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Effect of the Te/Si ratio on the electrical characteristics of the amorphous chalcogenide switches

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The effect of composition on amorphous chalcogenide threshold switches of the system $Si_xTe_{60-x}As_{30}Ge_{10}$, where $x = 5, 10, 12$ and 20, has been studied. The composition $x = 5$ shows the best switching characteristics, e.g. the smallest holding voltage ($V_h = 0.4$ V), the highest ON state current ($I_h = 45\,\mu A$) and smallest threshold voltage ($V_s = 1.5$ V). Applying the three mechanisms of conductance of Mott *et al.* (*Phil. Mag.* **37** (1975) 961), it is found that for a particular composition $\sigma_2 < \sigma_1 < \sigma_0$ (the pre-exponential factors) and $W_2 < (E_a - E_f + W_1) < (E_c - E_f)$ (where E_a, E_c and E_e = activation energies at band edge, fermi level and conduction band; W_1 and W_2 = activation energy for hopping). It was found that the density of states at the fermi level $N(E_f)$ increases with the decrease of silicon content. The results provided further evidence against thermal interpretations and thereby support electronic models of threshold switching for these glass systems.

1. Introduction

The operation of electrical switching prepared from films of chalcogenide semiconducting glasses has attracted much interest, as described by Ovshinsky [1] and Ovshinsky and Adler [2]. A general survey of the significant results has recently been provided by Adler *et al.* [3].

Interpretations have been divided between those who consider switching a thermal process, and those who maintain its essentially electronic origin. Homma *et al.* [4] in 1980 provided further evidence against thermal interpretations and thereby supported the electronic model of threshold switching for chalcogenide glass $Si_{18}Te_{40}As_{35}Ge_7$. The study reported here has investigated the electronic properties of thin film for the systems $Si_xTe_{60-x}As_{30}Ge_{10}$.

2. Device preparation

Four glasses of the system $Si_xTe_{60-x}As_{30}Ge_{10}$, with $x = 5, 10, 12$ and 20 had been prepared from very pure silicon, tellurium, arsenic and germanium (99.999% purity) by melting together the constituents under vacuum (10^{-6} torr) in precleaned silica tubes at 800° C for about 8 h which were subsequently quenched in liquid nitrogen. The specimens employed for the d.c. conductivity measurements were prepared by thermal evaporation of chalcogenide source material onto a substrate of insulating mica, the latter having previously been equipped with coplaner gold electrodes, and separated by a gap of width 0.1 mm.

The specimens employed for switching measurements were prepared by evaporation of chalcogenide material onto substrate of pyrographite. Edward 306 Coating Unit (West Sussex, England) was used for thin film. The thickness of the prepared thin film samples has been measured by using the thickness monitor type (FM3). The prepared thin films were confirmed to be amorphous by testing thin film samples from the same preparation by X-ray diffraction and transmission electron microscopy. Measurements of d.c. conductivity and the details of the measuring arrangements are described elsewhere [5]. A Keithly type 616 digital electrometer was used for the resistance measurements.

A special cell was constructed for the switching measurement. The cell was made of teflon block in order to give a high insulation. Details of the construction and the method of measuring are described elsewhere [5].

3. Experimental results

3.1. Effect of composition on the electrical conductivity of thin films

The d.c. conductivity of four glasses in the system $Si_xTe_{60-x}As_{30}Ge_{10}$, with $x = 5, 10, 12$ and 20 has been studied as a function of temperature. In this respect, two arrangements for the measurements of conductivity were considered. The first covers the temperature range from room temperature to + 85° C and the second from room temperature to near liquid nitrogen temperature. The high temperature limit has been chosen to be far below the softening temperature of the samples (the lowest $T_g = 165°$ C for $x = 5$). The specimens used for conductivity measurements

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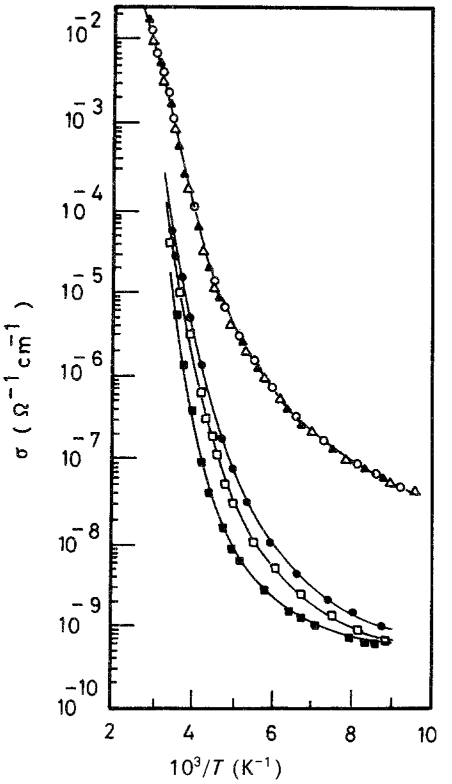

Figure 1 Temperature dependence of d.c. conductivity for glasses in the system $Si_xTe_{60-x}As_{30}Ge_{10}$, where (○ $x = 5$; (●) $x = 10$; (□) $x = 12$; (■) $x = 20$, and the measurements of reproducibility for $x = 5$ in the range +85° C to −160° C; (○) run 1; (▲) run 2; (△) run 3.

were prepared by evaporation of chalcogenide materials on substrates of mica.

