

# Mercury(II) selective sensors based on AlGaN/GaN transistors

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## Abstract

This work presents the first polymer approach to detect metal ions using AlGaN/GaN transistor-based sensor. The sensor utilised an AlGaN/GaN high electron mobility transistor-type structure by functionalising the gate area with a polyvinyl chloride (PVC) based ion selective membrane. Sensors based on this technology are portable, robust and typically highly sensitive to the target analyte; in this case  $\text{Hg}^{2+}$ . This sensor showed a rapid and stable response when it was introduced to solutions of varying  $\text{Hg}^{2+}$  concentrations. At pH 2.8 in a  $10^{-2}$  M  $\text{KNO}_3$  ion buffer, a detection limit below  $10^{-8}$  M and a linear response range between  $10^{-8}$  M- $10^{-4}$  M were achieved. This detection limit is an order of magnitude lower than the reported detection limit of  $10^{-7}$  M for thioglycolic acid monolayer functionalised AlGaN/GaN HEMT devices. Detection limits of approximately  $10^{-7}$  M and  $10^{-6}$  M in  $10^{-2}$  M  $\text{Cd}(\text{NO}_3)_2$  and  $10^{-2}$  M  $\text{Pb}(\text{NO}_3)_2$  ion buffers were also achieved, respectively. Furthermore, we show that the apparent gate response was near-Nernstian under various conditions. X-ray photoelectron spectroscopy (XPS) experiments confirmed that the sensing membrane is reversible after being exposed to  $\text{Hg}^{2+}$  solution and rinsed with deionised water. The success of this study precedes the development of this technology in selectively sensing multiple ions in water with use of the appropriate polymer based membranes on arrays of devices.

**Keywords:** AlGaN, mercury, heavy metal detection, ISFET, Polymer membrane

## 1. Introduction

Mercury is known to be an extremely toxic metal that can lead to irreversible damage to human, animal and plant life. Furthermore, it has a tendency to bio-accumulate in living organisms meaning that even a very low level of exposure to mercury over a long period of time can lead to adverse effects. Therefore, it is essential that mercury levels in drinking water and other bodies of water are monitored carefully. In recent years, ion-selective electrodes (ISEs) have become a focus of attention due to their excellent selectivity, portability and cost advantages over traditional laboratory-based detection methods such as cold vapour atomic fluorescence spectroscopy (CVAFS), inductively coupled plasma emission spectrophotometry (CVICP-AES), gas chromatography (GC), neutron activation analysis (NAA) and inductively coupled plasma mass spectrometry (ICP-MS) [1, 2]. *In situ* techniques such as ISEs also have the added advantage that the sample is more likely to be representative of the environment and less likely to have degraded during transport from the field to the lab. In many applications this outweighs the benefits of higher sensitivity that may be obtained for laboratory-based methods [3, 4]. However for ISEs themselves, the underlying electrode configuration requiring a reference electrode and a filling solutions limits their widespread use. Si-based ion selective field effect transistor (ISFET) devices have been investigated to solve the portability and robustness issues related to ISEs; however, chemical/thermal instability of silicon in aqueous solutions and the requirement for a reference electrode remain [5]. Alternative microfluidic-based miniature, portable sensors have been investigated with similar reported sensitivity to ISEs [6]. Investigations into AlGaIn/GaN high-electron-mobility transistor (HEMT) based sensors seek to improve upon other portable sensor technologies to achieve both ruggedness and high sensitivity, with AlGaIn/GaN-based materials being both robust and highly sensitive to surface charge. This paper reports the development of an AlGaIn/GaN HEMT-based sensor to accurately and robustly measure  $\text{Hg}^{2+}$  in experimental solutions with Nernstian

response and a high degree of sensitivity and selectivity. Performance characteristics such as working range, response time/slope and selectivity coefficients for several interfering ions are reported.

