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Etching of GaN layers at electrolysis under UV-irradiation

T K Zubenko¹, M V Puzyk^{1,2}, V M Stozharov¹, I A Ermakov², D S Kovalev², S A Ivanova², A S Usikov^{2,3}, O S Medvedev⁴, B P Papchenko², S Yu Kurin⁵, A A Antipov⁵ and A E Chernyakov⁶

¹ Herzen University, Nab.r.Moyki 48, St.Petersburg 194186, Russia

² University ITMO, Kronverkskiy pr. 49, St.Petersburg 197101, Russia

³ Nitride Crystals Inc., 181 E Industry Court, Suite B, Deer Park, NY 11729, USA

⁴ St. Petersburg State University, St. Petersburg, Russia

⁵ Nitride Crystals Group, Ltd., pr. Engel'sa 27, St. Petersburg 194156, Russia

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

E-mail: zubenko_1993@bk.ru

Abstract. Etching of the GaN layers in 1M KOH aqua solution under irradiation was studied by the electro-stimulated photolysis using N₂-laser (337 nm, 60 W/m²) as a light source. It was observed that the size and the depth of the failure monotonically depend on the optical power and the irradiation time of the N₂ laser and the GaN layer type of conductivity. The GaN layers etching rate was evaluated. A mechanism of the failure in the n-GaN layers is discussed.

1. Introduction

GaN is wide band-gap semiconductor for application in prospective power electronic devices that require rapid charge carrier transport and high breakdown voltage. Because of the chemical resistance to aggressive environment and the large energy gap ($E_g = 3.43$ eV), GaN is also intensively studied as a base material to be use as working electrode at the water photoelectrolysis to produce molecular hydrogen, a candidate for clean, non-polluting energy storage [1-4].

In the last few years, appreciable rate of hydrogen generation at the water photoelectrolysis (0.37 - 1.44 ml/cm² × h) was demonstrated using working anode electrode based on n-GaN and n-GaN/n-InGaN structures [5]. However, systematic studies of the GaN-anode stability were not carried out. In this work we performed investigation of failure in the GaN layers immersed in 1M KOH aqua solution under UV irradiation using N₂-laser (337 nm, 60 W/m²) as a light source. Portion of the UV light in the solar spectrum is about 3%. However these experiments allow making clear a mechanism of the GaN failure in the electrolyte to prevent the electrode corrosion in real photo-electrochemical cells.

2. Experimental

Hydride vapor phase epitaxy (HVPE) was used to grow 5-10 μm thick GaN layers on c-plane 2-inch sapphire substrates. Undoped and Si-doped GaN layers had net donor concentration ($N_D - N_A$) measured by C-V method of $(1-5) \times 10^{16}$ cm⁻³ and $(1-2) \times 10^{18}$ cm⁻³, respectively. The sapphire substrate orientation allows breaking the 2-inch sample into near equal six sectors having an area of about 3 cm². The sectors



were used for contacts deposition and electrodes producing. The contacts were protected by a chemical resistant varnish.

Diffuse reflectance spectrum of n-GaN is obtained on the Shimadzu UV 2400 spectrophotometer.

The electro-stimulated photolysis (scheme in figure 1) was carried out in a quartz cuvette in 1.0 M aqueous KOH using an external power source (Mastech DS POWER SUPPLY HY 3010E), GaN working electrode (anode) and the Pt plate as the counter electrode (cathode). The current from the power source was 0.5 mA in all experiments. N₂-laser (LGI-21-type, 337 nm, 100 Hz, 60 W/m²) was used as a light source.

After experiments, the samples were cleaved and their surface morphology were examined in both top-view and cross-sectional configurations by high-resolution scanning electron microscopy (SEM)

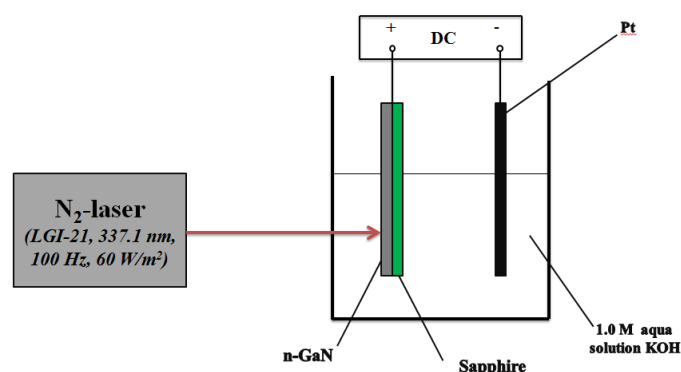


Figure 1. Experimental set-up.

