AD 725487

June 1, 1971

Research on

Contacts Between Chalcogenide Glasses, Metals and Semiconductors

sponsored by the
Advanced Research Projects Agency
ARPA Order No. 1562

Semi-Annual Technical Report

Program Code No. 61101D

Contract No. DAHC04700C 0047

Contractor: Pennsylvania State University

Principal Investigator: H. K. Henisch

Telephone: 814-865-1194

Effective Date of Contract: June 1, 1970

Contract Expiration Date: May 31, 1971 (renewal proceedings in hand)

Amount of Contract: $41,666.06

Materials Research Laboratory
The Pennsylvania State University
University Park, Pennsylvania 16802

D D C
JUN 24 1971

The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the Advanced Research Projects Agency or the U. S. Government.

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
Springfield, Va 22151

BEST
AVAILABLE COPY

The Director
Advanced Research Projects Agency
Washington, D. C. 20301

Attention: Program Management

Contacts Between Chalcogenide Glasses, Metals and Semiconductors

The two main purposes of the research here described are to elucidate the mechanism of threshold switching and to explore new possibilities through the use of contact materials which can be electronically altered in situ.

In pursuit of these objectives, four lines of research have been followed. They are concerned with

(a) the nature of the ON-state,

(b) the effect of semiconductor electrodes and contact asymmetry on the switching process,

(c) the statistical nature of threshold switching, and

(d) scaling problems, i. e. the variation of switching parameters with thickness of the chalcogenide glass film.

The last sub-project is still in its initial stages, and will be reported on when the work is a little more advanced. The first three sub-projects are covered by Appendices A, B and C of the present report. These Appendices are papers now ready for publication. In addition, Appendix D represents a review paper presented at the European Semiconductor Device Research Conference, Munich (Germany) in March, 1971.

Among the highlights of recent results are

(a) the discovery of a "blocked ON-state", of high resistance but operationally quite distinct from the OFF-state and convertible to the normal ON-state without the necessity of going through any threshold switching process, and

(b) the discovery of a sharp boundary (in terms of applied voltage) which separates the statistical operating regime from a sharply defined regime.

The current measurements are performed in part on threshold devices of commercial origin (provided by Energy Conversion Devices, Inc., through the courtesy of Mr. S. R. Ovshinsky) and in part on systems locally made from chalcogenide alloy (also supplied by E. C. D.) by flash evaporation and sputtering. The results continue to support a primarily non-thermal interpretation of threshold switching, as outlined in the detailed papers.

APPENDIX A: "Nature of the ON-state in Chalcogenide Glass Threshold Switches", by R. W. Pryor and H. K. Henisch.

APPENDIX B: "Statistical Aspects of Threshold Switching", by S. Lee and H. K. Henisch

APPENDIX C: "Characteristics of Ovonic Threshold Switches with Crystalline Semiconductor Electrodes", by H. K. Henisch and G. Vendura, Jr.

APPENDIX D: "Amorphous Semiconductor Switching", by H. K. Henisch.

(submitted to physica status solidi) APPENDIX A

Nature of the ON-state in Chalcogenide Glass Threshold Switches

by

R. W. Pryor and H. K. Henisch
Materials Research Laboratory
The Pennsylvania State University
University Park, Pennsylvania 16802

GERMAN ABSTRACT

Durch Überlagerung von vorübergehenden Spannungspulsen, während ein Dünnfilm-Glashalbleiterelement sich im AN-Zustand befindet, ist die kurzfristige Strom-Spannungskennlinie des AN-Zustandsfadens für zwei verschiedene Arten von Graphitelektroden gemessen worden. Mit beiden Elektroden wurden Schichten aus $Te_{40}As_{35}Ge_7Si_{18}$ von ungefähr 1μ Dicke verwendet. Aus den Resultaten kann man die Lebensdauer der freien Ladungsträger während einer Unterbrechung des AN-Zustandes ableiten. Solange noch solche Ladunsgträger überleben, kann der AN-Zustand ohne neuen Schaltprozess wieder hergestellt werden. Wenn der AN-Strom sich seinem Minimalwert nähert, dann nähert sich seine maximal-zulässige Unterbrechung auf Null. Es wird aus den Beobachtungen geschlossen, dass der Verfall von Ladungsträgern in Haftstellen dem Verfall freier Ladungsträger mit einer Zeitkonstante von etwa 1μ Mikrosekunde folgt. Die kurzfristige Strom-Spannungskennlinie des AN-Zustands hängt vom Elektrodenmaterial ab. Die gegenwärtige Arbeit unterstützt die elektronische Deutung von Schwellenspannung-Schaltungsvorgängen in amorphen Halbleitern.

Nature of the ON-state in Chalcogenide Glass Threshold Switches

by

R. W. Pryor and H. K. Henisch*
Materials Research Laboratory
The Pennsylvania State University
University Park, Pennsylvania 16802

ABSTRACT

By superimposing transient voltage pulses during the ON-state of a threshold switching cycle, the transient voltage-current characteristic of the ON-state filament has been determined for two types of switching systems, using different forms of graphite electrodes. Both systems employed ~1μ films of $Te_{40}As_{35}Ge_7Si_{18}$ as the active material. From the data, the lifetime of free charge carriers following cessation of the ON-state can be inferred. Until the free carrier decay is complete the ON-state can be re-established without any switching process. As the ON-current approaches the minimum holding current, the maximum permissible interruption period approaches zero. It is concluded that the decay of non-equilibrium carriers in trapping centers follows the decay of free charge carriers until complete equilibrium is restored (after 1μsecs approximately). It is shown that the transient ON-state characteristics are dependent on the electrode material. The conclusions heavily reinforce electronic interpretations of threshold switching.

*Also affiliated with the Department of Physics.

1. Introduction

In previous papers (1-4) concerned with the mechanism of threshold switching in thin ($\sim 1\mu$) chalcogenide glass films, it was concluded that the ON-state involves a gross electronic disequilibrium. According to present understanding, this disequilibrium is maintained by carrier injection (presumably at both contacts but not necessarily to the same extent), against the prevailing recombination mechanism. If the current density drops below a certain value, then recombination 'wins' and the system returns to the OFF-state. This explains at least qualitatively the existence of a well defined minimum holding current I_{MH} (Fig. 1d). It has long been known (5, 6) that the ON-current is filamentary and that the potential drop along the filament prevails largely near the contacts. These are not assumptions, but are necessary inferences drawn from the facts that (a) ON-currents are independent of superficial electrode area, and (b) ON-resistances depend only slightly on film thickness. Beyond that, the nature of the ON-state has long remained somewhat of a mystery. The experiments described below should prove helpful towards achieving a more complete understanding. Most were carried out on encapsulated switches* based on 1μ thick films of $Te_{40}As_{35}Ge_7Si_{18}$ starting material, deposited on two highly polished electrodes of pyrolytic graphite by vacuum evaporation and later assembled into a "double film sandwich". The high conductivity direction of the graphite was perpendicular

*Supplied by Energy Conversion Devices, Inc., through the courtesy of E. A. Fagen and R. Shaw.

to the film surface. A few measurements were performed on locally prepared (un-encapsulated) switches, made by RF sputtering the same alloy onto (a) graphite substrates as described above, and (b) clean (electrically isotropic) solidification surfaces on vitreous graphite. In both cases, the films were probed with pyrolytic graphite contacts. The three types of systems thus differed in structure, as shown by (a), (b) and (c) on Fig. 1.

2. Operational Considerations

If the ON-state is completely interrupted for a very short time, it can be re-established without a new switching process. The maximum value of t_s for which this can be done under prevailing conditions will be called $(t_s)_{max}$. The corresponding voltage-time and current-time relationship is shown in Fig. 2. If the interruption is slightly longer (Figs. 3a and b), a new switching process takes place upon reimposition of the voltage. This switching process is characterized by a lower-than-normal threshold voltage V_{THS}. For sufficiently long values of t_s, the full original value V_{TH} is restored. This form of behavior is shown on Fig. 3c.

It is important to note that the precise shape of these relationships is influenced by the operational conditions and, in particular, by the prevailing overvoltage. In principle, this is related to the total duration (t_p) of the test pulse following the interruption (Fig. 3a). The smaller t_p, the larger will be the effective overvoltage when the ON-pulse is restored. For the present mea-

surements, we always have $t_p >> t_{Ds}$, which means that the effective overvoltage is close to zero. These conditions contrast with those reported in a previous paper (4) which was concerned mainly with the measurements at a fixed value of t_p (2 microseconds). Such conditions imply a substantial overvoltage, varying with t_s. Moreover, before one can designate a time-interval as a switching delay, one needs a safe criterion for switching as such. When V_{THS}/V_H is high, this presents no problem. When the two voltages are comparable, as they are for small values of t_s, voltage transients arising from specimen and stray capacitances can simulate switching processes (i. e. can themselves cause voltage peaks) and thereby lead to erroneous conclusions. To avoid these, it is necessary to observe current as well as voltage as a function of time. When switching proper occurs (Fig. 2b), the current shows a rapidly decaying transient when the switching voltage is first applied. After that, the current remains close to zero, until the switching delay is over; then it rises very rapidly to its stable ON value. In the present work, switching delay t_{Ds} is defined by reference to this time interval on the current trace, a relationship which is much less likely to be disturbed by transients than the simultaneous voltage trace.

Measurements of $(t_s)_{max}$ depend also on the external circuit capacitance C_{ext}. This is so because, following an interruption of the ON-state, there is a certain amount of charge exchange between the switching system and C_{ext}. It can be shown that, contrary to intuitive expectation, the larger C_{ext}

and the smaller any resistance that may be in series with it, the more rapidly will the after-effects of the ON-state decay during its interruption. Accordingly, $(t_s)_{max}$ diminishes with increasing C_{ext}, as can be simply demonstrated by measurements during which varying ballast capacitances are connected in parallel with the specimen. The absolute value of $(t_s)_{max}$ is therefore clearly defined only as an extrapolation to $C_{ext} = 0$.

3. The Transient ON-characteristic (TONC)

The nature of the ON-state cannot be fully explored by display procedures which yield Fig. 1c; much more information can be obtained by pulse measurements of the kind shown in Fig. 3, especially since V_s can have any value, positive or negative. By varying V_s, while keeping $t_s < (t_s)_{max}$, so as to avoid renewed switching, a "transient ON-characteristic" (TONC) is obtained, as shown in Fig. 4. For small departures from the original operating point, the TONC of the evaporated double-film units (Fig. 1a) coincides with the normal (stable) ON-characteristic. Because of the short pulse duration (low power dissipation) the voltage-current relationship can be pursued over a much wider current range than the systems can tolerate under steady-state conditions. For small negative departures from the original operating point $+V_{ON}$, the current diminishes very rapidly, so much so that (for some external circuit conditions) there is the appearance of a current jump. However, there is no reason for believing that zero current (or, at any rate, an

exceedingly low current) is not in fact smoothly approached at $+V_H$. As V_s tends via zero to $-V_H$, the current remains zero. At $-V_H$, there is a very rapid current increase, similar to that observed in the first quadrant but with a slope somewhat steeper than that of the standard V_{ON}-I_{ON} relationship. In accordance with Figs. 2 and 4, the interval $-V_H < V_s < +V_H$ represents a condition under which the high carrier disequilibrium characteristic of the ON-state still prevails, but the current is nevertheless zero or close to it. This condition might be called a "blocked ON-state", and is clearly quite different from the stable OFF-state, even though both are high resistance states. From the stable OFF-characteristic, the ON-state can be reached only through a threshold switching process. From any point of the TONC of these particular switches, on the other hand, the original ON-state is immediately restored when the probing pulse ceases. Even for the highest negative pulses, a direct transition from a positive ON-state to a negative ON-state and back is evidently possible, without going through any OFF-state.

The TONC of 'home-made' single film switches made with two pyrolitic graphite contacts is very similar. However, films deposited on vitreous graphite show very different characteristics (Fig. 5). In particular, it lacks the "blocked ON-state" condition, and shows a certain amount of asymmetry.

Figure 3c shows how the threshold voltage behaves as a function of t_s. The points in regions A and B satisfy the switching criterion discussed in

Section 1; the broken line represents transient peaks which do not satisfy it. In Fig. 6a the maximum permissible t_s value for which renewed switching is still avoided [i.e. $(t_s)_{max}$] after complete ON-state interruption is plotted against the original current I_{ON} (see Fig. 1d). The results suggest that increasing current involves at least some increase in current density and hence an increase in the degree of carrier disequilibrium. In a previous (4) experiment (limited to $t_s = 0.6\mu sec$) no such increase could be detected. It is now known that, under the conditions of that experiment, $(t_s)_{max}$ was $0.2\mu secs$ and it will be shown (see below) that, in the circumstances, a positive result cannot be expected. The present experiments, reaching smaller t_s values and being conducted essentially without overvoltage offer the necessary conditions for detection. The results also show that $(t_s)_{max}$ tends to zero as the operating point approaches the minimum holding current I_{MH}.

Figure 6b shows how $(t_s)_{max}$ depends on V_s. As long as $-V_H < V_s < +V_H$ no current flows and $(t_s)_{max}$ is therefore constant. As V_s approaches $\pm V_{ON}$, $(t_s)_{max}$ must obviously tend to infinity. For $+V_H < V_s < V_{ON}$ and $-V_{ON} < V_s < -V_H$ the $(t_s)_{max}$ increases smoothly and rapidly, as one would expect. The small amount of asymmetry shown by the curves is not at this time believed to be significant.

Experiments of this kind permit us also to test whether the temperature of the system shows any appreciable rise during the ON-period. This is done

by varying the epoch, t_e, of the interruption t_s (Fig. 2). Over most of the ON-period, $(t_s)_{max}$ and hence, presumably, the temperature are independent of t_e, as seen in Fig. 7. For very small values of t_e there are changes, but these cannot be ascribed to temperature with any certainty because the pulse edges tend to overlap under these conditions. In this region, the results are questionable. In the same way, over most of the t_e range, V_{THS} is also independent of t_e. The results show that if there is any temperature change while the ON-state prevails, it must be over after the shortest time interval $[t_e + (t_s)_{max}]$ accessible by this method. t_e can be made as small as 0.1 μsec, and $(t_s)_{max}$ tends to zero as I_{ON} tends to I_{MH}, as shown on Fig. 6a. In practice some margin, implying $(t_s)_{max}$ = 0.1 μsec is desirable, which makes the shortest total interval 0.2 μsec.

4. Temperature Dependence

The minimum holding current has been found to diminish with increasing ambient temperature. This is also shown in Fig. 5a and can be interpreted as follows. In accordance with a model previously proposed (1, 4) the ON-state corresponds to a condition under which all electron traps have captured electrons and all hole traps have captured holes, the two types of traps being present in equal concentrations on the basis of the Cohen-Fritzsche-Ovshinsky band theory (7). "All", in this connection, means all

the traps capable of holding carriers at the temperature concerned, i. e. traps which are separated from the mobility edges by more than kT. With increasing ambient temperature, the number of traps effective in this way obviously diminishes, and so does the current which is necessary to keep them full.

The transient ON-characteristics (in the above sense) examined at lower temperatures (e. g. -78°C) show behavior identical with those observed at room temperature, whereas threshold voltage and minimum holding current (see above) are, of course, temperature sensitive. The results can be interpreted as meaning that, in the short time interval $(t_s)_{max}$ here considered, no redistribution of carriers in traps is involved, since any such process would be expected to be temperature sensitive and to affect V_{THS}.

5. Discussion and Conclusions

A conclusion which may be derived from results of the kind shown on Fig. 3c is that two distinct relaxation processes are at work following the interruption of an ON-state. One of these is relatively fast (e. g. 0. 1 to 0. 4 microsecond) and is concerned with the decay of free carriers. This follows from the fact that the ON-state can be fully restored without renewed switching within such a time interval. The exact magnitude of this time interval depends on the interrupted current and hence, presumably, on

the density of the free carrier concentration prevailing before the interruption. The other process is slower (e.g. 1.0 - 1.2 microsecond) and is presumably concerned with the recombination of non-equilibrium carriers in traps. After a time interval of that order, the original equilibrium condition (and hence the original threshold voltage) is restored almost completely. [Some small residual effects can be observed after longer time intervals. These will be dealt with in a future paper.] If the interruption is short, then the initial nonequilibrium population prevailing in the ON-state (or, at any rate, a significant part of it) remains in the traps. This advances the starting point of the subsequent switching event and thereby lowers the threshold voltage, as compared with the value which ordinarily governs transitions from the OFF- to the ON-state. This interpretation is in harmony with the findings of Haberland (8) on the necessity of a fixed amount of charge storage before switching can occur. It is also in agreement with the temperature independence of the TONC mentioned above.

