

ELECTROFORMING, SWITCHING AND MEMORY EFFECTS IN OXIDE THIN FILMS

D. P. OXLEY

Department of Physics, Leicester Polytechnic, Leicester, England

(Received December 14, 1976)

Experiments on electroforming of Metal-Oxide-Metal thin film sandwiches which have been electroformed to exhibit voltage-controlled negative resistance are summarized and an outline of recent evidence in favour of localized or filamentary conduction is given.

A similar review is given of the experiments on oxide sandwich structures which have been formed to exhibit current-controlled negative resistance or threshold switching and memory switching. Current theories are reviewed briefly. Finally oxide memory devices are compared with those based upon the chalcogenide glasses.

1. INTRODUCTION

A wide range of amorphous and crystalline oxide thin films when sandwiched between suitably selected electrodes (usually metal) can be processed so that they exhibit a wide range of interesting electrical properties. Such sandwiches can be made to exhibit voltage-controlled negative resistance (VCNR), current-controlled negative resistance (CCNR), threshold switching, analog memory switching, bistable memory switching and other potentially useful electrical effects. These properties have been reviewed by Dearnaley *et al*¹ and a later bibliography listed by Agarwal² includes some references to switching phenomena. Further papers have appeared since these articles were written and the literature of these effects is now quite extensive. The present paper will give a brief, but hopefully representative, review of this literature summarizing the reported practical significance and compare these switching and memory phenomena with those found in chalcogenide glasses.

2. FORMING

The review by Dearnaley *et al*¹ summarized a significant body of experimental evidence to show that:

1) Many metal-amorphous or crystalline oxide-metal thin film sandwich structures could have their electrical properties changed in a radical and irreversible manner by the application of a bias to the electrodes. This process has become known as 'forming'.

2) A large class of metal-amorphous oxide-metal thin film sandwiches could be 'formed' to show an enhanced conductivity in a vacuum and a low frequency VCNR and analog memories. Many workers refer to this process as electroforming.

3) Other forming processes can lead to CCNR and threshold or memory switching.

4) Some oxides can undergo both types of forming.

5) That the models advanced to explain these effects divide into two main groups consisting of schemes envisaging a relatively homogenous modification of the insulator during each type of forming or those envisaging localized or filamentary conduction in the formed state.

The processes leading to the classes of behaviour in (2) and (3) will each be discussed in more detail and the properties of the formed states reviewed.

3. ELECTROFORMING LEADING TO VCNR

Devices to be electroformed usually consist of a central insulating layer of thickness in the range 20 nm to about 1000 nm, a thickness of 100 nm being typical. The insulator is frequently an amorphous oxide layer prepared either by vacuum deposition or anodic oxidation. The selection for the conducting electrodes to complete the sandwich is limited for the anode (the electrode held at a positive potential during electroforming and subsequent operation) to specific materials; the choice of cathode being less critical. The anode is usually chosen by

experiment although the balance of evidence¹ would indicate that inert metal anodes assist in obtaining the electroformed state. Electroforming is carried out in a vacuum. The following results (Figure 1) from the early paper by Verderber *et al*³ show the difference between the formed and unformed state for an Au-SiO_x-Al sandwich where the gold electrode is positively biased in a vacuum of better than 10⁻² torr. When the bias is first applied the current is commensurate with that expected on the basis of the conductivity of the unformed insulator, i.e. small. At a critical bias, V_F , the current increases quite rapidly and irreversibly. Verderber *et al*³ report that at a given temperature this voltage V_F is reasonably reproducible for nominally identical structures and that it does not depend strongly on the thickness of the insulator; this indicates that electroforming is not simply related to the macroscopic average field. Later work¹ indicated that V_F varied somewhat with insulator and electrode composition. As the bias is cycled at a constant low frequency between 0 and $\sim V_F$ the forming progresses until the I, V characteristic becomes reasonably reproducible (Figure 2, curve

