The mechanism of threshold switching in amorphous alloys

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This paper surveys the characteristics of threshold switching systems and examines the evidence for threshold switching as an electronic process. A semiquantitative model is proposed for the nature of the ON—state. The OFF—ON transition is also discussed in the light of recent experimentation, as are the principal aspects of the problem still in need of furthur clarification.

CONTENTS

I. INTRODUCTION

Observations of switching in thin semiconducting films go back over a considerable period. Since Ovshinsky (1968) reported threshold processes in thin layers of chalcogenide glass alloys, there have been many attempts to explain these observations. Several investigators have maintained that the phenomena are essentially thermal, the current in the ON-state being carried by a hot filament. While this may well be so for thick films, the present authors are convinced by many recent investigations that this is not true for thin films of the multicomponent chalcogenide glasses. The purposes of this article are to review this evidence, and to discuss the model to which it is believed to lead. Quantitative solutions of the transport equations from electrode to electrode are not yet available. Nevertheless, the accumulated body of results have made it possible, with a reasonable degree of confidence, to present an electronic interpretation of what is happening, at any rate in the ON-state. This is the principal aim, but the more difficult problem of the transition from OFF-state to ON-state will also be discussed.

A threshold switch is typically a sputtered film about 1-μm thick, with metal or graphite electrodes, though for experimental purposes electrodes of Ge and Si (n-type and p-type) have also been used (Henisch and Vendura, 1971; Henisch *et al.*, 1972; Reinhard *et al.*, 1973; Petersen and Adler, 1974; Adler *et al.*, 1974; Petersen and Adler, 1976). Alloy glasses of various compositions within the Te–As–Ge–Si system normally function as switching material, $Te_{40}As_{35}Ge_6Si_{18}$ being a typical example. These are semiconductors with an optical band gap at about 1 eV, and an activation energy for conduction, which is p-type, of about 0.5 eV. Their properties have been widely discussed in the literature, for example, by Fritzsche and co-workers (Fritzsche, 1973; Kastner *et al.*, 1976a), Street (1976), Tauc (1974), Grigorovici (1971; 1973), Kolomiets and co-workers (Kolomiets, Mamontova, and Babaev, 1972; Kolomiets, 1974; Domorid and Kolomiets, 1976), Owen and co-workers (Marshall *et al.*, 1972; Main and Owen, 1974; South and Owen, 1974), Bishop and co-workers (Bishop *et al.*, 1975), and others. Figure 1(a) shows a typical voltage-current characteristic of a switch, as obtained by continuous ac display in the presence of a series load resistance. Important features are:

(a) The OFF-current is highly temperature dependent, and non-Ohmic before switching. In previously unswitched ("unformed") devices, it is proportional to the electrode area. [Forming processes are sometimes observed (see below) in units made under insufficiently clean conditions, and these tend to destroy this proportionality.]

(b) The ON-state does not depend on the electrode area (unless very small—see Petersen and Adler, 1976), showing that a highly conductive "filament" or "channel" is formed during switching. The ON-voltage depends little on temperature and on film thickness. The last feature suggests that the electric field is low throughout most of the volume, and high only at the electrodes.

(c) The switching ("threshold") voltage decreases at high temperatures, but is almost constant below ~200 °K. It is proportional to the film thickness. Such scaling tests cannot be carried out with great accuracy but, inasmuch as they yield significant results, they

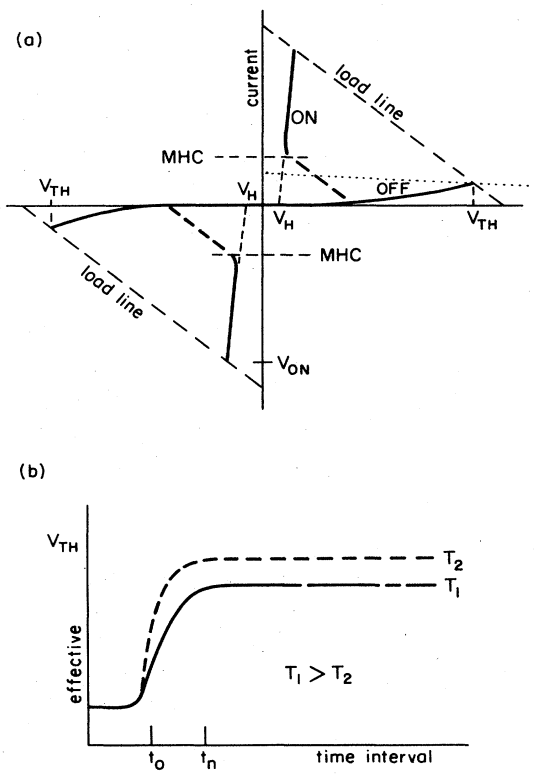

FIG. 1. Threshold switching; schematic characteristics. (a) Voltage–current relationship under continuous ac excitation in the presence of a series resistance which determines the load line. Resistance collapses when $V = V_{th}$; operating point shifts to the conductive branch (ON-state). (b) Transient aftereffects, and their temperature dependence. Effective threshold voltage as a function of the time interval since the cessation of the last ON-state. $t \approx 1$ μsec for switching layers of about 1 μm thickness.

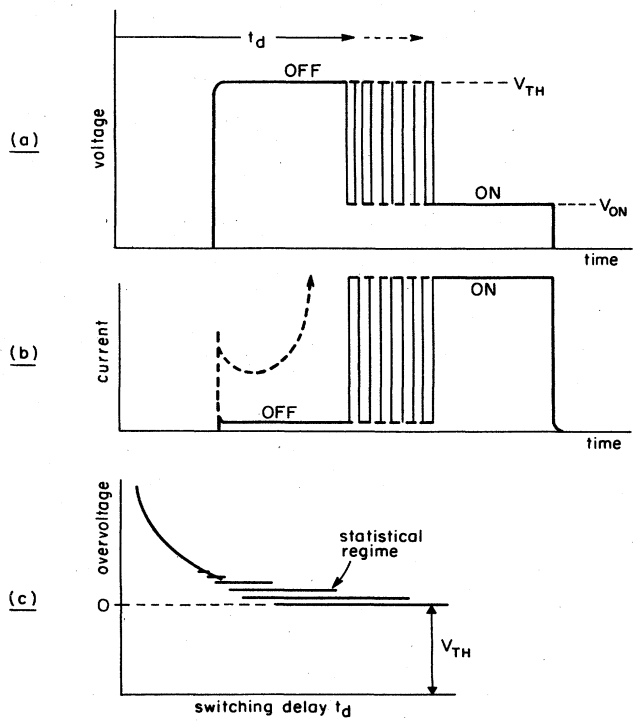

FIG. 2. The switching delay t_d. There is a waiting period at $V = V_{th}$ before the ON-state is established. (a) Voltage-time relationship; random variation (about a certain mean) of the t_d values associated with successive switching events. (b) Current-time relationship. Dotted line: current when appreciable overvoltage is applied. (c) Switching delay and width of the statistical regime as a function of overvoltage.

imply that the internal field is substantially uniform up to this point, and suggest the need for a critical switching field.