An interpretation of the TONC itself (and its correlation with structural features) is obviously more complicated, but a tentative picture can be formulated. It is known from observations by Ovshinsky (9) that asymmetric contact structures can lead to unequal values of the minimum holding current I_{MH} in the two directions of current flow. Similarly, Henisch and Vendura (10) have shown that highly asymmetric holding voltages (V_H) can be obtained under such conditions. Both sets of observations and results re-

ported by Altunyan and Stafeev (11) indicate that the ON-state is sensitive to the precise nature of the contacts. This is, inter alia, what one would expect from the potential profile (curve a) shown in Fig. 8. The high field regions arise, presumably, from some kind of barrier, through which electrons and holes tunnel. At this stage, nothing precise is known about their shape and nature. Complete electron-hole symmetry is assumed, if only for want of any definite evidence to the contrary, but this assumption is not essential. When transient probing pulses are applied, the potential profile must become distorted, and because of the high internal ON-state conductivity, any such experiment is primarily a test of barrier behavior. In the direction of increasing applied voltages (curve b), the distortion tends to make the barriers thinner and thus more highly conductive. For the systems with pyrolytic graphite electrodes, tunneling strongly suggests itself as the prevailing mechanism of charge transfer because of the steepness of the corresponding V-I relationship which also tends to make the system self-stabilizing (compare Fig. 4).

Since the TONC (Fig. 4) is symmetrical, it is necessary to conclude that the prevailing space charge configuration is also symmetrical with respect to applied voltage. The transition from $-I_{ON}$ to $+I_{ON}$ can be achieved within a time too short to be measured by the available instrumentation (50 n sec). It follows that the space charge adjustment from profile (a) to profile (c) on Fig. 8 must likewise be very fast. In view of the large number of free car-

riers present, this is not altogether surprising.

The situation is less clear within the voltage region $-V_H < V_S < V_H$. Figure 4 suggests that, in that region, the barrier is too thick to pass any current. The question is why there should be a barrier at all. Figure 8 does not contain this information explicitly because it is concerned only with the manner in which the external potential difference is distributed. Since no (or very little) current is flowing, it follows that whatever barriers may exist for $V_S = \pm V_H$ are maintained in some form when temporarily $-V_H < V_S < +V_H$. Their survival time must be at least as long as the lifetime of the free carriers within the bulk of the film, since no measurable change of current is observed during $(t_s)_{max}$. Though the OFF-state and the "blocked ON-state" are both characterized by high resistances, the functional and operational differences between the two states are clear and unmistakeable.

As shown on Fig. 5, the TONC of systems made with one pyrolytic and one glassy graphite electrode is "soft". This means that the nature of the barrier is evidently sensitive to the contact material. It is not yet known why it should be so; differences in barrier height may be responsible.

Under the present test conditions, the magnitude of the filamentary ON-current determines the magnitude of the electronic disequilibrium, using $(t_s)_{max}$ as a symptomatic criterion. The results on Fig. 6a suggest that the current density increases with increasing current, but not in proportion. The lack of proportionality could be due to a progessive increase of

filament diameter which would tend to keep the current density more nearly (but not entirely) constant.

****

This research was supported by the Advanced Research Projects Agency of the Department of Defense and was monitored by G. Boghosian, U. S. Army Research Office, Durham, under contract No. DAH C04-70C 0047. The authors wish to thank S. H. Lee and S. R. Ovshinsky for much valuable advice.

References

1. H. K. Henisch, E. A. Fagen and S. R. Ovshinsky, J. Non-cryst. Solids 4, 538 (1970).

2. H. Fritzsche and S. R. Ovshinsky, J. Non-cryst. Solids 4, 464 (1970).

3. N. F. Mott, Festkörperprobleme 9, 22 (1969).

4. H. K. Henisch and R. W. Pryor, Solid State Electronics (in print).

5. S. R. Ovshinsky, Phys. Rev. Letters 21, 1450 (1968).

6. B. K. Ridley, Proc. Phys. Soc. (London) 81, 996 (1963).

7. M. H. Cohen, H. Fritzsche and S. R. Ovshinsky, Phys. Rev. Letters 22, 1065 (1969).

8. D. R. Haberland, Solid State Electronics 13, 207 (1970).

9. S. R. Ovshinsky, personal communication.

10. H. K. Henisch and G. J. Vendura, Jr. (to be published).

11. S. A. Altunyan and V. I. Stafeev, Soviet Physics-Semiconductors 4, 431 (1970).

Figure Captions

FIG. 1 System configurations and schematic threshold switching characteristics.

(a) 'double-film' system.

(b) 'single-film' system, asymmetric contacts.

(c) 'single-film' system, symmetric contacts.

(d) voltage-current relationship observed under AC conditions.

Film thickness $\sim 1\mu$.

Contact area $\sim 20\mu$ diam.

V_{TH} = threshold voltage.

I_{MH} = minimum holding current.

V_{ON} = operating point after switching.

FIG. 2 Short interruption of the ON-state.

(a) shape of pulse voltage across system.

(b) current through the system for $t_s < (t_s)_{max}$ and $V_S = 0$.

FIG. 3 Long interruption of the ON-state.

(a) shape of pulse voltage across system; t_s variable.

(b) current profile corresponding to (a) when $t_s > (t_s)_{max}$ and $-V_H < V_S < +V_H$.

(c) V_{THS} versus t_s relationship.

Region A: ON-state re-established after switching at the original threshold voltage V_{TH}.

Region B: ON-state re-established after switching at a reduced threshold voltage V_{THS}.

Region C: Switching process not well defined, if defined by voltage criteria above.

Region D: ON-state re-established without switching, as in Fig. 2.

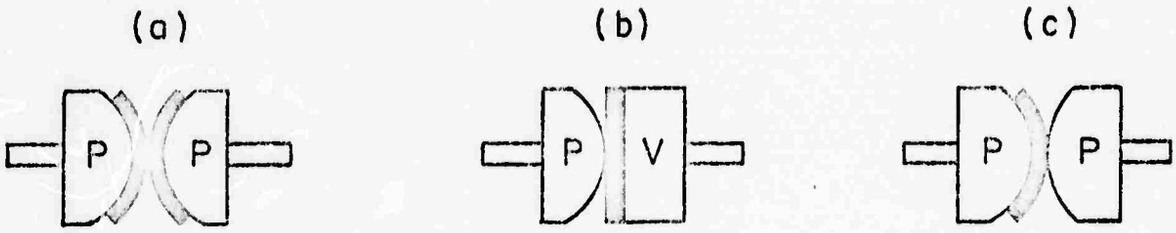
FIG. 4 Typical transient ON-characteristics of threshold switches for $t_s < (t_s)_{max}$; 'double-film' system as shown on Fig. 1a and 1c.

FIG. 5 Typical transient ON-characteristics of threshold switches for $t_s < (t_s)_{max}$; single film system as shown on Fig. 1b.

FIG. 6 Relationships between maximum permissible ON-state interruptions $(t_s)_{max}$ original ON-state current (I_{ON}) (a) and systems voltage V_S. (b) Double film system (Fig. 1a).

FIG. 7 Maximum permissible ON-state interruption as a function of epoch, for different ON-currents. Double-film system (Fig. 1a).

FIG. 8 Schematic representation of potential profiles within the amorphous semiconductor film during the ON-state.



P = pyrolytic graphite

V = vitreous graphite

= active material

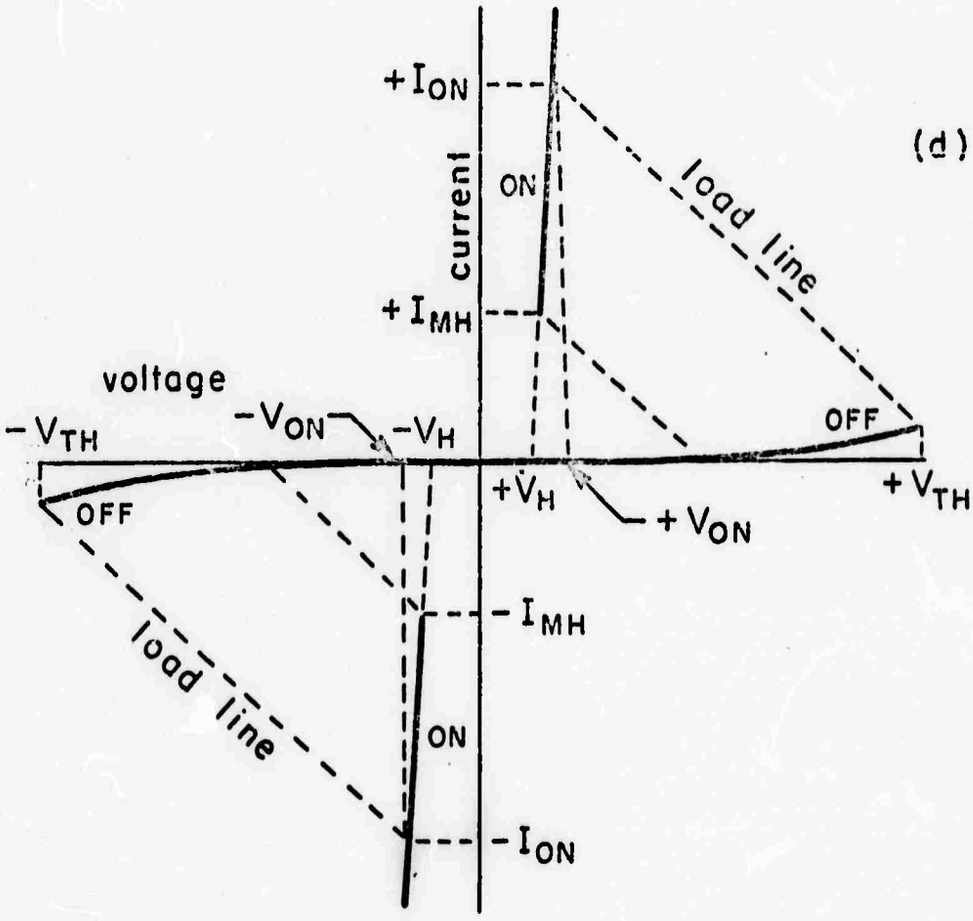


Fig. 1

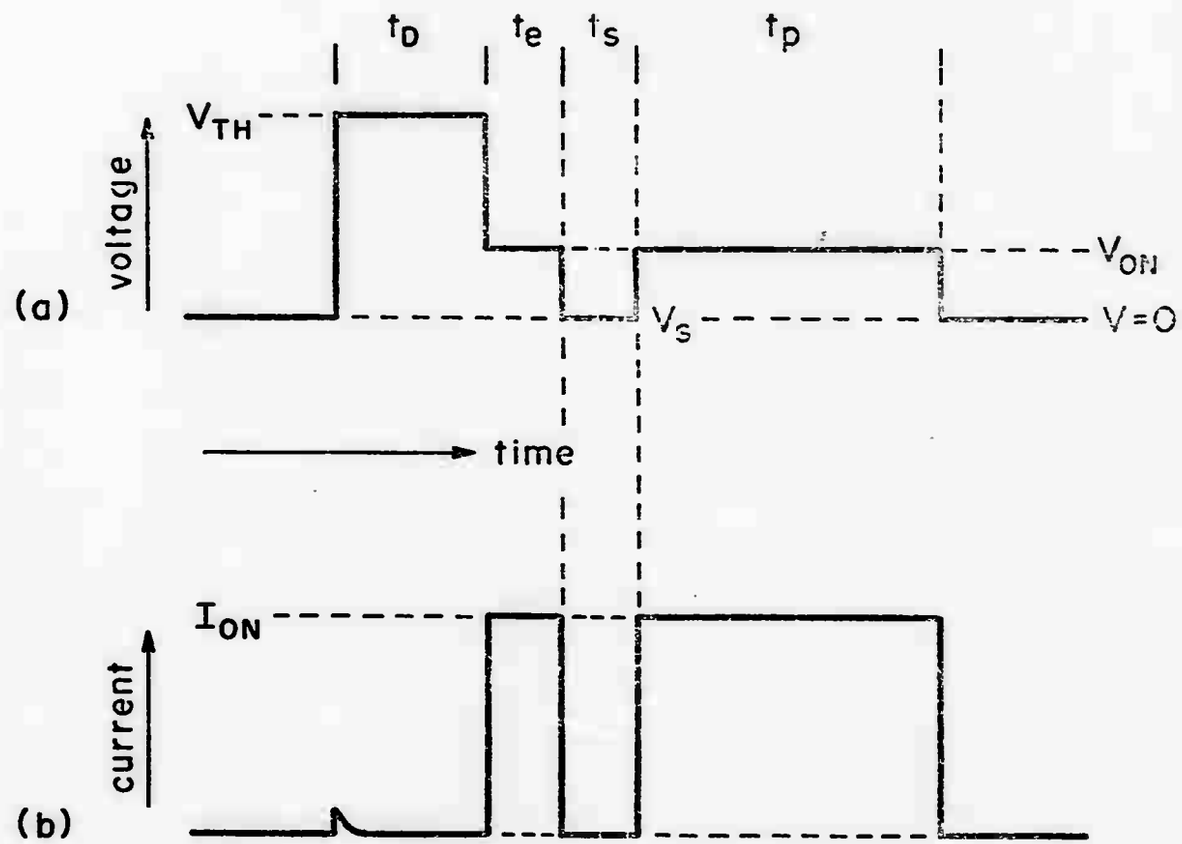


Fig. 2

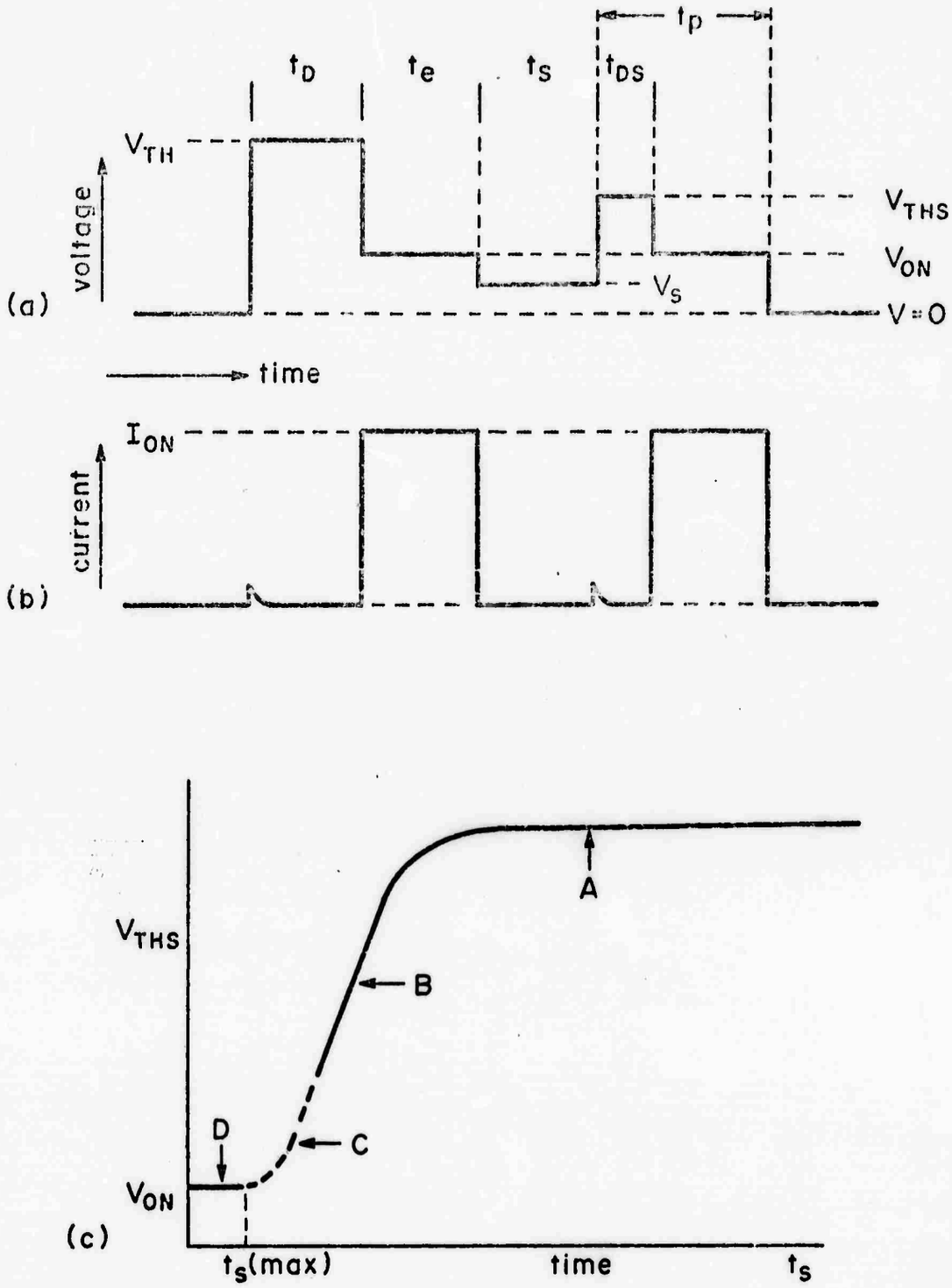

t_p
t_D
t_e
t_S
t_{DS}
V_{TH}
voltage
V_{THS}
V_{ON}
V_S
(a)
V = 0
time
I_{ON}
current
(b)
V_{THS}
A
B
D
C
V_{ON}
(c)
t_s(max)
time
t_s

