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Electrical switching behavior of bulk $In_{15}Se_{85-x}Tl_x$ chalcogenide glasses - A study of compositional dependence

G. Ravi Kolarkar, Department of Electronics, Maharani's Science College for Women, Bangalore-560 001, Karnataka, India.

Abstract

Electrical switching studies on melt quenched bulk $In_{15}Se_{85-x}Tl_x$ ($2 \leq x \leq 10$) glasses have been undertaken in order to understand the effect of Tl addition on these glasses. It has been observed that all the $In_{15}Se_{85-x}Tl_x$ glasses studied exhibit the threshold type switching behavior. Further, the switching voltage and the OFF state resistance are found to increase with Tl content, which indicates that, the network connectivity and rigidity of the dopant plays a dominant role in this system compared to the metallicity and chemical ordering factors. The composition dependence of switching voltage exhibits a sharp slope change at $\langle r \rangle = 2.42$ which is associated with rigidity percolation in the system. It has also been observed that the switching voltage increases with increase in sample thickness, which is due to thermal and electronic origin of the switching mechanism. The temperature variation of switching voltages reveal that the switching voltage of $In_{15}Se_{83}Tl_2$ glassy sample decreases with increasing temperature.

1. Introduction

Chalcogenide glasses are band gap semiconductors and are infrared transmitting [1]. Selenium is an indirect band gap semiconductor [2], and it becomes a direct band gap semiconductor at about 4.5 GPa pressure [3] and it also has tremendous potential in device applications namely rectifiers, photocells, xerography, switching and memory devices etc. [4]. Generally, selenides have a higher crystallization temperature in comparison with tellurides. Thallium containing amorphous chalcogenide semiconductors have attracted much attention in acousto-optical devices [5,6]. The addition of thallium to chalcogenide glasses is usually accompanied by a marked change in their structural and physical properties [7-11]. Certain chalcogenide amorphous glasses are found to exhibit a very interesting electrical effects involving a sudden decrease in the resistance, from high (OFF state) to low (ON state) under the application of an appropriate electric field commonly known as threshold electric field (V_{th}). The phenomenon of electrical switching in chalcogenide glasses is first observed by Ovshinsky almost four decades ago [12]. Chalcogenide glasses, which exhibit switching, are classified into memory and threshold type, based on the way they respond to the removal of the electric field, after switching to the ON state. On the removal of the electric field, threshold-switching glasses revert to the OFF state whereas memory-switching glasses remain locked to the ON state.

Thermal [13] and electronic models [14-17] are proposed, in order to understand the electrical switching mechanism in amorphous chalcogenide glasses. It is generally accepted that the origin of switching in both threshold and memory glasses are electronic in nature [18], and it occurs when the charged defect states in glasses are filled by the field-injected charge carriers. Additional thermal effects come into play in memory switching glasses, with the formation of a conducting crystalline channel in the electrode region due to Joule heating [19-21].

The present work deals with the effect of Tl on the electrical switching behavior of bulk $In_{15}Se_{85-x}Tl_x$ ($2 \leq x \leq 10$) glasses. Furthermore, the effect of composition, sample thickness (t), and temperature on the threshold voltage has been studied. Though, the single-beam overwrite experimental studies for phase change recording have been reported on amorphous InSeTl thin films earlier [21], studies have not been made so far on switching behavior of bulk $In_{15}Se_{85-x}Tl_x$ glassy samples.

2. Experimental procedure

2.1. Sample preparation

Bulk semiconducting $In_{15}Se_{85-x}Tl_x$ ($2 \leq x \leq 10$) glasses have been prepared by conventional melt-quenching technique. Appropriate amounts of spectroscopically pure (99.999%) constituent elements (total weight of about 1 gm) are weighed according to their percentages and sealed in quartz ampoule of about 1 mm wall thickness and 8 mm inner diameter under the vacuum of 10^{-5} Torr in order to prevent oxygen contamination with glasses at higher temperature. The sealed quartz ampoule containing sample is loaded in a horizontal rotary furnace and gradually heated (100 ^{0}C/hr) beyond the melting point of the constituent elements. The ampoules are maintained at 850 ^{0}C and rotated continuously at 10 rpm for about 36 hours to ensure the homogeneity of the melt. The molten materials are subsequently quenched in NaOH + ice water mixture to obtain bulk glassy samples. The amorphous nature of the quenched samples is confirmed by the X-ray diffraction technique as no sharp peaks are observed.

