Study on Surface Modification of GaN by Atmospheric Microplasma

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***Abstract* -- GaN is widely studied and developed as a material for new application in power electronics devices or as emitter of various color of light. GaN is usually formed by nitriding GaAs and grown on the sapphire substrate with a high dislocation density. For this dislocation, microchannel epitaxy (MCE) or regrowth of GaN is required to reduce dislocations. Recently, plasma treatment is used for interface treatment, regrowing of GaN crystal and nitridation process of GaAs. GaN surface was treated by atmospheric pressure microplasma using Ar and N_2 as process gases and powered by AC and pulse power supplies. Microplasma is atmospheric pressure nonthermal plasma and a type of dielectric barrier discharge which has small discharge gap and requires relatively low discharge voltage of only about 1 kV. Modifications of the surface were observed after the treatment and they depend on the gas process, treatment time and power supply. The surface was analyzed before and after the treatment using X-ray Photoelectron Spectroscopy (XPS) analysis and Field-Emission Scanning Electron Microscope (FE SEM).**

***Index Terms*— atmospheric microplasma, surface modification, GaN, pulse power**

I. INTRODUCTION

In this paper, surface modification of GaN crystal by atmospheric microplasma was performed. GaN is known as a material used for blue LED [1-4], power devices [5-8] and semiconductor lasers [9-12] after adjusting its band gap by mixing it with Indium or Aluminium. It is usually formed by nitriding GaAs and grown on the sapphire substrate with a high dislocation density [13-16]. The large lattice mismatch between GaN and sapphire leads to the possibility of high threading dislocations densities in the nitride layers [17]. Dislocations which occurred in the GaN crystal degrate its quality and electric characteristic. Microchannel epitaxy (MCE) or regrowth of GaN is required to reduce dislocations [18,19]. The use of these crystal growth method was shown to dramatically improve the morphology and defect density of the GaN in comparision in direct growth only at high temperature [20].

Recently, a plasma process for interface treatment, regrowth of GaN and nitridation process of GaAs was reported [21-26]. These reports produced the results which improved electric characteristics or produced high quality devices used the GaN crystal such as High-Electron-Mobility Transistors (HEMTs). Although these treatment and improvements by plasma were performed under the hard circumstance, low pressure or high temperature.

On the contrary, GaN surface modification by microplasma introduced in this article was carried out under atmospheric pressure. For applying to the industry, atmospheric pressure plasma would be the one of the solution to minimize cost or space. Microplasma used in this article is atmospheric pressure nonthermal plasma and a type of dielectric barrier discharge which has small discharge gap and requires relatively low discharge voltage of only about 1 kV [27-29] without vacuum equipment.

One of the aim of this research is reducing dislocations in the GaN crystal or its surface directly to expose atmospheric pressure microplasma. Surface treatment of the GaN substrate by atmospheric pressure microplasma was experimentally performed and the effect for the GaN surface was analyzed with X-ray Photoelectron Spectroscopy (XPS) and Field-Emission Scanning Electron Microscope (FE-SEM).

II. EXPERIMENTAL SETUP

A. Microplasma electrodes

Figure 1 shows a schematic image of microplasma electrodes which are perforated metallic plates covered with a dielectric layer and faced each other at small discharge gap under 100 μm with a spacer. Due to small discharge gaps (0 - 100μm) and to the assumed specific dielectric constant of dielectric layer which was about 10^4, a high intensity electric field (10^7 - 10^8 V/m) could be obtained with relatively low discharge voltage (about 1 kV). The electrodes have circular shape with Ø 40 mm diameter and holes to flow the gas, diameter Ø 1.6 mm. The gas was flown through an acrylic pipe Ø 10 mm connected to the electrodes. The GaN substrate to be treated was placed at 1 mm distance from electrodes inserting a spacer between the film and electrode. Therefore only a small size reactor is necessary and the power consumption is low. Streamers which were generated between electrodes could produce various radicals and ions. These active species could affect a target surface [27].

