A MODEL FOR FILAMENT GROWTH AND SWITCHING IN AMORPHOUS OXIDE FILMS

G. DEARNALEY, D. V. MORGAN and A. M. STONEHAM

Atomic Energy Research Establishment, AERE, Harwell, England

The forming process, by which changes are brought about in the electronic conduction of thin films of various binary amorphous oxides and halides, is first described, and experimental evidence is put forward which contradicts an earlier theory of the forming process in gold–silicon monoxide–metal structures. A theory is developed, in terms of the growth and thermal rupture of many conducting filaments through the insulating layer, to explain the observed voltage controlled negative resistance, electron emission, electroluminescence and memory phenomena. The model is presented firstly in its simplest phenomenological form, after which some atomic mechanisms which may be involved are tentatively discussed.

It is further shown that there is evidence to suggest that the forming process is important in a wide range of systems. These include metal–oxide–silicon capacitors and transistors, surface-barrier junctions on silicon, oxide-coated thermionic cathodes and anodic oxide layers. Electronic conduction in each of these cases is held to take place through localized filamentary paths.

The relationship between this and other filamentary conduction models is briefly discussed, and a general classification of negative-resistance devices into regenerative and non-regenerative systems is made.

1. Introduction

Some of the most interesting and potentially important aspects of the electrical behaviour of amorphous semiconductors are associated with the switching, negative resistance and memory properties that many of them display. Much attention has been given to chalcogenide glass structures in which there is evidence[1]) that current-controlled switching is a consequence of the growth of a monofilament, of a different character from the matrix material, bridging the gap between the electrodes. Various models have been proposed at this conference to account for the switching and memory phenomena in these cases, though there appears to be no consensus yet regarding the relative importance of thermal and field-induced transitions.

In this and earlier publications[2-4]) there is developed a different type of model to explain related but voltage-controlled phenomena which have been observed in another class of amorphous materials, sandwiched as a thin film between metal electrodes. These materials include the oxides of Si, Ta, Zr, Ti, together with certain halides, such as CaF_2 and LiF. The effects to be dis-

cussed appear most strikingly in silicon monoxide evaporated films, which have been thoroughly investigated by Verderber, Simmons and Eales[5]). We shall take their observations and our own on this material as exemplifying the application of our filamentary model, and its success in explaining diverse properties of silicon monoxide structures is regarded as justifying its physical validity. In some respects our model with many filaments is complementary to the monofilament models applicable to other amorphous systems[6]).

Although the metal–oxide–metal structures mentioned above offer a good example of a system in which filament formation may occur, we shall quote evidence that the same process occurs, to varying degrees, in other oxide systems. These include anodic oxide layers, MOS capacitors, oxide-coated thermionic cathodes and nuclear radiation detectors of the surface-barrier type. A better understanding of the mechanisms occurring in such a wide range of devices is felt to be both conceptually desirable and of practical importance.

In order to bring about the electrical and memory characteristics we are considering here it is necessary to subject the amorphous film to a process which has been termed "forming"[7]), and which had until recent years been regarded as merely a breakdown process. Before introducing our filamentary model of this phenomenon we shall briefly summarize the salient observations which we and others have made on forming and the properties of formed structures.

2. The forming process

Under suitable ambient conditions it has been shown[5, 7, 8]) that dramatic voltage-induced changes may be brought about in thin amorphous films of many oxides or halides evaporated between metal electrodes. Thus, prior to forming, the current–voltage behaviour of a Au–SiO$_x$–Al sandwich structure, with composition corresponding to $1 < x < 2$, shows[5]) a simple dependence (fig. 1) with $\log I$ proportional to $V^{\frac{1}{2}}$, explicable by Schottky or Poole–Frenkel emission processes. When a voltage in excess of a critical value called the forming voltage, V_F, is applied under reduced pressure (10^{-2} Torr or less) a striking change takes place over a period of the order of seconds (at room temperature), after which the characteristic exhibits a voltage-controlled negative resistance region (fig. 1). The degree of forming varies with the composition of the material and is governed also by the nature of the anode metal. Forming occurs readily in SiO$_x$, TiO$_x$, and to a lesser extent in LiF, CaF$_2$, Ta$_2$O$_5$ and other binary oxides and halides[9]). Metals which will act as suitable anodes include the noble metals, Cu, C, Si and Ni, while metals such as In, Be, Al and Mg rarely, if ever, induce
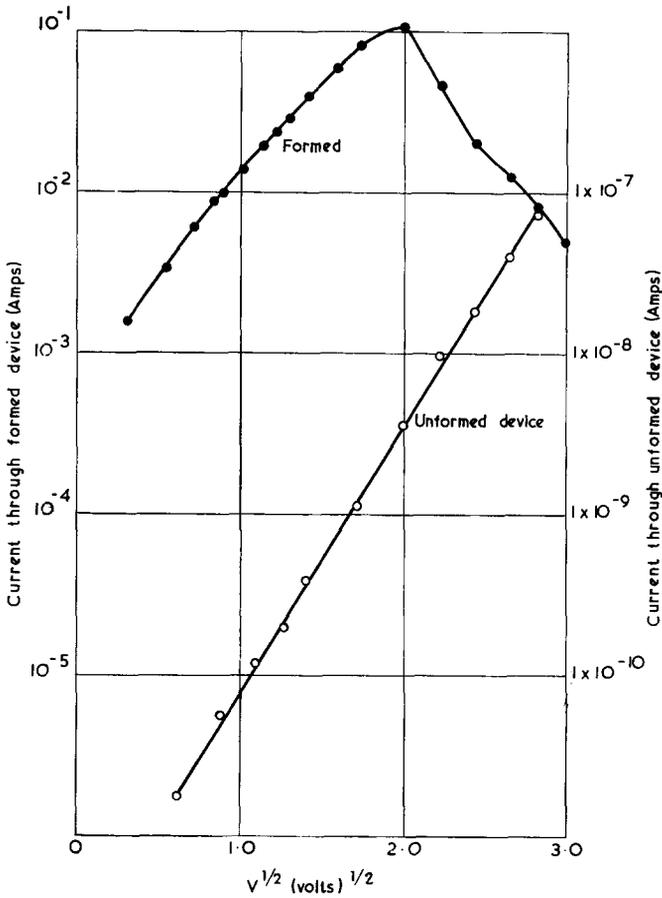
Fig. 1. Current-voltage characteristics of a gold–silicon monoxide-aluminium layer structure before and after forming, shown as a function of the square root of applied voltage. The oxide thickness was 400 Å [from Verderber et al.[5]].

