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Effect of Fluorine Ion/Neutral-Beam Irradiation on Ohmic Contact Formation to n-Type GaN

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The effect of fluorine neutral/ion-beam irradiation to an n-type GaN surface on the ohmic contact property of a Ti/Al/Au multilayer scheme was investigated. The contact formed after a fluorine neutral-beam treatment showed lower contact resistivity than that formed without the treatment and that formed after a fluorine ion-beam treatment. The irradiation of the fluorine neutral beam is believed to create nitrogen vacancies at the surface region of n-GaN due to the preferential removal of nitrogen, which acts as a donor impurity. In addition, the GaN surface treated by the fluorine neutral beam showed less GaF_x formation and smaller surface damage compared to the surface treated by the fluorine ion beam. This resulted in lower ohmic contact resistivity. After annealing at temperatures above 600°C, the contact formed after the fluorine neutral-beam treatment exhibited an excellent linear current-voltage characteristic.
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Obtaining excellent ohmic contact to GaN-based materials is one of crucial steps in the fabrication of high-performance light emitting diodes (LEDs) and laser diodes (LDs). There have been many efforts of ohmic contact formation to n-type GaN-based materials using different metal schemes such as Ti/Al- and V/Al-based metallization.[1-5] In conjunction with the above efforts, surface-treatment techniques such as wet treatment and plasma treatment have also been proposed as an additional route to realize a good ohmic contact.[6,7] In the case of n-type GaN contact formation, it is well known that the increase in donor concentration at the surface region of the GaN is one of important factors in achieving a good ohmic formation. In the case of the surface treatment, good ohmic contact can be obtained by generating nitrogen vacancy acting as a donor at the surface region of n-type GaN. Jang et al.[8,9] investigated the effects of Cl_2 inductively coupled plasma (ICP) on the n-type GaN contact properties and found that the Cl_2 plasma treatment improved the ohmic characteristics of metal contacts due to the formation of nitrogen vacancy on the surface of the GaN, resulting in the increase of donor carrier concentration.

In the case of plasma treatments, however, if the GaN surface is damaged by ion bombardment during the treatment, ohmic contact properties can be degraded. Ping et al.[7,10] studied the effects of reactive ion etching (RIE)-induced damage on the Schottky and ohmic characteristics of n-GaN contacts. The surface of n-GaN was treated with $SiCl_4$ and Ar plasmas prior to metallization. They found that the surfaces treated with $SiCl_4$ plasmas showed improved ohmic contact properties compared to those of the untreated samples for all treatment conditions investigated. The GaN surfaces treated with Ar plasmas showed severely degraded ohmic contact behavior except for the treatment conditions using low self-bias voltages.

In this study, the n-GaN surface was treated by fluorine ion and neutral beams and their effects on the n-GaN ohmic contact properties were investigated. Fluorine-based gas was used in the GaN surface treatment to increase the nitrogen vacancies further compared to chlorine-based gases such as Cl_2 and $SiCl_4$ by forming volatile NF_x on the surface. Also, to investigate the possible reduction of charge-induced damage on the GaN surface during the treatment, fluorine neutral beam was used in addition to fluorine ion beam and the n-GaN contact treated by fluorine ion beam was compared with the contact treated by fluorine neutral beam.

Experimental

The fluorine ion-beam treatment was carried out using a laboratory-built two-grid radio-frequency ICP ion gun (13.56 MHz) with SF_6 plasma. The fluorine ions from the plasma were extracted using the two-grid assembly. A potential of +400 V (V_a) was applied to the grid located close to the source (acceleration grid), and the grid located outside of the source (extraction grid) was grounded to obtain a 400 eV fluorine ion beam. In the case of the fluorine neutral beam, on the outside of the ICP gun, a low-angle planar reflector was attached to neutralize the extracted fluorine ion beam. The reflector was made from a parallel stack of polished stainless steel supported by an aluminum block and mounted onto the extraction grid with a tilted angle of 5° from the ion-beam (normal) direction. The parallel reactive fluorine ion beams extracted from the ion gun were reflected on the low-angle flat surface so that about 99% of the beams toward the substrate could be neutralized.[11-13]

The epitaxial layers were grown on sapphire substrates using a commercial metallorganic chemical vapor deposition system. The layers consisted of an AlN buffer layer grown on the sapphire substrate, followed by a 3 μm thick Si-doped n-type GaN layer having a carrier concentration of $7 \times 10^{17}/cm^3$ and a mobility of about 240 cm^2/V s. The samples were degreased and sonicated in acetone and isopropyl alcohol for 10 min each and blow-dried using N_2 to remove the organic contaminants on the surface before the fluorine beam treatments. The samples were then treated with a fluorine neutral beam or with a fluorine ion beam for 120 s at the acceleration voltage of +400 V, a chamber pressure of 0.3 mTorr, and a SF_6 gas flow rate of 5 sccm. The contact metal composed of Ti (15 nm)/Al (80 nm)/Au (50 nm) was then deposited onto the surface using an e-beam evaporator. The samples were annealed in a rapid temperature annealing system (RTA) under an N_2 atmosphere at the temperatures from 600 to 900°C for 30 s.

