Simultaneous four-photon luminescence, third-harmonic generation, and second-harmonic generation microscopy of GaN

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We demonstrate what is to our knowledge the first example of four-photon luminescence microscopy in GaN and apply it to quality mapping of bulk GaN. The simultaneously acquired second- and third-harmonic generation can be used to map the distribution of the piezoelectric field and the band-tail state density, respectively. Through spectrum- and power-dependent studies, the fourth power dependence of the band edge luminescence is confirmed. The superb spatial resolution of the four-photon luminescence modality is also demonstrated. This technique provides a high-resolution, noninvasive monitoring and tool for examining the physical properties of semiconductors. © 2005 Optical Society of America

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A recent demonstration of high-brightness LEDs and laser diodes has established III–V nitrides as key materials for optoelectronics operating in the green-ultraviolet wavelength range.¹ The optical behavior of the GaN layer has been found to be strongly affected by high densities of defect states and large residue piezoelectric fields that are due to unrelaxed strain and instantaneous polarization.² Because of the large piezoelectric constants in group III nitrides, built-in electric fields of 10–100 kV/cm are expected in bulk GaN films. Defect-related yellow luminescence (YL) and high density of band-tail states are frequently observed in GaN materials.³ A considerable amount of studies have been devoted to clarifying the roles of defects versus the piezoelectric field in the photoluminescence spectra that are related to the laser mechanism.^{4,5} To obtain more insight into the dominant emission properties of the bulk GaN substrate and the quantum wells grown on top of the bulk GaN substrate, it is essential to develop a microscopic tool for mapping the distributions of the defect-related band-tail states and the strain-induced piezoelectric field as well as studying their interactions.

Previously, we have demonstrated mapping of the piezoelectric field and the defect-related band-tail state distributions in bulk GaN by second-harmonic generation (SHG) and third-harmonic generation (THG) microscopies, respectively, based on the use of a Cr:forsterite laser.^{6,7} Comparing the optical harmonics images with results from a two-photon microscope pumped by a Ti:sapphire laser,⁸ we found connections among suppressed band-edge luminescence (BEL), increased YL, increased band-tail state densi-

ties, and decreased piezoelectric fields.⁶ However, the previous demonstration used two different, expensive solid-state lasers for luminescence and optical harmonics studies. Since BEL is an important indicator of growth quality in optoelectronics semiconductor research, four-photon excited BEL is required for simultaneous observation of THG without strong absorption inside the studied materials. Here, we demonstrate what are to our knowledge the first simultaneously acquired four-photon excited BEL, THG, and SHG microscopic images in bulk GaN, obtained by use of a single Cr:forsterite laser. This technique provides a functional imaging tool for semiconductor materials with highly localized excitation and submicrometer spatial resolution.

The 2.5 μm thick unintentionally doped GaN thin film under study was grown by metal-organic chemical-vapor deposition on a *c*-plane sapphire substrate.^{6,8} The crystal structure was wurzite. The excitation source for the four-photon scanning microscope⁹ is a Cr:forsterite laser operating at 1230 nm with a repetition rate of 110 MHz and a pulse width of 140 fs. The excitation power after an Olympus PlanApoIR (60 $\times$ /1.2) objective was kept around 30–50 mW. The nonlinear emission spectrum is forward collected with a 1.4 NA oil-immersion condenser and a spectrometer equipped with a cooled CCD. The images are formed by a pair of laser-scanning galvanometer mirrors and three signal-detecting photomultiplier tubes (PMTs) with an appropriate interference filter (10 nm bandwidth) in front of each PMT. The 410 nm THG and the ultraviolet BEL were forward collected because of the strong attenuation in the reflection path for blue-

Fig. 1. (A) Nonlinear emission spectrum of a 2.5- μm -thick GaN thin film excited by a femtosecond Cr:forsterite laser. Inset, enlarged view of the spectrum between 340 and 400 nm, where the 365 nm BEL and the 370–380 nm bandtail luminescence can both be observed. (B) Excitation power dependence of the BEL (rectangles) and THG (triangles) intensities. The well-fitted slope of 4 and the slope of 3 of the lines for BEL and THG, respectively, indicate that they are four-photon and three-photon processes, respectively.

ultraviolet light. The 615 nm SHG was collected in the backward mode. Comparing the SHG intensities in the forward and backward modes, we conclude that the backward-propagated SHG in bulk GaN is contributed mainly from the interface reflection of the forward-propagated SHG (bulk contribution). Thus-similar SHG images as well as information can be obtained from both the forward and the backward modes in this case.

