High resolution density of states spectroscopy in semiconductors by exact post-transit current analysis

C. Main a) and S. Reynolds
School of Science and Engineering, University of Abertay Dundee, Dundee, United Kingdom

R. I. Badran
Department of Physics, The Hashemite University, Jordan

J. M. Marshall
Dept of Materials Engineering, University of Wales Swansea, United Kingdom

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We show that the analysis of post-transit photocurrent i(t) to determine the energy distribution g(E) of trapping states in a semiconductor is capable of much finer energy resolution than has hitherto been realized. Existing methods use a Laplace inversion of i(t) data to find g(E) but employ a delta function approximation for trap release times. In this article we retain the exponential distribution function for the release time and solve the rate equations directly. The analysis is performed on computer generated post-transit data for distributed and discrete traps, and compared with the earlier method and other related transform methods for determining the density of states, g(E). © 2000 American Institute of Physics. [S0021-8979(00)08713-2]

Post-transit spectroscopy has been employed by numerous groups to determine the distribution of localized trapping states (DOS) in amorphous semiconductors, such as amorphous silicon and its alloys, 1–5 and in polymeric semiconductors. 6 The method is a variant of the time-of-flight technique in which excess carriers are created by pulsed illumination in a semiconductor structure (e.g., p-i-n). A high reverse field ensures that excess carriers emitted from any group of states which has a capture time longer than the transit time of free carriers, will transit the structure, to be collected, before retrapping in these states can occur. The resulting ‘‘post-transit’’ photocurrent decay i(t) then simply reflects progress with elapsed time t, of the rate of release of charge from traps distributed in the semiconductor’s energy gap, g(E). This situation is clearly simpler than the ‘‘pre-transit’’ photocurrent case in which retrapping occurs, and so is relatively easier to model and analyze. We note here the near equivalence between the post-transit situation in sandwich configuration, and ‘‘post-recombination’’ in coplanar geometry, if one carrier type predominates, and recombination is monomolecular.

All reports to date have made use of the approximate expression g(E) ~ i(t) to estimate the density of states, 7 together with the energy scale E = kT ln(ν), defined by associating the average release time from traps at energy depth E below the mobility edge with the elapsed time t, where ν is the attempt to escape frequency, assumed to be energy independent, k is Boltzmann’s constant, and T is the absolute temperature. We show in this article that the approximation used to obtain the above expression for g(E) is unnecessary and, most importantly, that a more exact method, which we term high resolution post-transit spectroscopy (HPT), is feasible, which has remarkably fine energy resolution.

Figure 1 compares the computed relative distribution of excess trapped charge in an exponential band-tail under conditions with no extraction (pretransit) and with extraction (post-transit), after the same elapsed time from initial excitation. The sharp variation in occupation in the latter case presents a clear advantage for a high resolution DOS spectroscopy, and is the stimulus for this work.

We consider that the continuous density of states may be represented by a very fine ladder of discrete trapping levels Nui, i = 1,2,...m, at associated energies Ei. Of the initial excess electron density N introduced by pulsed excitation, a fraction N’ is trapped, and the remainder is removed by collection, so that

\[ N' = N \frac{t_0}{t_0 + \tau_i}, \]

where \( t_0 \) is the transit time of free electrons and \( \tau_i \) is the trapping time into the ensemble of traps, of total density \( N_T \). The initial trapped fraction \( n_{\text{tr}}(0) \) is distributed according to the density of trapping states, assuming an energy independent capture coefficient, so we may write for the trapped electron distribution

\[ n_{\text{tr}}(0) = N_0 N'/N_T. \]

In the post-transit situation, the multitrapping rate equation for free electron density \( n \) reduces to

\[ \frac{dn}{dt} = \sum_i n_{\text{fr}}(t) \nu \exp \left( \frac{E_i}{kT} \right) \frac{n}{t_0}, \]

where the summation is necessarily only over deep-lying states whose combined trapping time is greater than the transit time. Retrapping terms are considered by definition to be negligible, so we can also write

a)Electronic mail: c.main@tay.ac.uk
The solution to Eq. (3) is

\[
n(t) = n(0) \exp \left( -\frac{t}{\tau_i} \right) + \sum_i n_a(0) \nu_i \exp \left( \frac{E_i}{kT} \right) \exp \left( -\frac{t}{\tau_i} \right) \exp \left( -\frac{t}{\tau_0} \right),
\]

which under post-transit conditions \((t, \tau_i \geq \tau_0)\), gives to a good approximation,

\[
i(t) = e \mu \mathcal{E} n(0) \exp \left( -\frac{t}{\tau_i} \right) = e \mu \mathcal{E} A \sum_i n_a(0) \frac{t_0}{\tau_i} \exp \left( -\frac{t}{\tau_i} \right),
\]

where \(e\) is the electronic charge, \(\mu\) is the electron mobility, \(\mathcal{E}\) is the applied field, and \(A\) is the conduction cross sectional area of the sample. At this point, the “standard” analysis converts the summation to an integral over a continuous distribution, to the form of a Laplace transform but with truncated limits, and replaces the exponential trap release time distribution factor in Eq. (6) with a delta function, \(\tau_i \delta(t - \tau_i)\). This approximation is equivalent to the assumption that all traps at a given depth release at the same time. The result is

\[
g(E) \approx ti(t) \frac{N_T}{N'e \mu \mathcal{E} A t_0 kT}.
\]

