JOURNAL OF MATERIALS SCIENCE 19 (1984) 1718–1725

Some electrical properties of thin film sandwich assemblies of SiO/V_2O_5

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

Thin films of the complex dielectric material SiO/V_2O_5 were prepared by a co-evaporation technique and used as the insulator material in MIM structures in which the metal M was copper. Most of the samples could be electroformed at between 4 and 9 V applied. They then exhibited a voltage-controlled negative resistance associated with an emission current into vacuum whose density was of the order of 10^{-5} A cm^{-2}. Voltage–memory, thermal voltage–memory and ambient pressure–memory effects were also observed. A polyfilamentary model was used to interpret these properties.

1. Introduction

It is now well established that a large variety of thin film amorphous oxides can be electroformed and show interesting and potentially useful electronic effects such as voltage-controlled negative resistance (VCNR), switching and memory effects, electron emission into a vacuum and electroluminescence. Electroforming is a process which takes place when a relatively low voltage, well below the normal dielectric breakdown voltage, is applied across the dielectric thin film sandwich so that the current increases rapidly, typically by two or more orders of magnitude at a fixed voltage. The process is accompanied by the development of the variety of effects listed above.

Much of the early work was reported by Hickmott on Al_2O_3 films [1] where VCNR and large circulating current densities were observed. The voltage–current (V–I) characteristics were explained by him in terms of a space-charge-limited conduction mechanism. Simmons and co-workers [2, 3] performed basic experiments using SiO as the dielectric material and the work on thin film complex dielectric materials initiated by Hogarth and Wright [4] was extended to the study of electroforming phenomena. Initially thin films of 70% SiO/30% B_2O_3 were studied by Taheri *et al.* [5] and found to give considerably higher electron emission currents than thin films of SiO investigated under similar conditions. Abidi and Hogarth [6] studied similar phenomena in the thin films of 70% SiO/30% BaO, and Rakhshani and Hogarth [7] also studied SiO/BaO samples having different compositions. They both reported electron emission; the latter paper also reported observations of the thermal voltage–memory effect and used the filamentary model originally postulated by Dearnaley *et al.* [8] to interpret the experimental results.

A number of models have been suggested to account for the forming process and related phenomena and these are of two main types. The first type of model deals with iso-energetic tunnelling of electrons through a band of localized states within the insulator band gap as in the models of Simmons and Verderber [2], Hickmott [9] and Verderber *et al.* [3], or describes the electrical conduction by means of a combination of ionic and tunnelling mechanisms as reported by Barriac *et al.* [10, 11], or by electron tunnelling through chains of defect centres produced during the forming process as a result of solid-state electrolysis as given by Greene *et al.* [12]. The second type of model, the polyfilamentary model which was first proposed by Dearnaley *et al.* [8] and extended by Ralph and Woodcock [13], has had considerable success in explaining the various electrical properties of the electroformed devices. Dearnaley *et al.* [8] have suggested that electrical conduction through each filament is ohmic in nature and Joule heating-assisted rupturing of the filaments is responsible for the differential negative

0022–2461/84 \$03.00 + .12

resistance effect. In the model of Ralph and Woodcock [13] a band structure is associated with each filament and conduction then occurs by isoenergetic tunnelling at low voltages. At higher voltages the electrons enter localized states both within and outside the filaments and eventually lead to a reduction in the current flow.

In earlier work at Brunel, much attention has been given to complex materials whose component oxides would form a glassy structure if melted together above the appropriate glass-forming temperature. Preparation of quasi-glassy films by the co-evaporation technique provides a series of interesting dielectrics in thin film form and which are capable of exploitation as passive or active electronic components. In this paper some results for thin films of oxide complexes based on the system SiO/V_2O_5 are reported. No information is reported in the literature on such amorphous thin-film complexes but much work has been published on V_2O_5 to which a glass former such as P_2O_5 has been added. This system was extensively studied as an example of displaying the semiconducting properties resulting from a hopping process due to the existence of reduced oxidation states of vanadium ions V^{4+}. Conduction is a consequence of small polarons hopping between V^{4+} and V^{5+} ions [14]. In such glasses even with as much as 90 mol% V_2O_5 as one constituent [15], the electrical conductivity is found to increase with increasing V_2O_5 content and at the same time the activation energy for conduction decreases.

