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Pulse duration and diffusion corrections in electron conductance transients

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The effects of excitation pulse duration and electron diffusion upon drift-velocity measurements are described. The correction procedure employed by Wada and Freeman is at least as accurate as that proposed by Cassidy and by Robson, but was perhaps not previously illustrated in enough detail.

There is confusion[1,2] about the Wada-Freeman (WF) analysis of electron-drift signals.[3,4] The cause appears to be that Ref. 3 contained an example trace of a signal obtained at high-electric-field strength, but not examples of traces for intermediate- and low-field strengths. Measurement of the high-field drift time t_d required a correction for the x-ray pulse duration τ, but not for diffusion. Signals at intermediate fields did not require correction for either τ or diffusion. Those at low fields required correction for diffusion but not τ. We had mistakenly thought that only the first case needed illustration. All three cases are illustrated below.

The discussion refers to uniformly irradiated cells with parallel plate electrodes.

I. HIGH FIELDS

A schematic and an experimental current-versus-time trace at high-field strengths are given in Fig. 1(a). The schematic trace was obtained from Fig. 1(d) of Ref. 3. The features are similar to the experimental trace beside it, and to the trace in Fig. 1(b) of Ref. 3. These experimental traces can be contrasted with the schematic curves in Fig. 8 of Ref. 1, which are unlike anything we have ever obtained.

The drift time obtained from Fig. 1(a) is[3]

$$t_d = t_0 - \tau/2 \ , \tag{1}$$

where t_0 is measured from the beginning of the x-ray pulse to the point where the extrapolation of the linear portion of the decay intersects the base line. In addition to Eq. (1), Cassidy's diffusion correction[1,2] might be appropriate to apply to t_d, which would be to multiply it by $1+2kT/eV$, where k is Boltzmann's constant, T is the temperature, e is the electron charge, and V the applied voltage. In Robson's notation of Eq. (24),[2] this factor is $1+1/l^*$. For Fig. 1(a) the factor equals 1.0007, which we take to be negligibly different from unity. Owing to the 1%–2% scatter in experimental values, we do not apply correction factors smaller than 1%.

It should be noted that on page 687 of Cassidy's paper,[1] there are two misprints, where the diffusion correction is given as $(4kT/eV)$, instead of the correct $(2kT/eV) = 2(D/\mu)/V$ given elsewhere in the text, where D is the diffusion coefficient and μ is the mobility.

When diffusion is negligible the same t_d is obtained by all treatments.[1-4] For example, as $(1/l^*) \rightarrow 0$, Eq. (21) of Ref. 2 reduces to the above Eq. (1).

WF also noted that when τ is not negligible compared to t_d,[3]

$$t_d = t_{\text{end}} - \tau \ , \tag{2}$$

where t_{end} is the point where the current trace merges (not asymptotically) with the base line.

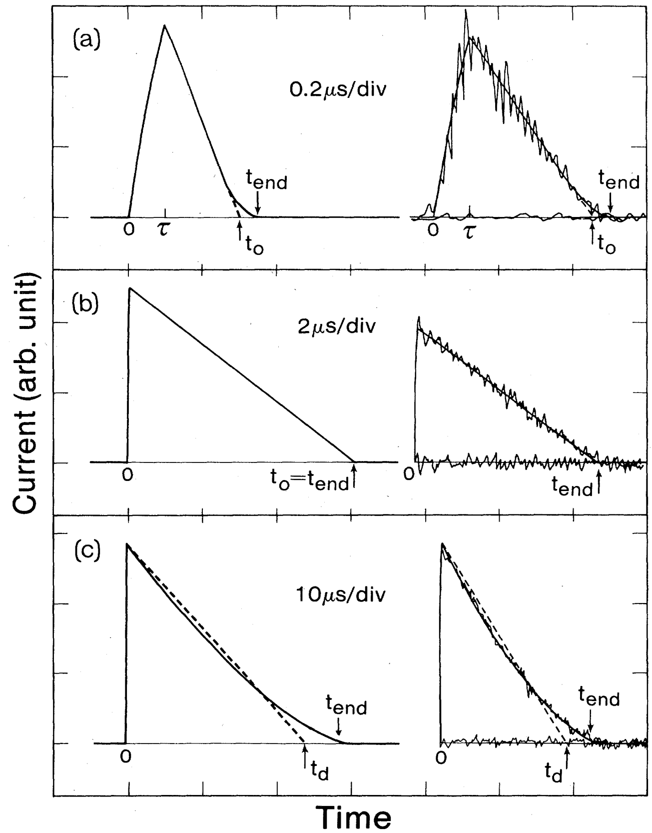

FIG. 1. Schematic and experimental electron current-vs-time traces. (a) High field: $\tau=$ pulse duration, $t_0=$ intersection of the linear extrapolation (dashed line) with the base line, and $t_{\text{end}}=$ where the trace merges with the base line. The drift time $t_d = t_0 - (\tau/2)$. (b) Intermediate field: as in (a) but $t_d >> \tau$, so $t_d = t_0 = t_{\text{end}}$. (c) Low field: dashed line indicates diffusion free equivalent of the signal trace (solid line), chosen so that $t_d = t_{\text{end}}/[1+(2kT/eV)^{1/2}]$. The experimental traces are for electrons in n-butane at 1.10×10^{25} molecules/m^3, 603 K, drifting across 7.27 mm at (a) 150 V, (b) 10.0 V, (c) 3.07 V applied potential.

