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# Mathematical Analysis of the Photovoltage Decay (PVD) Method for Minority Carrier Lifetime Measurements

O.H. von Roos



February 15, 1982

Prepared for  
U.S. Department of Energy  
Through an Agreement with  
National Aeronautics and Space Administration  
by

Jet Propulsion Laboratory  
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Combining Equations (15) and (12):

$$\lim_{\ell/L \rightarrow \infty} N(0,t) = TG e^{\alpha^2 Dt - t/\tau} \operatorname{Erfc}(\alpha\sqrt{Dt}) \quad (16)$$

a result quoted in the literature (Reference 4). Evidently Equation (16) is valid if the diffusion length  $L$  is small compared to the thickness of the base region  $\ell$  of the solar cell. On the other hand, Equation (11), being exact within the limitations of the underlying theory, is valid for all ratios  $\ell/L$ .

An alternative form to Equation (11) can be found if the hyperbolic functions of the integrand of Equation (9) are expanded in powers of  $\exp(-2\sqrt{u}\ell/L)$ . The first term of such a series would only yield Equation (16) upon integration, and subsequent terms would give corrections corresponding to situations in which  $\ell/L$  becomes progressively smaller. The complete series must, however, become identical with Equation (11) upon integration. Expanding the integrand of Equation (9) in the manner proposed gives

$$N(0,t) = TG \frac{e^{-t/\tau}}{2\pi i} \int_{-i^{a+b}}^{i^{a+b}} du e^{ut/\tau} \left\{ \frac{1}{\sqrt{u}(\sqrt{u} + \alpha L)} - \frac{2}{u - \alpha^2 L^2} \right. \\ \left. \times e^{-\alpha\ell - \sqrt{u}\ell/L} \sum_{n=0}^{\infty} \left[ \left( -e^{-2\sqrt{u}\ell/L} \right)^n + \frac{\alpha L}{\sqrt{u}} \sum_{n=1}^{\infty} \left( -e^{-2\sqrt{u}\ell/L} \right)^n \right] \right\} \quad (17)$$

The first term within the braces of Equation (17) gives Equation (16), as has been demonstrated. Since the infinite sums of Equation (17) converge absolutely on the integration path, summation and integration may be interchanged. One is then left with a series of integrals that can be handled in the

## ABSTRACT

When the diffusion length of minority carriers becomes comparable with or larger than the thickness of a p-n junction solar cell, the characteristic decay of the photon-generated voltage results from a mixture of contributions with different time constants. The minority carrier recombination lifetime  $\tau$  and the time constant  $\ell^2/D$ , where  $\ell$  is essentially the thickness of the cell and  $D$  the minority carrier diffusion length, determine the signal as a function of time. It is shown that for ordinary solar cells ( $n^+$ -p junctions), particularly when the diffusion length  $L$  of the minority carriers is larger than the cell thickness  $\ell$ , the excess carrier density decays according to  $\exp(-t/\tau - \pi^2 Dt/4\ell^2)$ ,  $\tau$  being the lifetime. Therefore,  $\tau$  can be readily determined by the photovoltaic decay (PVD) method once  $D$  and  $\ell$  are known.

An analysis of this matter was published recently in the Journal of Applied Physics. This report offers details of its mathematical development.

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## ANALYSIS

The author recently gave an account of the photovoltage decay (PVD) method for minority carrier lifetime measurements (Reference 1) in which he promised to furnish the details of the mathematical analysis in a separate report. This report fulfills that promise.

Since several cases (ordinary solar cells, BSF solar cells, etc.) have been treated in Reference 1, and since the mathematical formalism is similar for all cases considered, only one specific case will be considered in detail here. It consists of the determination of  $N_{21}(0,t)$ , the excess electron density at  $x = 0$  (the edge of the depletion layer of the p-type base) as a function of time. The subscript 21 identifies the mode of illumination (2 = excitation by a short flash) and the cell type (1 = an ordinary n<sup>+</sup>-p junction solar cell). The solar cell is subjected to a short pulse of duration T at  $t = 0$ ; the ensuing decay of the excess minority carriers given by  $N_{21}(0,t)$  is considered. For details, see Reference 1.

Mathematically, the problem of the determination of  $N_{21}(0,t)$  is expressed thus:  $N_{21}(x,t)$  satisfies the diffusion equation in the quasi-neutral base

$$N_{21}'' - L^{-2} N_{21} = D^{-1} \dot{N}_{21} - D^{-1} G e^{-\alpha x} T \delta(t) \quad (1)$$

where

L = electron diffusion length

D = electron diffusion constant

G = electron-hole pair generation rate in  $\text{cm}^{-3} \text{s}^{-1}$

$\alpha$  = light absorption coefficient

and a prime indicates differentiation with respect to x, a dot indicates differentiation with respect to time.

