

Photoluminescence Study of Plasma Etching-Induced Damage in GaN

Yoshitaka Nakano

Abstract: We investigated, by employing a photoluminescence technique, the etching damage introduced in near-surface regions of GaN by Ar and Kr plasmas and clarified the differences between the damage characteristics of these regions for the two plasma etching cases. For Ar plasma, the shallow donor-acceptor pair emission at ~ 3.28 eV was significantly weakened; additionally, a broad blue luminescence band arose at approximately ~ 3.0 eV. In contrast, for Kr plasma under high gas pressure, we found the recovery of the damage to the same level as the as-grown crystallinity. These differences in the damage characteristics for the two plasma etching cases probably depend upon which atom (N or Ga) is preferentially etched in these cases.

Keywords : *plasma etching, damage, GaN, Ar, Kr, photoluminescence*

1. INTRODUCTION

Gallium nitride (GaN) is a promising material for fabricating high-power, and high-frequency optoelectronic devices because of its remarkable features such as a wide band gap of 3.39 eV, a high breakdown field of 5×10^6 V/cm and a high saturation drift velocity of 2.7×10^7 cm/s.¹⁾ Recently, GaN-based devices have been developed with advances made in plasma etching techniques.²⁾ However, damage introduced in GaN surfaces by plasma etchings is a critical issue, because it is closely related to the degradation of device performance.^{3,4)} The plasma etching of GaN, composed of Ga and N atoms, is a preferential etching process that results in the etching of specific atoms from the GaN surface. This preferential etching causes an undesirable GaN surface, as in the case of Ga- or N-rich conditions, resulting in a significant decrease in electrical activity. Recently, Kawakami *et al.* reported, based on theoretical calculations and X-ray photoelectron spectroscopy (XPS) analyses, that N is preferentially etched by Ar plasma and that Ga is preferentially etched by Kr plasma.^{5,6)} Additionally, they also reported that anomalous surface defects are formed on GaN surfaces through Ar plasma etching under high gas pressures and for a long etching time; this phenomenon is probably associated with ultraviolet (UV) irradiation from the Ar plasma onto GaN surfaces.⁵⁾ However, these issues have yet to be completely understood. Thus, to educe the potential of GaN materials, we must perform a basic investigation of the plasma-etching damage in GaN using a multifaceted approach. In this study, we investigate damage introduced in GaN near-surfaces by fundamental Ar- and Kr-plasmas etching by employing a photoluminescence (PL) technique and clarified the differences in their damage characteristics.

2. EXPERIMENTAL

4 μm -thick Si-doped GaN films with n -type carrier concentrations of $5 \times 10^{17} \text{ cm}^{-3}$ were epitaxially grown on c -plane sapphire substrates at 1130 °C through metal-organic chemical vapor deposition (MOCVD). To verify the

electronic band-gap states in the as-grown GaN before plasma etching, planar Schottky barrier diodes (SBDs) were fabricated using Au as a Schottky metal. Steady-state photocapacitance spectroscopy (SSPC) measurements were performed on the fabricated SBDs at 100 kHz, measuring photo-capacitance transients as a function of incident photon energy from 0.78 eV (1600 nm) up to 4.0 eV (300 nm). For a detailed description of SSPC measurement methods, see refs. 7 and 8.

These GaN samples were exposed to radio-frequency (RF) Ar and Kr plasmas for 30 and 200 min, respectively, using a capacitively coupled plasma (CCP) reactor with gas pressures of 10 and 50 mTorr, as shown in Fig. 1. The cathode on which the GaN samples were placed was connected to a 13.56 MHz RF power supply with a maximum voltage V_{RF} of 200 V (electrical power $P_{RF} < 30$ W). The anode, which was located 4 cm from the cathode, was electrically grounded. The self-bias voltage V_{DC} generated at the cathode in the plasma was set at -200 V. After plasma etching, the surface morphologies and etching depths of the etched samples were examined using a scanning electron microscope (SEM) and a surface profile measuring system, respectively. Variable temperature photoluminescence (VT-PL) measurements were then performed between 17 and 277 K to study the optical properties of these samples. The PL was excited by the bright 313 nm line of a Hg-Xe lamp with an excitation power of ~ 1 W/cm². In this study, the penetration depth of the 313 nm line was estimated to be ~ 70 nm from the GaN surface.

