

Differential thermal analysis, structure and switching of thin chalcogenide films

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Differential thermal analysis (DTA) and electron diffraction techniques have been used to characterize thin chalcogenide alloy films by comparison with the properties of bulk alloys from which they were deposited. It is shown that the DTA technique is a valuable adjunct to structural studies on thin films since it helps to differentiate between the two non-crystalline states, amorphous and vitreous or glassy. It is observed that the former does not produce reproducible reversible threshold switching from a high impedance to a low impedance state whereas the latter does.

1. Introduction

Unusual methods of preparing glasses, for example, precipitation and sublimation [1] and splat cooling [2] have proved to yield glass transition temperatures (T_g) as measured by differential thermal analysis (DTA) which were, within the experimental error, the same as those obtained on glasses of the same composition produced by standard techniques. Because the threshold voltage at which amorphous semi-conducting alloys switch from a high to a low impedance state both in bulk [3] and thin film form [4] has a strong correlation with T_g it is pertinent to compare the structure and thermal properties of both bulk glass and thin films sputtered from that glass. As yet there does not appear to be enough data in the literature to say whether or not this is a second order correlation, T_g being related to the materials band gap (E_g) and hence to the threshold voltage so that the primary correlation is to E_g . But preliminary unpublished RRE data indicates that two materials with the same T_g can have very different E_g .

Two basic types of switches exist [5]:

(i) A memory switch, which at a specific threshold voltage V_T converts from a high impedance state to a permanent, stable, low impedance ON state which is generally considered to be crystalline and requires no power to remain in that state. The device is reset to the high impedance state with a high current pulse.

(ii) A threshold switch which again switches from a high impedance to a low impedance state at V_T but requires a holding current, i_H , and a commensurate holding voltage V_H to keep the device in the ON state. In general, provided that the current in the ON state is not too large, and short pulse lengths are applied, memory switches can be operated in the threshold mode. Memory switches, since crystallization is a necessary property, in the main come from the boundary of a glass forming region whilst threshold switches are manufactured from more stable glasses near the centre of such a region. In Fig. 1 this region is shown schematically for the GeTeAs system [6]. Apart from the obvious importance of crystallization processes in thin film samples, certain film compositions, although shown to be amorphous by transmission electron diffraction, could only be switched once from the high impedance to the low impedance state and could not be reset with a high current pulse so that it was necessary to characterize the difference between these compositions and switching compositions by some other technique.

Several questions arise, for example, is there a significant difference between the amorphous and glassy state and, if so, is the amorphous state really amorphous or microcrystalline? Dixmier and Guinier [7] have shown that experimentally the difference between the latter two cases can be elucidated despite each having an apparently amorphous diffraction pattern,

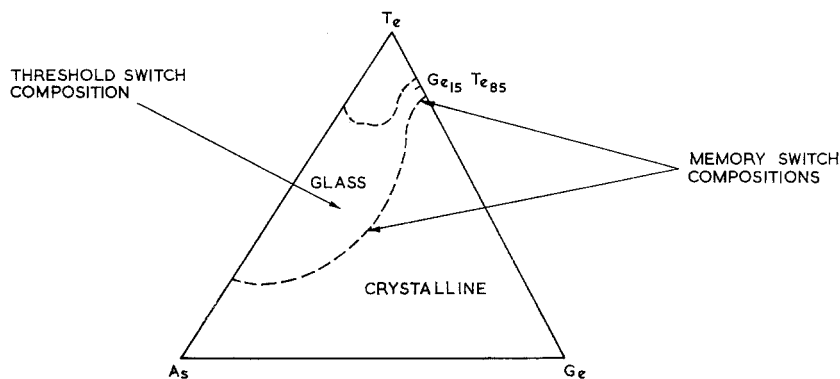


Figure 1 Glass forming region of GeTeAs system (schematic after [6]).

i.e., a diffraction pattern composed of a small number of broad rings. The former question has been broached by Bagley *et al* [8]. For a material to be defined as a glass (an amorphous solid formed by continuous solidification of a liquid in the normal definition), it is not sufficient to show that the solid has an amorphous diffraction pattern, some other classification like the change in viscosity or the heat absorbed or evolved as the temperature of the material is raised, which is preferably cyclable, is necessary. Because of the difficulties in making large amounts of material in thin film form DTA was chosen to highlight any differences between different film compositions, particularly whether or not a T_g existed in the films. Bagley *et al* note, however, that the absence of a T_g does not in itself prove the material is different from a glass. For example, T_g and the crystallization temperature, T_x may coincide or like some organic glasses, T_g may be below 0°C , a temperature range not covered in the present experiment. It is unusual to find glass transition temperatures in inorganic systems below 0°C . Furthermore, in the chalcogenide glasses, a T_g greater than 450°C is rare.

