

Laplace transform deep-level transient spectroscopic studies of defects in semiconductors

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A quantitative improvement in deep-level transient spectroscopy (DLTS) resolution has been demonstrated by using Laplace transform method for the emission rate analysis. Numerous tests performed on the software used for the calculations as well as on the experimental setup clearly demonstrated that in this way the resolution of the method can be increased by more than an order of magnitude. Considerable confidence in this approach was gained through measurements of a selection of well-characterized point defects in various semiconductors. The results for platinum in silicon and EL2 in GaAs are presented. For each of these cases conventional DLTS give broad featureless lines, while Laplace DLTS reveals a fine structure in the emission process producing the spectra.

I. INTRODUCTION

Following the work of Lang,¹ deep-level transient spectroscopy (DLTS) has become a technique commonly used for the characterization of semiconducting materials. Classical DLTS uses a simple form of signal processing to produce a spectrum of deep energy levels present in the band gap of the material. It analyzes the temperature-dependent emission transient to produce a sequence of peaks on the temperature scale. This form of standard DLTS, which uses boxcar or lock-in techniques to undertake the signal processing, has excellent sensitivity.

However, the time constant resolution of standard DLTS is too poor for studying fine structure in the emission process. Among numerous reasons for this is the fundamental way the spectrum is obtained, i.e., even a perfect defect, with no complicating factors, produces a broad line on the DLTS spectrum. Any variation of time constant present in the defect emission results in an additional broadening of the peak, so this structure is practically impossible to resolve unless the time constants are well separated. Numerous authors have tried to overcome this limitation, usually by applying sophisticated peak deconvolution methods; however, the problem of extracting multiple closely spaced decaying exponentially is fundamentally ill posed.

The task of separating multiple, closely spaced, decaying exponential components in measured data recurs throughout science. In DLTS there are two broad categories of approach: analog and digital signal processing. All analog signal processing is undertaken in real time as the sample temperature is ramped, picking out only one or two decay components at a time. Fixed filters produce an output proportional to the amount of signal that they see within a particular time constant range. This is done by multiplying the capacitance meter output signal by a time-dependent weighting function. Many weighting function wave forms have been investigated, i.e., double boxcar,¹ exponential,² and multiple

boxcar.³ In summary, it appears that the most elaborate weighting function wave forms are unable to provide a very significant selectivity improvement over Lang's original scheme.

Digital schemes digitize the analog transient output of the capacitance meter, typically with a sample held at a fixed temperature and averaging many digitized transients to reduce the noise level. All of the accessible decay time constants are then picked out of the acquired wave form by software. The problem of what algorithm to use is difficult. However, consideration in the DLTS specific context is given by Ikossi-Anastasiou and Roenker,⁴ who use a "method of moments" approach, and by Nolte and Haller,⁵ who used an approximation to the inverse Laplace transform. Nolte and Haller also consider the ultimate theoretical limit of time constant separation in the presence of noise. Eiche *et al.*⁶ use a method "Tikhonov regularization" to separate the constituent exponentials in a photo-induced current transient spectroscopy (PICTS) signal. Tikhonov regularization appears to produce results similar to those that we report. More recently a simple scheme using a binomial expansion of the boxcar weighting function was reported by Thurzo, Pogany, and Gmucova.⁷ This combined a temperature scanning measurement with simple digital signal processing to obtain sharper peaks although this resulted in considerably more noise.

A common approach to the quantitative description of nonexponentiality observed in the capacitance transients is to assume that they are characterized by a spectrum of emission rates,

$$f(t) = \int_0^\infty F(s) e^{-st} ds, \quad (1)$$

where $f(t)$ is the recorded transient and $F(s)$ is the spectral density function. For simplicity, this spectrum is sometimes represented by a Gaussian distribution overlaying the logarithmic emission rate scale.⁸ In this way it was possible to

describe the nonexponentiality of the transient in terms of broadening of the activation energy for emission. The possibility that the spectrum contains fine structure is ignored.