2. Experimental work

2.1. Sample fabrication

The samples were deposited on to cleaned 1 in. x 3 in. (2.54 cm x 7.62 cm) 7059 Corning glass substrates by the vacuum deposition of successive layers of metal–insulator–metal at pressures of about 8×10^{-6} torr in a Balzers BA 510 coating system, with a substrate temperature of 150° C for the dielectric and 100° C for the electrode depositions. The warming of the substrate improved the adhesion of the thin films. The rate of evaporation was monitored and controlled during the evaporation by the use of a number of quartz-crystal monitors and the rates were 2 nm sec^{-1} for V_2O_5 and about 0.8 nm sec^{-1} for the SiO and the metal electrodes, but the values were varied to obtain films of differing but controlled compositions. Two quartz crystal monitors were used so that the individual evaporation rates of the two oxides were continuously controlled and recorded following a co-evaporation technique developed by Hogarth and Wright [4]. Six samples were deposited on each substrate with a common base electrode of copper. This was followed by the deposition of six copper electrodes of different thicknesses (60 to 100 nm) as counter-electrodes. Each device had an active area of 10 mm^2. Fig. 1 shows the arrangement of the samples.

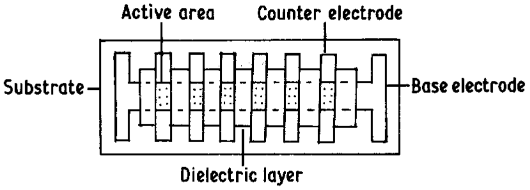

Figure 1 Arrangement of the specimens.

2.2. Forming experiments

Electrical measurements were made by conventional methods using a subsidiary vacuum system at a pressure of about 10^{-6} torr and the forming experiment was started by increasing the applied voltage by a 1 V step min^{-1} until the circulating current, I_c, through the device started to increase rapidly and continued to do so until no further change was noted and the forming process was then complete. The voltage–current characteristics were recorded and then emitted electrons were collected by a copper anode positioned 1.5 cm vertically above the substrate and biased at + 100 V with respect to the base electrode of the device. The emission current was measured using a Keithley 610 C solid-state electrometer. The sample temperature during the experiments could be monitored approximately by the use of a fine copper–constantan thermocouple attached to the counter-electrode. Silver paste was used to make good contact between the counter electrode and the pressure contacts.

2.3. D.c. voltage–current characteristics

Fig. 2a shows a reproducible V–I characteristic of a sample composition 68 mol% V_2O_5/32 mol % SiO, having a thickness of 159 nm, and with a 32 nm thick copper counter-electrode. Initially ohmic behaviour is observed but at an applied voltage of 9 to 10 V the current starts to increase rapidly to a level between 100 and 1000 times the current before forming. The new state of the sample is shown in the "formed" part of Fig. 2a and the sample does not revert to the initial

