Structural origin of set-reset process in a new bulk Si$_{15}$Te$_{83}$Ge$_2$ phase-change memory material

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A new phase-change memory material, in bulk, has been prepared by melt-quenching technique, which has a better glass forming ability. This sample is set and resettable relatively easily for several cycles at 2mA SET and RESET input currents, and is likely to be a suitable material for phase-change memory applications. Raman scattering studies have been undertaken during the SET and RESET operations to elucidate the local structural transformations that occur during these operations. © 2011 Author(s). This article is distributed under a Creative Commons Attribution Non-Commercial Share Alike 3.0 Unported License. [doi:10.1063/1.3560852]

I. INTRODUCTION

Chalcogenide based phase-change memories (PCMs), in which data is recorded by switching the material either into the amorphous or crystalline state, are being considered very promising for electrical and optical data storage and as an alternative to the current flash memories.1–3 The chalcogenide switches can be classified into two groups, namely threshold (mono-stable) or memory (bi-stable) devices depending on the type of switching (reversible or irreversible, respectively) exhibited by them. In threshold and memory glasses, the initiation of switching from the semiconducting OFF state to the conducting ON state, is electronic in nature; switching occurs when the charged defect states in a chalcogenide glass are filled by the field-injected charge carriers. Additional thermal effects come into play in memory materials which result in the formation of a conducting crystalline channel.7

The chalcogenide memory switches can be reset back to the OFF state by the application of a current or light pulse, during which local melting of the conducting channel and re-solidification into the amorphous state takes place.8 The RESET process is generally accomplished by applying a sharp current pulse of higher magnitude compared to the SET pulse.2

The thermal stability and glass forming ability are two important thermal attributes of phase change memory materials. While the poor thermal stability will lead to a rapid thermal degradation of the glass and lesser life time of the device, good glass formability is essential from the point of view of easy resetting of the memory device.

There are two classes of phase-change materials used so far in memory technology; those having short erasure times enabled by their fast crystallization speeds, known as the Nucleation Dominated Materials (NDM) and Fast Growth Materials (FGM). The NDM family comprises of the thermodynamically stable ternary compositions Ge$_2$Sb$_2$Te$_5$ (GST 225), Ge$_2$Sb$_2$Te$_4$, and Ge$_2$Sb$_2$Te$_7$.6 The FGM family is based on the binary composition Sb$_{69}$Te$_{31}$. Efforts are being made recently to develop newer phase change materials, understand their SET-RESET processes and optimize their electrical switching parameters such as amplitude, pulse width, etc., which are important from the viewpoint of the device performance.9–12 Attempts are also made being made to reduce the RESET current by modifying the device structure or by doping with other elements.13

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While the studies on the switching behavior of thin film samples are more relevant to memory applications, investigations on bulk samples help us to understand the basic properties better and also correlate various properties such as structure, thermal parameters, etc., with the switching behavior. In the present work, a new phase-change material Si$_{15}$Te$_{83}$Ge$_2$ (GSiT), in bulk, is identified which is relatively easily devitrifiable, and having better glass forming ability, which is likely to be a suitable material for phase-change memory applications. Electrical switching and Raman scattering studies have been undertaken during the SET and RESET operations to elucidate the local structural transformations which occur during these operations. Alternating differential scanning calorimetric (ADSC) studies also have been done to study the thermal stability of the GSiT glass.

II. EXPERIMENTAL

Bulk Si$_{15}$Te$_{83}$Ge$_2$ glass is prepared by vacuum sealed-melt quenching method. Appropriate quantities of high purity (99.999%) constituent elements are sealed in an evacuated quartz ampoule at $1 \times 10^{-5}$ Torr and slowly heated in a horizontal rotary furnace. The ampoule is maintained at 1100 °C and rotated continuously for about 36 h at 10 rpm to ensure homogeneity of the melt. The ampoule is subsequently quenched in a bath of ice water and NaOH mixture to get bulk glass sample.