Figure 1 shows the temperature dependence of d.c. conductivity (σ) as well as the measuring reproducibility of one sample of composition $Si_5Te_{55}As_{30}Ge_{10}$ over the two temperature ranges. The individual data point deviations are between 1–2%. It is worth noting that the conductivity measurements are carried out under equilibrium conditions, after the required temperature was attained and was constant for a while. Also, Fig. 1 shows the variation of the function $\sigma = f(1/T)$ for the compositions $Si_{20}Te_{40}As_{30}Ge_{10}$, $Si_{12}Te_{48}As_{30}Ge_{10}$, $Si_{10}Te_{50}As_{30}Ge_{10}$ and $Si_5Te_{55}As_{30}Ge_{10}$.

In the temperature range from +30 to −160° C, each plot can be divided into three linear ranges. Adopting the three mechanisms of conduction of Mott *et al.* [6], different values for the pre-exponential factors (σ_0, σ_1 and σ_2), and activation energies ($E_c - E_f$, $E_a - E_f + W_1$, W_2) have been obtained, where E_f is the activation energy at the fermi level.

Table I gives the compositional dependence of the electrical characteristic quantities (pre-exponent, σ (RT), and energy, where RT is room temperature). The increase of the Te/Si ratio in the sample leads to a decrease of the pre-exponential factor σ_0 and to an increase of both σ_1 and σ_2. Also, for each composition the values of W_2 and ($E_a - E_f + W_1$), are less than those of ($E_c - E_f$) and both energy terms ($E_a - E_f + W_1$) and W_2 increase while ($E_c - E_f$) decreases with increasing Te/Si ratio. The last result is very interesting since, it is expected that as the Te/Si ratio increases the localized states in the gap and the effective density of states near E_a (the limit of extended state from the conduction band) increases. When the localized states increase in the gap, the differences between W_2, ($E_a - E_f + W_1$) and ($E_c - E_f$) decrease and this is due to the lack of sharp band states in the gap.

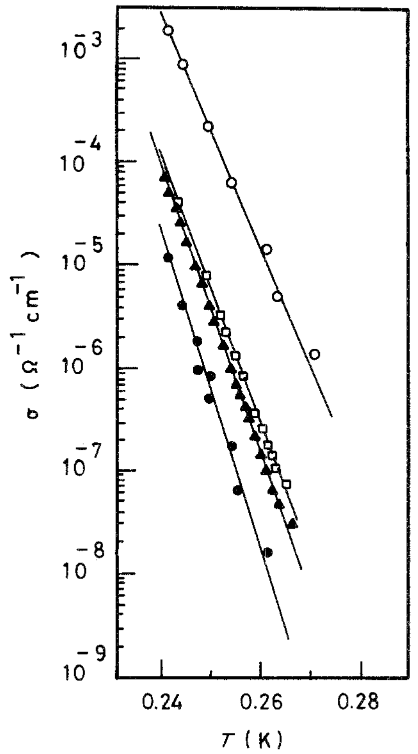

Figure 2 Variation of σ against $T^{-1/4}$ for the glasses investigated in the system $Si_xTe_{60-x}As_{30}Ge_{10}$ where (○) $x = 5$; (●) $x = 10$; (□) $x = 12$; (▲) $x = 20$.

Regarding conduction at low temperatures by variable-range hopping near the fermi energy, the function $\log \sigma = f(1/T)$ has been plotted on a ($T^{-1/4}$) scale Fig. 2. The latter, which is termed a Mott's plot, shows a linear dependence over a wider temperature range than that of $\log \sigma$ against $1/T$ plot in Fig. 1. The linear dependence of Fig. 2 behaves according to the Mott relationship [6, 7]. The density of states at the fermi level, $N(E_f)$ has been evaluated. The calculated values of $N(E_f)$ for the four compositions investigated are given in Table II. From this stable, it is clear that the value of $N(E_F)$ increases with the increase of the tellurium content in the glassy sample.

