Solar water splitting with III-N nanocolumn structures

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Abstract. HVPE – grown GaN/AlGaN p-n structures with nanocolumns fabricated on the top (1.0 µm of height and 100-130 nm of diameter) were used in a photoelectrochemical process to investigate direct water splitting. The H₂ production rate of 0.56 ml/cm² × h was measured for the GaN/AlGaN structures in KOH electrolyte under the Xe-lamp illumination. H₂ evolution was observed at the Pt electrode. However an etching and a small amount of generated gas was observed at the working electrode. Possible mechanisms of corrosion in GaN/AlGaN nanocolumn structures are discussed. A sacrificial agent (like HBr) or the surface passivation by nitrogen atoms is needed to prevent oxidation and etching of the III-N materials.

1. Introduction

Direct water photoelectrolysis using III-N materials is a way for the clean technology development for hydrogen production. In this process, III-N semiconductor, which is immersed in an aqueous solution of electrolyte, allows decomposition of water into H₂ and O₂ gases by solar irradiation of its surface. Required energy to split water molecule is generated by sunlight absorption in the semiconductor. The method is simple in comparison with other methods of hydrogen production. However, the technology is in the development stage.

The main challenges to enable broad application of this method include: research and development of the materials used as photoelectrodes for water electrolysis; slowing down the corrosion of electrodes for a long-term work; increase of the solar-to-hydrogen conversion; research and development of new materials and approaches for effective H₂ and O₂ storage.

Two major approaches of the direct water splitting under solar radiation are currently under investigation at nowadays. The first one is to separate electron-hole (e-h) pairs created by the solar irradiation inside the III-N materials in order to get oxygen evolution reaction and hydrogen evolution reaction at different electrodes in an electrochemical cell. It that case, electrons and holes participate in proper reactions separately at different electrodes, H₂ and O₂ gases generate separately too and can be collected in different reservoirs [1]. The second one is to transport electron-hole pairs created by the solar irradiation to the III-N material surface in order to get oxygen evolution reaction and hydrogen evolution reaction simultaneously on the same surface. It that case, H₂ and O₂ gases need to be separated in different reservoirs [2].

When a p-n structure is immersed into an electrolyte under illumination, an electric field created by space charge at the p-n junction in the volume of III-N structure should improve the efficiency of the e-h pairs separation to compare with the band bending at the semiconductor-electrolyte interface.
However, the same carriers separated by the p-n junction and the band bending have opposite flow direction in the semiconductor that reduces the total efficiency of the water splitting. When all illumination absorbs at the p-n junction (with p-layer on the tip), the flow of holes separated at the p-n junction toward the interface with electrolyte may be larger the opposite flow of the holes separated at interface by the band-bending. In that case, diminution of the barrier high at the interface with the electrolyte and increasing of the surface chemical resistance are the major tasks to be studied for III-N p-n structures for application for the direct water splitting.

In this work we used as working electrodes GaN/AlGaN p-n structures with nanocolumns on the top to investigate the hydrogen generation rate and the material corrosion during the photoelectrochemical (PEC) process.

2. Experimental details
The initial - thick AlGaN/GaN structures were grown by chloride HVPE on c-plane 2-inch sapphire substrates [3]. First, the growth procedure included in-situ sapphire substrate treatment followed by multilayer structure growth consisting of AlN-based buffer layer, AlxGa1-xN/AlxGa1-yN (x > y) stress control structure. Then, a p-n structure was grown on the top in the same run. The basic structure included a 50-100 nm-thick AlGaN active region, which was sandwiched between p- and n-AlxGa1-xN barriers (x ~ 0.05-0.12). A 0.5 μm-thick Mg-doped p-type GaN contact layer covers the structure. A net acceptor concentration N_A-N_D ~ (2-4) × 10^{18} cm^{-3} was determined on the surface by C-V measurements using Hg probe.

The nanocolumns on the structure top were processed by reactive ion etching in Cl2 plasma using self-aligned Ni/SiO2 masks as described in detail in [4]. A sketch of the structure used in the electrochemical experiments is shown on figure 1.

![Figure 1. The design of AlGaN/GaN p-n structure with nanocolumns](image)

The samples with nanocolumns used as working electrodes in the photoelectrochemical experiments. The samples were immersed in a KOH aqua electrolyte (0.75M KOH) under external electrical bias from 0 V to +0.5 V and irradiation with a Xe lamp (AM 1.5 standard spectrum, 3500 W/m²). Pt plate was used as counter electrode. The electrical contact to the sample (working electrode) was made through a metallic In pads. The In contact was protected by a fluorine-based varnish to prevent its etching in the electrolyte. The structures were partly immersed in the electrolyte. An area irradiated by the Xe lamp was about 2.5 cm².

A digital multi-meter and an UV-radiometer were used to measure the photo - current and the luminous flux (the optical power of light) of the incident light from the light sources on the GaN-electrode surface. Sample surfaces were characterized by field emission scanning electron microscope (SEM) at an accelerating voltage of 5 kV and with an electron beam current of 300 pA.

3. Results and discussion
Figure 2 shows scanning electron microscope (SEM) images of one of the S3 group GaN/AlGaN structures with nanocolumns (1.0 μm of height and 100-130 nm of diameter) before and after PEC process. The corrosion (etching) process penetrates deep into the structure and results in much thinner
nanocolumns. SEM plan-view images (figure 2 (a) and (d)) show that p-type top of nanocolumns was not etched and fell down between the columns. An investigation of cleavage section of the sample shows that the corrosion process was heterogeneous and the sample surface was covered by thinner columns of a 10-20 nm diameter and a 200-400 nm height. An approximately half of the nanocolumns volume was etched away during 1-hour operation of the PEC cell.

