Low electric field, easily reversible electrical set and reset processes in a $Ge_{15}Te_{83}Si_2$ glass for phase change memory applications

M. Anbarasu, and S. Asokan

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Low electric field, easily reversible electrical *set* and *reset* processes in a $Ge_{15}Te_{83}Si_2$ glass for phase change memory applications

M. Anbarasu[a] and S. Asokan
Department of Instrumentation and Applied Physics, Indian Institute of Science, Bangalore 560012, India

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We report here an easily reversible *set–reset* process in a new $Ge_{15}Te_{83}Si_2$ glass that could be a promising candidate for phase change random access memory applications. The I-V characteristics of the studied sample show a comparatively low threshold electric field (E_{th}) of 7.3 kV/cm. Distinct differences in the type of switching behavior are achieved by means of controlling the *on* state current. It enables the observation of a threshold type for less than 0.7 mA beyond memory type (*set*) switching. The *set* and *reset* processes have been achieved with a similar magnitude of 1 mA, and with a triangular current pulse for the *set* process and a short duration rectangular pulse of 10 msec width for the *reset* operation. Further, a self-resetting effect is seen in this material upon excitation with a saw-tooth/square pulse, and their response of leading and trailing edges are discussed. About 6.5×10^4 *set–reset* cycles have been undertaken without any damage to the device. © *2011 American Institute of Physics*. [doi:10.1063/1.3574659]

I. INTRODUCTION

Recent advancements in the field of phase change materials unveil three generations of optical storage media and also throw light on the possibility of electronic memories.[1] This class of material possesses a unique property of fast, reversible structural change between the amorphous and crystalline states by means of applied electrical or optical pulses. This pronounced property change is indicative of atomic rearrangement. Nevertheless, this local atomic rearrangement in the subnanosecond time scale is intriguing not only for flash memories but also for dynamic random access memories.[2,3] The first commercial products of phase change materials emerged in optical storage, although reversible electrical switching phenomena in chalcogenide glassy materials had actually been demonstrated much earlier.[4]

The phenomenon of electrical switching in chalcogenide glasses was first observed by Ovshinsky nearly four decades ago.[4] Chalcogenide switches are normally classified into two groups, namely, ovonic threshold switch (OTS) or ovonic memory switch (OMS) devices, depending on the type of switching (reversible or irreversible, respectively) exhibited by them. Electrical switching in these materials occur when an appropriate electric field, known as the threshold electric field (E_{th}), is applied and the glass switches to a high conducting *on* state from a low conducting *off* state. Upon the removal of the electric field, OTS switches revert to the initial high resistance *off* state, whereas OMS switches remain locked into the low resistance *on* state.

The process of initiation of electrical switching in both OTS and OMS glasses is believed to be primarily electronic in nature, and it occurs when the field injected charge carriers fill the charged defect states in a chalcogenide glass.[5–8] Nevertheless, an additional thermal effect such as Joules heating made by an *on* state current comes into play in memory materials and results in the formation of a conducting crystalline channel.[9,10]

Phase change memories (PCM) make use of chalcogenide materials of the OMS type. In these materials, the electrical *set* process occurs, in which the storage of information takes place due to a phase change from the amorphous to the crystalline state induced by the applied current pulse. Similarly, the *reset* process is accomplished by applying a higher, sharp current pulse in the conducting crystalline region formed during the *set* process, which locally melts and resolidifies into the amorphous state.[11,12] Generally, the *reset* process is accomplished by applying a sharp current pulse with a higher magnitude than the *set* pulse that increases the temperature above the melting temperature, whereas the *set* pulse raises the temperature only up to the crystallization point.[13,14]

Recently, tremendous efforts have been made to understand the *set* and *reset* processes, and optimizing input electrical parameters such as pulse amplitude, source resistance, and pulse width is very important with regard to the stable performance of a memory device.[15–18] For example, the reduction in the *reset* current is one of the most crucial parameters for developing high-density (lower programming volume) phase change random access memory applications. Many attempts have been made to reduce the *reset* current by modifying the device structure or by doping[19] other elements to reduce the melting temperature and to increase the crystalline resistivity (or stability of the amorphous phase) of the material, which eventually reduces the programming volume. In addition, properties such as latent heat transfer and cooling rate in the bulk material on the nanoscale level[20] play a significant role in optimizing electrical pulses. Another significant step forward has been made very recently by a novel scalable and stackable cell architecture comprising a layer stack of a storage element (OMS) and a selector (OTS), which are vertically integrated as in a cross

