Gallium nitride (GaN) is a III/V direct bandgap semiconductor that exhibits high-thermal, chemical, and mechanical stability and is relatively harmless to humans and the environment because it does not contain toxic substances such as arsenic (As). Most notably, GaN is a wide-bandgap material with 3.4 eV of energy, which can be varied from 0.65 to 6.0 eV by alloying it with indium nitride (InN) and aluminum nitride (AlN). On the basis of these excellent properties, various functional devices have been designed, for example ultraviolet (UV) laser diodes, chemical sensors, and photo-electrodes for water splitting.

Electrochemically formed porous structures, which have been applied for various materials, are promising nanostructures for the above-mentioned applications. Many researchers have reported the electrochemical formation of GaN-porous structures. However, their formation mechanism has not been fully understood. One of the reasons is that the photo-assisted electrochemical process is commonly used in which the formation process becomes more complicated due to the supply of photo-carriers generated by illumination. We previously argued that it is difficult with front-side illumination (FSI) to control the structural properties of GaN-porous structures. We believe that the optimization of the supply of photo-carriers is one of the key issues for controlling of the structural properties.

In this study, we formed GaN-porous structures using the photo-assisted electrochemical process in the back-side illumination (BSI) mode, for the first time, and compared with it that in FSI mode. From the experimental and theoretical aspects, we discuss the formation mechanism of GaN-porous structures in BSI mode.

The electrochemical setup used in this study is schematically shown in Figure 1. A custom-made cell equipped with a crystal window and Indium Tin Oxide (ITO) plate was used for both the photo-assisted electrochemical process and spectroscopic measurements. The electrochemical cell has three electrodes, i.e., a n-type GaN electrode as a working electrode (W.E.), Pt counter electrode (C.E.), and Ag/AgCl reference electrode (R.E.). We used GaN epilayers grown on freestanding GaN substrates or sapphire substrates as the W.E. The electrolyte consists of 1 mol/L H$_2$SO$_4$ and 1 mol/L H$_3$PO$_4$ (pH = 2.5).

The GaN-porous structures were formed using the photo-assisted electrochemical process both in the FSI and BSI modes using a xenon (Xe) lamp as a UV light source, as shown in Fig. 1. The photo-generated holes, $h^*$, are used at the electrolyte/n-GaN interface for the following anodic reaction.

$$2\text{GaN} + 6h^* \rightarrow 2\text{Ga}^{3+} + N_2 \quad [1]$$

Various electrochemical conditions such as applied voltage $V_a$, UV-intensity $P_{UV}$, and anodization time $t_a$ were precisely controlled using a potentiostat connected to a computer system monitoring the anodic-reaction current density $J_a$. The structural properties of the GaN-porous samples formed under different conditions were compared using a scanning electron microscope (SEM) with a Hitachi SU-8010 system. Spectroscopic properties, such as photo-reflectance, transmittance, and absorbance, were evaluated using an HR4000CG-UV-NIR spectrometer (Ocean Optics) under the voltage applied in the same setup shown in Fig. 1.

Figures 2a–2d show top and cross-sectional SEM images of the GaN-porous samples formed after $t_a = 600$ and 1800 s by comparing between the FSI and BSI modes. The $V_a$ and $P_{UV}$ were adjusted by monitoring the $J_a$ to be about the same between both modes. No anodic current and no porous structure was observed at the same bias condition in the dark. For the FSI mode shown in Figs. 2a and 2b, the pore diameter measured from top images increased with anodization time, whereas the pore depth $d_p$ measured from the cross-section did not increase. On the other hand, $d_p$ increased with anodization time in BSI mode, as shown in Figs. 2c and 2d, where the pore was the almost the same throughout all parts of the porous layer.