forming[9]). The nature of the cathode material does not appear to be critical[5])

Temperature affects the rate of forming, but only slightly influences the forming voltage. Devices of SiO_x will not form below about $-50\,°C$[9]). The forming voltage, typically around 5 V, increases only slowly with film thickness L, though the degree of forming (measured by the peak current density) decreases approximately as L^3, and forming rarely occurs in films over 3000 Å in thickness[5]).

Greene et al.[9]) observed that fluorine was evolved during the forming of CaF_2 films, while in the forming of $Au–SiO_x–Si$ devices we have observed the development of many tiny bubbles of gas, apparently trapped under the
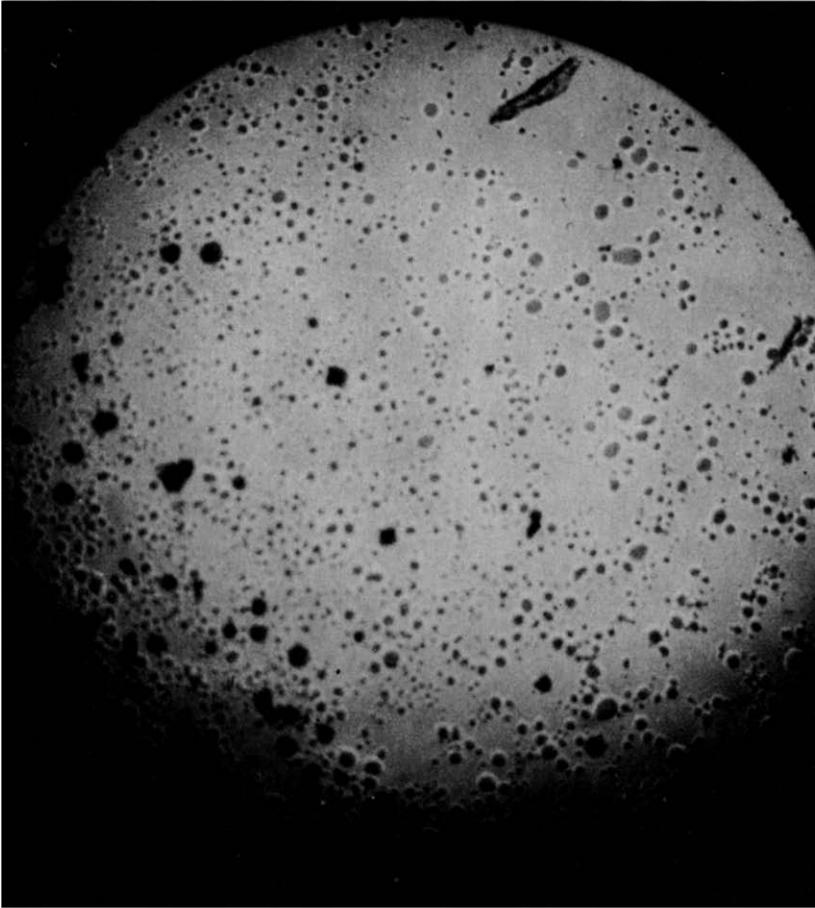
Fig. 2.   Photograph of a Au–SiO$_x$–Si device soon after forming, showing many small
bubbles under the anode layer. Magn. × 15.

anode layer (fig. 2). Over a period of hours these tend to collapse or aggregate
into a smaller number of larger blisters.

3. Properties of formed devices

Referring to fig. 3 [after Simmons and Verderber[10])] we see that up to a
threshold voltage, V_T (about 2.5 V) the current increases somewhat faster
than linearly. Up to about 1 kHz this characteristic is independent of
frequency and the conductivity varies only slowly with temperature[5])

$$\sigma = \sigma_0(1 + aT^2), \tag{1}$$

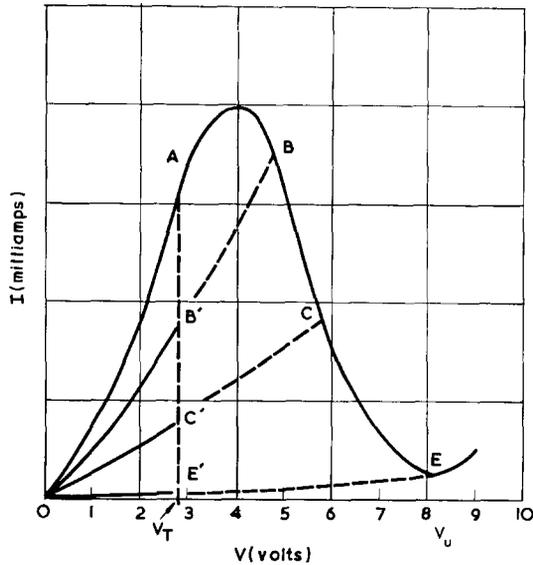where a is about 10^{-6} (deg)$^{-2}$.

Fig. 3. Solid line: the dc or low-frequency current–voltage characteristic of a formed Au–SiO$_x$–Al device, 400 Å thick. Broken lines: the dc (1 kHz) characteristics of the same structure [after Simmons and Verderber[10]].

Above V_T the low frequency and higher frequency behaviour differs, as shown in the figure. Only the dc or low frequency measurements demonstrate a negative resistance[5]), while at 1 kHz and above the current varies monotonically up to a maximum $I(V_a)$ determined by the peak voltage V_a. The dc characteristic forms the locus of the points $I(V_a)$. Once formed, the devices have a characteristic which is symmetrical with respect to the polarity of the applied voltage.

