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Conduction mechanism at high electric field and switching phenomena in V_2O_5–P_2O_5 and V_2O_5–P_2O_5–TeO_2 glasses

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A previous investigation [1] suggests that the conduction in some vanadate glasses is ohmic up to a field of the order of 10^5 V cm^{-1} with an activation energy range from 0.31 to 0.48 eV depending on composition, but independent of temperature above room temperature. In this work the electrical conductivity of these glasses at high electric field is reported. The results suggest that above a field of $\sim 4 \times 10^5$ V cm^{-1} conduction becomes non-ohmic, and this is found to be due to lowering the potential barrier to the carrier at high electric field. Memory switching is observed in thin blown film samples of both binary and ternary glass systems, and is associated with field-induced crystallization of a localized region and the formation of a conduction channel in the switched area due to a self-heating effect.

1. Introduction

Semiconducting glasses often show marked deviations from normal semiconductor behaviour, e.g. non-ohmic conduction under the influence of temperature and or in a strong electric field. The application of a high electric field to a free charge carrier system may influence both the mobility of the carriers and the number of available carriers. The mobility of the carrier may be influenced by the change in the effective energy distribution of the carriers, which would be described in terms of a rise of carrier temperature T_c above the lattice temperature. There are various conduction mechanisms at high electric field.

In the model of Schottky the emission of electrons occurs from the metal contact at negative potential into the high electric field region obtainable across thin insulating films. In this model, when an electron is at a distance r from the surface of a metal a positive charge will develop inside the metal, known as an image charge, whose effect is to change the shape of the potential barrier. The effect of high electric field not only lowers the height of the potential barrier, but also increases the emission current. At sufficiently high electric field the Coulombic barrier becomes thin and conduction at the Fermi level occurs as a result of tunnelling through the barrier rather than over it.

In the model proposed by Poole [2] and Frenkel [3], if a crystalline or amorphous semiconductor contains donors or traps in which the binding energy of an electron is E_b, the effect of the high electric field E is to lower the ionization energy of the centre by $\Delta\phi$ given by

$$\Delta\phi = \frac{\beta E^{1/2}}{kT} \qquad (1)$$

where β is the field-lowering coefficient given by

$$\beta = \left(\frac{e^3}{\pi\epsilon_R\epsilon_0}\right)^{1/2} \qquad (2)$$

in which ϵ_R is the relative dielectric constant and ϵ_0 is the permittivity of the free space. The physical basis of this effect is the lowering of a Coulombic potential barrier when it interacts with the electric field, and the increased thermal excitation of electrons from traps into the conduction band.

In the derivation of Equation 1 it is assumed

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that there is no tunnelling through the barrier at high temperature. As the temperature is lowered tunnelling through the barriers rather than excitation over the barrier can take place. The reduction in height of the Coulombic barrier $\Delta\phi$ due to the Poole–Frenkel effect in a uniform electric field is found to be twice that due to the Schottky effect at a neutral barrier [4].

The effect of high electric field E on the mobility of the carriers was discussed by Mott [5]. He assumed that if the hopping mobility μ of the carriers is of the form

$$\mu = \frac{ea^2\nu_{\mathrm{ph}}}{kT}\exp(-2\alpha a)\exp\left(\frac{-W}{kT}\right) \qquad (3)$$

in which hopping is to nearest neighbour sites, an electric field should reduce the activation energy (W) to $W-eaE$. It should also increase the tunnelling factor $e^{-2\alpha a}$, but calculations of this effect have not been made. In Equation 3 a is the mean atomic spacing, and ν_{ph} is a phonon frequency.

The effect of high electric field on polaronic conduction in low mobility solids, such as amorphous semiconductors in general, and glassy systems in particular, is of considerable interest. A small polaron may be considered to form on a neutral centre. The effect of a high electric field may be considered in two terms. Firstly the field may enhance the supply of electrons from donors to the medium, and their further transport between donor centres may then precede the polaronic transport. Secondly, the field may affect the hopping probability of the polarons themselves, by causing a lowering of the potential barrier of the short range field between nearest neighbours.

