Abstract

$\text{Ge}_{17}\text{Te}_{83-x}\text{TI}_x$ ($x=2, 3, 6, 8, 10$) glasses have been prepared by melt quenching method and their amorphous nature was confirmed by XRD spectra. I-V characteristics and repeatability of electrical switching were investigated for all the glasses in order to find out their suitability for phase change memory applications. A comparison has been given with $\text{Ge}_2\text{Sb}_2\text{Te}_3$ the most commonly used material for phase change memory application. The entire series of glasses exhibited memory type of electrical switching but only the composition $\text{Ge}_{17}\text{Te}_{81}\text{TI}_2$ was able to withstand SET-RESET pulses for more than 10 cycles. The other samples show repeatability for only a few cycles with the degradation of threshold voltage.
Chapter 7: Electrical SET-RESET phenomenon in thallium doped Ge-Te glasses

7.1 Introduction

Chalcogenide glasses show fast and reversible crystalline to amorphous phase transitions resulting in significant changes in resistivity and reflectivity which has attracted the attention of academic and industrial researchers to utilize them for electrical and optical memory applications as Phase Change Random Access Memory (PRAM) [1–7]. Phase Change Memories make use of chalcogenide glasses which show memory type of electrical switching [1]. Upon applying an appropriate current or voltage pulse to these glasses, if an amorphous to crystalline phase change occurs then a semi storage of information takes place and the phenomenon is called as SET process. Under application of another short and sharp current pulse of higher magnitude, if the conducting crystalline channel melts and re-solidifies quickly, the glasses regain their amorphous state and this process is called RESET after which the glass is ready for another SET process. Glasses that are capable of undergoing such SET-RESET processes are possible candidates for use in Non-volatile Random Access Memory (NVRAM) applications. So the development of new materials showing memory type switching and investigation of SET-RESET phenomenon in them is central to the development of NVRAM technology.

This chapter reports the results of SET-RESET process on the series of thallium doped chalcogenide glasses of the composition Ge_{17}Te_{83-x}Tlx with x= 2, 3, 6, 8, 10 as a preliminary study to select a suitable glass amongst them.

7.2 Experimental details

The ternary chalcogenide glasses have been prepared by vacuum-sealed melt quenching method as described in section 2.2. The amorphous nature of the quenched samples was confirmed by X-ray diffraction. The electrical switching and SET and
RESET operations on samples polished to about 0.3-0.45 mm thickness have been performed using a programmable dc source-meter (Keithley 2410c) controlled using LabVIEW 6.1.

7.3 Results and Discussion

Before discussing the response of the samples to SET-RESET process, a closer look at the processes taking place during memory switching is attempted. This will help understand what happens during SET-RESET process in a better manner.

7.3.1 Memory switching in chalcogenide glasses

Figure-1(a) shows a representative XRD spectra confirming the amorphous nature of as prepared sample. Electrical switching studies in the glasses Ge$_{17}$Te$_{83-x}$Tl$_x$ with $0 \leq x \leq 10$ were carried out by increasing the applied current from 0 to 3 mA in small steps and noting the voltage across the sample. All the samples in the series showed memory type switching behaviour as reported in chapter-3 and ref. [8]. Figure-1(b) is the I-V characteristics of a representative glass, Ge$_{17}$Te$_{81}$Tl$_2$, which shows memory type switching.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{(a) XRD spectra showing amorphous nature of the as prepared sample (b) the I-V characteristics with 3 mA input current showing memory type switching behaviour.}
\end{figure}
In the region AB shown in figure-1(b), the voltage across the sample increases monotonically until a threshold value $V_{th}$ is reached. At this point the material undergoes a transition from a high resistance state to a low resistance state. The region marked as BC shows the progress towards the attainment of the low resistance state. The region CA shows that the material remains locked in the low resistance state even when the current is reduced to zero. This kind of behavior is called memory switching and occurs when the material undergoes a phase change from amorphous to crystalline phase. The process of change from high resistance to low resistance is understood to occur in the following manner. When a current is passed through the sample, Joule heating nucleates islands of crystallinity due to the higher temperatures, which grow and finally form a crystalline path for the current [9]. At this stage the material has a low resistance, achieved through a phase change from amorphous to crystalline. To be able to use it as non-volatile memories, it must be possible to switch between the high and low resistance states many times. It is possible to re-amorphize the sample by the application of a high current pulse of short duration. This short high current pulse melts the material which on cooling becomes amorphous because of fast dissipation of heat from the channel.