Figure 3 shows the relationship between $d_p$ and the charge density $Q$ passing through the working electrode during the photo-assisted electrochemical process. In FSI mode, $d_p$ increased with $Q$ until around 400 mC/cm$^2$ ($t_a = 1200$ sec), but it largely decreased after that. In BSI mode, however, $d_p$ increased almost linearly with $Q$, showing no decrease in $Q$ over 1000 mC/cm$^2$ in this study. These results come from the difference in the supply method of holes used for the anodization reaction. The FSI mode generates holes near the top-surface due to FSI. As $Q$ increased to more than about 400 mC/cm$^2$ ($t_a = 1200$ sec), the pore wall thinned to breaking point and was removed from the top-surface. In BSI mode, the other hand, the holes were...
supplied from the back surface or supplied only at the pore tips due to BSI. Since the anodic reaction occurred only at the pore tips, the pore was etched in the vertical direction, whose depth linearly increased during photo-assisted electrochemical process. To clarify the formation mechanism of GaN-porous structures in BSI mode, we conducted the photo-assisted electrochemical process by changing monochromatic-light illumination using an optical filter. Table I summarizes the anodic-reaction current density, and the results of SEM observation on whether the porous structure was formed. The full width at half maximum of the band-path filter was 10 nm. From a series of experiments, we found that porous structures were formed on the GaN samples under monochromatic light with wavelengths of 370 and 380 nm, whereas neither porous formation nor anodic etching was observed at wavelengths of 350, 390, and 400 nm. It should be noted that the largest current density was observed at a wavelength of 370 nm, corresponding to hv of 3.35 eV, which is smaller than the bandgap of GaN. These results clearly indicate that the light with hv below the bandgap contributes to the formation of GaN-porous structures in BSI mode.

The Franz-Keldysh effect is one possible phenomenon to explain the present results. Franz $^{14}$ and Keldysh $^{15}$ pointed out that the high electric field may cause a red-shift of the absorption edge, leading to the presence of absorption below the bulk bandgap. Cavallini et al. reported that the Franz-Keldysh effect is applicable for GaN nanowires to argue that the photo-absorption properties depended strongly on the wire diameter. $^{16}$ We believe that this effect is similarly applicable to the present electrochemical process, where a high electric field is induced in the depletion region formed at the interface between the electrolyte and n-type GaN. In the depletion region, the Franz-Keldysh absorption coefficient is expressed as a function of both $hν$ and $V_a$, as follows: $^{17,18}$

$$\alpha(hν, V_a) = \alpha_0 \exp\left(-\frac{hν - E_{gap}}{\Delta E(V_a)}\right)^\frac{1}{2},$$

where $E_{gap}$ is the bulk bandgap (= 3.44 eV for GaN) and $\alpha_0$ is the absorption coefficient at $hν = E_{gap}$. The term $\Delta E$ in Eq. 2 is the red-shift energy of the absorption edge and expressed by

$$\Delta E(V_a) = \frac{2}{3} \left(\frac{\Delta h^2(V_a)}{m^*}\right)^\frac{1}{2},$$

where $\Delta$, $m^*$, $q$, and $\hbar$ are the electric field, effective mass, elementary charge, and Dirac’s constant, respectively.

To experimentally elucidate the Franz-Keldysh effect, we conducted spectroscopic measurements on the GaN samples in the electrolyte under $V_a$. Figure 4a shows the increases in photo-absorbance measured as a function of the wavelength of incident light, where the vertical axis shows the difference between the data obtained at $V_a = 3$ V and $V_a = 0$ V. The data clearly show that the red-shift of the absorption edge under $V_a = 3$ V was applied. The highest increase in absorbance was obtained at a wavelength of 370 nm, corresponding to the largest anodic-reaction current density obtained, as shown in Table I. The absorbance $A(hν, V_a)$ is expressed as

$$A(hν, V_a) = 1 - \exp(-\alpha(hν, V_a)W(V_a)),$$

where $W$ is the depletion layer width obtained by solving the Poisson’s equation in the depletion region. The solid line in Fig. 4a is the theoretical curve of the increase in absorbance obtained from Eq. 4 by considering the Franz-Keldysh effect expressed with Eqs. 2 and 3.
holes were generated near the back-surface due to so-called bandedge emission with photon energy above the bulk bandgap during the photo-assisted electrochemical process. In the case of illumination with photon energy above the bulk bandgap, the photons obviously penetrate thorough both the bulk GaN and porous layer as transmitted light. Thus, the illumination with $h\nu > E_{\text{gap}}$ plays the most important role in the formation of GaN-porous structures in BSI mode. This model explains very consistently the experimental results obtained in BSI mode in which the pores were etched only at the pore tips in the vertical direction.

In summary, we succeeded in forming GaN-porous structures by using photo-assisted electrochemical etching. The morphology of GaN-porous structures depends on the direction of light illumination. We experimentally demonstrated that the pore depth linearly increased with $Q$ in the BSI mode because the pores were etched only at the pore tips. Our proposed model by considering the Franz-Keldysh effect makes it possible to explain the experimental results consistently. From both the experimental results and theoretical analysis, the BSI mode is powerful for controlling the structural properties of GaN-porous structures such as pore diameter and depth.

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Acknowledgments

References


Figure 4. (a) Photo-absorbance measured as function of wavelength of incident light and (b) formation model of GaN-porous structure using photo-assisted electrochemical process.