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Observation and compositional studies of the metallic conducting filaments in the low-resistance state (ON-state) of SiO/V_2O_5 thin films used as memory elements

F. A. S. AL-RAMADHAN, C. A. HOGARTH
Department of Physics, Brunel University, Uxbridge, Middlesex, UK

Memory elements of SiO/V_2O_5 co-evaporated thin films with copper or silver electrodes were studied in the scanning electron microscope. Electron probe microanalysis revealed the existence of metallic filaments in the dielectric material when it was in the ON-state and the resistance was typically in the range 2 to 60 Ω at room temperature. When the sample resistance was in the range 10 to 100 kΩ at room temperature and the sample was in the OFF-state, no structural changes in the sample were observed. The properties in the ON-state are consistent with the diffusion of metal from the electrodes during the foming process to form conducting filamentary paths.

1. Introduction

An amorphous high-resistivity semiconductor or a dielectric material sandwiched between two electrodes can show very interesting properties as, for instance, memory switching, and for this an amorphous material is used whose structure can be changed reversibly between two structural states, the amorphous state which has a high resistance and a microcrystalline state which has a low resistance [1]. Switching effects have been reported by many workers on glasses and evaporated thin films alike. Switching properties of thin NiO films were studied by Gibbons and Beadle [2]. The switching action was thought to be due to the formation and subsequent rupture of a nickel filament in the NiO matrix. An S-type negative-resistance region in the voltage–current characteristics of thin films of both silicon oxide and aluminium oxide was reported by Argall [3]. A switching phenomenon was observed where the film could be switched from an insulating to a conducting state and vice versa, by the application of suitable pulses.

The switching effect of thin polycrystalline films of VO_2 has been identified [4–6] as being caused by self-heating to a phase transition at 68° C where the resistivity of VO_2 drops by a factor of some 10^3. Cope and Penn [7] have also studied VO_2 and concluded that the switching behaviour observed in vanadium oxide fused on to platinum electrodes, could be explained in terms of the thermal transformation of a central region of the material to another phase showing the metallic conduction mode.

The work of Ovshinsky [8] on the reversible electrical switching in the disordered chalcogenide semiconducting materials, initiated more research into the switching phenomena in glasses and thin films.

Argall [9] has shown that thin films of anodized titanium dioxide could be made to switch between three distinct conductivity states, and concluded that the reversible switching was not due to a phase change of the dielectric.

Bistable switching of various amorphous and polycrystalline materials has been reported by many workers. Hickmott and Hiatt [10] have reported on Nb_2O_5 diodes where switching appeared to be an electronic phenomenon, occurring at a small number of regions in the oxide. Sliva *et al.* [11] studied the CuO + epoxy system and Al_2O_3 and other materials including V_2O_5, and their diagnostic measurements enabled them to

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interpret the switching behaviour in terms of the formation and rupture of filamentary conduction paths. Park and Basavaiah [12] investigated Zr–ZrO_2–Au thin film samples and they observed physical changes during the forming and subsequent switching of their samples. A study of the physical changes indicated that in the low-resistance state the current was carried by a single filament centered around one of the spots formed while switching from the high-resistance state to the low-resistance state. A memory effect was observed in thin film Ta–SiO_2(B-doped)–Ag devices by Tronc [13] whose devices developed an ohmic conducting state on application of a few volts with the silver electrode positive, restoring the initial insulating properties achieved by the application of a few volts with the silver biased negatively. No explanation of this phenomenon was presented, but it was noted that no filament connecting the two electrodes was observed, contrary to observations on semiconducting chalcogenide glasses [14]. Switching effects have also been reported by Sutherland *et al.* [15] on Al–SiO_x–Ag and Al–ZnS–Ag devices. Regan and Drake [16] have reported memory and threshold switching in two-terminal devices made from a mixed transition metal oxide glass CuO–V_2O_5–P_2O_5 system. Cyclic switching of the memory devices showed a reproducible OFF-state resistance of order 1 MΩ and an ON-state resistance consistently less than 1 Ω. These devices were capable of passing a direct current of ~ 1 A when in the ON-state without either incurring physical damage or reverting to the OFF-state.

