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Formation of Thin Native Oxide Layer on n-GaN by Electrochemical Process in Mixed Solution with Glycol and Water

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In this paper, we report on the feasibility of oxidizing n-GaN by an electrochemical process in a mixture containing an aqueous solution of tartaric acid and propylene glycol. Photons generated by UV illumination were supplied at the electrolyte-GaN interface during the oxidation process. In the constant-voltage mode, X-ray photoelectron spectroscopy analysis revealed that relatively thick Ga oxide layer formed on the n-GaN surface. However, the oxide surface was very rough. In addition, we found metallic Ga components in the oxide layer or at the oxide-GaN interface for longer oxidation times. On the other hand, a thin Ga_2O_3 layer with a smooth surface was grown by a constant-current process.

KEYWORDS: GaN, oxide, electrochemical, anodic oxidation, XPS

GaN is a promising material for such applications as high-power and high-frequency devices operating at high temperatures. However, the process for device fabrication is generally difficult owing to the chemical bonding stability of GaN, which significantly limits the flexibility of the process.

For the formation of insulating layers on GaN and the etching of the GaN surface, dry processes utilizing plasma have generally been used in device fabrication. However, they require a vacuum environment. Furthermore, high energies during the plasma-assisted dry processes can generate defects such as vacancies at the processed GaN surfaces.^{1,2)} On the other hand, wet processes can be performed in air at lower temperatures. In addition, chemically or electrochemically low-energy reactions can be used, which minimize damage to the surfaces. As an example of a wet process for GaN, Ohkubo³⁾ reported the anodic etching of n-type GaN films in a NaOH electrolyte. For oxidation, Rotter *et al.*⁴⁾ carried out a photo-assisted electrochemical process on the n-GaN surface in KOH solution under potentiostatic control. Similarly, Mistele *et al.*⁵⁾ fabricated and characterized AlGaIn/GaN high electron mobility transistors in which photoanodically grown oxide layers were used as gate dielectrics.

In this work, we adopted a photoelectrochemical process utilizing a mixed solution of glycol and water.⁶⁾ Unlike the processes in alkaline solutions used in the previous studies,^{4,5)} the present method enables us to form a thin oxide layer on the GaN surface with a nearly neutral condition in the solution, which is important to avoid unexpected etching reactions on the oxidized GaN surface during the electrochemical process.

We used undoped GaN layers grown on sapphire substrates by metal-organic vapor phase epitaxy. The

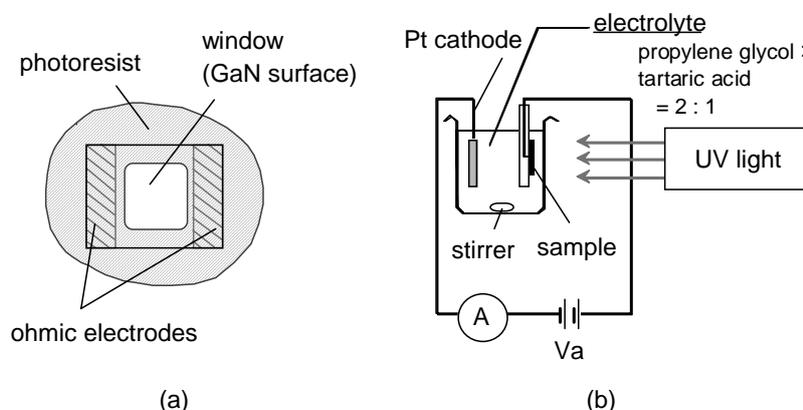


Fig. 1. (a) Schematic of preparation of GaN sample. (b) Experimental setup of photoelectrochemical process.

