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Doping level-dependent dry-etch damage in *n*-type GaN

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Abstract The electrical effects of dry-etch on *n*-type GaN by an inductively coupled $Cl_2/CH_4/H_2/Ar$ plasma were investigated as a function of ion energy, by means of ohmic and Schottky metallization methods. The specific contact resistivity (ρ_c) of the ohmic contact was decreased, while the leakage current in the Schottky diode was increased with increasing ion energy due to the preferential sputtering of nitrogen. At a higher rf power, an additional effect of damage was found on the etched sample, which was sensitive to dopant concentration in terms of the ρ_c of the ohmic contact. This can be attributed to effects such as the formation of deep acceptors as well as the electron-enriched surface layer within the depletion layer. Furthermore, the thermal annealing process enhanced the ohmic and Schottky properties of the heavily damaged surface.

Keywords GaN · Etch · Plasma · Damage

1 Introduction

During the last decade, a variety of etching methods for the reliable pattern transfer of GaN have been reported, and a dry etching method has proven to be effective for the fabrication of light emitting diodes (LED) and laser diodes [1–3]. However, energetic ion bombardment-induced damage, which accompanies the dry etch process can lead to the deterioration of the optical and electrical properties of the semiconductors [4–7]. The specific contact resistivity (ρ_c) and current-voltage (I-V) measurement, extracted from the ohmic contact and Schottky diodes, respectively, have been found to be very sensitive to surface damage induced by the dry-etching of semiconductors [8]. Although the effects of the ion bombardment of non-reactive gases in the plasma have been reported by exploiting a metal-semiconductor contact method [9–12], only a few results have been reported on the electrical characterization of dry-etched GaN under a actual device fabricating conditions. It is known that the depth of the damaged surface, etched with a chemical component, should be smaller than those etched using a physical component [12]. Thus, it would also be expected that the contact behavior of the surface etched with a chemical component would be different from those etched with a physical component, since ρ_c depends on the semiconductor doping concentration as well as the depth of the interfacial layer, formed by dry-etch between the metal and the semiconductor [13]. In this article, we report on effects produced by an inductively coupled $Cl_2/CH_4/H_2/Ar$ plasma (ICP) on *n*-type GaN surfaces, by exploiting an ohmic and Schottky metallization method. Furthermore, we also reports on the result of N_2 plasma treatment on etched surface and rapid thermal annealing (RTA) for the purpose of removing etch-induced damage.

2 Experimental

Two types of Si-doped GaN films, with a thickness of 1.5 μm, were grown on a c-plane sapphire substrate using a metalorganic chemical vapor deposition method by controlling the flow rate of SiH_4 as the *n*-type dopant source. The carrier concentration was assessed by Hall measurements. The etching

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of GaN was performed using $Cl_2/CH_4/H_2/Ar$ (30/8/8/16 sccm) plasmas, and the N_2-plasma treatment, under the same conditions, was carried out on the sample etched at different rf conditions. A detailed description of the etching and N_2 plasma treatment conditions can be found elsewhere [7]. The ρ_c was measured using a Ti (30 nm) as an ohmic metal by a transmission line method, and the current-voltage (I-V) curve were extracted from the Schottky diodes, which were fabricated using an Ti/Au (30/80 nm) and Ni/Au (30/80 nm) as ohmic and Schottky metals, respectively. A PL measurement at 10 K was performed in order to investigate the optical properties of the etched film using a He-Cd laser (325 nm). RTA treatments were also performed under a N_2-ambient for 1 min to evaluate the thermal stability of the etch-damage in Schottky diodes.

