*p*H response of GaN surfaces and its application for *p*H-sensitive field-effect transistors

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The *p*H-sensitivity of GaN surfaces in electrolyte solutions has been determined. For this purpose, GaN field-effect transistors and AlGaN/GaN high-electron-mobility transistor (HEMT) structures were used to measure the response of nonmetallized GaN gate regions to changes of the H⁺-concentration in an ambient electrolyte. We found a linear response to changes in the *p*H between pH=2 and pH=12 for both as-deposited and thermally oxidized GaN surfaces. Both surfaces showed an almost Nernstian behavior with sensitivities of 57.3 mV/*p*H for GaN:Si/GaN:Mg and 56.0 mV/*p*H for GaN/AlGaN/GaN HEMT structures. This suggests that the native metal oxide on the III-nitride surface is responsible for *p*H-sensitivity. The investigated devices showed stable operation with a resolution better than 0.05 *p*H over the entire *p*H range. © 2003 American Institute of Physics. [DOI: 10.1063/1.1589188]

Since the first report of an ion-sensitive field-effect transistor (ISFET) based on a Si n-channel transistor with a SiO₂ gate layer by Bergveld,^{1,2} the understanding and improvement of ISFETs operating as pH sensors³ or detectors for biochemical processes^{2,4-6} in aqueous solutions has been a subject of intense research. Apart from SiO₂ gate layers, which show low response and poor stability, other inorganic gate materials, such as Si_3N_4 , Al_2O_3 ,^{4,5,7} or Ta_2O_5 ,⁸ have been investigated, resulting in substantial improvement of both stability and sensitivity. Transistor structures based on GaN or AlGaN/GaN heterostructures grown on sapphire substrates can easily provide metal oxide gate layers and can benefit from the high chemical stability of the III-nitrides. Due to the optical transparency of both the thin semiconducting film and the sapphire substrate, GaN-based ISFETs allow simultaneous electronic and microscopic detection of processes on the device surface in biophysical and biochemical applications. Although some work on III-nitride-based chemical sensors has been done recently,^{9,10} the ion sensitivity of GaN surfaces in aqueous solutions has not been systematically investigated so far.

In this work, we have studied the electrical response of as-deposited and thermally oxidized GaN surfaces to variations of the H⁺ concentration in electrolyte solutions. As a readout device for the ion-induced changes of the surface potential, we have used transistor structures based on GaN:Si/GaN:Mg double layers and AlGaN/GaN heterostructures. GaN:Si/GaN:Mg field-effect transistors and AlGaN/ GaN high electron mobility transistor (HEMT) structures were grown by plasma-induced molecular beam epitaxy (PIMBE), as described in detail elsewhere.^{11,12}

The sample structures are shown in Fig. 1. Samples A and B consist of a 60-nm-thick Si-doped GaN channel grown on a 1.5- μ m-thick GaN buffer layer with N-face polarity. The latter was partially compensated with Mg to achieve a high resistivity compared to the thin Si-doped channel close to the surface. The carrier densities at room temperature were 3×10^{18} cm⁻³ in the Si-doped top layer and 5×10^{15} cm⁻³ in the Mg-compensated layer, as determined by C-V measurements. Sample B was thermally oxidized in dry oxygen at 700 °C for 2 h, leading to the formation of a thin Ga_rO_v layer, as observed by x-ray photoemission spectroscopy (XPS) measurements.¹³ XPS analysis of as-deposited GaN surfaces via the surface sensitive Ga 2p and the O1s core level spectra also revealed the almost immediate formation of a thin surface oxide after exposure to atmosphere. Similar results have been reported by other groups.¹⁴

The AlGaN barrier of the HEMT structure (sample C) had an Al content of 28% and a thickness of 35 nm. The two-dimensional electron gas (2DEG) carrier density was determined to $n_{2\text{DEG}}=6.1\times10^{12}$ cm⁻² by C-V measurements. Deposition of an additional 3-nm GaN cap layer on top of the AlGaN barrier allowed the comparison of similar sur-



FIG. 1. Schematic layout of the investigated transitor structures. All samples were grown by PIMBE. The surface of sample B was thermally oxidized at 700 $^\circ$ C for 2 h.