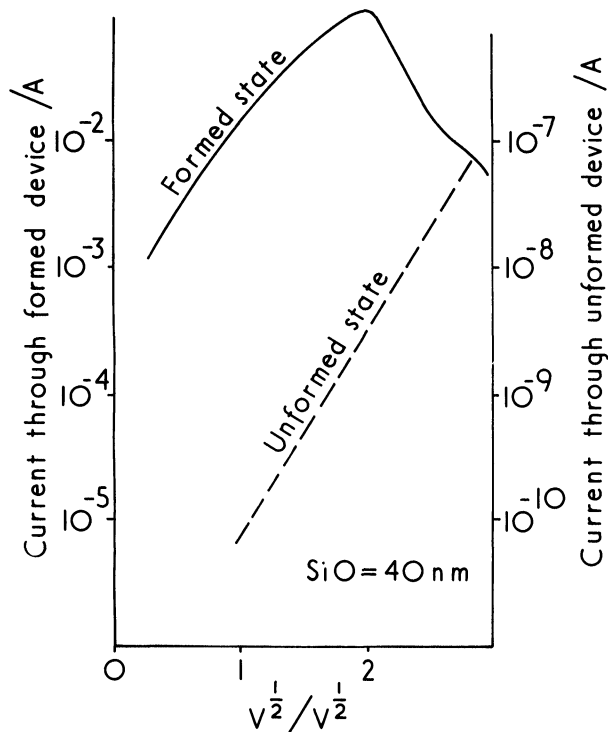


FIGURE 1 From Verderber³ *et al.* showing change in current upon electroforming Al-SiO_x-Au.

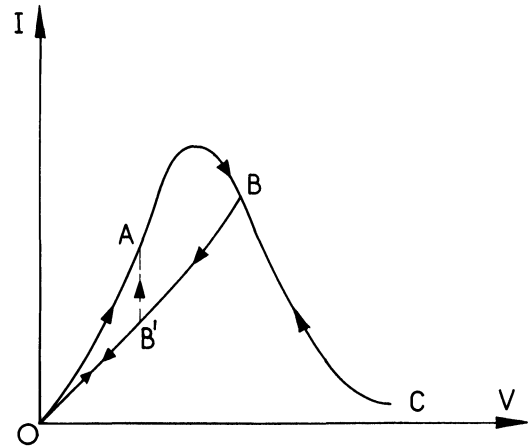


FIGURE 2 I, V characteristic of formed device and an analog memory state (schematic diagram).

OABC). The current in the pronounced region of VCNR is noisy. The VCNR is destroyed if the bias is cycled whilst the device is exposed to air (oxygen seems to be the important gas³) or if the temperature is reduced to about 100 K⁴ or if the device is operated under reverse bias.¹ After such treatments the average conductivity is low and the I, V characteristic non-ohmic. These effects can be reversed. Although prolonged operation in air usually causes degradation of the device.^{5,7}

The electroformed structure can be used as an analog memory as described by Simons and Verderber.⁴ They applied a bias $V_a > V_p$, the voltage for maximum current, to put the device into the region of VCNR. This bias was then removed rapidly, in about 0.1 ms. During this rapid removal, the downward sweep of the I, V locus does not show VCNR (Figure 2). After this process, for a bias below a value V_T , the I, V characteristic will be that for the previous downward sweep. Simons and Verderber⁴ claim that this state appeared to be stable indefinitely provided that the bias did not exceed V_T and that the memory state was reversible, and that the original low impedance memory state OA could be regenerated by applying a voltage slightly in excess of V_T . They reported that the sample could exist in any one of a 'continuum' of memory states corresponding to rapid removal of the bias within the VCNR region. The accepted functional form of these characteristics is that given by Simons and Verderber⁴ viz:

$$I = K(V_a) \sinh k(V_a)V$$

where both $K(V_a)$ and $k(V_a)$ decrease in magnitude

with increasing V_a . Typically for $V_a = 6V$, $K(V_a) = 1.1 \times 10^{-3} A$ and $k(V_a) = 0.5 V^{-1}$.

For a given memory state and a bias $V < V_T$ then the I, V characteristics are stable as the temperature is decreased with a slight quadratic dependence in the mean conductance σ . For applied voltages above $1V$ but less than V_T , Simmons and Verderber⁴ suggest that:

$$\sigma = \sigma_0(1 + \alpha T^2)$$

with

$$\alpha \approx 10^{-6} K^{-2}$$

After electroforming devices usually emit electrons and exhibit electroluminescence. Figure 3, after Collins and Gould⁶ shows representative results for the variation in emission current with device bias. Emmer⁷ has reported that all of the electroformed

