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Liquid-phase sensors using open-gate AlGaIn/GaN high electron mobility transistor structure

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Liquid-phase sensing characteristics of open-gate AlGaIn/GaN high electron mobility transistor (HEMT) structures were investigated in aqueous solutions and polar liquids. In de-ionized water, the open-gate HEMT clearly showed good drain I - V characteristics with current saturation and pinch-off behavior, very similar to I - V characteristics of typical Schottky-gate HEMTs. We observed a fine parallel shift in the transfer curves according to change in the pH value in a solution, indicating the corresponding potential change at the AlGaIn surface. The sensitivity for the potential change was 57.5 mV/ pH , very close to the theoretical value of 58.9 mV/ pH at 24 °C for the Nernstian response to H^+ ions. In the low drain bias region, the drain current linearly decreased with the pH value. This also indicated a systematic potential change at the AlGaIn surface due to pH change. The present open-gate device showed a fast response to the pH change and a stable operation at fixed pH values. A possible mechanism for the pH response of the AlGaIn surface is discussed in terms of equilibrium reactions of hydroxyls at the AlGaIn surface with H^+ in a solution. It was also found that the device was quite sensitive to changes in the electrostatic boundary conditions of the open-gate area by exposure to polar liquids. The drain current linearly decreased with increasing normalized liquid dipole moment. © 2006 American Vacuum Society.
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I. INTRODUCTION

Chemical sensors using semiconductors which can detect ions, polar molecules, surface adsorption process of molecules, etc., are very attractive not only for various chemical-but also for biological-sensing applications. Ion-sensitive field effect transistors (ISFETs) using Si metal-oxide-semiconductor (MOS) structures have extensively been studied. In particular, much effort at investigating pH -sensing membranes and device structures has improved sensitivity and stability of Si ISFET.¹⁻³ Utilizing heterostructures and quantum structures, on the other hand, III-V and II-VI compound semiconductors have demonstrated their capabilities in various types of chemical-sensing devices for biochemical processes such as the detection of molecule chemisorption, DNA hybridization, etc.⁴⁻⁷ However, such compound semiconductor surfaces are not chemically stable in solutions. Thus, a surface-coating layer is absolutely necessary for chemical sensor structures, causing low sensitivity and slow response of such sensors.

On the basis of excellent optical and electrical properties, significant progress has been achieved in the GaN-based devices, such as ultraviolet laser diodes, white light-emitting diodes, high electron mobility transistors (HEMTs), and high-power FETs. In addition, GaN-based materials are very attractive for various chemical and biological sensor applications because of their superb chemical stability and capability of high-temperature operation owing to their wide gap

nature. The pH response of GaN surfaces using ISFET structures was recently reported by Steinhoff *et al.*⁸ However, no work on the pH response to AlGaIn surfaces was done, and mechanism of pH response is not understood yet. Although Stutzmann *et al.*⁹ and Mehandru *et al.*¹⁰ reported preliminary results on the response of open-gate AlGaIn/GaN HEMTs to polar liquids, the sensing properties of such devices have not systematically been investigated so far.

The purpose of this study is to investigate pH -sensing and liquid-phase sensing characteristics of open-gate AlGaIn/GaN HEMT structures. We have investigated the basic transistor characteristics and liquid-phase sensing capability of open-gate devices with bare AlGaIn surfaces in aqueous solutions. In addition, the ion sensitivity of bare AlGaIn surfaces was compared to that of SiN_x -passivated surfaces. The results obtained seem to open up the feasibility of cointegration with AlGaIn/GaN HEMT circuits for sensor network applications.

II. EXPERIMENT

A. Device structure and fabrication process

As shown in Fig. 1, we used AlGaIn/GaN heterostructures with an Al composition of 0.23 and AlGaIn thickness of 22 nm, grown on sapphire by metal-organic vapor phase epitaxy (MOVPE). The electron mobility and density of the two dimensional electron gas (2DEG) were 950 cm²/V and 8.0×10^{12} cm⁻², respectively, at room temperature.

