

## Electrical Switching and Other Properties of Chalcogenide Glasses

S. Asokan\* and K.P. Lakshmi

Department of  
Instrumentation and  
Applied Physics, Indian  
Institute of Science,  
Bangalore 560012, India  
\*sasokan@isu.iisc.ernet.in

**Electrical switching:**  
The process of changing the material from a high resistance state to a low resistance state in a very short time by the application of an electric field.

**Amorphous materials:**  
Materials that do not possess long-range order which is a characteristic of crystal.

**Glassy materials:**  
Amorphous materials exhibiting the phenomenon of glass transition.

**Chalcogenides:**  
Compounds which are primarily constituted by VI group elements such as S, Se and Te

**PCRAM or phase change random access memory:**  
A non-volatile memory which is based on the phase transformation of a material from an amorphous to crystalline state.

**DRAM:** Type of memory in which data is stored as a charge in a capacitor

**MRAM:** Memory in which information is stored as different polarizations in a ferromagnetic material

**FeRAM:** A non volatile memory that records data on a magnetic surface

Abstract | Electrical switching which has applications in areas such as information storage, power control, etc is a scientifically interesting and technologically important phenomenon exhibited by glassy chalcogenide semiconductors. The phase change memories based on electrical switching appear to be the most promising next generation non-volatile memories, due to many attributes which include high endurance in write/read operations, shorter write/read time, high scalability, multi-bit capability, lower cost and a compatibility with complementary metal oxide semiconductor technology.

Studies on the electrical switching behavior of chalcogenide glasses help us in identifying newer glasses which could be used for phase change memory applications. In particular, studies on the composition dependence of electrical switching parameters and investigations on the correlation between switching behavior with other material properties are necessary for the selection of proper compositions which make good memory materials.

In this review, an attempt has been made to summarize the dependence of the electrical switching behavior of chalcogenide glasses with other material properties such as network topological effects, glass transition & crystallization temperature, activation energy for crystallization, thermal diffusivity, electrical resistivity and others.

### 1. Introduction

*Electrical switching*, which was discovered by Ovshinsky in 1969,<sup>1</sup> is a scientifically interesting and technologically important phenomenon exhibited by *amorphous/glassy chalcogenide* semiconductors. The application of this phenomenon in areas such as information storage, power control, etc., has been thought of for a long time; however, the commercial exploitation of electrical switching has become a reality only recently, with the advent of *Phase Change Memories (PCM)* also known as *Ovonic Unified Memories (OUM)*.

The phase change memory appears to be the most promising next generation non-volatile memory Technology, due to many attributes which include high endurance in write/read

operations, shorter write/read time, high scalability, multi-bit capability, lower cost and the compatibility with complementary metal oxide semiconductor technology.<sup>2</sup> In fact, only recently, Samsung Semiconductors announced the production of a 512Mbit chip based on PCM technology. According to Samsung, the PCM offers almost seven times faster operation than NOR-flash RAMs and is expected to gain importance in mobile devices.<sup>3</sup>

The success of PCMs over other conventional Random Access Memories like *DRAM*, *MRAM*, *FeRAM*, etc., depends on the development of newer phase change materials with better electrical switching characteristics. In this context, studies on the electrical switching behaviour of chalcogenide *glasses* help us in identifying newer

glasses which could be used for phase change memory applications. In particular, studies on the composition dependence of thermal properties and electrical switching parameters are necessary for the selection of proper compositions in a glassy system having easy crystallizability, good glass forming ability, low thermal diffusivity, lower switching voltages, etc., required for a good memory material.

In this review, an attempt has been made to summarize the dependence of the electrical switching behavior of chalcogenide glasses on other material properties. Particularly, the dependence of electrical *switching voltage* (also known as *threshold voltage*,  $V_t$ ) which is a key parameter in PCM applications, on other material properties such as network topological effects, glass transition ( $T_g$ ) & crystallization temperature ( $T_c$ ), activation energy for crystallization ( $E_c$ ), thermal diffusivity ( $\alpha$ ) and electrical Resistivity ( $\rho$ ) has been discussed.

## 2. The Phenomenon of Electrical Switching in Chalcogenides

At low electric fields, amorphous/glassy chalcogenides exhibit the DC electrical characteristics of an intrinsic semiconductor.<sup>1</sup> However, at higher fields, the electrical behavior becomes non-Ohmic and at a critical electric field, the material switches from a low conducting (OFF) state to a high conducting (ON) state.

The electrical switching in chalcogenide glasses can be either mono-stable (threshold behaviour) or bi-stable phenomenon (memory behaviour). Figure 1 (a, b) show the I-V characteristics of

$Al_5As_{35}Te_{60}$  and  $Al_{20}As_{20}Te_{60}$  glasses, exhibiting memory and threshold switching respectively.<sup>4</sup>

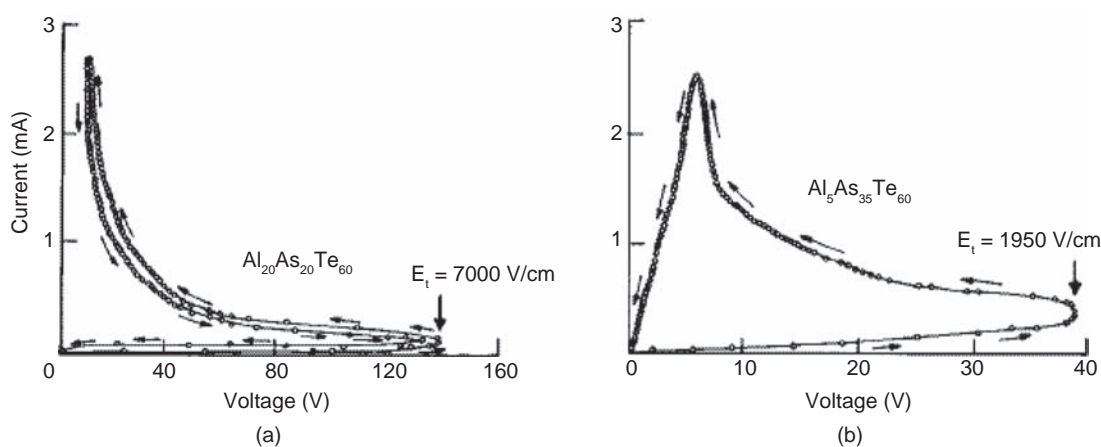
In threshold switching, the low resistance ON state is retained as long as a minimum holding current is maintained. For smaller currents, the device reverts to the high resistance state. However, the memory samples remain in the low resistance ON state even if the current is reduced to zero. The process of switching in both threshold and memory glasses is primarily electronic in nature. However, additional thermal effects come into play in memory materials which result in the formation of a conducting crystalline channel in the electrode region, even at lower ON-state currents. This process, known as phase change is induced by maintaining the current for a few milliseconds after switching. In order to reverse the phase change and restore the high resistance OFF state in the sample, the application of a high current/light pulse is required.<sup>5</sup> This reversible phase change is technologically important as the basis of the nonvolatile amorphous semiconductor memory device.

