

Investigation of AlInN barrier ISFET structures with GaN capping for pH detection

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ABSTRACT

The pH response of GaN/AlInN/AlN/GaN ion-sensitive field effect transistor (ISFET) on Si substrates has been characterized. We analyzed the variation of the surface potential ($\Delta V_{sp}/\Delta pH$) and current ($\Delta I_{ds}/\Delta pH$) with solution pH in devices with the same indium content (17%, in-plane lattice-matched to GaN) and different AlInN thickness (6 nm and 10 nm), and compared with the literature. The shrinkage of the barrier, that has the effect to increase the transconductance of the device, makes the 2-dimensional electron density (2DEG) at the interface very sensitive to changes in the surface.

Although the surface potential sensitivity to pH is similar in the two devices, the current change with pH ($\Delta I_{ds}/\Delta pH$), when biasing the ISFET by a Ag/AgCl reference electrode, is almost 50% higher in the device with 6 nm AlInN barrier, compared to the device with 10 nm barrier. When measuring the current response ($\Delta I_{ds}/\Delta pH$) without reference electrode, the device with thinner AlInN layer has a larger response than the thicker one, of a factor of 140%, and that current response without reference electrode is only 22% lower than its maximum response obtained using reference electrode.

1. Introduction

After the first introduction of the concept of ion sensitive field effect transistor (ISFET) by Bergveld [1] the interest of solid-state based devices as chemical sensors has increased. Gate voltages induced by ions adsorbed onto the gate region of a semiconductor field effect transistor (FET) modulate the source-drain currents, realizing the concept of ISFET. The first device was fabricated on silicon with SiO₂ as dielectric material on top of the gate region inducing a shift in the surface potential proportional to the ion concentration in the solution. Since then, the development has focused mainly on material selection to improve the performance of the ISFET as a pH sensor and on achieving integration between the ISFET and CMOS processing [2,3].

In the last decade the interest in nitride-based sensors has increased both in the field of gas and ion-detection [4–11], especially since the first evidence of pH-sensitivity of GaN surfaces [6] and its application in pH-sensitive AlGaIn/GaN field effect transistors [7]. In particular, the Ga_xO_y on the surface (native or promoted by wet oxidation) seems to follow the site-binding model [12] that explains the pH sensitivity. Compared to standard dielectric materials such as SiO₂, Si₃N₄ and Al₂O₃ used in commercial ISFET, improved sensitive response and robust surface properties can be ascribed to nitride materials like GaN [7] and InN [8]. Especially for chemical and biomedical applications in harsh environments,

nitride robustness can be a solution to avoid or reduce possible damages and contaminations. Devices with high electron mobility transistor (HEMT) hetero-structures have been frequently used in pH detection mode [7,9]. In structures such as AlGaIn/GaN [9,10] or AlN/GaN [11], the conductivity of two dimensional electron gas (2DEG) located at the interface between the barrier and the GaN is affected by surface potential modifications.

Recently, the AlInN barrier HEMT is substituting the conventional AlGaIn technology basically due to several facts. First of all, InAlN can be grown lattice matched (LM) to GaN for an indium composition of 16–18%, reducing the strain present in a typical AlGaIn-based transistor, and thus improving the long-term reliability of the device.

As InAlN can offer a high concentration of 2DEG density due to its much higher spontaneous polarization compared to AlGaIn, a thinner barrier can be used. From a point of view of an open gate sensor, this provides an advantage regarding the sensitivity of the 2DEG to changes in the environment. A constant sheet charge density down to approximately 10 nm barrier thickness has been observed. Even at 5 nm a sheet charge density of around $1.6 \times 10^{13} \text{ cm}^{-2}$ has been measured [13].