3.2. Effect of composition on the off–on state

Figure 3 shows the current–voltage characteristics for four compositions in the system $Si_xTe_{60-x}As_{30}Ge_{10}$ where $x = 5$, 10, 12 and 20. From this figure, it is clear that the composition $Si_{20}Te_{40}As_{30}Ge_{10}$ has the highest threshold voltage ($V_s = 5.5$ V) and holding voltage ($V_h = 4.5$ V) while the ON state current is not the highest. It is interesting to note that composition $Si_5Te_{55}As_{30}Ge_{10}$ shows the best switching characteristics, e.g. the smallest holding voltage ($V_h = 0.4$ V), the highest ON state current ($I_h = 45\,\mu$A) and smallest $V_s = 1.5$ V. A typical current–voltage characteristic of the compositions under investigation are shown in Fig. 4 for alternating current at a frequency of 500 Hz.

The temperature inside the conductivity channel of the switch is calculated at the threshold voltage and

TABLE I Compositional dependence of the electrical characteristic quantities associated with various processes for thin film glasses in the system $Si_xTe_{60-x}As_{30}Ge_{10}$

Composition	σ (RT)	$-\log \sigma$ (RT)	First slope			Second slope			Third slope		
			σ_0	$\log \sigma_0$	$E_c - E_f$ (eV)	σ_1	$-\log \sigma_1$	$E_a - E_f + W$ (eV)	σ_2	$-\log \sigma_2$	W_2 (eV)
$Si_{20}Te_{40}As_{30}Ge_{10}$	1.5×10^{-5}	4.82	6.0×10^4	4.78	1.10	1.4×10^{-7}	6.85	0.22	7.0×10^{-9}	8.16	0.11
$Si_{12}Te_{48}As_{30}Ge_{10}$	5.0×10^{-5}	4.30	2.3×10^4	4.36	0.94	7.0×10^{-7}	6.16	0.27	9.5×10^{-9}	8.02	0.13
$Si_{10}Te_{50}As_{30}Ge_{10}$	6.0×10^{-5}	4.22	1.2×10^4	4.08	0.86	1.2×10^{-6}	5.92	0.30	2.7×10^{-8}	7.57	0.15
$Si_5Te_{55}As_{30}Ge_{10}$	1.8×10^{-3}	2.77	8.0×10^3	3.90	0.70	9.0×10^{-5}	4.05	0.32	1.1×10^{-5}	4.96	0.17

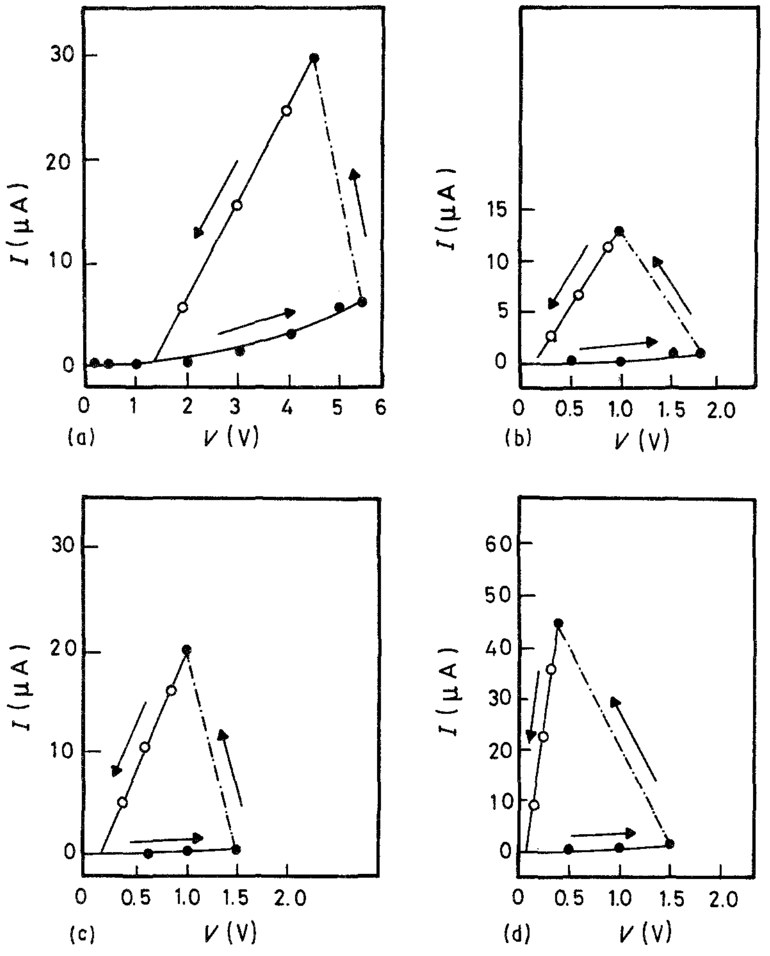

Figure 3 I–V characteristics of d.c. for the glasses $Si_xTe_{60-x}As_{30}Ge_{10}$, (a) $x = 20$; (b) $x = 12$; (c) $x = 10$; (d) $x = 5$.

after switching for the four compositions at room temperature using the numerical equation [8].

$$T = T_0 + Q/2\pi\lambda d \qquad (1)$$

where $Q = IV$ is the power generated inside the active region of the device, T_0 is the ambient temperature, λ is the thermal conductivity for the substrate = 0.009 cal cm^{-1} sec^{-1} C^{-1} d is the thickness of thin film sample.

