

## Photoelectrochemical corrosion of GaN-based p-n structures

**A D Fomichev<sup>1</sup>, S Yu Kurin<sup>2</sup>, I A Ermakov<sup>1</sup>, M V Puzyk<sup>1,3</sup>, A S Usikov<sup>1,4</sup>, H Helava<sup>4</sup>, A Nikiforov<sup>5</sup>, B P Papchenko<sup>1</sup>, Yu N Makarov<sup>2,4</sup> and A E Chernyakov<sup>6</sup>**

<sup>1</sup>University ITMO, Kronverkskiy pr. 49, St. Petersburg 197101, Russia

<sup>2</sup>Nitride Crystals Group Ltd., pr. Engel'sa 27, St. Petersburg 194156, Russia

<sup>3</sup>Herzen University, Nab. r. Moyki 48, St. Petersburg 194186, Russia

<sup>4</sup>Nitride Crystals Inc., 181 E Industry Court, Suite B, Deer Park, NY 11729, USA,

<sup>5</sup>Boston University, Photonics Center, 8 St. Mary's St., Boston, MA 02215, USA

<sup>6</sup>Submicron Heterostructures for Microelectronics Research & Engineering Center, RAS, 26 Polytekhnicheskaya Str., St. Petersburg 194021, Russia

**Abstract.** Direct water photoelectrolysis using III-N materials is a promising way for hydrogen production. GaN/AlGaIn based p-n structures were used in a photoelectrochemical process to investigate the material etching (corrosion) in an electrolyte. At the beginning, the corrosion performs through the top p-type layers via channels associated with threading defects and can penetrate deep into the structure. Then, the corrosion process occurs in lateral direction in n-type layers forming voids and cavities in the structure. The lateral etching is due to net positive charges at the AlGaIn/GaN interfaces arising because of spontaneous and piezoelectric polarization in the structure and positively charged ionized donors in the space charge region of the p-n junction.

### 1. Introduction

Hydrogen is considered to be a candidate as the substantial energy carrier. Direct water photoelectrolysis is a promising way for hydrogen production. In this process, a semiconductor material immersed in an aqueous solution of electrolyte allows decomposition of water into H<sub>2</sub> and O<sub>2</sub> gases by solar irradiation of its surface. The required energy to split water molecule is generated by sunlight absorption in the semiconductor. The solar water splitting process may be spontaneous under illumination if electrochemical redox potentials of oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) in an electrolyte are bracketed by the energy gap of the semiconductor. This is fulfilled for GaN and most of InGaIn materials [1, 2].

Not all of the electron-hole pairs generated in the semiconductor under illumination in an electrolyte can participate in OER and (or) HER. Carrier recombination at the surface and in the bulk of the layer reduces the gas generation rate. The corrosion or etching of the electrode material is another process having a negative effect on the gas evolution reaction [3]. The corrosion is an issue for n-type materials as photoelectrodes because upward band-bending at the photoelectrode/electrolyte interface promotes photo-generated holes to transfer to the electrolyte. The holes at the interface not only oxidize water (OER) but can oxidize and etch the photoelectrode. In p-type materials the band-bending promotes photo-generated electrons to transfer to the electrolyte for the HER process that almost leaves the surface of the photo-electrode chemically intact.



In this work we use GaN/AlGaIn p-n structures as working electrodes with a p-type GaN layer on the surface to investigate the material corrosion of the photoelectrochemical process. Several 8-10  $\mu\text{m}$ -thick AlGaIn/GaN p-n structures were grown by chloride HVPE on c-plane 2-inch sapphire substrates.

## 2. Samples and experimental techniques

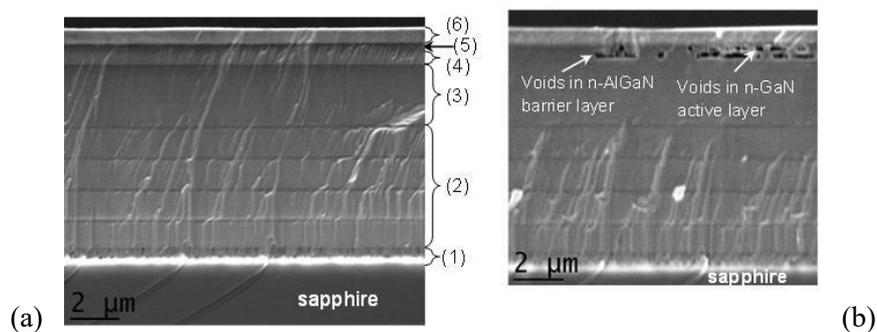
Several 8-10  $\mu\text{m}$ -thick AlGaIn/GaN p-n structures were grown by chloride HVPE on c-plane 2-inch sapphire substrates in a conventional horizontal-flow reactor. The basic structure included a 50-100 nm-thick GaN active region co-doped with Zn and Si to have emission at 420 nm [4], which was sandwiched between p- and n- Al<sub>x</sub>Ga<sub>1-x</sub>N barriers ( $x \sim 0.05\text{--}0.12$ ). A 0.5-1  $\mu\text{m}$ -thick p-type GaN contact layer doped with Mg covered the structure. The Mg doping produces hole concentration up to  $10^{18} \text{ cm}^{-3}$  in the contact layer. Details of the structure growth and characterization can be found elsewhere [5]. Note that it was the p-type GaN layer surface that served as a photoelectrode (working electrode) in this work.

