Photocarrier radiometric study of defect states in semi-insulating GaAs

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Abstract. Photo-Carrier Radiometry has been applied to semi-insulating (SI) GaAs wafers. Due to the ultrafast free carrier lifetime, the conventional diffusion based PCR theory was modified to reflect defect induced carrier radiometry. Modulated and spectrally-gated defect luminescence was measured and analyzed using rate-window detection, in both temperature and frequency domain. Five defect levels were identified through multi-parameter fitting of PCR theory to the experimental data.

1. Introduction
The defect characterization of SI-GaAs is of great importance for the performance and application of SI-GaAs based optoelectronic and microelectronics devices. In the past few years, significant efforts have been made on the identification of defect states using mixed techniques such as Photo-Induced Current Spectroscopy (PITS) [1] (optical and electrical), Piezoelectric Photo-Thermal (PPT) [2] (optical and thermoacoustic), and the newly developed Deep Level Photo-Thermal Spectroscopy (DLPTS) [3] (optical and thermoelectronic). All these techniques are based on a pump-and-probe rate-window detection [4] that measures the post excitation thermal resonance of current, thermal radiation or optical absorption. Although GaAs is known as an important radiative emission (photoluminescent, PL) material, few PL kinetic/dynamic studies have been reported due to its ultrafast recombination lifetime (within nanoseconds) [5]. In this study, defect PL in SI-GaAs is analyzed for the first time using photo-thermal emission kinetics and the rate-window technique. The modulated PL signals are detected by means of Photo-Carrier Radiometry (PCR) [6] which blocks the non-radiative components by judicious spectral matching of the detector bandwidth to the photon emission spectral range.

2. Carrier Recombination and Photoluminescence in GaAs
There are mainly two recombination mechanisms in SI-GaAs, namely, the band-to-band recombination and Shockley-Read-Hall (SRH) recombination [7]. The band-to-band recombination emits large photon fluences with bandgap energy (~1.5 eV) and is blocked by our spectral filter. The SRH recombination is the main contribution to our PCR signal since it emits photons below bandgap energy. The SRH recombination involves two distinct defect centers: the recombination center and the trap. The recombination center has similar electron and hole capture coefficients, while the trap has a larger capture coefficient for one carrier, and is more likely to hold carriers and allow carriers of opposite sign to recombine at a much slower rate [7]. It should be noticed that, although recombination
normally occurs between defect states and energy bands, it may also occur within defect states. Such transitions have been proposed for several PL bands in SI-GaAs.\[8, 9\]

Based on the foregoing discussion, a generalized PCR theory can be described by Eq. (1). The PCR signal in this case consists of carrier photo-thermal capture and emission rate equations \[10\], it is diffusionless in the frequency scale of our experiments due to the ns-scale recombination and is proportional to the density of trapped carriers, $n_T(t, T)$ (trap recombination) and the free carrier concentration $n(t)$ (recombination center).

$$L(t) = I(T) \left[ a n(t) + b \sum_j C_j m_j(t) n_j(t) \right]. \quad (1)$$

Here, $a$ and $b$ are constants; $I(T)$ is the un-normalized temperature dependent emission efficiency; for defect $j$, $C_j$ is the capture cross section, and $n_j(t)$ is the concentration of occupied defect states; $m_j(t)$ is the density of carriers with opposite sign available for recombination with trapped $n_j(t)$. In this expression, a constant rate is assumed for recombination involving free carriers. This is a valid assumption in SI-GaAs due to its ultrafast free carrier lifetime \[11\]. The second term in Eq. (1) represents recombination between defect states. In these transitions, since the activation energies of the two defects are different, one state always holds carriers for a longer period than the other, and will simply act as the source of carriers for recombination. For this reason we can assume $m_j(t)$ to be a constant. This will not affect the result for rate-window detection, since only defects with time constants matching (resonant with) the rate-window can be observed.

3. Experimental results and discussion

A detailed description of the system and sample used in the study can be found in our previous publications \[6, 10\]. Using an InGaAs detector, the PCR signal consists of near-IR carrier emissions from 1.0 to 1.8 $\mu$m (photon energy from 0.7eV to 1.24eV), which covers the typical defect PL bands (0.67, 0.68, 0.78, 0.8eV) in SI-GaAs \[12\]. It should be noticed that PL bands are always broadened up to 0.35 eV due to phonon coupling. So the 0.68 and 0.67 eV bands are still within our detection range.

Due to the small defect PL (and PCR) signal, an integration time of 3 s is used in the lock-in amplifier.

Figure 1 shows the temperature-scanned PCR spectra. The PCR amplitude is only slightly dependent on modulation frequency, and it decreases rapidly when temperature increases. This is because of the competing non-radiative recombination process which are more probable at high temperatures \[13\]. The PL efficiency $I(T)/I_0$ can be approximated by Eq. (2) \[13\]

$$I(T)/I_0 = 1 / \left[ 1 + A \exp \left( -E_a / kT \right) \right]. \quad (2)$$

where $A$ and $I_0$ are constants, and $E_a$ is the thermal activation energy for non-radiative recombination.