A mathematical representation of the capacitance transients given by Eq. (1) is the Laplace transform of the true spectral function $F(s)$. Thus, to find a real spectrum of the emission rates present in the transient it is necessary to use a mathematical algorithm that effectively performs an inverse Laplace transform for the function $f(t)$. The result of such a procedure is a spectrum of deltalike peaks for multi-, monoexponential transients, or a broad spectrum with no fine structure for continuous distribution. In this method it is not necessary to make any *a priori* assumptions about the functional shape of the spectrum, except that all decays are exponential in the same direction.

Despite the fact that we define the problem in a very general way, one has to remember that Eq. (1) has not a general solution for any given function $f(t)$.⁹ For an analytical multiexponential function such a solution exists and, according to Lerch's theorem,⁹ it is unique; however, if this function is superimposed with noise the number of possible solutions can be infinite. As a result, our problem is to find the best estimate for $F(s)$ and, according to the prior knowledge about the system being investigated, exclude unphysical solutions and chose only the simplest one, i.e., the one that reveals the least amount of detail or information that was not already known or expected. Following such a strategy one knows that the amount of information obtained from a fitting procedure is as much as necessary to satisfy statistical tests performed on the experimental data.

In this article the quantitative improvement in the DLTS measurement resolution due to the use of this method is presented. The actual algorithm employed is more involved than a simple Laplace transformation;¹⁰ however, we feel that the end product of a time constant versus spectral density plot justifies our describing this as Laplace DLTS (just as a spectral density-frequency plot is described as a Fourier plot). Besides a variety of tests performed on the software used for solving Eq. (1), a further test of the method has been done through a long series of measurements on different point and extended defects in different semiconductors. We have investigated the Laplace DLTS spectra starting from a simple point defect in an elemental semiconductor (the platinum-related center in silicon), then considering EL2 in GaAs, and finally applying the technique to very complicated centers, such as the DX defects in AlGaAs,¹¹ GaSb,¹² GaAsP, and δ -doped GaAs.¹³ The most important observation from this work is that in each of the cases the standard DLTS gave featureless peaks while the Laplace DLTS spectra revealed there is a fine structure in the thermal emission process, i.e., each of the defects has its characteristic signature.

In our previous work on this topic, Laplace DLTS has been used to study the influence of the local environment of the defect on the electron emission from the DX centers related to group-IV (silicon) in AlGaAs and δ -doped GaAs and group-VI (tellurium) donor elements in AlGaAs and GaAsP.^{11–13} It provided the experimental evidence that substitutional-interstitial atom motion is responsible for DX behavior and for the associated metastability effects. We

have concluded that the atom which is subjected to this transition for $DX(\text{Si})$ silicon itself, and so in the spectra only one group of peaks in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ and one peak in δ -doped GaAs are observed. For the case of $DX(\text{Te})$ such a transition can occur for either gallium or aluminum, so producing two groups of peaks in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ and three or four broad emission bands in $\text{GaAs}_{0.35}\text{P}_{0.65}$. Using these results we are able to rule out the possibility that the DX -type defect states are formed by a donor atom in stable substitution position with small lattice relaxation or with a fully symmetric large lattice relaxation effect.

II. EXPERIMENT

For the Laplace transform DLTS measurements a standard system for isothermal DLTS has been employed. The sample was placed in a cryostat which had temperature stability of better than 0.2 K (measured over a period of at least 1 h). As a capacitance meter we have used the Boonton 72B (with slightly modified electronics to speed up the response time), or the capacitance meter implemented in the standard DLTS spectrometer SemiTrap DLS82E. Both meters differ in the response time and noise-to-signal (N/S) ratio. The instruments were carefully checked in respect of the possible influence of nonlinearity in the capacitance-voltage relationship or noise on the spectra. In principle, the capacitance meter, due to its limited response time, acts as a low-pass filter in the system. It may cause a considerable distortion in the spectra when too high a sampling rate is applied. The time interval between subsequent samples of the signal t_s is usually chosen to be much larger than the response time of the capacitance meter so avoiding a possible distortion of the spectrum in the high-emission-rate region. This value has been established for each of the meters experimentally.

