Flat-Band Potentials of Ga-face and N-face in Free-Standing n-GaN Electrode and Their Effects on Water Electrolysis

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The flat-band potentials of (0001) face (Ga-face) and (000\bar{1}) face (N-face) of free-standing n-type GaN with a carrier concentration of 1×10^{18} \text{cm}^{-3} are measured by the bias dependence of photoluminescence intensity in electrolyte solution. The flat-band potentials of Ga-face and N-face are \(-1.5\pm0.1\text{ V}\) and \(-1.2\pm0.1\text{ V}\) in 0.1 molL\(^{-1}\) Na\(_2\)SO\(_4\) solution (pH7) on the basis of Ag/AgCl reference electrode, indicating the conduction band edge of N-face is about 0.3 eV lower than that of Ga-face. This result is consistent with the observation that the H\(_2\) gas generation occurs vigorously on N-face compared with Ga-face when the free-standing n-GaN electrode is at a fixed bias of \(-1.8\text{ V}\) vs. Ag/AgCl. [DOI: 10.1380/ejssnt.2009.847]

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I. INTRODUCTION

The photocatalyst, the material which induces redox reactions by photoexcited carriers, attracts much attention as a new type functional material recently. The hydrogen generation by direct water-splitting is one of the attractive applications of photocatalysts. Fujishima and Honda achieved the hydrogen generation on titanium dioxide (TiO\(_2\)) under the ultraviolet (UV) light irradiation with negative bias for the first time, well-known as the Honda-Fujishima effect [1]. From the viewpoint of generating hydrogen under sunlight, the shift of sensitivity to visible right region in photocatalyst is strongly desired as the development of photocatalyst sensitive to visible light. Sayama et al. achieved water splitting under visible light by using Pt–SrTiO\(_3\) and Pt–WO\(_3\) particles [2]. Maeda et al. reported the hydrogen generation owing to visible-light water-splitting by powder GaN:ZnO oxynitrides [3].

Recently, gallium nitride (GaN) semiconductors, materials for blue light-emitting diode [4], have become much interested also as a photocatalytic material. The applications of GaN and its related materials to working electrode [5, 6], counter electrode [7, 8], and oxynitride powder [3] have been reported. Especially the use of GaN as the working electrode is advantageous in hydrogen generation. In this case, water-splitting occurs by carrier injection from the conduction band of GaN to electrolyte solution. The backset of electron from H\(_2\) or H\(^+\) to electron is suppressed to realize a high efficiency of electron injection from GaN to electrolyte, because GaN working electrodes have higher conduction band-edge energy than the level of hydrogen generation potential [9]. The spontaneous hydrogen generation from UV irradiated p-GaN was reported by Kobayashi et al. [5]. Furthermore, Tokue et al. reported the water-splitting by the 405 nm visible light excitation of p-type InGaN passivated by nanocrystalline TiO\(_2\) [6].

In the hydrogen generation on GaN, the difference in chemical properties due to the surface orientation, as observed at wet etching process [10], is a key parameter to be studied. Because GaN and its related semiconductors are polar materials owing to the spontaneous and piezoelectric polarizations, it is expected that the polarity affects the surface conduction band-edge energy as well as the efficiency of electron injection. Especially, the (0001) face (Ga-rich surface: Ga-face) and (000\bar{1}) face (N-rich surface: N-face) of GaN have considerably different surface property owing to their configuration anisotropy of Ga and N atoms along c-axis, which remains positive charge for Ga-face and negative charge for N-face. And it is expected that the band-edge energy of N-face is lower than that of Ga-face because of the internal electric field, although the ionized surface state and ionized donors behave as screening dipoles and attenuate the potential difference [11, 12]. In this paper, the flat-band potential of Ga-face and N-face of free-standing n-type GaN sur-

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FIG. 1: Schematic image of the system for flat-band potential measurement and free-standing GaN electrode.
face in the electrolyte solution under UV light irradiation was measured by the dependence of photoluminescence intensity on applied external voltage to study the effect of surface polarity on flat-band potential. The use of free-standing GaN enables us to compare the flat-band potential for Ga-face and N-face in the same conditions for carrier concentration and the crystalline quality. Moreover, the direct observation of hydrogen gas generation and the measurement of the current-potential characteristics were done on each face. The effect of surface polarity on the water electrolysis system was also discussed.