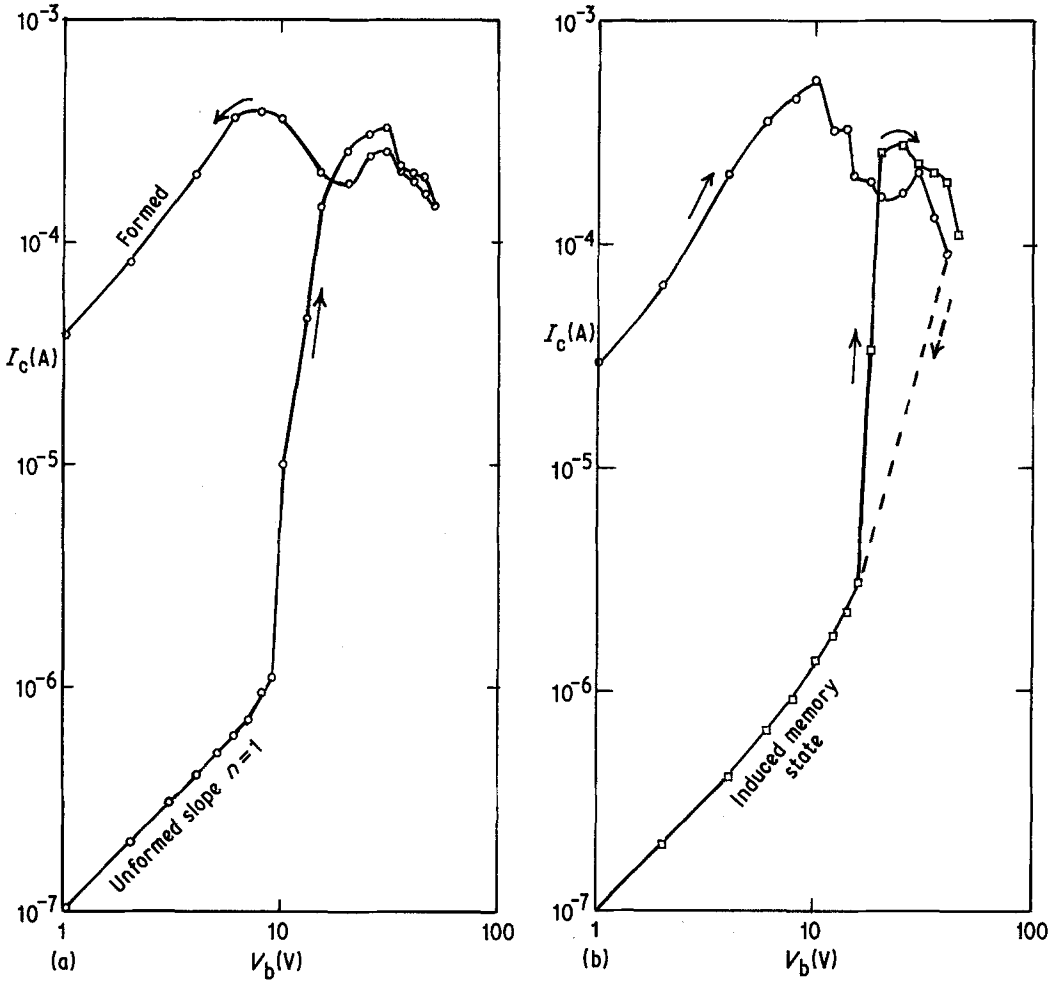

Figure 2 (a) Voltage–current characteristics of a 32 mol% SiO/68 mol% V_2O_5 sample. (b) Curves showing voltage–memory effect. (Memory state induced at 40 V applied.) (c) Curves showing thermal voltage–memory effect at – 67° C. (d) Effect of ambient pressure and curves for pressure voltage–memory in a Cu–67 mol% SiO/33 mol% V_2O_5–Cu sample.

unformed state when the applied voltage is reduced to zero. In the formed state regions of differential negative resistance are observed.

The power dissipated in the device just before the forming process starts is $\simeq 0.01$ mW but after forming the peak power is $\simeq 3$ mW, the type of power level often relevant to signal-translating electronic circuits.

2.4. Memory effects

A voltage–memory effect exhibited by the same sample at room temperature is shown in Fig. 2b. It was found that a high-resistance memory state could be induced if the voltage were lowered rapidly from any point on the VCNR trace to zero, followed by the switching off of the power supply for a very short time. When the voltage is re-applied the original high-resistance state is re-generated up to a particular threshold voltage where the current increases sharply to join up the previous high-conductivity state in the VCNR region.

A thermal voltage–memory effect can also be generated in our samples as shown in Fig. 2c when the sample temperature is reduced to – 67° C. The first curve traces the same V–I characteristic as normally recorded after forming but when the applied voltage is reduced to zero, a high-resistance memory state is generated and preserved during subsequent measurements of V–I characteristics. The high-resistance state is similar in characteristic to the original unformed sample. Raising the sample to room temperature again develops the low-