2.2 Electrical switching experiments

The electrical switching characteristics of the $In_{15}Se_{85-x}Tl_x$ ($2 \leq x \leq 10$) glasses have been studied using a Keithley Source-Meter® unit (Model 2410©) controlled by a PC using Lab VIEW 7 (National instruments). Samples are polished to a thickness of about 0.3 mm and is mounted in a holder made of brass between a flat bottom electrode and a point contact top electrode with a spring-loading mechanism to hold the sample. The source meter is capable of sourcing a current in the range of 0-20 mA at maximum compliance voltage of 1100 V. A constant current of 4 mA is passed through the sample and the voltage developed across the sample is measured. The consistency of the result obtained is checked by repeating the experiment for at least three samples of the same composition. Threshold voltage is found to be reproducible within ± 2%.

3. Results

X-ray diffraction patterns obtained for the investigated $In_{15}Se_{77}Tl_8$ and $In_{15}Se_{75}Tl_{10}$ glassy samples in bulk form are shown in figure 1 (a) and (b). The absence of sharp diffraction peaks in the XRD patterns confirm that, the samples are amorphous in nature. Figure 2 shows the I-V characteristics and switching behavior of representative $In_{15}Se_{85-x}Tl_x$ ($2 \leq x \leq 10$) glasses. It can be seen that, these samples exhibit an Ohmic behavior initially which is high resistance OFF state. The samples exhibit a current controlled negative resistance (CCNR) behavior, near a threshold voltage (V_{th}), which eventually leads to a low resistance ON state. It is interesting to note that the $In_{15}Se_{85-x}Tl_x$ glasses revert to their original low conducting OFF state, upon removal of the applied electric field indicating a threshold switching behavior. Glasses that are stable against devitrification are likely to exhibit threshold behavior. The variation of threshold voltages of $In_{15}Se_{85-x}Tl_x$ ($2 \leq x \leq 10$) glasses as a function of Tl composition is shown in figure 3, which shows that the threshold voltages increase with increasing Tl content. The variation of OFF state resistance (R) of the $In_{15}Se_{85-x}Tl_x$ ($2 \leq x \leq 10$) glasses with Tl composition is shown in figure 4. It is seen that the OFF state resistance increases with an increase in Tl content. Figure 5 shows the variation of threshold voltage with thickness for $In_{15}Se_{83}Tl_2$ glass, as a representative sample of the $In_{15}Se_{85-x}Tl_x$ ($2 \leq x \leq 10$) glasses indicating an increase in threshold switching voltage with thickness. Switching voltage of $In_{15}Se_{79}Tl_6$ glassy alloy decreases as the temperature is increased above the room temperature shown in figure 6, which is a common feature exhibited by many ternary chalcogenide glasses.

4. Discussion

4.1 I-V characteristics of $In_{15}Se_{85-x}Tl_x$ ($2 \leq x \leq 10$) glasses

The type of switching exhibited by glassy selenides and tellurides is determined by many thermal parameters namely activation energy for crystallization (ΔE), crystallization temperature (T_c), and thermal stability (T_c-T_g). The explaination can also be done based on the compressibility and atomic radii of the constituent elements. The compressibility and atomic radii of Se are 11×10^{-12} cm^2/dyn. and 1.17Ǻ respectively, whereas for Te they are 4.35×10^{-12} cm^2/dyn. and 1.37Ǻ respectively**.** During the switching process in Se based glasses, because of lesser atomic radii, higher compressibility and lower elasticity, the tendency of regaining their initial state is less after deformation. Therefore, they exhibit memory type switching.