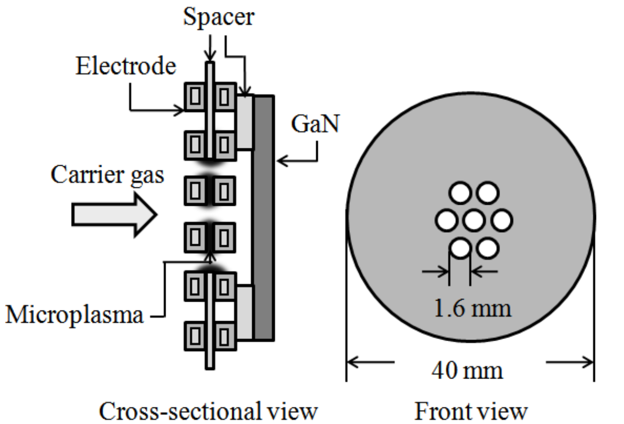


Fig. 1 A schematic image of the microplasma electrodes.

An image of microplasma generation is shown in Figure 2. Microplasma was generated around the holes of the electrode. The discharge area was controllable by a spacer.

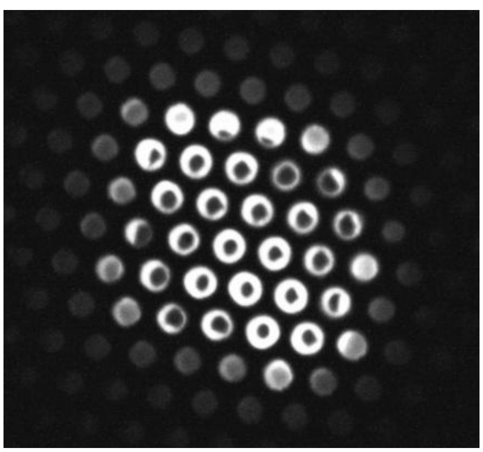


Fig. 2 An image of the microplasma generation.
(Process gas: Ar, Dsicharge voltage: 1 kV)

B. Experimental setup

The experimental setup for surface modification of GaN on a substrate is shown in Figure 3. GaN sample and the microplasma electrodes were placed into a chamber. In this study, Ar and N_2 were used as the process gases supplied from a gas cylinder. The gas flow rate was set at 5 L/min. Before carrying out the each experiment, both process gases were flown for about 4 minutes. Thus the effect of the impurity components in the chamber could be minimized. An AC high voltage and a negative pulse high voltage power supplies were used to compare their performance or the treatment effect. The waveforms of discharge voltage and corresponding discharge current for both AC and pulse power supplies are shown in Figure 4. Spike current occurred at rise and decay time of discharge voltage (Fig. 4 (a)). This is a typical waveform of a dielectric barrier discharge. The frequency of AC high voltage was 27 kHz. AC powered microplasma was confirmed at discharge voltage of 0.9 kV and at corresponding discharge current of 52 mA in Ar and at 1.6 kV and 100 mA in N_2 respectively. The negative pulse width was about 2 μs and frequency was set at 1 kHz (Fig. 4(b)). Pulsed powered microplasma was generated at discharge voltage of 1.3 kV and discharge current of 2.0 A in Ar and at 1.6 kV and 4.2 A in N_2 respectively.

