

## Temperature shift of short-circuit thermally-stimulated-current peaks of Teflon electrets with time after electron injection

G. M. Sessler and J. E. West

*Bell Laboratories, Murray Hill, New Jersey 07974*

(Received 17 June 1974)

A dependence of the temperature for the current maximum of thermally-stimulated-current (TSC) curves on storage time between electron injection and TSC experiment has been observed for 25- $\mu\text{m}$  Teflon electrets. The currents were measured with contacting electrodes on samples charged with 20-keV electrons. Typical peak temperatures are 40 and 100°C for storage times of  $10^3$  and  $10^8$  sec at room temperature, respectively. The peak shifts are explained by the time dependence of the radiation-induced conductivity generated during electron injection.

It has been recently noted that thermally-stimulated-current (TSC) curves obtained from certain electrets in short circuit (with contacting electrodes) differ from those obtained in open circuit (one electrode at a distance large compared to the sample thickness) in the sense that the former show a considerably lower temperature of the dominant current maximum (peak temperature) than the latter.<sup>1-3</sup> This effect was found with Teflon FEP (polyfluoroethylenepropylene) electrets charged by injection of 10- to 40-keV electrons. Such differences in peak temperature have been attributed to opposite carrier drifts under short-circuit and open-circuit conditions. In the former case, charge drifts occur primarily from the trapped charge layer through the volume penetrated (and made more conductive) by the injected charge carriers back to the surface of incidence. Under open-circuit conditions, however, the drifts occur through the remainder of the volume to the other surface. The increase in conductivity, caused by secondary carriers generated in the penetrated volume, has been investigated recently with respect to its delayed component persisting for long periods of time.<sup>4,5</sup>

In a series of new experiments with Teflon electrets we have found a dependence of the peak temperature  $T_p$  of short-circuit TSC's on open-circuit storage time  $t_0$  between electron injection and TSC experiment. Representative results are shown in Fig. 1 which depicts three short-circuit TSC spectra obtained from 25- $\mu\text{m}$  samples carrying an evaporated aluminum electrode ("rear electrode") and charged for a few seconds through the nonmetalized surface with a 20-keV electron beam and a dose rate of  $4 \times 10^4$  rad/sec prior to the TSC experiment. Parameter is the storage time  $t_0$  at room temperature. The short-circuit currents were obtained between the rear electrode and a polished gold-coated external electrode ("front electrode") pressed<sup>2</sup> against the polymer side of the neoprene-backed sample.

The short-circuit TSC curves in Fig. 1 show a

dominant low-temperature peak and a considerably smaller peak at higher temperature (see also Refs. 2 and 3). The curves demonstrate a pronounced dependence of the temperature of the dominant peak on time after charging. Comparison with an open-circuit TSC curve, also shown in the figure, reveals the expected difference in polarity of the currents as well as a large peak-temperature difference remaining even for samples with  $t_0$  in excess of one year. TSC curves obtained after storage at 100°C show, apart from the low-temperature peak, higher-temperature peaks, which are generally more prominent than those obtained after storage at room temperature.

Evaluation<sup>6,7</sup> of the dominant peak of the short-circuit TSC curves yields activation energies  $E$  of 1.8-1.9 eV, independent of  $t_0$  for  $2 \times 10^4 < t_0 < 10^8$  sec. For shorter  $t_0$ 's, such an evaluation is inaccurate because of the presence of short-circuit currents at room temperature.

This result suggests that the observed peak shift is not due to retrapping (during storage) of charges in traps emptying at higher temperatures. Similarly, measurements of the retained charge indicate<sup>2</sup> that discharge of trapped charges to the rear electrode is negligible over storage periods of the order of a year at room temperature.

To elicit the relation between peak temperature and storage time in short-circuit TSC, the logarithm of  $t_0$  is plotted in Fig. 2 against the inverse of  $T_p$  for a number of samples stored at 25 and 100°C. The dependence of  $T_p$  on  $t_0$  is again very prominent. The data can be represented by parallel straight lines having slopes corresponding to an activation energy of  $E = 1.95$  eV. The relation between this and the above values will be evident below.