However, the experimental results of $In_{15}Se_{85-x}Tl_x$ glasses showed threshold type switching behavior, which is due to the dominant role of the compressibility and atomic radii played by In and Tl constituent elements. For In, the compressibility and atomic radii are 2.43×10^{-12} cm^2/dyn. and 1.55Ǻ, and for Tl, they are 2.79×10^{-12} cm^2/dyn. and 1.56Ǻ respectively. During the process of switching, free movement of Se atoms will be obstructed because of larger Tl and In atoms, also, due to the formation of stronger heteropolar In-Se and Tl-Se bonds, the bond angles of In-Se and Tl-Se bonds which constitute the local structure of In-Se-Tl glasses, therefore cannot be deformed easily because of lower compressibilities of In and Tl [22,23]. Hence in the In-Se-Tl ternary glassy system, the tendency towards devitrification is less, which is responsible for the threshold switching behavior (figure 2).

4.2 Composition dependence of threshold voltage (V_{th})

There are several factors such as resistivity of the additive element [24], network connectivity and rigidity [25] and chemical ordering [26], which determine the composition dependence of switching voltage in chalcogenide glasses. In general the switching voltage of chalcogenide glasses is found to decrease with the addition of more metallic additives [27] which is due to enhanced conductivity ensuing from the decrease in activation energy for conduction. It has been reported that, the electrical conductivity of $In_{15}Se_{85}$ base glasses is based on the formation of Se-Se, Se-In, In-In bonds. It is known that in a-Se around 40 at.wt.% of atoms enter into ring structure and the remaining are bonded in polymeric chains [28]. When the atomic concentration of Indium is 15 and above, the chemical order-disorder transformation occurs in the system. The In-In bond length (325 pm) is larger than that of the Se-Se (232 pm) bond length, and the number of In-In bonds exceeds Se-Se bonds, which results in decrease in the molecular weight and density of localized states effectively [29], which leads to an increase in porosity forming a more disordered system [30]. Hence there is a decrease in the conductivity of the system. It has been established that, an increase in the number of heteropolar bonds leads to the increase of chemical order resulting in the decrease of V_{th}, whereas an increase in the number of homopolar bonds leads to the growth of chemical disorder resulting in the increase of V_{th} [31,32].

The switching voltages of the chalcogenide glasses are found to increase with an increase in network connectivity and rigidity, as the structural rearrangements become more difficult with increase in network rigidity [33]. In $In_{15}Se_{85-x}Tl_x$ $(2 \leq x \leq 10)$ system, the addition of Tl with a higher coordination number of 4, at the expense of Se with the coordination number 2 [25,34], results in a progressive increase in network connectivity and rigidity. Hence based on the network connectivity and rigidity, one could expect an increase in switching voltages with an addition of Tl (figure 3). An increase in V_{th} has also been observed due to increase in the chemical order and metallicity of the additive in GeTeI chalcogenide systems [35].

The average coordination number <r>, is an important parameter in determining the composition dependence of various physical properties of chalcogenide glasses. Using the coordination numbers 4, 2, and 4, for In, Se, and Tl atoms respectively, the average coordination number can be calculated by using the formula:

$$\langle r \rangle = \{ r_{In}(15) + r_{Se}(85-x) + r_{Tl}(x) \} / 100$$

In the $In_{15}Se_{85}$ system the average coordination number <r> is 2.3 i.e. the system is in floppy mode. The addition of thallium with $In_{15}Se_{85}$ base glasses is very important from the basic as well as application point of view because for $In_{15}Se_{85-x}Tl_x$ $(2 \leq x \leq 10)$ compositions <r> varies from 2.34 to 2.5, i.e., the system varies from floppy mode to rigid mode following a rigidity percolation [36,37,39]. According to Phillips' Constraint Theory [38] and Percolation Model [38,39], the rigidity percolation at which a percolation transition takes place from a polymeric glass to a rigid network or amorphous solid is expected to occur in the InSeTl system at <r> = 2.40. It is also suggested that the rigidity percolation threshold may be shifted towards higher values of <r> in certain glassy systems [40]. In the $In_{15}Se_{85-x}Tl_x$ glasses, at the average coordination <r> = 2.42, a sharp slope change is seen in the composition dependence of switching voltages corresponding to the shifted rigidity percolation threshold (RPT). Such a shifted RPT has been observed in AsTeSi glassy system also [41] which is consistent with these samples.

