

Electrical switching and topological thresholds in Ge-Te and Si-Te glasses

Department of Instrumentation, Indian Institute of Science, Bangalore 560012, India

ABSTRACT Melt-quenched $\text{Ge}_x\text{Te}_{100-x}$ glasses and $\text{Si}_x\text{Te}_{100-x}$ glasses ($15 \leq x \leq 25$) have been found to exhibit memory switching, with threshold fields of the order of 4–11 kV/cm and 6–25 kV/cm, respectively. It is found that the switching voltages of $\text{Ge}_x\text{Te}_{100-x}$ samples increase linearly with Ge content and the composition dependence of threshold voltage V_t shows a marked slope change at $x = 20$, which has been earlier identified as the rigidity percolation threshold (RPT) of the system. Above the RPT, V_t of Ge-Te glasses continues to increase with composition until the boundary of bulk glass formation ($x = 28$). On the other hand, the switching voltages of $\text{Si}_x\text{Te}_{100-x}$ glasses increase with x , exhibiting a broad maximum around $x = 20$ (RPT). The difference in the composition dependence of $\text{Si}_x\text{Te}_{100-x}$ and $\text{Ge}_x\text{Te}_{100-x}$ glasses has been understood on the basis of separation between the rigidity percolation threshold and the stoichiometric threshold (CT_{ST}) in these samples. The present results also indicate that the turnaround in the composition dependence of V_t and the subsequent minimum observed in the switching voltages of chalcogenide glasses is likely to be due to CT_{ST} and not to the chemical ordering threshold (CT_{COCRN}).

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1 Introduction

Studies of the composition dependence of properties of chalcogenide glassy semiconductors indicate the presence of two critical compositions, namely, the rigidity percolation threshold (RPT) and the chemical threshold, respectively [1–8].

The rigidity percolation deals with dimensionality and rigidity of a glassy network. According to Philip's constraints theory, for a covalent network glass, the rigidity percolation occurs at a mean coordination number $\langle r_c \rangle = 2.4$ [9–11]. If medium-range order is taken into account in the constraints theory, the percolation threshold is likely to be shifted to higher $\langle r \rangle$ values [12]. 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 $\langle r_c \rangle = 2.4$ [13, 14].

Usually, the critical composition defined by the chemically ordered covalent random network (COCRN) model is taken to be the chemical threshold (CT_{COCRN}). At CT_{COCRN} , the chemical ordering is maximized with the bonding being fully heteropolar [15]. In addition, the stoichiometric compositions at which equilibrium crystalline compounds occur have also attracted special attention because it is possible to directly relate the molecular structure of the stoichiometric glasses with their crystalline counterparts [15, 16]. In this sense, the stoichiometric composition is also considered to be a chemical threshold (CT_{ST}). CT_{ST} and CT_{COCRN} are often considered synonymous because, in the archetypal chalcogenide system $\text{Ge}_x\text{Se}_{100-x}$, the two thresholds coincide at $x = 33$. However, in many other glassy systems the two thresholds occur at different compositions. For example, in the $\text{Ge}_x\text{Te}_{100-x}$ system, CT_{COCRN} occurs at $x = 33$ whereas CT_{ST} occurs at $x = 50$. Further, CT_{ST} is not as uniquely defined as CT_{COCRN} , since there can be several stoichiometric compounds in a system.

It has been known for a long time that anomalies occur in various properties of chalcogenide glasses, at RPT and CT [1–8]. However, only recently, efforts have been made to understand the relation between the electrical switching and the topological thresholds of chalcogenide glasses. It has been found that the composition dependence of switching fields of certain memory and threshold switching glasses exhibits anomalies at both RPT and CT; a sharp slope change is seen in the composition dependence of switching fields at the RPT in memory switching glasses such as As-Te [17], Al-Te [18], Ga-Te [19], Ge-As-Te [6], Al-Ge-Te [8], etc., and threshold switching glasses such as As-Te-In [20]. Further, a minimum is seen in the switching fields of these glasses at a composition that is identified to be a possible chemical threshold [6, 8, 20]. In the present work, efforts are made to understand the effect of topological thresholds on the electrical switching behavior of bulk Ge-Te and Si-Te glasses, belonging to the IV-VI family.

