Fine structure of near-band-edge photoluminescence in He^+ -irradiated GaN grown on SiC

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The effect of He ion implantation on the optical properties of epitaxial GaN-on-SiC was studied. We observed that He^+ irradiation increases the relative intensity of the “blue emission” and resistivity of GaN films and decreases the intensity of the near-band-edge photoluminescence. Because the intensity of the main peak is drastically decreased, the fine structure of the near-band-edge photoluminescence in GaN after He^+ irradiation was observed. From a comparison of observed sharp lines with photoluminescence peaks of GaN doped with oxygen, we conclude that oxygen can produce a complex, which is characterized by a strong localization of free carriers and a large lattice distortion. The zero-phonon line of this defect has energy close to the band-gap energy of GaN.

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Recently, many efforts have been devoted to the investigation of the defect origin in GaN. One of the most important problems is the origin of the shallow donors observed in unintentionally doped GaN films. Hall measurements show that these defects still have a high concentration ($>1 \times 10^{17} \text{ cm}^{-3}$).^{1,2} The high concentration of point defects and high carrier concentration result in a perturbation of the GaN band gap.³ This perturbation is easily detected by a measurement of the full width at half maximum (FWHM) of the near-band-edge photoluminescence peaks at low temperatures.⁴ Nevertheless, the origin of these donors is still unknown despite their high concentration and simplicity of registration. There are different suggestions about their origin. One of these suggestions is the nitride vacancy (V_N) origin of the shallow donor.⁵ However, Neugebauer and Van de Walle⁶ showed that even at growth temperatures as high as 1000 °C the V_N concentration is orders of magnitude too small to explain the high unintentional carrier concentrations above 10^{18} cm^{-3} found in GaN epitaxial films. They also supported that Si and O could be unintentional donors in GaN. Chung and Gershenson studied the effect of high oxygen concentration (from 10^{19} to the 10^{20} cm^{-3} range) on optical properties of GaN.⁴ The photoluminescence (PL) peaks at 3.51, 3.47, 3.42, and 3.34 eV in GaN samples at 4.2 K were observed. They claimed that these peaks are a band-to-band recombination, an exciton bound to V_N , an oxygen-related recombination, and a LO-phonon replica of the peak at 3.47 eV, respectively.

In this letter we study the effect of a $^4\text{He}^+$ ion implantation during Rutherford backscattering spectroscopy (RBS) investigations on the optical properties of GaN films grown on (0001) SiC. We found that a near-band-edge photoluminescence of the GaN has a fine structure after He^+ ion irradiation.

These effects are discussed, and to explain these experimental results, a model is presented.

The GaN films which we used for our investigations were grown by metal-organic chemical-vapor deposition method on (0001) 6H-SiC substrates.⁷ The thickness of the GaN film was 2 μm . A virgin GaN film had a sheet resistance of $2 \times 10^3 \Omega/\square$. This film was characterized with RBS. The RBS analysis was done with a 1.8 MeV $^4\text{He}^+$ ion beam, an incident angle of 90° to the sample surface, and an incident ion-beam diameter of $<3 \text{ mm}$. During RBS analysis, channel searching, and channeling analysis, the sample was irradiated with a dose of 20 μC . This corresponds to a dose of $\sim 7 \times 10^{15} \text{ } ^4\text{He}^+/\text{cm}^2$. Projective range (R_p) of the 1.8 MeV $^4\text{He}^+$ in GaN calculated by TRIM is $\sim 3.6 \mu\text{m}$, $\Delta R_p \sim 0.12 \mu\text{m}$. The estimated maximum concentration of the implanted He is about $2 \times 10^{19} \text{ at/cm}^3$. Thus, the projected range for He^+ was greater than the thickness of the GaN film. Therefore, more of the He^+ ions stopped in the SiC substrate. The detector was mounted at an angle, corresponding to the scattering angle of 165° in the laboratory frame of reference. The value of χ_{min} was $\sim 4\%$, which indicates that the virgin sample had a good crystallinity.

The energy loss of the He^+ ion in the interaction with the solid GaN consists of two parts: (a) energy loss due to the interaction with electrons, and (b) energy loss due to the elastic interaction with nuclei. The first process prevails for the high-energy incident ions, thereby initiating ionization of the irradiated crystal. After the ions lose their energy near the surface, the second mechanism of energy loss will begin to dominate. As a result of this process, the atoms of the irradiated crystal move from their regular position in the lattice and form radiation defects.