Figure 1(A) gives the forward-collected nonlinear emission spectrum from the GaN thin film. Symmetric SHG and THG located at 615 and 410 nm, respectively, are easily observed. According to our previous studies,⁶ the piezoelectric field distribution can be mapped by SHG through an electric field induced SHG effect. On the other hand, the defect-related band-tail state distribution can be probed by closely resonant THG. Here, four-photon excited BEL of bulk GaN around 365 nm is observed simultaneously for what is believed to be the first time. The detailed spectrum of the four-photon excited BEL is shown in the inset of Fig. 1(A), where a main peak around 365 nm and a shoulder from 370 to 380 nm are observed, similarly to what was observed in previous single-photon reports.¹⁰ The 365 nm luminescence originates from direct band-to-band transition, while the 370–380 nm luminescence corresponds to the transition between a shallow donor and the valence

band.¹¹ The existence of band-tail luminescence thus indicates the existence of shallow donor states. An important observation is that there is no YL around 560 nm in the nonlinear emission spectrum of the bulk GaN. It is generally accepted that the YL in GaN arises from the transition between shallow donors and deep acceptors, which are related to defects in GaN.^{10,11} The four-photon excitation nature of the BEL is confirmed in Fig. 1(B), where a quartic power dependence of BEL is observed. The cubic power dependence of THG is also displayed in the figure for comparison. A previous study of multiphoton excited BEL with an $\sim 1.3 \mu\text{m}$ excitation had reported an approximately cubic power dependence due to the pump-saturation effect of the deep acceptor states.¹² However, our observed quartic power dependence can be explained by the absence of YL due to the diminishing deep acceptor state density, resulting in a negligible pump-saturation effect. Notice that our study indicates a relatively high four-photon absorption coefficient in GaN even under the condition that there is no real intermediate state (deep acceptor state) for resonant enhancement.

It is observed from the spectrum [Fig. 1 (A)] that the SHG and THG from bulk GaN are much stronger than the four-photon excited BEL. In fact, the powers of these harmonic signals are of the order of a nanowatt to tens of nanowatts and can be directly visualized by the naked eye. This gives us a good chance to examine the far-field pattern of the optical harmonics. Figure 2 shows the far-field forward emission profiles of SHG and THG from this bulk GaN thin film collected by a high-NA condenser and recorded directly with a CCD camera. The bidirectional nature of SHG is a composite result from the phase-matching requirement and the fact that the excitation light is subject to an effective increase in wavelength owing to a phase anomaly near the focal center.¹³ Unlike SHG, THG is more concentrated in the forward-propagated direction. This result confirms a previous theoretical prediction.¹⁴ The well-

Fig. 2. Far-field forward emission profiles of (A) SHG and (B) THG from GaN thin film, collected by an oil-immersion condenser and recorded by a CCD camera.

Fig. 3. Scanning (A) SHG, (B) THG, and (C) four-photon excited BEL images of GaN thin film. Scale bar, 10 μm .

Fig. 4. Normalized axial response of four-photon excited BEL (filled triangles), THG (circles), and SHG (rectangles) in 2.5 μm thick GaN thin film.

collimated beam means that THG, even excited by a high-NA objective, can be efficiently collected with a low-NA objective, as described in Ref. 14.

Figure 3 shows simultaneously acquired SHG, THG, and four-photon excited BEL microscopic images of the edge region of the bulk GaN thin film. The image acquisition time is ~ 10 s when a Kalman filter is used. All three images reveal a uniform intensity distribution. The unvaried intensity of these imaging modalities indicates a unanimous distribution of piezoelectric field (SHG), of band-tail state density (THG), and of luminescence quality (BEL). This is reasonable since the superb quality of this bulk GaN has been revealed by the absence of YL.

The axial responses of these three nonlinear imaging modalities are shown in Fig. 4. Examining their relative axial locations can reveal the physical origin of these nonlinear signals. THG has an interface-sensitive characteristic, and it has been previously reported that THG emission peaks at an interface with a larger refractive index mismatch.¹⁵ Thus, the THG peak (circles in Fig. 4) is located around the GaN–air interface as a result of the large refractive index difference. For SHG, on the other hand, the signal is strongest in the vicinity of the nucleation layer because of the unrelaxed strain and the induced piezoelectric field during crystal growth. It can be proved that in a tightly focused geometry the thickness of a bulk material is underestimated by a factor of its refractive index. In our specific case, the effective GaN thickness should be measured as $\sim 1 \mu\text{m}$, corresponding to the axial distance between the maximum of the SHG and THG signals. The four-photon excited BEL exhibits a maximum between those of THG and SHG, confirming the bulk generation origin of the four-photon BEL. The superior spatial resolution of four-photon microscopy compared with SHG and THG microscopy is also evident.

In summary, we have demonstrated what is believed to be the first four-photon microscopy in a bulk GaN thin film with simultaneously acquired SHG and THG imaging modalities. The four-photon exci-

tation mode is confirmed by spectral- and power-dependence measurements, and no pump-saturation effect is observed in the absence of YL (the deep acceptor state). The axial response of each nonlinear signal is used to study the generation mechanism, and higher spatial resolution for higher nonlinear imaging modality is manifested. This novel imaging technique allows the simultaneous acquisition of high spatial resolution third harmonics and band-edge luminescence imaging in a thick semiconductor sample with a single light source, providing a noninvasive and highly penetrative investigating tool for material research.

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