In both types of switching the ON-state is characterized by the formation of a conducting filament in the electrode region.<sup>5</sup> Threshold switching materials are generally chosen so as to be stable against *devitrification* and no phase change occurs in the filament during switching. However, the low resistance state of a memory material involves the crystallization of the current carrying filament.<sup>5</sup> Therefore, memory compositions are chosen so as to promote devitrification. It is known that poor structural cross-linking, weaker bonds, and more lone-pair interactions favor memory switching in chalcogenide glasses.

Switching voltage/  
Threshold voltage:  
The voltage at which  
a material exhibits electrical  
switching from a high  
resistance state to a low  
resistance state

Devitrification:  
The crystallization  
of a glassy material,  
usually by thermal means

Figure 1: The I-V characteristics of (a)  $Al_{20}As_{20}Te_{60}$  glass showing threshold switching and (b)  $Al_5As_{35}Te_{60}$  glass exhibiting memory switching.<sup>4</sup>



**Space Charge Limited Conduction:** Current arising because of a breakdown that occurs in a semiconductor placed in an electric field, due to the accumulation of charges at the electrodes

**Schottky emissions:** It is a thermionic emission occurring at a metal—semiconductor interface due to an applied electrical field

**Poole-Frenkel emissions:** Conduction mechanism arising due to the thermal emission of charge carriers from coulombic traps in the bulk of a material under an applied electric field

**Valence Alternation Pairs:** These are defects states such as under or over coordinated chalcogen atoms which get charged by electron transfer

**RPT (Rigidity Percolation Threshold):** The composition at which a covalently bonded glassy network exhibits a sudden change from an elastically floppy to an elastically rigid behavior in mechanical properties

**CT (Chemical Threshold):** Chemical threshold is the maximally ordered glass composition consisting of only hetero-polar bonds

**Coordination number:** The coordination number denotes the number of nearest neighbors around a particular atom

### 3. The Mechanism of Electrical Switching

There are mainly three models which have been put forward to explain the switching phenomenon in glassy chalcogenides, namely the electronic model,<sup>6</sup> the thermal model<sup>7</sup> and the electro-thermal model.<sup>6</sup> The electronic model is based on the assumption that the electric fields near the electron and the hole- injecting contacts are high because of the presence of hetero-space charge; it further assumes that the electron and hole traps are completely filled near the center. According to the electronic model, non-Ohmic conduction is mainly attributed to one of the three mechanisms namely, the *Space Charge Limited Conduction (SCLC)*, *Schottky emissions* and *Poole-Frenkel emissions*.

The electro-thermal model suggests that the electric fields near the contacts is high and is supposed to arise from the high-resistance cold layers of material adjacent to the metallic contacts. These cold layers depend only on the device geometry and are independent of the polarity of the applied bias voltage. Further, according to the electro thermal model, the electrical switching occurs in a chalcogenide glass when the charged defect states known as *Valence Alternation Pairs*<sup>8</sup> are filled by the field-injected charge carriers and the carrier mobility increases suddenly from a low to a high value. The larger current flowing through the sample after the initiation of switching leads to a higher Joule heating, which, in turn, leads to a further reduction in the resistance and more current flow. This cyclic mechanism is well depicted in figure 2, by a feed-back loop.<sup>6</sup>

### 4. Study of the Electrical Switching Behavior and the Scope of this Review

Studies on the electrical switching behavior of materials can be performed in two different ways. The first method is to apply a voltage ramp across the sample and measure the current flow

through the sample. This is referred to as Voltage Ramp Switching. Because of the exponential increase in current at high fields, this technique does not permit the accurate determination of the switching current. Near the switching field, a small increase in applied voltage results in a large increase in current and hence the immediate pre-switching region cannot be effectively accessed by this technique. Instead, a slow current ramp can be used to control the rate of increase of current and the voltage across the sample can be measured as a dependent variable. This second method is referred to as Current Ramp Switching.

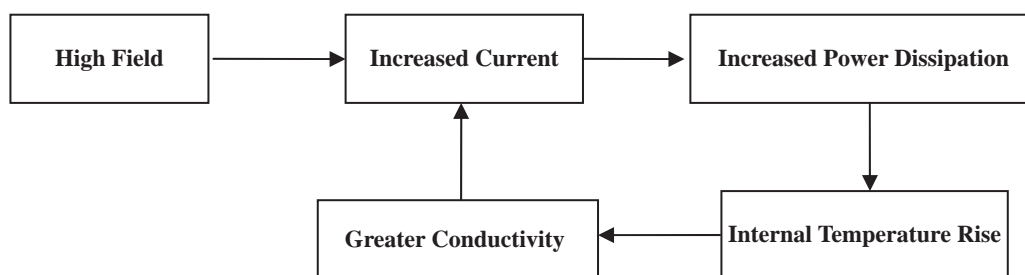
This review focuses on the dependence of the switching behavior of a variety of binary and ternary chalcogenide glasses on the two network topological thresholds in chalcogenide glasses, namely, the *Rigidity Percolation Threshold (RPT)* and the *Chemical Threshold (CT)*. In addition, the correlation between the switching parameters and other electrical and thermal properties has been discussed. The electrical switching results described in this review have been obtained using the current sweep.

### 5. Rigidity Percolation, Chemical Ordering and Extended Rigidity Transition in Chalcogenide Systems

In covalent network glasses, the connectivity, rigidity and ordering of the glassy network evolves with composition. As a function of composition, two important network topological effects are known to occur in chalcogenide glasses, namely rigidity percolation and chemical ordering.

Rigidity percolation deals with the dimensionality and rigidity of a glassy network and is decided by the average *coordination number*  $\langle r \rangle$  of the glass. According to the constraints theory of Phillips and Thorpe,<sup>9</sup> in a chalcogenide network glass, there exists a critical coordination ( $\langle r_c \rangle = 2.4$ ), at which the degrees of freedom

Figure 2: A block diagram depicting the cyclic mechanism of electrical Switching in glassy chalcogenides.<sup>6</sup>



per atom and the number of constraints acting on it become equal. This means a mechanical equilibrium is established at this composition which is referred to as the Rigidity Percolation Threshold (RPT) or Mechanical Threshold (MT) or Stiffness Threshold (ST) of the glass.

