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Electrical switching behavior of bulk $Si_{15}Te_{85-x}Sb_x$ chalcogenide glasses – A study of compositional dependence

R. Lokesh [a], N.K. Udayashankar [a], S. Asokan [b,*]

[a] *Department of Physics, National Institute of Technology, Karnataka, Surathkal 575 025, India*
[b] *Department of Instrumentation, Indian Institute of Science, Bangalore 560 012, India*

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ABSTRACT

Studies on the electrical switching behavior of melt quenched bulk $Si_{15}Te_{85-x}Sb_x$ glasses have been undertaken in the composition range ($1 \leqslant x \leqslant 10$), in order to understand the effect of Sb addition on the electrical switching behavior of $Si_{15}Te_{85-x}$ base glass. It has been observed that all the $Si_{15}Te_{85-x}Sb_x$ glasses studied exhibit a smooth memory type switching. Further, the switching voltages are found to decrease almost linearly with Sb content, which indicates that the metallicity of the dopant plays a dominant role in this system compared to network connectivity/rigidity. The thickness dependence of switching voltage (V_{th}) indicates a clear thermal origin for the switching mechanism. The temperature variation of switching voltages reveals that the $Si_{15}Te_{85-x}Sb_x$ glasses studied have a moderate thermal stability.

1. Introduction

Chalcogenide amorphous semiconductors are found to exhibit the interesting electrical switching behavior, which involves a sudden decrease in the resistance (of the order of $10^3\ \Omega$) under the application of a high electric field ($\cong 10^5$ V cm^{-1}). The phenomenon of electrical switching in chalcogenide glasses was first observed by Ovshinsky [1] and it is classified into two types, namely threshold switching (reversible) and memory switching (irreversible) [2,3].

It is now generally accepted that the origin of switching in both threshold and memory switching glasses is electronic in nature and occurs when charged defect traps that are present in chalcogenide glasses, are filled by field injected charge carriers excited by the applied electric field [4]. Additional thermal effects come into play in memory switching glasses, with the formation of a crystalline channel in the electrode region due to joules heating [5,6].

Recently, the property of electrical switching (especially memory switching) exhibited by chalcogenide has been exploited in the development Non Volatile Random access Memories (NVRAMs), popularly known as Phase Change Memories (PCMs) [7–10]. In practice, germanium telluride glasses containing Sb ($Ge_2Sb_2Te_5$ – GST) have been used in the development of commercial memories [11–14]. Sustained efforts are being made in literature, to develop newer phase change materials for RAM applications, which have greater performance, lower reset current and smaller power consumption compared to $Ge_2Sb_2Te_5$.

Earlier investigations reveal that binary Si–Te glasses [15] and ternary samples in bulk glassy and amorphous thin film form containing Si including As–Te–Si [16] Ge–Te–Si [17], exhibit electrical switching phenomenon. Further, the feasibility of replacing Ge in Ge–Sb–Te with Si for PCM applications is being explored, due to better properties of Si–Sb–Te glasses [18,19], such as smaller reset current, lower power consumption and a good data retention as compared to the $Ge_2Sb_2Te_5$ [18–21]. In this work, the electrical switching behavior of bulk $Si_{15}Te_{85-x}Sb_x$ glasses over a wide composition range ($1 \leqslant x \leqslant 10$) has been investigated. Furthermore, the thickness and temperature dependence of threshold voltage have carried out.

2. Experimental procedures

2.1. Sample preparation

Bulk glasses belonging to the $Si_{15}Te_{85-x}Sb_x$ series ($1 \leqslant x \leqslant 10$), were prepared melt quenching method; constituent elements of 99.995% purity were weighed according to their stoichiometric ratio and sealed in a cleaned and evacuated flat bottom quartz ampoule at a pressure of 10^{-5} mbar. The ampoules were heated gradually in a horizontal furnace to 1100 °C at the rate of 100 °C per hour. At this temperature, the ampoules were rotated at 10 rpm continuously for 48 h, to ensure homogeneity of the melt. The ampoules were subsequently quenched in a bath of ice cold water and NaOH solution. The amorphous nature of the bulk samples was confirmed from the X-ray diffraction using

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* Corresponding author. Tel.: +91 80 22932271; fax: +91 80 22933195.
E-mail address: sasokan@isu.iisc.ernet.in (S. Asokan).

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Phillips powder X-ray Diffractometer with Cu kα radiations ($\lambda = 1.541$ Å).

