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# Laplace deep level transient spectroscopy: Embodiment and evolution

A.R. Peaker [a,*], V.P. Markevich [a], I.D. Hawkins [a], B. Hamilton [a], K. Bonde Nielsen [b], K. Gościński [c]

[a] Photon Science Institute and School of Electrical and Electronic Engineering, University of Manchester, Sackville Str. Building, Manchester M13 9PL, UK
[b] Department of Physics and Astronomy, University of Aarhus, Ny Munkegade, DK 8000 Aarhus C, Denmark
[c] Institute of Physics, Polish Academy of Sciences, al. Lotnikow 32/46, 02-668 Warsaw, Poland

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ABSTRACT

This paper is to commemorate the work of Leszek Dobaczewski[1] who devoted much of his life to the development and application of high resolution DLTS.

Under good experimental conditions Laplace DLTS provides an order of magnitude higher energy resolution than conventional DLTS techniques. This has had a profound effect on electrical defect spectroscopy enabling the effect of external probes, such as uniaxial stress, and internal perturbations, such as the proximity of atoms isovalent with the host, to be quantified in terms of electronic behaviour. Laplace DLTS provides a synergy with other techniques that was difficult or impossible to achieve previously. In this paper we present an overview of the development of LDLTS and illustrate some of its uses by describing its application in a number of key areas of defect research.

Leszek Dobaczewski was born on 25th December 1954. He received his education in Warsaw taking his PhD in 1986 with Jerzy Langer at the Institute of Physics on "*Recombination Processes at defects with the large lattice relaxation*". He held a research position at the institute in Warsaw until he came to Manchester in 1990 and thereafter alternated between Manchester and Warsaw. He worked primarily on the development and application of high resolution DLTS. He was awarded the degree of DSc in 1994 for his work on DX centres and held an appointment as full professor in Warsaw with Visiting Professor posts at Manchester and Aarhus.



Leszek Dobaczewski (1954 to 2010).

## 1. Introduction

The capture and thermal emission of carriers from defects in semiconductors has been used as a characterisation tool for over half a century. In 1970 Sah et al. [1] reviewed the field and established a general formalism for the processes involved. This was important because a very significant advance came into general usage in the late 60s when the technique was applied to pn junctions or Schottky barriers. In these structures the carrier occupancy of the defects could be modulated within a depletion region. This was a stark contrast to the earlier work, which used bulk or compensated materials. This could result in ambiguities and much lower detectivities. In bulk or compensated material the carrier emission was observed as a current whereas in the depletion region case emission from the defect state could be monitored by current, or by a change of capacitance, reflecting the charge in the depletion region. In general a capacitance measurement is preferable as it distinguishes between the emission of holes and electrons by presenting a different sign of capacitance change and, in most practical cases, it also provides greater sensitivity.

Fig. 1 illustrates the generalised capture and thermal emission process with equations describing the behaviour. Measurements in this early era typically recorded the emission transient over a range of temperatures where the time constant of the decaying exponential transient was of the order of seconds or longer. The transient was usually saved on a chart recorder and the result analysed graphically by plotting on a semilog scale. This worked well if the transient could be represented by a single exponential but often, as shown in Fig. 1, the emission emanated from more than one defect. In such cases the longest time constant could be extracted and subtracted from the experimentally observed

* Corresponding author. Tel.: +44 161 306452.
*E-mail address:* peaker@manchester.ac.uk (A.R. Peaker).
[1] Professor Leszek Dobaczewski died in April 2010.

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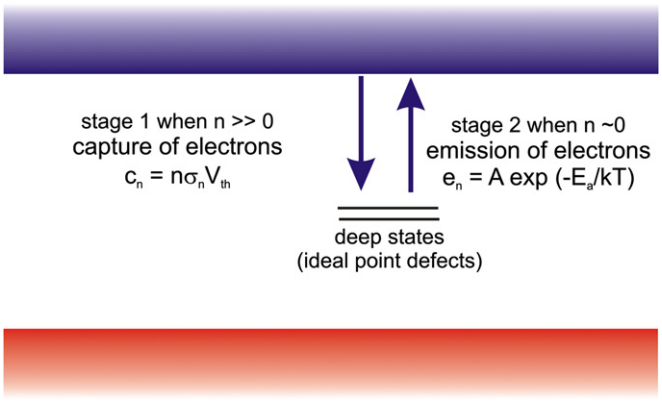



**Fig. 1.** Band diagram showing capture and emission processes from deep states.

transient, so leaving the difference to be analysed in the same way. Up to three well separated exponentials could be quantified with this method but the analysis was tedious particularly as the experiment had to be repeated several times at different temperatures to extract the activation energy of the emission process.

