4.1. Introduction

The phenomenon of electrical switching in chalcogenide glasses has been an important topic in the field of amorphous semiconductors. It has several technological applications including information storage, power control, etc. Chalcogenide glasses are found to exhibit a sudden change in the electrical resistance (from a low conducting “OFF” state to a high conducting “ON” state) under the application of an appropriate electric field (commonly referred as the switching/threshold electric field) [1]. This phenomenon, known as electrical switching, is classified into memory and threshold type based on the way the glasses respond to the removal of the electric field after the switching event. Upon the removal of the switching field, threshold-switching glasses revert to the OFF state, whereas memory switches remain locked to the ON state.

As discussed in detail in section 1.7, there are several models proposed to understand the memory and threshold type of electrical switching effects exhibited by chalcogenide glasses. They are generally classified into purely electronic [2, 3], thermal and electronically modified thermal [4-8] models. It is normally accepted that, the process of initiation of switching in chalcogenide glasses is electronic in nature [5]. The conducting state during switching is achieved when the charged defect states that are present in chalcogenide glasses are filled by charge carriers excited by the applied electric field. In memory switching glasses, additional thermal effects come into play, with the formation of a conducting crystalline channel in the electrode region due to Joule heating [9-11].
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Investigations on the current-voltage (I-V) characteristics and studies on the dependence of switching voltages on different material properties such as composition, thickness etc., help in understanding the local structural effects in chalcogenide glasses.

It is also known that the addition of metallic impurities to chalcogenide glasses brings about interesting variations in their properties. The metallic impurities enter the glassy network, thereby affecting the network connectivity, crystallizing ability, and the electrical conductivity of the glass [12, 13].

The addition of Tl to Ge-Se glasses has been found to bring about noticeable changes in their structural and physical properties [14]. The studies on Ge-Se-Tl glasses are also motivated by their interesting acousto-optical and electronic applications [12, 15, 16]. In literature, there are a few investigations on the I-V characteristics and switching behavior of Ge-Se-Tl glasses and amorphous thin films. For example, studies by Zope et al. [17], indicate that the room temperature I-V characteristics of Ge_{10}Se_{90-x}Tl_{x} glasses (1 ≤ x ≤ 9), is linear for lower voltages and it becomes non-linear at higher voltages. Earlier investigations also reveal that the amorphous Ge-Se-Tl films [18, 19] exhibit memory type electrical switching.

In the present work, the I-V characteristics of bulk Ge_{10}Se_{90-x}Tl_{x} glasses have been investigated over a wide range of compositions (15 ≤ x ≤ 34), in order to understand the switching behavior in these glasses. Further, the effects of composition, sample thickness on the switching behavior are studied. In addition, the compositional variation of switching voltages is correlated with the thermal properties.

4.2 Sample Preparation and Experimental Details

Bulk semiconducting Ge_{10}Se_{90-x}Tl_{x} (15 ≤ x ≤ 34) glasses are prepared by the conventional melt quenching technique as discussed in section 2.2. The amorphous nature of the samples prepared is confirmed by X-ray diffraction and differential scanning Calorimetry studies.
4.3. Electrical Switching Studies on Ge-Se-Tl glasses

Electrical switching studies have been carried out on samples polished to about 0.20 mm thickness, placed between a flat plate bottom electrode and a point contact top electrode made of brass (figure 2.10). A constant current is passed through the sample and the voltage developed across the sample is measured.

The switching behavior of Ge\textsubscript{10}Se\textsubscript{90-\textit{x}}Tl\textsubscript{\textit{x}} glasses of higher Tl concentrations (27 ≤ \textit{x} ≤ 34), has been investigated using a Keithley source-meter (Model 2410). The source meter is capable of sourcing current in the range 0-20mA at a compliance voltage of 1100V maximum (figure 2.10). As Ge\textsubscript{10}Se\textsubscript{90-\textit{x}}Tl\textsubscript{\textit{x}} glasses of lower Tl concentrations (15 ≤ \textit{x} ≤ 26) exhibit switching at voltages above 1100V, the I-V behavior of these glasses has been studied using lab-made programmable high voltage power supply [20] which is capable of sourcing constant current in the range 0-45mA at a maximum compliance voltage of 1750V (figure 2.12). The deviation in the switching voltages measured with the help of lab-made programmable high voltage power supply and the Keithley source-meter has been found to be within ± 2%.