![Figure 1](image-url)

Figure 1. The temperature-scanned PCR spectra at various frequencies. (a) amplitude spectra, and (b) phase spectra.
Using this equation, the 8 kHz amplitude spectrum is best fitted as shown in Figure 2. Discrepancies in the fitting are mainly due to the simplifications in Eq. (2), such as the temperature independent radiative recombination probability [13]. Thermal relaxation of defect states over the temperature range is also not considered in this model. For this reason, a more precise determination of the emission efficiency can only be obtained when the defect states have been identified.

![Figure 2](image)

**Figure 2.** Best-fit of the PL efficiency to the 8 kHz amplitude spectrum to Eq. (2).

The phase spectrum represents the ratio between the quadrature and in-phase components, and is not affected by $I(T)$. For this reason, the phase spectra can be easily analyzed without using $I(T)$. The frequency-scanned spectra, Figures 3b&c, are also unaffected by $I(T)$ due to their isothermal nature. For better illustration, the frequency domain amplitudes are normalized with respect to the maximum amplitude at each frequency, and all the data are intentionally separated by several magnitudes as indicated in the figure. The decay of amplitude at high frequencies clearly indicates the existence of slow photo-thermal kinetics consistent with long thermal emission times in SI-GaAs.

![Figure 3](image)

**Figure 3.** Experimental and theoretical PCR data: (a) temperature-scanned phase spectra, (b) frequency-scanned amplitude spectra, and (c) frequency-scanned phase spectra.

In our DLPTS studies [10], we have found that the combined analysis in three domains (temperature and frequency scans and time-transients) provides (so-far unavailable) consistency in the identification of defect states. In this study, the fitting is performed on both phase spectra of the temperature scan, and amplitude and phase spectra of the frequency scan. A hybridized Genetic and Nelder-Mead algorithm [13] is used for multiparameter fitting. During the fitting process, the number of defect levels is increased starting from one until a satisfactory result is obtained. The solid lines in Figure 3 show the best fitted spectra. Five defect states are identified and summarized in Table 1. The first two defects could both be EL2 levels considering the fact that EL2 consists of several charge
states with different activation energies ranging from 0.83 to 0.6 eV [14]. The EL4 defect is known to be a VGa defect [15], and has been suggested for the observed 0.8 eV PL [12]. A shallow defect state is also found. This could be the shallow donor state proposed by Yu [8] for the 0.77 eV band. The defect PL from EL17 level is detected for the first time. It was not reported on prior dc PL measurements probably due the reason that the conventional PL signal is very weak.

Table 1. Summary of defect states detected by PCR.

|     | $E_a$ (eV) | $\sigma$ ($\times 10^{-13}\text{cm}^2$) | $N_T$ ($\times 10^{15}\text{cm}^{-3}$) | $\Delta E$ (eV) |
|-----|------------|--------------------------------------|--------------------------------------|----------------|
| EL2 | 0.87       | 0.0131                               | 0.3275                               | 0.0151         |
| EL2 | 0.69       | 36.9581                              | 0.0326                               | 0.002          |
| EL4 | 0.52       | 4.1017                                | 0.0356                               | 0.0585         |
| EL17| 0.2        | 0.0053                                | 0.0521                               | 0.0166         |
| Shallow donor | 0.066 | 0.0623                               | 1.7707                               | 0.0374         |

Using the same fitting parameters, the 8 kHz PCR temperature-scanned spectra were simulated as shown in Figure 4a. In this simulation the PL efficiency $I(T)$ is assumed to be constant. It can be seen that even without applying $I(T)$, the simulated spectra show a decaying curve vs. temperature. Discrepancies start to appear near -100 °C. This is consistent with observations in thermoluminescence measurements, that the luminescence efficiency remains constant up to a critical temperature and then decreases rapidly [16]. This also confirms our argument that $I(T)$ cannot be precisely determined without taking account of defect states. By comparing the simulated spectra in Figure 4a and the experimental spectra, the PL efficiency can be derived, which gives $I_0=5.97$, $E_a=0.1$ eV, and $A=34.9$. Figure 4b shows the theoretical spectra after applying $I(T)$. It can be seen that the fitting is greatly improved. Small discrepancies still exist, however. This could be due to the fact that the same PL efficiency is used for all defect states, while it is possible that each defect has its own efficiency. Using different $I(T)$ for each defect, however, will increase uncertainties in the fitting parameters. The good agreement between the experiment and our theory on both temperature and frequency scans proves that our simplified PCR model is well suited for defect analysis.

![Figure 4](image-url)

**Figure 4.** Experimental and theoretical PCR temperature-scanned spectra at 8 kHz modulation frequency: (a) without using luminescence efficiency, and (b) after applying luminescence efficiency.

4. Conclusions
The PCR technique has been applied to Si-GaAs for the study of defect PL as a result of carrier emission photo-thermal processes. The temperature-scanned phase spectra and the frequency scans provide a convenient way to analyze the data without using the temperature dependent PL efficiency,
which can be determined independently once the defect states are identified. Five defect states were identified through a multiparameter fitting method applied to the experimental data. The calculated energy levels are consistent with studies in dc PL measurements. Our study indicates the PCR technique has great potential for the characterization of defect luminescence in semiconductor materials as it can provide combined results from temperature, time- and frequency-domain signals.

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