The 2-inch grown samples were immersed in a KOH aqua electrolyte (5.7 weight % of KOH, pH=14) under external electrical bias of +2.5 V and irradiation with a 150 W Xe lamp (AM 1.5 standard spectrum) having a concentration factor of 20x. As a counter electrode a 2-inch diameter Ni plate was used. The electrical contact to the sample (working electrode) was made through a metallic clamp with In pads. The structures were partly immersed in the electrolyte. A segment of the structure, which was used to hang the whole wafer by the clamp, was above the electrolyte to avoid a short circuit. The whole process of photoelectrolysis took about 6 minutes.

After experiments, the samples were cleaved and their surface morphology and luminescence properties were examined in both top-view and cross-sectional configurations by high-resolution scanning electron microscopy (SEM) and cathodoluminescence (CL) spectroscopy and monochromatic CL imaging, respectively.

## 3. Results and discussion

Figure 1 shows SEM images of cross sectional views of the same sample taken at an unetched area on the surface and an area underwent the corrosion (etching). All layers of the structure can be distinguished. The structure total thickness is about 9.5  $\mu\text{m}$ .

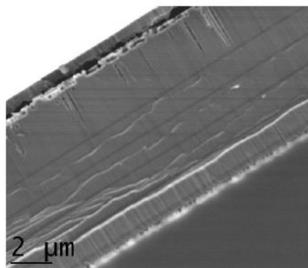


**Figure 1.** Cross-sectional SEM image of different areas of the AlGaIn/GaN p-n structure after photoelectrolysis. (a) Unetched area on the surface. No peculiarities related to the photoelectrochemical etching are observed. (1) AlN/AlGaIn buffer,  $\sim 0.65 \mu\text{m}$ ; (2) AlGaIn/AlGaIn four pairs of stress control layers,  $4.97 \mu\text{m}$ ; (3) n-GaN:Si contact layer,  $\sim 2.5 \mu\text{m}$ ; (4) n-AlGaIn barrier layer,  $\sim 0.5 \mu\text{m}$ ; (5) GaN:(Zn+Si) active layer,  $\sim 0.2 \mu\text{m}$ ; (6) p-GaN contact +p-AlGaIn barrier layers,  $\sim 0.66 \mu\text{m}$ . (b) an area underwent the corrosion (etching) on the surface.

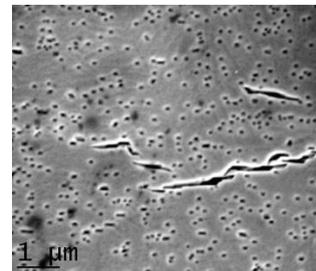
Note that in the experiment a +2.5V bias was applied to the p-type top layer of the structure from external power source, i.e the structure was a photo anode. During the experiment the measured value of photocurrent was found to decrease from 4.3 mA to 2.2 mA ( $0.5\text{--}0.25 \text{ mA/cm}^2$ ). The total thickness of the p-type layers is about 0.7  $\mu\text{m}$ . P-type conductivity on the surface was confirmed by C-V measurements. Two rows of micro-voids in Figure 1b can be ascribed to the photoelectrochemical

etching. The position of the voids in the stack of layers in the structure makes it possible to assume that these voids are formed in the GaN active layer and in the underlying n-AlGaN barrier layer. The micro-voids can spread laterally and overlap leading to formation of a large-size cavity.

Figure 2 shows the large-size cavity that formed after the photoelectrolysis process performed on another AlGaN/GaN p-n structure but having higher photocurrent of 5.6-9.7 mA (0.65- 1.1 mA/cm<sup>2</sup>) under the same illumination. The large-size cavity may result in delamination of the p-layers from the structure. Figure 3 shows a scanning micrograph of surface morphology of the etched area of the sample in figure 1. Pits and large open cavities on the surface are attributed to the photoelectrochemical process. The pits density is about  $4\text{-}7 \times 10^8 \text{cm}^{-2}$  and it varies over the sample surface up to  $(1\text{-}2) \times 10^9 \text{cm}^{-2}$  in the most defective areas near the microcracks. The CL spectra acquired from the sample surface have a weak emission at about 360 nm and a dominant broad peak centred around 420 nm as shown in figure 4a. The strongest luminescence was measured from the area illuminated by the Xe lamp (the etched area) where the density of non-radiative defects was likely decreased as a result of the photoelectrochemical etching. The coarser surface morphology in the etched area may also improve the light extraction efficiency. The dominant emission can be ascribed to the active layer located at a depth of 0.5-0.6 microns from the surface.