In the following, the peak shift apparent from Fig. 2 will be explained in terms of the delayed radiation-induced conductivity (DRIC) introduced above. The dark conductivity, being orders of magnitude smaller, is neglected. The DRIC is primarily due

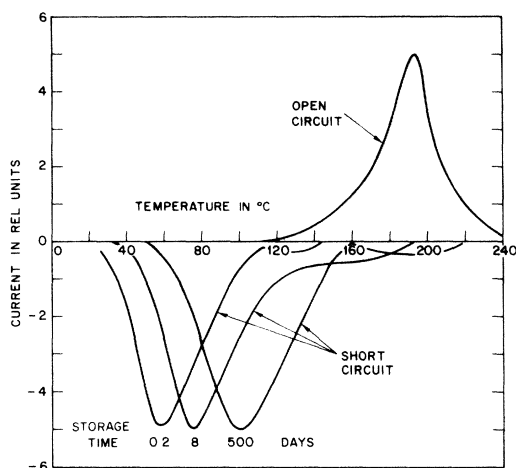


FIG. 1. Short-circuit and open-circuit TSC curves for 25- $\mu$ m-thick Teflon FEP films aluminized on one side, and charged with 20-keV electron beam to about  $3 \times 10^{-8}$  C/cm<sup>2</sup>. Heating rate 1 °C/min. Parameter on the short-circuit TSC curves is the open-circuit storage time  $t_0$  at 25 °C between charging by electron beam and TSC experiment. Since charge loss during open-circuit storage is negligible, the expected integrated areas under the short-circuit TSC curves are about the same. A minor normalization is used to equalize peak amplitudes exactly. Open circuit TSC is independent of storage time.

to secondary carriers and can be expressed as  $g = en\mu$ , where  $e$  is the electronic charge,  $n$  is the number of free electrons (or free holes, if holes are more mobile), and  $\mu$  the free mobility. Following Fowler<sup>8</sup> we assume  $n$  to be dependent on temperature  $T$  and time  $t$  after irradiation, as explained below, while  $\mu$  is assumed to be only weakly (nonexponentially) dependent on  $T$ . Thus  $g$  is written as

$$g(T, t) = en(T, t)\mu(T). \quad (1)$$

For a single trapping level and isothermal storage conditions,  $n$  may be represented by<sup>8,9</sup>

$$n(t) = n_0 / (1 + n_0 b t), \quad (2)$$

where  $n_0$  is the number of free carriers at  $t = 0$  and  $b$  is a modified recombination coefficient, considered weakly dependent on  $T$ . Equation (2) is valid if the rate of release of electrons from traps is sufficiently rapid to keep pace with recombination. Since retrapping is fast in Teflon,<sup>3</sup> this condition is met. Relations similar to Eq. (2) hold for uniform and exponential trap distributions. The hyperbolic time dependence expressed by Eq. (2) has been experimentally verified<sup>5</sup> for Teflon for time periods from 1 to  $10^4$  sec and for other polymers for time periods of less than 1 sec.<sup>10,11</sup> Since for Teflon  $n_0 b$  is about 1/sec at room temperature<sup>5</sup> in short circuit (but possibly much smaller in open circuit) and larger at elevated temperatures, Eq. (2) may be written for,  $t \gg 1$  sec,

$$n(t) = 1/bt. \quad (3)$$

If the sample temperature is changed, the number of free carriers is, under the above conditions, determined by thermal equilibrium with the trapped carriers. Assuming that a temperature change from  $T_0$  to  $T$ , commencing at  $t = t_0$ , is performed over a time interval so short that the number of recombining carriers can be neglected as compared to the number of trapped carriers,  $n(T, t_0)$  changes exponentially with temperature and is therefore determined by<sup>9</sup>

