Efficient blue light emission from $In_{0.16}Ga_{0.84}N$/GaN multiple quantum wells excited by 2.48-μm femtosecond laser pulses

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We report on the efficient blue light emission from $In_{0.16}Ga_{0.84}N$/GaN multiple quantum wells excited by femtosecond laser pulses with long wavelengths ranging from 1.24 to 2.48 μm. It is found that the trap states in GaN barrier layers lead to an efficient cascade multiphoton absorption in which the carriers are generated through simultaneous absorption of n ($n = 1$ and 2) photons to the trap states, followed by simultaneous absorption of m ($m = 3$, 4, and 5) photons to the conduction band. The dependence of the upconversion luminescence on excitation intensity exhibits a slope between n and $n + m$, which is in good agreement with the prediction based on the rate equation model.

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As important semiconductors operating in the ultraviolet-green spectral region, III-V nitrides have received intensive and extensive studies over the past two decades [1]. Among them, the physical properties of GaN and $In_xGa_{1-x}N$ epilayers have been the focus of many studies due to their importance in the fabrication of blue light-emitting diodes [2–4]. It has been demonstrated that the intrinsic defects present in GaN epilayers, such as the shallow donors related to Ga vacancy complexes and the trapped states related to Ga vacancies [5–8], play a crucial role in determining the luminescent properties of both GaN epilayers and $In_xGa_{1-x}N$/GaN quantum wells (QWs).

Apart from the linear optical properties under single photon excitation, the nonlinear optical properties of GaN epilayers were also investigated using pulsed laser light in the near-infrared spectral region. Early in 1997, Kim *et al.* studied the multiphoton luminescence (MPL) from GaN using tunable picosecond laser pulses and identified the existence of defect states that are located ~1.0 eV above the valence band [9]. In 2000, Sun *et al.* employed second-harmonic generation (SHG) and third-harmonic generation (THG) microscopy to map the piezoelectric field distribution in GaN and studied the two-photon absorption (TPA) [10–12]. The TPA in GaN, $In_xGa_{1-x}N$, and $Al_xGa_{1-x}N$ was also characterized by Krishnamurthy *et al.* [13]. Lately, Chu *et al.* demonstrated simultaneous four-photon luminescence (4PL), THG, and SHG microscopy of GaN using femtosecond (fs) laser light at 1230 nm [14]. Li *et al.* investigated the two-photon luminescence (TPL) and SHG in $In_xGa_{1-x}N$/GaN multiple quantum wells (MQWs) [15].

All these studies indicate that $In_xGa_{1-x}N$/GaN MQWs may exhibit highly efficient MPL due to the intrinsic defect states present in the GaN barrier and the short radiative recombination time in $In_xGa_{1-x}N$ QWs. It is expected that the existence of the trap states in the GaN barrier may significantly modify the multiphoton absorption (MPA) process in GaN and lead to efficient blue light emission from $In_xGa_{1-x}N$/GaN MQWs under the excitation of fs laser pulses in the infrared spectral region.

In fact, a solid state quantum counter for infrared and millimeter waves was proposed more than fifty years ago by Bloembergen [16]. The principle for the quantum counter is schematically depicted in Fig. 1(a). The energy separation between level E_1 (ground state) and level E_2 is much larger than kT so that the optical pump light $h\upsilon_{32}$ will not be absorbed because level E_2 is not populated. Once an infrared quantum $h\upsilon_{21}$ is absorbed, however, a second transition to level E_3 will be induced, provided that the pump light produces a faster rate than the decay from level E_2 back to level E_1. The detection of the

