Application of GaN for photoelectrolysis of water

M V Puzyk[1], A S Usikov[2,3], S Yu Kurin[4], A M Puzyk[1], A D Fomichev[2], I A Ermakov[2], D S Kovalev[2], B P Papchenko[2], H Helava[3], and Yu N Makarov[3,4]

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

E-mail: puzyk@mail.ru

Abstract. GaN layers of n-type and p-type conductivity grown by HVPE on sapphire substrates were used as working electrodes for water electrolysis, photoelectrolysis and hydrogen gas generation. Specifically the water splitting process is discussed. Corrosion of the GaN materials is also considered. The hydrogen production rate under 365-nm UV LED irradiation of the GaN and external bias was 0.3 ml/(cm^2*h) for an n-GaN photoanode (n~8×10^{16} cm^{-3}) in 1M Na_2SO_4 electrolyte and 1.2 ml/(cm^2*h) for an n-GaN photoanode (n~1×10^{17} cm^{-3}) in 1M KOH electrolyte.

1. Introduction

At present, several basic technologies are used for the production of hydrogen: the conversion of methane, technologies for converting biomass into valuable fuel, and the decomposition of water. Semiconductor material immersed in an aqueous solution of electrolyte allows decomposition of water into molecular hydrogen and oxygen by solar irradiation of its surface. The required energy to split water molecule is generated by sunlight absorption in the semiconductor. This method of H2 generation is a simple, low-energy consumption, carbon-free technology not demanding high temperatures and pressure. Another key benefit of this process is the high purity of the output hydrogen gas stream, an important requirement for its use in fuel cells.

The solar water splitting process may be spontaneous under illumination if the electrochemical redox potentials of the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER) in an electrolyte are bracketed by the energy gap of a semiconductor [1]. This is fulfilled for GaN and InGaN materials [2]. A generic diagram of photoelectrochemical water splitting using n-type GaN material and an alkaline electrolyte is given in figure 1. The absorption of solar photons in a semiconductor material forms excited electron–hole pairs that are split by a specific band-bending at the GaN electrode (anode)/electrolyte interface. The band-bending is due to the establishment of an equilibrium between the n-GaN material and the electrolyte. Excited electrons coming to the cathode through an external circuit take place in HER that gives ions of OH^- (anion) and molecules of H_2. The anions come to the GaN-anode to participate with exited holes leaving the semiconductor in OER that gives molecules O_2 and H_2O.

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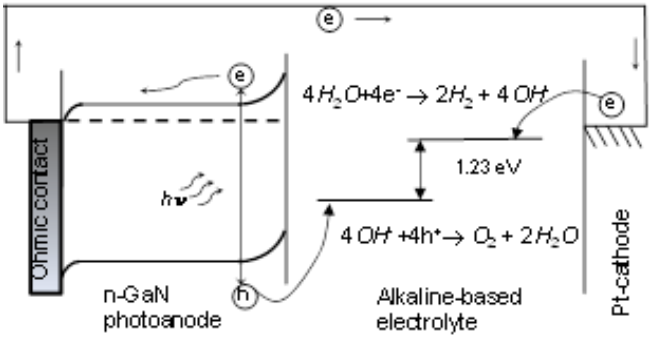

Figure 1. Schematic diagram showing photoelectrochemical water splitting using p-type GaN as a working electrode (photocathode).

In this work we report on first results of electrolysis and photoectrolysis of water using different electrolytes and n-type and p-type GaN layers as working electrodes (anodes or cathodes). GaN layers and multilayer structures were grown on sapphire substrates by chloride hydride vapor phase epitaxy.

2. Experimental

5-7 μm thick GaN layers and AlGaN/GaN p-n structures were grown by chloride hydride vapor phase epitaxy (HVPE) on c-plane 2-inch sapphire substrates. The growth procedure included in-situ sapphire substrate treatment and an AlN/AlGaN (x~ 0.6) buffer layer deposition followed by GaN or AlGaN/GaN multilayer p-n structure growth. Details of the structure growth and characterization can be found elsewhere [3].

The energetics of hydrogen reduction in water solutions of various pH-electrolytes using GaN-based working electrodes were evaluated under conditions of external electrical power and solar irradiation. Sulfuric acid (pH=1), sodium sulfate (pH=7) and potassium hydroxide (pH=14) were used as the electrolyte.

The sapphire substrate orientation made it possible to cut a 2-inch wafer into six sectors (plates). These sectors were used for contact deposition on selected areas of the plates and electrode preparation. As contacts, Ti/Ni/Au or Ni/Au thin films were evaporated on select areas of the p- or n-type GaN layer, respectively. Wire welding completed the electrode fabrication. The contact pads and contact wire were protected by chemical-resistant varnish (wax).