The boundary conditions are given by

$$N_{21}'(0,t) = 0, \quad N_{21}(\ell,t) = 0, \quad N_{21}(x,0) = 0 \quad (2)$$

The first condition expresses zero current flow (open circuit); the second implies a perfect ohmic contact at the back surface ( $l$  being the width of the base) and the last, an initial condition, presupposes that the device is quiescent just before it is illuminated by the pulse  $TG(t)$ .\*

A Laplace transformation of Equations (1) and (2) defined by

$$n(x,s) = \int_0^{\infty} e^{-st} N_{21}(x,t) dt \quad (3)$$

gives the following diffusion equation for the electron density in  $x$  and  $s$  space:

$$n'' - \mathcal{L}^{-2} n = -D^{-1} TG e^{-\alpha x} \quad (4)$$

where

$$\mathcal{L} = L(1 + \tau s)^{-1/2} \quad (5)$$

with  $\tau$  as the lifetime of the minority carriers. In deriving Equation (4) from Equation (1), use has been made of the connection between the diffusion constant  $L$  and the lifetime  $\tau$ , e.g.,  $L = (D\tau)^{1/2}$ , and the rules concerning Laplace transformations (Reference 2). The solution to Equation (4) that satisfies the boundary conditions (2) may be obtained by standard methods and reads:

$$n(x,s) = Ae^{-\alpha x} + A[\cosh(l/\mathcal{L})]^{-1} \{ \alpha l \sinh[(x-l)/\mathcal{L}] - e^{-\alpha l} \cosh(x/\mathcal{L}) \} \quad (6)$$

with

$$A = TG\tau(1 + \tau s - \alpha^2 L^2)^{-1} \quad (7)$$

---

\*  $\delta(t)$  is the Dirac  $\delta$ -function and  $T$  is again small compared with the minority carrier recombination lifetime  $\tau$  or other relevant time constants. The pulse illuminates the cell at  $t = \xi$  with  $\lim \xi = 0$  and the argument of the  $\delta$ -function in Equation (1) should read  $(t - \xi)$  in order to make Equation (1) consistent with the last expression of Equation (2).



The electron density at the edge of the depletion layer  $x=0$  is now found from Equation (6) by means of a back transformation (Reference 2), thus:

$$N_{21}(0,t) = \frac{1}{2\pi i} \int_{-i\infty+a}^{i\infty+a} e^{st} n(0,s) ds \quad (8)$$

Substituting  $u = 1 + \tau s$  and inserting Equation (6) into this expression yields the following integral for  $N_{21} = N$  (omitting the subscript 21 for simplicity):

$$N(0,t) = TGe^{-t/\tau} \frac{1}{2\pi i} \int_{-i\infty+b}^{i\infty+b} du \frac{e^{ut/\tau}}{u - \alpha^2 L^2} \left[ 1 - \frac{e^{-\alpha \ell}}{\cosh(\sqrt{u}\ell/L)} - \frac{\alpha L}{\sqrt{u}} \tanh(\sqrt{u}\ell/L) \right] \quad (9)$$

The path of integration in the complex  $u$ -plane is taken to the right of all singularities of the integrand, as indicated. The integrand of Equation (9) is a meromorphic function of  $u$  and has simple poles at

$$u_n = -\left(n + \frac{1}{2}\right)^2 \pi^2 L^2 / \ell^2 \quad (10)$$

for integer values  $n = 0, \pm 1, \pm 2, \pm 3, \dots$ \* the contour can be swung into the left-hand plane (Reference 2) and the residues may be picked up one by one, leading to the infinite series

$$N(0,t) = TGe^{-t/\tau} \sum_{n=0}^{\infty} 2 \frac{\alpha \ell^n + (-1)^n \pi(n + 1/2)e^{-\alpha \ell}}{(\alpha \ell)^2 + \pi^2(n + 1/2)^2} \exp[-\pi^2(n + 1/2)^2 Dt/\tau^2] \quad (11)$$

quoted as Equation (14) of Reference 1.

\* At first glance, a pole might be expected at  $u = \alpha^2 L^2$ , but its residue being zero, the integrand is regular at  $u = \alpha^2 L^2$ .