$$n(T, t_0) = (1/bt_0) e^{E/kT_0 - E/kT}, \quad (4)$$

where  $E$  is the activation energy and  $k$  is Boltz-

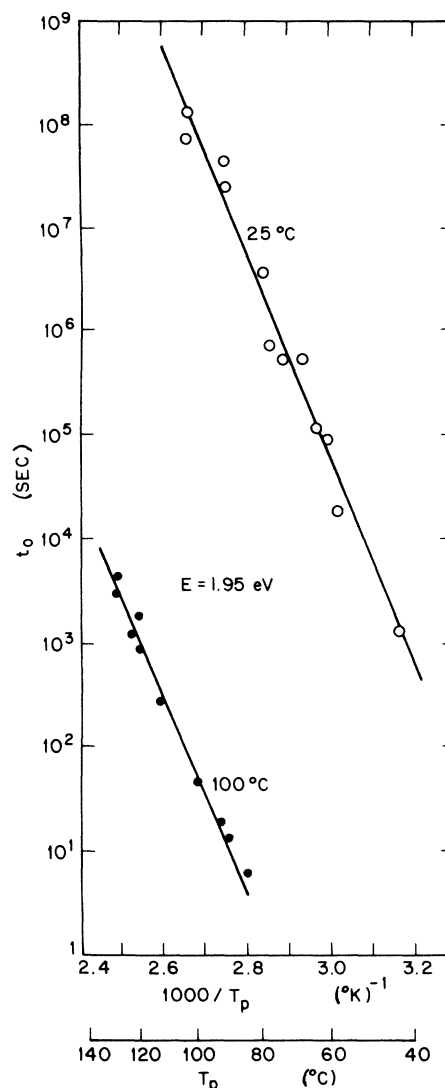


FIG. 2. Plot of storage time  $t_0$  at 25 and 100 °C vs inverse peak temperature  $1/T_p$  of short-circuit TSC curves for 25- $\mu$ m-thick Teflon FEP films aluminized on one side.

mann's constant. The temperature dependence of the conductivity is thus with Eq. (1)

$$g(T, t_0) = (e/bt_0)\mu e^{E/kT_0 - E/kT} \quad (5)$$

The current  $I(t) = dq(t)/dt$  as function of the induction charge  $q(t)$  on the rear electrode is given by [see Eq. (29) of Ref. 5]

$$\frac{dq(t)}{dt} = -Ag(T, t_0)q(t), \quad (6)$$

where  $A = (1 - R/D)/\epsilon$ , with  $R$  representing the mean spatial depth of the trapped electrons, measured from the front electrode,  $D$  is the sample thickness, and  $\epsilon$  is the dielectric permittivity. We assume now, as customary in TSC experiments, a linear temperature rise

$$T = T_0 + h(t - t_0), \quad (7)$$

where  $T_0$  is the starting temperature and  $h$  is the heating rate. Eliminating  $t$  with Eq. (7) from Eq. (6) and differentiating with respect to  $T$  (indicated by primes), one obtains for the temperature  $T_p$  at which the maximum of  $I(T)$  occurs

$$g'(T = T_p)/g(T_p) = Ag(T_p)/h, \quad (8)$$

where  $q'/q = -Ag/h$  has been used. The left-hand side of this equation may be determined from Eq. (5) with  $T = T_p$

$$g'/g = \mu'/\mu + E/kT_p^2. \quad (9)$$

Since  $E/kT_p \approx 60$  and  $\mu$  is weakly dependent on temperature, only the second term on the right-hand side has to be considered. With this, Eqs. (5) and (8) yield

$$t_0 = BT_p^2 \mu e^{E/kT_0 - E/kT_p}, \quad (10)$$

where  $B = ekA/bhE$ .

This equation explains the linear dependence of  $\ln(t_0)$  on  $E/kT_p$ , observed in Fig. 2, if the temperature dependence of the pre-exponential factors can be neglected. Because of the value of  $E/kT_p$  (see above), this neglect is readily justified. The vertical separation of the two lines in the figure reflects essentially the dependence of the exponential factor in Eq. (10) on storage temperature  $T_0$ . Comparison of Fig. 2 and Eq. (10) also yields  $\mu/b \approx 10^5$  (V cm)<sup>-1</sup>, practically independent of  $T$ . As is evi-

dent from Eq. (4), the activation energy of 1.95 eV determined from Fig. 2 applies to conductivity and agrees reasonably well with that evaluated above from individual TSC curves and also with values found for Teflon FEP by other methods.<sup>3,12</sup>

The recently observed dependence of peak temperature on temperature during electron injection<sup>13</sup> can similarly be explained with Eq. (10).