4.3.1. Electrical Switching Behavior of Ge\textsubscript{10}Se\textsubscript{90-\textit{x}}Tl\textsubscript{\textit{x}} Glasses

Figure 4.1 shows the I-V characteristics and switching behavior of representative Ge\textsubscript{10}Se\textsubscript{90-\textit{x}}Tl\textsubscript{\textit{x}} glasses (15 ≤ \textit{x} ≤ 34). It can be seen that, these samples exhibit an ohmic behavior at lower applied voltages, which is the high resistance OFF state. At the switching field \( E_T \) (corresponding to the switching voltage \( V_T \)), the samples show a deviation from the Ohmic behavior (current controlled negative resistance-CCNR), which eventually leads to a low resistance ON state.

It is interesting to note that, the Ge\textsubscript{10}Se\textsubscript{90-\textit{x}}Tl\textsubscript{\textit{x}} glasses revert back to their original low-conducting OFF state, upon removal of the applied electric field. This indicates that the bulk Ge\textsubscript{10}Se\textsubscript{90-\textit{x}}Tl\textsubscript{\textit{x}} glasses exhibit threshold type electrical switching behavior. Furthermore, the switching event in the present Ge\textsubscript{10}Se\textsubscript{90-\textit{x}}Tl\textsubscript{\textit{x}} glasses is accompanied by a noise, visible light generation, and material ablation leading to the fluctuations in the I-V characteristics of these glasses.
Figure 4.1. The I-V characteristics of representative samples of Ge\textsubscript{10}Se\textsubscript{90-x}Tl\textsubscript{x} (15 ≤ x ≤ 34) glasses.

Compared to other chalcogenide glasses, the threshold switching behavior observed in the present Ge\textsubscript{10}Se\textsubscript{90-x}Tl\textsubscript{x} glasses has been found to be not ideal with fluctuations seen in the I-V characteristics as shown in figure 4.1. Further, in contrast to the switching behavior of conventional threshold switching glasses, the switching event is accompanied by burning along with a loud noise and visible light generation. These observations suggest that an adiabatic joule heating of the material occurs during initial stages of switching because of the high resistance of the sample, leading to a sudden increase in the temperature in the electrode region. The temperature increases much faster
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at the electrode-material contact regions compared to the rest of the sample since these regions exhibit an extra contact resistance. As a consequence, local melting of the sample results around the periphery of electrode-material contact region. The local melting and subsequent re-solidification in the electrode region is responsible for the fluctuation present in the I-V characteristics of the Ge_{10}Se_{90-x}Tl_{x} (15 \leq x \leq 34) glasses. It is also known that the local melting and subsequent re-solidification generally depends upon the thermal conductivity/diffusivity of the sample, which in turn is decided by the local structure of the glass [12].

4.3.2. Composition Dependency of Switching Voltages of Ge-Se-Tl Glasses and its Correlation with Thermal Properties

The variation of switching voltages of Ge_{10}Se_{90-x}Tl_{x} glasses, as a function of composition for samples of 0.20 mm thickness, is shown in figure 4.2. It is found that \( V_{r} \) decreases with the increase in Tl content.

It has been reported that the composition dependence of switching voltages of chalcogenide glasses is determined by two main factors, namely the metallicity of the additive element and the rigidity percolation [21-23]. The addition of more metallic impurities generally results in the decrease of \( V_{r} \), which is due to enhanced conductivity ensuing from the decrease in the activation energy for conduction. It is interesting to note here that a decrease in the activation energy for electrical conduction with an increase in Tl content has been observed earlier in Ge-Se-Tl bulk glassy system [17], which has been attributed to the bonding of Tl and the resultant local structure. The observed decrease in \( V_{r} \) of Ge_{10}Se_{90-x}Tl_{x} glasses is therefore consistent with the decrease in conductivity activation energy with the Tl addition. A decrease in \( V_{r} \) with Tl addition has been also been observed in other Tl based chalcogenide systems such as As-Te-Tl glasses [21], Ge-Se-Tl amorphous thin films [18, 19].
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Figure 4.2. Composition dependence of switching voltage ($V_T$) of $\text{Ge}_{10}\text{Se}_{90-x}\text{Tl}_x$ glasses.