If we let  $l/L$  go to infinity in Equation (9) we obtain

$$\lim_{l/L \rightarrow \infty} N(0,t) = TGe^{-t/\tau} \frac{1}{2\pi i} \int_{-i\infty+b}^{i\infty+b} du \frac{e^{ut/\tau}}{\sqrt{u}(\sqrt{u} + \alpha L)} \quad (12)$$

The value of the integral can be found in a table of integral transforms such as that given by Doetsch (Reference 2) or it can be evaluated directly without undue labor. Here the latter option is taken; a number of similar integrals to be encountered below need not then be treated as extensively.

The integrand of Equation (12) has branch points at 0 and  $\infty$ . If we take the cut along the negative real axis and swing the contour so that the path of integration lies parallel and very close to the negative real axis in the complex  $u$ -plane, in such a manner that the part of the path above the cut lies on the first Riemann sheet and the part below the cut lies on the second Riemann sheet of the double-valued integrand, we obtain

$$\begin{aligned} I &= \int_{-i\infty+b}^{i\infty+b} \frac{e^{ut/\tau}}{\sqrt{u}(\sqrt{u} + \alpha L)} du = \lim_{\epsilon \rightarrow 0} \int_{-\infty-i\epsilon}^{-i\epsilon} \frac{e^{ut/\tau}}{-\sqrt{u}(-\sqrt{u} + \alpha L)} du \\ &+ \lim_{\epsilon \rightarrow 0} \int_{i\epsilon}^{-\infty+i\epsilon} \frac{e^{ut/\tau}}{\sqrt{u}(\sqrt{u} + \alpha L)} du \end{aligned} \quad (13)$$

with the substitution  $u = -x$ , this expression becomes

$$I = 2i\alpha L \int_0^{\infty} \frac{e^{-xt/\tau} dx}{\sqrt{x}(\alpha^2 L^2 + x)} = 4i\alpha L \int_0^{\infty} dy \frac{e^{-y^2 t/\tau}}{y^2 + \alpha^2 L^2} \quad (14)$$

The last integral can be found in a table of integrals (Reference 3) with the result that

$$I = 2\pi i e^{\alpha^2 Dt} \operatorname{Erfc}(\alpha\sqrt{Dt})^* \quad (15)$$

\* The complementary error function  $\operatorname{Erfc}(x)$  is defined by  $\operatorname{Erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^{\infty} e^{-\eta^2} d\eta$ .

Combining Equations (15) and (12):

$$\lim_{\ell/L \rightarrow \infty} N(0,t) = TGe^{\alpha^2 Dt - t/\tau} \operatorname{Erfc}(\alpha\sqrt{Dt}) \quad (16)$$

a result quoted in the literature (Reference 4). Evidently Equation (16) is valid if the diffusion length  $L$  is small compared to the thickness of the base region  $\ell$  of the solar cell. On the other hand, Equation (11), being exact within the limitations of the underlying theory, is valid for all ratios  $\ell/L$ .

An alternative form to Equation (11) can be found if the hyperbolic functions of the integrand of Equation (9) are expanded in powers of  $\exp(-2\sqrt{u}\ell/L)$ . The first term of such a series would only yield Equation (16) upon integration, and subsequent terms would give corrections corresponding to situations in which  $\ell/L$  becomes progressively smaller. The complete series must, however, become identical with Equation (11) upon integration. Expanding the integrand of Equation (9) in the manner proposed gives

$$N(0,t) = TG \frac{e^{-t/\tau}}{2\pi i} \int_{-i^{a+b}}^{i^{a+b}} du e^{ut/\tau} \left\{ \frac{1}{\sqrt{u}(\sqrt{u} + \alpha L)} - \frac{2}{u - \alpha^2 L^2} \right. \\ \left. \times e^{-\alpha\ell - \sqrt{u}\ell/L} \sum_{n=0}^{\infty} \left[ \left( -e^{-2\sqrt{u}\ell/L} \right)^n + \frac{\alpha L}{\sqrt{u}} \sum_{n=1}^{\infty} \left( -e^{-2\sqrt{u}\ell/L} \right)^n \right] \right\} \quad (17)$$