The situation changed dramatically in 1974 when Lang published a paper describing an elegant way of displaying emission data spectroscopically in which a signal related to the magnitude and time constant of the exponential was plotted as a function of temperature [2]. Lang adopted a very simple approach to analyse the transient, which he called "Deep Level Transient Spectroscopy" and is now universally referred to as DLTS. He simply took two samples of the transient at different times and displayed the difference as a function of the temperature of the semiconductor device.

The emission rate increases rapidly as a function of temperature:

$$e_n(T) = \sigma_n \langle \nu_n \rangle \frac{g_0}{g_1} N_c \exp\left(-\frac{E_c - E_t}{k_B T}\right) \quad (1)$$

where $E_c - E_t$ is the energy separation of the deep state from (in this case) the conduction band. The degeneracy terms $g_0$ and $g_1$ refer to the state before and after electron emission, respectively. The parameter $\sigma_n$ is the electron capture cross section, which may be temperature dependent. In this equation the thermal velocity of electrons $\langle \nu_n \rangle$ and the effective density of conduction band states $N_c$ are temperature dependent.

If the transient is very fast there is no difference between the two sampled values and similarly if the transient is very slow the values are identical. However at some intermediate value, (a time constant roughly equal to the time difference between the samples taken of the transient), the difference is a maximum. The emission rate corresponding to this time constant was called the rate window. The output provided the user with an immediate picture of the defect population, in the material under test, in the form of a series of peaks on a temperature scale. The magnitude of a peak is proportional to the defect concentration and the position of the peak on the temperature scale is related to the energy required to emit a carrier. DLTS outperformed previous techniques for deep level measurements in terms of signal to noise because, unlike older methods such as Thermally Stimulated Current, the transient was repetitive and could be averaged many thousands of times. Lang also chose to develop DLTS with transient time constants of the order of milliseconds or a tenth of a millisecond. This region of the spectrum (0.5 to 50 kHz) is particularly free from noise.

DLTS made thermal emission measurements user-friendly and the appearance of commercial equipment on the market to undertake such measurements made it a routine technique in thousands of labs worldwide. However Lang's simple and elegant approach to the problem of exponential analysis came at a cost, namely that the ability to resolve similar time constants was poor. In Fig. 1 this can be thought of as being able to resolve the two energy levels representing defects with similar emission rates. The precise figure for DLTS depends on the actual sampling times but typically DLTS cannot resolve emission rates clearly, which have a ratio of less than 15. This results in similar emission rates appearing as a single broad peak. In consequence the linewidth is due primarily to the instrumental broadening of the technique. This is far greater than the thermal broadening in the measurement. It is a major barrier to the use of DLTS to obtain the sort of detailed physical information about the defect, which is typical of optical techniques. This review is about the quest for higher resolution in thermal emission measurements and Leszek Dobaczewski's pivotal role in achieving that in the form of Laplace DLTS.

## 2. The quest for higher resolution

Lang was acutely aware of the resolution problem associated with DLTS and so his colleagues at Bell labs [3] and many others [4] began working on analogue correlation techniques, which might provide a better resolution of emission rates. In Manchester although we initially followed this development of analogue filters, we soon moved to digitising DLTS transients. This was because a digital approach offered much greater flexibility in subsequent analysis. A timeline of a selection of the key developments on the road to Laplace DLTS is given in Table 1.

A central issue here is that extracting exponentials with similar time constants from experimental data, on which noise is superimposed, and which has an unknown baseline, is an extremely difficult task both mathematically and experimentally. The many aspects of this problem are discussed elsewhere [5–8] but the key issue is that noise sets the fundamental limit for extraction of time constants of exponential decays. It can be shown, in general, that the ability to distinguish closely spaced time constants, the dynamic range of transient amplitudes and the emission rate range measurable are all dependent on signal to noise ratio.

A 1987 paper by Nolte and Haller [8] highlighted these issues but it was not until 1999 that a comprehensive review of the experimental and analytical issues associated with exponential analysis was published by Istratov and Vyvenko [5].

