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Glass Forming Region and DTA Survey in the Ge-As-Te Memory Switching Glass System

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The glass forming region for 2.0 gm melts in the Ge-As-Te system is reported together with a comparison of glass transition temperatures and metastable glass melt crystallisation temperatures for bulk glass pieces of different compositions, heated at 20° C/min under standardised conditions in a nitrogen atmosphere. The crystallisation characteristics of certain compositions are correlated with published compositional data on device quality memory switches.

1. Introduction

The work of S. R. Ovshinsky [1, 2] has shown that switching devices can be made from bulk glasses or thin films of a variety of compositions taken from chalcogenide glass forming systems. These glasses consist of the Group VIa elements S, Se and Te of the periodic table combined with Group IVa elements Si and Ge and Group Va elements P, As or Sb plus, in some cases, Group IIIa elements such as Tl or Ga. Amorphous semiconductor compositions can thus be made from binary, ternary or quaternary systems and there have been many device and materials studies reported in the literature. In particular the two systems most often quoted are Ge-As-Te and Si-Ge-As-Te from which can be made the "Memory" and "Threshold" switching devices respectively. The mechanism of operation of these devices is controversial in that there are electronic [3] thermal [4] and structural models [5], but it is possible that more than one mechanism is operating depending on device geometry, mode of operation and chemical composition. However, there is a basic difference between the two devices after switching into the low resistance state. The memory device can be disconnected from its circuit and will remain in this state, but the threshold device requires a holding current otherwise it reverts to the high resistance state.

It has been suggested [6] that these devices could find application in controlling electroluminescent lamps or panels and in memory arrays of the "read mostly" type. In order to assess the new circuit elements for these or other applications, it would be advantageous if not essential to have knowledge of the relevant physical properties of the glasses from the two systems quoted so that one might use this knowledge to understand and optimise the operation of these devices. Memory switches from the Ge-As-Te system are bistable, probably due to a glass/crystalline phase change during each switching cycle, therefore some study of the crystallisation characteristics of these memory glass compositions should prove to be fruitful. Differential thermal analysis is a powerful tool in studying phase changes and other exothermic and endothermic transitions, so that this technique has been employed in the present survey of Ge-As-Te glasses.

2. Experimental

2.1. Glass Preparation

Glasses were prepared from the elements by weighing in air the appropriate amounts of Johnson & Matthey spectrographically standardised Ge, As and Te to make 2.0 gm of glass. To minimise oxygen pick up, the arsenic was weighed immediately after removal from an inert gas ampoule and the elements were quickly transferred to an outgassed silica tube of ID 4 mm and wall 1.5 mm which was then evacuated to a pressure of 10^{-5} torr. Each tube was pumped at this pressure for 30 min, after which it was sealed under vacuum. The sealed tubes were heated to a temperature of 950° C in a rocking furnace, held at this temperature for 24 h of which 10 h was rocking time, then removed from the furnace and subjected to a static air, water or liquid nitrogen quench. When cool, the tubes were broken and the melts were assessed as vitreous or crystalline, initially from evidence of conchoidal fracture, and subsequently by evidence of glass transition temperature, T_g, and X-ray diffraction.

2.2. Thermal Analysis Apparatus and Calibration

A Du Pont 900 thermal analyser console and differential scanning calorimeter cell were employed in this work. During the experiments nitrogen purge gas was passed through the cell at a rate of 0.4 l/min while nitrogen cooling gas was passed over the outside of the silver heating block to increase the cooling rate when the DSC cell was in the cooling mode. It was possible to cool at rates up to 20° C/min down to 350° C, but between 350 and 200° C the maximum cooling rate was of the order of 10 to 15° C/min. The aluminium sample pans and empty reference pans with close fitting lids were placed on a constantan disc in the silver heating block. The measurement thermocouples were attached to the underside of the constantan disc and were not, therefore, in direct contact with the samples. There was no sign of attack by most of the chalcogenide materials on the aluminium pans even after repeated melting and crystallisation cycles. However, compositions near the Ge 15 Te 85 eutectic after two to three melting cycles did begin to attack the pans, resulting in satellite peaks just below the main melting endotherm in the DSC traces. The sample weight loss after six cycles below 450° C was negligible for some glasses, but the maximum loss of any glass cycled between 250 and 500° C was 1 wt.%. With empty pans the DSC baseline was flat and reproducible, and the melting points of metals in the range 150 to 420° C were obtained within 2.5° C of their published values.