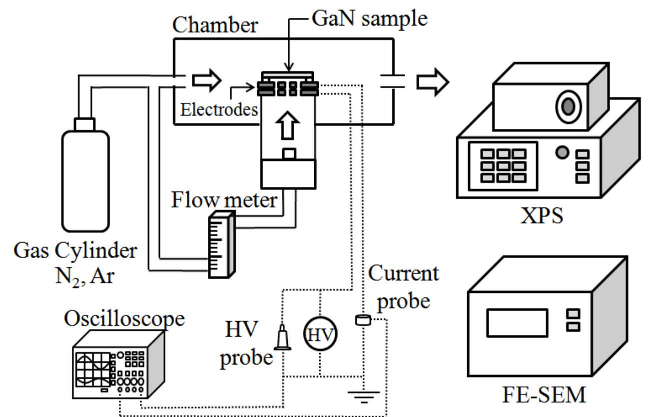
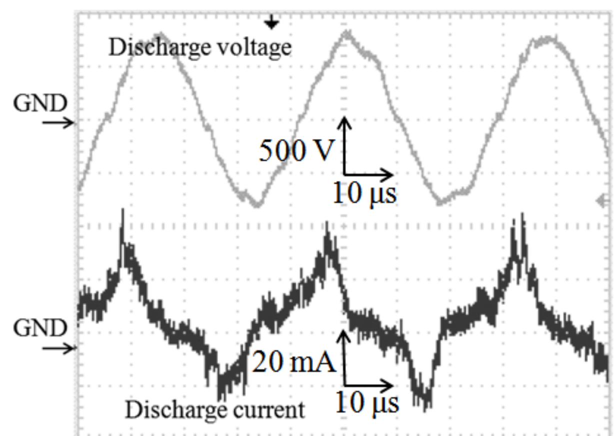
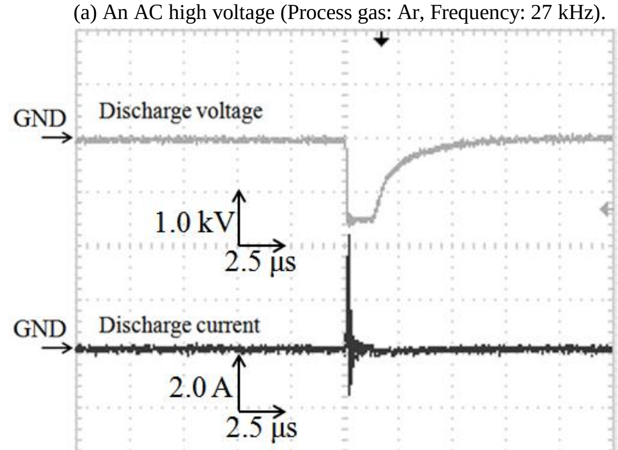


Fig. 3 An experimental setup for surface modification of the GaN substrate.



(a) An AC high voltage (Process gas: Ar, Frequency: 27 kHz).



(b) A negative high voltage (Process gas: Ar, Frequency: 1 kHz).
Fig. 4 Waveforms of discharge voltage and current during discharge.

Pulse powered microplasma was prepared for expecting the relatively moderate GaN surface compared with the high frequency AC power supply. Also pulse powered microplasma has an advantage over AC powered microplasma for power consumption which is lower.

XPS analysis (Shimadzu, ESCA-3400) was performed for surface analysis. FE-SEM (Nippon Denshi, JSM-6320F) was used to confirm the physical changes of GaN surface before and after microplasma treatment.

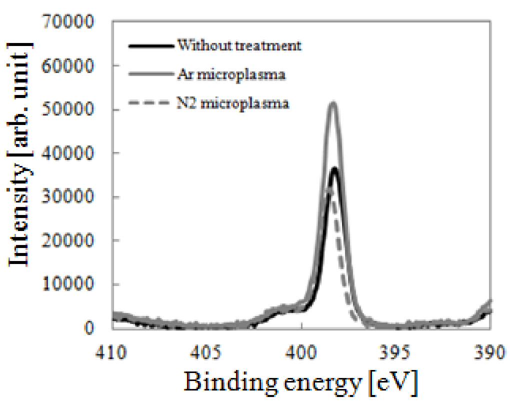
III. RESULTS AND DISCUSSIONS

A. XPS analysis

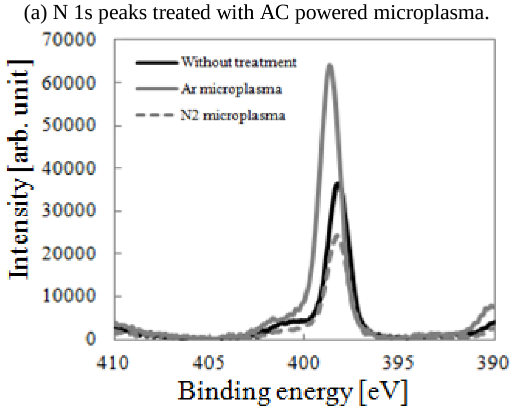
Chemical bonds on the GaN substrate surface were analyzed by XPS. Excited Ar species [30,31] and metastable N_2 species [32,33] generated by microplasma mainly contributed to surface modification of GaN substrate.