Another important point, following the usual definition of a glass, is that the solid-liquid transition is reversible, that is, it takes place in thermal equilibrium. This must be contrasted with the amorphous-polycrystalline transition which is irreversible [9] indicating that the amorphous state is much more unstable than the vitreous state. Furthermore, since the liquid state of Ge exhibits metallic-like conduction whereas both the amorphous and crystalline forms are semiconductors, it is not necessarily correct to equate the amorphous state with the liquid state in terms of structure and other

physical properties; to call it "liquid-like" can be a misnomer. In general in alloy systems, amorphous phases are found in the vicinity of eutectic compositions [10] i.e. in regions of low liquidus temperature, but there is little experimental phase diagram data in the amorphous-vitreous state nor theoretical guide lines on which to build.

2. Experimental details

Reasonable control of bulk to film stoichiometry is achievable by rf sputtering even from four component alloys of the chalcogenides [11], although the low sputtering yield of elements like Si and Al can cause some problems. A range of substrate temperatures from 77 to 700 K was available in the apparatus but in general, liquid nitrogen or water-cooled substrates were used. Transmission electron diffraction (AEI EM6) was done by floating the films ($\leq 1000\text{\AA}$) off substrates either in 2% HF or by precoating the substrates with boric oxide and floating off in water. For DTA, films of the order of $5\ \mu\text{m}$ thick were required to give sufficient material for the ΔT range $0.2^\circ\text{C}/\text{in.}$ of a Du Pont 900 console and differential scanning calorimeter cell [6] (RT to 600°C).

In general, DTA should be done at the same rate as the quench rate of the glass but this is obviously impossible with thin films which have an apparently high quench rate. The sensitivity of T_g to the rate of temperatures rise is illustrated in [1], for example, where T_g does not seem to vary too widely for As_2S_3 glass made by different methods if the measurement is done at the same heating rate.

Because of the well-reported phenomena of surface crystallization in the chalcogenides due

to the change in stoichiometry of the surface layers when heated in oxygen or water vapour, any post deposition heat-treatment must be done in ultra-pure argon or in a vacuum which experimentally was found to be less than 10^{-5} torr. Great care must be taken to avoid crystallization due to the electron beam during transmission experiments.

Elemental and binary compositions were generally produced by electron beam evaporation in a well trapped oil diffusion pumped system whilst glasses which were easy to make in large quantities were rf sputtered. Some materials, particularly memory glasses, could only be made as a glass in very small quantities by quenching 2 g melts in liquid nitrogen so that it was preferred to cast these in the crystalline form and use DC triode sputtering.

3. Results

3.1. Amorphous elements: Ge, Si, Se

3.1.1. Ge, Si

The problems associated with varying deposition conditions affecting the properties of amorphous elemental films have been discussed recently by Theye [12] and Chopra and Bahl [13], for example. Deposition conditions employed in this case were outlined in a previous publication [14] and are compatible with their findings. DTA on these two materials showed no sign of a T_g up to 500°C only a crystallization peak at 320°C for Ge which is typical of the amorphous-polycrystalline transition temperature in that material, the crystallization temperature (about 800°C) of amorphous silicon, hereafter a-Si, being higher than the maximum available on the apparatus. This result is consistent with the reported calorimetric data of Chen and Turnbull [15]. It is conceivable that T_g and T_x coincide due to the breadth of the crystallization peak. Unlike the true glasses to be reported later, the amorphous state could not be regained by quenching from the melt even into liquid nitrogen, i.e. the amorphous films were in a less stable state. Furthermore, it proved to be impossible to switch either a-Ge or a-Si repeatedly. The films went into the memory state at a specific breakdown field even when care was taken to limit the current at switch on by a high load resistance, e.g. 47 k Ω , in series with the device to limit the ON current to less than 1mA. Typical field values are given in Table I together with an approximate band gap [16]. This "memory" state could not be erased with a high

TABLE I

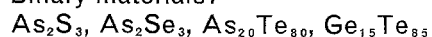
Material	E_g in eV	E_T volts cm^{-1}	Comments
a-Si	1.6	9×10^4	Could not be reset after one switch to high conductivity state. Material is amorphous
a-Ge	1.2	7×10^4	As above
Se	2.5	10^7	Destructively switched open circuit, blew top contacts. Single phase glass
As_2S_3	2.1	10^6	As Se case
As_2Se_3	1.5	2×10^5	Some switching. Tendency to be diphasic
$\text{As}_{20}\text{Se}_{30}\text{Ge}_{30}$	Not known	5×10^5	Some switching. Tendency to be diphasic
$\text{Ge}_{15}\text{Te}_{31}\text{Al}_4$	0.8	6×10^4	Reproducible switching, diphasic, partly crystalline
$\text{Ge}_{10}\text{Si}_{12}\text{Te}_{48}\text{As}_{30}$	1.0	9×10^4	Reproducible switching Diphasic films produced

current pulse as normal chalcogenide memory switches can; only complete device destruction occurred.

