PHYSICAL REVIEW B, VOLUME 63, 092203

Influence of chemical disorder on electrical switching in chalcogenide glasses

R. Aravinda Narayanan,[1,*] S. Asokan,[2] and A. Kumar[1]
[1]*Department of Physics, Indian Institute of Science, Bangalore 560012, India*
[2]*Department of Instrumentation, Indian Institute of Science, Bangalore 560012, India*

(Received 18 August 1999; revised manuscript received 18 July 2000; published 13 February 2001)

We report the results of the electrical switching and thermal studies performed on the bulk $Al_{20}Ge_xTe_{80-x}$ chalcogenide glasses which are a sequel to similar experiments on the $Al_{20}As_xTe_{80-x}$ glasses to ascertain the role of the crosslinking elements Ge and As in memory and threshold switching glasses. Anomalously large switching fields are seen for relatively smaller crystallization temperatures contradicting the thermal model for memory switching phenomenon. The present findings when viewed in conjunction with the data on other glassy alloys suggest that chemical ordering, the well known topological feature in chalcogenide glasses, influences the type of switching. A simple chemical bond and electronic band picture is developed to comprehend the results.

DOI: 10.1103/PhysRevB.63.092203 PACS number(s): 61.43.Fs, 72.80.Ng, 85.30.Fg

Electrical switching phenomenon was first observed[1] in chalcogenide (containing chalcogen elements S, Se, or Te) glasses some 30 years ago, by which they are classified into memory and threshold switching materials. Electrical switching occurs when an appropriate electric field, known as the threshold or the critical field (E_c), is applied and the glass switches to a high conducting ''on'' state from a low conducting ''off'' state. The difference between the two classes lies in the way they respond to the removal of the electric field which enabled them to switch. On the removal of the switching field, threshold switching glasses revert to the off state whereas memory switches remain locked to the on state.

In this article, we provide electrical switching and differential scanning calorimetry (DSC) results on $Al_{20}Ge_xTe_{80-x}$ glasses. The motivation for this study is the following: Al_xTe_{1-x} glasses[2] exhibited memory switching phenomenon but in $Al_{20}As_xTe_{80-x}$, a crossover from memory to threshold switching was observed[3] at $x=5$. It is known that network connectivity has a stabilizing influence on the glass and is an important factor contributing towards threshold switching.[4,5] In this study, we provide greater connectivity by replacing the threefold coordinated As by the fourfold coordinated Ge, expecting a crossover to threshold switching phenomenon for even smaller percentages of Ge. But remarkably the glasses exhibited only memory switching. Anomalously large switching fields are observed although the crystallization temperatures are lower, contradicting the existing thermal model[5] to understand memory switching phenomenon. These results are understood using a simple chemical bond and electronic band picture, which suggests a causal relationship between chemical disorder and the threshold switching phenomenon.

Bulk semiconducting glasses $Al_{20}Ge_xTe_{80-x}$ with $2.5 \leqslant x \leqslant 15$ were prepared by the melt-quenching technique and their glassy nature was confirmed by DSC. For the DSC scan, samples of about 0.1 mm grain size were used. All the glasses showed a single glass transition temperature (T_g) and multiple crystallization temperatures (T_c). To prepare a particular composition, appropriate quantities of high purity constituent elements sealed in evacuated carbon coated ampoules were kept in rotation in the furnace at 1000 °C continuously for 48 h and then quenched in ice-water mixture.

The *I-V* characteristics were studied using a PC based custom built system.[6] The sample polished to 0.2 mm thickness is placed between a point contact top electrode and a flat plate bottom electrode. A constant current is passed through the sample and the voltage developed across it is measured.

Figure 1 shows the *I-V* characteristics of the glasses studied in the $Al_{20}Ge_xTe_{80-x}$ system. All the glasses exhibited memory switching. The switching fields were found to be reproducible to within $\pm 1\%$.