There is a memory state of the system. If the voltage is taken beyond V_M (corresponding to the peak current) and then switched off rapidly (in $< 10^{-3}$ sec) the ensuing current, for $V < V_T$, is determined by the voltage at switch-off. The impedance may vary over a factor of 10^3 in the memory state, and this state may be erased by applying $V > V_T$, when the current rises to that corresponding to the normal I–V characteristic[5]). This switching from high to low impedance can be accomplished by a pulse of duration 100 nsec or greater. Switching in the reverse direction can be achieved in only 2 nsec, but a "dead time", τ_d, must elapse before the device can be switched again to as low an impedance as before. Depending upon the mode of fabrication and the temperature τ_d varies between 10^{-6} and 10^{-1} sec and Greene et al.[9]) also report that the current growth during switching shows many small steps of non-uniform amplitude (fig. 4). The memory storage appears to be

of indefinite duration[11]). The existence of a dead time demands that two different high-impedance memory states must exist, and other observations[10]) show that the relaxation between them is thermally activated.

Up to voltage V_T the electrical noise is relatively low, but between V_T and the voltage corresponding to the current minimum the noise reaches much higher values. Beyond the current minimum the noise is again low until at still higher voltages catastrophic breakdown begins to occur[9]). We shall see that this behaviour is a natural outcome of our model.
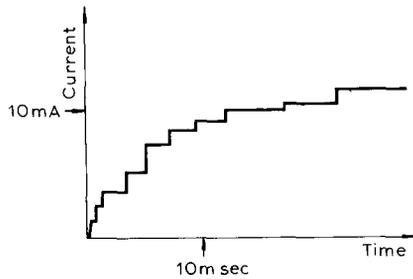

Fig. 4.   Step-line increases of current as a function of time in the switching of a formed SiO_x film [after Greene et al.[9]].

At voltages beyond V_M, electron emission into a vacuum has been observed by Lomax and Simmons[12]), and the electron emission current rises steeply with increasing voltage. Some energetic electrons are emitted, with energies extending in some cases up to the full applied potential difference across the device. The electron emission takes place from small centres over the surface of the film, and the intensity of emission varies with time at each point[12]). This electron emission is accompanied by weak, scintillating light spots emitted from local areas of the layer[13]).

Models have earlier been presented to account for many of these effects, e.g. in terms of impurities present within the material[14]), or the migration of metal ions from the anode[10]), or electrolysis of the material[9]), in each case resulting in a band of localized energy levels within the band-gap of the insulator. Conduction was then envisaged as taking place by a hopping mechanism between these localized states[10]). These theories treat the material as an essentially uniform medium to which a modified band theory may be applied.

In order to test the model of Simmons and Verderber[10]) we carried out an analysis of the composition of a film of formed SiO_x on a silicon substrate, after removal of the gold anode film by solution in aqua regia. The analysis was made by the back-scattering of a collimated beam of 1.2 MeV protons

from the Harwell 5 MV Van de Graaff accelerator. Energy analysis of the scattered protons, detected in a silicon surface-barrier detector, is capable of distinguishing the masses of those nuclei present near the surface of the target, and since the atomic number of Au is so much greater than those of Si and O the sensitivity was ample to detect that concentration ($\sim 10^{19}$
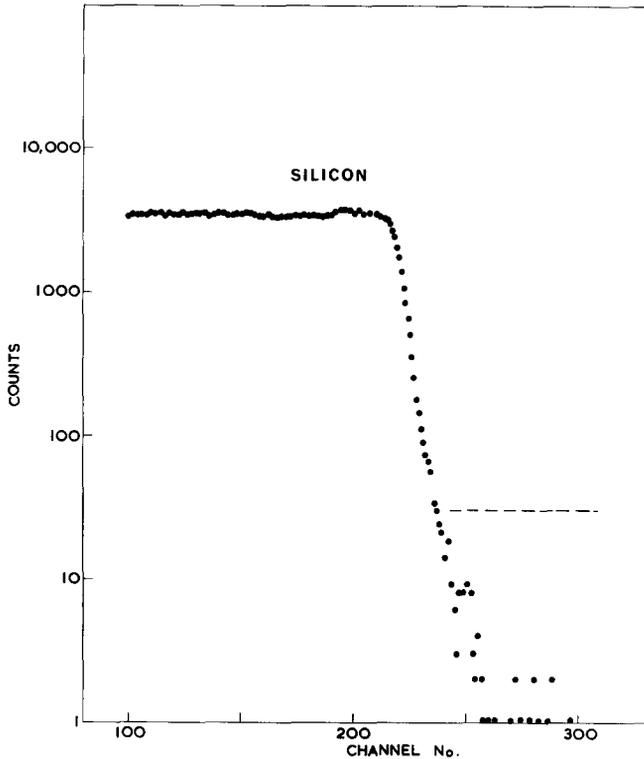

Fig. 5. The energy spectrum of 1.2 MeV protons back-scattered from a formed SiO_x film from which the gold anode had been removed. The dotted line indicates the level of counts to be expected (in that region of the spectrum) from 10^{19} gold atoms per cm^3 in the formed oxide.

atoms per cm^3) of gold demanded by Simmons and Verderber[10]). No evidence was found, however, for the presence of any gold within the formed oxide (fig. 5). This, together with the long-term stability of the memory state of the systems discussed above led us to reject the earlier theory, and to propose instead one based upon the growth of conducting filaments through the amorphous medium.

4. The filamentary model

Observations mentioned above such as the localized electro-luminescence of formed layers, localized emission of gas to create bubbles during forming, steplike increments in current during switching, large current fluctuations and localized electron emission all suggest that one should not consider the structure as a homogeneous insulator for which band theory is the most natural approach. We shall rather take an opposite view and consider a model in which the conduction, memory storage and emissive properties reside in highly localized regions and that the rest of the matrix plays almost no part in the observed phenomena. The forming process is considered to bring about the growth of conducting filaments, extending from the anode through the insulating film in the manner already discussed by Dearnaley[2]). The mechanism of filament formation and possible atomic models for the process are considered later, and such detailed models remain speculative as yet, besides varying from one system to another.