3.1.2. Se

In contrast to a-Ge and a-Si it is possible to prepare vitreous Se in bulk as well as thin film form. DTA data yields a definite T_g at 47°C (Fig. 2), at a heating rate of 20°C per min which is close to the usually quoted value for bulk (42°C [17]). The exothermic peak at 102°C is probably associated with the nucleation and crystallization processes which have been shown to occur above 70°C [18] rather than any polymerization transition which has been found to occur at 360 K [17]. The melting point endotherm at 210°C is a little lower than the usual bulk value of 220°C . Once again, it proved impossible to switch the material repeatedly; complete dielectric breakdown only was observed at a high value of electric field (Table I).

3.2. Binary materials:



3.2.1. As_2S_3

No evidence of crystallization was seen by

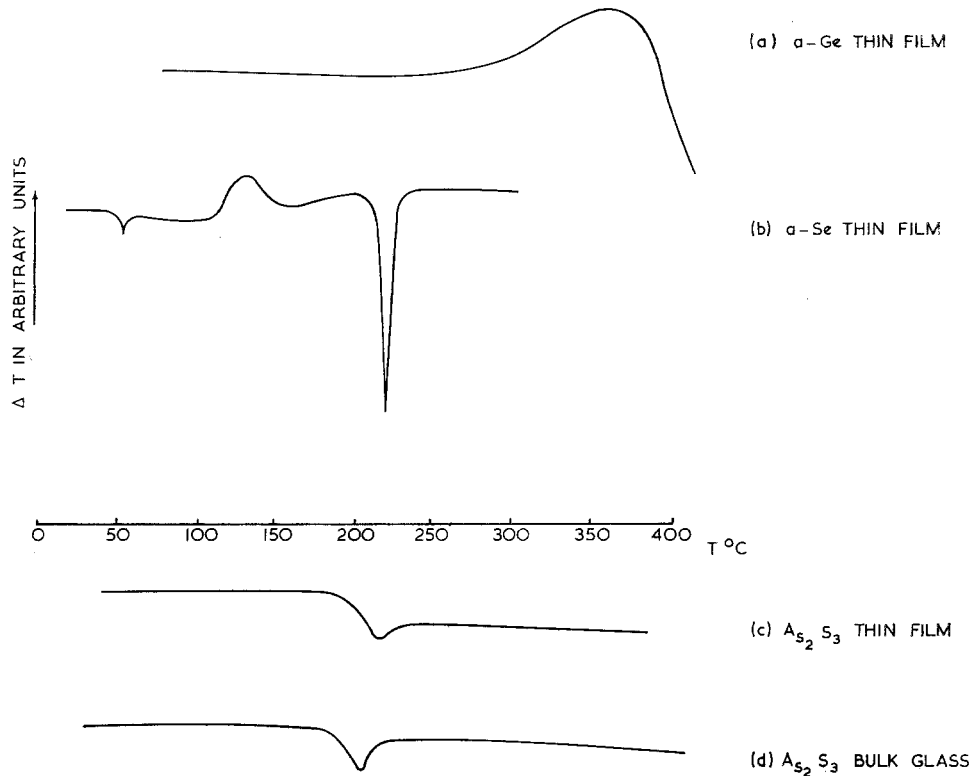
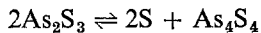


Figure 2 Differential thermal analysis traces of (a) Amorphous Ge thin film at a heating rate of 20°C per min. (b) Se thin film at 20°C per min. (c) As₂S₃ thin film at 20°C per min. (d) As₂S₃ bulk glass at 5°C per min.

electron microscopy on annealing thin film samples up to 400°C, the films being homogeneous on 16000 times magnification. Furthermore, breakdown again occurred when attempts were made to switch thin film samples of the material sandwiched between electrodes. It has been pointed out [19] that in laser irradiation of As₂S₃ the likely outcome is the following reaction:



Also, As₂S₃ seems to be the least likely of the glasses under discussion to phase separate; good homogeneous glass and thin films are relatively easy to prepare provided that the stoichiometric composition is achieved, otherwise microheterogeneities occur [20]. X-ray fluorescence and β-probe analysis of the films showed that they were stoichiometric to within the accuracy on the experiment. The DTA data (Fig. 2) confirms the electron diffraction result showing no crystallization peaks up to 500°C. The T_g is somewhat lower than both the precipitated and melt quenched data of Onodera *et al* [1] but is slightly higher than the bulk starting material which was

188°C. It would seem therefore that like pure Se, As₂S₃ films behave like their bulk glass equivalents and that the differences in apparent quench rates between film and bulk do not have a very large effect on their glass transition temperature. The heating rates were 20°C per min for the film and 5°C per min for the bulk.