Memory switching in SiO has also been studied by Manhart [17, 18], and by Morgan and Howes [19], who reported on the reversible switching of SiO films and suggested a metallic diffusion from the electrodes as the reason for switching to the low-resistance state, and presented a model to account for it. The later workers [20] have ascribed the switching effects in copper oxide films to the formation of a copper monofilament resulting from the reaction $Cu_2O \rightarrow CuO + Cu$. Rakhshani and Hogarth [21] reported a switching effect in SiO/BaO thin films at atmospheric pressure and interpreted the characteristics in terms of a monofilamentary model. Recently, Moridi and Hogarth [22] studied memory switching in copper-calcium–phosphate glass devices and demonstrated that switching ON was associated with a local amorphous-to-crystalline transition and vice versa. Memory switching has also been observed in GeO_2 films [23]. Bipolar threshold switching in vanadate glasses has been reported by Dimitriev *et al.* [24]. An attempt was made to describe the switching using a model in which the electrostatic field increases the number of nuclei of the metal-like phase so that the device switched on.

Following our work [25] on a variety of memory effects which may be observed in thin film samples of Cu–SiO/V_2O_5–Cu, we have studied the structural changes resulting from the switching processes and have been able to identify filamentary regions which are responsible for conduction in the ON-state.

2. Experimental work

Preparation of the samples was performed as described in earlier work [25], but the evaporation pressure was different (4 to 2×10^{-5} torr). The electrical measurements were made by conventional methods. Scanning electron microscope studies were performed using a Cambridge Stereoscan microscope S4 which was operated at 20 kV, together with the electron microprobe analyser to observe the termination of the conducting filaments and study their compositions. Another Cambridge Stereoscan microscope type 250 MK 2 was used at 10 kV to observe the formation of what are thought of as metallic filaments in the dielectric material. The counter-electrode was etched away before the sample was prepared for microscopic examination. The etching off of the counter-electrode was achieved by the use of a d.c. sputtering unit where a continuous beam of argon ions at angles from between 25° and 65° to the surface bombarded the active area of a sample. This treatment lasted typically for some 5 h but the period depended on the thickness of the counter-electrode.

3. D.C. voltage–current characteristics

Fig. 1 shows a V–I plot for a sample of 650 nm thick and 83 mol% SiO/17 mol% V_2O_5 composition with silver counter- and base-electrodes of thickness 30 and 200 nm, respectively. The measurements were made at room temperature and the plot represents a typical characteristic for the electroforming or memory switching in such samples. The threshold voltage was 6.5 V after which forming occurred, switching the device to the ON-state, characterized by a low resistance of typically 46 to 62 Ω, which was found to be

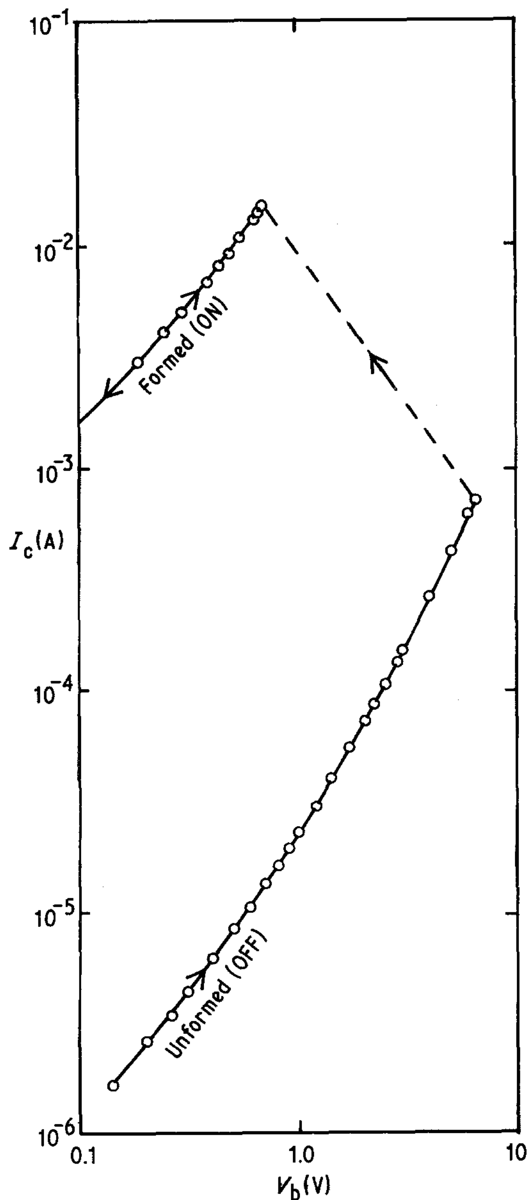


Figure 1 Voltage–current characteristics showing forming in an Ag–SiO/V_2O_5–Ag thin film assembly.