Obviously, the observed photoelectrochemical corrosion (etching) follows paths of the photo-current flow. The current flow paths in III-N GaN/AlGaN or GaN/InGaN materials, especially at low current, are non-uniform and can be associated with shunt conductivity in an extended defect system of grain boundaries, threading dislocations, local regions with irregular alloy composition enriched by metallic atoms (Ga or In), and other extended defects [5]. Note that the nanocolumn density is 7×10⁸ cm⁻² that is close to the threading defects density in the initial structure (3-5×10⁸ cm⁻²) estimated by X-ray diffraction measurements. It means that near 40-60% of nanocolumns may have a threading defect that may act as a leakage path for the photocurrent promotion the structure corrosion.

In addition, dry etching at the nanocolumns processing produces radiation damage defects in the near surface area of nanopillars. These defects consist of donor-like centers, such as nitrogen vacancies, gallium interstitials, and acceptor defects including nitrogen vacancy complexes, interstitial nitrogen, gallium vacancies and their complexes. The net result depends on the dry etching conditions and post-etching annealing. The dry etching defects in nanocolumns create another path for the photocurrent leakage that is favorable for the electrochemical etching but not for controllable water splitting and H₂ generation.

It is know that spontaneous and piezoelectric polarization between AlGaN/GaN layers in the structure results in formation of a net positive charge at their interface [6]. The GaN/AlGaN structures in this work had a stack of doped GaN and AlGaN layers that also influences the net positive charge in the structure. In addition, a thin n-AGaN layers in the structure are not fully relaxed and may have additional positive piezoelectric polarization charge at the n-AlGaN /AlGaN layer interfaces.

An additional positive charge at the layer interfaces can be associated with positively charged ionized donors, which are Si⁺ presumably, in a space charge region of the p (AlGaN)-n (AlGaN) junction. This
positive charge is located in the n-AlGaN active region too. Note that negatively charged ionized acceptors (Mg\textsuperscript{2+}) in the p-GaN and p-AlGaN layer may screen positive polarization charge at the p-AlGaN barrier layer/n-AlGaN active layer interface.

The net positive charge at the GaN/AlGaN n-n and p-n interfaces causes OH\textsuperscript{-} ions from the electrolyte to form Ga(OH)\textsubscript{3} and Al(OH)\textsubscript{3} or their soluble forms [3, 7] at the nitrogen vacancy sites and to continue the etching process along the positive charge sites resulting in narrowing of the nanocolumns.

\(H_2\) evolution was observed at the Pt electrode. However no \(O_2\) was observed at the working electrode. Obviously, a sacrificial agent (like HBr) or passivation of the surface by nitrogen atoms are needed to prevent oxidation (etching) the III-N materials at the direct water splitting process. As a whole, GaN based structures grown on c-plane sapphire have Ga-terminated surfaces, as a result one to be easily oxidized to \(Ga_2O_3\), which may even dissolve in acidic conditions, thereby leading to instability and degradation of the PEC cells. On the other hand the reverse crystal polarization (N-terminated) could enhances an efficient of separate and transport of electron-hole pairs to the photoelectrode/electrolyte interface so improving the direct water splitting process [2]. N-terminated surfaces protect the GaN-based nanowire surfaces against attack by the electrolyte (oxidation and photocorrosion) and thus, the engineered optimum surface band bending can be maintained during the photocatalytic overall solar water splitting reaction.

Figure 3 shows changing of a photocurrent at the electrochemical process under irradiation by Xe lamp. External bias of \(+0.5\) V was applied. Hydrogen evaluation reaction was observed on Pt counter electrode. The \(H_2\) production rate of \(0.56 \text{ ml/cm}^2 \times \text{h}\) was measured for GaN/AlGaN structures with nanocolumns fabricated on the top in KOH electrolyte under the Xe-lamp illumination. The nanocolumn GaN/AlGaN p-n structures worked as a sacrificial anode. The nanocolumns size decreased remarkably, as shown SEM images. Accordingly, a decrease of the photo-current was observed too during the experiment. At the end of the experiment (after 1 hour), the photocurrent decreased almost twice. We believe it is due to the electrochemical corrosion of nanocolumns. A small amount of gas was released on the GaN/AlGaN photo-anode. This gas can be \(O_2\) and/or \(N_2\), taking into account the corrosion of GaN/AlGaN structure (as shown in figure 2 (d-f)).

![Figure 3. A photocurrent at the electrochemical process under irradiation by Xe lamp](image)

4. Conclusions

Corrosion of the p-n GaN/AlGaN nanocolumn structures at the electrochemical process in a KOH aqua electrolyte under the Xe-lamp illumination penetrates deep into structure and results in much thinner nanocolumns. The top portions of the nanocolumns that had p-type conductivity were not etched and simply fall dawn from the top. \(H_2\) evolution was observed at the Pt electrode at an external bias of \(+0.5\) V. The \(H_2\) production rate of \(0.56 \text{ ml/cm}^2 \times \text{h}\) was measured. However, only a few gas bubblers generated on the working electrode. Obviously, a sacrificial agent (like HBr) or passivation of the surface by
nitrogen atoms are needed to prevent oxidation (etching) the III-N materials at the direct water splitting process.

Acknowledgments
The authors thank to Dr A. Y Polaykov and Prof. I.H. Lee for help in the nanocolumn fabrication. Work at University ITMO was financially supported by the Ministry of Education and Science of Russian Federation (grant agreement 14.575.21.0054, unique identifier of research activities is RFMEFI57514X0054).

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