

Estimation of residual nitrogen concentration in semi-insulating 4H-SiC via low temperature photoluminescence

E. R. Glaser,^{a)} B. V. Shanabrook, and W. E. Carlos
Naval Research Laboratory, Washington, DC 20375-5347

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The conditions and limitations are presented for using low-temperature photoluminescence to estimate the total residual nitrogen concentration in semi-insulating (SI) 4H-SiC substrates where all N shallow donors are compensated in the dark. The ratio of the nitrogen-bound exciton line (Q_0) to the free excitonic-related emission (I_{77}) was tracked as a function of excitation power density for a set of samples with varying residual N concentration ($\sim 6 \times 10^{14}$ – 5.2×10^{16} cm⁻³) as determined by secondary ion mass spectroscopy. A linear relationship was empirically found between the Q_0/I_{77} ratio and [N] for [N] < 1×10^{16} cm⁻³. However, a sub-linear behavior was observed for samples with higher N levels attributed to incomplete photo-neutralization of the N shallow donors. [DOI: 10.1063/1.1857079]

Due to possible trapping effects such as observed for SiC metal–semiconductor field-effect transistor devices,¹ several efforts^{2–5} are under way to develop large-area, semi-insulating (SI) 4H- and 6H-SiC substrates without introduction of transition metals such as vanadium or chromium. To achieve this goal it is important to track quantitatively the common residual shallow donor (nitrogen) and acceptor (boron) impurities within a single boule and for different growth runs. Secondary ion mass spectroscopy (SIMS) is typically employed to monitor the N and B levels in SiC. While the SIMS detectivity limit for B of ~ 3 – 5×10^{13} cm⁻³ appears to be quite sufficient, significant advances in the purity of the source materials, for example, have resulted in SiC substrates with N impurity concentrations approaching or below what can be presently detected (\sim mid– 10^{14} to 10^{15} cm⁻³) via SIMS (Ref. 6). Previously, both destructive and nondestructive techniques were employed to determine the concentration of uncompensated (neutral) N donors in *n*-type SiC. These included electrical measurements such as capacitance–voltage (*C*–*V*) and Hall effect and optical methods such as below band gap absorption spectroscopy.⁷ In particular, a calibration procedure based on low-temperature photoluminescence (PL) was developed by two groups^{8–10} in which a linear relationship was found between the ratio of bound and free excitonic recombination (I_{BE}/I_{FE}) and the concentration of uncompensated N determined via *C*–*V* measurements in *n*-type 4H- and 6H-SiC with *n* between 10^{14} and 10^{17} cm⁻³. However, the use of such transport techniques for calibration purposes is not feasible in SI SiC because all residual N shallow donors are compensated in the dark. In addition, it was suggested¹⁰ that this PL technique would not be applicable for such highly compensated SiC.

In this letter we discuss the conditions and limitations of using low-temperature band edge PL to estimate the *total* N in semi-insulating 4H-SiC substrates. SIMS was employed for calibration to provide the total [N] for each of the samples. The PL experiments were performed on samples cut from 2- to 4-in.-diam SI bulk 4H-SiC substrates as summarized in Table I. Transport measurements confirmed that most of the samples were semi-insulating with $\rho > 10^5$ Ω cm at

300 K except sample K that was found to be *p*-type. For reference, an intentional N-doped 4H-SiC substrate was also examined with net carrier concentration (i.e., $N_d - N_a$) of 1 – 2×10^{17} cm⁻³. The PL at 2 K was excited by the 351 nm UV line of an Ar⁺ ion laser with excitation power density varied from 0.3 to 200 W/cm². The emission was analyzed by a 0.25 m double-grating spectrometer and detected by a GaAs photomultiplier tube.

Detailed SIMS measurements¹¹ were performed on the *same* samples as used for the PL experiments in order to determine the residual N, B, Al, and V impurity concentrations. The residual Al levels were below 2×10^{14} cm⁻³ (consistent with the absence of Al-bound excitonic recombination in these samples) and V close to the detection limit of 2×10^{12} cm⁻³. The average N and B concentrations are summarized in Table I. In particular, a raster scan technique⁶ was employed to enhance the sensitivity for detection of N close to the system background levels. We note that the residual N concentration for sample A was at or below the SIMS back-

TABLE I. Summary of 4H-SiC samples investigated in this work with N and B concentrations as determined from SIMS (NP≡not profiled). The standard deviations in the determination of the N levels are also given.

