Composition dependence of threshold electrical switching behavior of bulk $In_{10}Se_{90-x}Tl_x$ (x =7,9,11,13,15) chalcogenide glasses.

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ABSTRACT

Bulk melt quenched $In_{10}Se_{90-x}Tl_x$ ($7 \leq x \leq 15$) chalcogenide glasses have been found to exhibit threshold type electrical switching behavior. Further it is observed that the switching voltage and the OFF state resistance of $In_{10}Se_{90-x}Tl_x$ glasses decrease with the increase in Tl concentration. The composition dependence of switching voltage exhibits a sharp slope change at $\langle r \rangle = 2.46$ which is associated with rigidity percolation in the system. A linear increase in switching voltage has been found in these samples with increase in thickness which is consistent with the threshold type electrical switching. At the same time, the switching voltage have been found to decrease with an increase in temperature as expected which is due to the decrease in the activation energy for crystallization since the energy barriers for crystallization are reduced at higher temperature.

1. Introduction

Amorphous chalcogenide glassy semiconductor has been a great deal of interest due to their higher photosensitivity, greater hardness, higher crystallization temperature, smaller aging effects and are relatively easy to fiberize. Because of these advantages, such glasses are nowadays used in various solid state devices and in particular as an optoelectronic device material [1,2]. The effect of incorporation of metallic impurities to binary chalcogenide glassy alloys is always been a topic of interest, because the metallic impurities enter the glassy network, and helps in getting relatively stable glasses, which in turn improves the network connectivity and rigidity, crystallizing ability and change in the conduction type from 'p' to 'n' [3].

In chalcogenide semiconducting glasses, the electrical switching phenomenon is of two types, namely threshold (reversible) switching and memory (irreversible) switching [4-6].

Electrical switching mechanism occurs when a suitable voltage also known as threshold voltage is applied, and the glass switches from low conducting OFF state to high conducting ON state. However, if the ON state of the material is retained even after the removal of electrical field, known as memory type switching; on the other hand, if the material revert to the OFF state then it is called threshold type switching. Hence it is clear that the memory switching is having bistable states and that of a threshold is monostable state. Generally the threshold switching is an electronic process and occurs when charged defect states are filled by field injected charge carriers [7,8]; whereas memory switching is a thermal process, in which the Joule heating in the current carrying path will form a conducting crystalline channel, which leads to phase transformation from amorphous to crystalline [9]. The present work deals with electrical switching studies on bulk $In_{10}Se_{90-x}Tl_x$ ($7 \leq x \leq 15$) glasses. Further, the effect of composition, sample thickness (t) and temperature on the threshold voltage is also studied.

2. Experimental procedure

2.1 Sample preparation

Bulk $In_{10}Se_{90-x}Tl_x$ ($7 \leq x \leq 15$) glasses have been prepared by vacuum sealed melt quenching method. High purity (99.999%) In, Se and Tl in appropriate atomic percent proportions are weighed using an electronic balance and are sealed in quartz ampoules (length ~ 5 cm and inner diameter ~ 8 mm) under the vacuum of 10^{-5} Torr in order to avoid the reaction of glasses with oxygen at higher temperature. The sealed quartz ampoule containing sample is loaded in a horizontal rotary furnace and heated up to 850 °C at the rate of 100-120 °C/h and rotated at 10 rpm continuously for about 36 h to ensure a high degree of homogeneity of the melt. Quenching has been done subsequently in ice water + NaOH mixture. The ingots of the samples are taken out by breaking the quartz ampoules. The amorphous nature of the quenched sample is confirmed by the absence of sharp peak in the X-ray diffraction pattern.

2.2 Electrical switching experiments

The electrical Switching characteristics of the as prepared $In_{10}Se_{90-x}Tl_x$ ($7 \leq x \leq 15$) glasses have been studied using a Keithley Source-Meter® unit (Model 2410^c) controlled by a PC using Lab VIEW 7 (National instruments). Samples polished to a thickness of about 0.3 mm are mounted in sample holder consisting a flat bottom electrode and a point contact top electrode made of brass with a spring-loading mechanism to hold the sample. The source meter is capable of sourcing a current in the range 0-20 mA at maximum compliance voltage of 1100 V. A constant 4 mA current is passed through the sample and the voltage developed across the sample is measured. The experiment is repeated for at least three samples of the same composition to check the consistency of the result. Threshold voltage is found to be reproducible within ± 2%.