We studied the influence of these defects on the photo-

FIG. 1. Distribution of the normalized intensity of the PL peaks across the GaN sample, irradiated by $^4\text{He}^+$: (a) distribution of the $I_{3.38}/I_{3.35}$ ratio; (b) distribution of the $I_{3.38}/I_{2.23}$ ratio; (c) distribution of the $I_{3.35}/I_{2.23}$ ratio; and (d) distribution of the $I_{2.8}/I_{2.3}$ ratio. Where $I_{3.38}$, $I_{3.35}$, $I_{2.8}$, and $I_{2.3}$ are the PL peak intensities of the 3.38, 3.35, 2.8, and 2.3 eV PL peaks, respectively.

luminescence of GaN. To make this investigation, we used the typical scheme for PL measurements with a lock-in amplifier and a cw He–Cd laser (the wavelength of the excited beam was 325 nm, the beam power was 7 mW, and the beam was focused into a 100 μm spot). The room-temperature PL spectra of as-grown GaN has intensive near-band-edge emission with a main peak at 3.38 eV and two low-intensive broad peaks at 2.8 and 2.3 eV. The intensity ratios $I_{3.38}/I_{2.23}$ and $I_{3.38}/I_{2.8}$ of the PL peaks are larger than 200 ($I_{3.38}$, $I_{2.8}$, and $I_{2.3}$ are the PL peak intensities of the 3.38, 2.8, and 2.3 eV PL peaks, respectively). Figure 1 shows the distribution of the intensity of different room-temperature PL peaks across the sample. To study the PL intensity distribution, the sample was moved in the focal plane with a velocity of 20 $\mu\text{m}/\text{s}$. The He^+ ion irradiated area was localized from 4 mm through 7.4 mm (7.6 mm is the edge of the investigated part of the sample). If we compare the extinction length of the laser beam with R_p of the He^+ ions, we can conclude that the change in PL mainly was determined by the point defects caused by a cascade process produced by the He^+ ions rather than by the presence of implanted He atoms. These defects produce nonradiative recombination of electron–hole pairs resulting in a decrease of the near-band-edge PL intensity. The significant increase of the native defects is confirmed by the analysis of the secondary ion mass spectroscopy (SIMS) profiles of the irradiated films. The profiles reveal the gettering of the oxygen at the irradiation-induced damage region localized at the depth of $R_p/2$. The similar gettering by He-irradiation-induced defects is well known for silicon.⁸ Another effect of the He irradiation is a remarkable increase in the sheet resistance. The irradiated area is semi-insulating, which could be due to an increase of electron traps or acceptors in the irradiated area. It is very important to note that a gallium vacancy could cause this high compensation of GaN. We also observed an increase in the blue emission with an increase in the He^+ irradiation dose (Fig. 1, curve d). The same effect was observed in all the GaN samples after Ga, Mg, Ca, N, and P implantation before annealing.

Figures 2 and 3 show the results of the investigation of

FIG. 2. The room-temperature PL spectra of the near-band-gap emission for different $^4\text{He}^+$ ion irradiation doses. The irradiation dose increases from the a curve to the d curve. The a curve is related to an unirradiated point on the GaN sample.

the near-band-edge PL across the sample at room temperature and at liquid-nitrogen temperature, respectively. The investigated points were located in a range from 3.6 to 5.4 mm. Change in the He^+ ion irradiation dose is correlated with the position of the investigated points. We observe three features in these PL spectra. The first feature is an increase in nonradiative electron traps (or acceptors) producing a decrease in the intensity and in the FWHM of the near-band-edge PL peaks. This narrowing effect can be explained by a significant increase of the Debye length due to the high compensation.

FIG. 3. Liquid-nitrogen PL spectra of the near-band-gap emission for different $^4\text{He}^+$ ion irradiation doses. The irradiation dose increases from the a curve to the c curve. The a curve is related to an unirradiated point on the GaN sample.

TABLE I. Collected data of low-temperature GaN photoluminescence.

