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CW Blue-Green Light Emission from GaN and SiC by Sum-Frequency Generation and Second Harmonic Generation

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Continuous wave (CW) back-scattered sum-frequency generation (SFG) and second harmonic generation (SHG) have been obtained from GaN and SiC. GaN samples were obtained from GaN films grown by molecular-beam epitaxy (MBE), metalorganic chemical-vapor deposition and hydride vapor-phase epitaxy. The SiC samples were obtained from 3C SiC/Si grown by chemical vapor deposition (CVD), 4H and 6H single crystal SiC substrates. The samples were optically excited with two CW lasers at the red (840 nm) and the infrared (1.0 μm). SHG at 420 nm and 500 nm and SFG at 455 nm were observed. SFG and SHG were verified by measuring their relative intensities against the pumping laser power. The SHG signals from GaN and SiC samples are compared with that from KH_2PO_4 (KDP).

Key words: GaN, SiC, nonlinear optical properties

GaN and SiC are wide band gap semiconductors (WBGS) well known for their chemical and thermal stability and are widely used in optoelectronics,[1,2] and high-power, high temperature[3,4] devices, respectively. The initial interest in GaN was centered on the fabrication of blue light emitting diodes (LEDs) and laser diodes. However, the band gap of GaN can also be tailored by alloying with In and Al to produce light emission from UV to infrared. Recently, the success of the incorporation of rare earth elements into GaN has ushered in a new technique of making light-emitting diodes.[5] On the other hand, the research and development in SiC technology has also produced significant progress over the past five years. A major factor in this rapid growth has been the development of SiC bulk crystals and the availability of crystalline substrates. An interesting, but less explored, area is the nonlinear optical (NLO) properties of these WBGS materials. Both GaN and SiC have large NLO coefficients.[6–8] By combining their excellent electronic/optical properties with NLO properties, a truly integrated optical circuit can be envisioned where light sources, detectors, modulators, switches and processing circuits can be fabricated monolithically. It has been shown that the second-order nonlinearities of GaN[6] and SiC[7,8] are an order of magnitude larger than $LiBnO_3$ and KH_2PO_4 (KDP). Four-wave mixing experiments have also been performed on GaN films using picosecond[9] or femtosecond[10] probes. In this paper, we report the observation of tunable CW second-harmonic generation (SHG) and sum-frequency generation (SFG) for GaN and SiC.

Our experiments utilized GaN and SiC thin films and powders obtained from a variety of sources. The powder approach was inspired by the Kurtz powder technique[11,12] which is a standard method of screening a large number of candidate nonlinear materials to determine whether a material has large or small nonlinearities and whether it is phase matchable or not. The GaN powders for these experiments were obtained from scribing GaN and SiC films with diamond scribers. This produces powders with particle sizes <0.5 μm. GaN films were grown by molecular-beam epitaxy (MBE), metalorganic chemical-vapor deposition (MOCVD), and hydride vapor-phase epitaxy (HVPE), all on c-axis (0001) sapphire substrates. The MBE samples were grown at University of Cincinnati (UC) in a Riber MBE-32 system. Solid sources were employed to supply the Ga and Al fluxes, while an SVTA rf-plasma source was used to generate atomic nitrogen. The substrate was initially nitrided at 750°C for 30 min. Chamber pressure throughout growth was mid-10^{-5} torr. An AlN or GaN buffer layer was deposited at 550°C for 10 min. Growth of the main

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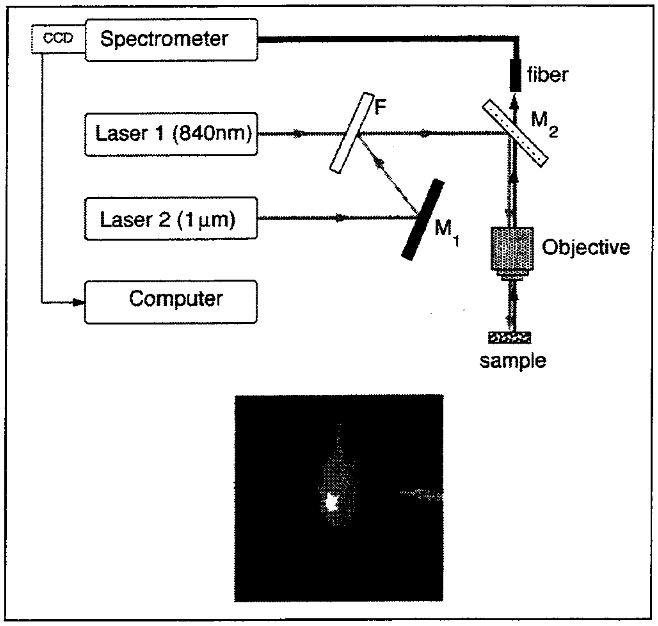

Fig. 1. Optical set up for the measurement of three color light emission. Laser 1: tunable diode laser, 835–855 nm. Laser 2: tunable diode laser, 1–1.02 μm. F: band pass filter, transmittance = 90% at 840 nm, reflectivity = 91% at 1 μm. M1: High reflector at 1 μm. M2: dichroic mirror. The insert shows the blue-green light emitted under excitation from a 6H SiC sample.