The composition dependence with OFF state resistance of the $In_{15}Se_{85-x}Tl_x$ glasses is shown in figure 4. It has been reported that, there is a direct relationship between the composition dependence of switching voltages and OFF state resistance (R) of chalcogenide glasses [42]. The observed increase in R and V_{th} with Tl in $In_{15}Se_{85-x}Tl_x$ glasses is consistent.

4.3 Thickness dependence of threshold voltage (V_{th})

The dependence of threshold voltage (V_{th}) with the thickness (t) of the sample provides an insight into the mechanism of switching. It has been suggested that threshold voltage will vary as t, $t^{1/2}$ or t^2 depending on whether the switching mechanism is purely electronic, purely thermal or based on carrier injection . In the present sample, it is seen that V_{th} is neither exactly linear nor does it vary as $t^{1/2}$ as shown in figure 5. It indicates that the switching mechanism is complex, involving both electronic and thermal effects. Such a result has been reported earlier in As-Te-Tl [44] and Ge-Se-Tl glasses.

4.4 Temperature dependence of threshold voltage (V_{th})

Thermal stability of the amorphous state is a term often used while ascertaining the performance of a glass for its practical applications [43]. By the addition of Tl as a third element, it is reported that the stability is improved [44]. Switching voltage of $In_{15}Se_{79}Tl_6$ glassy alloy decreases as the temperature is increased above the room temperature as shown in figure 6. It is a common feature exhibited by GeTeTl, GeSeTl, and AsTeTl, chalcogenide glasses [45]. The decrease in V_{th} with increase in temperature is expected due to decrease in the energy barrier for crystallization. Further, at higher temperature, the charge defect centers are filled up by thermally excited charge carriers along with field injected carriers which cause a decrease in switching voltage.

5. Conclusions

Melt quenched bulk $In_{15}Se_{85-x}Tl_x$ ($2 \leq x \leq 10$) glasses are found to exhibit threshold type electrical switching behavior. Also, there is an increase in switching voltage with increase in Tl content. This clearly indicates that the network connectivity and rigidity factor play a stronger role compared to the resistivity factor. The composition dependence of switching voltage exhibits a sharp slope change at <r> = 2.42 which is associated with rigidity percolation in the system. The thickness dependence of switching voltage (V_{th}) indicates that the switching mechanism is electro- thermal in nature. Further, the temperature variation of switching voltage reveals that the samples studied have a moderate thermal stability.

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FIGURE CAPTIONS.

FIG. 1. XRD patterns of the two representatives (a) $In_{15}Se_{77}Tl_8$,(b) $In_{15}Se_{75}Tl_{10}$ samples showing absence of sharp diffraction peaks.

FIG. 2. I-V characteristics of $In_{15}Se_{85-x}Tl_x$ $(2 \leq x \leq 10)$ glasses.

FIG. 3. Composition dependence of threshold voltages of $In_{15}Se_{85-x}Tl_x$ $(2 \leq x \leq 10)$ glasses as a function of atomic percentage of Tl.

FIG. 4. The variation of OFF state resistance (R) of the $In_{15}Se_{85-x}Tl_x$ $(2 \leq x \leq 10)$ glasses with Tl composition.

FIG. 5. Variation of threshold voltage of a representative sample $In_{15}Se_{83}Tl_2$ with respect to thickness (t).

FIG. 6. Variation of threshold voltage for the sample $In_{15}Se_{79}Tl_6$ in the temperature range from 30 – 100 ^{0}C.