The electrical switching behavior of Si$_{15}$Te$_{83}$Ge$_2$ sample is studied by recording $I-V$ characteristics using a Keithley source-meter (Model 2410$^{th}$) controlled by LabVIEW 6i (National Instruments). Sample polished to about 0.20 mm thickness is mounted between a flat-plate bottom and a point-contact top electrode made of brass. A constant current of 0-2 mA is passed through the sample and the voltage developed across the sample is measured.

The thermal analysis is carried out by ADSC (model DSC822$^{c}$, METTLER TOLEDO). The ADSC scans of all samples are taken at 3 °C min$^{-1}$ scan rate and 1 °C min$^{-1}$ modulation rate in the temperature range 50 – 410 °C. Typical error in the measurement of thermal parameters is within ±1°C.

The X-ray diffraction pattern of GSiT sample is recorded at RT, 250 °C ($T_{c1}$), 275 °C ($T_{c2}$) and 350 °C using a Bruker D8 instrument in high temperature mode. The confocal micro-Raman studies on Si$_{15}$Te$_{83}$Ge$_2$ glass has been carried out in back scattering geometry using HORIBAJOBIN YVON LabRAM HR instrument equipped with a charge coupled device detector (CCD) at a working temperature -70 °C. The sample is illuminated by the 514.5 nm line of an argon ion laser focused using a 100 X objective on a flat surface of the sample. All the data have been recorded using 2 mW of laser power and for 120 s of acquisition. The spectral resolution is 0.3 – 1.0 cm$^{-1}$.

III. RESULTS AND DISCUSSION

The current-voltage characteristics of the GSiT glass (of thickness 0.2 mm), is shown in Fig. 1, indicating that the sample exhibits memory type switching behavior for a 2 mA input current pulse at a threshold electric field ($E_{th}$) of 9.9 kV cm$^{-1}$ (corresponding $I_{th}$ = 100 µA). The inset in Fig. 1 shows the $I-V$ characteristics of the same sample at a lower input current of 1mA, which indicates a threshold-type switching behavior at a threshold electric field of 9.5 kV cm$^{-1}$ (corresponding $I_{th}$ = 100 µA). Upon increasing the current in the ON state about 2 mA (for sample thickness 0.2 mm), the Joule heating in the current carrying path and the consequent increased mobility of atoms lead to local structural rearrangements and crystallization, which set the sample in the low resistance ON state.$^7,14$

The most interesting aspect of the electrical switching in chalcogenide glasses is the behavior exhibited during the ramping down of the applied current. In memory switching glasses, which normally have a lower thermal diffusivity,$^{15,16}$ the dissipation of heat from the electrode region is poorer; consequently, the cooling of the switched region is slower and the crystalline state is retained even after reducing the applied current to zero (SET state). In such cases, it is necessary to externally RESET the memory state by applying a short duration current pulse, usually of higher magnitude than that required for setting the device in the ON state.$^2$

Fig. 2(a) shows that the SET and the RESET processes in GSiT sample are achieved by applying 2 mA triangular and short-width rectangular pulses respectively, for a sample thickness of 0.2 mm.
During the ramp-up process of the SET operation, the electrical switching from the OFF to ON state occurs at about 100 µA current and the SET state is reached at 2 mA ON-state current. During the ramp down of the applied triangular current pulse, the SET state is retained (memory behavior); the electrical resistance in the OFF state is \( \approx 8 - 9 \) MΩ and in the SET state is \( \approx 50 - 100 \) kΩ. The variation seen in the resistance of sample is due to error in thickness measurement which is of the order of \( \pm 0.01 \) mm.

The RESET process in GSIT glass is accomplished by applying a rectangular current pulse of 2 mA magnitude and 10 ms width, which heats up the crystallized conducting channel rapidly; this causes the local melting of the conducting channel and its subsequent re-solidification into high resistance amorphous state. Usually, in most of the chalcogenide glasses, the resetting pulse is of
higher magnitude compared to the setting pulse. However, the present results show that the current pulse of the same magnitude, with different wave forms, can perform both the SET and RESET processes in the GSiT glass.