Sample	Growth	Conductivity	[N] (cm ⁻³)	[B] (cm ⁻³)
A	PVT	SI	$< 7.0 \times 10^{14}$	8.0×10^{14}
B	PVT	SI	$5.5 \pm 3.4 \times 10^{14}$	1.1×10^{15}
C	PVT	SI	$1.0 \pm 0.2 \times 10^{15}$	1.2×10^{15}
D	PVT	SI	$1.1 \pm 0.8 \times 10^{15}$	1.3×10^{15}
E	PVT	SI	1.2×10^{15}	NP
F	PVT	SI	1.3×10^{15}	NP
G	PVT	SI	$1.5 \pm 0.4 \times 10^{15}$	1.8×10^{15}
H	PVT	SI	1.5×10^{15}	NP
I	HTCVD	SI	$2.2 \pm 1.0 \times 10^{15}$	9.6×10^{14}
J	PVT	SI	$2.6 \pm 1.4 \times 10^{15}$	1.2×10^{15}
K	PVT	<i>p</i> -type	$3.6 \pm 1.6 \times 10^{15}$	9.9×10^{15}
L	PVT	SI	$4.9 \pm 1.8 \times 10^{15}$	2.1×10^{15}
M	PVT	SI	$8.5 \pm 2.0 \times 10^{15}$	4.8×10^{15}
N	PVT	SI	$2.1 \pm 0.2 \times 10^{16}$	1.8×10^{16}
O	PVT	SI	$3.0 \pm 1.0 \times 10^{16}$	2.0×10^{16}
P	PVT	SI	$5.2 \pm 0.5 \times 10^{16}$	1.3×10^{16}
Q	PVT	<i>n</i> -type	$1.5 \pm 0.2 \times 10^{17}$	5.0×10^{16}

^{a)}Electronic mail: glaser@bloch.nrl.navy.mil

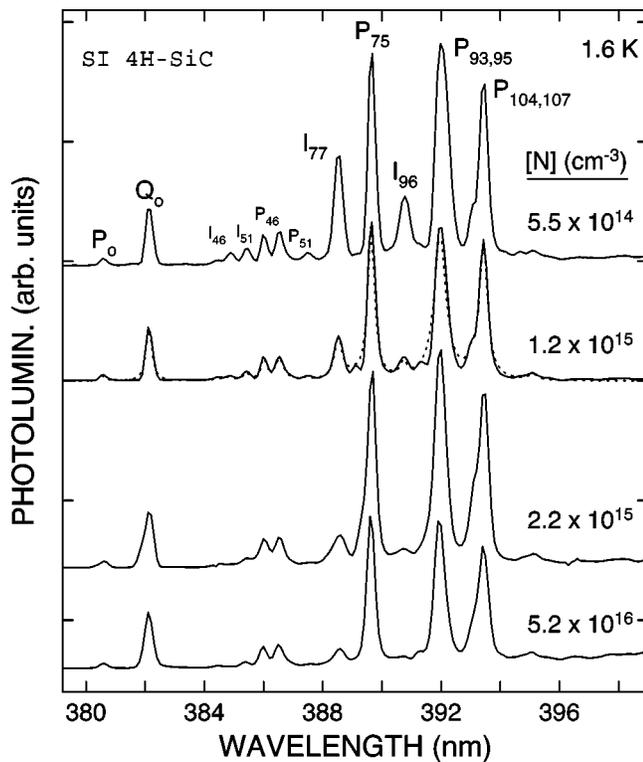


FIG. 1. Near-band-edge PL spectra obtained at 1.6 K for several SI 4H-SiC samples with varying residual nitrogen concentration (excitation power density of ~ 100 W/cm 2). The various assignments are discussed in the text. The dashed curve is a simulation of the PL.

ground level of 7×10^{14} cm $^{-3}$ for that particular measurement while a lower N background level was achieved prior to analysis of sample B.

