Measurements of AlGaN/GaN heterostructures for sensor applications

Mikołaj Ryszard Hojko, Dorota Paszuk, Bogdan Paszkiewicz[*]

Faculty of Microsystem Electronics and Photonics, Wrocław University of Technology,
ul. Janiszewskiego 11/17, 50-372 Wrocław, Poland

[*]Corresponding author: bogdan.paszkiewicz@pwr.wroc.pl

In the paper, the behavior of AlGaN/GaN HEMT-type heterostructures in a water solution of (KOH + HCl) with differing pH was studied. The influence of the electrolyte pH on channel pinch-off voltage was measured using impedance spectroscopy methods. It was observed that the change of the pH of electrolyte has a strong effect on the pinch-off voltage of AlGaN/GaN HEMT-type heterostructures independently of the concentration of other ions. In high-pH environment the so-called memory effect of heterostructures was revealed. Its possible origin was discussed. A general theory to explain all results was proposed.

Keywords: sensor, AlGaN/GaN heterostructure, electrolyte, two-dimensional electron gas (2DEG), pH.

1. Introduction

In recent years, bio- and chemical sensors have been in rapid development. Many material systems can be applied for transducers fabrication, from silicon to compound semiconductors such as arsenides or phosphorides. AlGaN/GaN heterostructures are more promising. Among their numerous advantages are: high resistance to temperature, to chemicals and to mechanical damage.

The high sensitivity of the AlGaN/GaN heterostructure-based sensors is caused by the presence of a two-dimensional electron gas (2DEG) formed on the heterointerface. The distribution of charges in the heterostructure results in the formation of a quantum well on the GaN/AlGaN junction, where 2DEG can effectively conduct electrical current even without intentional doping of the AlGaN layer. The most important feature of this heterostructure is that the 2DEG is very sensitive to any change on the surface of heterostructure. This results in the capacity to detect even small changes in the concentration of detected chemicals.

Many semiconductor-based sensors have already been designed and fabricated. However, sensors based on silicon, which are the ones most widely used, are unsuit-

able for many applications. They are especially inappropriate as chemical sensors or pH sensors because of their insufficient chemical stability [1–3]. It is likely that nitride-based sensors will not share this failing.

2. Experiment

All experiments were conducted using impedance spectroscopy methods. A specialized Teflon electrolyte cell, connected with a PC-driven Picotest M3500A voltmeter and an HP 4192A impedance analyzer, was used to form the electrolyte/heterostructures interface. The HEMT-type AlGaN/GaN/sapphire heterostructures, grown by MOVPE technique, were used as a pH sensing electrode.

The influence of the solution pH on channel pinch-off voltage was examined. Such dependence gives information about the pinch-off voltage change in different fluids, which is caused by the interaction of an AlGaN layer with certain particles in the electrolyte. Samples with different thicknesses of the AlGaN layer and differing Al concentration were selected for analysis.

Measurements were conducted while changing the pH value of the electrolyte in order to determine how pinch-off voltage changes with pH value. Three sets of experiments were performed. In the first one, the mixtures of HCl and KOH were used [4, 5] to test the influence of the H^+ and OH^- ions on the channel pinch-off voltage. Another set of experiments was conducted in a pure water solution of KCl of different concentrations. It was designed to test the channel pinch-off voltage dependency vs. K^+ and Cl^- ions concentrations. The last set of experiments was designed to test deoxidant properties of NH_4Cl. It could be possible to use the compound to remove oxygen bridges formed on the surface of heterostructure in contact with solutions with high pH.

3. Results

The strong dependence of the pinch-off voltage of the AlGaN/GaN HEMT-type heterostructure on the pH value is shown in Fig. 1. It was observed that this dependence was linear for some samples (see sample 011), while for others it had a more complicated form (see sample 029). Additionally, the dependence of the pinch-off voltage of the AlGaN/GaN HEMT vs. pH for some samples (*e.g.*, sample 061 and sample 064) was strongly affected by the "memory effect" caused by dipping in high-pH electrolytes; the same effect was much smaller for the other two samples.

We also observed that the KCl concentration in the solution had no effect on the pinch-off voltage of the channel of the AlGaN/GaN heterostructure. This remained the same for a wide range of KCl concentrations, indicating no changes in surface states of the sample. The results are shown in Fig. 2.

