Effect of $Be^+ + O^+$ coimplantation on Be acceptors in GaN

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P-type regions were produced in undoped GaN films by Be^+ and $Be^+ + O^+$ implantation and subsequent annealing at temperatures between 1000 and 1050 °C. From thermal admittance spectroscopic measurements, the activation energy of the Be acceptor level was found to decrease from ~240 to ~163 meV by the implantation of additional O atoms, which is in reasonable agreement with the improvement in *p*-type doping characteristics determined by room-temperature Hall-effect measurements. These results indicate that $Be^+ + O^+$ coimplantation reduces the depth of the Be acceptor level based on a site-competition effect. Therefore, these acceptor levels are most probably attributable to Be atoms at interstitial and Ga-lattice sites. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1564641]

In GaN device fabrication, acceptor doping has long been a serious problem. Beryllium (Be) is one of the more promising acceptor impurities for GaN because the theoretical value of its ionization energy when residing on a Ga-lattice site in wurtzite GaN is calculated to be ~60 meV.[1,2] For electronic device design, especially from a selective-area doping point of view, the light Be^+ ions can be implanted deeper into GaN for a given implantation energy, and they cause less damage in the lattice than Mg^+ ions, the most commonly used *p*-type dopant.

Recently, we have reported that some slight electrical *p*-type activity was achieved for Be-implanted GaN and that the Be-related acceptor level was located ~231 meV above the valence band from thermal admittance spectroscopy (TAS) measurements.[3] This is much deeper than that theoretically expected. This deepening of the activation energy of Be acceptors is considered to be associated with imperfect incorporation of the implanted Be^+ ions. In the case of conventional Be^+ implantation, where one kind of dopant is used, the generation of many N vacancies may occur in the implanted region after the activation annealing process, resulting in Be atoms residing at interstitial sites in GaN. Therefore, in order to suppress the N vacancies, a N-rich condition should be created prior to Be^+ implantation.[4–8] Considering that O atoms are apt to substitute at N-lattice sites, the implantation of additional O atoms into GaN might be expected to increase the probability that Be atoms will occupy a Ga-lattice site. In this study, the acceptor levels in Be+O coimplanted GaN have been investigated electrically, and the results are compared to those of conventional Be-implanted GaN.

The epitaxial GaN films used in these experiments were 2.5 μm thick. They were grown on *a*-plane sapphire substrates by atmospheric pressure metalorganic chemical-vapor deposition (MOCVD) at 1130 °C, with a pre-deposited 20 nm AlN buffer layer grown at 420 °C. The GaN films were not intentionally doped, but had a background *n*-type carrier concentration of $\sim 5\times 10^{15}$ cm^{-3}. After growth, the GaN samples were implanted, using O_2 gas and Be metal as the sources of the $^{16}O^+$ and $^{9}Be^+$ species, respectively. Prior to the O^+ implantation, a 100 nm thick Ni layer was deposited on the top surface of the samples by electron-beam evaporation in order to reduce the implantation induced damage. Then, multiple step O^+ implantation was performed as follows. The O^+ ions were implanted at 400, 300, 250, 200, 150, and 110 keV with dosages of 4.5×10^{14}, 8×10^{13}, 1.2×10^{14}, 1.3×10^{14}, 7×10^{13}, and 1.5×10^{14} cm^{-2}, respectively, to produce a mean O concentration of 2×10^{19} cm^{-3} to a depth of ~0.4 μm. After removing the Ni layer, a 300 nm thick Ni layer was deposited again prior to the Be^+ implantation. Then, multiple step Be^+ implantation was performed; the Be^+ ions were implanted at 350, 250, and 170 keV with dosages of 6×10^{14}, 2.5×10^{14}, and 4×10^{14} cm^{-2}, respectively, to produce a mean Be concentration of 2×10^{19} cm^{-3} to a depth of ~0.4 μm. Conventional Be- and O-implanted GaN samples were also prepared with mean concentrations of 2×10^{19} cm^{-3} (depth=0.4 μm) for reference. In the case of the $Be^+ + O^+$ coimplantation, the O/Be ratio was kept at about 1 for optimum doping.[5–7] All of the implants were carried out at room temperature at an incident angle 7° off the surface normal. After implantation, the Ni layer was removed and then a 500 nm thick SiO_2 capping layer was deposited on the surface by radio-frequency sputtering at room temperature to provide an encapsulation cap for the subsequent implant activation anneal. All of the samples were annealed at temperatures between 950 and 1100 °C for 5 min in flowing N_2 gas. Following the annealing step, HF was used to remove the SiO_2 cap. From secondary ion mass spectrometry (SIMS) measurements, the Be concentration to a depth of ~0.4 μm was confirmed to be about 2×10^{19} cm^{-3} for both Be- and Be+O-implanted GaN samples before the activation anneal, which is in reasonable agreement with a calculation made using transport of ions in matter (TRIM) software. Additionally, annealing caused the implanted Be atoms to diffuse slightly towards the near-

