold [19] and the average coordination for this composition ( $\langle r \rangle$ ) is 2.4, the mean field estimate of the RPT according to a Phillips theory [10-13]. Hence the sharp slope change in the switching voltages of  $\text{Ge}_x\text{Te}_{100-x}$  glasses observed at  $x = 20$  can be associated with the Rigidity Percolation. In this system, it has not been possible to see the influence of Chemical Threshold on the switching voltages, as the composition range of bulk glass formation is below the CT. Fig. 2 (a) shows the I-V characteristics of  $\text{Ge}_{7.5}\text{As}_{50}\text{Te}_{42.5}$  glass, representing the series  $\text{Ge}_{7.5}\text{As}_x\text{Te}_{92.5-x}$  ( $15 \leq x \leq 60$ ). It can be seen from this figure that Ge-As-Te samples exhibit memory type electrical switching at fields around 7 kV/cm. The composition dependence of threshold fields ( $E_t$ ) of  $\text{Ge}_{7.5}\text{As}_x\text{Te}_{92.5-x}$  glasses, is shown in Fig. 2 (b), which indicates that  $E_t$  increases linearly with x in the composition range  $15 \leq x \leq 25$ . At  $x = 25$ , a distinct change in slope is observed. It is interesting to note that the composition  $x = 25$  corresponds  $\langle r \rangle = 2.4$ , the RPT of the  $\text{Ge}_{7.5}\text{As}_x\text{Te}_{92.5-x}$  glassy system, and the slope change seen in  $E_t$  of Ge-As-Te glasses, can therefore be clearly associated with rigidity percolation. Above the RPT, the switching fields of  $\text{Ge}_{7.5}\text{As}_{50}\text{Te}_{42.5}$  increase again with composition, but with a higher slope. Further, a reversal in trend is observed at the composition  $x = 50$ , which leads to a minimum in  $E_t$  at  $x = 52.5$ . The composition at which a minimum is seen in  $E_t$  of  $\text{Ge}_{7.5}\text{As}_x\text{Te}_{92.5-x}$  glasses, is likely to correspond to the chemical threshold of the system. The memory switching in chalcogenide glasses is known to involve crystallization of the sample, which in turn requires structural reorganization [20]. With increasing rigidity, the network becomes less flexible and structural reorganization becomes more difficult. Hence, memory-switching fields is likely to progressively increase with increasing network rigidity and one could expect a slope change (from a lower to a higher value) in the composition dependence of switching voltages/fields across the percolation threshold [7].

Further, in a glassy system, the chemically ordered glass can be considered to be energetically closest to the crystalline phase [7,8]. Therefore, the driving force required for the crystallization is the least for this sample. Based on this, one could expect the memory-switching voltages to exhibit a minimum at the chemical threshold of a glassy system. Thus the observed anomalies in the composition dependence of switching voltages/fields of Ge-Te and Ge-As-Te glasses at the RPT and CT, are consistent with the expectations.

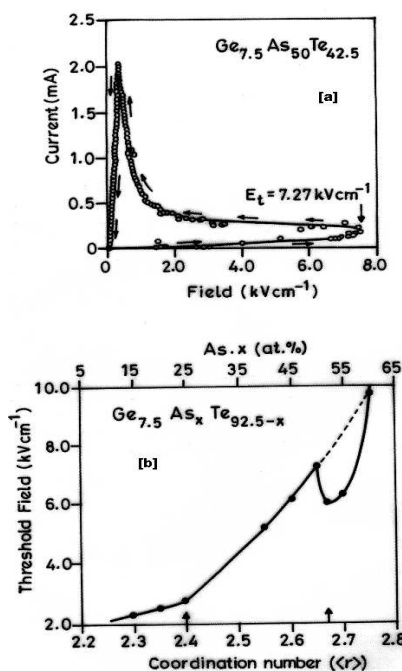


Fig. 2. a) I-V characteristics of a representative Ge<sub>7.5</sub>As<sub>50</sub>Te<sub>42.5</sub> Glass, b) The composition dependence of threshold fields of Ge<sub>7.5</sub>As<sub>x</sub>Te<sub>92.5</sub> Glasses.