3 Results and discussion

Figure 1 shows ρ_c as a function of rf table power on the surfaces that were (a) moderately-doped ($n = 1 \times 10^{18}$ cm^{-3}; MDG), (b) more highly-doped ($n = 5 \times 10^{18}$ cm^{-3}; HDG), and (c) N_2-plasma treated (NPT) GaN after the dry etching of HDG. The contact resistance (R_s) generally remained unchanged, consistent with the result of Thomas et al. [8] Since the doping concentration for the field emission or tunneling to dominate the transport mechanism [14] is calculated to be about $\sim 10^{19}$, it can be assumed that both thermionic and tunneling mechanisms dominate the carrier transport between the metal and GaN. For this reason, the HDG sample shows a lower ρ_c than that of the MDG sample in an as-grown state due to the increased tunneling. It is well known that the ρ_c value for a dry-etched GaN surface decreases due to nitrogen vacancies on the GaN surface, which act as shallow donors [15] and the resulting n-layer localized at the metal/GaN interface [16]. Samples etched at 100 W of table power show a lower ρ_c than those of as-grown samples regardless of the carrier concentration, and, correspondingly, a monotonic decrease in the ρ_c for a MDG sample was observed as the rf power was increased up to 200 W (induced dc-bias of –220 V), reaching $5.34 \times 10^{-4}\ \Omega\,\text{cm}^2$. This indicates that the degree of plasma damage, assumed to be a nitrogen vacancy, is enhanced and, as a result, the ρ_c is decreased with increasing the ion energy, due to the severity of nitrogen loss at a higher rf power. However, a further increase in the rf table power of 250 W for the MDG sample caused the ρ_c to increase, as can be seen in Fig. 1(a). Pearton et al. [5, 17] reported that if the system undergoes energetic ion bombardment, then electrical compensation could occur by forming deep acceptor states. It is evident that the additional damage which compensates the Si-donor dominates the ρ_c when the rf table power was increased above 200 W, consistent with our previous results [9]. A similar behavior was observed for an HDG sample. Figure 1(b) shows the initial decrease in ρ_c down to $1\times 10^{-3}\ \Omega\,\text{cm}^2$ and a subsequent increase as the rf power is increased over 100 W, indicating that the additional damage is also dominant. Note that the "threshold rf power" for the introduction of additional damage is much smaller for the HDG than for the MDG, indicating that highly doped GaN is more vulnerable to the introduction of such additional damage. It is known that highly doped layers are quite resistant to plasma-induced damage such as the introduction of deep acceptor states because it is difficult to produce a sufficient number of deep levels to affect the conductivity or the layer [17]. However, the presence of the electron-enriched surface layer within the depletion layer may change the transport properties of the etched surface. Popovic [13] proposed that ρ_c gradually decreases with increasing depth of the electron-enriched surface layer X_n due to the reduction in barrier height [18]. When X_n is greater than the width of the depletion region (W_n), i.e. $W_n \leq X_n$, however, ρ_c should not be influenced by the electron-enriched surface layer. From this result, one can intuitively expect that the "threshold rf power" in Fig. 1 is the very condition in which W_n is equal to X_n, and that the compensation effect of deep acceptors dominate the ρ_c over the threshold rf power. Thus, the threshold rf power of the HDG sample is lower than that of the MDG sample since W_n is inversely proportional to donor concentration. This result clearly shows that additional damage by dry etching can be expected, though the chemical components present in the plasma.