II. EXPERIMENTS

Schematic images of the free-standing GaN working electrode and the system for measuring flat-band potential are shown in Fig. 1. The free-standing Si-doped n-GaN substrate having (0001) face and (0001) face terraces (FURUKAWA Co., LTD) grown by hydride vapor phase epitaxy method was used for electrodes. The carrier concentration of the substrate was $1 \times 10^{18}$ cm$^{-3}$, the thickness was 322 µm and there were no significant differences about the roughness and the sheet resistance between Ga-face and N-face. The working electrode was fabricated by depositing Al/Au ohmic contact on N-face of substrate and covered by epoxy to avoid the exposure Al/Au contact to the electrolyte. The three-electrode system mediated by potentiostat (HAB-151, Hokuto Denko) with platinum counter electrode and Ag/AgCl reference electrode was used for flat-band potential measurement and observing hydrogen generation. 0.1M Na$_2$SO$_4$ aqueous solution (pH7) was used for electrolyte. The flat-band potential of each surface was determined by measuring the photoluminescence intensity against applied electropotential by using that system according to the study by Morita et al. [13]. The 325 nm light of He-Cd laser (2mmφ, Intensity: 387 mWcm$^{-2}$) was used for excitation. The hydrogen generation on Ga/N-face at $-1.80$ V (vs. Ag/AgCl) was observed with an optical microscope by using system shown in Fig. 1 without excitation light. The other side was masked by Teflon tape during observation. Cyclic-voltammetry was also measured with the same system. The sweep rate was 200 mVs$^{-1}$ and the sweep span was from $-1.8$ V to 1.5 V.

III. RESULTS AND DISCUSSION

Figures 2(a) and 2(b) shows the dependence of PL spectra on Ga-face and N-face between the intensity-saturated
FIG. 4: Direct observation of hydrogen gas generation on (a) Ga-face / (b) N-face of free-standing GaN electrode in 0.1M \( \text{Na}_2\text{SO}_4 \) (pH7). \(-1.8\) V vs. Ag/AgCl was applied. The dependence of photoluminescence intensity on electropotential vs. Ag/AgCl reference electrode in 0.1M \( \text{Na}_2\text{SO}_4 \) is shown in Figs. 3(a) and 3(b). The intensity was normalized by that at 0.0 V vs. Ag/AgCl. Photoluminescence intensity increases by increasing applied negative bias because the surface depletion layer decreases, and it saturates at a flat-band potential [13, 14]. Hence the flat-band potential was determined from the intersection of increasing line and saturated line of Figs. 3 which means the point at the photoluminescence intensity saturated. The flat-band potential of Ga-face and N-face were estimated \(-1.50\) V and \(-1.22\) V, respectively. Although the absolute potential was fluctuated \(\pm 0.1\) V, the flat-band potential of N-face and was always 0.2-0.3 V lower than that of Ga-face. No significant difference was observed whether determined from bandedge intensity or yellow-luminescence intensity.

Figures 4(a) and 4(b) show the hydrogen generation on Ga-face and N-face of free-standing GaN in 0.1M \( \text{Na}_2\text{SO}_4 \) solution at \(-1.8\) V bias vs. Ag/AgCl without photexcitation. On the Ga-face, the hydrogen bubbles were found only at the edge of the surface. In contrast, many bubbles on the terrace of the substrate were also observed at the N-face. Moreover the maximum cathodic current during hydrogen generation on N-face was around 360 \( \mu \)A, much larger than that of Ga-face, around 210 \( \mu \)A. Figure 5 shows the cyclicvoltammogram of Ga-face and N-face using the system shown in Fig. 1 without excitation. The results of hydrogen bubble formation in Figs. 4(a) and 4(b) and cyclicvoltammograms in Fig. 5 are consistent each other. The cathodic current of the N-face was around four times as large as that of Ga-face. Because there are no significant differences between each face in surface roughness and in sheet resistance, it can be said from these results that the more hydrogen generation occurs on N-face than Ga-face owing to the influence of surface polarity.

The behavior of each surface on hydrogen generation can be explained by the bandedge potential of each face. In the electrolyte solution, upward band-bending to solution on \(n\)-GaN surface and it works as the energy barrier for electron injection [5]. The flat-band potential determines with the energy barrier height for electron injection, i.e., the degree of the band-bending in the electrolyte solution, that is why the result shown in Figs. 3(a) and 3(b) indicates that the bandedge potential of the N-face surface is \(0.2-0.3\) eV lowers than that of Ga-face. This result is consistent with ref. [12], which says the band-edge energy of N-face is lower than that of Ga-face because the accumulation of two-dimensional electron gas occurs due to the positive polarization of Ga-face [12]. Unlike the inside of GaN crystal, where the electrical field weakens by the screening dipole, the potential difference remains on the Ga-face and N-face of the electrode. The upward bending becomes as an energy barrier for the electron injection from conduction band and the height of the barrier depends on the band-edge potential. Therefore it is concluded that the N-face of free-standing GaN is suitable for electron injection than the Ga-face due to the lower band-edge potential.
edge potential. It suggests that the surface orientation of the GaN electrode influences the carrier injection process in water-splitting because of the difference of band-edge potential. This result can also apply to the hydrogen generation on p-GaN by photo-excitation because the band-edge potential is independent of the carrier concentration and dopant.

IV. CONCLUSIONS

The flat-band potential on (0001) face (Ga-face) and (0001) face (N-face) of n-GaN was investigated by measuring the dependence of photoluminescence intensity on applied external voltage. The flat-band potential of N-face was 0.2-0.3 V lower than that of Ga-face. Furthermore, from the direct observation of gas generation, more hydrogen bubbles and cathodic current were found on N-face. It was considered that the lower flat-band potential of N-face, due to the surface polarization, is effective than Ga-face for electron injection because of the lower energy barrier due to lower bandedge potential.

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