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CONTACTS BETWEEN CHALCOGENIDE GLASSES, METALS AND SEMICONDUCTORS

S. H. Lee, et al

Pennsylvania State University

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Contacts Between Chalcogenide Glasses, Metals

and Semiconductors

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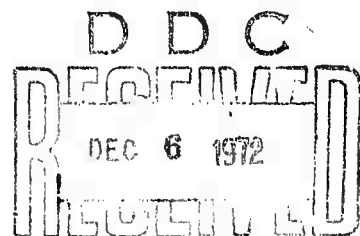
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Contacts Between Chalcogenide Glasses, Metals

and Semiconductors

Contents

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

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1. General Summary of Current Work

The two main purposes of the research here described are to elucidate the mechanism of threshold switching, and to explore systems with contact materials which can be electronically altered in situ. With this end in view, the experimental work performed during the last six months has concerned itself with the following problems:

(a) calculation of the voltage-current characteristics in the ON-state, based on a free-carrier space charge model;

(b) establishment of a criterion for the instability (threshold) point, based on the equivalence of dielectric relaxation time and carrier lifetime; and

(c) attempts at correlating carrier lifetime with the short-term memory and minimum holding current of threshold switches.

2. Status Report

(items correspond to those listed above)

(a) A variety of ON-state experiments carried out in the past have yielded evidence which cannot be reconciled with ionic space charge models. The barriers which evidently control the ON-

state react too quickly to deformation by externally applied voltages and are too temperature-independent to be ascribed to carriers in traps. However, barriers can also be formed by a deficiency or excess of free carriers. The questions were, how can such barriers be maintained and, if maintained, what would their voltage-current characteristics be. A paper, given below as Appendix A, addresses itself to this problem. The barriers are assumed to be transparent to electrons (Fowler-Nordheim model applied) in the voltage-region over which the ON-state is observed. The sharp dependence of tunnelling current on barrier thickness explains the steepness of the ON-state characteristic, and also the sharp cut-off exhibited by ON-state transients. The comparison between theory and experiment is not yet extensive, but the available results are in good agreement. The paper has been accepted for publication in Applied Physics Letters.

(b) Past experiments have yielded a good deal of information about the ON-state, but the nature of the threshold point has remained a controversial matter. On the basis of polarization arguments, the equality $\tau_d = \tau_\ell$ is proposed as the critical condition, τ_d being the relaxation time and τ_ℓ the carrier lifetime. It has been shown that this is the condition under which a "neutral pulse" (i.e. a region with an excess of electrons and holes in equal concentrations) will polarize completely, to the extent of electron and hole clouds drifting apart before recombination. Such a polarization has long been known to exist (see above) in the ON-state, but it was never clear how its formation might be initiated. The statistical nature of the switching delay suggests that the original neutral pulse arises

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from shot noise. It decays harmlessly if $\tau_d < \tau_\ell$, but polarizes completely (as far as the film thickness will allow) for $\tau_d = \tau_\ell$. Because the conductivity is field-dependent, τ_d diminishes with increasing field. On this basis, a number of other properties of threshold switches can be predicted and successfully compared with experiment. Appendix B of this report is concerned with these matters. A modified form of this paper has been accepted for publication by Applied Physics Letters.

(c) As is well known, the threshold voltage, V_{TH}, of the chalcogenide switches depends on frequency of addressing pulses. If a switching pulse is followed by another pulse after a time τ, the V_{TH} of the second pulse is reduced in comparison to the first pulse (Fig. 1). A characteristic time τ_k can be defined as shown, to mark the position of the knee. The interpretation of this curve has long been a problem, in particular because τ_k is almost independent of temperature. This mitigates against interpretations in terms of trapping and argues for a free carrier model. It was therefore of interest to compare τ_k with the lifetime τ_ℓ of free carriers, as determined in the course of experiments on the transient response of the ON-state. [S. H. Lee and H. K. Henisch, Solid State Electronics (in print)] There is a good deal of scatter, but within the spectrum of results obtained on a variety of switches τ_k varies by a factor of 10 whereas τ_k / τ_ℓ is virtually constant at 4 ± 1.4. One can say that τ_k is roughly proportional to τ_ℓ. More experimentation is needed to sharpen these relationships. An attempt to correlate τ_k and the minimum holding current I_{MH} was not successful. What ought to correlate is, of course, the minimum current density, and we

do not actually know how much the diameter of the ON-state filament varies from switch to switch.