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FIG. 2. Dependence of the channel current I_{DS} on the gate voltage V_G . I_{DS} was normalized to drain-source current at $V_G = 0$ mV.

faces on different readout devices (samples A and C), whereas the sensitivity of different surfaces on equal device structures was analyzed by comparison of samples A and B. For electrical characterization in aqueous solutions, the potential V_G of the electrolyte gate with respect to the source contact was adjusted via an Ag/AgCl reference electrode by a potentiostat. All measurements were performed in a 100-mM NaCl/10-mM Hepes solution, titrated with diluted NaOH or HCl for pH adjustment. The pH of the solution was measured with a digital pH-meter (WTW pH90) with a precision of $\pm 0.01 \text{ pH}$ after calibration with standard buffer solutions. All measurements were carried out in the dark at a constant temperature of 23 °C to avoid parasitic effects.¹⁵ The electrolyte solution was mechanically stirred to ensure homogeneous ion concentration in the electrolyte and a constant flow to the gate surface. Figure 2 shows the drainsource current, $I_{\rm DS}$, normalized to $I_{\rm DS}$ at $V_G = 0$, as a function of the gate potential V_G for a drain-source voltage V_{DS} of 250 mV and pH 5.3 for all investigated devices. These $I_{\rm DS}$ versus V_G curves have exhibited a high reproducibility without hysteresis during cyclic measurements. Therefore, it can be concluded that the device surfaces are chemically stable in the investigated gate voltage range ($V_G < 500 \text{ mV}$).

The chemical response of the gate surface to changes in the electrolyte composition was measured by adjusting the gate potential V_G via the Ag/AgCl reference electrode in such a way, that the ion-induced changes in the channel current $I_{\rm DS}$ at constant $V_{\rm DS}$ were compensated. For these measurement conditions, the *p*H-dependent change in the gate voltage (ΔV_G) is a direct measure for the potential change at the GaN/electrolyte interface.

Figure 3 shows the interface potential charge as a function of *p*H for the three investigated samples. A linear behavior over the entire investigated range from *p*H 2 to 12 is observed and a sensitivity of 57.3, 56.6, and 56.0 mV/*p*H \pm 0.5 mV/*p*H was measured for structures A, B, and C, respectively. These sensitivities are close to the Nernstian response to H⁺ ions, which is 58.7 mV/*p*H at 23 °C. Identical surface layers on different device structures (samples A and C) lead to almost identical sensitivities, demonstrating that the *p*H response is a pure surface effect. As surfaces with native oxide and thermally oxidized samples showed almost



FIG. 3. Variation at the GaN/electrolyte and Ga_xO_y /electrolyte interface potential as a function of *p*H. For clarity the datasets are shifted by a constant potential offset.

no difference in sensitivity, we assume that a Ga_xO_y surface layer is responsible for the observed behavior in both cases.

The *p*H response of metal oxide surfaces has been explained in terms of the site-binding model by Yates *et al.*,¹⁶ first applied to ISFETs by Siu and Cobbold,¹⁷ and further developed by Bousse *et al.*¹⁸ and Fung *et al.*¹⁹ According to this model, amphoteric hydroxyl groups are formed at oxidic surfaces in contact with aqueous solutions. These hydroxyl groups may be neutral, protonized, or deprotonized, depending on the H⁺ concentration and the equilibrium constants for the relevant dissociation reactions, and therefore lead to a *p*H-dependent net surface charge and an additional voltage drop at the solid/liquid interface.

To investigate the transient behavior of the GaN-based ISFET devices, we performed time-resolved measurements of the drain-source current for $V_{\rm DS}=250$ mV and V_G = 0 mV. The *p*H of the electrolyte was changed in steps between 0.1 and 0.3 *p*H by titration with diluted NaOH every 30 s. The results of these measurements for samples B and C are displayed in Fig. 4. In contrast to reported delay times of some seconds for SiO₂ gate ISFETs,¹⁹ all investigated GaN-based devices showed immediate response to changes in the *p*H. As expected from the $I_{\rm DS}/V_G$ characteristics shown in Fig. 2, the relative change of the channel



FIG. 4. Transient behavior of the source–drain current $I_{\rm DS}$ during changes of the electrolyte *p*H by titration with NaOH. $V_{\rm DS}$ and V_G were kept constant at $V_{\rm DS}$ =250 mV and V_G =0 mV. Numbers correspond to *p*H values measured with a calibrated *p*H meter.

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current, $\Delta I_{\rm DS}/I_{\rm DS}$ in the GaN/AlGaN/GaN HEMT structure is larger than for the GaN:Si-channel device. We estimate a resolution of 0.05 *p*H for the HEMT structure and of 0.1 *p*H for the other two devices. However, the investigated structures have not been optimized for ISFET applications. An enhanced transconductance due to a larger channel width to length ratio or optimization of other important device parameters, such as barrier thickness, doping concentration, and layer thicknesses, is likely to further improve the device resolution.

In conclusion, we have shown that native and thermally oxidized GaN layers feature a linear, nearly Nernstian pH response of about 56 mV/pH in aqueous solutions, both for GaN:Si/GaN:Mg and GaN/AlGaN/GaN ISFET devices. Nonoptimized ISFETs already provide stable operation in the range from pH 2 to 12 with a resolution better than 0.05 pH.

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