**Table 1**
Laplace DLTS Timeline.

| | |
|---|---|
| 1970 | CT Sah publishes milestone paper in Solid State Electronics [1] |
| 1974 | Lang DLTS [2] |
| 1975 | Miller et al. analogue correlation techniques for DLTS [3] |
| 1981 | Crowell and Aliphani use analogue filters with proper account of baseline [4] |
| 1987 | Nolte and Haller review fundamental requirements for high resolution DLTS [8] |
| 1989 | Hawkins et al. build low noise digital DLTS system in Manchester |
| 1990 | Dobaczewski takes up appointment in Manchester |
| 1991 | CONTIN [9] with Tikhonov regularisation used for LDLTS by Dobaczwski[11] |
| 1991 | First LDLTS results (paper on DX centres at ICDS 16) [11] |
| 1993 | UK National Physical Laboratory prize for LDLTS technique |
| 1995 | Honerkamp's group writes new Laplace algorithms (EU contract) |
| 1996 | Goscinski, Dobaczewski and Hawkins create "usable" LDLTS |
| 1997 | UK Royal Academy of Engineering award (uniaxial stress DLTS techniques) |
| 1998 | Onwards … use of LDLTS by the defect community |

In Manchester during the 80s we developed several DLTS systems including the one that was extensively marketed by Polaron and subsequently by BioRad. We also developed a very low noise digital system. There are many sources of noise in a DLTS experiment the most obvious are broad spectrum noise, digitisation noise and repetitive noise e.g. 50/60 Hz. In general these can be reduced by good engineering and signal averaging. However 1/f noise is particularly insidious and is often the limiting issue.

A form of noise, often overlooked, but which is central to thermal emission measurements is the variation in emission rate, which results from temperature instabilities during transient averaging. It can be seen from Eq. (1) that the emission rate is a rapidly moving function of temperature. In consequence very small variations in the temperature result in important changes in the transient.

This is an issue, which had not been given adequate consideration in work published in the 80s. The logical conclusion of attaching high importance to temperature stability is the need to conduct the measurements isothermally. It is necessary to repeat the isothermal measurement at different temperatures in order to obtain the activation energy but it is highly desirable to consider each temperature as a separate problem for analysis.

The central issue to this analysis is how to convert the transients from the time domain to the frequency domain. As we are dealing with the exponential decays it is self-evident that the appropriate mathematical procedure is an inverse Laplace transform. However applying Laplace in the presence of noise and an unknown baseline presents a serious challenge to mathematicians and experimentalist alike. It was at this point that Leszek Dobaczewski joined the team addressing these problems at Manchester.

Dobaczewski was familiar with CONTIN *"A general purpose constrained regularization program for inverting noisy linear algebraic and integral equations"* written by Provencher [9], who had made the FORTRAN source code available. Any extraction of time constants from an experimental exponential decay is ill posed—i.e. it has more than one solution or perhaps no mathematical solution. In applying CONTIN the main challenge was to constrain the solutions to physically feasible ones. This process is referred to as regularisation and there are numerous ways of computing such regularisation, which are specific to particular cases. CONTIN is used with Tikhonov regularisation [10] via a function written by Dobaczewski for thermal emission of carriers from defects.

Although the Laplace DLTS analysis has evolved substantially over the 20 years since Dobaczewski did this pioneering work, the basic constraints imposed by the regularisation are essentially unchanged. Basically the user must see a spectroscopic output, which is a genuine representation of the number of exponentials contained in the transient (this is crucially important in many experiments, for example uniaxial stress); it must present a measure not only of the time constant but also the magnitude of that component and if the transient contains a continuum of time constants (e.g. resulting from inhomogeneous strain or field effects) the output should reflect that rather than make an attempt to resolve, unrealistically, many discrete time constants.

It took almost a year to develop the system to a level at which we began to get novel scientific results. The first results were presented at ICDS 16 on "*Laplace transform DLTS studies of the DX centers in AlGaAs and GaSb*" [11]. To give an example of the performance of the system at this stage it would typically take an entire day to capture a set of transients at five temperatures and then an overnight run on a VAX computer to evaluate the results. Signal to noise performance for a defect at around 5% of the carrier concentration was $\sim$1000 and states with a separation $e_1/e_2=4$ could be resolved ($\sim$4 meV). This was a factor of four improvement on conventional DLTS and enough to enable some new science to be achieved.

Several papers on Laplace DLTS of III–V compounds followed and in 1993 the UK National Physical Laboratory Prize for Measurement was awarded to Dobaczewski, Hawkins and Peaker for the development of Laplace DLTS.