Another problem related to τ_k is its observed dependence on film thickness. If it were a lifetime-related property and all other parameters were constant, there should be no such relationship. A possible answer may be found in the dependence of film structure (and hence lifetime) on film thickness. It is known that thicker films are far more readily crystallized than thin films under small thermal or even mechanical perturbation. This shows that thicker films are under larger internal stress. In order to investigate this aspect of film structure, sputtered films on graphite are beginning to be studied with Reflection High Energy Detection Diffraction (RHEED) techniques.

3. Note on Personnel

In addition to the Principal Investigator, Dr. S. H. Lee (Research Associate), Mr. D. Burgess (Graduate Assistant)*, Mr. R. W. Pryor (Graduate Assistant)** and Mr. G. J. Vendura, Jr. (Graduate Assistant)*** have been employed on the contract.

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*up to July 31, 1972.

**up to September 29, 1972.
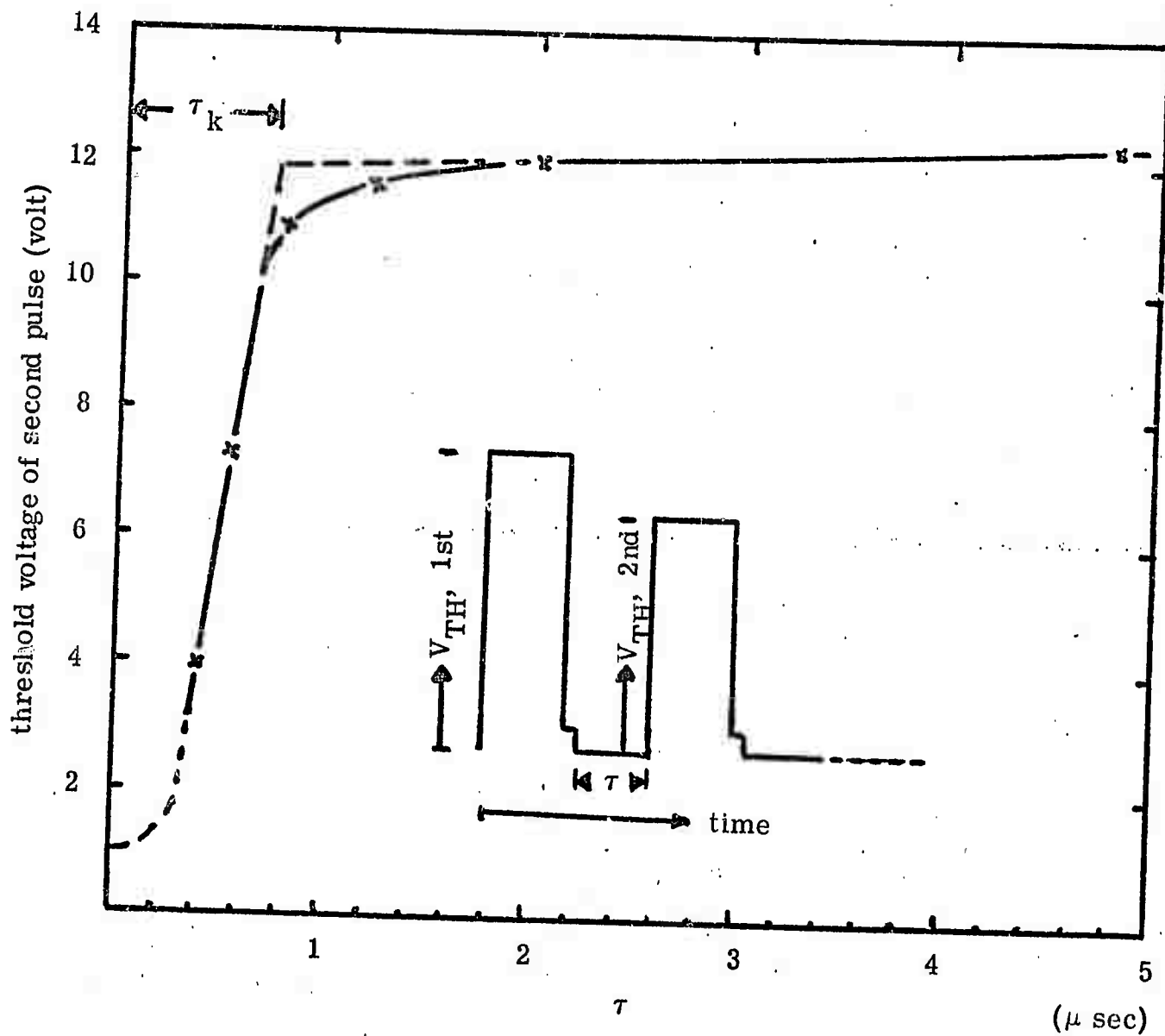
***up to June 15, 1972.

FIG. 1.   Relationship between threshold voltage and pulse interval; the double-pulse experiment.