(d) The ON-state ("minimum holding") voltage (V_H) is of the order of the optical band gap for each material, though an extensive series of comparative measurements on alloys of different composition is still lacking.

(e) Switching at the threshold voltage is subject to a switching delay (of a few microseconds), after which the transition to the ON-state is exceedingly rapid ($\sim 10^{-10}$ sec). The delay times of successive events are statistically distributed [Fig. 2(a)]. The average delay can be reduced and the spread diminished by the application of *overvoltages*. Above a certain overvoltage, the process ceases to be statistical, and the delay time eventually decreases to the order of the switching time.

(f) When the voltage across a switch in the ON-state is removed, the threshold voltage for a subsequent switching is temporarily reduced [Fig. 1(b)]. These aftereffects last, typically, for about 1 μsec, the exact shape of the relationship depending on the operating current before turnoff.

(g) The characteristics represented by Fig. 1(a) are those the system undergoes in the absence of major parallel capacitance. In the presence of such capacitance, additional (transient) discharge currents pass through the system when the internal resistance collapses. This can result in electrical and thermal overload which modifies switch behavior, and can also lead to irreversible breakdown.

(h) When the series resistance is high, so that the load line fails to intersect an operative part of the ON-characteristic, then the system goes into self-oscillation [see dotted line on Fig. 1(a)]. The detailed characteristics of these oscillations have been studied by Schmidt and Callarotti (1977a).

A great deal of effort has been devoted to the explanation of these features, most of it on the basis of conventional semiconductor theory, but some also within the framework of relaxation theory (Van Roosbroek, 1973), and some on the basis of special assumptions on the nature of the nonequilibrium processes involved (Vezzoli *et al.*, 1975). The proposed models can be divided into two main classes, depending on whether the ON-state arises primarily from heating (*thermal* models) or from a nonequilibrium enhancement of either carrier concentration or mobility or both (*electronic* models). Feature (c) above is a convincing symptom of nonthermal behavior up to the threshold point. Another early indication of this came from the work of Kolomiets *et al.* (1969), who found that the switching field is indeed constant up to film thicknesses of $\sim 10^{-3}$

cm, i.e., an order of magnitude greater than those ordinarily used. Only for thicknesses greater than 10^{-3} cm does the switching field diminish, suggesting thermally assisted processes. This conclusion has since been confirmed in a number of other ways (see below).

Because thermal and nonthermal effects are inherently difficult to distinguish by electrical measurements on two-terminal systems alone, experiments which purport to "prove" one contention or another have often shown themselves, upon closer examination, to be misleading, and the resolution of these problems has taken a good deal of time. Moreover, the fact that some switches show a "forming" effect, in which the threshold voltage changes drastically after the first switching event, or else more gradually until stability is reached, has introduced additional difficulties. It is now clear that "forming" is by no means an inherent feature of threshold switching systems; switches made under closely controlled conditions, as regards stray ion concentrations, do *not* exhibit any such variations in threshold. The modifying processes are therefore incidental, arising from faulty preparation or operation (overload). In contrast, most of the results reported in the literature refer to switches made under less-than-perfect conditions, and therefore to devices which become "formed" in the above sense during the first switching operation (Coward, 1971). One of the consequences of forming, when it occurs, is to make the OFF-current likewise independent of (or, at any rate, less dependent on) the superficial contact area. Another is to produce a certain amount of OFF-state asymmetry (rectification). Also, because some of the forming processes are reversible and relatively fast, they can affect detailed modes of switch behavior in ways which depend on experimental procedure. Observations like those reported by Schmidt and Callarotti (1974), and Burgess and Henisch (1973) are likely to owe their character to such factors, and Popescu (1975) has shown that lateral heterogeneity introduced during forming can have important thermal consequences. This difficulty affects some measurements more than others, as discussed below. Accordingly, it is a further purpose of this paper to indicate which aspects of the problem have been clarified and which are still in need of further research.

II. THERMAL MODELS AND STABILITY EXPECTATIONS

The thermal–nonthermal controversy arose many years ago for two opposing reasons: (a) It was obvious that power dissipation in the minute volume of a threshold switch would cause *some* heating. The magnitude of the effect could not be determined as long as the volume of the conducting channel in the ON-state was unknown, but it was natural to question whether the entire switching phenomenon might perhaps be described in thermal terms. (b) Detailed features of the switching process suggested from the beginning that nonthermal mechanisms might be at work, and the notion grew that research on threshold switching might eventually be used to throw light upon the nature of amorphous alloys, just as research on transistor physics was used to add greatly to our knowledge of crystalline semiconductors. Moreover, it was felt that thermal mechanisms would inevitably be associated with instability, and in this way the thermal-versus-nonthermal controversy came to be linked with an assessment of commercial device prospects. The matter will here be reconsidered in the light of new experiments.

Thermal theory predicts ON-state "filament" temperatures of the order of several hundred degrees centigrade, depending on the assumptions made (Popescu, 1975; Kroll, 1974; Kroll and Cohen, 1972; Kaplan and Adler, 1972; Popescu and Croitoru, 1972; Böer and Döhler, 1969), whereas the glass transition temperatures of the multicomponent chalcogenide alloys generally used for threshold switching are in the range 150°–350°C. This leads to the expectation of gross instability, whereas threshold switches made under clean conditions and operated without excessive power dissipation are in fact highly stable (more than 10^{14} operations under pulse conditions). It is now known that the term "filament," often used for the geometry of the conducting region of the ON-state, is a misnomer, because the diameter is generally larger, not smaller, than the length, and we shall therefore use the word "channel." It has become clear that the ON-state channel in thin chalcogenide switches is not ordinarily hot (see below), and this is strong evidence against a thermal model. However, even if it were hot the expectation of instability resulting from elevated temperatures may be false. Popescu (1977, personal communication) has drawn attention to the fact that the glass transition temperature is known to us only from experiments on homogeneous bulk systems. In contrast, thermal theory deals by supposition with a hot region of large surface-to-volume ratio surrounded by cold matter, whether comprised of electrode material or of nonconducting portions of the glass, i.e., a very nonuniform temperature distribution. In such circumstances, the cold envelope might act as an "anchor" which inhibits the glass transition. The notion is that the "filament" core could be "superheated" and might survive repeated pulse excitation, even if high temperatures were involved during each pulse. Such a system would be stable, as long as the duration of each ON-state is less than the (presumably augmented) time constant of the glass transformation. In *memory* switches, which are made from Te-rich glasses of lower transition temperature, a crystallization of Te does indeed occur in the conducting channel, but the power dissipation is a great deal higher in such cases, partly because of the higher conductance and partly because memory switching is routinely carried out with substantial overvoltages. However, the argument for or against thermal mechanism does not depend on considerations of phase stability alone, but on other features of switching behavior, on demonstration of the fact that the power dissipation can be substantially varied (by illumination) without affecting the threshold voltage (Smith and Henisch, 1973; Henisch *et al.*, 1974), and, ultimately, on actual determinations of channel temperature in the ON-state.

