



AlGaIn/GaN Based All-Solid-State pH Sensor for Micro-Liter Solution Measurements

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Abstract

The realization of pH measurement of micro-liter solutions may open up many new applications in biomedicine. However, traditional pH sensors are generally large thus failed to measure pH values of micro-liter solutions. In this paper, an AlGaIn/GaN based all-solid-state ion-sensitive heterostructure field-effect-transistor (ISHFET) to accurately measure pH values was realized through integrating a noble metal (Au) quasi-reference electrode close to the active area of sensor. By introducing the Au quasi-reference electrode, the size of the pH sensor can be significantly reduced down to micrometer scale. According to the leakage-current and time-resolved measurements, this all-solid-state ISHFET sensor was proved to be stable enough for pH reading of pH values ranging from 4 to 10.01, with the solution volume between 3 to 6 μ L. The sensitivity of this sensor is 54.73mV/pH at room temperature, which is close to the ideal Nernst ultimate value. The response time of the pH sensor is estimated to be 1.0 second in a change pH solution

Keywords: AlGaIn/GaN heterostructure, All-solid-state, Quasi-reference electrode

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Introduction

Accurately measuring of the pH value of solutions can bring in new opportunities of applications in chemistry, medicine, biology, pharmacy and agriculture^[1-4]. Recent years, there has been increasing interest in measuring the pH values of micro-liter solutions, especially in the fields of biomedicine. However, conventional pH measurement systems are too large for micro-liter solutions' measurements. Therefore, the AlGaIn/GaN-based ion-sensitive field-effect-transistor (ISFET) pH sensor has gained a lot of attention due to its small dimensions and its potential for measuring solutions with tiny volumes^[5-7].

There have been a significant number of studies detailing the development of silicon-based ISFET pH sensors due to their compatibility with the silicon MOSFET manufacturing processes^[8-10]. However, Si-based ISFET has challenges in high-temperature environment due to its narrow band gap (1.12 eV) and in special solutions for the device can also be easily corroded^[11]. In contrast, AlGaIn/GaN based ISHFET pH sensors have three major advantages compared to the Si-based: (1) AlGaIn/GaN-based ISHFETs have better light stability, chemical stability and are capable of being used in high-temperature operation, due to the wider band gap of III-Nitride; (2) The two-dimensional electron gas (2DEG) induced at the AlGaIn/GaN interface has a higher electron mobility and density, which provides a much higher signal sensitivity and faster response time^[12-14]; (3) The native metal oxide layer (aluminum and gallium oxides) developed on the surface of the AlGaIn/GaN heterostructure has a high chemical sensitivity to different concentrations of H⁺^[15-16]. Because of these desirable properties, new developments in AlGaIn/GaN-based ISHFET

pH sensors have increasingly been reported in recent years^[12-19]. However, neither the Si-based nor the AlGaIn/GaN-based pH sensors reported in these studies were able to realize measure pH values of micro-liter solution volumes. The reason is mainly due to the glass reference electrode which is too large for this purpose.

In this paper, we integrated a noble metal (Au) quasi-reference electrode near the active sensor area of the pH sensor and successfully fabricated an all-solid-state AlGaIn/GaN-based ISHFET pH sensor on the basis of this improvement. Due to the introduction of the noble metal quasi-reference electrode, the size of the chip can be significantly reduced. We recently have investigated the dimensional impact of the quasi-reference electrode to the ISHFET performance^[17]. With an optimized noble metal quasi-reference electrode, stable measurements of pH values in micro-liter solutions were achieved with a sensitivity of 54.73mV/pH at room temperature. This sensitivity is very close to the physical limit of the ideal Nernst response. And the response time is estimated to be 1.0 second.

Device Fabrication

The AlGaIn/GaN heterostructure was fabricated by growing a 35% Al composition and 25-nm-thick AlGaIn film onto a 2.2- μm -thick i-GaN buffer layer using a metal organic chemical vapor deposition (MOCVD)

system. The electron mobility and the charge density of the 2DEG were measured to be 1230 cm^2/V and $1.37 \times 10^{13} \text{ cm}^{-2}$ respectively at room temperature. After the AlGaIn film was grown, the fabrication process of all solid-state ISHFET pH sensors was shown as followed.

