Fabrication of GaN nanowires containing \(n^+\)-doped top layer by wet processes using electrodeless photo-assisted electrochemical etching and alkaline solution treatment

Michihito Shimauchi, Kazuki Miwa, Masachika Toguchi, Taketomo Sato, and Junichi Motohisa

Graduate School of Information Science and Technology, and Research Center for Integrated Quantum Electronics, Hokkaido University, North 14, West 9, Sapporo 060-0814, Japan

© 2021 The Japan Society of Applied Physics

We attempted to fabricate GaN nanowires by electrodeless photo-assisted electrochemical (PEC) etching and successive alkaline solution treatment. The sample consisting of \(n^+\)-doped and unintentionally doped GaN grown on a GaN substrate was selectively etched using a Ti mask in a mixed solution of \(\text{K}_2\text{S}_2\text{O}_8\) and KOH under UV light radiation. This specific layer structure required a relatively concentrated KOH solution for etching. The PEC etching resulted in the formation of a tapered cone structure of GaN with its top diameter determined by the mask size. Successive KOH treatment after PEC etching yielded GaN nanowires with diameters of about 220 nm.

© 2021 The Japan Society of Applied Physics

**Gallium nitride (GaN) is studied for its application to various types of devices owing to its excellent properties, i.e. wide band gap, high saturation velocity, high breakdown voltage, high thermal conductivity, and so forth. Many research studies on GaN-based optical devices, such as light-emitting diodes (LEDs) or lasers, and electron devices for power electronics have been reported.**

**Nanowires, which have a one-dimensional structure with a diameter of a few tens or a few hundreds of nanometers, have been attracting much attention because they are used to fabricate devices with unique structures, such as vertical surrounding-gate transistors**

**LEDs for micro-LEDs**

**–**

**addition, the etching of unintentionally doped epitaxial layers (residual donor density \(\sim 10^{16} \text{cm}^{-3}\)) was carried out, whereas the etching of heavily doped layers is crucial for practical device application.**

In this study, we conducted selective electrodeless PEC etching and successive alkaline solution treatment to realize nanowires with submicron diameters. The etching was carried out on a GaN epitaxial layer consisting of \(n^+\)-doped and unintentionally doped layers grown on GaN, where the \(n^+\)-doped layer was intended as the top contact layer of vertical devices. GaN nanowires with an average diameter of 220 nm were successfully fabricated by alkaline solution treatment following PEC etching using a titanium mask of less than 1 \(\mu\)m diameter.

The starting sample is an \(n^+\)-GaN/i-GaN epitaxial layer grown by metal-organic vapor-phase epitaxy on a free-standing GaN substrate. The doping density in the \(n^+\) layer was \(10^{19} \text{cm}^{-3}\), and the i-GaN referred to here is an unintentionally doped layer with a residual donor density of about \(10^{16} \text{cm}^{-3}\). The thicknesses of \(n^+\)-GaN and i-GaN were 100 and 2000 nm, respectively. The Ti masks for etching were formed by electron-beam (EB) lithography, EB evaporation (Ti: 150 nm), and a standard liftoff process. The Ti masks were designed to be hexagonal and were arranged in a triangular lattice with pitch \(a\). The mask size \(d\) was defined as the distance between facing vertices. Details of the setup for electrodeless PEC etching are described in Ref. 38. The intensity of the UVC light on the electrolyte surface was adjusted to 4.0 mW cm\(^{-2}\). The electrolyte was a mixture of equal volume of potassium hydroxide (KOH) and potassium peroxodisulfate (K\(_2\)S\(_2\)O\(_8\)). The concentration of KOH was
changed from 0.01 to 0.03 M, and that of $\text{K}_2\text{S}_2\text{O}_8$ was 0.05 M. After the PEC etching, alkaline solution treatment was conducted. In this study, 5% tetramethylammonium hydroxide (TMAH) and 5% KOH solution were used for the alkaline solution.

Figures 1(a)–1(c) show typical results of electrodeless PEC etching for 60 min under different KOH concentration. The pitch $a$ and mask size $d$ were 4 and 2 μm, respectively. The etch rate was found to be dependent on KOH concentration (and pH), and, for a KOH concentration of 0.01 M [Fig. 1(a)], the etching depth seems to be much smaller than the thickness of n$^+$-GaN. In our previous study, etching in an acid electrolyte (a mixture of phosphoric acid and $\text{K}_2\text{S}_2\text{O}_8$) is successful for the i-GaN layer and we concluded that pH is not relevant.39) We consider that the difference between the previous and present studies is in the n$^+$-doped layer on top of the sample and in the band structure associated with the doping profile as follows. The PEC etching of GaN is considered to proceed with the following reactions:\textsuperscript{42})

\begin{align}
2\text{GaN} + 6\text{OH}^- + 6\text{h}^+ &\rightarrow \text{Ga}_2\text{O}_3, \\
\text{Ga}_2\text{O}_3 + 6\text{OH}^- &\rightarrow 2\text{GaO}_3^{3-} + 3\text{H}_2\text{O}. \quad (2)
\end{align}

Reactions (1) and (2) represent the oxidation of GaN and the dissolution of $\text{Ga}_2\text{O}_3$, respectively, and both reactions indicate the importance of OH$^-$. Holes required in reaction (1) are supplied by the photoinitiation. Note that the number of holes contributing to the reaction depends on the hole lifetime as well as the illumination intensity, and it is expected that the hole lifetime is shorter (i) when the doping is heavier in n-type semiconductors. Therefore, the etching rate of n$^+$-GaN becomes slower than that of i-GaN. Lee et al. also reported a low-etching rate in heavily doped n-GaN if the UV light intensity was high.\textsuperscript{43} In addition, the extraction of electrons from GaN through the cathode is important in preventing the rapid recombination of photogenerated electron–hole pairs. The calculated band structure of the present sample is shown in Fig. 1(d). The calculation shows that electrons are likely to reside beneath the depletion layer over the i-layer. This becomes an obstacle for the extraction of electrons through the bottom substrate. In addition, the pH of the electrolyte changes the position of the energy level of the surface by 58.1 meV pH$^{-1}$ (at 20°C), and a high pH enhances the extraction of excess electrons from the surface via tunneling through Schottky barriers between the electrolyte and n$^+$-GaN. Thus, the large dependence of etching rate on the pH of the electrolyte in the sample with n-type doped layers is expected, as opposed to the i-GaN samples reported thus far.