[a]Author to whom correspondence should be addressed. Electronic mail: manivannan@physik.rwth-aachen.de. Present address: I. Physikalisches Institut (IA), RWTH Aachen University, 52056 Aachen, Germany.

point memory cell.[21] This specific new design that has an OTS element as a selector overcomes the limitations of other selectors such as size of array, array efficiency, stackability, etc. and enables promising nonvolatile memory technology for building fast and dense memory devices. Therefore, a resurgence of interest has developed with regard to understanding both the OTS and the OMS properties of various PCM materials.

The $Ge_{15}Te_{85}$ eutectic alloy in the Ge_xTe_{1-x} system has a low melting temperature.[22] The low melting temperature is advantageous in terms of the reamorphization of the crystallization phase. However, the thermal stability of the amorphous phase is poor in this composition. Furthermore, it is reported in the literature that the thermal stability of the amorphous phase of $Ge_{15}Te_{85}$ glass is improved significantly with the addition of silicon at the expense of tellurium.[23] In the present work, investigations of the electrical, phase change characteristics of $Ge_{15}Te_{83}Si_2$ glass—which belongs to the $Ge_{15}Te_{85-x}Si_x$ glass forming tie-line and has distinct, current controllable OTS and OMS behavior—have been carried out. Also, properties such as easy reversibility of the *set* and *reset* states, nearly 3 orders of magnitude difference in resistance between the two states, and a better thermal stability with a long endurance have been demonstrated.

II. EXPERIMENTAL DETAILS

Bulk $Ge_{15}Te_{83}Si_2$ glass has been prepared via the vacuum-sealed melt quenching method: Appropriate quantities of high purity (99.95%) constituent elements are sealed in an evacuated (at 10^{-6} mbar) quartz ampoule and are slowly heated at the rate of 100 °C/h up to 1100 °C in a horizontal rotary furnace. The ampoules are maintained at 1100 °C and rotated continuously for about 24 h at 10 rpm to ensure homogeneity of the melt. The ampoules are subsequently quenched in a bath of ice water and NaOH to get bulk glassy samples. The amorphous nature of the as quenched sample has been confirmed by x-ray diffraction.

Electrical switching analysis and the electrical *set* and *reset* processes have been carried out using a Keithley 2410-C dc sourcemeter controlled by LABVIEW 6.1. Samples polished to the required thickness (about 150 μm) are mounted in a holder made of brass, between a flat bottom (~2 cm diameter) electrode and a point contact (~500 μm diameter) top electrode, using a spring loading mechanism. To study the electrical switching properties and the *set* and *reset* states of the sample, various waveform types such as triangular, rectangular, saw-tooth, and square current pulses are used. The time duration of each data point is 1 ms. These higher pulse widths are due to mainly the limitations of the larger sample thicknesses that are used.

III. RESULTS AND DISCUSSION

A. Electrical switching behavior

The current-voltage characteristics and electrical switching behavior of the $Ge_{15}Te_{83}Si_2$ sample are shown in Figs. 1(a) and 1(b). It is observed that the sample exhibits electrical switching at a threshold electric field (E_{th}) of 7.4 kV/cm (corresponding to $I_{th} \sim 50$ μA). The threshold fields are found to be reproducible within ±2%. The measured threshold field of the $Ge_{15}Te_{83}Si_2$ sample is 1 order lower as compared with the other phase change materials reported in the literature.[12,24] We admit that it is difficult to directly compare the properties of bulk glassy material with thin film devices reported in the literature. Nevertheless, it is likely that the threshold-switching event driven by the threshold electric field is nearly constant, even when scaling down to lower sample thicknesses.

It is interesting to note in Fig. 1(a) that the sample exhibits OTS behavior until the *on* state current of 0.7 mA is maintained. This reversible OTS behavior is found to be reproducible more than 10^2 times. Therefore, it is clear that the *on* state current up to about 0.7 mA does not considerably alter the state of the sample in the switched region/conducting channel. In the next step, the *on* state current is further increased up to 1 mA. It can be clearly seen in Fig. 1(b) that the sample exhibits memory switching (OMS) behavior once the current is increased up to 1 mA. This implies that the Joule heating in the current carrying path and the consequent increased mobility of atoms lead to local structural rearrangements and crystallization, which result in the *set* state.