The ON-state in the Chalcogenide Threshold Switches

S. H. Lee
Materials Research Laboratory
The Pennsylvania State University
University Park, Pennsylvania 16802

Abstract

The ON-state of the chalcogenide glass threshold switch is analyzed. on experimental results which call for thin free-carrier space charge regions at the electrodes. Carriers are assumed to tunnel through the corresponding barriers which are, in turn, maintained by the joint action of the electron and hole flow. The calculated voltage-current relationship is in excellent agreement with observations.

The ON-state in the Chalcogenide Threshold Switches

S. H. Lee
Materials Research Laboratory
The Pennsylvania State University
University Park, Pennsylvania 16802

The nature of threshold switching in chalcogenide glass films has been subject to much discussion and controversy in recent years. Here, we present an analysis of the ON-state based on field emission from the electrodes into the chalcogenide glass film. Experimental evidence supporting the present discussions is obtained from 1.2 μ thick chalcogenide films of composition $Te_{40}As_{35}Ge_7Si_{18}$, sandwiched between two graphite electrodes.

During the ON-state, the voltage across the threshold switch is known to be insensitive to the thickness of the film, the voltage being slightly greater than 1 volt. This implies that there is very small potential drop across most of the film. Three possible potential profiles could thus apply during the ON-state: (a) potential drop mainly at anode and cathode; (b) potential drop at the anode only; or (c) potential drop at the cathode only. The electrothermal and thermal theories[1,2] support (a), while van Roosbroeck's analysis[3] takes the view of (b). Although compelling evidence for either one of the above views is lacking, it is here assumed that the potential profile (a) prevails. The reasons are as follows: when a switch is relatively new, it is sometimes observed that the switching process consists of two steps as shown in Fig. 1, suggesting that the breakdown takes place in two locations. Since the chalcogenide glass is considered as a nearly intrinsic semiconductor, electron and hole are placed on equal footing in this discussion, but strict equality is not actually an essential part of the argument.

Here, we propose a double injection model, as discussed by Mott[4] and

Henisch, Fagen and Ovshinsky[5], consistent with (a). Space charges of opposite signs are established at the electrodes; holes and electrons are assumed to tunnel through the potential barrier (Fig. 2).

It should be noted that the double injection model demands that the lifetime of the carrier be longer than the transit time of the carriers across the switch. That transit time is estimated to be 10^{-7} sec or less[4] in the chalcogenide glass of thickness of about 1 μ. In the same films, the lifetime of carriers as observed by Lee and Henisch is about 10^{-7} sec[6].

The presence of space charge after, and therefore also during, the ON-state has been established[6]. The distribution of that space charge will now be discussed. There are two possible modes: (1) a bound space charge is uniformly distributed as in the case of Schottky barrier, where ionized donors or acceptors provide the necessary potential fall on the side of semiconductor. Alternatively, (2) the space charge is made up of free carriers, under the dynamic conditions which prevail in the presence of electron and hole flows. However, the first hypothesis involves a difficulty. An analysis by Mott[4] showed that such a space charge would have to occupy deep traps if the potential barrier were to be thin enough to let the carrier tunnel through. Yet, this is inconsistent with the temperature independence of the ON-state and with the speed of space charge reversal (about nanoseconds) as observed[7] by reversing the polarity across a switch in the ON-state. Such a rapid polarity reversal implies that very shallow traps or, more probably, mobile carriers are involved in the process. This difficulty is removed by the choice of the second alternative of space charge distribution. Moreover, the consequences of this distribution can be shown to be in harmony with experimental results, as will now be discussed.

Consider the conditions at the cathode. During the ON-state, electrons are injected in the chalcogenide glass film by the field emission. These elec-

trons are accelerated across the potential fall, thereby becoming 'hot', but are then thermalized once they are in the region beyond the knee. On the other hand, slow holes move into that region from the opposite direction. Since current continuity prevails, this must result in the positive space charge at the knee of the potential fall. Thus, the process is self-sustaining. If the direction of the field is reversed during the lifetime of the free carriers, space charges of opposite sign (and thus barriers) are regenerated. The process is rapid, because the interior of the film is highly conductive.

The dependence of the current on the applied voltage during the ON-state may be estimated as follows: In the barrier, the potential is linear. This means that the main portion of potential fall is free from space charge (Fig. 2). This is possible because the carrier speed in this region is very high and does not contribute to charge density. All the space charge is assumed located at the knee of potential fall.