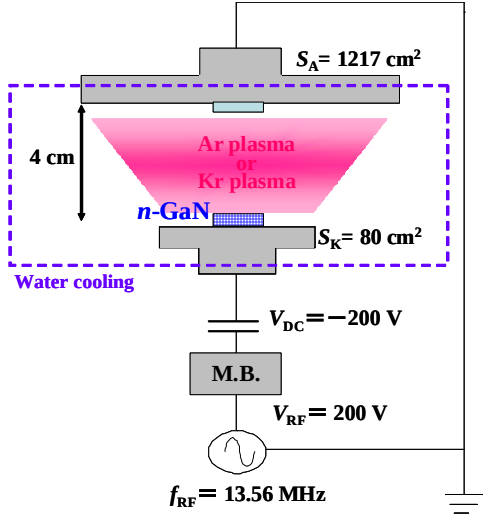


Figure 1. Capacitively coupled RF plasma reactor.

3. RESULTS AND DISCUSSION

Figure 2 shows typical room-temperature SSPC spectra of an SBD sample based on the as-grown GaN. In these measurements, the measured bias voltage V_G was fixed at -5.0 V. Five photoemission states are clearly observed with onsets at ~ 1.35 , ~ 1.70 , ~ 2.08 , ~ 2.80 , and ~ 3.20 eV below the conduction band, which are denoted as deep levels D1, D2, D3, D4, and D5, respectively, in addition to near-band-edge (NBE) emissions of GaN around ~ 3.4 eV. For all of the deep levels, electron emissions into the conduction band are a dominant process because of their positive photo-capacitance transients. These deep levels are almost identical to the deep-level defects that have previously been reported for GaN.⁸⁻¹⁰⁾ The D2, D3, and D5 levels are attributable to threading dislocations, Ga vacancies V_{Ga} , and shallow Carbon acceptors C_N .⁷⁻⁹⁾ In addition, the D4 level is believed to originate in $V_{Ga}-C_N$

complexes, which is associated with the yellow luminescence (YL) band generally observed in the PL spectra of GaN.^{10,11)} In this case, carbon is an unavoidable impurity in MOCVD growth. The deep level concentrations of D1, D2, D3, D4, and D5 are estimated to be, respectively, $\sim 1.3 \times 10^{15}$, $\sim 5 \times 10^{15}$, $\sim 3 \times 10^{15}$, $\sim 2.5 \times 10^{15}$, and $\sim 1.8 \times 10^{16}$ cm^{-3} .

Figure 3 shows the typical VT-PL spectra of an as-grown GaN sample. A broad YL band and a sharp donor-acceptor pair (DAP) emission are observed at approximately ~ 2.2 and ~ 3.28 eV, respectively. Additionally, a donor-bound excitation (DBE) emission of GaN at approximately ~ 3.47 eV is observed. This YL band is believed to be attributed to radiative transitions from a shallow donor to a deep acceptor, presumably a $V_{Ga}-C_N$ complex, as stated above.¹²⁾ Additionally, the shallow DAP emission probably corresponds to radiative transitions from Si and/or O donors to a shallow C_N acceptor.

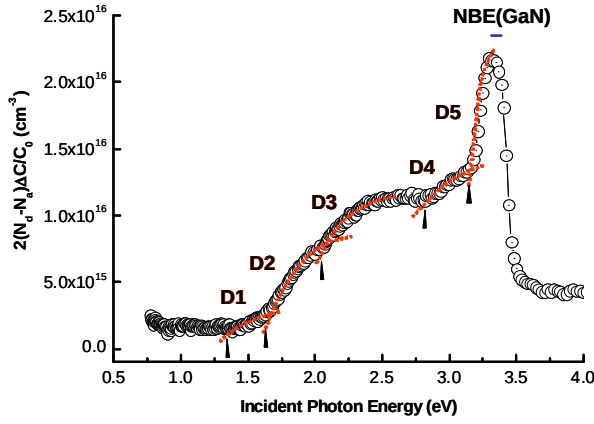


Figure 2. Room-temperature SSPC spectra of SBD based on as-grown GaN.