Application of a sufficiently high electric field to a disordered material sooner or later leads to deviations from linearity in the resultant current, indicating non-ohmic conduction.

It was found that in contrast to many other disordered systems, the transition metal oxide glasses show ohmic behaviour at fields up to about $10^5\,\mathrm{V\,cm^{-1}}$ and at higher fields the conductivity varies as [6]

$$\sigma(\mathrm{E}) = \sigma(0)\left[\sinh\left(\frac{ea\mathrm{E}}{2kT}\right)\Big/\left(\frac{ea\mathrm{E}}{2kT}\right)\right] \qquad (4)$$

where σ (0) is the ohmic conductivity, a is the site separation and the sinh term implies a departure from the ohmic behaviour at a field $E = kT/ea$. The estimated value of a, the jump parameter, can be determined by measuring the field at a point at which the non-linear I–V characteristic, occurs.

This paper describes electrical measurements on glass samples of composition V_2O_5–P_2O_5 as well as V_2O_5–P_2O_5–TeO_2 in order to study the effects of high electric field on these glasses, including switching effects in thin blown films in both the binary and ternary glass systems.

2. Sample preparation and measuring techniques

Thin blown films of glass samples of V_2O_5–P_2O_5–TeO_2 were prepared using the method described in an earlier paper [7]. The thicknesses of the samples were measured using a Sigma comparator. Silver paste was used as the electrode material and the samples, after painting on the electrodes, were annealed at 100° C for 2 h.

Fig. 1 shows the sample holder device, and Fig. 2 illustrates the circuit used to observe the V–I characteristic. The two high resistors (1 M Ω each) were used as current limiters across the sample at high electric fields. The measurements were carried out by using a stabilized d.c. voltage supply and a Keithley 610C electrometer for measuring the current. Experiments were carried out under a vacuum of ~ 10^{-5} torr.

3. Experimental results and discussion

A typical voltage–current characteristic is shown in Fig. 3 for a glass sample containing 65 mol% V_2O_5, 35 mol% P_2O_5 and in Fig. 4 for glass con-

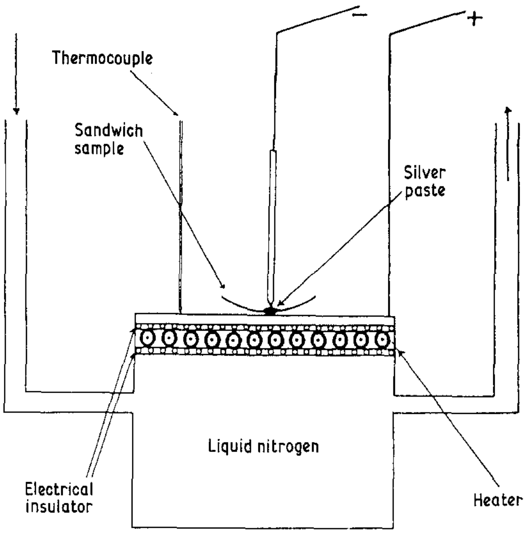

Figure 1 Sample holder, cooling and heating system used for high electric field experiments.

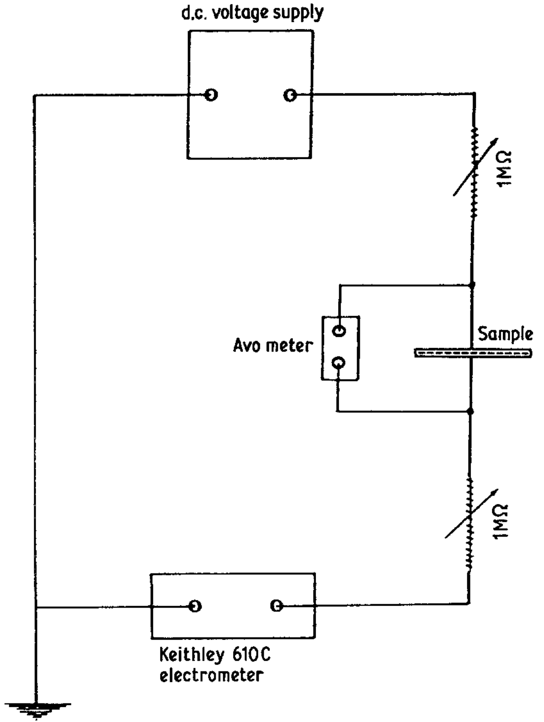

Figure 2 Electrical circuit for non-ohmic characteristics at high electric field and switching measurement.