The observed composition dependence of $V_T$ in $\text{Ge}_{10}\text{Se}_{90-x}\text{Tl}_x$ ($15 \leq x \leq 34$) glasses can also be understood on the basis of nature of chemical bonds involved, using Chemically Ordered Network (CON) model [23]. According to CON model, the formation of heteropolar bonds is always favored over the formation of homopolar bonds. For a compound $A_xB_y$, this model envisages only $A-B$ type of bonds. In addition, $A-A$ and $B-B$ types of bonds are present for the $A$-rich and $B$–rich compositions, respectively. Based on the CON model, the selenium rich $\text{Ge}_{10}\text{Se}_{90-x}\text{Tl}_x$ ($15 \leq x \leq 34$) glasses can be pictured to be made up of cross linked three dimensional structural units consisting of Ge-Se, Se-Se and Se-Tl bonds. Bond strengths of various possible bonds in this system namely, Ge-Se, Se-Se, Ge-Ge, Se-Tl and Tl-Tl, are 49.1 kcal/mole, 44 kcal/mole, 37.6 kcal/mole, 37.98 kcal/mole and 15.4 kcal/mole, respectively [24]. As the Ge-Se heteropolar bonds and the Se-Se homopolar bonds have comparatively more bond strength compared to Se-Tl bonds, they are more probable. So, as thallium content increases, more and more Se-Se bonds are broken and the probability of ionic Se-Tl bond formation increases.
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It is known that, an increase in the number of heteropolar bonds leads to the increase of chemical order resulting in the decrease of $E_T / V_T$, whereas increase in the number of homopolar bonds leads to the growth of chemical disorder resulting in an increase of $E_T / V_T$ [25, 26]. In the present study of Ge-Se-Tl glasses, with the increase in the Tl content, the number of heteropolar Se-Tl bonds increase in comparison with the Se-Se homopolar bonds. With more number of heteropolar bonds in the Ge-Se-Tl system, the chemical disorder is reduced and therefore, charge carriers are less localized resulting in an enhanced conductivity. The resultant increase in the conductivity helps switching and accounts for the decrease in $E_T / V_T$ with the increase in the Tl content in Ge$_{10}$Se$_{90-x}$Tl$_x$ glasses (figure 4.2). A decrease in $V_T$ due to increase in the chemical order and due to metallicity of the additive has been observed in other chalcogenide systems also [19, 27, 28].

In chalcogenide glasses, both $T_g$ as well as $V_T$ are known to increase with network connectivity and rigidity [25, 29]. Such an increase is seen in both glass transition temperatures and the switching voltages of many chalcogenide systems, with an addition of metal atoms (which coordinate tetrahedrally) [30, 31]. However, in the present Ge-Se-Tl samples, the network connectivity is attained only by the interaction of $TI^+Se^-GeSe_{2/2}Se^-TI^+$ structural units containing weaker ionic Se-Tl bonds. A decrease in the cross-linking of Se-chains and an increase in the number of Se-Tl weaker bonds with the addition of Tl, leads to a net decrease in the network connectivity and rigidity of Ge-Se-Tl glasses. The decrease in network connectivity with Tl content, as illustrated by the variation of $T_g$ (figure 3.3), also contributes for the decrease in the switching voltages in Ge$_{10}$Se$_{90-x}$Tl$_x$ glasses.

Thus, a decrease in network connectivity, an increase in chemical order, the decrease in the activation energy for electrical conduction [26] and the metallicity factor of the additive, all contribute to the observed significant decrease in $V_T$ with Tl addition in Ge-Se-Tl samples.

