Broadening effects and ergodicity in deep level photo-thermal spectroscopy of defect states in semi-insulating GaAs: a combined temperature-, pulse-rate- and time-domain study of defect state kinetics

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Abstract. The technique of Deep Level Photo-Thermal Spectroscopy (DLPTS) is extended to the low temperature region in order to cover several defect states in semi-insulating GaAs. Measurements are taken at three different modes, temperature-scanned, pulse-rate-scanned, and time-scanned DLPTS. It is demonstrated that each mode provides unique information about the defect configuration, and the combination of the different modes offers a powerful tool for DLPTS studies of physical optoelectronic processes in SI-GaAs. The non-exponentiality/broadening of experimental data is extensively studied using the two prevalent broadening theories: the stretched exponential and the Gaussian distribution of activation energies. A hierarchical carrier emission model has been proposed for the stretched exponential behavior. Simulations indicate that the two broadening theories exhibit roughly similar broadening effects and good fits to the experimental data. The origin of this similarity indicates an ergodic equivalence of random energy distribution and the constrained hierarchical emission process.

1. Introduction
Deep Level Transient Spectroscopy (DLTS), first introduced by Lang [1], is a powerful tool for detection and characterization of deep-level generating defects in semiconductors. In DLTS, the systems under study have often been assumed to have a sharp, well-defined energy level, represented by a Dirac delta function, which leads to a single exponential decay in the ideal DLTS transient. This assumption, however, is not true for real semiconductor systems. In recent years, considerable amounts of work have been reported on the non-exponential behavior of DLTS transients [2, 3]. The non-exponentiality is also observed in the temperature scans as a broadened spectrum [4]. Three models have been mainly proposed for the fitting of non-exponential data. These are the multi-exponential model [2], the William-Watts model [3], and the distribution of defect parameters [4]. Although all these models have been successfully used for the fitting of experimental data, they are based on different physical assumptions, and are usually studied independently without comparative evaluation. In this paper, the newly developed DLPTS [5] is used to study broadening phenomena in
SI-GaAs, and seeks to provide a comprehensive comparison in different broadening models with the combined study in temperature-, pulse-rate- and time-domain measurements.

2. Overview of photo-thermal spectrum broadening theories

The broadening of DLTS spectra is a common feature observed in various types of semiconductor samples [2, 4]. A possible origin of this broadening is the distribution of defect parameters caused by i) the random distribution of specific atoms and/or ii) the fluctuating random Coulomb potential of ionized shallow impurities [4, 6]. Due to the random nature of these phenomena, the distribution function is usually assumed to be Gaussian based on the central-limit theory [4].

In the time domain, broadening is presented as a non-exponential transient. A convenient way of characterizing non-exponentiality is to write it in the form of a stretched exponential (William-Watts decay) [3]

$$I(t) = \exp[-(\epsilon_n t)^\beta]; \quad \beta \leq 1,$$

where $\beta$ is the stretching factor, $I(t)$ is the transient signal, and $\epsilon_n$ is the thermal emission rate of trapped carriers. Properties of the stretching factor $\beta$ in SI-GaAs have been studied by Giri and Mohapatra [3], who found that $\beta$ was smaller at lower temperatures. Due to the limited number of sampled temperatures, they did not derive a relation between $\beta$ and temperature. The physical origin of the stretched exponential has been proposed in various models: i) depth dependent photo generation, ii) parallel relaxation, and iii) hierarchical relaxation. [6,7] Of all these models, the hierarchical relaxation originally proposed for glassy systems is best suited for SI-GaAs because it includes a possible temperature dependence of $\beta$ and the constrained thermal emission caused by changes in defect state energetics. A generalized expression for hierarchical relaxation model is shown in Eq. (2)

$$\beta = 1 / [1 + \mu_0],$$

where $\mu_0$ is a spin number defined in the model [7].