The values of temperature calculated from experimental I–V curves of Fig. 3 as well as the corresponding values of current passing through the switch with their corresponding values of threshold voltages and holding voltages (or holding currents) are given in Table III. From this table it was clear that the maximum temperature after switching (70° C) for the composition $Si_{20}Te_{40}As_{30}Ge_{10}$ is less than the glass transition temperature (T_g = 185° C). Also the temperature of the active part after switching of composition $Si_5Te_{55}As_{30}Ge_{10}$ was found to be 30° C (room temperature 20° C), which is reasonable.

4. Conclusion

The results can be summarized as follows:

1. All the thin specimens under investigation show an amorphous structure.
2. The deviations from the straight plot of log σ against $1/T$ shown in Fig. 1 may possibly be the beginning of variable range hopping, a consequence of overlap between the (D^+) and (D^-) bands due to centres with positive U (barrier energy) as has been emphasized by Mott *et al.* [6]. Another explanation follows, however, from the analysis of Marshall and Owen [9] who combine it with drift mobility curves to identify a spinless hole trap 0.13 eV below E_f, the defect responsible being present in sufficient concentration to allow hopping from one to another.
3. As regards the switching process, there have been many suggestions of its cause, including tunnelling from the electrodes, impact ionization. Mott *et al.* [6] have suggested that there is evidence that it cannot be the carriers in the conduction and valence band that cause switching in this or any other way, since,

TABLE II Composition dependence of the values of T_0 and N (E_f) evaluated from σ against $T^{-1/4}$ for the glasses in the $Si_xTe_{60-x}As_{30}Ge_{10}$ system

Composition	$N(E_f)$ (cm^{-3} eV)
$Si_{20}Te_{40}As_{30}Ge_{10}$	9.82×10^{17}
$Si_{12}Te_{48}As_{30}Ge_{10}$	1.03×10^{18}
$Si_{10}Te_{50}As_{30}Ge_{10}$	1.23×10^{18}
$Si_5Te_{55}As_{30}Ge_{10}$	1.94×10^{18}

TABLE III Values of filament at the switching voltage (V_s) and after switching as calculated from experimental I–V curves and the corresponding values of current for samples of $Si_xTe_{60-x}As_{30}Ge_{10}$ of thickness 0.5 μm at room temperature (20° C)

Composition	Filament temperature (° C)		Current (μA)		
	At V_s	After V_s	At V_s	After V_s	V_h
$Si_{20}Te_{40}As_{30}Ge_{10}$	35	70	5.5	30	4.5
$Si_{12}Te_{48}As_{30}Ge_{10}$	23	27	1.7	13	1.0
$Si_{10}Te_{50}As_{30}Ge_{10}$	22	29	1.5	20	1.0
$Si_5Te_{55}As_{30}Ge_{10}$	22	30	1.5	45	0.4

Where V_s is the switching voltage and V_h the switching hold.

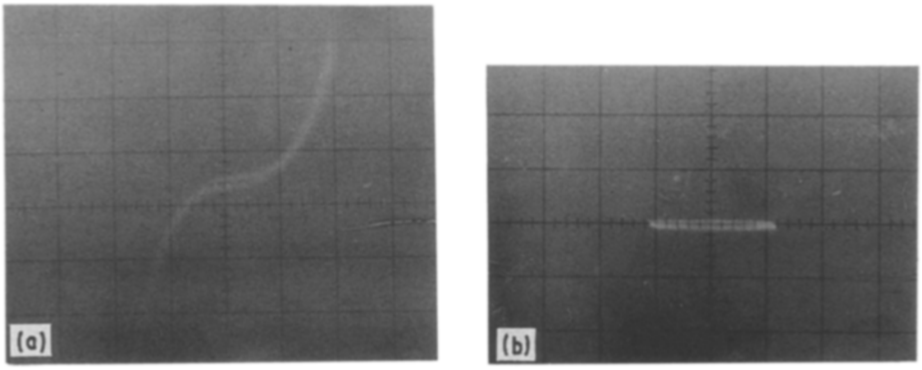

Figure 4 The ON–OFF states for alternating current, (a) ON; (b) OFF.

Henisch *et al.* [10] show that strong illumination which increases the number of free carriers by an order of magnitude, does not affect the switching voltage nor the delay time.

4. The composition $Si_5Te_{55}As_{30}Ge_{10}$ shows good switching results and may be used as a switching device in computer applications.

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