The capacitance transients were sampled by a high-speed 12 bit analog-digital (A/D) converter. In any one scan 16 000 samples of the signal are typically recorded. Assuming that to establish the emission rate for the fastest process in the spectrum it takes at least the first five samples [$e_{\max} = 1/(5t_s)$] and for the longest one all 16 000 samples [$e_{\min} = 1/(16\,000t_s)$], in one spectrum the processes differing in the emission rate by three and a half orders of magnitude can be observed. The high speed of the sampling allows us to record approximately one transient per second allowing the averaging of hundreds of transients within minutes. This procedure was used to reduce N/S [proportionally to $1/\text{SQRT}(n)$, where n is the number of transients averaged] and so had a substantial influence on the resolution of the method.

In the realization of the system used now the inverse Laplace transformation of the transient is performed by using a constrained regularization method for inverting the integral equations.¹⁰ In practice, the limits in Eq. (1) are never between 0 and infinity. Usually the emission rate span in the spectrum is defined by the values of e_{\min} and e_{\max} . The important experimental condition, which must be fulfilled, is that the sampling rate and the sample temperature must be chosen in a way to assure that the spectra function $F(e_{\min}) = F(e_{\max}) = 0$, otherwise the emission rates in the transient are not properly revealed by the program. A test

spectrum is calculated initially using 50 points equally spaced on the logarithmic scale. The final spectrum is calculated using 200 points.

III. RESULTS

A. Numerical tests

The validity of the software used for the calculation has been thoroughly checked by performing a series of inverse Laplace transforms on computer-generated simulated transients. The purpose of this was to test the capability of the program to properly reveal the emission rates of the transients, the resolution of the method, and its susceptibility to noise present in real transients. In principle, the noise-to-signal ratio present in the real single transient depends on the concentration of a particular defect in the crystal. For defects with a high concentration, e.g., the DX centers (after normal averaging procedures), the N/S ratio can be as low as 10^{-4} . Consequently, the accuracy of the software and its ability to recognize the emission rates in the transient properly was tested initially at a N/S equal to 3×10^{-4} ; however, it was found that for monoexponential function, even for a N/S ratio equal to 0.5, the emission rate was still calculated properly.

Figure 1(a) shows two artificially generated transients [referred to as (i) and (ii) with added noise]. For one of them a broad double Gaussian-like spectral function [see dashed line in Fig. 1(b)] was assumed, while the other consisted of a series of monoexponential functions with the emission rates equally spaced on the logarithmic scale [see dashed line in Fig. 1(c)]. In the latter case the envelope for the preexponential amplitudes is a function identical to that given by the dashed line in Fig. 1(b). In Fig. 1(a) it is seen that the difference between these two transients is not easy to distinguish. Figures 1(b) and 1(c) present the results of calculations (transient simulation then Laplace analysis) with these assumed forms of input data. As one can see, the software perfectly reveals the difference between these transients. The left-hand band in the "continuous" spectrum [Fig. 1(b)] is slightly broader, as it was assumed in the input data, than the right-hand one. The peaks for the transient (ii) are correctly positioned with similar amplitudes compared to the original for each of them.

There is also the important question of how long a transient should be in order to contain all information about the spectral function. A simple test for this is to calculate a spectrum from only a fragment of the transient. The dotted line in Fig. 1(c) shows the spectrum where only first 33% of the transient is taken for the calculations. For the case of the discrete spectrum there is a substantial distortion of the left-hand peak. This distortion can be expected as this peak represents the longest time constant in the transient.