The results of XPS analysis of the GaN surface treated for 5 s in various process gases and power supplies are shown in Figure 5

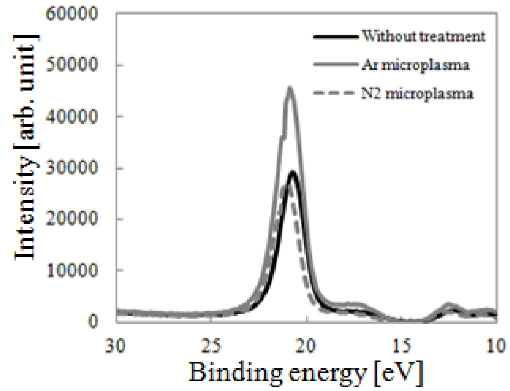
An increase of N-Ga bonds which formed GaN substrate was observed at N 1s and Ga 3d peaks when the surface was treated by Ar microplasma. Distinct change of N 1s and Ga 3d peaks were observed when the GaN surface was treated with pulse powered microplasma. In contrast, a decrease of N 1s and Ga 3d peaks were observed when the surface was treated with N_2 both AC and pulse powered microplasma.



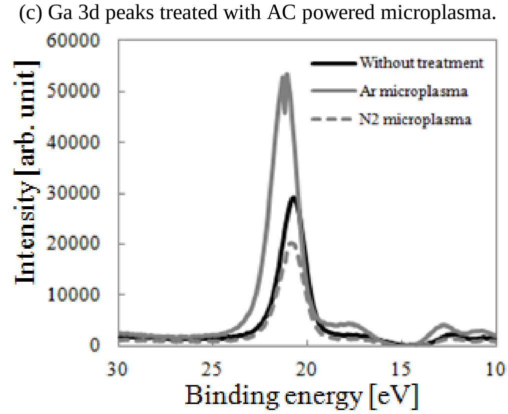
(a) N 1s peaks treated with AC powered microplasma.



(b) N 1s peaks treated with pulse powered microplasma.



(c) Ga 3d peaks treated with AC powered microplasma.

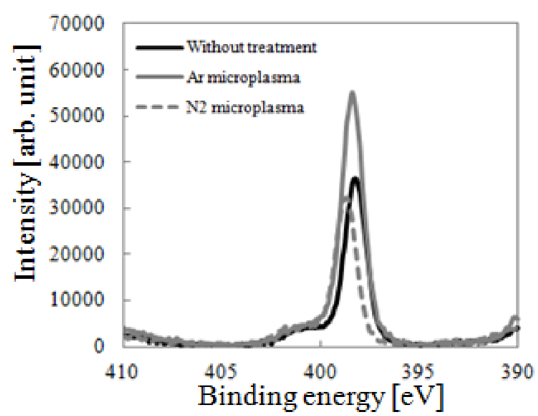


(d) Ga 3d peaks treated with pulse powered microplasma.

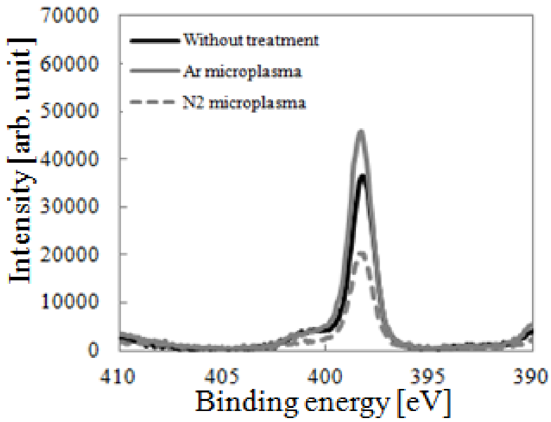
Fig. 5 XPS analysis of GaN surface treated for 5 s.

The results of XPS analysis which obtained from the GaN surface treated for 30 s are shown in Figure 6.

