Photoelectrochemical Water Splitting using GaN Nanowires with Reverse-Mesa Structures as Photoanode Material

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ABSTRACT

We report improved photoelectrochemical water splitting (PEC-WS) using GaN nanowires (NWs) with reverse-mesa structures (RMNWs) formed on Si(111) as a photoanode material. The GaN-RMNW photoanode exhibited a current density of 2.62 mA/cm\textsuperscript{2} and an applied photo-to-current efficiency of 1.65\% at 0.6 V versus a reversible hydrogen electrode (RHE). These values are considerably higher than those (1.16 mA/cm\textsuperscript{2} and 1.24\%) of the photoanode based on GaN NWs with uniform hexagonal-pillar structures. The improved PEC-WS using the GaN-RMNW photoanode is attributed to the increase in the number of carriers participating in the PEC-WS reaction. The increase in the effective carriers is primarily due to the high crystallinity of the GaN RMNWs and the increase in the absorption rate of the incident light by the reverse-mesa structures. In addition, the energy-band structure between the GaN RMNWs and Si(111) promotes the separation of photogenerated carriers. Consequently, it reduces carrier recombination inside the photoanode, thereby enabling a high-performance PEC-WS.

Keywords: Photoelectrochemical water splitting, GaN nanowire, Reverse-mesa structure, High crystallinity, Photoanode

1. Introduction

Photoelectrochemical water splitting (PEC-WS) is a promising method for providing clean and sustainable hydrogen energy [1–3]. Recently, metal oxides (MOs) with large energy band gaps have been actively used as photoanode materials owing to their nontoxicity and cost-effectiveness [4,5]. For example, Seabold et al. [6] reported a Cu\textsubscript{3}V\textsubscript{2}O\textsubscript{8} photoanode with a current density of 0.3 mA/cm\textsuperscript{2} at 1.2 V versus a reversible hydrogen electrode (RHE). Peng et al. [7] reported a CuWO\textsubscript{4} nanoflake photoanode with a current density of 0.36 mA/cm\textsuperscript{2} at 0.6 V versus RHE. However, Ebad et al. [8,9] demonstrated that new materials should be developed to replace MOs that have poor visible-light absorption. The PEC-WS performance of photoanodes fabricated using MOs may be limited, owing to their wide bandgap. Therefore, more effective photoanode materials that are capable of providing high performance, including high current density, should be developed for practical applications.

For a PEC-WS system, a semiconductor-based photoelectrode is considered a promising approach because it absorbs solar light and promotes redox reactions [10,11]. Currently, photoanodes based on III-nitride material systems are receiving considerable attention, owing to their wide and tunable energy bandgap, high carrier mobility, and chemical stability [12–14]. Most importantly, the energy band structure of GaN is suitable for water redox reactions [15]. GaN nanowires (NWs) are a promising photoanode material for high-performance PEC-WS, owing to their large surface-to-volume ratio, fast mobility, and spatial separation of photogenerated carriers [16–18]. However, to date, the PEC-WS performance of GaN NWs is insufficient for practical applications. For example, Bae et al. demonstrated a graphene/GaN-NW photoanode with a current density of ~0.24 mA/cm\textsuperscript{2} at 0.6 V versus RHE [19]. Kim et al. reported a GaN-nanocone photoanode with a current density of ~0.3 mA/cm\textsuperscript{2} at 0.6 V versus RHE [20]. The low current density of photoanodes fabricated using GaN NWs is primarily related to the poor crystal quality of the NWs. GaN NWs are typically formed on a Si(111) substrate, which results in the generation of unwanted defects at the interface due to large differences between material parameters of GaN and Si(111), which propagate into the NWs [21,22]. Therefore, numerous trap levels are generated in the energy band gap of GaN NWs, and they work as trap sites for carriers. Furthermore, the light-absorption rate of GaN NWs formed on Si(111) is low owing to the significant loss of light reflected on the surface of Si(111), which limits the generation of carriers that contribute to the PEC-WS. Based on these considerations, a new approach is required to form high-crystalline GaN NWs and increase the degree of light absorption for the practical application of PEC-WS.