2 Experimental

Semiconducting $\text{Ge}_x\text{Te}_{100-x}$ and $\text{Si}_x\text{Te}_{100-x}$ glasses ($15 \leq x \leq 25$) have been prepared by a melt-quenching method. Constituent elements (99.999% pure) are weighed appropriately and sealed in a quartz ampoule under a vacuum

✉ Fax: +91-80-2360-0135, E-mail: sasokan@isu.iisc.ernet.in

of about 10^{-5} Torr. The sealed ampoules are heated in a rotary furnace to about 950°C for Ge-Te samples and about 1100°C for Si-Te samples, at a rate of $100^\circ\text{C}/\text{h}$. The ampoules containing the melt are continuously rotated for nearly 48 h to ensure homogenization and subsequently quenched in ice water + NaOH mixture. The amorphous nature of the samples was confirmed by X-ray diffraction experiments.

The measurement of I - V characteristics has been undertaken in an electrical switching analyzer developed in the laboratory [21]. It consists of a micro-controller-based excitation source, a high-speed data-acquisition system, a sample holder, a temperature controller, a personal computer and the software developed for experimentation. Samples (having thickness of about 0.2–0.4 mm) are mounted in a holder made of brass and are kept in a temperature-controlled chamber. The sample holder consists of a flat-plate bottom electrode and a point-contact top electrode with a spring-loading mechanism to hold the sample. The output of the excitation source (voltage/current) is fed to the sample through a reference resistor. The voltage across the reference resistor and the voltage across the sample (V) are measured using an isolated dual-channel digital storage oscilloscope (DSO) having a sampling rate of 1 Gigasamples/s (Tektronix THS-730A). The voltage across the reference resistor provides the information about the current (I) flowing through the sample. The excitation source and the DSO are interfaced to a personal computer to acquire and store the I - V characteristics of the sample. Measurements have been undertaken for about 10 samples for each composition.

3 Results and discussion

Figures 1 and 2 show the current–voltage characteristics of $\text{Ge}_{15}\text{Te}_{85}$ & $\text{Ge}_{17}\text{Te}_{83}$ and $\text{Si}_{15}\text{Te}_{85}$ & $\text{Si}_{17}\text{Te}_{83}$ glasses, respectively, which represent the two series of glasses studied. The I - V behavior of other $\text{Ge}_x\text{Te}_{100-x}$ and $\text{Si}_x\text{Te}_{100-x}$ glasses is found to be similar; both $\text{Ge}_x\text{Te}_{100-x}$ and $\text{Si}_x\text{Te}_{100-x}$ glasses exhibit memory switching above a critical field. Also, a marginal threshold tendency is seen in these glasses, before they latch on to the low-resistance state. The switching fields of $\text{Ge}_x\text{Te}_{100-x}$ glasses lie in the range 4–11 kV/cm, whereas those of $\text{Si}_x\text{Te}_{100-x}$ glasses are of the order of 6–25 kV/cm.

Figure 3a and b show the variation of switching voltages (V_t) with composition of $\text{Ge}_x\text{Te}_{100-x}$ and $\text{Si}_x\text{Te}_{100-x}$ glasses, respectively. It is seen from these figures that the switching voltages of $\text{Ge}_x\text{Te}_{100-x}$ samples increase with Ge content in the composition range $15 \leq x \leq 20$ and, at $x = 20$, a change in slope is observed (lower to higher). On the other hand, V_t of $\text{Si}_x\text{Te}_{100-x}$ glasses increases with x , with a maximum exhibited around $x = 20$.

In both Ge-Te and Si-Te glassy systems, in the entire composition range of glass formation, Ge/Si and Te are four-fold and two-fold coordinated, respectively [22, 23]; the progressive replacement of Te by Ge/Si leads to an increase in the network connectivity and rigidity. Further, the composition $x = 20$ in $\text{IV}_x\text{VI}_{100-x}$ glasses corresponds to an average coordination $\langle r \rangle = 2.4$, the mean-field estimate of the RPT. In several chalcogenide glassy systems such as Ge-As-Te (memory) [6], Al-Ge-Te (memory) [8], As-Te-In (threshold) [20], etc., an increase in switching voltages with network connec-

