Self-termination of contactless photo-electrochemical (PEC) etching on aluminum gallium nitride/gallium nitride heterostructures

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Contactless photo-electrochemical (PEC) etching was successfully demonstrated on AlGaN/GaN heterostructures using a K2S2O8 aqueous solution. The etching was conducted by a simple method such as just dipping the sample with Ti-cathode pads into the solution under UVC illumination. The etching morphology of the AlGaN surface was very smooth with an root mean square roughness of 0.24 nm. The etching was self-terminated in the AlGaN layer, whose residual thickness was 5 nm uniformly throughout the etched region. These contactless PEC etching features are promising for the fabrication of recessed-gate AlGaN/GaN high-electron-mobility transistors with high recessed-gate thickness reproducibility.

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Gallium nitride (GaN), which has a wide bandgap (3.4 eV) and a high electron saturation velocity (2.7 × 107 cm s−1),1,2 is a very promising material for power electronic devices. GaN p-n junction diodes3 and trench-gate metal-oxide-semiconductor field-effect-transistors4–5 are typical examples showing superior performance over silicon devices such as high breakdown voltage devices and low specific ON-resistance devices. In addition to the superb material properties of GaN, the high-density two-dimensional electron gases (2DEGs) are yielded at the heterointerface of nitride semiconductors, such as an aluminum gallium nitride (AlGaN)/GaN heterointerface, due to the superposition of spontaneous- and piezoelectric-polarization field. Recently, high-power RF operation with f1 and fmax over 400 GHz has been achieved in AlGaN/GaN high-electron-mobility transistors (HEMTs), which are desirable for the next generation wireless communication system.6,7

AlGaN/GaN HEMTs are basically normally-on devices with a negative threshold voltage (Vth) originating from the high-density 2DEGs. From the viewpoint of fail-safe and low-power consumption design of power switching devices, however, it is necessary to attain normally-off operation. One of the promising approaches to attain such operation is adopting a recessed-gate structure,8–10 which can be fabricated by thinning the AlGaN layer beneath the gate electrode. For thinning the AlGaN layers, the plasma-assisted dry etching process has commonly been used. However, various types of damage and defects induced by the bombardment of reactive ions and radicals leads to severe operational stability problems such as gate leakage, current collapse, and Vth instability on AlGaN/GaN HEMTs.11,12

Photo-electrochemical (PEC) etching probably solves these problems on nitride semiconductors.13–26 PEC etching has some big advantages such as low-damage processing and well-controlled etching in depth compared with dry etching.19–22 Various PEC etching applications have been reported on nitride semiconductors, including the formation of the recessed-gate structure of AlGaN/GaN HEMTs.23–26 Recently, simple contactless PEC etching utilizing a sulfate radical (SO4−) has been reported.27–33 The SO4− radical, which is a strong oxidizing agent, functions as a cathode electrode in the PEC system,34,35 where electrical contact with the samples was not required. The well-controlled etching depth and smooth surface morphology were obtained on n-type GaN by contactless PEC etching utilizing K2S2O8-containing electrolyte under UVC illumination.36,37 However, there are few reports on AlGaN/GaN heterostructures,38,39 and the basic properties of recess etching were not clear.

In this study, we aimed to clarify the basic properties of contactless PEC etching on AlGaN/GaN heterostructures to apply them to recessed-gate AlGaN/GaN HEMTs. Two desirable features for the recessed-gate structures were obtained by our contactless PEC etching process: (1) the etched surface of the AlGaN layer was very smooth (which was comparable to the previous data obtained on the GaN surface) and (2) the etching depth was precisely controlled by the self-termination of the etching in the AlGaN layer.

The schematics of the experimental setup and sample procedure for the contactless PEC etching are shown in Figs. 1(a) and 1(b), respectively. As previously reported in detail,36,37 the etching was conducted by dipping the sample into a 0.025 mol l−1 K2S2O8 aqueous solution under illumination of UVC light. As a light source, we used an SK-BUV-C0860 (Shikoh Tech LLC), which is a deep-UV flexible surface light with a luminous array film with a center wavelength λ of 260 nm and a full width at half maximum of 55 nm. The working distance from the light source to the sample surface was fixed throughout the experiment, where a light power density of 4 mW cm−2 was obtained in the atmosphere. In this study, the optical-path length in a solution was set to 5 mm, and the solutions were not stirred during the etching.