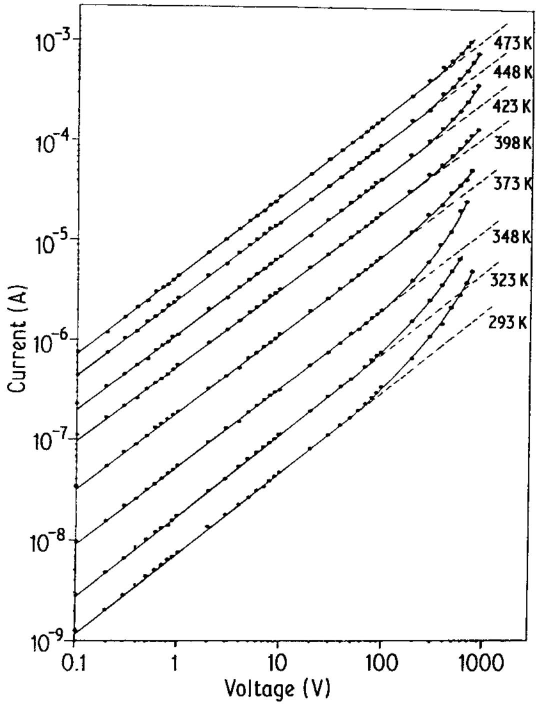

Figure 3 Typical V–I characteristic at high electric field for a binary glass at different temperatures (sample thickness 25 μm).

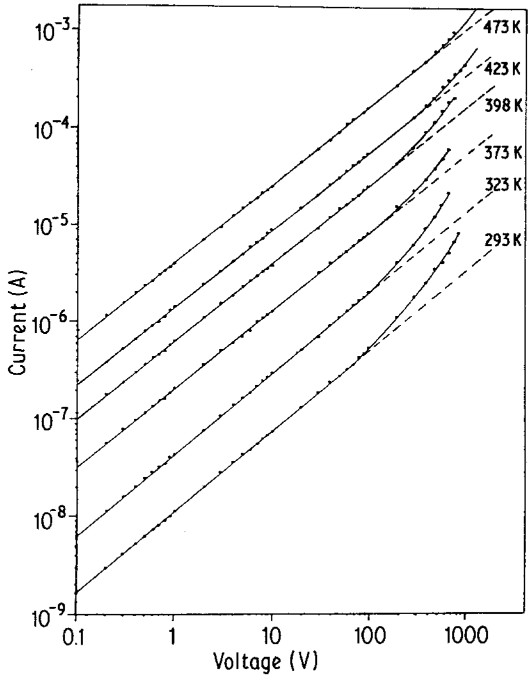

Figure 4 Typical V–I characteristic at high electric field for a ternary glass at different temperatures.

taining 60 mol %V_2O_5–20 mol% P_2O_5–20 mol% TeO_2, and similar curves were obtained for samples of other compositions listed in Table I.

In the present work it was found that for vanadium phosphate glasses at fields below 4×10^5 V cm^{-1} the conduction is ohmic and plots of log V versus log I give straight lines. The departure from linearity and the appearance of non-ohmic behaviour occurs at fields above 4×10^5 V cm^{-1}.

It was also found that with increasing temperature the linear region extends to higher values of field as has been observed generally for oxide glasses. A similar characteristic has been observed for a glass containing TeO_2 but the departure from linearity in the V–I characteristic occurs at a field slightly less than 4×10^5 V cm^{-1}.