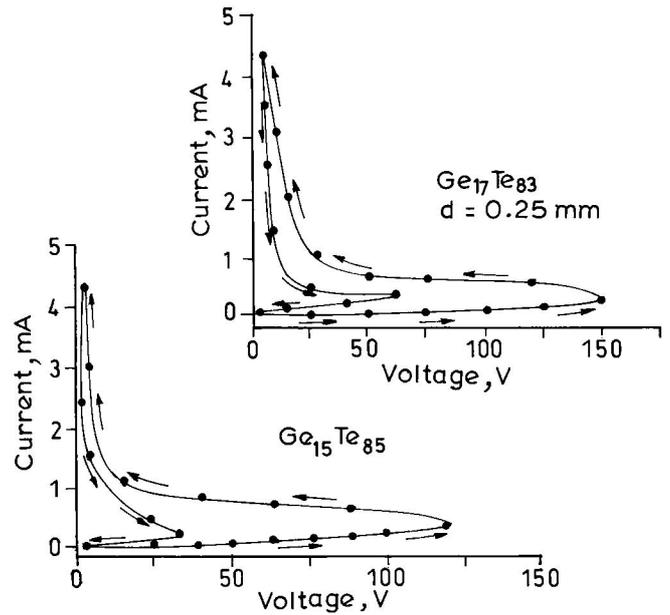


FIGURE 1 I - V characteristics of $\text{Ge}_{15}\text{Te}_{85}$ and $\text{Ge}_{17}\text{Te}_{83}$ glasses, representing the $\text{Ge}_x\text{Te}_{100-x}$ series

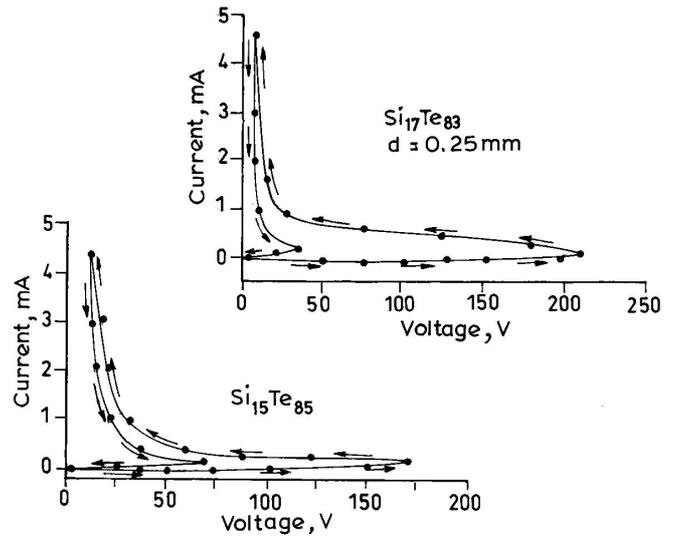


FIGURE 2 The current–voltage characteristics of $\text{Si}_{15}\text{Te}_{85}$ and $\text{Si}_{17}\text{Te}_{83}$ glasses, representing the $\text{Si}_x\text{Te}_{100-x}$ series

tivity has been seen earlier. The increase in V_t with Ge/Si content is therefore consistent with earlier observations.

The most interesting outcome of the present studies is the composition dependence of V_t of Ge-Te and Si-Te glasses above the RPT. Above the RPT, V_t of $\text{Ge}_x\text{Te}_{100-x}$ glasses is found to increase more sharply with x , which is continued until the upper boundary of bulk glass formation ($x = 28$). On the other hand, V_t of $\text{Si}_x\text{Te}_{100-x}$ glasses decreases with x above the RPT, which results in a maximum in V_t around the RPT of the system.

The variation with composition of switching voltages of Ge-As-Te and Al-Ge-Te glasses provides a clue for understanding the composition dependence of V_t of Ge-Te and Si-Te glasses, above the RPT. In both Ge-As-Te and Al-Ge-Te glasses, a turnaround in the composition dependence of V_t is seen above the RPT and a subsequent minimum is exhib-