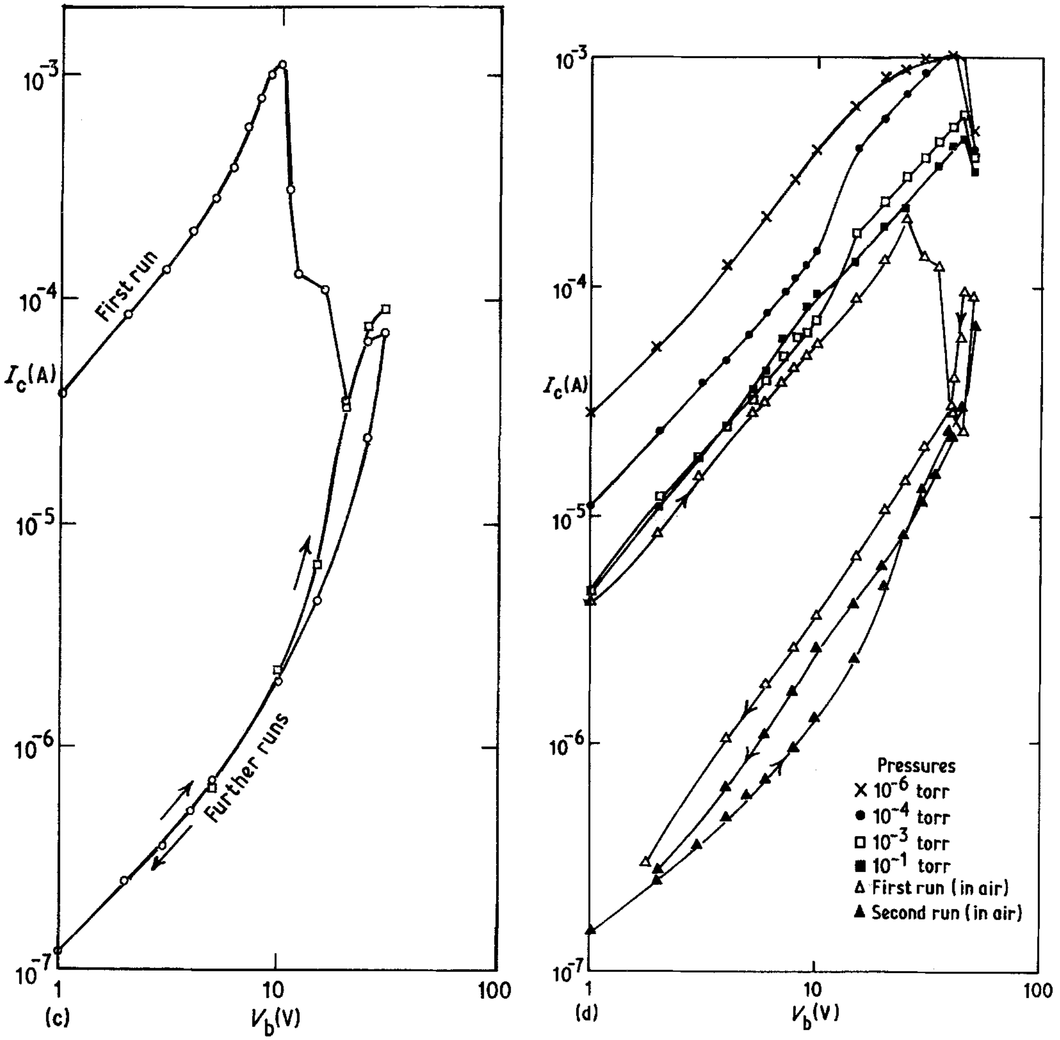

Figure 2 Continued.

resistance state characteristic of an electroformed device. The latter state may also be obtained by temperature cycling of the sample.

Pressure voltage–memory effects could be observed using another procedure involving changes in the ambient atmosphere around the sample. An electroformed sample having an insulator thickness of 500 nm and a composition 33 mol% V_2O_5/67 mol% SiO was tested at different ambient pressures from ~ 1×10^{-6} to 760 torr as indicated in Fig. 2d. The current passing through the sample was found to follow more or less the same V–I characteristic as is seen in a good vacuum (1×10^{-6} torr) with the peak current decreasing as the pressure increases. At atmospheric pressure the current followed the same characteristic up to a certain threshold voltage V_T. Increasing the voltage above V_T caused a decrease in the current and the development of a high-resistance state. This was maintained by reducing the voltage to zero, when the current then assumed a different value depending on the ambient pressure. Increasing the voltage again and then reducing it to zero generated a high-resistance memory state at atmospheric pressure. This could be erased by reducing the air pressure to 10^{-6} torr again and applying a bias voltage of 40 V across the sample.

The value of the voltage corresponding to the change in the conduction state and to the loss of the memory depends on the character of the change in pressure [16]. When it increases the threshold voltage is 25 V while for a decrease it is about 40 V. In the first case the degree of forming decreases; in the second it increases.