We used a GaN/Al0.22Ga0.78N/GaN heterostructure grown by metal organic vapor phase epitaxy on a semi-insulating SiC substrate with an AlN nucleation layer. The thickness of the AlGaN barrier layer and the GaN cap layer were 24 nm and 5 nm, respectively. The epitaxial wafer was cut into small pieces of about 20 × 20 mm2, which is much smaller than the illumination area of 80 × 60 mm2. In this study, a 330 nm
thick SiO2 film was formed on an AlGaN surface by the spin-on-glass method and patterned by buffered hydrofluoric acid (BHF) with a photoresist mask to define the etching region. Part of the SiO2 mask was additionally etched to produce apertures, in which a 50 nm thick Ti film was deposited as cathode pads. There were no annealing processes for ohmic alloying of Ti contacts. We have recently reported that the appropriate cathode design was very important for the contactless PEC etching of a sample grown on semi-insulating substrates. The etching rate of the n-GaN layer grown on a sapphire substrate increased with the total area ratio of cathode pads and the mask aperture area. This result suggests that the cathodic reaction occurs predominantly on the cathode pad, even though the side of the sample is in contact with the solution. In this study, the total area ratio of cathode pads and the mask aperture area were set to 8.4% and 21%, respectively. After the etching, the SiO2 mask and Ti pads were removed by the BHF and the HCl-H2O2 (1:1) treatment, respectively. The etching depth, $d_{\text{etch}}$, thickness of the remaining AlGaN layer, $d_{\text{AlGaN}}$, and surface morphology were evaluated using a surface profiler, transmission electron microscope (TEM), and atomic force microscope (AFM), respectively.

Figures 2(a) and 2(b) show the typical AFM images obtained on the as-grown sample surface and the AlGaN surface appearing after the contactless PEC etching with $d_{\text{etch}} = 23.2$ nm, respectively. The corresponding RMS roughness values were 0.14 and 0.24 nm, respectively, which were obtained from $1 \times 1 \mu m^2$ area measurement. The smooth etched surface was obtained on the etched AlGaN layer, whose overall roughness was comparable to that of the etched GaN surface. Note that small bumps were observed on the AlGaN surface after the etching, as shown in Fig. 2(b). In a previous work on n-GaN, the bumps that originated from the dislocation, which appeared as dark spots in a cathodoluminescence image, were almost flattened by the TMAH post-treatment. Similarly, the as-etched AlGaN surface with bumps that were 3–15 nm in height were remarkably flattened by BHF and HCl-H2O2 post-treatments, which were conducted to remove the SiO2 mask and Ti pads after the contactless PEC etching.

The $d_{\text{etch}}$ obtained in the AlGaN layer was plotted in Fig. 3 as a function of the etching time of the contactless PEC etching. The filled circles with error bars indicate the average values of $d_{\text{etch}}$, which were measured at 16 points, and their standard deviation values. The solid- and dashed-line indicate the eye-guide of etching behavior and the position of two heterointerfaces in the present epitaxial structure, respectively. After the 30 min etching, a $d_{\text{etch}}$ of 16.2 nm was obtained, where the etching rate was roughly estimated to be about 0.5 nm min$^{-1}$. Such a slow etching rate is desirable for precisely-controlled etching in depth by time. Furthermore, $d_{\text{etch}}$ did not increase over 25 nm, indicating that the etching was stopped before reaching the AlGaN/GaN heterointerface (29 nm), as shown in Fig. 3. One might think that the
degradation of the solution reactivity caused the termination of the AlGaN etching, but this is not the case here. The etching did not progress any further even though the solution was freshly prepared. We have also confirmed that the generation ratio of SO₄⁻ radicals, which was used for the AlGaN etching as described later, kept a constant value over 120 min etching. In other words, the contactless PEC etching definitely self-terminated in the middle of the etching of the AlGaN layer.

TEM observation was conducted to evaluate the exact thickness of the remaining AlGaN layer after the self-termination of the etching. Figures 4(a) and 4(b) show the cross-sectional TEM image of the sample after 60 min-etching and its magnified image on the etched region, respectively. The surface of the etched region was smooth and flat overall. From the magnified image shown in Fig. 4(b), the \( d_{\text{AlGaN}} \) obtained at the etched region was 4.7 nm, indicating that the self-termination of the contactless PEC etching was estimated as \( d_{\text{etch}} = 24.3 \) nm since the total thickness of the GaN cap and AlGaN barrier layers was 29 nm. This value was very consistent with those values obtained by using the data in Fig. 3.