The electron current, j_e, at the cathode is given by an expression, first obtained by Fowler and Nordheim, in M. K. S. unit[8]:

$$j_e = \frac{1.54 \times 10^{-10}}{w} \cdot E^2 \cdot \exp(-6.83 \times 10^9 [w]^{3/2} \cdot \Delta/E), \ (A/m^2) \qquad (1)$$

where E is the field at the electrode, w is the barrier height, here at least 1/2 electron-volt during the ON-state. Δ is the Nordheim elliptic function which is in practice equal to unity. For field strength of 10^9 v/m, and 10^{10} v/m, the exponential term is exp(-2.34) and exp(-0.234) respectively. This means that for plausible barrier fields, as estimated from the current density[9], the exponential term may be approximated as unity. The current density can thus be written as,

$$j_e \simeq \frac{1.54 \times 10^{-10}}{w} \cdot E^2 \cdot (A/m^2) \qquad (2)$$

An ON-state characteristic is schematically shown on Fig. 3. V_{ON} is always greater than a certain minimum voltage V_{MON}. Accordingly, E in eqn. (2) is also greater than the minimum field required for the onset of emission. Using the technique shown by Rose, current density can be calculated as follows. The charge density per unit area, σ, accumulated at the electrode, is given by,

$$\sigma = \frac{\varepsilon V}{\lambda} = \frac{\varepsilon (V - w/e)}{\lambda - \lambda_b} \tag{3}$$

and the transit time, T_r, across the barrier of thickness, λ, is given by

$$T_r = \frac{\lambda - \lambda_b}{E \cdot \mu_e} = \frac{(\lambda - \lambda_b)^2}{(V - w/e) \cdot \mu_e} \tag{4}$$

where V is the potential drop across one barrier. λ_b is the tunneling distance, which is assumed to be small; and μ_e is the effective hot electron mobility. If a certain fraction θ of the surface charge takes part in tunneling, the electron current density, j_e, becomes,

$$j_e = \frac{\theta \sigma}{T_r} = \frac{\theta \varepsilon (V - w/e)^2 \mu_e}{(\lambda - \lambda_b)^3} \tag{5}$$

With $j = j_e + j_h$ and $E = (V - w/e)/(\lambda - \lambda_b)$, the thickness of the potential fall, λ, can be eliminated as between eqns. (2) and (5),

$$j = \frac{1}{4}\left(\frac{1.54 \times 10^{-10}}{w}\right)^3 \left(\frac{1}{\theta \varepsilon \mu^*}\right)^2 (V_{ON} - 2w/e)^2 \quad (A/m) \tag{6}$$

where

$$\left(\frac{1}{\mu^*}\right)^2 = \left(\frac{1}{\mu_e}\right)^2 + \left(\frac{1}{\mu_h}\right)^2, \text{ and } V_{ON} \simeq 2V$$

and the subscript h stands for hole. Assuming that the cross-section of the cur-

rent remains the same, eqn. (6) shows that j is expected to be proportional to the square of $(V_{ON}-w/e)$. This is indeed observed, as shown in Fig. 3.

The field emission process is further supported by the following observations. First, the current-voltage relationship during the ON-state is insensitive to the ambient temperature[7]. Second, the electrodes during the ON-state appear to be hotter than the chalcogenide glass film itself[9, 6]. Third, the fluctuation in the delay time can be interpreted as the reciprocal of the probability of an incident electron having enough energy to tunnel through the barrier. Accordingly, the fluctuation of the delay time should be smaller at the higher ambient temperature and this is actually observed.

In the discussions above, it is assumed that ON-state is already established, and maintained by the field-injection of carriers, resulting in a high carrier concentration in the bulk of the film. A similar process is found by von Hippel and his colleagues in KBr with a large concentration of color centers[10]. When the density of color centers and the level of the photo-excited carrier concentration exceed a certain limit, field emission from the electrode sets in. The difference between the photoexcited KBr and the chalcogenide glass are as follows: the former involves excitation of carriers by light and a gradual increase of conductance as the field is increased, while the latter involves well defined switching from the OFF-state to the ON-state at the threshold voltage.