TABLE I Some parameters of thin V_2O_5/SiO thin films

Sample thickness (nm)	Forming voltage (V)	Voltage for maximum current (V)	Composition (mol %)		Maximum current (A)	Power dissipated (mW)
			V_2O_5	SiO		
190	–	50*	100	–	5×10^{-6}	0.25
159	9	8	68	32	3.8×10^{-4}	3
500	6	15	33	67	8.0×10^{-3}	128
545	9	15	30	70	9.7×10^{-3}	146
750	9	20	24	76	9.5×10^{-3}	190
340	6	12	17	83	1.3×10^{-2}	33
520	2–4	4	–	100	1.6×10^{-2}	64†

*For 100 mol% V_2O_5 there is no forming at our applied voltage and the current shown is simply the value at 50 V our maximum applied p.d.

†Data taken from Gould [17].

2.5. Composition studies

It is known that the electrode material used can have a major effect on the properties of formed MIM devices since some of this material is introduced into the insulator during the electroforming. In the present work we have kept to copper as an electrode material as it has been shown to lead to good forming and emission effects in many materials used in this type of experiment.

The effect of the composition of the oxides on the maximum current, I_{max}, and the power dissipated, P_{max}, at this current has been studied for a variety of samples as listed in Table I. In general it is found that the addition of V_2O_5 to the complex material leads to a decrease in the electrical conductivity of the film, unlike the result for vanadate glasses when the addition of V_2O_5 generally increases the conductivity. The pure V_2O_5 film reported in the table displayed an ohmic characteristic with very low values of current and as the SiO content increased so did the conductivity. Another general result was that thinner films generally displayed a low power dissipation at I_{max} and in any application of these devices this feature may be of technical importance in the design of precisely specified devices.

2.6. Transmission coefficient measurements

Significant electron emission was observed in a number of samples. The results of one such experiment are shown in Fig. 3a for a sample of insulator thickness 500 nm, composition 33 mol% V_2O_5/67 mol% SiO, and with 80 nm thick copper electrodes. The bias voltage was increased gradually in 1 V steps. The circulating current started to increase substantially at 6 V applied and it was left at this value for some 16 min at which point the current flowing stabilized. During this period the emission current started to increase. The bias voltage was then further increased in 1 V steps and at 13 V the circulating current again rose sharply to 8×10^{-3} A at 16 V applied and in this range the emission current rose by over four orders of magnitude to a value of ~ 2×10^{-6} A at 26 V applied. On reducing the value of V_b to zero the sample remained in the formed condition. Fig. 3b shows how the emission current is reduced rapidly by several orders of magnitude when the applied voltage is reduced to zero, following a curve only slightly displaced from the curve obtained for an increasing value of V_b.

The second run for the formed sample is shown in Fig. 4a where the initial curve up to 40 V shows an ohmic characteristic and a fairly high current level suggesting a stable arrangement of conducting filaments as discussed later. At 45 V applied there is a major change in the disposition of the conducting paths and a rapid decrease in current by one or two orders of magnitude. On reducing the applied voltage a further ohmic regime with a current level about one-tenth of the original current level for increasing applied voltage is seen. Fig. 4b shows how the transmission coefficient varies with applied voltage for the first and second runs. In the second run the transmission coefficient, α, defined as the ratio of emission current to circulating current for a given applied voltage ($\alpha \simeq I_e/I_c$) is found to increase rapidly at about 40 to 45 V and to show much less fluctuation for the applied voltages at which significant electron emission is recorded. Maximum values of α are ~ 2.5×10^{-4} for the first run and 6.4×10^{-4} for the second run.