E_c is plotted against atomic percentage of Ge/As in Fig. 2. The E_c increases with Ge content, with a sharper rise above

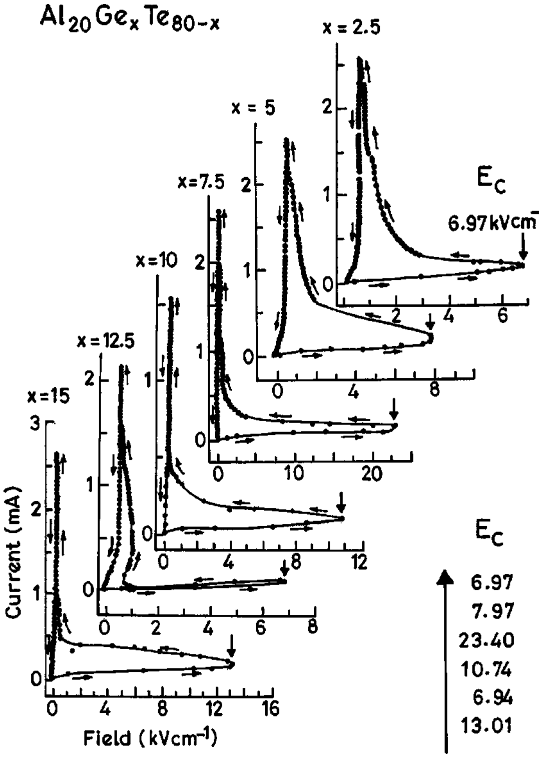

FIG. 1. Representative *I-V* characteristics of the glasses in the $Al_{20}Ge_xTe_{80-x}$ system.

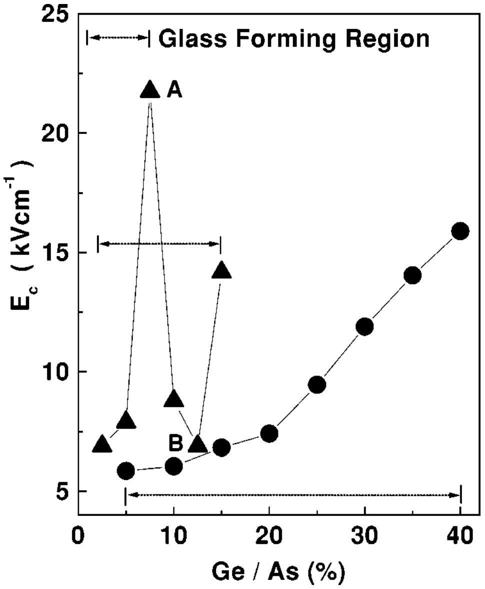

FIG. 2. The dependence of E_c on Ge and As atomic percentages in $Al_{20}Ge_xTe_{80-x}$ (triangle) and $Al_{20}As_xTe_{80-x}$ (circle) glass systems, respectively. Unusually high switching fields in Al-Ge-Te glasses and the greater glass forming extent of the Al-As-Te glass system can be seen.

$x = 5$. This trend continues until $x = 7.5$, when E_c begins to decrease and reaches the minimum at $x = 12.5$; for $x > 12.5$ it increases again.

Figures 3(a) and 3(b) show the compositional variation of T_g and T_{c1}, the glass transition and the first crystallization temperatures, respectively, in the $Al_{20}Ge_xTe_{80-x}$ glass system along with the corresponding data for $Al_{20}As_xTe_{80-x}$ from previous literature.[7] The $T_g(x)$ in Al-Ge-Te exhibits a nearly discontinuous jump at $x = 5$ and shows a broad maximum centered around $x = 12.5$, while in Al-As-Te, only a monotonic variation is seen. Also, the glasses in the Ge-based system crystallize during heating whereas in the As-based system, glasses with $x > 10$, do not crystallize.[7]

