

# Formation of Self-aligned Pore Arrays on n-GaN Substrates by Photo-assisted Electrochemical Etching Process

Yusuke Kumazaki, Taketomo Sato and Zenji Yatabe

Research Center for Integrated Quantum Electronics, Hokkaido Univ.  
North 13, West- 8, Kita-ku, Sapporo, 060-8628, Japan  
Phone: +81-11-706-7172, E-mail: kumazaki@rciqe.hokudai.ac.jp

## Abstract

On the basis of the spectroscopic measurements, we developed the photo-assisted electrochemical etching process for the formation of self-aligned pore arrays on n-GaN substrates. The illumination with photon energy below the bulk bandgap plays an important role in the formation of straight and size-controlled pores.

## 1. Introduction

High-density array of semiconductor nanostructures have been widely investigated as building-blocks of energy conversion devices such as solar cells and photo-electrodes. Among various semiconductor materials, GaN is getting a lot more attention lately because of their chemical stability and their potential to achieve direct photoelectrolysis by solar power. Electrochemically formed porous structures are promising nanostructures for the above-mentioned applications [1-3], and the control of the structural properties such as a pore diameter and depth is urgently needed. In this study, we aimed to develop the photo-assisted electrochemical etching process for the formation of self-aligned pore arrays on n-GaN substrates on the basis of data obtained by the spectro-electrochemical measurements.

## 2. Experimental

n-type GaN substrate ( $N_D = 1.1 \times 10^{18} \text{ cm}^{-3}$ ) with thickness of 400  $\mu\text{m}$  thick were used in this study. The spectro-electrochemical measurements and the electrochemical etching process were performed using a custom-made cell with three electrodes, as schematically shown in Fig. 1. Transmittance of the GaN substrates was measured in the back-side illumination (BSI) mode by controlling the electrochemical potential. For the formation of porous structures, the photo-assisted electrochemical etching was carried out under UV light in the front-side irradiation (FSI) mode.

## 3. Results and Discussion

### Spectro-electrochemical Properties of n-GaN substrates

Transmittance spectra obtained by applying 0 and 10 V are shown in Fig. 2. The transmittance,  $T$ , was not observed under illumination with wavelength lower than 370 nm. On the other hand,  $T$  obtained with wavelength above 375 nm showed strong dependence on applied voltage, and  $T$  decreased as applied voltage increased. The inset of Fig. 2 shows a plot of the difference between the  $T$  values obtained at 0 and 10 V, indicating that the absorption in-

creased under the higher voltage applied.

The present data are very consistent with the prediction of the Franz-Keldysh effect that the photoabsorption was enhanced by the high-electric field under illumination with  $h\nu$  below the bandgap [4]. The red-shift energy of the absorption edge,  $\Delta E_g$ , is expressed by

$$\Delta E_g = \frac{2}{3} \frac{(e\hbar\xi)^{\frac{3}{2}}}{(m^*)^{\frac{1}{3}}}, \quad (1)$$

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

The effective bandgap,  $E_g - \Delta E_g$ , calculated using Eq. (1) is plotted in Fig. 3(a) as a function of the applied voltage. The presence or absence of the electrochemical reactions are also shown as true or false in Fig. 3(a) for the sample anodized at 3 V by changing the wavelength of the UV light in the BSI mode. From a series of experiments,

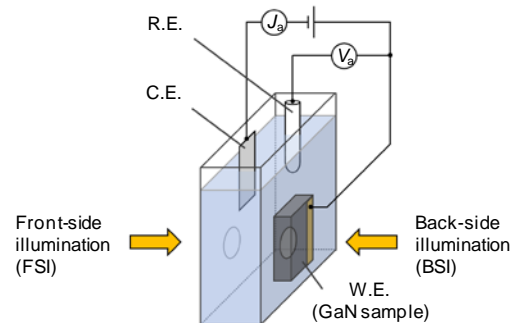


Fig. 1 Schematic illustration of the electrochemical setup used for both spectroscopic measurements and formation of porous structures.

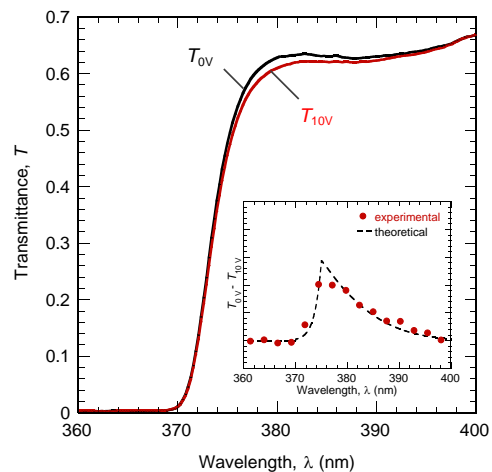


Fig. 2 Transmittance spectra of GaN-planar electrode measured in BSI mode. Inset shows the difference between transmittances obtained at 0 V and 10 V.