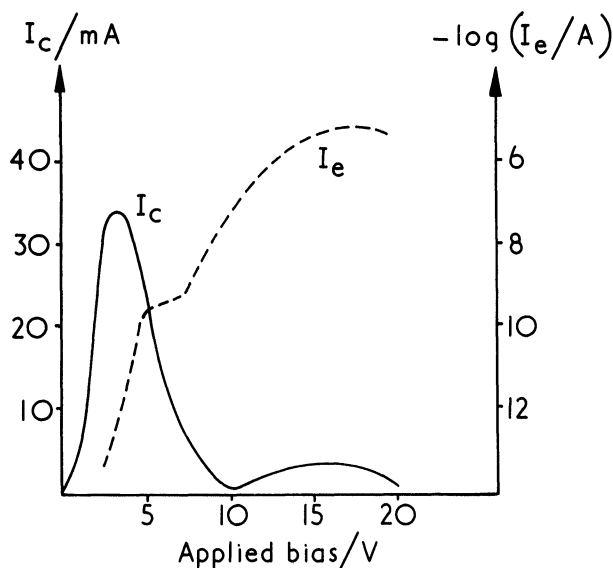


FIGURE 3 From Collins and Gould⁶, showing variation in circulating current I_c and emission current I_e with device bias for $Al-SiO-Au$ structure.

$Al-Al_2O_3-Au$ structures examined exhibited varying amounts of anode damage which could enhance electron emission. Attempts to use this emission process to infer hot-electron mean-free paths or attenuation lengths have recently been shown to be in error,⁸ and although this analysis was criticized⁹ the authors have replied.¹⁰

4. CONDUCTION AND MEMORY STATES AFTER ELECTROFORMING

Work performed since the review by Dearnaley *et al* has seriously reduced the credibility of models involving homogenous forming. Single shot pulsed bias studies¹¹ have added weight to filamentary approaches. The interpretation of experimental data cited as indicating the existence of local regions of high electric fields near the anode or cathode in electroformed structures has been criticized on simple fundamental grounds,^{12,13} which seriously weakens many band approaches. Equally disconcerting from a band model viewpoint are the experiments of Emmer⁷ giving evidence for localized electron emission.

It would thus appear that the conduction in electroformed structures is localized and that the conduction, memory phenomena, electron emission, electroluminescence and current noise are related to the processes envisaged by Dearnaley *et al*¹⁴ in terms of voltage controlled selective rupture and regrowth of filamentary conduction paths. Dearnaley *et al*¹⁴ suggest that the number of such filaments would be about $5 \times 10^4 mm^{-2}$ with diameters of the order of 1 nm. The detailed nature of the filaments was not specified.

Recently Bischoff and Pagnia¹⁵ have made gold island structures and report electroforming and d.c. and a.c. I-V characteristics which resemble those in electroformed diodes. They claim that their structures are suitable for electron microscope investigations of the forming and switching process and provide an excellent tool to clarify the fundamental behaviour of electroformed diodes.

5. BISTABLE SWITCHING AND CCNR

The detailed forming procedures used to obtain CCNR and bistable switching vary rather more than the procedures used to produce VCNR. Equally the device characteristics after forming are more varied than for devices showing VCNR. Despite these variations many of these forming processes have a common advantage in that forming need not take place in a vacuum. The formed devices are potentially more useful as their properties can be stable under bias in air. Dearnaley *et al*¹ have reviewed the earlier work in this area to show that some oxides can separately exhibit both VCNR and CCNR after suitable forming. This review cites the early reports of Chopra on thermally grown 50 nm oxide layers of Nb, Ta, Ti . Metal-metal oxide-

metal sandwiches exhibiting rectifying characteristics are formed under reverse bias, by increasing the reverse current to above 1 mA mm^{-2} to transform the I, V characteristic to a symmetrical shape exhibiting CCNR followed by a region where the dynamic impedance approaches zero (Figure 4). The holding voltage to sustain this state is conveniently small and is independent of oxide thickness and electrode material (as in Ovshinsky¹⁶ threshold switches for metal electrodes); the CCNR persists at frequencies of up to 1 MHz, in contrast with the VCNR in electroformed structures which is limited to lower ($\lesssim 10 \text{ kHz}$) frequencies, and on this basis it was argued that the mechanism leading to such CCNR was electronic. Chopra¹⁷ in his original paper emphasised the reproducibility of his devices compared with those exhibiting VCNR and established their relative insensitivity to ambient air.