In this study, we propose an improved PEC-WS using high-crystalline GaN NWs with reverse-mesa structures (RMNWs) as the photoanode material by increasing the number of photogenerated car-
The GaN NWs used as photoanodes were grown on Si(111) using plasma-assisted molecular-beam epitaxy. As a first step of growing the NWs, the oxide layer naturally formed on the Si(111) substrate was eliminated by annealing in a chamber at a temperature of 900°C. Subsequently, a SiNₓ layer was formed by supplying an N flux on the Si(111) substrate at a temperature of 800°C. Thereafter, only Ga flux was supplied to form nucleation seeds [14,25–28]. Finally, the GaN NWs were grown by simultaneously supplying Ga and N plasma fluxes. During the growth process, the V/III ratios were fixed at 213 (Ref-NW), 258 (RMNW1), 322 (RMNW2), and 471 (RMNW3) for 4 h to obtain reverse-mesa structures of the GaN NWs. The growth conditions for GaN NWs have been described in detail in our previous study [25].

Structural characterization of the GaN NWs was conducted using FE-SEM (SU-70, Hitachi) and DCXRD (Max-2500, Rigaku). To investigate the optical properties of the GaN NWs, PL spectroscopy using a diode-pumped solid-state laser with a wavelength of 266 nm and a UV-visible spectrophotometer (UV-2550, Shimadzu) with a fixed slit size of 5 nm were performed. For the absorbance measurements of the GaN NW samples, the baseline was first set using two Si substrates. Then, one of the Si substrates was replaced with the GaN-NW sample. The relative number of carriers that participated in the PEC-WS reactions was manipulated from a hexagonal pillar to a reverse mesa by varying the V/III ratio, where one of the Si substrates was replaced with the GaN-NW sample. The relative number of carriers that participated in the PEC-WS reaction was measured using an incident photon-to-electron conversion efficiency (IPCE) system (K3100, McScience). All PEC-WS measurements were conducted using a potentiostat (Reference-3000, Gamry Instruments Inc.) in a three-electrode configuration composed of a Pt counter electrode, Ag/AgCl reference electrode, and GaN-NW working electrode as the photoanode. A 0.5-M H₂SO₄ solution with a pH value of 0.3 was used as the electrolyte. According to the Nernst equation, the measured voltage was converted into a potential versus RHE [29]. A xenon lamp (MAX-303, McScience) with a power density of 400 mW/cm² was employed as the light source. The photoelectrochemical properties of the GaN-NW photoanodes were recorded by sweeping the voltage from 0 to 1.2 V versus RHE.

3. Results and discussion

The cross-sectional FE-SEM images of the (a) Ref-NW, (b) RMNW1, (c) RMNW2, and (d) RMNW3 samples are shown in Fig. 1. The insets show the plan-view FE-SEM images. The average heights (diameters) of the Ref-NW, RMNW1, RMNW2, and RMNW3 samples were measured to be 332.8±15.9 (66.8±9.6), 304.6±17.8 (71.3±5.7), 177.5±40.7 (74.8±16.1), and 98.3±47.3 nm (57.4±11.6 nm), respectively; these measurements were summarized in Fig. 1(e). Because the width of the NWs varies with the vertical position, the average diameters of the GaN-NW samples were measured at half the maximum height. The NWs were approximated as cylindrical, and their volumes were calculated using the diameters and heights obtained above. The volumes of the single NWs for the Ref-NW, RMNW1, RMNW2, and RMNW3 samples were 1.166×10⁶, 1.216×10⁶, 0.780×10⁶, and 0.254×10⁶ nm³, respectively. The difference in the NW volume between Ref-NW and the RMNW samples was less than 4% and was negligible considering the calculation error in the structural dimensions. The spatial densities of the NWs for the Ref-NW, RMNW1, RMNW2, and RMNW3 samples were measured to be 4.2×10⁹, 5.0×10⁹, 5.4×10⁹, and 6.2×10⁹/cm², respectively. An increase in the spatial density of the GaN NWs was clearly observed in the plan-view FE-SEM images as the V/III ratio increased. Moreover, the shape of the GaN NWs changed from hexagonal pillars to reverse mesas as the V/III ratio increased. These results can be explained by the N-blocking effect [25]. Under N-rich conditions, the number of Ga atoms migrating towards the upper region of the GaN NWs is restricted. Thus, the Ga atoms that cannot migrate toward the upper region of the GaN NWs form nucleation seeds on the Si(111).