In the present study, the SET state (low resistance state of sample) is confirmed by applying two triangular SET pulses and a rectangular RESET pulse of 2 mA. It can be seen from Fig. 2(b) that after the first SET pulse, the sample exhibits an Ohmic behavior for the second SET pulse. However, the sample gains its initial high resistance state upon application of the 2 mA rectangular RESET pulse. It is also observed that the resistance of sample after the first RESET pulse is slightly less (∼2 MΩ) that of its initial resistance before switching. Similarly, the sample resistance observed after the second SET pulse is slightly larger (∼150 kΩ) than that of the resistance in the first SET state of the sample. It is interesting to note that there is no considerable variation in the sample resistances of each state during several subsequent SET-RESET cycles.

Glass transition temperature ($T_g$) is one of the important parameters which helps to understand the thermal stability of the material, which is significant for phase change memory applications. The ADSC studies have been undertaken to know the thermal parameters such as glass transition temperature ($T_g$) and crystallization temperature ($T_c$) of GSiT sample. The benefits of MDSC/ADSC technique over conventional differential scanning calorimetry (DSC) have been documented well in several recent papers. From the Fig. 3, it is found that the present GSiT glass exhibits one endothermic glass transition ($T_g$) and two exothermic crystallization reactions at $T_{c1}$ and $T_{c2}$ respectively. The measurements of $T_g$ and $T_{c1}$ and $T_{c2}$ are made from reversing heat flow (RHF) and non-reversing heat flow (NHF) curves respectively and are as follows: $T_g = 150.2$ °C; onset temperatures of first and second crystallization peaks are 249.3 °C ($T_{c1}$) and 274.8 °C ($T_{c2}$) respectively. On comparison with several Ge-Sb-Te (GST) glasses which have been widely used in phase-change memory applications, the glass transition temperature of the present GSiT material is considerably high. The glass transition temperatures are indicative of network connectivity and thermal stability of the glass. Therefore, from the point of view of thermal stability, the present GSiT material is relatively more suitable for phase change memory applications compared to GST glasses.

High temperature X-ray diffraction (HTXRD) studies undertaken in the present work (Fig. 4) indicate that the microscopical phases present in the GSiT glass at $T_{c1}$ and $T_{c2}$ are hexagonal-Te (Space group (SG): R3m (160)) and orthorhombic-GeTe (SG: Pnma (62)) and cubic-GeTe4 (SG: P*3* (221)) respectively. The HTXRD spectrum of GSiT glass recorded at 350 °C is found to be similar to the spectrum obtained at $T_{c2}$.

Raman studies have been undertaken on GSiT glass sample during various stages of switching, namely OFF, SET, and RESET states (Fig. 5). The Raman spectrum is recorded by focusing the laser beam on the flat sample surface (OFF state), at a spot in the conducting crystalline channel formed during the SET process (SET state) and at the position where resetting is carried out. The nature
FIG. 4. HTXRD pattern of (a) as-prepared GSiT glass (b) at first crystallization temperature $T_{c1}$ and (c) at second crystallization temperature $T_{c2}$. Crystalline phases presented at $T_{c1}$ and $T_{c2}$ are identified as $c$-Te and $c$-GeTe and $c$-GeTe$_4$ respectively. Two peaks presented commonly (shown with cross in circle symbol) in (a), (b) and (c) belong to tantalum (Ta) element which is used as HTXRD heating element. ($h, k, l$ values are not indexed here as are not important in results discussion.)

of the three different phases of sample has been confirmed by measuring the electrical resistance between electrodes.

From Fig. 5 it can be seen that there are three main bands in the Raman spectra of the Si$_{15}$Te$_{83}$Ge$_2$ (GSiT) sample in the amorphous (Fig. 5(a)) and RESET states (Fig. 5(c)) in the wave-number range 50 – 250 cm$^{-1}$. Approximate wave-numbers of the band positions in both the states are as follows: band $B \sim 117.4$ cm$^{-1}$; band $C \sim 137.8$ cm$^{-1}$; and a weak hump band at $A \sim 89.7$ cm$^{-1}$. The peak $B$ can be attributed to the $A_1$ mode and peaks $A$ and $C$ to the $E_{TO}$ modes of crystalline Te-Te chain.$^{21}$

