Impurity Characterization in Device Quality Hot Filament Chemical Vapor Deposition (HFCVD) Grown 3C Silicon Carbide (3C-SiC)

Cooperative Research and Development Final Report

CRADA Number: CRD-17-00684

NREL Technical Contact: Kirstin Alberi

NREL is a national laboratory of the U.S. Department of Energy
Office of Energy Efficiency & Renewable Energy
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Technical Report
NREL/TP-5K00-77694
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Cooperative Research and Development Final Report

Report Date: **August 21, 2020**

In accordance with requirements set forth in the terms of the CRADA agreement, this document is the final CRADA report, including a list of subject inventions, to be forwarded to the DOE Office of Scientific and Technical Information as part of the commitment to the public to demonstrate results of federally funded research.

Parties to the Agreement: BASiC 3C

CRADA Number: CRD-17-00684

CRADA Title: Impurity Characterization in Device Quality Hot Filament Chemical Vapor Deposition (HFCVD) Grown 3C Silicon Carbide (3C-SiC)

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Sponsoring DOE Program Office(s): Office of Energy Efficiency and Renewable Energy (EERE), Advanced Manufacturing Office (AMO), Small Business Voucher (SBV) Program

Joint Work Statement Funding Table showing DOE commitment:

Estimated Costs	NREL Shared Resources a/k/a Government In-Kind
Year 1	$70,000.00
TOTALS	$70,000.00

Executive Summary of CRADA Work:

BASiC-3C needs advanced characterization of material properties to continue making progress towards high quality 3C-SiC. For over 190 growth runs, BASiC 3C has relied almost exclusively on feedback from commercially available metrology such as cross-sectional FESEM, AFM, Raman, XRD and SIMS. This standard feedback loop has enabled BASiC 3C to “rough-in” growth conditions and achieve growth of epitaxial growth over a 4” wafer size, at respectable growth rates (Figure 1). Still, the material quality deduced from X-ray rocking FWMH and APB density must be further improved to be viable for our industry partners. Electron Spin Resonance (EPR) and time-resolved photoluminescence (TRPL) data and interpretation by an experienced scientist is identified as a critical, yet not commercially readily available feedback that would enable further material improvement.

Summary of Research Results:

The intent of this project was to investigate the impact of impurities in SiC semiconductor material grown by BASiC-3C through optical, structural and chemical characterization. This information was used by BASiC-3C to supplement data from other measurement methods and more thoroughly evaluate material growth issues as well as the suitability of their material for electronic device applications. Below is a summary of the tasks outlined in the Statement of Work and the results that were generated.

Task 1: Establish baseline PL (photoluminescence) and ESR (electron spin resonance) measurements on material with known impurity concentration.

Elemental impurities can substantially impact the optical and transport properties of semiconductors and their performance in devices. Impurity incorporation is strongly governed by the synthesis conditions, and prior to the start of the project, BASiC-3C identified impurities as a potential source of non-ideal behavior in their SiC material. Both PL and ESR were initially specified as two methods of optically detecting impurities that can could provide complementary information to other characterization techniques performed by BASiC-3C.

Photoluminescence was performed around 5 K using a 375 nm or 325 nm laser source. Figure 1a shows the spectrum of a SiC 3C epilayer grown on a 6H substrate. The intense sharp peaks just below 2.3 eV correspond to radiative recombination of nitrogen impurity-bound excitons and their phonon replicas. The other sharp emission lines between 2.1 and 2.26 eV have also been attributed to additional radiative recombination processes involving nitrogen impurities [1]. The spectral features below 2.0 eV are tentatively attributed to recombination at sites involving vacancies and dislocation defects as well as donor acceptor pair recombination. Figure 1b shows the spectrum of a nitrogen-doped SiC 4H substrate for reference. The sharp spectral features near 3.1 and 3.2 eV are attributed to excitonic recombination from nitrogen impurity states and their photon replicas. This emission was very weak in comparison to the 3C epilayer in Fig. 1a. The broad emission centered around 2.1 eV is attributed to donor-acceptor pair luminescence [2]. These two spectra serve as starting points for understanding how impurities and defects introduced through changes in processing parameters affect the optical properties of the material.

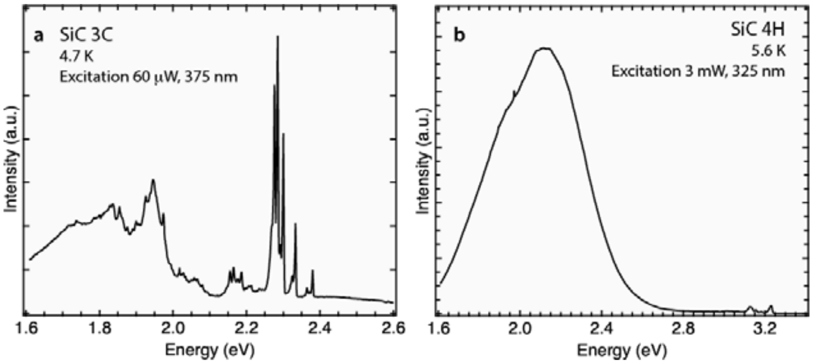

Fig. 1. Photoluminescence of SiC material. (a) SiC 3C epilayer on a 6H substrate. (b) SiC 4H substrate.