3.2.2. As₂Se₃

This glass in bulk form is readily crystallizable with a well defined T_x at 314°C and a T_g at 180°C. The thin film on the other hand only has a hint of a T_x just before the melting point of 367°C, which is confirmed by the fact that transmission electron diffraction showed only a slight hint of crystallization on annealing. The apparent lack of film structure in transmission electron diffraction would imply little or no second phase (Fig. 3). However, unlike As₂S₃, etching the films did reveal areas of different etch rates. The T_g of the film was slightly higher than the bulk, being 185°C as with As₂S₃ but again there was the same difference in the heating rate as the As₂S₃ case. Coultts and Levin [21]

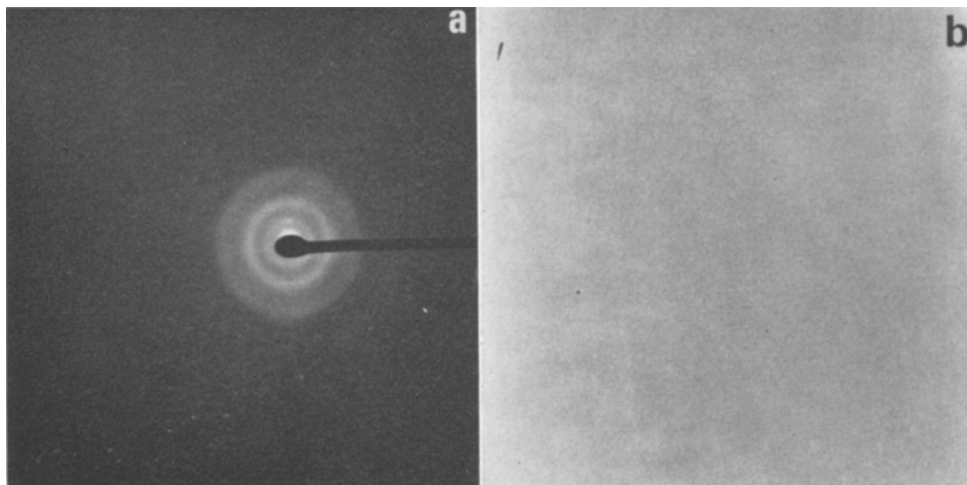


Figure 3 Transmission electron diffraction pattern and photomicrograph of As_2Se_3 thin film at room temperature. (a) Typical diffuse electron diffraction pattern. (b) Photo-micrograph (16000 times magnification).

reported that untreated As_2Se_3 films show no structure on transmission electron diffraction and that heat-treatment caused no change, so that the results reported above are consistent with their result. It is difficult to explain this conflict between DTA and transmission electron diffraction since crystallization is readily achievable in bulk material. On the other hand it proved relatively easy to switch the film and to produce a reversible memory transformation, so that the switching action obviously produces crystallization. However, the reproducibility in V_T and the overall switch lifetime were poor, the latter being of the order of 100 operations only.

3.2.3. $\text{As}_{20}\text{Te}_{80}$

The extent of the glass forming region in this system has been reported previously [6] (see Fig. 1). By quenching at room temperature from the melt, it proved to be impossible to make $\text{As}_{20}\text{Te}_{80}$ as a glass. If however the material is sputtered or evaporated onto cold substrates then an amorphous layer is produced when observed in transmission electron diffraction (Fig. 4). DTA confirms that this is a glassy layer with a $T_g = 91^\circ\text{C}$ followed by a well-defined crystallization peak at 129°C and two subsidiary ones at 212 and 268°C ; these latter two are also mirrored in the melting endotherm. Liquid nitrogen quenching of the bulk shows a very similar result on DTA at $5^\circ\text{C}/\text{min}$ compared with $20^\circ\text{C}/\text{min}$ for the film: $T_g = 84^\circ\text{C}$, $T_{x1} = 117^\circ\text{C}$, $T_{x2} = 207^\circ\text{C}$, $T_{x3} = 252^\circ\text{C}$ and

$T_{mp} = 363^\circ\text{C}$. (See Fig. 5.) Annealing studies reveal that the first peak is due to nearly pure Te but the quantities of material associated with the secondary peaks prevented positive identification (Fig. 4). Like the well-documented eutectic $\text{Ge}_{15}\text{Te}_{85}$, these films switch both in the memory and threshold modes depending upon the input power in the on state and behave in a more regular manner with a much longer life than the As_2Se_3 films. The As-Te phase diagram [22] shows that a eutectic occurs at the composition $\text{As}_{20}\text{Te}_{80}$. The importance of eutectic points in the generation of amorphous phases has been outlined above (see [10]).

