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ELECTRICAL SET-RESET PHENOMENON IN THALLIUM DOPED Ge-Te GLASSES SUITABLE FOR PHASE CHANGE MEMORY APPLICATIONS

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$Ge_{17}Te_{83-x}Tl_x$ (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 $Ge_2Sb_2Te_5$ 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 $Ge_{17}Te_{81}Tl_2$ 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.*

Keywords: *CHALCOGENIDE GLASS, THALLIUM DOPING, ELECTRICAL SWITCHING, SET-RESET, PHASE CHANGE MEMORY.*

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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 a 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 paper reports the results of SET-RESET process on the series of thallium doped chalcogenide glasses of the composition $Ge_{17}Te_{83-x}Tl_x$ with x = 2, 3, 6, 8, 10.

2. EXPERIMENTAL DETAILS

The ternary chalcogenide glasses have been prepared by vacuum-sealed melt quenching method. Appropriate quantities of high purity (99.99%) constituent elements were sealed in an evacuated quartz ampoule (at 10^{-5} Torr) and slowly heated in a horizontal rotary furnace. The ampoules were maintained at 950 °C and rotated continuously for about 24 h at 10 rpm to ensure homogeneity of the melt. The ampoules were subsequently quenched in a bath of ice water and NaOH mixture to get bulk glassy samples. 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 LabVIEW6.1.

3. RESULTS AND DISCUSSION

3.1 Memory switching in chalcogenide glasses

Figure 1a shows the XRD spectra confirming the amorphous nature of as prepared sample. Electrical switching studies in the glasses $Ge_{17}Te_{83-x}Tl_x$ with $0 \le x \le 10$ 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 [8]. Figure 1b is the I-V characteristics of a representative glass, $Ge_{17}Te_{81}Tl_2$, which shows memory type switching.

In the region AB (Fig. 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 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.

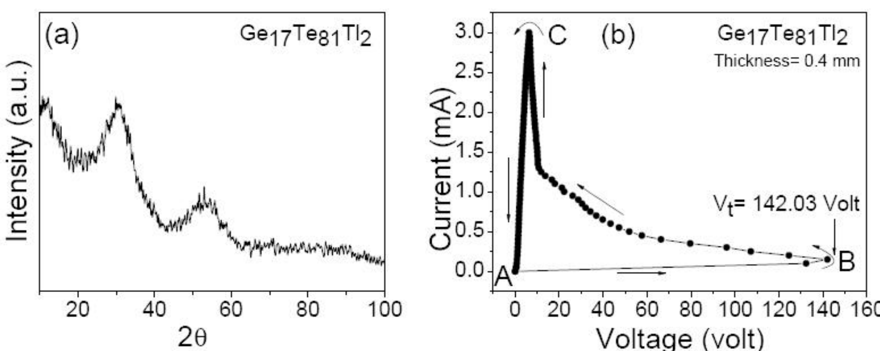

Fig. 1 *– XRD spectra showing amorphous nature of the as prepared sample (a); the* I-V *characteristics with* 3 *mA input current showing memory type switching behaviour (b)*

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 3 mA for samples of 0.3 mm thickness and 4 mA for samples of 0.4 mm thickness. The width of the pulse was ≈ 1 sec, hence the current changed slowly at the rate of about 30 μA in 10 ms, 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].

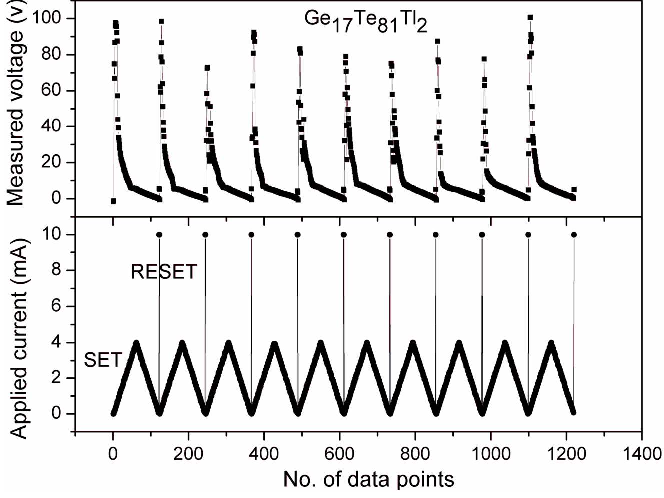

Fig. 2 *– The response of $Ge_{17}Te_{81}Tl_2$ to SET-RESET pulse cycles (sample of thickness* 0.4 *mm) (*1200 *data points)*

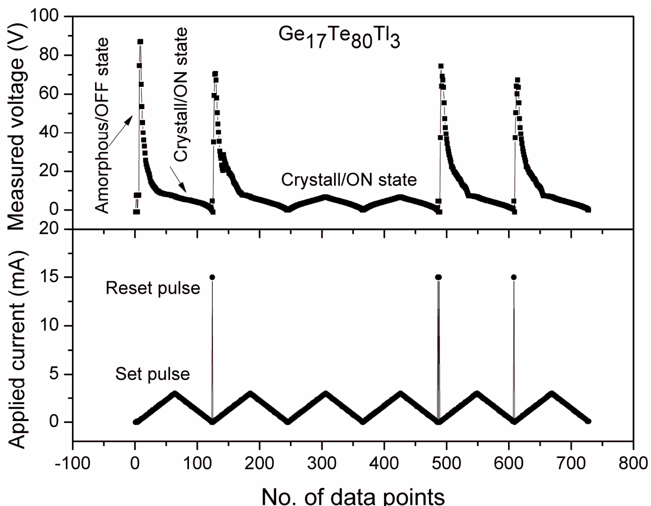

Fig. 3 – Response of $Ge_{17}Te_{80}Tl_3$ to SET-RESET pulses (sample thickness 0.3 *mm)*