Band edge PL spectra observed for several SI 4H-SiC samples with varying residual N concentration are shown in Fig. 1 under excitation power density of ~ 100 W/cm 2 . For display purposes, the spectra are normalized to the intensity of the line labeled Q_0 . The individual line assignments are well known from previous optical studies¹² of N-doped 4H-SiC. In particular, the features labeled P_0 and Q_0 are the zero-phonon-lines (ZPLs) of excitons bound to neutral N shallow donors at the hexagonal and cubic lattice sites, respectively. Free excitonic recombination without the assistance of phonons is “forbidden” for indirect band gap semiconductors such as 4H-SiC. However, the nitrogen donors break the translational invariance and no-phonon, impurity-related excitonic transitions become allowed. The much stronger intensity of Q_0 reflects the higher binding energy (\sim twice) and, hence, more localized wave function of the N donors at the cubic sites compared to that for N at the hex. sites. The series of lines labeled $P_{46}, P_{51}, \dots, P_{104,107}$ are phonon-assisted transitions of excitons bound to N donors at the hexagonal site. Following previous convention, the index refers to the energy separation in milli-electron-volts of the particular replica from the P_0 ZPL position. Finally, the features labeled $I_{46}, I_{51}, I_{77},$ and I_{96} are phonon-assisted transitions of free excitonic recombination. These spectra clearly show that this series of lines diminish rapidly in absolute intensity and relative to the Q_0 bound-exciton PL as a function of increasing residual N concentration.

Following the procedure¹⁰ established for calibration of N in *n*-type bulk and epi 4H-SiC, we determined the ratio of

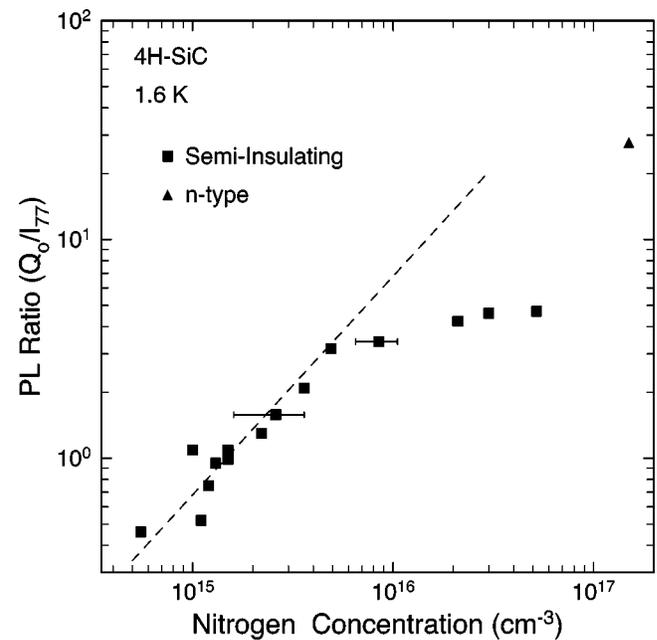


FIG. 2. Plot of the Q_0/I_{77} excitonic PL ratio vs total nitrogen concentration as determined from SIMS ($P_{\text{exc}} \sim 100$ W/cm 2). The dotted line is a least-squares fit to the data with $[N] < 8.5 \times 10^{15}$ cm $^{-3}$.

the integrated intensities for the Q_0 and I_{77} emission lines from fits to all PL features in the near bandedge spectral region. As shown by the composite dashed line in Fig. 1 for sample E with $[N] = 1.2 \times 10^{15}$ cm $^{-3}$, use of Lorentzian line shapes for the individual PL lines gave reasonable fits. A plot of the Q_0/I_{77} PL ratio for the entire set of samples (excluding sample A) under excitation power density of ~ 100 W/cm 2 vs the total N concentration as determined from SIMS is shown in Fig. 2. Most notably, a linear relationship (within the errors of the SIMS measurements as given in Table I) is found between the Q_0/I_{77} ratio and $[N]$ for the samples with residual $[N] < 8.5 \times 10^{15}$ cm $^{-3}$. This implies that all of the compensated N donors have been photo-neutralized and the Q_0/I_{77} ratio is proportional to the total N concentration.