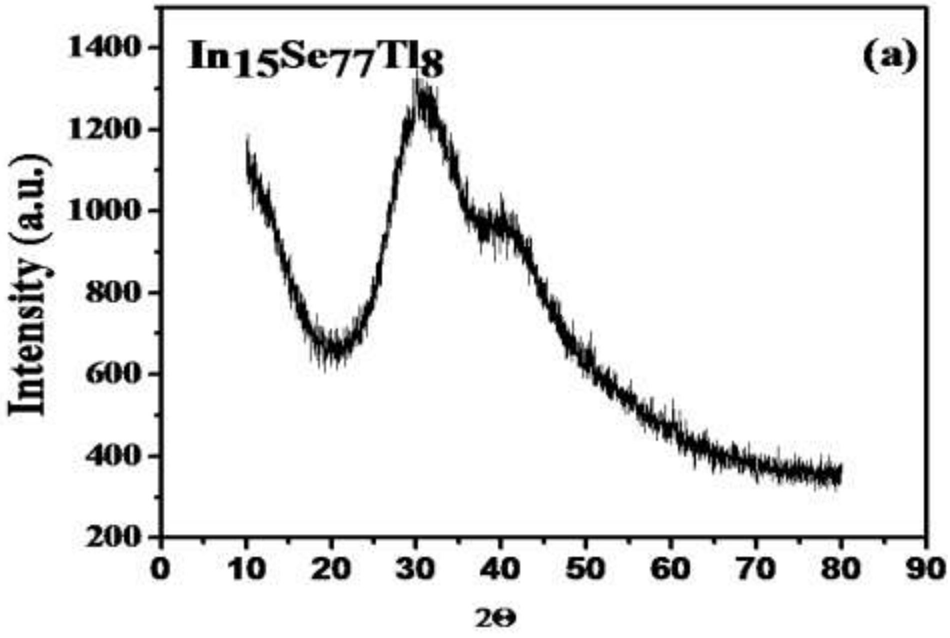

Figure 1(a)

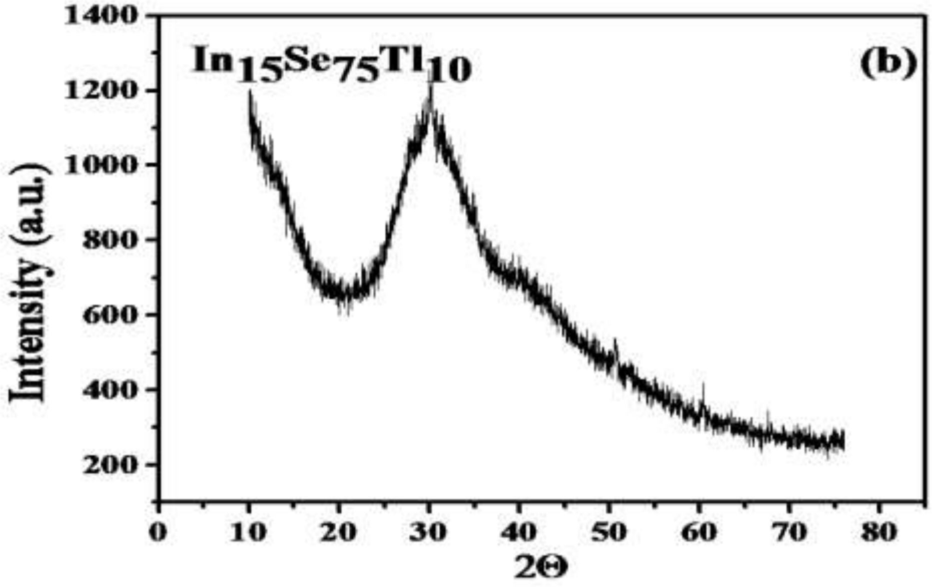

Figure 1(b)