(1) Mesa Isolation: The mesa isolation with a depth of 100 nm was etched by using the inductively coupled plasma reactive ion etching (ICP-RIE) system.

(2) Source & Drain Metallization: Ti/Al/Ni/Au (15/80/20/60 nm) layers were then deposited, which passed a rapid thermal annealing (RTA) process with N₂ ambient at a temperature of 850°C for 30 seconds to form the ohmic contacts for the drains (D) and sources (S).

(3) Interconnection & Reference Electrode: Ti/Au (5/200 nm) metal layers was then evapored to form noble metal quasi-reference electrodes and metal interconnections.

(4) Isolation Process: An insulating layer was employed to protect the device from the electrical influence of the solutions, leaving the active area between source and drain and part of the quasi-reference electrode alone to contact with the target solution. The testing pads were also exposed to air for testing. The exposed portion of the solid-state quasi-reference electrode was near the active sensor area with a length of 500 μm and a width of 200 μm , as shown in Fig. 1 (b).

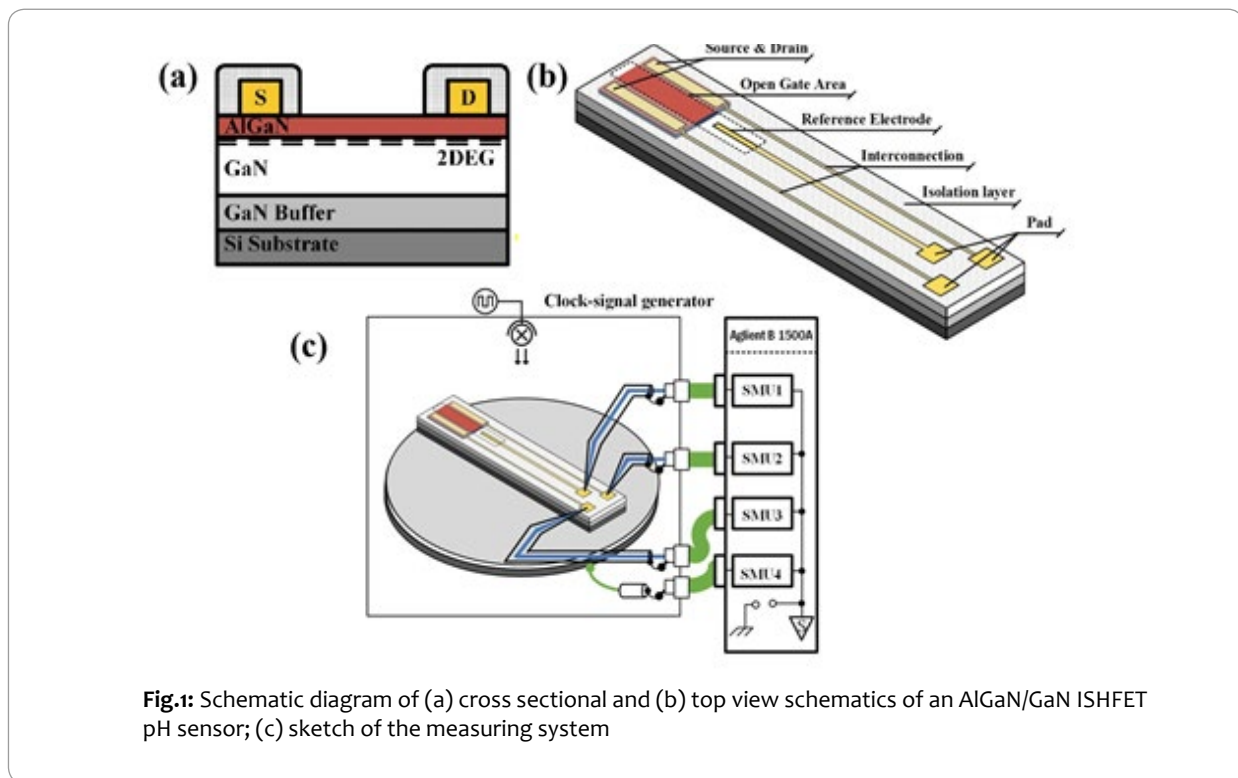


Fig.1: Schematic diagram of (a) cross sectional and (b) top view schematics of an AlGaIn/GaN ISHFET pH sensor; (c) sketch of the measuring system

