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Non-linear I-V characteristics and threshold switching in As-Te-In glasses

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ABSTRACT

Non-linear I-V behaviour and electrical switching exhibited by chalcogenide glassy semiconductors, find applications in variety of areas including information storage and power control. In this work, semiconducting chalcogenide \( \text{As}_4\text{Te}_{60-x}\text{In}_x \) glasses \( (7.5 \leq x \leq 16.5) \) have been prepared by melt quenching technique. The current-voltage and electrical switching behaviour of these glasses have been studied using a custom-built PC based system. The results obtained clearly indicate that all the glasses studied exhibit current controlled negative resistance behaviour, which leads to the low resistance state. The switching to the low resistance state is found to be reversible (threshold behaviour) and the samples revert back to the high resistance state on reducing the current. Threshold switching over such a wide range of compositions has been observed only in very few systems so far. The most interesting outcome of the present studies is the variation of the switching voltage with composition. It is observed that there is an increase in the switching voltage (threshold voltage) \( V_t \) with the increase in indium concentration in the composition range \( 7.5 \leq x \leq 12.5 \). Further, the composition dependence of switching field is found to exhibit a distinct change in slope at \( x=12.5 \) (mechanical threshold) and \( V_t \) continues to increase with \( x \) until \( x=13.5 \). Around \( x=13.5 \), the trend is reversed and \( V_t \) starts decreasing with \( x \). A minimum in \( V_t \) is seen around the composition \( x=14.3 \), which corresponds to the chemical threshold of the As-Te-In system. Beyond \( x=14.3 \), switching voltage is found to increase with composition again. The present results are consistent with earlier observations, which indicate the composition dependence of switching voltages of chalcogenide glasses are influenced by chemical ordering and rigidity percolation.

1. INTRODUCTION

Electrical switching in chalcogenide glasses was first observed by Ovshinsky, when an appropriate electric field known as the threshold or the critical field \( (E_t) \) is applied, the glass switches from a semiconducting OFF state to a conducting ON state. Chalcogenide glasses, which exhibit switching, are classified into memory (irreversible) or threshold (reversible) types. Threshold-switching glasses revert to the OFF state upon the removal of the switching field, whereas memory switches remain locked to the ON state.

The relation between the electrical switching and the network topological thresholds of chalcogenide glasses, has been a topic of interest in the recent times. Theoretical investigations have revealed the existence of two topological effects namely, Rigidity Percolation and Chemical Ordering in chalcogenide glasses. The rigidity percolation deals with dimensionality and rigidity of a glassy network and is decided by the average co-ordination number \( <r> \) of the glass. The constraint theory of Phillips and Thorpe proposes that in a chalcogenide network glass, at an average critical co-ordination \( <r_c> \), a mechanical equilibrium is established. At \( <r_c> \), the degrees of freedom per atom and the number of constraints acting on it become equal. Chalcogenide network glasses with \( <r> < <r_c> \) are under constrained and are elastically floppy, whereas glasses with \( <r> > <r_c> \) are over constrained and rigid. The composition corresponding to \( <r_c> \) is known as the Rigidity Percolation Threshold (RPT) or mechanical threshold (MT) of the glass. For a glassy network with purely covalent bonding, rigidity percolation occurs at a mean co-ordination number \( <r> = 2.4 \). However, it is pointed out that if ionic interactions are taken into account, the percolation threshold may shift to higher \( <r> \) values.

At a composition known as the chemical threshold (CT), a chalcogenide glass is considered to be chemically ordered consisting of only heteropolar bonds. The chemical threshold is expected to occur at a mean co-ordination \( <r> = 2.67 \).
Anomalies in various properties of chalcogenide glasses have been observed at the Rigidity Percolation and Chemical
thresholds. In this work, an attempt is made to understand the effect of topological thresholds on the switching
behaviour of As-Te-In glasses.

2. EXPERIMENTAL

Bulk semiconducting As$_{40}$Te$_{60-x}$In$_{x}$ (7.5 ≤ x ≤ 16.5; 2.55 ≤ <r> ≤ 2.73), glasses have been prepared by melt quenching
method. The amorphous nature of the quenched samples is confirmed by X-ray diffraction. The I-V characteristic of these
glasses is studied using a custom built PC based system. Samples polished to different thickness are mounted between a
flat plate 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 and corresponding current through the sample is measured.

