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# Comparison of memory switching operation in a number of amorphous chalcogenide systems

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A number of chalcogenide glasses were investigated for thin film switching applications. Two ranges of threshold voltage were of interest, 15 and 30 V. The switching performance of thin film devices was evaluated and rated on a simple numerical scale. The memory glasses based on the Ge–Te eutectic gave generally satisfactory performance. Selenium-based glasses exhibited high threshold voltage in thin film form, but had limited lifetime. Threshold voltages of about 30 V were obtained from Bi–As–Se glasses; these proved difficult to lock "ON" and possible reasons for this are discussed.

Measurements on the bulk properties were used to give an indication of the properties to be expected from thin films of the corresponding glasses.

## 1. Introduction

Non-oxide glasses based on the chalcogen elements have many unusual and characteristic properties. These glasses exhibit, depending primarily on composition, two different types of switching behaviour termed threshold and memory switching [1-3]. This paper deals with a number of different chalcogenide glass memory compositions which have been used in an attempt to produce switching devices with stable behaviour and with parameters suitable for two possible applications; one as a Read Mostly Memory (RMM) which would be compatible with Transition-Transistor Logic (TTL) and the other as a latching element for large area electroluminescent displays. The requirements for these applications differ in that RMM's require low ($< 15$ V) threshold voltage memory devices, while latching applications require devices operating at higher voltages ($> 30$ V).

One possible way of increasing the threshold voltage of a device is to increase the thickness of the active layer of the device. However, this method has limitations and therefore the use of different compositions for different voltage ranges has to be adopted. This also allows the control of other characteristics of the switching device (e.g. OFF and ON resistances).

The object of this work was, therefore, to prepare and investigate, both in the bulk and thin film forms, binary, ternary and quaternary glasses using combinations of the chalcogen elements, S, Se, Te with one or more other elements, e.g. Ge, As, Si, Sb, Bi etc., in order to determine the properties of these glasses relevant to the above mentioned applications.

The switching performance of thin film devices based on the prepared glasses have been rated (and categorized), judged on both life and stability of switching, by a single factor which is a number ranging from zero upwards. Zero rating implies one catastrophic switching event, the number assigned to a glass increases as the life and stability of the device improves.

These experiments were complemented by measurements on bulk materials. Apart from switching experiments, differential scanning calorimetry, optical microscopy and X-ray diffraction were employed to interpret the results of thin film device performance.

TABLE I DTA results for RMM glasses

| Glass composition (at. %) | Reference | $T_g$ (°C) | $T_x$ (°C) | $T_m$ (°C) |
|---|---|---|---|---|
| 50As 40Te 10Ge | A | 203 | 322 | 376 (413) |
| 85Te 15Ge | C | 132 | 229 | 373 |
| 81Te 15Ge 4Si | F | 150 | 243 (330) | 319 |
| 81Te 14Ge 5Si | G | 155 | 235 (340) | 384 |
| 81Te 14Ge 5As | H | 125 | 215 | 372 |
| 81Te 14Ge 5Sb | N | — | — | 385 |
| 81Te 14Ge 5S | E | 130 | 260 (350) | 377 (399) |
| 81Te 15Ge 2As 2S | B | 130 | 203 (253) | 342 (365) |

Figures in brackets indicate secondary peaks.

TABLE II Resistivity and DTA results for display glasses

| Composition | Reference | Resistivity Ω cm | $T_g$ (°C) | $T_x$ (°C) | $T_m$ (°C) |
|---|---|---|---|---|---|
| 40Te 30Ge 30Se | I | $1 \times 10^9$ | — | — | — |
| 80.8Te 14.2Ge 5Se | K | — | — | — | — |
| 59.5Te 10.5Ge 30Se | M | — | 100 | 360 | 400 |
| 80Se 20Ge | P | $6 \times 10^{15}$ | 160 | > 600 | > 600 |
| 60Se 40Ge | Q | $2 \times 10^{14}$ | 345 | 470 (498) | > 600 |
| 50Se 50Ge | R | — | — | — | > 600 |
| 85 Te 15Si | O | $8 \times 10^4$ | 110 | 250 (310) | 405 |
| 90Te 10Si | U | $2 \times 10^4$ | — | — | — |
| 60Se 40Sb | V | $2 \times 10^5$ | 115 | 215 | 555 |
| 50Se 50Sb | W | — | — | — | — |
| 4Bi 36As 60Se | X | $>7 \times 0 \times 10°$* | 165 | 290 | 343 |
| 8Bi 32As 60Se | Y | $5 \times 1 \times 10x^1$* | 175 | 314 | 375 |
| 16Bi 24As 60Se | Z | $3 \times 2 \times 10x^1$* | 183 | 313 | 373 |