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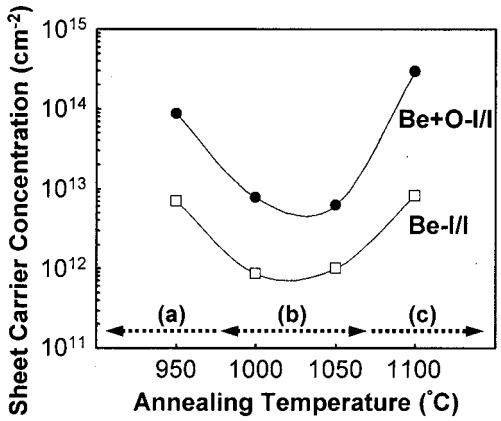

FIG. 1. Sheet carrier concentration as a function of the annealing temperature of Be- and Be+O-implanted GaN.

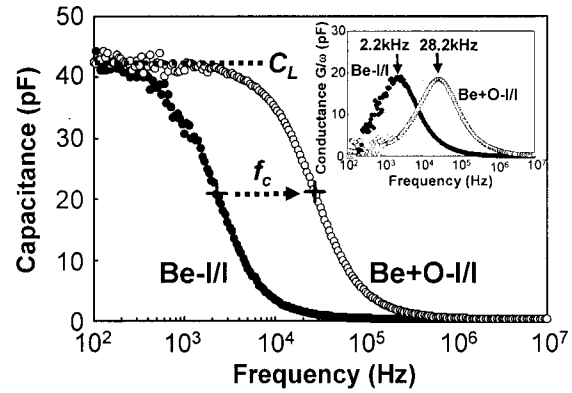

FIG. 2. Room-temperature frequency dependence of the capacitance of Be- and Be+O-implanted GaN after annealing at 1050 °C. The inset shows the frequency dependence of the conductance at room temperature.

surface region (~100 nm from the surface) regardless of whether there was implantation of additional O atoms. The Be-diffusion level was almost the same under all annealing conditions, resulting in identical Be SIMS profiles regardless of the annealing temperature. Moreover, the SIMS profiles of implanted O atoms both before and after annealing were unchanged, in agreement with the profiles calculated by TRIM. Furthermore, no Ni atoms were detected in any of the implanted samples. This suggests that the diffusion of Ni atoms into GaN from the Ni layer does not occur during the implantation process and consequently that the use of the Ni layer to reduce the implantation induced damage does not influence the Be-doping characteristics, as discussed later. The type of carrier of the Be- and Be+O-implanted GaN samples was determined by room-temperature Hall-effect and electrical measurements. For the conventional O-implanted samples, the implanted O atoms became electrically active as an *n*-type dopant after annealing at 1100 °C. Some electrical measurements were conducted on lateral dot-and-ring Schottky diodes fabricated using Pt as the Schottky metal.[3,9,10] Capacitance–frequency ($C-f$), conductance–frequency ($G/\omega-f$), and capacitance–voltage ($C-V$) measurements were performed at room temperature at an ac modulation level of 30 mV and frequencies ranging from 100 Hz to 10 MHz. TAS measurements were performed at an ac modulation level of 30 mV and frequencies ranging from 100 Hz to 30 kHz, covering the temperature range from 85 to 480 K.

