JOURNAL OF MATERIALS SCIENCE 7 (1972) 64–67

Glass-Forming Region and DTA Survey of Some Glasses in the Si-Ge-As-Te Threshold Switching Glass System

J. A. SAVAGE
Royal Radar Establishment, Great Malvern, Worcs, UK

The glass forming region for 2.0 g melts in the Si-As-Te system and pseudo ternary Si 5%-Ge-As-Te and Si 10%-Ge-As-Te systems are reported together with 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.

1. Introduction

It has been demonstrated by S. R. Ovshinsky [1, 2] that switching devices can be made from glasses in the Si-Ge-As-Te system and that these devices are of potential use in many applications such as the control of electroluminescent display panels [3]. In particular a glass of composition Si 12, Ge 10, As 30, Te 48 at. % has been quoted as a suitable material for the manufacture of threshold switches. These threshold switches are monostable, requiring a minimum holding current to maintain them in their high conductivity state, and hence it is unlikely that any crystallisation process plays a part in their operating mechanism. It would appear therefore that for threshold switching devices a material is required possessing a high degree of stability to crystallisation. Consequently a knowledge of the limits of glass formation and stability to crystallisation of glasses within this system would be useful in order to ensure that the most suitable composition is used to meet a particular requirement.

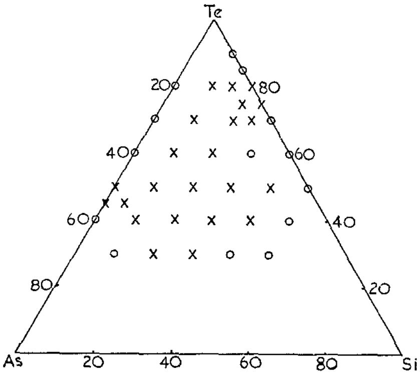

Figure 1 Glass forming region in the Si-As-Te system for 2.0 g melts. Atomic percentages.
× Glass ⎫
○ Crystalline ⎭ static room temperature air quench

Within the Si-Ge-As-Te system, a DTA survey and the glass forming region for Ge-As-Te glasses have been previously reported [4, 5] and these compositions have been shown to be suitable for memory switching devices [6]. In the present work, glass forming regions and DTA data are reported for the ternary system Si-As-Te and pseudo ternary systems Si 5%-Ge-As-Te and Si 10%-Ge-As-Te.

2. Experimental

2.1. Glass Preparation

The glasses were prepared as previously described [4] and were assessed as vitreous or crystalline by evidence of conchoidal fracture, glass transition and X-ray diffraction.

2.2. DSC Calibration and Measurement Technique

A Du Pont 900 thermal analyser console and differential scanning calorimeter cell were employed in this work. It was calibrated with metals melting in the range 150 to 420°C and the melting points were obtained within 2.5° C of their published values. Determinations were made on quenched lump material because this technique had already been shown to be satisfactory for survey work in the Ge-As-Te system [4]. Glass transition temperatures, temperatures of crystallisation of the metastable glass melts, and temperatures of onset of melting were all determined on 52 mg ± 5 mg of quenched glass heated at a rate of 20°C/min in a nitrogen atmosphere. The glass transitions resulted in endothermic baseline shifts of the order of 0.3°C, while the exothermic metastable melt crystallisation peaks and endothermic melting peaks were of the order of 3°C high. A DSC trace consisted of a glass transition, followed by a metastable melt crystallisation peak, and a subsequent melting peak or peaks. However, some glasses did not crystallise at a heating rate of 20°C/min and the DSC trace of these consisted solely of an endothermic glass transition. The extrapolated onsets of the baseline shift, the exothermic peak and endothermic peak were taken respectively as the glass transition temperature T_g, the metastable melt crystallisation temperature T_x and the onset of melting T_m. These values were obtained with a reproducibility of better than ±2.5°C when several determinations were made on any particular glass composition.