2.2. Electrical switching experiments

Electrical switching studies of the as prepared $Si_{15}Te_{85-x}Sb_x$ glasses ($1 \leqslant x \leqslant 10$) were undertaken using a Keithley Source-Meter® (model: 2410^c), controlled by a PC using Lab VIEW-6.1 (National Instruments). Samples polished to the required thickness were mounted in a sample holder made of brass, in-between a flat bottom and a spring loaded point top electrodes. A constant current is passed through the sample and the voltage developed across the sample is measured. Temperature dependence of threshold voltage was studied in the range of 30–110 °C using a custom built heater cell provided with a thermocouple.

3. Results and discussions

3.1. XRD studies

Fig. 1 shows the XRD patterns of the as prepared, representative $Si_{15}Te_{85}Sb_1$ and $Si_{15}Te_{75}Sb_{10}$ glasses. The absence of any sharp diffraction peaks in the XRD patterns indicates that the as-prepared samples are amorphous in nature.

3.2. I–V characteristics of the $Si_{15}Te_{85-x}Sb_x$ glasses

Figs. 2 and 3 show the *I–V* characteristics of $Si_{15}Te_{85-x}Sb_x$ ($1 \leqslant x \leqslant 10$) glasses, which indicate that the samples exhibit an initial Ohmic behavior with high resistance (OFF state). Near a critical voltage (V_{th}), the samples exhibit a negative resistance region and electrical switching to the low resistance ON state. The samples are found to be remain in the high conducting ON state and do not revert back to the original high resistance OFF state even after the removal of the applied electric field. This observation clearly indicates that $Si_{15}Te_{85-x}Sb_x$ glasses ($1 \leqslant x \leqslant 10$), exhibit a memory switching behavior at comparatively lower applied currents (≅2 mA). At currents lower than 2 mA, an unstable threshold behavior is seen for few switching cycles (e.g. 10 cycles at 0.5 mA) and the samples set into the memory state after few switching cycles.

There are several factors which determine the nature of switching in chalcogenide glasses. As we mentioned earlier, that memory switching in chalcogenide glasses is due to the formation of a conducting crystalline channel in the sample which is favored in glasses that are easily prone to devitrification or in glasses with lower thermal diffusivity values [22]. It is also found that Te based glasses usually exhibit memory switching at lower currents, because of their greater conductance which results in larger power dissipation and higher Joule heating. Telluride glasses also exhibit a clean electrical switching behavior without any fluctuations in the *I–V* characteristics during the transition to the ON state. The present results indicate that the electrical switching behavior of $Si_{15}Te_{85-x}Sb_x$ glasses is similar to other binary and ternary telluride glasses such as Si–Te [15], As–Si–Te [16], Ge–Te–Si [17], etc. and also thin film amorphous tellurides like Si–Te–Sb [18,19].

3.3. Composition dependence of threshold voltage (V_{th})

Fig. 4 shows the variation of threshold voltages of $Si_{15}Te_{85-x}Sb_x$ glasses as a function of composition, for the samples of thickness (d) = 0.3 mm. It is found that the switching voltages decrease monotonically and almost linearly with Sb content. It is well known from the earlier studies that the composition dependence of the switching voltages is primarily determined by the metallicity of the additive, the network connectivity/rigidity and the chemical ordering of the network. The incorporation of higher coordinated additives in chalcogenide glasses increases the network connectivity and rigidity and the switching voltages are generally found to increase with an increase in network connectivity and rigidity [17]. On the other hand, addition of more metallic dopants tends to decrease the activation energy for electrical conduction, which in turn decreases the switching voltages (V_{th}) [23]. In any given glassy system, the actual composition dependence of switching voltages will be decided by the relative dominance of each of these factors.

In the present $Si_{15}Te_{85-x}Sb_x$ system of glasses, based on the network connectivity, the addition of three fold coordinated Sb (at the expense of the two fold coordinated Te) is expected to increase the switching voltages. However, the addition of more metallic Sb ($\rho_{Sb} = 40 \times 10^{-8}$ Ωm and $\rho_{Te} = 10 \times 10^{-5}$ Ωm) is expected to result in a decrease in the switching voltages with Sb addition, as the switching voltages are directly related to electrical conductivity of the material [24].