Suffice it initially to postulate that forming creates filamentary paths between the electrodes, the conduction being essentially ohmic, i.e. with a negligible activation energy for migration of carriers. The filaments are not considered to be perfectly uniform but to have weak spots which determine their resistance and which become heated by the flow of electrons. Since conduction must arise due to unusual interatomic spacing, interbond angles or defect configuration it is reasonable to argue that thermal vibration will interfere with conduction; in other words electrons will suffer phonon scattering particularly at the weak, hot spots of the filament and the conducting chain may actually be ruptured. This is the novel aspect of the filamentary model that will account for negative resistance and memory properties of formed layers. We shall next see that is it possible, with this very simple model, to explain all the observed dc and ac conduction phenomena, the memory characteristics and the effects of thermal cycling.

We now consider the current–voltage characteristics of an array of conducting filaments embedded in an insulating matrix. Each filament will be assumed to exhibit ohmic conduction and we will ignore hopping conduction, tunnelling and space-charge effects which probably play a role: by ignoring these effects we shall be unable to predict the non-linear dependence of current upon voltage at very small voltages. The novel current–voltage characteristics occur because filaments can rupture.

Once each filament bridges the gap between the electrodes, electronic conduction begins and Joule heating will occur. We then associate a local lattice temperature, T, with each filament and assume that rupture will occur if T exceeds T_{max}. The filaments can re-form subsequently, but this will

depend on their temperature, the ambient temperature, the electric field and possible space-charge effects: the precise conditions will not be specified in detail. The filament temperature, T, is not a thermodynamically well-defined quantity. It will only be used as a measure of the local heating in the filament. Physically both T and the resistance, ρ, of each filament can best be imagined by associating them with local regions of high resistance on a highly-conducting filament or chain of defects. Two terms contribute to changes in T: the usual Joule heating, and heat loss to the insulator, which we assume simply to be proportional to the temperature difference between the filament and its environment. Thus the local temperature is given by

$$\frac{dT}{dt} = \alpha \frac{V^2(t)}{\rho} - \frac{1}{\tau_c}(T - T_0),\tag{2}$$

where α measures the heating and τ_c characterizes the cooling.

We first consider the static characteristic. From the steady-state solutions of (2) we see that, at voltage V, only filaments with resistance greater than

$$\rho_{min} = \tau_c \alpha V^2/(T_{max} - T_0)\tag{3}$$

remain unfractured. The total current is thus

$$I = \int_{\rho_{min}}^{\infty} d\rho \frac{V}{\rho} P(\rho),\tag{4}$$

where $P(\rho)$ gives the probability distribution of the various resistances, and

$$\int_0^{\infty} d\rho\, P(\rho) = 1.\tag{5}$$

We have assumed implicitly that the filaments are either permanently broken or permanently unbroken at the given voltage, and that an equilibrium has been achieved so that the previous history of the specimen can be ignored. Clearly the detailed shape of the characteristic is determined by the distribution $P(\rho)$. Two features of $P(\rho)$ are immediately apparent. First, there are very few filaments with resistances below

$$\rho_T = \tau_c \alpha V_T^2/(T_{max} - T_0),\tag{6}$$

since the devices can be cycled below V_T without showing signs of filaments breaking. Secondly, there are very few filaments with resistances above

$$\rho_u = \tau_c \alpha V_u^2/(T_{max} - T_0),\tag{7}$$

where V_u is the voltage at which $I(V)$ is a minimum. Above V_u the current is

close to that of the unformed device, and extra conduction mechanisms can
be ignored. We can derive $P(\rho)$ from $I(V)$ by noting:

$$P(\rho)/\rho \sim \mathrm{d}(I/V)/\mathrm{d}(V^2), \tag{8}$$

this distribution is shown in fig. 6a. The apparently negative value of $P(\rho)$
for small ρ simply reflects the contribution of tunnelling at small voltages.
We also show a simple triangular distribution in fig. 6b, and in fig. 7 we
show that the $I(V)$ characteristics for the two distributions are strikingly
similar. The absence of very low resistance filaments is only to be expected in
view of the small dimensions we postulate. The absence of high resistance
filaments presumably reflects a natural selection mechanism in the forming
process, that is to say that a filament will cease to propagate rather than
continue as high resistance path, if conditions (such as the composition of the
medium) are unfavourable. The mode of growth of filaments will be consid-
ered later in this section.

The distribution of resistances shown in fig. 6 is merely qualitative unless
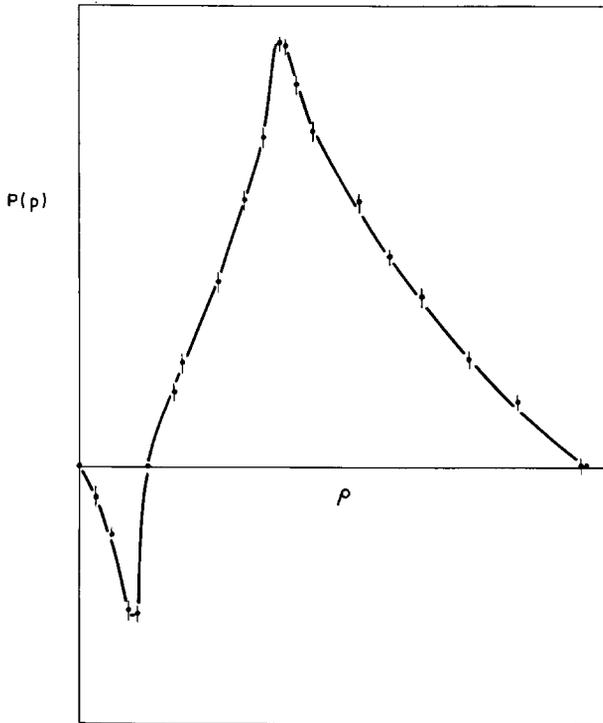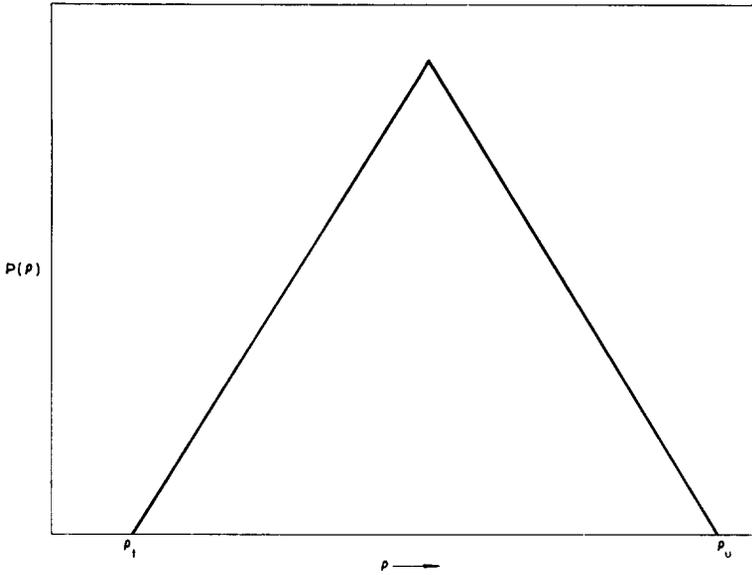we can estimate N, the number of filaments per unit area. We now make

