

Annealing of defect states in reactive ion etched GaN

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Abstract

The Al_{0.11}Ga_{0.89}N-based photodiodes fabricated under different annealing ambient after inductively coupled plasma reactive ion etching process were studied. The dark current and photocurrent with different illuminated wavelengths were characterized. Higher photocurrent for the diode annealing in H₂ ambient can be observed and attributed to the defect-assisted photocurrent. This photocurrent shows a strong annealing ambient dependence and causes the shift of cutoff wavelength in the responsivity spectrum. The surface state was characterized by the capacitance analysis with Schottky contact.

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1. Introduction

Gallium nitride (GaN) materials have been intensively studied for the fabrication of the high-temperature and high-power electronic device applications [1–4]. The device fabrication has to utilize the inductively coupled plasma reactive ion etching (ICP-RIE) method. However, the ion bombardment can induce dislocations or formation of dangling bonds on the surface effects and may cause material and/or device damage after the ICP etching process. Several groups have found that the studies of the GaN defects induced by the ICP etching process [5–9]. The optical and electrical properties of semiconductor can be degraded due to ICP-induced defects, and these related process defects are reduced by thermal treatment [10–12].

In this work, we have studied the Al_{0.11}Ga_{0.89}N-based photodiode devices characteristics depending on different annealing ambients. Moreover, in order to investigate the ICP-induced defects after annealing in different ambients, the Si-doped gallium nitride (GaN:Si) is also studied. The interfacial states density is characterized and determined by capacitance–frequency (*C*–*f*) measurements over a frequency range (100 Hz–1 MHz) at room temperature. The

spectral responsivity for Al_{0.11}Ga_{0.89}N-based photodiode devices after annealing in different ambients at 600 °C is analyzed. From this, the surface-treated effects and the ICP-induced defects are discussed. We have found that the ICP-induced defects caused by the ICP etching process can be partially eliminated by annealing process.

2. Experimental details

In this experiment, samples of GaN epitaxial layers were grown on sapphire substrate by metal–organic chemical vapor deposition (MOCVD). The epitaxial structure consisted of a low-temperature GaN nucleation layer, 2 μm of undoped GaN, 2 μm of n⁺-GaN:Si (2 × 10¹⁸ cm⁻³), 50 nm of n-GaN:Si (5 × 10¹⁷ cm⁻³), 200 nm of undoped i-Al_{0.11}Ga_{0.89}N, 100 nm of p-Al_{0.11}Ga_{0.89}N (2 × 10¹⁷ cm⁻³) and 50 nm of p⁺-GaN (5 × 10¹⁷ cm⁻³). Then, the samples were etched to n⁺-GaN region by ICP etching process with standard photolithography. After the ICP etching process, some certain damages were incorporated in GaN. Followed by annealing in N₂ ambient at 600 °C for 30 min (“N₂-treated” sample) or in H₂ (“H₂-treated” sample) ambient at 600 °C for 30 min. A sample without annealing treatment (“non-treated” sample) was used for comparison. The above-mentioned samples were then chemically

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treated by an HCl:H₂O (1:1) solution for 3 min. The p-type ohmic contacts of the Al_{0.11}Ga_{0.89}N-based photodiode devices were processed by evaporation of Ni/Au (5 nm/8 nm) with standard photolithography technology, followed by annealing process at 550 °C in air in a furnace. The specific contact resistance (ρ_c) is around $1.2 \times 10^{-3} \Omega \text{cm}^2$. Evaporations of Cr/Al/Cr/Au (15 nm/300 nm/15 nm/300 nm) were processed through the thermal evaporation as n-type ohmic contacts and bonding pad, and they were subsequently annealed at 600 °C for 20 min in N₂ ambient. The current–voltage (I – V) measurements of Al_{0.11}Ga_{0.89}N-based photodiode devices were characterized by a Hewlett-Packard 4156 semiconductor analyzer. The spectral responsivity of Al_{0.11}Ga_{0.89}N-based photodiode devices was measured by using a Xenon arc lamp and a monochromator (SPX1000). All the optical systems were calibrated by using a UV-enhanced silicon photodiode.

For comparison, 2 μm of undoped GaN epitaxial layer was grown on sapphire by MOCVD with same low-temperature GaN nucleation layer, and subsequently 2 μm of Si-doped n-GaN was grown on the undoped GaN epitaxial layer as described above. The n-type ohmic contact was formed with the above described process. Then, the mesa layer was etched by the ICP etching process. The same annealing processes (N₂-treated, H₂-treated and non-treated) were performed, then the Schottky contacts were evaporated by the Ni/Au (100 nm/300 nm). The capacitance was measured by Hewlett-Packard 4284 analyzer at room temperature with series resistance correction [13,14].