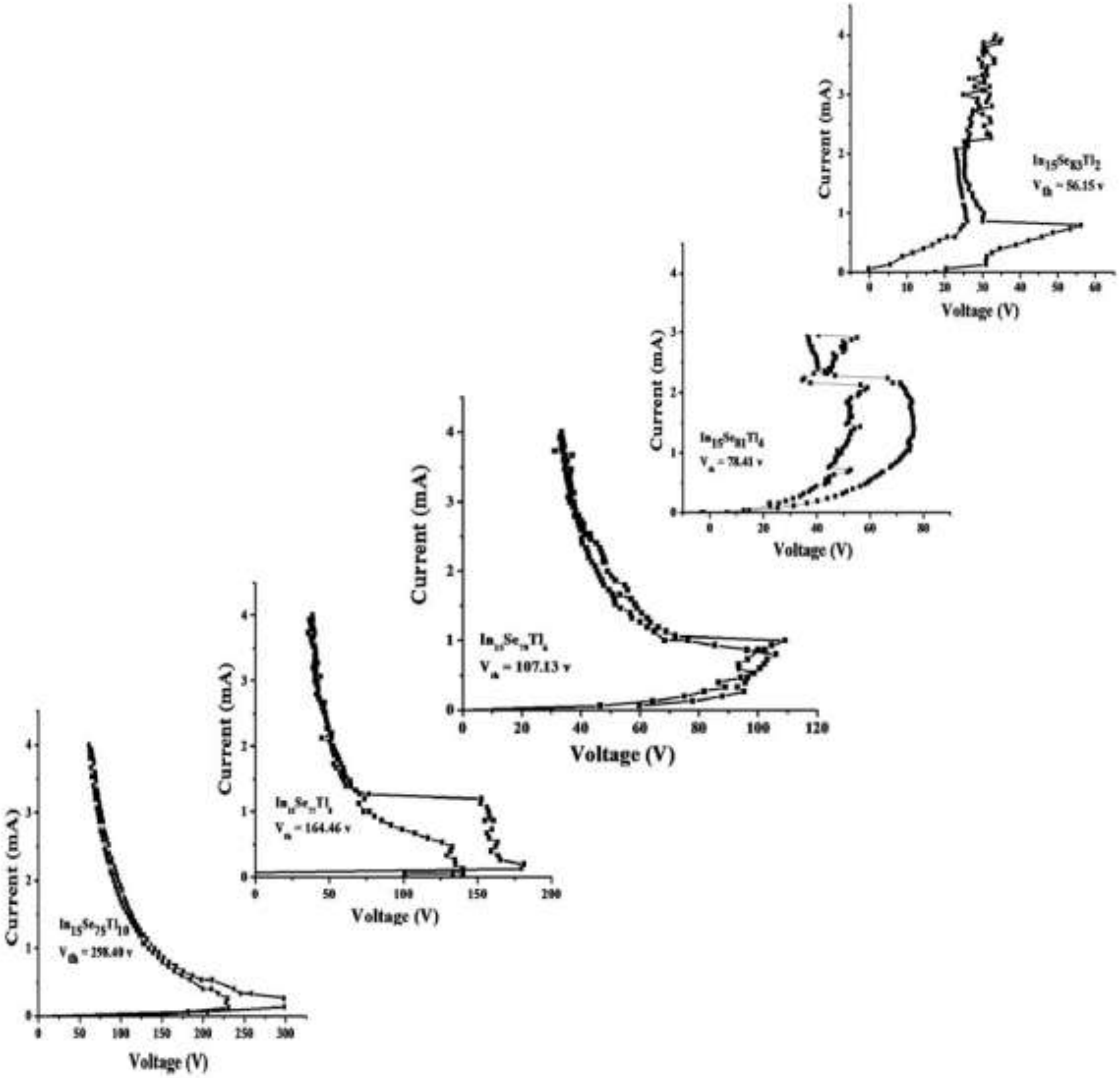
Current (mA)
Voltage (V)
In$_{15}$Se$_{83}$Tl$_2$
V$_{th}$ = 56.15 v
In$_{15}$Se$_{81}$Tl$_4$
V$_{th}$ = 78.41 v
In$_{15}$Se$_{79}$Tl$_6$
V$_{th}$ = 107.13 v
In$_{15}$Se$_{77}$Tl$_8$
V$_{th}$ = 164.46 v
In$_{15}$Se$_{75}$Tl$_{10}$
V$_{th}$ = 258.40 v