Due to the lack of lattice-matched materials, sapphire and silicon carbide are commonly used as substrates. Recently, the Si(1 1 1) substrate has attracted more attention because of its low cost, good thermal conductivity, availability of wafers up to 30 cm in diameter, and more especially, the possibility of integrating Si electronics on the same chip. Up to now, encouraging results have been achieved in the fabrication of devices based on GaN/Si(1 1 1) layers. InAlN barrier HEMTs grown on silicon substrate have been

reported with channel electron sheet density of $2.6 \times 10^{13} \text{ cm}^{-2}$ mobility $\mu = 400 \text{ cm}^2/\text{Vs}$ and frequency operation up to 102 GHz [14]. Therefore, it opens a way to a technology compatible with CMOS fabrication standards and low cost substrates with electronic performances consistent with the state of the art of AlGaN technology.

In this work we investigate in detail the feasibility of InAlN HEMTs as pH sensors, determining their surface sensitivity ($\Delta V_{sp}/\Delta \text{pH}$) and current sensitivity ($\Delta I_{ds}/\Delta \text{pH}$) working with an without reference electrode. As GaN has been recognized to have pH-sensitivity of the order of the theoretical Nernstian limit (59 mV/pH at room temperature) [6,7] we use HEMT structures always with a GaN capping layer as sensitive surface, but with different thicknesses of the AlInN barriers (either 6 nm or 10 nm), so different distances between the surface and the 2DEG that suffers modulation due to surface potential changes.

2. Experimental

The samples used in this work are HEMT structures grown by MOCVD on silicon substrates, and their structure is schematized in Fig. 1a. An AlN nucleation layer of nominal 60 nm thickness was grown on high resistivity (HR) Si(1 1 1) substrate ($\rho > 5 \text{ k}\Omega \text{ cm}$) and after that a HR GaN epilayer of 600 nm. In a typical InAlN/GaN heterostructure, a very thin AlN interlayer (in this case, 1 nm thick) is introduced at the interface to improve electron confinement by increasing the effective barrier, and at the same time to reduce alloy scattering [15]. The InAlN barrier was of two different thicknesses, namely 6 nm (sample A) and 10 nm (sample B). Finally a GaN cap layer of 1 nm covered the samples.

(0002) $\theta/2\theta$ X-ray reflection diffraction (XRD) has been performed on the samples (not shown here). In the spectra, the GaN and AlN peaks are identified respectively at $\theta = 17.283^\circ$ and $\theta = 18.025^\circ$, as well as the band related to the InAlN barrier with a LM composition (at around $\theta = 17.5^\circ$ for In content of 17%).

We patterned the device structure with ICP dry etching (MESA) creating a channel between two ohmic contacts (Fig. 1b), having this conduction channel a length (L) and width (W) of 1.2 mm and 0.5 mm, respectively. The ohmic metallization of source and drain contacts (S and D in the image) consisted in a multilayer scheme of Ti/Al/Ni/Au (30 nm/200 nm/50 nm/150 nm) annealed at 850°C during 30 s, assuring a good contact resistance in all the samples investigated ($R_C \leq 1 \Omega \text{ mm}$). The resistance of the devices (in air)

measured between source and drain was $1.5 \text{ k}\Omega$ (sample A) and $0.7 \text{ k}\Omega$ (sample B).

Previous to the characterization of the devices as pH-sensor, we extracted the electron concentration in the 2DEG (n_s) and the field effect mobility (μ_{fe}) of the structures. By short circuiting the source and drain terminals and negative biasing the electrolyte-gate with respect to them, we could extract the dependence of the density of electron from gate-source voltage ($n_s(V_{gs})$) by electrolyte capacitance-voltage measurements (ECV). The mobility is extracted from the source-drain current (I_{ds}) versus electrolyte-gate voltage (V_{gs}) characteristics at a fixed low source-drain voltage ($V_{ds} = 50 \text{ mV}$), together with the relation $n_s(V_{gs})$ extracted before [16]. For sample A, the maximum value of μ_{fe} is $739 \text{ cm}^2/\text{Vs}$ when $n_s = 8.481 \times 10^{12} \text{ cm}^{-2}$, and for sample B, $\mu_{fe} = 1283 \text{ cm}^2/\text{Vs}$ when $n_s = 6.955 \times 10^{12} \text{ cm}^{-2}$. These values are consistent with the state of the art of AlInN/GaN HEMT structures grown on silicon (1 1 1) [17].

