Investigation of the p-GaN layer thickness of InGaN-based photoelectrodes for photoelectrochemical hydrogen generation

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We investigated photoelectrochemical hydrogen generation using InGaN-based photoelectrodes with different p-GaN layer thicknesses. It was confirmed that the photocurrent density and hydrogen generation can be enhanced at zero bias between the photoelectrode and counterelectrode. We found that the maximum energy conversion efficiency was 2.0% when using an InGaN-based photoelectrode with a 20-nm-thick p-GaN layer; this was one order larger than for a photoelectrode without a p-GaN layer. The p-GaN layer can pull the potential of the InGaN layer upward, leading to efficient electron–hole separation in the photoabsorption layer and improving carrier transfer from the InGaN layer. By measuring incident photon to current efficiency, it was confirmed that the InGaN layer worked as a photoelectrode since the absorption edge wavelength was around 400 nm.

1. Introduction

Hydrogen generation technology using photocatalytic phenomena can use light energy to separate water into hydrogen and oxygen. This technology has attracted attention as a source of renewable energy and can be implemented in future green energy solutions. The generation of hydrogen and oxygen from the splitting of water using semiconductor photoelectrodes has been reported previously. The absorption phenomenon creates electron–hole pairs in the region of the semiconductor surface. These electrons and holes cause a redox reaction with water, and hydrogen and oxygen can be generated. The bandgap energy of the material and the valence and conduction band potentials are significantly related to the photoelectrochemical properties of the photocatalyst. Highly efficient and durable photoelectrodes for water splitting have been reported. III-nitride semiconductors can also be used as photoelectrodes for photoelectrochemical hydrogen generation from water. In general, III-nitride semiconductors are widely used in light-emitting devices but they also have an excellent light absorption capability because of their tunable bandgap energy from 0.67 to 6.04 eV, which comprises most of the energy range of the solar spectrum. Therefore, III-nitride semiconductor materials are expected to be suitable for use in efficient photoabsorption devices such as solar cells and photocatalysts. We previously developed NiO/GaN photoelectrodes, which do not need extra bias to work and last for more than 500 h. The discovery of the NiO/GaN heterostructure substantially affected the efficiency of the photoelectrode in the photoelectrochemical reaction. As long as GaN is used as the photoabsorption material in photocatalysts, the solar-to-hydrogen energy conversion efficiency should be low because of its bandgap of 3.42 eV. To enhance this energy conversion efficiency, InGaN could absorb more sunlight by narrowing the bandgap energy. However, it is well known that a piezoelectric field is induced in strained InGaN layers due to the large lattice mismatch between InGaN and GaN. With a high In content in InGaN, the piezoelectric field is strong. A strong piezoelectric field induces potential barriers for the excited carriers and the carrier distribution in the semiconductor’s layers is affected by the change in band potential. Thus, the transfer of carriers in photoabsorption devices (i.e. solar cells, photocatalysts, etc.) is influenced by the piezoelectric field. According to several reports, a high doping concentration in the n-layer can screen the internal electric field, pulling down the potential between the n-layer/absorption layer interface. These techniques lead to inhibition of carrier recombination in the photoabsorption layer. Such band engineering is an important factor for improving device performance.

In this paper, we report hydrogen generation at zero bias using InGaN-based photoelectrodes with different p-GaN layer thicknesses and investigate the effect of the p-GaN layer on the photoelectrochemical phenomena. The p-GaN layer can pull the potential in the top InGaN layer upward, causing the generated carriers to smoothly transfer to n- and p-layers.