The alternative proposed in the present work, is to retain the trap release time distribution function of Eq. (6) and simply perform a fit to the photocurrent \(i(t)\) of Eq. (6), with a finely spaced set of model functions, \((A_j/\tau_j) \exp(-t/\tau_j)\), using in the first instance, a general least-squares fitting technique LMDIF1,\(^8\) where the set \(A_j\) are the adjustable fitting parameters. Values of \(\tau_j\) are preselected so that the energy range covered is appropriate to the time range of the \(i(t)\) data set. Normally values are chosen to give a uniform spacing \(\delta E(<kT)\) between levels on the energy scale. We note that since the distribution of states is assumed to be continuous, the choice of \(\tau_i\) is arbitrary, and thus not necessarily identical to \(\tau_i\), as long as the energy spacing is very close \((<kT)\). In general a very good fit may be obtained, with overall standard error value of <1%. The amplitude parameters \(A_j\) are equated with \(e \mu \mathcal{E} n_a(0)\) and we obtain the HPT result for the density of states at energy \(E_i\),

\[
g(E_i) \approx A_i \frac{N_T}{N'e \mu \mathcal{E} A t_0 \delta E}.
\]

To evaluate the proposed method, we computed the \(i(t)\) response under post-transit conditions for several representative distributions of traps, using a numerical procedure developed by the authors,\(^9\) ensuring that the value of \(t_0\) in the simulation was short enough to include any important features in the trap distribution within the post-transit time regime. We then calculated the density of states from the \(i(t)\) data using the relations of Eqs. (7) and (8), respectively. In addition to this comparison, we calculated the density of states from pre-transit \(i(t)\) data for the same representative distributions, using a Fourier transform (FT) method developed by the authors.\(^10\) We note that the FT method also involves a delta function approximation to simplify an integration, and so is also subject to a broadening effect.

In Fig. 2, we show the reproduced \(g(E)\) when the original distribution is a steep exponential tail of characteristic energy \(E_0 = 35\) meV, with superimposed, sharp Gaussian feature peaking at \(E_b = 0.3\) eV of the form \(g(E) = D \times \exp(-(E-E_b)^2/2\sigma^2)\). The energy \(E_1 = 25\) meV [full width at half maximum (FWHM) = 41.6 meV] and the factor \(D\) is chosen to give a peak 100 times the background tail density at the center of the feature. The very substantial broadening of the FT method is evident, particularly at energies below the Gaussian peak. The approximate post-transit expression of Eq. (7) is significantly better, as expected. However, the HPT method proposed in the present work follows the original density well, including the Gaussian feature.

Lastly, we present the extreme case of a DOS consisting of two discrete levels of equal density, \(1.0 \times 10^{17} \text{ cm}^{-3}\), at

\[
\delta E(<kT)\]
depths 0.3 and 0.5 eV. Computing the DOS from $i(t)$ curves gives the results shown in Fig. 3, where we have scaled the results to ease comparison. We note that the discrete levels are represented now by a $g(E)$ distribution, which when integrated should represent the same total density. The symmetrical broadening is evident in the FT method, which gives a FWHM as high as 67 meV, or 2.6 kT while the approximate post-transit analysis is only marginally sharper, and asymmetrically broadened. At the shallow energy side of the recovered DOS for each level, broadening is evident, similar to that of the FT method, while the deep energy side is rather sharper in form as expected from the observations of Fig. 1. This is a consequence of fitting the asymmetric exponential release time distribution function with a delta function. It is clear however, that the proposed HPT method gives a much sharper and symmetrical reproduction, with FWHM estimated as $\sim$12 meV, or 0.48 kT in this case.

In conclusion, we have shown that a simple procedure may be applied to post-transit pulse photocurrent data to reveal the density of localized states with very high resolution. It is often thought that this type of experiment necessarily has a resolution limited by kT broadening effects. This is not the case, as this work shows. The broadening associated with the other methods employed in the study arises because of the approximation, in each case, of a distribution function, with a delta function, in order to simplify an integral. In addition, the versatility of the new method in handling cases with either distributed traps or with discrete traps means that it can be applied to disordered materials or to crystalline materials with well-defined defect levels. We note that further improvements may be possible using optimized fitting procedures.

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