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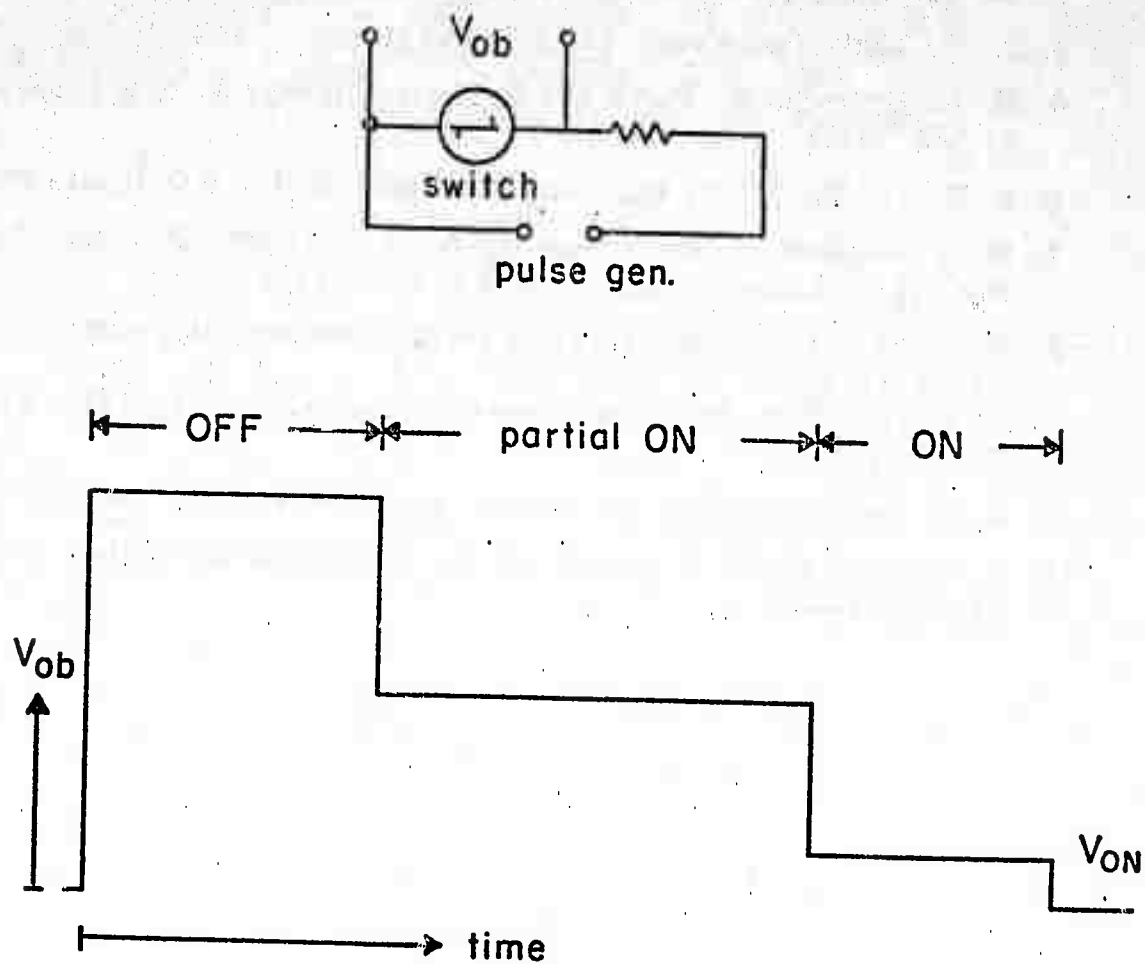
FIG. 1 Schematic diagram showing the observed voltage V_{ob} across the specimen during double switching.
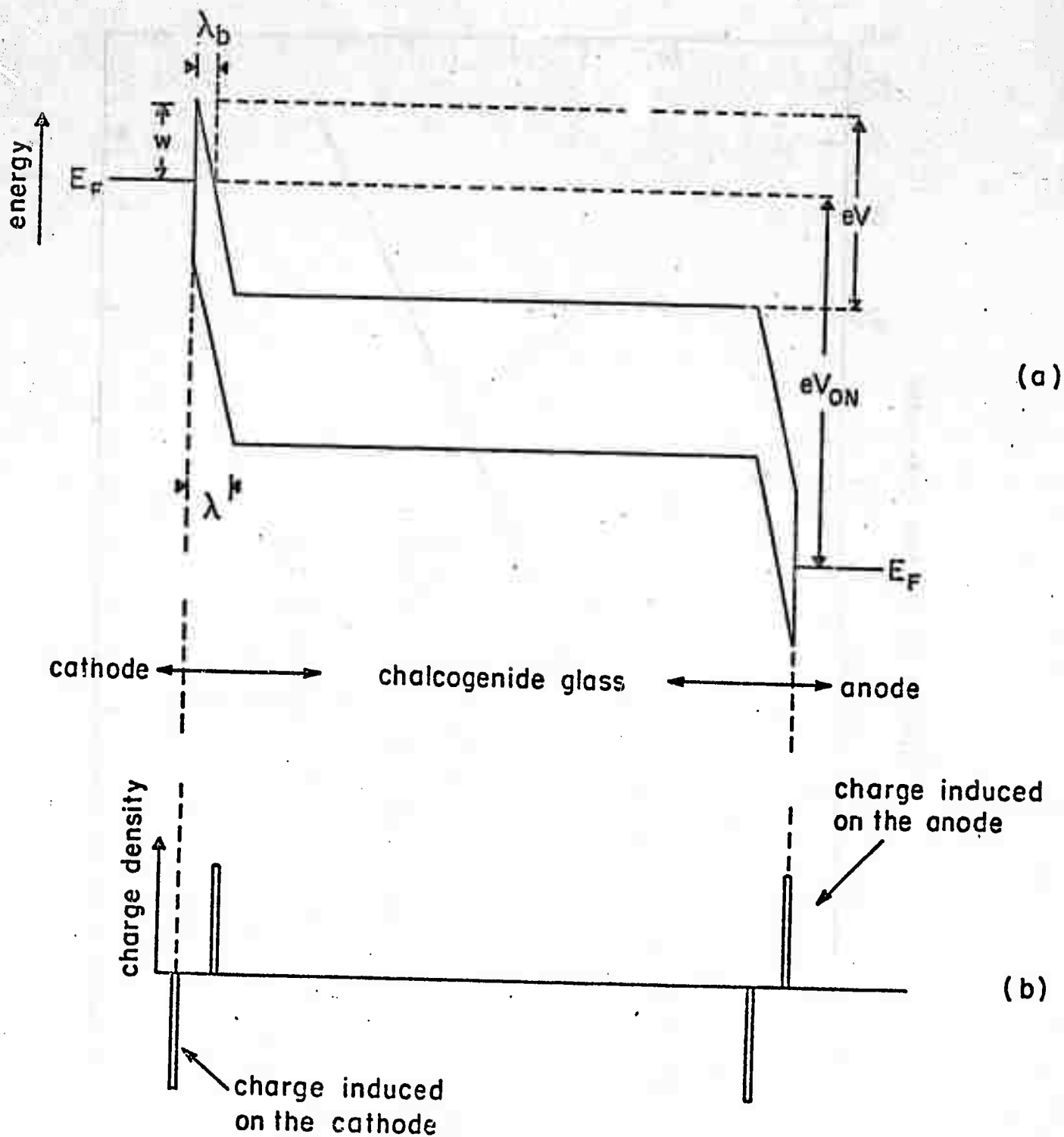
FIG. 2 Potential profile and space charge distribution during the