According to the chemically ordered covalent network model, the Te atoms are arranged as one dimensional chains in Te-rich Si (or Ge)-Te glasses and any dopant atom added leads to the cross linking of Te-Te chain.$^{22}$ Thus, the structural network in the base glass is primarily decided by Te-Te chains, which are interlinked by Ge-Te bonds. It is also seen from the Raman spectra that in addition to three bands observed in amorphous and RESET state, the GSiT sample exhibits a new Raman band at $D \sim 199.6$ cm$^{-1}$ in the SET state (Fig. 5(b)). Also, here is no considerable shift observed in Te-Te chain Raman bands $A$, $B$ and $C$. Form this observation, it can be concluded that the only phase responsible for set-reset process is crystalline GeTe/GeTe$_4$.

Further, it is interesting to note that the Raman band ($D$) is temperature dependent and is assigned to $D[\nu_3(F_2)]$ mode of amorphous GeTe (or GeTe$_4$) structural unit at its crystallization temperature, $T_{c2}$ (274.83 °C). Earlier studies on $a$-GeTe also indicate that the Raman band ($D$) is temperature dependent and it shifts towards lower wave-number side with temperature.$^{22}$ The observation of Raman band ($D$) at $D \sim 199.6$ cm$^{-1}$ during SET process can be understood in the following manner.

During the SET process, the voltage across the sample increases initially with input current, till the initiation of switching due to the passivation of charged defect states in the glass. The sudden increase in the mobility of charge carriers and the consequent increase in Joule heating, lead to the formation of a conducting crystalline channel across the sample. At this stage sample will switch from high resistance amorphous state to low resistance crystalline state and this results in decreasing the voltage with further increase in current due to negative differential resistance. The formation of conducting channel is possible only if the temperature in the conducting region is equal to the crystallization temperature of the sample, in this case that of the GeTe (and GeTe$_4$) phase.

In order to verify the temperature effect on Raman shift, the Raman spectrum of GSiT sample has been recorded at 350 °C, which is well above crystallization temperature and below the melting point of GeTe/GeTe$_4$ phase (Fig. 5(d)). It can be seen from Fig. 5(d) that the Raman peak presented during SET process at $\sim 199.6$ cm$^{-1}$ (band $D$) is now shifted to $\sim 177.6$ cm$^{-1}$ (lower wave-number side). On the other hand, the Raman modes $A$ ($\sim 93.26$ cm$^{-1}$), $B$ ($\sim 121.9$ cm$^{-1}$) and $C$ ($\sim 141.3$ cm$^{-1}$)
are shifted towards higher wave-number side at 350 °C temperature. This shift in peak positions at different temperatures strongly supports the temperature dependence of Raman band $D$.

The previous reports\textsuperscript{23} on Pb-Ge-Se glasses indicate that the Raman peaks at 177.6 cm$^{-1}$ and 199.6 cm$^{-1}$ are associated with Ge in tetrahedral position. However, the shift in peak $D$ with temperature is not fully understood. The possible reason may be the structural transformation of Te-Te, GeTe and GeTe$_4$ units presented in GSiT glass. The details of peak positions at different thermal stages of the GSiT sample are consolidated in Table I.

**TABLE I. Peak positions of Raman spectra at different stages of Si$_{15}$Te$_{83}$Ge$_2$ sample.**

| Peak Identity | Frequency [cm$^{-1}$] | Amorphous | SET | RESET | at 350 °C |
|---------------|-----------------------|-----------|-----|-------|-----------|
| $E_{TO}$      | 89.7                  | 89.7      | 89.7| 93.3  |
| $A_1$         | 117.4                 | 117.9     | 117.4| 121.9 |
| $E_{TO}$      | 137.8                 | 137.8     | 137.8| 141.4 |
| $D[\nu_3(F_2)]$ | -                    | 199.6     | -   | 177.6 |

In summary, a new phase-change material Si$_{15}$Te$_{83}$Ge$_2$ (GSiT), in bulk, is prepared by melt quenching technique. Electrical switching studies show that the present GSiT glass, of thickness 0.2 mm, can be easily set and resettable using a 2 mA triangular SET pulse and a 2 mA short rectangular RESET pulse respectively. The thermal parameters of GSiT glass are estimated by using