The glass compositions with  $\langle r \rangle < \langle r_c \rangle$  are referred to as *floppy* or under-constrained systems while compositions for which  $\langle r \rangle > \langle r_c \rangle$  are referred to as over-constrained systems. Anomalous variations in various properties of many different chalcogenide glasses have been observed at the rigidity percolation threshold.<sup>9</sup>

Careful experimental and theoretical investigations have shown that in certain glassy systems, rigidity percolation spans an extended composition range and mean coordination numbers. As a result, these systems exhibit two stiffness transitions, namely from the floppy polymeric phase to an isostatically rigid phase (the intermediate phase) and from the isostatically rigid to a stressed rigid phase.<sup>10</sup> The three phases, the floppy, the intermediate and the rigid phases are characterized by distinct elastic behavior.

Further, it is suggested that the intermediate phase constitutes a thermally reversing window and is characterized by a vanishing non-reversing enthalpy,  $\Delta H_{NR}$ , suggesting that glass compositions in this phase are configurationally close to their liquid counterparts, i.e. self-organized. The compositional width (and the centroid) of the intermediate phase is determined by the glass structure. In random covalent networks, the width of the intermediate phase almost vanishes, and a solitary floppy to rigid phase transition is observed. In certain chalcogenide systems, some degree of self-organization occurs which opens up a thermally reversing window between the floppy and rigid phases.<sup>10</sup> Glasses in the intermediate phase composition range are self-organized, near-ideal and stress-free. They are also found to be good glass formers.

In addition to the rigidity and extended rigidity percolation, chemical ordering also occurs in chalcogenide glasses (usually at higher coordination numbers). A chemically ordered chalcogenide glassy network comprises of only hetero polar bonds and has maximum molar volume and minimum density. Energetically, the maximally ordered glassy network is closest to its crystalline state. Further, the glass-forming ability of chalcogenide glasses is found to be minimal at the composition corresponding to the chemically ordered network as they attain their crystalline state easily.

As mentioned earlier, the Chemical Threshold (CT) in chalcogenide glassy systems usually refers to the composition at which hetero-polar bonds

dominate the network ( $CT_{COCRN}$ ). In addition to  $CT_{COCRN}$ , the stoichiometric compositions at which equilibrium crystalline compounds occur are also considered as chemical thresholds (referred to as  $CT_{ST}$ ). In some systems like  $Ge_xSe_{100-x}$ , the two thresholds coincide at a particular composition ( $x = 33$ ). However, in many other glassy systems the two thresholds occur at different compositions.<sup>11</sup> (eg. In  $Ge_xTe_{100-x}$ ,  $CT_{COCRN}$  occurs at  $x = 33$  whereas  $CT_{ST}$  occurs at  $x = 50$ ).

## 6. The Effect of Topological Thresholds on the Switching Voltages ( $V_t$ ) of Chalcogenide Glasses

Unusual variations in various properties have been observed at the rigidity percolation and chemical thresholds; however, the exact nature of the variation depends on the property studied and it also varies from one system to another. For example, binary telluride glasses such as  $Ge-Te$ <sup>11</sup> and  $Si-Te$ <sup>11</sup> and ternary tellurides such as  $Ag_xGe_{15}Te_{85-x}$ <sup>12</sup> show a minimum in the glass transition temperature  $T_g$  at the rigidity percolation threshold, whereas the glassy selenide systems such as  $Ge-Se$ ,  $Ge-Ga-Se$ ,  $Ge-In-Se$ , are reported to show a slope change in  $T_g$  at the RPT.<sup>12</sup>

Generally, the switching voltages of memory-switching chalcogenide glasses increase with the addition of higher coordinated atoms due to the increase in the network connectivity and rigidity of the system. This effect can be seen as an increase in  $V_t$  and  $T_g$ . With the increase in network connectivity and rigidity, the structural reorganization required for memory switching becomes more difficult, causing an increase in switching voltages. It is seen in a variety of memory glasses such as  $As_{30}Te_{70-x}Si_x$ ,<sup>13</sup>  $As_xTe_{100-x}$ ,<sup>14</sup>  $Ge_xTe_{100-x}$ ,<sup>11</sup>  $Si_xTe_{100-x}$ ,<sup>11</sup>  $Al_xTe_{100-x}$ ,<sup>15</sup>  $Al_xAs_{40}Te_{60-x}$ <sup>4</sup> and  $Ge_{7.5}As_xTe_{92.5-x}$ <sup>16</sup> that the switching voltages increase with an increase in network connectivity and rigidity and a sharp change in slope (lower to higher) is seen in the composition dependence of switching voltages at the rigidity percolation threshold of the system.

Figures 3 and 4 show the composition dependence of switching voltages of two representative glassy systems,  $Ge_xTe_{100-x}$ <sup>11</sup> and  $Ge_xSe_{35-x}Te_{65}$ <sup>17</sup> respectively, indicating an increase with composition and a sharp slope change in switching voltages at the RPT.

Usually, a minimum is seen in the composition dependence of switching voltages of glassy chalcogenides at the chemical threshold (CT); with chemical ordering, the charge carriers are likely to be less localized, leading to an increased conductivity and a reduction in switching voltages.

Elastically floppy:  
A condition that facilitates  
easy rearrangement of  
constituent atoms