ON-state. (a) Mobility edge and the double barrier system. (b) Induced space charge distribution.
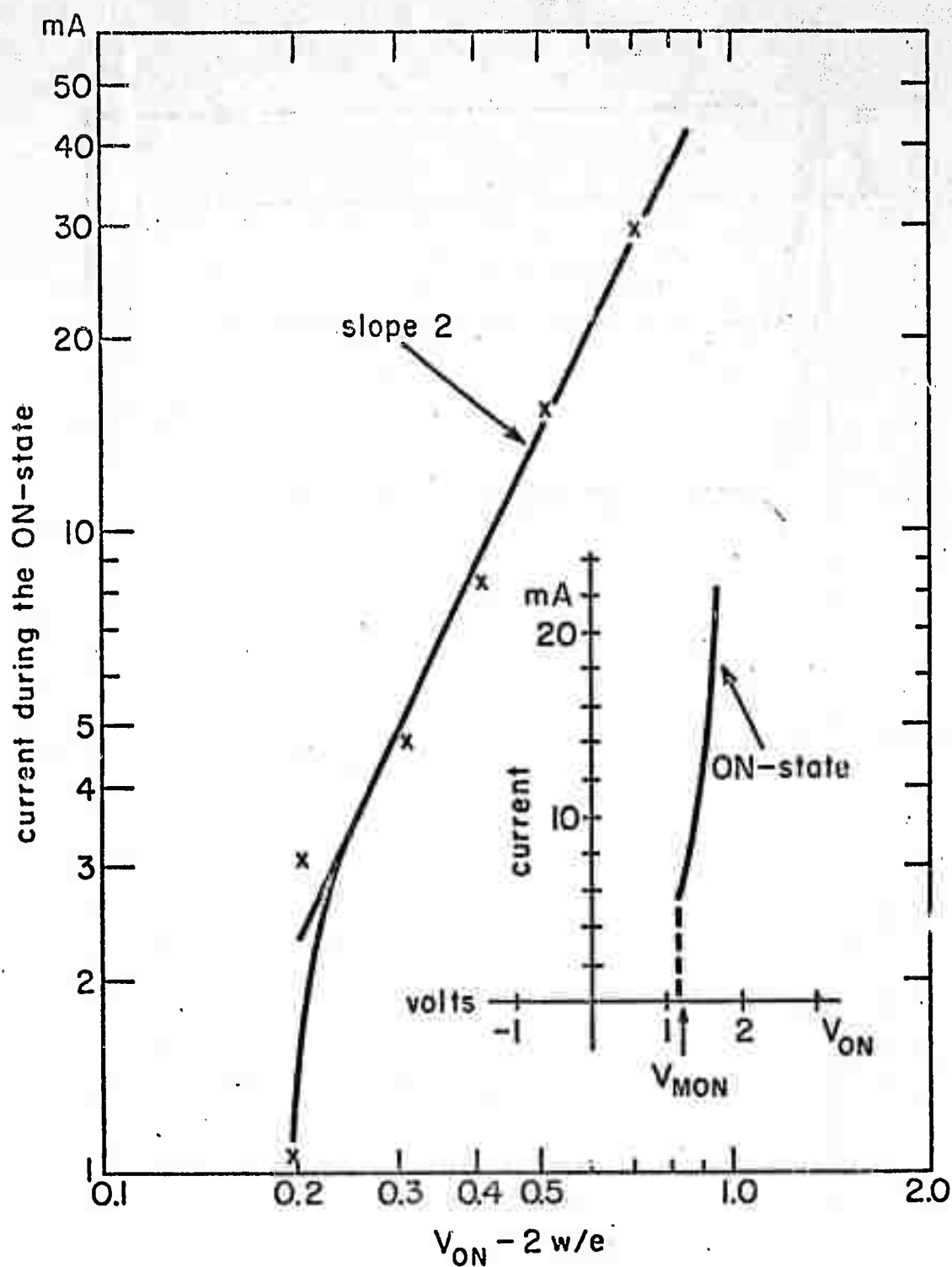
FIG. 3 Current during the ON-state.   (Henisch, Pryor and Vendura, Jr., loc. cit.) The ON-current is measured by a pulse technique (pulse frequency: 10 Hz, pulse length: ~3 μsec).