Fig. 3

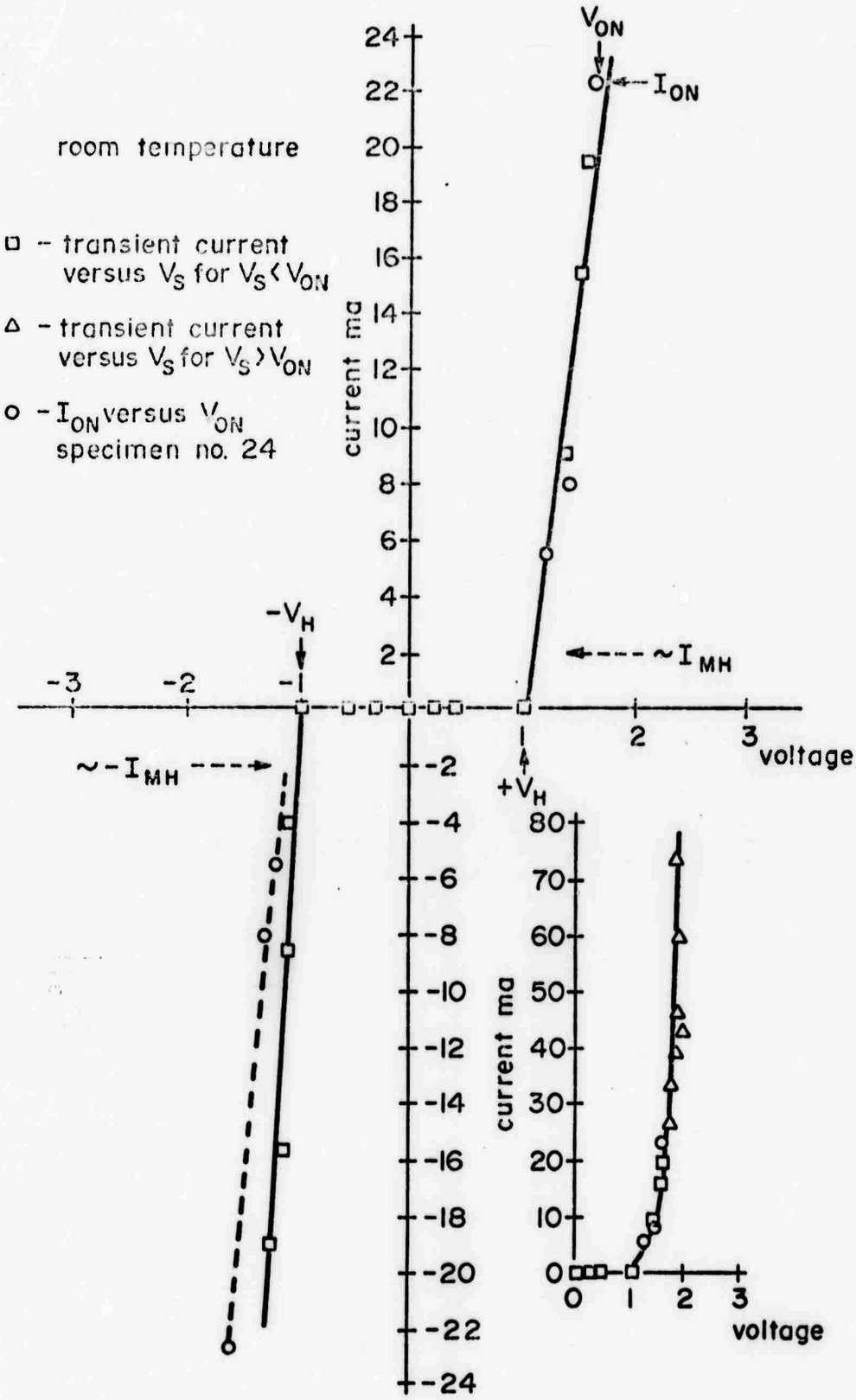

room temperature
□ - transient current versus V_S for $V_S < V_{ON}$
△ - transient current versus V_S for $V_S > V_{ON}$
○ - I_{ON} versus V_{ON} specimen no. 24
V_{ON}
I_{ON}
$-V_H$
$+V_H$
$\sim I_{MH}$
$\sim -I_{MH}$
current ma
voltage
24
22
20
18
16
14
12
10
8
6
4
2
-2
-4
-6
-8
-10
-12
-14
-16
-18
-20
-22
-24
-3
-2
-1
1
2
3
80
70
60
50
40
30
20
10
0

Fig. 4

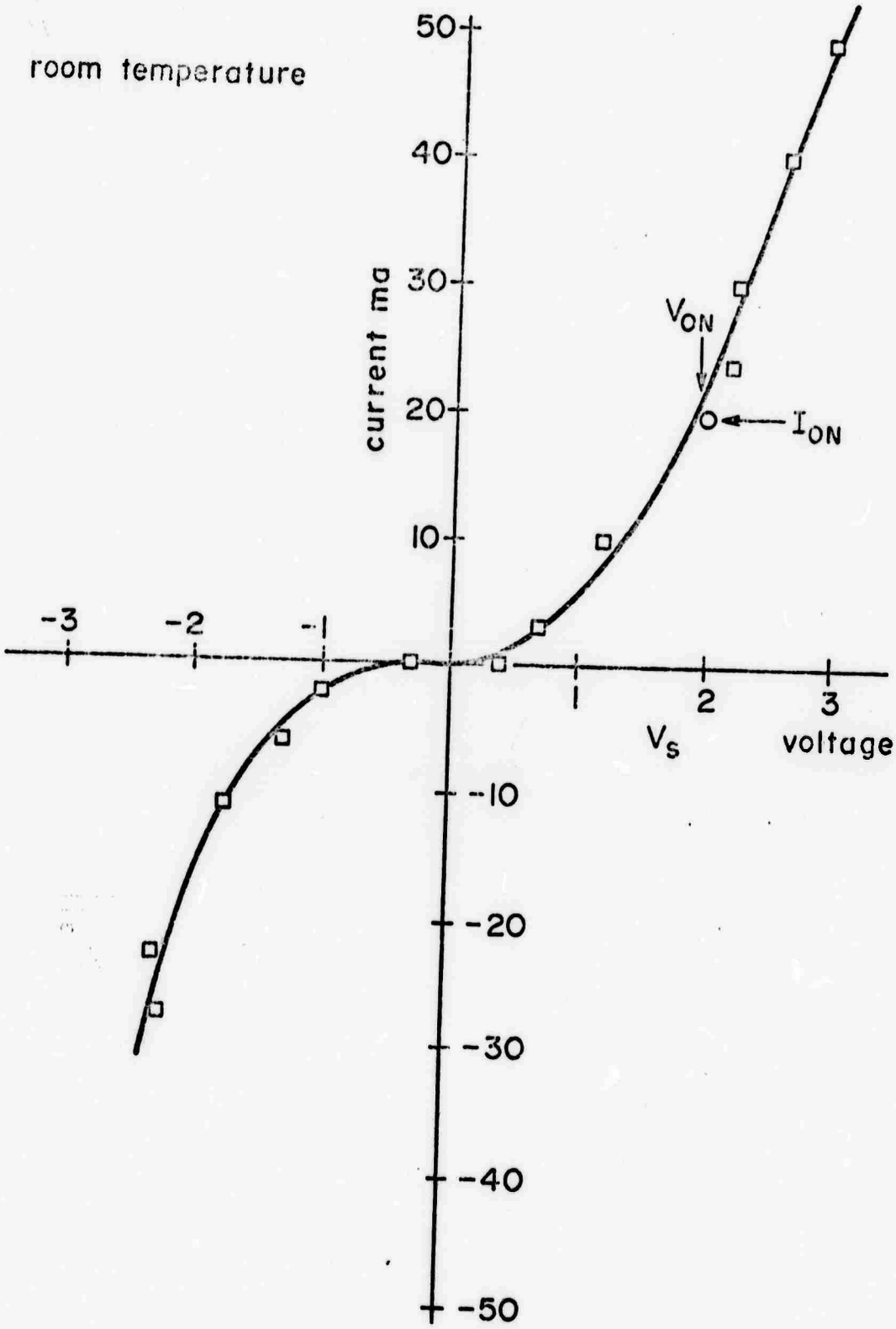
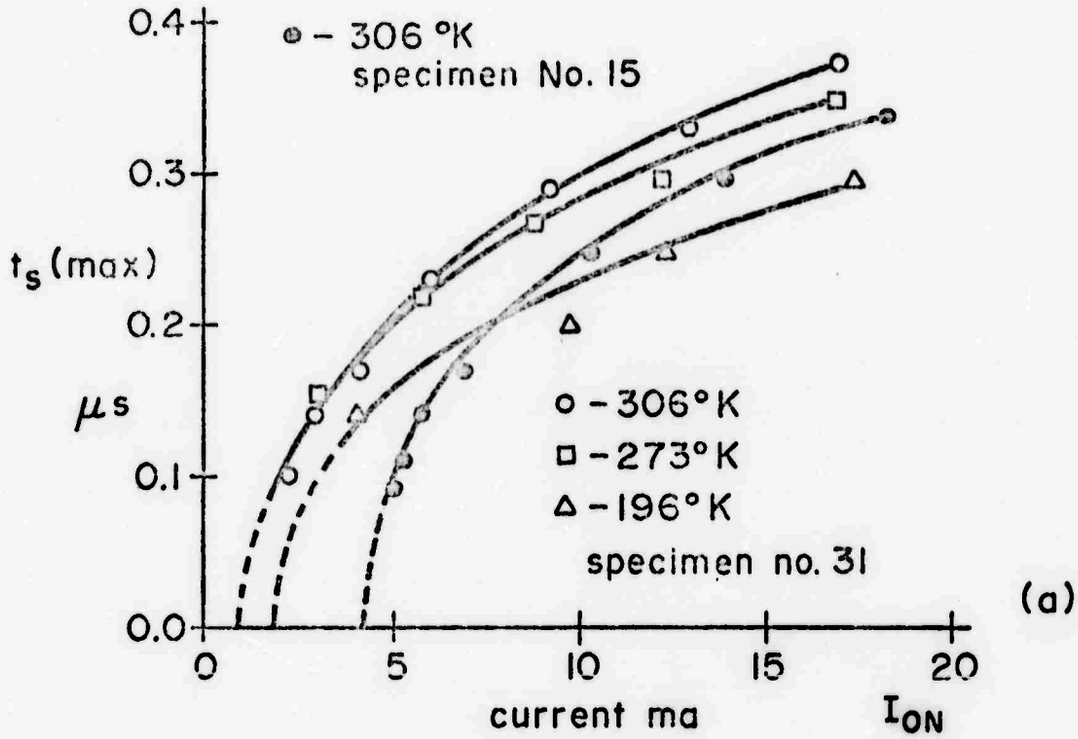

room temperature
50
40
30
20
10
-10
-20
-30
-40
-50
current ma
-3
-2
-1
1
2
3
V_S
voltage
V_{ON}
I_{ON}

Fig. 5


0.4
0.3
0.2
0.1
0.0
t_s (max)
μs
● - 306 °K
specimen No. 15
○ - 306° K
□ - 273° K
△ - 196° K
specimen no. 31
0
5
10
15
20
current ma
I_{ON}
(a)

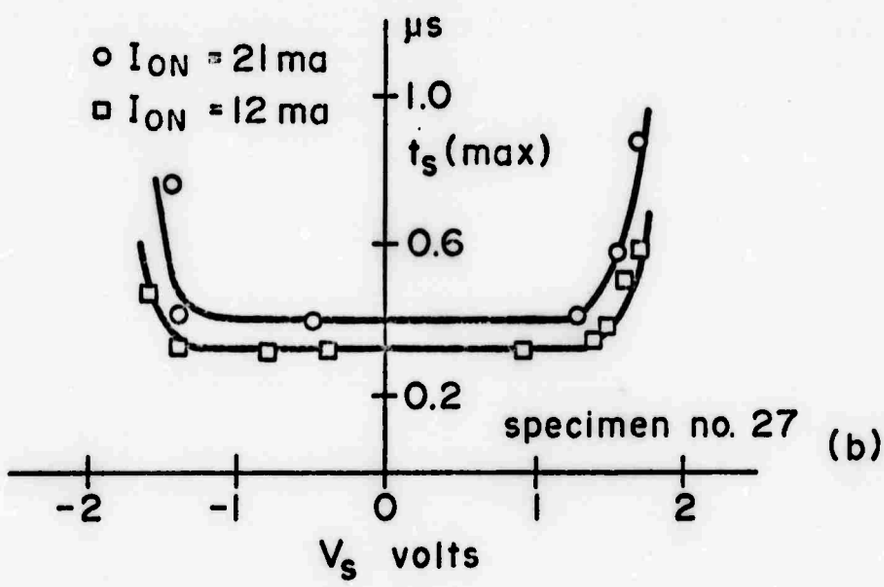

○ I_{ON} = 21 ma
□ I_{ON} = 12 ma
μs
1.0
t_s (max)
0.6
0.2
specimen no. 27
(b)
-2
-1
0
1
2
V_s volts

Fig. 6

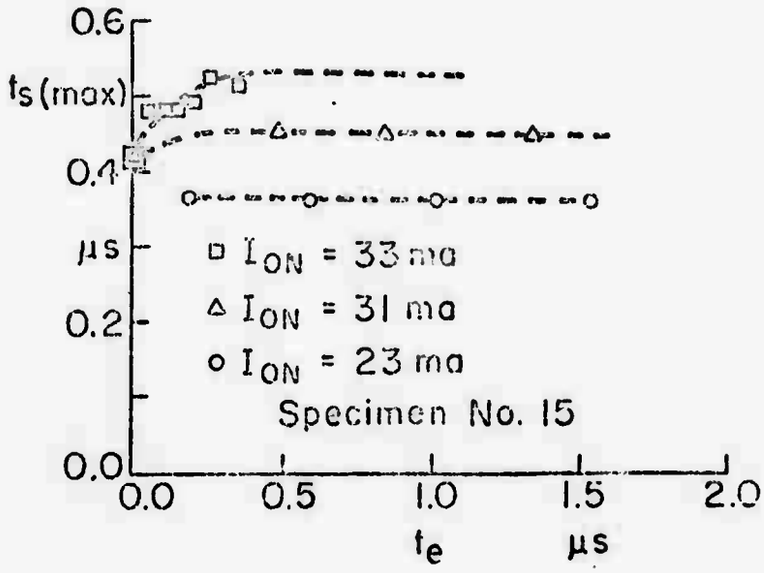

0.6
t_s(max)
0.4
μs
0.2
0.0
□ I_{ON} = 33 ma
△ I_{ON} = 31 ma
○ I_{ON} = 23 ma
Specimen No. 15
0.0
0.5
1.0
1.5
2.0
t_e
μs