*Crystalline bulk values – see Fig. 1.

## 2. Preparation and assessment of materials

### 2.1. Glass and target preparation

The composition of glasses which were prepared and investigated is given in Tables I and II. The boules of glass were prepared by weighing and mixing the constituents (minimum purity 99.99 %) in a nitrogen atmosphere and melting them in silica ampoules under reduced argon pressure or under vacuum. During melting, which was carried out at temperatures up to 1000°C depending on composition, the ampoules were continuously rocked and rotated for a time sufficient to ensure that a homogeneous melt was obtained. The boules of glass were used to provide specimens for bulk measurements and also to prepare r.f. sputtering targets.

After initial experiments with hot-pressing of powdered glasses, the procedure adopted for the preparation of r.f. sputtering targets was to cast discs of glass about 3 mm thick. These discs were then bonded to metal backing plates which were screwed into position in the r.f. sputtering apparatus to form a cathode in the sputtering process. This method proved to be satisfactory, provided that the discs were carefully annealed after casting to prevent cracking.

### 2.2. Thin film preparation

Two techniques were considered for the preparation of thin glass films – flash evaporation and r.f. sputtering. The flash evaporation was found to be unsatisfactory because the composition of the film was considerably different from that of the initial powder and varied from run to run. Flash evaporation was also a very wasteful technique in that a large proportion of the powdered glass was ejected from the heated boat and fell to the bottom of the vacuum chamber. This probably explains why the composition of the films was considerably different from that of the initial powder, as preferential evaporation may have been taking place during the time the powder was moving

about the boat. It was therefore decided to use a sputtering technique and r.f. sputtering was chosen because some of the target material is non-conducting. The sputtering gas used was argon which was admitted through a gas purification system after the system was pumped to about $1 \times 10^{-4}$ Pa. By a proper balance of argon flow and pumping rate, the system was maintained at a pressure of about 1.0 Pa during the sputtering and a typical deposition rate used was 0.25 nm $sec^{-1}$ for an r.f. power of 80 W.

The suitability of a new glass composition was initially evaluated by using a simple structure consisting of a matrix of 25 μm diameter tungsten wires fused into a glass substrate and separated by 2 mm. A thin film (1 to 2 μm) was sputtered onto this pin structure, followed immediately by an evaporation of thin chromium/thick gold which forms the ground plane. From these preliminary tests glasses were selected for evaluation in an improved test structure. This employed a sandwich arrangement consisting of a photolithographically defined oxide layer, which determines the active area of the device (this ranged from 20 to 100 μm diameter), active glass film and metal electrodes. A 0.3 μm film of molybdenum was found to be suitable as an electrical contact to the underside of the active chalcogenide film, whereas for the top contact a 1 to 2 μm thick gold layer was found to be necessary because thinner layers led to premature device failure due to poor thermal conductance.

### 2.3. Assessment

The performance of a new glass composition, both in bulk and thin-film form, was assessed by a number of methods. In the bulk, differential thermal analysis (DTA) was used to detect glass formation and to determine glass transition temperature ($T_g$), crystallization temperature ($T_x$) and crystal melting point ($T_m$). Electrical resistivity, activation energy, switching mode (threshold or memory) and current-voltage characteristics were also determined for particular glasses using discs cut from boules.