3. Results

Figure 1. (a) and (b) show the X-ray diffraction patterns of the $In_{10}Se_{83}Tl_7$ and $In_{10}Se_{81}Tl_9$ glasses representing $In_{10}Se_{90-x}Tl_x$ glassy system. The absence of sharp diffraction peaks in the XRD-pattern confirms the amorphous nature of the samples. Figure 2. shows the I-V characteristics of bulk $In_{10}Se_{90-x}Tl_x$ ($7 \leq x \leq 15$) series of glasses. It is evident from figures 2 (a-e) that the samples exhibit an Ohmic behavior at lower applied voltages, which is the high resistance OFF state. Near threshold voltage, the sample shows a current controlled negative resistance (CCNR) behavior, which eventually leads to a low resistance ON state. The samples are found to revert to their original high resistance OFF state, after the current is reduced below the holding current, indicating a threshold type electrical switching behavior.

The variation of switching voltages of $In_{10}Se_{90-x}Tl_x$ glasses as a function of Tl composition for 0.3 mm sample thickness is shown in figure 3. It is found that the switching voltage decreases with an increase in Tl content. A similar decrease in switching voltage with memory/threshold behavior with an increase in Tl addition has been reported in AsTeTl, GeSeTl bulk glasses [10,11]. The composition dependence versus the resistance of the $In_{10}Se_{90-x}Tl_x$ glasses in the OFF state is shown in figure 4. It has been observed that the OFF state resistance decreases with an increase in Tl content. Figure 5 shows the variation in the switching voltage with thickness for $In_{10}Se_{81}Tl_9$ glass, a representative sample of the $In_{10}Se_{90-x}Tl_x$ glasses indicating an increase in threshold switching voltage with thickness. The switching voltage of $In_{10}Se_{81}Tl_9$ glass is found to decrease with increase in temperature as shown in figure 6, which is a common feature exhibited by other Tl content ternary glasses namely Ge-Se-Tl films [12].

4. Discussion

4.1. Threshold electrical switching behavior of $In_{10}Se_{90-x}Tl_x$ ($7 \leq x \leq 15$) glasses

It has been observed that compared to Te based glasses, Se based ternary and binary glasses always exhibit memory type switching. This can be explained on the basis of the compressibility and atomic radii of the constituent atoms. In case of Se, the compressibility and atomic radii are 11×10^{-12} cm^2/dyn. and 1.17Ǻ respectively and for Te they are 4.35×10^{-12} cm^2/dyn. and 1.37Ǻ respectively. Memory switching is, in general, explained on the basis of the thermal, which involves phase transformation from amorphous to crystalline state. During the process of switching, Se atoms can easily move because of lesser atomic radii and also bond angles can be easily deformed due to the higher compressibility. In addition, the elasticity of Se based glasses is less compared to Te glasses. Consequently, the tendency towards regaining its initial state is less after deformation and as a result they exhibit memory.

The present studies, however, reveal that $In_{10}Se_{90-x}Tl_x$($7 \leq x \leq 15$) glasses exhibit threshold switching behavior. It can be attributed due to role played by the compressibility and atomic radii of the In and Tl. 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 movements of Se atoms will be hindered because of larger Tl and In atoms and also due to the formation of stronger heteropolar In-Se and Tl-Se bonds. Also the bond angles of In-Se and Tl-Se bonds which constitute the local structure of In-Se-Tl glasses cannot be deformed easily because of lower compressibilities of In and Tl [13]. 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. The composition dependence of switching voltages of In-Se-Tl glasses

It is well known from the earlier studies that, the composition dependence of the switching voltages in chalcogenide glasses is determined by three main factors, namely the metallicity of the additive, the network connectivity, rigidity and the chemical ordering of the network [14-16]. The addition of more metallic impurities usually brings down the switching voltages [17, 18], which is due to enhanced conductivity and also the metallic dopants tends to decrease the activation energy for electrical conduction [19]. This is also the case in the present $In_{10}Se_{90-x}Tl_x$ system in which Tl is more metallic compared to Se (ρ_{Tl} = 15x10^{-8} Ωm and ρ_{Se} ~ 10^{16} Ωm). It is interesting to note here that a decrease in the activation energy for electrical conduction with an increase in Tl content has been observed in bulk and thin film glassy systems [20-22].