The device fabrication process started with isolation patterning using electron-cyclotron resonance (ECR)-assisted

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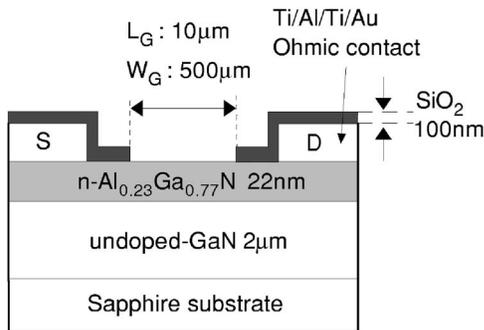


FIG. 1. Structure of the open-gate AlGaN/GaN HEMT.

reactive ion beam etching with a CH_4 -based gas system consisting of CH_4 , H_2 , Ar, and N_2 . The addition of N_2 to the gas system is very effective in achieving a smooth and stoichiometric surface.¹¹ The drain and source electrodes were formed by deposition of Ti/Al/Ti/Au multilayers and annealing at 800°C for 1 min. Then, the device surface was covered with SiO_2 film to a thickness of 100 nm using plasma-enhanced chemical vapor deposition (PECVD) at 300°C . The open-gate area, length of $10\ \mu\text{m}$ and width of $500\ \mu\text{m}$, was formed through photolithography and wet etching processes in a buffered HF solution. The final structure is as shown in Fig. 1.

B. Electrochemical cell and measurement circuit

Figure 2 shows an electrochemical cell and a measurement circuit consisting of a potentiostat (EG&G, 273AEC) and a semiconductor parameter analyzer (Agilent, 4156C). The open-gate devices were set on a Teflon holder, and the source and drain electrodes were covered by a negative-type photoresist. The gate bias was applied from the semiconductor parameter analyzer to the electrolyte/AlGaN interface at the open-gate area via a saturated calomel electrode (SCE). For pH-sensing measurements, we prepared de-ionized (DI) water and a mixed solution with HCl and NaOH in DI water.

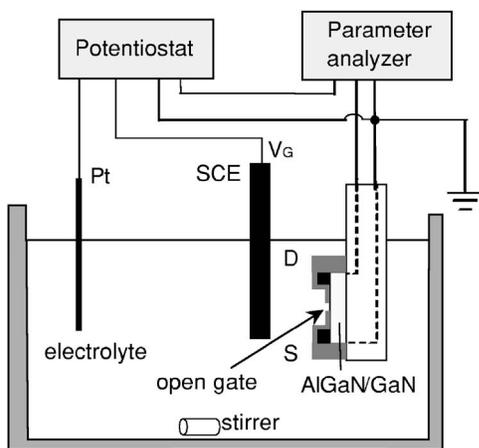


FIG. 2. Schematic of the electrochemical cell and the measurement circuit. The open-gate devices were set on a Teflon holder. The source and drain electrodes were covered by a negative-type photoresist.

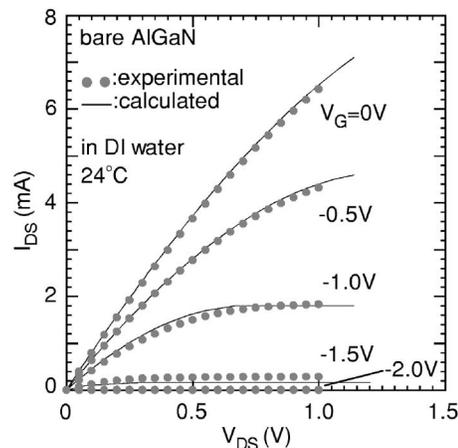


FIG. 3. Typical drain I - V characteristics of the open-gate HEMT in DI water at 24°C under dark conditions. The gate bias was applied to the open-gate area via a SCE.

The pH values in solutions were measured using a digital pH meter (CyberScan, pH100). For polar liquids, we used ethanol and acetone. All measurements in solutions were performed at 24°C under dark conditions.