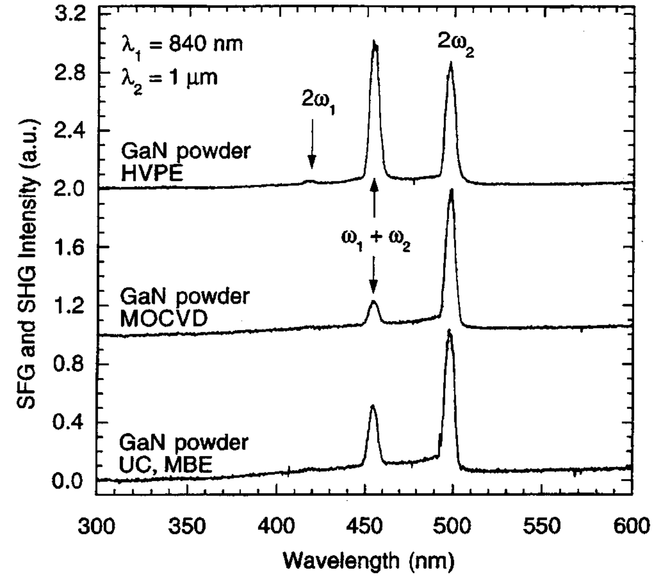

Fig. 2. SHG and SFG from GaN powders obtained from GaN films grown by MBE, MOCVD, and HDPE. Laser 1 = 840 nm, Laser 2 = 1 μm.

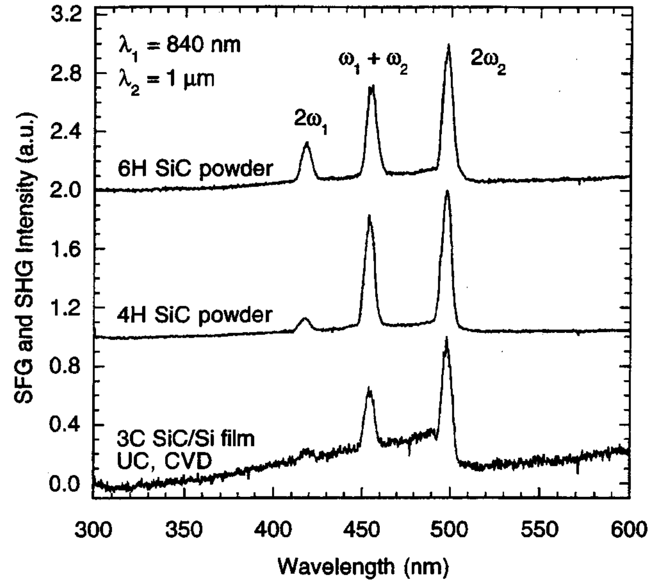

Fig. 3. SHG and SFG from SiC powders/films obtained from SiC films/substrates with 3C, 4H, and 6H polytype. Laser 1 = 840 nm, Laser 2 = 1 μm.

GaN layer proceeded at 750–800°C for 3 hours with a constant Ga beam pressure in the mid-10^{-7} torr range. This produces a film thickness of 1.5 μm.

SiC powders from 3C, 4H, and 6H polytypes were prepared by scribing SiC films and substrates with diamond scribers. The cubic SiC films were grown at UC on 3 inch Si(111) substrates (p-type, 150–300 Ω-cm, off-axis) using trimethylsilane (3MS) at 1200°C and 4 torr. Prior to CVD growth, the Si surface was carbonized using propane at 1300°C and 1 atm to reduce the effects of large lattice mismatch and thermal coefficient difference between SiC and Si(111). The flow rate was 10 sccm for propane, 40 sccm for 3 MS. H_2 and N_2 were used as carrier gas and dopant, respectively. The H_2 flow rate was 2 slm during carbonization and 1 slm during growth. The N_2 flow rate of 1 sccm was the same for both carbonization and growth. The SiC film thickness is about 1 μm as measured by cross-sectional SEM. X-ray diffraction shows that the SiC film is highly ordered with (111) orientation. 4H and 6H SiC substrates were research grade single crystal substrates purchased from Cree Research, Inc.

