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Electrical switching and short-range order in As-Te glasses

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The local structural order in chalcogenide network glasses is known to change markedly at two critical compositions, namely, the percolation and chemical thresholds. In the As_xTe_{100-x} glassy system, both the thresholds coincide at the composition $x=40$ (40 at. % of arsenic). It is demonstrated that the electrical switching fields of As-Te glasses exhibit a distinct change at this composition.

Recent theoretical and experimental investigations on chalcogenide glassy semiconductors reveal the existence of two critical compositions, namely, the percolation and chemical thresholds, connected with the local structural order in the material. The percolation (or mechanical) threshold refers to the composition at which the material undergoes a transformation in the structural rigidity.[1-3] The chemical threshold corresponds to the stoichiometric composition of the system, at which chemical ordering takes place.[4] In glassy systems like Ge-Te, Si-Te, Ge-Se, etc., the chemical and mechanical thresholds occur at different compositions. Anomalies in physical properties such as density,[5,6] dielectric constant,[7] optical band gap,[8,9] ultrasound attenuation,[10] conductivity activation energy,[11,12] high-pressure resistivity behavior,[4,12,13] etc. have been found to occur in these systems at both the threshold compositions. In the As_xTe_{100-x} glassy system, it is interesting to note that the percolation and chemical thresholds coincide at the composition $x=40$. The present studies indicate that there is a sharp change in the electrical switching fields of As-Te glasses at the $x=40$ composition.

Bulk, semiconducting As_xTe_{100-x} glasses $(25<x<60)$, were prepared by the melt quenching method and their glassy nature was confirmed by x-ray diffraction and differential scanning calorimetry. The I-V and switching characteristics of these glasses were studied using a personal computer (PC) based system. Samples polished to about 0.2-mm thickness were mounted between a flat plate and a point-contact electrode. A constant current was passed through the sample, and the voltage developed across the sample was measured. The details of the system and the experimental procedures[14] are described elsewhere.

The current-voltage and electrical switching characteristics of As_xTe_{100-x} glasses are shown in Fig. 1 for a representative composition $As_{32}Te_{68}$. The behavior is similar for other compositions. The "off" state electrical resistivity of as-quenched As_xTe_{100-x} glasses, measured by four probe technique, is of the order of $10^6\ \Omega\,cm$. With the increasing current, the voltage across the samples initially increases linearly (Fig. 1). Near a critical field (E_t), corresponding to a critical current, the samples show a small nonlinearity. At the critical field, the samples start exhibiting a current-controlled negative resistance behavior. The negative resistance behavior eventually leads to a very low-resistance "on" state (the dynamic resistance being almost zero), and the samples are latched in that state. The samples do not revert to the initial high-resistance state even if the applied current is reduced to zero. This indicates that the As_xTe_{100-x} glasses studied exhibit a current-controlled negative resistance behavior with memory. In the low-resistance state, the I-V characteristic is linear for higher currents, and a slight deviation is observed from linearity for lower currents (Fig. 1).

A significant feature of the present experiments is the composition dependence of the critical field E_t of As_xTe_{100-x} glasses, as shown in Fig. 2. It is found that the switching fields increase linearly with the increase in arsenic content. Further, a sharp change in the slope of E_t versus the concentration curve is observed at a composition $x=40$. It is very interesting to note that the variation of switching fields of As_xTe_{100-x} glasses with

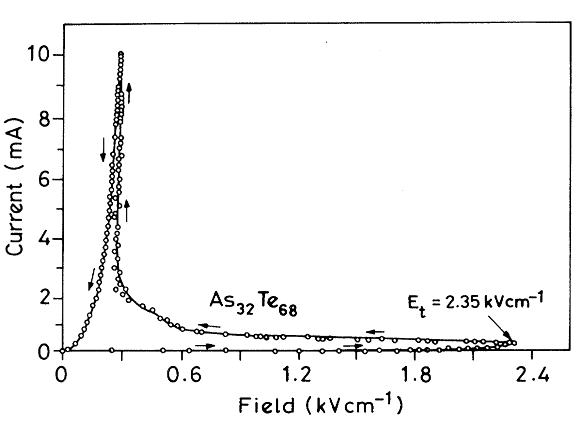

FIG. 1. I-V characteristics of a representative $As_{32}Te_{68}$ glass.