III. RESULTS AND DISCUSSION

A. I - V characteristics of the open-gate HEMT in de-ionized water

Figure 3 shows typical drain I - V characteristics of the open-gate HEMT in DI water at 24°C under dark conditions. The device clearly exhibits current saturation and pinch-off behavior, which is very similar to I - V characteristics of typical Schottky-gate HEMTs. This shows that the potential of the AlGaN surface in the open gate can effectively be controlled by the solution potential. The solid lines in Fig. 3 indicate the calculated curves based on the gradual-channel approximation together with a field-dependent mobility formula. The source and contact resistances were considered in the calculation. The experimental I - V curves were reproduced very well by the calculation. From the calculated results, we estimated the value of $1.5\ \text{eV}$ for the flat-band potential at the water/AlGaN interface, which is very close to the charge neutrality level (CNL) of $1.6\ \text{eV}$ for $\text{Al}_{0.23}\text{Ga}_{0.77}\text{N}$.¹² Fujii and Ohkawa recently reported¹³ that the flat-band potential of n -GaN was about $1.0\ \text{eV}$ in Na_2SO_4 solution ($\text{pH}=6.7$). This value is also very close to CNL of $1.03\ \text{eV}$ for GaN.¹²

The gate-leakage characteristics of the open-gate HEMT in de-ionized water is shown in Fig. 4, together with a typical I_{GS} - V_{GS} curve of the Ni/Au Schottky-gate HEMT in air. The Schottky-gate device showed large leakage currents with a pronounced bias dependence, which can be explained by enhancement of electron tunneling transport through the metal-AlGaN interface caused by the unintentionally induced surface donors.^{14,15} In comparison, the open-gate HEMT brought low gate currents in solution, probably due to few carriers (electrons and holes) in the electrochemical system

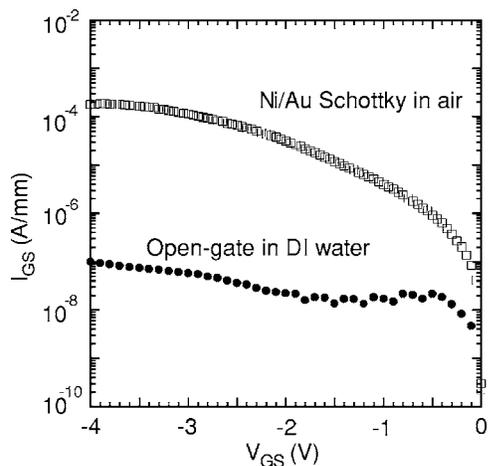


FIG. 4. Gate I - V characteristics of the open-gate HEMT in DI water at 24 °C under dark conditions. For comparison, typical I_{GS} - V_{GS} curve of a Schottky-gate HEMT is plotted.

under dark conditions. Similar gate I - V characteristics were observed in other solutions. This indicated that the effects of gate leakage on the potential control of solution/AlGaIn interfaces can be ignored, resulting in good gate control of drain current via the SCE, as shown in Fig. 3.

B. pH response of the open-gate HEMT

Figure 5 shows the transfer characteristics of the open-gate HEMT in a mixed solution of HCl and NaOH in water with different pH values. To evaluate the transfer characteristics in the linear region, we set the drain bias at 0.2 V. A fine parallel shift was observed in the transfer curves, when the pH value changed from 4.0 to 10.0, indicating the corresponding potential change at the AlGaIn surface. The sensitivity for the potential change is 57.5 mV/pH, very close to the theoretical value of 58.9 mV/pH at 24 °C for the Nernstian response to H^+ ions.