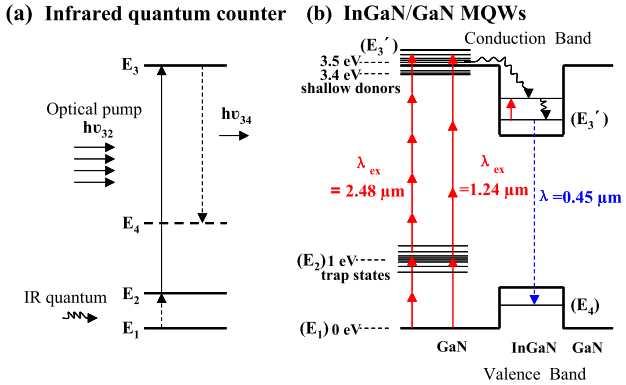

Fig. 1. (a) Solid state quantum counter for infrared and millimeter waves proposed by Bloembergen more than fifty years ago. (b) Energy band diagram for $In_{0.16}Ga_{0.84}N$/GaN MQWs in which the upconversion of infrared light to blue light through cascade multiphoton absorption is indicated. The correspondences between the energy states in $In_{0.16}Ga_{0.84}N$/GaN MQWs and the energy levels in the infrared quantum counter are also indicated.

spontaneous emission from level E_3 to another level E_4 will form a counter for infrared quantum hv_{21}.

If we compare the energy diagram of the quantum counter with that of $In_xGa_{1-x}N/GaN$ MQWs, which is schematically shown in Fig. 1(b), then a scenario for realizing efficient upconversion of infrared light by utilizing cascade MPA is generated. Apparently, the valence band of GaN corresponds to level E_1 while the trap states in GaN correspond to level E_2. The conduction band of GaN or equivalently the ground state of electrons in $In_xGa_{1-x}N$ QWs corresponds to level E_3 while the ground state of holes in $In_xGa_{1-x}N$ QWs corresponds to level E_4. There exist two major differences between the infrared quantum counter (IQC) model and the proposed MPA scheme. First, the transitions from low energy levels to higher energy ones are initiated by single photon absorption (SPA) in the IQC model while most of the transitions in our case are induced by MPA. Second, an upconversion luminescence produced by a pump light is employed to detect an infrared wave with much lower energy in the IQC model. In our case, an upconversion luminescence is generated through a cascade MPA of the pump light. The larger absorption cross section for the E_1 to E_2 transition, as compared with that for the E_2 to E_3 transition, ensures the population of level E_2.

In this Letter, we demonstrate such an efficient upconversion from 2.48 to 0.45 μm in $In_{0.16}Ga_{0.84}N/GaN$ MQWs, which normally requires at least simultaneous absorption of seven photons in the absence of the trap states.

The sample used in our study was composed of a GaN buffer layer of ~2 μm, five periods of $In_{0.16}Ga_{0.84}N/GaN$ QWs with a well thickness of 3 nm and a barrier thickness of 10 nm, and a GaN cap layer of ~10 nm. They were grown on a sapphire substrate by metal–organic chemical vapor deposition [17]. In experiments, the fs laser light, with a repetition rate of 1 kHz and a pulse duration of ~100 fs delivered by an optical parametric amplifier (OperA Solo, Coherent), was used to excite the sample at an angle of 45°. The excitation wavelength (λ_{ex}) was tuned from 1.24 to 2.48 μm. A focusing lens with $f = 150$ mm was used to focus the fs laser light and the sample was placed 2 cm away from the focus to avoid the optical damage of the sample. In this case, the diameter of the excitation spot was estimated to be ~400 μm and the maximum laser fluence was calculated to be ~7.96 mJ/cm^2, which is much lower than the damage threshold reported previously for GaN (~250 mJ/cm^2) under the excitation of nanosecond pulses [18]. In our case, the damage threshold was found to be ~24 mJ/cm^2 and ~40 mJ/cm^2 for 1.24 μm and 2.48 μm excitation, respectively, based on scanning electron microscopy (SEM) observation. The absence of optical damage was confirmed by both the SEM observation after excitation and the repeatability of the measurement results. The emitted light was collected using another lens in the direction normal to the sample surface and directed to a spectrometer for analysis. The photoluminescence spectra of the MQWs under single photon excitation were measured by a spectrometer (F-4600, Hitachi).