The conduction channel of AlGaIn/GaN heterostructures is characterised by high sheet electron density, high electron mobility, and high saturation velocity, which arises from a confined electron layer at the AlGaIn/GaN interface, induced by piezoelectric polarization of the strained AlGaIn layer, also referred to as a two-dimensional electron gas (2DEG) [7]. In such structures, the immobilisation or capture of charged species at the heterostructure surface modulates the 2DEG sheet density in the conducting channel, and the resulting change in 2DEG channel conductivity thus provides an effective mechanism whereby chemical sensing can be deployed [5, 8]. Consequently, AlGaIn/GaN heterostructures can be utilised as robust and sensitive ion sensors, with applications in the fields of biosensing [5, 9, 10] and environmental pollutant screening [5, 10, 11]. Furthermore, unlike conventional Si-based transistors, AlGaIn/GaN HEMTs are normally-on and therefore can easily be operated without a reference electrode [8, 11]. Without the necessity for a reference electrode, the disadvantages currently faced by miniaturised reference electrodes such as instability, short lifetimes and drift are eliminated. Miniaturised systems can be integrated more easily and manufacturing costs can be lowered as a result.

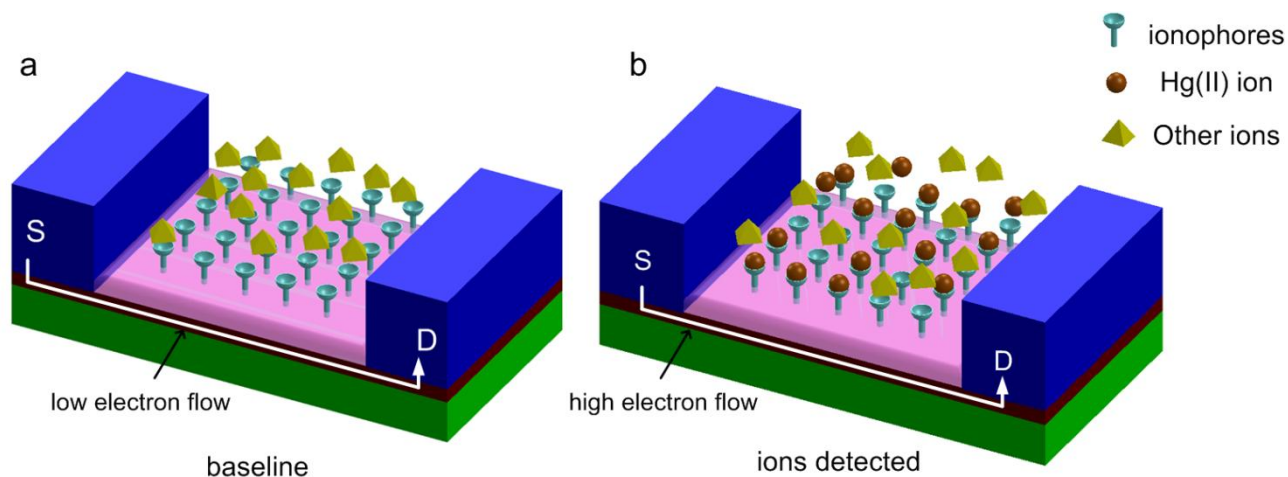
ISEs typically consist of a chemical component (a membrane) that is selective for a particular ion of interest. These membranes can be utilised as the ion selection element for ISFETs. Plasticized polyvinyl chloride (PVC)-based membranes of varying formulations have been used to detect a wide variety of both anions and cations in solution [12].

Ionophores are added to the membrane formulation and are designed to fit a specific ion in the ionophore cavity and bind with this ion to form a molecular complex, while having a low affinity for other ions [13].

In a previous study, we demonstrated AlGaIn/GaN heterostructure-based devices coated with a PVC-based membrane to detect nitrate ions in solution without a reference electrode [11]. It has been shown that GaN-capped AlIn/GaN devices without a reference electrode can successfully measure pH in solution [14]. Very few studies on detecting heavy metal ions using AlGaIn/GaN high electron mobility transistor-based sensors have been published in the past, other than those by one group [10, 15, 16]. This group has shown that a thioglycolic acid monolayer on a gold-coated AlGaIn/GaN device can detect  $\text{Hg}^{2+}$  with a detection limit of  $10^{-7}$  M in aqueous solutions [10]. They hypothesised that the carboxylic acid functional groups from the thioglycolic acid monolayer form a dimer chelate with  $\text{Hg}^{2+}$  (i.e.  $R\text{-COO}^-(\text{Hg}^{2+})\text{-OOC-R}$ ), when the sensors are exposed to the  $\text{Hg}^{2+}$  ion solution. It is expected that the adsorption of  $\text{Hg}^{2+}$  on the surface would lead to a build-up of positive charge on the surface causing an increase in the channel conductivity. However, this was not the case and a decrease in channel conductivity was observed. It has been hypothesized that the charges of trapped  $\text{Hg}^{2+}$  ion in the  $R\text{-COO}^-(\text{Hg}^{2+})\text{-OOC-R}$  chelates changes the polarity of the thioglycolic acid molecules, which were bonded to the Au gate through  $\text{-S-Au}$  bonds. Selectivity by a factor of 100 against  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  has been demonstrated; however, the mechanism for this selectivity has not been unambiguously established and might not apply to other cations [15, 16]. It should also be noted that in their work a reference electrode was not used but this was because the device itself was not in solution; only the gate area was exposed.