It was shown previously^{9,10} that residual Al shallow acceptors ($E_a \sim 200$ meV) at levels comparable to that of N in 4H- and 6H-SiC offer an alternate channel for capture of free excitons and, thus, highly impact the Q_0/I_{77} ratios. However, based on the absence of B-bound excitonic recombination in the present samples (even with $[B]$ of $\sim 10^{15}$ – 10^{16} cm $^{-3}$), the deeper B acceptors ($E_a \sim 300$ meV) do not appear to offer a secondary pathway for capture of free excitons. In addition, we note that SIMS detects nitrogen regardless of the particular lattice site but, following previous work,¹⁰ only the bound-excitonic emission associated with the N donors on the cubic site (Q_0) was used in the PL ratio. However, the ratio of the Q_0 to P_0 donor-bound excitonic recombination did not change appreciably ($< 15\%$) over this N concentration range (i.e., $< 8.5 \times 10^{15}$ cm $^{-3}$) and, thus, use of the Q_0/I_{77} PL ratio alone appears to be sufficient for calibration of the total residual N level.

Following the analysis in Ref. 10, the dashed line in Fig. 2 is a least-squares fit, defined by $R(=Q_0/I_{77}) = A \cdot [N]$, to the data with $[N] < 10^{16}$ cm $^{-3}$. The proportionality constant of $A = 6.8 \times 10^{-16}$ cm 3 is similar to those found with this technique for (uncompensated) *n*-type 4H- and 6H-SiC where the ratio was plotted against the carrier concentration (*n*) deter-

mined from $C-V$. However, this simple correspondence is not applicable for the present SI 4H-SiC substrates with residual $[N] \geq 8.5 \times 10^{15} \text{ cm}^{-3}$. In particular, a deviation (outside of experimental error) of the PL ratio from this linear dependence is seen for sample M with $[N] = 8.5 \times 10^{15} \text{ cm}^{-3}$ while a strong sublinear behavior is observed for all other SI SiC samples with higher residual N and B levels.

The sublinear dependence of the Q_0/I_{77} PL ratio found for the SI 4H-SiC substrates with $[N] \geq 10^{16} \text{ cm}^{-3}$ and P_{exc} of 100 W/cm^2 is attributed to the incomplete photo-neutralization of the residual N shallow donors. This was established from an excitation power dependence study of the ratio for several samples. In particular, a weak dependence was observed with P_{exc} between 0.3 and 200 W/cm^2 for the substrates with $[N] < 8.5 \times 10^{15} \text{ cm}^{-3}$. This suggests that all the compensated N donors are fully neutralized under these readily attainable excitation power conditions. However, a very different power dependence was observed for samples with $[N] \geq 8.5 \times 10^{15} \text{ cm}^{-3}$. The Q_0/I_{77} PL ratio was approximately constant for $P_{\text{exc}} \leq 10 \text{ W/cm}^2$ but monotonically increased under higher power levels to values approaching the dashed line shown in Fig. 2. The increase of the ratio was particularly rapid for the sample with the largest concentration (i.e., $5.2 \times 10^{16} \text{ cm}^{-3}$) of compensated N donors. These results indicate that larger excitation power levels are clearly required in order to completely photo-neutralize the residual N donors for SI substrates with $[N] \geq 8.5 \times 10^{15} \text{ cm}^{-3}$ and, furthermore, suggests that this PL technique can be extended to samples with such high residual N levels if sufficiently high power conditions are used while avoiding significant heating.

In summary, detailed near-band-edge PL at 2 K has been performed on a large set of semi-insulating 4H-SiC substrates with varying residual N concentration as determined by SIMS. A simple one-to-one correspondence was found between the Q_0/I_{77} PL ratio obtained under excitation power conditions of ~ 10 – 100 W/cm^2 and the total N concentration for samples with $[N] < 8.5 \times 10^{15} \text{ cm}^{-3}$. The sublinear behavior of the ratio observed under similar excitation conditions for samples with higher N levels can be understood

from the incomplete photo-neutralization of the N shallow donors. We propose this low-temperature PL technique would be particularly useful to map nondestructively the residual N concentration in large-area, semi-insulating 4H- and 6H-SiC substrates, especially for wafers with N levels close to or below the present SIMS detection limit of $\sim 1 \times 10^{15} \text{ cm}^{-3}$.

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¹¹The SIMS was performed at Charles Evans and Associates (West) during a 12 month period of time.

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