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Molecular gated-AlGaN/GaN high electron mobility transistor for pH detection

A molecular gated-AlGaN/GaN high electron mobility transistor (HEMT) with hybrid detection groups serves as a platform for pH detection, which exhibits good performances like chemical stability, good sensitivity and low hysteresis.

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Molecular gated-AlGaN/GaN high electron mobility transistor for pH detection

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A molecular gated-AlGaN/GaN high electron mobility transistor has been developed for pH detection. The sensing surface of the sensor was modified with 3-aminopropyltriethoxysilane to provide amphoteric amine groups, which would play the role of receptors for pH detection. On modification with 3-aminopropyltriethoxysilane, the transistor exhibits good chemical stability in hydrochloric acid solution and is sensitive for pH detection. Thus, our molecular gated-AlGaN/GaN high electron mobility transistor acheived good electrical performances such as chemical stability (remained stable in hydrochloric acid solution), good sensitivity (37.17 µA/pH) and low hysteresis. The results indicate a promising future for high-quality sensors for pH detection.

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# 1. Introduction

pH represents the acidity or basicity of an aqueous solution. According to the definition, pH can be calculated as  $-\log_{10} (a_{\rm H})$ , where  $a_{\rm H}$  is the activity of the hydrogen ion. The detection of pH is widely used in medicine, environmental science, agriculture, physiology, and so on.<sup>1</sup>

Since pH detection is very important, novel devices such as optical-based pH sensors,<sup>2</sup> mass-sensitive-based pH sensors<sup>3</sup> and metal–oxide-based pH sensors<sup>4</sup> have been proposed. However, the usage of these devices can be time-consuming, expensive, and require professional training for use. To overcome these issues, an ion-sensitive field-effect transistor (ISFET) based pH sensor has been developed, which showed advantages of quick response, compatibility with integrated

circuit technology and high sensitivity.<sup>5,6</sup> Among all electrical parameters of ISFET, sensitivity and chemical stability are the two most significant parameters for evaluating the performances of a sensor. Appropriate gate insulators can be developed using nanostructures or a certain combination of materials to improve these parameters. For example, high-*k* stacking materials,<sup>7</sup> multilayer materials<sup>8</sup> or nanowires<sup>9,10</sup> were utilized as sensing materials. Additionally, novel structures have been proposed such as dual gate<sup>7</sup> and local gate controlled ISFET,<sup>10</sup> both of which can achieve high response.

However, devices of Si-based ISFET may still suffer from several issues such as degradation of gate insulators<sup>11</sup> and instability in aqueous solution.<sup>12</sup> On the contrary, GaN is a rather stable material with high sensitivity to surface potential.<sup>13-15</sup> The first GaN-based pH sensor was proposed by Eickhoff et al. in 2003, and oxidized GaN surfaces were formed by native oxidization and thermal oxidization.<sup>16</sup> In contrast to the reported Si-based FET, the GaN-based sensor showed great pH sensitivity. However, with these fabrication methods, deep traps may exist at the interface of native oxide and semiconductor under these fabrication methods, which will result in response. To reduce the deep traps, dielectric materials such as Sc<sub>2</sub>O<sub>3</sub> have been explored.<sup>17</sup> This sensing material was epitaxially deposited on the GaN-based sensor by RF plasmaactivated molecular beam. This inorganic gated sensor exhibited great performances with sensitivity of 40 µA/pH and resolution of 0.1 pH, which are superior to those of the oxide-gated GaN formed by native oxidation or UV/O3 treatment. The above processes of high-energy deposition may still induce defects in the devices and cause deterioration of material composition. Liu et al. proposed a chemical wetness oxidation process with

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hydrogen peroxide, and the pH sensor exhibited high sensitivity and low hysteresis.<sup>11</sup>

Self-assembled monolayers (SAMs) can serve as insulation films, which can also reduce the surface energy at the interface between solid and liquid. Some SAMs can serve as the sensing membranes for pH detection.<sup>18</sup> Pioneered by Cui *et al.*,<sup>19</sup> 3-aminopropyltriethoxysilane (APTES, a common aminosilane reagent used to covalently link molecules) coating on the sensing region of ISFET proved quite useful for pH detection, and this approach has been studied by many researchers ever since.<sup>18–20</sup> However, it is still unclear whether the molecular gated-AlGaN/GaN HEMT (MG-AlGaN/GaN HEMT) will be stable for pH detection. In this work, we study, for the first time, the feasibility, sensitivity and chemical stability of the MG-AlGaN/GaN HEMT pH sensor modified by APTES.