Figure 2(a) shows the DCXRD rocking curves of the Ref-NW, RMNW1, RMNW2, and RMNW3 samples. The two strong peaks observed at 28.32 and 34.5° in the DCXRD curves correspond to Si(111) and GaN(0002), respectively [30]. An asymmetric property was observed in the peak corresponding to Si(111), which is related to the lattice mismatch between SiNₓ and Si(111). For the peak corresponding to GaN(0002), shown in the expanded plot in the inset, slight shifts in the peak position were observed as the average height of the GaN NWs increased. This is owing to the reduction in tensile strain due to the lattice mismatch between GaN and Si(111) [31]. In other words, an increase in the height of the GaN NWs enables a reduction in the tensile strain generated at the interface between GaN and Si(111). The peak intensities of GaN(0002) for the Ref-NW and RMNW1 samples were almost equal, primarily owing to their similar volumes. For the RMNW2 and RMNW3 samples, the peak intensity of GaN(0002) was significantly lower than that of the Ref-NW and RMNW1 samples, which is related to the reduced volume of the RMNWs and the effect of defects generated at the interface between GaN and Si(111). The full widths at half maximum (FWHMs) of the GaN(0002) peak were measured as 0.15, 0.16, 0.17, and 0.19° for the Ref-NW, RMNW1, RMNW2, and RMNW3 samples, respectively. All FWHMs of the GaN NWs in this study are considerably narrower than those (~1.5°) of previous reports [32,33], which indicates that GaN...
NWs formed on Si(111) with high crystal quality. Figure 2(b) shows the PL spectra of GaN NWs measured at room temperature (RT). The free-exciton peaks of the Ref-NW, RMNW1, RMNW2, and RMNW3 samples were clearly observed at 368 nm. In most previous studies, the PL peak related to the GaN NWs was observed at a low temperature (10 K) [34,35]. This result can be explained by the significant influence of defects that are typically formed in Si-based GaN NWs, which work as trap sites for photogenerated carriers and consequently reduce the radiative recombination rate [14,36]. However, the GaN NWs in this study exhibited strong free-exciton peaks at RT. The intensities of the PL peaks for the Ref-NW and RMNW1 samples were higher than those of the other samples, which is also related to their higher volume. The PL spectra were consistent with the DCXRD rocking curves.

Figure 3(a) shows a schematic of the PEC-WS cell with a three-electrode configuration in 0.5-M H$_2$SO$_4$ electrolyte. Figures 3(b) and 3(c) show the current density of the GaN-NW photoanodes as a function of voltage versus RHE under dark and illuminated conditions, respectively. Under dark conditions, the Ref-NW, RMNW1, RMNW2, and RMNW3 photoanodes exhibited current densities of 100, 400, 1, and 5 mA/cm$^2$ at 0.6 V versus RHE, respectively. For the illuminated condition, the Ref-NW, RMNW1, RMNW2, and RMNW3 photoanodes exhibited current densities of 1.16, 2.62, 0.15, and 0.37 mA/cm$^2$ at 0.6 V versus RHE, respectively. From this result, we can estimate that the photoanodes in this study exhibit a better performance than those of previous studies [19,37]. For example, Bae et al. and Li et al. reported GaN-NW photoanodes with current densities of approximately 0.15 and 0.13 mA/cm$^2$ at 0.6 V versus RHE, respectively [19,37]. In addition, the current densities of the GaN-NW photoanodes were also higher than the theoretical value for GaN, which is largely related to the use of NW structures with a large surface-to-volume ratio, fast mobility, and high spatial separation of photogenerated carriers [16–18]. Among the photoanodes in this study, the RMNW1 photoanode exhibited the highest current density. The higher current density of the RMNW1 sample compared with the Ref-NW photoanode can be explained by the increase in the light-absorption rate, which enhances light confinement inside the photoanode using the reverse-mesa NW structures, which will be discussed in Fig. 4. For the RMNW2 and RMNW3 photoanodes, the current density was significantly reduced compared to the Ref-NW and RMNW1 photoanodes, which was due to the increase in the degree of influence of the defects generated at the interface between GaN and Si(111) on the carriers participating in the PEC-WS reaction. Typically, photoelectrode materials with a low crystal quality are more corroded, which generates a higher corrosion current. However, the RMNW2 and RMNW3 photoanodes exhibited almost no corrosion currents. This result is attributed to the outstanding mechanical stability of III-nitride NWs in an electrolyte, owing to their growth in a N-rich growth condition [14,15]. Figure 3(d) shows the applied photon-to-current efficiencies (ABPEs) of the Ref-NW, RMNW1, RMNW2, and RMNW3 photoanodes derived from the current densities measured under illuminated conditions. The maximum values of the ABPEs of the Ref-NW, RMNW1, RMNW2, and RMNW3 photoanodes were measured to be 1.24, 1.65, 0.14, and 0.23%, respectively. Among the photoanodes, RMNW1 exhibited the highest value for the maximum ABPE. Figure 3(e) shows the open-circuit potentials (OCPs) of the Ref-NW, RMNW1, RMNW2, and RMNW3 photoanodes. All the GaN-NW photoanodes showed a decrease in the OCP immediately after illumination, which indicates the photoanodic property [38]. The changes in the OCP value of the Ref-NW, RMNW1, RMNW2, and RMNW3 photoanodes were measured to be 9.18, 15.02, 4.71, and 4.17 mV versus RHE, respectively. Among the photoanodes, the transition rate in the OCP curve was the highest for the RMNW1 photoanode, which is evidence of efficient carrier extraction to the electrolyte for the PEC-WS reaction [39,40]. As described earlier, the improved results obtained by the PEC-WS with the GaN-RMNW photoanode is mainly attributed to the increase in the degree of light absorption, owing to the reverse-mesa structure of the GaN NWs. Figure 4 shows a three-dimensional schematic and the energy-band structure of the GaN-RMNW photoanode to explain the working mechanism of the improved PEC-WS performance. Because the difference in the NW volume between the Ref-NW and RMNW1 samples was negligibly small, it was assumed that the effect of the difference on the volume of the PEC-WS was negligible. That is, under illuminated conditions, the amount of light absorbed directly by the GaN NWs and GaN RMNWs is considered to be almost the same, owing to their similar volumes. However, for the RMNW1 photoanode, the probability of absorbing light reflected from the Si substrate increases, owing to the structural characteristics of GaN RMNWs compared to those of GaN NWs with a uniform hexagonal pillar structure. As shown in Fig. 4, the GaN RMNWs can absorb not only directly incident light, but also light reflected by the surface of the Si(111) substrate. This increase in the degree of light confinement and consequent absorption enables the GaN RMNWs to generate more carriers, thereby contributing to the PEC-WS reaction. Fur-
Figure 4. Three-dimensional schematic image and the energy-band structure of the GaN-RMNW photoanode to explain the working mechanism for the improved PEC-WS.