The subsequent development of Laplace DLTS into a higher performance and more generalised system proceeded under a European Union Research Contract within the Copernicus Scheme (1995–1998). In addition to the University of Manchester and the Institute of Physics Warsaw this involved the Semiconductor Physics Institute, Vilnius, Lithuania (A. Matulis and Z. Kancleris), and the University of Freiburg, Germany (J. Honerkamp, D. Meier, J. Winterhalter). These two groups had considerable expertise in the mathematics of inverse problems and developed routines for the Laplace DLTS system, which extended the capabilities of the original equipment beyond those established by Dobaczewski using variants on CONTIN.

A subsequent UK EPSRC award funded The University of Manchester in collaboration with the Warsaw Institute of Physics to develop a user-friendly system and to undertake some research on specific defects.

## 3. Application of Laplace DLTS

The most obvious application is simply to separate defects with similar emission rates, a situation often resulting from very similar energy levels in the semiconductor band gap. The performance of Laplace DLTS today is that for a signal to noise ratio of 1000 and a temperature stability of $\pm 20$ mK $e_1/e_2=2$ can be resolved translating into $\sim$2 meV energy separation at 100 K. In general the transient capture continues until the magnitude of the transient above its quiescent value is comparable with the RMS noise.

An example of the use of this in the solution of a long standing problem is shown in Fig. 2 reprinted with the permission from [12] copyright 1998, American Institute of Physics. In this diagram the inset shows a conventional DLTS scan of a silicon sample doped with gold, which had been processed in such a way that it had become contaminated with hydrogen. The main figure shows a Laplace DLTS measurement of the same sample. Two peaks relating to different defects are evident. One is due to substitutional gold in silicon the other to a gold–hydrogen complex known as G4. Although the presence of G4 had been inferred previously by other workers from the slight broadening of the conventional DLTS peak, the clarity achieved through the higher resolution of Laplace DLTS is stark. The paper describes experiments where the hydrogen is dissociated from the gold by annealing and G4 transformed into substitutional gold, a deduction supported by precise quantative measurements of the concentration of G4 and the gold using LDLTS [12].

Fig. 3, which is based on data first published by Gościński et al. [15], illustrates a perturbation to the emission properties of gold in silicon–germanium resulting from the proximity of germanium to the gold in a predominantly silicon lattice. This internal perturbation can be seen in the Laplace DLTS spectrum in the form of separated emission rates for gold surrounded by four silicon atoms or three silicon atoms and one germanium and the case where there are two germanium and two silicon atoms in the nearest neighbour positions. The measurements shown were made on unstrained bulk SiGe grown by the Czochralski process with 0–5% Ge. In conventional DLTS the effect is not detectable. The distribution is easily quantified by Laplace DLTS and when compared statistically to a random distribution it is evident that

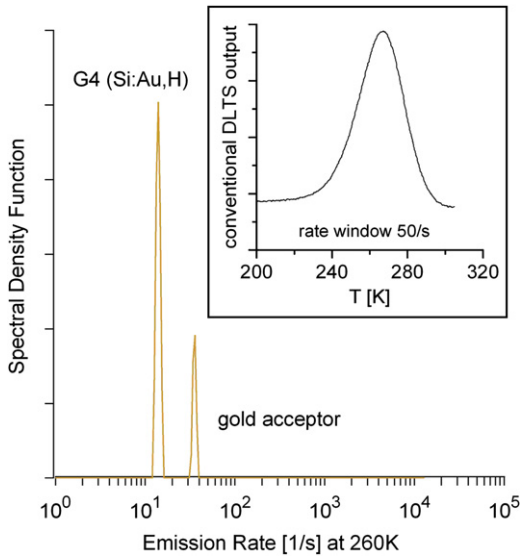



**Fig. 2.** DLTS and LDLTS spectra of hydrogenated silicon containing gold. The conventional DLTS spectrum is shown as an inset at the top right of the figure. The broad peak centred at 260 K is due to electron emission from the gold-acceptor and gold–hydrogen G4. The main spectrum uses the Laplace technique to separate the gold-acceptor level and the gold–hydrogen level.