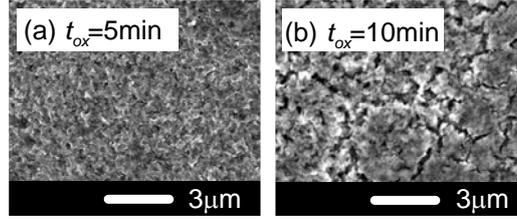


Fig. 2. SEM images of GaN surfaces after (a) 5 and (b) 10 min oxidation with constant voltage supply.

thickness of the GaN layer was 1.8 μm . The residual electron concentration and mobility of GaN were $1 \times 10^{16} \text{cm}^{-3}$ and $200\text{-}300 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, respectively. Figure 1(a) shows a schematic of a sample undergoing the electrochemical process. A multilayer consisting of Ti/Al/Ti/Au with thicknesses of 20/50/20/200 nm was formed on the GaN surface. After the deposition of the multilayer, the samples were annealed at 800°C for 1 min in N_2 to give the electrodes an ohmic property. Then, the sample was fixed on a Teflon holder using silver paste. The ohmic electrodes and edges of the sample were covered with photoresist (SPR6809) so as to make the current flow only through the window opening, as shown in Fig. 1(a). The size of the window was $5 \times 5 \text{mm}^2$.

The electrochemical setup is shown in Fig. 1(b). We prepared a mixed solution of propylene glycol $[(\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{OH})]$ and 3% tartaric acid $[\text{HOOC}-\text{CH}(\text{OH})-\text{CH}(\text{OH})-\text{COOH}]$ solution in the ratio of 2:1.⁶⁾ The pH value of the tartaric acid solution was adjusted to 7.2-7.9 by the addition of ammonium hydroxide (NH_4OH). The propylene glycol plays an important role in improving the electrolyte stability.^{6,7)}

The sample fixed on the Teflon holder was immersed in the solution and connected to an anode of a constant-voltage source or a constant-current source. As a counter electrode, a platinum plate was connected to the source cathode. The sample surface was illuminated by UV light from outside of the beaker to generate electron-hole pairs in GaN, which are essential for electrochemical reactions at the electrolyte/n-GaN interface. We used a xenon lamp (Asahi Spectra LAX-100) as the UV light source. The power density was 130mW/cm^2 . For the process with a constant voltage, the voltage ranged from 5 to 20 V. The voltage supply time t_{ox} was set to 5 or 10 min. When the voltage was applied to the sample, a current of up to $2\text{-}5 \text{mA/cm}^2$ immediately flowed and then decreased gradually. The current decreased to about 70% of the initial current density for the 5-min process, and about 10% for the 10-min process. A current of 0.5mA/cm^2 was applied to the samples for 2 min for the constant-current process. During the oxidation process, the voltage monitored increased monotonously and reached about 0.2 V in 2 min. The oxidized GaN surfaces were characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS).

We characterized the structural and chemical properties of the oxide layers on n-GaN grown in the constant-voltage and the constant-current modes. On the basis of the cyclic voltammetry characteristics with and without the UV illumination, we assigned the bias conditions, i.e., the bias voltage for the constant-voltage mode and the bias current for the constant-current mode. First, we characterized the oxidized GaN surfaces in the constant-voltage mode. Figure 2 shows the SEM images obtained from the samples after oxidation at the bias voltage of 10 V for the voltage supply times t_{ox} of 5 and 10 min. For the sample with $t_{\text{ox}}=5$ min, as shown in Fig. 2(a), we found that the surface was very rough. The longer processing time resulted in a peculiar surface morphology with pronounced roughness and many cracks, as shown in Fig. 2(b). Similar features appeared for the samples processed at the bias voltages of 5 and 20 V.

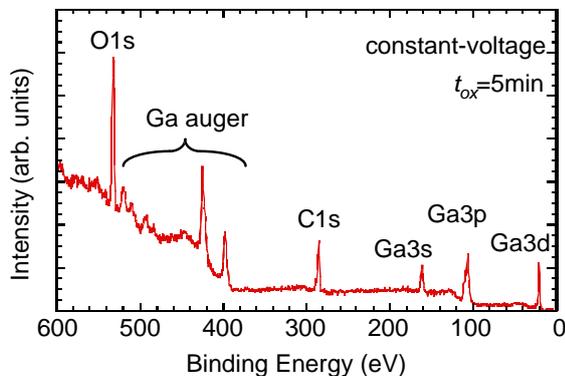


Fig. 3. Survey XPS spectrum obtained from GaN after constant-voltage process for 5 min.