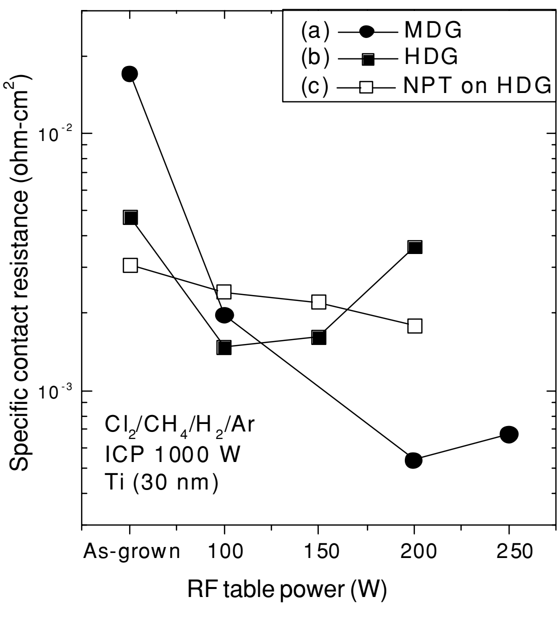

Fig. 1 Specific contact resistivity (ρ_c) as a function of rf table power using as-deposited Ti on surfaces of (a) MDG and (b) HDG, and (c) NPT sample for HDG after dry etch. All samples were etched using a $Cl_2/CH_4/H_2/Ar$ (30/8/8/16 sccm) plasma at 10 mTorr for 1 min. Note that the rf power in X-axis is the dry-etching condition

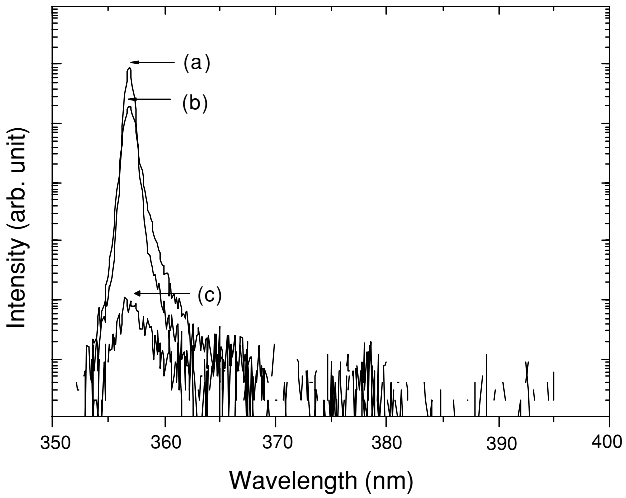

Fig. 2 PL spectra of HDG samples at 10 K from (a) as-grown, (b) etched HDG at 100 W of rf table power, (c) etched HDG at 200 W of rf table power

In order to investigate the effect of the damage on the optical properties of the HDG sample, PL measurements were performed at 10 K. In Fig. 2, the dominant transition line at 356.5 nm (3.475 eV), the I_2 line, is due to the recombination of excitons that were bound to donors [19]. Cheung et al. [20] observed an additional transition in the PL spectrum of undoped GaN after Ar-reactive ion etching, which were donor-bound excitons, confirming the proposed formation of shallow donors. In our PL results, however, the additional transition was not observed, indicating that the shallow donors by nitrogen vacancies are restricted to the topmost surface due to the reduced contribution to the luminescence of the surface than that of the bulk, in accordance with the R_s value. On the other hand, the PL intensity of the I_2 peak decreased with increasing rf power, as shown in Figs. 2 (a), (b), and (c). At an rf power of 200 W, the PL intensity drastically decreased by 4 orders of magnitude, compared to the PL intensity of the as-grown sample. These results also confirm that the HDG sample etched at a higher rf power suffers from other types of damage, which are different from those etched at a lower rf power, in accordance with the result of Fig. 1.

Damage-recovery is of great importance since it would be expected that the degradation in the performance and the lifetime of an LED by etch-damage in the n-GaN would be inevitable, by analogy with the growth optimization of n-GaN to reduce the resistance [21]. In this regard, we also investigated the effect of NPT on the etched HDG sample, and the results are shown in Fig. 1(c). The NPT at 380°C were performed under the same conditions. While the ρ_c of the as-deposit HDG sample was slightly decreased after the N_2-plasma treatment, which may be due to the removal of contaminants, the ρ_c of the NPT sample, which had been etched in the range of 100–150 W of rf power, was slightly increased due to an excess supply of nitrogen on the nitrogen-deficient HDG surface. However, an NPT sample that had been etched previously at an rf power of 200 W showed a further decrease in ρ_c after the N_2 plasma treatment, indicating that a different type of damage, as proposed earlier, can be removed by an NPT, thus leading to improved ohmic properties. It should be noted that the ρ_c of the NPT sample decreases slightly with increasing rf power during the etching, confirming that the depth of the nitrogen-deficient layer increases as the rf power increased, since it becomes too thick to be fully compensated by the NPT, as the rf power is increased.