It is known that the events constituting the *set* process in a phase change material consist of three sequential stages.[14] In the first stage, the electric field across the sample increases monotonously until it reaches the threshold value; at the threshold electric field (E_{th}), the material undergoes a transformation from a high resistance state to a low resistance state, and thereby a conducting path is established. In the second stage, the low resistance state established during switching is preserved. The process at this stage is reversible, as no permanent change takes place in the conducting path. The subsequent increase in current flow leads to the third stage, during which the phase change from the amorphous to the crystalline state occurs in the conducting channel. The

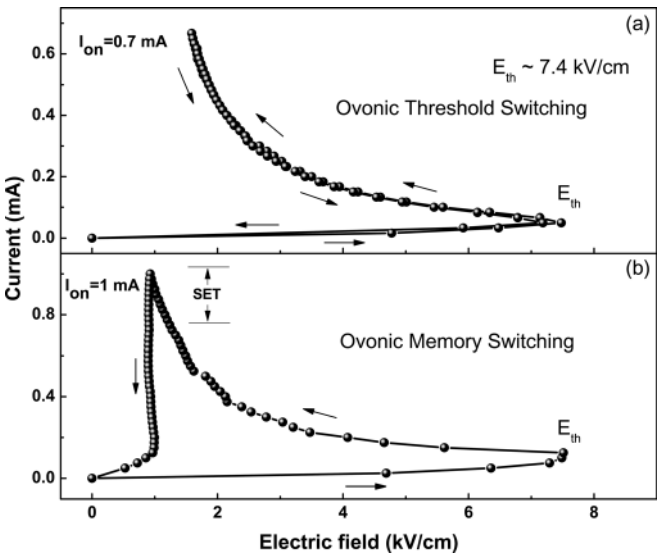

FIG. 1. (a) The I-V characteristics of $Ge_{15}Te_{83}Si_2$ glass with an input current of 0.7 mA, showing a threshold type switching behavior. (b) I-V characteristics of the same sample exhibit memory type switching behavior with an input current of 1 mA.

crystallization of the material in the conducting channel is likely to commence via a nucleation mechanism. The nucleation of crystallites might trigger an enhanced electrical conduction, which might lead to more Joule heating, and as a result of such heating the crystallites might grow rapidly to replace an amorphous matrix.

Therefore, it is clear that $Ge_{15}Te_{83}Si_2$ exhibits a distinctly different type of switching, such as OTS behavior, for the current up to 0.7 mA, and a *set* state can be achieved with an *on* state current of 1 mA. The most interesting aspect of the electrical switching in chalcogenide glasses is its behavior during the ramping down of the input current. In memory switching samples, the slow cooling that occurs during this process maintains the crystalline region formed in the *set* state. In these cases, it is necessary to electrically *reset* the memory state by applying a current pulse of short duration, and usually of higher magnitude than that required for setting the device in the *on* state.

B. Set and reset processes

In the present experiments, the electrical *set* and *reset* processes in the $Ge_{15}Te_{83}Si_2$ sample are achieved by applying a 1 mA triangular current pulse (the pulse width is 80 ms, with a fixed 40 data points for both the leading and the trailing edge) for the *set* process and a rectangular pulse 10 ms in width for the *reset* operation, as shown in Fig. 2(a). It can be seen clearly from Fig. 2(b) that the sample is initially in the amorphous state. When the programming current pulse of a triangular shape is applied to the sample [Fig. 2(a)] during the leading edge, at low currents the device remains in the high resistance amorphous state [0.7 MΩ, as indicated in Fig. 2(b)]. When a sufficiently high current is reached beyond the threshold value ($I_{th} \sim 50\ \mu A$, $E_{th} = 7.4$ kV/cm), the device switches into the low resistance *on* state. Further current flow in the *on* state between 0.7 and 1 mA (I_P) crystallizes the conducting channel, and hence the *set* process is accomplished. During the trailing edge, the current is reduced with a longer time leading to a controlled slow cooling of the material, which maintains the crystallized conducting channel (*set* state), as is demonstrated by the measured low resistance [11 kΩ as indicated in Fig. 2(b)] of the device at the end of each programming triangular pulse.

