C-Implanted N-Polar GaN Films Grown by Metal Organic Chemical Vapor Deposition *

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C-implantation N-polar GaN films are grown on c-plane sapphire substrates by metal organic chemical vapor deposition. C-implantation induces a large number of defects and causes disorder of the lattice structure in the N-polar GaN film. Raman measurements performed on the N-polar GaN film before C-implantation after C-implantation and subsequent annealing at 1050°C for 5 min indicate that after annealing the disordered GaN lattice is almost recovered. High resolution x-ray diffraction shows that after implantation there is an obvious increase of screw-dislocation densities, and the densities of edge dislocation show slight change. Carbon implantation can induce deep acceptors in GaN, thus the background carriers induced by the high oxygen incorporation in the N-polar GaN film will be partially compensated for, resulting in 25 times the resistivity, which is demonstrated by the temperature-dependent Hall-effect measurement.

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The growth of group Ⅲ-nitrides (Al,Ga,In)N have generated significant research interest within the past three decades due to their tremendous potential to create light-emitting diodes (LEDs), laser diodes, and electronic devices with excellent properties.[1–3] Due to their wurtzite structures, group Ⅲ-nitrides exhibit large spontaneous and piezoelectric polarization oriented along the (0001) *c*-axis.[4] Generally, LEDs are grown on the Ga-face (0001) polarity GaN films, and the electronic devices utilize the polarization discontinuities at the AlGaN/GaN interface on the Ga-face to induce a two-dimensional electron gas (2DEG).[5] Rajan *et al.* pointed out the potential benefits of N-face GaN transistors such as low reverse-bias gate leakage, enhancement mode operation and reduced output conductance in short gate length devices, and improved carrier confinement under reverse bias.[6] Although there are many proposed theoretical benefits of N-face-based devices, high-performance devices require improvement of material quality, including reducing the concentrations of impurities, where leak currents can limit the device performance and lifetime.[7–9] Both theoretical and experimental investigations show that oxygen in the N-$(000\bar{1})$ face is much higher than the Ga-(0001) face.[10] Previous work showed that the incorporation of oxygen impurities in the N-face GaN film grown on sapphire (Al_2O_3) was 100 times higher than Ga-face samples.[10–13] It is well-known that oxygen is a shallow donor in GaN,[10,13,14] and can induce high background carriers that degenerate device performance and limit the application of N-polar GaN devices. Ion-implantation is a very attractive technological tool for the doping of the GaN film. To improve the device performance, a feasible method is used to introduce deep acceptors such as carbon by ion-implantation to compensate for the background carriers which will result in higher resistivity N-polar GaN materials.[15,16] Ion-implantation in Ga-polar GaN films, including C-implantation, has been studied in detail.[17–22] However, there are few reports on ion-implanted N-polar GaN films. In this study, we examine the properties of the N-polar GaN films before and after C-implantation and annealing at 1050℃ by Raman scattering, high resolution x-ray diffraction (HRXRD) and temperature-dependent Hall-effect measurement.

The N-polar GaN film was grown on *c*-plane sapphire substrates by metal organic chemical vapor deposition (MOCVD). The *c*-axis direction of the substrate was inclined toward the *m*-plane by 4°. H_2 was used as carrier gas and the growth pressure was kept at 40 Torr. The substrate was first annealed in H_2 for 2 min to clean any organic material on the sapphire substrate. The sample was then of nitridation with an NH_3 flow of 150 mmol/min at 1100℃ for 2 min. Then an AlN nucleation layer was deposited at 1100℃. Lastly, a GaN layer was deposited by using a TEGa flow of 100 μmol/min and an NH_3 of 130 mmol/min at 1100℃. Since 1×10^{15} cm^{-2} is a typical dose in ion-implantation, the N-polar GaN layer was implanted with 200 keV C ions at room temperature with a total dose of 1×10^{15} cm^{-2} after growth.[21,22] After im-

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plantation, the sample exhibited a much darker color. The annealing experiment was carried out at 1050℃ for 5 min under nitrogen with a chamber pressure of 40 Torr.