Figure 1 shows the room-temperature sheet carrier concentration, n_s, of the Be- and Be+O-implanted GaN samples as a function of the annealing temperature. The behavior of n_s may be classified into three regions: (a), (b), and (c) with respect to carrier type. In region (b) where the annealing temperature is between 1000 and 1050 °C, n_s tends to decrease significantly for both Be- and Be+O-implanted samples. These samples are the only ones displaying *p*-type characteristics, with small mobility, μ, in the region of 1–3 $cm^2/V\,s$. Furthermore, the n_s of the Be+O-implanted samples is relatively higher than that of the Be-implanted samples, indicating that the implantation of additional O atoms improves electrical *p*-type activation. On the other hand, samples annealed in regions (a) and (c) show *n*-type characteristics, which may be caused by the implantation induced damage and the formation of N vacancies during the anneal, respectively. In particular, the significant increase in n_s seen for the Be+O-implanted sample after annealing at 1100 °C is considered to be due to the combined effect of N-vacancy formation and electrical O-activation induced by high-temperature annealing, as mentioned above.

Figure 2 shows room-temperature $C-f$ curves at zero dc bias for Schottky diodes based on Be- and Be+O-implanted GaN samples after annealing at 1050 °C. Regardless of the O implantation, the capacitance measured varies markedly with the frequency for both samples. This variation in capacitance is most likely due to a typical dispersion effect characteristic of deep Be acceptors; depending on frequency, there is competition between deep impurities and the dopant character.[11,12] Here, the low-frequency capacitance C_L is determined by carrier exchange between the Be-related impurity level and the valence band, reflecting the electrical activity of the implanted Be atoms, whereas above the capacitance cutoff frequency f_c (impurity transition frequency), hole modulation of the depletion layer edge governs the electrical response. In view of the fact that there is a peak at f_c in the conductance G/ω, the characteristic frequencies f_c are estimated to be ~2.2 and ~28.2 kHz for the Be- and Be+O-implanted samples, respectively, as shown in the inset of Fig. 2. Thus, a significant increase in f_c occurs due to the implantation of additional O atoms. This result indicates that shallower acceptor levels may be newly formed by coimplantation of Be^+ and O^+ based on a site-competition effect.[10] From $C-V$ measurements at 1 kHz, the net acceptor concentration (N_a-N_d) was calculated to be $\sim 1.5 \times 10^{17}\ cm^{-3}$ for the Be+O-implanted sample. As shown in Fig. 2, C_L is estimated to be about 43 pF for both samples, which suggests that the effective acceptor concentration of the Be-implanted sample is at the same level as that of Be+O-implanted sample. These acceptor concentrations are much smaller than the Be concentration of $2\times 10^{19}\ cm^{-3}$ determined by the SIMS measurements. This result indicates that much implantation induced damage still remains and may compensate for the holes generated by the deep Be acceptors in both samples. Therefore, the higher Be activation rate caused by the introduction of O atoms is most likely to be the dominant factor for improvement of the *p*-type doping characteristics, as mentioned in Fig. 1.

Figures 3(a) and 3(b), respectively, show typical TAS spectra measured under zero dc bias for Schottky diodes fab-

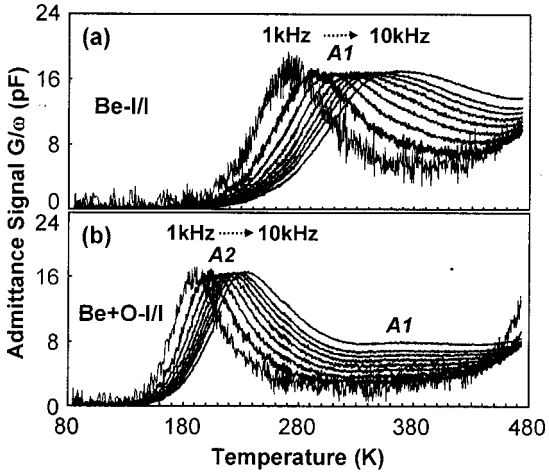

FIG. 3. TAS spectra at various frequencies between 1 and 10 kHz of (a) Be- and (b) Be+O-implanted GaN after annealing at 1050 °C.