It is interesting to note that the composition dependence of switching voltages of Ge$_{10}$Se$_{90-x}$Tl$_x$ glasses exhibit a small cusp around the composition $x = 22$; the glass
transition temperatures of these samples also exhibit an inflexion around this composition. Further, a broad minimum is seen in the $T_{cl}$ of Ge$_{10}$Se$_{90-x}$Tlx glasses in the composition range $22 \leq x \leq 30$ (figure 3.5). Also, the thermal stability ($T_{cl} - T_g$) of Ge$_{10}$Se$_{90-x}$Tlx glasses is found to exhibit a minimum in the composition range $22 \leq x \leq 30$ and increases with further addition of Tl as shown in figure 3.6. These observations indicate that Ge$_{10}$Se$_{90-x}$Tlx glasses in the composition range $31 \leq x \leq 34$ are more stable against devitrification. It is also interesting that Ge$_{10}$Se$_{90-x}$Tlx glasses with $31 \leq x \leq 34$ exhibit a better threshold switching behavior with less fluctuations in the I-V characteristics, as seen in figure 4.1. Further, a minimum is seen in the composition dependence of non-reversing enthalpy $\Delta H_{nr}$ of Ge$_{10}$Se$_{90-x}$Tlx glasses around 22 atom % of Tl (figure 3.7). Based on the ADSC studies, it has been proposed that the composition range $22 \leq x \leq 30$ in Ge$_{10}$Se$_{90-x}$Tlx glasses constitutes a thermally reversing window [32]. The cusp seen in the composition dependence of $V_T$ of Ge$_{10}$Se$_{90-x}$Tlx glasses can therefore be associated with the thermally reversing window in this system.

4.3.3. Thickness Dependence of Switching Voltage

It is clear from the figure 4.3 that, the switching voltage, $V_T$ of the Ge$_{10}$Se$_{57}$Tl$_{33}$ sample increases with an increase in thickness. In some of the chalcogenides, such as Al-Te-Ge [33], Ge-Se-Tl films [18] etc., $V_T$ has been found to be proportional to thickness “t”. However, $V_T$ is found to be proportional to $t^{1/2}$ in certain memory switching glasses (Ge-Te [34], Ge-As-Te [35]). Earlier, It has been suggested that the 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[36]. However, in the present study, it is observed that, the variation of $V_T$ with thickness does not fit with any of the suggested dependences. The above result suggests that the mechanism of switching in these Ge$_{10}$Se$_{90-x}$Tlx samples is complex and may involve both thermal and electronic effects.
4.4. Summary

Electrical switching behavior of melt quenched bulk Ge\textsubscript{10}Se\textsubscript{90-x}Tl\textsubscript{x} (15 \leq x \leq 34) glasses have been investigated. Unlike Ge-Se-Tl thin films which exhibit memory switching, the bulk Ge\textsubscript{10}Se\textsubscript{90-x}Tl\textsubscript{x} glasses are found to exhibit threshold type switching with fluctuations seen in their I-V characteristics. The local melting and the subsequent re-solidification in point-electrode/material contact region is responsible for the fluctuation present in the Current-Voltage characteristics of the Ge\textsubscript{10}Se\textsubscript{90-x}Tl\textsubscript{x} glasses. Further, the threshold switching voltages of Ge-Se-Tl samples are found to decrease with the addition of Tl atoms. The observed variation of $V_T$ with the Tl content seems to be associated with the nature of Tl bonding in the Ge-Se matrix and the resultant increase in the chemical order due to formation of large number of Se-Tl heteropolar bonds. The network connectivity and metallicity factors also contribute for the decrease in the switching voltages of Ge\textsubscript{10}Se\textsubscript{90-x}Tl\textsubscript{x} glasses with Tl addition.

It is interesting to note that the composition dependence of switching voltages of Ge\textsubscript{10}Se\textsubscript{90-x}Tl\textsubscript{x} glasses exhibit a small cusp around the composition $x = 22$, which is understood on the basis of the presence of a thermally reversing window in this system.
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References

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