The observed decrease in the switching voltages of $Si_{15}Te_{85-x}Sb_x$ glasses with Sb addition indicates that the metallicity of the dopants plays a dominant role in this system compared to network connectivity/rigidity. It is interesting to note that a similar decrease in V_{th} has been observed in the $Sb_xSe_{55-x}Te_{45}$ glassy system, with the progressive replacement of Se by Sb [23]. In the Ge–Se–Sb glassy system also, a decrease in the switching voltages has been observed with the increase in Sb content [25], indicating that the present results are consistent with earlier observations.

It has not been possible to probe the effect of network topological thresholds such as rigidity percolation on the composition dependence of V_{th} of $Si_{15}Te_{85-x}Sb_x$ glasses, as the composition

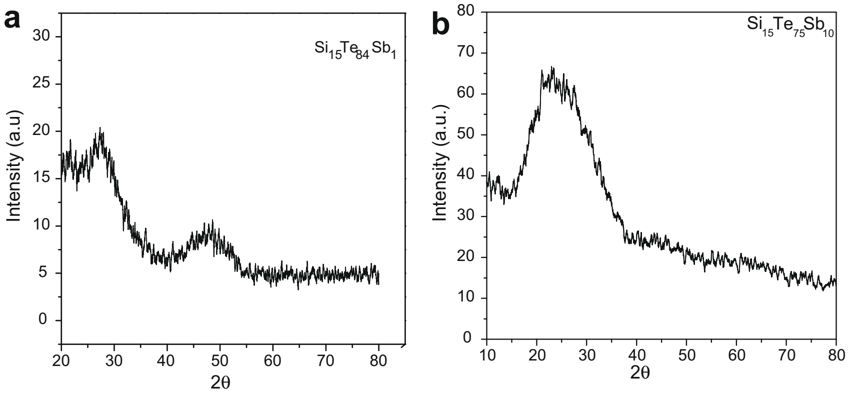

Fig. 1. XRD patterns of the two representatives (a) $Si_{15}Te_{83}Sb_1$ and (b) $Si_{15}Te_{75}Sb_{10}$ samples showing absence of sharp diffraction peaks.