When we tuned the excitation wavelength from 1.24 to 2.48 μm, efficient blue light emission from the sample was clearly observed, as shown in Fig. 2. In Figs. 3(a) and 3(b), we show the emission spectra obtained at

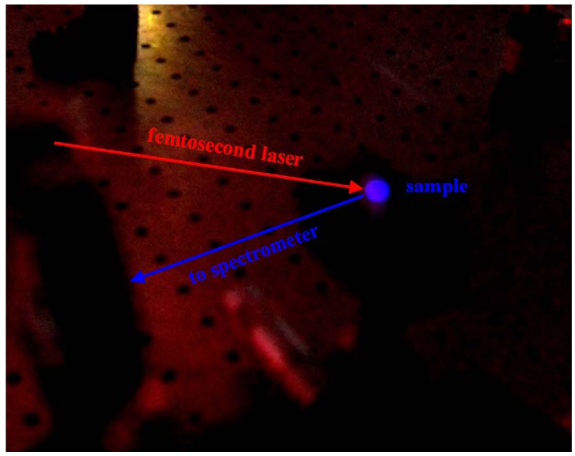

Fig. 2. Photo showing the blue light emission from $In_{0.16}Ga_{0.84}N/GaN$ MQWs under the excitation of 2.48-μm fs laser pulses.

$\lambda_{ex} = 1.24$ μm under the lowest and highest excitation intensities. In Fig. 3(b), a weak SHG located at 0.62 μm was observed because the transition from the valence band to the trap states is caused by SPA with a large absorption coefficient and the excitation light is depleted mainly by SPA. In Fig. 3(c), the excitation intensity dependence of the upconversion luminescence intensity is presented in a logarithmic coordinate. A slope of ~3.64 is observed at low excitation intensities. It is reduced to ~1.55 at high excitation intensities, implying the saturation of the upconversion luminescence.

When we excite the MQWs at 1.24 μm (~1.0 eV), electrons will be lifted from the valence band to the trap

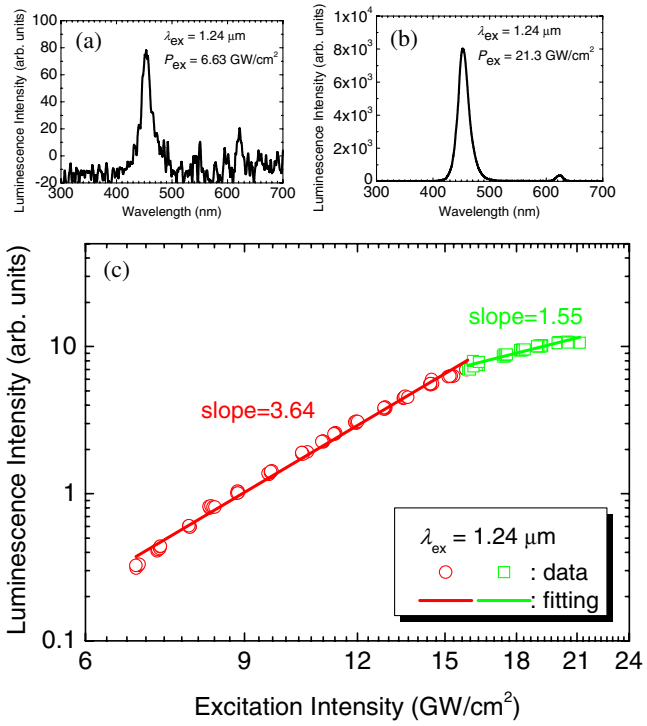

Fig. 3. (a) and (b) Luminescence spectra of $In_{0.16}Ga_{0.84}N/GaN$ MQWs under the excitation of 1.24-μm fs laser pulses with the lowest and highest excitation intensities. (c) Dependence of the upconversion luminescence intensity on excitation intensity.

states by SPA and the transition back to the valence band was found to be nonradiative with a lifetime ~430 ps [19], which is long enough for electrons to be further pumped to the conduction band through three-photon absorption (3PA). Since the SPA possesses a cross section much larger than that of the 3PA, the trap states are generally filled with electrons that can be continuously pumped to the conduction band, provided the intensity of the fs laser light is sufficiently strong for the 3PA process. In addition, the electrons pumped to the conduction band will be rapidly captured into InGaN QWs, leading to efficient upconversion from 1.24 to 0.45 μm.