3.2.4. $\text{Ge}_{15}\text{Te}_{85}$

This eutectic composition can be made in the vitreous state in bulk samples by quenching at liquid nitrogen temperatures [6], with a T_g of 131°C , T_x of 217°C and $T_{mp} = 379^\circ\text{C}$ at a scan rate of 20°C per minute. Films deposited onto a water-cooled substrate from a crystalline target by DC triode sputtering or from a glass phase by RF sputtering showed similar behaviour with a $T_g = 137^\circ\text{C}$ and $T_{mp} = 375^\circ\text{C}$. However, although the primary crystallization peak was comparable to the bulk value being at 210°C for the film, a satellite exotherm appears at 250°C in the case of the film when scanning at the same rate on DTA (Fig. 5). Transmission electron diffraction reveals that the primary peak is due to almost pure Te, whereas the higher temperature exotherm is associated with $\text{Ge}_{50}\text{Te}_{50}$ as would be

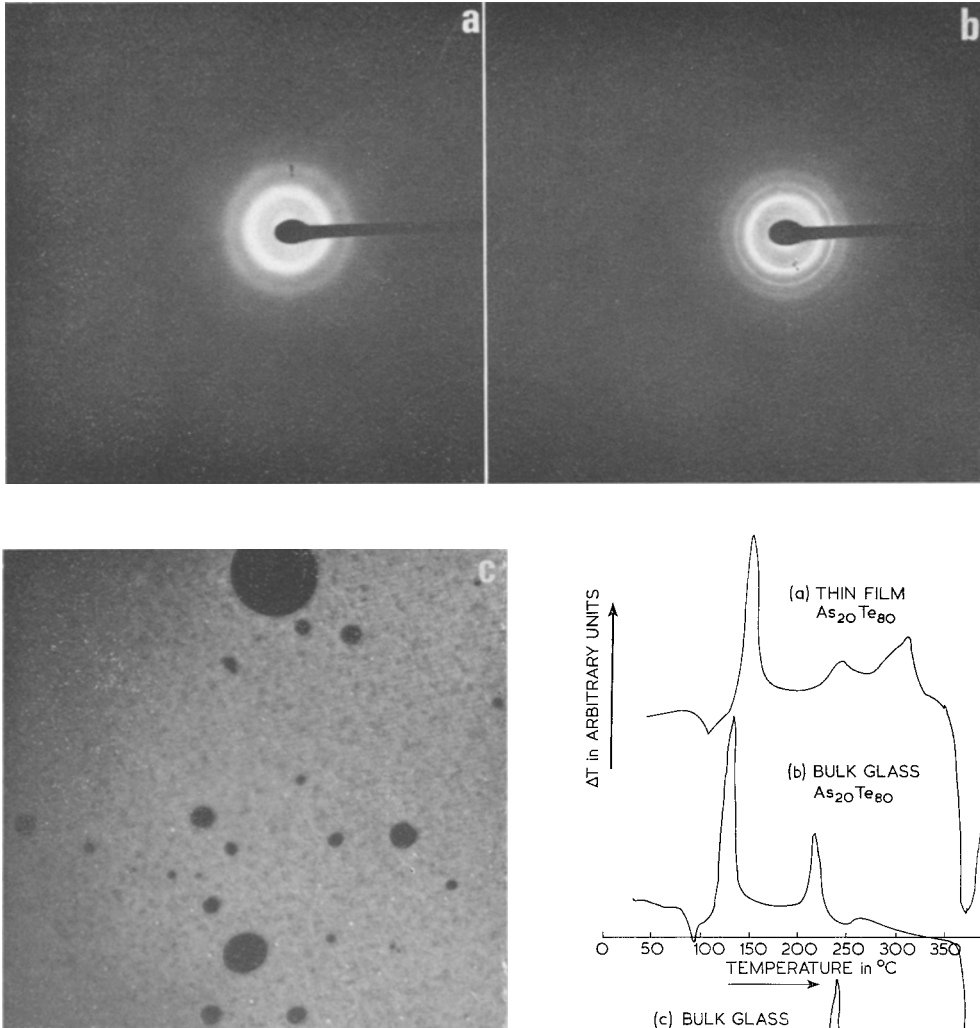


Figure 4 (a) Transmission electron diffraction of $As_{20}Te_{80}$ thin film at room temperature. (b) Same film after 1 h anneal between 270 and 300°C. (c) Photomicrograph of the film after annealing as (b) (16000 times magnification).

