Broadband light-absorption InGaN photoanode assisted by imprint patterning and ZnO nanowire growth for energy conversion

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Abstract
In this research, an InGaN-based photoanode with a broadband light-absorption range from ultraviolet to green, patterned by imprint lithography and branched by ZnO nanowires, has been applied to water splitting. Over the solar spectrum range, the absorbance increases due to the scattering effect of the micro-structure compared to that of flat surface InGaN, which reaches a maximum of over 90% at 380 nm as ZnO nanowires are further employed in this novel photoanode. Consequently, the induced photocurrent density of the InGaN photoanode with a domelike structure and ZnO nanowires on the surface shows a remarkable enhancement of seven times that of the one with a flat surface. Further investigation indicates the wet-etching process for defect removal has an essential impact on photocurrent efficiency. This design demonstrates an innovative approach for water splitting.

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(Some figures may appear in colour only in the online journal)
The patterned surface with a strong light-scattering effect could also enhance the light-absorption efficiency [10]. Furthermore, the massive reaction sites within the increased surface area facilitate the charge transportation and oxidation process at the electrolyte and material interface. For instance, 3D core–shell hierarchical GaN nanowires grown by the vapor–liquid–solid method could increase the photocurrent density fivefold [11]. GaN nanowire material with a larger surface area by molecular beam epitaxy (MBE) synthesis for stable and effective water splitting was also observed systematically [12]. With regard to device reformation, which usually relates to growth and indium composition, various kinds of methods have been used to improve the performance. For example, Alvi reported an InN/InGaN quantum dot (QD) photode electrode for water splitting at zero voltage, which showed high photo-to-current efficiency at long wavelength [13]. Caccamo demonstrated a GaN/InGaN core–shell rod array photoanode grown by selective area growth for visible water splitting [11]. The indium composition on various facets was different, which could facilitate light absorption over a wide range.

In previously reported results, an InGaN nanowire photoanode grown by MBE with different indium composition in different quantum layers was studied [14]. Moreover, tunnel junction connected InGaN heterojunction showed higher energy conversion efficiency with a separate light-absorption region [15]. However, few reports with regard to a broadband light-absorption photoanode in an individual quantum well (QW) region have been demonstrated using metal organic chemical vapor deposition (MOCVD). Furthermore, nanoimprint lithography technology is a facile way to obtain nano- or micro-scale structure on diverse kinds of flat material [16]. In our previous research, we reported, and fabricated moth-eye or photonics crystal structure for a solar cell or light-emitting diode (LED) [17, 18]. The light absorbance or transmittance is abundantly increased due to the light-scattering effect on the structured surface.

In this paper, by optimizing the InGaN growth technology, a broadband light-absorption InGaN-based photoanode grown by MOCVD is demonstrated and fabricated. With applying the imprint lithography (IL) method and hydrothermal ZnO nanowire growth, the InGaN-based photoanode with micro- or nano-structure on the surface is achieved. We believe that a novel design with higher light absorption and greater surface area could further enhance the electrochemical properties. The performance of this innovative photoanode is investigated in detail.

2. Experiment

2.1. Growth of InGaN material

Prior to the device fabrication, an Aixtron horizontal MOCVD reactor was used to grow the broadband light-absorption monolithic InGaN wafer on c-plane (0001) patterned sapphire substrates. The precursors were trimethylgallium (TMGa), triethylgallium (TEGa), trimethylindium (TMIn), and ammonia (NH₃). Silane (SiH₄) and bis-cyclopentadienyl magnesium (Cp₂Mg) were used as n-type and p-type dopants, respectively. Before the deposition of a GaN nucleation layer, the sapphire wafer was thermally cleaned at 1150 °C under an H₂ atmosphere for 10 min. Then, a 30 nm thick GaN buffer layer was grown at 500 °C under a reactor pressure of 650 mbar, followed by the deposition of a 3 μm thick undoped GaN (uGaN) layer and a 3 μm thick nGaN layer (Si-doped 8 x 10¹⁸ cm⁻³) at 1030 °C and a reactor pressure of 300 mbar, respectively. Nine pairs of In₀.₉Ga₀.₁N(3 nm)/GaN(15 nm) multiple quantum wells (MQWs) were grown at a temperature of 735 and 815 °C, respectively. After that, a thin 0.5 nm In₀.₁₀Ga₀.₉₀N wetting layer was inserted before the InGaN well layer grown at the same temperature as that of the wells. During the MQW growth, the V/III ratio was set at 1.15 x 10⁶, the reactor was at 600 mbar and the TMIn flow for the wetting layer and the InGaN QD layer were 8 μmol min⁻¹ and 68 μmol min⁻¹, respectively. Finally, the temperature was increased to 920 °C for the growth of a 20 nm pAlGaN electron blocking layer and 200 nm pGaN layer (p-doping 3 x 10¹⁹ cm⁻³). Other information can be found elsewhere [19, 20].