In the thin-film form, a memory device was assessed using a purpose built unit consisting of four pulse generators each with separately variable amplitude, pulse shape and length, and output impedance which were gated to provide a train of four pulses. The first pulse was used for switching the device into the ON state, the second to determine that this had occurred and to measure the resistance in this state, the third and fourth pulses to switch the device OFF and measure its OFF resistance. Current through the device was monitored by measuring the voltage across a 100 Ω series resistor.

## 3. Results and discussion

### 3.1. Bulk properties of glasses

A summary of DTA results for bulk glasses prepared for the RMM application is given in Table I. With the exception of glass A, these glasses were based on the Ge–Te eutectic and contained minor additions of Si, As, Sb and S. The eutectic composition itself (glass C) had much lower values of $T_g$ and $T_x$ than glass A and a simple, well-defined crystallization peak on the DTA curve. The occurrence of a single peak precludes the possibility of interference with the switching process by another crystal phase and a low $T_x$ is expected to produce an early and positive switch-ON.

The addition of Si to the eutectic composition (glasses F and G) was found to increase both $T_g$ and $T_x$ and to introduce a second crystallization peak. Arsenic had little effect on either $T_g$ or $T_x$ and produced no detectable secondary peaks for a 5% addition. The same (atomic) percentage of Sb resulted in a completely crystalline boule. The addition of sulphur gave the same $T_g$ as glass C but increased $T_x$ and produced additional crystallization peaks. A combination of As and S (2 at. % of each element) added to glass C had no effect on $T_g$ but gave the lowest value of $T_x$.

On the basis of these results, glasses C and H, having single crystallization peaks and lower values of $T_g$ and $T_x$ than glass A, appeared to be most suitable for the RMM application. A number of glasses from different systems were prepared for the higher voltage display application. Table II lists these glasses together with relevant resistivities and DTA results. Glasses were initially selected on the basis that materials with higher electrical resistivities would be expected to exhibit higher threshold fields.

The Ge–Te–Se glass I, with a resistivity of $10^9$ Ω cm (25°C) was used as a starting point. This, together with glasses K and M, having 5 and 30% additions of Se to the Ge–Te eutectic, were prepared in target-form for thin film evaporation.

The simpler binary system Ge–Se was also investigated in the hope that a higher threshold analogue of the Ge–Te eutectic would be found.

The resistivity of these glasses (P, Q and R) was much greater than that of glass I, but was associated with high $T_x$ values, which could inhibit switching.

The Si–Te glasses O and U were expected to have higher resistivities and bulk switching voltages than the Ge–Te glasses but both these properties were found to be lower in value than for many of the RMM glasses in Table I. The possibility of partial bulk crystallization of these glasses which have a low $T_x$ value cannot be excluded, however, and this may account for the low measured resistivities.

Glasses V and W from the Sb–Se system had lower $T_x$ values than Ge–Se glasses, but their resistivities were still within the typical RMM range of $10^4$ to $10^6$ Ω cm. Glasses, X, Y and Z from the $Bi_2Se_3$–$As_2Se_3$ pseudobinary system showed phase separation in the as-quenched form. Fig. 1 shows an optical micrograph of a polished section of glass Z (16 Bi 24 As 60 Se) with a probe resting on a conducting needle-shaped crystal. The crystals were identified as $Bi_2Se_3$, dispersed in vitreous $As_2Se_3$. The resistance between probe and lower electrode was $4 \times 10^5$ Ω with the probe contacting a crystal, and $1.7 \times 10^{12}$ Ω with the probe contacting the $As_2Se_3$ matrix. Glass X (4 Bi 36 As 60 Se) shows a similar two-phase structure, but with a different morphology of the dispersed phase. SEM of a polished section (Fig. 2) shows the reduced diameter of the $Bi_2Se_3$ crystals.

The DTA traces of these glasses were identical with the $As_2Se_3$ glass and the resistivities were low (Table II). Switching experiments were performed on bulk devices prepared from the three glasses. The devices were found to be in the ON-state as prepared, but could be RESET to the OFF-state and thereupon switching action (both memory and threshold) could be demonstrated. The threshold voltage was found to increase with decreasing Bi contents, but the devices were increasingly difficult to lock-ON and RESET.