The possible model for the contactless PEC etching was discussed on the basis of the carrier transport between the electrolyte and the AlGaN/GaN heterostructure. The \( \text{S}_2\text{O}_8^{2-} \) ion absorbs the UV light with \( \lambda < 310 \) nm and produces two \( \text{SO}_4^- \) radicals.\(^{40,41}\) The \( \text{SO}_4^- \) radical is known as a strong oxidizing agent that immediately changes itself to the reduced form, sulfate ion (\( \text{SO}_4^{2-} \)), as \( \text{SO}_4^- + e^- \rightarrow \text{SO}_4^{2-} \). Here, the PEC reaction of GaN in the present system is represented as follows.

\[
\text{AlGaN} + \text{photo carriers}(6h^+ + 6e^-) + 6\text{SO}_4^- \rightarrow \text{Al}^{3+} + \text{Ga}^{3+} + 6\text{SO}_4^{2-} + \frac{1}{2} \text{N}_2, \tag{1}
\]

where the description of intermediate products such as Al₂O₃ and Ga₂O₃ are omitted for simplification. As described in Eq. (1), the generation of photo carriers in the AlGaN layer is the trigger for the etching reaction.

Figure 5(a) shows the schematic illustration of our model for self-termination in contactless PEC etching. The photo carriers (holes and electrons) generated in the AlGaN layer are separated by the built-in electric field, as schematically shown in Fig. 5(a). The holes directly move to the electrolyte interface, where they are consumed by the etching of the AlGaN surface. On the other hand, the electrons are collected in the 2DEG channel and move to Ti pads, where the electrons are consumed by the reduction of \( \text{SO}_4^- \) in the electrolyte. Here, it may seem a little strange that the electrons in the 2DEG channel overcome the potential barrier formed at the AlGaN/GaN interface. In fact, the electrical measurements showed no ohmic-connection between the Ti pad and the 2DEG channel. We believe that the motive force of the electrons in 2DEGs comes from two factors: (1) the photovoltage that increase the potential energy of the 2DEG electrons under illumination and (2) the low potential barrier formed at the Ti/GaN or Ti/AlGaN interface. Several groups have reported that the Schottky barrier heights of Ti/GaN and Ti/AlGaN contacts were 0.6–0.8 eV which were much lower than those obtained when other metals were used.\(^{42,43}\) Such a low Schottky barrier comes from the small metal work-function of Ti (4.33 eV).\(^{44}\) On the other hand, the surface potential of the AlGaN layer in the electrolyte (\( \text{pH} \sim 2 \)) is estimated to be 1.25 eV from the previous report on the water (\( \text{pH} \sim 7 \))/AlGaN interface.\(^{45}\) Since, the potential barrier formed at the Ti pad is lower than that formed at the solution/AlGaN interface, the 2DEG electrons move into the solution through the Ti pad by a photovoltaic force.
the etching progresses at the unmasked region, the 2DEG density underneath decreases due to the thinning of the AlGaN layer. When the $d_{\text{AlGaN}}$ reaches a certain value, the 2DEGs at the AlGaN/GaN interface should be completely depleted for the same reason as for a normally-off operation observed in AlGaN/GaN HEMTs.

Figure 5(b) shows the 2DEG density calculated for the AlGaN/GaN heterostructure as a function of $d_{\text{AlGaN}}$. For calculation, the surface potential of the AlGaN layer was set to 1.25 eV as previously mentioned. It was found that the self-termination of the etching occurred, as shown in Fig. 4(b). These results suggest that the self-termination of the etching is originated from the depletion of 2DEGs. The phenomenon of self-terminating etching was first observed during the contact (or wired) PEC etching on AlGaN/GaN heterointerface (29 nm). Such a self-terminating etching was most probably originated from the disconnection of the 2DEG channel, which was depleted by the thinning of the AlGaN layer. These contactless PEC etching features are promising for fabricating recessed-gate AlGaN/GaN HEMTs with a high reproducibility of recessed thickness.

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