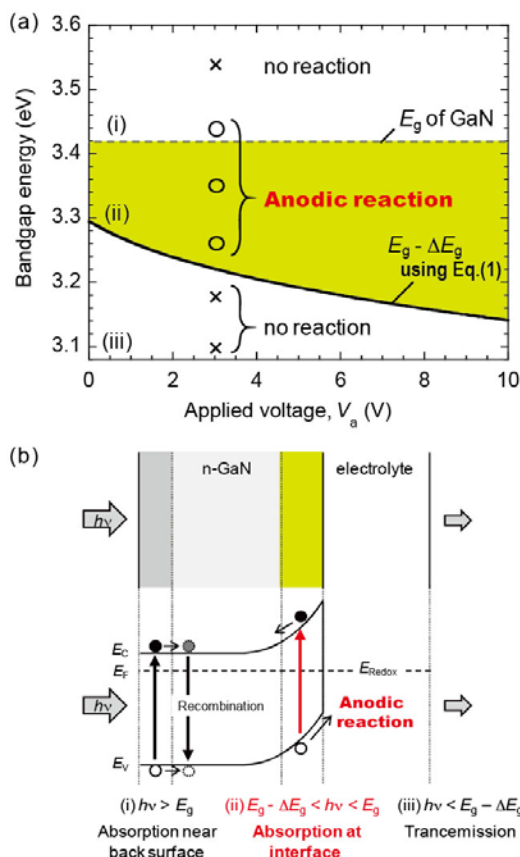


Fig. 3 (a) The bandgap energy calculated with the Franz-Keldysh effect as a function of applied voltage and (b) model for the photo-absorption and the electrochemical reaction at GaN/electrolyte interface.

we found that the electrochemical reactions were occurred on the GaN samples under the light with photon energy,  $h\nu$ , of 3.26, 3.35, and 3.44 eV, whereas neither porous formation nor anodic etching was observed at  $h\nu$  of 3.54, 3.18, and 3.1 eV. These results clearly indicate that the light with  $h\nu$  below the bulk bandgap contributes to the electrochemical reactions at the GaN/electrolyte interface.

**Figure 3 (b)** shows our model for the photo-absorption and the electrochemical reaction. In the case of illumination with photon energy for  $E_g - \Delta E < h\nu < E_g$ , the photons coming from the back-surface penetrated through the bulk GaN but were absorbed by Franz-Keldysh effect near the GaN/electrolyte interface in which the high-electric field was induced (ii). In such a situation, the photo-generated holes contribute to the anodization of GaN.

#### Formation of GaN Porous Structures

On the basis of the spectroscopic measurements, we developed the photo-assisted electrochemical etching process for the formation of self-aligned pore arrays on n-GaN substrates. **Figures 4(a)** and **(b)** show the cross-sectional SEM images of the porous sample formed in the FSI mode using a monochromatic light with  $h\nu$  of 3.54 and 3.26 eV, respectively. Under the illumination with  $h\nu > E_g$ , as shown in **Fig. 4(a)**, the surface roughness increased by the photoelectrochemical etching about 200 nm in depth near

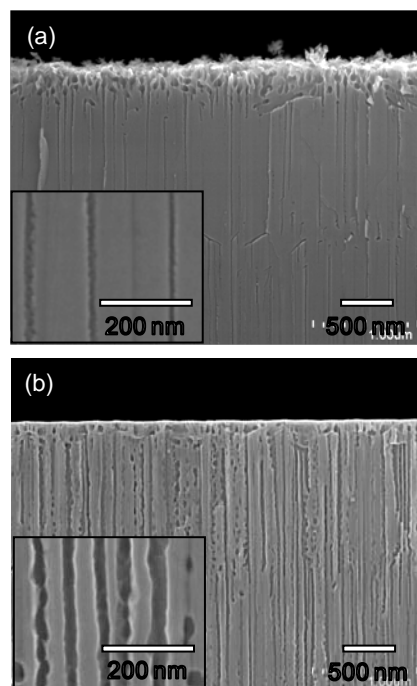


Fig. 4 SEM images of GaN-porous samples formed in FSI mode with  $V_a = 10$  V for 3600 s: (a) under the light with  $h\nu$  of 3.54 eV and (b) with  $h\nu$  of 3.26 eV.

the GaN surface [2]. On the other hand, the relatively flat surface was obtained under the illumination with  $h\nu$  of 3.26 eV, where the pores diameter was larger than that obtained with  $h\nu$  of 3.54 eV, as shown in **Fig. 4(b)**. The light with  $h\nu < E_g$  was not absorbed at the GaN surface but it was absorbed at the pore tips during the electrochemical etching process, resulting in the larger pore diameter without surface roughing. Thus, the illumination of light with  $h\nu$  between  $E_g - \Delta E$  and  $E_g$  plays the most important role in controlling the structural properties of GaN-porous structures.

#### 4. Conclusions

The photo-absorption was observed even under illumination with  $h\nu < E_g$  at the GaN/electrolyte interface. The phenomena can be explained as the red-shift of the absorption edge due to the high-electric field. The photo-assisted electrochemical etching process utilizing the light with  $h\nu < E_g$  has a great potential to control the structural properties of the GaN porous structures.

#### Acknowledgements

This work was supported in part by a Grant-in-Aid for JSPS Fellows – 14J01371, Grant-in-Aid for Scientific Research (B) – 25289079 and a Grant-in-Aid for Challenging Exploratory Research – 15K13937 from Japan Society for the Promotion of Science (JSPS).

#### References

- [1] R. Jinbo et al., *Thin Solid Films* **520** (2012) 5710.
- [2] Y. Kumazaki et al., *J. Electrochem. Soc.* **161** (2014) H705.
- [3] A. Watanabe et al., *ECS Electrochem. Lett.*, **4** (2015) H11.
- [4] A. Cavallini et al., *Nano Lett.* **7** (2007) 2166.