One other general indication is provided by experiments with crystalline semiconductor electrodes. The original argument (Henisch and Vendura, 1971; Henisch *et al.*, 1972) was that (say) n-type and p-type Ge, when used as

electrode materials, would have the same thermal conductivity, but different electrical properties. If thermal aspects alone were relevant, the switching results should be the same for the two electrode materials, but they are in fact highly asymmetrical, and thus strongly indicative of electronic interaction, as further discussed in Sec. VI.

III. OTHER STABILITY CONSIDERATIONS

Apart from thermal factors, stability is believed to be governed (a) by considerations of composition and structure, and (b) by the presence of accidental impurities. It is a common experience that threshold switches made under insufficiently clean conditions (e.g., in the presence of etch residues) are more stable under ac than under dc operation, and this is bound to have an interpretation in terms of ionic movement. Such movement would, in due course, lead to a change of composition along the path between the cathode and the anode, and such a change could move the material out of the stable composition region of the phase diagram (Fritzsche, 1977, personal communication). As a result, a major fraction of the volume might crystallize. Before total failure one first observes a decrease in threshold voltage. The original state can be recovered by reversing the polarity until the switch fails again due to electromigration in the other direction. By choosing a composition which has a wide stability region for adjacent compositions around it, it is possible to make dc stable devices (Ovshinsky, 1974, personal communication). There is thus an intrinsic problem, which can be dealt with by the correct choice of switching material, and a stray ion problem which can be avoided by clean deposition techniques.

If unwanted ions were present, they could take part in "forming processes," whether drastic or slight, when electric fields are applied. In any event, it has recently been shown that whereas these smaller changes influence the OFF-resistance (of "formed" switches), they do not influence the threshold voltage (Esqueda and Henisch, 1976). Accordingly, it must be concluded that electrolytic aftereffects involve only the region which surrounds the formed channel region on which (alone) the actual switching process depends.

As regards the choice of switching material, it is important to note that whereas many amorphous materials "switch" in one sense or another, the multicomponent chalcogenide glasses (e.g., of the type $Te_{40}As_{35}Ge_7Si_{18}$) are the only ones which have thus far proved stable enough to permit the design and preparation of stable devices. Other chalcogenides such as As_2Te_3 show similar effects, but without the required stability. Cross-linking in the alloy glass doubtless accounts for its superior stability. It is believed that the capacity of the chalcogenides to switch without immediate recrystallization can be understood in terms of the electronic band structure. On the basis of the electronic process proposed in this article, one likely stability condition is that the highest occupied band in these materials should result from interaction between the nonbinding electrons, e.g., the lone pairs on chalcogen atoms (Kastner, 1972). Intense electronic excitation is then possible *without* disrupting the bonding strengths of the material (Ovshinsky, 1973, 1976; Kastner *et al.*, 1976b). In addition, three-dimensional structural stability is promoted by the presence of tetrahedrally linked elements like Ge and Si. Switching processes in other materials, e.g., in polymers (Henisch and Smith, 1974), which show a superficial resemblance to "ovonic" switching, are in fact rather different and much less stable (Henisch *et al.*, 1977). Their ON-state currents are much more voltage dependent, and their minimum holding voltages substantially greater.

IV. INFORMATION DERIVED FROM FAST-PULSE MEASUREMENTS

Another point which has to be borne in mind is that thermal theory (i.e., the models so far developed) is a *steady state* theory. As such it concerns itself with the temperature distribution which prevails (or which, on the basis of simplifying assumptions made, is believed to prevail) *after* several thermal time constants have elapsed. In its present state of development, therefore, it cannot make predictions concerning the outcome of experiments carried out within shorter time intervals. Thus, for instance, it has nothing to say about the *transient* ON-characteristic (TONC) [Henisch and Vendura (1971); Henisch *et al.* (1972)] illustrated in Fig. 3. Of course, the converse is also true. In order to "disprove" thermal theory as it stands, it is necessary to conduct experiments *within* its claimed range of validity. Fast-pulse experiments (Shaw *et al.*, 1973; Buckley and Holmberg, 1975) can be highly informative in other ways, but do not address themselves directly to this particular problem. Thus the establishment of the ON-state with a voltage pulse shorter than the thermal time constant is not by itself proof of electronic mechanisms at work. Many such experiments prove only that events happen faster when higher voltages are applied, and that would

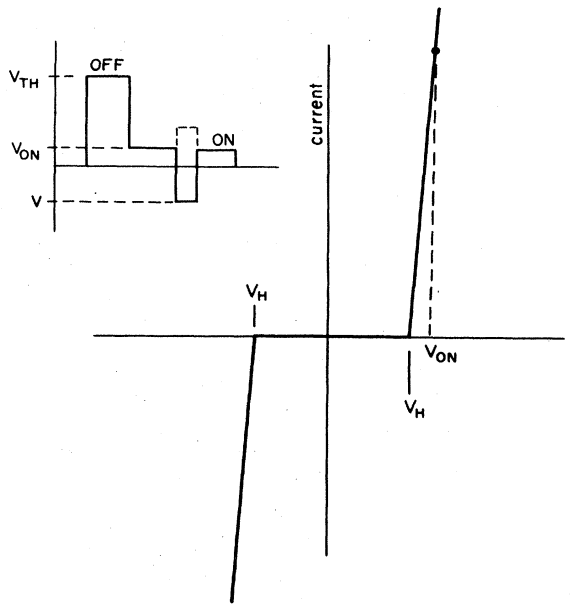

FIG. 3. Transient ON-characteristics (TONC) of a threshold switch. A transient voltage excursion from $V = V_{ON}$ to a variable V is made when the switch is in its ON-state. (After Henisch, Pryor, and Vendura, 1972.)

be true no matter what particular switching mechanism is envisaged. Since the thermal behavior is never simple, one would in any event have to contend with a whole distribution of thermal time constants. However, it has been possible to show (Shaw *et al.*, 1973) that the ON-state can be established by means of nanosecond pulses, with total energy dissipations too small to cause any appreciable temperature rise (for plausible current distributions), even on the assumption of zero heat loss from the channel area. Such results are far more convincing than fast switching as such.

Experiments to determine the TONC begin from a steady point on the ON-characteristic and involve pulsed displacements from that point. Because the displacements are very fast, they take place under virtually isothermal conditions. The highly characteristic shape (Fig. 3) of the TONC itself suggests very strongly that electronic processes play a dominant role under these conditions, no matter whether the ON-state is essentially "hot" or "cold."