reversible in both directions of the applied field and which could be maintained even in the absence of the electric field. The OFF-state could be restored by applying a short duration pulse or passing a high current pulse. When these devices were electroformed, voltage-controlled negative resistance and emission currents were also observed, but in the present work we are devoting our attention to the physics of the forming process.

4. Scanning electron microscope studies

4.1. General details

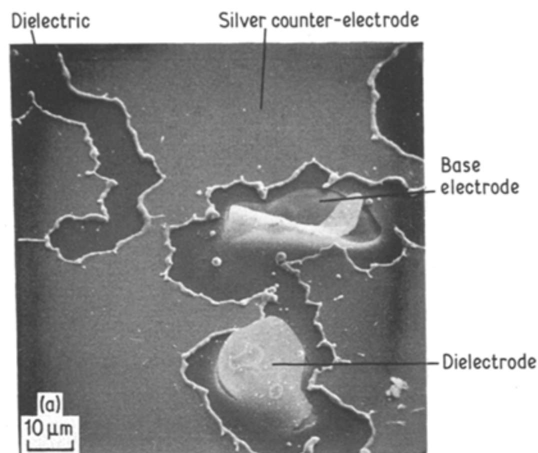
One of the new devices on the same substrate as the above sample was examined and biased under the scanning electron microscope. By applying a small voltage, it switched to the ON-state without incurring any damage and was very stable; its active area was free from obvious defects or pinholes which have been seen on many electrically operated thin film MIM devices [26]. When a high current (0.9 A) was allowed to pass through it, the device started to break down and switched to a high-resistance state showing pronounced damage at the edge of the active area, which is usually considered to be a weak region in the device. It is obvious that this damage could be caused by a thermal runaway due to very hot channels passing through that region and leading to the peeling off of the counter-electrode with the appearance of many tiny gas bubbles as shown in the scanning electron micrographs (Fig. 2a and b). Inspection of the feature in Fig. 2b shows that the hot channel has reached the surface obliquely as shown by the gradations in extent of molten material at its edge. A special feature seemed to be a large gas bubble observed at the centre of the active area (Fig. 2c) probably due to the migration of oxygen gas to the positive electrode due to the electrolytic process previously described by Rakhshani *et al.* [26].

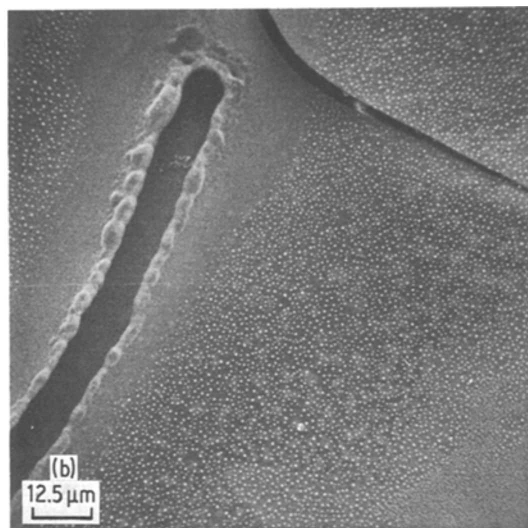
No significant emission current was observed in this case and it seems that the unbroken oxygen bubble probably blocked the creation of pinholes or craters characteristic of the termination of a filament regarded as centres for electron emission.

Fig. 3 shows the V–I plot for such a device whose threshold voltage for switching on was 7 V. By increasing the current flowing to 0.9 A the device reverted to a different high-resistance state. Another device on the same substrate was examined under vacuum but not in the scanning electron microscope and when a high current was passed with the device in the ON-state the resistance changed back to the original high-resistance state. Further cycles of applied voltage, however, led to the new high-resistance state shown by the first device. The V–I plot is shown in Fig. 4.