**Figure 2.** Cross-sectional SEM image of the etched area of another AlGaN/GaN p-n structure. Overlapped micro-voids created large-size cavities that may peel the p-type layer.



**Figure 3.** SEM image of surface morphology after the photoelectrochemical etching of the AlGaN/GaN p-n structure. Pits density is about  $4\text{-}7 \times 10^8 \text{cm}^{-2}$ .

Obviously, the photoelectrochemical 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 [6].

The voids observed in the SEM images in figures 1-2 suggest that the process of their formation proceeds in two stages. During the first stage, the etching process starts via channels (or shunts) in the extended defect system of the structure penetrating the p-type layers all the way into the underlying n-type layers. The shunts could be threading defects, grain boundaries and micro-cracks attributed to mosaic structure of the structures as-grown. During the second stage, the etching on the n-type AlGaN barrier and GaN active layer proceeds in a lateral direction resulting in formation of voids and cavities underneath the p-type layers. Although the p-type layers of the structure remained unetched, the top surface exhibited a lot of pits.

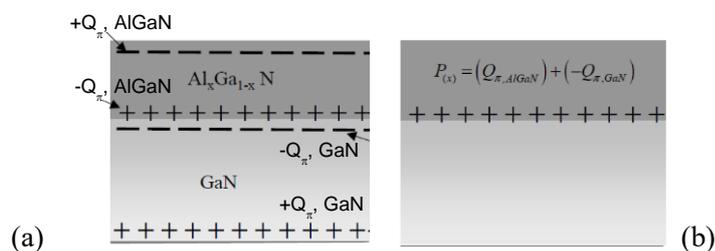
The UV portion of the illumination light gets effectively absorbed in the p-GaN contact layer (at a depth of about 0.2-0.3 μm from the surface) leading to formation of excited electron-hole pairs. These pairs can be separated further by either the internal electric field of the space-charge region in the p-n junction of the structure when they drift towards it or by the specific band-bending at the p-GaN layer/electrolyte interface. The photo-generated carriers may participate in two competitive processes in the structure employed as an anode and immersed into an electrolyte under irradiation: (1) oxygen evolution reaction (OER) and (2) photo-etching of GaN and GaN-based materials. However, because of a too thick p-GaN layer (0.5-0.6 μm thick) the excited electron-hole pairs recombine mostly at the structure surface and in the p-layer before being separated by the p-n junction producing as a result a

relatively low photocurrent. It appears that relatively low photocurrent flows non-uniformly through the structure selecting higher conductivity paths that are threading defects and micro cracks.

We speculate that photo-generated holes could assist in oxidative decomposition of p-GaN, primarily in the vicinity of the threading defects forming dangling bonds of  $\text{Al}^{3+}$  and  $\text{Ga}^{3+}$  atoms. Hydroxide ions ( $\text{OH}^-$ ) from the electrolyte would then attack the  $\text{Al}^{3+}$  and  $\text{Ga}^{3+}$  dangling bonds and form hydroxides  $\text{Al}(\text{OH})_3$  and  $\text{Ga}(\text{OH})_3$  [7, 8]. Dissolution of the hydroxides would lead to formation of soluble  $\text{Al}_2\text{O}_3$  and  $\text{Ga}_2\text{O}_3$ . Continuous formation and dissolution of the oxides in the solution would further simulate the etching process.

The etching process may move deeper into the layers via the threading defects. The Mg-doped p-type GaN and AlGaN layers have ionized Mg- acceptors and may screen partly the positive charge of the dangling bonds preventing the etching of the p-type layers but still allowing the etching to proceed along the threading defects. Indeed we did not observe any appreciable etching of the top p-layers. However, some micro-cracks and numerous pits associated with etching were observed on the top surface as can be seen in figure 3.

The step involving lateral etching in figures 1-2 can be explained on effects resulting in a positive charge at layer interfaces. It is known that spontaneous and piezoelectric polarization between AlGaN/GaN layers in the structure results in formation of a net positive charge at their interface [9]. Figure 4 shows a net positive charge at the AlGaN/GaN interface in the AlGaN layer caused by the sum of the net spontaneous polarization and piezoelectric polarization between the AlGaN and GaN layers in the structure growing along the c-direction [9].  $Q\pi$ , AlGaN includes the contribution of spontaneous and piezo-electric charges for the AlGaN layer and  $Q\pi$ , GaN is the only spontaneous polarization for the GaN layer as it has been assumed to be relaxed due to a much larger thickness than that of the AlGaN layer.



