

## Evidence concerning the effect of topology on electrical switching in chalcogenide network glasses

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Electrical switching properties of Ge-As-Te glasses have been investigated over a wide range of mean coordination numbers ( $\langle r \rangle$ ) in a single composition tie line. The results obtained clearly indicate the modulation of the composition dependence of switching fields by network topology. Distinct change is observed in the slope of the composition dependence of switching field, at  $x=25$  ( $\langle r \rangle=2.4$ ) and  $x=52.5$  ( $\langle r \rangle=2.67$ ), which correspond to mechanical and chemical thresholds, respectively. Present results also rule out the earlier suggestions such as shifting of percolation threshold to higher  $\langle r \rangle$  values and the likelihood of two isolated rigidity percolation thresholds in such glass systems. [S0163-1829(96)02531-3]

The relation between the network topology and physical properties of chalcogenide glasses has been intensely investigated recently.<sup>1-6</sup> Theoretical studies have revealed the existence of two critical compositions, namely rigidity percolation and chemical threshold.<sup>7-9</sup> Extrema in various physical properties have been observed<sup>1-6,10-16</sup> at both of these thresholds. We have recently established<sup>5</sup> that electrical switching can be effectively used to probe the local structural order in chalcogenide glasses. The present study is motivated by our earlier work<sup>5</sup> on As-Te glasses in which an anomaly in electrical switching fields has been observed at a composition at which chemical and mechanical thresholds coincide. Hence, in this system it is difficult to quantify the relative contribution of rigidity percolation and chemical ordering to the anomaly in the switching field. We have undertaken electrical switching studies on Ge-As-Te glasses, in which rigidity percolation is expected to occur at  $\langle r \rangle=2.4$  and chemical threshold at  $\langle r \rangle=2.67$ , with an idea of isolating the contributions of the two thresholds.

Also, there are reports<sup>13,14,17</sup> that propose a shift in the percolation threshold of Ge-As-Ch glasses (Ch=chalcogen), from  $\langle r \rangle=2.4$  to higher values. Contrarily, there are results that indicate the possibility of rigidity percolation remaining<sup>18</sup> at  $\langle r \rangle=2.4$  in Ge-As-Ch glasses. It has even been suggested that there can be two percolation thresholds connected with network rigidity in  $IV-V-VI$  glasses with a layered structure.<sup>19</sup> The present studies are aimed at clearing these ambiguities.

Semiconducting glasses  $\text{Ge}_{7.5}\text{As}_x\text{Te}_{92.5-x}$  with  $15 \leq x \leq 60$  (covering both  $\langle r \rangle=2.4$  and  $2.67$ ) were prepared by melt quenching and their amorphous nature was confirmed by x-ray diffraction. It is worth mentioning that earlier investigations of topological effects on physical properties of Ge-As-Ch glasses have used glasses belonging to *different* composition tie-lines<sup>20</sup> to tune the coordination numbers. Such studies cannot present a true picture of the topological effects

as the influence of each constituent element cannot be accurately ascertained. Hence, in the present study efforts have been made to tune the coordination number over a wide enough range in a single composition tie line. This involved preparation by exhaustive trials of glasses in the composition regions where glass formation is difficult.

The  $I$ - $V$  characteristics were studied by using a PC based system<sup>21</sup> developed in the laboratory. Samples polished to a 0.2-mm thickness were mounted 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. The veracity of the results obtained was checked by repeating the experiments on two different batches of glasses and on different samples of the same composition in a given batch. The switching fields were found to be reproducible to within  $\pm 1\%$ .

The current-voltage characteristics of a representative  $\text{Ge}_{7.5}\text{As}_{50}\text{Te}_{42.5}$  glass is shown in Fig. 1. The behavior is similar for other  $\text{Ge}_{7.5}\text{As}_x\text{Te}_{92.5-x}$  glasses. The resistivity of as quenched  $\text{Ge}_{7.5}\text{As}_x\text{Te}_{92.5-x}$  samples is of the order  $10^6 \Omega \text{ cm}$ . With an increase in current, there is an initial linear increase in the voltage across the sample (OFF state). Above a critical field  $E_t$  (corresponding to a critical current  $I_t$ ), the samples exhibit a current-controlled negative resistance (CCNR) behavior, which leads to a low resistance ON state. The samples get latched onto that state and do not revert to the initial OFF state if the applied current is reduced to zero. This indicates that  $\text{Ge}_{7.5}\text{As}_x\text{Te}_{92.5-x}$  glasses ( $15 \leq x \leq 60$ ) exhibit a current-controlled negative resistance with memory.

