

Characterization of plasma etching damage on *p*-type GaN using Schottky diodes

M. Kato,^{1,a)} K. Mikamo,¹ M. Ichimura,¹ M. Kanechika,² O. Ishiguro,² and T. Kachi²

¹*Department of Engineering Physics, Electronics and Mechanics, Nagoya Institute of Technology, Gokiso, Showa, Nagoya 466-8555, Japan*

²*Toyota Central R&D Laboratories, Inc., Nagakute, Aichi, 480-1192 Japan*

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The plasma etching damage in *p*-type GaN has been characterized. From current-voltage and capacitance-voltage characteristics of Schottky diodes, it was revealed that inductively coupled plasma (ICP) etching causes an increase in series resistance of the Schottky diodes and compensation of acceptors in *p*-type GaN. We investigated deep levels near the valence band of *p*-type GaN using current deep level transient spectroscopy (DLTS), and no deep level originating from the ICP etching damage was observed. On the other hand, by capacitance DLTS measurements for *n*-type GaN, we observed an increase in concentration of a donor-type defect with an activation energy of 0.25 eV after the ICP etching. The origin of this defect would be due to nitrogen vacancies. We also observed this defect by photocapacitance measurements for ICP-etched *p*-type GaN. For both *n*- and *p*-type GaN, we found that the low bias power ICP etching is effective to reduce the concentration of this defect introduced by the high bias power ICP etching. © 2008 American Institute of Physics. [DOI: 10.1063/1.2908227]

I. INTRODUCTION

Wide band gap semiconductors are promising material for the next generation power devices. In particular, gallium nitride (GaN) has a band gap three times larger than Si and almost the same electron mobility as Si. These properties can lead to high power devices with both the high breakdown voltage and the low electric resistance.¹ However, power electronic devices based on GaN have never been in commercial production. There are several reasons for that, such as the absence of good gate insulators and difficulty to make vertical device structures. In addition, the damage introduced by device fabrication processes is also a crucial problem. It is well known that a GaN crystal shows degraded electrical properties after a dry etching process,^{2–8} which is an essential process to fabricate GaN devices. Therefore, suppression of the damage originating from the dry etching process is important to improve GaN devices.

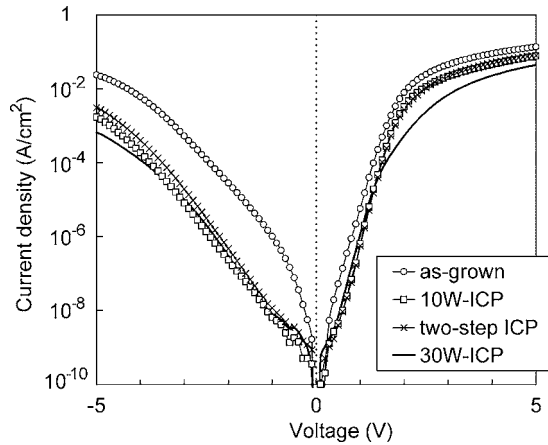
In order to establish a method to suppress the damage, we should characterize deep levels in GaN introduced by the inductively coupled plasma (ICP) etching, which is the most commonly used dry etching process. In particular, since there are only few reports on the deep levels introduced by the etching damage in *p*-type GaN, we focus on deep levels in *p*-type GaN. Although the capacitance deep level transient spectroscopy (*C*-DLTS) is usually employed to characterize deep levels, *p*-type GaN does not have enough conductivity to perform measurements of the capacitance transient. Therefore we employed current DLTS (*I*-DLTS) and photocapacitance (PHCAP) measurements.⁹ We also characterized *n*-type GaN to obtain complementary information of deep levels in the upper half of the band gap by the *C*-DLTS.

These characterizations are performed for ICP-etched samples with several etching conditions to discuss how the etching damage can be diminished.