Fig. 7

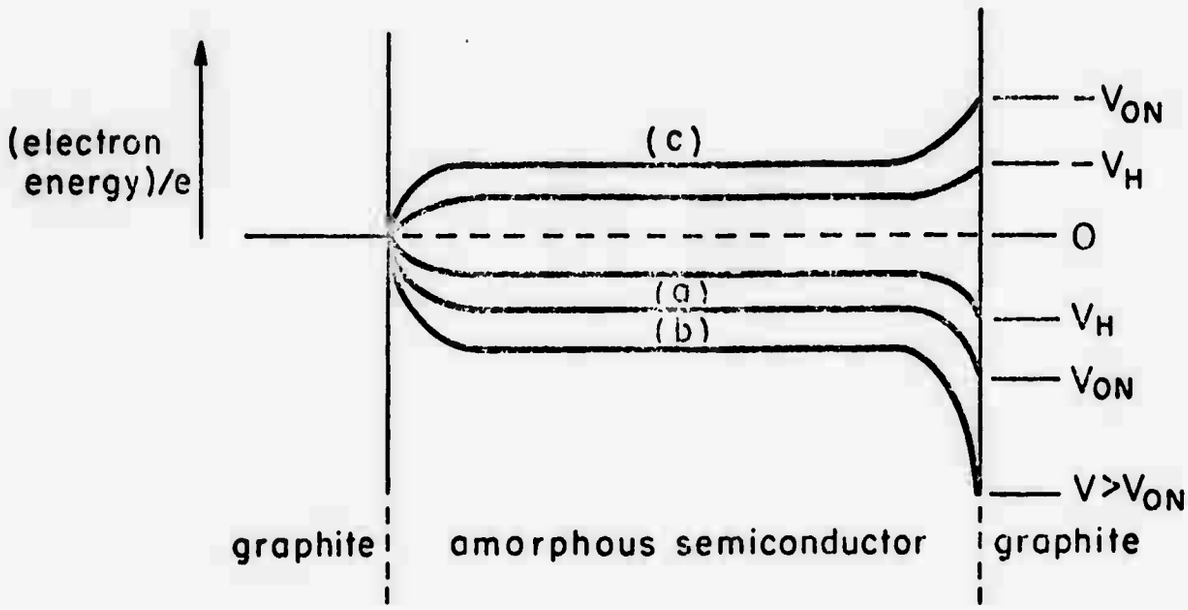

(electron energy)/e
(c)
(a)
(b)
$-V_{ON}$
$-V_H$
0
V_H
V_{ON}
$V>V_{ON}$
graphite
amorphous semiconductor
graphite

Fig. 8

(Intended for Ann Arbor Conference) APPENDIX B

On the Time-delay in Chalcogenide Glass Threshold Switches

by

S. H. Lee, H. K. Henisch* and W. D. Burgess
Materials Research Laboratory
The Pennsylvania State University
University Park, Pennsylvania 16802

ABSTRACT

It is shown that two distinct operating regimes exist, a low voltage regime (close to the threshold point) under which the switching delay is subject to substantial fluctuations and a high voltage regime (high over-voltages) for which the delay is closely determined. The results suggest that the origin of the scatter lies not primarily in the mechanism whereby the threshold point is approached but in the transient and semi-permanent after-effects of previous switching events. These after-effects can be detected in terms of a diminished pre-threshold conductance.

1. Introduction

Threshold switching processes in a variety of amorphous semiconductors (1) and especially in chalcogenide glasses (2) have been extensively studied in recent years. However, although many important observations have been available for some time, the fact that these processes are statistical in character has received very little attention. When

*also affiliated with the Department of Physics.

switches are repeatedly "addressed" with pulses of constant voltage and substantial duration, the statistical character shows itself as a spread in the observed switching delays; when switches are addressed with voltage pulses of fixed width and adjustable amplitude, it shows itself as a spread in the observed switching voltage V. The two variations are given schematically in Fig. 1, which also shows that the (mean) switching delay t_D is a function of the applied voltage V. This relationship has been represented (3, 4) by the empirical equation

$$t_D = t_{Do} \exp -(V - V_{TH})/V_o \qquad (1)$$

where t_{Do} and V_o are constants, and V_{TH} is the threshold voltage, below which switching is not ordinarily observed (see below). On the basis of various assumptions, eqn. (1) has also been derived from operational models of threshold switching, e.g. one involving a charge-controlled double injection process (5), and one involving thermally assisted double injection coupled with a field-dependent bulk conductivity (6).

Since t_D is the subject of a statistical distribution, it is reasonable to explore, whether this arises from a corresponding fluctuation of V_{TH}. Of course, if V_{TH} is defined as the lowest voltage at which switching is <u>ever</u> observed, then there can be no such fluctuation. In practice, however, and for simple operational reasons, V_{TH} is usually taken as the "most probable" switching voltage, and that practical definition leaves scope for fluctuations. When V is large, such fluctuations are obviously

unimportant, but the overvoltage concept $V-V_{TH}$ ceases to have a precise meaning when V and V_{TH} are comparable.

All the results here discussed were obtained on encapsulated threshold switches*, consisting of thin ($\sim 1\mu$) chalcogenide glass films between polished graphite electrodes. The films had been prepared by vacuum evaporation, using $Te_{40}Si_{18}Ge_7As_{35}$ as starting material. It is known that the properties of such switches (except for aspects connected with working life) do not depend at all sensitively on composition, and the results should therefore have a more general validity than a single composition would suggest. For temperature runs the specimens were immersed in a liquid bath.

2. Experimental Results

In general the threshold switching delay time shows not only a scatter but also a systematic drift. The latter is most prevalent in new specimens, especially if large ON-currents are permitted. By using small currents, and pulse repetition frequencies smaller than 1000 per second, the drift can be made negligibly smaller, and this was done in the experiments here presented.

Figure 2a shows a series of switching time delays associated with a hundred successive events at each applied voltage. Each event was pro-

*obtained from Energy Conversion Devices, Inc., through the courtesy of Mr. S. R. Ovshinsky.

duced by means of a single voltage pulse of 6μsec duration at 30 sec intervals and of a fixed amplitude close to the threshold voltage (overvoltage $<$0.5 volts).

If eqn. (1) were the only relevant relationship and V_{TH} the only fluctuating quality, then it would follow that the uncertainty Δt_D would be directly proportional to t_D, i.e.

$$\Delta t_D \cong (t_D / V_o) V_{TH} \qquad (2)$$

Figure 2a shows, however, that this is not the case. There is no statistical regime at all for small values of t_D. As the overvoltage diminishes, the onset of scatter is very sudden. Moreover, the locus of mean values is not a continuation of the high voltage relationship. For the case under investigation, $V_o \sim 2$ volts, $\Delta V_{TH} < 0.2$ volts and the longest delay t_D = 4μsecs. This would give Δt_D = 0.4μsecs whereas the observed value is about 2 secs. Figure 2 also shows the temperature dependence of the V-t_D relationship. The width of the statistical regime decreases towards higher-temperatures. Its general form follows

$$N_{t_D} / N_o = \exp(-t_D / t_o) \qquad (3)$$

where N_{t_D} / N_o is the probability of encountering a delay of time t_D, and t_o is a constant. Equation (3) is well obeyed except at high values of t_D where N_{t_D} / N_o diminishes sharply. The results also show that for ON-currents less than about 6mA, the spread of t_D values and their mean value remain constant during a long series of successive switching events. For higher cur-

rents (e.g. 15mA or more) there is a substantial increase in scatter and also a systematic drift towards higher V_{TH} values as the number of events increases.

3. Discussion

The results show that there are two distinct switching regimes: a low voltage (close to threshold) regime of statistical character and a high voltage regime in which the switching time is closely defined. The statistical nature of switching at $V \approx V_{TH}$ can itself be regarded as a proof of the fact that switching is not primarily due to self-heating. At room temperature, t_D commonly fluctuates by a factor of 2, and at low temperatures by as much as 4, as shown in Fig. 2a. Since the threshold current is almost constant, this implies fluctuations of input energy by the same factor, and corresponding variations of the maximum temperature reached in the course of self-heating. If thermal filament formation due to self-heating were the essential cause of switching, there would seem to be no conceivable reason for such a pronounced random fluctuation of the energy requirements.

It is evident that close to $V \approx V_{TH}$ the switching conditions (possibly the length, condition or location of the ON-state filament in the course of its formation) are not closely defined. Increasing over-voltages imply ultimately an increasing local temperature, even if the switching mechanism at $V \approx V_{TH}$ is essentially non-thermal. The inevitable result of increasing the applied voltage would therefore be a more precise localization of the

switching event and a corresponding reduction of Δt_D. However, there is no reason for believing that this process should set in very abruptly, as shown on Fig. 2a (considering the logarithmic scale). Thus, although heating may play some localizing role, it is more plausible to conclude that two distinct electronic processes are at work. This is also indicated by the discontinuities in the t_D versus V relationships on Fig. 2a. At low voltages the two mechanisms may be taken to compete with one another; at high voltages the process responsible for the fluctuations evidently disappears.

The question of what these processes are cannot as yet be unequivocably answered, but some general comments can be made. In previous work (7, 8), "complete trap filling" has been proposed as the criterion for the threshold point, and still appears as the most appropriate assumption. However, different mechanisms can be envisaged whereby this state is reached. One of these, impact ionization, is favored by Hindley (9), Rockstadt (10), and Mott (11); another is trap-to-trap hopping, as proposed by Fritzsche (12). Yet another, favored by low temperature, is space charge overlap, as suggested by Henisch, Fagen and Ovshinsky (7). Of these processes, impact ionization is the most "obviously statistical" but difficulties are encountered on other grounds, e.g. because $V_{TH} \rightarrow 0$ as $T \rightarrow \sim 170°C$, and also because of the observed relationships between V_{TH} and film thickness.

In principle, there is an alternative possibility, namely that the statistical fluctuation results not from the peculiarities of the excitation mechanism itself, but from the residual consequences of the previous switching event. It is known (13) that the pre-threshold resistance of a switch is reduced by a previous switching event. A large part of this reduction is very short-lived ($\sim 1\,\mu$sec), but a part lingers demonstrably for up to several minutes and, below the limits of measurement, presumably for longer. In some way not yet understood (but under active investigation), a threshold switch is in a different 'state' after each switching event, either because of a re-distribution of residual charge or because of some very minor structural change. In either case, it would have to be assumed that the effect is obliterated when a sufficiently high voltage is applied. The random nature of the fluctuations would seem to favor a non-structural interpretation, e.g. possibly one dependent on carrier trapping in association with the compositional heterogeneity of the materials (14, 15). Whereas the role of the excitation process in producing fluctuating threshold conditions remains uncertain, the fluctuating after-effects are not in doubt and are bound to influence subsequent switching events.

References

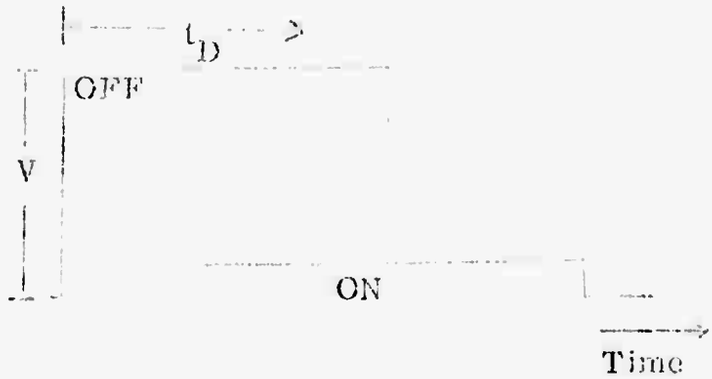
1. J. G. Simmons, Contempt. Phys. 11, 21 (1970).
2. See for instance, J. Non-cryst. Sol. 2 and 4 (1970).
3. R. R. Shanks, J. Non-cryst. Sol. 2, 504 (1970).
4. S. R. Ovshinsky, Phys. Rev. Letters 21, 1450 (1970).
5. F. Schmidlin, Phys. Rev. 1, 1583 (1970).
6. K. W. Boer, J. Appl. Phys. 41, 2675 (1971).
7. H. K. Henisch, E. A. Fagen and S. R. Ovshinsky, J. Non-cryst. Sol. 4, 538 (1970).
8. H. K. Henisch and R. W. Pryor, Solid State Electronics, in print (1971).
9. N. K. Hindley, J. Non-cryst. Sol. 5, 17 (1970).
10. H. K. Rockstadt, J. Appl. Phys. 42, 1159 (1970).
11. N. F. Mott, personal communication.
12. H. Fritzsche, J. Non-cryst. Sol. 2, 393 (1970).
13. S. H. Lee and H. K. Henisch, to be published.
14. W. Heywang and D. R. Haberland, Solid State Electronics 13, 1077 (1970).
15. H. Fritzsche, personal communication.

Figure captions

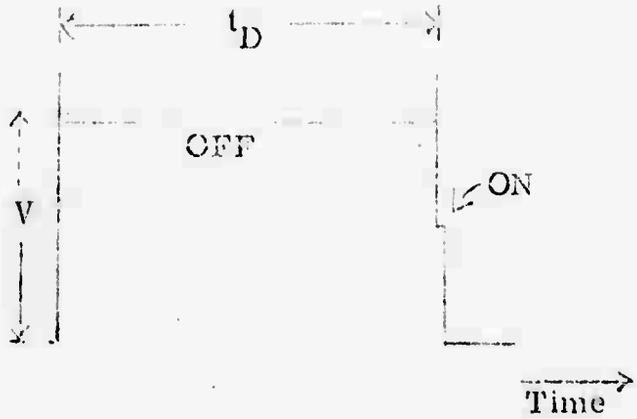
FIG. 1 Schematic representation of statistical threshold switching aspects. (a) constant voltage; spread of delay times, $V \approx V_{TH}$. (b) constant delay time; spread of switching voltages. (c) relationship between applied voltage and switching time t_D.

FIG. 2 Characteristics of statistical switching effects. (a) distinct high and low voltage regimes. V_{TH} = 13.5 volts at 293°K and 16.5 volts at 210°K. Dots denote mean values. (b) effect of ON-current on statistical behavior. Results up to broken line correspond to constant over-voltage within 0.2 volt. Events at 30 second intervals.