Fig. 6a.

Fig. 6b.

Fig. 6. (a) The calculated distribution of filament resistances, ρ, deduced from experimental current–voltage behaviour. Negative values near the origin arise because tunnelling at the electrodes has been neglected. (b) The simple triangular distribution of filament resistances assumed as an approximation in fitting the current–voltage characteristic.

a rough estimate of N assuming that all filaments have the same resistance, ρ. The initial resistance of the device per unit area is ρ/N, apart from small tunnelling effects, and the filaments all burn out when $V \sim V_{\text{max}}$. Thus, from eq. (2),

$$\rho \sim \tau_c \alpha V_{\text{max}}^2 / (T_{\text{max}} - T_0). \tag{9}$$

The cooling time, τ_c, is estimated by regarding each filament as a cylinder of radius d and temperature T cooling to a cylindrical sink of radius D and temperature T_0; D is taken to be the mean filament separation defined by $ND^2 = 1$, but could be smaller than this. It is then easy to show that

$$\tau_c \alpha = \frac{\ln(D/d)}{4.18 \times 2\pi KL}, \tag{10}$$

where K is the thermal conductivity of the insulator and L is the length of the filaments. Note that the choice of D and d is not very critical in this equation. Combining (9) and (10) we may find ρ and N. Reasonable values of most of the parameters are easily introduced, e.g. an initial resistance ρ/N of 5 ohm for a filament length of 400 Å, a thermal conductivity of 0.002 cal/cm$^2 \cdot$ sec $\cdot \,^\circ$K
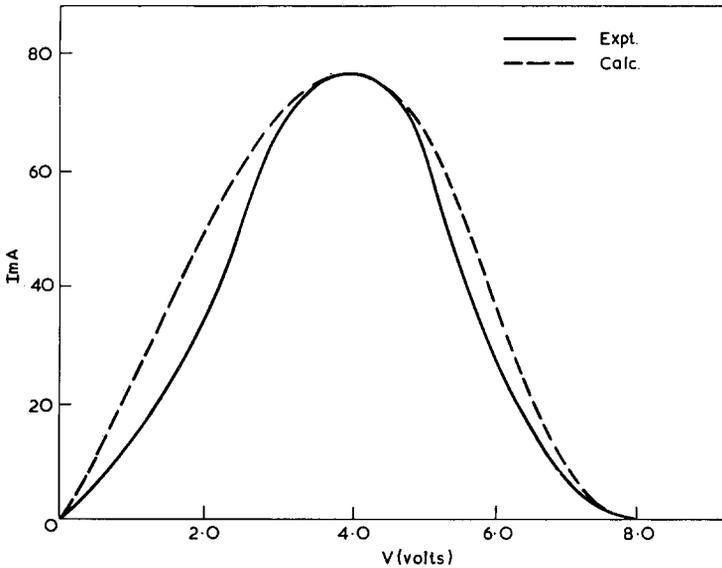
Fig. 7. The low-frequency or dc current–voltage behaviour calculated with the distri-
bution of filament resistances shown in fig. 6b, compared with the experimental results of
Simmons and Verderber[10]) in a formed Au–SiO$_x$–Al device and after subtraction of the
current before forming.

and $(T_{max} - T_0)$ of $1000°$K. It is harder to estimate d, but in the next section
we show that the dependence of forming voltage upon film thickness suggests
$d \sim 10$ Å. Using these values we find ρ, the mean resistance per filament, to
be about 2.5×10^7 ohm and N to be 5×10^6 filaments per cm^2. These lead to
$D \sim 2.5$ μm and a specific resistance of about 0.2 ohm·cm for the material of
the filament. We emphasize that these calculations give only order-of-
magnitude estimates since, for example, end effects have been neglected in
deriving τ_c. However the results appear to be both plausible and consistent.
We have since learned that microphotographs of formed silicon monoxide
films [Hall[15])] do in fact reveal about 10^6 minute holes per cm^2, in close
agreement with our estimate.