2.3. DSC Measurement Technique

During preliminary trials it was found that approximately 50 mg of glass was sufficient to observe all transitions without resorting to the maximum sensitivity of the instrument. Two to three pieces of material were used to make up the 50 mg rather than sieved powder. The values of T_g and the onset of melting of the crystallised glasses were similar for lump or powdered material. However, as would be expected, the temperature of onset of crystallisation during heating was lower for the powdered material than for the bulk material and the resolution of the details of these exothermic crystallisation peaks was greater with the powdered sample. In the first instance, for the type of survey work reported here, it was decided to utilise lump material and to postpone the determination of the more detailed crystallisation characteristics of selected compositions to a later date.

Glass transition temperatures were determined on 52 mg ± 5 mg of quenched sample utilising a 20° C/min heating rate which gave an endothermic baseline shift of the order of 0.3° C. The extrapolated onset of this baseline shift was taken as T_g and the measured reproducibility for ten determinations on one glass was better than ± 2.5° C. Crystallisation peaks of the metastable glass melts and subsequent melting and recrystallisation peaks were also determined on 52 mg ± 5 mg quenched samples at the same heating rate, which resulted in endothermic and exothermic peaks of the order of 3° C high. The extrapolated onsets of the crystallisation, T_X, from the metastable glass melt, and subsequent onset of melting, T_M, were obtained with a reproducibility of ± 2.5° C.

2.4. X-ray Diffraction

Standard Debye-Scherrer techniques with CuKα radiation were employed in determinations on the quenched glass melts.

3. Results

The glass forming area for 2.0 gm melts shown in fig. 1 is larger than that given for 20 gm melts by the author in a previous paper [7]. Several of the tellurium rich compositions obtained in the crystalline form by air quenching were obtained in the glassy state by water or liquid nitrogen quenching, as shown in fig. 1. The whole glass forming area is in good agreement with that reported by Iizima *et al* [8] for water quenched melts and by Takamori *et al* [9] for water quenched and splat cooled melts in the Ge-Te system. Under the melting conditions described in section 2.1 some compositions rich in tellurium were found to attack the inside surface of the melting tubes slightly, resulting in an etched appearance. However, a glass doped with oxygen in the form of TeO_2 had identical T_g, T_X and T_M to an undoped sample, so that the very slight contamination by oxygen would be unlikely to affect the

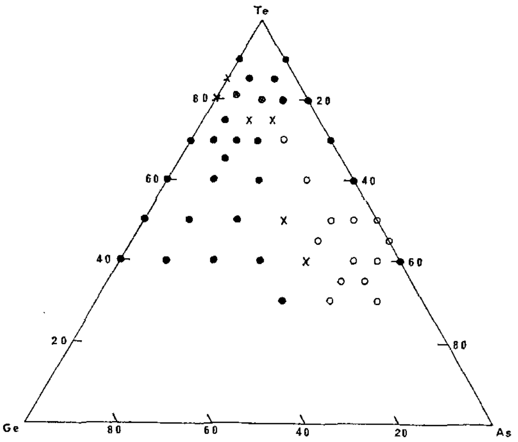

Figure 1 Glass forming region in the Ge-As-Te system for 2.0 gm melts. Atomic percentages.

● Crystalline } static room temperature air quench.
○ Glass
⊗ Glass static room temperature water quench.
× Glass static liquid nitrogen temperature quench.