Chemical bond picture. There are mainly two factors which affect the atomic arrangement in a glass system and is reflected in the sign of the slope of the plot E_c vs x (Fig. 2). (i) As x increases, the bonds of greater strength are formed and the atomic network connectivity increases. This implies greater E_c to reach the higher conducting state and hence, the slope is positive. (ii) With increasing x, growth of chemical order (heteropolar bonds) decreases E_c, while growth of chemical disorder (homopolar bonds) increases E_c.[8] Let us now see in more detail how these factors determine the curves of E_c versus x, in Al-Ge-Te and other relevant systems. Table I provides the bond strengths of various possible bonds in these systems. Before proceeding, we mention that the sharp features seen in E_c versus x, such as the slope change at $x = 5$ and the minimum at $x = 12.5$ in Al-Ge-Te, are discussed in detail in Ref. 9, in terms of Phillip's constraint theory[10] and shall not concern us in this article.

In $Al_{20}Ge_xTe_{80-x}$ system, Ge-Te heteropolar bonds have the maximum strength and hence are more probable. So, as x increases, more and more Ge-Te bonds are formed and the network connectivity increases due to the crosslinking of Te chains. Thus, any rearrangement of the bonds to reach a higher conducting state becomes difficult which is reflected by the positive slope in Fig. 2 until $x = 7.5$, when the effect of chemical ordering takes over. With more heteropolar bonds, chemical disorder is reduced and therefore, charge carriers are less localized: The resultant increase in conductivity aids switching and accounts for the decrease in E_c between $x = 7.5$ and 12.5. After $x = 12.5$, there is again a proliferation of homopolar bonds which is due to Ge (and lack of Te) and E_c again increases. As mentioned earlier, all the glasses exhibited memory switching proving that network connectivity alone does not guarantee threshold switching characteristics.

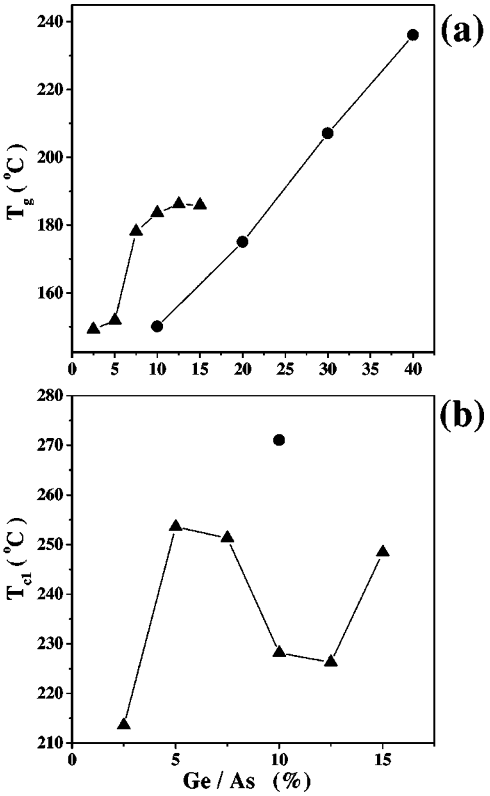

FIG. 3. Shows the composition dependence of (a) T_g in $Al_{20}As_xTe_{80-x}$ (circle) and $Al_{20}Ge_xTe_{80-x}$ (triangle) glass systems and (b) first crystallization temperature (T_{c1}) with composition for Al-Ge-Te (triangle). Note that for $x > 10$ in the Al-As-Te (circle) system the glasses do not crystallize (Ref. 7).

In $Al_{20}As_xTe_{80-x}$ system, Fig. 2 shows a distinct change in slope at $x = 20$, at which E_c shows a significant increase and continues so for all higher x. No minimum is observed in E_c versus x plot, indicating the absence of chemical order. The reason is the following: In the Al-As-Te system, As homopolar bond strength is much higher than any other possible bonds, and hence, has the highest probability for bond formation. So, as the As content is increased, its homopolar bond concentration increases and as a result the chemical disorder grows, along with bond energy. In this system, a crossover from memory to threshold switching characteristics at $x = 5$ was observed earlier.[3] Also, along two other composition tie-lines in the Al-As-Te glass system,

TABLE I. Bond energies of the possible bonds in the Al-Ge-Te, Al-As-Te, and Ge-As-Te systems (Ref. 11).