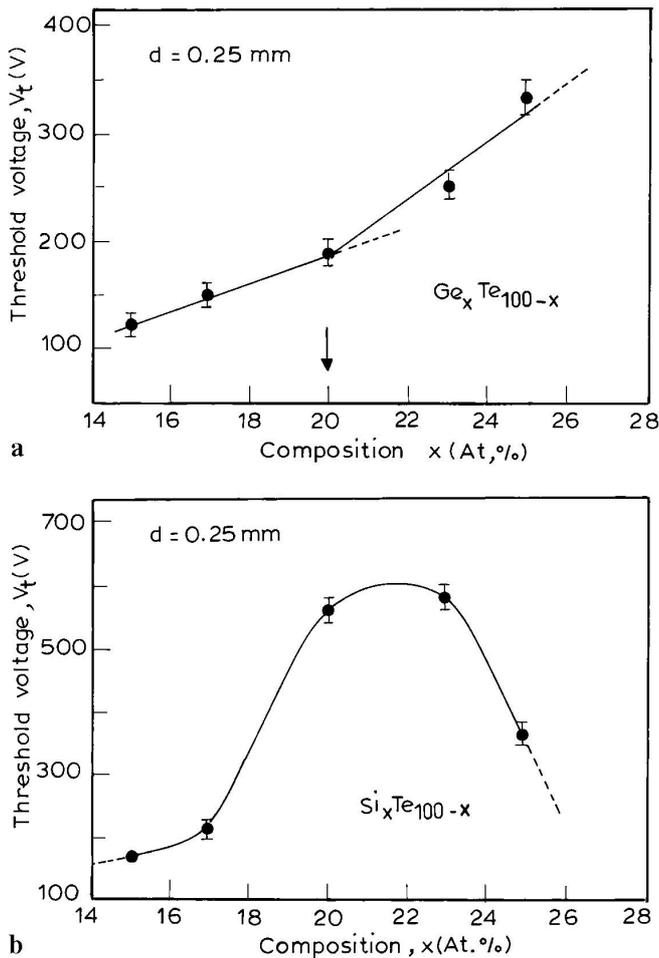


FIGURE 3 **a** The composition dependence of switching voltages of $\text{Ge}_x\text{Te}_{100-x}$ glasses; **b** the variation with composition of switching voltages of $\text{Si}_x\text{Te}_{100-x}$ glasses

ited at the composition suggested to be the CT of the system (which is not clearly identified to be CT_{COCRN} or CT_{ST}) [6, 8]. Further, the composition at which the turnaround occurs in the switching voltages of Ge-As-Te and Al-Ge-Te samples is found to depend on the separation between the RPT and the CT; in the $\text{Ge}_{7.5}\text{As}_x\text{Te}_{92.5}$ glasses, the RPT occurs at $x = 25$ ($r = 2.4$) and the turnaround in V_t occurs at $x = 50$ ($r = 2.65$), which leads to a local minimum in V_t at $x = 52.5$ ($r = 2.67$). A similar effect is seen in $\text{Al}_{20}\text{Ge}_x\text{Te}_{80-x}$ glasses, in which the RPT, the turnaround and the CT are observed in the composition dependence of V_t at $x = 5$ ($r = 2.5$), $x = 7.5$ ($r = 2.55$) and $x = 12.5$ ($r = 2.65$), respectively. It can be noted here that the separation between the RPT and the CT is closer in the Al-Ge-Te glasses ($\Delta x = 7.5$ at. %), whereas it is much larger in the Ge-As-Te system ($\Delta x = 27.5$ at. %). Consequently, the turnaround in V_t occurs closer to the RPT in the Al-Ge-Te system, compared to Ge-As-Te.

The above results suggest that the observed difference in the composition dependence of V_t of Ge-Te and Si-Te glasses is closely connected with the chemical effects. Normally, IV-VI crystals exist in 1:1 or 1:2 stoichiometry, whereas crystalline silicon telluride belongs to a small group having the 1:2 and 2:3 stoichiometries [24, 25]. Thus, we have two stoichiometric chemical thresholds (CT_{ST}) in the $\text{Si}_x\text{Te}_{100-x}$ sys-

tem, corresponding to SiTe_2 and Si_2Te_3 , respectively. In the $\text{Ge}_x\text{Te}_{100-x}$ system, on the other hand, we have only one CT_{ST} , occurring at $\text{Ge}_{50}\text{Te}_{50}$ [26]. As mentioned earlier, in both $\text{Ge}_x\text{Te}_{100-x}$ and $\text{Si}_x\text{Te}_{100-x}$ systems, CT_{COCRN} occurs at $x = 33$.