**FIG. 5.** Raman spectrum of Si$_{15}$Te$_{83}$Ge$_2$ glass at different stages.
ADSC technique, which shows that the glass is thermally more stable. Raman scattering studies indicate that in GSiT glass, Te-Te chain Raman modes are present in all the OFF, SET and RESET stages and no considerable shift is observed in peak positions. In SET stage, the GSiT sample shows a new Raman peak corresponding to the structural unit formed during crystallization of α-GeTe (or GeTe₄), which is responsible for the set-reset process. This phase is also observed in the sample annealed at 350°C which is well above the crystallization temperature and it is found to shift towards lower wave-number side with temperature. However there is a shift in Te-Te Raman modes at 350°C towards higher wave-number side.

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1 S. R. Ovshinsky, Phys. Rev. Lett. 21, 1450 (1968).
2 S. Hudgens, B. Johnson, MRS Bull. 29, 829 (2004).
3 M. H. R. Lankhorst, B. W. S. M. M. Ketelaars, R. A. M. Wolters, Nat. Mater. 4, 347 (2005).
4 N. Yamada, E. Ohno, K. Nishiuchi, N. Akahira, M. Takao, J. Appl. Phys. 69, 2829 (1991).
5 H. Iwasaki, Y. Ide, M. Harigaya, Y. Kageyama, I. Fujimura, Jpn. J. Appl. Phys. 31, 461 (1991).
6 N. K. Abrikosov, G. T. Danilova-Dobryakova, Izv. Akad. Nauk SSSR Neorgan. Mater. 1, 204 (1965).
7 R. Aravinda Narayanan, S. Asokan, A. Kumar, Phys. Rev. B 63 092203 (2001).
8 Matthias Wuttig, Nat. Mater. 4, 265 (2005).
9 A. Pironavo, A. L. Lacaita, A. Benvenuti, F. Pellizzer, R. Bez, IEEE Trans. Electron Devices 51, 452 (2004).
10 A. Redaelli, A. Pironova, F. Pellizzer, A. L. Lacaita, D. Lemini, R. Bez, IEEE Electron Device Lett. 25, 684 (2004).
11 You Yin, Akihita Miyachi, Daisuke Niida, Hayato Sone, Sumio Hasaka, Jpn. J. Appl. Phys. 45, L726 (2006).
12 V. G. Karpov, Y. A. Kryukov, S. D. Savransky, I. V. Karpov, Appl. Phys. Lett. 90, 123504 (2007).
13 Baowei Qiao, Jie Feng, Yunfeng Lai, Yun Ling, Yinyin Lin, Ting’ao Tang, Bingchu Cai, Bomy Chen, Appl. Surf. Sci. 252, 8404 (2006).
14 Dae-Hwan Kang, Byung-ki Cheong, Jeung-hyun Jeong, Tack Sung Lee, In Ho Kim, Won Mok Kim, Joo-Youl Huh, Appl. Phys. Lett. 87, 253504 (2005).
15 S. Manohar, S. Murugavel, S. Asokan, Solid State Commun. 135, 323 (2005).
16 Pulok Pattanayak, N. Manikandan, M. Paulraj, S. Asokan, J. Phys.: Condens. Matter 19, 036224 (2007).
17 M. Reading, A. Luget, R. Wilson, Thermochimica. Acta. 238, 295 (1994).
18 B. Wunderlich, Y. Jin, A. Boller, Thermochimica. Acta. 238, 277 (1994).
19 P. S. Gill, S. R. Sauerbrunn, M. Reading, J. Thermal Analysis 40, 931 (1993).
20 J. A. Kalb, M. Wuttig, F. Sapeen, J. Mater. Res. 22, 748 (2007).
21 A. T. Pine, G. Dresselhaus, Phys. Rev. B 4, 356 (1971).
22 K. S. Andrikopoulos, S. N. Yannopoulos, G. A. Voyiatzis, A. V. Kolobov, M. Ribes, J. Tominaga, J. Phys.: Condens. Matter. 18, 965 (2006).
23 B. Vaidhyanathan, S. Murugavel, S. Asokan, K. J. Rao, J. Phys. Chem. B 101, 9717 (1997).