A similar expression can be derived in the semiconductor system by assuming a defect occupancy dependent activation energy Eq. (3).

$$\epsilon_n [T, n_i (t)] = \phi (T) \exp \left( -\frac{E_0 \pm \Delta E_0 [n_i (t)]}{k_B T} \right) = \epsilon_n (T) \exp \left( -\frac{\pm \Delta E_0 [n_i (t)]}{k_B T} \right).$$

Comparing Eq. (3) with the stretched exponential (Eq.(4))

$$\epsilon_n [T, n_i (t)] \cdot t = [\epsilon_n (T) t]^\beta,$$

we obtain [6]:

$$\beta (T) = 1 / [1 + \Delta E_0 / (k_B T)].$$

Here $\Delta E_0$ reflects the variation on trap activation energy during the thermal emission/capture process. Compared with the general expression in Eq.(2), $\Delta E_0 / (k_B T)$ here represents the number of electronic degrees of freedom (measured in units of the carrier thermal quantum $k_B T$) available to each trapped carrier during the activation process of the trap. The nature of $E(t)$ as emission/capture processes under way change the activation energy for the remaining emission/capture events is consistent with the more general hierarchical origins of stretched exponentials in kinetic systems [7]. Since $\Delta E_0$ depends on the local environment of interacting defect states under study, it should have a correlation with energy distribution functions. Simulations of DLPTS theory in the next section demonstrates that for equivalent energy-level broadening effects between stretched exponential, $\Delta E$, and Gaussian, $\delta E$, distributions, $\Delta E_0 = \delta E / 1.5$, and helps elucidate the physical implications of this equality. The Gaussian and stretched exponential broadening are incorporated into the simplified solution of rate equations [8], and are used for simulations in the following sections.

3. Experimental results and discussion.
The sample used in the experiment is a Vertical Gradient Freeze (VGF) growth SI-GaAs with an EL2 concentration around $10^{16}$ cm$^{-3}$. Details of the experimental setup can be found in previous publications [5, 6].

Figure 1 shows the DLPTS temperature-scanned spectra at various pulse repetition frequencies. For better illustration, the amplitude spectra are normalized and separated by 0.2 (normalizing factor) and the phase spectra are separated by 20°. There are two major peaks in the amplitude photo-thermal spectra and the peaks shift to higher temperatures as the frequency increases. The defect states of the two main peaks can be obtained through an Arrhenius plot and were identified to be the EL3 (0.59 eV) and EL6 (0.21 eV) levels [6]. However, using the two main defects, the temperature scanned spectra did not fit well[6]. Since there are several defect states in SI-GaAs [9], more defects are added into the simulation until a satisfactory fit is obtained. The solid lines in figure 1 show the best fitted temperature scanned spectra and table 1 summarizes the defect parameters obtained from the fitting. It should be noticed that the best-fit parameters to DLPTS spectra presented here are primarily based on the temperature-scanned spectra; however data from other DLPTS modalities have been derived and used. The optical generation rate, $G_{op}(t)$, used here is determined from the pulse-rate scans, and the relative contribution of $n(t)$ and $nT(t)$ absorption is determined from the time-domain transients. As a result, Table 1 reflects the final best fitting parameters, and was also used in the pulse-rate- and time-domain theoretical fits. A detailed discussion of these parameters is presented in the following sections.

![Figure 1](image_url)

**Figure 1.** Experimental and simulated temperature scanned DLPTS spectra at various frequencies. (a)\&(c): Gaussian activation energy broadening. (b)\&(d): stretched exponential broadening.