In chalcogenide glasses, memory switching has a thermal origin; it involves the formation of a conducting crystalline channel<sup>22</sup> between the electrodes and the energy required for crystallization is provided by the electric field. Memory switching is usually observed in Te-rich glasses, because of their greater conductance that results in greater power dissipation and therefore a conducting channel could be easily

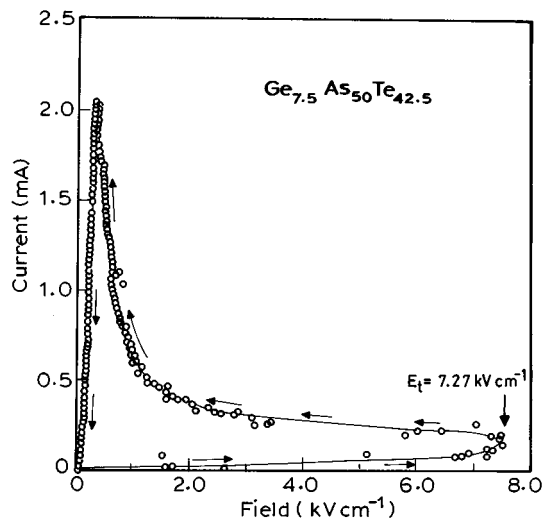


FIG. 1.  $I$ - $V$  characteristics of a representative  $\text{Ge}_{7.5}\text{As}_{50}\text{Te}_{42.5}$  glass.

formed. Smaller switching fields perform mean easier conducting channel formation, which is a result of greater conductance.

Figure 2 shows the variation of switching fields with composition for  $\text{Ge}_{7.5}\text{As}_x\text{Te}_{92.5-x}$  glasses ( $15 \leq x \leq 60$ ). It can be seen that  $E_t$  increases linearly with  $x$ , in the composition range  $15 \leq x \leq 25$  ( $2.3 \leq \langle r \rangle \leq 2.40$ ). At  $x = 25$  ( $\langle r \rangle = 2.4$ ), a distinct change in slope is observed. In the composition region  $25 < x \leq 50$  ( $2.4 < \langle r \rangle \leq 2.65$ ),  $E_t$  varies linearly again with  $x$ , but with greater slope. At the composition  $x = 50$  ( $\langle r \rangle = 2.65$ ), the trend is reversed and  $E_t$  hits a minimum at the composition  $x = 52.5$  ( $\langle r \rangle = 2.67$ ). Beyond  $x = 52.5$ ,  $E_t$  increases with composition again.

As mentioned earlier, property extrema in chalcogenide glasses are associated with two topological effects, namely,

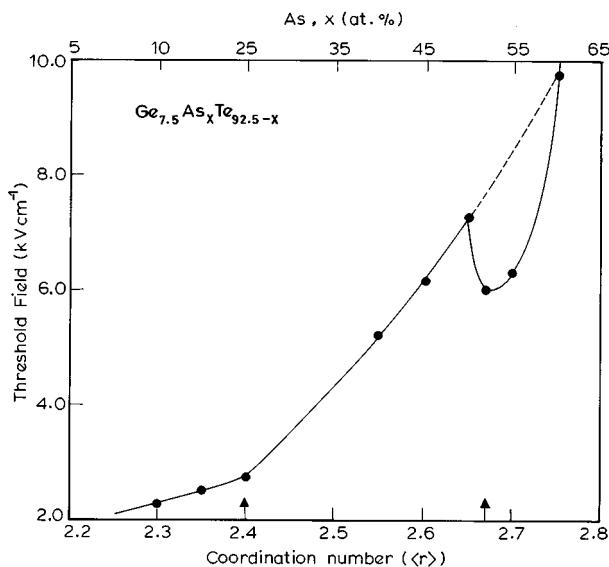


FIG. 2. Composition dependence of the electrical switching fields ( $E_t$ ) of  $\text{Ge}_{7.5}\text{As}_x\text{Te}_{92.5-x}$  glasses. The vertical arrows at  $\langle r \rangle = 2.4$  and  $2.67$  indicate the mechanical and chemical thresholds, respectively.

rigidity percolation and chemical ordering. Rigidity percolation transition takes place when the zero-frequency floppy modes disappear and a rigid amorphous network appears from a polymeric glass.<sup>7-9</sup> Applying mean-field approximation and assuming a perfectly covalent network, it was deduced<sup>7,8</sup> that rigidity percolation occurs at a mean coordination number  $\langle r \rangle = 2.4$ . Several binary chalcogenide glasses, such as Ge-Te, Ge-Se, and Si-Te exhibit<sup>10-12</sup> rigidity percolation at  $\langle r \rangle = 2.4$ . In a system with van der Waals interaction between unbonded neighbors, the percolation phenomenon can be smeared out.<sup>3,9</sup> It has also been suggested that in certain chalcogenides glasses, with a layered structure, the rigidity percolation may shift<sup>12,13</sup> to higher  $\langle r \rangle$  values. For example, in Ge-As-S (Se) glasses, it has been pointed out that rigidity percolation occurs<sup>13,14,17</sup> at  $\langle r \rangle = 2.67$ .