In order to characterize the electrical properties of the contacts, a linear transmission line method (L-TLM) was used. A series of contacts with a subsequent separation of 5, 10, 20, 40, 80, and 160 μm were photolithographed on the n-GaN surface and their current-voltage characteristics were measured using a semiconductor parameter analyzer (HP4145B). The surface chemistry after the beam treatments was measured using X-ray photoelectron spectroscopy (XPS) (Mg kα 1253.6 eV, resolution 0.05 eV, Axis Kratos). For the calibration of the XPS peak, residual carbon peak was used. And, to analyze the surface damage after the beam treatments, room-temperature photoluminescence (PL) spectra were measured.

Results and Discussion

Figure 1 shows the current-voltage characteristics of the contact formed with Ti/Al/Au patterned using TLM on the n-GaN surfaces. The n-GaN surfaces were treated by the fluorine neutral beam and the fluorine ion beam, respectively, for 120 s, then cleaned with a

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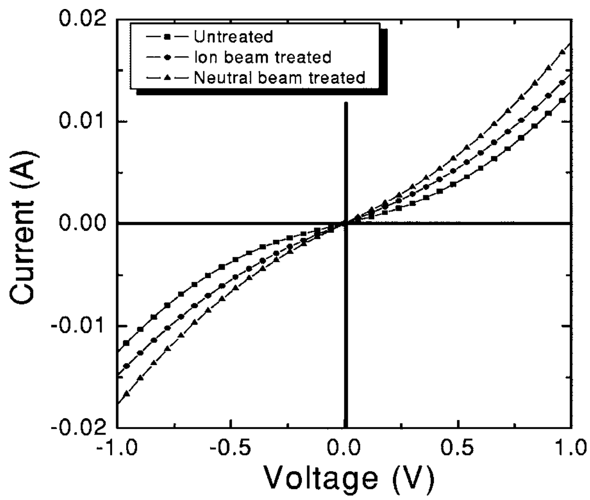

Figure 1. Current-voltage characteristics of as-deposited Ti/Al/Au contacts on n-GaN treated by fluorine ion beam and neutral beam. As a reference, the current-voltage characteristic of the contact fabricated on the untreated n-GaN was included.

buffered oxide etching (BOE) for 1 min and rinsed with deionized water before the evaporation of Ti/Al/Au. As a reference, an n-GaN ohmic contact formed without fluorine beam treatment was fabricated and its current-voltage characteristic was compared. As shown in the figure, all the three n-GaN contacts formed after the evaporation of the contact metal showed rectifying characteristics. However, the contact formed after the fluorine neutral-beam treatment showed the lowest contact resistivity and that formed after the fluorine ion-beam treatment showed the next lower resistivity. Therefore, the contacts formed after the fluorine beam treatments showed the better contact properties compared to untreated contacts.

The above contacts were annealed at 600, 700, 800, and 900°C for 30 s using RTA and their current-voltage characteristics were investigated again. The results are shown in Fig. 2a for the untreated sample, (b) for the fluorine ion-beam-treated sample, and (c) for the fluorine neutral-beam-treated sample. The calculated variations of the specific contact resistivity and sheet resistance measured as a function of annealing temperature for all of the samples are also shown in (d). As shown in the figures, the increase in annealing temperature decreased the contact resistivity for all the samples; however, the neutral-beam-treated sample showed the lowest contact resistivity at a given annealing temperature. After annealing at 900°C, the specific contact resistivities of the untreated sample, the