3. Results and discussion

First, the over potential on GaN working electrodes needed for H_2 generation was measured using different aqua electrolytes and an external power source. The aqueous contact area of the GaN electrode was about 2.5-3 cm^2. A Pt plate (4 cm^2) was used as the counter-electrode. The reference electrode was made of Ag/AgCl/KCl (potassium-chloride-saturated silver-chloride electrode). The potential of hydrogen reduction at the GaN electrode (Na_2SO_4-based electrolyte, pH=7) was -0.80 V that is -0.40 V lower (over potential) than that at the Pt electrode. The over potentials measured on GaN electrodes in other electrolytes were -0.4 V (H_2SO_4, pH=1) and -1.20 V (KOH, pH=14). The over potentials could be due to a potential barrier for carriers on the GaN/electrolyte interface, higher specific resistivity and worse current spreading on the GaN electrode. Optimization of the GaN electrode contact configuration is required.

Then, the effectiveness of water electrolysis with GaN working electrodes to produce one milliliter of hydrogen was studied. Figure 2 shows the I-V (V-I) characteristics and energy consumption in relation to the type of electrolyte and the electrolyte concentration. Graduated tube was used to collect generated hydrogen. I-V characteristics showed linear dependencies with various slopes that are in line with different resistivity of GaN electrodes and the electrolyte.

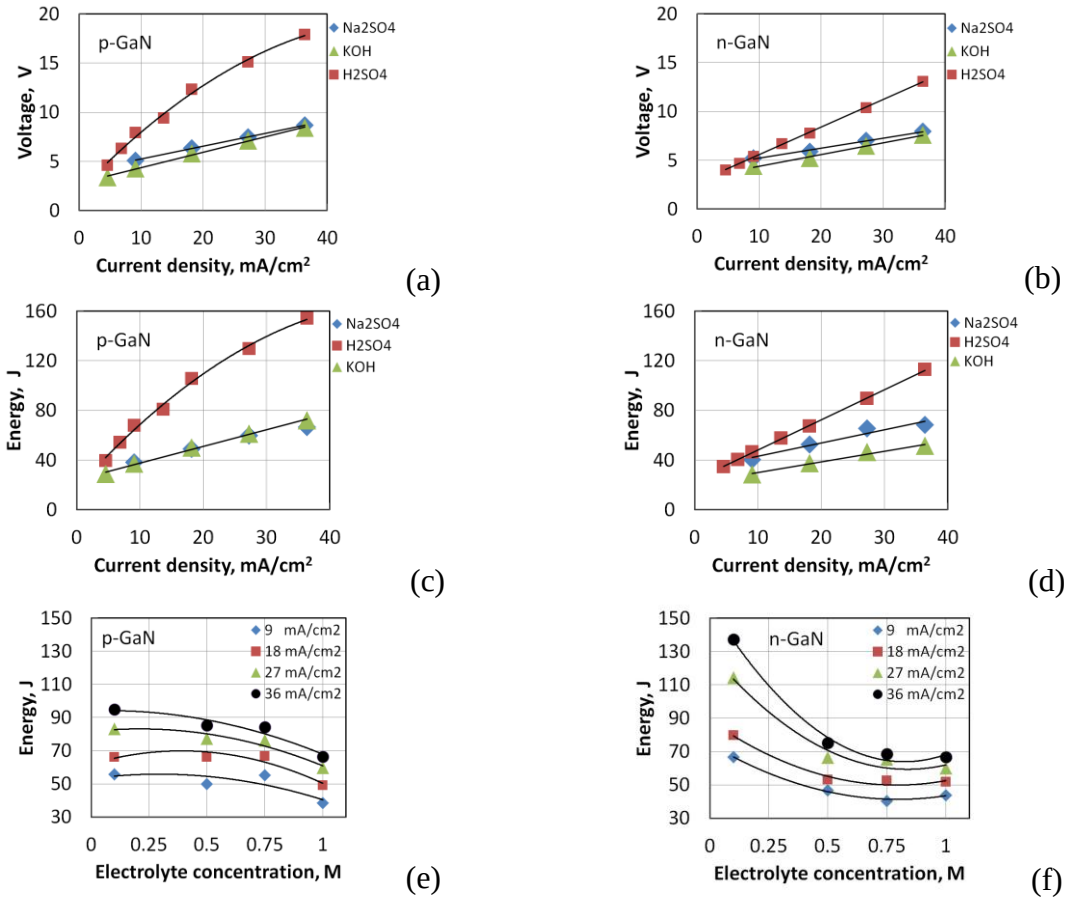

Figure 2. I-V characteristics (a, b) and energetics of a 1 ml H_2 generation (c, d, e, f) using n-GaN and p-GaN working electrodes (as cathode), different 1.0 M-aqua electrolytes (a, b, c, d) and different concentration of Na_2SO_4-based electrolytes (c, d).