(a)


t_D
OFF
V
ON
Time

(b)


t_D
OFF
ON
V
Time

(c)

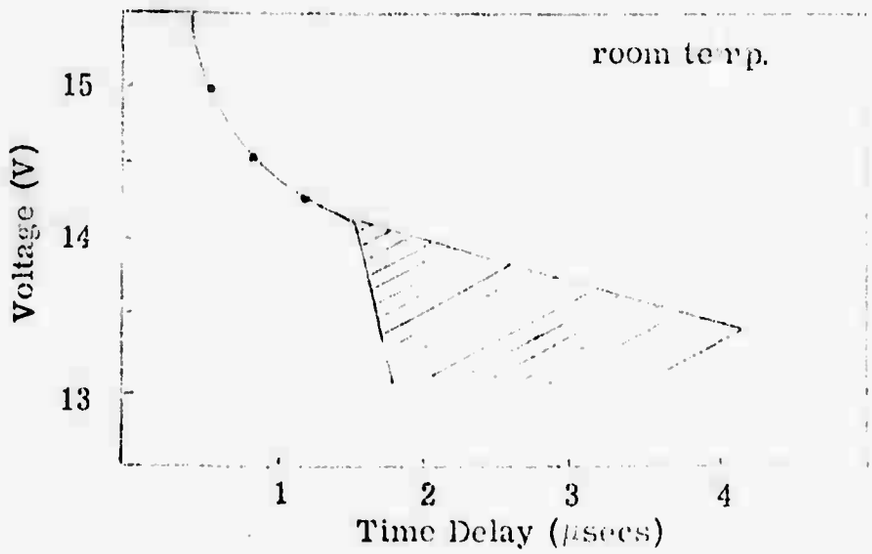
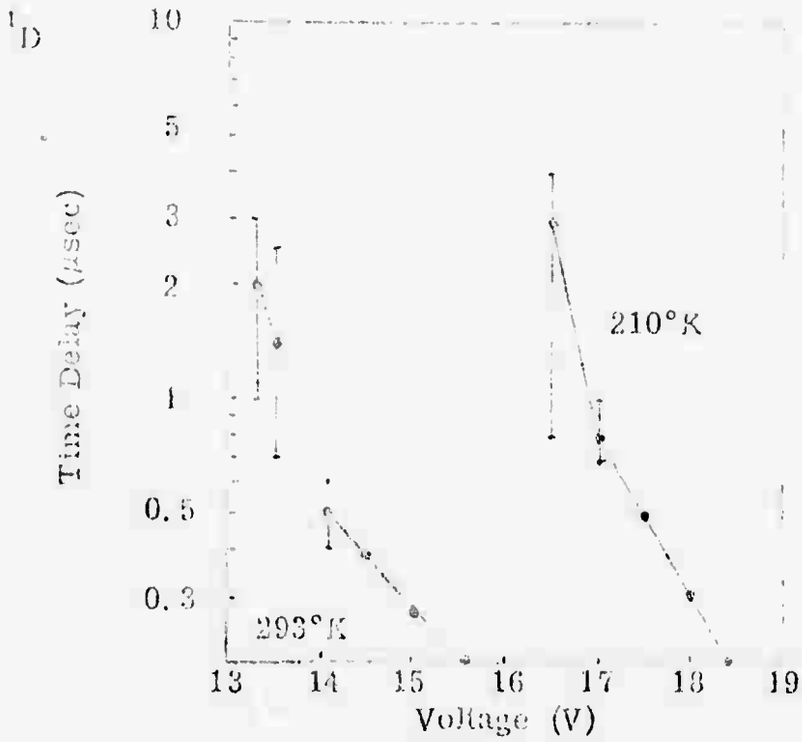

room temp.
15
14
13
Voltage (V)
1
2
3
4
Time Delay (μsecs)

FIG. 1

(a)


t_D
10
5
3
2
1
0.5
0.3
Time Delay (μsec)
210°K
293°K
13
14
15
16
17
18
19
Voltage (V)

(b)

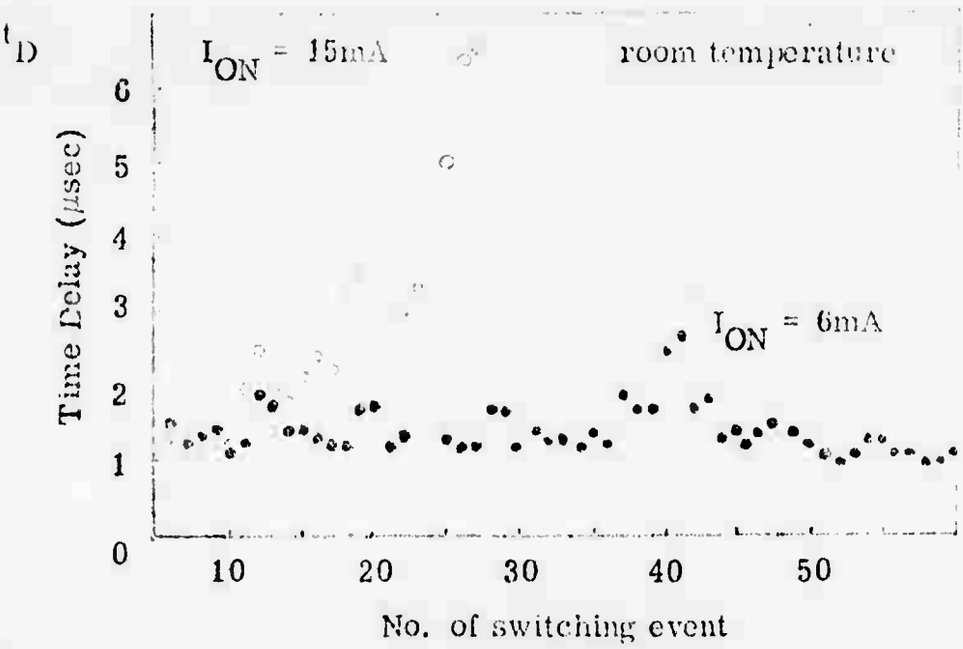

t_D
I_{ON} = 15mA
room temperature
6
5
4
3
2
1
0
Time Delay (μsec)
I_{ON} = 6mA
10
20
30
40
50
No. of switching event

Fig. 2

(Submitted to Applied Physics Letters) APPENDIX C

Characteristics of Ovonic Threshold Switches with Crystalline Semiconductor Electrodes

by

H. K. Henisch* and G. J. Vendura, Jr.
Materials Research Laboratory
The Pennsylvania State University
University Park, Pennsylvania 16802

ABSTRACT

The paper describes asymmetric threshold switching phenomena observed on thin films of $Te_{40}As_{37}Ge_7Si_{18}$ (0.2 to 1.9μ), deposited by flash evaporation on crystalline Ge and surface probed by means of a pyrolytic graphite counter-electrode. "Dynamically tristable" systems can be made in this way. The asymmetries are reversed for n-type and p-type Ge. Suitably biased systems can be switched by illumination. The differences between the present results and those obtained on conventional threshold switches with two graphite electrodes call for an interpretation in terms of electronic interface phenomena.

The voltage-current switching characteristics of threshold devices based on multicomponent chalcogenide glasses and graphite or metal electrodes are well known (e.g. 1-4). Such effects are observed for a wide variety of alloy compositions and their detailed features (apart from operational life) do not ordinarily depend on the choice of

*also affiliated with the Department of Physics.

the electrodes in any sensitive way. However, changes in the characteristics can make themselves felt after repeated use, as a result of diffusion and chemical interaction. It is conceivable that the variable holding voltages reported by Altunyan and Stafeev (5) originate in this manner. The situation is very different when one or other of the electrodes is a crystalline semiconductor. The chalcogenide layer (in this case of $Te_{40}As_{35}Ge_7Si_{18}$)* was deposited onto carefully etched substrates of single crystal germanium by flash evaporation. X-ray diffraction measurements confirmed the amorphous character of the resulting films. Such systems lend themselves better than metals to an investigation of the role played by the electrode material, because of (a) the wider range of carrier concentrations offered, (b) the possibility of changing that concentration in situ by irradiation with absorbed light, (c) the possibility of irradiating the contact interface with infrared light (to which the crystalline material is transparent), and (d) the opportunity of experimenting with n-type and p-type contact systems. Preliminary results show that such systems exhibit a variety of phenomena not observed with metallic electrode materials.

Figure 1 shows a cross-section of the specimens. Typical switching characteristics of thin films ($\sim 0.2\mu$ thickness) on n-type Ge substrates are given in Fig. 2 (a to d). Symmetry was observed up to and including threshold while the ON-states showed asymmetry. For p-type substrates this asymmetry is of opposite polarity. A similar film, simultaneously deposited on a graphite substrate and tested in the same way, yielded conventional (symmetrical) characteristics.

---

*Obtained from Energy Conversion Devices, Inc., through the courtesy of Dr. John de Neufville.

Observations of asymmetry as shown in Fig. 2 suggest the possibility that one might be dealing simply with a non-interacting series combination of a conventional (symmetric) switch and a contact rectifier, the rectifying action being ascribed to the interface between the amorphous film and the substrate. However, inspection shows that this cannot be the case. If rectifying action were to prevail at low currents, the OFF-characteristic would be asymmetrical, and this is not observed (Fig. 2a and b). If rectification were assumed to be absent for low and present only for high currents (and such an assumption would be perfectly reasonable), then the ON-states should be asymmetric (as actually observed) but the OFF-state should have identical threshold voltages. In fact, a threshold point is not reached in the first quadrant until much higher external voltages are applied to the system (Fig. 2c). Moreover, especially in the first quadrant, the threshold current and the minimum holding current in the ON-state are almost equal and thus not subject to different degrees of control by a series rectifier.

It is thus clear that a simple "non-interacting rectifier-in-series" hypothesis cannot apply. Nevertheless, conduction asymmetries one aspect of the overall behavior. According to their direction, it is necessary to conclude that the amorphous layer behaves as if it were "relatively p-type" compared with the n-type Ge substrate, and "relatively n-type" compared with the p-type substrate. This is qualitatively in harmony with previously formulated models which assume that the multi-component chalcogenide glasses are almost intrinsic semiconductors. It is necessary to ascribe the above asymmetries to the detailed nature of the contact interfaces and, in particular, to the differences between graphite and germanium as contacting materials. On the basis of previous work (6-8), the ON-condition is believed to be sustained by a

double injection process. Accordingly, it would be necessary to conclude that Ge on the one hand and graphite (or similarly conducting materials, such as Mo, W, etc.) on the other are injecting contacts of very unequal injecting efficiency. The same conclusion is suggested by the magnitude of the observed holding voltages (as assessed by extrapolation of the ON-characteristic to the voltage axis). On conventional systems these voltages are of the order of 1-2 volts, and this was found to be correct when the particular layers here used were tested between a pair of graphite electrodes. On the systems with one Ge and one graphite electrode, the holding voltages varied between 2 and 10 volts in the first and 2 and 8 volts in the third quadrants, while the film thickness varies from 0.2μ to 1.9μ. The detailed mechanism of these holding voltage relationships remains to be ascertained.

Typical characteristics of thicker switches (e.g. 1.6 to 1.9μ) are similar to those shown on Fig. 2d, but always with symmetrical OFF-states. For these systems the V-I relationships are symmetrical up to and including both threshold points, whereas the ON-characteristics are not. Again, the threshold currents and the minimum holding currents are almost equal, which means that the above argument concerning rectification must apply. Characteristics of the type shown on Fig. 2d are "dynamically tristable", in the sense that they have one stable OFF-state and two distinct quasi-stable ON-states.

For the effects here observed, a thermal interpretation is implausible. It is clear that the first order thermal properties of n-type and p-type substrates are the same. Thermal interpretations of threshold switching (e.g. 9-11) depend on the magnitude of the electrode heat sink and therefore lead, in the present circumstances, to the expectation of identical characteristics. This is contrary to the observations reported above.

Though some degree of heating is inevitable as a result of internal power dissipation, the results indicate that the switching mechanism must be essentially electronic. This is in harmony with experiments by the "rare double-pulse technique" (7) previously described.

The thin film characteristics described above were found to be light sensitive, as shown in Fig. 3. Inter alia, this means that, for a suitable voltage bias close to threshold, the switching process can be light activated. The light sensitivity was greatest at low temperatures (-70°C). During such measurements, the specimens were completely immersed in alcohol. Tests showed that incidental heating effects were not responsible for these observations. In principle, the light effects could thus be due either to the action of light-generated carriers on the Ge-amorphous interface or, more simply, to photoconduction in the germanium layer which acts inevitably as a series resistance. For the latter explanation to hold, the light effect on the specimen voltage at a given current level would have to be symmetrical. In practice (Fig. 4), the light effect is considerably greater in the third than in the first quadrant. Thus, although photoconduction no doubt plays some part, it is not by itself sufficient to account for the observed behavior. It is necessary to conclude that light has an effect on the switching mechanism itself, and the most plausible point of interaction is the Ge-amorphous interface.

Acknowledgements

This research was supported by the Advanced Research Projects Agency of the Department of Defense and was monitored by G. Boghosian, U. S. Army Research Office, Durham, N. C., under contract No. DAH C0470C 0047. The authors also wish to thank S. Lee, S. R. Ovshinsky and R. W. Pryor for extensive discussions.

References

1. S. R. OVSHINSKY, Phys. Rev. Letters 21, 1450 (1968).
2. H. K. HENISCH, Scientific American 221, 30 (1969).
3. H. FRITZSCHE and S. R. OVSHINSKY, J. Non-cryst. Solids 2, 393 (1970).
4. D. R. HABERLAND, Solid State Electronics 13, 207 (1970).
5. S. A. ALTUNYAN and V. I. STAFEEV, Soviet Physics-Semiconductors 4, 431 (1970).
6. H. K. HENISCH, E. A. FAGEN and S. R. OVSHINSKY, J. Non-cryst. Solids 4, 538 (1970).
7. H. K. HENISCH and R. W. PRYOR, Solid State Electronics (in print) (1971).
8. R. W. PRYOR and H. K. HENISCH, Appl. Phys. Letters 18, 324 (1971).
9. N. CROITORU and C. POPESCU, phys. stat. solidi (a)3, 1047 (1970).
10. A. C. WARREN, J. Non-cryst. Solids 4, 613 (1970).
11. K. W. BÖER, G. DOHLER and S. R. OVSHINSKY, J. Non-cryst. Solids 4, 573 (1970).

Figure Captions

FIG. 1 Cross-section of the test assembly. Chalcogenide glass 0.2 - 1.9μ thick. Ge (n-type or p-type) 0.02 cm thick, with low resistance contact attached.

FIG. 2 Typical switching characteristics of thin ($\sim$0.2μ) film systems on n-type Ge substrates. Externally applied voltage (60 Hz) increases from (a) to (d). The first quadrant corresponds to negative graphite. OFF-states as shown in (d) are usually but not always asymmetrical.

FIG. 3 Effect of light on switching characteristics of a 'thin' ($\sim$0.2μ) system; D - dark, L - light. Illumination from below as shown in Fig. 1.