The observed composition dependence of threshold switching voltage in $In_{10}Se_{90-x}Tl_x$ ($7 \leq x \leq 15$) glasses can also be understood with the help of chemically ordered network (CON) model [23]. In the CON-model, the formation of heteropolar bonds is favored over the formation of homopolar bonds, for a glassy system A_xB_{1-x}, this model envisages formation of A-B type of bonds. Further, for A rich compositions of the system, the CON-model envisages formation of A-B type and then A-A type bonds; similarly for B rich compositions, A-B type and then B-B type bonds are formed. Based on the CON-model, the Se rich $In_{10}Se_{90-x}Tl_x$ ($7 \leq x \leq 15$) glassy system can be described as a completely cross-linked three-dimensional structural units consisting of In-Se, Se-Se and Se-Tl bonds. The bond energies of various possible bonds involved in the formation of this network system namely, In-Se, Se-Se, In-In, Se-Tl and Tl-Tl are 247, 205.8, 100, 158, and 64.5 kJ/mol respectively [23]. When Tl concentration increases, more and more Se-Se bonds are broken and the probability of ionic Se-Tl bond formation increased. As the In-Se heteropolar bonds and the Se-Se homopolar bonds have more bond energies compared to Se-Tl bonds, this attribute to the reduction of the energy of the conduction band edge resulting in a decrease in $V_{th.}$

It has been reported that, an increase in the number of heteropolar bonds leads to the increase of chemical order resulting in the decrease of $V_{th,}$ whereas increase in the number of homopolar bonds leads to the growth of chemical disorder resulting in the increase of V_{th} [24, 25]. In $In_{10}Se_{90-x}Tl_x$ glasses, with the increase in the Tl content, the number of heteropolar Se-Tl bonds increases in comparison with the Se-Se homopolar bonds resulting in the reduction of chemical disorder and less localized charge carriers enhancing the conductivity, which is responsible for the decrease in V_{th} (figure 3). A similar composition switching behavior has been observed in other chalcogenide systems [26,27].

The average coordination number <r>, is an important parameter in determining the composition dependence of various physical properties of chalcogenide glasses. In $In_{10}Se_{90}$ system the average coordination number <r> is 2.2 i.e. the system is in floppy mode. The addition of Tl with $In_{10}Se_{90}$ base glass is very important from the basic as well as application point of view because for $In_{10}Se_{90-x}Tl_x$ ($7 \leq x \leq 15$) compositions <r> varies from 2.34 to 2.5 i.e. the system varies from floppy mode to rigid mode around 2.4. According to Phillips Constraint theory [28], the rigidity percolation is expected to occur in the In-Se-Tl system at <r> =2.40. It is also know that the rigidity percolation threshold may be shifted towards higher values of <r>, in certain glassy systems [29,30]. In the present study, at <r> =2.46 a sharp slope change is seen in the composition dependence of switching voltages corresponds to the shifted rigidity percolation threshold (RPT) of the In-Se-Tl glasses.

The composition dependence with OFF state resistance of the $In_{10}Se_{90-x}Tl_x$ glasses is shown in figure 4. It has been reported that, there is a direct relationship between the composition dependence of switching voltage and OFF state resistance (R) of chalcogenide glasses [31]. The observed decrease in R and V_{th} with Tl in $In_{10}Se_{90-x}Tl_x$ glasses are consistent.

4.3 Thickness (t) dependence of switching voltage.

In literature, it has been suggested that the switching voltage is found to be proportional to either t, $t^{1/2}$ or t^2 depending upon whether the mechanism responsible for switching is purely electronic, purely thermal or based on carrier injection. Figure 5 shows the variation of V_{th} of a representative sample $In_{10}Se_{77}Tl_{13}$ with thickness in the range of 0.15-0.40 mm. In the present sample, the variation of threshold voltage with t has been observed to be increasing. This observation indicates that it is not possible to infer clearly the mechanism of switching in these samples and the switching may involve both electronic and thermal effects.