expected although the analysis of the diffraction spots is ambiguous. If, however, stoichiometry is not achieved, then both for Te rich films, greater than 95 at. % Te and for films in the region $Ge_{20}Te_{80}$ to $Ge_{50}Te_{50}$, the DTA showed no sign of a T_g only crystallization followed by melting. Even on melting followed by rapid cooling the films remained crystalline, so that in rapidly quenched films there is only a limited glass forming region around the $Ge_{15}Te_{85}$ eutectic. Amorphous films can be made but they are much less stable. The extent of this vitreous region seems to be consistent with the splat-cooled data [23].

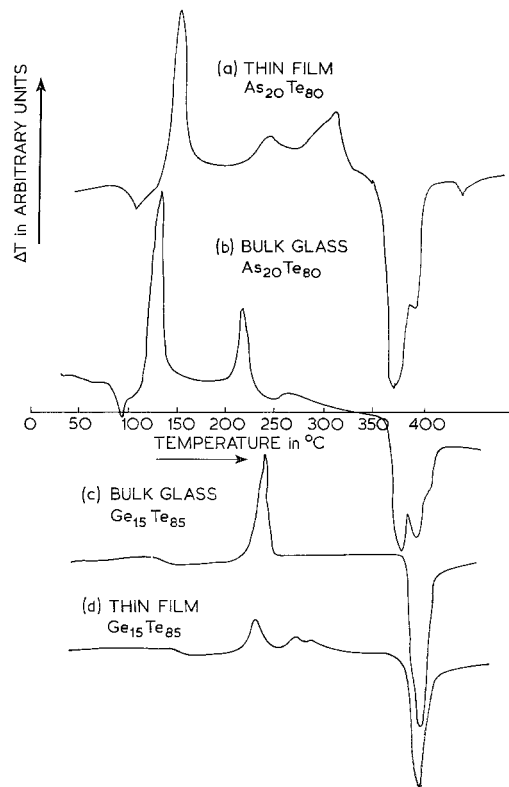


Figure 5 DTA traces of: (a) $As_{20}Te_{80}$ thin film. (b) $As_{20}Te_{80}$ bulk glass. (c) $Ge_{15}Te_{85}$ bulk glass. (d) $Ge_{15}Te_{85}$ thin film. Thin film heating rate 20°C per min, bulk glass 5°C per min.

The fact that Te rich films readily crystallize is consistent with the fact that pure Te films can only be made amorphous by deposition onto liquid nitrogen substrates becoming crystalline on anneal at about 10°C. Differences in crystal-

lization temperatures of powdered and bulk glass have been emphasized recently by Takamori *et al* [24] for the $\text{Ge}_{15}\text{Te}_{81}\text{As}_4$ system so that some disagreement between film and bulk is to be expected. Films outside of this narrow glass forming region could only be switched destructively into the memory state, whereas within the glass forming region both threshold and memory operation was obtained and the device could be readily cycled between the on and off states in the memory mode.

3.3. Ternary compositions:

$\text{Ge}_{15}\text{Te}_{81}\text{Al}_4$, $\text{Ge}_{10}\text{Te}_{35}\text{As}_{55}$, $\text{Ge}_{30}\text{As}_{20}\text{Se}_{50}$
and $\text{As}_{40}\text{Se}_{40}\text{Te}_{20}$

3.3.1. $\text{Ge}_{15}\text{Te}_{81}\text{Al}_4$

Compositions based on the $\text{Ge}_{15}\text{Te}_{85}$ eutectic have been reported to give good memory switch characteristics [25]. A wide variety of additions to the basic eutectic will switch in this fashion. The one reported here is difficult to make in thin film form because of the low sputtering rate of Al, so that the film composition approaches the $\text{Ge}_{15}\text{Te}_{85}$ eutectic with only a little Al present (0.2 wt %). The T_g of this film was 140°C , followed by crystallization at 202°C and melting at 369°C compared with the bulk values of 142, 248 and 368°C respectively. The films switched reproducibly for greater than 10^5 operations in both threshold and memory modes despite the fact that the as-prepared films often contained crystalline nuclei visible in a polarizing microscope.

