

Electrochemical oxidation of GaN for surface control of GaN-based device structures

Naohisa Harada, Nanako Shiozaki, Eri Ogawa, and Tamotsu Hashizume

Reserch Center for Integrated Quantum Electronics, Hokkaido University
Sapporo 060-8628, Japan
E-mail: (harada, hashi)@rciqe.hokudai.ac.jp

1. Introduction

GaN-based semiconductors are now recognized as important material candidates for high-power/frequency electronic devices and high efficiency LDs and LEDs. For a fabrication processing and a stable device structure, we need a low-energy etching technique or a suitable passivation structure, so that the method itself does not damage the semiconductor surface. From this point of view, a wet process should be paid attention for its advantages such as low energy and RT process with a simple setup in the air.

In this paper, we firstly present a fundamental study on an electrochemical oxidation of GaN surfaces. It is also shown that the present oxidation method is effective in enhancing the PL intensity and reducing electronic state density at the GaN surface.

2. Experimental Method

We used Mg-doped p-GaN (Mg: $3 \times 10^{19} \text{ cm}^{-3}$) and Si-doped n-GaN (Si: $8 \times 10^{16} \text{ cm}^{-3}$) grown by MOCVD. Ohmic contacts were fabricated on GaN surfaces with a Ni/Au structure for p-GaN and a Ti/Al/Ti/Au structure for n-GaN. The electrochemical setup is schematically shown in Fig. 1 (a). We used an electrolyte consisting of propylene glycol and 3-wt% tartaric acid at a ratio of 2:1. The electrolyte was adjusted to pH = 7.0 by adding NH_4OH into the solution. The potential of the GaN surface was controlled by a potentiostat via an Ag/AgCl reference electrode. When a positive bias was applied to the GaN surface, the following oxidation reaction is expected:



As indicated by this equation, holes(h^+) are absolutely

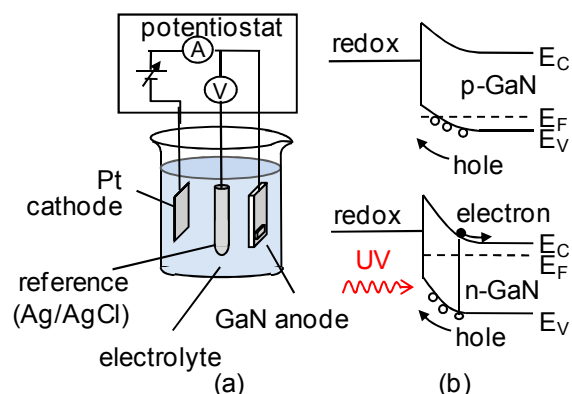


Fig. 1.(a) Experimental setup for oxidation (b) Band structures of electrolyte/GaN interfaces at positive bias to GaN.

necessary at the electrolyte/GaN interface for electrochemical oxidation reaction. Thus, the UV illumination was introduced to the surface to generate holes for the oxidation of n-GaN, as shown in Fig.1 (b).

3. Results and discussion

First, we investigated the oxidation of p-GaN surface. The waveform of applied voltage to the GaN ohmic electrode was shown in Fig.2 (a). At an initial stage of oxidation, we applied a ramp voltage with a sweeping rate of 25 mV/s. Then, the bias was changed to a constant form. Figure 2 (b) shows the reaction current as a function of the process time. A rapid current increase was observed at around 70s, corresponding to the voltage amplitude of 1.75 V. At zero bias, there seems to be an initial potential barrier, E_{B0} , opposite to the potential shown in Fig. 1(b), at the electrolyte/p-GaN interface like Schottky barrier. In this case, holes are far from the interface, preventing the electrochemical oxidation. When the positive bias was applied to the GaN ohmic electrode, the potential barrier at

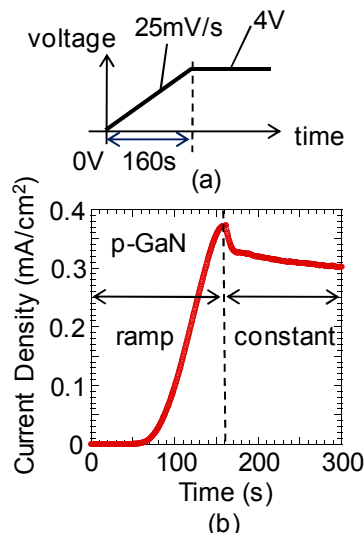


Fig. 2. (a) Waveform of applied voltage. (b) I-t characteristics of oxidation current for oxidation of p-GaN.

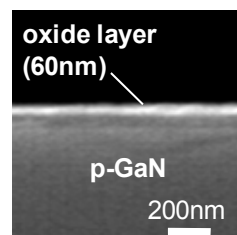


Fig. 3. Cross-sectional SEM image of oxidized p-GaN.