We did not end up performing the ESR measurements that were planned in the original project scope due to loss of relevant ESR expertise at NREL. We found that a combination of PL, TRPL and SIMS measurements served as an effective substitute for ESR in the following tasks.

Task 2: Measure PL and ESR on sample series where key process conditions are varied.

Photoluminescence measurements were performed on 3C SiC epilayers grown on 6H and 4H substrates. The spectra varied between samples and as a function of the position within the sample in some instances. In some cases where 3C epilayers were grown on 4H substrates, the epilayers had low PL intensity that could not be distinguished from the substrate (see Fig. 2a). To understand the lack of PL, we also performed PL measurements on 4H epilayers grown on 4H substrates. Those samples also showed a lack of near-band edge luminescence associated with nitrogen impurity-bound states and mainly show lower-energy PL associated with donor-acceptor pairs (see Fig. 2b).

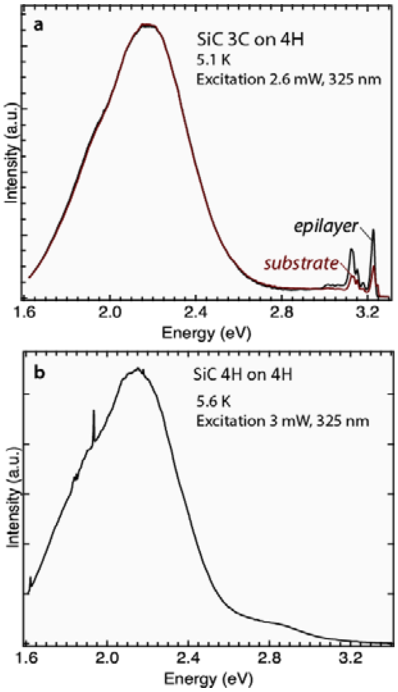

Fig. 2. Photoluminescence of SiC material. (a) SiC 3C epilayer on a 4H substrate. (b) SiC 4H epilayer on a 4H substrate.

To further understand whether the lack of high-energy PL was due to excessive non-radiative recombination induced by impurities or some other process, we performed secondary ion mass spectrometry (SIMS) measurements to understand whether the epilayers contained unintentional impurities. Figure 3 shows SIMS profiles of a nitrogen-doped 3C epilayer and an undoped 4H SiC epilayer, which contained varying degrees of impurities. In particular the 4H epilayer in Fig. 3b contained a very high concentration of boron and a higher than expected concentration of Al. The feedback from these measurements was that the impurity concentrations in these samples did not vary in a way that was linked to intentional processing changes and allowed BASiC 3C to identify the sources of these unintentional impurities so that they could reduce them. They subsequently have made changes to their growth system configuration and heater design to minimize impurity incorporation. The SIMS measurements also indicated that it would be difficult to evaluate PL spectra without accompanying quantitative data on impurities, since they did not vary as expected.

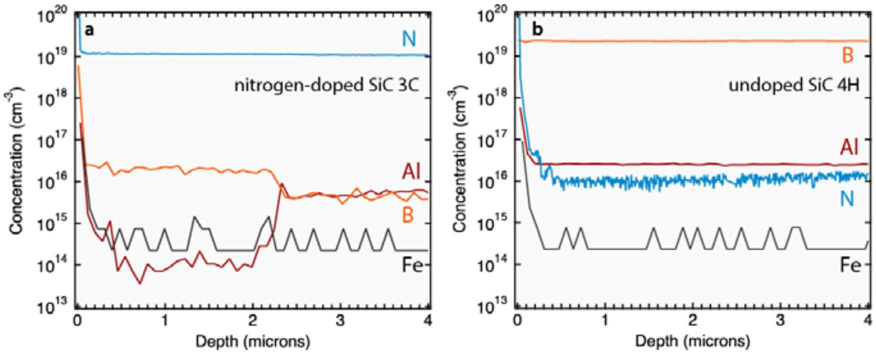

Fig. 3. Secondary ion mass spectrometry (SIMS) profiles of two different SiC epilayers, showing intentionally-added N and unintentionally added Al, B and Fe impurities.