A similar principle is applied to fs laser light with a much longer wavelength of 2.48 μm (~0.5 eV). In this case, the transition from the valence band to the trap states can be realized by a TPA process while that from the trap states to the conduction band can be accomplished by a five-photon absorption (5PA) process.

For $\lambda_{ex} = 2.48$ μm, the upconversion efficiency is thought to be small because a 5PA process is required. However, the SHG in this case is suppressed because the existence of the trap states whose energy matches the energy of two photons. Previously, the suppression of SHG with decreasing excitation wavelength from 795 to 750 nm was observed in ZnO nanorods [20]. It originates from the competition of TPL, which becomes dominant when the energy of two photons is larger than the exciton energy of ZnO. In contrast to the SHG observed at 0.62 μm for $\lambda_{ex} = 1.24$ μm, no SHG was observed at 1.24 μm for $\lambda_{ex} = 2.48$ μm, confirming the suppression of SHG. This implies that the TPA process is facilitated, leading to a larger population of the trap states and an enhancement of the upconversion luminescence. In Fig. 4, we present the upconversion luminescence intensity as a function of excitation intensity. As expected, we observe a slope of ~4.13 at low excitation intensities and a smaller slope of ~2.65 at high excitation intensities, indicating the saturation of the upconversion luminescence. In the inset of Fig. 4, we show the PL spectra of the MQWs under single photon excitation at different wavelengths. Similar to the previous reports for the yellow band in GaN epilayers [5,6,8], a broad emission band was observed at ~550 nm, confirming the existence of the trap states in the GaN barrier layers [9].

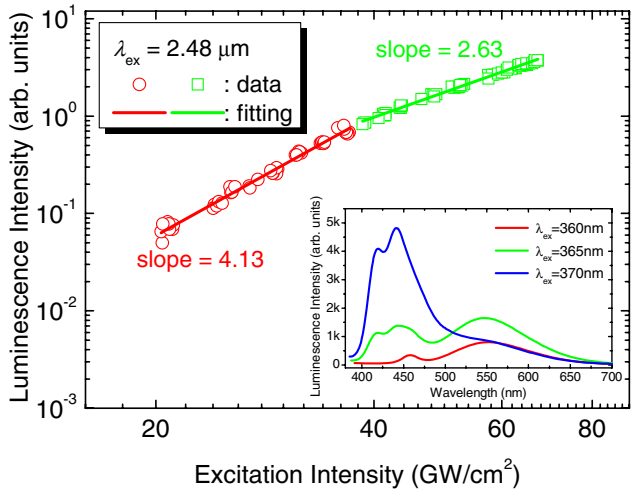

Fig. 4. Excitation intensity dependence of the upconversion luminescence intensity under the excitation of 2.48-μm fs laser pulses. The PL spectra obtained by single photon excitation at different wavelengths are shown in the inset.

Now let us try to explain the excitation intensity dependence of the MPL observed at $\lambda_{ex} = 1.24$ and 2.48 μm. Early in 2000, Pollnau *et al.* investigated theoretically, with a simple rate equation model, the power dependence of upconversion luminescence mediated by a set of intermediate states [21]. It was revealed that the upconversion luminescence excited by sequential absorption of n photons may exhibit a dependence on excitation intensity P in the range of P^n to P^1. The two limits are identified as the cases of infinitely small and infinitely large upconversion rate. They verified their theoretical results by experiments carried out in several typical rare-earth-ion-doped crystals.

Now we employ the similar rate equation model to analyze the excitation intensity dependence of the upconversion luminescence generated in the MQWs. The energy diagram of the MQWs is considered as a three-level system, including the valence band (E_1), the trap states (E_2), and the conduction band (E_3). Suppose that the transition from E_1 to E_3, which is mediated by E_2, is achieved by simultaneous absorption of n photons, followed by the simultaneous absorption of m photons, then the rate equations dominating the carrier dynamics in E_2 and E_3 can be written as

$$\frac{dN_2}{dt} = \sigma_1 P^n N_1 - \sigma_2 P^m N_2 - \frac{N_2}{\tau_2}, \tag{1}$$