It can be seen that both Gaussian and stretched exponential theories fit very well at all frequencies. The similarities between the two broadening configurations offer major physical insight. Ergodic systems are equilibrium statistical ensembles in which time statistics is equivalent to statistics based on energetically random distributions in an appropriate phase space of microstates. The experimental proof of validity of an ergodic hypothesis in the case of trapped carriers in SI-GaAs and other semiconductors is tantamount to a statement that all accessible trap microstates are equally probable
over a long period of time [10]. This period can be on the order of the time required to empty (emission) or fill (capture) the trap and it is much longer than the interaction time among the member electron or hole population of a trap or defect. The existence of this type of equivalence in the case of semiconductors, and SI-GaAs in particular as revealed by temperature-scanned DLPTS, points to a photo-carrier ensemble statistical ergodic relationship and thus renders the Gaussian energy distribution a meaningful statistical mechanical quantity. The nature of the trapped carrier ergodicity needs to be investigated further. In Table 1, the ratio between $\delta E$ and $\Delta E$ is 1.5 for most defect levels. Some discrepancies exist on shallow (small activation energy) defect levels, where the ratios are significantly smaller than 1.5. Considering semiconductor systems are usually less disordered at low temperatures than at high temperatures, observations here indicate that the statistical relation between $\delta E$ and $\Delta E$ is influenced by the degree of disorder in the system and defines the temperature extent of ergodicity. The obvious ergodic inference of the relation $\delta E = \text{const.} \times \Delta E$ is that the extended electronic carrier microstate distributions within the trap levels for which the relation holds are equivalent to the hierarchical emission/capture kinetics of the carrier ensemble out of/into the energy distributed levels, respectively.

| Table 1. Summary of defect states detected by DLPTS |
|------------------------------------------|
| $E_n$ (eV) | $\sigma_n \times 10^{13}$ (cm$^2$) | $N_T \times 10^{15}$ (cm$^3$) | $\delta E$ (eV) | $\Delta E_0$ (eV) | $\delta E / \Delta E_0$ |
| EL2 | 0.76 | 6.0 | 0.03 | 0.06 | 0.04 | 1.5 |
| HL3 | 0.65 | 6.7 | 0.03 | 0.03 | 0.020 | 1.5 |
| EL3 | 0.58 | 2.7 | 1.0 | 0.035 | 0.021 | 1.67 |
| EL4 | 0.52 | 13.67 | 0.2 | 0.075 | 0.05 | 1.5 |
| EL5 | 0.48 | 3.53 | 0.15 | 0.083 | 0.055 | 1.5 |
| HB5 | 0.40 | 8.39 | 0.239 | 0.068 | 0.055 | 1.24 |
| EL6 | 0.34 | 4.0 | 0.232 | 0.057 | 0.038 | 1.5 |
| EB7 | 0.29 | 5.38 | 0.40 | 0.032 | 0.027 | 1.19 |
| EL14 | 0.24 | 7.0 | 0.40 | 0.029 | 0.027 | 1.07 |
| EL17 | 0.21 | 9.4 | 0.364 | 0.027 | 0.025 | 1.08 |

Figure 1c,d shows experimental and theoretical phase spectra. The phase spectrum is neglected in most DLTS based techniques, mainly because it does not exhibit defect peaks like the amplitude spectrum. Our simulation demonstrates that each peak in the amplitude spectrum has a correlated reversed peak in the phase spectrum. An unexpected decrease at the high temperature end can be seen in the 4 kHz phase spectrum. This decrease is most likely due to the onset of another phase peak. Simulations on the broadened DLPTS theory indicate the decrease is due to the superposition of the HL3 and EL2 levels. The EL2 concentration in Table 1 is much lower than the value provided by the vendor ($10^{16}$ cm$^{-3}$). This is because the DLPTS theory uses the same absorption coefficient for all defect states[8]. The real defect concentration needs to be corrected once the defect absorption can be accurately determined.