One of the important insights derived from experiments with ultrafast pulses concerns the detailed features of the voltage-current relationship close to and beyond threshold (Buckley and Holmberg, 1975). When overvoltages are applied, the switching delay becomes very short [Fig. 2(c)], but if the pulse duration is shorter still (e.g., 0.5 μsec), switching can be prevented, and the appropriate OFF-current measured. Such experiments have revealed the existence of a new and highly nonlinear conductance region, beginning immediately below the threshold point. With overvoltages, the power dissipation also increases sharply, which, in all likelihood, contributes to the disappearance of the statistically varying switching delay [Fig. 2(b)]. Indeed, operations at high overvoltage, preferred by many casual investigators on account of their relative simplicity, are expected to have increasingly thermal components, of which there is no sign in connection with switching at and close to threshold. The distinction between switching close to threshold and switching at high overvoltages must therefore be borne in mind in the course of any comparison of results published in the literature.

V. GENERAL NATURE OF THE ON-STATE

According to thermal theory, the ON-state has a negative resistance slope. In fact, one finds a positive slope (Fig. 1) over most of the current range when tests are made with ac, and over the entire range when tests are made with fast pulses. Thermal models tend to cope with the situation in the following way. When the material is cold and its bulk resistance high, contact resistances are negligible, at any rate over the contact area of the filament. The overall performance is then controlled by the bulk. As the material gets hot, its bulk resistance collapses; the residual contact resistances then become important and yield the positive slope. Such contact resistance may then be associated with secondary effects, e.g., tunneling through contact barriers, of which the TONC may be a symptom, and with carrier injection, of which radiative recombination furnishes the external evidence. Therefore neither the existence of the TONC nor the demonstration of radiative emission by itself constitutes conclusive proof against thermal models; the emission could be merely an interesting adjunct phenomenon, not directly associated with switching. Conversely, qualitative demonstrations of heating prove nothing by themselves. In particular, they do not show that switching is thermal, and it is therefore necessary to devise other criteria.

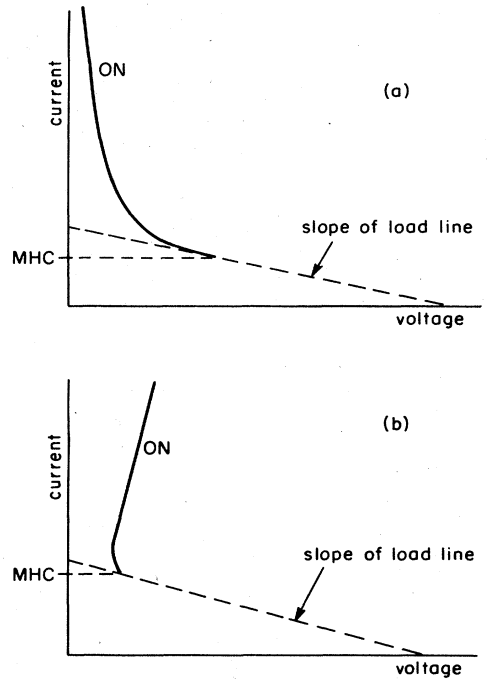

FIG. 4. Cessation of the ON-state. (a) Typical behavior of thermal systems (Ovshinsky, 1973); slope of characteristic matches slope of load line at the minimum holding current (MHC). (b) Observed behavior of "ovonic" systems (Popescu and Croitoru, 1972); slopes do not match.

ac displays of the threshold switching characteristic (and displays based on slow ramp voltages) show that the slope is indeed negative at the lower end of the current scale, and to that extent the common observations are similar to the prediction of thermal theory. A distinction arises, however, in connection with the nature and status of the *minimum holding current* (MHC) [Fig. 1(a)]. Within the framework of electronic models the MHC, considered as the limiting point of a steady ON-state, denotes a situation which is entirely controlled by internal conditions, e.g., carrier injection and recombination. (Observations under dynamic conditions must, of course, involve also the external circuit conditions.) In contrast, thermal theory envisages *no* minimum current of this kind, except in a trivial sense, applicable only to infinite series resistances. According to thermal theory, the system must return to the OFF-state at a point at which the slope of the voltage–current relationship is equal to the slope determined by the load line. Varying the series resistance should therefore lead to varying cutoff points, in accordance with the slope-matching requirement (Fig. 4), and cases are known in which this actually happens (Hughes *et al.*, 1975), although these involve film thicknesses greater than those ordinarily used in ovonic

switching. However, recent experiments (Esqueda and Henisch, 1976) on normal switches ($\lesssim 1$ μm thickness) have yielded quite different results. Although the apparent minimum holding current is not in practice *totally* independent of procedural details (because some stray capacitance is always involved), it has been demonstrated beyond doubt that there is no matching of slopes at the cutoff point. Indeed, some situations involve gross mismatch. In other words, there is a minimum holding current below which the ON-state cannot be sustained. This conclusion is further confirmed by the work of Schmidt and Callarotti (1977b), who concluded from observations of relaxation oscillations in threshold switches that the ON-state does not gradually decay, but comes to an abrupt, discontinuous end.

For such an abrupt cutoff there is no known explanation in terms of any thermal model, but electronic theory provides a plausible explanation. To sustain the high current density in the ON-state, it is necessary to envisage the existence of a high-density (nonequilibrium) electron-hole plasma (Henisch, 1969; Henisch, Fagen and Ovshinsky, 1970). The two types of charge carriers must be present to avoid enormous space charges. Such a plasma can be maintained in the steady state only if some replenishment process (the nature of which will be discussed later)balances the losses due to recombination and due to transfer out of the glass into the electrodes. In such terms, the MHC represents that condition for which the replacement rate becomes insufficient to keep up with the recombination or diffusion rate, whichever predominates. The system must then revert to the OFF-state, and will do so very quickly, within the order of a carrier lifetime.

VI. AREA AND TEMPERATURE OF ON-STATE CHANNEL

In his original paper on the threshold switch, Ovshinsky (1968) suggested that in the ON-state the current density in the conducting channel might be constant, with the cross section increasing with increasing current. The first experimental evidence that this is so was provided by Henisch and Pryor (Henisch, Ovshinsky, and Pryor, 1970; Pryor and Henisch, 1971; Henisch and Pryor, 1971), who showed that the effect of a pulse A on the switching voltage of a pulse B at a later time t_0 [beyond the point of inflection on Fig. 1(b)] did not depend on the total current in pulse A. They deduced that the current density in pulse A must be independent of the total current. Since the time required for the restoration of the full threshold voltage is also essentially independent of temperature, the authors concluded that carrier trapping cannot play any appreciable part in these aftereffects; an explanation had to be sought on the basis of free-electron models.

