Degenerate four-wave-mixing spectroscopy on epitaxially laterally overgrown GaN: Signals from below the fundamental absorption edge

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We performed photoluminescence (PL) and degenerate four-wave-mixing (FWM) spectroscopy in epitaxially laterally overgrown GaN at 10 K. Optical transitions based on exciton complexes such as biexciton emission, exciton–exciton scattering, electron–hole plasma, and so on, were revealed by PL under a wide range of excitation densities. The FWM signals were observed from states below the fundamental excitonic absorption edge, showing that nonlinear photoswitching can be performed with a transmitance geometry. The origin of such nonlinearity was discussed by correlating with feasible many-body effects between excitons, biexcitons, and free carriers.


A number of breakthroughs in the fabrication technology of GaN-based semiconductors have opened the way to the commercialization of laser diodes, as well as of light-emitting diodes. Such progress has also contributed detailed studies on linear and nonlinear spectroscopy of excitonic transitions in hexagonal GaN (h-GaN) epilayers with relatively high optical quality. 1-3 Free excitons in h-GaN are composed of three bands labeled \( E_{XA} \) (A exciton), \( E_{XB} \) (B exciton) and \( E_{XC} \) (C exciton), which are transitions from the conduction \((\Gamma_{7v})\) to the A \((\Gamma_{9u})\), B \((\Gamma_{7uv})\), and C \((\Gamma_{71u})\) valence bands, respectively. The binding energy \( E_b \) (\( E_{BA} \)) and the effective Bohr radius \( r_B \) of the A exciton \((E_{XA})\) in h-GaN have been reported to be about 28 meV and about 2.9 nm, respectively. 4 Fisher et al. performed transient four-wave-mixing (FWM) studies on a GaN epilayer and observed quantum beating between the A and B excitons. 1 Furthermore, Zimmermann et al. discussed the beating period and \( v \) (\( v \)) of the two beams is below 10°. The external-crossing angle of the two beams is below 10°. The whole spectra were taken at 10 K.

Figure 1 shows the reflection and the cw PL spectra of the sample. By comparison between the two, PL peaks at 3.4945 and 3.5025 eV are attributed to the A free exciton \((E_{XA})\) and the B free exciton \((E_{XB})\), respectively. These energy positions are shifted towards the higher photon energy side by about 17 meV compared to that of the nearly strain-free homoepitaxial h-GaN layer. 6 This is because the epilayer suffers biaxial compression of the order of 13 kbar at the face perpendicular to the (0001) direction, which is mainly induced by the difference of the thermal expansion coefficient between the substrate and the epilayer. The main PL peak located at 3.4880 eV is attributed to the excitons bound to the neutral donor \([D^0, X]\). This energy position is very close to that of biexcitons which appear under moderately high photoexcitation. 7 It should be noted that the spec-
FIG. 1. PL spectrum of an ELO-GaN sample at 10 K under cw excitation with a He–Cd laser. Reflection spectrum is also inserted in the figure.

tra in Fig. 1 are taken under macroscopic condition where a lot of stripes composed of wing/window regions are included within the area of photoexcitation. In order to assess the correlation between dislocation densities and optical properties, the microscopic PL was performed under the site-selective configuration. It was found that the spectral shape of the spectra taken at the wing region is almost the same as that at the window region, besides the former is blueshifted by 0.3 meV with respect to the latter due to a slight difference of compressive strain. This suggests that the optical quality is insensitive to macroscopic dislocation densities, and that the transition energies can be determined within the accuracy of 0.3 meV even with a macroscopic measurement.

Figure 2(a) shows the picture of transmitted laser beams used for the FWM measurement, the directions of which are defined as \( k_1 \) and \( k_2 \), respectively. Since the striped SiO\(_2\) mask acts as a grating, each beam is diffracted to the direction perpendicular to the periodic structures of an ELO GaN. The wavelength is 357 nm (3.473 eV), so that the incident beams transmit the sample with almost no photoabsorption. If the timings of the two beams are tuned, FWM signals appear in the phase matching directions, showing third (2\( k_2 - k_1 \)), fifth (3\( k_2 - 2k_1 \)), seventh (4\( k_2 - 3k_1 \)), ninth (5\( k_2 - 4k_1 \)), eleventh (6\( k_2 - 5k_1 \)), thirteenth (7\( k_2 - 6k_1 \)), and fifteenth (8\( k_2 - 7k_1 \))-order nonlinearity, as shown in Fig. 2(b). To the naked eye, signals up to eleventh-order nonlinearity can be observed. If the incident energy density is less than about 20 \( \mu \)J/cm\(^2\), such optical nonlinearity is not observed at energies below the fundamental absorption edge. It should be noted that similar high-order nonlinearities have been observed in ZnSe-based semiconductors. The finding of optical nonlinearity at the transparent energy range is interesting not only from the physics viewpoint but also from applications related to the high-speed multisignal processing with low optical conditions.

The FWM spectra at 10 K, taken under various pumping spectral conditions, are shown in Fig. 3. Each signal is measured at each time \(( t = 0 - 275 \text{ fs} )\) when the maximum intensity is reached. Unlike the case under lower photoexcitation energy density, the nonlinear signals originating from the transitions of \( E_{XB}, E_{XA}, \) and \( E_{XX} \) are not detected in this condition probably because the carrier density exceeds the Mott's screening density of excitons. FWM signals are pinned instead at two energy ranges, labeled \( A \) (3.473–3.476 eV) and \( B \) (3.442–3.459 eV) if the incident is covered beam in the vicinity of these energy positions. Since the absorption tail in GaN is negligibly small in such energy ranges at cryogenic temperature, almost no real exciton population is involved in these nonlinear processes. Moreover, if the incident laser wavelength is in the range of 354–358 nm, the time when the maximum intensity is reached is delayed with respect to that of the laser pulse. The spectra taken under such wavelength conditions are pinned at the energy positions of \( A \) and \( B \). From these results, the origin of the \( A \)- and \( B \)-nonlinear bands in the FWM spectra may be ascribed to virtual excitonic states related to the many-body effect of excitons such as exciton–exciton scattering or to exciton–phonon complex systems.

The spectrally integrated intensities of the FWM signals as a function of pumping laser energies are shown in Fig. 3(b). The maximum intensity is obtained at the pumping energy of 3.473 eV, which is almost the same as the energy position of \( A \). However, it should be noted that the peak of the FWM spectrum jumps to the \( B \) range if the incident laser energy is tuned to peak \( A \), as shown in the spectrum in Fig. 3(b).
...energy of the EEX + 1LO (longitudinal optical phonon) band (3.409 eV) (see, also, Fig. 4).

As mentioned before, the origin of the A-nonlinear band in the FWM spectra may be related to virtual exciton–exciton $P_2$ scattering comparing with FWM and PL spectra. However, no clear correspondence was observed between the B-nonlinear band and PL peak energies. This $B$ band (3.442–3.459 eV) is located between $P_2$ and the $E_{EX} + 1$LO bands. It may be related to three or more exciton scattering processes, or other complicated many-body processes where excitons, biexcitons, and free carriers are involved. However, it is difficult at the current stage to make a clear assignment of the $B$ band. This finding is important for the future development of nonlinear optical switching devices operated under transmittance geometry with low optical loss conditions.

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