Extrapolation of the straight lines in Fig. 2 to the temperature of the open-circuit peak in Fig. 1 at 195 °C yields storage times  $t_{00} = 10^{13}$  and  $10^7$  sec for 25 and 100 °C, respectively. This is the time required for the DRIC to decay to the conductivity of a virgin sample. The conductivity under these conditions can be determined from Eqs. (1) and (3) with the above value of  $\mu/b$  to be  $10^{-27}/\Omega$  cm and  $10^{-20}/\Omega$  cm, respectively, at the two temperatures. The former value is, however, not realistic in the sense that other processes (such as ambient radiation) induce conductivities greater by several orders of magnitude.

It is of interest that time constants of the open-circuit charge decay on Teflon electrets<sup>12</sup> are also of the order of  $10^{13}$  (extrapolated value) and  $10^7$  sec at 25 and 100 °C. The closeness of these and the above figures for  $t_{00}$  may be explained by the fact that both are representative of the carrier transit time (including retrapping) through the thickness of the sample or a substantial fraction thereof. In case of DRIC, the carriers are the secondaries which have to drift distances increasing with time (due to their gradual depletion) before recombining or reaching the electrodes. For charge decay, the carriers are either intrinsic, drifting to the injected (stored) charge layer, or the stored charges drifting to the electrodes.

The change of DRIC with time, as evident from the above relation between peak temperature and storage time, is believed to be of fundamental importance for the interpretation of short-circuit TSC and isothermal charge decay. Present analyses<sup>14</sup> are based on the assumption of dielectrics with isotropic and time-independent properties. In the light of the present results, a reexamination of these assumptions is necessary.

The authors are greatly indebted to Professor B. Gross for stimulating discussions on the subject of this paper.

<sup>1</sup>G. M. Sessler and J. E. West, in 1970 *Annual Report, Conference on Electrical Insulation and Dielectric Phenomena* (National Academy of Sciences, Washington, D. C., 1971), pp. 8-16.

<sup>2</sup>G. M. Sessler and J. E. West, in *Electrets, Charge Storage and Transport in Dielectrics*, edited by M. M. Perlman (The Electrochemical Society, Inc., Princeton, N. J., 1973), pp. 292-299.

<sup>3</sup>J. van Turnhout, in Ref. 2, pp. 230-251.

<sup>4</sup>B. Gross, G. M. Sessler, and J. E. West, *Appl. Phys. Lett.* **22**, 315 (1973); **24**, 351 (1974).

<sup>5</sup>B. Gross, G. M. Sessler, and J. E. West, *J. Appl. Phys.*, **45**, 2841 (1974).

<sup>6</sup>R. A. Creswell, M. M. Perlman, and M. A. Kabayama, in *Dielectric Properties of Polymers*, edited by F. E. Karasz (Plenum, New York, 1972), pp. 295-312.

- <sup>7</sup>H. J. Wintle, *J. Appl. Phys.* 42, 4724 (1971).  
<sup>8</sup>J. F. Fowler, *Proc. R. Soc. A* 236, 464 (1956).  
<sup>9</sup>A. Rose, *RCA Review* 12, 362 (1951).  
<sup>10</sup>E. H. Martin and J. Hirsch, *J. Appl. Phys.* 43, 1001 (1972); J. Hirsch and E. H. Martin, *J. Appl. Phys.* 43, 1008 (1972).  
<sup>11</sup>D. M. J. Compton, G. T. Cheney, and R. A. Poll, *J. Appl. Phys.* 36, 2434 (1965); R. C. Hughes, *J. Chem. Phys.* 58, 2212 (1973).  
<sup>12</sup>P. W. Chudleigh, R. E. Collins, and G. D. Hancock, *Appl. Phys. Lett.* 23, 211 (1973).  
<sup>13</sup>M. M. Perlman and S. Unger, *Appl. Phys. Lett.* 24, 579 (1974).  
<sup>14</sup>J. van Turnhout, thesis (Leiden, 1972) (Krips Repro, Meppel, 1972), and references therein.