Further evidence for the correctness of this assessment comes from the work of Petersen and Adler (1974, 1976; see also Adler *et al.*, 1974), who also obtained a measurement of the channel cross section by several methods:

(a) They used an n-type silicon electrode and made use of the velocity saturation effect in that material. By measuring the I–V characteristic of the ON-state in the velocity–saturation regime (Fig. 5) and assuming that the current in the silicon spreads laterally at 45°C (Fig. 6), they estimated the current density and thus the channel radius up to the point when the silicon avalanches. The results are shown in Fig. 7 (full line).

FIG. 5. Switching characteristics of a glass/n-Si heterojunction device. Polarities refer to the top Mo contact. The OFF-state on this scale is just the horizontal line at zero current. When the glass switches into the ON-state, the current levels rise to 2–10 mA, as shown. The high-current branch, (>15 mA), is due to avalanching in the n-Si epitaxial layer. Vertical scale: 10 mA/div; horizontal scale: 5V/div.

(b) They increased the current until the resulting channel occupied the whole cross-sectional area of the glass, after which further increase of current necessarily increased the current density. At very high current levels, deterioration effects due to heating were observed. Devices with small cross-sectional areas of diameter of 6 μm and 25 μm were used for these experiments. The results are also shown in Fig. 7.

(c) TONC experiments (involving current changes within a time too short for the channel area to change) gave a measure of the resistance of the channel. This was found to be inversely proportional to the current. If the area is taken from the measurements above, the resistivity of the resulting channel can be assessed and is found to be

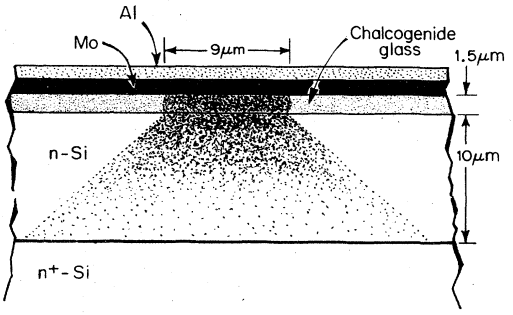

FIG. 6. Pattern of current flow. Scale drawing of current flow at about 7 mA in the ON-state of a glass/n-Si heterojunction device. The 45° lateral current spread in the Si is an approximation used in many calculations. Note pancake shape of conducting channel in the glass.

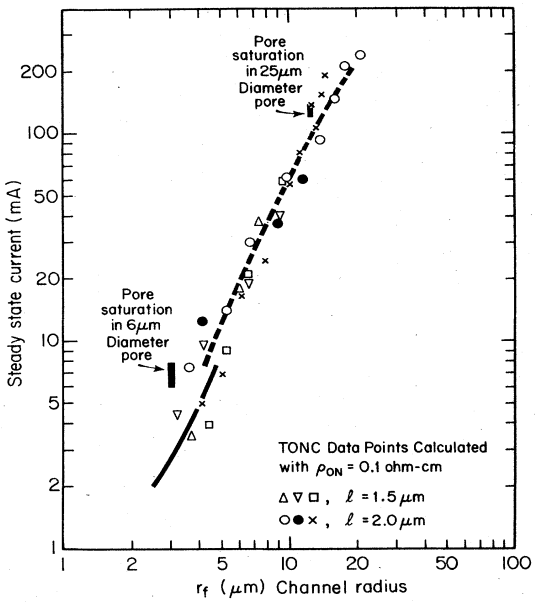

FIG. 7. Channel radius as a function of steady-state current. Determination by four methods. The pore saturation points referred to in the text (at 7 and 130 mA) are indicated, as the TONC data. The solid line is calculated from current saturation effects in glass/n-Si heterojunction devices.

$$\rho = (0.08 \pm 0.02)\Omega - \text{cm}.$$

From this and the total current the field within the film was deduced. It was found that a potential drop of about 0.1 V occurs across the channel, the rest (≈0.7 eV) being at the electrodes.

Various workers have measured the maximum interruption time allowed during an ON-state before reswitching is required. This has sometimes been ascribed to recombination of electrons and holes (Mott, 1975), but Petersen and Adler have concluded it to be due mostly to the diffusion of carriers out of the channel. This follows from the observation that the recovery time is proportional to the cross-sectional area of the channel, a relationship obeyed with remarkable accuracy (Petersen and Adler, 1976). On this basis, a diffusion coefficient can be deduced, and from it a mobility, about 10 cm^2/V sec. From this and the resistivity, the carrier concentration ($\sim 7 \times 10^{18}$ cm^{-3}) can be found.

(d) A further estimate was obtained as follows. If V_B is the effective barrier to carriers entering the glass from outside, and V_B (eff) the extrapolation of the V–I curve to zero current, then, as a schematic approximation, one would expect

$$V_B(\text{eff}) = V_B + \rho l J.$$

Here ρ is the ON-state resistivity, l the thickness, and J the (constant) current density. This again [given values of J from (a) and (b)] enabled Petersen and Adler to find ρ. The method yielded 0.07 Ω cm, in good agreement with the above value.

Knowing the cross section of the ON-state channel, the current density, resistivity, and thermal constants of the material, one can calculate the temperature rise. Petersen and Adler found this to be less than 60°C. This is much less than thermal models predict, because the channel is so much wider. Estimates of surface temperature have recently been made by Neto and Henisch (unpublished) on switches of co-planar design and 10 μm electrode spacing, on the basis of measurements with a focused pyroelectric radiation detector. The procedure yields a time-maximum temperature, *averaged* over the field of view. Estimates of the channel temperature itself would therefore depend crucially on the exact size of the channel. If the temperature were uniform over an area of 10 μm diameter, the measurements (at minimum switching power, corresponding to zero overvoltage) would assess this temperature as 13°C above ambient. However, two corrections must still be applied, one to take account of the fact that the co-planar switch dissipates six times as much power as the devices with which we are ordinarily concerned (i.e., 1 μm layers with massive graphite electrodes), and another to allow for the more efficient cooling of the conventional units. Together, these factors suggest a space-averaged temperature rise of the order of 1°C with a central region somewhat hotter. We are dealing with a rough estimate, but one which is unlikely to be in error by a substantial factor. While the exact value may be in doubt, there is no sign of any temperature as high as thermal models demand, e.g., several hundred degrees above ambient (Warren, 1969; Male, 1970; Thomas and Male, 1972). Similar conclusions follow from the results of Adler and Sokolowski (1977), who found (by means of delicate thermocouple measurements on the hottest point of a small-area electrode) that only a very small temperature rise (less than 1°C) takes place in the electrode temperature of a Mo/glass/Mo switch under normal ON-state operating conditions. That some Joule heating takes place is not, of course, in doubt, but predictions relating to the resulting temperature distribution depend *inter alia* on assumptions made concerning the pattern of the current distribution. Since these parameters are difficult to assess, thermal models have up until now involved a wide margin for error.