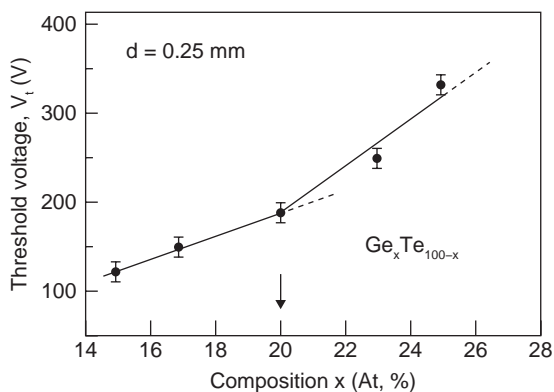
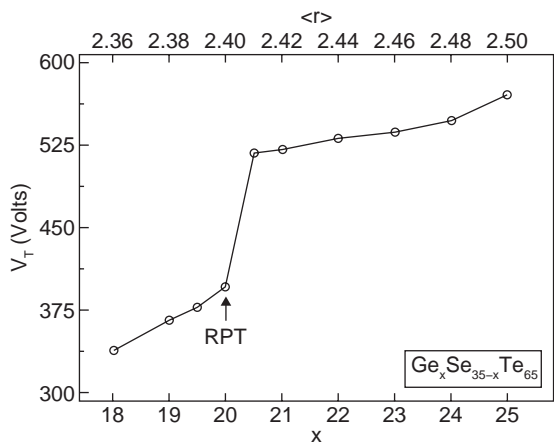
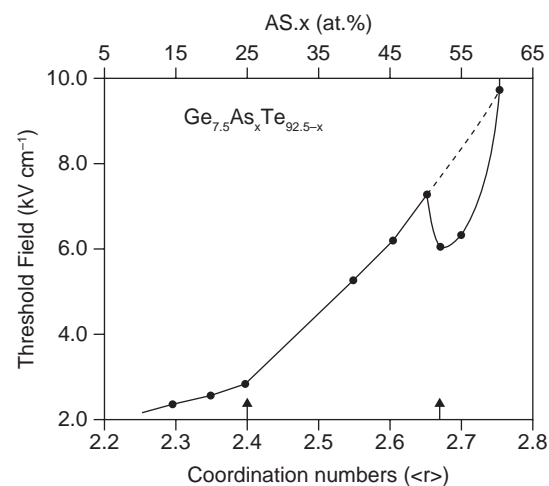
Figure 3: The compositional dependence of  $V_t$  in  $\text{Ge}_x\text{Te}_{100-x}$  glasses.<sup>11</sup>

 Figure 4: The variation with composition of  $V_t$  of  $\text{Ge}_x\text{Se}_{35-x}\text{Te}_{65}$  glasses.<sup>17</sup>

 Figure 5: Compositional dependence of  $V_t$  of  $\text{Ge}_{7.5}\text{As}_x\text{Te}_{92.5-x}$  glasses.<sup>16</sup>


Figure 5 shows the composition dependence of switching voltages of  $\text{Ge}_{7.5}\text{As}_x\text{Te}_{92.5-x}$  glasses in which a sharp slope change at the RPT and a minimum at the CT are clearly seen.

The sharp slope change in the switching fields has also been observed in chalcogenide systems, in which the stiffness transition is shifted to average coordination numbers higher than  $\langle r \rangle = 2.4$ , due to the partial ionicity of the bonds. For example in the  $\text{As}_{40}\text{Te}_{60-x}\text{In}_x$  glassy system<sup>18</sup> (figure 6), the four-fold coordination of In atoms involve coordinate bond formation with the chalcogen, which results in the shifting of the RPT to  $\langle r \rangle = 2.65$ . Further, the minimum observed in  $V_t$  around  $\langle r \rangle = 2.69$  is associated with the chemical threshold.

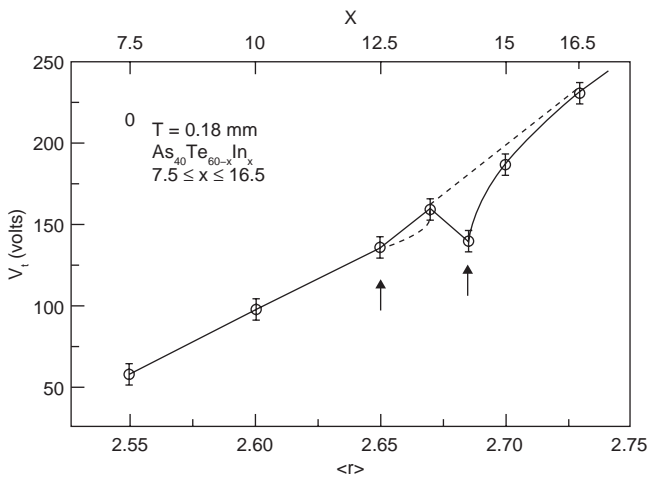
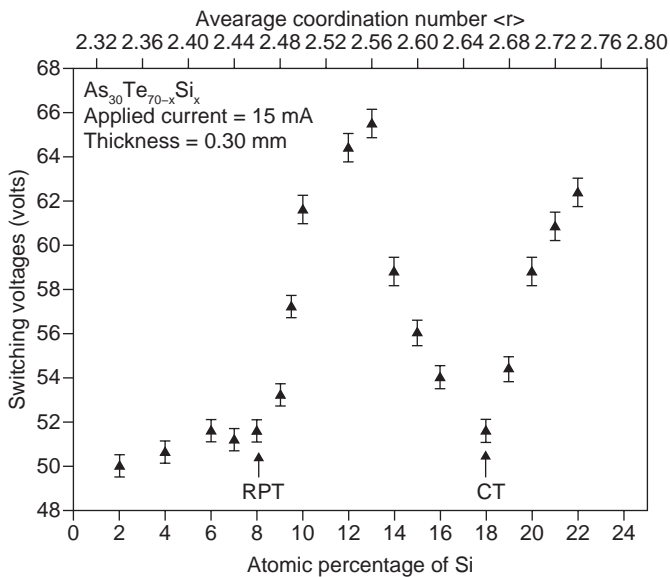
Figure 7 shows the composition dependence of switching voltages of the  $\text{As}_{30}\text{Te}_{70-x}\text{Si}_x$  glassy system, in which similar effects, namely the slope change at the shifted mechanical threshold and a minimum at the CT are seen.

In certain glassy systems, a maximum is observed in switching voltages at the Rigidity Percolation Threshold (RPT). Figure 8 shows the variation with the composition of switching voltages of the  $\text{Si}_x\text{Te}_{100-x}$  glassy system exhibiting a maximum in  $V_t$  at the mechanical threshold. In these systems, it has been suggested that one of the chemical thresholds ( $\text{CT}_{\text{COCRN}}$  or  $\text{CT}_{\text{ST}}$ ) is quite close to the RPT. Due to the proximity between the chemical and mechanical thresholds, there is a turnaround in  $V_t$ , which occurs very close to the RPT and results in an apparent maximum in  $V_t$ . This turn-around eventually leads to a minimum in  $V_t$  at the CT.

Apart from the general behavior discussed above, there are glassy systems in which the variations in switching voltages at the network thresholds, especially at the mechanical threshold, are different. For example, in  $\text{Ge}_{20}\text{Te}_{80-x}\text{Pb}_x$  glasses, though there is an increase in network rigidity, a decrease is seen in the composition dependence of  $V_t$  with the lead addition, and a subtle change in slope at the RPT (figure 9);  $V_t$  decreases with a further increase in lead, reaching a minimum at the composition corresponding to the CT (figure 9). In this glassy system, the observed composition dependence has been understood on the basis of the dominance of the metallicity factor (more metallic nature of the dopant) over network rigidity.