In order to analyse the basis of this behaviour, the effect of the sample thickness and electrode material on the conductivity of our samples was examined first, and it was found that the conductivity is independent of these factors, which suggests that space-charge-limited conduction and Schottky emission do not determine the conductivity and consequently the field dependence was a property of the bulk material. Secondly the value of β in Equation 2 was determined from the slope of the log I versus $V^{1/2}$ curves, and the result

TABLE I Glass composition for binary V_2O_5–P_2O_5 and ternary V_2O_5–P_2O_5–TeO_2 systems

Glass number	V_2O_5 (mol%)	P_2O_5 (mol%)	TeO_2 (mol%)	Softening temperature (°C)	Colour
101	50	50	0	595	Black*
102	55	45	0		Black*
103	60	40	0		Black*
104	65	35	0		Black*
105	70	30	0		Black*
106	75	25	0		Black*
107	80	20	0		Black*
108	85	15	0		Black*
109	90	10	0	420	Black*
210	60	35	5	555	Black*
202	60	30	10		Black†
203	60	25	15		Black†
204	60	20	20		Black†
205	60	15	25		Black†
206	60	10	30		Black†
207	60	5	35	435	Black†

*Blown films of V_2O_5–P_2O_5 glasses 2–10 are dark green.
†Blown films of V_2O_5–P_2O_5–TeO_2 glasses 2–10 are dark brown.

compared with the theoretical value of β calculated from Equation 2.

Figs. 5 and 6 show the plots of log I versus $V^{1/2}$ for V_2O_5–P_2O_5 and V_2O_5–P_2O_5–TeO_2 glasses respectively. These figures show that the dependence of log I on $V^{1/2}$ is linear at high fields and the value of β obtained from the slope of the linear part of these curves is about 1.37×10^{-4} eV$(\text{cm}V^{-1})^{1/2}$ sec^{-1} for V_2O_5–P_2O_5 glasses. Theoretical values of β calculated from Equation 2 are $\beta_{PF} = 1.02 \times 10^{-4}$, and $\beta_S = \frac{1}{2}{}_{PF} = 0.51 \times 10^{-4}$ eV $(\text{cm}\,V^{-1})^{1/2}\,\text{sec}^{-1}$. This calculation shows that the experimental value of β fits the Poole–Frenkel formula much better than the Schottky equation.

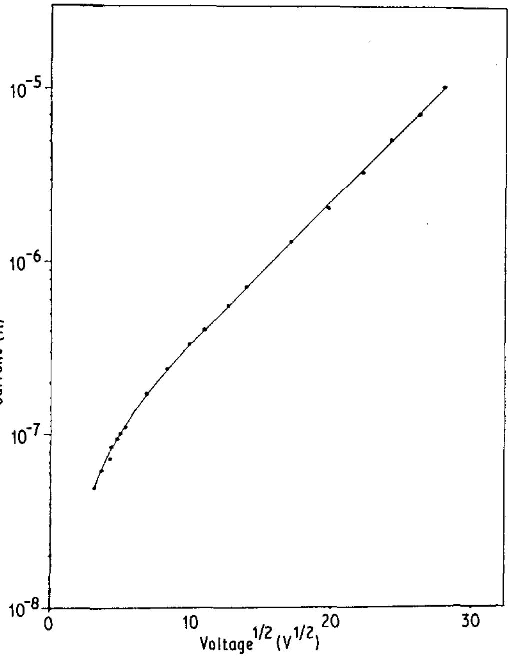

Figure 5 Current as a fuction of $V^{1/2}$ for a glass containing 65 mol% $V_2O_5$35 mol% P_2O_5.

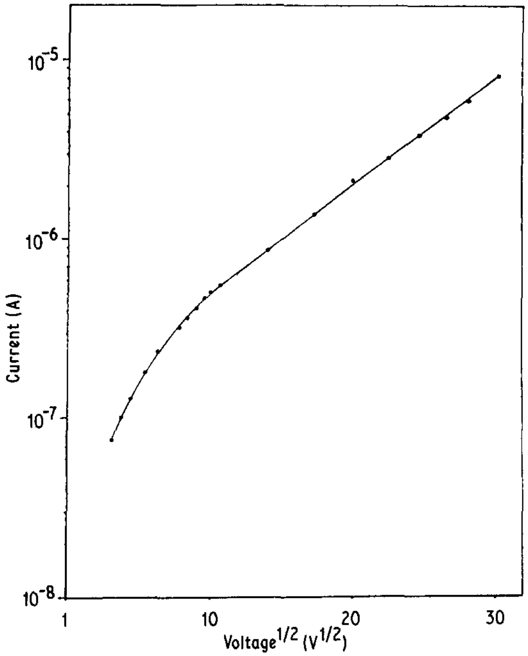

Figure 6 Current as a function of $V^{1/2}$ for a glass containing 60 mol% V_2O_5–20 mol% P_2O_5–20 mol% TeO_2.