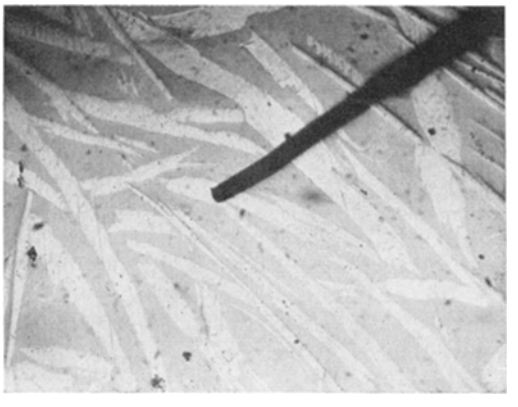

*Figure 1* Optical micrograph of a polished section of glass Z showing $Bi_2Se_3$ crystals in $As_2Se_3$ matrix, × 56.

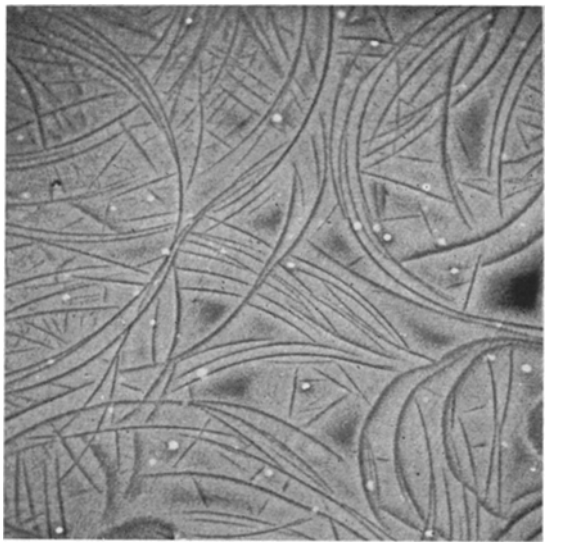

*Figure 2* SEM of a polished section of glass X showing the smaller diameter $Bi_2Se_3$ crystals, compared with glass Z, × 1000.

### 3.2. Switching in thin films

The performance of an amorphous material when switched repeatedly from the high to low resistance state and back again is judged by several criteria and the most important of which are the variation of $V_T$ from one switching cycle to another and the maximum number of switching operations.

The threshold voltage for the first operation of a virgin device is normally higher than the subsequent mean steady value, generally by a factor of 1.5 or more [5]. A forming process is therefore carried out, before evaluating a device to determine typical characteristics, during which $V_T$ reduces to a stable value after few (typically 10), to as many as 200, cycles of operations. The variation in the threshold voltage is presently taken as an indication of the stability of the switch. On this basis, the performance of the various glasses has been rated and the rating factor was arrived at using the classifications given on the next page.

| *Factor* | *Performance* | *Glass* |
|---|---|---|
| 0 | One catastrophic switching operation | I, M, Q, R |
| 1 | 1 - < $10^2$ switching operations, Unstable | A, K, P, U, V, W, X, Y, Z |
| 2 | $10^2$ – $10^3$ switching operations, not very stable | B, G, H, J |
| 3 | $10^3$ - $10^4$ switching operations | F, O |
| 4 | $10^4$ – $10^5$ switching operations, fairly stable | |
| 5 | $10^5$ upwards, Stable | C, E, L, N, S, T |

A summary of the performance of various glasses is given in Table III. Glass A is not stable from cycle to cycle and often fails to SET. This glass has a typical threshold voltage of 4 to 5 V for a 1 μm thickness. Most effort has been concentrated on glass compositions around the $Te_{85}Ge_{15}$ eutectic (C glass), with any additional material replacing in part the Te content. It has been found that adjustments of the composition about the basic eutectic show generally small variations in the performance (threshold voltages are nearly all in the region of 6 to 12 V for a 1 to 1½ μm layer thickness), with two exceptions. E glass has an improved stability over the basic C glass but at the expense of a higher ON resistance, 500 Ω as opposed to 250 to 300 Ω. A 1.8 μm film of E glass gave 2.5 × $10^5$ memory operations with a threshold voltage of 9.5 V, and a stability of the threshold voltage of ± 0.25 V over 200 switching operations. L glass, with 10% rather than 5% S, shows a stability similar to that of E glass, but the ON resistance increases again, this time to approximately 1000 Ω.