We now turn to consider the dynamic characteristics of formed devices, in
much the same manner as the dc behaviour was treated. If the applied voltage
has amplitude V_0:

$$V = V_0 \sin \omega t, \qquad (11)$$

then, after a time of order τ_c when the transients have disappeared, the
filaments with resistance greater than

$$\rho_{min}(\omega, V_0) = \rho_{min}(0, V_0) \, \phi(\omega\tau_c) \qquad (12)$$

remain unfractured. Here $\rho_{\min}(0, V_0)$ is equivalent to (3), and

$$\phi(\omega, \tau_c) = \tfrac{1}{2}\{1 + [1 + (2\omega\tau_c)^2]^{-\frac{1}{2}}. \tag{13}$$

At higher frequencies more filaments survive. The current is given by

$$I = \int_0^\infty d\rho \, \frac{V}{\rho} \, P(\rho) \, f(\rho, \omega), \tag{14}$$

where $f(\rho, \omega)$ is the fraction of the time for which a filament of resistance operates at frequency ω. Clearly $f(\rho, \omega)$ is unity if ρ is greater than $\rho_{\min}(\omega)$. The dynamic characteristic differs from the static characteristic in that the filaments which are broken reform only after a number of cycles, and the conduction is dominated by those which remain unbroken throughout. There is no negative resistance régime in the dynamic case. As long as ω is sufficiently large that the re-forming of a ruptured filament is unlikely during the cycle, we may treat $f(\rho, \omega)$ as zero for ρ less than $\rho_{\min}(\omega)$. Other cases can, and do, arise at lower frequencies. We may relate the dynamic and static characteristics and, using the simplified triangular distribution of resistances (fig. 6b) with $\phi(\omega, \tau_c) = 1$ we obtain:

$$I = \frac{2V}{(\rho_T + \rho_n)} \left[\frac{(1 - (V_a/V_n)^2}{(1 - (V_T/V_n)^2} \right]. \tag{15}$$

These ac characteristics are shown in fig. 8. (These are straight lines since we have again ignored the effects of tunnelling.) Further, we find that for V_0 less than $V_T/\sqrt{\phi(\omega, \tau_c)}$ then no filaments should break, and the initial slopes of the static and dynamic characteristics should be the same. At 1000 Hz it seems that $\phi(\omega, \tau_c)$ is close to unity, since the fracture of filaments occurs at very similar voltages in the two cases. Using $\phi(\omega, \tau_c) \approx 1$ we find that, for V_0 greater than V_T, the dynamic and static characteristics should meet at $I(V_0)$, that is

$$I_{\text{dynamic}}(V) = (V/V_c) I_{\text{static}}(V_0). \tag{16}$$

This has been observed by Simmons and Verderber[10]), and it is illustrated in fig. 3. Their static characteristics were measured at 50 Hz. From the observations at two frequencies we can deduce that τ_c is shorter than 1 msec and than the mean reforming times of filament are typically longer than 1 msec but shorter than 20 msec at room temperature. Reforming appears to be thermally activated, as it occurs slowly, if at all, at low temperatures. As reforming does not occur for an applied voltage (rather than an applied field) below V_T it is likely that both the fracture and the reforming only in-
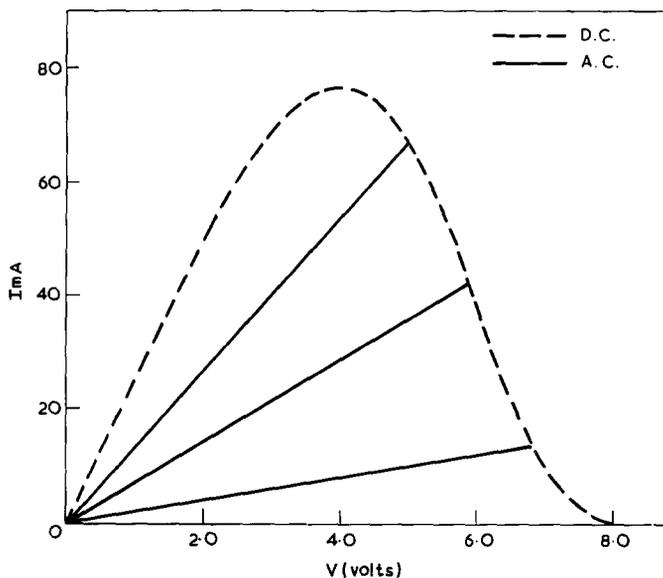
Fig. 8.   The ac (1 kHz) current–voltage characteristic calculated in the filamentary model, assuming a simple triangular distribution of resistances (fig. 6b), and after the transient period has elapsed.

volve a well-localized region of space. After fracture the filament must be in one of several distinct states. The dead time, discussed earlier, is a measure of the time between the filament breaking and reaching a state from which it may reform. This transition appears to be thermally activated.

The model we have so far discussed is simple and phenomenological, and we have avoided any assumptions regarding the detailed atomic structure and other properties of the filaments. We shall now consider some processes which may provide a physical basis for the model: further work will be needed to test the ideas put forward here, but modification of these details would probably not greatly alter the model as discussed above.

A possible mechanism of growth of conducting channels was proposed by Dearnaley[2]) who argued that the high electric stress at the tip of a fine conducting filament extending from the anode could bring about a migration of anions in such a way as to extend the filament. The release of gas at localized areas during forming may well be due to the electrolytic transport of anions as suggested by Greene et al.[9]), or equally as an inward migration of anion vacancies. The fact that it occurs only at certain points suggests that a nucleation process is involved in the initiation of filament growth, which may depend upon the existence of suitable structural conditions in the material

near to the anode, as well as the nature of the anode metal and its interaction with the anions.

The forming process is voltage, rather than field dependent, which again suggests that the filaments are initiated in well-localized regions. The size of these regions (say, diameter R) can be estimated from the dependence of the forming voltage on the insulator thickness, L. If $L \gg R$ then the field $E(R)$ at the boundary of this local region is given approximately by

$$E(R)_L = E(R)_{L=\infty} (1 + \eta R/L),\qquad (17)$$

where η is of order unity and depends on the detailed structure of the imperfection. The observed [5]) dependence of the forming voltage V_F upon thickness then suggests that R is less than about 20 Å. This makes it unlikely that the filaments could be observed microscopically.

The mechanism of electronic conduction in normally insulating materials such as SiO_x have been discussed by Revesz[16]) and Dearnaley[2]) who independently suggested that the overlap of π-orbitals in the –Si–O–Si– chain might under certain conditions allow conduction. On the other hand, such a mechanism is incapable of explaining conduction in all those materials which undergo forming. One must infer that more general mechanisms, perhaps involving chains of metal atoms alternating with anion vacancies, are responsible for the effect. This possibility was also postulated by Dearnaley[2]) and is better able to account for the subsequent observations of gas release during forming.