The variation in forming conditions leading to CCNR in oxide layers is illustrated by comparison of the previous method of Chopra¹⁷ with that followed by Hickmott and Hiatt¹⁸ for their $\text{Nb-Nb}_2\text{O}_5\text{-Bi}$ structures. They developed empirically a complex breakdown (forming) procedure using both pulsed and steady but limited currents to produce devices with stable characteristics (Figure 5). The final device has two distinct non-ohmic states with high and low average values of conductance. Switching between these states was described but in view of the reported sporadic nature of the switching, the device degradation under sinusoidal drive at 100 kHz, and the general absence of long term stability in any state,

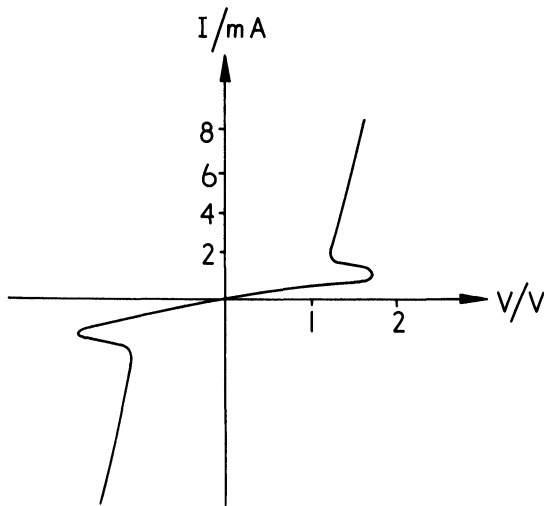


FIGURE 4 Showing CCNR in Nb-Nb oxide-Au structure. After Chopra¹⁷.

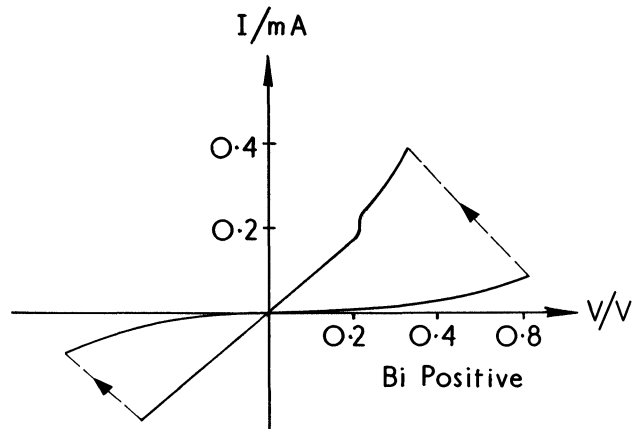


FIGURE 5 Showing memory states for $\text{Nb-Nb}_2\text{O}_5\text{-Bi}$ structure. After Hickmott and Hiatt¹⁸.

they are of little direct interest for memory application in reported form. It is of interest to note however that Hickmott and Hiatt¹⁸ confirmed earlier reports¹⁹ that the forming results from the modification of a very small region of the oxide of less than 10^{-3} mm^2 in contrast with Chopra¹⁷ who suggested that the whole structure was active in his devices. Further variations in forming methods and characteristics of the formed devices are reported in the work of Basavaiah and Park²⁰ for $\text{Nb-Nb}_2\text{O}_5\text{-Bi}$ junctions. They used a simple forming procedure, applying a bias of +30 V via a $50 \text{ K}\Omega$ resistor to the bismuth electrode to reduce the resistance from about $10^7 \Omega$ to about $5 \text{ K}\Omega$. Memory switching between two states with a binary signal ratio of 8:1 for more than 10^6 operations was reported. Typical switching times were $1 \mu\text{s}$ and $20 \mu\text{s}$ from the high to low and low to high resistance states respectively. Conduction in the formed state was associated with the modification of a small ($\sim 2 \mu^2$) region in the oxide layer which was observed on the top bismuth film. It was suggested that the conduction in the high resistance state was related to a Schottky mechanism whereas that in the low conductivity state was not identified. More recently Lalevic *et al*²¹ reported a further variation; this work used $\text{Nb-Nb}_2\text{O}_5\text{-Nb}$ structures with Nb doped amorphous Nb_2O_5 films. Forming was initiated using a bias of 14 V and a current density of 1.34 mA mm^{-2} . During this process the resistivity changed from $1.4 \times 10^{10} \Omega\text{m}$ to $2.9 \times 10^8 \Omega\text{m}$. At this state a reduced bias of 1.25 V at a current of 3.0 mA was necessary to bring the device to a final state with a resistivity of $5 \times 10^7 \Omega\text{m}$. Repetitive switching between bistable states was then claimed

