Damage Characteristics of $n$-GaN Crystal Etched with N$_2$ Plasma by Soft X-Ray Absorption Spectroscopy*

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$n$-GaN crystals were plasma-etched with N$_2$ gas, and their surfaces were analyzed mainly by X-ray photoelectron spectroscopy (XPS) and soft X-ray absorption spectroscopy (XAS). In the samples etched with a high self-bias voltage of $\sim 400$ V, the surface morphology changed, roughening under the treatment conditions of higher gas pressures ($\sim 100$ mTorr) and longer treatment times ($\sim 200$ min). In these samples with a roughened surface, the N/Ga composition ratios measured by XPS deviated greatly in the Ga-rich direction from the normal N-preferentially etched sample. Moreover, N-K near-edge X-ray absorption fine structure (NEXAFS) spectra changed greatly from that normally observed in GaN crystals. New peak features were also observed in the O 1s XPS and the O-K NEXAFS spectra. The surface roughening, the composition deviation, and the anomalous spectral changes in XPS and the NEXAFS correlated well with each other, which indicated the formation of another compound in the surface-roughened sample. [DOI: 10.1380/ejssnt.2016.9]

Keywords: X-ray photoelectron spectroscopy; Near-edge X-ray absorption fine structure (NEXAFS); Ion bombardment; Surface roughening; Gallium nitride

I. INTRODUCTION

Gallium nitride (GaN) is expected to be applied as a wide-gap semiconductor in electronic devices, not only in light-emitting devices [1], but also in processing devices for high frequency [2] and high voltages [3, 4]. Plasma-etching techniques are frequently used to fabricate those microdevices. However, plasma process have many underlying issues [5, 6], such as composition deviation from the stoichiometry, because GaN is a binary compound and degradation of device performance.

We have investigated the damage of $n$-GaN crystals etched by various plasmas (Ar, He, and N$_2$) using a capacitively coupled radio frequency (RF) plasma reactor [7–9]. The Ar plasma generated at a high gas pressure of 50–100 mTorr caused a morphological change (surface roughening and defect formation) in the surfaces as the etching time increased more than sixty minutes [7]. However, in the samples etched by N$_2$ plasma with a lower self-bias voltage of $\sim 200$ V, the surface morphologies changed little, and their surfaces were equivalent to that of the as-grown sample [8]. We have further investigated and found that in the samples etched with a higher self-bias voltage of $\sim 400$ V, the surface morphology changed, roughening with higher gas pressures (50–100 mTorr) and longer treatment times (60–200 min). A part of the investigation has been reported elsewhere [9], but it was insufficient to understand the details of the etching damage and their effects on the microdevices.

In this paper, we report the characteristics of the etch-induced damage of an $n$-GaN crystal etched with N$_2$ plasma using mainly X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy methods. XPS and NEXAFS are effective techniques for investigating the details of the local chemical bonding and electronic structure of solids [10–12]. We used a surface-sensitive total electron yield (TEY) method and bulk-sensitive total fluorescence yield (TFY) method to investigate the depth analysis of the etch-induced defects. We also noted the effect of oxygen on the damage, although oxygen was not a constituent element of the GaN crystals.

II. EXPERIMENTAL

The specimen used in this study was an $n$-type (Si-doped) GaN wafer grown on a sapphire substrate by the metal-organic chemical vapor deposition (MOCVD) method (Nichia Corp.). The film thickness of the GaN was 2 μm. The concentration of doped Si was $8 \times 10^{18}$ cm$^{-3}$. All of the samples for etching were cut from one wafer. Plasma etching was carried out using...
a capacitive coupled radio frequency (RF) plasma reactor [13] using N₂ as an etching gas. The reactor was constructed with two asymmetric electrodes: the anode, with a 1217-cm² area, and the cathode, with an 80-cm² area; the distance between the two electrodes was 4 cm. The anode was connected to ground, and an RF voltage of 13.56 MHz was applied to the cathode through a capacitance. The generated self-bias voltage (V_{DC}) was almost equal to the peak value of the RF voltage (V_{RF}); namely, V_{DC} = -|V_{RF}| regardless of the etching gas pressure. In this study, plasma etching was carried out with an applied V_{RF} of 400 V, and gas pressures and treatment times were varied in the ranges of 10–100 mTorr and 5–200 min, respectively. The etching rate of the sample was about 0.5 nm/min.

The surface morphology of the etched sample was observed by a scanning electron microscope (SEM, JEOL JSM-6390). The composition change of the surface was determined by XPS (Shimadzu ESCA-1000). The probing depth of the XPS method was estimated to be less than 5 nm. The N/Ga ratio on the surface was determined from the integrated intensity of N 1s and Ga 3s peaks. The relative composition deviation was calculated with the N/Ga ratio of the as-grown sample equaling one. The O 1s XPS spectrum was obtained by the same apparatus. A particle collision model simulation named “PIS”, developed by the authors [8], was employed to calculate the composition change of the etched surface.