3. Results and discussion

As seen in figure 2, a n-GaN effectively absorbs short-wave radiation up to 352 nm. Therefore, in a nitrogen laser was chosen as the radiation source.

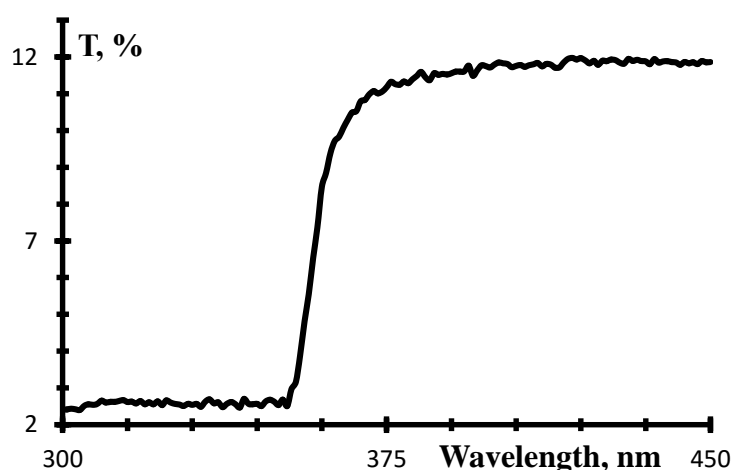


Figure 2. Diffuse reflectance spectrum of n-GaN.

The GaN failures under the laser illumination had a circular spot of a ~2.5 mm in diameter (figure 3a). Honeycombs-like defects of the GaN layer surface in the spot area seems to be due to specific of the etching process in the mosaic (domain) structure attributed to the III-N materials and to HVPE-grown GaN layers in particular (figure 3b).