TABLE I

Ref.	Anode	Oxide and thickness mm	SWITCHING		Maximum repetition rate/Hz	Long term stability claimed	Suggested conduction mechanisms		Remarks
			Cathode	Bistable			'on' state	'off' state	
24)	Au	Al ₂ O ₃ 5-10 (V)	Al		Yes	No	Joule heating of oxide	Low conductance due to trapped charge	Small operating current (~μA)
25)	Au	Al/Al ₂ O ₃ * 15-100 (V)	Au		Yes	Yes	Metallic filament formed	Metallic filament ruptured	
26)	Point contact	Cu ₂ O ~10 ⁶ (T)	Ag		Yes	No	Metallic filament Cu ₂ O→CuO + Cu at 1000°C	Metallic filament ruptured	High operating voltage ~1 kV
27)	Ag	Cu ₂ O ~10 ⁵ (T)	Ag		Yes		Joule heating of oxide	Formation of copper filament prevented	High operating voltage ~1 kV
28)	Metal or graphite probe	Cu ₂ O 20-200 (T)	Cu		Yes	0	Copper filament reaction Cu ₂ O→CuO + Cu	Switched 'on' state stable	
17)	Au	Nb oxide 50 (T)	Nb		Yes	~10 ⁶	Avalanche injection	Space charge limited current	(T) better than (A)
18)	Bi	Nb ₂ O ₅ 150 (A)	Nb	Limited CCNR	Yes	~10 ⁵	Via local region in oxide. No evidence for metallic filament when Nb goes superconducting traps ionized to yield low conductance	Traps neutralized to yield 'off' state	Very low power to switch cf. Chalcogenides. Complex forming procedure
20)	Bi	Nb ₂ O ₅ 100-150 (A)	Nb	Limited	Yes	~10 ⁴	Via local region (2μ') mechanism not specified in detail	Activated process Schottky mechanism suggested	Simpler forming than about case

21)	Nb	Nb ₂ O ₅ (Nb doped) 140 (A)	Nb	Yes	10 ⁴	10 ⁷ operations	Double injection	Power handling capacity comparable with chalcogenides
29)	Ni	Ni/LiO 2 × 10 ³ → 10 ⁴ (T)	Ni	Yes		No	4 different conductivity states reported	Li doping reduces switching voltage
30), 31)	Ag	SiO 80→140 (V)	CO or Al	Yes		Yes 10 ⁵ operations	Metallic filament	Filament ruptured in local region
32)	Al	SiO 150 (V)	Al	Yes T > 70°C		No	Al filament	Filament ruptured in local region
33)	Al	SiO ₂ 20-100 (T)	Si	Yes	Single shot only studied		Filamentary, with electron tunneling into conduction band of SiO ₂	Local electrode damage reported
17)	Ta	Ta oxide 19 (T)	Au	Yes but with some hysteresis	10 ⁶		Avalanche injection with trapping	Space charge limited current (T) much better than (A)
17)	Ti	Ti oxide	Au	Yes but with some hysteresis	10 ⁶		Avalanche injection with trapping	Space charge limited current (T) much better than (A)
22)	Au	TiO ₂ 5-80 (A)	Ti	Yes	Low		No definite method proposed	No definite model proposed
23)	Cr	TiO ₂ 3 × 10 ³ (T)	Ti	Yes	3 × 10 ⁶	8 × 10 ¹¹ cycles	Two carrier space charge limited current	Filamentary double injection Stable oscillations in 1-3 MHz range using CCNR

Note: a) Letter (A), (T), (V) denote method of preparation of oxide layer as a nodic oxidation, thermal oxidation and vacuum deposition respectively.
b) *Metal/Oxide composites prepared by evaporation of metal in presence of oxygen.

with the switching state characterized by a CCNR. The observed delay time in switching was >1 ms which was used to argue a double-injection model of the switching mechanism. They also claimed that their devices could switch in times and sustain power levels which compared favourably with amorphous chalcogenide thin film structures.

The earlier work by Chopra^{1,7} included reports of high frequency CCNR in formed Ti-TiO₂-Au structures. The later data obtained by Soukup^{2,2} on Ti-TiO₂-Au structures who reported CCNR only under slowly varying bias would appear to be in conflict. Recently Taylor and Lalevic^{2,3} have obtained stable oscillations in the 1–3 MHz range using the CCNR in a Ti-TiO₂-Cr device. These variations may be associated with electrode composition or forming procedures. Taylor and Lalevic^{2,5} suggest that the measured I , V characteristics for their devices are in agreement with the theory of filamentary double injection of space charge limited current.