Figure 1 shows the optical setup used to measure the nonlinear signals of GaN and SiC samples. Spectra were obtained at room temperature by pumping the sample with two CW tunable diode lasers, the SDL 8630 GaAs/AlGaAs at 835-855 nm (Laser 1, λ_1) and SDL TC30 InGaAs/AlGaAs at 1–1.02 μm (Laser 2, λ_2). Both lasers were coupled into collinear beams and focused to a 10 μm diameter beam spot through a modified Nikon Eclipse E600-FN Physiostation microscope with a CFI Super Flour 40X 0.9NA objective. The lasers produce a maximum power of 200 mW on the sample. Backscattered light was collected through the same objective and coupled into an optical fiber located on top of the microscope. The signal is analyzed in a 0.27 meter SPEX 270M spectrometer outfitted with a Spectrum One 1024 × 256 pixel liquid nitrogen cooled SiCCD array detector. A grating of 300 grooves/mm blazes at 500 nm was selected for spectra collection. As shown in the insert of Fig. 1, blue-green light emission was observed by focusing these two lasers on either GaN or SiC samples.

Figure 2 shows the SFG and SHG from GaN powders. The GaN powders were excited with the two lasers at $\lambda_1 = 840$ nm and $\lambda_2 = 1.0$ μm. The spectra in Fig. 2 show emission from SFG at 455 nm ($\omega_1 + \omega_2$) and from SHG at 500 nm ($2\omega_2$). A small peak due to SHG at 420 nm ($2\omega_1$) was also observed. In Fig. 2, each

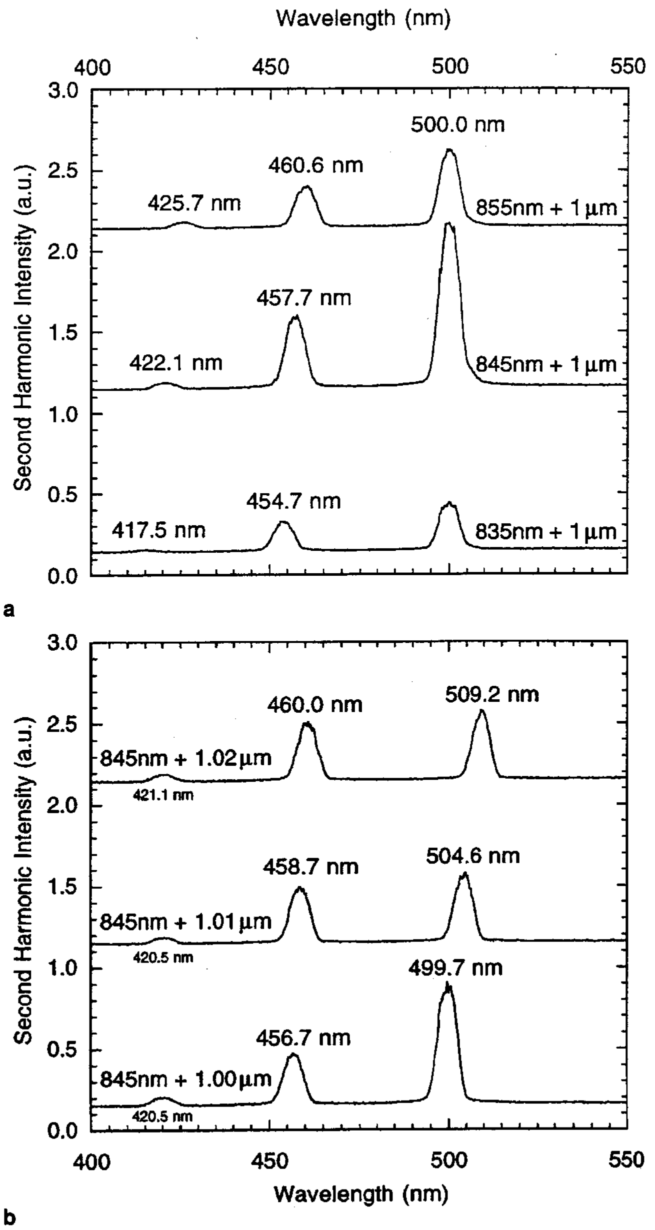

Fig. 4. SFG and SHG from peak shift from a GaN film due to pumping laser tuning: (a) 840 nm laser is adjusted from 835 nm to 855 nm; (b) 1.0 µm laser is adjusted from 1.0 µm to 1.02 µm.