4.2. Observation of metallic filaments

In order to study the structure of the dielectric film used in the switching experiments, an argon ion bombardment of the samples was carried out





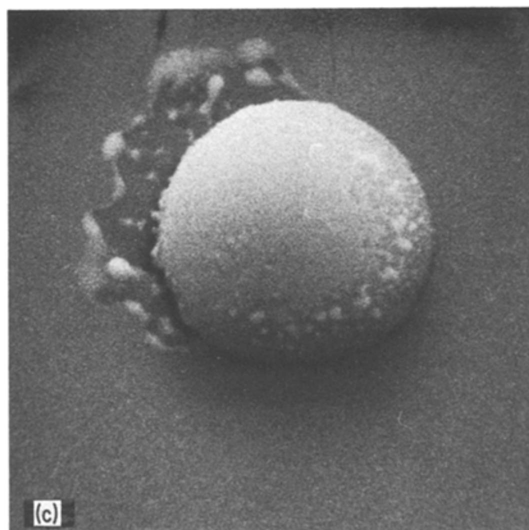


Figure 2 (a) Micrograph showing complete thermal breakdown in a sample of Ag–83 mol% SiO/17 mol% V_2O_5–Ag (magnification ×780). (b) Damage at the device edge with occurrence of tiny gas bubbles (magnification ×624). (c) Oxygen gas bubble at the centre of the active area, diameter $\simeq 5.6\,\mu m$ (magnification × 7800).

to etch away the counter-electrodes of a device left in the ON-state and one left in the OFF-state, both on the same substrate and having the same thickness, 190 nm. The dielectric composition was 56 mol% SiO/44 mol% V_2O_5 and the Cu counter-electrode was 110 nm thick. Fig. 5, for the formed device, shows a number of features which seem to be the termination of filaments at the surface, probably microcrystalline in nature following local melting and produced by some sort of diffusion process during the electroforming process. A number of such features were observed across the surface of the sample. Fig. 6 shows one of the same features in more detail. The mottled background appearance is likely to be due to slight surface damage caused by the etching process.

4.3. Electron microprobe analysis

Initially, the counter-electrodes of the samples were etched off and the samples were then carbon-coated to prevent them being charged during electron scanning. Two devices were examined, one left in the ON-state and the second in the OFF-state.

The ON-state device was observed to have developed on the dielectric many features or defects (Fig. 7) which were clearly characteristic of the termination of the conducting filaments.

Using a Stereoscan scanning electron microscope (Cambridge S4) with a dispersive system for X-ray detection, by setting the detector to pick up only X-rays of a particular wavelength, it is possible to display the spatial distribution of a particular element in the sample. We have used this technique to study the central region of the termination of a filament. The silicon $K\alpha$ (0.7126 nm) line, vanadium $K\alpha$ (0.2505 nm) line and copper $K\alpha$ (0.1542 nm) line were used for the scan display.

Fig. 8 shows the vanadium scan and the line tends to decrease slightly in the centre of the defect and indicates a slight deficiency in vanadium metal in that region. Fig. 9 shows the silicon and