Bond	Bond strength $\mathrm{K\,J\,mol^{-1}}$
Ge-Te	456
As-As	382
As-Te	324.3
Al-Te	267.8
Ge-Ge	263.6
Te-Te	259.8
Al-As	202.9
Al-Al	133

TABLE II. Lists the type of switching in various binary, ternary, and quaternary Te-based glass systems.

Glass system	Type of switching	Reference(s)
As-Te	Memory	15
Ge-Te	Memory	16
Al-Te	Memory	2
Ge-As-Te	Memory	8
Al-As-Te	Memory and threshold	3,12
Si-Te-As-Ge	Memory and threshold	1
Al-Ge-As-Te	Memory and threshold	17

$\mathrm{Al}_x\mathrm{As}_{40}\mathrm{Te}_{60-x}$ and $\mathrm{Al}_x\mathrm{As}_{40-x}\mathrm{Te}_{60}$, in which a similar crossover with composition was observed,[12] no chemical ordering is seen. In the present bond picture, when As replaces Ge, chemical disorder prevails; and As is a necessary component in all threshold switching chalcogenide glasses. Is there a causal relationship?

To further strengthen the argument, consider the Ge-As-Te glass system, an interesting example of a ternary system in which both the crosslinking elements Ge and As are present. The composition dependence of E_c in $\mathrm{Ge}_{7.5}\mathrm{As}_x\mathrm{Te}_{92.5-x}$ system revealed the effect of network connectivity and chemical ordering and notably all the glasses in the system exhibited memory switching.[8] This perhaps complicated situation is understood better by our chemical bond picture. In this system, Ge-Te bonds have a greater bond strength than that of As-As and other bonds. Hence, the presence of homopolar bonds is considerably reduced and maximum chemical ordering is observed at $x=52.5$. Also, note from Fig. 2 that the drop in the E_c from A to B in the $\mathrm{Al}_{20}\mathrm{Ge}_x\mathrm{Te}_{80-x}$ is about 14 $\mathrm{kV\,cm^{-1}}$ whereas in $\mathrm{Ge}_{7.5}\mathrm{As}_x\mathrm{Te}_{92.5}$ (Ref. 8) it is only about 1.2 $\mathrm{kV\,cm^{-1}}$ which is a compelling evidence of the influence of As on chemical ordering. Further, the greater positive slope for Al-Ge-Te compared to Al-As-Te in Fig. 2, can be attributed to Ge-Te bond strength being greater than As-As.

Thermal stability. Figures 3(a) and 3(b) show T_g and T_{c1} as a function of composition for the Al-Ge-Te and Al-As-Te glasses. The difference $(T_{c1}-T_g)$, which represents the thermal stability of a glass, is distinctly greater for the As-based system as glasses in it do not crystallize with increasing As content. This is also reflected in their glass forming ability as can be seen in Fig. 2: The As-based system has a wider glass forming region and this could be ascribed to broken chemical order engendered by As, the evidence for which is to be found in Fig. 3(a): The S-shaped variation of $T_g(x)$ in $\mathrm{Al}_{20}\mathrm{Ge}_x\mathrm{Te}_{80-x}$ indicates network polymerization whereas its linear variation in $\mathrm{Al}_{20}\mathrm{As}_x\mathrm{Te}_{80-x}$ points to fragmentation[13] and a molecular phase separation due to homopolar bonds. The promotion of glass formation due to homopolar bonds has been earlier established, microscopically as well, using Mössbauer spectroscopy.[14] Furthermore, this evidence for broken chemical order supports the chemical bond picture developed in the previous subsection, where the absence of chemical ordering in Al-As-Te glass systems is understood as due to the increased presence of As-homopolar bonds and the electronic band picture to be developed in the next subsection to comprehend the memory and threshold switching phenomenon.

Models of electrical switching. The following simple inferences can be drawn from Table II, which serves to focus the attention on the correlation between presence of chemical disorder and threshold switching phenomenon: Threshold switching glasses are rare, occur in systems with at least three components and always contain As. Let us now briefly look at the existing understanding on memory and threshold switching phenomenon.