P1	FX_B	FX_A	D_1, X	A_1, X	D_2, X	P2	1LO	P3	2LO	DAP	Dopant	Substrate	Ref.
3.512	3.5	3.492	3.485	3.48	3.462		3.402 3.393 3.385 3.375 (0.027) ^a 3.365 (0.028) ^a	3.37 3.345 (0.025) ^a	3.31		Undop.	Al ₂ O ₃	8
3.485 (0.027) ^a	3.48 (0.02) ^a	3.465 (0.027) ^a	3.46 (0.025) ^a		3.436 (0.026) ^a						Undop.	6H-SiC	8
3.504 (0.008) ^a			3.47 (0.015) ^a 3.474 (-0.004) ^b 3.472 (-0.002) ^b		3.448 (0.014) ^a	3.424 3.422 (0.002) ^b 3.42 (0.004) ^b				3.297 3.33 3.27	Oxygen Undop. Undop.	Al ₂ O ₃ Al ₂ O ₃ Al ₂ O ₃	4 9 10
3.515 (-0.011) ^b (-0.003) ^a			3.465 (0.005) ^b (0.02) ^a		3.45 (-0.002) ^b (0.012) ^a	3.425 (-0.001) ^b	3.37 (0.032) ^a 3.36 (0.033) ^a	3.335 (0.035) ^a	3.265 (0.036) ^a	3.245	Undop.	6H-SiC	This work

^a() the value in parentheses is a difference between the energy of the related PL peak in Ref. 8 and data in the current reference.

^b() the value in parentheses is a difference between energy of the related PL peak in Ref. 4 and data in the current reference.

The second feature corresponds to the full width at half maximum of the peaks in Fig. 2 (curve d) and Fig. 3 (curve c) becoming less than the FWHM associated with temperature broadening. This means that these peaks belong to strongly localized states. If we take into account that the investigated peaks have energy very close to the band-gap energy, we can conclude that we observed intercenterlike recombination. The third feature is that the observed peaks (Fig. 3, curve c) coincide with the PL peaks observed by Chung and Gershenson,⁴ which shows that the defects are possibly associated with an oxygen complex.

In Table I we have collected the data of the near-band-edge emission observed by different authors in GaN. The results of Skromme *et al.*⁸ illustrate the emission of a high-purity GaN grown on sapphire and silicon carbide substrates. The data of Smith *et al.*⁹ and Fisher *et al.*¹⁰ represent the low-temperature photoluminescence of GaN with significant oxygen concentrations according to the authors' analysis. It is noted that an accuracy of the peak energy determination was about 10 meV in the Chung and Gershenson work⁴ and about 2 meV in our investigations. Thus, we have good agreement with our data and the data of Chung and Gershenson for the peak position of the P1; D1, X; D2, X; and P2 emissions. A lesser correlation between the LO replicas and donor-acceptor pair (DAP) peaks is explained by different concentrations of the point defects in these films. As a result, our samples reveal the phonon replicas of the point defects, while the phonon replicas of more perfect films⁸ are related to band-to-band recombination in GaN.¹¹ As we showed, peaks P1 and P2 in our sample have a sharp-line structure and are related to the PL peaks observed in samples with a very high oxygen concentration ($>1 \times 10^{19} \text{ cm}^{-3}$).⁴ From this we can conclude that the origin of these peaks is due to an oxygen complex. This result is confirmed by the analysis of the SIMS profiles of the investigated film. These profiles show that the studied film has a two-order increase of the oxygen concentration in the "under-the-surface layer" (the "layer" thickness is about $0.3 \mu\text{m}$, the observed maximum oxygen concentration in the "layer" is $1 \times 10^{18} \text{ cm}^{-3}$). It is important to note that the oxygen and carbon SIMS profiles

are not changed in the top part of the GaN film after He⁺ ion irradiation. The next interesting property of these peaks is the energy difference between the P1 and P2 peaks, which is equal to the LO phonon energy in GaN. In addition, these peaks have the same behavior with respect to changes in temperature (Figs. 2 and 3). Thus, we suggest that P2 is a LO phonon replica of peak P1 and the oxygen complex is related to a significant lattice distortion. These features of the oxygen complex should explain the disappearance of the P1 peak and an increase of the P2 peak with an increase in the oxygen doping level as observed by Chung and Gershenson.

To summarize, we studied the effect of ⁴He⁺ ion irradiation during RBS investigation on the optical properties of GaN films grown on (0001) 6H-SiC. We found that the near-band-edge photoluminescence of GaN has a fine structure after He⁺ ion irradiation. We suggested that the observed sharp peaks in GaN belong to the intercenter recombination of electron-hole pairs on the oxygen complex.

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