3. Results and discussion

Fig. 1 shows the schematic of cross-section of the Al_{0.11}Ga_{0.89}N-based photodiode devices in this work. Since the mesa layer was defined by ICP etching process, some damage may be formed on the etched surface as shown in the shadow region of Fig. 1.

Fig. 2 shows the current–voltage (I – V) characteristics of the Al_{0.11}Ga_{0.89}N-based photodiode devices with different annealing ambients. The illumination power is 0.13 μW with a wavelength of 340 nm, and the photon energy is higher than the band gap of the Al_{0.11}Ga_{0.89}N (3.6 eV). The inset in Fig. 2 shows the three different dark currents of the samples by using different annealing ambients. After the annealing process, the dark currents are reduced compared to the non-treated sample. The N₂-treated sample shows the lowest dark current in this work, and a little higher dark current of H₂-treated sample can also be observed in the figure. After the ICP etching process, the sample with annealing in N₂ ambient can reduce defects [15]. Under the illumination, the photocurrent of the non-treated sample remains nearly constant and increases rapidly as the reverse-bias is higher than 6 V. After annealing in N₂ ambient, a small amount of photocurrent can be observed and remains nearly constant even though the reverse-bias is 10 V. Fewer defects can be expected for

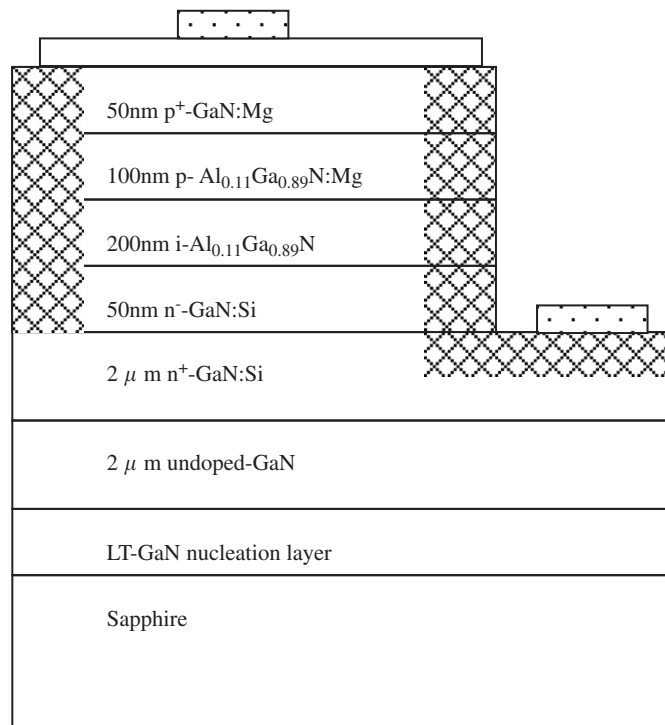


Fig. 1. Schematic of cross-section of Al_{0.11}Ga_{0.89}N-based photodiode devices. After ICP etching process, ICP-induced defects and the effects of thermal treatment in different ambients are observed in the deep sidewall regions and n-GaN layer as shown in shadow regions of this figure.

the Al_{0.11}Ga_{0.89}N-based photodiode devices after N₂ annealing process. In case of H₂-treated sample, a little higher photocurrent can be observed and increases more rapidly than the non-treated sample with reverse-bias higher than 6 V. The external quantum efficiency of the H₂-treated photodiode may increase more than two times of magnitude as compared to that of the N₂-treated photodiode. Several reviews have reported the properties of hydrogen in compound semiconductor. They have demonstrated that hydrogen passivation of defects may help to reduce the trapping or recombination centers and create new hydrogen-related donors or acceptors in structures [16–20]. Some electrons may be generated by these defects under higher reverse-bias and cause the high photocurrent [21]. To clarify these hydrogen-caused defect complexes effects, illumination with photon of energy less than the band gap was studied.

Fig. 3 shows the I – V characteristics under illumination with a wavelength of 400 nm (0.4 μW). In dark and under the illumination, the I – V curves of the non-treated and the N₂-treated samples are almost the same. Yet, the photocurrent of the H₂-treated sample increases by a small amount. This result indicates that these Al_{0.11}Ga_{0.89}N-based photodiode devices may respond at a wavelength of 400 nm (3.1 eV) with hydrogen-caused defect level in higher reverse-bias.