II. EXPERIMENT

The samples were *c*-face GaN layers grown on *a*-face sapphire substrates, with low temperature (420 °C) grown aluminum nitride (AlN) buffer layers, by metalorganic chemical vapor deposition at the atmospheric pressure. The source gases were trimethylgallium and ammonia and the carrier gas was hydrogen. The growth temperature was 1100 °C and the grown GaN layer was 1.4 μm thick. The full width at half maximum of the x-ray rocking curve for the as-grown *p*-type GaN is 52 arc sec. Biscyclopentadienyl magnesium (Cp₂Mg) and monomethylsilane gases were employed for acceptor (Mg) and donor (Si) dopings, respectively. After the growth, only for Mg doped *p*-type GaN, activation annealing was performed at 800 °C for 20 min in nitrogen atmosphere. The doping concentrations, as confirmed by secondary ion mass spectrometry, are 3×10^{19} – 5×10^{19} and 2×10^{17} cm⁻³ for Mg doped *p*-type GaN and Si doped *n*-type GaN, respectively (they are not the carrier concentrations). After the growth and annealing, the samples were cut into many pieces and some of them were employed as the as-grown samples (annealed *p*-type GaN is referred to as “as grown” in this paper for convenience). We performed the ICP etching for the rest of pieces. The etching gas was Cl₂ with a flow rate of 30 SCCM (SCCM denotes cubic centimeter per minute at STP) at a pressure of 1 Pa, and the plasma power was 300 W. We prepared samples etched with a bias power of 30 W for 120 s (30W-ICP), samples etched with a bias power of 10 W for 60 s (10W-ICP), and samples etched with a bias power of 30 W for 120 s and additionally etched with a bias power of 10 W for 60 s (two-step ICP).

^{a)}Electronic mail: kato.masashi@nitech.ac.jp.

FIG. 1. I - V characteristics for p -type GaN.

The etching depths for the 30W-ICP and 10W-ICP samples are 300 and 30 nm, respectively, and these etching conditions are the same as in our previous report about carrier lifetime.⁴ These etching conditions are typical ones used in the device fabrication process, and we did not investigate the etch time dependence of the damage generation. For the bias power of 30 W, we applied an ac bias of 310 V, and for the bias power of 10 W, we applied 140 V.

We fabricated Schottky diodes using those samples. The samples were cleaned by organic solvent and dilute HF just before the metal evaporation. For p -type GaN, NiMg₂/Au was evaporated as the Ohmic contact, and the samples were annealed at 600 °C for 5 min. Al was evaporated as the Schottky contacts. Al is known to be a good Schottky metal for p -type GaN owing to its relatively small work function.¹³ On the other hand, for n -type GaN, Al was evaporated and annealed at 500 °C for 10 min as the Ohmic contact and Au was evaporated as the Schottky contact. The Schottky contacts had a diameter of 0.5 or 1.0 mm, and the larger one, used in the PHCAP measurement, was made thin enough (less than 50 nm) to be transparent for a light from a 100 W Xe lamp employed in this measurement. All the Ohmic contacts have a relatively large area of approximately 5×10 mm² to reduce the contact resistance. Current-voltage (I - V) and capacitance-voltage (C - V) measurements were performed for the Schottky diodes. In addition, we performed I -DLTS and PHCAP measurements for p -type GaN and C -DLTS measurements for n -type GaN by our homemade systems. A Keithley 428 current amplifier was employed for the I -DLTS measurement, and a Boonton 72B capacitance meter for the C -DLTS measurements. The C - V and PHCAP measurements for p -type GaN were performed with an Agilent 4284A LCR meter at a measurement frequency of 1 kHz. Before the DLTS and PHCAP measurements, we confirmed that the rectification properties of the diodes were good enough for the capacitance measurements.