Memory switches developed by Energy Conversion Devices, Inc. ("Ovonic" memories) are made of alloys with a lower percentage of cross-linking elements, e.g., with a typical composition $Ge_{14}Te_{81}Sb_2S_3$. Moreover, considerably higher operating temperatures may occur, even in the OFF-state, owing to the higher conductivity of the materials employed. Though such devices can be repeatedly *threshold switched* with sufficiently short pulses without going into the memory ON-state, they are ordinarily operated under very different conditions, i.e., with long pulses (milliseconds) and high overvoltages. The total power dissipation is then substantially greater than that involved in the processes discussed above. Nevertheless, Feinleib, de Neufville, Moss, and Ovshinsky (1971) have suggested that, even under those conditions, the crystallization of the memory glass is promoted not only by the elevated temperature, but by the electronic disequilibrium which characterizes the ON-state, and we consider this very plausible.

VII. DOUBLE INJECTION; GENERAL CONSIDERATIONS

The experiments quoted above seem to show with little doubt the following:

(a) In the ON-state there is a conducting channel normally thicker than the glass film, and the cross-sectional area of this channel is proportional to the total current.
(b) Most of the voltage drop is at the electrodes.
(c) The channel is not hot.
(d) The density of carriers is in the range 10^{18}–10^{19} cm^{-3}, and the mobility of order 10 cm^2/V sec.

Since the carriers are not thermally excited, and could hardly be produced by either impact ionization or Zener tunneling in the small internal field in the ON-state, the conclusion is inescapable that they come from the electrode region. Moreover, since a density of 10^{19} carriers/cm^2 in a film 1 μm thick would produce an enormous space charge, we are forced to the conclusion that electrons *and* holes are injected. We therefore are led to the double injection model, first put forward in this context independently by Mott (1969) and by Henisch (1969). This situation is illustrated in Fig. 8. It assumes that narrow barriers are formed at both electrodes, which allow holes and electrons to tunnel into the glass.

It will be seen that the model at once explains why the holding voltage is of the order of the gap, accepting Petersen and Adler's conclusion that a potential drop of only 0.1 eV occurs in the bulk of the film. Also, by assuming that the band structure and gap are essentially maintained in the ON-state, the model explains the radiation with $h\nu \simeq 1$ eV observed by Kolomiets, Lebedev, Rogachev, and Shpunt (1972), and by Vezzoli *et al.* (1974). However, the model also introduces a major problem: What maintains the barriers? A further problem concerns recombination. The transit time is given by

$$\text{transit time} = \text{thickness/field} \cdot \text{mobility}$$
$$= 10^{-4}\ \text{cm}/(10^3\text{V/cm}) \cdot (10\ \text{cm}^2/\text{V sec})$$
$$= 10^{-8}\ \text{seconds},$$

and the question is, will there be any appreciable recombination of free carriers in this time? If so, the space charge set up should increase the holding voltage. This is illustrated in Fig. 8(b), where a plot of voltage against position across the film is given, under conditions which involve considerable recombination.

Before we attempt to answer these questions, we shall survey briefly some of the relevant properties of the chalcogenide glasses as electronic conductors.

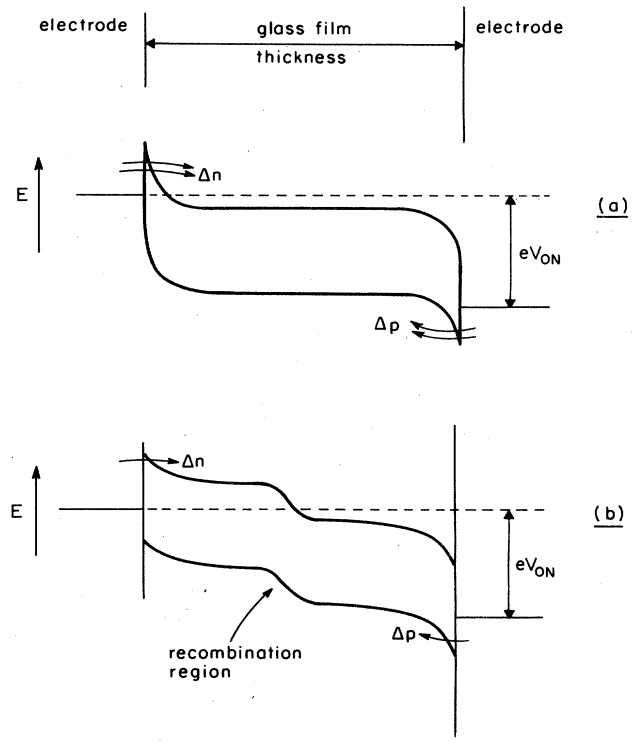

FIG. 8. Energy profile in the ON-state. (a) Transit time long; double injection without recombination. (b) Transit time short; recombination region between the electrodes.

VIII. PROPERTIES OF CHALCOGENIDE GLASSES

As_2Te_3 and the alloy glasses are ordinarily p-type semiconductors. This is deduced from the thermopower, Hall coefficients giving no simple indication of the sign of the carriers for amorphous semiconductors (Emin, 1977). The Fermi energy is thought to be pinned near mid-gap (but slightly below it) by defect states.

For As_2Te_3 containing 1% Si, rather extensive observations of conductivity, thermopower, and Hall effect made by Nagels *et al.* (1974) could be interpreted by the assumption that the valence band has a mobility edge at $E = 0.1$ eV from the band edge. 10 cm^2/V sec is a reasonable value for the mobility of holes at a mobility edge. For holes with energies between the mobility and band edges, a hopping activation energy of 0.03 eV is deduced by these authors. On the other hand, in chalcogenide alloy glasses, the drift mobility for holes seems to be limited by discrete traps, ~0.17 eV from the valence band edge, and probably due to defects. An alternative hypothesis proposed by Emin *et al.* (1972) is that carriers form polarons. Mott, Davis, and Street (1975), however, have given several arguments to show that this is not so in chalcogenides [though it may be so for holes in SiO_2 (Hughes, 1975)]. For electrons in chalcogenides the mobility is also likely to be trap limited, and we have no information about the existence of a mobility edge. [Mott (1977) has pointed out that in glassy SiO_2, for instance, any mobility edge in the conduction band would have to be so close to the band edge as to be unobservable.]

These arguments are relevant to the ON-state. From the mobility (10 cm^2/V sec) and the carrier concentration one infers:

(a) that *degenerate* carrier gases carry the current, with their Fermi energies on the extended state side of the mobility edges, if any.
(b) that the discrete traps are full.

For reasons of space-charge compensation, this must be so for electrons as well as holes, and information about the mobility edge for electrons would therefore be

desirable, but is not available. However, Rockstad *et al.* (1975) found a reversal of the sign of the thermopower of certain (Se–Te) alloys under strong illumination, which suggests that $\mu_e > \mu_h$, where μ_e and μ_h are the electron and hole drift mobilities, respectively. This is consistent with the transistor results of Petersen *et al.* (1976). The two mobilities are nevertheless believed to be of the same order of magnitude. (Yoffa and Adler, 1977).