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Threshold Switching in Chalcogenide Glass Films

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

ABSTRACT

On the basis of polarization arguments, the equality $\tau_d = \tau_\ell$ is proposed as the critical condition for the threshold point of chalcogenide glass switches, τ_d being the dielectric relaxation time and τ_ℓ the carrier lifetime. It is shown that this switching criterion is in good agreement with measurements, and that it explains the temperature dependence of the threshold voltages as well as the voltage-dependence of the delay time.

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The nature of threshold switching in chalcogenide glass films has been the subject of much discussion and controversy in recent years. In previous work, the present authors[1] and others[2,3] have drawn attention to the essentially electronic nature of the switching process. Arguments are here presented which relate switching parameters directly to the measured electrical properties of the glass film. Experimental evidence, some new, some taken from the literature, which supports this discussion was obtained on films sandwiched between pyrolytic graphite electrodes.

Previous workers have noted four characteristic features of threshold switching systems:

1. The threshold voltage V_{TH}, when measured with square-wave pulses, is temperature dependent in accordance with an equation in the

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*Also affiliated with the Department of Physics.

form[4]

$$V_{TH} = A - BT \tag{1}$$

where A and B are constants. Such an equation is valid up to (say) 450°K above which V_{TH} diminishes asymptotically, rather than linearly. This may be associated with changes of a permanent nature, as the glass goes through a phase change at a temperature of that order.

2. The switching delay time t_d of a thin chalcogenide glass film with applied voltage V can be expressed by an equation of the form[5]

$$t_d = t_{do} \exp(-V/V_o) \tag{2}$$

where t_{do} and V_o are constants. Two restrictions have already been noted on previous occasions: (a) When $(V - V_{TH})$ is large, i.e. at high overvoltage, temperature changes may have to be envisaged. (b) When $V \approx V_{TH}$, t_d is no longer well defined, but is subject to a wide statistical spread[6].

3. According to Haberland and co-workers[7], switching cannot occur until a certain __minimum__ charge q_H has been stored in the system, and that charge turned out to be independent of temperature, at any rate between 273°K and 360°K.