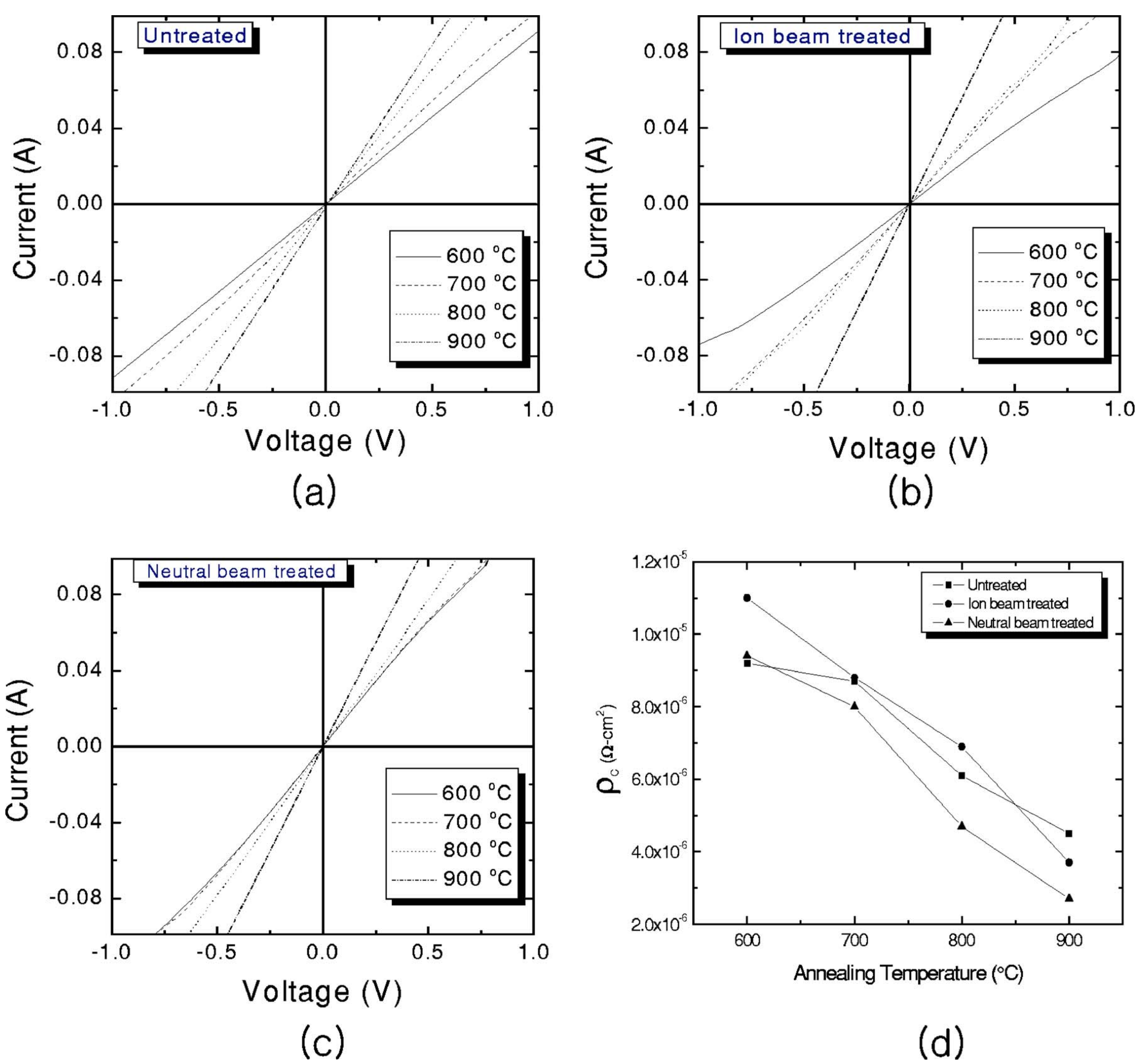

Figure 2. (Color online) Current-voltage characteristics of annealed Ti/Al/Au contacts on n-GaN treated by (c) fluorine neutral beam and (b) fluorine ion beam. (a) As a reference, the current-voltage characteristic of the contact fabricated on the untreated n-GaN was included. The variations in the specific contact resistivity and sheet resistance for all samples are also shown in (d).