2. Experimental procedure

All samples were grown by metalorganic vapor-phase epitaxy in a single-wafer horizontal reactor. Figure 1 shows a schematic view of the cross section of the sample structures. Structure A of the InGaN-based photoelectrode consisted of a 2.5-μm-thick n-GaN (n = 1 × 10^{17} cm^{-3}) layer grown on c-plane sapphire-covered with a low-temperature GaN buffer layer, a 3.5-μm-thick Si-doped n-GaN (n = 3 × 10^{18} cm^{-3}), a 10-μm-thick compositional graded n-In_{x}Ga_{1-x}N layer (x = 0–0.065), a 95-μm-thick unintentionally doped (uid) In_{0.065}Ga_{0.935}N layer, a 13-μm-thick uid-GaN layer and a Mg-doped p-GaN layer. The thickness of p-GaN was varied from 5 to 80 nm. In both structures, the highly n-doped linearly graded In_{x}Ga_{1-x}N (x = 0–0.065) layer pulls down the potential in the InGaN/n-layer interface by screening the polarization charge. In comparison with structure A, structure B of the InGaN-based photoelectrode does not contain the uid- and p-GaN layers. After growth of the
photoelectrode structures, the p-layer was activated by annealing. The annealing was in a nitrogen ambient at 700 °C. Then, NiO co-catalyst was deposited on the sample surface. This NiO deposition procedure is the same as in previous works.\textsuperscript{17,18} The setup for the photoelectrochemical experiment consists of an InGaN-based photoelectrode as the working electrode and Pt as the counter electrode, with a 1 M NaOH aqueous solution as the electrolyte and a Xe lamp as the irradiation light source. The irradiation power density was adjusted at 100 mW cm\textsuperscript{-2} and the irradiated sample area was adjusted to 1.0 cm\textsuperscript{2} using an epoxy resin coating. The photocurrent between the InGaN-based photoelectrode and Pt counter electrode was measured using an ammeter during light irradiation. The applied bias is defined as the potential difference between the InGaN-based photoelectrode and the Pt counter electrode. We used gas chromatography to analyze the purity of the gas generated from the Pt counter electrode. The incident photon to current efficiency (IPCE) was measured using a monochromatic light source under irradiation from the Xe lamp at 100 mW cm\textsuperscript{-2}.\textsuperscript{22} Measurement of the photoluminescence (PL) can identify the bandgap energy of InGaN. PL measurement was performed using a wavelength of 325 nm with a He–Cd laser. The excitation power density was 10 W cm\textsuperscript{-2} at room temperature.

3. Results and discussion

Figure 2 shows the schematic band diagrams for the equilibrium state. We assumed that the residual donor concentrations in InGaN were $1 \times 10^{17}$ cm\textsuperscript{-3}.\textsuperscript{21} Structure A can pull the potential in the p-GaN/uid-InGaN interface upward. It is expected that the excited carriers enhance the charge transport. Therefore, the deposition of p-GaN layers in InGaN-based photoelectrodes would be helpful for transferring the carriers to n- and p-layers at zero bias. Figure 3(a) shows the time dependence of the photocurrent from structures A and B without extra bias. Structure A exhibited an average photocurrent of 1.7 mA, but for structure B (without a p-GaN layer) the photocurrent was only 0.2 mA. We obtained a large enhancement of the photocurrent and H\textsubscript{2} generation by introducing a p-GaN layer into the photoelectrode structure. We evaluated the rate of hydrogen generation rate during light irradiation, as shown in Fig. 3(b). The energy conversion efficiency was estimated from the amount of hydrogen generated. The conversion efficiency of Xe lamp light energy to hydrogen energy was calculated by

$$ \eta = \frac{\Delta G^0 \times n}{P \times A}, $$

Figure 1. (Color online) Schematic views of structures A and B: (a) with a p-GaN layer and (b) without a p-GaN layer.

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Fig. 2. (Color online) Schematic band diagrams of structures A and B: (a) with a p-GaN layer and (b) without a p-GaN layer. These band diagrams are for the equilibrium state (i.e. in the dark and without extra bias).

Fig. 3. (Color online) Photocurrent and hydrogen generation from structures A and B at zero bias.
where $\Delta G^0$ is the Gibbs energy of H$_2$ combustion (237.13 kJ mol$^{-1}$), $n$ is the H$_2$ generation rate (mol s$^{-1}$), $P$ is the power density of the irradiating light and $A$ is the irradiated area.

Figure 4 shows the energy conversion efficiency and Faradaic efficiency as a function of the thickness of the p-GaN layer at no extra bias. The Faradaic efficiency was estimated from the ratio of current contributed by the evolution of hydrogen from water to the total observed current. For structure A we found that the maximum energy conversion efficiency was 2.0% when a 20-nm-thick p-GaN layer structure was used. The maximum Faradaic efficiency reached approximately 95%. On the other hand, structure B showed a very low energy conversion efficiency; this is discussed below. We achieved an improved energy conversion efficiency with the use of a p-GaN layer. The p-GaN layer structure has the benefit that the excited electrons can easily transfer into the n-GaN layer.