Time-resolved PL (TRPL) measurements were also performed on SiC samples with varying degrees of impurity-related PL signatures to understand how strongly these impurities act as non-radiative recombination centers. Measurements were performed with a frequency doubled Ti:Sapphire laser and streak camera. Results are shown in Fig. 4. The cleanest samples exhibited a fast decay curve (T_1) followed by a much longer component (T_2), indicating that minority carriers can live for very long lifetimes. In other samples, the T_2 component was shorter, indicating shorter minority carrier lifetimes. The lifetimes will be governed by the specific mixture of impurities and defects in each sample. However, they provide an overall picture of which material will support good device performance and which material will not. This data was correlated with transport measurements performed by BASiC 3C to better determine the factors limiting their device performance.

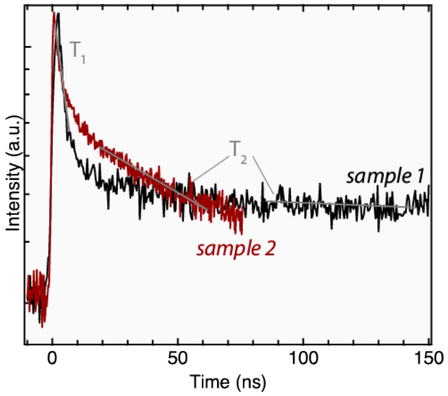

Fig. 4. Time-resolved photoluminescence of two SiC samples exhibiting different decay curves governed by non-radiative recombination.

We also noticed through optical microscopy measurements that some of the SiC samples had noticeable extended defects, which could also affect the transport properties. We performed PL measurements at regions near and far from these defects to determine what types of electronic states those defects introduce into the bandgap. That information was helpful in understanding the sources of defect-related luminescence and non-radiative recombination in these samples and also provided feedback about general material quality.

Finally, we performed x-ray diffraction (XRD) measurements as a function of position on some samples to probe the general structural integrity of the epitaxial SiC material. Strain and lattice relaxation are other factors that can affect carrier transport in electronic devices, and our measurements provided information on whether these factors existed and how they change across the substrate (an indication that the growth conditions are not optimized).

Task 3: Measure PL and ESR on N-doped sample series

To supplement the as-grown samples with N-type doping that were measured as part of Tasks 1 and 2, we implanted SiC material with systematically varying concentrations of nitrogen and then measured PL and TRPL. Representative PL spectra from the as-grown and implanted samples are shown in Fig. 5a. Bound exciton lines associated with the nitrogen dopants were detected. The low-energy portion of the spectrum also shifted after implantation. This is likely due to a re-distribution of nitrogen impurity and defect states, which can change the donor-acceptor pair emission energies. The decay curves from the TRPL measurements exhibited similar behavior and relatively fast T_2 components, suggesting that the minority carrier lifetimes in both samples are limited by the same aspect of the material. Devices were subsequently fabricated from this material at BASiC 3C. This data was used to supplement their transport measurements with information about nitrogen activation and the relative extent of defects that could limit radiative recombination.

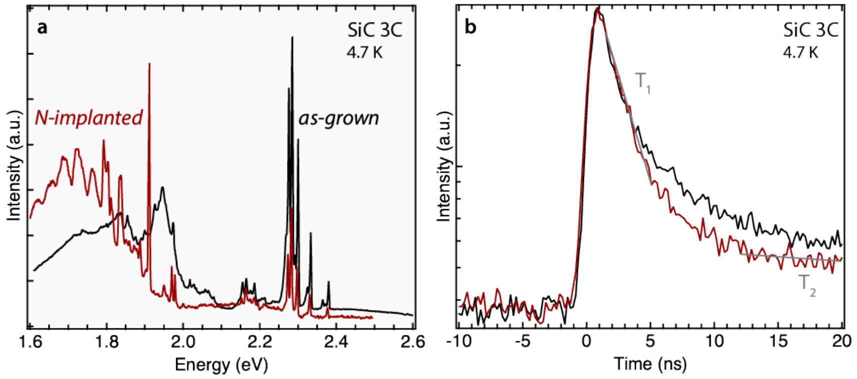

Fig. 5. Photoluminescence measurements of as-grown and nitrogen-implanted SiC 3C samples. (a) PL spectra. (b) time-resolved PL decay curves. The intensity scales are not the same for the two samples in each plot.

References

[1] W.J. Choyke, Z.C. Feng and J.A. Powell. (1988). Low-temperature photoluminescence studies of chemical-vapor-deposition-grown 3C-SiC on Si. *J. Appl. Phys.* **64 (**3163), https://doi.org/10.1063/1.341532.

[2] A. Suzuki, H. Matsunami and T. Tanaka. (1977). Photoluminescence due to Al, Ga and B acceptors in 4H-, 6H-, and 3C-SiC grown from a Si melt. *J. Electrochem. Soc.* **124** (241), https://doi.org/10.1149/1.2133274.

Subject Inventions Listing: None

ROI #: None