Values of emission current density at the higher

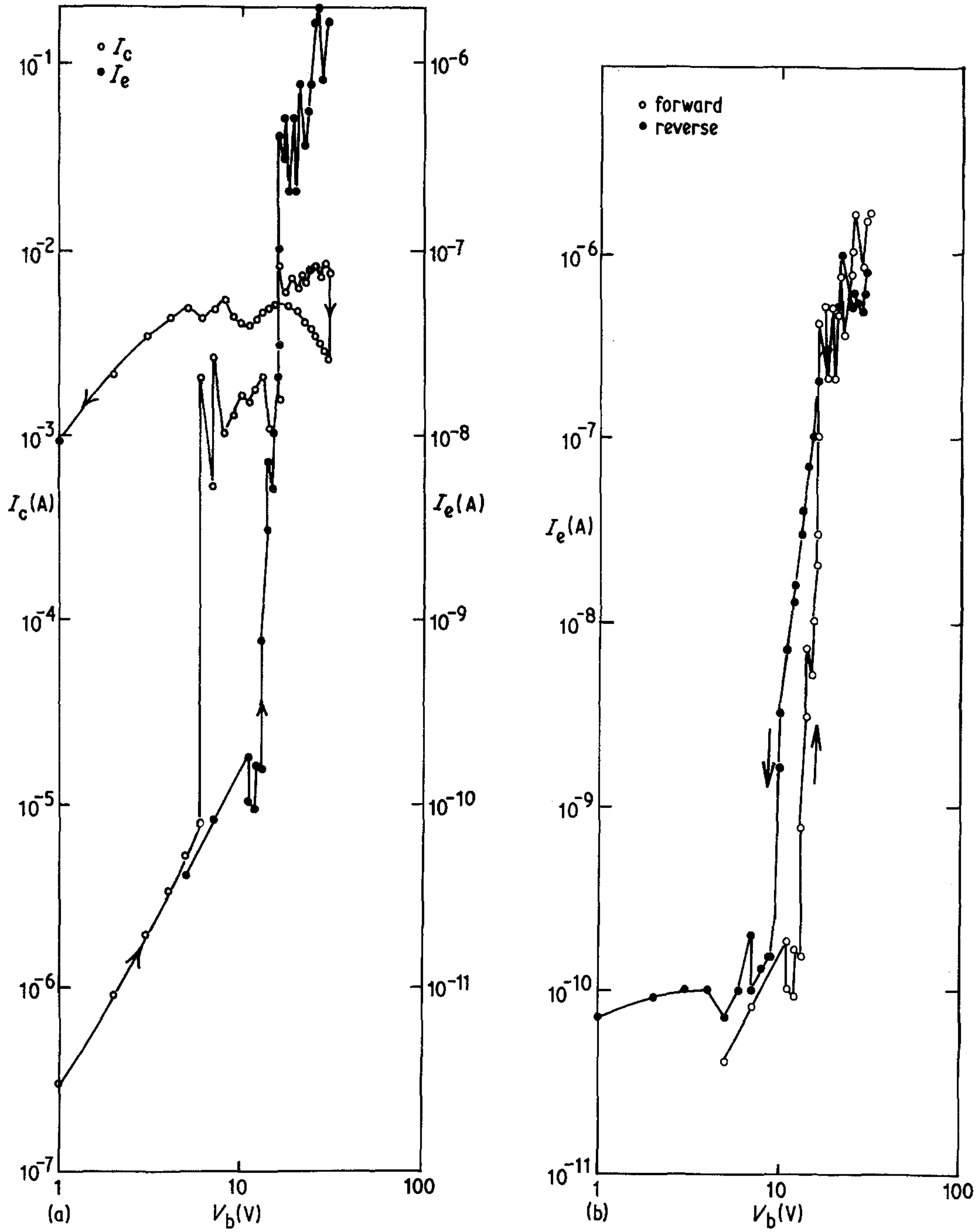

Figure 3 (a) Formed characteristics with emission current, I_e, as a function of bias voltage, V_b. (b) Variation of emission current with bias voltage for the sample in (a).

ends of the curves given in Figs. 3b and 4b are of order 10^{-5} A cm^{-2}.

3. Discussion of results

The generation of conducting filaments during the electroforming process as originally suggested by Dearnaley *et al.* [8], developed by Ralph and Woodcock [13] and by Rakhshani *et al.* [18], and their subsequent rupturing at the higher applied electric fields can explain many of the details of the properties of active MIM devices. So far as the memory effects are concerned a qualitative explanation may be offered based on the filamentary theory.