A strong interplay between the two counteracting factors, namely the metallicity of the dopant and the rigidity, on the composition dependence of  $V_t$  is more clearly brought out in  $\text{As}_{20}\text{Te}_{80-x}\text{Ag}_x$  glasses (figure 10). In these



Figure 6: Compositional dependence of  $V_t$  of  $As_{40}Te_{60-x}In_x$  glasses.<sup>18</sup>Figure 7: The variation of switching voltages of  $As_{30}Te_{70-x}Si_x$  glasses with composition.<sup>13</sup>

samples, both the metallicity and network rigidity increase with the addition of silver; while the increase in metallicity tries to decrease  $V_t$ , the increase in rigidity tries to increase it. As a result of these two opposing factors, an initial decrease, a minimum and a subsequent increase is seen in the threshold voltages of  $As_{20}Te_{80-x}Ag_x$

samples. The region of decrease in  $V_t$  indicates the dominance of the metallicity factor and the subsequent increase is due to the influence of the rigidity factor.

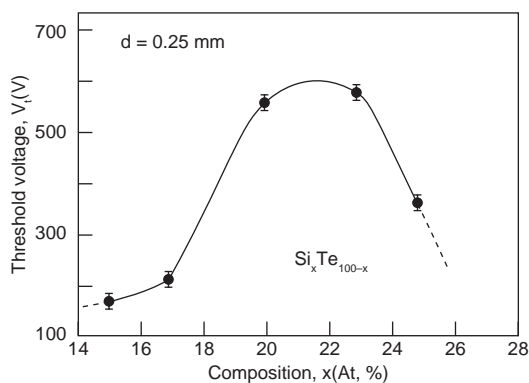
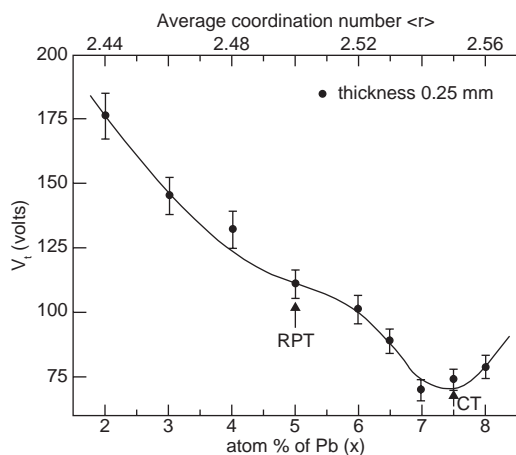
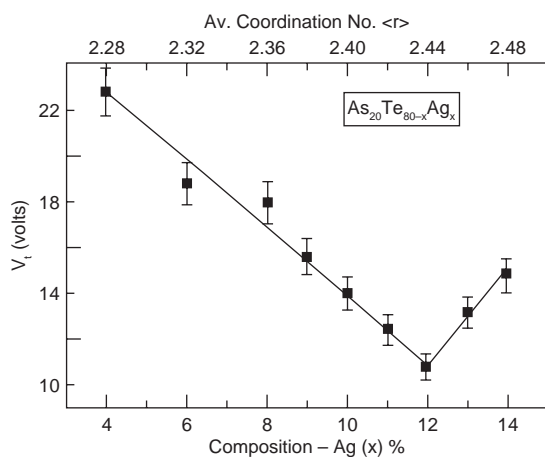
The competing effects of metallicity and rigidity leading to a minimum in  $V_t$  at the stiffness threshold is also seen in the  $Ge_{15}Te_{85-x}In_x$ <sup>21</sup> glassy system (figure 11). The extended glass formation region in this system allows us to notice the other minimum exhibited at the CT at a higher composition.

Another interesting deviation in the variation of switching voltages at the topological thresholds is seen in the  $Ge_{15}Te_{85-x}Si_x$ <sup>22</sup> system, shown in figure 12. In this system,  $V_t$  increases with the increase in Si content (as the network gets rigid), with the conventional slope change seen at the RPT. However, there is no decreasing trend observed above the RPT which could lead a minimum in  $V_t$  at the CT.  $V_t$  continues to increase even up to the CT, with only a slope change and saturation of  $V_t$  at the chemical threshold instead of the minimum seen in other systems.

In glassy systems exhibiting extended rigidity percolation and an intermediate phase, more interesting features are seen. In these systems, the onset and completion of the extended rigidity transition are exemplified by a sudden increase and a slope change in electrical switching voltages. For example, in the  $Ge_{15}Te_{85-x}In_x$ <sup>21</sup> system, an initial decrease is seen in  $V_t$ , in spite of the addition of higher coordinated indium atoms, which is due to the higher metallicity of indium atoms (shown earlier in figure 11). However, at the onset of the extended rigidity percolation, the trend reverses leading to a maximum in  $V_t$ , at the composition corresponding to the completion the intermediate phase.  $V_t$  decreases again, above the completion of the extended rigidity percolation, reaching a minimum at the composition corresponding to the CT (figure 11).

In the  $Al_{15}Te_{85-x}Si_x$ <sup>23</sup> glassy system, which also exhibits extended rigidity percolation, different behavior is seen (figure 13). With the addition of higher coordinated Si atoms, the switching voltages increase and a cusp is seen in  $V_t$  at the onset of rigidity percolation. There is a sharp increase in the switching voltages in the intermediate phase and saturation in  $V_t$  is observed at the composition corresponding to the completion of an extended stiffness transition.

It is to be noted here that unlike at rigidity percolation and chemical thresholds, the exact variation of switching voltages during an extended stiffness transition is not yet fully understood.

Figure 8: The variation of switching voltages of  $\text{Si}_x\text{Te}_{100-x}$  glasses with composition, exhibiting a maximum at the RPT.<sup>11</sup>Figure 9: Compositional dependence of  $V_t$  of  $\text{Ge}_{20}\text{Te}_{80-x}\text{Pb}_x$  glasses.<sup>19</sup>Figure 10: The variation with composition of  $V_t$  of  $\text{As}_{20}\text{Te}_{80-x}\text{Ag}_x$  glasses.<sup>20</sup>

## 7. The Correlation Between Switching Voltages and Material Properties

### 7.1. Switching Voltages and Electrical Properties of Chalcogenide Glasses

The switching voltages of chalcogenide glasses have a strong correlation with the resistivity of the sample. The addition of more metallic impurities to a base glass system, in general, lowers the conductivity activation energy, resistivity and the switching voltages of the sample.