The value of jump parameter a in Equation 4 is calculated by measuring the field at the point at which the departure from linearity in plots of log I versus log V occurs and an average of 2.1 nm was found for a which is nearly 5 times greater than the values derived from the results of electron spin resonance and chemical analysis measured by the present authors in earlier work [1]. Austin and Sayer [6] reported a similar enhancement factor for the V–V spacing in V_2O_5–P_2O_5 glasses and they concluded that this factor may be a characteristic of any individual glassy system depending on the structure of glass. However many authors [8] have suggested that a modification to the formula

$$\sigma = \sigma(0)\,\frac{\sinh\,(eaE/2kT)}{eaE/2kT} \tag{5}$$

is necessary in order to explain the experimental results for the value of a, and concluded that the sinh law is only applicable in a relatively small range of electric field.

4. Switching phenomena in vanadate glasses

It has been known for many years that when the interelectrode distances in samples of amorphous or glassy semiconductors are reduced to sufficiently small values (typically a few μm), the current–voltage characteristics are no longer governed by Ohm's law after a certain threshold voltage has been reached. At this point a partial breakdown takes place and the conductance of the sample appears to increase abruptly. This phenomenon is described as a switching effect and has many potentially useful applications in electronics.

Two kinds of switching have been recognised, threshold [9–11], and memory [12]. In both types of device the switching process occurs when an increasing applied voltage exceeds the threshold voltage V_{th}, or after a delay time t_{D} when a voltage pulse V_{p} larger than V_{th} is applied.

The switching process takes place very rapidly within a switching time $t_{\text{s}} \leqslant 10^{-10}$ sec. However there is a delay time t_{D}, typically about 10^{-6} sec at the threshold voltage, and the delay time decreases exponentially with over-voltage [13]. It has been reported [14] that if the applied voltage is about 50% above threshold voltage, the delay time will be reduced to 10^{-9} sec. The voltage dependence is also composition-dependent. Sugi *et al.* [15] reported that the decrease in delay time is proportional to the inverse square of the over-voltage. In the case of the threshold switch, during the switching process the atomic arrangement and structure of the sample do not change permanently, but in the case of memory switching the process is associated with a structural change.

When low voltages are applied to a device typically 1 to 50 μm thick, sandwiched between two electrodes, the conduction is ohmic. Above fields of about 10^4 to 10^5 V cm^{-1} a non-ohmic characteristic becomes evident and the current rises exponentially with applied voltage [16]. Switching occurs at a critical field, generally of the order of 10^5 V cm^{-1}, from a high resistance (off-state) to low resistance (on-state). As long as a holding voltage V_{h} is maintained across the device the material remains in the conducting state. In the case of threshold switching, if the holding voltage is removed the device switches back to the high resistance state (off-state) in about 5×10^{-7} sec. The switching process is reversible and independent of polarity. The threshold voltage decreases with increasing temperature and it has been reported [17] that the threshold voltages appear to increase exponentially with glass transition temperature [18] for a large number of disordered materials.

A typical memory switch behaves initially like a threshold switch. At low fields the conductivity is low and obeys Ohm's law until the applied voltage reaches the threshold voltage. Above this voltage, after a delay time there is rapid switching from high resistance (off-state) to low resistance (on-state). After switching, if the current is quickly reduced below a critical value, the device will switch back to the high-resistance state, exactly like a threshold switch. However, if the device is held in the conductive state for about 10^{-3} sec, it will remain highly conductive, even after the external field is removed. This time is called the lock-on time (t_1). Memory-switched material can usually be returned to the original high resistance (off-state) by applying a short intense current pulse of either polarity.