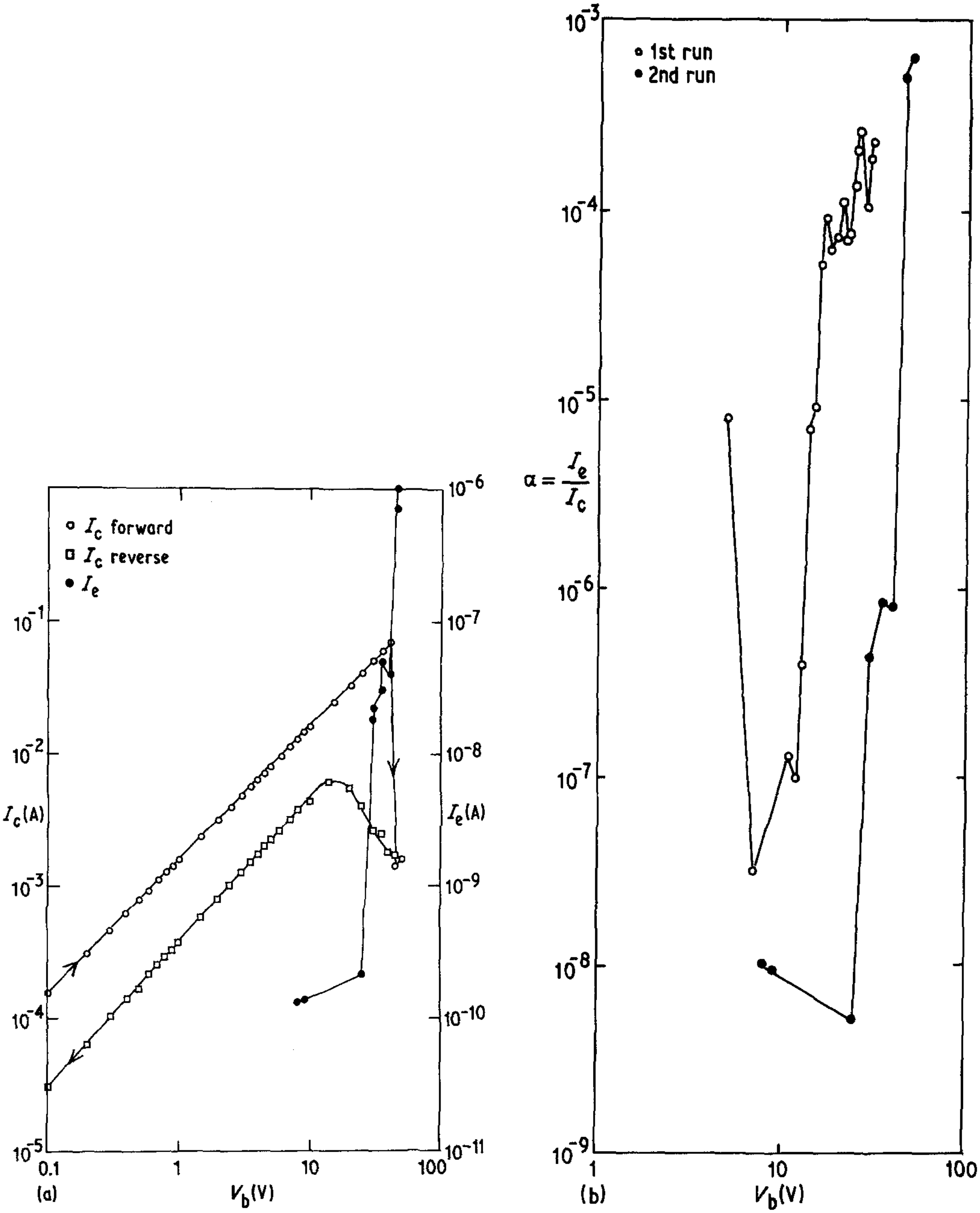

Figure 4 (a) Second run for the sample of Fig. 3a giving an emission current virtually free from fluctuations. (b) Transmission coefficient, α, as a function of bias voltage.

The simple voltage–memory effect (as shown in Fig. 2b) arises as follows. On the initial application of a higher voltage to the formed device the VCNR region is developed as the filaments rupture under the high rate of Joule heating dissipated in the conducting filaments surrounded by a poorly thermally conducting matrix. On reducing the applied voltage rapidly to zero the current falls rapidly to zero but the ruptured filaments have no time to reform and thus the sample finds itself in a high-resistance state and only reverts to the low-resistance state when an adequate voltage is applied to provide a healing of the original rupturing and filamentary re-establishment.