Also, the low resistivity samples are most likely to exhibit memory switching as the low resistivity facilitates higher currents which are carried by the sample. This causes an increase in Joule heating; as a result, the temperature rise inside the sample is higher and structural transformation becomes more favorable. These effects will result in a low value of switching voltages. Further, the low resistivity samples require less energy for phase transformations and are likely to exhibit memory switching.

It has been shown long ago that in Al-As-Te<sup>31</sup> memory samples, the switching voltage varies with the resistivity of the sample as

$$2 \log (V_t) = \log (R) - 2.08 \quad (1)$$

Where, R is the resistance of the sample.

The decrease in switching voltages with the addition of more metallic impurities has been observed in chalcogenide systems including  $\text{Cu}_x\text{Ge}_{15}\text{Te}_{85-x}$ ,<sup>25</sup>  $\text{Ag}_x\text{Ge}_{15}\text{Te}_{85-x}$ ,<sup>25</sup>  $\text{Si}_{15}\text{Te}_{85-x}\text{Sb}_x$ ,<sup>26</sup>  $\text{Ge}_{18}\text{Te}_{82-x}\text{Bi}_x$ ,<sup>27</sup>  $\text{Ge}_{17}\text{Te}_{83-x}\text{Tl}_x$ ,<sup>28</sup> etc. Figures 14, 15 and 16 show the variation of switching voltages of representative  $\text{Ge}_{18}\text{Te}_{82-x}\text{Bi}_x$ ,<sup>27</sup>  $\text{Ge}_{17}\text{Te}_{83-x}\text{Tl}_x$ <sup>28</sup> and  $\text{Si}_{15}\text{Te}_{85-x}\text{Sb}_x$ <sup>26</sup> glasses with composition thus indicating the effect of resistivity/metallicity of the constituents.

### 7.2. Switching Voltage ( $V_t$ ) and Thermal Properties

#### 7.2.1. Switching Voltages and Thermal Diffusivity ( $\alpha$ )

Thermal diffusivity ( $\text{cm}^2/\text{s}$ ) indicates the rate at which heat gets conducted away from a sample or from a region in the sample. As mentioned earlier, memory switching occurs due to the formation of a filamentary channel (crystalline conducting channel) between the electrodes. If the heat that is generated due to Joule heating in this filamentary region is not removed at a higher rate, phase transitions become easy and hence the  $V_t$  required would be less. Accordingly, samples with low values of thermal diffusivity are likely to exhibit memory switching while those with high values of thermal diffusivity are likely to show threshold switching.

Figure 11: The compositional dependence of  $V_t$  of  $Ge_{15}Te_{85-x}In_x$  glasses.<sup>21</sup>

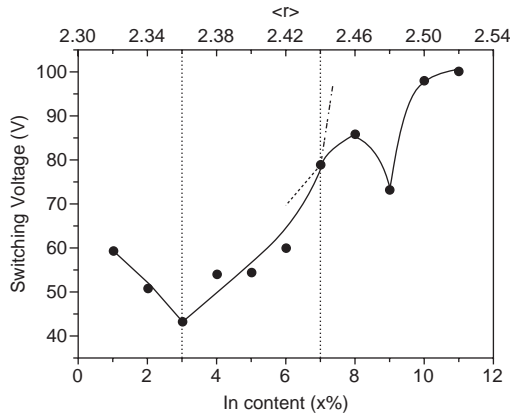
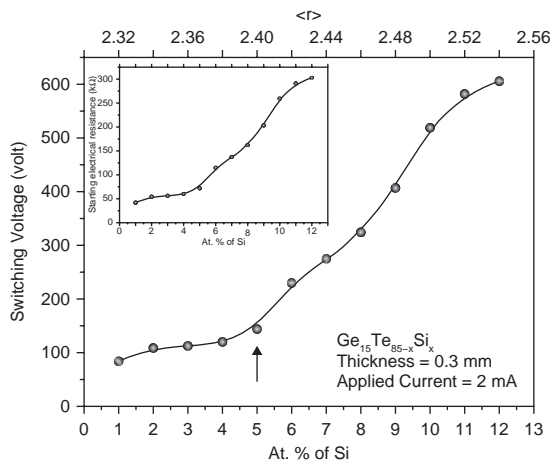
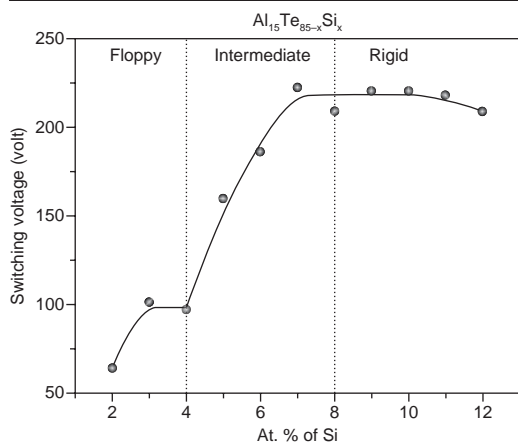


Figure 12: The variation with composition of  $V_t$  of  $Ge_{15}Te_{85-x}Si_x$  glasses.<sup>22</sup>



Glass transition temperature: Temperature at which an amorphous solid exhibits a transition from a solid to a super-cooled liquid state upon heating

Figure 13: Compositional dependence of switching voltages of  $Al_{15}Te_{85-x}Si_x$  glasses.<sup>23</sup>



For example, in the  $Al_{20}As_{80-x}Te_x$  glassy system, samples with higher  $\alpha$  show threshold behavior and those with lower  $\alpha$  exhibit memory behavior. The observed change in switching behavior with thermal diffusivity has been understood as follows: The higher the thermal diffusivity, the higher will be the rate at which heat is dissipated away and hence the lower will be the temperature rise in the conducting filament. Consequently, the structural reorganization required for phase change becomes more difficult and the sample exhibits threshold behavior.

On the other hand, lower thermal diffusivity means a higher impedance to the flow of diffusing thermal waves. It also means that the rate at which heat is dissipated away from the sample is low. As a consequence, the temperature rise in the conducting channel is higher and hence the structural transformation becomes easy. These effects facilitate memory behavior.