5. Sample preparation and experimental procedures

Thin blown films of glass samples of some compositions listed in Table I were prepared using the method described before [7].

Binary glass samples of the compositon 65 mol% V_2O_5–35 mol% P_2O_5 and ternary glass samples of the composition 60 mol% V_2O_5–15 mol% P_2O_5–25 mol% TeO_2 were prepared and two-terminal devices were made by using silver paste as the electrode material. The cross-sectional area of the silver paint was 0.2 to 0.3 cm^2.

The sample holder and the circuit used to observe V–I characteristics were the same as were used in the high electric field measurement (Figs. 1 and 2).

6. Experimental results and discussion

A typical V–I characteristic of memory switching for a binary glass is shown in Fig. 7 and similar characteristics were observed for glasses with various compositions. As the applied voltage increases in the high-resistance state, the conduction is ohmic at low field and the current becomes increasingly non-ohmic at higher fields, as described earlier.

When the applied voltage excees a threshold voltage V_{th}, the device switches from high resistance to an ordered state. Thus a rapid current increase and a large decrease in voltage drop across

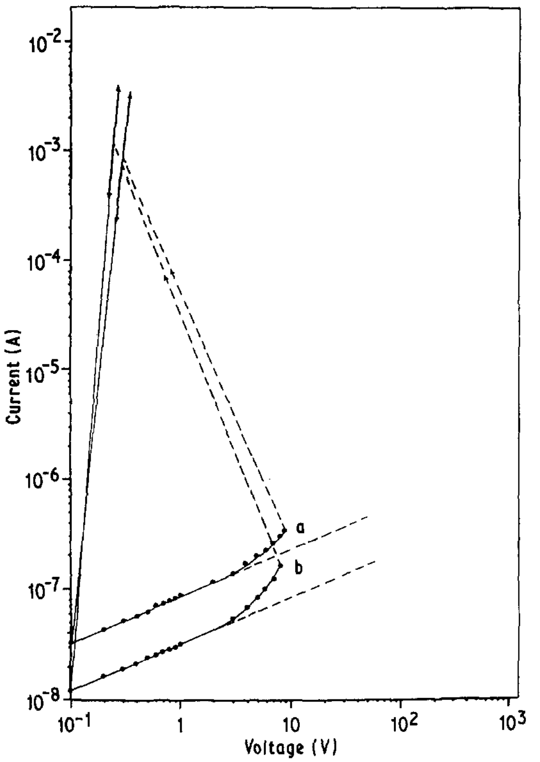

Figure 7 Typical V–I characterisitic of a binary glass switching at room temperature (memory). (a) Sample thickness 12 μm, (b) Sample thickness 19 μm.

the sample occurs. As the applied voltage increases further the current continues to increase, and in the case of the samples the log V versus log I curve after switching was linear as is shown in Fig. 7. The device remains in its conductive state even when the current decreases to zero, which is characteristic of a memory switch. The switched device can be returned to its high resistance state by applying a high d.c. pulse (0.2 to 1 mA).

It was found that the threshold voltage is not reproducible and depends on the external switching condition as was reported by Drake *et al.* [19]. For all devices the first switching voltage was much higher than for the subsequent switching. All glasses with different thicknesses show a similar switching effect and it seems that the on-state of devices is nearly independent of the sample thickness as indicated in Fig. 7. In any event the current in the on-state is largely determined by the high value series resistors.

It was found that the threshold voltage decreases with increasing temperature. Figs. 7 to 9 show memory switching for binary glass at three differ-