The Raman measurement was performed at room temperature by using the 514 nm line of an Ar^+ laser as an excitation source. The laser beam was focused by a microscope lens system (×50 ulwd) yielding a spot size of 1 μm. The scattered light was detected in backscattering geometry by using an 1800 g/mm spectrometer with a charge coupled device (CCD) detector.

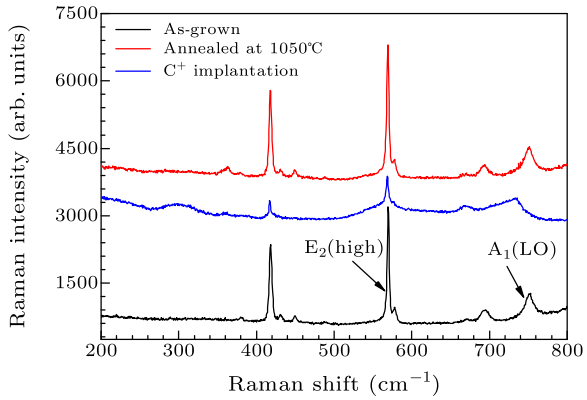

Fig. 1. Raman scattering spectra measured for the N-polar GaN before and after C^+-implantation and subsequent annealing at 1050℃ for 5 min.

Raman scattering spectra of the N-polar GaN film before and after 200 keV C implant at room temperature at a dose of $1 \times 10^{15}\,\mathrm{cm}^{-2}$ is shown in Fig. 1. The spectra covered the range of 200–800 cm^{-1} and recorded the Z-direction along the c-axis of the wurtzite phase. In the as-grown sample there were two peaks at 569 cm^{-1} and 750 cm^{-1} due to the E_2 (high) and A_1 (LO) modes, respectively, characteristic of the wurtzite-type structure. This result is consistent with the Raman selection rules.[18,19,23] There were two additional peaks, one peak at 418 cm^{-1} stems from the sapphire substrate and the other weak peak at 680 cm^{-1} originates from the AlN nucleation layer since the penetration depth of the incident laser light is larger than the thickness of the GaN layer.[24–26] After C-implantation three additional peaks were observed at 300 cm^{-1}, 360 cm^{-1}, and 670 cm^{-1} and were accompanied by an increase of the background signal and the E_2 (high) and A_1 (LO) line widths. Previous reports also observed the same peak in polar Ga-face GaN films, and ascribed this peak to the disordered GaN structure induced by implantation, independent of the ion species.[18,20] High dose C-implantation in the GaN film would introduce a large number of defects and cause disorder of the lattice structure. The high defect densities break the selection rules in the Raman scattering process. Therefore, phonon modes that are forbidden by the selection rules can be observed in the Raman spectrum. This phenomenon is called the disorder activated Raman scattering (DARS). The broadband at 300 cm^{-1} was assigned to the highest acoustic-phonon branch at the zone boundary which has been attributed to the breathing mode of Ga vacancy (V_{Ga}). The peak at 670 cm^{-1} probably arises from the optical-phonon branch at the zone boundary, which was assigned to N vacancy (V_N) in Limmer's work.[21] Due to the gap between the acoustic- and the optical-phonon branches from 300 to 530 cm^{-1}, DARS cannot explain the peak at 360 cm^{-1}. The most likely reason for this 360 cm^{-1} peak was due to the large amount of point defects induced by C implantation.[20–25]

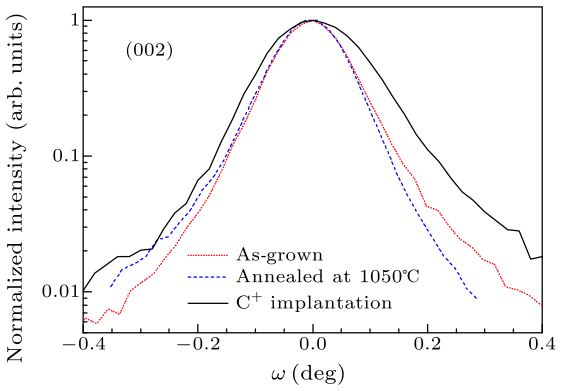

Fig. 2. X-ray rocking curves measured for (002) planes of N-polar GaN films before C-implantation and after annealing the implanted GaN at 1050℃.