2.2. Fabrication process of domelike patterned InGaN

After the growth, the highly periodic InGaN-based domelike pattern was fabricated by the IL method, which is shown in figure 1. First, a poly(dimethylsiloxane) (PDMS) polymer was dropped onto the micro-patterned mask shown in figure 1. After that, the stamp was degassed under low pressure for 5 min and put into the oven with a curing temperature of 90 °C for 2 h. Later, the PDMS mold with a duplicated pattern was detached from the micro-patterned mask. Then, a Fox-16 solution, containing 22 wt.% hydrogen silsesquioxane (HSQ) in methyl isobutyl ketone solvent was used as the HSQ solution for the formation of the HSQ layer on the PDMS mold in figure 1(b). During the spin coating, the thickness of the HSQ layer could be modulated by the rotation speed. In this study, the spin coating of the HSQ solution was carried out at 3000 rpm s⁻¹ for 30 s. Later, the HSQ spin-coated PDMS mold was transferred onto the pre-cleaned InGaN wafer shown in figure 1(c). A direct IL process was conducted at 5 x 10⁻² Pa for 5 min. The PDMS mold was detached from the InGaN wafer, but the patterned HSQ remained on it. Finally, the InGaN wafer was loaded into the reactive ion etching (RIE) and inductively coupled plasma system for the HSQ and InGaN dry etching process, as shown in figures 1(d) and (e), respectively. The chemicals used in each step are O₂ and Cl₂/BCl₃ plasma, respectively. The HSQ residual was removed by diluted HF wet chemical etchant, as can be seen in figure 1(f). The detailed IL process can be found elsewhere [16].

2.3. Characterization of domelike patterned InGaN

To further indicate the light-absorption peak and range of the sample, temperature-dependent photoluminescence (PL) measurement of the sample was carried out with an excitation source of a 377 nm pulsed laser, with 50 ps pulse width.
1 MHz repetition rate, and approximately 8 mW average laser power. Two main band-to-band optical emission peaks around 410 and 600 nm are obvious in the spectrum. The emission peak with a wavelength of 410 nm is from the QW region. From wavelength 450–700 nm, the emission has a broad range, which is for the first time achieved in InGaN thin film (sample A) and which originated from the indium fluctuation in the QW region, as shown in figure 3(a). The mechanism of broadband light absorption was discussed in our previous result [19, 21]. The internal quantum efficiency (IQE) is estimated to be 2%, which is normally lower than that of the reported commercial InGaN-based laser or LED. Here, we emphasize that the broadband light emission deliberately matches with the solar spectrum regardless of the relatively low efficiency. The scanning electron microscope (SEM) images of the InGaN structures were performed with a field-emission SEM (S-4300). An acceleration voltage of 1.5 kV and an emission current of 1.5 μA were applied. The x-ray diffractometry (XRD) was carried out to investigate the crystal quality of the InGaN sample and ZnO nanowires by the D1 system. UV–vis spectra of the photoanodes were recorded using a Jasco V-650 spectrophotometer.