Moreover, the energy-band structure between Si(111) and the GaN RMNWs promotes the separation of photogenerated carriers and reduces the carrier-recombination rate inside the photoanode, enabling an improved PEC-WS.

PEC-WS using GaN RMNWs as the photoanode was significantly influenced by the degree of light absorption. The wavelength-dependent absorption of the GaN-NW photoanodes was investigated to understand the influence of light absorption on PEC-WS. Figure 5(a) shows the absorption spectra of the Ref-NW, RMNW1, RMNW2, and RMNW3 photoanodes measured at wavelengths ranging from 360 to 700 nm. The degree of light absorption of the GaN-RMNW photoanodes is considerably higher than that of the Ref-NW photoanode, which indicates that the GaN-RMNW photoanode can absorb more light than the GaN NWs with a uniform hexagonal pillar structure, as explained earlier. Figure 5(b) shows the IPCE spectra of the GaN-NW photoanodes as a function of wavelength, ranging from 360 to 700 nm. The IPCE values of the Ref-NW, RMNW1, RMNW2, and RMNW3 photoanodes were measured to be 43.4, 55.4, 29.2, and 15.7%, respectively, at a wavelength of 360 nm, which corresponds to the energy bandgap of GaN. Above 360 nm, there were no significant changes in the IPCE curves of the photoanodes. The IPCE value of the RMNW1 photoanode was higher than that of the Ref-NW photoanode, which is attributed to the reverse-mesa structure, which allows for an increase in the amount of light absorption. However, for the RMNW2 and RMNW3 photoanodes, the IPCE values were significantly lower than those of the other anodes. This resulted from an increase in the degree of influence of the interface between GaN and SiNₓ/Si(111), as shown in Fig. 2. These results are in good agreement with the PL spectra of the GaN-NW photoanodes, thereby indicating that the RMNW1 photoanode generates more effective carriers by increasing the absorption of incident light.

4. Conclusion

In summary, we demonstrated an improved PEC-WS using GaN RMNWs as a photoanode. The GaN-RMNW photoanode exhibited a current density of 2.62 mA/cm² and ABPE of 1.65% at 0.6 V versus RHE, which are improved results compared to those of previous studies. The improvement in PEC-WS using the GaN-RMNW photoanode was attributed to the increase in the number of carriers participating in the PEC-WS reaction, owing to the formation of high-crystalline GaN RMNWs. In addition, the degree of light absorption at the GaN-RMNW photoanode was significantly higher than that of the GaN NWs with a uniform hexagonal pillar structure, owing to an increase in the confinement of incident light by the reverse-mesa structure. The energy band structure between the GaN RMNWs and Si(111) induced the separation of photogenerated carriers, and consequently, reduced the carrier recombination rate inside the photoanode.

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Conflicts of Interest

The authors declare no conflicts of interest.

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