spectrum was normalized relative to its own highest peak intensity. The relative intensity between SFG ($\omega_1 + \omega_2$) and SHG at 500 nm ($2\omega_2$) varies due to the crystal orientation of various GaN particles. Similar SFG and SHG results were obtained from SiC powders. Figure 3 shows the spectra obtained by exciting SiC powders with the same two lasers. Both 4H and 6H SiC powders show strong violet-blue-green light emission. Spatially uniform light emission was obtained when performing the experiment over an entire 3C SiC/Si wafer. Si, quartz and sapphire powders were also prepared in the same fashion and optically excited with these two lasers. No SFG or SHG signals were observed. This may due to the fact that the pumping power density is too low to observe any nonlinear signals from these samples.

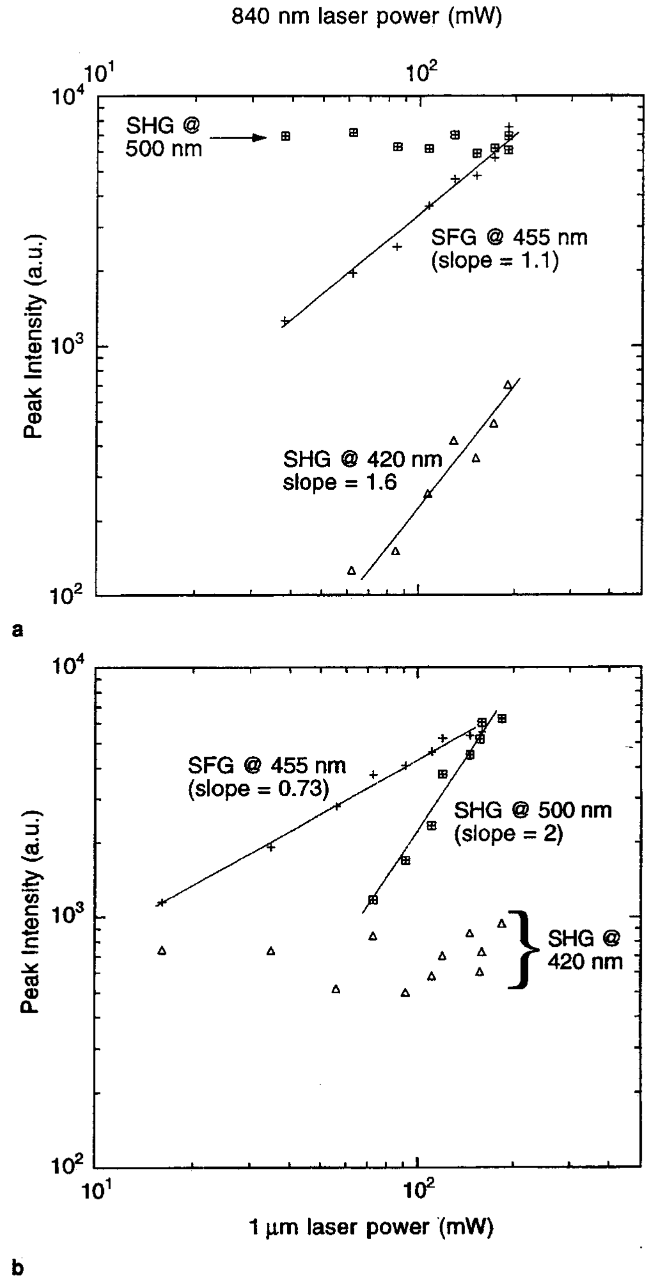

Fig. 5. SFG and SHG intensity from a GaN film as a function of pumping laser powers.

Blue-green light emission was also obtained from GaN films grown by MBE. After growth, a GaN film was annealed by rapid thermal annealing (RTA) at 1100°C in a N_2 ambient. SFG and SHG were observed across the sample. SFG and SHG were verified by tuning pumping laser wavelengths and measuring SFG and SHG intensities against pumping laser powers. Figure 4 contains spectra which show the SFG and SHG peak shift corresponding to the change of pumping wavelengths. Figure 4a shows the SFG and SHG peaks for three choices of Laser 1 wavelength (λ_1 = 835 nm, 845 nm, and 855 nm) while the wavelength of Laser 2 ($\lambda_2 = 1.0\,\mu$m) remains unchanged. It shows clearly the corresponding change of the $2\omega_1$ signal, from 417.5 nm, to 422.1 nm to 425.7 nm. The