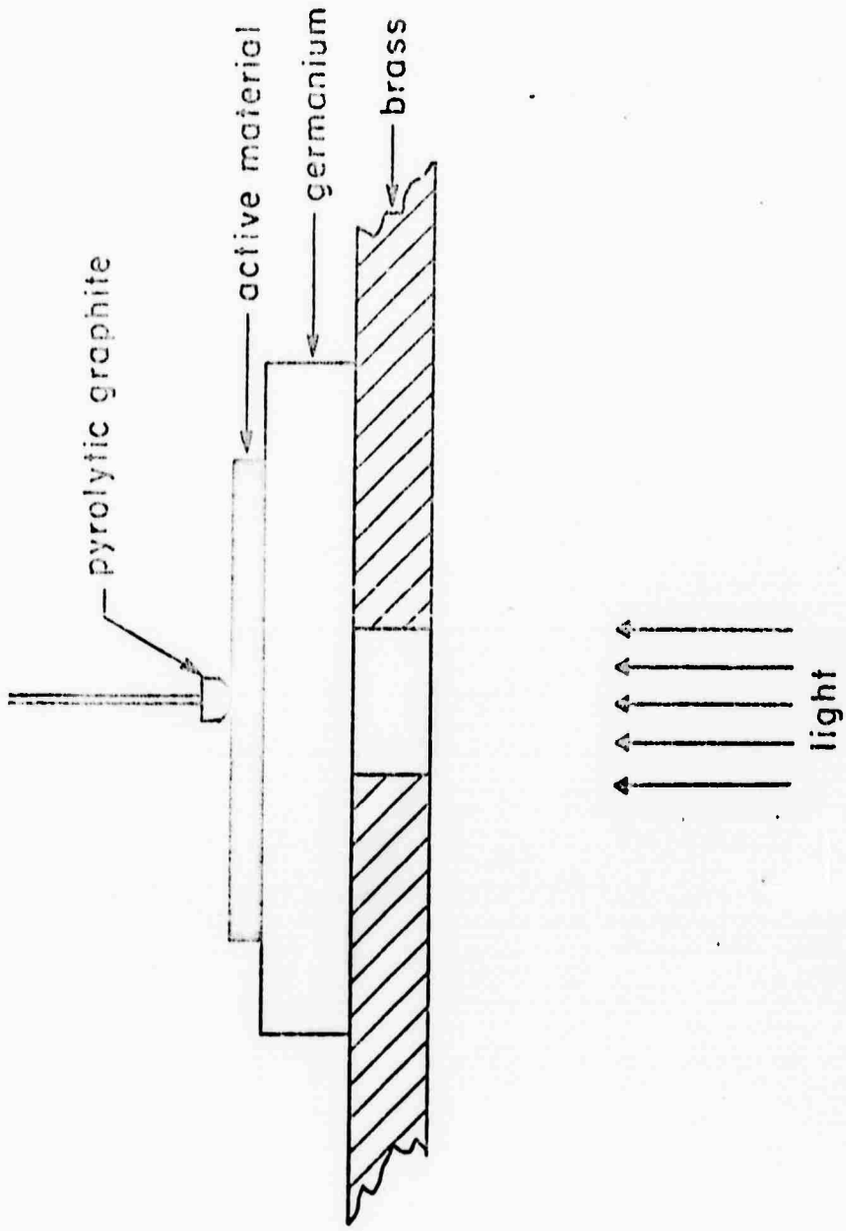

pyrolytic graphite
active material
germanium
brass
light

Fig. 1

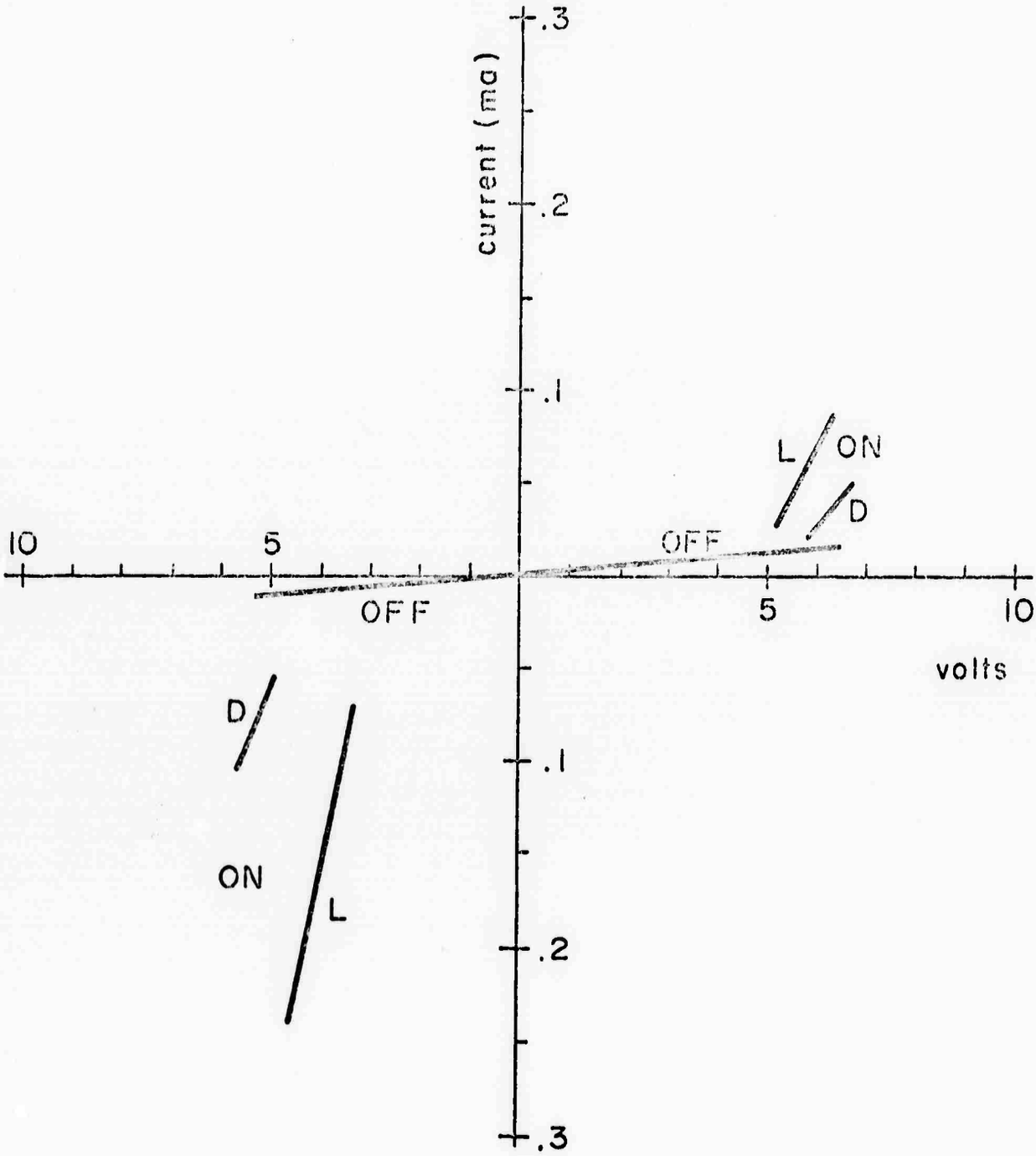


Fig. 3

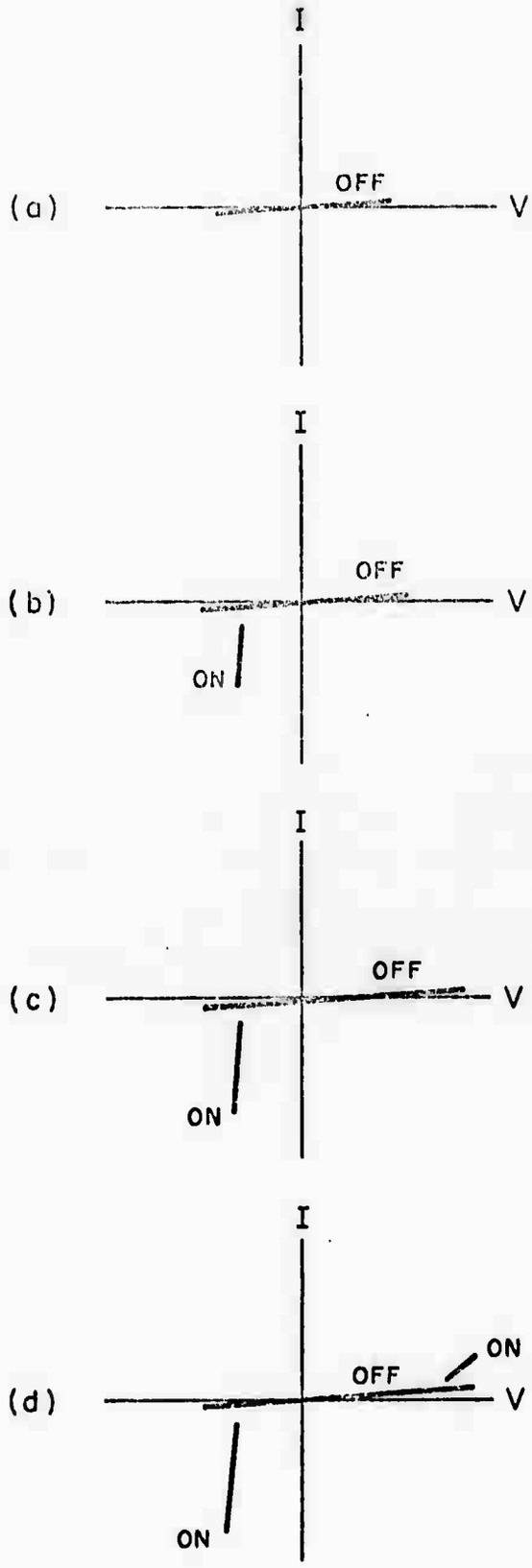


Fig. 2

AMORPHOUS SEMICONDUCTOR SWITCHING:
Thermal and Non-thermal Processes in Chalcogenide Glasses[Δ]

by

H. K. Henisch*
Materials Research Laboratory
The Pennsylvania State University
University Park, Pennsylvania 16802

Introduction

Phenomena of various kinds which are often discussed under the loosely defined heading of "switching" have been observed in thin film structures of many different materials. Switching ratios, speeds and other parameters vary enormously from case to case and, as far as is known, only switches based on chalcogenide glasses (1-5) have reached the degree of overall effectiveness required for practical devices. They have been called "ovonic", after their inventor, S. R. Ovshinsky, and the present paper is confined to devices and device-like structures of this kind.

The first switches were made by coating graphite electrodes with chalcogenide glass layers and pressing them together. Experimental specimens are still made in this way, but this is not the manner in which the devices are at all likely to find their most important applications. Modern switches are pure thin film devices, of the general type shown on Fig. 1a. In this form, as many as 2500 can be accommodated in an area of 6 cm^2, and the method of their deposition is fully compatible with normal integrated circuit techniques. It is obvious that the small size of these switches implies certain power limitations which must be borne in mind by the user and,

*also affiliated with the Department of Physics.

Δ For presentation at the European Semiconductor Device Research Conference, Munich, March 1971.

of course, by the investigator of their properties. Deposition of the amorphous films can be accomplished by flash evaporation or sputtering of the electrodes and of the chalcogenide glass. The glasses used are 4-component or even 5-component mixtures of Ge, Si, Se, S, As, Te, In, etc. For every selection of components, there is a composition range within which materials tend to be crystalline or at least partially ordered, and another within which they tend to be amorphous. We know now that there can be no strict boundary betwen these ranges: whether something is deposited in glassy or crystalline form depends, amongst other things, on the rate of cooling.

As far as electrical characteristics are concerned, the devices can be made in two forms, called threshold switches and memory switches. Their characteristics are shown on Figs. 1b and 1c respectively. For threshold switches (see below) one needs a material which is highly stable in the glassy state; for memory switches one which is close to the boundary of the glassy-crystalline composition range. The process of compositional optimization must, of course, concern itself not only with performance but also with manufacturing consistency and working life. The materials used have low-field room temperature resistivities between $10^4 \Omega$cm and $10^7 \Omega$cm. Switching phenomena can be observed over a wide range of compositions and can therefore be discussed in quite general terms.

It has long been known that the change of a memory switch from the OFF to the ON state involves phase transformation of a type that can be observed on bulk specimens of the same glasses. On such specimens, transformations which lead to a large increase in conductivity can be brought about by purely thermal means. Accordingly, it was at one time believed that the ovonic memory switch is a purely thermal device. Also, there is an extensive literature on thermal breakdown processes in dielectrics, and it was at once tempting to ascribe threshold switching likewise to purely thermal

processes. Both conclusions are now believed to be false. The present paper gives a summary of the situation as far as the controversy between thermal and non-thermal interpretations is concerned.

Mechanism of Memory Switching

The basic mechanism of the memory switch involves an ordering process, in the course of which new (and more highly conductive) phases are also formed. The ordering process has been convincingly monitored by differential thermal analysis (6, 7), and such results also explain how the device can return from the ON to the original OFF state: by heating to the softening point and subsequent quenching. This is accomplished by a sharply cut-off pulse, the power being dissipated not in the device as a whole but in the filamentary channel which is known to sustain the ON condition. In one chalcogenide alloy, Adler and co-workers (8) identified the conductive components present in the ON-state as degenerative GeTe and metallic Te.

There is no doubt that such a transformation takes place and, in that sense, the thermal character of the memory switch has been established. However, at least two other processes have come to light which accompany the transformation and which are not thermal. One was reported by Utrecht and co-workers (9, 10) whose experiments were performed with wide (e.g. 0.5 mm) electrode spacings. After application of a constant voltage, a "streamer" was seen to move slowly from the anode to the cathode. It was distinguished from the rest of the material by its reflectivity. Voltage reversal before completion of the process caused the streamer to reverse its direction of movement, accompanied by a new streamer emerging from the (new) anode. Completion of the process (streamer reaching cathode) constituted "lock-on" of the memory device. Only then was the ON condition stable. The polar nature of the phenomena naturally suggests interpre-

tations in electrolytic terms (11) or else in terms of an "electron wind" (12, 13), a process which is believed to have been observed in a variety of metallic alloys, but is perhaps less firmly established. At this time, it is still uncertain to what extent similar processes play a role in the thin film structures actually used for memory switching. On the other hand, it is difficult to believe that they play no significant role at all.

The other reports (14) concerns memory transformations by means of laser beams. In one sense, a pulsed laser beam is merely a convenient way of dissipating energy in an amorphous film in order to bring about its transformation to the more conductive (or, in the present context, to the more light scattering) form. However, when the situation is examined in detail, it is found that the transformation is greatly accelerated by the presence of light, as opposed to heat, presumably as a result of the electronic disequilibrium. This conclusion was in fact derived from a much more sophisticated experiment, but its consequences can be simply represented in the schematic manner shown on Fig. 2. In this highly idealized arrangement, a sharply defined laser beam would produce a temperature profile in the amorphous film as shown. If that profile were allowed to prevail for a sufficiently long time, the film area converted to the crystalline form would be considerably larger than the area actually irradiated. The time involved would be of the order of minutes, as is known from conversion experiments with conventional heat sources. In contrast, laser heating achieves the conversion in times of the order of microseconds. Even for considerably longer heating times (i.e. long enough to guarantee a stable temperature distribution, but shorter than minutes), conversion to the crystalline form would be observed only in the region actually irradiated. Cohen (15) has suggested that this is due to bond-breaking by incoming photons, and the resulting increase of atomic mobility.

The matter is directly relevant to memory switching of the electrical kind, because of the controversy concerning the status of the device

at the points P_1 and P_2 (Fig. 1c). At these points, the device has just completed a stage of threshold switching. According to thermal theories of threshold switching (see below) the system is then hot, but not in electronic disequilibrium whereas, according to electronic theories, gross electronic disequilibrium prevails at P_1 and P_2. Such a disequilibrium could explain why the memory transformation which follows (if sufficient power is dissipated at these points) is so much faster in a switch than it is in bulk or even in ordinary thin film form. Such an argument does not, of course, constitute a proof of the disequilibrium, but it lends a certain amount of support to the non-thermal interpretations pursued below.

Thermal Interpretations of Threshold Switching

Thermal interpretations are based partly on analogies with other known instances of resistive breakdown and partly on calculations. Inevitably such calculations make simplifying assumptions which may or may not be valid for the devices under consideration. The general contention is (16-21) that self-heating leads to the formation of a highly conductive filament, a process which can occur very rapidly because of inherent positive feedback. In support, Stocker (21) and Pearson (22) have demonstrated the existence of high temperatures over substantial regions of their system. However, such demonstrations prove no more than that some device-like systems become very hot when excessive power is dissipated within them. They do not by themselves distinguish between cause and effect, nor do they prove that switching in devices of fully commercial design is essentially due to heating. Fritzsche and Ovshinsky (23) for instance, have shown that thermal interpretations become increasingly plausible, as the layer thickness increases beyond 10μm, whereas commercial devices employ layers of 0.7 to 1.5μm thickness.

A number of specific arguments and demonstrations are now avail-

able which mitigate very strongly against thermal interpretations; for instance:

(a) Fritzsche and Ovshinsky (23) have shown that the very short switching times observed (e.g. of the order of a nanosecond) do not permit even a thin filament to be heated to temperatures which can be reconciled with the observed conductances. Diminishing the (hypothetical) filament diameter does not solve the problem. It increases the temperature for a given power dissipation, but also calls for higher temperatures to produce comparable conductances. The argument is dependent on the assumption that the activation energy is constant.

(b) Male and Warren (24) have found that thermal theories do not lead to a correct scaling of threshold voltage with layer thickness. The discrepancies can be reconciled by assuming that the electrical bulk conductivity is field dependent, but such an ad hoc assumption would seem to call for an electronic explanation of almost as great in complexity as the switching process itself. Moreover, no thermal model has as yet reproduced the observed switching characteristics as a function of temperature, nor has any yielded a V-I discontinuity at the minimum holding current I_H, as shown on Fig. 1c.

(c) Systems which are known to be thermal, e.g. turnover in ~~print~~ point control diodes (25), always exhibit a V-I loop which is strongly frequency dependent in relation to the thermal time constant. By way of contrast, the loop shape and area of a threshold switch is almost constant up to about a MHz and, what is equally important, down to zero frequency. It is true, that filament formation has been experimentally established in the latter case and

not in the former, but whether this is a critical or incidental difference is not yet fully understood. Indeed, it is doubtful whether thermal breakdown can ever occur without filament formation. Moreover, as far as is known, there is as yet no convincing thermodynamic proof that such a loop is possible at all at zero frequency on thermal grounds alone.