We treated the open gate of the devices with piranha solution (1:1 $\text{H}_2\text{O}_2:\text{H}_2\text{SO}_4$) to increase the native oxide (Ga_xO_y) concentration, therefore the amphoteric hydroxyl groups responsible for pH sensitivity according to the site-binding theory [12]. In fact, we observed a clear increment in sensitivity after this treatment.

3. Results and discussion

The response to aqueous solutions with pH of 4, 7 and 10 (commercial buffer solutions purchased at VWR) was systematically investigated at room temperature. Measurements of $I_{ds} - V_{gs}$ were recorded using an HP4156C parameter analyzer, while an HP4284 LCR-meter was used for capacitance-voltage measurements. An Ag/AgCl electrode was used as the reference electrode during the measurements.

In Fig. 2 we report on the source-drain current (I_{ds}) and transconductance ($g_m = dI_{ds}/dV_{gs}$) versus V_{gs} , at $V_{ds} = 200 \text{ mV}$ and $\text{pH} = 10$, for both samples A and B. The maximum transconductance can be expressed as

$$g_m^{\max} = \left(\frac{dI_{ds}}{dV_{gs}} \right)^{\max} = \left(\frac{W}{L} \right) V_{ds} \mu^{\max} C_i,$$

where $C_i = (\epsilon \cdot \epsilon_0)/z$ is the capacitance per unit area between the electrolyte and the 2DEG channel, and μ^{\max} is the maximum electron mobility. Leaving post-growth design parameters (W/L) and V_{ds} aside, μ/z is the main key parameter to obtain a high

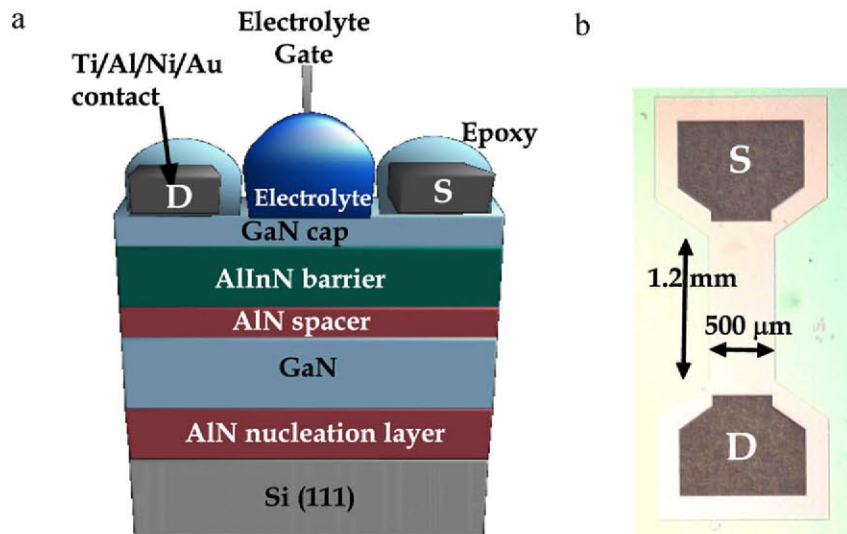


Fig. 1. Structure of the samples investigated and configuration of the device used for the characterization and pH-response measurements. (a) Side view and (b) top view.

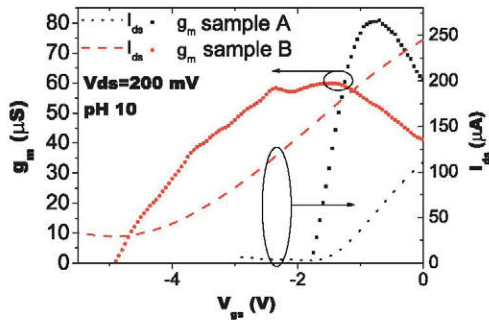


Fig. 2. Transconductance (g_m) and source-drain current (I_{ds}) versus gate voltage for the two samples recorded at pH 4 and $V_{ds} = 200$ mV.

transconductance value and therefore, high transduction sensitivity. The improvements in LM AlInN growth on GaN allow to create high quality AlInN/GaN HEMT structure with thin barrier (lower z) and keeping high mobility values.