Figure 2

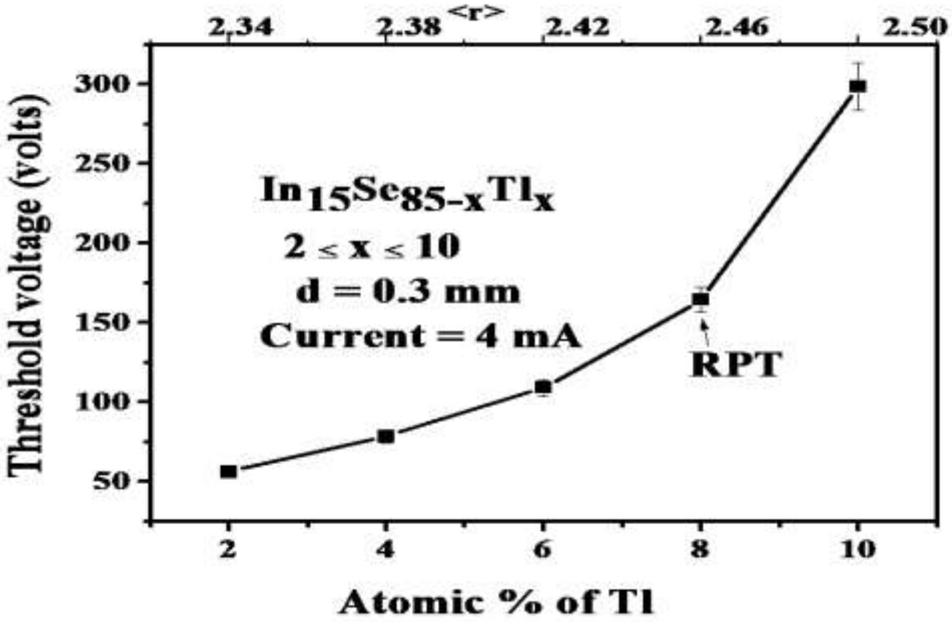

Figure 3

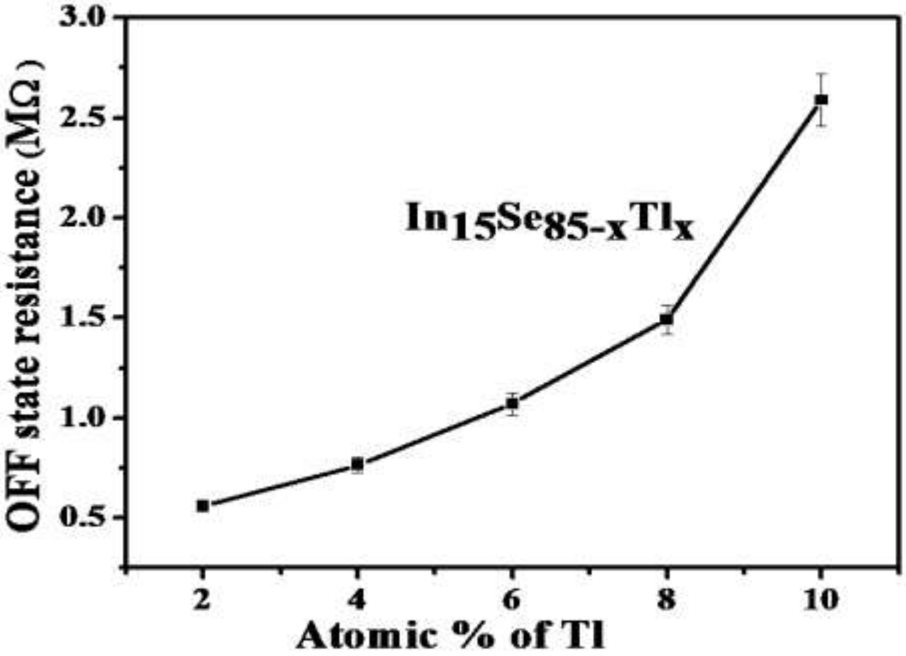