Once conducting filaments are established between the electrodes the applied field will cause electronic conduction to begin and the electron temperature will rise sharply, if we assume that the carrier mobility is high. The lattice temperature will follow and phonon scattering will increase, particularly at the weak regions which we have supposed to be present in most filaments. At these points thermal vibration will increase until at some stage conduction will cease. In this process many electrons will have been scattered into the surrounding matrix of insulator where they will be trapped. The dielectric in such a region will be highly polarized and will relax by thermally-activated Poole–Frenkel emission of trapped charges over a period corresponding to the dielectric relaxation time. We believe this to be the origin of the two "broken states" of a filament referred to above. At low temperatures the state described will persist for a very long time as the high-impedance memory state: at higher temperatures relaxation will occur to a state in which the filament is broken but polarization is absent. Under such conditions the electric field will tend to re-grow the filament by ionic migration, but this relaxation process will take a finite time and hence we can explain the transient phenomena which appear at frequencies between 50

and 1000 Hz. Furthermore, filaments which have been broken remain non-conducting for almost the whole of the time since the time constant for the heating process is short compared with the time to re-establish conduction. In this way we can understand the relatively long switching time from the high to the low impedance state ($\sim 10^{-7}$ sec) while switching back to the high impedance state is rapid ($\sim 10^{-9}$ sec). It is likely that the difference occurs because in the former case ionic migration must take place, while in the latter the controlling mechanism is the scattering of "hot" electrons leading to polarization of the dielectric. Likewise we can understand why the "dead time" of many milliseconds must elapse before the cycle can be repeated: this corresponds to the relaxation of space-charge polarization.

Electronic noise in the devices will clearly be large over that range of voltages, between V_T and V_u, over which filaments are rupturing and re-growing: fluctuations are occurring both in the number of carriers which are mobile and in their mobility. In some ways the noise may be regarded as occurring in a one-dimensional analogue of the two-dimensional conducting channel of a metal–oxide–semiconductor transistor, in which Flinn et al.[17] have shown that scattering of carriers results in their being temporarily trapped in the overlying oxide matrix. On the other hand, as is observed, the noise is expected to be far less at voltages below V_T (when essentially no filaments are rupturing) and above V_u (when most of the filaments are broken). It is interesting that the noise in thin-film formed insulators, MOS transistors, surface-barrier diodes and in oxide-coated cathodes exhibits a $1/f$ dependence upon frequency, often referred to as "flicker noise", the origin of which has never been well understood.

Electron emission from the surface of the devices will, in our model, be due to the generation of hot carriers by the high electric fields which exist at high-resistance spots of the filaments. It is possible, in the case of a filament with a weak spot near to the anode, for electrons to be accelerated through a large potential difference just below the anode layer. Emitted electron energies are observed[12] to spread almost up to that corresponding to the full applied potential difference. One can further understand why electron emission should first be detectable[10] near to the voltage V_T at which filaments are beginning to rupture.

Since the processes we have discussed will lead to energetic electrons (with energies $\sim 100\,kT$) being scattered into wide band-gap material, we can understand the electroluminescence which occurs in scintillating pin-point regions over the surface of a number of metal–oxide–metal structures[13,18].

Our discussion of filamentary conduction differs from that of Ridley[19] for example. Ridley discussed the instabilities associated with systems showing current-controlled differential negative resistance, and put forward thermo-

dynamic arguments to show that the instability would be associated with the appearance of high-current filaments. In our model the devices, once formed, contain filaments which may rupture as a result of the current flow; such a system will exhibit differential negative resistance which is voltage-controlled.

There are some similarities between our model and that of Gibbons and Beadle[20]), proposed to explain switching in thin NiO films. In their model, however, a single filament of metallic nickel was considered to migrate through the oxide: switching occurs but negative resistance does not result in this case. In our model, very many filaments are postulated to develop from nucleation sites at the anode interface, and this is feasible as long as the applied voltage exceeds the forming voltage V_F.

As a general classification of negative-resistance devices it appears that current-controlled (S-shaped) I–V characteristics result from filament formation which is *regenerative*, i.e. when creation of a single filamentary conducting path leads to conditions in the medium which bring about a rapid radial growth or conductivity rise of the filament (e.g. by thermally-induced transitions). On the other hand, in our model, voltage-controlled (N-shaped) I–V characteristics result from *non-regenerative* filament formation. Here the creation of a filament is not followed by its sudden radial growth, and the resistance of the device is only slightly perturbed. Conditions are therefore retained for the further development of other filaments wherever appropriate nucleation and propagation can take place.

5. Evidence for forming in other structures

Although the effects of forming on the electrical characteristics of amorphous oxide films appear to the greatest degree in the systems we have considered above, we believe that the phenomenon is of more widespread significance than has been suggested hitherto. For instance, the behaviour of many semiconductor devices depends upon effects which occur at the surface, where, as a rule, there will be an amorphous oxide layer.

Thus, in MOS capacitors prepared by evaporating gold on to thermally-grown SiO_2 on silicon, Worthing[21]) observed time-dependent breakdown phenomena which occurred only when the gold was made positive with respect to the silicon. Although the current was limited to 10^{-10} A a permanent and cumulative change took place in the oxide. The 'breakdown' was accompanied by visible scintillations of light: tests were therefore made for revealing pinholes in the oxide but none were found. The effects did not occur if the devices were cooled to $77°K$. These phenomena appear compatible with a small amount of forming taking place in the SiO_2 under the applied electric field. It is desirable to minimise the likelihood of this in

capacitor fabrication as well as in MOS transistors, and the techniques which result in optimum stability of such devices seem aimed at inducing the maximum degree of oxidation. Although ion transport (particularly of Na^+ ions) has been proved to account for some of the instability of MOS transistors[22,23] some additional effects may arise due to local forming of the oxide. We consider the observations of Hofstein[24] to be an instance of this. The role of phosphorus in stabilizing MOS transistor characteristics[25] may thus be linked with its observed behaviour[26] of suppressing local crystallization in silicon dioxide films.