Energy consumption in Joules (J) was evaluated based on I-V characteristic and a time needed to generate 1 ml of hydrogen. The water electrolysis took place with lower energy consumption for n-GaN and p-GaN electrodes in the alkaline electrolyte (pH=14). Opposite to that, the process is more energy-consuming for n-GaN electrodes in sodium sulfate (pH =7) electrolyte at lower electrolyte concentration and higher currents (figure 2 c, d). The energy consumption showed sublinear dependencies that demonstrate a band bending effect at the GaN electrode surface that creates an energy barrier in n-GaN to be overcome by electrons in order to participate in the redox reactions in the electrolyte (figure 2 e, f). It seems that the polarity of the external bias (+2.5 - +5 V on the GaN cathode to begin H_2 generation) was a driving force to form an additional barrier for electrons at the interface the n-GaN electrode/electrolyte and to reduce the barrier at the p-GaN electrode surface. At high concentration of electrolyte and high current the band bending effectively becomes lower and overall energy consumption for the process on the n-GaN electrode is somewhat lower than at the p-GaN electrode due to higher carrier mobility and better current spreading in the n-GaN material.

Experiments on water photoelectrolysis were performed under irradiation by 365-nm UV LED and with external power source. Optical power of the UV LED was of 16 mW that corresponds to a concentration factor of ~20x in comparison to the AM1.5-Global standard spectrum of solar radiation in the UV spectral range. Hydrogen generation was observed on Pt cathode using n-GaN as the photoanode. It started at low potential values depending on pH of the electrolyte. n-GaN layers were found to be electrochemically inactive (no corrosion) at potentials from -1.5 V to +1.5 V in all

aqueous electrolytes applied in this work. Oxygen generation on the p-GaN anode began at potential more than +2 V (hydrogen was observed on Pt-counter electrode in this case) and accompanied by the p-GaN electrode corrosion. Under UV LED irradiation and with external bias of + 2.5- +3.0 V photocurrent (I_{photo}) was in a range of 3-7 mA/cm^2 and sufficient for hydrogen evolution.

The hydrogen production rate was as high as 0.3 ml/(cm^2*h) for the n-GaN photoanode (n~8×10^{16} cm^{-3}) in 1M Na_2SO_4 electrolyte (UV LED irradiation and +2.5- +3.0 V of external bias). Under the similar conditions using an other n-GaN photoanode (n~1×10^{17} cm^{-3}) in 1M KOH electrolyte, the hydrogen production rate was as high as 1.2 ml/(cm^2*h). These values compare to those from GaN with NiO catalyst (no external bias, Xe lamp irradiation, 0.37 ml/(cm^2*h)) [4], n-$In_{0.18}Ga_{0.82}N$ photoanode (with external bias, Xe lamp irradiation, 1.44 ml/(cm^2*h), and p-n $GaInP_2$/GaAs double electrode (no bias, 5 suns, 1.1 ml/(cm^2*h).

The experiments have shown that the doping and crystalline qualities of the GaN electrodes need to be optimized. A surface passivation and (or) catalyst application are required to increase the hydrogen production rate and diminish the GaN electrode corrosion. Utilizing GaN/InGaN structures as working electrodes may improve hydrogen evolution by effectively absorbing a larger portion of the solar spectrum.

4. Conclusions

In this paper we report on comparative studies of electrolysis and photoectrolysis of water using different electrolytes and n-type and p-type HVPE-grown GaN layers as working electrodes (anodes or cathodes). GaN layers and multilayer structures were grown on sapphire substrates by chloride hydride vapor phase epitaxy.

Potential of hydrogen reduction at the GaN electrode (Na_2SO_4-based electrolyte, pH=7) was -0.80 V that is -0.40 V lower (over potential) than that at the Pt electrode. The over potentials measured on GaN electrode in other electrolytes were -0.4 V (H_2SO_4, pH=1) and -1.20 V (KOH, pH=14). The lowest energy of hydrogen generation was observed in 0.5 M-1.0 KOH electrolyte.

Corrosion of the GaN working electrode used as a cathode was not observed. Obvious corrosion was observed on GaN-anode electrodes.

Hydrogen generation at n-GaN cathode started at low external bias values depending on pH of the electrolyte. The hydrogen production rate was as high as 0.3 ml/(cm^2*h) for n-GaN photoanode (n~8×10^{16} cm^{-3}) in 1M Na_2SO_4 electrolyte (UV LED irradiation and +2.5- +3.0 V of external bias) and 1.2 ml/(cm^2*h) n-GaN photoanode (n~1×10^{17} cm^{-3}) in 1M KOH electrolyte.

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