II. INTERMEDIATE FIELDS

A schematic diagram and an actual trace of signals at intermediate-field strengths are shown in Fig. 1(b). The current decay is linear and $t_d >> \tau$, so

$$t_d = t_0 = t_{\text{end}} \quad . \tag{3}$$

Equation (3) is equal to Eqs. (1) and (2) with τ negligible. Another example of this type of trace is given in Fig. 1 (top) of Ref. 5. The Cassidy diffusion correction[1,2] for the experimental trace in Fig. 1(b) would be 1.01, which we neglect. For all of our experimental conditions where the current trace was linear the Cassidy correction was ≤ 1.01. The Cassidy correction can be larger at other experimental conditions, but then the trace would probably be curved. The value of t_0 from a single experimental trace such as that in Fig. 1(b) is precise to ±1% to 2%.

III. LOW FIELDS

Schematic and experimental traces of signals obtained at low-field strengths are shown in Fig. 1(c). Such decay curves do not possess the distinct linear portion suggested[1,2] by Cassidy and Robson. The Cassidy correction factor is 3% for this trace. The upper two thirds of the experimental decay could be approximated by a straight line and extrapolated to the base line, with the intersection occurring 4% short of t_d. The fraction of the decay that must be approximated by a straight line to agree with the Cassidy correction is a function of the temperature and applied voltage. The choice is subjective, especially in the presence of signal noise. Reasonable lines through the experimental trace in Fig. 1(c) would give intersections 0%–8% short of t_d.

The WF treatment also involves a degree of subjectivity with low-field signals, but we find it to be as satisfactory as any other method. The diffusion term $(2kT/eV)^{1/2}$ corresponds to the Gaussian dispersion parameter of the broadening that would occur to a thin slice of electrons, that started at the negative electrode, by the time it reached the positive electrode. The drift of a nonbroadening slice would produce a rectangular trace. The clearing of electrons from a uniformly irradiated volume produces a right triangular trace when pulse duration and random diffusion are negligible, as in Fig. 1(b). When diffusion is appreciable, the current decay becomes curved. Time-dependent Gaussian broadening is superimposed on the triangular trace. The full diffusion parameter $(2kT/eV)^{1/2}$ applies only to the portion of electrons that arrive at the electrode at times near t_d. If one had fine enough experimental resolution, one should find that the last bit of the Gaussian-broadened trace approaches the base line asymptotically, so t_{end} in this case is not sharply defined. Empirically, we have found that the place where the signal disappears into the noise of the base line is an appropriate place to take t_{end} for use in Eq. (4)

$$t_d = t_{\text{end}}/[1+(2kT/eV)^{1/2}] \quad . \tag{4}$$

For the experimental trace in Fig. 1(c), $(2kT/eV)^{1/2} = 0.18$. This refers to a low field and high temperature and is an extreme case. The mobility calculated from this trace and the WF equation,[3]

$$\mu = l^2[1+(2kT/eV)^{1/2}]/Vt_{\text{end}} \tag{5}$$

(where l is the distance between the electrodes), is 1.02 $\text{m}^2/\text{V s}$. The value calculated from the experimental trace in Fig. 1(b) and Eq. (6),

$$\mu = l^2/Vt_{\text{end}} \quad , \tag{6}$$

is 1.06 $\text{m}^2/\text{V s}$. The average of eleven values obtained at potentials up to 70 V is 1.04 $\text{m}^2/\text{V s}$, with a mean deviation of 1.2%.

Robson suggested that the generalized Nernst-Einstein relation should be used to determine l^*, except at very weak fields.[2] By neglecting inelastic collisions and assuming that the field dependence of mobility was small, he obtained [Eq. (32) of Ref. 2]

$$l^* = 0.5elE \Big/ \left[kT + \frac{Mw^2}{3}\right] \quad , \tag{7}$$

where M is the mass of a gas molecule and w the electron drift velocity. Applying Eq. (7) to electrons in *n*-butane at 603 K and 10 V ($w = 1.46$ km/s) or 150 V ($w = 18.9$ km/s) gave a Cassidy correction of 1.10 ($l^* = 10.4$) or 1.96 ($l^* = 1.04$), respectively. Both are large diffusion corrections. With $l^* = 10$, the trace was predicted to have a long curving portion (Fig. 1 of Ref. 2), which Fig. 1(b) does not contain. The $l^* = 1.04$ predicted at 150 V should give an even longer curved portion, in even worse conflict with the actual shape in Fig. 1(a). Equation (7) may be invalid for electrons in *n*-butane, because Eq. (31) of Ref. 2 refers to energy loss by elastic collision.[6] Energy loss in hydrocarbon gases is dominated by inelastic collisions even near the thermal region.[7] When the electrons are near thermal, the thermal Nernst-Einstein relation is adequate. Equation (7) may not be valid in polyatomic molecular systems.

IV. SUMMARY

The Wada-Freeman treatment is at least as precise as that of Cassidy and Robson.

We are grateful to Dr. Robson for bringing to our attention the confusion that resulted from our too-brief presentation of procedures in Ref. 3. The shapes of the curves in Figs. 7 and 8 of Ref. 1 were beyond our experience, which unfortunately decreased our perception of the need to respond to that article.

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[3] T. Wada and G. R. Freeman, Can. J. Chem. **57**, 2716 (1978).

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[5] T. Wada and G. R. Freeman, *Proceedings of the 1980 Conference on Electrical Insulation and Dielectric Phenomena* (National Academy Press, Washington, DC, 1980), p. 386.

[6] G. H. Wannier, Phys. Rev. **83**, 281 (1951), Eqs. (1) and (2).

[7] N. Gee and G. R. Freeman, Phys. Rev. A **23**, 1390 (1981).