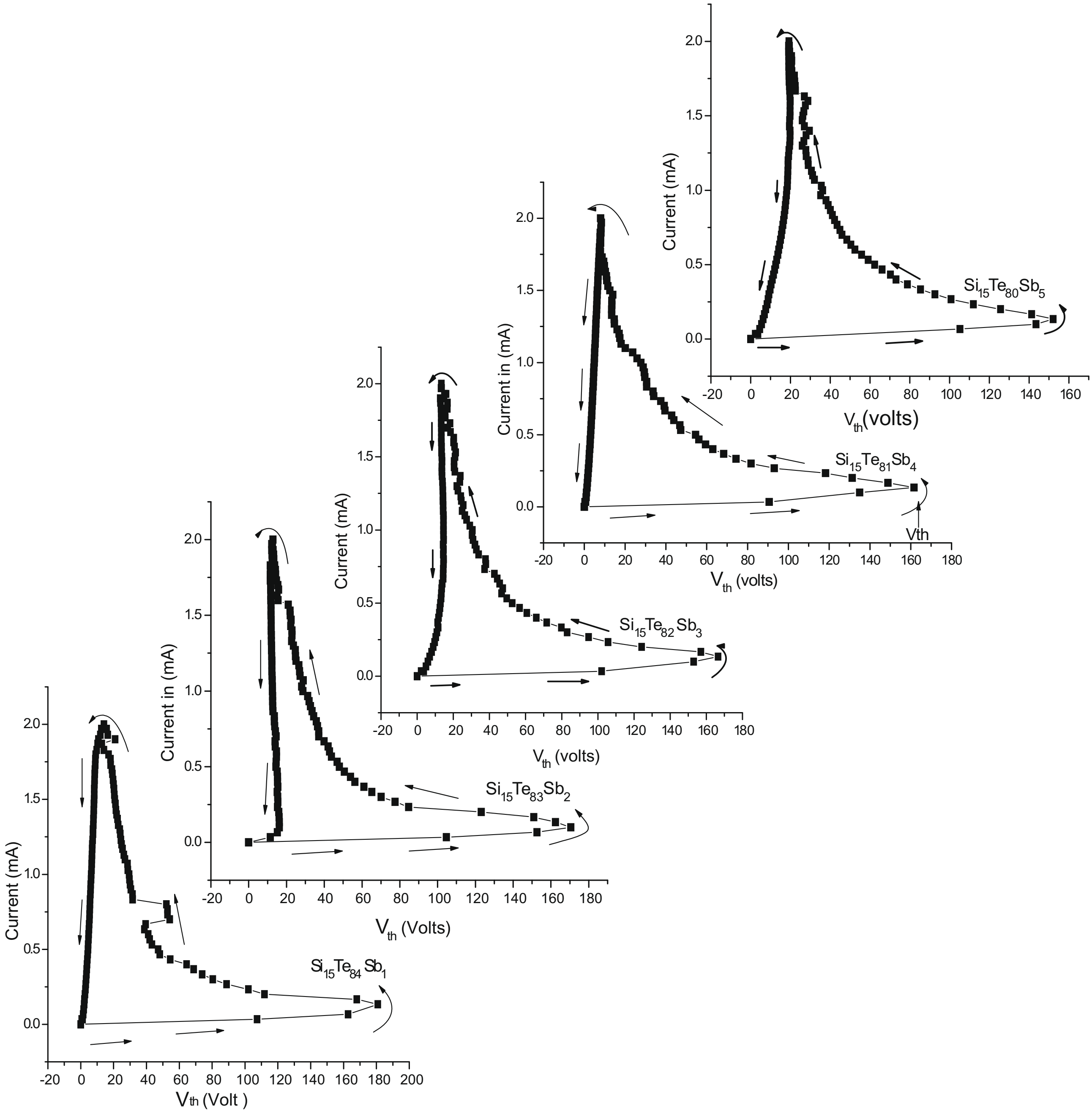

Fig. 2. *I–V* characteristics of $Si_{15}Te_{85-x}Sb_x$ glasses in the composition ranges $X = 1$ to $X = 5$.

range of glass formation is restricted to a narrow range of average coordination numbers ($2.31 \leqslant \langle r \rangle \leqslant 2.40$).

3.4. Thickness dependence of threshold voltage (V_{th})

The investigation of thickness (d) dependence of threshold voltage (V_{th}) provides an insight into the mechanism of switching [26]. In case of samples exhibiting memory switching, either a linear or square root dependence of threshold voltage with thickness is reported. This dependence is based on whether the sample behaves as thermally thin slab or thermally thick slab respectively, which in turn is decided by the thermal conductivity (k) of the sample and external heat conductivity (λ) which quantify the heat lost by sample through electrode surface.

If $\lambda d \ll 2$ k, the sample behaves as thermally thick slab and it is thermally thin if $\lambda d \gg 2$ k. In the first case, the temperature drop within the material is greater than the temperature drop at the boundary and a non uniform temperature distribution results within the sample. In the second case, the temperature drop at the boundary is higher due to larger heat loss at electrodes and a more uniform temperature distribution occurs with in the sample; V_{th} has a dependence of type square root for thermally thin slab and a linear dependence is seen for a thermally thick slab [27]. For example, in samples like Al–Ge–Te [28], Ge–Te–Pb [29], As–Te–Si [16] etc., V_{th} is found to increase linearly with thickness and in samples like Ge–As–Te [30], a square root variation of threshold voltage with thickness has been observed.

Fig. 5 shows the variation of V_{th} of a representative sample $Si_{15}Te_{80}Sb_5$ with thickness '*d*' in the range 0.2–0.6 mm. It has been