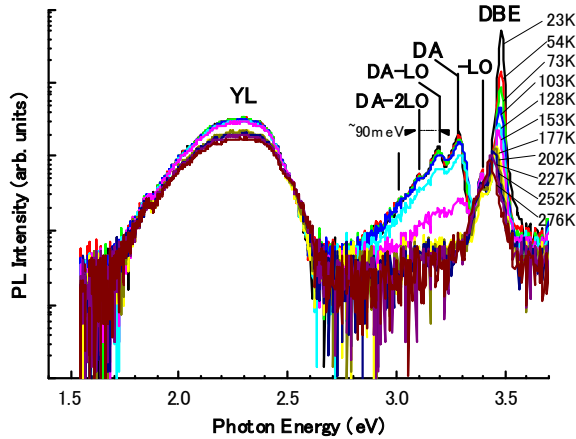


Figure 3. VT-PL spectra of as-grown GaN.

Figures 4 and 5 show typical VT-PL spectra for GaN samples etched by Ar and Kr plasmas, respectively. The plasma conditions were set at gas pressures of 10 and 50 mTorr for 30 and 200 min. For both plasmas, the plasma characteristics can be classified into two regions, (i) and (ii), based on the UV emissions from the plasmas. In region (i), with relatively low gas pressure (between 10 and 40 mTorr), the plasmas have high ion energies and

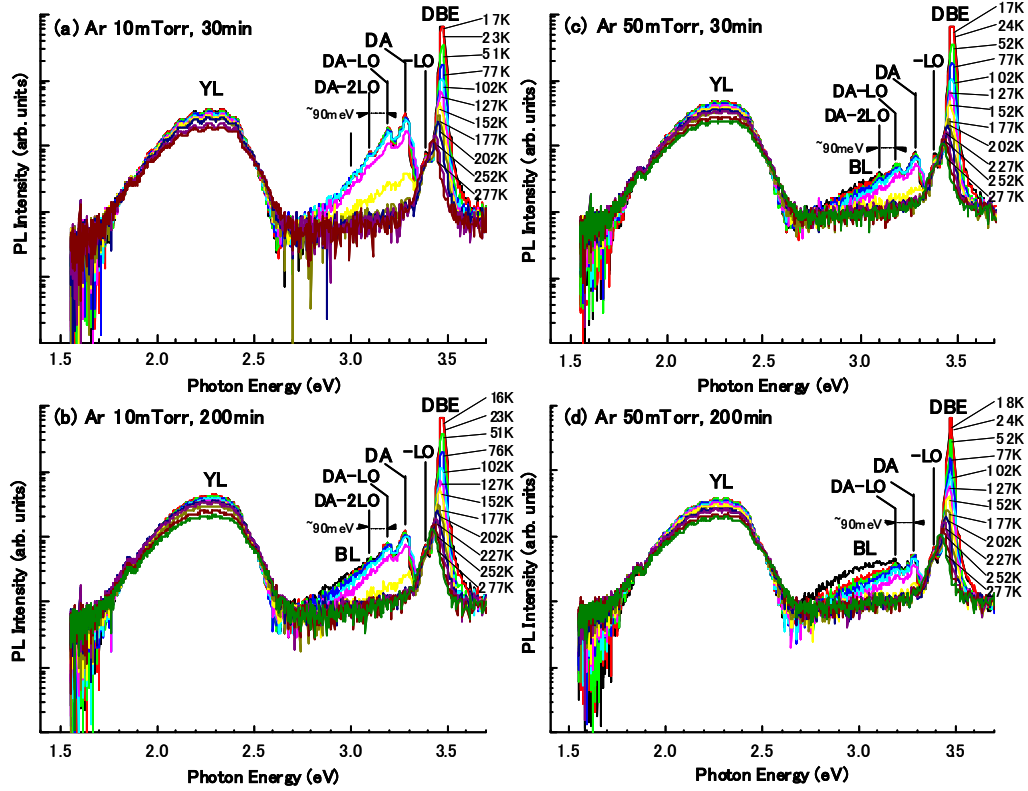


Figure 4. VT-PL spectra of GaN etched by Ar plasma under gas pressures of 10 and 50 mTorr for 30 and 200 min.