Figure 6 shows the drain current measured under $V_{GS} = -0.5$ V and $V_{DS} = 0.2$ V as a function of the pH value. As

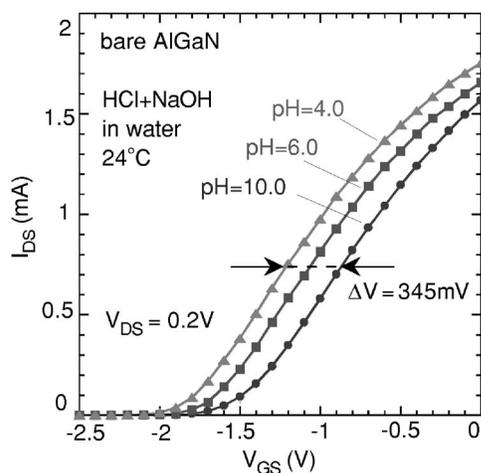


FIG. 5. Transfer characteristics of the open-gate HEMT in a mixed solution of HCl and NaOH in water with different pH values.

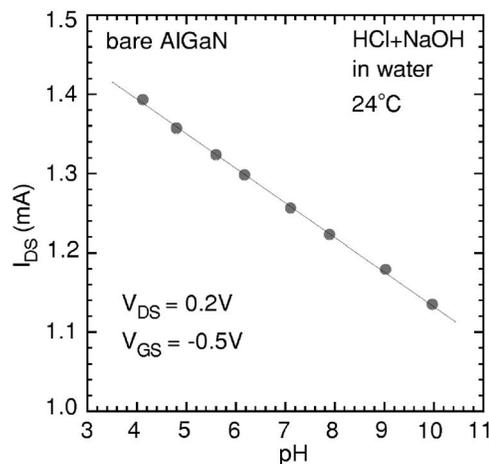


FIG. 6. Drain current measured under $V_{GS} = -0.5$ V and $V_{DS} = 0.2$ V as a function of the pH value.

expected from the result in Fig. 5, the drain current decreased with the pH value. We obtained a large current change, over 200 μ A, when the pH value was changed from 4.3 to 10.0, because of high mobility and 2DEG density of the AlGaIn/GaN HEMT. In addition, a linear behavior was clearly observed, reflecting systematic change in potential at the AlGaIn surface in the linear bias region.

The exact mechanism of how these changes occur is still unknown. For electrolyte-insulator interfaces (SiO_2 , SiN_x , Al_2O_3 , AlN, etc.) in Si-based ion-sensitive FETs, a site-binding model is generally accepted.^{1,2,16} According to this model, hydroxyl groups (MOH : M represents Si or metals) are formed at insulator surfaces in contact with aqueous solutions, and can dissociate to or combine with H^+ , depending on the H^+ concentration and the equilibrium constants for the relevant reactions, as follows:



When the H^+ concentration decreases in solution, the right-direction reaction in the equilibrium equation (1) becomes dominant, resulting in negative charges at the insulator surfaces due to deprotonized hydroxyls (MO^-). On the other hand, the increase of H^+ can induce positive charges at the surfaces due to protonized hydroxyls (MOH_2^+), represented by Eq. (2). This leads to a pH-dependent net charge at the insulator surfaces, and the liquid-solid interfacial potential thereby follows the Nernst equation.

The simplest model for the present open-gate HEMT is an analogy of this mechanism. To investigate the control mechanism of the interfacial potential, we fabricated and characterized another device with a SiN_x -covered AlGaIn surface, as shown in Fig. 7(a). A thin SiN_x film with a thickness of 10 nm was deposited on the surface by ECR-assisted CVD at 270 °C. It is known that SiN_x /AlGaIn structures show good interface properties with low interface state densities,¹⁷ and that a SiN_x -based surface passivation improves operation stability of AlGaIn/GaN HEMTs.^{18,19}