results shown in table I. The main features of the phase diagram of fig. 1 are an island of glass formation adjacent to the composition As 50 Te 50 and a band of glass formation extending from this island along the 10% germanium line and terminating at the Ge 15 Te 85 eutectic [10]. All of the glass compositions on first heating showed a DSC curve consisting of an endothermic glass transition, an exothermic crystallisation peak and endothermic melting peaks. Thereafter on cycling at 20°C/min the materials remained in the crystalline state and showed reproducible exothermic crystallisation peaks and endothermic melting peaks. The DSC traces for the binary glasses were simple as shown in figs. 2a and b for the compositions As 50 Te 50 and Ge 15 Te 85. These glasses crystallised above T_g at a temperature, T_X, well below the onset of melting of the crystalline material so formed at T_X. The subsequent melting endotherm was simple as shown in figs. 2a and b. Three-component glasses along the 10% germanium line containing low percentages of arsenic also showed similar behaviour, as can be seen in fig. 2c for glass Ge 10 As 20 Te 70. However, with increasing arsenic content in glasses along the 10% Ge line of fig. 1, several endothermic melting peaks were observed and the metastable melt crystallisation temperature, T_X, moved to higher temperatures. Finally, as shown in figs. 3a and b for glass compositions Ge 10 As 50 Te 40 and Ge 15 As 50 Te 35 the metastable glass melt crystallisation temperature, T_X, increased to a value almost within the range of the first onset of melting of some of the crystal products formed at T_X. Results of T_g, T_X, ($T_M - T_X$ peak) the temperature interval between the onset of melting and T_X peak, and T_M are given in table I for the glass compositions shown in fig. 1.

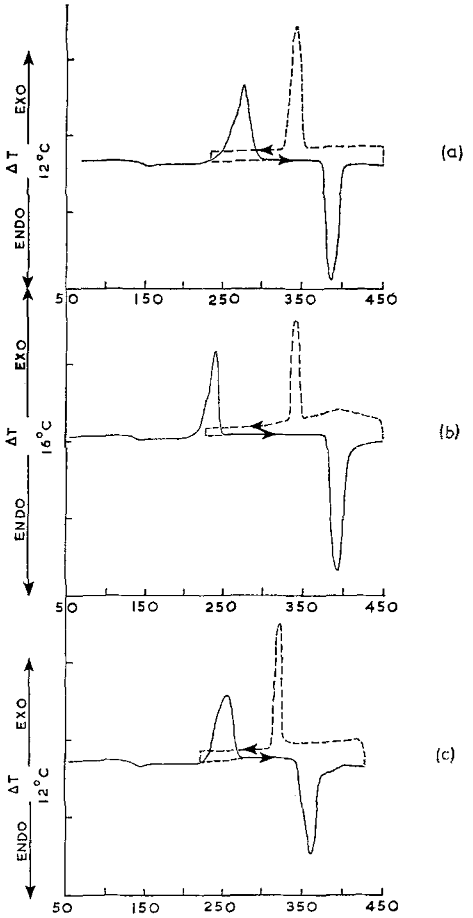

Figure 2 DSC traces for compositions (a) As 50 Te 50
(b) Ge 15 Te 85
(c) Ge 10 As 20 Te 70

—— first heating of glasses showing endothermic glass transitions exothermic crystallisation peaks and endothermic melting peaks.

---- subsequent cycling of the crystallised materials showing exothermic crystallisation and endothermic melting peaks.

4. Discussion

The main features of the results can be summarised as follows. The binary As 50 Te 50 metastable glass melt can be crystallised of the order of 100°C below the onset of melting of the

TABLE I Data obtained on quenched glasses heated at 20°C/min.

Glass composition at. %	T_g °C	T_X °C	$T_M - T_X$ peak temperature interval	Onset of melting T_M °C				
As 50 Te 50	137	245	105					378
As 55 Te 45	147	273	64					378
Ge 5 As 45 Te 50	148	271	45		357			
Ge 5 As 55 Te 40	171	323	*		358			
Ge 10 As 10 Te 80	116	219	112		356			
Ge 10 As 15 Te 75	123	244	101		354			
Ge 10 As 20 Te 70	127	234	99	344				
Ge 10 As 30 Te 60	147	218	107	343				
Ge 10 As 40 Te 50	173	300	*		357			
Ge 10 As 50 Te 40	195	330	*		357			
Ge 10 As 55 Te 35	213	338	*		359			
Ge 10 As 60 Te 30	231	347	*		357			
Ge 15 Te 85	132	229	134				379	
Ge 15 As 4 Te 81	134	238	114				372	
Ge 15 As 10 Te 75	134	242	99			361		
Ge 15 As 40 Te 45	204	338	*		358			
Ge 15 As 50 Te 35	231	353	*			360		
Ge 20 Te 80	155	228	147				380	
Ge 20 As 30 Te 50	213	324	15		357			
Ge 20 As 40 Te 50	240	372	*		359			

*In close proximity to the onset of melting.

