Electrical switching studies on Ge–Te–Tl chalcogenide glasses: Effect of thallium on the composition dependence of switching voltages

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ABSTRACT

Bulk Ge17Te83–xTlx glasses (0 ≤ x ≤ 13), have been found to exhibit memory type electrical switching. The switching voltages (also known as threshold voltage — Vth) of Ge17Te83–xTlx glasses are found to decrease with increasing thallium content. The rate of decrease of Vth is greater at lower concentrations and Vth falls at a slower rate for higher thallium concentrations (x ≥ 6).

The addition of thallium to the Ge–Te network fragments the covalent network and introduces ionic nature to it; the reduction in network connectivity leads to the decrease in switching voltages with thallium content. The decrease in the glass transition temperatures of Ge17Te83–xTlx glasses with increasing thallium concentration supports the idea of decrease in network connectivity with Tl addition. The more metallic nature of Tl also contributes to the observed reduction in the switching voltages of Ge17Te83–xTlx glasses with Tl content.

Further, there is an interesting correlation seen between the threshold voltage Vth and the average bond energy, as a function of Tl content. In addition, the switching voltages of Ge17Te83–xTlx glasses have been found to decrease with sample thickness almost linearly. The set–reset studies indicate that the Ge17Te83Tl2 sample can be switched for more than 10 cycles, whereas other glasses could not be reset beyond two switching cycles.

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1. Introduction

Chalcogenide glasses exhibit two types of electrical switching behavior, known as memory switching which is irreversible and threshold switching which is reversible [1]. The electrical switching in glassy chalcogenides has been explained based on electronic [2,3], thermal or electro-thermal mechanisms [4–7]. It is generally accepted that in both threshold and memory switching glasses, the onset of switching is electronic in nature, involving charged defect states known as Valence Alternation Pairs (VAPs). In memory materials, an additional thermal effect comes into play in the form of Joule heating which leads to a phase change with the formation of a conducting crystalline channel in the electrode region. Since the phase change is permanent, the material does not revert back to the original OFF state unless it is reset back externally by the application of a current or light pulse.

Chalcogenide glasses, which exhibit memory type electrical switching, find applications in Phase Change Memories (PCM) which are being considered as possible replacement for conventional Random Access Memories. It is desirable for PCM applications that the switching glasses have comparatively low switching fields.

Earlier studies on ternary chalcogenides containing thallium [8–11] indicate that the addition of this metallic element modifies the glassy network to a large extent and brings down the switching voltages making them attractive candidates for phase change memory applications. The formation of Te–Tl+ dipoles which fragment the network as well as the higher metallicity of thallium have been thought to be the cause for the observed decrease in the threshold voltages of Tl doped chalcogenide glasses.

In the present work, electrical switching studies have been undertaken on Ge17Te83–xTlx glasses, both with a view to obtain a suitable material for memories as well as to understand the mechanism underlying the switching phenomenon. The variation of Vth with both composition as well as the thickness of the sample has been studied. The response of the sample to continuous set–reset processes has also been evaluated.

2. Experimental details

Ge17Te83–xTlx glasses (0 ≤ x ≤ 13) were prepared by the melt quenching method. Appropriate amounts of constituent elements (99.999% pure) were weighed to ± 0.01 mg accuracy and taken in a dry, clean, flattened quartz ampoule. The ampoules were evacuated to...
a vacuum better than $10^{-5}$ mbar and sealed. The ampoules were heated in a horizontal rotary furnace up to 950 °C, at a rate of about 100 °C/h. The ampoules were maintained at this temperature for 24 h, under continuous rotation (10 rpm), to ensure homogeneity of the melt. The ampoules were subsequently quenched in a bath containing mixture of ice water and NaOH. The amorphous and glassy nature of the samples was confirmed by X-ray diffraction and Differential Scanning Calorimetry (DSC) respectively.

The electrical switching studies were undertaken using a Keithley source-meter (Model 2410) interfaced with a personal computer and the data was acquired using the LAB VIEW program (National Instruments). Samples polished to a uniform thickness of 0.3 mm were mounted between a flat-plate bottom and a point-contact top electrode made of brass. A constant current (0 – 3 mA) was passed through the sample and the voltage developed across it was measured. The variation of threshold switching voltage with sample thickness was also studied using the same setup.