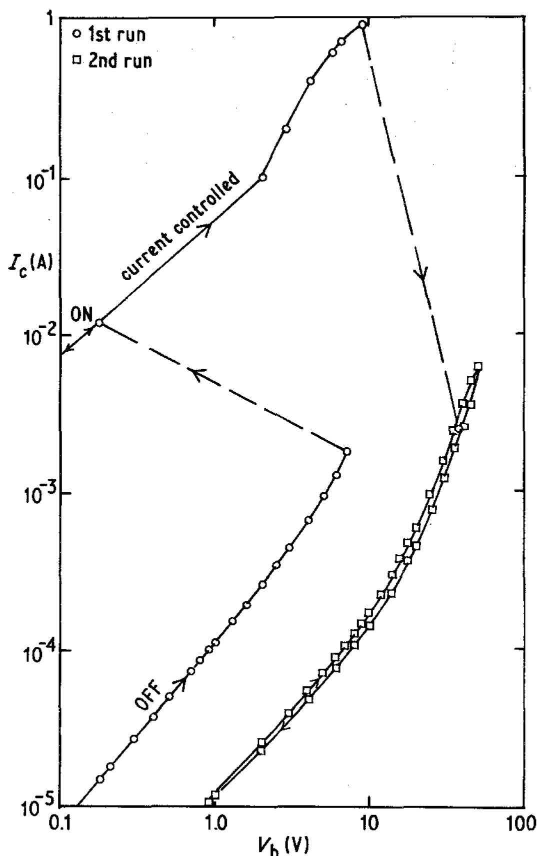


Figure 3 Voltage–current characteristics of a device switched back to a higher resistance state.

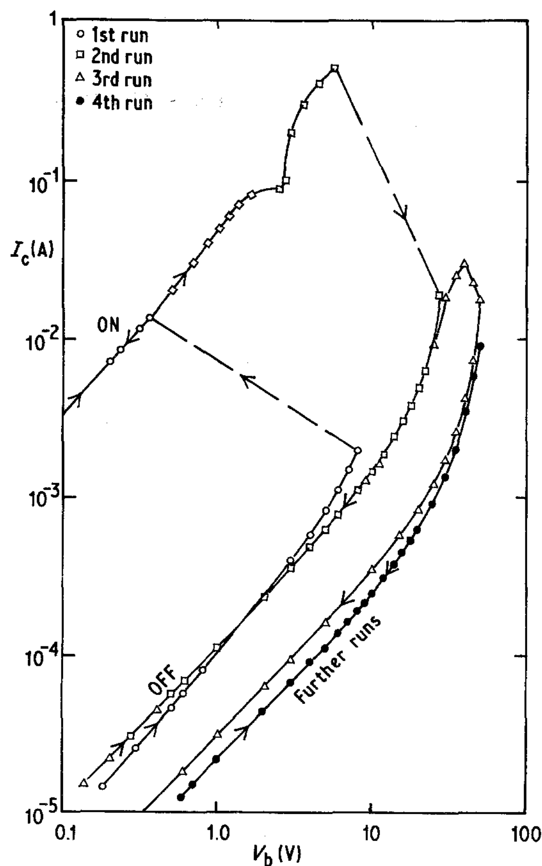


Figure 4 Voltage–current characteristics of another device on the same substrate as in Fig. 3, but switched back to the original OFF-state. Higher resistance state is retained in further runs.

copper scan lines superimposed on each other. The upper line near the edge on the micrograph is for silicon; the lower is the copper line.

These micrographs show clearly the composition of the ends of the conducting filaments where they have a deficiency in silicon and a higher composition of copper probably due to copper having diffused from the electrodes and forming relatively highly ordered metallic filaments. Fig. 10 shows a micrograph of a device left in the OFF-state and no significant change in the structure of the dielectric material was observed.

5. Discussion of results

Restoring the high-resistance state of an electroformed sample by passing a high current resulted in the development of gas bubbles on the surface of the counter-electrode, which is indicative of high local heat dissipation. Part of the evolution of gas at this time is due to this local heating.

The electrolytic process suggested by Rakhshani *et al.* [26] was tested in the following

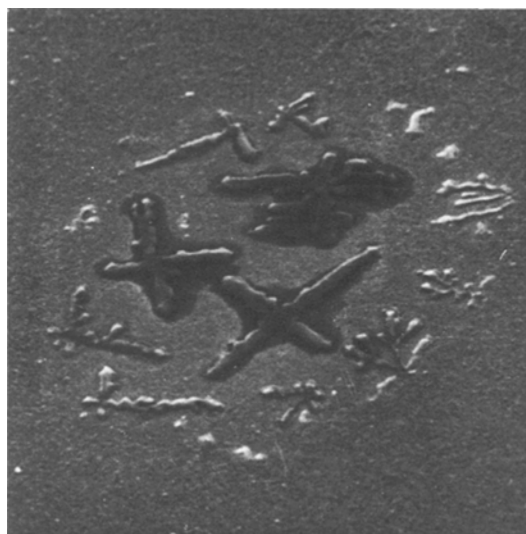


Figure 5 Formation of conducting filaments in Cu–56 mol% SiO/44 mol% V_2O_5–Cu sample.