Figure 4

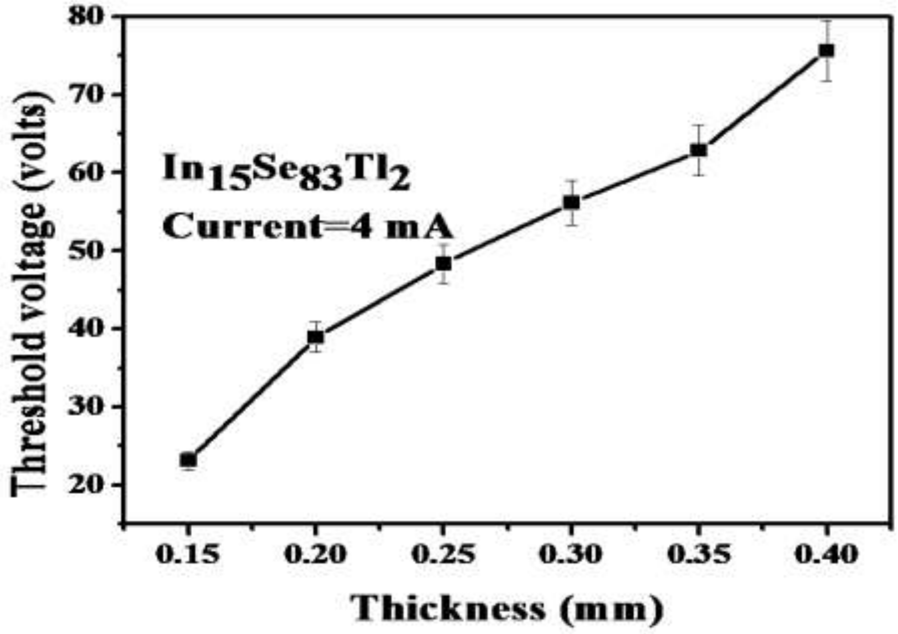

Figure 5

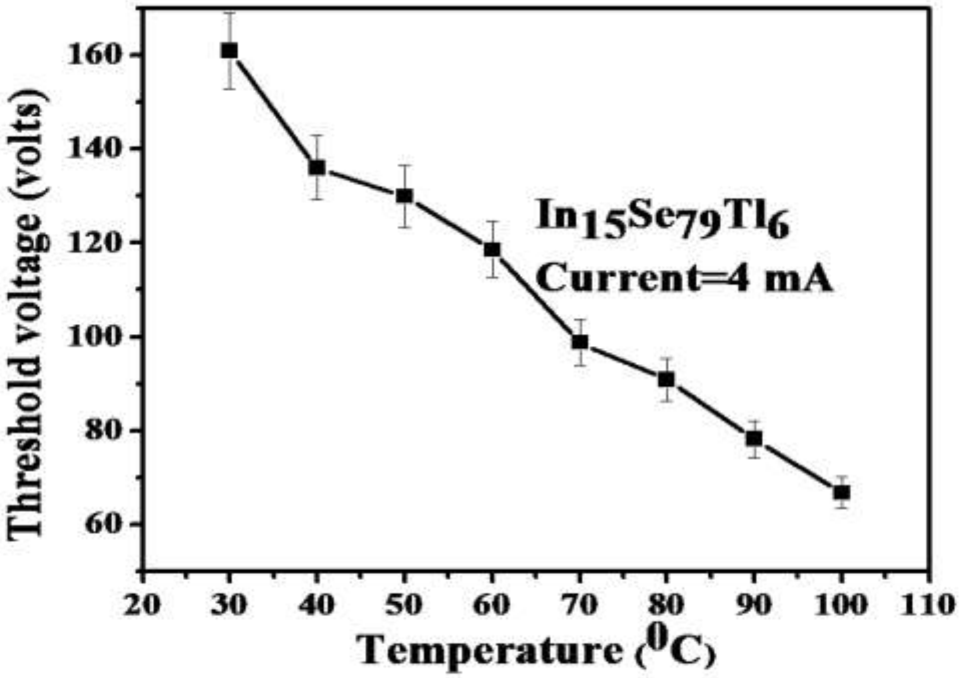

Figure 6