2.3. X-ray Diffraction

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

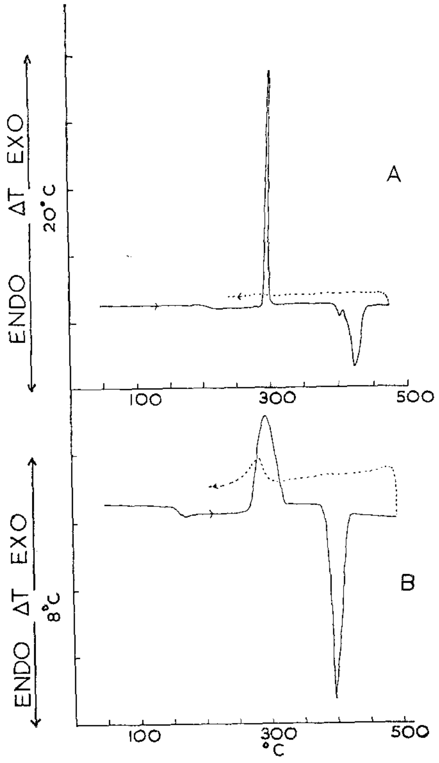

Figure 2 DSC traces for compositions. (a) Si 25, Te 75. (b) Si 10, Ge 10, Te 80.

3. Results

3.1. Si-As-Te Glasses

The glass forming region for 2.0 g melts shown in fig. 1 is in good agreement with that reported by Hilton and Brau [7] and is much larger than the corresponding Ge-As-Te system [4]. The phase diagram of fig. 1 consists of an area of three component glass formation near the Te apex and two small regions of binary glass formation in the Si-Te and As-Te [4] systems. The glasses in the three component system can be divided into two groups: (1) those containing more than 70% Te which crystallised during the DSC experiments and (2) those containing less than 70% Te which did not crystallise during the DSC experiments. Ternary glasses in group (1) containing 70 to 75% Te showed either very weak metastable melt crystallisations or none at all. Only the compositions Si 10, As 10, Te 80; Si 20, Te 80 and Si 25, Te 75 showed any strong tendency to crystallise under the experimental conditions given in section 2.2. The DSC trace for the composition Si 25, Te 75 is shown in fig. 2a and values of T_g, T_x and T_m are shown in table I for all compositions.

3.2. Si-Ge-As-Te Glasses

Work on the whole of the Si-Ge-As-Te glass forming system was not attempted but was restricted to the two pseudo ternary systems Si5%-Ge-As-Te and Si 10%-Ge-As-Te. The glass forming region for the latter is shown in fig. 3 while the glass forming compositions for the former are given in table II together with the values of T_g, T_x and T_m for both systems. It can be seen from table II that glasses from the Si 5%-Ge-As-Te pseudo ternary had a tendency to crystallise while those from the Si 10%-Ge-As-Te pseudo ternary were much more stable. A DSC trace for the composition Si 10 Ge 10, Te 80 is shown in fig. 2b.

4. Discussion

Glasses containing less than 70 at. % Te in the Si-As-Te system and those containing 10 at. % Si in the Si-Ge-As-Te system were sufficiently stable towards crystallisation to be considered as a possible source of threshold device material. Of the remainder of the glasses it is possible that the composition Si 25, Te 75 might be the basis of a

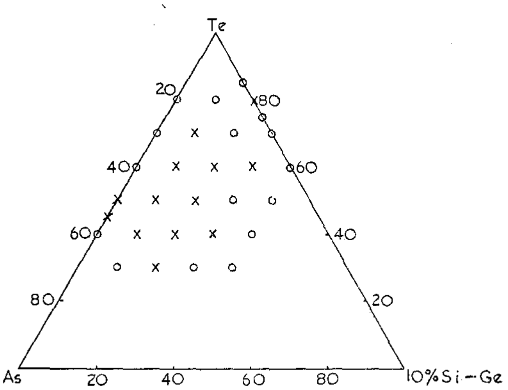

Figure 3 Glass forming region in the Si 10%-Ge-As-Te system for 2.0 g melts. Atomic percentages.
× Glass } static room temperature air quench
○ Crystalline }