The switching experiments were repeated for at least five samples for each composition and the threshold voltages were found to be reproducible within ±5%. The data displayed in the graphs indicate error bars which were obtained as the root mean square deviation of the number of trials conducted.

3. Results

Fig. 1 shows the I–V characteristics of representative Ge$_{17}$Te$_{83}$ – xTl$_x$ glasses, which indicates that all the samples studied show memory type electrical switching. The variation of the switching voltages ($V_{th}$)/threshold electric field ($E_{th}$) of Ge$_{17}$Te$_{83}$ – xTl$_x$ glasses with Tl content is shown in Fig. 2, which shows that the threshold voltages/fields decrease with increasing thallium content. A fast, near-linear decrease is seen in $V_{th}$ at lower Tl concentrations ($x \leq 6$), whereas, the decrease in $V_{th}$ is much less at higher thallium atomic percentages.

The variation of the switching voltage with the thickness of the sample is known to provide an insight into the mechanism underlying the type of switching observed and is shown in Fig. 3.

The suitability of a chalcogenide material for use as Phase Change memory depends on its ability to withstand many cycles of write and erase. The present samples have been subjected to recurrent set–reset pulses to evaluate their suitability for memory applications. During the set process, a small current in triangular form (of 4 mA amplitude) is applied to the sample to switch it from the high resistance state to low resistance state (phase change). The reset process is achieved by applying a short square pulse of higher current (10 mA) which converts the material back to the amorphous phase having a high resistance so that it is ready for another set process. The response of two representative glasses, Ge$_{17}$Te$_{81}$Tl$_2$ and Ge$_{17}$Te$_{73}$Tl$_{10}$, is shown in Figs. 4 and 5 respectively.

4. Discussion

4.1. Electrical switching behavior of Ge–Te–Tl glasses

In Tl containing chalcogenide glasses, the introduction of thallium into the network is known to create smaller unconnected units which may facilitate easy crystallization [8,11]. The composition tie-line
chosen in this study (Ge17Te83−xTlx) is tellurium rich and hence Te–Te bonds are present throughout the range studied. The presence of flexible Te chains which aid structural reorganization and devitrification [12,13], is likely to contribute to the memory switching observed in Ge17Te83−xTlx glasses.

In this context, it is interesting to compare the electrical switching behavior of Ge17Te83−xTlx glasses with other Tl doped chalcogenide glasses. While bulk As–Te–Tl glasses [8] exhibit memory type switching, Ge10Se90−xTlx glasses [9] undergo threshold type of switching with fluctuations seen in the I–V characteristics. The present results reveal that all the Ge17Te83−xTlx glasses (0 ≤ x ≤ 13) show memory type switching without any fluctuations in the I–V characteristics, as in the case of As–Te–Tl glasses.

4.2. Composition dependence of switching voltages in Ge–Te–Tl glasses

The threshold electric fields for switching of Ge17Te83−xTlx glasses range from 15 × 10^4 V/m to 55 × 10^4 V/m in our samples. The GeSb2Te3 (GST) film of 100 nm thickness, which is the commonly used phase change memory material, has a threshold voltage of 0.6 V [14] which translates to an electric field of the order of 6 × 10^5 V/m. Thus, a simple comparison indicates that the threshold fields of the present Ge–Te–Tl samples are lesser. GST however withstands nearly 10^5 sessions of switching and erasure while most of the Ge17Te83−xTlx studied are able to withstand only few switching cycles.

Another interesting aspect of the present results is the variation with the composition of threshold voltages of Ge17Te83−xTlx glasses; a fast, near-linear decrease is seen in Vth of Ge17Te83−xTlx glasses at lower Tl concentrations (x ≤ 6), whereas, the decrease in Vth is much lesser at higher thallium atomic percentages.

It is known that in Ge–Te–Tl glasses, thallium does not bond directly with Ge, and only forms Te–Tl bonds [11]. Hence the bulk glass is made up of Ge–Te4/2 tetrahedral units, Te–Te chains and Tl containing units similar to those shown in Fig. 6a, b, and c. When a Te–Tl bond is formed, Te gets negatively charged and Tl positively charged forming a dipole, as Te is more electronegative than Tl. The glassy network is broken with the formation of this dipole and the structural cross linking can occur further through weaker electrostatic interactions, only when another similar dipole of opposite polarity aligns nearby forming a quadrupole [Fig. 6c] [8,11]. This fragmentation of the network with the addition of thallium is responsible for the observed decrease in the threshold switching voltage with increasing thallium in the Ge17Te83−xTlx glassy system. A decrease in Vth with thallium atomic percent has been observed earlier in the As–Te–Tl glasses as well as the Ge–Se–Tl glasses and has been explained in an analogous manner [8,9]. A decrease in switching voltages with a decrease in network connectivity has been seen in many other glassy systems also.