Figure 2 shows the pulse-rate scanned spectra at various temperatures. In these measurements, the laser pulse duty cycle is fixed at 1% while the repetition frequency is scanned. The pulse-rate spectra exhibit a broad peak, which shifts to higher pulse rates as the temperature increases. The theoretical fits indicate this peak corresponds to the EL3 level, which is also the above room temperature peak in the photo-thermal temperature spectrum. The theoretical consistency of the EL3 peak positions between temperature-scanned and pulse-rate-scanned DLPTS spectra enhances the trap energy state diagnostic capability of DLPTS over other single-signal producing methodologies. This self-consistency check can only be made by comparing the photo-thermal pulse-rate scan with the
temperature spectrum. Theoretical pulse-rate-scanned spectra are also shown in figure 2. It can be seen that the two broadening theories give similar results in the pulse-rate scans in further agreement with the ergodic considerations of the trapped photo-carrier ensemble. Discrepancies, mainly in the high pulse-rate regime, are reflected as a narrower theoretical peak than the experimental one. Compared with the temperature-scanned results, these discrepancies could be related to the disagreements between theory and experiment at high pulse-rates in the temperature phase spectrum. Origins of these discrepancies are likely due to the approximations used in deriving the time domain theory, such as neglecting the re-capture components[8].

Figure 2. Experimental and simulated pulse-rate scanned DLPTS spectra at various temperatures. (a): theory with Gaussian activation energy broadening. (b): theory with stretched exponential broadening.

Unlike the temperature spectra, the peak position in the pulse-rate spectrum is also sensitive to the optical generation rate, $G_{op}(t)$, where a higher $G_{op}(t)$ shifts the peak to higher frequencies. Although $G_{op}(t)$ could in principle be calculated from the laser power, the actual amount of light entering the sample after reflection and scattering is hard to determine. Our fitting of the pulse-rate domain spectrum indicates $G_{op}(t)=2\times10^{23}$ cm$^{-3}$s$^{-1}$, and it takes on only half of the calculated value. This fact helps determine the actual optical power that couples into the sample, and also turns pulse-rate DLPTS into a useful tool for power sensitive optoelectronic measurements. In addition, pulse-rate-scanned DLPTS measurements are performed under isothermal conditions, which are very useful for precision analysis of temperature-sensitive defect state kinetics.

Figure 3. Experimental and simulated DLPTS transients at various temperatures. (a): theory with Gaussian activation energy broadening. (b): theory with stretched exponential broadening.

The DLPTS time-domain transients, which represent the raw signals as captured by the photodiode detector, are shown in Figure 3. Transients are normalized and separated by 0.0003 (normalizing factor) as shown in the figure. All transients consist of three parts: (a) a sharp decrease of the signal at the beginning of the pulse, followed by (b) a rapid recovery of the signal at the end of the pulse, further followed by (c) a slower long-time recovery of the signal [8]. The rapid decrease is caused by
the generation of free carriers from the excitation pulse, which increases the free carrier absorption and thus decreases the DLPTS signal in diffuse reflection from the back-surface. The fast increase is due to the recombination of free carriers, while the slow recovery is a result of thermal emission of carriers from deep energy states in the band-gap. The three stage relaxation clearly indicates the DLPTS signal consists of both \( n(t) \) (fast relaxation) and \( n_T(t) \) (slow relaxation). The transients are fitted with the Gaussian and stretched exponential theory using the parameters in Table 1. It can be seen that both broadening theories give excellent fits to transients at all temperatures thus further supporting the ergodicity of the thermal emission process from the active trap state(s). Small discrepancies are seen at certain temperatures. However, the discrepancies are negligible compared to those observed in the temperature-scanned and pulse-rate-scanned spectra. This fact indicates that the transient DLPTS response has the lowest energy-state resolution, and is not sufficient for the study of multi-exponential or stretched exponential decays. This conclusion has far-reaching consequences, as transients obtained at fixed temperature are the commonest diagnostic modality in conventional electronic deep-level studies of semiconductors. To overcome this lack of resolution, some researchers have proposed a spectral analysis, which gives the inverse Laplace transform of the transient [11]. Due to the complexity of the transient, this transformation can only be done numerically, and it requires estimated minimum and maximum emission rates for calculation. For the DLPTS transients with the aforementioned three stages, the inverse Laplace transformation requires a very large range of emission rates and computational results are not stable. Therefore, our combined-modality approach clearly shows that lock-in amplifier emission-level analysis combining thermal and pulse-rate spectra is the optimal defect-level diagnostic method for DLPTS.