4.4 Temperature dependence of threshold voltage.

The switching voltage of $In_{10}Se_{77}Tl_{13}$ glasses are found to decrease as the temperature is increased above the room temperature (figure 6). This is a common feature exhibited by many chalcogenide glasses. According to the configurational free-energy diagram [32], the decrease in V_{th} is due to the decrease in the energy barrier required for crystallization at higher temperatures, and also due to the fact that the charge defect centers are filled up by thermally excited charge carriers in addition to field-injected carriers, which also accounts for the decrease in switching voltage [33].

5. Conclusions

The composition dependence of switching voltage of the $In_{10}Se_{90-x}Tl_x$ glassy system is investigated for five compositions namely x = 7, 9, 11, 13, 15 by studying the I-V characteristics of bulk samples. The study shows a typical threshold switching behavior. The composition dependence of switching voltage exhibits a sharp slope change at $<r> = 2.46$ which is associated with shifted rigidity percolation in the system. Further, the sample thickness dependence of V_{th} is found to be increasing with t. Finally, the variation of V_{th} with temperature reveals that, V_{th} decreases with increasing temperature.

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FIGURE CAPTIONS.

FIGURE 1. XRD patterns of the two representatives (a) $In_{10}Se_{83}Tl_7$ and (b) $In_{10}Se_{81}Tl_9$ samples showing absence of sharp diffraction peaks.

FIGURE 2. I-V characteristics of $In_{10}Se_{90-x}Tl_x$ ($7 \leq x \leq 15$) glasses.

FIGURE 3. Composition dependence of threshold voltages of $In_{10}Se_{90-x}Tl_x$ ($7 \leq x \leq 15$) glasses at a function of atomic percentage of Tl.

FIGURE 4. The variation of OFF state resistance (R) of the $In_{10}Se_{90-x}Tl_x$ ($7 \leq x \leq 15$) glasses with Tl composition.

FIGURE 5. Variation of threshold voltage of a representative sample $In_{10}Se_{77}Tl_{13}$ with respect to thickness(t).

FIGURE 6. Variation of threshold voltage for the sample $In_{10}Se_{77}Tl_{13}$ in the temperature range from 30 – 100^0C.

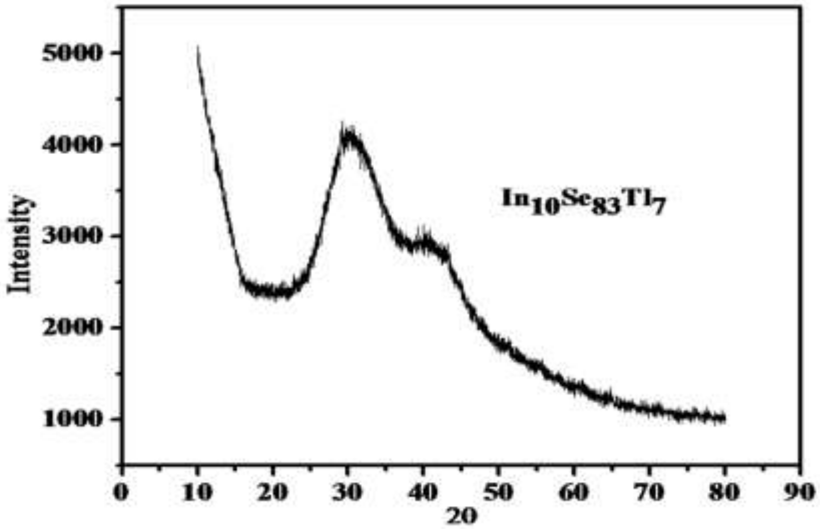

Figure 1(a)