small ion fluxes, whereas in region (ii), with relatively high gas pressure (above 50 mTorr), the plasmas have low ion energies and large ion fluxes. In particular, in region (ii), both plasmas are found to emit distinct, bright UV lines between 300 and 380 nm.⁵⁾ Significant differences in PL behavior can be seen in between the Ar-plasma etched and Kr-plasma etched GaN samples. In general, the damage done to the GaN surfaces by the Ar-plasma etching is known to produce two defective layers, N-deficient surfaces limited to the top few monolayers and defect propagation regions down to ~ 100 nm, due to the preferential etching of N.¹³⁾ Thus, for the Ar-plasma etching in this study, any N-deficiency-related non-radiative recombination centers are expected to be generated on the top surfaces; however, no significant decrease in the DBE peak in the PL spectra was observed, as shown in Fig.4. This implies that the material information obtained from the PL measurements is mainly for the near-surface regions (down to ~ 70 nm) rather than the top surfaces. Additionally, for the Ar-plasma etching, the intensity ratio of the shallow DAP emission to the DBE peak is significantly decreased with increasing Ar gas pressure and etching time; this suggests that the Ar-plasma etching induces inactivation of Si and/or O donors. Simultaneously, a broad, blue luminescence (BL) band centered at ~ 3.0 eV arises in the spectra with increasing Ar gas pressure and etching time. In particular, this spectral variation is significantly enhanced in region (ii) under Ar gas pressures of 50 mTorr for 200 min. These experimental results suggest that the Ar-plasma etching induces the BL band in the near-surface regions of GaN, which is similar to the BL bands that have previously been reported for plasma etching and ion implantation of GaN.^{14,15)} This BL band observed may correspond to radiative transitions from the conduction band to the $V_{Ga}-C_N$ level, because it is the same metastable center as the YL band.^{15,16)} Additionally, SEM observations reveal anomalous surface defects in the GaN sample etched by the Ar plasma under a gas pressure of 50 mTorr for 200 min. This phenomenon is probably associated with a significant enhancement in the