The threshold voltage (V_{th}) of the two devices rescale with the barrier thickness, being in the case of sample A $V_{th} = -1.8$ V while in case of sample B $V_{th} = -4.9$ V. Moreover, higher maximum g_m is obtained for sample A which present a thinner barrier and a lower mobility in comparison with sample B.

We extracted the variation of the surface potential with the pH (Fig. 3) by fixing V_{ds} at 200 mV and measuring $I_{ds} - V_{gs}$ for the three different pH values. Shifts on the $I_{ds} - V_{gs}$ curves depending on the pH reflect the surface potential dependence on the pH of the electrolyte, and the obtained slopes are -53.7 mV/pH and -52.1 mV/pH for samples A and B, respectively, close to the Nernstian theoretical limit at 25°C of 59 mV/pH [6].

Whereas the variation of surface potential depends on surface properties, the dependence of I_{ds} with the pH of the solution ($\Delta I_{ds}/\Delta\text{pH}$) is strongly affected by the electrical characteristic of the structure and therefore by g_m . In fact, the relationship between ($\Delta I_{ds}/\Delta\text{pH}$) and ($\Delta V_{sp}/\Delta\text{pH}$) is

$$\left(\frac{\Delta I_{ds}}{\Delta\text{pH}}\right) = g_m \cdot \left(\frac{\Delta V_{sp}}{\Delta\text{pH}}\right).$$

The results of ($\Delta I_{ds}/\Delta\text{pH}$) for samples A and B are shown in Fig. 4. V_{gs} is set to the voltage at which the device shows its maximum g_m , i.e. $V_{gs} = -0.7$ V for sample A, and $V_{gs} = -2$ V for sample B. In both cases $V_{ds} = 200$ mV. A linear dependence has been observed in the two cases, with a higher slope for sample A ($4.16 \mu\text{A}/\text{pH}$) than for sample B ($2.83 \mu\text{A}/\text{pH}$), as expected due to the higher g_m of sample A because of its smaller barrier thickness in spite of its lower mobility.

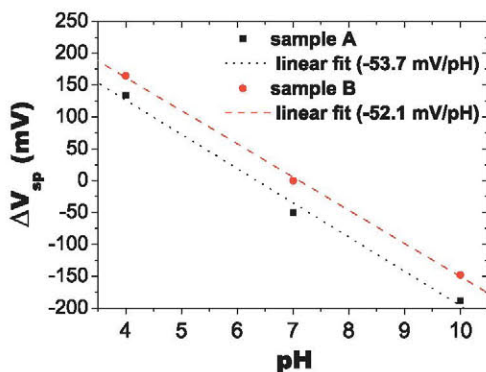


Fig. 3. Variation of the surface potential (ΔV_{sp}) versus pH of the solution and linear fits for the two samples.

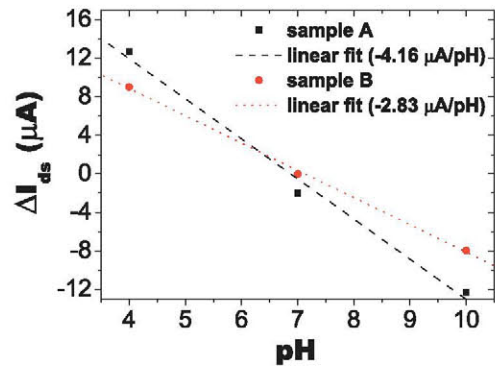


Fig. 4. Variation of the drain-source current (ΔI_{ds}) versus pH of the solution and linear fits for the two samples.