### 2. Theory and experimental

# 2.1 The operational mechanism of the MG-AlGaN/GaN HEMT

Several mechanisms of pH response have been proposed including<sup>21–23</sup> (i) hydrogen ion exchange in the membrane of the sensing material; (ii) redox reaction at the interference between electrolyte and sensing material; (iii) corrosion of the sensing membrane by acidic or basic solution; (iv) surface potential change caused by binding sites; and (v) combination of various electrical characteristics. Among the above mechanisms, change of surface potential can explain the operational mechanism of our MG-AlGaN/GaN HEMT. At the interface between the GaN surface and electrolyte, the processing of two reactions at the binding sites, namely, protonation and deprotonation (*i.e.*,  $-OH + H^+ = -OH^{2+}$ ,  $-OH^{2+} + OH^- = -OH + H_2O$  and  $-NH_2 + H^+ = -NH_3^+$ ,  $-NH_3^+ + OH^- = -NH_2 + H_2O$ ) will positively or negatively change the surface potential. Generally, the expression of surface potential can be defined as follows:<sup>24,25</sup>

$$\psi = 2.3 \frac{kT}{q} \frac{\beta'}{\beta' + 1} (\mathrm{pH}_{\mathrm{pzc}} - \mathrm{pH}), \qquad (1)$$

where,  $\beta'$  is the acidic equilibrium constant of the reaction related to added electrolyte, which represents the capacity of the sensing material. It should be noted that  $\beta'$  is the result of two different binding sites (-OH, -NH<sub>2</sub>); if  $\beta'$  is large enough,  $\beta'/(\beta' + 1)$  can be regarded as 1. As mentioned above, the AlGaN/GaN HEMT is quite sensitive to surface potential. The potential change will be capacitively coupled with 2DEG in the channel of AlGaN/GaN HEMT, thus changing the source-drain current as described by the following equation:<sup>26</sup>

$$I_{\rm ds} = \frac{\varepsilon_{\rm AlGaN} \mu_{\rm 2DEG} W}{LD} \left[ (V_{\rm G} - V_{\rm T}) V_{\rm ds} - \frac{V_{\rm ds}^2}{2} \right]$$
(2)

where  $\varepsilon_{AlGaN}$ ,  $\mu_{2DEG}$ , *W*, *L*, *D*, *V*<sub>G</sub>, *V*<sub>T</sub> and *V*<sub>ds</sub> are the permittivity of AlGaN, electron mobility of the 2DEG, width and length of the channel, gate voltage, threshold voltage and source–drain

voltage, respectively. Therefore, the source-drain current will change with surface potential.

#### 2.2 AlGaN/GaN HEMT fabrication

The AlGaN/GaN HEMT consists of a sapphire substrate, a GaN buffer layer, an AlGaN barrier layer and a GaN cap layer. The wafer was pre-cleaned with acetone and isopropanol, and then dried with nitrogen. The main process of fabrication is shown in Fig. 1. First, the device active area was defined by photolithography and etched by inductively coupled plasma with Cl<sub>2</sub>/BCl<sub>3</sub> gases. A multilayer metal with a matrix of 200 Å-thick Ti, 1200 Å-thick Al, 700 Å-thick Ni and 1000 Å-thick Au was evaporated, followed by rapid thermal annealing in nitrogen environment to form the ohmic contacts. An overlapping multilayer consisting of 200 Å-thick Ti, 700 Å-thick Ni and 1000 Å-thick Au was later evaporated on the wafer. The wafer was encapsulated with photoresist, diced into units, and mounted on the printed circuit board (PCB). Finally, the electrodes were bonded to the pads of PCB with gold wire and sealed with polydimethylsiloxane (PDMS).

#### 2.3 Modification of MG-AlGaN/GaN HEMT

After the AlGaN/GaN HEMT was fabricated, the sensor was modified with APTES. First, the device was treated in a UV/O<sub>3</sub> chamber (400 W, 10 min) to achieve a clean oxide sensing surface. Then, the sensing surface was immersed in ethanol (AR) solution with 20  $\mu$ L 5% APTES (by volume, purchased from Sigma-Aldrich Co. LLC., Shanghai, China) for 2 hours with periodic supply of the vaporized solution. The physically absorbed APTES surface was rinsed with deionized water five times.