2.4. PEC measurements

Photocurrent density versus voltage (J–V) and photocurrent density versus time curves were recorded using the IVIUM TECHNOLOGIES system. A 150 W xenon lamp (PEC-CELL) calibrated to 100 mW cm⁻² with a standard Si solar cell (BS-500BK) was used as the light source. All the samples were investigated by three-electrode cell configuration in 0.5 M L⁻¹ Na₂SO₄ near neutral electrolyte at room temperature. The samples, Pt mesh and Ag/AgCl electrode acted as working, counter, and reference electrodes, respectively. The potentials versus Ag/AgCl was changed into that versus RHE. RHE denotes the reversible hydrogen electrode, which is defined by the formula:

\[ E(\text{vs. RHE}) = E(\text{vs. } Ag/AgCl) + E_{Ag/AgCl} - \text{pH} + 0.0591 \text{ pH}, \]

where \( E_{Ag/AgCl} \) (reference) is 0.1976 V and the pH value is 7 in this experiment. The incident-photon-to-current-efficiency (IPCE) was conducted with the electrode potential of 1.23 V versus RHE by the equation \( IPCE = 1240I_{sc}/P_{in} \), where \( I_{sc} \) is the current density, \( \lambda \) is the wavelength of the incident light, and \( P_{in} \) is the incident light intensity. The standard solar cell was used as calibration reference. More information can also be found elsewhere [13].

3. Results and discussion

Figures 2(a) and (b) show the image of dry-etched GaN wafer with a domelike array on the surface. The diameter and height of the domelike GaN are both approximately 2 μm. The spacing of each domelike InGaN is about 200 nm. Because the GaN layer on the surface is usually partly damaged during the dry etching process, a wet-etching process was applied to remove the damaged GaN in this study. The commonly used GaN solution, according to our previous result, is diluted in KOH at 1 ml⁻¹ and 60 °C. Tseng also observed the impact of plasma-induced surface damage on the PEC properties of GaN pillars fabricated by the dry etching process, which showed the undamaged GaN layer. The photocurrent density had an obvious enhancement and the onset potential shifted to a low-voltage part [7]. In our study, the wet-etching process was conducted in KOH solution for 1 h at 60 °C. As shown in figures 2(c) and (d), the domelike InGaN (sample B) has a diameter change compared to figure 2(a). The white spot on the center of each domelike GaN is a small GaN pillar, as also shown in figure s1, which indeed further confirms that the wet-etching process works. Later, a hydrothermal method was
used to grow ZnO nanowires on the domelike GaN surface. Prior to the growth process, ZnO seed layer was distributed on the GaN surface by the spin-coating method. The ZnO nanowire growth rate is approximately 1 μm per h. More information is also provided in the supplementary section.

Figures 2(e) and (f) show the morphology of the domelike GaN branched ZnO nanowires (sample C). The length and diameter of the ZnO nanowires are 300 and 100 nm on average, respectively. To further evaluate the ZnO nanowire crystal quality of sample C, the XRD for the structure information was carried out. The results indicate that obvious intrinsic peaks exist in both the InGaN and ZnO. ZnO nanowire intrinsic peaks of (100), (002), and (101) demonstrate high intensity, which is half of the intensity of the GaN intrinsic peak of (1001), as shown in figure 3(b). More than eight ZnO nanowire peaks could be clearly observed in the XRD spectrum. As can also be seen in online supplementary figure s2, the high-quality ZnO nanowires are mainly vertically aligned while grown on the flat InGaN-based surface. Without ZnO nanowires on the surface, only the GaN and Al2O3 intrinsic peaks could be observed in the XRD spectrum.

The optical spectra properties of sample A, sample B, and sample C were conducted by Jasco V-650 spectrophotometer. In figure 4(a), the transmittance of sample A is lower than that of sample B over the whole solar spectrum range. However, sample C has more transmittance than sample B at a wavelength around 400 nm, which means patterned InGaN and ZnO could cause less scattering or backward reflection in the sample. The reflectance spectra also confirm that with InGaN patterning or ZnO nanowire growth, less light reflective light is observed over the solar spectrum range, as shown in figure 4(b). As a consequence, sample C has a better light absorbance of over 90% from 300–400 nm than that of sample B and C, as shown in figure 4(c). The light-scattering effect by patterned InGaN and UV light absorption by ZnO nanowire material together influence the performance of the samples. Even though the
dry etching process might partly remove the QW area, the light absorbance decreases less at a wavelength around the visible range, which is also supported by reference [10]. The schematic photoanode of sample C is demonstrated in figure 4(d). Multiple layer metals of Cr/Pt/Au with thicknesses of 10 nm/100 nm/1000 nm, which were commonly utilized in the LED industry were deposited to form the ohmic contact on the partly dry-etched nGaN surface.