B glass, which contains less S than E but has an addition of 2% As, was not as good a memory material as C or E, achieving only 1000 operating cycles. F, G and H were all inferior in stability and performance generally to the C glass.

N glass, containing Sb in the basic eutectic, shows good stability and improved immunity to

TABLE III Summary of results on switching in thin films

| Reference | Composition (at. %) | Comments on switching performance | Rating |
|---|---|---|---|
| A | 50As 40Te 10Ge | A few unstable switches | 1 |
| B | 81Te 15Ge 2As 2S | Some hundreds of switches; not very stable | |
| C | 85Te 15Ge | Good life, about $10^5$ switches, reasonably stable | 5 |
| E | 81Te 14Ge 5S | Good life (several × $10^5$ switches) stable | 5 |
| F | 81Te 15Ge 4Si | A few thousand switches | 3 |
| G | 81Te 14Ge 5Si | A few hundred switches, not very stable | 2 |
| H | 81Te 14Ge 5As | A few hundred switches, not very stable | 2 |
| I | 40Te 30Ge 30Se | One catastrophic switch | 0 |
| J | G + 0.1% Ag | A few hundred, not very stable switches | 2 |
| K | 80.8Te 14.2Ge 5Se | A few unstable switches | 1 |
| L | 76.5Te 13.5Ge 10S | Several × $10^5$ switches. Stable | 5 |
| M | 59.5Te 10.5Ge 30Se | One catastrophic switch | 0 |
| N | 80.8Te 14.2Ge 5Sb | Several × $10^5$ switches. Stable | 5 |
| O | 15Si 85Te | Some few thousand switches | 3 |
| P | 20Ge 80Se | A few unstable switches | 1 |
| Q | 40Ge 60Se | One catastrophic switch | 0 |
| R | 50Ge 50Se | One catastrophic switch | 0 |
| S | 81Te 15Ge 2Sb 2S | Many × $10^5$ switches. Stable | 5 |
| T | 83.3Te 14.7Ge 2Sb | Several × $10^5$ switches. Stable | 5 |
| U | 90Te 10Si | A few unstable, badly defined switching operation | 1 |
| V | 60Se 40Sb | Variable threshold, first threshold high, switches with a low SET current | 1 |
| W | 50Se 50Sb | Very unstable and highly polarity dependent | 1 |
| X | 4Bi 36As 60Se | Very difficult to lock-ON, requires very high SET currents | 1 |
| Y | 8Bi 32As 60Se | Difficult to lock-ON | 1 |
| Z | 16Bi 24As 60Se | Difficult to turn ON and OFF | 1 |

irreversible locking in the ON state – devices SET with currents as high as 1 A are capable of being RESET by 100 to 200 mA 5 μsec pulses. However, this glass shows a tendency to have a less stable ON resistance from cycle to cycle than C and E glass, and also has a relatively low threshold field. Under the optimum drive conditions, a 2 μm thick film of N glass gave a threshold voltage of 7 V with a standard deviation of 70 mV over 200 switching operations.

A polarity effect was found in some of the glasses in which stable operation depended upon the polarity of the pulses applied to the top electrode. The basic $Te_{85}Ge_{15}$ eutectic, C glass gave stable operation with either positive or negative polarity of the top electrode. However, with glasses N and T, more stable operation was achieved when positive pulses were applied to the top electrode while with glasses E and L, negative pulses gave a stable operation. Because of this polarity effect, it is not possible to use E and L glasses for RMM applications since the polarity effect they show is opposite to that required by the silicon isolation diodes [4].