Fig 1(a) and (b) is the microphotograph of the cross sectional and top view schematics of the all-solid-state AlGaIn/GaN-based ISHFET pH sensor incorporating with a noble metal (Au) quasi-reference electrode. The structure and electrical characteristics of the ISHFET pH sensor are similar to those of a typical AlGaIn/GaN heterostructure field effect transistor (HFET), the only difference is that the gate metal of a HFET was replaced by an electrolyte solution and the Au quasi-reference electrode.

The transfer and output characteristics of the ISHFET were plotted against four pH values. Four kinds of standard pH buffer solutions

were prepared and each had a different pH value of 4.00, 7.00, 9.18 and 10.01. The pH values of the solutions were confirmed with a standard pH tester (pH400, Lab-Alalis Instrument, China). During the measurements, a 3-6 μL droplet was delivered by a micropipette onto the sensor, which can cover both the active area and the exposed quasi-reference electrode, as shown in Fig. 1 (b). The electronic characteristics of the ISHFET pH sensor were then measured by a semiconductor device parameter analyzer (Agilent 1500 – Key sight Technologies, United States) at room temperature, as shown in Fig. 1 (c).

Results and Discussion

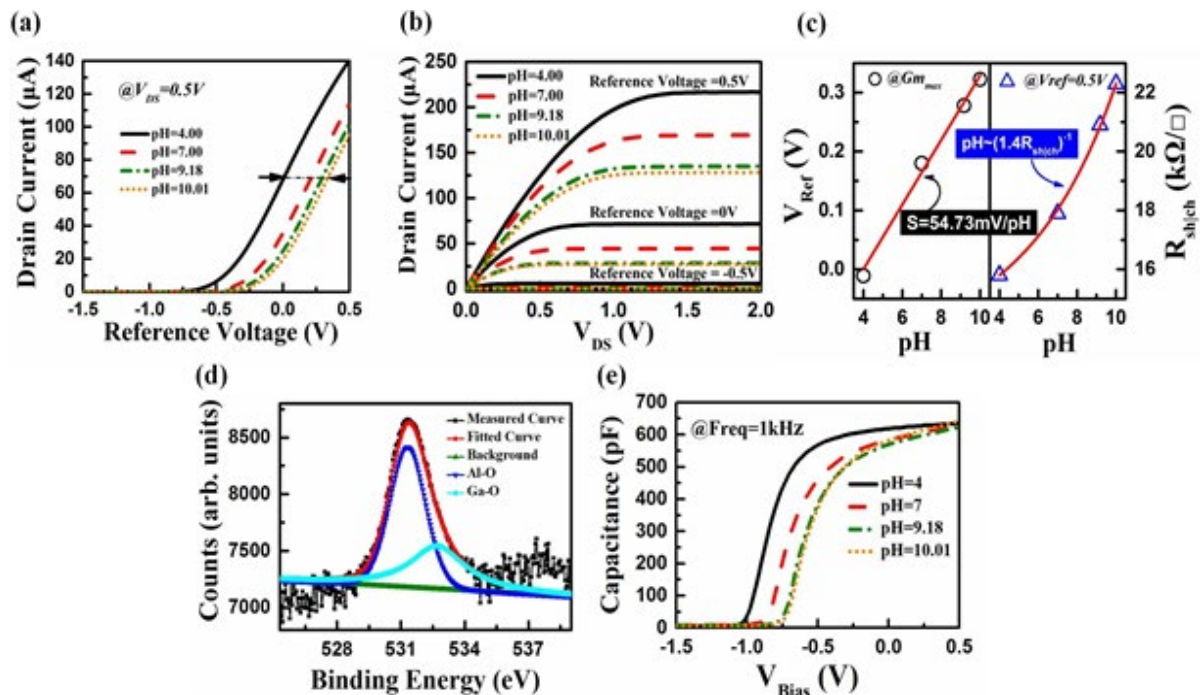


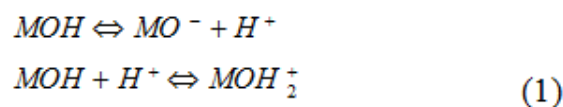
Fig.2: (a) Transfer characteristics,(b) output characteristics and (e) capacitance- voltage characteristics measured with four aqueous solutions with different pH values,