Fig. 4 shows the spectral response of these samples under reverse-bias 8 V. The cutoff wavelength is around at a

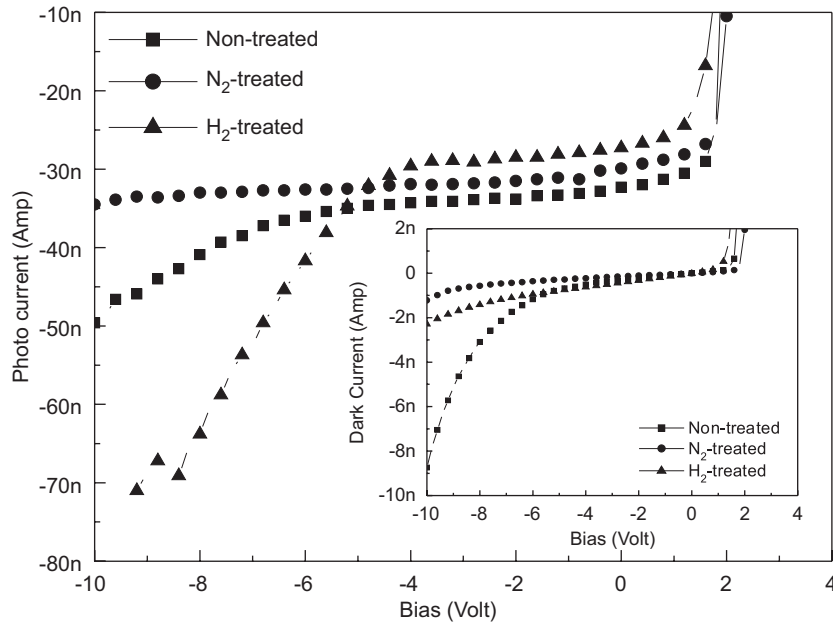


Fig. 2. Current–voltage (I – V) characteristics of $\text{Al}_{0.11}\text{Ga}_{0.89}\text{N}$ -based photodiode devices after annealing in different ambients under illumination with a wavelength of 340 nm ($0.13 \mu\text{W}$). A lower dark current could be observed and is also near a constant at various reverse-biases as shown in the inset of the figure.

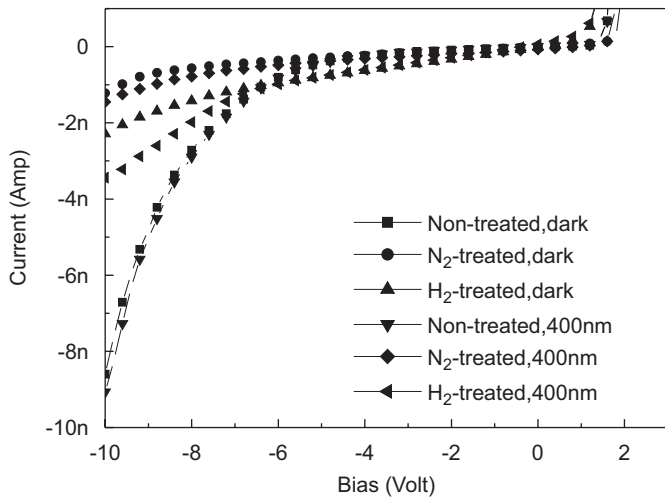


Fig. 3. Current–voltage (I – V) characteristics of $\text{Al}_{0.11}\text{Ga}_{0.89}\text{N}$ -based photodiode devices after annealing in different ambients under illumination with a wavelength of 400 nm ($0.4 \mu\text{W}$).

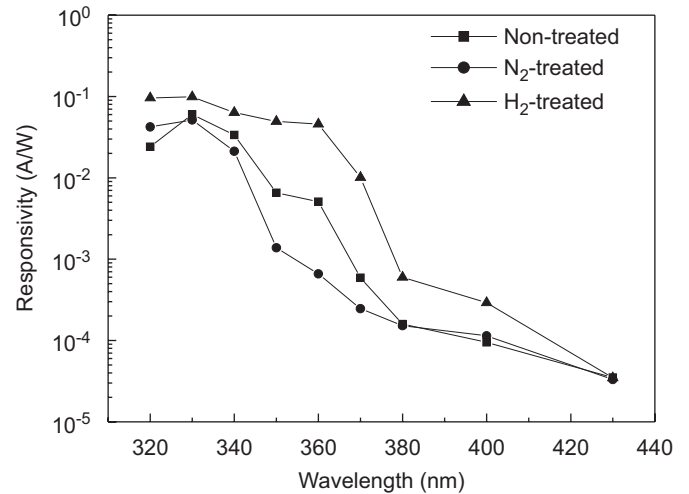


Fig. 4. Spectral response of surface-treated samples after annealing in different ambients under reverse-bias voltage 8 V.