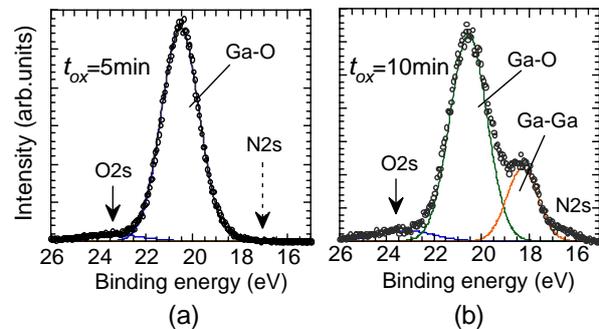
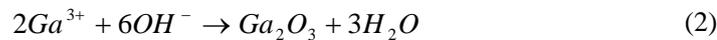
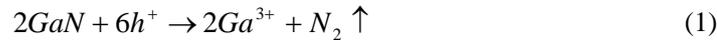


Fig. 4. Ga 3d XPS spectra from GaN surfaces after constant-voltage process for (a) 5 and (b) 10 min.

The chemical properties of the surface obtained from the sample with $t_{ox}=5$ min were characterized by XPS. As shown in Fig. 3, the XPS wide-scan spectrum showed clear peaks from the Ga 3d, Ga 3p, Ga 3s, O 1s, C 1s, and N 1s core-levels. The large peak from O 1s indicated the formation of oxides on the GaN surface. Note that the C 1s peak originates from the surface contaminants, such as C-H chemicals. Its high intensity probably reflects the significant roughness at the oxidized surface.

Figure 4 shows the XPS spectra of the Ga 3d core levels from the samples with $t_{ox}=5$ and 10 min. As shown in Fig. 4(a), the Ga 3d peak obtained from the sample with $t_{ox}=5$ min can be fitted with a single peak at 20.5 eV, which corresponds to the Ga-O bond. In addition, the O 2s peak clearly appeared, whereas the N 2s peak from the underlying Ga-N bond was not detected. We also observed a symmetric and single feature in the O 1s peak at 531.8 eV (not shown here). These results indicated that the Ga oxide mainly in the form of Ga₂O₃ grew on the GaN surface. As shown in Fig. 4(b), however, the Ga 3d spectrum obtained from the sample with $t_{ox}=10$ min showed a peak at around 18.2 eV in addition to that of the Ga-O bond. This peak corresponded to the Ga-Ga component, indicating the generation of metallic Ga in the oxide layer and/or at the oxide/GaN interface.

During the photo-assisted electrochemical process, oxidation generally takes place at the n-GaN surface according to the following reaction equations^{4,8}.



Some kinds of defects, such as dislocations, nanoclusters, and vacancies with dangling bonds, exist even at the initial GaN surface.^{9,10} Around such surface defects, the electrochemical reaction can be enhanced via dangling bonds or by the ionization of point defects. In addition, a localized concentration of electric field near the defects can occur under the constant-voltage condition. This probably leads to nonuniform oxidation in the microscopic scale, resulting in a roughly oxidized surface in the constant-voltage mode. Similar behaviors were predicted for the dry oxidation of GaN in O₂ gas at high temperatures. Wolter *et al.*¹¹ suggested that discrete crystallites of oxide could grow preferentially at dislocations at the early stage of oxide growth on GaN in dry O₂ at 800 and 900°C. As expected from eq. (2), the reaction rate for oxidation is limited by the supply of OH⁻ ions at the GaN surface. For longer oxidation times, the supply of OH⁻ ions to the oxide film/GaN interface may become insufficient. Consequently, one Ga atom combines with a neighboring one before forming a Ga-O bond with an OH⁻ ion. Thus, Ga clusters form at the interface causing a rougher surface and the generation of cracks.

To reduce such an impact on the surface at the initial stage of the electrochemical reaction, we adopted the constant-current process with the bias current of 0.5 mA/cm² for 2 min. Figure 5(a) shows the SEM image of the oxidized GaN surface. A significant improvement in surface morphology was obtained in the constant-current mode. The AFM image of the oxidized surface, as shown in Fig. 5(b), also represents a smooth surface with an rms roughness of 1.6 nm. During the process, we observed a monotonous increase in voltage, indicating an almost constant reaction rate for the oxidation of the GaN surface. For longer oxidation times, it is expected that the oxidation rate will gradually decrease, being limited by the diffusion of OH⁻ in the oxide layer. In this case, the electrochemical system may include reactions for the dissolution of the oxide surface and the oxidation of the GaN surface, probably causing the degradation of the oxide layer.