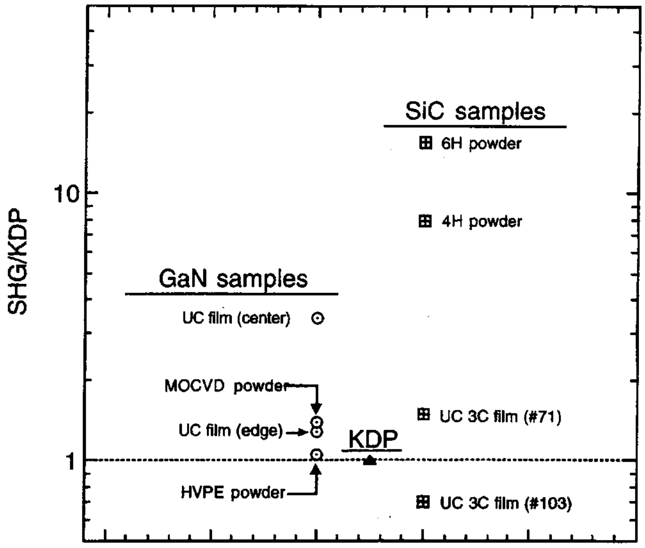

Fig. 6. A comparison of SHG intensity from GaN and SiC films and powders with KDP powders. The SHG from KDP powders is taken to be unity and the SHG signal strength of GaN and SiC samples is obtained relative to that from KDP. The comparison shows that SHG from GaN and SiC is ~5 to 10 times stronger than that from KDP.

SFG $\omega_1 + \omega_2$ was changed correspondingly from 454.7 nm, to 457.7 nm to 460.6 nm. Figure 4b shows the complementary results with the Laser 1 wavelength being fixed at 845 nm and the Laser 2 wavelength being changed from 1.00 µm to 1.01 µm to 1.02 µm.

The SFG and SHG signals from the GaN films were further verified by measuring their intensity against pumping laser power. Figure 5a shows the change of the nonlinear signal intensity as the pumping power of Laser 1 varies. It shows that the 455 nm peak has a linear dependence on the pumping power of Laser 1 (840 nm), which is an indication of sum-frequency generation. The slope of the SHG 420 nm peak is ~1.6, which is probably due to the fact that the SHG signal at 420 nm is too weak to be measured correctly. This is supported by noting that the 420 nm peak spreads over a wide range in Fig. 5b, while Laser 1 (840 nm) remains unchanged and only the pumping power of Laser 2 (1 µm) was varied. In Fig. 5b, the SFG 455 nm peak still exhibits a slope of ~0.73 which is very close to unity, while the 500 nm peak shows clearly a quadratic dependence on the pumping power of the 1 gm laser. In Fig. 6, we compare the SHG from SiC and GaN powders and films with that from KDP powders under the same experimental conditions. KDP powders were obtained by scribing KDP single crystals (Keon Optics, Haverstraw, NY) with diamond scribers. The SHG from KDP powders is taken as unity. The two 3C SiC samples were grown under the same condition but different runs. The UC GaN sample was grown by MBE and RTA annealed at 1100°C. This GaN sample has stronger SHG signal at the center than at the edge. The data indicates that both GaN and SiC films and powders can have a stronger SHG than KDP (~5 to 10 times stronger).

A good nonlinear optical material should have the following characteristics: sufficient birefringence to meet phase matching conditions, high nonlinearity and high mechanical stability, high optical power damage threshold and be economically available in bulk form.[13] These requirements put $LiNbO_3$ and KDP as two of the most popular nonlinear crystals. The use of GaN and SiC in nonlinear optical applications is also affected by the above mentioned requirements. Recently, promising results have also shown that a multi-layer strategy[6] and artificial periodic structures[14] can be employed to improve phase matching.

In summary, we have obtained CW back scattered sum-frequency generation and second harmonic generation from GaN and SiC. GaN powders and films grown by MBE, MOCVD and HVPE were optically excited with two lasers at the red (840 nm) and the infrared (1.0 µm). SFG and SHG at 455 nm, 420 nm, and 500 nm, respectively, were obtained. SiC powders and films with 3C, 4H, and 6H polytypes show similar results. SFG and SHG were verified by tuning of the pumping laser wavelengths and by measuring the SFG and SHG signals versus the pumping laser powers. Given the high SHG and other properties, GaN and SiC appear to have a promising future in nonlinear optical applications. The authors would like to acknowledge the assistance of B.K. Lee and C.J. Chi with the measurements and of J. Chen and R. Birkhahn with the growth of the SiC and GaN samples. This work was supported by MRL-DOD, NSF and BMDO/ARO contracts.

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