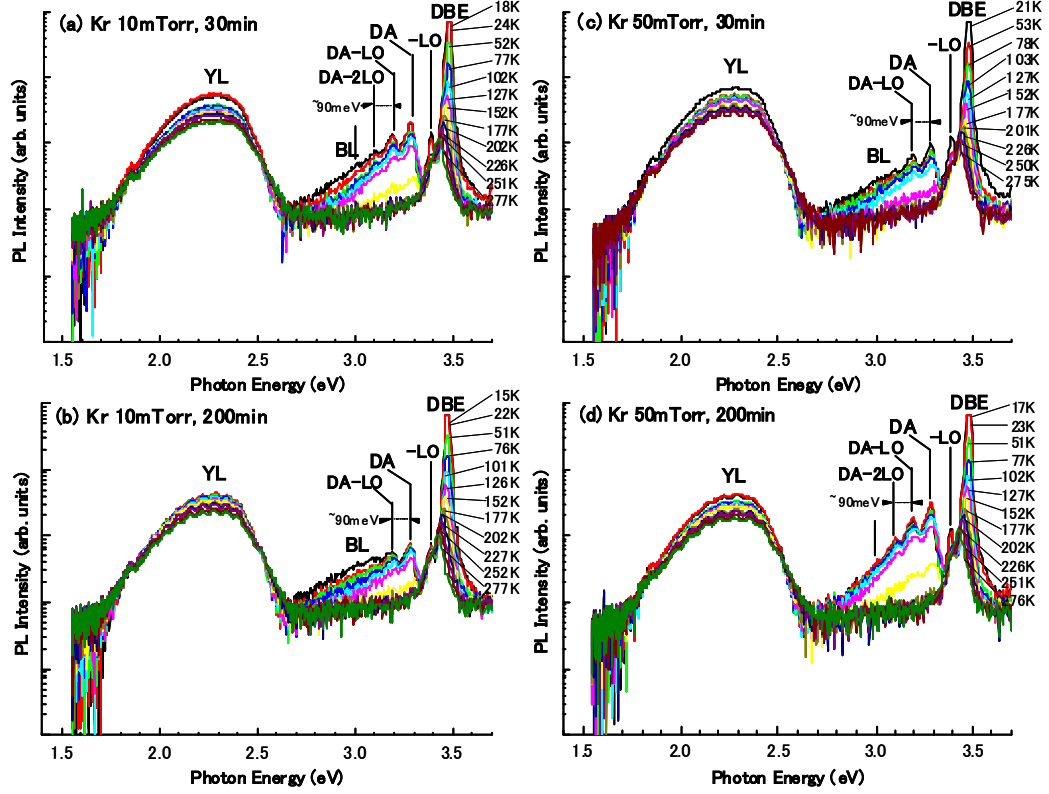


Figure 5. VT-PL spectra of GaN etched by Kr plasma under gas pressures of 10 and 50 mTorr for 30 and 200 min.

N-deficiency induced by the Ar-plasma etching; in this etching, UV irradiation on the GaN probably plays an important role in enhancing the redox reaction on the GaN surfaces because of the generation of numerous electron-hole pairs by absorption of UV light.⁵⁾ As shown in Fig.4, for the Kr-plasma etching, the same phenomena as in the case of Ar-plasma etching can be observed with increasing etching time in region (i). In region (ii), in sharp contrast, the PL spectra that were modified by the etching damage are found to recover to the same level as those of the as-grown GaN with increasing etching time. Thus, the etching damage tends to be accumulated in the GaN top and near-surfaces in the region (i) for both the Ar and Kr plasmas, whereas an opposite behavior of “damage accumulation” or “damage recovery” can be clearly seen in the region (ii) for the Ar and Kr plasmas, respectively. In particular, in region (ii) with long etching time for both plasmas, the plasma etching is considered to proceed remarkably because of the combined effect of UV irradiation and high ion fluxes, as stated above. These experimental results are in reasonable agreement with the plasma-etching-induced variation in the N/Ga ratio that has previously been reported by Niibe *et al.*; the Ar-plasma etching results in a decrease in the N/Ga ratio ($N/Ga < 1$), whereas for Kr-plasma etching, the N/Ga ratio is maintained at ~ 1.0 . In the case of the Kr plasma, the residual N atoms produced by the preferential etching of Ga are considered to form N_2 gases on the surfaces of the etched GaN and then be desorbed from those surfaces.⁶⁾ Resultantly, the Ga-deficiency damage layer formed on the GaN surfaces may well disappear with an increase of etching time by the combined effect of UV irradiation and high ion fluxes. Thus, the differences between the damage characteristics in the cases of Ar- and Kr-plasmas etching probably depend on which atom of N or Ga is preferentially etched; this dependence is in reasonable agreement with the theoretical calculations that have previously been reported by Kawakami *et al.*, i.e., N is preferentially etched by the Ar plasma, whereas Ga is preferentially etched by the Kr plasma.⁵⁾

4. CONCLUSIONS

We have clarified the differences between the damage characteristics in the near-surface regions of GaN for Ar- and Kr-plasma etching, using the PL technique. The etching damage tends to be accumulated in the GaN surface and near-surface regions for Ar plasma etching, whereas GaN surfaces etched by Kr plasma become less damaged until reaching the same level as that of the as-grown GaN via N₂ desorption of residual N atoms from the etched GaN surfaces. The differences in the damage characteristics between these cases probably result from the difference in etching mechanism regarding which atom (N or Ga) is preferentially etched, in addition to the UV irradiation from the plasmas.

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