(c) the sensitivity for the voltage variation at the maximum of transconductance (G_{m-max}) and the relationship between pH value and $R_{sh|ch}$, (d) XPS O 1s spectra and de-convoluted to Al-O and Ga-O peaks of the the active sensor area of the ISHFET pH sensor.

Fig 2 (a) and (b) are the transfer and output characteristic curves of the ISHFET pH sensor for the four kinds of solutions with different pH value. The transfer characteristic curves were measured with a bias applied via the quasi-reference electrode and a fixed drain bias of 0.5 V. In Fig. 2(a), the measured drain currents resembled the typical shape of a HFET, with the current linearly increasing for forward reference voltages (linear region) but shutting off for reverse reference voltages (shut-off region). As the pH value increased, the shut-off threshold of the drain current shifted to the right, which requires a higher reference voltage for the drain current to conduct to cross into the linear region. Fig. 2 (b) shows the full output characteristic curves of the ISHFET pH sensor under a range of reference voltages from -0.5 V to 0.5 V for the solutions with four kinds of pH value.

The left of Fig. 2 (c) was used to estimate the sensitivity of the ISHFET pH sensor in which the reference voltages were recorded at a fixed drain current of 73 μA (at the peak of transconductance) under the four different pH values. The sensitivity was fitted to be 54.73mV/pH, which was slightly under the ideal Nernst response (58mV/pH) at room temperature^[5].

The channel sheet resistance $R_{sh|ch}$ can be extracted from the output characteristics. For a fixed reference voltage, the drain current decreased as the pH value increased. As shown in the right figure of Fig. 2(c), the drain current change was measured to be -5.6 μA/pH in the linear region ($V_{DS}=0.5V$) when the reference voltage was set at 0.5V. This indicates that the channel sheet resistance $R_{sh|ch}$ was inversely proportional to the pH value. The $R_{sh|ch}$ can be expressed as $R_{sh|ch}=1/(\mu_{sh|ch} \cdot Q_{sh|ch})$, where $\mu_{sh|ch}$ is the channel mobility, and $Q_{sh|ch}$ is the sheet carrier concentration of 2DEG. $\mu_{sh|ch}$ can be considered to be constant in small current mode^[24]. Thus the 2DEG carrier concentration is inverse-linearly proportional to the pH value. The response of ISHFET pH sensor can be explained by the site-binding model and electrical double layer theory. Native metal oxide layers of amphoteric hydroxyl groups can be formed on the surface of AlGaIn when the surface is contacted with the aqueous solutions. As shown in Fig. 2 (d), the XPS O 1s spectra of the AlGaIn surface are de-convoluted into Al-O and Ga-O bonds, which prove the existence of the aluminum and gallium oxides. The amphoteric hydroxyl groups at the surface can be dissociated and became neutralized, protonized or deprotonized, depending on the pH value of the aqueous solutions^[10]. The dissociative interactions on the surface can be described by the following chemical equations,



where M represents the metal atom. The dissociative interactions can build up a pH-dependent net charge on the oxide surface and this surface net charge concentration is denoted as σ_{DL} . According

$$\sigma_{DL} = -C \times \phi_{DL} \tag{2}$$

where C is the integral double layer capacitance. By introducing the Nernst equation, it can be determined that there is a linear relationship between pH value and ϕ_{DL} (20-22). For this reason, the electrostatic potential of the AlGaN/solution interface is affected by the H^+ concentration of the solution, which in turn enhancing or depleting the 2DEG for the channel underneath (23). Therefore, this

explains why the shut-off threshold voltage shifts to higher reference voltages as the pH increases. This is due to the dissociation of H^+ from the metal oxide as the pH value increases, resulting in a reduction of 2DEG between the source and the drain. These were demonstrated by the capacitance-voltage measurement with different pH value, as shown in Fig. 2 (e).