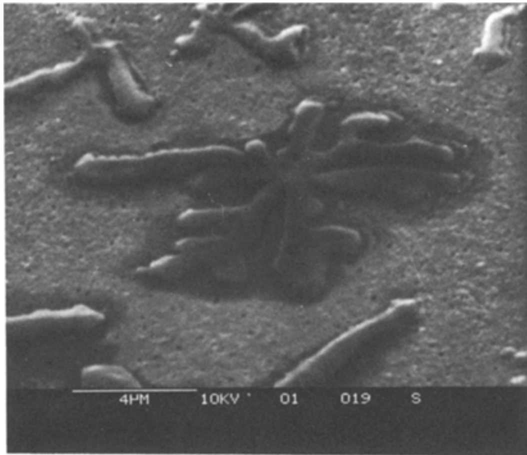


Figure 6 Magnified region from Fig. 5 showing details of the filaments.

manner: a high current (1 A) was allowed to pass for 3 min in a formed sample until finally the filaments melted or broke down thermally. This high circulating current was accompanied by an emission current of compensating electrons detected by the electrometer in the range 2×10^{-10} to 2×10^{-8} A, with liberation of oxygen gas which led to an increase in the pressure of the sample chamber indicated by the Penning gauge reading. This was initially 1×10^{-5} torr and then increased to 6×10^{-4} torr after the passage of the high current.

The switching behaviour of our samples may be summarized as follows.

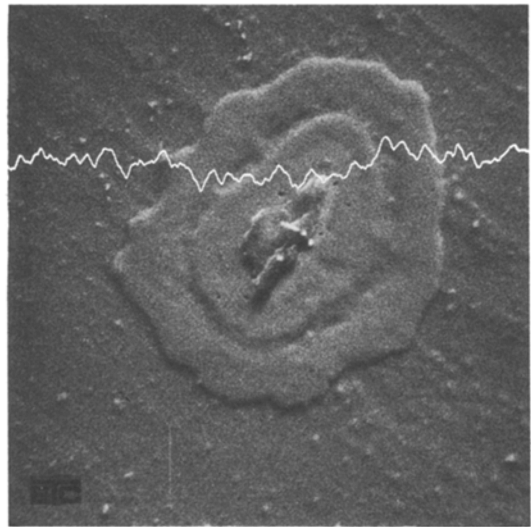


Figure 8 Vanadium scan line in the centre of the filament termination showing slight deficiency in vanadium metal (magnification × 1404).

1. The memory switches can be used to control the flow of electric current.
2. They are very stable while operating up to 0.5 A, but some samples were capable of passing a direct current of 1 A when in the ON-state without either incurring physical damage or reverting to the OFF-state.
3. The current can be made to pass through the sample in either direction i.e. the V–I characteristic is symmetrical with respect to the direction of the applied voltage.

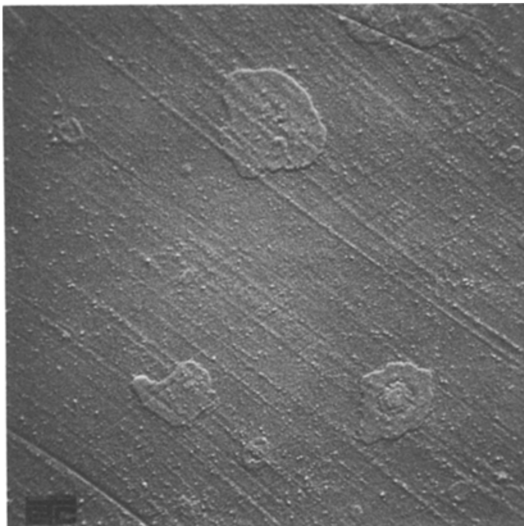


Figure 7 Micrograph showing several terminations of filaments (magnification × 351).