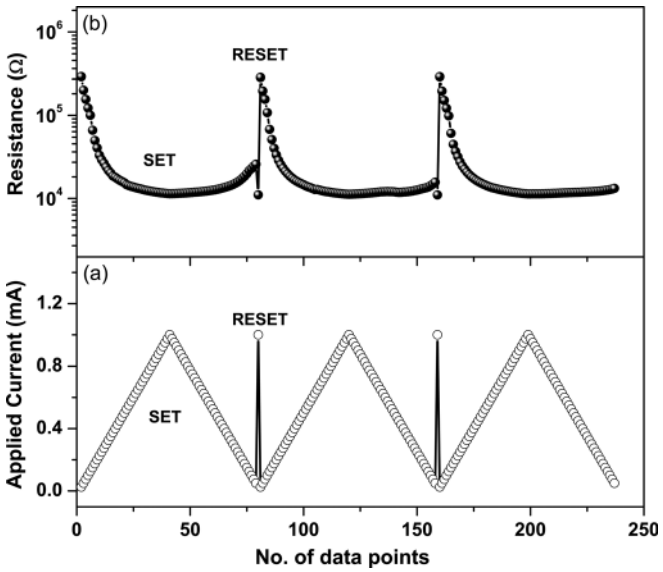

FIG. 2. (a) The *set–reset* operations in the $Ge_{15}Te_{83}Si_2$ sample are carried out with an applied current of 1 mA with a triangular pulse (for *set*) and a rectangular pulse of short duration with a width of 10 ms (for *reset*). (b) The corresponding resistance states across the device are measured.

The *reset* operation is accomplished by applying a rectangular pulse of a short duration with a width of 10 ms (the magnitude is the same as in the *set* current I_P), which heats up the crystallized conducting channel rapidly; this causes local melting of the conducting crystalline channel. The quick dissipation of heat from the molten conducting channel to the surrounding matrix during the sharp trailing edge results in the reamorphization of the region (*reset* process); the measured device resistance of 0.7 MΩ is equal to that of the amorphous state. Consecutive applied *set* and *reset* pulses [Fig. 2(a)] confirm the consistency of the change of the *set* and *reset* states as indicated by their resistance [Fig. 2(b)].

It is well known that the *set* and *reset* states are achieved by means of an appropriate choice of both pulse height/magnitude and pulse width/duration. The *set* state is realized when the *on* state current flow is of sufficiently long duration or large magnitude to raise the temperature to the crystallization point.[16] In contrast, the *reset* state is achieved by applying a pulse of sufficiently large magnitude to raise the local temperature up to melting point. As discussed above, the current required to *reset* the chalcogenide glass must be of a larger magnitude than the *set* current.[13,14] However, in the present $Ge_{15}Te_{83}Si_2$ glassy sample, it is found that the *set* and *reset* processes can be achieved using current pulses of the same magnitude with different types of waveforms, such as triangular and short width rectangular pulses, respectively. Both of these waveforms have different leading and trailing edges. Therefore, we made an attempt to understand the affect of the leading and trailing edges with various waveform types on switching behavior, and their significance is discussed below.

C. Response of various waveform excitations

In order to probe the influence of the current waveform on the switching behavior, experiments have been carried out by applying a saw-tooth type current pulse [Fig. 3(a)] to the $Ge_{15}Te_{83}Si_2$ glass. It is interesting to note from Fig. 3(b) that the sample exhibits threshold type switching (reversible switching) with a current of 1 mA, and memory behavior is seen with triangular pulses of same magnitude, as indicated in Fig. 1(b). Generally, the trailing edge is abrupt in a saw-tooth pulse, whereas the leading edge remains the same in both. The threshold behavior seen in the experiment using the saw-tooth pulse means that the abrupt trailing edge results in a fast cooling of the material, leading to the reamorphization of the switched region. Therefore, it is obvious that the crystallized conducting channel during the leading edge of the saw-tooth pulse of 1 mA is reamorphized in the trailing edge of the same pulse. This event of crystallizing and reamorphizing in a single saw-tooth pulse is seen clearly