Because of the way the spectrum is calculated, it is the area under the peak which is proportional to the magnitude of each component in the transient. Consequently, when the emission rate is presented on a logarithmic scale, the height of the peak does not represent the true magnitude of each component in the emission process. Thus, a series of monoexponential functions with equal amplitudes produces

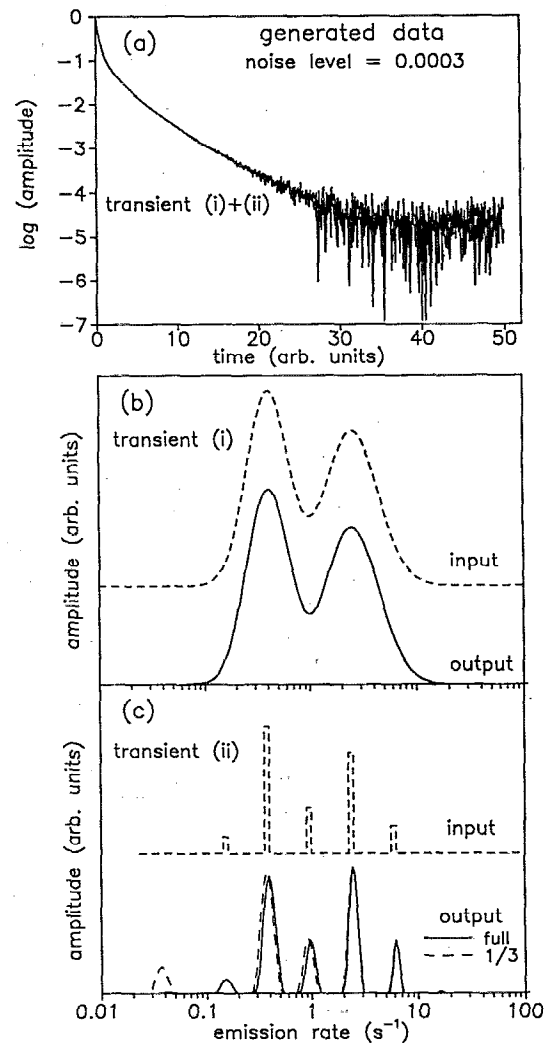


FIG. 1. (a) Two computer-generated capacitance transients with $N/S=3 \times 10^{-4}$, assumed (dashed line) and calculated (solid line) spectra for (b) transient (i) and (c) (ii).

peaks with exponentially increasing amplitudes on a spectrum.

For the discrete spectrum it was found that the calculation method gives less satisfactory results compared to those presented in Fig. 1(c) in the following circumstances: (i) the number of exponential functions is increased for the same ratio between subsequent emission rates [equal to 2.5 in Fig. 1(c)]; in this case the spectrum becomes too broad and the condition $F(e_{\min})=F(e_{\max})=0$ is not fulfilled within the allowed three and a half orders of magnitude span of the emission rates; (ii) the N/S ratio is increased; i.e., more noisy signals result in an effective decrease of resolution—in particular the position of peaks in the middle of the spectrum is not necessarily correct; and (iii) the ratio between the subsequent emission rates is decreased; i.e., in reality the peaks should be closer to each other, while in the obtained spectrum they start to merge, especially in the middle part of the spectrum. From other tests we have noticed that when a spectrum contains a large number of peaks the software has a

tendency to calculate preexponential amplitude which are smaller than the actual values for the left-hand-most peak (-s) in the spectrum. This is especially true when on the right-hand side there are peaks with considerably larger amplitudes.

B. Defects in semiconductors

In the DLTS measurements there are numerous phenomena which may lead to nonexponentiality in the thermal emission transients even for perfect point defects in homogeneous materials. The most common are caused by the fact that the defect investigated has a higher concentration than shallow centers.¹⁴ An additional universal problem is that the space region is never abrupt (the Debye tail of carriers) and the defects present in this region have different emission characteristics.¹⁵ Less commonly the nonuniform electric field always present in that region may enhance the emission process due to the Poole-Frenkel effect.¹⁶ In our study we found it essential to recognize these effects and by applying special experimental conditions, minimize their influence on the obtained spectrum. For each of the cases discussed below and in Refs. 11–13 these conditions were always established through a series of measurements until the optimum resolution of the method was achieved.