3.3.2. $\text{Ge}_{10}\text{Te}_{35}\text{As}_{55}$

Memory switch compositions of this type generally crystallize into several components with the crystallization temperature approaching the onset of melting in bulk form [6]. The bulk values of T_g , T_x and T_{mp} were 213, 338 and 359°C respectively compared with 215 and 360°C for T_g and T_x respectively for the film. The onset of melting was inseparable from the crystallization exotherm (Fig. 6). The material readily crystallized in the electron beam of the EM6 electron microscope (Fig. 7). These films, which were obviously diphasic (see the photomicrograph of the annealed film in Fig. 7), switched well both in the memory and threshold modes.

3.3.3. $\text{Ge}_{30}\text{As}_{20}\text{Se}_{50}$

Pinto and Ramanathan [26] have recently reported memory switching in a glass of this composition despite the fact that neither DTA nor

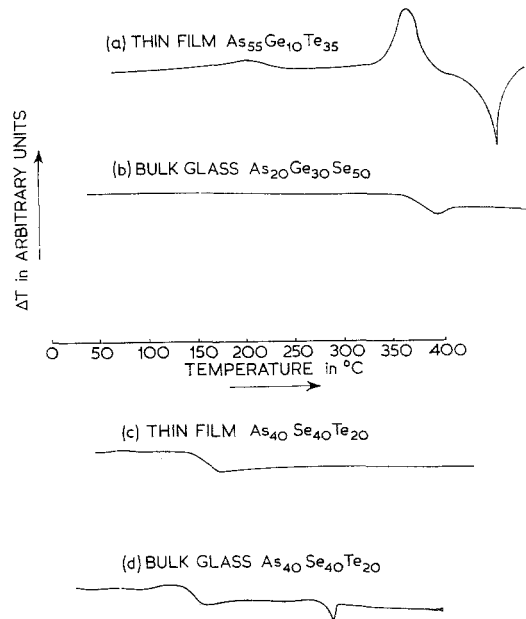


Figure 6 DTA traces of: (a) Thin film of $\text{As}_{55}\text{Ge}_{10}\text{Te}_{35}$. (b) Bulk $\text{As}_{20}\text{Ge}_{30}\text{Se}_{50}$. (c) Thin film $\text{As}_{40}\text{Se}_{40}\text{Te}_{20}$. (d) Bulk $\text{As}_{20}\text{Se}_{40}\text{Te}_{20}$.

X-ray diffraction showed any sign of crystallization. DTA on bulk samples measured by us likewise showed no evidence of crystallization (Fig. 6) up to 550°C , neither did transmission electron diffraction of annealed thin films. However, it is possible to switch the films into the memory state confirming Pinto and Ramanathan's result. The enhancement of the rate of phase separation of a glass when subjected to high electric fields has been pointed out by de Vekey and Majumdar [27] and at high temperatures under the influence of an electric field the presence of cristobalite was inferred in a silica glass sample [28]. This crystallization enhancement in an electric field could be the key to achieving the memory state in $\text{Ge}_{30}\text{As}_{20}\text{Se}_{50}$ when heating alone will not do so. However, in some cases, in the relatively high field strengths involved in switching this material (Table I), electrode damage could be seen even with molybdenum electrodes so that it requires further work to confirm that electrode transport is not taking place.

3.3.4. $\text{As}_{40}\text{Se}_{40}\text{Te}_{20}$

Unlike the $\text{Ge}_{30}\text{As}_{20}\text{Se}_{50}$ alloy, this material showed a hint of a crystallization exotherm in the bulk at 250°C . DTA at 20°C per minute on