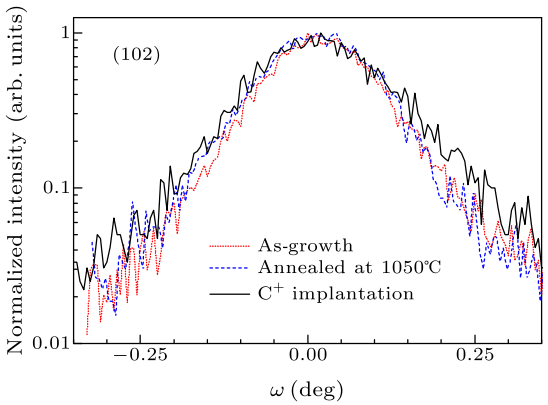

Fig. 3. X-ray rocking curves measured for (102) planes of N-polar GaN films before C-implantation and after annealing the implanted GaN at 1050℃.

To ascertain the origin of the additional peaks, HRXRD measurement was performed. The HRXRD measurement was performed by using a Bruker D8-discover system equipped with a Ge(220) monochromator and a channel-cut analyzer operating in the triple-axis mode, delivering a pure CuKα line of wavelength $\lambda = 0.15406$ nm. It has been reported that the densities of edge dislocation including the edge component of mixed dislocation are indirectly represented

by the x-ray rocking curve (XRC) full width at half maximum (FWHM) at the (102) planes while the densities of screw-dislocation are represented by FWHM at (002).[27,28] The XRCs of as-grown, C-implanted and annealed sample for the (002) and (102) plane are shown in Figs. 2 and 3. For the (002) plane, the XRC FWHMs of the as-grown, C-implanted, and annealed N-polar sample are 518.50 s, 694.34 s and 500.73 s, respectively. The FWHM at the (102) plane of the as-grown sample is 641.83 s, while these of the C implanted and annealed sample are 649.36 s and 686.14 s, respectively. These results show that after implantation there is an obvious increase of screw-dislocation densities while the densities of edge dislocation show almost no change. After annealing at 1050℃ for 5 min, the change of XRD FWHM disappears, indicating that the disordered N-polar GaN film is almost recovered. This result is consistent with the Raman scattering spectra described above. As shown in Fig. 1, the disordered GaN lattice is almost recovered after annealing temperature up to 1050℃ for 5 min, the peaks at 300 cm^{-1} and 670 cm^{-1} disappear, and the 360 cm^{-1} mode becomes very weak. Based on these results, we can obtain that the recoverable peaks located at 300 cm^{-1} and 670 cm^{-1} may be associated with the vacancy defects or screw dislocations that disappear after annealing. In contrast, the peak at 360 cm^{-1} appearing after annealing does not originate from dislocations, while it likely results from the introduction of C or complex by ion-implantation.

To study the effect of C-implantation on the electrical properties of the N-face GaN film, a temperature-dependent Hall-effect measurement was carried out in the temperature range of 300–470 K for both the as-grown sample and the sample with C-implantation and annealing at 1050℃.

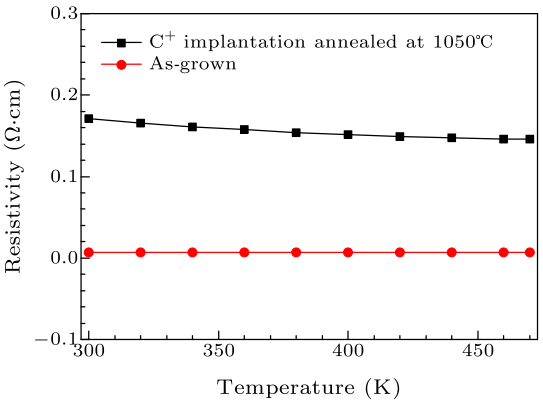

Fig. 4. Evolution of resistivity of N-polar GaN with measurement temperature.