The irreversible memory switching is understood by a thermal model,[5] according to which switching occurs due to the formation of a crystalline conducting channel,[18] by using the energy provided by E_c. The reversible threshold switching has been ‘‘traditionally’’ understood by an electronic model[19]: When the carriers generated by the applied field completely fill up the unique charge traps, known as the valence alternation pairs (VAP), found in chalcogenide glasses, mobility and the concentration of the carriers suddenly increases resulting in the switch to the high conducting state.

Since there is no discernible difference in the I-V characteristics of the memory and threshold switching glasses[3] when they switch from the off to on state, the justification for different models for memory and threshold switching is not clear from the existing literature: The two classes differ only in their reaction to the removal of the field. In principle, since, VAP defect centers are also present in memory switching glasses, the above electronic model should be equally valid for memory switching as well.

Our view, considering the above arguments, is that threshold switching will be observed in glasses, in which crystallization is impeded; otherwise they exhibit memory switching phenomenon. We now look into the role played by As in this: In $\mathrm{Al}_{20}\mathrm{As}_x\mathrm{Te}_{80-x}$, for As concentration greater than 5% the glasses exhibit threshold switching[3] and it is observed that the number of I-V cycles for which this remains so before the glass ‘‘degrades’’ and gets locked permanently in the high conduction state, increases with As[12] and significantly, T_c also increases with As percentage and is higher than that of $\mathrm{Al}_{20}\mathrm{Ge}_x\mathrm{Te}_{80-x}$ glasses [Fig. 3(b)]. If T_c is less, the case with most memory switching glass, it becomes that much easier for the phase transformation, due to the Joule heat generated by the collision between the surging free electrons and the lattice. Therefore, we state that the *formation of a crystalline channel in a memory switching glass is only consequential* and probably not the reason behind switching. In this context, the present experiments have given an intriguing result: E_c of Al-Ge-Te glasses are greater than that of Al-As-Te glasses whereas T_c of Al-Ge-Te glasses are lower than that of Al-As-Te glasses, contradicting the thermal model of memory switching.

An electronic band picture is now presented, which clarifies, (i) why As-based glasses may not crystallize easily while switching, (ii) the role of chemical disorder (due to As) in threshold switching, and (iii) the results that contradict the thermal model of memory switching. This picture is a modified version of the three-dimensional (3D) model[4] of structure and electronic properties of chalcogenide glasses proposed 25 years ago. In this model, the lone-pair (LP) electrons, which are known to influence the electronic properties of chalcogenide glasses, play a crucial role. Chalcogens contain LP electrons in the *s* and *p* orbitals of the outer shell. Of the crosslinking elements As and Ge, only As possesses LP electrons.

In $Al_{20}As_xTe_{80-x}$, as we replace Te with As, according to the chemical bond picture, As homopolar bonds (chemical disorder) are formed. In such a situation, the repulsive interaction between the LP's present in the surrounding atoms will be very strong. This would catapult the nonbonding (LP) *s* orbital of As to higher energies such that its ionization energy becomes smaller. The LP orbitals which are positioned spatially and energetically by the covalently bonded surroundings, are distorted due to their interactions, resulting in a shift in their energy positions both lower and higher: A LP electron band is formed above the valence band. It is thus easier to excite electrons from this band rather than the valence band formed by the bonding orbitals. This LP band satisfies the demand for free electrons which leaves the ''underlying'' bonding structure unaffected: crystallization is prevented. Absence of structural change, when an electric field is applied on threshold switching materials, having a high percentage of As, is thus understood.

In $Al_{20}Ge_xTe_{80-x}$ system, as Te is replaced with Ge, LP electron concentration decreases and importantly, Ge-Te bond concentration increases, with the result, the LP-LP interaction among neighboring Te atoms is considerably reduced and the formation of LP band becomes difficult. Under these circumstances, the demand for free electrons is met by the valence band. This affects the bonding structure, leading to structural reorganization and crystallization that is observed in memory switching materials. Also, absence of an LP band coupled with high Ge-Te bond strength means that, to switch, greater energy or E_c is required, as the electrons have to be excited from the valence band, in contrast to the Al-As-Te system (Fig. 2).