In the experiment that followed, the concentration of KOH in the electrolyte was set to 0.02 M to obtain a reasonable etching rate. We found that the pH decreases with time and reached the neutralization point at 53.6 min after the start of the illumination. This is owing to the reaction between sulfate radicals ($\text{SO}_4^{2-}$) with water and resultant generation of H$^+$ ions.30,39) To maintain basic electrolyte condition, we replaced electrolyte every 60 min. Thus, the etching rate discussed hereafter should be considered as an average during the processing time of 60 min.

Figure 2(a) shows the relationship between the etching time $t_{\text{PEC}}$ and the etching depth $h$. The etching depth $h$ increased with the etching time $t_{\text{PEC}}$. The etching rate is not constant over time; the initial etching rate was low, and it increased and appeared constant up to $t_{\text{PEC}} = 240$ min. This is due to the difference in the carrier concentration in the etched layer and the resulting difference in the lifetime of holes in the layers, as discussed earlier. The average etching rates deduced from $t_{\text{PEC}} = 120$ to 240 min was 3.74 nm min$^{-1}$ [solid lines in Fig. 2(a)]. One can also see that the etching rate decreases for $t_{\text{PEC}} > 240$ min. Part of the reason would be the reduction in the rate of extraction from the top Ti cathode as the distance from the etched surface to the cathode electrode increased. In addition, the decrease in etching rate seems to be accompanied by the variation in the etching depth, namely, surface roughness. The surface roughness was partly due to the bumps formed during etching, as reported in our previous study,\textsuperscript{38} but it was found that other factors degraded the surface flatness, as discussed later.

Figure 2(b) shows a scanning electron microscopy (SEM) image of an etched surface with Ti masks (black regions). In
with treatment time. As shown in the inset, the sidewall became vertical after the treatment. As can also be seen in Fig. 3(a), a longer treatment time resulted in the nonuniformity of the nanowire diameter. Therefore, to obtain uniform nanowire arrays with a much smaller diameter, it is important to decrease the initial size of GaN before the alkaline solution treatment and to optimize the alkaline solution treatment time. Figure 3(b) shows the results of KOH treatment for 90 min after the PEC etching for 180 min. The parameters of the mask pattern were $d = 500$ nm and $a = 1$ μm. The average diameter of the nanowires in this image was about 223 nm. Finally, to show the possibility of a combination of PEC etching and alkaline solution treatment, an SEM image of the nanowire with the smallest diameter (∼10 nm) obtained in this study is shown in Fig. 3(c).

It was found that unetched bumps [indicated by the black circle in Fig. 2(b)] formed by the electrodeless PEC etching were completely removed by the alkaline solution treatment. Thus, this type of roughness can be eliminated from nanowire samples in the present process. However, the RMS surface roughness improved very little after the alkaline solution treatment. We consider that the roughness is due to the inhomogeneous oxidation of GaN in PEC etching. The inhomogeneity arises and is enhanced by the difference in etching rate between n-GaN and i-GaN at the initial etching stage. To reduce the roughness originating from PEC etching, etching under diffusion-limited conditions is assumed to be useful, so a smooth etched surface is expected to be obtained by using a higher UVC light intensity and a more dilute KOH solution. In fact, the surface roughness is larger for higher concentrations of KOH in the electrolyte, as shown in Figs. 1(a)–1(c). It is necessary to compromise between surface smoothness and rapid etching rate and associated lower processing time.

In conclusion, we successfully fabricated GaN nanowires by electrodeless PEC etching and alkaline solution treatment. Selective electrodeless PEC etching using a Ti mask was performed and the etching rate showed large dependence on the doping concentration in the GaN layer. For a mask size of 500 nm, side etching was very small, so electrodeless PEC etching is useful for submicron processes. The etched surface was very rough, and this roughness should be eliminated by optimizing the PEC etching conditions. GaN nanowires could be obtained by alkaline solution treatment following PEC etching.

Acknowledgments. The authors thank Prof. Katsuhiro Tomioka and Dr. Fumimasa Honkari for fruitful discussions and useful comments. This work was financially supported in part by the Japan Society for the Promotion of Science (JSPS) via Grant-in-Aid for Scientific Research, KAKENHI Grant Nos. JP 17H05323 and JP 19H04528.

ORCID iDs
Taketomo Sato https://orcid.org/0000-0001-5032-6947
Junichi Motohisa https://orcid.org/0000-0001-9529-4299

1) M. S. Wang, S. Nakamura, and S. P. DenBaars, ECS J. Solid State Sci. Technol. 9, 015012 (2020).
2) T. Hamaguchi, M. Tanaka, and H. Nakajima, Jpn. J. Appl. Phys. 58, SC0806 (2019).
3) H. Amano et al., J. Phys. D: Appl. Phys. 51, 163001 (2018).
4) K. Tomioka, M. Yoshimura, and T. Fukui, Nature 488, 189 (2012).
5) F. Yu et al., Nanotechnology 28, 095206 (2017).
6) M. F. Fataihah et al., Sci. Rep. 9, 10301 (2019).