$$\frac{dN_3}{dt} = \sigma_2 P^m N_2 - \frac{N_3}{\tau_3}. \tag{2}$$

Here, N_i ($i = 1, 2, 3$) is the population density of state i, P is excitation intensity, σ_i ($i = 1, 2$) is the MPA cross section of state i, and τ_i ($i = 2, 3$) is the decay time of state i. In the steady state, we have $dN_2/dt = dN_3/dt = 0$, and Eqs. (1) and (2) are reduced to be

$$\sigma_1 P^n N_1 = \sigma_2 P^m N_2 + \frac{N_2}{\tau_2}, \tag{3}$$

$$\sigma_2 P^m N_2 = \frac{N_3}{\tau_3}. \tag{4}$$

If state E_2 is dominated by linear decay (i.e., the second term in the right side of Eq. (3) is much larger than the first one), then we have $N_2 \propto P^n$ and $N_3 \propto P^m N_2 \propto P^{m+n}$. In the case when state E_2 is governed by upconversion instead of decay, we have $N_2 \propto P^n/P^m$ and $N_3 \propto P^m N_2 \propto P^n$. Therefore, it is expected that the excitation intensity dependence of the upconversion luminescence will exhibit a slope between n and $m + n$, which is considered as the index of the corresponding nonlinear process.

For $\lambda_{ex} = 1.24$ μm, it is apparent that the transition from E_1 to E_2 is a SPA process ($n = 1$) while that from E_2 to E_3 is a 3PA one ($m = 3$). Therefore, the excitation intensity dependence of the upconversion luminescence

will exhibit a slope between 1.0 and 4.0. For $\lambda_{ex} = 2.48$ μm, the transition from E_1 to E_2 becomes a TPA process while that from E_2 to E_3 becomes a 5PA one. As a result, a slope between 2.0 and 7.0 is anticipated. In experiments, we observed a slope of 3.64 for $\lambda_{ex} = 1.24$ μm at low excitation intensities, which is close to the upper limit of the theoretical value. It implies that the dynamics of the trap states is dominated by linear decay. With increasing excitation intensity, the trap states are gradually governed by upconversion, leading to a smaller slope, which is close to the lower limit. Previously, the saturation intensity of 3PA was reported to be 44 and 210 GW/cm^2 for ZnO and ZnS, respectively [22]. In our case, GaN is expected to have a lower saturation intensity of 3PA because it occurs between the trap states, which possess a lower density of states than the valence or conduction bands. Therefore, it is reasonable to observe that the saturation of upconversion appears at ~16 GW/cm^2. For $\lambda_{ex} = 2.48$ μm, the slope observed at low excitation intensities is in the middle of the lower and upper limits, implying similar rates for upconversion and linear decay at the trap states because the excitation intensity is several times larger than that used for $\lambda_{ex} = 1.24$ μm. At high excitation intensities, the slope also approaches the lower limit.

Apparently, the trap states formed by Ga vacancies spread over a wide energy region, as shown in Fig. 4. This characteristic significantly releases the constraint of resonant excitation to the trap states, making it possible to realize efficient upconversion over a wide wavelength region. To demonstrate this feature, we also investigated the upconversion luminescence generated by using $\lambda_{ex} = 1.8$ and 2.1 μm. It was found that efficient blue light emission could still be achieved. For $\lambda_{ex} = 1.8$ μm, the transition from the trap states to the conduction band can be achieved by 4PA process. However, the observed upconversion luminescence is not much stronger than that observed at $\lambda_{ex} = 2.48$ μm because the first transition to the trap states does not occur at the energy position, where the density of states is the largest. With increasing excitation intensity, a gradual saturation of the MPL is also observed. For $\lambda_{ex} = 2.1$ μm, similar reduction in the slope is also found, however, the saturation occurs at higher excitation intensities.