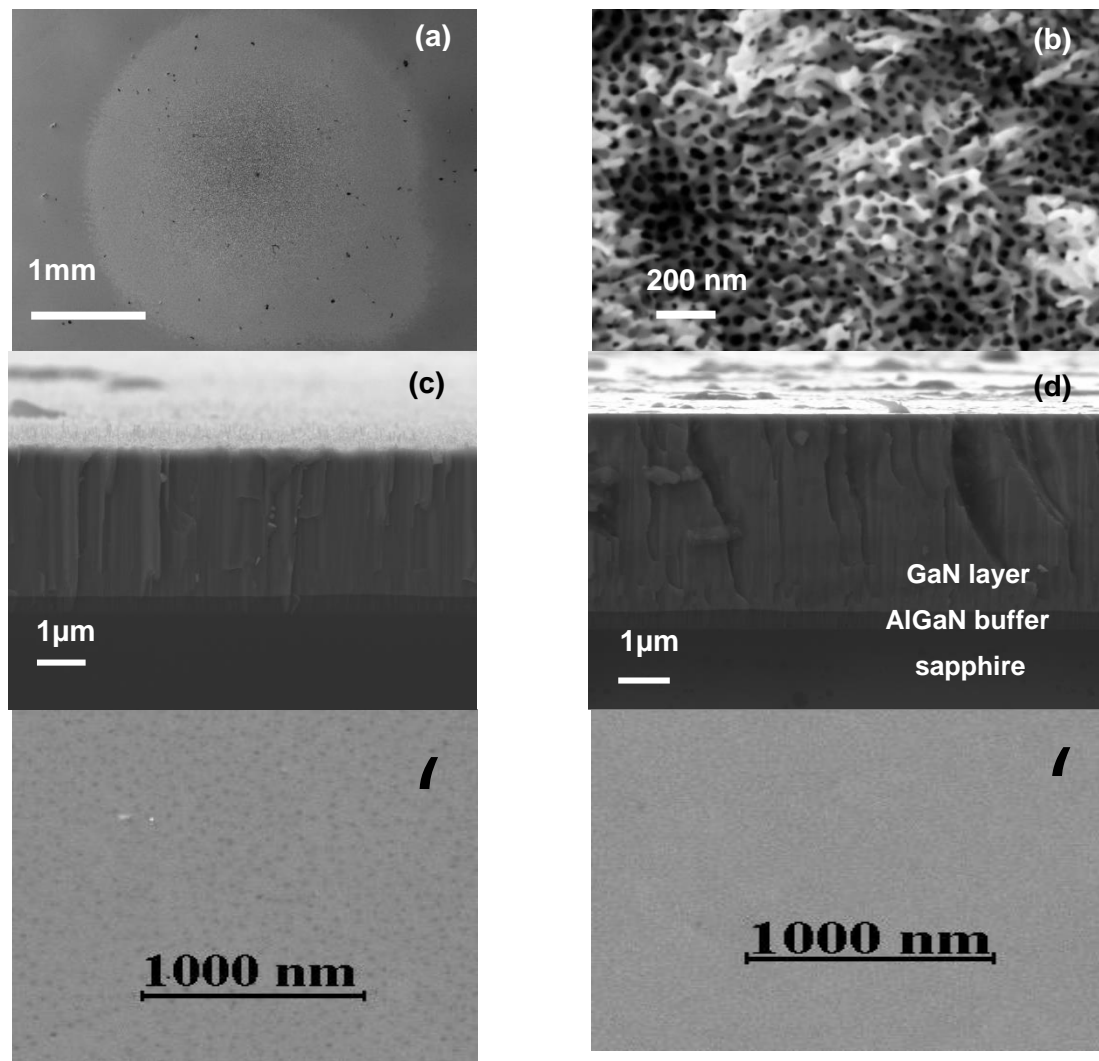


Figure 3 (a-f). SEM images of a GaN sample ($N_D-N_A = 1 \times 10^{18} \text{cm}^{-3}$) after the electro-stimulated photolysis. (a) The spot on the GaN surface. (b) Over etched GaN surface in the spot under higher magnification after a 40-min experiment. (c) Cross-sectional view of the sample in the spot area after a 40-min experiment. The GaN layer thickness is $6.9 \mu\text{m}$. (d) Cross-sectional view of the sample in unetched area. The GaN layer thickness is $9 \mu\text{m}$. (e-f) Produced nanodefects on the GaN-surface at a distance of 2 mm (e) and 5 mm (f) from the spot.

To determine the depth of the photodestruction of the samples were studied from the end (in the area of exposure and beyond figure 3 c-d, respectively).

The etching process may have a preferable way at the domain boundaries. Formation of nanodefects due to the scattered light is observed exposure spot at a distance of 2 mm and 5 mm (figure 3 e-f, respectively). The farther from the spot was, the smaller the formed nanodefects.

In the KOH aqua solution the n- GaN layers underwent etching with an average speed of 46 nm/min (figure 4). The photolysis process with n-GaN electrodes depended on the doping and electrolyte concentration and type and had the max effect at $\sim 0.75 \text{M KOH}$ and $N_D-N_A = (3-5) \times 10^{18} \text{cm}^{-3}$. Photo-destruction of low-alloy specimens n-GaN ($N_D-N_A < n \times 10^{18} \text{cm}^{-3}$) absent. This fact may be useful for creating electrode gallium nitride for splitting water under the influence of UV-light.

The most likely equation describing the processes in the alkaline environment (pH=14) for n-GaN layers may be as follow: $2 \text{ GaN} + 8 \text{ OH}^- = 2 [\text{Ga}(\text{OH})_4]^- + \text{N}_2\uparrow$. About excreted nitrogen indicates a small amount of gas bubbles formed on the illuminated part of the anode.

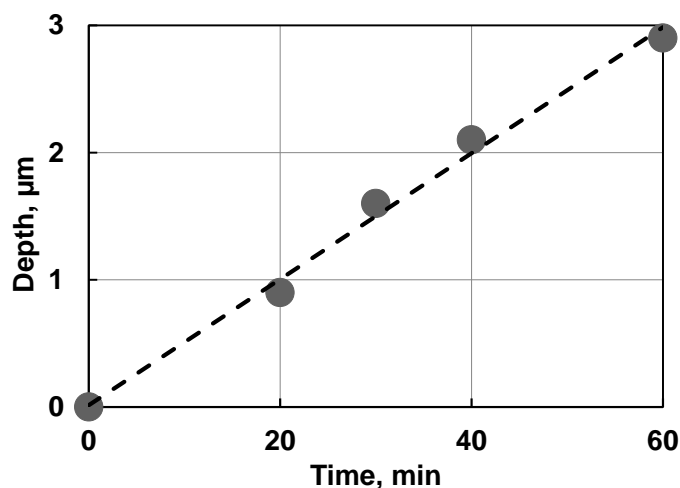


Figure 4. The dependence of the failure depth in n-GaN layer ($N_D - N_A = 1 \times 10^{18} \text{ cm}^{-3}$) vs. the irradiation time by the N_2 laser. Dashed line is a linear approximation.

4. Conclusions

For the first time held a photo-electro-stimulated destruction of high n-GaN-samples grown by HVPE. Experimentally established linear relationship depth photo-electro-etching n-GaN on the time of UV irradiation.

Acknowledgments

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