7.3.2 Response to SET-RESET pulses

Since all the samples in the series Ge$_{17}$Te$_{83-x}$Tl$_x$ showed memory type switching behaviour, the samples with $x = 2, 3, 6, 8, 10$ were subjected to cycles of SET-RESET pulses to evaluate their suitability for use as PRAM material. SET was performed by a triangular pulse whose height was fixed at 3mA for samples of 0.3mm thickness and 4mA for samples of 0.4mm thickness. The width of the pulse was ≈1sec, hence the current changed slowly at the rate of about 30µA in 10ms, to switch the material from amorphous to crystalline. The reset pulse is a short rectangular pulse
of 10 ms (fixed) whose amplitude was varied in steps until the material switches from crystalline (low resistance) to amorphous (high resistance). Generally the current required to RESET the chalcogenide glass is much larger than the SET current [10, 11].

Figure 2: The response of Ge$_{17}$Te$_{81}$Tl$_2$ to SET-RESET pulse cycles (sample of thickness 0.4 mm (1200 data points) [8].

Figure 2 is the response of Ge$_{17}$Te$_{81}$Tl$_2$ to the pulses where a RESET pulse height of 10 mA was able to reset the sample. The sample could withstand 10 cycles of SET-RESET. Figure 3 shows the response of Ge$_{17}$Te$_{80}$Tl$_3$ to SET-RESET pulses of height 3mA/15mA and here it is clearly seen that in the absence of a reset pulse, the material retains its crystalline low resistance state.
Figure-3 Response of $\text{Ge}_{17}\text{Te}_{80}\text{Tl}_3$ to SET-RESET pulses (sample thickness 0.3mm).

Figure-4: The response of (a) $\text{Ge}_{17}\text{Te}_{77}\text{Tl}_6$ and (b) $\text{Ge}_{17}\text{Te}_{73}\text{Tl}_{10}$ to SET-RESET pulse cycles (sample of thickness 0.3 mm).

Figure-4a and 4b [8, 12] show the results of experiments on $\text{Ge}_{17}\text{Te}_{77}\text{Tl}_6$ and $\text{Ge}_{17}\text{Te}_{73}\text{Tl}_{10}$ respectively. In the case of the former, a reset pulse height of 20mA was required and the material was able to withstand only 4 cycles of set-reset without degradation of the threshold voltage. In the latter case, a reset pulse height of 15mA
was necessary and the material could withstand only 2 cycles of set-reset before degradation of threshold voltage takes place.

7.3.3 **Comparison with Ge$_2$Sb$_2$Te$_5$**

The SET-RESET processes require two different attributes in the phase change glasses; for SET process an easy devitrification which causes easy crystallization is necessary, whereas a good glass forming ability i.e. an easy re-amorphizibilty is required for easy resettability.

**Table-1: Comparison of the thermal and electrical properties of Ge$_2$Sb$_2$Te$_5$ (GST) and Ge$_{17}Te_{83-x}Tl_x$ glasses**