III. RESULTS AND DISCUSSION

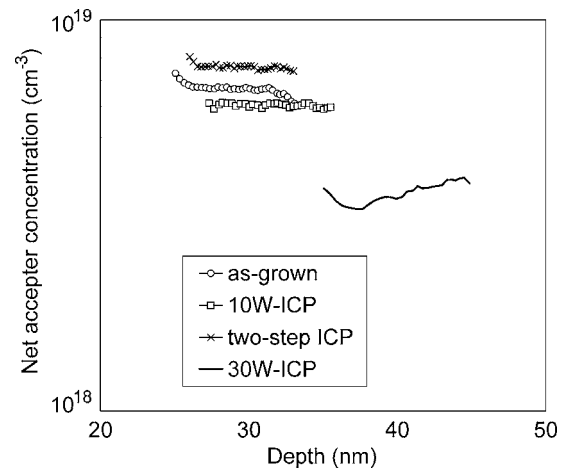
The I - V characteristics for the Schottky diodes on the p -type GaN are shown in Fig. 1. The samples showed a rectifying property but large leakage currents were observed for all the diodes. The series resistances of the forward char-

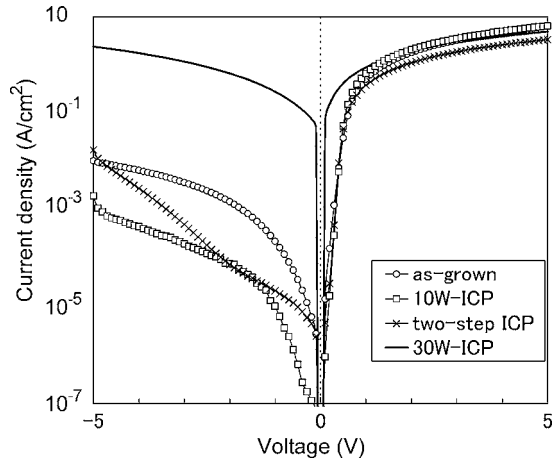
TABLE I. Leakage currents and series resistances of the Schottky diodes on GaN.

Sample (conductivity type)	Leakage current at -5 V (A/cm ²)	Series resistance (kΩ)
As grown (p)	2.4×10^{-2}	10
10W-ICP (p)	1.7×10^{-3}	17
Two-step ICP (p)	3.1×10^{-3}	15
30W-ICP (p)	7.0×10^{-4}	18
As grown (n)	1.1×10^{-2}	0.32
10W-ICP (n)	2.0×10^{-3}	0.35
Two-step ICP (n)	1.8×10^{-2}	0.66
30W-ICP (n)	2.4	0.49

acteristics estimated by the method in Ref. 4 are larger than 10 kΩ. The leakage current at a reverse bias of -5 V and the series resistances for the diodes on p -type GaN are listed in Table I. The as-grown sample shows the largest leakage current and the lowest series resistance among all the samples. The net acceptor concentrations estimated from the C - V measurements are uniformly distributed and are approximately 7×10^{18} cm⁻³ except for the 30W-ICP sample, as shown in Fig. 2. These net acceptor concentrations are almost the same as previously reported values for p -type GaN.^{11,12} It should be noted that the free hole concentration should be much smaller than those concentrations because of the deep Mg acceptor level. For the 30W-ICP sample, the net acceptor concentration is 4×10^{18} cm⁻³ and the depletion layer is wider than the other samples. Thus the high bias power ICP etching seems to decrease the net acceptor concentration. Reduction of the sheet carrier concentration and increase of the sheet and contact resistance in p -type GaN after the dry etching have been widely reported,⁵⁻⁷ and the present results are in agreement with those previous results.