The change in bonding states of the surface atoms was characterized by the X-ray absorption spectroscopy (XAS) method. XAS measurement was conducted at the high-energy resolution beamline BL09A [14] at the NewSUBARU synchrotron radiation facility at the University of Hyogo. The NEXAFS spectra of N-K (~400 eV) and the O-K (~530 eV) edges of the plasma-etched GaN samples were measured by the TEY method (surface sensitive) and the TFY method (bulk sensitive). The TEY method was carried out with a sample current mode. The TFY method was carried out by measuring the amount of fluorescent X-rays with a photodiode. As a secondary emission (yellow-band, visible) by X-ray absorption was significant for the GaN samples, a 40 nm Al-coated photodiode was used to avoid the influence of the secondary emission. The probing depths of the TEY and TFY methods have been measured to be less than 3 nm and more than 100 nm, respectively [15]. All XPS and XAS measurements were carried out for the samples exposed to air after the plasma etching.

III. RESULTS

Figure 1 shows SEM images of the GaN surfaces etched with a V_{DC} of −400 V and at a gas pressure of 100 mTorr [9]. As shown in Fig. 1(b) and (c), the surface of the sample treated with 5–60 min is as smooth as that of the as-grown sample shown in Fig. 1(a). However, the surface morphology changes with roughening (Fig. 1(d)) under a longer treatment time (200 min). The surface roughening was observed even with a treatment time of 60 min in the sample treated under a gas pressure of 50 mTorr (not shown here). The surface roughening is remarkable in the sample treated for 200 min, and the defect is pit-like. In contrast, the surface morphology did not change for the samples etched with a lower V_{DC} of −200 V (not shown here) [8].

Figure 2(a) shows the N/Ga composition ratio of the plasma-etched samples under a V_{DC} of −400 V and a gas pressure of 100 mTorr. The solid circles denote the measurement points by the XPS method, and the solid lines denote the calculated values by the PIS simulation. The measured N/Ga ratio nearly agrees with the calculated values in the samples under a shorter treatment time of 5–60 min. However, the N/Ga ratio greatly deviated in the Ga-rich direction (N/Ga > 1) from the PIS-simulated value in the samples treated at 100 mTorr with 200 min. Figure 2(b) shows the O 1s XPS spectra of the samples treated at 100 mTorr. It is noted that oxygen atoms exist even on the surface of the as-grown sample. The O 1s peak intensity increases gradually with an increasing treatment time of 5–60 min, though the peak shape does not change. In the sample with a treatment time for 200 min, the peak shape changes; a new peak is formed at the binding energy near 536 eV, though the peak intensity becomes smaller than that treated for 5–60 min.

The anomalous changes in the N/Ga ratio and O 1s peak shape of the sample with a treatment time of 200 min correlated well with the result of surface roughening observed by SEM, as shown in Fig. 1(d). Our PIS simulation method deals with only the physical etching effect based on the simple two-body collision model of particles. Therefore, deviation from the physical simulation should become obvious under the condition of remarkable chemical etching effect. We think that UV-light emitted from the N₂ plasma affects the anomalous change of the surface morphology and composition change in the sample treated with 200 min. The details of the “synergy effect” of UV-irradiation and ion-impacts have been discussed in elsewhere [9].

Figure 3(a) shows the N-K NEXAFS spectra of samples treated under a gas pressure of 100 mTorr as measured by the TEY method (surface sensitive). The NEXAFS spectrum of the as-grown sample has a complicated shape
FIG. 2. N/Ga ratio and (b) O 1s spectra of n-GaN crystal surfaces etched by N₂ plasma generated with a high applied voltage of V_{RF} = 400 V and at a gas pressure of 100 mTorr as a function of etching time. In (a), the solid circles denote the measured points by the XPS method, and the solid curves denote the calculated value by the PIS model simulation.

with a maximum peak at 405 eV; this shape largely agrees with that previously reported elsewhere [16, 17]. According to Katsikini et al. [16], the absorption shape at the photon energy of 400–414 eV can be explained by the superposition of six Gaussian peaks. As shown in the spectra of samples etched with a treatment time of 5 min, broadening of the above six peaks occurs, as compared with the as-grown sample. This broadening can be explained by the disordering of the crystalline structure of the GaN crystal induced by the N₂⁺ ion bombardment. The broadening is more significant with a treatment time of 60 min. The shape of the NEXAFS spectrum of the sample treated for 200 min is quite different from that previously reported for the GaN crystal.