One of the sensitive methods for evaluating damage is to investigate the diode characteristics of the Schottky contacts. Figure 3(a) shows typical I–V characteristics of the Schottky diodes on the HDG sample. The diodes were leaky when the sample was etched at 100 W and 200 W of rf power due to the collective effects of etch-induced damage [11, 12], while the NPT showed a decrease in leakage current for 100 W etched samples, especially in the reverse current region (not shown). This indicates that NPT treatment is an effective method for recovering the stoichiometry of the nitrogen deficient surface, consistent with the result of Figs. 1(b) and (c). On the other hand, the NPT sample that was etched at 200 W of rf power shows a drastic decrease in both the forward and reverse

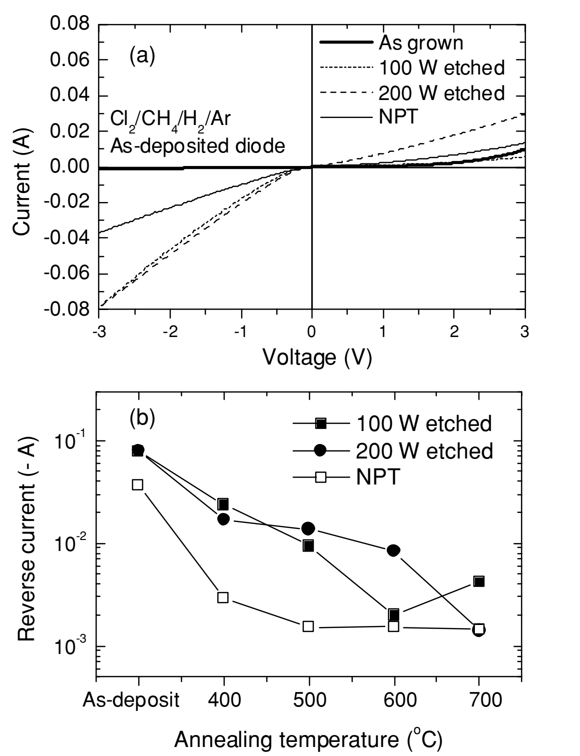

Fig. 3 (a) I-V characteristics of Schottky diodes on an HDG sample in an as-deposit state as a function of rf table power, and (b) Reverse current variation with annealing temperature measured at a bias of –3 V. NPT sample was etched at 200 W of rf power prior to N_2-plasma treatment

current regions, indicative that NPT can restore the transport property which was affected by the deep level compensation.

We also investigated the effects of RTA on the reverse currents of Schottky diodes, as shown in Fig. 3(b). The annealing process of the as-grown sample showed no detectable change in the I–V characteristics of the Schottky contact up to 600°C, indicating the absence of any metallurgical interaction between metal and GaN. The reverse currents for the 100 W etched sample shows a linear decrease up to temperatures of 600°C, while those at 200 W show a non-linear recovery mechanism, indicating that the full recovery of the etch-induced damage require a higher temperature than those for 100 W etched sample such as 700°C in this experiment. However, NPT sample shows a more rapid decrease in leakage current than those of the etched samples. From these results, we conclude that the NPT lowers the activation energy for the recovery of etch-damage.

4 Conclusion

In summary, we studied the effect of ion-bombardment on the electrical properties of n-type GaN using and ohmic and Schottky metallization methods under actual device process conditions. Additional effects of damage were found on the etched GaN sample prepared at a higher rf power, which is more sensitive to doping concentration in terms of the specific contact resistivity in the ohmic contact. The N_2 plasma treatment on the etched GaN surface along with the RTA process enhanced the ohmic and Schottky properties of the heavily damaged surface.

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