Switching has also been reported by other workers, some using other oxides (Table 1) and it can be seen that a clear theoretical understanding has yet to emerge. For memory switching the balance of evidence perhaps points to filamentary conduction in the on state whilst for the threshold switches the picture is less clear.

6. COMPARISON WITH OVSHINSKY DEVICES

Ovshinsky^{1,6} switches, both memory and threshold, are based upon layers of chalcogenide glass, sandwiched between suitable electrodes. The mechanism of operation of the memory switch has for some time been understood to be associated with the growth of a highly conducting polycrystalline filament during the lock-on process whilst reversion of the polycrystalline region occurs during the reset process to a lower conductance state. Etching techniques have verified these ideas in detail and led to improved device performance.

Threshold switching, using rather more stable, chalcogenides, has only recently been understood in detail. Petersen and Adler^{3,4} have cited excellent evidence to show that in the case of chalcogenide threshold switches the conduction in the on state is that for a semi-conductor whose electronic band structure is essentially unchanged from the off state, but in which a concentration of about 10^{20} electrons m^{-3} yields the high conductivity. They have refined the accepted filamentary model of conduction by measuring the filament size as a function of current.

This was achieved using velocity saturation effects in amorphous/crystalline Si heterojunctions and transient on state conductivity measurements. They emphasize that at a high current density in a 1–2 μm layer of chalcogenide glass the 'filament' diameter will be $\approx 50 \mu m$ provided that pore saturation is not evident, hence their comment "Note that the filament . . . has the appearance of a pancake rather than a long narrow channel". Such filament diameters lead to relatively low ($< 100^\circ C$) pore temperatures and may assist in long term stability.

Reference to Table 1 shows that oxide sandwich structures can exhibit threshold and memory switching. However, in view of the present limited use of chalcogenide switches which, most importantly are of established compatibility with silicon technology, are relatively more reliable, and also better understood, it seems unlikely that oxide switches will be sold in the next decades. It will be interesting from a fundamental viewpoint to continue to examine switching in oxides as a clear theoretical position has yet to emerge. For the development of any possible future application of oxide switches it is perhaps best to attempt to understand the memory switches. These can be used, like chalcogenide switches, to perform read-mostly functions not accessible by silicon technology alone.^{3,5}

REFERENCES

1. G. Dearnaley, A. M. Stoneham and D. V. Morgan, "Electrical phenomena in amorphous oxide films", *Repts. Prog. Phys.*, **33**, 1124 (1970).
2. V. K. Agarwal, "Breakdown conduction in thin dielectric films: a bibliographical survey", *Thin Solid Films*, **24**, 55 (1974).
3. R. R. Verderber, J. G. Simmons and B. Eales, "Forming processes in evaporated SiO thin films", *Phil. Mag.*, **16**, 1049 (1967).
4. J. G. Simmons and R. R. Verderber, "New conduction and reversible memory phenomena in thin insulating films", *Proc. Roy. Soc.*, **A301**, 79 (1967).
5. P. D. Greene, E. L. Bush and I. R. Rawlings, "The forming process in metal-insulator-metal thin film memory and cold cathode devices", *Proc. Symp. on Deposited Thin Dielectrics, Montreal ed.*, 167 (1969).
6. R. A. Collins and R. D. Gould, "Hot electron transport and emission in Au-SiO-Au thin film cathodes", *Solid-State Electron*, **14**, 805 (1971).
7. I. Emmer, "Conducting filaments and voltage-controlled negative resistance in Al-Al₂O₃-Au structures with amorphous dielectric", *Thin Solid Films*, **20**, 43 (1974).
8. D. P. Oxley and R. E. Thurstans, "Criticism of some hot-electron attenuation length measurements", *Thin Solid Films*, **26**, 157 (1975).