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

Glass Composition at.%	T_g°C	T_x°C	T_m°C
Si-As-Te Glasses			
Si 10, As 10, Te 80	112	225	274
Si 10, As 20, Te 70	125	246	319 *
Si 10, As 30, Te 60	145	282	322 *
Si 10, As 40, Te 50	169	—	— †
Si 10, As 50, Te 40	198	—	— †
Si 15, As 5, Te 80	133	266	372
Si 20, Te 80	157	265	386
Si 20, As 5, Te 75	166	—	— †
Si 20, As 10, Te 70	177	—	— †
Si 20, As 20, Te 60	202	—	— †
Si 20, As 30, Te 50	226	—	— †
Si 20, As 40, Te 40	258	—	— †
Si 20, As 50, Te 40	288	—	— †
Si 25, Te 75	201	292	413
Si 25, As 5, Te 70	214	329	350 *
Si 30, As 20, Te 50	307	—	— †
Si 30, As 30, Te 40	350	—	— †
Si 30, As 40, Te 30	353	—	— †
Si 40, As 10, Te 50	377	—	— †
Si 40, As 20, Te 40	414	—	— †
Si 5, As 50, Te 45	158	—	— †

*Partially crystallised.
†Not crystallised.

memory material due to its high glass transition temperature and rapid crystallisation indicated by the sharp exothermic peak in fig. 2a. The latter crystallisation characteristic is in contrast to the more usual slower crystallisation indicated by the broad exothermic peak shown in fig. 2b for the composition Si 10, Ge 10, Te 80.

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

Glass Composition at. %	T_g°C	T_x°C	T_m°C
Si 5%-Ge-As-Te Glasses			
Si 5, Ge 5, As 20, Te 70	123	246	315
Si 5, Ge 5, As 30, Te 60	149	258	321 *
Si 5, Ge 5, As 40, Te 50	169	—	— †
Si 5, Ge 5, As 50, Te 40	193	—	— †
Si 5, Ge 15, Te 80	149	259	379
Si 5, Ge 15, As 10, Te 70	163	295	329 *
Si 5, Ge 15, As 20, Te 60	185	330	422 *
Si 5, Ge 15, As 30, Te 50	210	393	433 *
Si 5, Ge 15, As 40, Te 40	239	—	483 *
Si 5, Ge 15, As 50, Te 30	268	443	482 *
Si 10%-Ge-As-Te Glasses			
Si 10, Ge 10, Te 80	153	267	377
Si 10, Ge 10, As 20, Te 60	187	—	— †
Si 10, Ge 10, As 30, Te 50	219	—	— †
Si 10, Ge 10, As 40, Te 40	249	—	— †
Si 10, Ge 10, As 50, Te 30	282	520	ND *
Si 10, Ge 20, As 10, Te 60	169	—	— †
Si 10, Ge 20, As 30, Te 40	289	466	ND

*Partially crystallised.
†Not crystallised.
ND not determined.

It has recently been reported [8] that some threshold device compositions from the Si-Ge-As-Te system possess a diphasic non-crystalline structure and that compositions containing more than 70% Te possess a crystalline tellurium second phase within a glass matrix. Therefore it is likely that in the present work the compositions which crystallised during the DSC experiments, did so due to the presence of existing nuclei in the form of a crystalline second phase, or due to the presence of a very easily crystallisable second glass phase. The glass compositions of the threshold type which did not crystallise during the DSC experiments probably contained no crystalline second phase or easily crystallisable second glass phase. It would appear that the memory materials require built in crystal nuclei to initiate crystallisation during the lock on process, whereas the threshold materials need to be free from such nuclei.

Acknowledgements

The author is indebted to his colleagues W. Bardsley, C. Hilsum, J. Kirton, J. R. Bosnell, and C. B. Thomas for numerous discussions, and gratefully acknowledges the expert experimental assistance of Miss P. J. Penny.

References

1. S. R. OVSHINSKY, *Phys. Rev. Letts.* **21** (1968) 1450.
2. H. FRITZSCHE and S. R. OVSHINSKY, *J. Non-Cryst. Solids* **2** (1970) 148.
3. D. ADLER, *Electronics* **49** No. 20 (1970) 61.
4. J. A. SAVAGE, *J. Mater. Sci.* **6** (1971) 964.
5. S. IIZIMA, M. SUGI, M. KIKUCHI, and K. TANAKA, *Solid State Comm.* **8** (1970) 153.
6. H. J. STOCKER, *Appl. Phys. Letts.* **15** (1969) 55.
7. A. R. HILTON and M. BRAU, *Infrared Phys.* **3** (1963) 69.
8. G. V. BUNTON, *J. Non-Cryst. Solids* **6** (1971) 72.

Received 30 July and accepted 24 August 1971.