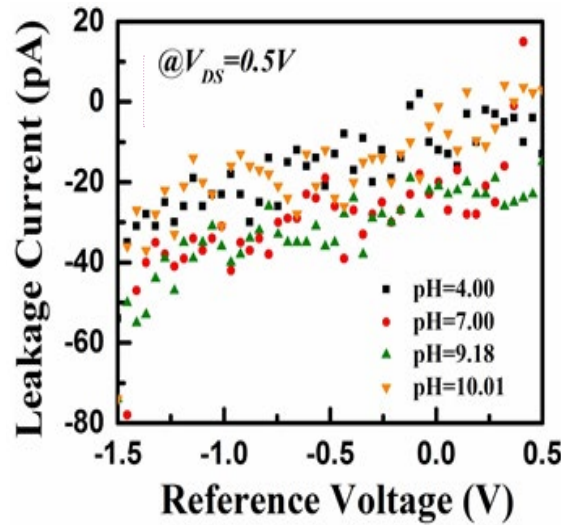


Fig.3: Leakage currents measured with different voltages of the reference electrode.

It's worth mentioning that the ISHFET pH sensor demonstrates a high electrochemical stability, which is indicated by an extremely low leakage current. As shown in Fig3, the leakage current was measured

to be less than 80 pA with no pH dependence. Larger leakage current is generally not desirable since it can cause electrochemical reactions for the Au quasi-reference electrode and for the AlGaN surface, which can affect measurement consistency of pH values.

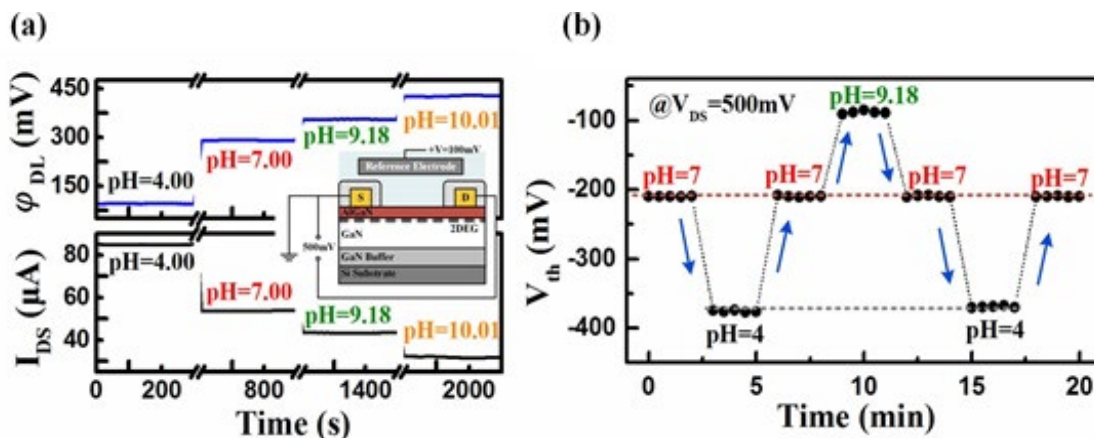


Fig.3: (a) Time-resolved measurements of the drain current with a fixed $V_{DS} = 500\text{ mV}$ and $V_{Ref} = 100\text{ mV}$, variations of the drain current measured and the corresponding potential calculated as a function of time. (b) Hysteresis effect of ISHFET pH sensor.