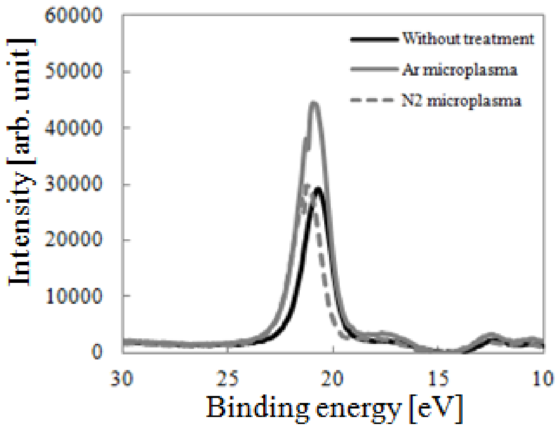
Same tendency of changing N 1s and Ga 3d peaks were observed by changing the treatment time. There was no significant change of peaks comparing with the XPS analysis of the GaN surface treated for 5 s in AC powered microplasma treatment. Although in pulse powered microplasma treatment, N 1s and Ga 3d peaks became small especially Ar microplasma treatment compared with the peaks which obtained from the GaN surface treated for 5 s (Fig. 5 (b) and (c)).



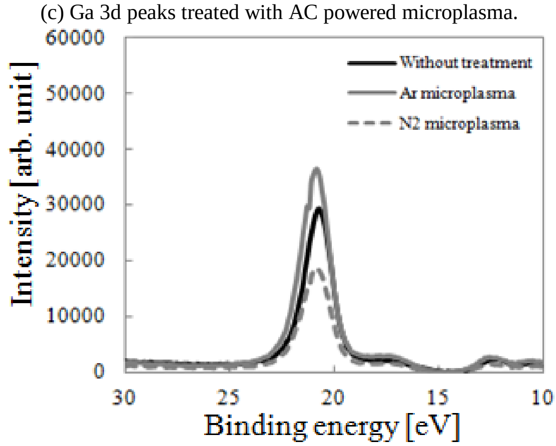
(a) N 1s peaks treated with AC powered microplasma.



(b) N 1s peaks treated with pulse powered microplasma.



(c) Ga 3d peaks treated with AC powered microplasma.



(d) Ga 3d peaks treated with pulse powered microplasma.
Fig. 6 XPS analysis of GaN surface treated for 30 s.

For AC powered microplasma electron temperature is determined by the slope of the electron energy distribution function (EEDF) at low energy and usually in the 1–3 eV range which are effective in exciting the vibrational states of gas molecules but they do not have enough energy to cause ionization. Only a small number of electrons have sufficiently high energies, in the 10–15 eV range, to be capable of ionization.

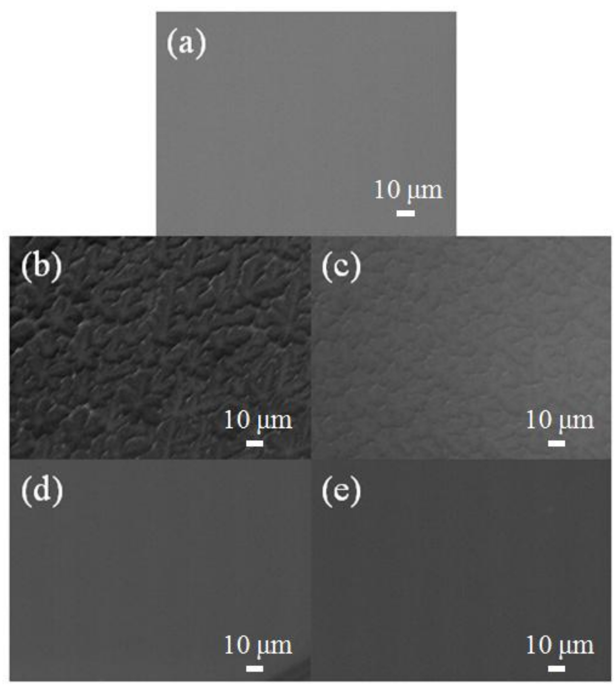
２ ２２２ ｂ ｙ In the case of pulse powered microplasma, the peak electron density is larger and the EEDF is toward its high energy tail. A faster rising voltage by the pulse power supply shift the EEDF and produce a higher proportion of high energy electrons for inducing ionization [34]. Considering this and a lower discharge power due the plasma off period, we can conclude that microplasma generated by pulse power supply is a more effective and efficient way for the surface treatment of GaN while considering same tendency of changing N-Ga bonds on a GaN surface. The peaks became smaller in the area of the GaN surface in which treatment time was longer. The secondary electron emission coefficient of argon metastable atoms (Ei = 11.55 eV) is high [35], thus after Ar microplasma treatment, etching effect to the GaN surface could be occurred [36,37]. This etching effect could be arisen a clear thin layer of the GaN surface, then increase of N 1s and Ga 3d peaks occurred.