wavelength of 340 nm as the absorption of $\text{Al}_{0.11}\text{Ga}_{0.89}\text{N}$ (3.6 eV). Under the illumination at a wavelength of 360 nm, the photon energy is less than the band gap. The responsivity of the non-treated sample around $5 \times 10^{-3} \text{ A/W}$ can be observed. After annealing in N_2 ambient, the reduction of responsivity and a clear cutoff can be observed. The below band gap absorption may be attributed to these defects. For the N_2 -treated sample, few ICP-induced defects as discussed above can be achieved, and a higher rejection ratio which is around three to four orders of magnitude in the spectral response could be observed. For the H_2 -treated sample, the responsivity around $3 \times 10^{-4} \text{ A/W}$ can be observed even under illumi-

nation with a wavelength of 400 nm. Thus, more defect levels can be expected for the H_2 -treated sample. Although the defect level may cause recombination center and reduce the photocurrent, the defect-assisted photocurrent may be enhanced [21] and may increase the responsivity. These defects may cause in the epitaxial procedure or the followed process such as ICP etching and cause these below gap response.

On the other hand, in order to quantitate the surface defect complexes for these samples, n-GaN with same ICP etching process was performed. The interface capacitance for the Schottky contact with different frequency was characterized. The interfacial states capacitance depending

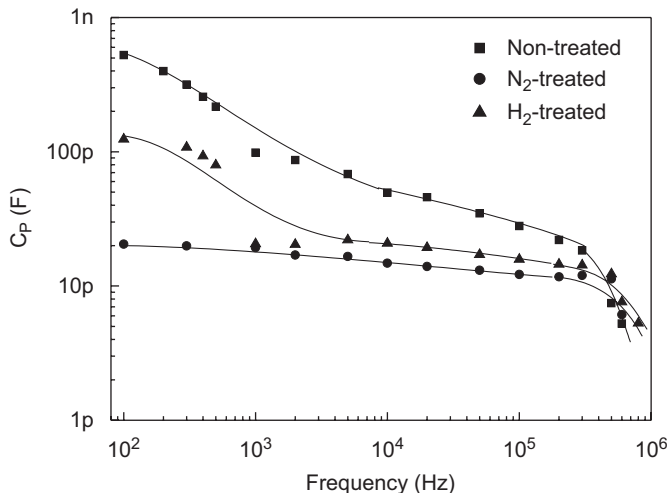


Fig. 5. Frequency dependence of the interfacial states capacitance of the n-GaN Schottky contacts after annealing in different ambients.

on the interfacial states density N_{ss} with the relaxation time τ is given in [22–27] as

$$C_p = qAN_{ss} \frac{\arctan(\omega\tau)}{\omega\tau}, \quad (1)$$

where q is the electron charge, A is the contact area and $\omega = 2\pi f$ is the angular frequency.

Frequency dependence of the interfacial states capacitance of the n-GaN samples after annealing in different ambients for the Schottky contacts is shown in Fig. 5. The interfacial states density of the non-treated sample may reach higher than $5.4 \times 10^{12} \text{ eV}^{-1} \text{ cm}^{-2}$. However, the interfacial states density reduces more than one order of magnitude after annealing in both the N_2 and H_2 ambients, for which its values are around 2.2×10^{11} and $1.3 \times 10^{12} \text{ eV}^{-1} \text{ cm}^{-2}$, respectively. The N_2 ambient shows a better effect in removing these ICP-induced defects after annealing at 600°C . For the H_2 -treated sample, some hydrogen-caused defects may be formed on the ICP-etched surface, and may enhance the defect-assisted photocurrent on the photodiode.

4. Conclusion

In conclusion, the $\text{Al}_{0.11}\text{Ga}_{0.89}\text{N}$ -based photodiode devices characteristics with different annealing ambients are investigated. The N_2 -treated sample shows the lowest dark current in this work, and a little higher dark current is observed for the H_2 -treated sample. Under the illumination, the H_2 -treated sample shows the highest photocurrent compared to the non-treated and N_2 -treated samples. Worst rejection ratio in the responsivity can be observed for the H_2 -treated sample and more defect levels can be expected for it. Although the defect level may cause recombination center and reduce the photocurrent, the defect-assisted photocurrent may be enhanced and may increase the responsivity [21]. This result could be

attributed to some electron–hole pairs generated by the defects which may be in the structure and/or on the surface under high reverse-bias. On the other hand, the Schottky contact characteristics with different annealing ambients have also been studied to quantitate the defects density on the surface after the ICP etching process. The interfacial states density of the non-treated sample may reach higher than $5.4 \times 10^{12} \text{ eV}^{-1} \text{ cm}^{-2}$. However, the interfacial states density reduces more than one order of magnitude after annealing in both the N_2 and H_2 ambients, for which its values are around 2.2×10^{11} and $1.3 \times 10^{12} \text{ eV}^{-1} \text{ cm}^{-2}$, respectively. The N_2 ambient shows a better effect in removing these ICP-induced defects after annealing at 600°C .

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