To further characterize the stability of pH sensor, we performed time-resolved measurements of the drain current with a fixed $V_{DS} = 500$ mV and $V_{Ref} = 100$ mV, as shown in the insert of Figure 4 (a). These experimental conditions allowed the drain current as low as possible to avoid self-heating. Fig. 4 (a) plotted the drain current as a function of time while holding the pH value to be the same for at least 300 seconds. Solutions with different pH values were changed at several time points by rinsing the sensor with de-ionized water between the solutions. At pH = 4.00, 7.00, 9.18 and 10.01, ΔI_{DS} were measured to be 0.5 μ A, 0.23 μ A, 0.4 μ A and 0.5 μ A, respectively. Calculated from

the IDS data, there was a small potential variation, $\Delta\phi$, of 1.5 mV at pH = 7 within 300 seconds. The drain current I_{DS} stayed relatively stable for all pH values, but sometimes a significant current variation occurred at the very beginning of the experiments. The small potential variation demonstrates that the all-solid-state ISHFET pH sensor based on the AlGaIn/GaN heterostructure integrated with Au quasi-reference electrode could be used to stably measure pH values of micro-liter solution. The hysteresis phenomena of ISHFET pH sensor was shown in Fig. 4. (b). We tested the sensor in a pH cycle (7-4-7-9.18-7-4-7), the repeated test results show that the same pH value solutions keep a similar V_{th} , which confirmed the retention stability of the pH sensor.

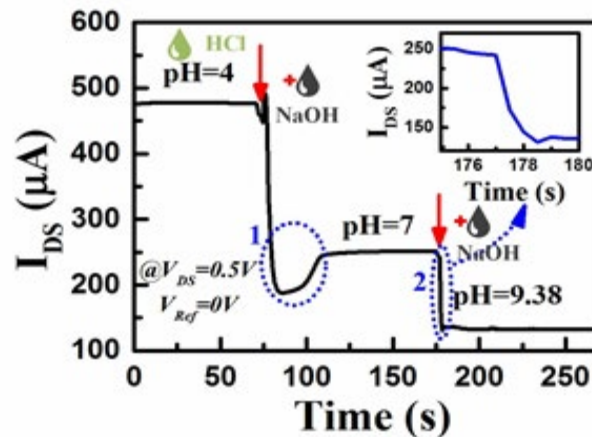


Fig.5: Transient behavior of IDS as a function of the pH value. The inset was the partial enlarged detailed of blue loop 2.

A fast response time of the sensor makes a significant sense to dynamic biological systems and related topics. Here we performed a measurement to monitor the response time of the ISHFET, as shown in Fig 5.

We performed time-resolved measurements of $V_{DS} = 500$ mV. V_{Ref} was set at 0V to avoid having an impact on the solutions, which simulated the fluid in vivo environment. First, a 3- μ L-HCl droplet (pH=4) was delivered by a micropipette onto the open-gate region. Then, a 3- μ L-NaOH droplet (pH=10) was added to neutralize. We found that the current changed rapidly but it had a long time to be stable (close to 20s). Finally, with another 3- μ L-NaOH droplet (pH=10) added, the current changed and tended to steady rapidly.

The response time test was usually carried out in the large volume solution, and the titration experiment was carried out with a stirrer to accelerate the reaction. However, the measurements for aqueous solutions of micro-liter volume were unable to use the stirrer, so the diffusion and neutral reaction between HCl and NaOH solutions would need a lot of time. Therefore, the response time shown in the blue loop 1 included the neutral reaction time, as shown in Fig. 5. However, when the alkaline solutions were added in the neutral solution, the ISHFETs showed a fairly good stability and immediate response to change in pH. The response time was estimated to be 1.0 second, as there was no chemical reaction in it. This data was limited not by the intrinsic sensor response but by the pH exchange rate in the solution. This paper proposed and demonstrated an all-solid-state AlGaIn/GaN ISHFET pH sensor. By adding a noble metal (Au) quasi-reference electrode, the ISHFET pH sensor was able to detect a large range of pH values in aqueous solutions with micro-liter volumes. The transfer

characteristic and current-voltage characteristic curves of the ISHFET were shown to have high linearity for the range of pH values from 4.00 to 10.01. Sensitivity of the pH sensor was measured to be 54.73mV/pH at room temperature over this pH value range. The sensitivity was very close to that of an ideal Nernst response. The sensor also has a low leakage current, which translates to a high electronic stability for pH measurements. The stability was demonstrated with time-resolved and hysteresis effect measurements. With a fast response time of 1.0 second, the sensor, therefore, may be useful in satisfying important applications in many areas, including chemistry, biology and medicine, for measuring the pH values of precious aqueous samples with very small volumes.

Acknowledgments

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