9. R. A. Collins and R. D. Gould, "Hot-electron attenuation measurements: comments relating to recent criticisms", *Thin Solid Films*, **30**, L1 (1975).
10. D. P. Oxley and R. E. Thurstans, "A reply to 'Hot-electron attenuation measurements: comments relating to recent criticisms'", *Thin Solid Films*, **16**, L5 (1975).
11. R. E. Thurstans, P. C. Wild and D. P. Oxley, "Enhanced forming in Al-SiO_x-Au structures under pulsed bias", *Thin Solid Films*, **20**, 281 (1974).
12. D. P. Oxley and P. C. Wild, "Potential distribution in electro-formed M1M and M1M1M structures", *Thin Solid Films*, **23**, 353 (1974).
13. D. P. Oxley and D. A. Bean, "Comments on 'Experiments on M-I-M-I-M triode structures using SiO_x/B₂O₃ as the insulating material'", *Int. J. Electron.*, **44**, No. 3, 309 (1976).
14. G. Dearnaley, D. V. Morgan and A. M. Stoneham, "A model for filament growth and switching in amorphous oxide films", *Journ. of Non-Cryst. Solids*, **4**, 593 (1970).
15. M. Bischoff and H. Pagnia, "Electroluminescence spectra from gold island structure thin films", *Thin Solid Films*, **29**, 303 (1975).
16. S. R. Ovshinsky and H. Fritzche, "Amorphous semiconductors for switching, memory, and imaging applications", *IEEE Trans. Electron. Dev.*, Ed. 20, No. 2, 91 (1973).
17. K. L. Chopra, "Avalanche-Induced Negative Resistance in Thin Oxide Films", *J. Appl. Phys.*, **36**, 184 (1965).
18. T. W. Hickmott and W. R. Hiatt, "Electrode effects and bistable switching of amorphous Nb₂O₅ diodes", *Solid-State Electron*, **7**, 1033 (1970).
19. T. W. Hickmott, "Electroluminescence, bistable switching and dielectric breakdown of Nb₂O₅ diodes", *J. Vac. Sci. & Tech.*, Vol. 6 No. 5, 828 (1969).
20. S. Basavaiah and K. C. Park, "Bistable Switching and Conduction Mechanisms in Nb-Nb₂O₅-Bi Junctions", *IEEE Trans. Electron. Dev.*, Ed. 20, No. 2, 150 (1973).
21. B. Lalevic, N. Fuschillo and W. Slusark (Jr.), "Switching in Nb-Nb₂O₅ amorphous films", *IEEE Trans. Electron. Dev.*, Ed. 22, 965 (1975).
22. R. J. Soukup, "Observations of negative resistance in Ti-TiO₂-Au diodes", *J. Appl. Phys.*, **43** No. 8, 3431 (1972).
23. G. Taylor and B. Lalevic, "R.F. relaxation oscillation in polycrystalline TiO₂ thin films", *Solid-State Electron*, **19**, 669 (1976).
24. A. Roybardhan, P. C. Srivastava and D. L. Bhattacharya, "Negative resistance and bistable switching in very thin Al₂O₃ films", *Thin Solid Films*, **24** 541 (1974).
25. H. Birey, "High-field transport properties of aluminium-embedded aluminium oxide films", *App. Phys. Lett.*, **23**, No. 6, 316 (1973).
26. E. L. Cook, "Model for the resistive-conductive transition in reversible resistance-switching solids", *J. Appl. Phys.*, **41** No. 2, 551 (1970).
27. M. J. Zarabi and M. Satyam, "Switching in copper oxide", *J. Appl. Phys.*, **45** No. 2, 775 (1974).
28. D. V. Morgan and M. J. Howes, "Electroforming and switching in copper oxide films", *Phys. Stat. Sol. (a)*, **21**, 191 (1974).
29. N. Fuschillo, B. Lalevic and B. Leung, "High-field transport in NiO and Ni_{1-x}Li_xO thin films", *Solid-State Electron*, **19**, 209 (1976).
30. S. Manhart, "Memory switching in SiO films with Ag and Co electrodes", *J. Phys.D: Appl. Phys.*, **6**, 82 (1973).
31. S. Manhart, "Conduction and switching characteristics of SiO films with Al and Ag electrodes", *Journ. Non-Cryst. Solids*, **11**, 293 (1973).
32. D. V. Morgan and M. J. Howes, "Threshold and memory switching in silicon oxide films", *Thin Solid Films*, **20**, S7 (1974).
33. M. Shatzkes, M. Av-Ron and R. M. Anderson, "On the nature of conduction and switching in SiO₂", *J. Appl. Phys.*, **45**, No. 5, 2065 (1974).
34. K. E. Petersen and D. Adler, "On state of amorphous threshold switches", *J. Appl. Phys.*, **47**, No. 1, 256 (1976).
35. J. Tauc, "Amorphous semiconductors", *Physics Today*, Oct. (1976).