Figure 6(a) shows the XPS Ga 3d spectrum for the anodically oxidized GaN surface by the constant-current process. For comparison, the XPS spectra of the thermally oxidized and air-exposed GaN surfaces are plotted in Figs. 6(b) and (c), respectively. The spectra can be deconvoluted into three peaks, consisting of the Ga-N bond, the Ga-O bond, and the O 2s peak. For the anodically oxidized surface in the constant-current mode, the Ga-O peak was dominant, whereas the Ga-N peak was very low. Moreover, the O 2s peak, not seen in the air-exposed sample, appeared. These results indicate that a thin oxide layer was successfully grown on the GaN surface during the anodic process with the constant-current supply. The chemical status of the layer was very similar to that of the oxide surface formed by the thermal process in dry O₂ at 900°C for 30 min, as shown in Fig. 6.

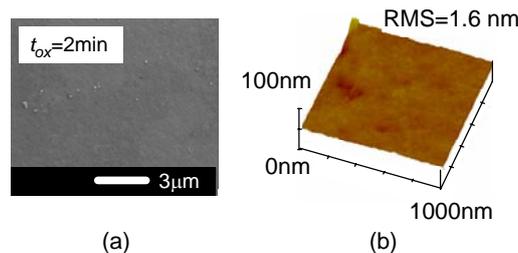


Fig. 5. (a) SEM and (b) AFM images of GaN surfaces after anodic oxidation in constant-current mode.

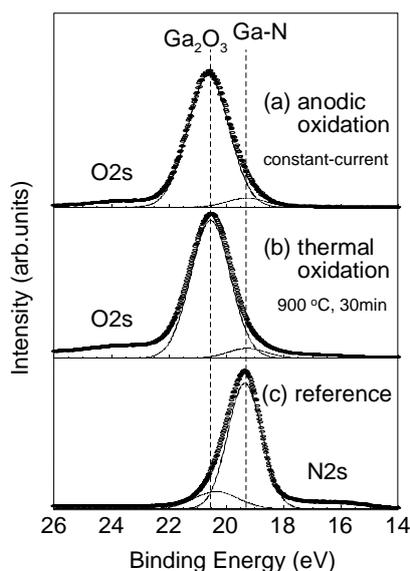


Fig. 6. Ga 3d XPS spectra of GaN surfaces after (a) anodic oxidation in the constant-current mode for 2 min, (b) thermal oxidation in dry O₂ at 900 °C for 30 min, and (c) air exposure.

We determined the ratio of the integrated intensities of Ga 3d to O 1s using the corresponding XPS sensitivity factors and found that the composition of the Ga oxide was very close to Ga₂O₃. In addition, from the angle-resolved analysis of the Ga 3d integrated intensities, the Ga₂O₃ thickness was estimated to be 2-3 nm. In this case, we assumed an electron escape depth of 2 nm from the Ga 3d orbit.¹²⁾ The XPS analysis indicated relatively good uniformity in composition and thickness for the oxide layer with the area size of 5x5 mm². These results indicate that the photoelectrochemical process using a constant-current source can yield a native oxide layer with good uniformity on the GaN surface, although further characterization of the oxide layers and optimization of the process are necessary.

In summary, we examined the feasibility of oxidation on an n-GaN surface by a photoelectrochemical process in the mixed solution containing glycol and water. With the constant-voltage supply, rough oxide layers were formed on the GaN surface, and we found that the metallic Ga emerged when the processing time increased. On the other hand, we succeeded in forming a uniform oxide layer on the GaN surface in a constant-current mode. With a low constant current density of 0.5 mA/cm², we observed the formation of thin Ga₂O₃ layer with rms roughness of 1.6 nm, which is sufficiently smooth for use as an interfacial control layer in GaN metal-insulator-semiconductor structures.

Acknowledgements

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