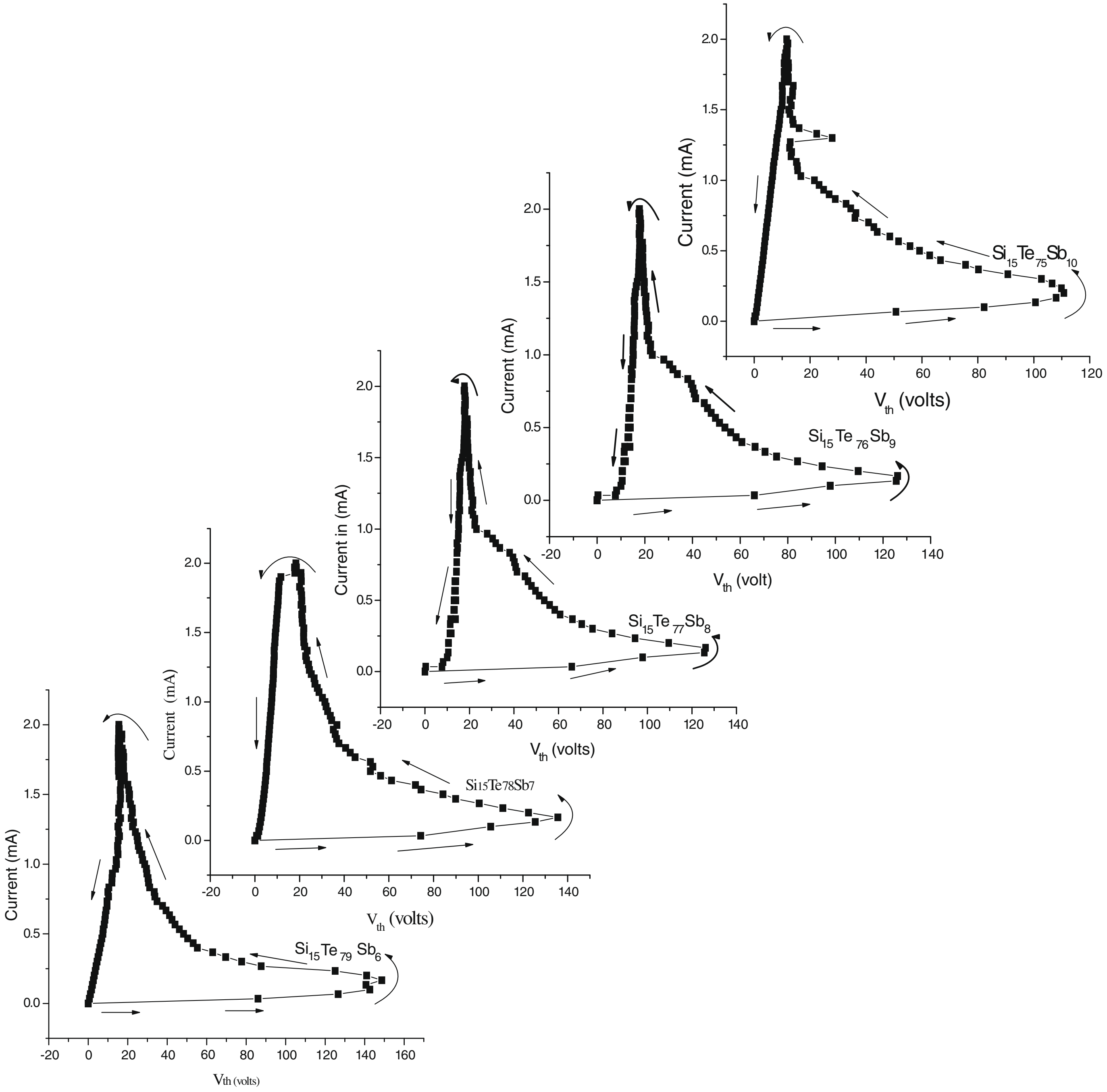

Fig. 3. *I–V* characteristics of $Si_{15}Te_{85-x}Sb_x$ glasses in the composition ranges $X = 6$ to $X = 10$.

noted that thickness dependence of switching voltage fits exactly to the square root dependence and this observation is a clear indication of the domination of thermal effects in the switching mechanism of $Si_{15}Te_{85-x}Sb_x$ glasses.

3.5. Temperature dependence of threshold voltage (V_{th})

Temperature dependence of threshold voltage is an important factor which characterizes the material against thermal degradation and hence stability of the material for device applications [7]. In both threshold and memory samples, V_{th} is found to decrease with increasing temperature [31–33]. As mentioned earlier, the memory switching in chalcogenide glasses involves the formation of conducting crystalline channel in the material and a decrease in threshold voltages is expected, as the energy barriers for crystallization are reduced at higher temperatures. According to Algeria et al. [31], the threshold voltages of chalcogenide glasses vary with temperature as $V_{th} = CT \exp(E/2Ki)$ where E is the activation energy for electrical conduction and T_g the glass transition temperature.

Fig. 6 shows the variation of threshold voltages for the sample $Si_{15}Te_{79}Sb_6$ in the temperature ranges of 30–110 °C. It can be seen that there is a continuous decrease in the V_{th} with increase in temperature, which is consistent with the decrease in energy barriers for devitrification decrease at high temperatures [34]. It is also interesting note that the decrease in V_{th} of $Si_{15}Te_{79}Sb_6$ glasses over the range 30–110 °C is moderate (130–30 V) compared to related glasses such as As–Te–Si, As–Te–Ag, As–Te–Tl, etc. [16,33,35].