#### 2.4 Measurement of MG-AlGaN/GaN HEMT

Three groups of solutions were prepared in our experiment; each group had different pH values with the same ionic strength (*i.e.*, group I: 0.01 M H<sub>2</sub>SO<sub>4</sub> and 0.01 M Na<sub>2</sub>SO<sub>4</sub>; group II: 0.1 M NaHCO<sub>3</sub> and 0.1 M Na<sub>2</sub>CO<sub>3</sub>; group III: 0.2 M



**Fig. 1** Schematic drawing of the MG-AlGaN/GaN HEMT fabrication process. (a) ICP to form mesa isolation. (b) Evaporation of Ti/Al/Ni/Au and subsequent annealling to form ohmic contact. (c) Evaporation of Ti/Ni/Au to form overlap layer. (d) Encapsulation with photoresist.



Fig. 2 Characteristics of the MG-AlGaN/GaN HEMT. (a) Schematic model of MG-AlGaN/GaN HEMT. The sensing region of the device is modified with APTES to provide  $-NH_2$ , the unmodified region may provide -OH, constituting the hybrid binding sites for pH detection. The sensor is passivated with a photoresist. (b) Top view of our MG-AlGaN/GaN HEMT. The sensor is mounted on the designed printed circuit board and sealed with polydimethylsiloxane (PDMS).

NaH<sub>2</sub>PO<sub>4</sub> and 0.2 M Na<sub>2</sub>HPO<sub>4</sub>). All devices were soaked in deionized water for 12 hours before measurements to improve hydrolytic stability.<sup>20</sup> The device was connected to a Keithley 2636A for data acquisition with source–drain voltage fixed at constant voltage of 1 V and sampling interval of 1 s. The response was represented as current change  $(I - I_0)$  to minimize device-to-device response variability.

The main difference between our MG-AlGaN/GaN HEMT and other AlGaN/GaN HEMT is the origin of detecting groups. Fig. 2a gives a schematic illustration of the device and the GaN surface provides hybrid detection groups of both hydroxyl and amine. The photomicrograph of the MG-AlGaN/GaN HEMT mounted on PCB is shown in Fig. 2b.

### Results and discussion

#### 3.1 Characteristic of the MG-AlGaN/GaN HEMT

Before performing measurements, we illustrated that APTES was successfully immobilized onto the surface of AlGaN/GaN HEMT. Electrostatic adsorption between the carboxyl-terminated gold nanoparticles (AuNPs) and APTES-coated GaN surface was utilized. GaN sample with APTES coating was dipped into a solution of AuNPs, rinsed and sonicated adequately. Well-distributed AuNPs were anchored on the surface. Contrast test was conducted to illustrate that there was hardly any adsorption between the unmodified GaN surface and AuNPs. The results reveal that functional amine groups were provided on the surface of GaN (Fig. 3).

#### 3.2 The detection capability of the MG-AlGaN/GaN HEMT

To validate whether the device works properly and to examine the maximum response of the sensor, the MG-AlGaN/GaN HEMT was applied to detect acidic (group I) and basic (group II) solutions. To compare with the traditional AlGaN/GaN HEMT-based pH sensor (the sensing area of GaN is treated in UV/O<sub>3</sub> chamber with 400 W, 20 min), we conducted the same experimental steps. The results are illustrated in Fig. 4. To provide a clearer comparison, the data in these figures were



**Fig. 3** Scanning electron microscopy (SEM) images of two samples. (a) GaN surface modified with APTES will electrostatically adsorb carboxyl-terminated AuNPs; (b) GaN surface with no APTES coating exhibits hardly adsorption with carboxyl-terminated AuNPs.