In any glassy system, the composition dependence of switching fields is determined by three factors, namely, resistivity of the additive element, rigidity percolation, and chemical ordering. Typically, taking the example of  $\text{As}_x\text{Te}_{100-x}$  or  $\text{Ge}_{7.5}\text{As}_x\text{Te}_{92.5-x}$ , the switching field can be expected to increase with composition owing to the lesser metallic character of As compared to that of Te. Rigidity percolation, due to increasing dimensionality of the network, can influence switching in two ways. First, there can be an increase in the resistivity of the material and hence, an increase in the switching field. Secondly, with increasing rigidity the network becomes less flexible and structural reorganization can become more difficult. Therefore, switching fields needed progressively increase with increasing network rigidity. Considering the above aspects, one should expect an increase in  $E_t$  with  $x$  and a slope change (from a lower to a higher value) across the percolation threshold. It is seen from Fig. 2 that such a slope change is, indeed, observed in  $E_t$  at  $\langle r \rangle = 2.4$ , which shows clearly that rigidity percolation threshold occurs at this  $\langle r \rangle$  value and that there is *no* shifting in the threshold in contrast to earlier suggestions. Elastic constant measurements as a function of composition of Ge-As-Se glasses also indicate the occurrence<sup>18</sup> of rigidity percolation at  $\langle r \rangle = 2.4$ .

The third factor, which influences the composition dependence of switching fields, is the ordering of the chemical species. In any system, the stoichiometric glass is considered to be maximally ordered and hence closer to the crystalline phase. Therefore, the energy barrier and the driving force, required for the crystallization of the ordered glass are the lowest. Interestingly, in many glassy systems, the molar volume is found to be maximum at the chemical threshold,<sup>23</sup> which implies that the network is least constrained for any structural reorganization. Consequently, the energy required for crystallization of this glass is the lowest. Therefore, memory switching fields should exhibit a minimum at the chemical threshold of a glassy system. The minimum observed in the composition dependence of glassy semiconductor-crystalline metal transition pressure of chalcogenide glasses at the chemical threshold also strengthens this idea.<sup>12</sup> Hence, the minimum in  $E_t$  of Ge-As-Te glasses at  $\langle r \rangle = 2.67$  in Fig. 2, can be clearly associated with chemical ordering and *not* to another threshold connected with network rigidity.

We would also like to emphasize that the composition dependence of any physical property of chalcogenide glasses, is determined by the combined effect of rigidity and chemical ordering. In the Ge-As-Te system, the rigidity percolation dominates in the region  $2.3 \leq \langle r \rangle \leq 2.65$ . At  $\langle r \rangle = 2.65$ , the chemical ordering starts dominating, accounting for the reversal in trend in  $E_t$  at  $\langle r \rangle = 2.65$ . The chemical ordering continues to influence  $E_t$  in the region  $2.65 < \langle r \rangle \leq 2.67$ , until the minimum at the chemical threshold at  $\langle r \rangle = 2.67$ . The positive slope with higher magnitude in  $E_t$  versus  $\langle r \rangle$  above 2.67 reveals a renewed domination of network rigidity. The enhanced slope in this range is also a reflection of the less metallic character of the additive element As in comparison to Te.

An important outcome of the present investigations is that the switching fields depend on both the network topology, as well as chemical composition. It is found that the switching

fields for As-Te<sup>5</sup> and Ge-As-Te glasses are quite different for a given  $\langle r \rangle$ . For example, the threshold fields for As<sub>40</sub>Te<sub>60</sub> and Ge<sub>7.5</sub>As<sub>25</sub>Te<sub>67.5</sub> glasses with  $\langle r \rangle = 2.4$  are 3.2 kV cm<sup>-1</sup> and 2.75 kV cm<sup>-1</sup>, respectively. The relative shift in the switching fields of samples having the same  $\langle r \rangle$ , belonging to different composition tie lines, may arise due to the departure of the network from covalency. The most important assumption<sup>8</sup> of the constraint theory is the covalency of the network and this, in principle, requires that the physical properties solely depend on the network topology. The departure from covalency could be attributed to the presence of the metallic atoms and the Coulomb forces (long-range forces) can no longer be neglected.

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