7.2.2. Switching Voltages/Fields and Glass Transition Temperature ( $T_g$ )

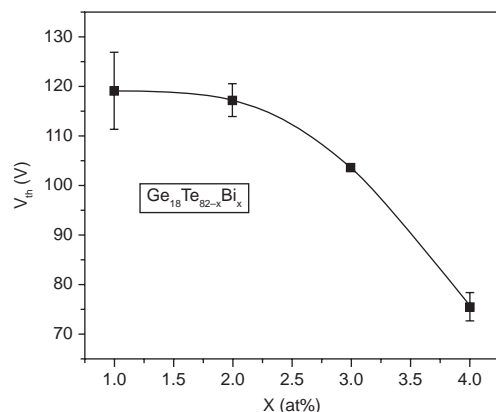
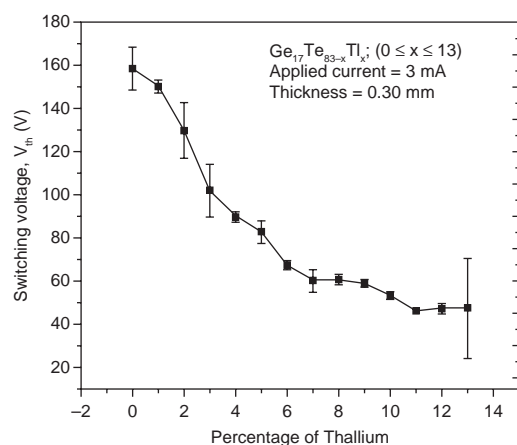
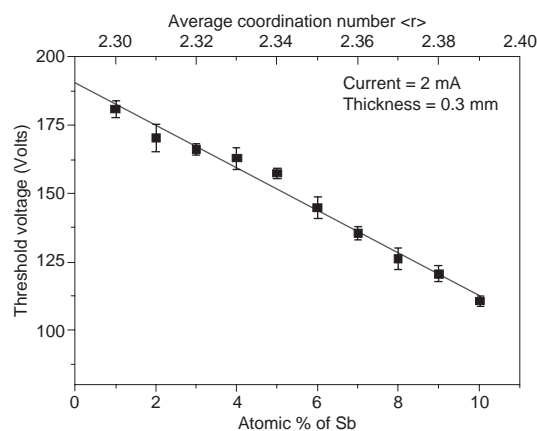
The glass transition temperature can be taken as indicative of the connectivity of the glassy network. An increase in  $T_g$  usually indicates an increase in network connectivity. Similarly, a decrease in  $T_g$  upon adding dopants has been attributed to nano-phase separation caused by the segregation of homo-polar bonds. There have also been efforts reported in the literature to link the glass transition temperature with parameters quantifying the network connectivity such as the average coordination number  $\langle r \rangle$ . In general, an increase in the  $V_t$  of chalcogenide glasses can be expected with an increase in  $T_g$ .

Figure 17 shows the composition dependence of switching fields ( $E_t$ ) and the glass transition temperature of  $Al_xTe_{100-x}$  glasses, which shows that the variation in  $E_t$  nearly follows the variation of  $T_g$  with Al content.<sup>15</sup> Further, the glass transition temperature can be taken to be indicative of the energy required for the phase change from amorphous to crystalline states during memory switching. Based on a configurational free energy model, an empirical relation<sup>15</sup> between the switching fields and  $T_g$  has been suggested in the literature:

$$E_t^2 = C_1 \exp [C_2 * k(T_g - T)/kT]$$

Where  $E_t$  is the switching field,  $C_1, C_2$  are constants,  $T$  is the ambient temperature and  $k$  is the Boltzmann constant. Figure 18 shows the variation of  $\text{Log}(E_t^2)$  versus  $(T_g - T)/T$  of  $Al_xTe_{100-x}$  glasses, which confirms the validity of this relation.



Figure 14: The variation with composition of switching voltages of  $\text{Ge}_{18}\text{Te}_{82-x}\text{Bi}_x$  glasses.<sup>27</sup>

 Figure 15: The variation with composition of switching voltages of  $\text{Ge}_{17}\text{Te}_{83-x}\text{Tl}_x$  glasses.<sup>28</sup>

 Figure 16: The variation with composition of switching voltages of  $\text{Si}_{15}\text{Te}_{85-x}\text{Sb}_x$  glasses.<sup>26</sup>

**Glass forming ability:**

It is defined as the ability of a material to form a bulk non crystalline solid, from the melt, by sudden cooling

**Set process:** Switching the material from the high resistance state to the low resistance state

**Reset state:** Switching the material back to the high resistance state from the low resistance state attained during the set operation

### 7.2.3. Switching Voltages/Fields and Crystallization Temperature ( $T_c$ )

Glasses with a high value of  $T_c$  are considered strong glasses, and it is seen that glasses with a low value of  $T_c$  crystallize easily and, consequently, are more likely to exhibit memory switching. Further, the switching fields required for strong glasses can be expected to be more as compared to the systems with low  $T_c$ .

In a glassy system, as the network gets more rigid,  $T_c$  generally increases, crystallization becomes more difficult and hence  $V_t$  can be expected to increase. Figure 19 shows the composition dependence of switching fields and crystallization temperatures of  $\text{As}_x\text{Te}_{100-x}$  glasses exhibiting memory switching, which shows that the variation of switching fields exactly mimics the variation of crystallization temperatures with composition.

### 7.2.4. Switching Voltages and Activation Energy for Crystallization ( $E_c$ )

In addition to the crystallization temperature, the activation energy for crystallization ( $E_c$ ), which denotes the energy barrier to overcome for crystallization, can be taken as indicative of the easiness/difficulty of devitrification. Consequently, a correlation between the switching voltages/fields and activation energy for crystallization can be expected, especially in memory switching samples. This clear correlation has been recently demonstrated in the  $\text{Ge}_{18}\text{Te}_{82-x}\text{Bi}_x$  system, in which there is a decrease in both activation energy for crystallization ( $E_c$ ) and memory switching voltage with the addition of Bi (Table 1). Further, a low value for  $E_c$  could also mean fast crystallization and hence a good switching speed.

### 7.2.5. Switching Voltage ( $V_t$ ) and Glass Forming Ability (GFA)

The *glass forming ability* ( $\Delta T$ ) of a system is given by the difference between  $T_c$  and  $T_g$ , which is also taken to define the thermal stability of a glass. The *set* and *reset* processes in a phase change memory require two different attributes of 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. Recent experiments indicate that the  $\text{Ge}_{15}\text{Te}_{83}\text{Si}_2$  glass composition is relatively easily devitrifiable, as seen by the ease 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).