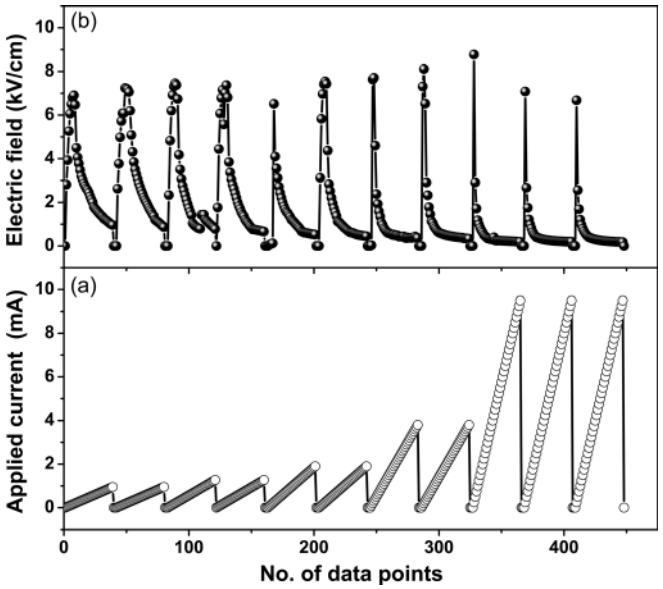

FIG. 3. The electrical switching behavior of the $Ge_{15}Te_{83}Si_2$ sample obtained with a saw-tooth current pulse. (a) Applied saw-tooth current pulses with varying peak heights from 1 to 10 mA. (b) The response electric field measured across the device.

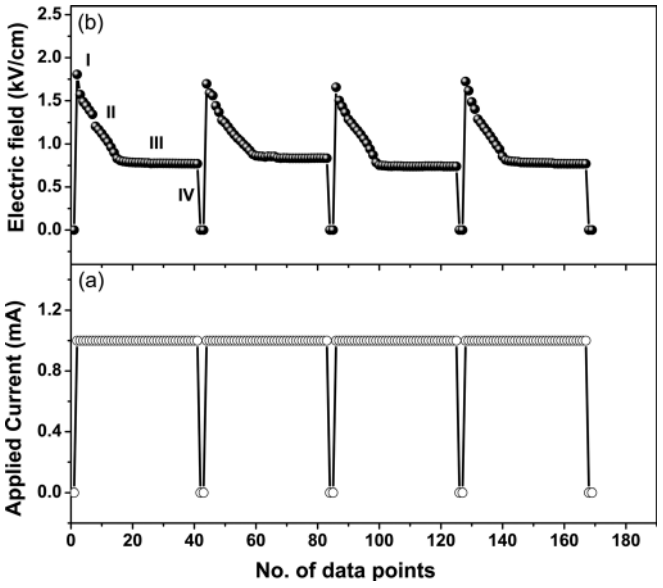

FIG. 4. The electrical switching response of the $Ge_{15}Te_{83}Si_2$ sample obtained with a square current pulse. (a) The applied square current pulses and (b) the response electric field measured across the device.

even with a current of a higher magnitude [up to 10 mA with the corresponding electric field, as shown in Figs. 3(a) and 3(b), respectively]. This indicates that the $Ge_{15}Te_{83}Si_2$ sample is easily resettable, and the sharp trailing edge with the saw-tooth current pulse results in self-*reset* (the *reset* state is realized due to the sharp trailing edge of the same applied single current pulse) of the sample. A similar effect of self-*reset* has also been observed with the application of a square type current pulse.

Figures 4(a) and 4(b) show the four stages of sequential response for excitation with a square input current pulse. It can be seen clearly in Fig. 4(b) that, during the first stage, electrical switching occurs due to the fast rising 1 mA of the applied current pulse. As we mentioned earlier, the $Ge_{15}Te_{83}Si_2$ sample requires an I_{th} of $\sim$50 μA in order to switch the sample into the *on* state. At Stage II, the steady state current flow increases the temperature and the glass starts to crystallize. The nucleation and growth of crystallites might trigger an enhanced electrical conduction, as observed in the reduction in the *on*-state voltage. The reaching of a constant *on*-state electric field at Stage III indicates the phase change in the material leading to the *set* state. During the last stage (Stage IV), the abrupt termination of the square pulse causes fast cooling of the material to induce a self-*reset* effect, as the material melts locally and resolidifies into the amorphous state.

The *set–reset* processes require two different attributes of the phase change glasses. An easy devitrification is essential for a fast *set* operation, whereas a good glass forming ability is required for it to be easily *reset* by means of low melting temperature. The present experiments indicate that the $Ge_{15}Te_{83}Si_2$ glass composition is relatively easily devitrifiable, as seen by the easiness of the *set* process, and, at the same time, the sample is a better glass former (as seen by the ease with which it is *reset*).