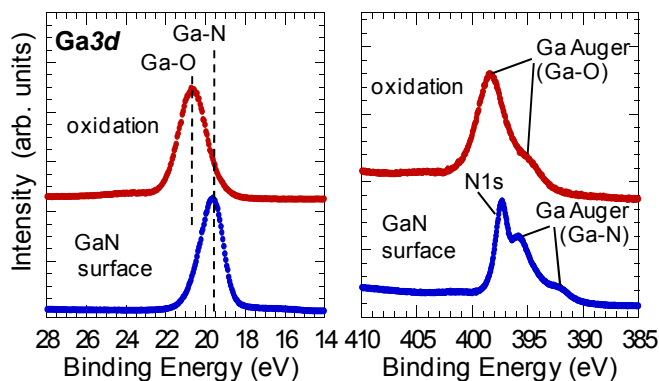


Fig. 4. XPS spectra of N1s and Ga3d core levels with and without oxide.

the p-GaN surface became lower. Then holes were supplied to the electrolyte/p-GaN interface, resulting in the oxidation reaction, as shown in Fig. 1(b). The initial potential barrier nearly equals to the onset of reaction current, i.e., $E_{B0}=1.75$ eV. In constant bias region, the decrease of oxidation current was observed. This indicated a voltage drop in the oxide layer.

Figure 3 shows a cross-section SEM image of the oxide/p-GaN structure. We observed a good structure with a uniform thickness of oxide and a flat interface. The thickness of oxide was estimated to be 60 nm, corresponding to a growth rate of 0.2 nm/s for an average current density of 0.35 mA/cm^2 .

Then, the oxidized p-GaN surface was characterized by X-ray photoelectron spectroscopy (XPS). **Figure 4** shows XPS spectra of Ga3d and N1s core levels before and after the oxidation. Before oxidation (bare surface), the peak positions of Ga3d and N1s spectra were in good agreement with those from the Ga-N bond. In addition, the Ga Auger signals in Ga-N bond appeared at the lower energy side of the N1s peak. After oxidation, the peak position of the Ga3d spectrum shifted to the higher energy. Furthermore, the N1s peak disappeared, while the Ga Auger peaks in the oxide-bond configuration became dominant, as shown in the upper parts of Fig. 4. This indicated that the GaN surface was successfully oxidized during the present electrochemical process. The energy position of Ga-O bonding peak in the Ga3d spectrum showed that the main composition of the oxidized GaN surface was Ga_2O_3 . The separate TEM analysis showed that the present oxide was not crystalline but amorphous.

Our oxidation technique is promising for surface control because the resulting layer consists of native oxide of semiconductor, not deposited oxide. Therefore, with a good interface expected between the GaN and oxide, the luminescence was investigated through PL measurement using a He-Cd laser. **Figure 5** shows PL spectra of p-GaN before and after oxidation. Even for the as-grown GaN surface, the luminescence related deep levels remarkably appeared in addition to the band-edge luminescence, which is typical in p-GaN with doping of Mg [1]. After oxidation, we observed the intensity enhancement of the band-edge emission, as shown in Fig.5. Through oxidation, some defects near the GaN surface could have been consumed

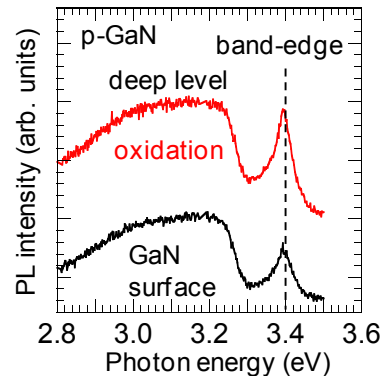


Fig. 5. PL spectra from p-GaN areas with and without oxide film.

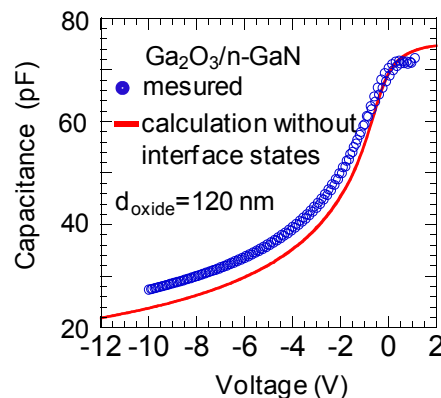


Fig. 6. C-V characteristics measured at 1 MHz and calculated with Terman method.

into the oxide layer: namely, defects near the surface could be reduced by oxidation. Another possible cause for the enhancement of PL intensity is surface passivation effects due to oxidation. The native oxide of the *n*-GaN was expected to form a good interface, resulting in a smooth transition of the bonding configuration, so that dangling bonds were passivated.

To investigate properties of the $\text{Ga}_2\text{O}_3/\text{GaN}$ interface, we prepared a MOS structure. The p-GaN sample was doped with a high concentration of Mg ($3 \times 10^{19} \text{ cm}^{-3}$). This is not suitable for the C-V characterization because the change in the depletion layer at the GaN surface is insensitive to the gate potential. Thus, we used n-GaN with Si doping concentration of $8 \times 10^{16} \text{ cm}^{-3}$. **Figure 6** shows the C-V curve of the $\text{Ga}_2\text{O}_3/\text{n-GaN}$ structure with a Ga_2O_3 thickness of 120 nm, together with the calculation result without taking account of interface states. The experimental result was very close to the calculated one. From the capacitance difference of them, interface state density was calculated using the so-called Terman method. As a result, we found relatively low densities of interface states at the $\text{Ga}_2\text{O}_3/\text{n-GaN}$ interface. The minimum density was $5 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$ at around $E_C - 1.0 \text{ eV}$.

These results predict that the present electrochemical oxidation process is promising for a selective oxidation of p-type region and a suitable surface passivation structure.

References

- [1] U. Kaufmann *et al.* Appl. Phys. Lett. **72**, 1326 (1998)