1. Platinum-related defects in silicon

Further confidence in the method was gained through measurements of the well-known and well-characterized point defect resulting from platinum in silicon. This center is thought to be a very good example of the point defect, and a high quality of the silicon crystals offered by today's technology allowed us to minimize the influence of possible crystal inhomogeneities. Figure 2(a) shows the standard DLTS spectrum for the sample of Si:Pt.¹⁷ The Laplace spectrum taken at temperature corresponding to the low-temperature peak in Fig. 2(a) showed [Fig. 2(b)] one narrow peak, with no subsidiary peaks over a range of almost two orders of magnitude above and below as would be expected from an ideal point defect in a homogeneous matrix under the measurement conditions used. Moreover, the emission behavior analyzed by the Laplace technique agreed exactly with published data for this defect and with our own conventional DLTS measurements on the same samples.

2. EL2 in GaAs

The standard DLTS method has been used for the EL2 defect by many groups to determine the characteristic parameters of the center, i.e., the activation energy for electron emission ($E_e=0.82$ eV) and electron capture cross section ($\sigma_e=4.7 \times 10^{-16}$ cm²). In our comparative study five liquid-encapsulated-Czochralski (LEC) grown GaAs:Te crystals designated no. 1 to no. 5 with electron concentrations around 10^{17} cm⁻³ but originating from different sources were investigated. We found that unlike the Si:Pt case the emission activation energy and the directly measured electron capture cross section derived from the standard DLTS measurements are in reality caused by a convolution of a group of features.

In the Laplace DLTS spectra for the EL2 defect a family of four peaks is observed.¹⁸ In Fig. 3 these lines are assigned

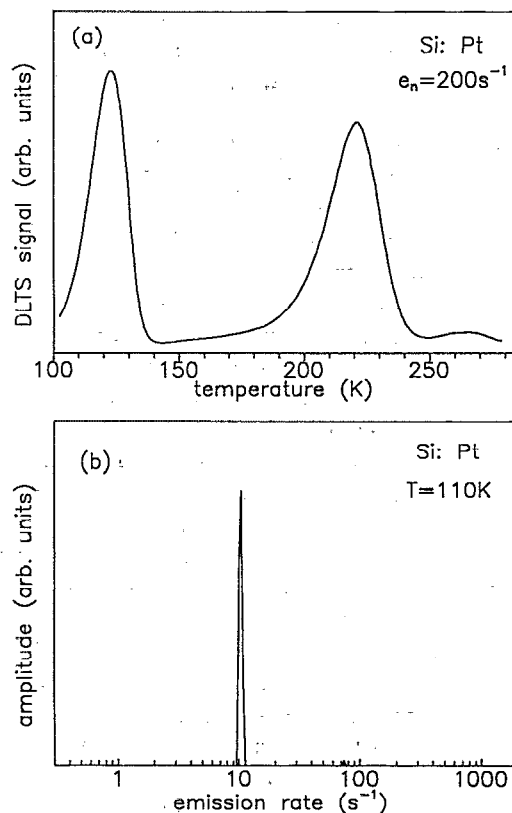


FIG. 2. (a) Standard DLTS and (b) Laplace DLTS spectra for Si:Pt. A featureless spectrum (b) indicates a perfectly monoexponential emission from the defect observed in (a) as a low-temperature peak.

by the letters A–D. For samples no. 1 and no. 2 in the spectra the peaks are much sharper which is a result of a much smaller noise-to-signal ratio in these cases. A simple inspection of the spectra presented in Fig. 3 shows that the general