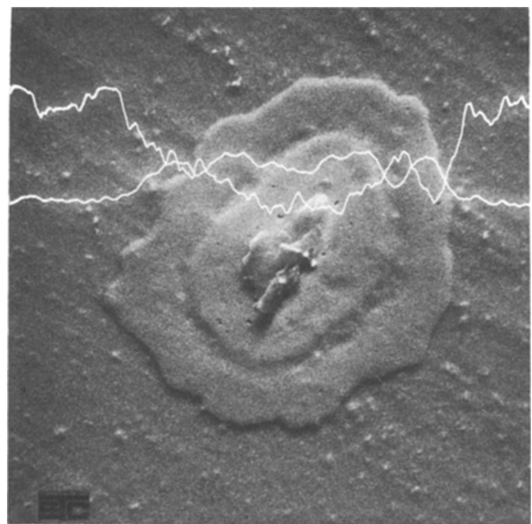


Figure 9 Silicon and copper scan lines superimposed. The upper line near the edge of the micrograph is for silicon; the lower is a copper line (magnification × 1404).

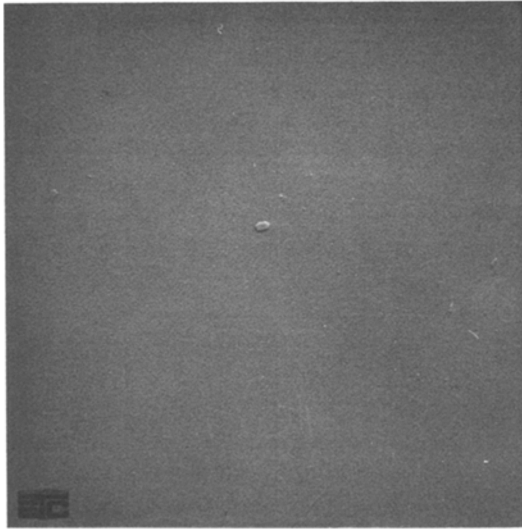


Figure 10 Micrograph of a device left in the OFF-state showing no structural change in the dielectric material (magnification × 293).

4. The magnitude of the power consumption (~ 2 to 10 mW) in the ON-state is evidence for the electronic nature of this switching.

5. Observation of isolated formations of filaments and their isolated terminations from the rest of the material after switching took place, suggests that a separation of the dielectric material and the metallic filaments has taken place because of the difference in their freezing points. In addition it means that the rest of the dielectric did not play any major part in the conduction and kept cool and disordered during switching while hot channels of highly ordered structure, probably microcrystalline in nature, were the main current-carrying paths.

6. The high current required to restore the high-resistance state was sufficient to melt the filament, mixing it with the dielectric constituents and because of the rapid cooling that follows, a new amorphous phase is frozen in place resembling to a certain extent the properties of non-linearity of the original pre-forming phase or giving rise to the production of a phase of even higher resistance.

The conduction thermal activation energy, ΔE, of the final high resistance state has been determined by measuring directly the resistance of the device as a function of temperature at zero applied voltage and at constant rate of rise of temperature (0.7° C min^{-1}) and found to be 0.125 eV. Assuming Schottky emission at the contact, the value of the relative dielectric constant was found to lie in the range 1.6 to 3.7, the lower value being characteristic of the pre-switching off-state and the higher was measured for a sample in post-switching high resistance state. The potential barrier height at the contact was found to be of order 0.6 to 0.7 eV at $V = 0$.

It is found that samples with composition less than 50 mol% V_2O_5 exhibited switching action of the above type provided their preparation pressure was of the order of $4\text{–}2 \times 10^{-5}$ torr or lower.

7. Switching action was observed with copper and silver electrodes and since both metals are known to have a high diffusivity and mobility, it is assumed that metal diffusion takes place from the electrodes when a channel is heated by a thermal instability above a critical field of about 10^5 V cm^{-2}. The power fed into the device exceeds the power dissipated and thus thermal equilibrium is destroyed, the resistance decreases rapidly and the high mobility of the electrode metal will facilitate charge transport to a continuous metallic filament produced through the dielectric film as a result of applying a high current during the forming process.

The ON-state now has a stable linear $V\text{–}I$ characteristic nearly ohmic in nature and has a positive temperature coefficient of resistance. The suggestion of metallic diffusion into the dielectric material is further supported by the high metallic composition of the terminations of the conducting filaments carried out using electron microprobe analysis. Our observations agree with a model of switching proposed by Manhart who suggested metal diffusion from the electrodes for the conduction in the ON-state and a field dependence mechanism for conduction in the OFF-state.

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