In summary, we investigated, by comparing with the solid state quantum counter, the upconversion luminescence in $In_{0.16}Ga_{0.84}N$/GaN MQWs and demonstrated efficient blue light emission mediated by cascade MPA. It was revealed that the intrinsic trap states present in the GaN barrier play a crucial role in the realization of efficient upconversion luminescence. The slope in the excitation intensity dependence of the upconversion luminescence intensity was found to be determined mainly by the carrier dynamics in the trap state. The wide spread trap states in GaN barrier layers make it possible to generate efficient blue light over a wide wavelength range. The efficient upconversion in $In_{0.16}Ga_{0.84}N$/GaN MQWs will find applications in making optoelectronic devices.

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References

1. I. Vurgaftman, J. R. Meyer, and L. R. Ram-Mohan, J. Appl. Phys. **89**, 5815 (2001).
2. S. Nakamura, M. Senoh, and T. Mukai, Appl. Phys. Lett. **62**, 2390 (1993).
3. S. D. Lester, F. A. Ponce, M. G. Craford, and D. A. Steigerwald, Appl. Phys. Lett. **66**, 1249 (1995).
4. C. A. Tran, A. Osinski, R. F. Karlicek, Jr., and I. Berishev, Appl. Phys. Lett. **75**, 1494 (1999).
5. D. M. Hofmann, D. Kovalev, G. Steude, B. K. Meyer, A. Hoffmann, L. Eckey, R. Heitz, T. Detchprom, H. Amano, and I. Akasaki, Phys. Rev. B **52**, 16702 (1995).
6. T. Suski, P. Perlin, H. Teisseyre, M. Leszczyński, I. Grzegory, J. Jun, M. Boćkowski, S. Porowski, and T. D. Moustakas, Appl. Phys. Lett. **67**, 2188 (1995).
7. J. Neugebauer and C. G. Van de Walle, Appl. Phys. Lett. **69**, 503 (1996).
8. M. A. Reshchikov and H. Morkoç, J. Appl. Phys. **97**, 061301 (2005).
9. D. Kim, I. H. Libon, C. Voelkmann, Y. R. Shen, and V. Petrova-Koch, Phys. Rev. B **55**, R4907 (1997).
10. C.-K. Sun, S.-W. Chu, S.-P. Tai, S. Keller, U. K. Mishra, and S. P. DenBaars, Appl. Phys. Lett. **77**, 2331 (2000).
11. C.-K. Sun, S.-W. Chu, S.-P. Tai, S. Keller, A. Abare, U. K. Mishra, and S. P. Denbaars, Scanning **23**, 182 (2001).
12. C.-K. Sun, J.-C. Liang, J.-C. Wang, F.-J. Kao, S. Keller, M. P. Mack, U. Mishra, and S. P. DenBaars, Appl. Phys. Lett. **76**, 439 (2000).
13. S. Krishnamurthy, K. Nashold, and A. Sher, Appl. Phys. Lett. **77**, 355 (2000).
14. S.-W. Chu, M.-C. Chan, S.-P. Tai, S. Keller, S. P. DenBaars, and C.-K. Sun, Opt. Lett. **30**, 2463 (2005).
15. Q. Li, S. J. Xu, G. Q. Li, D. C. Dai, and C. M. Che, Appl. Phys. Lett. **89**, 011104 (2006).
16. N. Bloembergen, Phys. Rev. Lett. **2**, 84 (1959).
17. T. Lu, S. Li, C. Liu, K. Zhang, Y. Xu, J. Tong, L. Wu, H. Wang, X. Yang, Y. Yin, G. Xiao, and Y. Zhou, Appl. Phys. Lett. **100**, 141106 (2012).
18. T. Akane, K. Sugioka, and K. Midorikawa, Appl. Phys. A **69**, S309 (1999).
19. H. Haag, B. Hönerlage, O. Briot, and R. L. Aulombard, Phys. Rev. B **60**, 11624 (1999).
20. J. Dai, Q.-F. Dai, J.-H. Zeng, S. Lan, X. Wan, and S.-L. Tie, IEEE J. Quantum Electron. **49**, 903 (2013).
21. M. Pollnau, D. R. Gamelin, S. R. Lüthi, H. U. Güdel, and M. P. Hehlen, Phys. Rev. B **61**, 3337 (2000).
22. B. Gu, J. He, W. Ji, and H.-T. Wang, J. Appl. Phys. **103**, 073105 (2008).