In this context, it is interesting to note from the ADSC measurements that the glass transition temperature Tg of Ge17Te83−xTlx glasses, also
also contributes to the observed decrease in switching voltages of composition. Hence, Ge and Tl form only heteropolar bonds and only and there are no dangling bonds and vacancies.

In addition to the network connectivity, the more metallic nature of thallium (electrical resistivity $\rho_Tl = 15 \times 10^{-8} \Omega \cdot m$) also contributes to the observed decrease in switching voltages of $\text{Ge}_{17}\text{Te}_{83-Tl}$ glasses with the addition of Tl; the increased metallicity of the dopant decreases the activation energy for conduction and reduces the switching voltage. A similar decrease in switching voltages due to metallic additives has been observed in many other systems also [8,16,17].

Apart from simple connectivity and metallicity considerations, a plausible argument based on the Tl bonding and chemical ordering can also explain the observed composition dependence of switching voltages of $\text{Ge}_{17}\text{Te}_{83-Tl}$ glasses.

Recently, the idea of resonant bonding has been invoked [18,19] in tellurides where the pi-electrons are shared between two bonds giving rise to a high contrast between amorphous and crystalline regions. This does not seem to happen in this case as the electrical switching does not show any sharp change in behavior.

4.2.1. Thallium bonding, chemically ordered network and the variation of electrical switching voltages

Thallium NMR studies on the present series of amorphous materials are not available. However NMR studies on similar samples of Tl–As–Se [20] have indicated the possibility that thallium can enter the network with either a valence of one or three. NMR on the crystalline chalcogenides containing thallium [21,22] also indicates two valencies for the thallium. The chemical shift values tend to indicate that the valency of one leads to a bonding similar to that in thallous chloride which is ionic in nature. The valency of three, however, is similar in bonding to thallic chloride which is covalent.

The idea of two valencies for thallium can be incorporated into the existing theory of the Chemically Ordered Network (CON) model [23] for the glassy network to calculate the numbers of the various bonds in the case of the present Ge–Te–Tl glasses as follows:

4.2.1.1. Method of calculation of average bond energy. The CON model states that heteropolar bonds are more probable than homopolar bonds as the former leads to a more ordered network. Also, bonds with higher energy are formed first and those with lower energy are formed later. The model also assumes that all the bonds are satisfied and there are no dangling bonds and vacancies.

In the present $\text{Ge}_{17}\text{Te}_{83-Tl}$ glassy system, the possible bonds are Ge–Te, Ge–Ge, Ge–Tl, Te–Tl and Te–Tl, which have bond energies of 37.4 kcal/mole, 37.6 kcal/mole, 33.0 kcal/mole, 26.3 kcal/mole and 15.4 kcal/mole respectively [9,24,25]. Since the tie-line studied is tellurium rich, there is enough Te to bond with Ge and Tl at each composition. Hence, Ge and Tl form only heteropolar bonds and only Te forms homopolar bonds. Therefore, the bonds present in this system are Ge–Te, Tl–Te and Te–Te only. Ge has a co-ordination of 4, hence 4 x NGe bonds of the type Ge–Te are formed (NGe is the number of germanium atoms per mole). Similarly, Tl$^{3+}$ will form 1 Tl–Te bond and Tl$^{3+}$ will form 3 Tl–Tl bonds each. The remaining Te will form Te–Te bonds. The average bond energy is the total energy of all the bonds divided by the total number of bonds. The numbers of Tl$^{3+}$ and Tl$^{3+}$ are varied such that the average energy varies in a manner analogous to the switching voltage and this is used to fix the numbers of each type of thallium.

Table 1 shows the number of bonds of each type for the various compositions studied and the average bond energy in each case. The average bond energy is seen to decrease with increasing thallium and by assuming two species of thallium in the network, one with valency one and the other with valency three, it has been possible to adjust their numbers within the CON model and obtain a variation in average bond energy that is similar to the variation in the threshold switching voltage, as seen in Table 1.