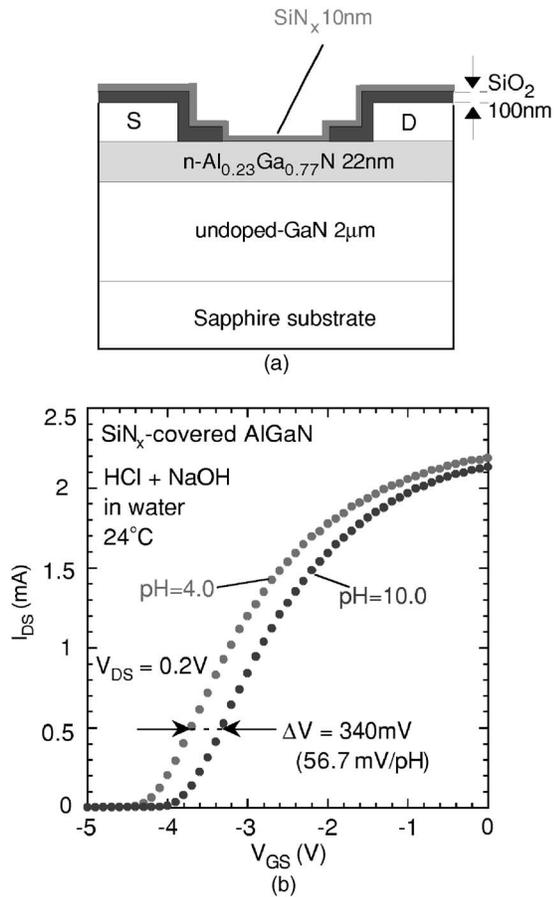


FIG. 7. (a) Structure of the open-gate HEMT with a SiN_x -covered AlGaIn surface. (b) The transfer characteristics of the open-gate HEMT with SiN_x -covered AlGaIn in a mixed solution of HCl and NaOH in water with different pH values.

Figure 7(b) shows the transfer characteristics of the open-gate HEMT with SiN_x -covered AlGaIn in a mixed solution of HCl and NaOH in water with different pH values. It is noted that the insertion of the SiN_x layer on the AlGaIn surface caused the shift in intrinsic threshold voltage toward deeper gate bias. We observed a parallel shift in the transfer characteristics with change in pH , similar to the device without the SiN_x layer. The pH sensitivity obtained was 56.7 mV/pH , very close to that of the device without the SiN_x layer. Almost the same value of 55.8 mV/pH was reported for the AlN-gate Si ISFET.³ Thus, it is likely that the mechanism explained above controls the potential of the solution-AlGaIn interface for the present AlGaIn/GaN open-gate HEMT. Steinhoff *et al.* pointed out⁸ that natural oxide such as GaO_x on the GaN surface could be responsible for the pH response of GaN-based pH -sensitive FETs. However, it is known that Ga oxides are soluble in alkaline solutions.^{20,21} Thus it seems impossible that such a natural oxide acts as a stable insulator layer at GaN surfaces in a solution with a wide pH range. There still remains the possibility that the potential at the solution-AlGaIn interface is governed by direct adsorption of

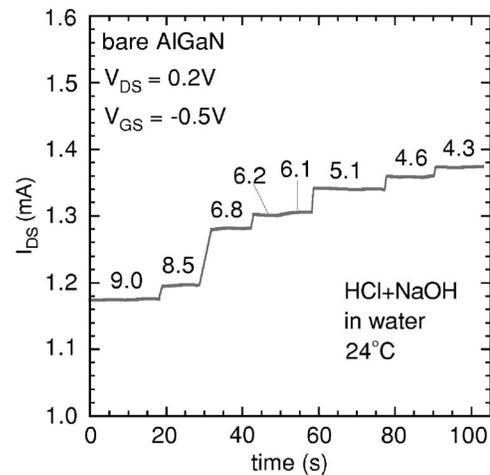


FIG. 8. Transient behavior of I_{DS} as a function of the pH value. The numbers indicate corresponding pH values in a mixed solution of HCl and NaOH in water.

ions at the given sites of the AlGaIn surface. Further investigation is necessary to confirm the exact mechanism of pH response of the AlGaIn surface.

To investigate the operational stability of the AlGaIn/GaN ISFET, we performed time-resolved measurements of I_{DS} under $V_{GS} = -0.5 \text{ V}$ and $V_{DS} = 0.2 \text{ V}$. The device showed a fairly good stability and immediate response to change in pH , as shown in Fig. 8. The response time was estimated to be 100–200 ms which seems to be limited not by the intrinsic device response but by the pH exchange rate in the solution.