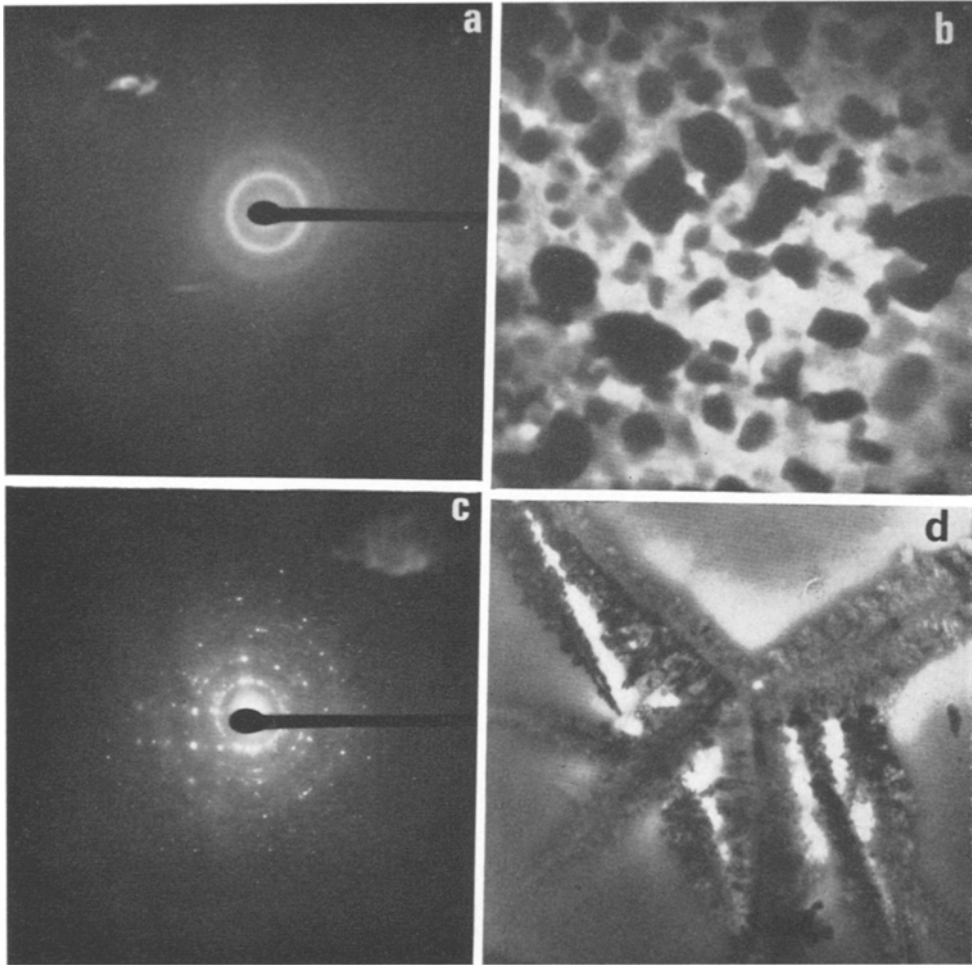
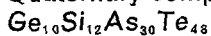


Figure 7 Electron diffraction patterns of $\text{Ge}_{10}\text{Te}_{35}\text{As}_{55}$ thin films; (a) Room temperature transmission diffraction patterns. (b) Photomicrograph of same film after 300°C anneal (16000 times magnification). (c) Transmission diffraction pattern after annealing. (d) Photomicrograph of the film after crystallization by the electron beam (16000 times magnification).

thin film samples gave a T_g of 150°C compared with 138°C for the bulk material at 5°C per minute. However, unlike the bulk glass, there was no sign of crystallization and associated melting but, like the $\text{Ge}_{30}\text{As}_{20}\text{Se}_{50}$ alloy, the film could be switched into the memory mode. Annealing for 1 h at greater than 300°C did produce some evidence of crystallization in thin film samples when viewed in transmission electron diffraction. The switching was much more erratic than the GeAsTe alloy devices.

3.4. Quaternary composition:



This composition has been widely reported as a
1242

suitable material for threshold switch manufacture. The mode of operation of threshold switches is still, unlike the memory switch, a matter for debate. It is generally agreed that the memory action is due to a crystalline filament which provides a locked on low resistance path in the on state of the device. Hence to obtain good stable threshold switching this latter mode of operation should be inhibited and a glass which is stable to crystallization chosen (unless electric field effects are important).

The composition of the film showed some loss of Si compared with the bulk alloy [11] but this did not change the T_g of the film significantly, it being 220°C compared with 223°C for the bulk

at the same heating rate of 20°C per minute. There was similarly little evidence in transmission electron diffraction of any crystallization but possibly some sharpening of the diffuse rings. On the other hand, if the anneal was performed at a pressure greater than 10⁻⁵ torr, crystallization readily occurred and was mirrored by a sharp increase in conductivity. Currents of greater than about 5 mA dc in the ON state for long periods of time can also convert the material into the crystalline or memory state.

4. Conclusions

Unless T_g coincides precisely with T_x or is below room temperature, and therefore out of range of the apparatus, it would seem from the above results that there is a distinction between the two non-crystalline states, amorphous and vitreous or glassy, in line with the theoretical ideas of Stevels [29]. Furthermore, this distinction is of more than academic interest since it is mirrored in the switching behaviour of the material. It seems that reproducible switching also requires a tendency on the part of the material to phase separate, see Table I. Crystallization may be enhanced by the presence of an electric field so that some materials can be switched into the memory state when heating alone will not do so. Devices made from Se alloys, which in general have a wider band gap than the equivalent Te alloy system, tend to have shorter lifetimes and break down more readily.

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