4.2.1.2. Results of calculations under the CON model. The superposition of the variation in $V_{th}$ and variation in average bond energy as a function of composition (percentage of thallium), are in good agreement (Fig. 7). It is also seen from this model that thallium enters the network as a trivalent, more covalently bonded species, at lower concentrations. However, as the concentration is increased, it enters as monovalent ionic species. While the concentration of monovalent species increases with increasing thallium concentrations, the concentration of trivalent species remains almost a constant. Fig. 8 shows the variation of the number of monovalent and trivalent Tl ions with composition in the $\text{Ge}_{17}\text{Te}_{83-Tl}$ glassy system. The monovalent thallium leads to fragmentation of the network and easy crystallization which favors memory type switching and also lowerings of $V_{th}$.

4.3. Thickness dependence of $V_{th}$

The variation of the switching voltage with the thickness of the sample ($t$) is known to provide insight into the mechanism underlying the type of switching observed. Generally, in memory switching glasses such as Ge–Te [26], Ge–As–Te [27], etc., $V_{th}$ has been found to be proportional to $t^{1/2}$. In bulk Al–Te–Ge [28] and Ge–Se–Tl films [29], $V_{th}$ has been found to be proportional to the thickness “$t”$. It has been suggested that switching voltage will vary as $t$, $t^{1/2}$ or $t^2$ depending on whether the mechanism responsible for switching is purely electronic, purely thermal or based on carrier injection [30]. In the case of the

**Table 1**

<table>
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<tr>
<th>Sl. No.</th>
<th>Composition</th>
<th>Ge–Te bonds</th>
<th>No. of Ti$^{3+}$</th>
<th>No. of Ti$^{3+}$</th>
<th>Te–Te bonds</th>
<th>Te–Tl bonds</th>
<th>Average energy (Kcal/mole)</th>
<th>Switching voltage (volt)</th>
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</table>
Ge–Te–Tl glasses, it is seen that $V_{th}$ increases nearly linearly with increasing thickness as shown in Fig. 3.

4.4. Response to the set–reset process

The suitability of a chalcogenide glassy material for phase change memory applications depends on its ability to withstand recurrent cycles of switching and erasure (i.e. resetting back to the original state). In the present experiments, during the set process, a small current in triangular form (of 4 mA height) is applied to the sample to switch it from the high resistance state to low resistance state (phase change). The reset process is achieved by applying a short square pulse of higher current (10 mA) which converts the material back to the amorphous phase having high resistance so that it is ready for another set process. The response of two representative glasses, Ge$_{17}$Te$_{83}$Tl$_2$ and Ge$_{17}$Te$_{73}$Tli$_0$, are shown in Figs. 4 and 5 respectively, and hence no error bars are shown. The continuous line is a guide to the eye.

The hypothesis of resonant bonding in tellurides [18,19] indicates that stressed rigid structures lead to a material which can be switched recurrently. The reason that samples with higher thallium content do not withstand large number of cycles of set–reset may lie in this idea as higher thallium content is conjectured to lead to more fragmentation and less rigidity. More work needs to be done for arriving at undisputed conclusions.

5. Conclusions

Electrical switching studies on tellurium rich Ge$_{17}$Te$_{83-x}$Tlx glasses reveal that all of them show memory type switching. The threshold switching voltages ($V_{th}$) of these glasses have been found to reduce with increasing thallium content, which is understood as due to the fragmentation of the network by the addition of thallium and also due to the more metallicity of Tl. In addition, the average bond energy is seen to correlate well with the composition dependence of threshold voltages; Thallium is covalently bonded at low concentrations, but for higher concentrations, it is more ionic in nature. It is the ionic thallium that contributes to the fragmentation of the network and subsequent lowering of the switching voltage. Further, the switching voltages of Ge$_{17}$Te$_{83-x}$Tlx glasses have been found to decrease with sample thickness almost linearly. The set–reset studies undertaken on Ge$_{17}$Te$_{83-x}$Tlx glasses indicate that the Ge$_{17}$Te$_{83}$Tl$_0$ sample is comparatively better in the series and can be switched for more than 10 cycles. The other glasses could not be reset beyond two switching cycles.

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References