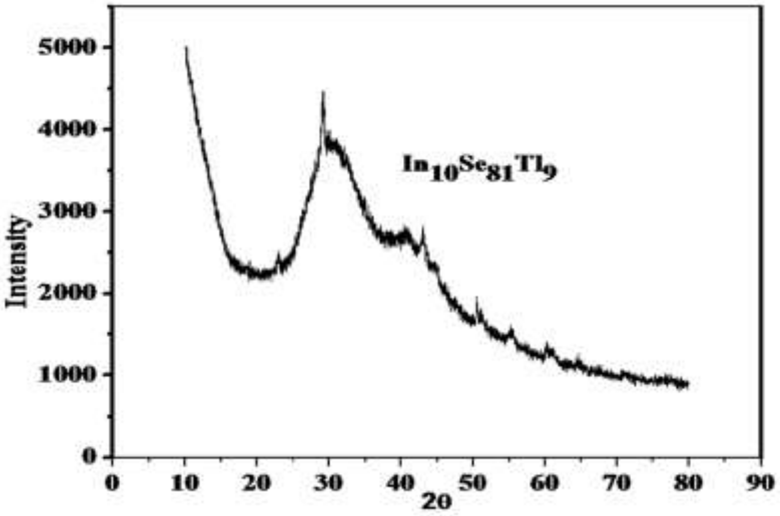

Figure 1(b)

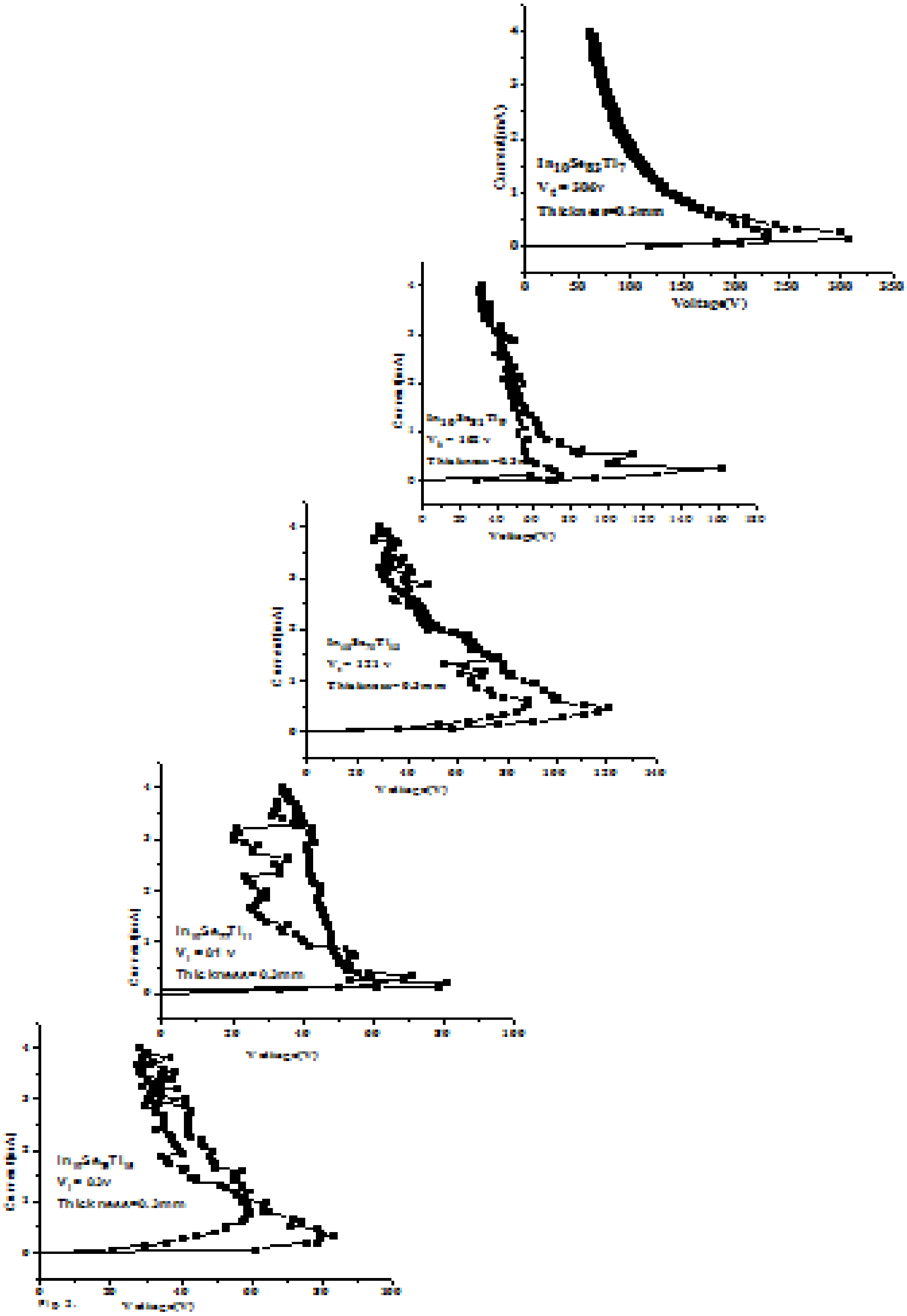
Current(mA)
0
1
2
3
4
Thickness=0.2mm
0
50
100
150
200
250
300
350
Voltage(V)
0
20
40
60
80
100
Fig. 2.