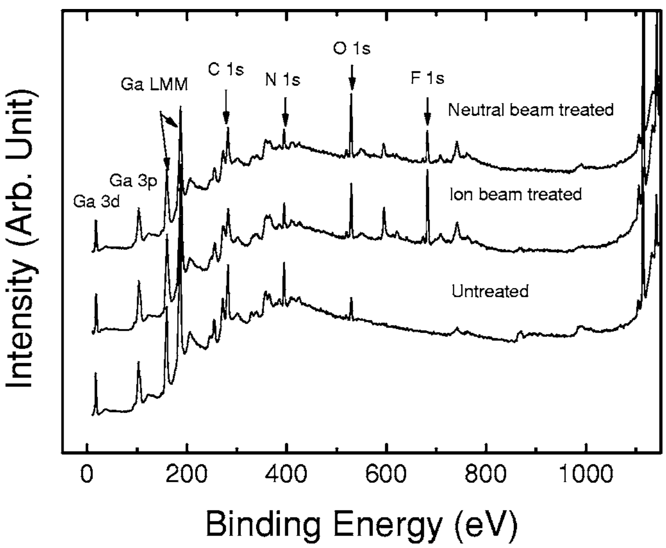

Figure 3. XPS wide-scan spectra for n-type GaN surfaces before and after treatments using both fluorine ion and neutral beams before BOE cleaning.

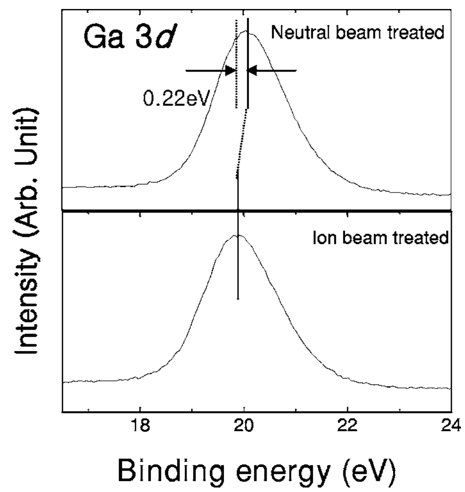

Figure 4. XPS narrow scan spectra of Ga 3d core level for n-type GaN surfaces after treatments using both fluorine ion and neutral beams.

ion-beam-treated sample, and the neutral-beam-treated sample were 4.5, 3.7, and 2.7×10^{-6} ohm-cm^2, respectively. Therefore, the neutral-beam-treated sample showed an improvement of specific contact resistivity of about 60%. However, in the case of the sheet resistance, no significant variation was observed for all of the samples.

To investigate the reason for the improvement of ohmic contact property after the beam treatments, the n-GaN surface chemistries before and after the treatments were measured using XPS and the results are shown in Fig. 3 (before BOE cleaning) and Table I. The treatment conditions are the same as those in Fig. 1. As shown in Fig. 3, the GaN surfaces treated by the fluorine ion beam and the fluorine neutral beam showed higher oxygen and fluorine due to the oxygen and fluorine existing in the processing chamber during the processing. The oxygen and fluorine on the GaN surface appear to exist in the form of Ga compounds such as GaO_x and GaF_x, respectively. After cleaning with BOE, as shown in Table I, the excessive fluorine and oxygen remaining after the beam treatments were significantly removed. Also, even though the ratio of Ga/N became higher than 1 after the beam treatment, the ratio of Ga/N showed further increase after the BOE cleaning, possibly due to the removal of the oxygen- and fluorine-related compound formed during the treatment and the nitrogen loosely bound on the GaN surface. When the GaN surfaces after the fluorine neutral-beam treatment and the fluorine ion-beam treatment are compared, as shown in Table I, the ratio of Ga/N remained similar around 1.4 after the BOE cleaning for both cases; however, a little more fluorine was remaining on the surface for the fluorine ion-beam-treated GaN surface.

Table I. Atomic percentages of Ga, N, F, and O for the untreated without BOE cleaning, ion-beam-treated, and neutral-beam-treated n-GaN surfaces with and without BOE cleaning.

		Ion-beam-treated		Neutral-beam-treated	
	Untreated	Without BOE	With BOE	Without BOE	With BOE
Ga	45	25.8	52.9	27.3	53.4
N	45	24.9	37.8	24.4	37.9
F	0	25.3	0.95	14.4	0.4
O	10	24	8.35	33.8	8.3
Ga/N	1	1.04	1.4	1.12	1.41

Fluorine irradiated to the GaN surface dissociates the GaN bonding and forms GaF_x and NF_x on the surface. In the case of NF_x, due to the high vapor pressure (boiling point of N_2F_2, NF_3, and N_2F_4: −106, −129, and −73°C, respectively),[14] it is easily removed from the surface by vaporization. However, in the case of GaF_x, due to the low vapor pressure (boiling point of GaF_3:950°C),[15] it is removed only through sputtering by energetic particle bombardment. In our experiment, the fluorine neutral beam was formed by reflecting the fluorine ion beam at a low angle while keeping the processing conditions the same. Therefore, the similar ratio of Ga/N obtained after the treatment by both beams appear to be related to the similar physical characteristics of the beams. However, more fluorine on the GaN surface obtained after the fluorine ion-beam treatment might be related to the higher chemical reactivity of fluorine ion compared to fluorine neutral with Ga atom in the formation of GaF_x.