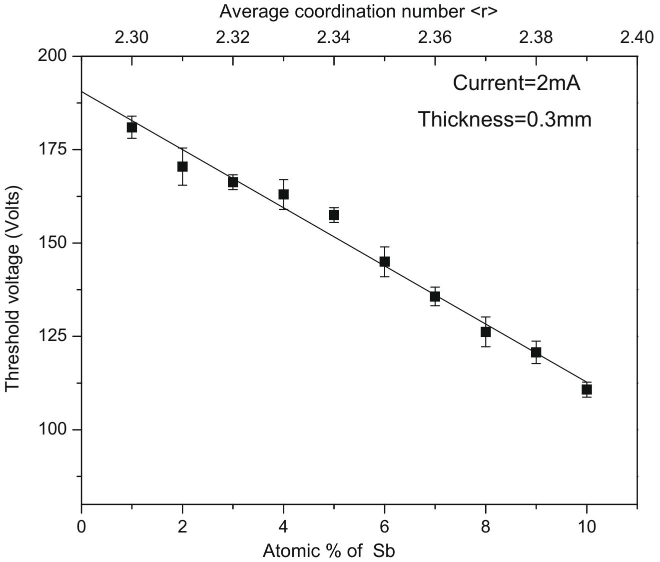

Fig. 4. Composition dependence of threshold voltages (V_{th}) of $Si_{15}Te_{85-x}Sb_x$ ($1 \leqslant x \leqslant 10$) glasses as a function of atomic percentage of Sb.

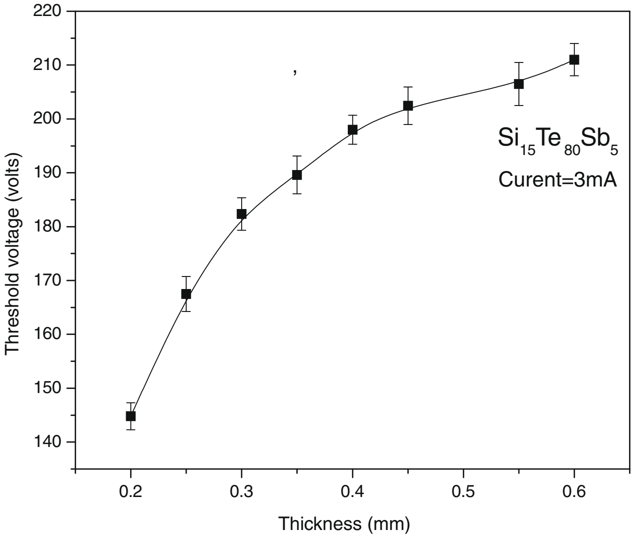

Fig. 5. Variation of Threshold voltage (V_{th}) of a representative sample $Si_{15}Te_{80}Sb_5$ with respect to thickness (d).

4. Conclusions

Electrical switching behavior of the bulk $Si_{15}Te_{85-x}Sb_x$ glasses has been investigated over a wide composition range ($0 \leqslant x \leqslant 10$). All the samples are found to exhibit a smooth memory type switching behavior. It is found that the switching voltages decrease monotonically and almost linearly with Sb content, which indicates that the metallicity of the dopant plays a dominant role in this system compared to network connectivity/rigidity. The thickness dependence of switching voltage (V_{th}) indicates a thermal origin for the switching mechanism. Further, the temperature variation of switching voltage reveals that the samples studied have a moderate thermal stability.

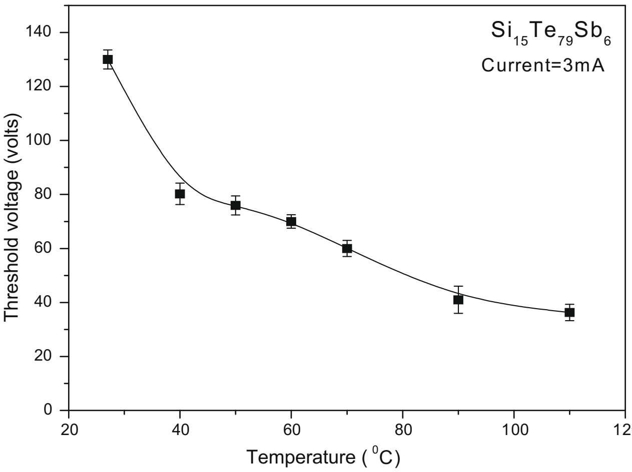

Fig. 6. Variation of threshold voltage (V_{th}) for the sample $Si_{15}Te_{79}Sb_6$ in the temperature ranges of 30–110 °C.

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