Figure 2

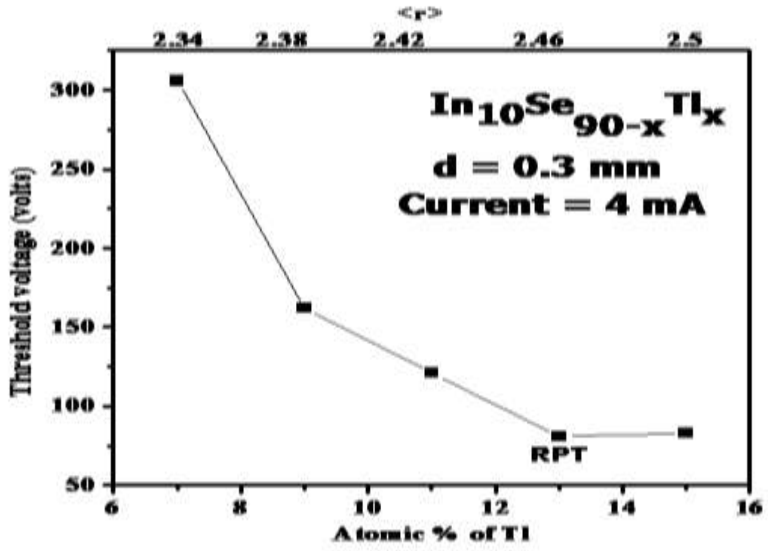

Figure 3

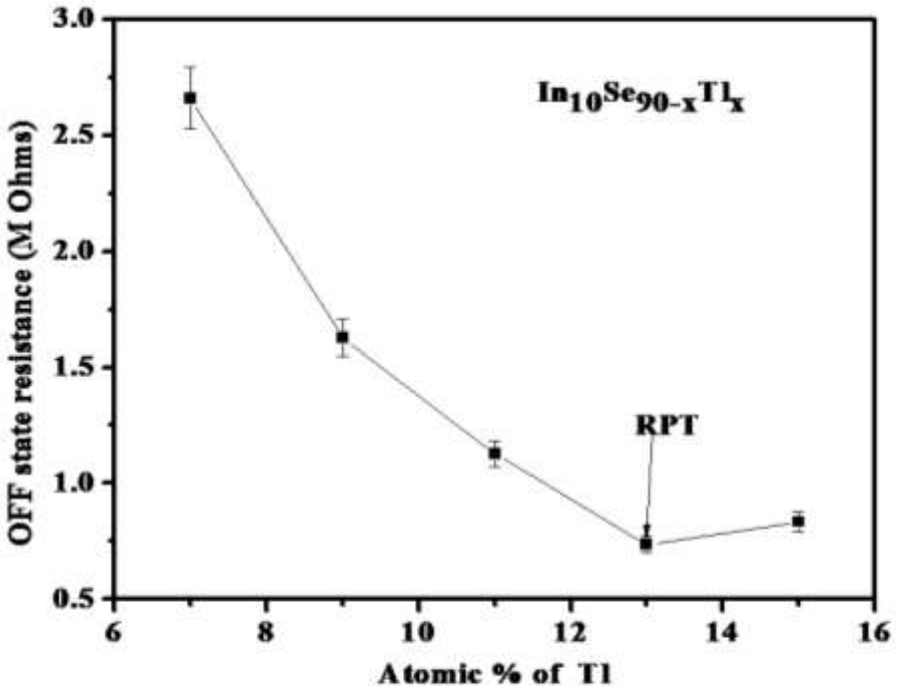