The first term within the braces of Equation (17) gives Equation (16), as has been demonstrated. Since the infinite sums of Equation (17) converge absolutely on the integration path, summation and integration may be interchanged. One is then left with a series of integrals that can be handled in the

same manner as the integral of Equation (13). The result of the integrations is given by

$$\begin{aligned}
 N(0, t) = & TGe^{-t/\tau + \alpha^2 Dt} \left\{ \operatorname{Erfc}(\alpha\sqrt{Dt}) - \sum_{n=0}^{\infty} (-1)^n \left[ e^{2n\alpha\ell} \operatorname{Erfc}\left(\alpha\sqrt{Dt} + (2n+1)\ell/2\sqrt{Dt}\right) \right. \right. \\
 & - e^{-(2n+2)\alpha\ell} \operatorname{Erfc}\left(\alpha\sqrt{Dt} - (2n+1)\ell/2\sqrt{Dt}\right) \\
 & + \sum_{n=1}^{\infty} (-1)^n \left[ e^{2n\alpha\ell} \operatorname{Erfc}\left(\alpha\sqrt{Dt} + n/\sqrt{Dt}\right) + e^{-2n\alpha\ell} \right. \\
 & \left. \left. \times \operatorname{Erfc}\left(\alpha\sqrt{Dt} - n/\sqrt{Dt}\right) \right] \right\} \quad (18)
 \end{aligned}$$

Equation (18) is the alternative expression to Equation (11) and is in fact identical with it. First, since  $\operatorname{Erfc}(0) = 1$ ,  $\operatorname{Erfc}(\infty) = 0$  and  $\operatorname{Erfc}(-\infty) = 2$ , the limit of  $t = 0$  yields for Equation (18)

$$\lim_{t=0} N(0, t) = TG \left[ 1 + 2e^{-2\alpha\ell} \sum_{n=0}^{\infty} (-e^{-2\alpha\ell})^n + 2 \sum_{n=1}^{\infty} (-e^{-2\alpha\ell})^n \right] = TG, \quad (19)$$

since the sums cancel. This result is identical with the limit obtained from Equation (11). Furthermore, in the limit of very large absorption ( $\alpha \gg 1$ ), it is possible to use the asymptotic approximation for  $\operatorname{Erfc}$

$$\operatorname{Erfc}(x) = \frac{e^{-x^2}}{\sqrt{\pi x}} \quad (20)$$

Under the assumption that  $\alpha\sqrt{Dt} \gg n\ell/\sqrt{Dt}$ , it can be shown that Equation (18) becomes

$$\lim_{t \rightarrow \infty} N(0, t) = \frac{TG e^{-t/\tau}}{\sqrt{\pi Dt}} \left( 1 + 2 \sum_{n=1}^{\infty} (-1)^n e^{-n^2 \ell^2 / Dt} \right) \quad (21)$$

But this expression is related to a theta function (Reference 5).

$$\theta_1(1/2, i\pi Dt/\ell^2) = \frac{\ell}{\sqrt{\pi Dt}} \left( 1 + 2 \sum_{n=1}^{\infty} (-1)^n e^{-n^2 \ell^2 / Dt} \right) \quad (22)$$

so that Equation (21) becomes

$$\lim_{t \rightarrow \infty} N(0, t) = \frac{TG e^{-t/\tau}}{\alpha \ell} \theta_1(1/2, i\pi Dt/\ell^2) \quad (23)$$

Furthermore (Reference 5),

$$\theta_1(y, t) = 2 \sum_{n=0}^{\infty} e^{-\pi(n+1/2)^2 t} (-1)^n \sin[(2n+1)\pi y] \quad (24)$$

so that finally

$$\lim_{t \rightarrow \infty} N(0, t) = TG e^{-t/\tau} \frac{2}{\alpha \ell} \sum_{n=0}^{\infty} e^{-\pi^2 (n+1/2)^2 Dt/\ell^2} \quad (25)$$

an expression that is identical with Equation (11), provided that  $\alpha \ell = 1$ . Since both series, Equation (11) and Equation (21), are identical, the question arises: which is to be preferred? As an example, take  $\alpha = 10^4/\text{cm}$ ,  $\ell = 10^{-2}/\text{cm}$  and  $D = 36 \text{ cm}^2/\text{sec}$ , corresponding to values for Si at a doping level of  $N_A = 10^{15}/\text{cm}^3$  and a wavelength of  $0.55 \mu\text{m}$  (maximum solar intensity). If  $t$  is measured in  $\mu\text{sec}$ , the arguments of the complementary error functions of Equation (18) become  $60\sqrt{t} + 3/2\sqrt{t}$  and for  $t > 1 \mu\text{sec}$ , the approximation (25) already is very good. If  $t$  is small, however, the photon energy being near the band gap, many terms of Equation (18) must be used for longer times; for the

series (11), only the first term need be retained. Therefore, Equation (11) is to be preferred. It was used in Reference 1.

Calculations similar to those made on these pages for the other cases discussed in Reference 1 lead to analogous results.

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