As a part of the present work, a detailed study has been made of the local structural changes in the $Ge_{15}Te_{83}Si_2$ sample using *in situ* Raman scattering on the amorphous, *set*, and *reset* states, which is reported elsewhere.[25] The Raman spectra have been recorded in three sequential steps. In the first step, the Raman spectrum of amorphous sample is obtained by focusing at a spot on the chalcogenide glass. In the second step, the spectrum has been acquired by focusing the laser beam at a spot in the conducting crystalline channel formed during the *set* process, as described above. In the third step, the spectrum is obtained after resetting the conducting channel by applying a short width rectangular current pulse. The nature of the three different phases of sample namely, the amorphous, *set*, and *reset* states has

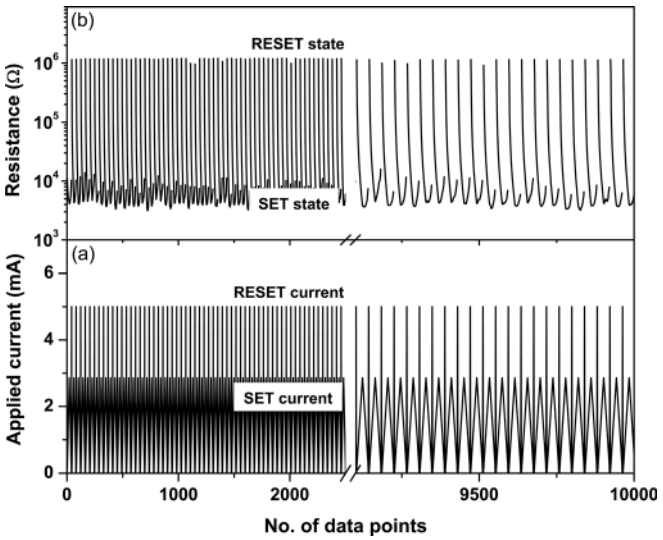

FIG. 5. The representative *set–reset* cycles for 10 000 data points undertaken with the $Ge_{15}Te_{83}Si_2$ sample. (a) The applied current amplitude of 3 mA/5 mA for the *set*/*reset* process, respectively. (b) The corresponding resistance states across the device.

been confirmed by measuring the electrical resistance between the electrodes. *In situ* Raman scattering on the *set* and *reset* states reveal that the local structures in the glassy (*off*) and *reset* states are not very different from the local structure in the *set* state.[25] This implies that the *set* and *reset* states are close to each other in terms of local structure, and thus transitions between them are likely to be less energy intensive. Therefore, the present study of electrical switching behavior and the easily reversible electrical *set* and *reset* processes in $Ge_{15}Te_{83}Si_2$ glass is consistent with their structural properties as reported elsewhere.[25,26]

D. Cycling measurements

Figures 5(a) and 5(b) show the representative *set–reset* cycles for 10000 data points. It is interesting to note that the $Ge_{15}Te_{83}Si_2$ samples withstand a large number of *set–reset* cycles without any degradation. It can be seen clearly from Fig. 5(b) that there is a contrast of nearly three orders of resistance between the *set* and *reset* states. In the present study, about 6.5×10^4 *set–reset* cycles have been undertaken without any damage to the device. For the cycling experiment (with a sample thickness of 0.4 mm), amplitudes of 3 mA/5 mA for *set*/*reset* processes, respectively [as indicated in Fig. 5(a)], have been used in order to improve the understanding of the better thermal stability of the $Ge_{15}Te_{83}Si_2$ sample.

IV. CONCLUSIONS

The studied $Ge_{15}Te_{83}Si_2$ glassy material exhibits memory type switching with the *on* state current of 1 mA with a comparatively low threshold electric field (E_{th}) of 7.3 kV/cm. Also, this $Ge_{15}Te_{83}Si_2$ sample has been found to exhibit easily reversible *set–reset* processes with a 1 mA triangular current pulse of a similar magnitude for the *set* process and a rectangular pulse of short duration with a width of 10 ms for the *reset* operation. Further, a self-resetting effect is seen in this material upon excitation with a saw-tooth/square pulse. More than 6.5×10^4 stable *set–reset* cycles have been carried out in the $Ge_{15}Te_{83}Si_2$ sample without any damage to the device.

ACKNOWLEDGMENTS

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