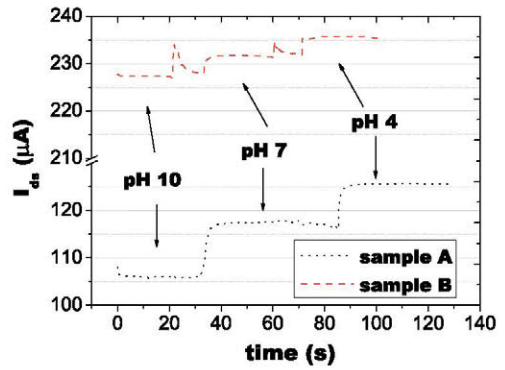


Fig. 5. Transient behaviors of the two samples when pH is changed by means of droplets of buffer solutions (pH 4, 7 and 10), without reference electrode.

After that, we also performed real-time I_{ds} measurements for the two samples changing the pH of the solution without the use of an external reference electrode which bias at maximum g_m . If possible, the current readout in pH sensing without the need of a reference electrode may be very practical. Without a reference electrode, the current I_{ds} is then just controlled by the surface potential that depends on the pH of the electrolyte, but most probably the operation point would be away from the maximum g_m .

We fixed the drain-source voltage at 200 mV as in previous experiment and measured the variation with time of the source-drain current by applying to the open gate a drop of the different buffer solutions by means of Pasteur pipettes (Fig. 5).

No substantial drift of the current was observed after the application of the buffer solution on the open gate, and high reproducibility and stability are observed.

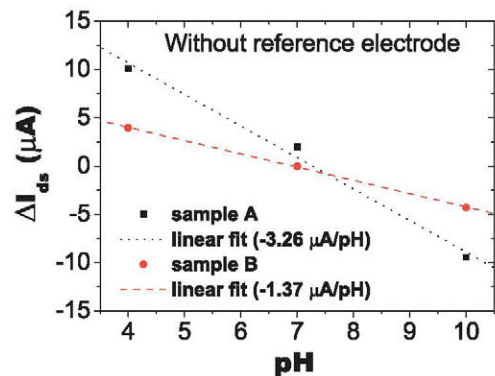


Fig. 6. Variation of the drain source current (ΔI_{ds}) versus pH of the solution without the use of reference electrode, and linear fits for the two samples.

A linear behavior of ΔI_{ds} versus the pH of the solution is found (see Fig. 6), although as expected, working without reference electrode reduces the sensitivity of both devices. The response decrease in the sample A (from 4.16 $\mu\text{A}/\text{pH}$ to 3.26 $\mu\text{A}/\text{pH}$, reduction of 22%) is less pronounced than in sample B (from 2.83 $\mu\text{A}/\text{pH}$ to 1.37 $\mu\text{A}/\text{pH}$, reduction of 52%). This is reasonable taking into account that maximum transconductance for sample A is achieved at a V_{gs} value less negative (closer to zero) than in the case of sample B (see Fig. 2); thus, when working without reference electrode, sample A is spontaneously closer to its maximum transconductance than sample B.

4. Conclusions

We have investigated the pH-sensitivity of InAlN/GaN heterostructure grown on Si substrates. The devices tested showed potential sensitivity of the order of the Nernstian limit. Even though the sample with larger barrier showed higher field effect mobility, the device with the thin barrier presented an enhanced $\Delta I_{ds}/\Delta\text{pH}$, related to the higher influence on the 2DEG density from the environment, being the 2DEG closer to the surface.

Measurements without reference electrode confirmed how the thin barrier improves the sensor performance working at a point closer to the maximum transconductance.

Therefore we can conclude that sample A, with a barrier thickness of only 6 nm, has the best performance for pH sensing current readout; even working without reference electrode its sensing response is better than the one of sample B with a 10 nm barrier thickness.

In conclusion, the AlInN barrier ISFET with a LM thin barrier and grown on silicon is a very promising candidate for chemical sensors which can be integrated with CMOS technology.

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