In summary, the present electrical switching and thermal studies on $Al_{20}Ge_xTe_{80-x}$ glasses, (i) indicate that chemical disorder due to the presence of As homopolar bonds is crucial for the observance of threshold switching in chalcogenide glasses, (ii) contradict the thermal model of memory switching. The results are explained through a simple bond and band picture. Recent local structure studies on As-Te (Ref. 20) and Ge-As-Te (Ref. 21) glasses provide strong evidence for the presence of chemical disorder due to As. Similar studies on Al-Ge-Te and Al-As-Te systems are awaited.

We gratefully acknowledge discussions with E.S.R. Gopal, P.K. Thiruvikraman, J. Jacob, and B.M. Jaffar Ali. We thank Department of Science and Technology, Government of India for financial support.

---

*Present address: Department of Chemistry, Indiana University, Bloomington, IN 47405.

[1] S.R. Ovshinsky, Phys. Rev. Lett. **21**, 1450 (1968).

[2] S. Prakash, S. Asokan, and D.B. Ghare, Semicond. Sci. Technol. **9**, 1484 (1994).

[3] S. Murugavel and S. Asokan, J. Mater. Res. **13**, 2982 (1998).

[4] S. R. Ovshinsky and K. Sapru, in *Proceedings of the Fifth International Conference on Amorphous and Liquid Semiconductors*, Garmisch-Bartenkirchen, FRG, 1973, edited by J. Stuke and W. Brenig (Taylor and Francis, London, 1974), p. 447.

[5] D. Adler, Sci. Am. **236** (5), 36 (1977).

[6] R. Chatterjee, K.V. Acharya, S. Asokan, and S.S.K. Titus, Rev. Sci. Instrum. **65**, 2382 (1994).

[7] J. Colmenero and J.M. Barandiaran, Phys. Status Solidi A **62**, 323 (1980).

[8] R. Aravinda Narayanan, S. Asokan, and A. Kumar, Phys. Rev. B **54**, 4413 (1996).

[9] R. Aravinda Narayanan and A. Kumar, Phys. Rev. B **60**, 11 859 (1999).

[10] J.C. Philips, J. Non-Cryst. Solids **34**, 153 (1979).

[11] *CRC Handbook of Chemistry and Physics*, edited by D. R. Lide (CRC Press, Baton Rouge, 1998).

[12] S. Murugavel and S. Asokan, Phys. Rev. B **58**, 3022 (1998).

[13] M.B. Myers and E.J. Felty, Mater. Res. Bull. **2**, 535 (1967).

[14] W.J. Bresser, P. Boolchand, P. Suranyi, and J.P. de Neufville, Phys. Rev. Lett. **46**, 1689 (1981).

[15] S.S.K. Titus, R. Chatterjee, S. Asokan, and A. Kumar, Phys. Rev. B **48**, 14 650 (1993).

[16] P. Dargan, P. Burton, S.V. Phillips, A.S. Bloor, and P. Nesvadba, J. Mater. Sci. **9**, 1595 (1974).

[17] S. Prakash, S. Asokan, and D.B. Ghare, IEEE Electron Device Lett. **18**, 45 (1997).

[18] H. Fritzche, in *Amorphous and Liquid Semiconductors*, edited by J. Tauc (Plenum, London, 1974), p. 313.

[19] D. Adler, M.S. Shur, M. Silver, and S.R. Ovshinsky, J. Appl. Phys. **51**, 3289 (1980).

[20] Q. Ma, D. Raoux, and S. Bénazeth, Phys. Rev. B **48**, 16 332 (1993).

[21] P.E. Lippens, J.C. Lumas, J. Olivier-Fourcade, and L. Aldon, J. Non-Cryst. Solids **271**, 119 (2000).