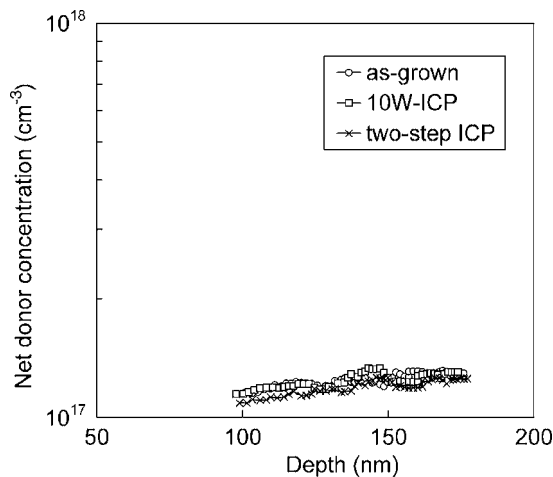
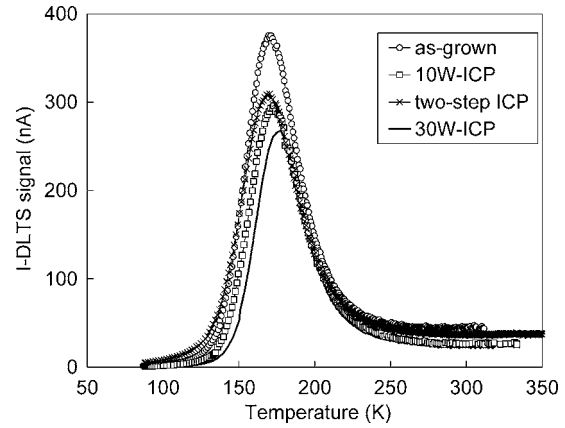
We also obtained the I - V characteristics for the Schottky diodes on the n -type GaN samples as shown in Fig. 3. The series resistances for n -type GaN are one order of magnitude lower than those for p -type GaN, while the leakage currents are almost the same as those for p -type GaN. The leakage current for the 30W-ICP sample is very large and thus the rectifying property of this sample is poor. The poor rectifying

FIG. 2. Net acceptor distributions in p -type GaN.

FIG. 3. *I-V* characteristics for *n*-type GaN.

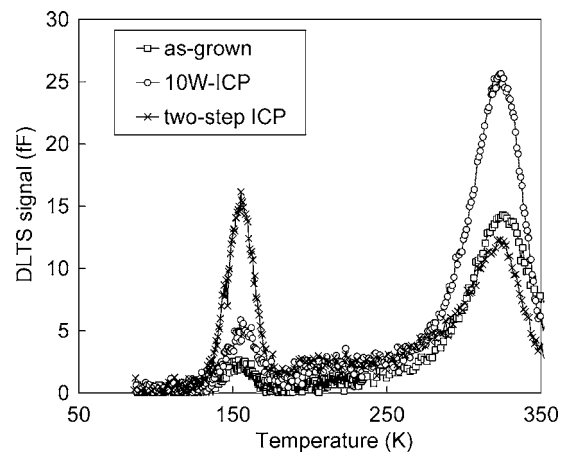
property after the dry etching is also consistent with the previous report.⁸ The leakage current at a reverse bias of -5 V and the series resistance for the diodes on *n*-type GaN are also listed in Table I. The net donor concentrations in *n*-type GaN obtained by the *C-V* measurements are shown in Fig. 4. The net donor concentration for the 30W-ICP sample was not measured because of its large leakage current. The net donor concentrations for the as-grown, 10W-ICP, and two-step ICP samples are approximately $1 \times 10^{17} \text{ cm}^{-3}$, and we do not find any effects of the ICP etching.

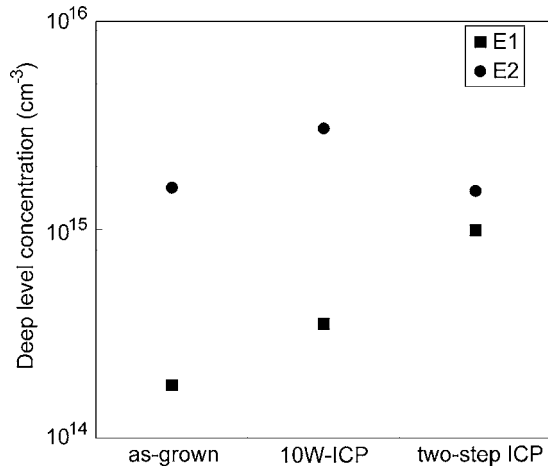
In order to detect deep levels in *p*-type GaN, the *I*-DLTS measurements were performed. Figure 5 shows the *I*-DLTS spectra for the emission time constant of 9 ms. Since, at temperatures higher than 350 K, the *I*-DLTS signal had a large noise, the *I*-DLTS measurements were performed only up to 350 K. A peak is observed around 170 K in all the spectra. From the Arrhenius plot, the activation energy and the capture cross section of this peak are estimated as 0.1 eV and $8 \times 10^{-21} \text{ cm}^2$, respectively. Since the position and the activation energy of this peak are almost the same as those reported for the Mg acceptor level,^{10,11} this peak can be identified as the Mg acceptor level. There is no other peak in all the spectra and thus deep levels with a concentration higher than the detection limit ($\sim 10^{17} \text{ cm}^{-3}$) are not present near