The traps which limit the drift mobilities of holes appear to have concentrations variously estimated as between 10^{17} and 10^{18} cm^{-3}. Their origin has been discussed by Street and Mott (1975), Mott, Davis, and Street (1975), Kastner *et al.* (1976), and others. We doubt if their intrinsic nature is relevant to threshold switching, but their role in the following contexts must be considered:

(a) pinning the Fermi energy;
(b) determining a screening length at the metal/glass interface;
(c) acting as recombination centers;
(d) conceivably acting as centers for the accumulation of space charge near the electrodes (see below, however).

As regards the interface between a metal electrode and a semiconductor, various theoretical investigations show why the Fermi energy will normally be near mid-gap. The defects will determine the screening length at the interface.

The precise conditions at the metal-glass interface are not yet well understood. Meanwhile, it may be concluded from the linearity of the OFF-state resistance with film thickness that no appreciable barrier resistances come into play before threshold. For strong fields, the OFF-state behaves nonlinearly (Telnic *et al.*, 1973; Stubb *et al.*, 1972; Croitoru *et al.*, 1972), but this, in the circumstances, must be ascribed to bulk processes. There are indications (Reinhard *et al.*, 1973b) that the effect arises from a field-dependent carrier concentration. Mott and Street (1977) have given a discussion based on this model of the defects which confirms this, and goes some way towards explaining non-ohmic behavior in bulk materials.

IX. ORIGIN OF THE ON-STATE BARRIERS

The reasons for believing that such barriers exist have already been given above. For their formation an excess positive charge must be present near the electrode at which the electrons enter, and a negative charge where the holes come in. It would appear that this cannot be due to charge trapped in slow defect states [as proposed in an early paper by Mott (1971)] because, as shown by Henisch and Pryor (1971), when the polarity of a switch in the ON-state is reversed the high conductance is not disturbed. There is no time delay as we would expect if electrons had to be released and holes trapped in the place, nor are the aftereffects of switching temperature dependent in a manner consistent with the postulate of nonequilibrium carriers in traps. What the experiments demand is a *dynamic* theory. Electrons that have tunneled into the glass are hot, and may thus move away more quickly than the holes which come from the other electrode. Irrespective of the barriers and their origin, the experiments also demand a model that leads to a constant current per unit area in the ON-state (Petersen and Adler, 1976).

Such a model, in schematic form, was first proposed by Lee (1972) and extended by Mott (1975). It is supposed that the mobility of a carrier increases rapidly with energy, so these carriers move faster than those of opposite sign which have traversed the film and have had time to get thermalized. Since the hot carriers are drifting faster, their density is less, and this leads to a positive space charge in the glass near the cathode, and negative near the anode. These space charges can produce the two quasi-Schottky barriers of Fig. 8(a). Moreover, the model predicts that a tendency to maintain a constant current per unit area would be expected. The reason is that the current due to tunneling through the barrier must depend sensitively on the barrier's width, but since the barrier width is itself determined by the number of "hot" carriers that get through, an equation which fixes the current in terms of the parameters of the system must result. Particulars of the model are given in Mott's paper, but its detailed features, including stability and solution of the transport equation with appropriate boundary conditions, have not yet been ascertained. Meanwhile, we note it as very probable that a dynamic process, sustained by free carriers, is responsible for the electrode barriers and for the constant current density. Mott has also proposed that, if electrons and holes are injected, their steady-state density in the interior will be that for which the energy of the electron-hole gas is a minimum. The theory is similar to that worked out for electron-hole droplets in crystalline germanium. For parabolic energy bands, the kinetic energy is

$$\text{const}\ \hbar^2 n^{2/3}/m_{\text{eff}}\,,$$

and the potential energy

$$-\text{const}\ e^2 n^{1/3}/\kappa\,.$$

The minimum energy occurs at a density determined by

$$n^{1/3} a_H = \text{constant}, \quad \text{where } a_H = \kappa\hbar^2/me^2\,.$$

Evaluation of the constant, however, even for crystals, presents great difficulties, and depends both on band structure and correlation forces. The adaptation of the theory to amorphous material, where the parabolic form of the band edge cannot be assumed, has not yet been made. Nonetheless, values of n in the range of 10^{18}–10^{19} cm^{-3} seem reasonable.

X. RECOMBINATION OF ELECTRONS AND HOLES

The values of mobility and field deduced by Petersen and Adler give an ON-state transit time of 10^{-8} sec. For the previously discussed model to be valid, the recombination of electrons and holes in this time must be small. Radiationless recombination is thought to be via defect states. Investigations (Mott *et al.*, 1975) of the time decay of the photocurrent, in the OFF-state, in the regime where photoexcited carriers exceed those thermally excited, show that recombination follows the law

$$dn/dt = -bn^2\,,$$

where $b \simeq 10^{-10}$ cm^3 sec^{-1} and is independent of T. The mechanism proposed is that electrons fall rapidly into (N) defect centers, and that the rate-determining step is the recombination of a hole with one of these. In the conducting channel of a switch, however, all these N centers are likely to be occupied, since they coexist with a very high concentration of free carriers. The recombination time is then

$$\tau = 1/bN .$$

If this is to be greater than 10^{-8} sec, N must be less than 10^{18} cm^{-3}.

XI. THE OFF-ON TRANSITION

We turn now to the question of how the OFF-state resistance might be caused to collapse. This question must be discussed in the light of the following information, derived from experiment:

(a) The proportionality of V_{th} and film thickness. This also implies that the field is sensibly uniform between the electrodes up to the threshold point. There are indeed cases in which the linearity criterion fails, but in the absence of corroborative injection-relaxation effects, the simplest hypothesis is that there are no *effective* OFF-state barriers. Indeed with Mo electrodes on glass, the estimated barrier height is only about 0.15-eV at zero current (Petersen *et al.*, 1976). These barriers may distort somewhat in the immediate prethreshold region, giving a slight excess of field nearer one electrode, and that is where the OFF–ON transition would be initiated.

(b) The statistical distribution of the switching delay, at or just above threshold, during which the OFF-current is *constant* [Fig. 2(b)]. Nonconstant currents during the delay are always associated with substantial overvoltages, and these also reduce the delay.

(c) Illumination, of an intensity capable of modulating the conductance by an order of magnitude, leaves V_{th} (and thus the switching field) unchanged (Smith and Henisch, 1973; Henisch *et al.*, 1974) (Fig. 9), at any rate in switching materials of sufficiently high photoconductive sensitivity. [Some results have been reported (Rogers *et al.*, 1976) which involve a lowering of V_{th}, and one would ordinarily expect to see this when the carrier lifetime is small.]