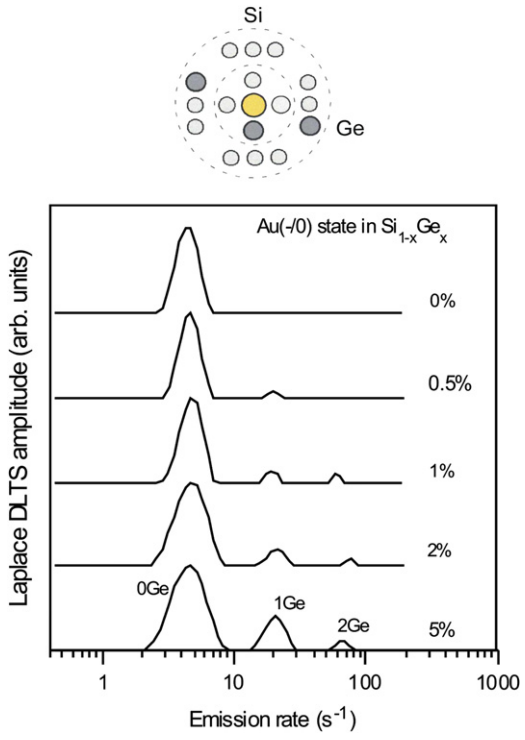
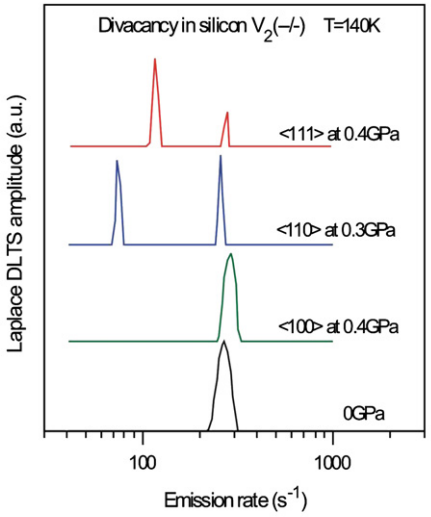



**Fig. 3.** Laplace DLTS spectra of gold-diffused SiGe samples having different germanium content. For each of the spectra the main lines have been aligned and normalised to the 5% sample.

there is a marked preference for gold to site near to germanium [13–15].

One of our early motivations in trying to achieve higher resolution in DLTS measurements was the possibility of determining defect symmetry from electrical measurements. This is immensely valuable data in identifying a defect and its lattice siting. Although using uniaxial stress to lift the degeneracy in optical absorption and photoluminescence is well established, the splitting observed in DLTS is usually too small to be conclusive unless extreme levels of stress are applied with the resultant experimental problems and sample breakages [16]. Fig. 4, which is based on work by Dobaczewski et al. [17], shows a clear resolution of the symmetry of the double acceptor state of the di-vacancy in silicon using Laplace DLTS with stresses of around 0.4 GPa being applied to bars orientated in the major crystallographic directions. This level of stress is easily manageable and breakages of the samples are not common in well prepared bars of silicon. However in germanium the situation is rather different and considerable care is required to avoid breakages and so to obtain useful information [18].

As well as determining the symmetry of the defect from the splitting it is also possible to extract quantative values for the piezo-elastic tensor. This combined with ab-initio modelling and the symmetry information can sometimes be used to establish the detailed structure of a defect [e.g. 19].




| | splitting ratios | | |
|---|---|---|---|
| system | <111> | <110> | <100> |
| trigonal ($D_{3d}$) | 3:1 | 3:3 | 3:0 |

**Fig. 4.** Laplace DLTS spectra of the double acceptor state of the di-vacancy in silicon taken without stress and with stress applied along the three major crystallographic directions. The splitting indicates the defect has trigonal ($D_{3d}$) symmetry.

**Fig. 5.** Leszek Dobaczewski talking to Dave Lang and Tony Peaker at ICDS in Albuquerque during 2007.

Many other types of defect studies have been undertaken including defect reorientation kinetics, in-situ measurements of unstable species, the transmutation of radioactive nuclides in semiconductors at ISOLDE (CERN), studies of MOS interfaces and of quantum dots. More details of these can be found in the literature and are catalogued on the Laplace DLTS website [20].

## 4. Epilogue

The fact that we have Laplace DLTS as a tool for defect studies is due to the efforts of many people and help and advice from researchers working in a wide spectrum of specialities. However what is quite certain is that without the dedication of Leszek Dobaczewski it is unlikely that Laplace DLTS would exist as a usable technique. Leszek was a regular and very active contributor to the ICDS conference series; Fig. 5 shows him with Dave Lang and Tony Peaker at ICDS in Albuquerque in 2007. Sadly this was the last ICDS he was able to attend and he is sorely missed by his many friends and colleagues in the defect community.

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