FIG. 4. Net donor distributions in *n*-type GaN.FIG. 5. *I*-DLTS spectra for *p*-type GaN.

the valence band. The effect of the ICP etching is not observed in the *I*-DLTS spectra. Zhu *et al.* has reported that many levels are present near the valence band of *p*-type GaN even without any etching.¹³ The reason for difference from our results could be due to difference in the doping source gas; they employed bisethylcyclopentadienyl magnesium (EtCp_2Mg), while we employed Cp_2Mg . Difference in other growth parameters may also contribute to the above difference, but we do not have enough information for detailed discussion. At least we may suppose that those levels observed in Ref. 13 are not of intrinsic origin, since they are absent in our samples.

In order to observe deep levels near the conduction band edge, the *C*-DLTS measurements were performed for *n*-type GaN. As in the *C-V* measurements, we did not perform the *C*-DLTS measurement for the 30W-ICP sample because of its large leakage current. The measurement temperature ranges were also limited up to 350 K as in *I*-DLTS for *p*-type GaN, because capacitance became unstable at temperatures higher than 350 K. Figure 6 shows the *C*-DLTS spectra for *n*-type GaN at the emission time constant equal to 9 ms. Two peaks are observed around 155 and 325 K in all the spectra. The activation energy and the capture cross section for the peak at 155 K are 0.25 eV and $1 \times 10^{-15} \text{ cm}^2$, respectively, while those for the peak at 325 K are 0.55 eV and $1 \times 10^{-15} \text{ cm}^2$, respectively. These values are similar to those

FIG. 6. *C*-DLTS spectra for *n*-type GaN.

FIG. 7. Deep level concentrations in *n*-type GaN.

for the levels named E1 and E2,¹⁴ and thus the peaks can be attributed to E1 and E2. The peak heights for E1 and E2 in the spectra are different among the samples, and we compare E1 and E2 concentrations in Fig. 7. The concentration of E2 ranges between 1×10^{15} and $3 \times 10^{15} \text{ cm}^{-3}$, and it does not seem to be affected by the ICP etching. On the contrary, the concentration of E1 increases from 2×10^{14} to $1 \times 10^{15} \text{ cm}^{-3}$ with bias power of the ICP etching. (We can expect that the two-step ICP sample has more damage than the 10W-ICP sample.) Thus, as reported previously,^{2,3} the concentration of E1 is enhanced by the damage of the ICP etching. In the previous reports, the origin of E1 is considered as nitrogen vacancies,^{2,3} whose concentration is increased by the plasma etching. In addition, it has been reported that the nitrogen vacancy acts as a donor and increases the leakage current of the Schottky diode on *n*-type GaN.¹⁵ We observed electric field dependence of the activation energy for E1 as shown in Fig. 8. The activation energy depends linearly on the square root of the electric field, which means that this level acts as a donor. The large leakage current for the 30W-ICP sample will be due to the large amount of nitrogen vacancies acting as a donor. Cl is another possible origin of the deep level after the ICP etching as discussed in Ref. 4. From the bias power for the ICP etching,