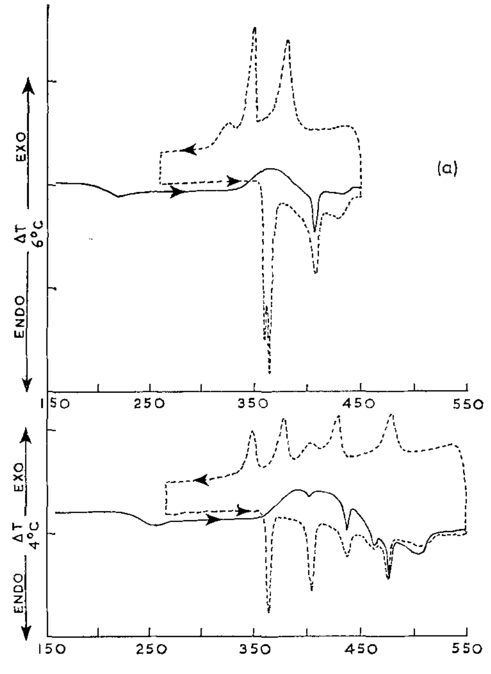

Figure 3 DSC traces for compositions
(a) Ge 10 As 50 Te 40
(b) Ge 15 As 50 Te 35
——— first heating of glasses showing endothermic glass transitions, exothermic crystallisation peaks and endothermic melting peaks.
- - - subsequent cycling of the crystallised materials showing exothermic crystallisation and endothermic melting peaks.

crystal phases produced at T_X. Metastable glass melts of compositions containing low percentages of arsenic near the Ge 15 Te 85 eutectic also show similar behaviour, and the small number of melting endotherms indicate that few crystalline phases are present in the crystal products. However, the metastable glass melts of compositions rich in arsenic do not begin to crystallise until almost in the temperature region of the onset of melting of the crystal phases produced at T_X. The melting endotherms are multiple indicating the presence of many crystalline phases in these crystallised materials. The glass transition temperatures increase smoothly along the Ge 10% line of fig. 1 on replacing Te with As, and the values quoted in table I are in good agreement with those of Iizima *et al* [8]. Thus T_g can be increased at the expense of a much more complicated crystal phase structure of the crystallised melts.

The original Ovshinsky memory compositions quoted in the literature were from the island of glass formation adjacent to As 50 Te 50 while the more recently quoted compositions were based on the Ge 15 Te 85 eutectic. It is likely that one of the reasons for the change in composition was to gain the simpler crystal phase structure of the compositions based on Ge 15 Te 85. Also experiments have been reported [11, 12] in which crystalline filaments have been produced on the surface of bulk glass between two tungsten point contacts after switching between the two contacts. Analysis of these filaments showed that the average crystalline composition was closely similar to that of the glass for materials near the Ge 15 Te 85 eutectic. However, for glasses rich in arsenic adjacent to the As 50 Te 50 composition, the crystallised filaments were of an average composition very different to that of the original glass. But in the latter case no indication of whether the filaments could be switched back into their glass state was given, or if this was possible, whether the original glass composition was regained. One should use caution in correlating results of this type for bulk glass with results switching in thin films, but they suggest that atomic motion of the constituents plays an important role, in the devitrification of glasses rich in arsenic during filament formation. It is probable that this effect would lead to a non-uniform distribution of constituents in the films over many switching cycles resulting in a permanent "lock on" of the crystalline state due to the inability of the compositionally segregated film to vitrify. On the other hand if atomic motion plays a minimal role in the devitrification of compositions near the Ge 15 Te 85 eutectic, there would be a higher probability of the film retaining its ability to vitrify after repeated switching cycles and device failure by a permanent "lock on" of the crystalline state would be less likely.

It has been reported that memory device threshold voltage is some function of the glass transition temperature [8] so that if it were required to adjust the threshold voltage to suit a particular application it would be advantageous to be able to adjust the T_g of a particular memory material. Therefore it would appear profitable in looking for improved or alternative memory compositions to study in some detail the crystallisation characteristics of glasses based on As 50 Te 50 or Ge 15 Te 85 and in particular to establish means of control of T_g by compositional substitutions whle still retaining a preferred crystallisation characteristic.

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