4. Conclusions

In comparison among all the DLPTS modalities, the temperature-scanned spectrum is the easiest to interpret theoretically, since the amplitude spectrum is shown to be a superposition of various defect levels. The phase spectrum also contains additional information not easily garnered in the amplitude spectrum, like the HL3 and EL2 levels in SI-GaAs. The combination of temperature and pulse-rate DLPTS enhances the specificity of the DLPTS technique to trapped carrier energetics and kinetics. The pulse-rate-scanned spectrum yields a single peak in the measured pulse-rate (frequency) range. The pulse-rate scan requires a much broader bandwidth in order to cover all defect states accessible to photo-thermal temperature scans. The pulse-rate peak position is found to be sensitive to the optical power of the excitation laser. DLPTS time-domain transients represent the raw signal from the detector and provide a clear illustration of DLPTS kinetics. Although transients suffer from low trap-level resolution, the clearly shown three stage relaxation can be used to determine the relative contributions of \( n(t) \) and \( n_T(t) \) absorptions, which are essential for wider applications of DLPTS.

With regard to the physical implications of the DLPTS broadening mechanisms, a hierarchical carrier emission theory was developed capable of generating good fits to DLPTS temperature spectra, pulse-rate scans and photo-thermal transients. Our theory provides a possible explanation for the stretched exponential behavior commonly observed in DLTS measurements, and also confirms the existence of electron-to-electron constrained kinetics from trapped states in SI-GaAs. The hierarchical theory gives similar broadening compared with the commonly used Gaussian theory. This theory allows a wider application of stretched-exponential characterization in semiconductor systems, and also provides an energetic broadening parameter \( \Delta E \) as in the Gaussian distribution theory. For equivalent broadening effects, the ratio \( \Delta E / \Delta E = 1.5 \) for defect states with higher activation energies (higher resonance temperatures), while it decreases and is close to 1 for defects with lower activation energies (lower resonance temperatures). The existence of a relationship between the Gaussian and stretched exponential-induced trap-state energy broadening mechanisms demonstrates a statistical relation between the emission kinetics of the trapped electron system, and their random energetic distribution in the trap microstate manifold. The evidence of a changing \( \Delta E / \Delta E \) ratio at low temperatures also indicates this statistical relation depends on degrees of disorder in systems. The ergodic nature of the emission process is supported by all three DLPTS modalities.
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References
[1] D. V. Lang, J. Appl. Phys. 45, 3023 (1974).
[2] M. J. S. P. Brasil, and P. Motisuke, J. Appl. Phys. 68, 3370 (1990).
[3] P. K. Giri, and Y. N. Mohapatra, J. Appl. Phys. 78, 262 (1995).
[4] A. Das, V. A. Singh, and D. V. Lang, Semicond. Sci. Technol. 3, 1177 (1988).
[5] J. Xia, and A. Mandelis, Appl. Phys. Lett. 90, 062119 (2007).
[6] J. Xia, and A. Mandelis, J. Appl. Phys. 105, 103712 (2009).
[7] R. G. Palmer et al., Physical Review Letters 53, 958 (1984).
[8] A. Mandelis, and J. Xia, J. Appl. Phys. 103, 043704 (2008).
[9] P. Kaminski, and R. Kozlowski, Mater. Sci. Eng. B 91-92, 398 (2002).
[10] K. E. Petersen, Ergodic Theory, Cambridge Studies in Advanced Mathematics (Cambridge University Press, 1990)
[11] L. Dobaczewski et al., J. Appl. Phys. 76, 194 (1994).