Most of the work described so far has been related to an attempt to produce a stable, relatively low threshold voltage glass. However, the need exists also for a high threshold glass. The obvious method of using thicker films of these same glasses (based on the $Te_{85}Ge_{15}$ eutectic) is limited to the production of devices with threshold below $\sim$ 25 V, and further increase in thickness, produce very little, if any, increase in the long term value of the threshold voltage. Hence a search was initiated for different glass systems which had higher intrinsic threshold fields. The first group of glasses were selected on the basis, as mentioned in Section 3.1, that materials with high resistivities were expected to exhibit high threshold fields. Compositions based on TeGe (with high percentage addition of Se, glass M), Ge–S (glasses P, Q and R) and Si–Te (U glass), Se–Si (V and W glasses) were investigated. The Se containing glasses (M, P, Q, U, V and W) did indeed exhibit increased threshold fields but only for the first switching pulse and in most cases these glasses were extremely unstable. The glasses that could be switched more than once exhibited a much reduced threshold voltage after the first SET/RESET cycle – often from $\sim$ 100 V for a 1 μm film for the first operation to a few volts subsequently. The catastrophic switching failures on these systems are thought to be due, at least in part, to the inability of these glasses to form a highly conducting phase. The absence of such a phase allows excessive Joule heating and hence thermal breakdown.

The requirement, therefore, is for a glass capable of separating out into two phases, that is,

OFF state: homogeneous (single phase), highly resistive and having a high threshold field.

ON state: phase separated structure – conducting minor phase embedded in a non-conducting matrix.

Additionally, the material must have the capability of having electrically switched from state to state; this generates the following requirements. On threshold operation the material must phase separate into crystalline conducting phase in a non-conducting matrix. This conducting phase must be constrained to channel and must join up electrodes to give conducting path. This crystalline channel will be thermally grown during an operation; this means that the crystallization temperature $T_x$ should be within the range that will be likely to be produced by Joule heating during the SET operation. Additionally, the minor phase must be soluble in the matrix at somewhat higher temperature $T_m$ (RESET operation) and the material thus formed must remain glassy during fast quenching.

The system Bi–As–Se (glasses X, Y and Z), which was known to consist, as discussed in Section 3.1, of a highly insulating matrix with a highly conducting dispersed phase, was investigated for its suitability as a high threshold material. Films 1 to 2 μm thick of the glasses X ($Bi_4As_{36}Se_{60}$) and Y ($Bi_8As_{32}Se_{60}$) were sputtered on to the pin glass structure. Threshold voltages for these glasses were 30 and 12 V respectively for a 1 μm film. Both of these were difficult to lock-ON, in agreement with the bulk switching measurements, even with quite large SET currents. Some devices could be made to switch for a short period with $i_{SET}$ as low as 4 mA (compared with 2 mA for C glass) but for most devices SET currents as large as 25 mA were required to cause lock-ON, and after a few switching operations many of the devices failed to switch. For Z glass, for which the Bi content was increased to 16%, $V_T$ for a 1 μm film dropped to as low as 4 V. Thus, the introduction of small amount of Bi into As–Se glass (glass X) led to the required high threshold voltages being

obtained in thin film switches. However, the lock-ON and RESET operation was difficult to achieve in these glasses. This may be associated with the high melting point of the $Bi_2Se_3$ dispersed phase ($T_m$ = 700°C) and a correspondingly high electrical energy requirement to obtain this temperature region.

## 4. Conclusion

Of several chalcogenide glass compositions evaluated for RMM application, those based on the $Te_{85}Ge_{15}$ eutectic have the most acceptable switching characteristics, giving more than $10^5$ stable operations at a threshold voltage of < 15 V which is sufficiently high for this application. Attempts to increase $V_T$ to 30 V were partially successful. BiAsSe thin films switched at 30 V but the lock-ON and RESET characters were unsatisfactory. The reason for the poor memory action is attributed to the high melting point of the conducting $Bi_2Se_3$ phase and it is thought that the memory operation could be improved by replacing Bi by some suitable addition which would provide a low melting point conducting compound dispersed in the basic $As_2Se_3$ glass.

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