Figure 3. (a) PL spectra of as-grown InGaN wafer under different temperatures. (b) XRD 2-theta scan of as-grown InGaN wafer with and without ZnO nanowires on the surface.

Figure 4. (a) Transmittance, (b) reflectance and (c) absorbance spectra properties of the samples measured as a function of wavelength. (d) Schematic device of the domelike InGaN photoanode with ZnO nanowires on the surface.
The J–V properties of these three types of photoanode were studied under one sunlight illumination with a sweep rate of 10 mV s\(^{-1}\), as shown in figure 5(a). The photocurrent density of sample B at a potential of 1.23 V (versus RHE) is significantly enhanced threefold from 0.024–0.079 mA cm\(^{-2}\), which is mainly attributed to the light-scattering effect of the InGaN micro-pattern on the surface. Meanwhile, the increased contact area between the photoanode and electrolyte interface plays an important role in enhancing the photon-to-current efficiency. Even though there is a reduction of the QW area due to the dry etching process, the light-scattering effect and the surface flake, which resulted from the wet-etching process, dominate the light absorption. When ZnO nanowires are applied onto sample C, the photocurrent density is further improved sevenfold to 0.17 mA cm\(^{-2}\) with more light absorption at UV range and more reaction sites on the photoanode and electrolyte interface. The turn-on potentials (versus RHE), which are dependent on the kinetics of the photo-generated electron and hole pair, are slightly increased by the enhanced light absorption and interfacial charge carrier separation. Furthermore, all the photoanodes show a long duration of hours under constant light exposure. The image of O\(_2\) bubbles on the sample surface is provided in figure s3.

The J–T properties under externally applied potential of all samples at 1.23 V versus RHE are shown in figure 5(b). The photocurrent density of sample B is approximately threefold higher than that of sample A, which corresponds to the previous J–V results. At the same time, the photocurrent density of sample C is further increased sevenfold compared to that of sample A. The enhancement could be attributed to the increased light absorption and surface area of the patterned InGaN and ZnO nanowires for redox reaction, resulting in enhanced charge separation. There are photocurrent overshoots at the beginning of each switching, which disappear slowly. As a result, constant photocurrent density is achieved in all samples. The overshoots might be caused by the separation of photo-generated electron and hole pairs, resulting in the accumulation of holes at the photoanode surface. As for InGaN material, the hole diffusion distance is relatively low compared to that of other material, which is usually investigated by time-resolved PL and Hall measurement.

The IPCE curves of all samples were measured at 1.23 V versus RHE, as shown in figure 6. For sample A, the IPCE value reaches the maximum of 1% at a wavelength of 360 nm. However, for sample B and C, the IPCE values at a wavelength of 360 nm enhance to 6% and 9.5%, respectively. The IPCE change in sample B and sample C could be attributed to the light-absorption increase due to the domelike pattern on the surface, ZnO nanowire decoration, and extended photoanode/electrolyte interface. The IPCE value exhibits less change at a long wavelength of 500 nm, which means the partial removal of the QW area has a minimal effect on our sample. The existing band diagram alignments are shown in online supplementary figure s4, which together influence the total efficiency. As the IQE of our sample is relatively low, the relation of QW loss and interface extension or light-
scattering effect should be reconsidered if a high IQE sample is involved in the future. All samples demonstrate a broadband light absorption from 300 to near 550 nm, which is less than the corresponding PL spectra range. The causes are probably the low light-absorption factor and solar spectrum portion at long wavelength, which should be further confirmed in the future.

4. Conclusions

In summary, the PEC properties of the domelike InGaN with a ZnO nanowire photoanode is investigated in this research. The InGaN wafer grown by MOCVD has intentionally broadband light absorption from the UV–vis range, which is suitable for solar energy harvesting. By using the IL method for surface patterning and ZnO nanowire decoration, the photocurrent density is inevitably enhanced sevenfold at 1.23 V versus RHE. The IPCE results also confirmed that the photoanode/electrolyte interface and light-scattering effect together influence the energy conversion efficiency in nitride semiconductor material.

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