**Figure 4.** Polarization charges in an AlGaN/GaN structure. (a) Charge polarization in individual layers of the structure (b) a net positive charge at the AlGaN/GaN interface in the AlGaN layer [8].

The structures in this work had a stack of doped GaN and AlGaN layers at the top (i.e the n-GaN active layer was sandwiched between n- and p-AlGaN barrier layers) that influences the net positive charge compared to that depicted in figure 4. First of all, negatively charged ionized acceptors (Mg-) in the p-AlGaN layer may screen positive polarization charge at the p-AlGaN barrier layer/n-GaN active layer interface. In addition, a thin n-GaN active layer is not fully relaxed and may have additional positive piezoelectric polarization charge at the n-GaN active layer/n-AlGaN barrier layer interface.

Then, n-AlGaN barrier also has a positive piezoelectric polarization charge at the interface with n-GaN contact layer beneath (see figure 1a for reference to the structure design). Note also that all thin AlGaN layers having higher composition in the AlGaN/AlGaN four-pair structure, beneath the n-GaN contact layer, have a net positive polarization charge. However these layers are located deep in the structure, further away from the structure surface. Only two thin n-GaN active and n-AlGaN barrier layers are near the p-type layers and have positive piezoelectric polarization charge. An additional positive charge at the layer interfaces can be connected with positively charged ionized donors, which are  $\text{Si}^+$  presumably, in a space charge region of the p (AlGaN)-n (GaN) junction. This positive charge is located in the n-GaN active region too. Our separate experiments on photoelectrolysis with GaN layers only demonstrated porous-like etching of 5-6  $\mu\text{m}$  thick n-GaN layers through the layer to the substrate whereas in p-n GaN structures having a p-GaN layer on the top the etching process was terminated at the p-n junction.

The net positive charge at the GaN/AlGaN n-n and p-n interfaces promotes  $\text{OH}^-$  ions from the electrolyte to form  $\text{Ga}(\text{OH})_3$  and (or)  $\text{Al}(\text{OH})_3$  hydroxides and the nitrogen vacancy sites and continue the etching process along the positive charge position forming lateral voids and large-size cavities. When the etching process via threading defects reaches a layer with positive net charge it changes the etching direction from vertical to lateral presumably because of a stronger charge at the layer interface than that in the channel associated with threading defects and dangling bonds.

#### 4. Conclusions

The corrosion of GaN/AlGaN p-n structures performs through the top p-type layers via channels associated with threading defects and can penetrate deep into the structure. Then, the corrosion process occurs in lateral direction in n-type layers forming voids and cavities in the structure. The lateral etching is due to net positive charges at the AlGaN/GaN interfaces arising because of spontaneous and piezoelectric polarization in the structure and positively charged ionized donors in the space charge region of the p-n junction.

#### Acknowledgements

Work at University ITMO was supported by the Ministry of Education and Science of Russian Federation (grant agreement 14.575.21.0054, unique identifier of research activities is RFMEFI57514X0054).

#### References

- [1] Ohkawa K, Ohara W, Uchida D, and Deura M 2013 *Japan. J. Appl. Phys.* **52**08JH04.
- [2] Aryal K, Pantha B N, Li J, Lin J Y and Jiang H X 2010 *Appl. Phys. Lett.* **96** 052110- 1-3.
- [3] Wolff N, Rapp M and Rotter T 2005 *Phys. Status Solidi C* **2** 990–993.
- [4] Usikov A S, Tsvetkov D V, Mastro M A, Pechnikov A I, Soukhoveev V A, Shapovalova Y V, Kovalenkov O V, Dmitriev V A, O'Meara B, Gurevich S A, Arakcheeva E M, Zakhgeim A and Helava H 2003 *Phys. Status Solidi C* **0** 2265-2269.
- [5] Kurin S, Antipov A, Barash I, Roenkov A, Usikov A, Helava H, Ratnikov V, Shmidt N, Sakharov A, Tarasov S, Menkovich E, Lamkin I, Papchenko B and Makarov Yu 2014 *Phys. Status Solidi C* **11** 813-816.
- [6] Shmidt N, Shabunina E, Usikov A, Chernyakov A, Kurin S, Helava H and Makarov Yu 2015 *Phys. Status Solidi C* **12** 1136-1139.
- [7] Zhuang D and Edgar J H 2005 *Mat. Sci. and Eng. Rep.* **R48** 1-46.
- [8] Macht L, Kelly J J, Weyher J L, Grzegorzczak A and Larsen P K 2005 *J. Cryst. Growth* **273** 347-356.
- [9] Mishra U K, Parikh P and Wu Y F 2002 *Proc. IEEE* **90** 1022-103.