<table>
<thead>
<tr>
<th>Thermal and electrical properties</th>
<th>Ge$_2$Sb$_2$Te$_5$</th>
<th>Ge$<em>{17}Te</em>{83}$.Tl$_2$</th>
<th>Ge$<em>{17}Te</em>{80}$.Tl$_3$</th>
<th>Ge$<em>{17}Te</em>{77}$.Tl$_6$</th>
<th>Ge$<em>{17}Te</em>{75}$.Tl$_8$</th>
<th>Ge$<em>{17}Te</em>{73}$.Tl$_{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Threshold electric field (Eth)</td>
<td>~60 kV/cm, thickness 100nm [16]</td>
<td>4.319 kV/cm, thickness 0.3 mm [8]</td>
<td>3.94 kV/cm, thickness 0.3 mm [8]</td>
<td>2.23 kV/cm, thickness 0.3 mm [8]</td>
<td>2.01 kV/cm, thickness 0.3 mm [8]</td>
<td>1.76 kV/cm, thickness 0.3 mm [8]</td>
</tr>
<tr>
<td>Change in resistance (OFF-ON state)</td>
<td>1.58 MΩ–6.8 kΩ [17]</td>
<td>5 MΩ–2 kΩ</td>
<td>4.27 MΩ–15 kΩ</td>
<td>100 MΩ–25.9 kΩ</td>
<td>0.68 MΩ–6.23 kΩ</td>
<td>1.25 MΩ–39 kΩ</td>
</tr>
<tr>
<td>SET current</td>
<td>1.31 mA for 200 nm thickness. [17]</td>
<td>4 mA for 0.4 mm thickness</td>
<td>3 mA for 0.3 mm thickness</td>
<td>3 mA for 0.45 mm thickness</td>
<td>3 mA for 0.3 mm thickness</td>
<td>5 mA for 0.3 mm thickness</td>
</tr>
<tr>
<td>RESET current required</td>
<td>~0.45 mA for 100 nm Thickness [17]</td>
<td>10 mA for 0.4 mm thickness</td>
<td>15 mA for 0.3 mm thickness</td>
<td>20 mA for 0.30mm thickness</td>
<td>10 mA for 0.3 mm thickness</td>
<td>15 mA for 0.3mm thickness</td>
</tr>
<tr>
<td>Thermal stability</td>
<td>Poor</td>
<td>better</td>
<td>better</td>
<td>better</td>
<td>better</td>
<td>better</td>
</tr>
<tr>
<td>Cycling</td>
<td>10$^3$ cycles achieved [18]</td>
<td>More than 10 cycles without degradation</td>
<td>4 cycles only</td>
<td>6 only</td>
<td>3 with degradation</td>
<td>3 with degradation</td>
</tr>
</tbody>
</table>
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Table-1 shows the comparison of the thermal and electrical properties of the present Ge$_{17}$Te$_{83-x}$Tl$_x$ glasses with Ge$_2$Sb$_2$Te$_5$ (GST) which is the most common material used in PRAMs. The change in ON resistance to OFF resistance in the two systems, Ge-Te-Tl and GST, is similar, and nearly by three orders of magnitude (a few kΩ to a few MΩ).

It is seen that the crystallization temperature, $T_c$, in Ge-Te-Tl samples are nominally higher than GST. The glass transition temperatures, $T_g$, are also higher in Ge-Te-Tl samples compared to GST. The threshold electric field is however nearly two orders of magnitude smaller in Ge-Te-Tl and this is attributed to the network fragmentation effect of thallium [8, 14, 19, 20]. The reduced threshold field is expected to translate into lower currents for switching the sample and if a linear variation of $V_{th}$ with thickness is assumed by extrapolating the results of section 3.4 of chapter-3 [8], it must be possible to switch Ge-Te-Tl films of nanometer thickness with nano-amperes of current. The above aspects seem to indicate that Ge-Te-Tl samples may be better than even GST. However it is known that simple extrapolation or the linear scaling does not work for every thin films. Further, even though they showed promise, the glasses with higher thallium content were not able to withstand repeated cycles of crystallization and re-amorphization.

Of all the samples, Ge$_{17}$Te$_{81}$Tl$_2$ seems most suitable for memory applications as it can withstand more than 10 cycles of SET-RESET without degradation. The reason for the degradation of threshold voltage in the case of samples having higher thallium content may lie with the way Tl bonds in these samples [8, 14, 19, 20]. As Te is more electronegative than Tl, the Te-Tl bonds in these samples become polarized and introduce electrostatic forces inside the material. The presence of these forces may inhibit repeated re-amorphization of the sample.
7.4 Conclusions

In summary, a new material, Ge-Te-Tl glass, has been investigated for suitability for use in Phase change Random Access Memory applications. All the samples studied show memory type switching necessary for use in PRAMs. The composition Ge$_{17}$Te$_{81}$Tl$_2$ was found to be the most promising as it could withstand more than 10 cycles of SET-RESET operations. Glasses with higher thallium content however show degradation in the threshold voltage after a few cycles.
References


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