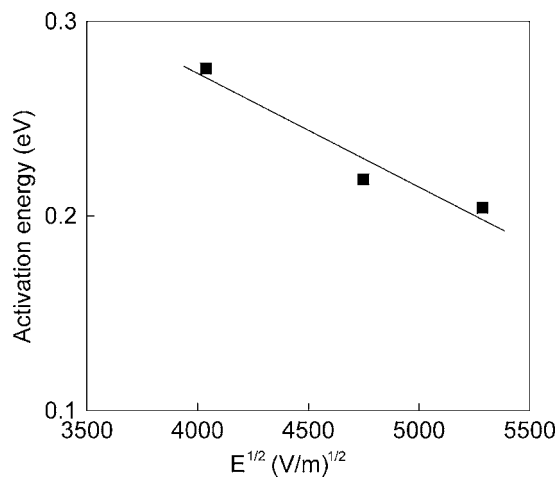
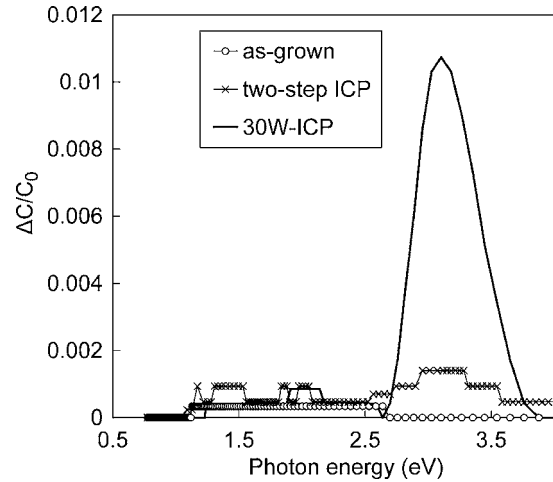


FIG. 8. Electric field dependence of the activation energy for E1.

FIG. 9. PHCAP spectra for *p*-type GaN.

the generated ac and dc bias voltages are 310 V and less than 300 V, which are estimated from Fig. 1 of Ref. 16, respectively. At these accelerating voltage, the Cl implantation depth would be too shallow for the Cl-related defects to be observed by DLTS. Therefore, the origin of E1 should not be Cl, and the nitrogen vacancy can be the most probable origin.

Using *I*-DLTS, we did not observe any deep levels in *p*-type GaN caused by the ICP etching damage, probably because the detection of levels close to the surface or at energies above the middle of the gap is not possible by *I*-DLTS. Therefore, we employed the PHCAP measurement to detect such deep levels in *p*-type GaN. The PHCAP spectra for *p*-type GaN at 300 K are shown in Fig. 9, where we plot the capacitance variation after 15 s from the start of the illumination normalized by the capacitance at equilibrium. (We did not perform this measurement for the 10W-ICP sample.) At each light energy, the diodes are forward biased before the measurements to initialize the charge state of deep levels to the equilibrium condition. In the spectra for the as-grown and two-step ICP samples, no peak appears with the illumination of any energy, while the spectrum for the 30W-ICP sample shows a large peak at illumination with 3.15 eV light. When we observe a positive PHCAP signal in *p*-type semiconductors, it means that negative charges increase in the depletion layer. Therefore, this signal is caused by photoemission of holes from the level located 3.15 eV above the valence band edge ($E_v + 3.15 \text{ eV}$) to the valence band. Since the band gap of GaN at room temperature is 3.39 eV, this level should be located 0.24 eV below the conduction band edge ($E_c - 0.24 \text{ eV}$). The peak at 3.15 eV, thus, will correspond to E1 observed in DLTS for *n*-type GaN. For the two-step ICP sample, there is no peak originating from E1 in the PHCAP spectrum. The concentration of E1 introduced by the high bias power (30 W) ICP etching can be reduced by the additional low bias power (10 W) ICP etching.

IV. CONCLUSIONS

We characterized deep levels in as-grown and ICP-etched GaN by the DLTS and PHCAP measurements. DLTS

spectra for *n*-type GaN showed a level (E1) with an activation energy of 0.25 eV whose concentration increased after the ICP etching. We also observed E1 in the ICP-etched *p*-type GaN from the PHCAP measurements. Electric field dependence of the activation energy of E1 indicated that this level acts as a donor. The high bias power ICP etching increased the concentration of E1, and the additional ICP etching with low bias power can reduce this concentration.

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