There is still room for conjecture, but we are led to the following tentative conclusions:

(i) The OFF-ON transition demands a critical field, irrespective of carrier concentrations. It *is* the process whereby the internal resistance (characterized by field uniformity) collapses, and the field pattern changes, from almost uniform at the threshold point to that of the established ON-state [Fig. 8(a)].

(ii) The existence of the critical field is a necessary but not a sufficient condition for switching to occur. In addition, the system awaits a "random event" which occurs after the (statistically distributed) switching delay (t_d). The constancy of the current during t_d implies that the delay does not arise from any buildup of space charge or temperature. Since t_d is also independent of

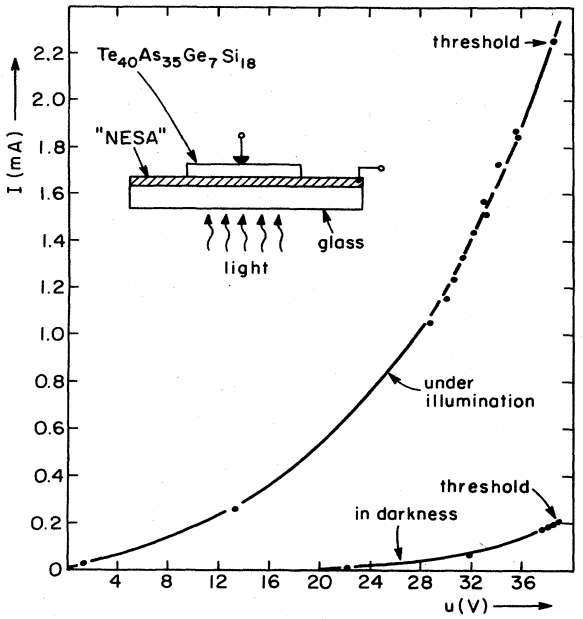

FIG. 9. Effect of illumination on threshold switching. Graphite/glass/NESA system (Kroll, 1974) at room temperature. Nominal glass thickness of the switching glass 0.4 μm. V_{th} = 39v. Pulsed illumination and pulsed applied voltage to avoid heating. V_{th} unchanged, despite order-of-magnitude increase to threshold current.

illumination, we must conclude that the transition nucleates in a place where the effects of illumination are nullified. This could happen at the electrodes where the carrier lifetime might be extremely small. The "random event" itself could be the arrival of a tunneling or a field ionizing carrier from one of the electrodes. The results suggest that the statistical component of the total delay dominates the switching event near threshold, and the formative component dominates in the presence of appreciable overvoltages (Silver, 1977, private communication).

A second possibility is the interpretation of t_d as a propagation time. This is linked with the notion that the OFF–ON transition is initiated at one of the electrodes, e.g., by avalanche, after which the augmented carrier concentrations would have to spread through the interelectrode space (Shaw, 1977, private communication. The difficulty is, however, to account for the constancy of the OFF-current while this happens. Additional hypotheses would be needed.

XII. AFTEREFFECTS OF SWITCHING

When the ON-state ceases, three processes must be presumed to go on:

(a) the radical diffusion of carriers out of the bulk of the original ON-state channel, as investigated by Petersen and Adler (1976), who have shown that this is the process which *initially* dominates the situation;

(b) bulk recombination of excess carriers in the interior of the channel, a volume effect;

(c) collapse of the electrode barriers, through recombination (bulk or surface) and/or axial diffusion.

The aftereffects show themselves as a diminution of threshold voltage, but it has already been shown that excess carriers as such do not have the effect of V_{th}. It is therefore very unlikely that the characteristic decay curve of Fig. 1(c) arises from either (a) or (b) above. It arises very plausibly from (c), since that process would involve a gradually decaying field concentration at the electrodes. While any field nonuniformity of this kind persists, the critical field criterion could be fulfilled (in one location) for a lower external voltage than the normal V_{th}, and switching could be initiated thereby.

XIII. OUTSTANDING PROBLEMS

Though a good deal is now understood, it is important to list at least some of the aspects which are still in need of clarification. Some of these are concerned with the nature of the materials involved, others with transport theory as such. Detailed questions apart, we see four principal needs:

(1) We still lack a detailed and comprehensive comparison (including V-I relationship, pulse and optical characteristics, temperature dependence, etc.) of the switching properties which characterize different amorphous alloys. Of particular interest in this connection would be a systematic assessment of chalcogenide and non-chalcogenide alloys of comparable mobility gap. The question is not only one of durability, but one which concerns intrinsic switching behavior, whether ultimately durable or not. In the absence of such an experimental comparison, the specific function of the lone-pair electron band remains a matter of conjecture. In any event, we lack detailed information concerning the relationships between the transport properties of materials in bulk and their switching behavior.

(2) We still lack solutions of the transport equations for a two-electrode system with dynamically self-maintaining contact barriers. Such solutions cannot be achieved by analytic methods, because the complete transport equations cannot be explicitly solved, even for the one-dimensional case, whereas the radial inhomogeneity would actually require a full three-dimensional calculation.

(3) There is still no satisfactory explanation of the nonlinear behavior in the OFF-state and, in particular, of the sharply field-dependent conductance at fields near threshold and, under transient conditions, beyond threshold (overvoltage). This is a gap in our understanding of bulk properties.

(4) We concluded that switching at minimum power levels is essentially nonthermal, but do not as yet understand with sufficient precision at what point (e.g., during operation with overvoltage or low load resistance) thermal factors intervene. Nor can we assess the immediate consequence of this intervention (sometimes referred to as "thermal trimming") in any degree of detail.

A great deal of progress has been made but a complete quantitative solution of the switching problem will have to await the answers to these more specific questions.

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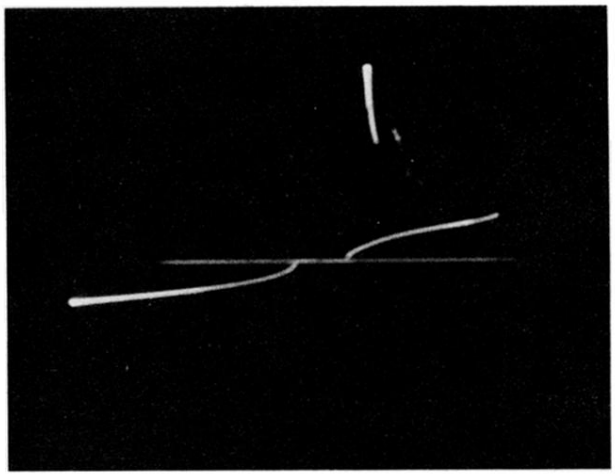

FIG. 5. Switching characteristics of a glass/n-Si heterojunction device. Polarities refer to the top Mo contact. The OFF-state on this scale is just the horizontal line at zero current. When the glass switches into the ON-state, the current levels rise to 2–10 mA, as shown. The high-current branch, (>15 mA), is due to avalanching in the n-Si epitaxial layer. Vertical scale: 10 mA/div; horizontal scale: 5V/div.