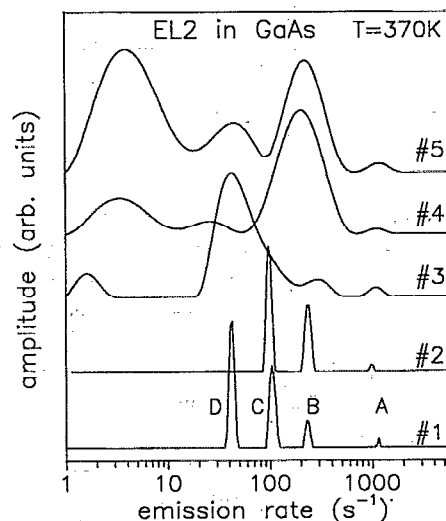


FIG. 3. Laplace DLTS spectra related to the EL2 defect in GaAs in five different samples.

pattern of the peaks (understood here as their position on the emission rate scale) is very similar for all samples. Comparing the spectrum for the sample no. 1 with that for the sample no. 2 we find that three lines from A to C perfectly match and line D is missing for the sample no. 2. For the sample no. 3 exactly the same lines as for no. 1 were seen but they are much broadened. For samples no. 4 and no. 5 the pattern of peaks is similar but the lines B and C are merged. From the Laplace DLTS spectra taken at different temperatures we obtained the activation energy for the emission process. For line A this energy is very close to $E_e = 0.82$ eV. For the other lines differences between the activation energies and E_e are smaller than few tens of meV.

The electron capture experiment revealed that the center represented by the line D and observed in the highest (among these four) concentration has an electron capture cross section orders of magnitude lower than that found for the other defect (line A). Moreover, for the peak associated with the large capture cross section (line A) a high electric field present in the space-charge region of the diode enhances the emission process (an effect whose existence in EL2 has been debated for a long time^{19–21}), while such a phenomenon is not observed for the dominant peak.

The Laplace DLTS, similarly to conventional DLTS, allows the concentration profiles for each component of the spectrum to be investigated. The defect represented in the spectrum by line A has a uniform distribution in the diode space-charge region, and this defect among all four has the lowest concentration. The concentrations of the defects represented by lines B and C increase slightly with the increasing distance from the crystal surface, while the concentration of the defect represented by line D steeply decreases.

These results show that there is a possibility that the EL2 center commonly observed in the GaAs crystals is always accompanied by another defect which slightly modifies its emission characteristics as a result of the electrostatic potential. Such a defect configuration has been debated for a long time, in relation to interstitial arsenic present close to the center being responsible for some ambiguity seen in other local environment sensitive experiments. Alternative interpretations of the EL2 data involving oxygen-related centers in the crystal have also been proposed.¹⁸

IV. SUMMARY

The quantitative improvement in the DLTS measurement resolution has been demonstrated when an algorithm that effectively performs an inverse Laplace transform is used. Numerous tests performed on the software used for the data analysis and on the experimental setup clearly demonstrate that the resolution of standard DLTS can be increased by orders of magnitude. This improvement is achieved due to fundamental reasons: The standard DLTS method, even for perfect point defect in a homogeneous semiconductor, gives a broad peak, while the isothermal Laplace DLTS in such a case results in a sharp narrow peak. The efficiency of the method is illustrated by the results of measurements on different point defects in different semiconductors. For each of the cases the standard DLTS gives broad featureless peaks,

while the Laplace DLTS revealed a fine structure in the emission process producing the spectra, these often being definitive fingerprints of the defects. We have compared conventional and Laplace DLTS spectra from simple point defects such as the platinum-related center in silicon, from EL2 in GaAs, and complicated centers such as the *DX* defects in alloys.

The most promising avenue for the future development seems to be a combination of the Laplace DLTS with an internal or external disturbance of the emission process. A good example of the former case is an influence of the local alloy environment (similar to the case of the *DX* centers) on the emission. The latter case can be realized by using uniaxial stress, hydrostatic pressure, magnetic or electric fields. The high resolution offered by the method may, in these cases, successfully measure the small influence these perturbation have on the emission process giving the scientific community a new tool for the defect identification.

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