Figure 3 schematically illustrates the experiment undertaken to counter the "memory effect" that high-pH solutions had on AlGaN/GaN heterostructures. We found that the ammonia chloride was useful for restoring the starting state of the AlGaN/GaN
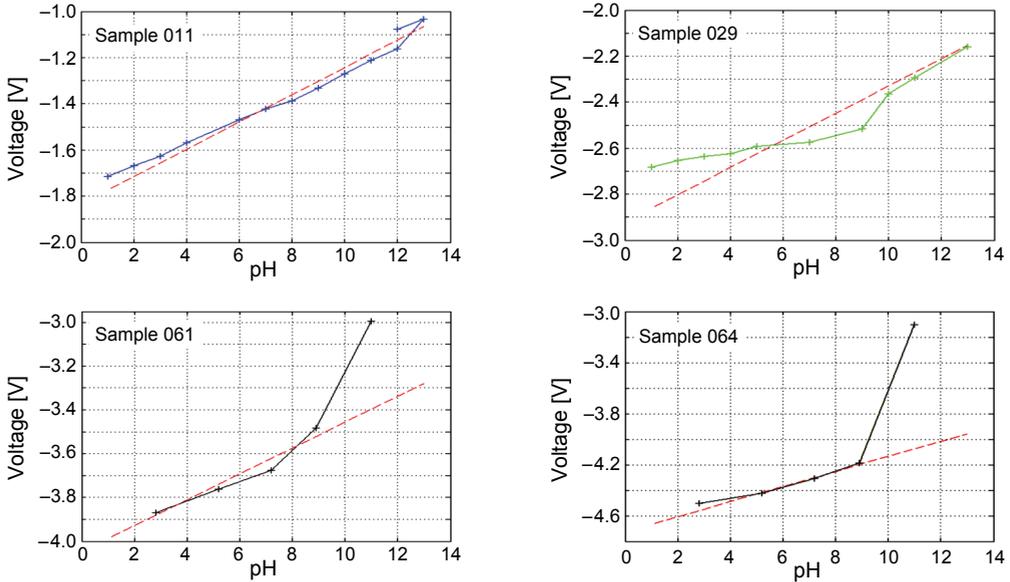
▲
Fig. 1. Plot of pinch-off voltage dependence on pH values. The dashed line in all graphs shows the theoretical dependence derived from the Nernst equation.
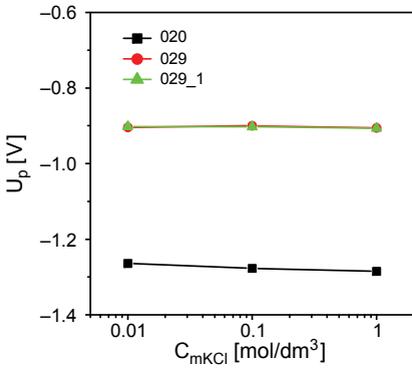
◄ Fig. 2. The pinch-off voltage dependence vs. KCl concentration in electrolyte.
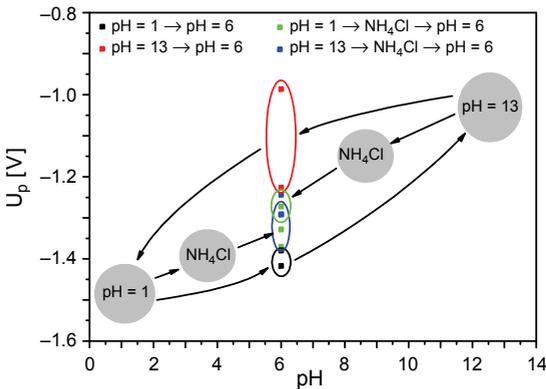
◄ Fig. 3. Schematic illustration of the observed "memory effect" for AlGaN/GaN heterostructures.

heterostructure surface, but a stronger deoxidizing agent would be needed to fully restore the surface to its starting, non-oxidized state.

4. Discussion and conclusions

The obtained results clearly show that the pinch-off voltage of HEMT-type AlGaN/GaN heterostructures is influenced by the pH of the electrolyte. But not every type of ion can change the properties of 2DEG. We conclude that the OH-groups can bind to the surface, lowering its positive electrical charge and therefore depleting the 2DEG.

In solutions with higher concentration of OH-groups, and therefore with higher pH, more and more termination sites can be occupied by OH-groups. The chemical binds are formed between Ga or Al atoms, terminating the surface, and O atoms in OH-groups. This process was reversible in electrolytes with moderate pH values, where the "memory effect" in AlGaN/GaN heterostructure was not observed.

The "memory effect" manifests itself in the persistent change of pinch-off voltage. In order to explain this phenomenon, the theory was proposed that, when most of the termination sites of the crystal are occupied by OH-groups and there remains a high quantity of OH-groups in the electrolyte, the Al atoms can break some of the Al–N bonds and form additional Al–O bonds. Those cannot be broken so easily, and a strong deoxidizing agent is needed to restore the surface to its original state.

AlGaN bonding with oxygen can be used to fabricate very sensitive and selective sensors by bonding different molecules to the surface. At the same time, AlGaN/GaN HEMT heterostructures are not a good choice for fabricating pH-sensors, aside from specific applications where the range of pH values is relatively low – for instance, in medicine.

References

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