The proposed interpretation of these features is as follows. When an equal number of electrons and holes are injected into a semiconductor, e.g. by a short light pulse or by any other mechanism, the electron-hole cloud will become polarized by the prevailing electric field. According to Kielson[8] and van Roosbroeck[9], the polarizability, α is given by

$$\alpha = e \left| (\mu_n + \mu_p)/(\tau_\ell^{-1} - \tau_d^{-1}) \right| \tag{3}$$

where μ_n and μ_p are the electron and hole mobilities in that field, τ_ℓ is the carrier lifetime and τ_d the dielectric relaxation time. Equation (3) ap-

plies, no matter whether $\tau_d \gg \tau_\ell$ or $\tau_d \ll \tau_\ell$. Inspection shows that an instability is expected for $\tau_d = \tau_\ell$. Under these conditions, the approximations involved in the derivation of eqn. (3) are not actually valid, and a new formal derivation must be sought. This will be given in a separate paper[10], but the same result can be arrived at intuitively. When the dielectric relaxation time and the carrier lifetime are equal, the electron and hole clouds will drift apart before any substantial amount of recombination has taken place. Once apart, recombination stops altogether. For an infinite semiconductor, the polarizability would become time-dependent simply in accordance with

$$\alpha = et \left[\mu_n + \mu_p\right]. \tag{4}$$

Meanwhile, reference to experiment shows that the carrier lifetime and the dielectric relaxation time are in fact approximately equal at the switching point. The former has been estimated by Lee and Henisch[11] as 10^{-7} seconds before $199°K$ and $306°K$, and that value is in agreement with the dielectric relaxation time (8×10^{-8} sec), as calculated from the measured conductance and capacitance ($Te_{40}As_{35}Ge_7Si_{18}$ alloy). Though the experiment accuracy is not very high, there is what must be considered good support for the contention that $\tau_\ell = \tau_d$ at the threshold point. It must be remembered that τ_d at $V = V_{TH}$ is always much smaller than τ_d in equilibrium ($V \approx 0$) because the effective conductivity increases with field. This is, in fact, the principal claim here made. Inter alia, it leads at once to an explanation of eqn. (1). A temperature-independent τ_d implies a constant conductivity, since there are no significant changes of dielectric constant. The differential conductivity may be expressed approximately as

$$\sigma = \sigma_0 \exp\left[-\frac{W-eaE}{kT}\right] \tag{5}$$

where a is a characteristic distance. The threshold conductivity σ_{TH} cor-

responds to a threshold field $E_{TH} = V_{TH}/L$, L being the film thickness. With $(W-eaE_{TH})/kT$ constant, eqn. (5) directly implies eqn. (1), with A = WL/ea. Experimentally, we may compare W, obtained from thermal activation energy of the film, with Aea/L, obtained from the empirical relation of eqn. (1). For most of the specimens used by Walsh, Vogel and Evans[12] the agreement is excellent, as Table I shows.

TABLE I

Comparison of Experimental Results Obtained by
Walsh, Vogel and Evans with Present Model.

Walsh and Evans Sample Nos.	0-20-1	0-30-2	0-30-1	0-30-4	0-20-Ref. 5
W (ev)	0.35	0.35	0.35	0.35	0.35
$\frac{eaA}{L}$ (ev)	0.37	0.37	0.38	0.39	0.23

[The first four samples ranged in thickness from 1μ to 3μ. The last sample was described as "much thinner".]

Equation (5) also means that the current is given by

$$I = I_0 \exp\left[-\frac{W-eaE}{kT}\right] \qquad (6)$$

This equation applies on a stable basis up to the threshold point I_{TH}, E_{TH}, and for times such that $0 < t < t_d$ it is also valid for small overvoltages. This permits us to calculate the charge passing in the time t_d, this being here taken as the minimum delay time for a given applied voltage. Since I_{TH} has been shown[12] to be constant during t_d,

$$q_H = I_{TH}t_d \qquad (7)$$

from which, with eqn. (6), we obtain

$$t_d = q_H C \exp\left[-\frac{eaV}{kTL}\right] \qquad (8)$$

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where C is a constant (independent of voltage). This is clearly of the form of eqn. (2).

The existence of a minimum charge q_H as such is also plausible within the model here suggested. When $\tau_\ell = \tau_d$, the polarization within the film proceeds in time until charge accumulates near the electrodes. An appropriate free-carrier space-charge system has already been discussed[13]. However, this system is self-sustaining only if the contact barriers are thin enough to permit tunneling, and that, in turn, demands the accumulation of a certain minimum charge. One would expect this charge to be independent of temperature, as in fact is is, because it does not matter in this context whether it consists of free or trapped carriers.

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