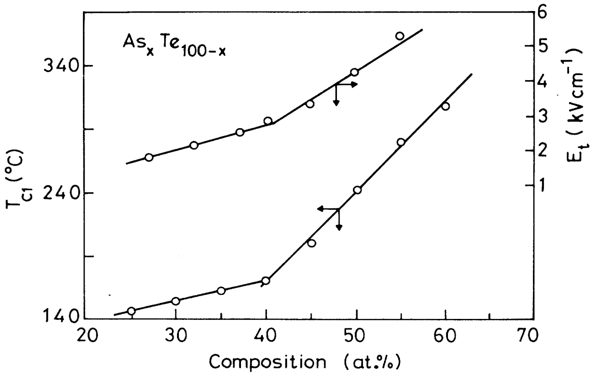

FIG. 2. Composition dependence of the electrical switching fields (E_t) and crystallization temperature (T_{cl}) of As_xTe_{100-x} glasses. The open circles represent the experimental data points, and the solid lines are the guides to the eye.

composition displays a striking similarity to the composition dependence of the thermal crystallization temperature (T_{cl}) of these glasses. T_{cl} of As_xTe_{100-x} glasses increases linearly[15] with composition (x), exhibiting a similar change of slope at $x=40$ composition (Fig. 2). The strong correlation between the crystallization temperatures and the switching fields of As-Te glasses confirms the idea that the memory switching of chalcogenide glasses involves the crystallization of the material. The increase in T_{cl} is suggestive of the increase in the thermal stability against devitrification of the glasses. Hence the composition dependence of memory switching fields of As-Te glasses follows the composition dependence of the crystallization temperatures.

The sharp change of slope occurring in E_t and T_{cl} can be attributed to the local structural effects in the glass. It is known that in $A_x\mathrm{VI}_{100-x}$ chalcogenide glassy semiconductors ($A=$Ge, Si, As, etc.), the regions of bulk glass formation usually involve a large amount of twofold-coordinated chalcogen atoms. The local structural order in these glasses is essentially one dimensional, consisting of distorted chalcogen atom chains which are weakly interlinked by the higher coordinated additive atoms. These glasses are elastically floppy, as they can be compressed easily without costing much energy. When the concentration of the higher coordinated A-type atoms increases, the network becomes more and more cross linked,[1-3] and it becomes rigid. The floppy to rigid transformation in chalcogenide network glasses is identified as a percolation transition, commonly known as the "rigidity percolation,"[1-3] occurring at a definite composition "x_c." The composition x_c depends on the coordination of the constituent atoms and is 20 for $\mathrm{IV}_x\mathrm{VI}_{100-x}$ glassy systems, and 40 for $\mathrm{V}_x\mathrm{VI}_{100-x}$ glassy systems.

The stoichiometric composition of a glassy system is also critical like the rigidity percolation threshold, as there is a change in the local structural order at this composition.

As mentioned earlier, the percolation and chemical thresholds coincide in the As_xTe_{100-x} glassy system at $x=40$ composition. Though it will be difficult to separate the contributions of the chemical ordering and the rigidity percolation, unusual property variations can be expected in As_xTe_{100-x} glasses at this composition due to both the effects. Earlier investigations of these glasses indicate anomalies in properties such as microhardness,[16] high-pressure resistivity,[17] thermal crystallization,[15-18] thermal diffusivity,[19] etc. at the $x=40$ composition. The present investigations indicate clearly that there is a pronounced change in the electrical switching fields of As-Te glasses at this composition. Such a remarkable change in the electrical switching fields at the critical threshold composition has to our knowledge not been observed so far in any other chalcogenide glassy system.

It is more likely that the rigidity percolation, rather than the chemical ordering, induces the sharp increase in the electrical switching field at $x=40$. During the crystallization of a glass, atoms and molecules have to reorient themselves. If the network is more and more rigid, the atomic readjustments will become more and more difficult. Consequently, the magnitude of external parameters (like temperature, electric field, etc.) needed to induce crystallization may be enhanced noticeably at the rigidity percolation threshold. Hence there is a sharp increase in the crystallization temperature and memory switching field at the $x=40$ composition.

The above idea needs to be corroborated in glasses for which the rigidity and chemical ordering thresholds differ distinctly.

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