The easy resettability of the memory state has been found to be intimately linked to the

Figure 17: The composition dependence of switching fields of  $\text{Al}_x\text{Te}_{100-x}$  glasses. The inset in the figure shows the variation with composition of the glass transition temperature.<sup>15</sup>

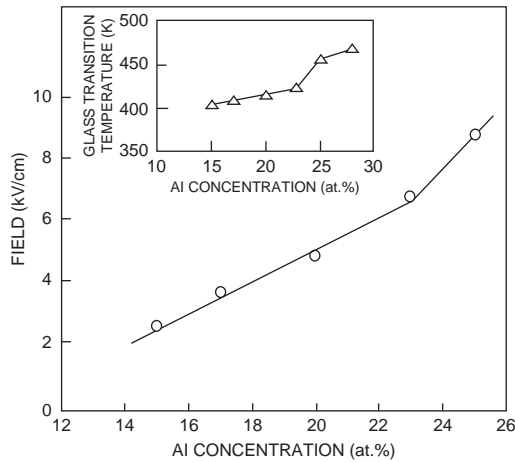


Figure 18: The variation of  $\text{Log}(E_t^2)$  with  $(T_g - T)/T$  for  $\text{Al}_x\text{Te}_{100-x}$  glasses.<sup>15</sup>

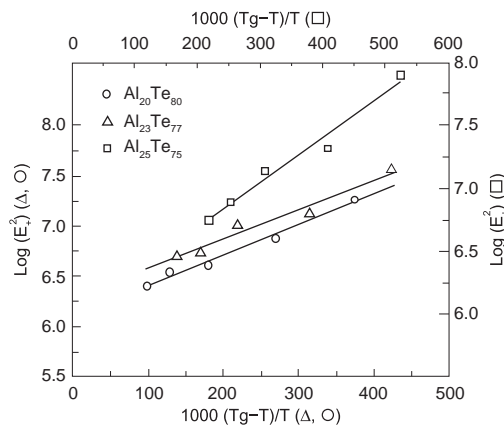


Figure 19: Compositional dependence of  $E_t$  and  $T_{c1}$  of  $\text{As}_x\text{Te}_{100-x}$  glasses.<sup>14</sup>

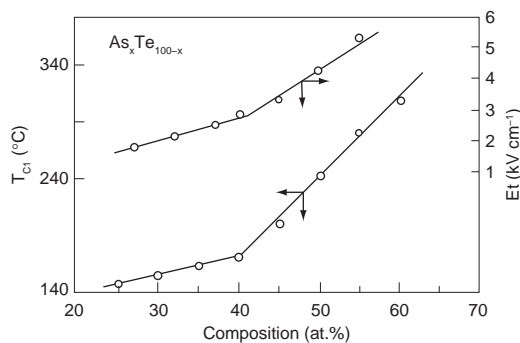


Table 1: Activation energy for crystallization ( $E_c$ ) and memory switching voltages of  $\text{Ge}_{18}\text{Te}_{82-x}\text{Bi}_x$  glasses.<sup>27</sup>

At. % of Bi	$E_c$ KJ/mol	$V_t$
1	27.5	≈119 V
2	12.9	≈117 V
3	11.8	≈109 V

Table 2: The correlation between GFA and resettability of Ge-As-Te glassy samples.<sup>24</sup>

Composition	GFA	Resetting pulse
$\text{Ge}_{10}\text{As}_{35}\text{Te}_{55}$	0.529	20 mA;50 $\mu\text{s}$
$\text{Ge}_{10}\text{As}_{40}\text{Te}_{50}$	0.390	20 mA;50 $\mu\text{s}$
$\text{Ge}_{10}\text{As}_{45}\text{Te}_{45}$	3.9	10 mA;30 $\mu\text{s}$
$\text{Ge}_{10}\text{As}_{50}\text{Te}_{40}$	3.13	10 mA;30 $\mu\text{s}$

glass-forming ability of chalcogenide glasses. Table 2 shows the values of GFA and the magnitudes of the resetting pulse for Ge-As-Te<sup>24</sup> memory glasses. One can easily observe that samples with higher GFA are easily resettable.

## 8. Conclusion

The phenomenon of electrical switching in chalcogenide glasses has many technological applications including information storage, power control, etc. Non-Volatile Random Access Memories (NVRAMs) based on electrical switching in chalcogenides, known as Phase Change Memories, have many advantages including include high endurance, shorter write/read time, high scalability, lower cost, compatibility with complementary metal oxide semiconductor technology, etc. Studies on the electrical switching behavior of chalcogenide glasses help us in identifying newer glasses which could be used for phase change memory applications. In particular, investigations on the variation with composition of electrical switching parameters and studies on the correlation between switching behavior with other material properties are necessary for the selection of proper compositions which make good memory materials. In this review, an attempt has been made to summarize the dependence of the electrical switching behavior of chalcogenide glasses with other material properties such as network topological effects, glass transition & crystallization energy for crystallization, thermal diffusivity, electrical resistivity, etc.

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**S. Asokan** received the M.Sc. degree in Materials Science from the College of Engineering, Anna University, Madras, India, and the Ph.D. degree in Physics from the Indian Institute of Science, Bangalore, India. In 1987, he joined the Department of Instrumentation, Indian Institute of Science, where he is currently a Professor. He

has published more than 150 papers in international journals/Books. He was the recipient of The Martin J. Forster Gold Medal of the Indian Institute of Science for the best Ph.D. thesis in the division of Physical and Mathematical Sciences for the year 1986–1987, the Young Scientist Award of the Indian National Science Academy (1990), and the Young Scientist Research Award of the Department of Atomic Energy (1995), India. He was a JSPS Visiting Scientist at the Department of Electronics and Computer Engineering, Gifu University, Gifu, Japan, during 1991, INSA-Royal Society Visiting Scientist at the Imperial College of Science, Technology and Medicine, London, U.K., in 1998, and a Visiting Scholar at Lyman Laboratory, Harvard University, Cambridge, MA, in 1999. Dr. Asokan is the Chief Editor of the Journal of Instrument Society of India and Member, Editorial Board of J. Indian Institute of Science. He was elected Fellow of the National Academy of Sciences, India in the year 2008.



**K.P. Lakshmi** received B.E. degree in Instrumentation and Electronics from the Bangalore University in 1997 and M.Tech degree in Electronics from Visveswaraya Technological University in 2002. She joined B.M.S. College of Engineering in 1999, where she is presently an Assistant Professor. She has been currently

deputed to pursue research work on 'Chalcogenides for phase change memory applications' at the department of Instrumentation and Applied physics, IISc, Bangalore.