Fig. 4 Current responses of MG-AlGaN/GaN HEMT and device with UV/O<sub>3</sub> treatment for the sensing region, for comparison. The data were extracted when the current was relatively steady during the measurements. (a) Detection of the acidic solution by mixing different volumes of 0.01 M H<sub>2</sub>SO<sub>4</sub> and 0.01 M Na<sub>2</sub>SO<sub>4</sub>. The sensitivities are 37.03  $\mu$ A/pH and 20.11  $\mu$ A/pH, respectively. (b) Detection of the basic solution by mixing different volumes of 0.1 M Na<sub>2</sub>CO<sub>3</sub> and 0.1 M Na<sub>2</sub>CO<sub>3</sub>. The sensitivities are 37.32  $\mu$ A/pH and 24.4  $\mu$ A/pH, respectively.

extracted when the current response of the devices was steady without any further treatment. It is clear that our MG-AlGaN/ GaN HEMT exhibits slightly higher sensitivity for pH detection. The sensitivities of the MG-AlGaN/GaN HEMT are calculated as 37.03  $\mu$ A/pH for acidic solution and 37.32  $\mu$ A/pH for basic solution, while the device with UV/O<sub>3</sub> treatment shows sensitivities of 20.11  $\mu$ A/pH and 24.4  $\mu$ A/pH in acidic and basic solution, respectively. The improved sensitivity results from the predominant role played by amine groups although the un-immobilized sensing area of GaN (without APTES, GaN exposed) still presents hydroxyl groups for detection.<sup>27,28</sup>

We further evaluated the performance of the sensor using solution for the detection range 7.0–8.0, which is the range relevant for human blood.<sup>17</sup> The pH of electrolyte used in the experiment was measured with a commercial digital pH meter with precision of 0.01. The calibrated range is from pH = 6.84 to pH = 7.94. The current change is quite clear during the measurement, as shown in Fig. 5a. The calculated sensitivity is 31.29  $\mu$ A/pH and the change of current response is significant according to our results. It should be noted that the sensitivity of this group is different from those of groups I and II. On the one hand, this may result from device variabilities that cannot be totally eliminated; on the other hand, p*K* values of amino groups may affect the sensitivity of our MG-AlGaN/GaN HEMT. The hysteresis measurement with the loop path of pH



6.84–7.94–6.84 is revealed in Fig. 5b. To give a clear illustration, each step of the steadiest current response within 60 seconds is extracted instead of real time detection. The device showed a relatively low hysteresis characteristic.

#### 3.3 The investigation of the chemical stability of MG-AlGaN/ GaN HEMT after hydrochloric acid soaking

Undesired corrosion may occur during application, which will definitely cause the degradation of stability and sensitivity, thus shortening the durability of sensors.<sup>29,30</sup> Former studies on AlGaN/GaN HEMT-based pH sensors rely on the formation of amphoteric hydroxyl groups at oxide surfaces in aqueous solution  $(-OH + H^+ = -OH_2^+ \text{ and } -OH_2^+ + OH^- = -OH + H_2O)$ ,<sup>16</sup> in which the oxide deposition will be dissolved in various acidic (like HCl and HF)<sup>31</sup> or basic (like NaOH and NH<sub>4</sub>OH) solutions.<sup>32</sup> In other words, both stability and sensitivity will most likely decline after soaking in the aforementioned solutions regardless of the methods of formation of oxide deposition in GaN-based pH sensors. It has been reported that the modification with APTES can make the ZnO nanowires resistant to etching by acid,<sup>33</sup> while it remains unknown whether APTES can improve the chemical stability of MG-AlGaN/GaN HEMT.

Chemical stability can be investigated by measuring the water contact angle.<sup>34</sup> Therefore, we measured water contact angles on the GaN surface upon the introduction of 10  $\mu$ L DI water (contact angle system OCA20). All groups of tested samples were rinsed with deionized water five times and measured immediately before our treatments. It is quite clear that the contact angle is less than 20° before modification with the APTES. On the contrary, the contact angle at GaN surfaces with APTES modification were measured to be around 50° even after soaking in HCl solution (10% by volume, soaking time: 2 min). These results indirectly suggest that on modifi-



**Fig. 5** MG-AlGaN/GaN HEMT for pH detection in the range 6.84–7.94, the step is 0.1 pH, calibrated with a commercial pH meter. (a) Real time response of pH detection using sensors with and without APTES modification. PBS buffers with pH ranging from pH = 6.84 to pH = 7.94, were prepared by mixing 0.2 M NaH<sub>2</sub>PO<sub>4</sub> solution and 0.2 M Na<sub>2</sub>HPO<sub>4</sub> solution. (b) The hysteresis measurement of MG-AlGaN/GaN HEMT, with the loop path 6.84–7.94–6.84.