A decrease of nitrogen on the GaN surface means that GaN surface became a nitrogen deficiency state. In this state there are some possibilities of applying the nitriding process or regrowth of GaN. Thus a different tendency in modification of N 1s and Ga 3d was observed with the treatment time.

B. *Observation of GaN surface by FE-SEM*

Images of GaN surface were taken by the FE-SEM in order to analyze the physical modifications of GaN surfaces after the microplasma treatment.

Images of GaN surface before and after treatment are shown in Fig. 7.



(a) Without treatment.
(b) Treated with Ar AC powered microplasma for 10 s.
(c) Treated with Ar pulse powered microplasma for 10 s.
(d) Treated with N_2 AC powered microplasma for 10 s.
(e) Treated with N_2 pulse powered microplasma for 10 s.
Fig. 7 SEM images of the GaN surface before and after treatment.

Compared with the surface images, before treatment [Fig. 7(a)] and after the Ar microplasma treatment [Fig. 7(b) and Fig. 7(c)], the effect of the surface treatment was visible for both cases: AC powered and pulse powered. While N_2 microplasma seems to have the smooth surface after the microplasma treatment [Fig. 7(d) and Fig. 7(e)].

A significant physical modification was observed only with Ar microplasma treatment which attributed to a higher amount of radicals and excited species. This could be due to the etching effect which affected a thin layer from the GaN surface as shown in Fig. 8 left. Even pure Ar was used as the process gas, due to the impurities in the chamber wall, OH radicals were generated. Thus excited Ar and also OH radicals could have contributed to the surface modification effect [27]. N_2 microplasma treatment could have affected the dangling bonds due to the reaction with excited N_2 or N radicals generated by the microplasma as shown in Fig. 8 right [38,39].

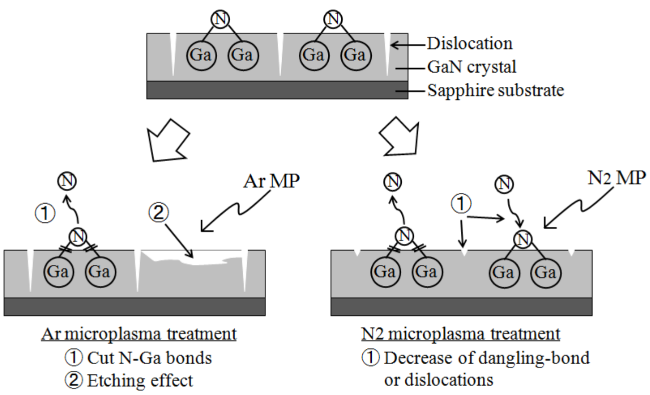


Fig. 8 Image of microplasma treatmentr of the GaN surface.

IV. Conclusions

The possibility of the GaN surface modification by atmospheric pressure remote microplasma method was studied and the results were confirmed by XPS and FE-SEM analysis:

1. The XPS analysis showed an increase of N1s and Ga 3d peaks on a GaN surface treated with Ar microplasma and a decrease of the same peaks on a GaN surface treated with N_2 microplasma. Physical effects were observed by the FE-SEM analysis only with the Ar microplasma treatment. This could be explained by an etching effect to cut the N-Ga bonds under the action of excited Ar and OH radicals. In the case of N_2 microplasma treatment, the action of excited N_2 or N radicals on the GaN surface could affect the dangling bonds of Ga and reduce the dislocations.
2. Pulse powered microplasma showed similar results with the AC powered microplasma in treating the GaN surface, but it proved to be more efficient due to lower energy consumption for obtaining almost same effect. Faster rise time of discharge voltage shifted the EEDF and produced a higher proportion of high energy electrons for inducing ionization and furthermore generating active species which affected the GaN surface.

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