We found that the energy conversion efficiency can be increased by increasing the p-GaN layer thickness until it reaches approximately 20 nm. However, the energy conversion efficiency should not be improved by increasing the p-layer thickness if Mg is uniformly incorporated in the p-GaN layer. Thus, we believe that Mg doping was actually delayed and the desired doping level was achieved when the p-GaN layer reached a thickness of 10–20 nm rather than during the early stage of growth (the first 5–10 nm). The results also indicate another phenomenon: the energy conversion efficiency started to decrease when the thickness of the p-GaN layer exceeded 20 nm. Such an effect might occur because the light irradiated on the InGaN layer was degraded due to its passage through the p-GaN layer. In general, the photoabsorption changes exponentially with the p-GaN thickness. The saturation current indicates the maximum rate of transfer of the generated carriers. Thus, this value indicates the energy loss due to photoabsorption by the p-GaN layers, supporting the results of Fig. 4(b). The photocurrent is substantially affected by the influence of the internal electric field at zero bias; however, the band potential can be changed by applying an electrical bias. This result means that the transfer of carriers strongly depends on the electric field strength in the crystal. Thus, we believe that structure B has an unfavorable band potential caused by an internal piezoelectric field at zero bias, causing the excited carriers to recombine inside the layer instead of being transported and contributing to the photocurrent. This phenomenon would explain the significantly lower photocurrent value found for structure B at zero bias. Therefore, control of the internal electric field is necessary to improve the energy conversion efficiency of the photocatalyst. On the other hand, increasing the thickness of the p-GaN layer would increase the turn-on bias due to an increase in the potential barriers at the interface between the p-GaN layer and the electrolyte. The ideal p-GaN thickness is less than 20 nm so it is within the thickness of the depletion zone.

Figure 6 shows the IPCE obtained for structure A with a 20-nm-thick p-GaN layer. This confirms that the InGaN layer

GaN increases due to the existence of acceptor levels (~170 meV). Considering this, our value for photoabsorption seems to be reasonable. With such a large photoabsorption coefficient the photoabsorption should be strong even in thin layers. Thus, the p-GaN layer can also generate free carriers by photoabsorption. However, we consider that the generated carriers are trapped by recombination centers in the p-GaN layer because of the large number of defects usually present in the p-GaN layers.

We therefore concluded that one of the reasons why conversion efficiency degrades is photoabsorption by p-GaN. The energy conversion efficiency would be improved after optimization of the Mg concentration and p-GaN layer thickness.

The characterization of photocurrent density as a function of applied bias is shown in Fig. 5. We found that the saturation current decreases with increasing p-GaN layer thickness. The saturation current indicates the maximum rate of transfer of the generated carriers. Thus, this value indicates the energy loss due to photoabsorption by the p-GaN layers, supporting the results of Fig. 4(b). The photocurrent is substantially affected by the influence of the internal electric field at zero bias; however, the band potential can be changed by applying an electrical bias. This result means that the transfer of carriers strongly depends on the electric field strength in the crystal. Thus, we believe that structure B has an unfavorable band potential caused by an internal piezoelectric field at zero bias, causing the excited carriers to recombine inside the layer instead of being transported and contributing to the photocurrent. This phenomenon would explain the significantly lower photocurrent value found for structure B at zero bias. Therefore, control of the internal electric field is necessary to improve the energy conversion efficiency of the photocatalyst. On the other hand, increasing the thickness of the p-GaN layer would increase the turn-on bias due to an increase in the potential barriers at the interface between the p-GaN layer and the electrolyte. The ideal p-GaN thickness is less than 20 nm so it is within the thickness of the depletion zone.
works well as a photoelectrode under light irradiation. The IPCE edge of the In$_{0.065}$Ga$_{0.935}$N layer was 400 nm, which is in good agreement with the PL emission peak wavelength. On the other hand, it was not possible to obtain the IPCE of structure B because the photocurrent density generated by monochromatic light was especially low.

4. Conclusions

We investigated photoelectrochemical hydrogen generation using InGaN-based photoelectrodes with various p-GaN layer thicknesses. The energy conversion efficiency was drastically improved by including a p-GaN layer on top of the photoabsorption layer. The pulling upward of the band potential at the top of the InGaN layer led to enhanced transfer of the excited carriers. After optimization of the growth conditions and the thickness of the p-GaN layer, we expect that the energy conversion efficiency can be even further enhanced. Such band engineering is one of the key technologies for improving the energy conversion efficiency of photocatalysts.

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