## ii) Role of coordination of constituents in switching behavior

Fig. 3 shows the I-V characteristics and switching behavior of Al<sub>20</sub>As<sub>x</sub>Te<sub>80-x</sub> glasses, which indicates that there is a change in the switching behavior of the sample with composition. Al-As-Te samples with lower arsenic concentrations (<5 at. %) exhibit memory switching and those with higher Al concentrations (> 5 at. %) show threshold behavior. Magic Angle Spinning Nuclear Magnetic Resonance (MASS NMR) studies show that in Al<sub>20</sub>As<sub>x</sub>Te<sub>80-x</sub> glasses [21], aluminum has two different coordination environments, namely 4-fold and 6-fold respectively. At lower arsenic concentrations, the ratio between 4-fold and 6-fold coordinated Al atoms is around 50 %. With increasing x, the fraction of 4-fold coordinated Al atoms decreases and it becomes zero around 25-atom % of arsenic. It is clear from the MASS NMR studies that in glasses, which exhibit threshold behavior, Al is predominantly 6-fold coordinated. The 6-fold coordinated aluminum atoms lead to increased structural cross-linking. In these samples with higher network connectivity, structural reorganization required for memory switching becomes difficult and threshold behavior is favored. On the other hand, in samples with lower arsenic content, the 4-fold coordinated Al atoms provide the structural flexibility and promote memory switching.

It is also interesting to note here that the As-As bond length is much smaller than that of Te-Te. Therefore, the free rotation of molecules becomes difficult at higher arsenic proportions, because of the higher energy barrier for rotation. The formation of arsenic pair-locks also contributes for the change in the switching type observed at higher arsenic content.

## iii) Thermal diffusivity and switching behavior

The variation of thermal diffusivity of Al<sub>20</sub>As<sub>x</sub>Te<sub>80-x</sub> glasses with x, has been obtained using Photo-Acoustic Spectroscopy (PAS) [22]. The thermal diffusivity ( $\alpha_s$ ) of Al<sub>20</sub>As<sub>x</sub>Te<sub>80-x</sub> glasses has been found to increase progressively with arsenic content and culminates in a peak around x = 20. Further, the PAS measurements reveal that the thermal diffusivity of the Al-As-Te samples that show memory behavior, is lower than that of samples exhibiting threshold switching [22]. Also, the electrical conductivity of samples with lower arsenic content is higher than that at higher arsenic content. Under the influence of electric field, the glass specimens with lower arsenic content will experience a higher Joule heating due to the higher conductance. The lower  $\alpha_s$  in these samples also implies a higher resistivity to the flow of diffusing thermal waves. This means that the rate at which the heat is removed from the regions carrying the current (filament region), is lower in samples with lower arsenic content. As a consequence, there will be a rise in temperature, which can trigger phase transformation and memory switching. On the other hand, in samples with higher arsenic percentages, the lower electrical conductivity in conjunction

with higher thermal diffusivity may preclude high enough temperature rise in their conducting region to cause any structural phase transformation. In such a case, the threshold behavior is seen.

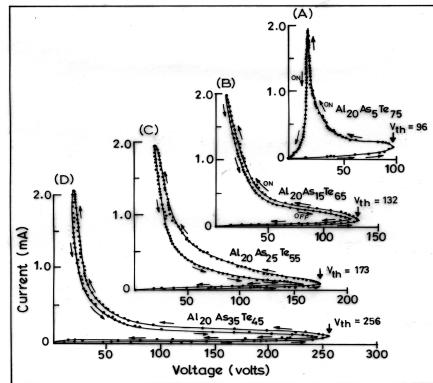


Fig. 3. Composition dependent switching behavior of  $\text{Al}_{20}\text{As}_x\text{Te}_{80-x}$  glasses.

#### 4. Conclusion

Electrical switching studies on a variety of chalcogenide glasses indicate that the network topological effects such as Rigidity Percolation and the Chemical Threshold influence considerably the composition dependence of the switching voltages of these materials. Further, factors like coordination of the constituent atoms, thermal diffusivity, etc., are found to determine type of switching exhibited (memory or threshold) by chalcogenide glasses.

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