**Fig. 6** Water contact angle measurements with the conditions: (a) GaN surface treated with UV/O<sub>3</sub> only, contact angle: 11.7°; (b) GaN surface treated with UV/O<sub>3</sub> and then soaked in HCl solution, contact angle: 18.9°; (c) GaN surface with APTES modification directly: 52.9°; (d) GaN surface with APTES modification and then soaked in HCl solution, contact angle: 54°.

cation by APTES, the transistor is quite chemically stable against HCl soaking and our MG-AlGaN/GaN HEMT may still work after this treatment (Fig. 6).

The MG-AlGaN/GaN HEMTs were soaked in HCl solution and rinsed with deionized water adequately right before the



**Fig. 7** MG-AlGaN/GaN HEMT for pH detection after treatment with hydrochloric acid, calibrated using a commercial pH meter. (a) Real time response of pH detection with APTES modification from pH = 6.84 to pH = 7.94, by mixing 0.2 M NaH<sub>2</sub>PO<sub>4</sub> solution and 0.2 M Na<sub>2</sub>HPO<sub>4</sub> solution. (b) Sensor was subsequently treated with UV/O<sub>3</sub> and soaked in hydrochloric acid solution. (c) Two types of detection modes are schematically represented. Hybrid binding sites will be obtained before treatment with hydrochloric acid, while the sensor remains chemically stable after soaking in hydrochloric acid.

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lable 1	Summary of our sensor w	with different treatments

Treatment	Sensitivity (µA/pH)	
UV/O <sub>3</sub>	22.25	
APTES modification	37.17	
APTES + HCl	24.34	
UV/O <sub>3</sub> + HCl	0	

measurements. Fig. 7a shows the results of the MG-AlGaN/GaN HEMT with range of pH from 6.84 to 7.94. The device exhibits stable response during the entire measurement. The sensitivity was calculated to be 24.34  $\mu$ A/pH. In comparison with the previous results shown in Fig. 5a, the decreased sensitivity results from the absence of hydroxyl groups, as depicted in Fig. 7c.

After the measurement, the MG-AlGaN/GaN HEMT was instantly treated with UV/O<sub>3</sub> (400 W, 20 min) to remove most of the binding APTES, dipped in HCl solution for two minutes, and then rinsed thoroughly in deionized water. This was done to ensure that the surface retains only GaN (the hydroxyl groups will be etched away by HCl solution). Significant drift occurred with no response of pH ranging from 6.84 to 7.94, as illustrated in Fig. 7b. We speculate that negligible amount of hydroxyl groups are continuously formed in the oxygenous solution,<sup>35</sup> while the number of binding sites formed is far from the lowest detection level of our HEMT. We hypothesize that the sensing mechanism is mainly attributed to the presence of the APTES after soaking in HCl solution, as given in Fig. 7c.

Table 1 summarizes the sensitivity of our sensor with different treatments. Relative to  $UV/O_3$  treatment, the sensitivity of our MG-AlGaN/GaN HEMT after APTES modification is almost 1.8-times higher. After soaking in HCl, the sensitivity of the MG-AlGaN/GaN HEMT declined by around 22.21% and the sensor treated with  $UV/O_3$  and HCL failed to detect the same pH range.

## 4. Conclusion

In summary, this study demonstrates the feasibility of covalently linked molecular gating for AlGaN/GaN HEMT-based sensors, and it shows great sensitivity to change of surface potential. The modification of APTES can provide binding sites of amine groups, which are sensitive to pH and quite stable after HCl soaking.

Additionally, MG-AlGaN/GaN HEMT exhibits outstanding performance in terms of good chemical stability (in HCl solution), high sensitivity (37.17  $\mu$ A/pH) and low current hysteresis with resolution of 0.1 pH. In comparison, the UV/O<sub>3</sub>-treated device shows relatively low sensitivity (22.25  $\mu$ A/pH). More importantly, after soaking in HCl solution, sensors with oxide sensing surfaces are unable to detect pH, while the MG-AlGaN/GaN HEMT still works with sensitivity of 24.34  $\mu$ A/pH and resolution of 0.1 pH.

# Conflicts of interest

There are no conflicts to declare.

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