Figure 3(b) shows the N-K NEXAFS spectra of samples treated under a gas pressure of 100 mTorr as measured by the TFY method (bulk sensitive). The spectral shapes of the etched samples were similar to that of the as-grown sample, although a small change was observed in the sample treated for 200 min. According to our previous investigation of the depth sensitivity of the TEY and TFY measurements for the N-K absorption edge [15], the disordering of the crystalline structure induced by ion bombardment does not extended to a depth of more than about 5 nm.

The anomalous shape of the N-K NEXAFS as observed by the TEY method in Fig. 3(a) with a treatment time of 200 min has not been previously reported. It may consist of a π⁺ peak near 400 eV and a broad σ⁺ peak around 410 eV, superposed with a deformed N-K NEXAFS of the original GaN. The shape is also quite different from that of the oxygenated gallium nitride films reported previously [18]. Therefore, assignment of the origination of the anomalous spectral shape is quite difficult. According to the report of the N-K NEXAFS of the sample of ZrAl₂O₄/Al₂O₃ powder catalyst adsorbed with NO molecules [19], two sharp π⁺ peaks and a broad σ⁺ peak were observed at the photon energies of 401 eV, 403 eV, and near 410 eV, respectively. The overview of the anomalous shape of the N-K NEXAFS spectra of the sample treated for 200 min resembles the spectrum above. On the other hand, similar N-K NEXAFS spectra are also reported in carbon nitride CNₓ thin films [20–22]. The large chemical shift of the new O1s peak (~536 eV) ob-
FIG. 4. O-K edge NEXAFS spectra of an n-GaN crystal etched by N₂ plasma generated at a gas pressure of 100 mTorr as a function of the treatment time measured with the TEY method (a) and the TFY method (b).

served in the XPS spectrum, as shown in Fig. 2(b), is in concert with the bonding of oxygen to nitrogen or carbon atoms. Therefore, formation of the N–O and N–C bonds may be suggested by a mixing of oxygen and/or carbon with the longer time of plasma treatment.

Figure 4(a) shows the O-K NEXAFS spectra of samples treated under a gas pressure of 100 mTorr as measured by the TFY method. In these spectra, peak intensities were shown without normalization. The intensity of the O-K NEXAFS as measured by the TFY method increased with increasing treatment time. This intensity change is quite different from the surface concentration of oxygen atoms measured by 1s XPS (Fig. 2(b)) and the TEY-measured O-K NEXAFS (Fig. 4(a)). This result indicates that oxygen entered to a deep degree (more than 100 nm) from the surface of the GaN crystal with increased treatment time. Additional oxygen may penetrate to a deep level of the sample when the sample is exposed to air, after 200 min etching. Moreover, the pre-edge, similar to the spectrum obtained by the TEY method, was also observed in the sample treated for 200 min. This suggests that in the surface-roughened sample, oxygen penetrates to a deep level of the sample and forms another compound.

Comparing the results of Fig. 4(b) to Fig. 3(b), the N-K NEXAFS spectra were found to be not so much affected by the incorporated oxygen. It may be because as follows. NEXAFS spectroscopy gives the information of only the local structure of the interesting atoms. In the case of N atoms interested in the sample, Ga atoms may remain properly around the N atoms and form the Ga-tetrahedral local structures, even when the surface roughening occurred and oxygen penetrated deeper region in the film. In other words, formation of N–O bonds may be much difficult even in the penetration of oxygen without ion bombardment.

The generation of surface roughening, the N/Ga composition deviation from the normal N-poorly etched sample, the formation of a new peak in the O 1s XPS spectrum, the anomalous spectral shape of the N-K NEXAFS, and observation of a pre-edge in the O-K NEXAFS spectra also occurred in the samples under a gas pressure of 50 mTorr (not shown here); these anomalous behaviors were found to correlate well with each other.

IV. CONCLUSIONS

From the SEM observation, significant surface roughening was found to be generated in the plasma-etched n-GaN crystal surface treated with a self-bias voltage of −400 V, a gas pressure of 100 mTorr, and a treatment time of 200 min. In the samples observed with surface roughening, the N/Ga composition ratio greatly deviated in the Ga-rich direction from the value predicted by the particle collision model (N/Ga < 1). The N-K and O-K NEXAFS spectra became broader with increasing treatment times, which suggests the generation of disorder in the crystalline structure of the surface atoms. In the sam-
ples observed with surface roughening, the N-K NEXAFS spectra changed to an anomalous shape, and a pre-edge was observed in the O-K NEXAFS. No remarkable change was observed in the N-K NEXAFS spectra obtained by the TFY method, which suggests that the structural deformation did not extend to the deeper range of 100 nm from the surface. In contrast, the peak intensity of the O-K NEXAFS obtained by the TFY method increased with treatment time, which suggests the entering of the oxygen atom into the crystal and the formation of another compound.

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