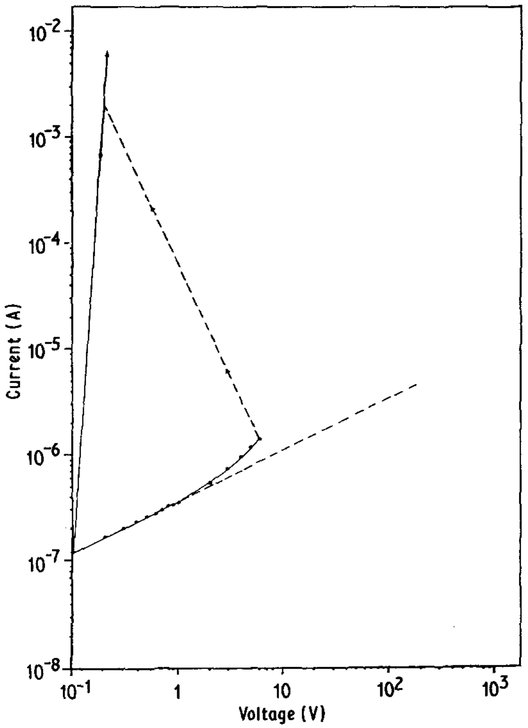

Figure 8 Switching of a binary glass sample at 40° C (memory).

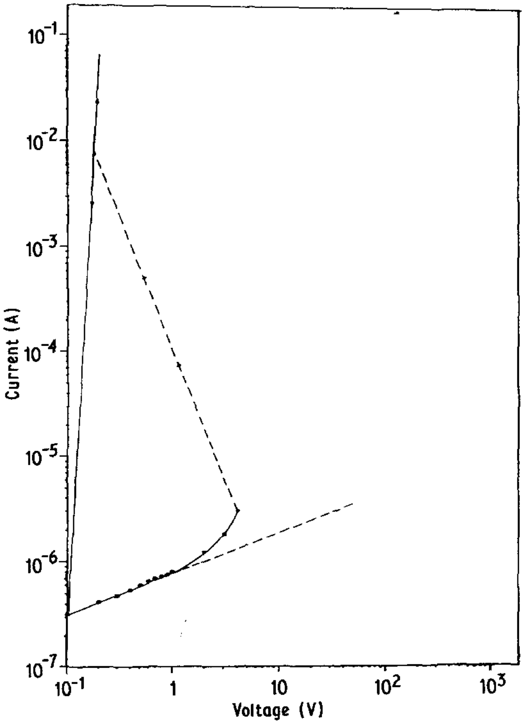

Figure 9 V–I characteristic of a binary glass sample memory switch at 55° C.

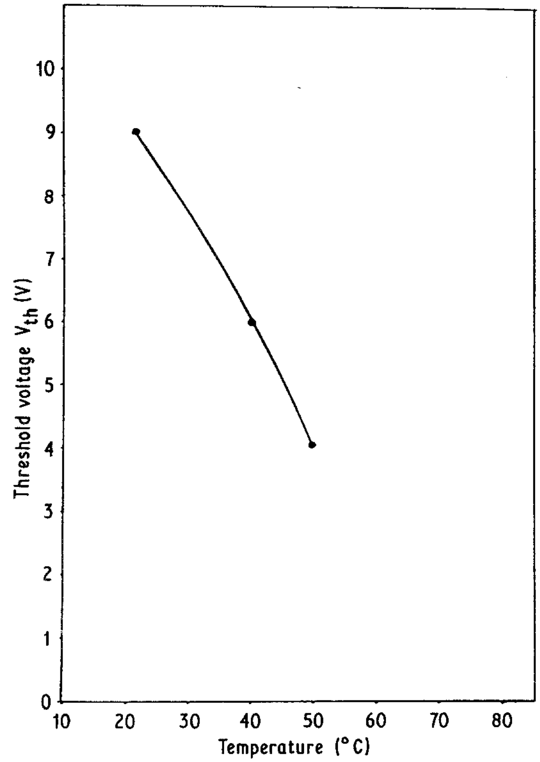

Figure 10 Variation of threshold voltage with temperature for a glass containing 65 mol% V_2O_5–35 mol%–P_2O_5.

ent temperatures; the variation of threshold voltage with temperature is shown in Fig. 10.

It is known that during a memory switching process, a crystalline channel is formed between the electrodes at the switching voltage leading to the low-resistance state. The high current re-setting pulse succeeds in melting the crystalline material and cools it rapidly to a glassy state. Decreasing the threshold voltage with increasing temperature supports the idea that a thermally produced crystalline filament is responsible for switching. As the temperature is increased molecular rearrangement and relaxation becomes easier in the glass, which causes further formation of the crystalline filament.