The GaF_x remaining on the GaN surface is insulating material.[16] Therefore, the higher contact resistivity of the ion-beam-treated sample than that of the neutral-beam treated sample appears to be partially related to more GaF_x remaining on the fluorine ion-beam-treated sample. In addition, the differences in the contact resistivities appear to be related to the differences in carrier concentration. Figure 4 shows the XPS narrow scan spectra of Ga 3d peaks of the GaN surfaces after treatments by the fluorine ion beam and the fluorine neutral beam. As shown in the figure, the Ga peak positions for the neutral-beam-treated sample and ion-beam-treated sample were located at 20.32 and 20.1 eV, respectively. In the case of the untreated sample, the peak was at 19.5 eV (not shown). Therefore, after the ion-beam treatment, the Ga peak was shifted to a higher binding energy by about 0.6 eV, and after the neutral-beam treatment, the peak was shifted to 0.82 eV. The Ga peak position is related to the Fermi level in the GaN and the movement to the higher binding energy implies that the Fermi level was moved toward the conduction band, possibly due to the increase in the carrier concentration in the GaN, resulting in the lower specific contact resistivity. The differences in the shifts of Fermi level for both treatments are believed to be from the less GaF formation for the neutral-beam-treated sample even though the ratios of Ga/N were the same for both treated samples.

Figure 5 shows PL spectra of the GaN before and after treatments by the fluorine neutral beam and the fluorine ion beam. As shown in the figure, the untreated GaN showed the highest PL intensity among the samples investigated, while the neutral-beam-treated GaN showed higher PL intensity compared to the ion-beam-treated GaN. The decrease of PL intensity is believed to be related to the defects formed near the GaN surface by the beam treatments.

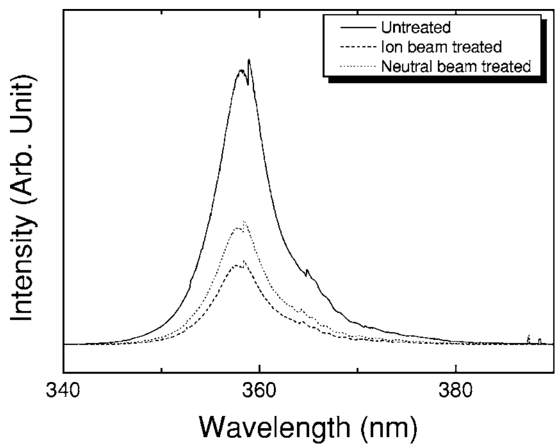

Figure 5. Room-temperature PL spectra of n-type GaN before and after treatments using both fluorine ion and neutral beams.

Therefore, the GaN surface treated by the neutral beam was damaged less than the surface treated by the ion-beam. The lattice disorder and point defect can occur for both the fluorine ion-beam treatment and the fluorine neutral-beam treatment due to the similar particle bombardment energy to the GaN surface during the treatment. However, the lower damage, showing higher peak intensity, obtained by the neutral-beam treatment compared to that by the ion-beam treatment appears to show the effect of charge during the treatment, which is possibly related to the charge-induced defect formation, and resulted in the creation of a larger amount of impurity states in the GaN.

Conclusions

Ohmic contacts were fabricated on the n-type GaN surfaces treated by fluorine neutral beam and fluorine ion beam by evaporating Ti/Al/Au contact metals, and their electrical characteristics were investigated. The GaN ohmic contact showed the lower contact resistivity after the beam treatments and the GaN contact treated by the fluorine neutral beam showed the lowest contact resistivity of about $2.7 \times 10^{-6}\ \Omega\ \text{cm}^2$ after the annealing at 900°C for 30 s. The treatment of the GaN surface by both the neutral beam and the ion beam removed nitrogen preferentially from the surface; therefore, by increasing the donor concentration near the surface, the contact resistivity was decreased. The decrease of contact resistivity by the beam treatment was limited by the formation of the surface defects and GaF_x compound during the beam treatment. The fluorine neutral-beam treatment showed lower surface defects and less GaF_x on the GaN surface possibly due to the lack of charge-induced defect formation and less reactivity of fluorine neutral compared to fluorine ion. Therefore, lower contact resistivity could be obtained for the fluorine neutral-beam-treated GaN compared to the fluorine ion-beam-treated GaN.

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