C. Drain current response to polar liquids

Finally, we investigated the sensitivity of the present device to polar liquids. The drain current in the linear bias region was measured in DI water (pH of 6.8), methanol (pH of 6.9), and acetone (pH of 6.9). It was found that the device was also quite sensitive to changes in the electrostatic boundary conditions of the open-gate area by exposure to polar liquids.

Figure 9 shows I_{DS} as a function of the p/ϵ value for each liquid, where p and ϵ are the dipole moment and the relative permittivity, respectively, of the liquid. In the simplest approximation, the potential drop ΔV at the liquid-solid interface due to the molecule's dipole moment can be described by the well-known Helmholtz model:⁴

$$\Delta V = \frac{N_s p (\cos \theta)}{\epsilon \epsilon_0}, \quad (3)$$

where p is the dipole moment, N_s is the dipole density per unit area, θ is the angle between the dipole and the surface normal, ϵ is the relative permittivity of the liquid, and ϵ_0 is the permittivity of free space. The present device showed a good linear behavior shown in Fig. 9, indicating the potential change at the AlGaIn surface due to change in dipole moment in each liquid. The response time was estimated to be several hundred milliseconds. Bastide *et al.* reported⁴ a simi-

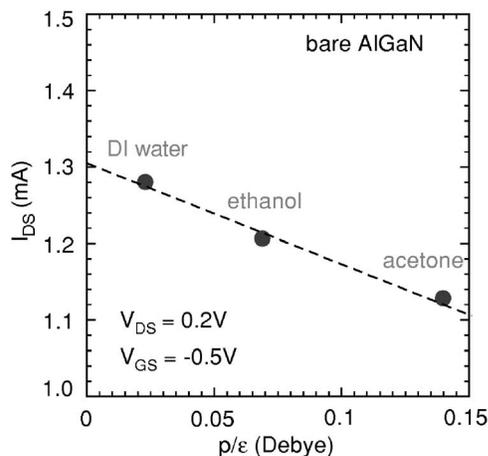


FIG. 9. Drain currents in DI water, ethanol, and acetone, as a function of the p/ϵ value for each liquid, where p and ϵ are the dipole moment and the relative permittivity of the liquid.

lar behavior in the surface potential of GaAs by adsorption of benzoic acid. Luber *et al.*⁷ reported that an AlGaAs/GaAs device coated by a self-assembled biphenyl layer showed a similar response to polar liquids. However, the response time is very long, e.g., several tens of minutes, probably due to the coating layer. On the other hand, no surface passivation is necessary for the present device, thereby resulting in an immediate response to polar liquids. Thus, the results obtained indicate that the present open-gate AlGaIn/GaN HEMT can effectively distinguish molecules with different dipole moments.

IV. SUMMARY

We have investigated the pH -sensing and liquid-phase sensing characteristics of open-gate AlGaIn/GaN HEMT structures in aqueous solutions and polar liquids. In DI water, the open-gate HEMT clearly showed good drain I - V characteristics with current saturation and pinch-off behavior, which is very similar to I - V characteristics of typical Schottky-gate HEMTs. We observed a fine parallel shift in the transfer curves according to change in the pH value in a solution, indicating the corresponding potential change at the AlGaIn surface. The sensitivity of the potential change is 57.5 mV/ pH , very close to the theoretical value of 58.9 mV/ pH at 24 °C for the Nernstian response to H^+ ions. In the low drain bias region, the drain current linearly decreased with the pH value. This also indicated a systematic potential change at the AlGaIn surface due to the pH change.

The present open-gate device showed a fast response to the pH change and a stable operation under the fixed pH value. A possible mechanism for the pH response of the AlGaIn surface was discussed in terms of equilibrium reactions of hydroxyls at the AlGaIn surface with H^+ in a solution. It was also found that the device was quite sensitive to changes in the electrostatic boundary conditions of the open-gate area by exposure to polar liquids. The drain current linearly decreased with increasing normalized liquid dipole moment. These results indicate that the open-gate AlGaIn/GaN HEMTs are very promising as high-sensitivity liquid-phase sensors for chemical and biological sensor-chip applications.

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