To observe the existence of a conduction channel at the on-state, contact points between electrodes and samples were removed to a place nearby to the switched area and it was found that this part of the sample was still in the high-resistance state.

It has been suggested by Suji and Kao [20] that the filament formed by the application of a threshold voltage in the case of threshold switching may consist of a mixture of amorphous and crystalline regions in the switching area, but the filament responsible for memory switching may consist of crystalline region only as has been observed by Moridi and Hogarth [21]. Cohen *et al.* [22] suggested that the memory action occurs by switching initially to a filamentary threshold on-state and that the maintained current causes the slow crystallization to take place and a memory state to be formed. Chunghi *et al.* [23] reported that the *V–I* characteristics of vanadate glasses in the switching process can be interpreted in terms of thermal effects. As the voltage in the high-resistance state is increased, the current becomes increasingly non-ohmic due to self-heating. The conductivity increases and an internal temperature rise yields a collapse of the current region into a filament at a critical temperature at which devitrification takes place. Thus the irreversible switching action occurs once on the surface of the glasses, if the filament is devitrified completely during the delay and switching time, and the structure is not reversible. The observation of a devitrified filament formed after switching reveals that the switching action is associated with a phase transition from a disordered glassy state to an ordered devitrifed state due to self-heating effects.

Drake and Regan [24] worked on the switching phenomena of V_2O_5–P_2O_5–CuO glasses and reported that these glasses exhibit different switching properties depending upon the glass compositon and switching arrangements. They found that glasses with high vanadium content exhibit two types of switching, memory and threshold, dependent upon the switching circuit, and glasses made with a lower vanadium content do not show threshold switching properties but only show a memory effect.

7. Conclusions

The high electric field experiments show that the electrical conductivity of these glasses is ohmic at fields below 4×10^5 V cm^{-1} and above this field the behaviour becomes non-ohmic as a result of lowering of the potential barriers at high electric fields. The ohmic region of the *I–V* characteristics tends to be extended to higher fields as the temperature rises. The value of the jump parameter (*a*) was found for V_2O_5–P_2O_5 glasses to of the order of 2.1 nm, which is some five times higher than actual *V–V* ion spacing determined from chemical analysis and ESR data.

The glasses show memory switching phenomena independent of electrode material, but the

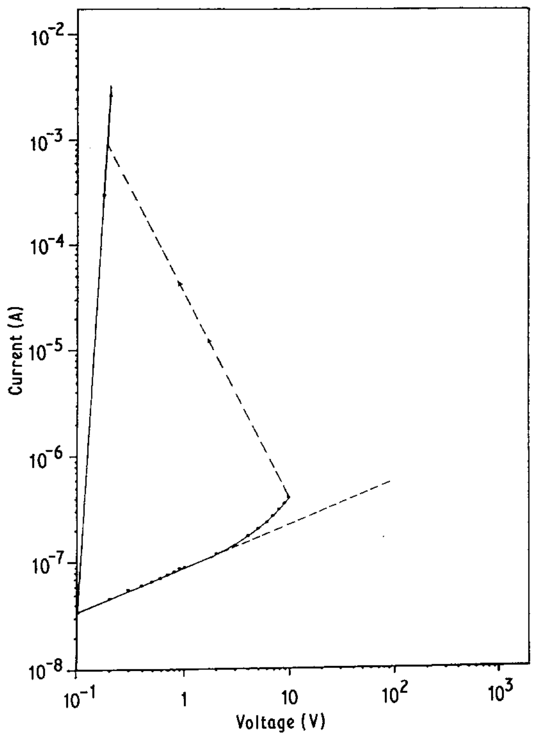

Figure 11 *V–I* characteristic (memory) of a ternary glass sample at room temperature.

threshold voltage decreases with increasing temperature and depends on the thickness of the sample. Thicker samples of the same composition switch at a higher voltage. The experiments reported here suggest that during the switching action a devitrified filament (conducting channel) forms after the first switching and this reveals that the switching action is associated with a phase transition from a disordered glassy state to an ordered devitrified state due to a self-heating effect, and that the conductive zone consists of VO_2 crystals which possess a more metal-like conductivity.

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