(d) The switching process is statistical in character, i.e. switching delays at a given overvoltage are subject to a distribution. For low overvoltages, this can imply time variation by a factor of 2 or so (26). In thermal switching models, the delay is a heating-up period, and a statistical variation of switching times at a constant voltage would imply an enormous variation of switching temperatures. While it is true that no model has as yet accounted convincingly for such observations, the thermal model seems peculiarly unsuitable as an interpretational framework.

(e) Thermal theories which make very different assumptions concerning the behavior of the model, e.g. as regards the role of the contacts as heat sinks (18-20), and arrive at very different estimates for the maximum temperature reached (varying from 20°C to several hundred degrees above ambient) nevertheless achieve equally good agreement with limited sets of experimental results. The inevitable conclusion is that the criteria employed are not sensitive to functional differences, and the range of observations not wide enough to permit a critical evaluation.

(f) Although switching processes are observed on a great variety of materials, the chalcogenide glasses appear to occupy a very special position. As far as is known, no other system appears

to have precisely the features which distinguish the switching process shown on Fig. 1a. On a thermal model, with only one key requirement: a sufficiently high activation energy, the special position is hard to understand.

(g) Henisch and Pryor (29, 30) have shown by means of a "rare double pulse" technique, that the energy dissipated by a first switching pulse (A) does not, within wide limits, affect the switching parameters of a subsequent pulse (B) (0.8 μsec) later. On the other hand, the threshold voltage of the B-pulse is lowered for time delays up to ~1-2 μsec. The experiment confirmed (29) that switching has after effects, but demonstrated that these are non-thermal in character and are therefore, presumably, electronic. In a similar way, it was shown (31) that voltage reversals before completion of the switching process (i.e. during what would ordinarily be the switching delay) led to a substantial postponement of switching, inexplicable on thermal (and, indeed, any other non-polar) grounds. This is shown in Fig. 3. The total energy dissipated before switching occurs is at least 50% higher in case (b). The results of pulse experiments by Haberland (4) likewise proved to be inconsistent with a purely thermal hypothesis, and could be most readily interpreted in terms of charge, rather than other operational parameters.

(h) It has been demonstrated (32) that the nature of the electrodes can have a profound effect on switching characteristics, even when materials of identical thermal properties and chemical ~~interaction~~ inertness are used. Thus, films with asymmetrical electrode systems show asymmetric switching characteristics in a manner quite inconsistent with thermal interpretations.

These, in summary form, are the reasons which lead to the adoption of non-thermal switching models. On the other hand it is, of course, undeniable that energy is being dissipated in the devices and that the materials are highly temperature sensitive. In the circumstances, one would expect that heating would give rise to some demonstrable side effects, even if it does not account for switching itself. Such side effects, amounting to a small power-dissipation dependent reduction of threshold voltage, have been identified (30).

Non-thermal Interpretations of Threshold Switching

Models, albeit in tentative and qualitative form, are available which aim at an explanation in non-thermal terms. They can be divided into two classes: polar and non-polar. Polar interpretations (e.g. in terms of space charge formation and eventual space-charge overlap) are most plausible in the lower temperature range. In that range (roughly from room temperature down to the limit of convenient experimentation) polarity dependent effects have been observed (29, 30). In particular, it has been shown that the switching parameters (and, indeed, other features of the V-I characteristic) depend on the polarity of voltages (whether switching or not) previously applied to the system. Their after-effects persist for a few microseconds. The direction of these effects is qualitatively in harmony with a double injection space charge model previously advanced (2,33), and specifically with a predicted space charge reversal during threshold switching (Fig. 4). A detailed quantitative analysis has not yet been possible, but order-of-magnitude agreement prevails between the total charge injected during the switching delay and the total number of traps believed to be present. The polarity effects are experimentally significant, but not so pronounced as to suggest that they are in sole control of the switching process. In the absence of calculations this is, of course, an intuitive judgment, but it is believed that the non-polar

mechanism which is evidently active at room temperature and above is not completely inactive at low temperatures. However, the predominating mechanism of reaching the threshold point appears to change with temperature. A symptom of this can be found in the temperature dependence of the pre-threshold V-I characteristic. Figure 5 shows this, as given by Fritzsche (34). At high temperatures, the threshold point is approached almost linearly, at low temperatures very non-linearly.

The above observations can be interpreted by envisaging one criterion for the threshold point, and two different mechanisms of reaching it. The threshold criterion is taken to be that condition under which all space charges in the material are eliminated through the mutual neutralization of electron and hole traps, it being assumed that electron and hole traps are present in equal concentrations (2). Such a model is supported by the Cohen, Fritzsche and Ovshinsky band theory (35) of amorphous semiconductors. The automatic equality of electron and hole traps is one of the essential features of this theory, which was originally put forward not in the context of threshold switching, but in order to explain the electrical and optical properties of amorphous semiconductors in bulk. Neutrality (and thus conduction free of space-charge control) would prevail if all electron traps (effective at the temperature concerned) were full of electrons and all hole traps full of holes. This state of affairs can indeed come about in two ways, of which one is more likely at low and the other more likely at high temperatures. At low temperatures, carrier trapping is effective, and the screening mechanism is not. Space charges are thus likely to be established near the electrodes as a result of carrier injection. This can be readily understood by reference to the considerations of van Roosbroeck and Casey (36) concerning materials in which the dielectric relaxation time is much longer than the non-equilibrium carrier lifetime. These circumstances certainly prevail in the materials used for switching. With increasing applied voltage, these would eventually

overlap and thus neutralize each other throughout most of the bulk. Such a mechanism is believed to be the origin of the polarity effects mentioned above. Towards higher temperatures space charge formation would become unlikely because of more efficient screening. This means that the traps could become filled, either through injection, or through field-assisted hopping, as proposed by Fritzsche and Ovshinsky (3) or through both mechanisms, without space charge formation. A model by Mott (37) emphasizes the possibilities for impact ionization, especially in view of the fact that the carrier mobilities are believed to increase with increasing energy. Impact ionization would create free charge carriers and, albeit indirectly, would also lead to trap filling.

In accordance with the arguments here advanced, the notion of two mechanisms arises naturally from the C-F-O band theory. In a similar way one can explain the existence of a sharply defined minimum threshold current which diminishes with increasing ambient temperature as observed. If the trap-filled state is to be maintained, this must be done against the prevailing recombination mechanism. A minimum current density (injection rate) is necessary to do this. When the current falls below this value, recombination wins and the traps empty. The effective traps are those which are (a) within the conduction filament, and (b) deep enough not to be thermally ionized. Condition (b) implies that their number diminishes with increasing temperature; therefore the current density required to keep them filled should likewise diminish. It is believed that the filament diameter increases with increasing ON-currents (29, 30). Why a filament is formed in the first place is another issue, and the actual cause is not yet known. The formation might indeed be thermally initiated or else might arise from essential plasma relationships.

Problems and Needs

There is no doubt that the present interpretations of switching phenomena in amorphous semiconductors rely heavily on analogies with crystalline materials. It may be that these analogies will continue to be sustained as more experimental evidence becomes available. On the other hand, the experience with bulk properties (e.g. conflicting signs of thermo-power and Hall effect) leads one to believe that such interpretations of switching will not ultimately prove satisfactory. They will certainly have to be reviewed in the light of new insight into the meaning of band concepts for amorphous materials and the significance of transport relationships in the presence of very slow dielectric relaxations. Another issue in need of clarification concerns the differences between "thick" (e.g. 10μ or more) and "thin" (e.g. 1μ) switches. In the former, thermal effects are believed to play a greater role, but the switching characteristics of thin and thick switches are, superficially at any rate, very similar. Double pulse experiments of the kind referred to above have not yet been performed on thick switches. Meanwhile, there are also many problems of an operational nature which call for urgent attention: the nucleation (if any) of the conversion process in memory switches, the mechanism of light-accelerated ordering, the real cause of filament formation, the exact nature of the ON-state of threshold switches and the role contacts under these conditions play, failure mechanisms and, on the positive side, the exploration of three-terminal systems.

Acknowledgements

This research was supported by the Advanced Research Projects Agency of the Department of Defense and was monitored by G. Boghosian, U. S. Army Research Office, Durham, North Carolina, under contract DAHC 0170 C 0017. Thanks are also due to S. Lee, S. R. Ovshinsky, R. Pryor and G. Vendura for many valuable discussions.

References

1. S. R. OVSHINSKY, Phys. Rev. Letters 21, 1450 (1968).
2. H. K. HENISCH, Scientific American 221, 30 (1969).
3. H. FRITZSCHE and S. R. OVSHINSKY, J. Non-cryst. Solids 2, 393 (1970).
4. D. R. HAMBERLAND, Solid State Electron. 13, 207 (1970).
5. R. G. NEALE, J. Non-cryst. Solids 2, 558 (1970).
6. H. FRITZSCHE and S. R. OVSHINSKY, J. Non-cryst. Solids 2, 148 (1970).
7. A. BIENENSTOCK, F. BETTS and S. R. OVSHINSKY, J. Non-cryst. Solids 2, 347 (1970).
8. D. ADLER, J. M. FRITZ, C. R. DEWES, B. P. KRAEMER, D. J. SELLMYER and S. D. SENTURIA, J. Non-cryst. Solids 4, 330 (1970).
9. R. UTTECHT, H. STEVENSON, C. H. SIE, J. D. GRENIER and K. S. RAGHAVAN, J. Non-cryst. Solids 2, 358 (1970).
10. C. H. SIE, J. Non-cryst. Solids 4, 548 (1970).
11. D. ADLER (M. I. T.), personal communication.
12. S. G. EPSTEIN and A. PASKIN, Phys. Letters 24A, 309 (1967).
13. J. D. VERHOEVEN and E. E. HUCKE, Am. Soc. Metal, Trans. Quart. 55, 866 (1962).
14. J. FEINLEIB, J. de NEUFVILLE, S. C. MOSS and S. R. OVSHINSKY, Appl. Phys. Letters (1971) (in print).
15. M. H. COHEN (University of Chicago), personal communication).
16. H. J. STOCKER, C. A. BARLOW, JR. and D. F. WEIRAUCH, J. Non-cryst. Solids 4, 523 (1970).
17. A. CSILLAG, J. Non-cryst. Solids 4, 518 (1970).
18. F. M. COLLINS, J. Non-cryst. Solids 2, 496 (1970).
19. N. CROITORU and C. POPESCU, phys. stat. solidi (in-print) [illegible]
20. A. C. WARREN, J. Non-cryst. Solids 4, 613 (1970).
21. H. J. STOCKER, J. Non-cryst. Solids 2, 371 (1970).
22. A. D. PEARSON, J. Non-cryst. Solids 2, 1 (1970).

23. H. FRITZSCHE and S. R. OVSHINSKY, J. Non-cryst. Solids 4, 464 (1970).

24. J. C. MALE and A. C. WARREN (Central Electric Research Lab.), personal communication.

25. H. K. HENISCH and J. W. GRANVILLE, Semiconducting Materials (London: Butterworths), p. 87 (1951).

26. S. LEE (Pennsylvania State University), personal communication.

27. A. C. WARREN, Electronics Letters 5, 461 (1970).

28. K. W. BÖER, G. DOLLER and S. R. OVSHINSKY, J. Non-cryst. Solids 4, 575 (1970).

29. H. K. HENISCH, S. R. OVSHINSKY and R. W. PRYOR, Proc. Int. Congress on Thin Films, Cannes, France, October 5-10, p. 437 (1970).

30. H. K. HENISCH and R. W. PRYOR, Solid State Electron. (1971) (in print).

31. R. W. PRYOR and H. K. HENISCH, Appl. Phys. Letters (in print).

32. R. K. HENISCH and G. VENDURA, JR. (in preparation).

33. H. K. HENISCH, E. A. FAGEN and S. R. OVSHINSKY, J. Non-cryst. Solids 4, 538 (1970).

34. H. FRITZSCHE, IBM Journal of Research & Development 13, 515 (1969).

35. M. H. COHEN, H. FRITZSCHE and S. R. OVSHINSKY, Phys. Rev. Letters 22, 1065 (1969).

36. W. VAN ROOSBROECK and H. C. CASEY, JR., Proc. 10th Intern. Conf. on Semiconductors, Boston, August (U. S. Atomic Energy Commission), p. 832 (1970).

37. N. F. MOTT (Cambridge, U. K.), personal communication.

Figure Captions

FIG. 1. Threshold and memory switching.

(a) switch design [Energy Conversion Devices, Inc.]

(b) voltage-current characteristics of an ovonic threshold switch

(c) voltage-current characteristics of an ovonic memory switch

FIG. 2. Idealized demonstration of glass-to-crystalline transformation, accelerated by laser-beam photons. Boundaries of laser beam assumed to be sharply defined. [Representation derived from experiments by Feinleib, deNeufville, Moss and Ovshinsky (14)]

FIG. 3. Effect of voltage reversal during the delay t_D before threshold switching: $t'_D \gg t_D$. [After Pryor and Henisch (31)]

FIG. 4. Space charge reversal in the course of threshold switching. Symmetrical double injection here assumed, but not essential. [After Henisch, Fagen and Ovshinsky (33)]

FIG. 5. Conductance of a 0.8μm thick chalcogenide glass alloy as a function of applied voltage. [After Fritzsche (34)]

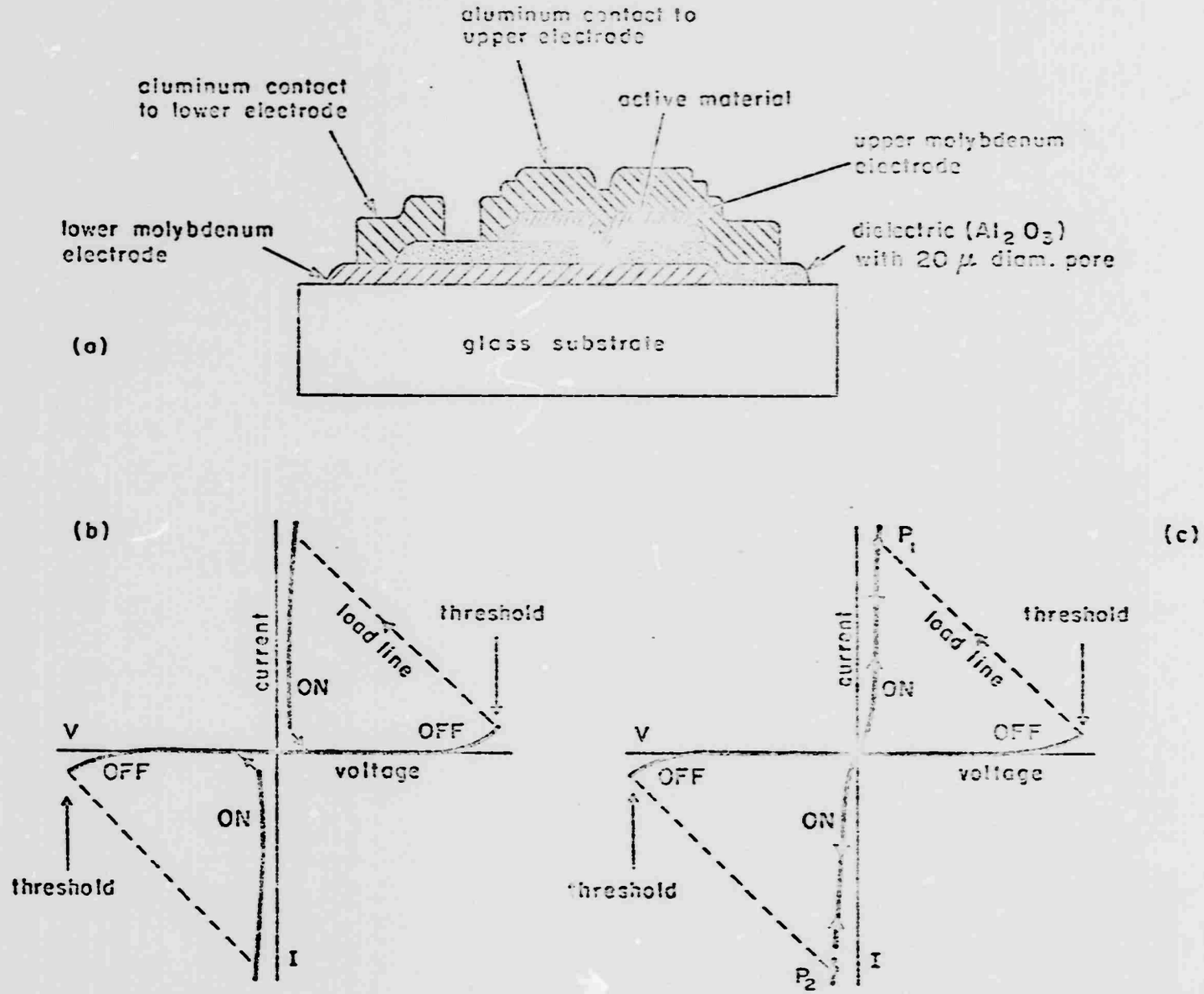

aluminum contact to upper electrode
aluminum contact to lower electrode
active material
upper molybdenum electrode
lower molybdenum electrode
dielectric (Al_2O_3) with 20 μ diam. pore
(a)
glass substrate
(b)
current
load line
threshold
ON
OFF
V
voltage
OFF
ON
threshold
I
(c)
P_1
current
load line
threshold
ON
V
OFF
voltage
OFF
ON
threshold
P_2
I