Fig. 2 [8] 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. Fig. 3 shows the response of $Ge_{17}Te_{80}Tl_3$ to SET-RESET pulses of height 3 mA / 15 mA and here it is clearly seen that in the absence of a reset pulse, the material retains its crystalline low resistance state. Figs. 4a and 4b [8] show the results of experiments on $Ge_{17}Te_{77}Tl_6$ and $Ge_{17}Te_{73}Tl_{10}$ respectively. In the case of the former, a reset pulse height of 20 mA 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 15 mA was necessary and the material could withstand only 2 cycles of set-reset before degradation of threshold voltage takes place.

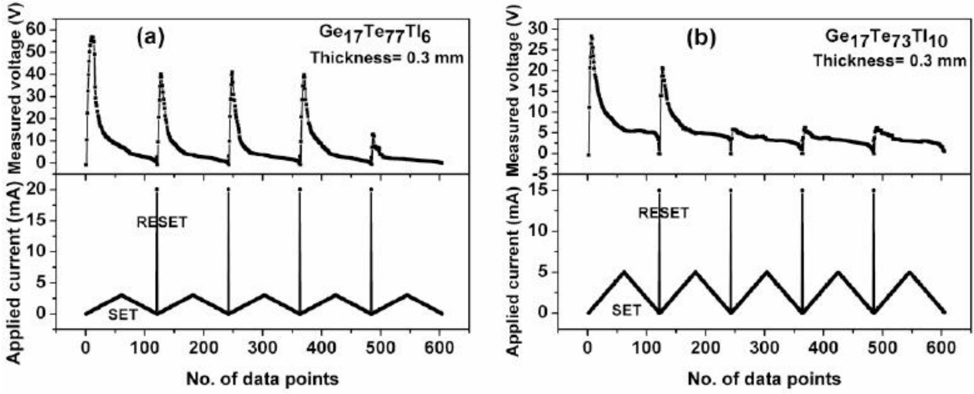

Fig. 4 – The response of (a) $Ge_{17}Te_{77}Tl_6$ and (b) $Ge_{17}Te_{73}Tl_{10}$ to SET-RESET pulse cycles (sample of thickness 0.3 *mm)*

3.3 Comparison with $Ge_2Sb_2Te_5$

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 shows the comparison of the thermal and electrical properties of $Ge_{17}Te_{83-x}Tl_x$ glasses with $Ge_2Sb_2Te_5$ (GST) which is the most common material used in PRAMs. The change in ON resistance to OFF resistance in the two

Table 1 *– Comparison of the thermal and electrical properties of* $Ge_2Sb_2Te_5$ *(GST) and* $Ge_{17}Te_{83-x}Tl_x$ *glasses*

Thermal and electrical properties	$Ge_2Sb_2Te_5$	$Ge_{17}Te_{83-x}Tl_x$ glasses				
		$Ge_{17}Te_{81}T_2$	$Ge_{17}Te_{80}Tl_3$	$Ge_{17}Te_{77}T_6$	$Ge_{17}Te_{75}T_8$	$Ge_{17}Te_{73}Tl_{10}$
Method		SET RESET Current/voltage Time				
Crystallization temperature (T_c)	~ 142 °C [16]	207.52 °C [12]	197.55 °C [12]	209.95 °C [12]	201.14 °C [12]	209.76 °C [12]
Glass transition temperature (T_g)	~ 100 °C [17]	134.12 °C [12]	137.28 °C [12]	125.37 °C [12]	128.2 °C [12]	128.28 °C [12]
Threshold electric field (E_{th})	~ 60 kV/cm, thickness 100 nm [18]	4.319 kV/cm, thickness 0.3 mm [8]	3.39 kV/cm, thickness 0.3 mm [8]	2.23 kV/cm, thickness 0.3 mm [8]	2.01 kV/cm, thickness 0.3 mm [8]	1.76 kV/cm, thickness 0.3 mm [8]
Change in resistance (OFF-ON state)	1.58 MΩ – – 6.8 kΩ [15]	5 MΩ – – 2 kΩ [8]	4.27 MΩ – – 15 kΩ [8]	1.06 MΩ – – 259 kΩ [8]	0.68 MΩ – – 6.23 kΩ [8]	1.25 MΩ – – 39 kΩ [8]
SET current	1.31 mA for 200 nm thickness. [15]	4 mA for 0.4 mm thickness	3 mA for 0.3 mm thickness	3 mA for 0.45 mm thickness	3 mA for 0.3 mm thickness	5 mA for 0.3 mm thickness
RESET current required	~ 0.45 mA for 100 nm Thickness [15]	10 mA for 0.4 mm thickness	15 mA for 0.3 mm thickness	20 mA for 0.30 mm thickness	10 mA for 0.3 mm thickness	15 mA for 0.3 mm thickness
Thermal stability	Poor	better	better	better	better	better
Cycling	10^{11} cycles achieved	More than 10 cycles without degradation	4 cycles only	6 only	3 with degradation	3 with degradation

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, 13, 14]. 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 [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. In spite of all these advantages, 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, 13, 14]. 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.

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 suitable 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.

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