Figure 4

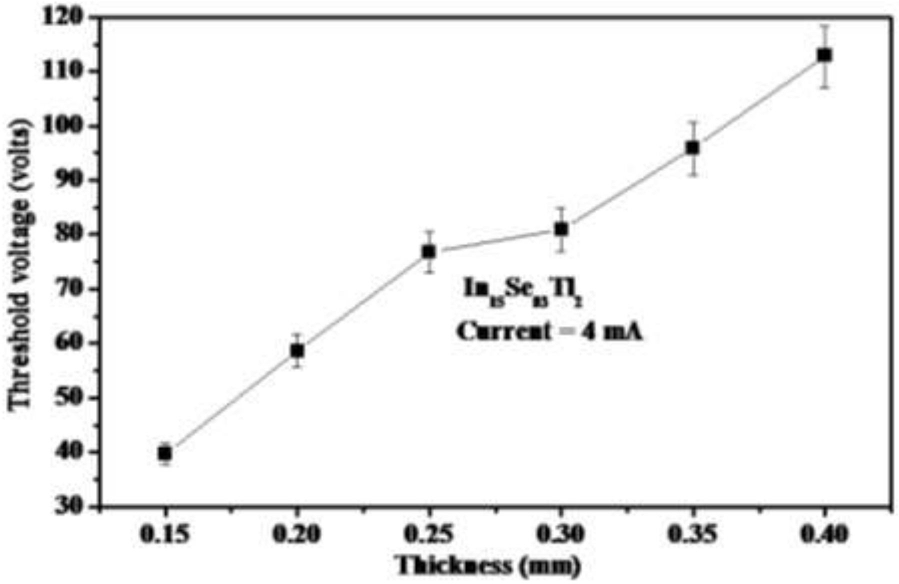

Figure 5

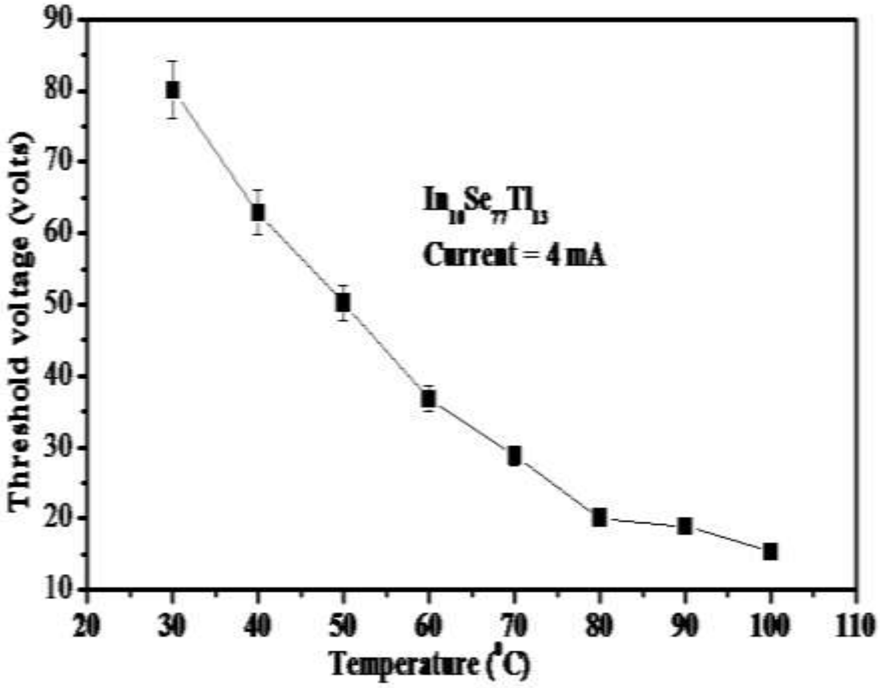

Figure 6