Fig. 1

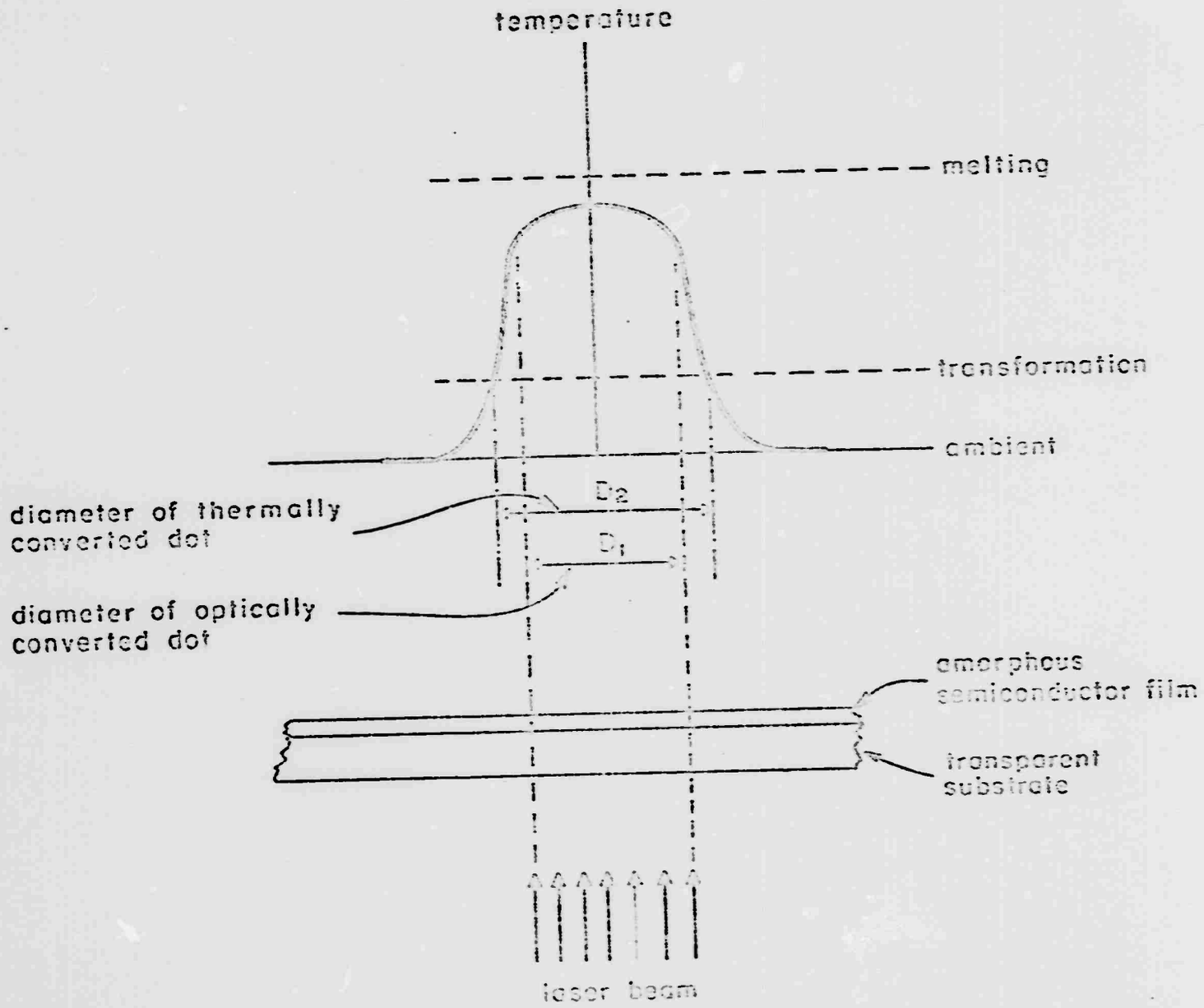

temperature
melting
transformation
ambient
diameter of thermally converted dot
D_2
D_1
diameter of optically converted dot
amorphous semiconductor film
transparent substrate
laser beam

Fig. 2

(7)

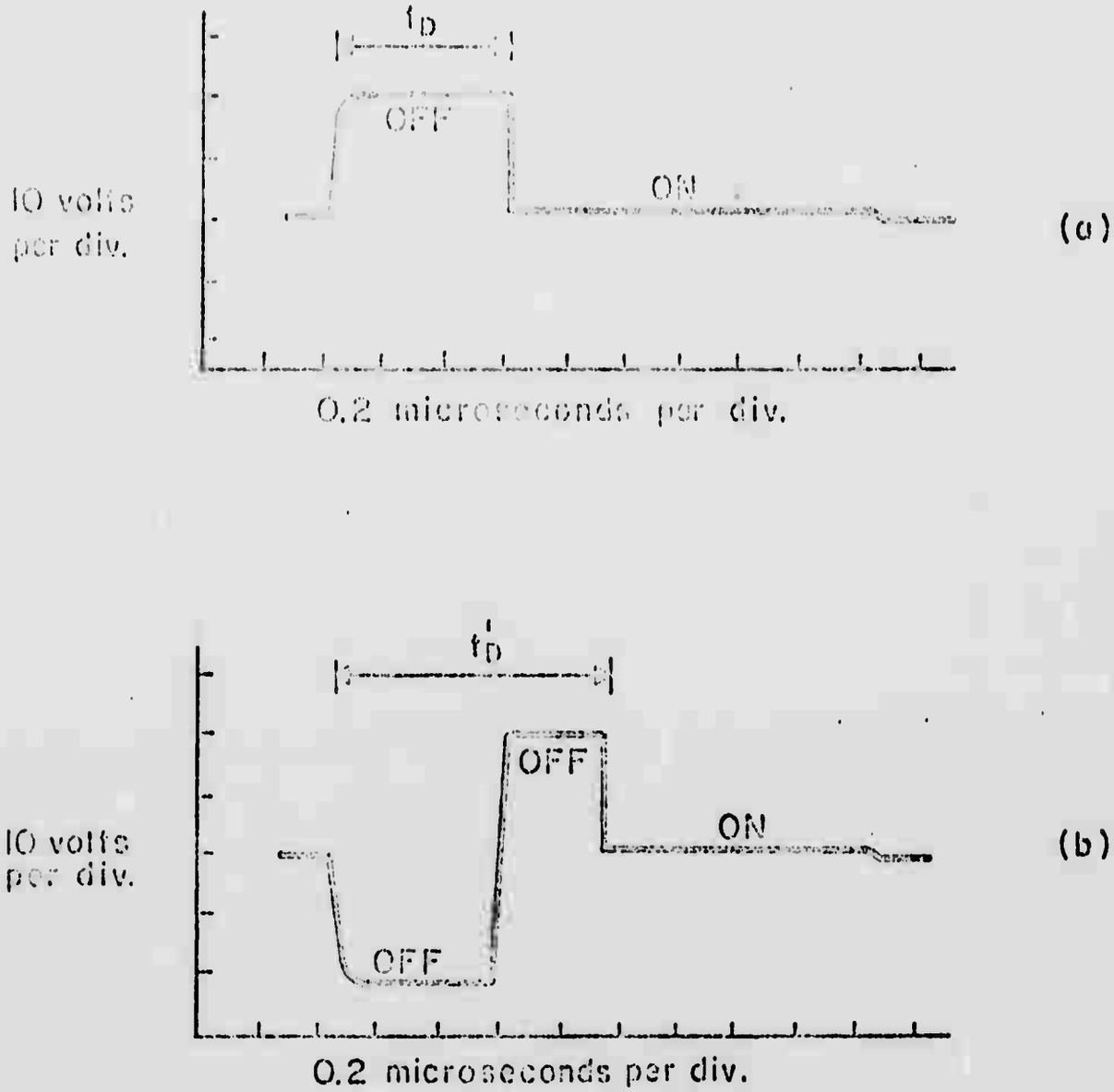
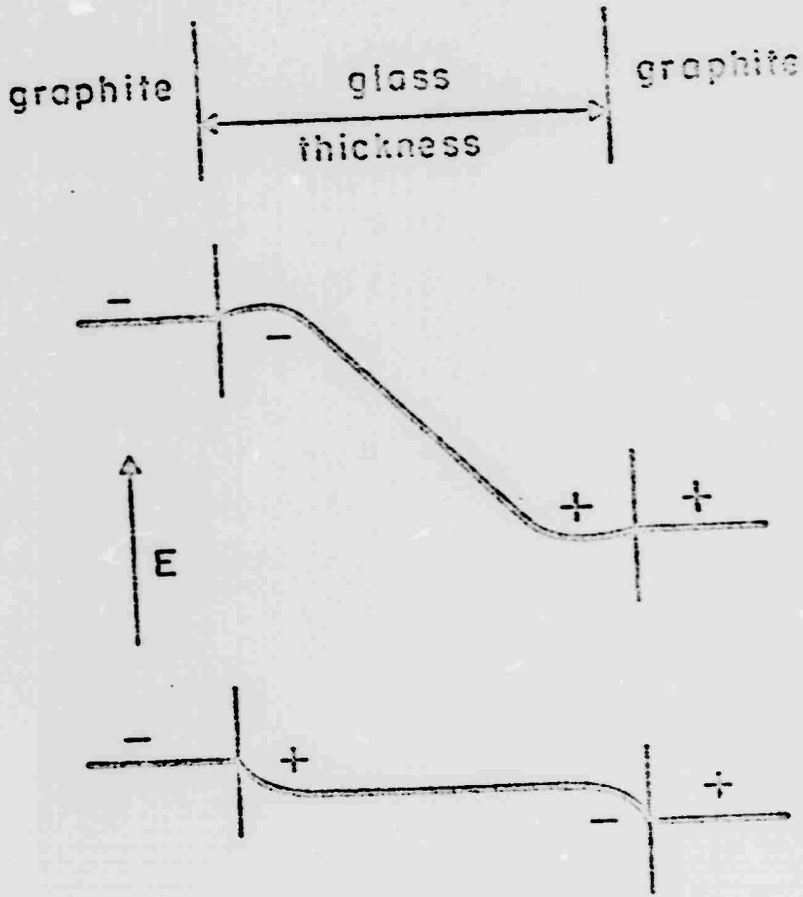

t_D
OFF
ON
10 volts per div.
(a)
0.2 microseconds per div.
t_D'
OFF
ON
OFF
10 volts per div.
(b)
0.2 microseconds per div.

Fig. 3



Electron energy profile in the OFF-state, as a result of double carrier injection; maximum field in interior.

Electron energy profile in the ON-state; most of voltage drop near contacts. Resistance almost independent of thickness.

Fig. 4

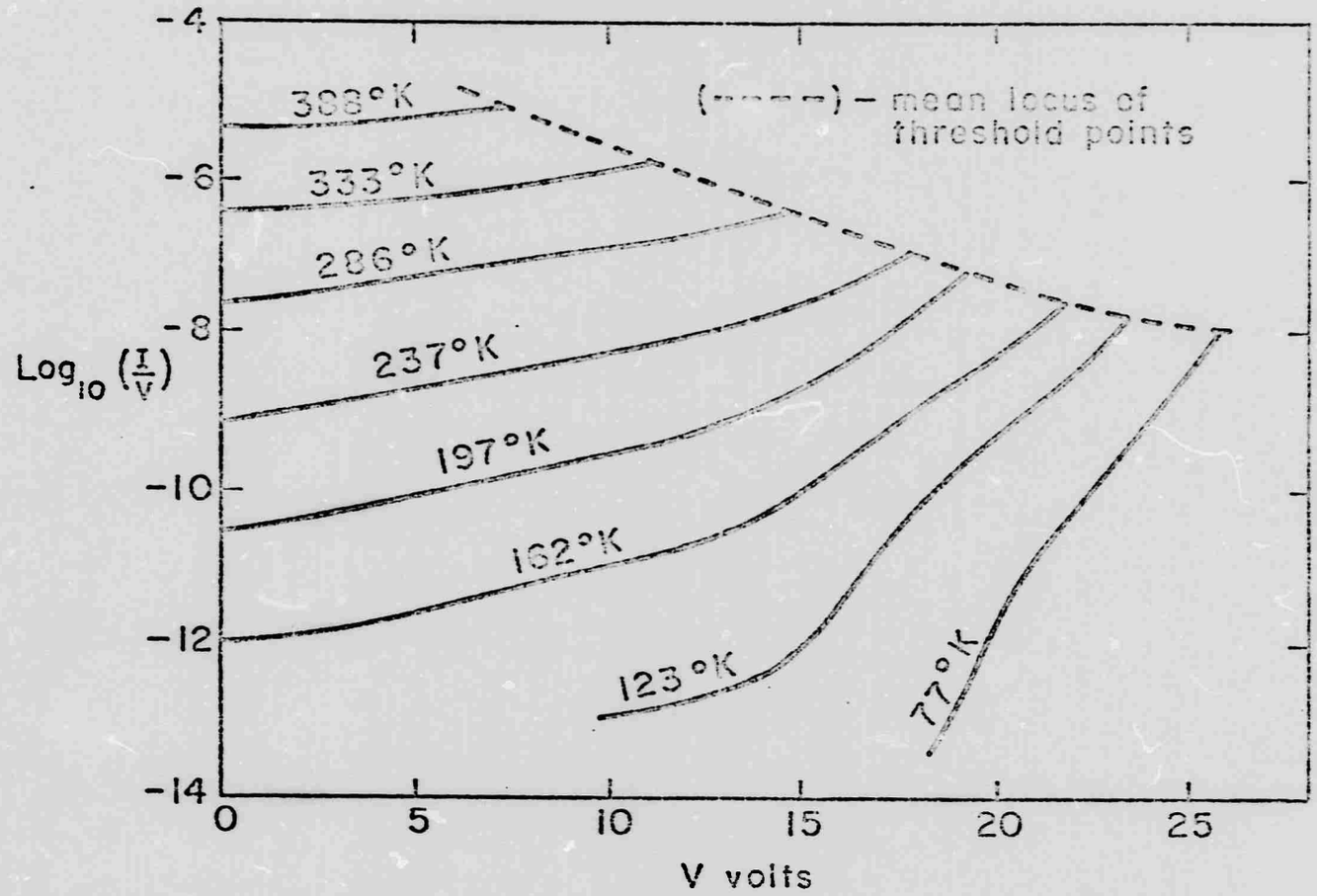

-4
-6
-8
-10
-12
-14
$\mathrm{Log}_{10}\left(\frac{I}{V}\right)$
0
5
10
15
20
25
V volts
388°K
333°K
286°K
237°K
197°K
162°K
123°K
77°K
(- - - - -) – mean locus of threshold points

Fig. 5