It can be seen that in the $\text{Si}_x\text{Te}_{100-x}$ system, one of the stoichiometric thresholds (SiTe_2) is quite close to the RPT. Due to the proximity between the chemical and mechanical thresholds, the turnaround in V_t occurs in Si-Te glasses just above the RPT, which results in an apparent maximum in V_t around the RPT. However, in this case, it is not possible to deduce whether CT_{COCRN} or CT_{ST} is responsible for the observed effects, as the composition SiTe_2 also happens to be CT_{COCRN} .

In the $\text{Ge}_x\text{Te}_{100-x}$ system, CT_{COCRN} and CT_{ST} occur at $x = 33$ and $x = 50$, respectively. If CT_{COCRN} were responsible for the composition dependence of V_t above the RPT, a turnaround in V_t and a possible maximum would have been seen in Ge-Te glasses, as in Si-Te samples. However, there is no turnaround in V_t of $\text{Ge}_x\text{Te}_{100-x}$ glasses above the RPT until the composition limit of glass formation ($x = 28$), which is quite close to CT_{COCRN} ($x = 33$). This suggests that the turnaround and the minimum seen in V_t in different chalcogenide glasses are mainly due to CT_{ST} and not CT_{COCRN} .

In this context, it is also interesting to note that the composition dependence of electrical resistivities of Si-Te and Ge-Te glasses is similar to the composition dependence of switching fields; the variation with composition of electrical resistivity (ρ) of $\text{Si}_x\text{Te}_{100-x}$ glasses exhibits a maximum at $x = 20$ (RPT) [27], whereas the composition dependence of ρ of $\text{Ge}_x\text{Te}_{100-x}$ glasses shows only a slope change at $x = 20$ [28]. Thus we find that the effect of separation between RPT and CT_{ST} is also seen in composition dependence of ρ of $\text{Si}_x\text{Te}_{100-x}$ and $\text{Ge}_x\text{Te}_{100-x}$ glasses. Further, it has been known for a long time that there exists a direct correlation between switching voltages and electrical resistivities of chalcogenide glasses [29] and hence the observed composition dependence of V_t and ρ of $\text{Ge}_x\text{Te}_{100-x}$ and $\text{Si}_x\text{Te}_{100-x}$ glasses is consistent with the earlier observations.

The present results also help us in understanding the topological thresholds in the $\text{Ge}_x\text{Se}_{100-x}$ glassy system. Anomalies have been observed [2] in several properties of these glasses such as density, metallization pressure, etc., at compositions $x = 20$ and $x = 33$. While the effect at $x = 20$ has been identified with certainty with the RPT, it has not been possible to ascertain the origin of the anomaly at $x = 33$, because both CT_{COCRN} and CT_{ST} coincide at this composition. It has been thought for a long time that the anomaly at $x = 33$ is due to chemical ordering (CT_{COCRN}). Based on the present results, it may be proposed that the anomalies seen in $\text{Ge}_x\text{Se}_{100-x}$ glasses at $x = 33$ are likely to be due to CT_{ST} and not CT_{COCRN} . Raman scattering and Mossbauer spectroscopic investigations [16, 30–32], which show that the chemical order is intrinsically broken in GeSe_2 glass, also support this conjecture.

4 Conclusions

Melt-quenched $\text{Ge}_x\text{Te}_{100-x}$ glasses and $\text{Si}_x\text{Te}_{100-x}$ glasses have been found to exhibit current-controlled negative-resistance behavior with memory. The switching voltages of

$\text{Ge}_x\text{Te}_{100-x}$ samples increase with Ge content and the composition dependence of V_t shows a marked slope change at $x = 20$, the rigidity percolation threshold (RPT) of the system. There is no reversal observed in the variation of V_t of $\text{Ge}_x\text{Te}_{100-x}$ glasses with composition above the RPT. On the other hand, V_t of $\text{Si}_x\text{Te}_{100-x}$ glasses increases with Si content and a maximum is seen around $x = 20$ (RPT). The difference in the composition dependences of $\text{Si}_x\text{Te}_{100-x}$ and $\text{Ge}_x\text{Te}_{100-x}$ glasses has been found to be due to the extent of separation between the rigidity percolation threshold and the stoichiometric threshold (CT_{ST}) in these samples. Further, the present results clearly show that the turnaround in the composition dependence of V_t and the subsequent minimum observed in the switching voltages of several chalcogenide glasses are likely to be due to CT_{ST} and not to the chemical ordering threshold (CT_{COCRN}).

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