The thermal voltage–memory effect may be explained by considering a resistance distribution of the filaments as postulated by Dearnaley *et al.* [8] and as considered for the SiO/B_2O_3 dielectric system by Hogarth and Kompany [19]. Once a thermal voltage–memory is induced, it remains in the high-resistance state until all the broken filaments are re-joined. The recovery of the low-resistance state will be delayed until the high polarization of the dielectric near the ruptured region of the filament is reduced by a relaxation process involving thermally activated Poole–Frenkel emission of trapped electrons. The sample may be heated up to room temperature in an unbiased condition or the sample may be loaded with a bias voltage for a very long time. In general, as the maximum resistance of the broken filaments increases, it takes longer for the filaments to rejoin. This is consistent with the field-assisted emission of trapped electrons at lower effective electric fields around the broken parts of the high-resistance filaments.

The pressure–memory effect may be explained by stating that as with the case of Al_2O_3 films reported by Emmer [16] we assume the decrease in electrical conductivity associated with the increase of gas pressure to be due to the voltage-stimulated adsorption of oxygen. The low resistance regime has for the main conduction process electrons crossing the insulator via the filaments and the motion of these electrons will be to a certain extent controlled by surface states on the walls of the conducting filaments. By the adsorption of oxygen these electrons become immobilized since the surface states are occupied or satisfied and the quasi-hopping mechanism cannot take place. By again reducing the ambient oxygen pressure and gradually reducing the trapped oxygen, the low-resistance state may again be restored. It is clear that any effects of this nature will be more readily observed in thin film rather than bulk dielectric samples.

The other basic effects, i.e. the development of VCNR and electron emission, have been discussed at length in the references cited in this paper.

Acknowledgements

We should like to thank Dr S. A. Y. Al-Ismail and Dr A. Kompany for helpful discussions. One of us (FAS Al-R) would like to acknowledge the grant of study leave from the University of Basrah, Iraq.

References

1. T. W. HICKMOTT, *J. Appl. Phys.* **33** (1962) 2669.
2. J. G. SIMMONS and R. R. VERDERBER, *Proc. Roy. Soc. A* **301** (1967) 77.
3. R. R. VERDERBER, J. G. SIMMONS and B. EALES, *Phil. Mag.* **16** (1967) 1049.
4. C. A. HOGARTH and L. A. WRIGHT, Proceedings of the International Conference on the Physics of Semiconductors, Moscow, July 1968 (Academy of Sciences of the USSR, Nauka, Leningrad, 1968) p. 1274.
5. E. H. Z. TAHERI, C. A. HOGARTH and R. D. GOULD, *Phys. Status Solidi (a)* **12** (1972) 563.
6. A. A. ABIDI and C. A. HOGARTH, *Thin Solid Films* **22** (1974) 203.
7. A. E. RAKHSHANI and C. A. HOGARTH, *Int. J. Electron.* **42** (1977) 465.
8. G. DEARNLEY, D. V. MORGAN and A. M. STONEHAM, *J. Non-crystalline Solids* **4** (1970) 593.
9. T. W. HICKMOTT, *J. Appl. Phys.* **35** (1964) 2679.
10. C. BARRIAC, P. PINARD and F. DAVOINE, *Compt. Rend. Acad. Sci. Paris* **266** (1968) 423.
11. *Idem, Phys. Status Solidi* **34** (1969) 621. *Status Solidi* **34** (1969) 621.
12. P. D. GREENE, E. L. BUSH and I. R. RAWLINGS, "Proceedings of the Symposium on Deposited Thin Film Dielectric Materials", edited by F. Vratny (The Electrochemical Society, New York, 1968) p. 167.
13. J. E. RALPH and J. M. WOODCOCK, *J. Non-Crystalline Solids* **7** (1972) 236.
14. J. HAEMERS, E. BAETENS and J. VENNICK, *Phys. Status Solidi (a)* **20** (1973) 381.
15. T. N. KENNEDY, R. HAKIM and J. D. MACKENZIE, *Mat. Res. Bull.* **2** (1967) 193.
16. I. EMMER, *Thin Solid Films* **20** (1974) 43.
17. R. D. GOULD, PhD thesis, Physics Department, Brunel University, Uxbridge (1973).
18. A. E. RAKHSHANI, C. A. HOGARTH and A. A. ABIDI, *J. Non-Crystalline Solids* **20** (1975) 25.
19. C. A. HOGARTH and A. KOMPANY, *Int. J. Electron.* **53** (1982) 301.

Received 30 August
and accepted 21 September 1983