3. RESULTS AND DISCUSSION

Figure 1-2 shows the current-voltage characteristics of all composition studied in the composition tie line As$_{40}$Te$_{60-x}$In$_{x}$
glasses for 0.28mm thick samples. It can be seen from figure 1-2 that all the As$_{40}$Te$_{60-x}$In$_{x}$ glasses exhibit non-linear I-V
characteristics and switching above a critical voltage $V_t$. Further, the samples revert back to the high resistance OFF state
on reducing the current (threshold switching behaviour).

Figure 3 shows the variation of the switching (threshold) voltage $V_t$ as a function of composition (x)/average co-ordination
number (<r>) for As$_{40}$Te$_{60-x}$In$_{x}$ glasses for 0.28mm thick samples. It can be seen from figure 3 that $V_t$ increases linearly
with increase in indium content in the range 2.55 ≤ <r> ≤ 2.65 (7.5 ≤ x ≤ 12.5). At <r> = 2.65 (x=12.5), a sharp slope change
(lower to higher) is seen in the <r> dependence of $V_t$. Above <r> = 2.65, $V_t$ continues to increase, until a reversal in trend
is observed around <r> = 2.67 (x=13.5). Subsequently, $V_t$ decreases with <r>, reaching a minimum around <r> = 2.69
(x=14.3). Beyond <r> = 2.69, $V_t$ increases with composition again.

In chalcogenide glasses, the composition dependence of switching voltage/field is determined by factors such as
co-ordination of the additive element, rigidity percolation, chemical ordering, etc. Metallic dopants usually take up 4-fold
coordination in chalcogenide glasses and based on a coordination of four for indium, it can be concluded that the
network connectivity and rigidity increases with indium concentration. The increase in the switching voltages with <r> in
the range 2.55-2.65, can be associated with the increase in network connectivity and rigidity percolation. Further, the
mean co-ordination <r> = 2.65 at which a slope change is seen in $V_t$ is likely to correspond to the RPT of the As-Te-In
system. A similar increase in $V_t$ and the slope change in the composition dependence of $V_t$ at RPT, have been observed
erlier in many other chalcogenide samples.

Usually, non-covalent interactions in a covalent network shift the rigidity percolation threshold from its ideal value of
2.4, to higher values of <r>. The four fold or higher co-ordination of metallic atoms in a chalcogenide network demands
partially ionic bonding, which explains the shifting in the RPT to <r> = 2.65 in As-Te-In samples.

Above <r> = 2.65, the switching voltages of As-Te-In glasses can be expected to exhibit a continued increase with <r>. The
observed turn-around in the switching voltage of As-Te-In glasses around <r> = 2.67 occurs due to the onset of chemical
ordering. With increasing chemical order, the charge carriers are likely to be less localised. The increased
conductivity aids switching, leading to a reduction in switching voltage. Further, the minimum seen in the threshold fields
of As-Te-In samples at the mean co-ordination number <r> = 2.69 can be taken as an indication of a possible chemical
threshold at the corresponding composition. A local minimum in $V_t$ at CT has been reported earlier in other systems such
as Ge-As-Te.
Figure 1. I-V characteristics of $\text{As}_{40}\text{Te}_{60-x}\text{In}_x$ glasses with (a) $x=7.5$, (b) $x=10$ and (c) $x=12.5$.

Figure 2. I-V characteristics of $\text{As}_{40}\text{Te}_{60-x}\text{In}_x$ glasses with (a) $x=13.5$, (b) $x=14.3$, (c) $x=15$ and (d) $x=16.5$. 
4. CONCLUSION
Bulk As$_{40}$Te$_{60-x}$In$_x$ glasses ($7.5 \leq x \leq 16.5$) have been found to exhibit threshold switching over a wide range of composition. The composition dependence of switching fields with indium concentration bears the signatures of rigidity percolation and chemical ordering at $\langle r \rangle = 2.65$ and $\langle r \rangle = 2.69$ respectively.

REFERENCES