The measured resistivity of the N-polar GaN film from $T = 300$ to 470 K are shown in Fig. 4. The resistivity of the implantation sample decreases by 15% over this temperature range, while the as-grown sample does not show a change of resistivity. In addition, the resistivity of the implantation sample is 25 times larger than the as-grown sample at room temperature. This difference in resistivity is consistent with damage-related trap sites removing carriers from the conduction band.[19] The measured electron concentration and mobility shown in Figs. 5 and 6 are in accordance with this phenomenon.

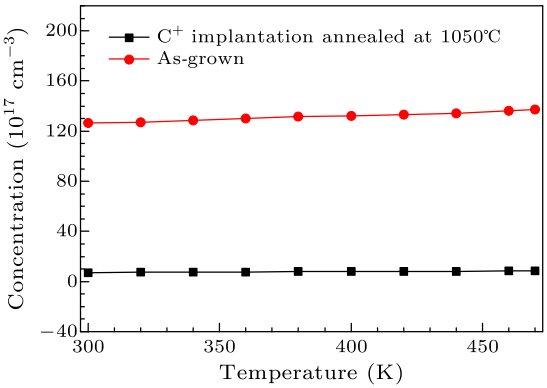

Fig. 5. Evolution of electron concentration of N-polar GaN with temperature.

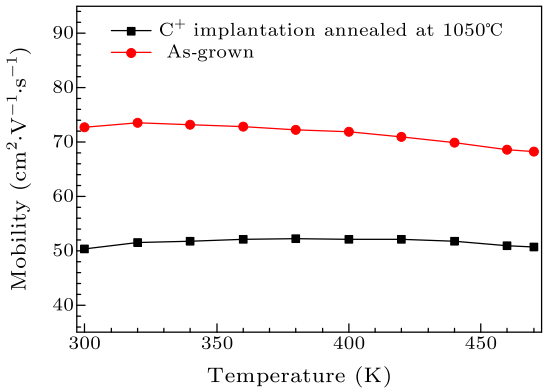

Fig. 6. Evolution of electronic mobility of N-polar GaN with measurement temperature.

Figure 5 shows the temperature dependence of electron concentration for the C-implanted N-polar GaN film. The as-growth electron concentration was over 17 times greater than the as-implanted sample due to the C-implantation induction of a large number of deep acceptors such as C_N,[22] thus the background carriers induced by oxygen are partially compensated for by C_N. The measured electron mobility is shown in Fig. 6, and the as-grown sample and the C-implanted GaN sample show the same trend. This behavior can be attributed to the competition between phonon and impurity scattering. Compared with the mobility of the as-grown sample, the C-implanted GaN sample shows lower electron mobility due to the increasing impurity scattering.

In summary, we have studied N-polar GaN films grown by MOCVD and implanted with C ions. Raman spectra show that C-implantation induces a large

number of defects and causes disorder of the lattice structures, introducing three additional peaks at 300 cm^{-1}, 360 cm^{-1}, and 670 cm^{-1}. After annealing, the disordered lattice almost recovers and the additional peaks at 300 cm^{-1} and 670 cm^{-1} disappear while the 360 cm^{-1} peak remains. The HRXRD results are consistent with the Raman scattering spectra. After C-implantation, there is an obvious increase of screw-dislocation densities, while it turns to the original level after annealing. The temperature-dependent Hall-effect is consistent with the higher resistivity of the N-polar GaN materials after C-implantation. The background carriers induced by oxygen incorporation in the N-polar GaN film are partially compensated for by the deep acceptor of C_N. Due to the increasing impurity scattering, the electron mobility of the as-grown sample was higher than the C-implanted GaN sample.

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