ricated on Be- and Be+O-implanted GaN and annealed at 1050 °C. Depending on the implant conditions, the TAS spectra reveal two kinds of peak, denoted $A1$ and $A2$. These peaks shift towards higher temperatures with an increase in the hole emission rate, which can be calculated from the measurement frequency. This implies that these peaks are associated with Be-related deep acceptor levels.[3] As shown in Fig. 4, the thermal activation energy for hole emission into the valence band is estimated from Arrhenius plots of the hole emission rate e_p/T^2 for the corresponding level in the both spectra. Here, the data are analyzed under the assumption that the cross section is temperature independent. For the conventional Be-implanted sample, a dominant $A1$ peak is clearly observed, which corresponds to a Be-related acceptor level with thermal activation energy of ~240 meV. This value is very close to the previously reported one.[3] For the Be+O-implanted sample, a dominant $A2$ peak is seen in addition to the $A1$ peak. This newly observed A_2 peak is located ~163 meV above the valence band. Thus, the Be-related acceptor level is found to decrease significantly with the introduction of O atoms. This behavior of the acceptor level, i.e., becoming shallower, seems to be in good agreement with the increase in impurity transition frequency f_c by implantation of additional O atoms (Fig. 2). The characteristic frequencies corresponding to the $A1$ and $A2$ peaks at room temperature (300 K) are calculated to be ~1.3 and ~43.1 kHz, which can be extracted from the Arrhenius plots shown in Fig. 4. These values are in reasonable agreement with the values of f_c of ~2.2 and ~28.2 kHz estimated from the room-temperature $C-f$ and $G/\omega-f$ curves in Fig. 2. Therefore, this confirms that these acceptor levels are attributable to the implanted Be atoms. Bearing in mind the site-competition effect caused by the implantation of additional O atoms, the $A1$ and $A2$ levels can probably be assigned to Be atoms that occupy interstitial and Ga-lattice sites, respectively. Therefore, the decrease in the Be-related acceptor level with the introduction of O atoms most likely enhances the Be activation rate, which results in improvement of the p-type doping characteristics, as mentioned above. In addition, a significant reduction in residual n-type carriers that act in competition with the p-type carriers is required in order to realize increasing p-type doping characteristics.

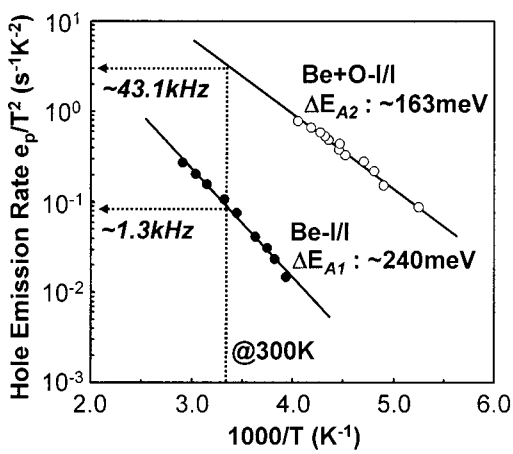

FIG. 4. Arrhenius plots of the hole emission rate e_p/T^2 of Be- and Be+O-implanted GaN after annealing at 1050 °C.

In summary, we have electrically investigated the effect of $Be^+ + O^+$ coimplantation of Be acceptors in GaN. From TAS and $C-f$ measurements, the implantation of additional O^+ ions is found to decrease the Be-related acceptor level from ~240 to ~163 meV due to a site-competition effect. This behavior of the acceptors is in reasonable agreement with the improvement of p-type doping characteristics determined by room-temperature Hall-effect measurements. Therefore, this acceptor level can probably be assigned to Be atoms that reside at interstitial and Ga-lattice sites in GaN.

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