It has been realized for many years that anodic oxides on materials such as silicon and zirconium show a much greater electronic conductivity than thermally-grown oxides, a fact which renders them unsuitable for many device applications. Ramasubramanian[27] showed that current transport through anodic ZrO_2 takes place at small localized regions. Revesz and Zaininger[28] consider that under the high electric field which accompanies anodic oxidation conducting channels are created through the oxide, these channels having a greater degree of order than the surrounding matrix. We would regard this phenomenon as another instance of forming in SiO_2, brought about by the high electric field. Under high electric stress Ilahi[29] has observed the emission of gas from an anodic SiO_2 layer, producing small blisters under a surface layer of metal; these blisters closely resemble the ones we have observed on $Au-SiO_x-Si$ structures on forming.

Forming in SiO_2 layers on silicon substrates may be expected to alter the surface states present at the oxide–semiconductor interface. This is undesirable in transistors but it appears that it may be beneficial to the production of surface-barrier diodes on silicon. Thus the metals which are most successful in yielding surface barriers are just those which most effectively induce forming in SiO_x, whereas the metals which most strongly inhibit forming are used for ohmic contacts[30] ,when a rectifying barrier is to be avoided. Oxygen is essential to the preparation of surface-barrier diodes[31] and it has been shown that the rectifying characteristics are induced more rapidly if an electric field is established within the oxide layer. We have shown that if SiO_x is evaporated on to etched silicon and a gold electrode is evaporated on top of this, a good surface barrier diode results from forming the oxide. We postulate therefore that forming plays a major part in the development of surface barriers on silicon.

Finally, it may be argued[4] that many of the properties of oxide-coated cathodes may be explained in terms of a process analogous to forming taking place during activation of the cathode. The high emission efficiency of the oxide-coated cathode can be shown to result from a model based upon the one to be described to account for forming. Electron emission from these

cathodes and from the "cold-cathode" SiO_x devices is thus seen to have a common origin.

6. Conclusions

We have seen that a model involving the filed-induced growth and thermal rupture of many slender filaments can explain the observed behaviour of metal–oxide–metal sandwich structures. Electronic conduction after forming is believed to be dominated, in many cases, by these filamentary conducting paths, which are in a more ordered state than the surrounding matrix. There is evidence that metal ions do not, as hitherto suggested, migrate into the medium from the anode.

It is suggested that the localized formation of conducting filaments is important in a wide range of oxide-based structures of practical importance.

Negative resistance devices in general are classified into two types: those in which regenerative mechanisms lead to a single filament exhibiting current-controlled characteristics, and those (as in our model) in which filament formation is non-regenerative. In the latter case many filaments can develop and their thermal rupture leads to voltage-controlled negative resistance.

References

1) C. H. Sie, J. Non-Crystalline Solids 4 (1970) 548.
2) G. Dearnaley, Phys. Letters 25A (1967) 760.
3) G. Dearnaley, A. M. Stoneham and D. V. Morgan, AERE Report R-5992 (1969).
4) G. Dearnaley, Thin Solid Films 3 (1969) 161.
5) R. R. Verderber, J. G. Simmons and B. Eales, Phil. Mag. 16 (1967) 1049.
6) H. Fritsche and S. R. Ovshinsky, J. Non-Crystalline Solids 4 (1970) 464.
7) T. W. Hickmott, J. Appl. Phys. 33 (1962) 2669.
8) G. S. Kreynina, L. N. Selivanov and T. I. Shumskaya, Radio Eng. Electron. (USSR) 5 (1960) 219.
9) P. D. Greene, E. L. Bush and I. R. Rawlings, in: Proc. Symp. on Deposited Thin Film Dielectric Materials, Montreal, October 1968, Ed. F. Vratny (The Electrochemical Society, New York 1969).
10) J. G. Simmons and R. R. Verderber, Proc. Roy. Soc. (London) A 301 (1967) 77.
11) P. E. Lighty, private communication.
12) R. W. Lomax and J. G. Simmons, Radio Electron. Engineer 35 (1968) 265.
13) H. Kanter and W. A. Feibelman, J. Appl. Phys. 33 (1962) 3580.

14) T. W. Hickmott, J. Appl. Phys. **35** (1964) 2118, 2679.
15) R. Hall, private communication.
16) A. G. Revesz, Phys. Status Solidi **24** (1967) 115.
17) I. Flinn, G. Bew and F. Berz, Solid State Electron. **10** (1967) 833.
18) W. Chan, to be published.
19) B. K. Ridley, Proc. Phys. Soc. (London) **82** (1963) 954.
20) J. F. Gibbons and W. E. Beadle, Solid State Electron. **7** (1964) 785.
21) F. L. Worthing, J. Electrochem. Soc. **115** (1968) 88.
22) E. H. Snow, A. S. Grove, B. E. Deal and C. I. Sah, J. Appl. Phys. **36** (1965) 1664.
23) S. R. Hofstein, IEEE Trans. Electron. Devices **ED-13** (1966) 222.
24) S. R. Hofstein, Appl. Phys. Letters **10** (1967) 291.
25) D. R. Kerr, J. S. Logan, P. J. Burkhardt and W. A. Pliskin, IBM J. Res. Develop. **8** (1964) 376.
26) T. Sugano, K. Hoh, K. Kudo and N. Hishinuma, Japan. J. Appl. Phys. **7** (1968), 715.
27) N. Ramasubramanian, Atomic Energy of Canada Ltd. Report AECL-3082 (1968).
28) A. G. Revesz and K. H. Zaininger, RCA Rev. **29** (1968) no. 2, 22.
29) K. Ilahi, private communication.
30) P. T. Andrews, in: *Proc. Symp. on Nuclear Instruments*, Harwell, 1961 (Heywood, London, 1962).
31) P. Siffert, G. Laustriat and A. Coche, IEEE Trans. Nucl. Sci. **NS-11** (1964) 244.