As a part of our interest in developing ion selective sensors [11], a polymer-based membrane formulation is used. Depending on the selection of membrane, the selectivity of ionophore-based ISEs can be compromised to varying degrees by the presence of other ions in the analyte matrix [13, 17]. For this work we have utilised a membrane formulation that (in a suspended membrane over an electrochemical junction) has a high sensitivity for  $\text{Hg}^{2+}$  and selectivity against wide variety of cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,

$\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$  and  $\text{Cr}^{3+}$ ) with  $\text{Ag}^{+}$  being the exception with a slight interference [18]. Figure 1 schematically indicates the operation of an AlGaN/GaN HEMT with ionophore capture of  $\text{Hg}^{2+}$  ions.



**Figure 1:** Schematic of AlGaN/GaN HEMT with ion selective PVC membrane-coated gate area (a). In the absence of mercury ions the electron flow (channel current) is at the base level. (b)  $\text{Hg}^{2+}$  ions captured by ionophore in the membrane cause an increase in the channel (2DEG) density and therefore an increase in the electron flow.

## 2. Experimental

### 2.1 Chemical materials

Mercury ionophore I (1,10-dibenzyl-1,10-diaza-18-crown-6), dibutyl butylphosphonate, sodium tetraphenylborate (NaTPB), high molecular weight poly(vinyl chloride) and mercury (II) nitrate were purchased from Sigma-Aldrich and used without further purification.

Analytical grade potassium nitrate, nitric acid, lead(II) nitrate, cadmium(II) nitrate were purchased from ChemSupply (Australia) and used without further purification.

### 2.2 Mercury (II) selective membrane

A membrane formulation similar to the optimised formulation reported by Gupta et al. [18] was used. 8.5 mg of sodium tetraphenylborate, 50.2 mg of mercury ionophore I, 570 mg of high molecular weight poly(vinyl chloride) and 400mg of dibutyl butylphosphonate were dissolved in 20 mL THF. A micro-dispensing system (Vermes MDV 3200) was used to

deposit a uniform layer of this membrane (10  $\mu\text{m}$ ) on the gate area of the sensor. To ensure complete evaporation of solvent and to enhance membrane adhesion to the GaN layer, the sensor was kept under vacuum at room temperature overnight.

### *2.3 Device construction and operation*

The HEMT structure consists of an MOCVD-grown AlGaIn/GaN (AlGaIn layer 15.5 nm thick, Al with an AlN mole fraction of 0.23) structure grown on a sapphire substrate (see figure 2a). A GaN cap layer of 2.4 nm was also grown to improve the electrochemical stability of the device. From Hall effect measurements, the carrier concentration and mobility of the HEMT sample were  $8.257 \times 10^{12} \text{ cm}^{-2}$  and  $1472 \text{ cm}^2/\text{Vs}$ , respectively. To fabricate the devices mesa isolation was performed by inductively coupled plasma reactive ion etching with  $\text{Cl}_2/\text{Ar}$  based discharges. Four ohmic contacts in a Kelvin mode arrangement (see Figure 2b) were formed by deposition of Al (200 nm), Cr (600 nm), and Au (600 nm), followed by rapid thermal annealing (RTA) in nitrogen ambient at  $830^\circ\text{C}$  for 60s. To form the ISFET sensor, individual AlGaIn/GaN devices were packaged onto a printed circuit board (PCB); the devices were then electrically connected to the PCB using silver-loaded epoxy. Electrically conductive regions were encapsulated using silicone gel, yet ensuring that the device active area was free of traces of the encapsulating film. Figure 2c shows an optical image of the sensor after fabrication. An optical image of the AlGaIn/GaN ISFET device after packaging is shown in figure 2d. During the measurements, source to drain current was maintained at  $100 \mu\text{A}$  whilst the sense terminals were connected to a voltage input data acquisition card (National Instruments, model 9239, 24-bit resolution).

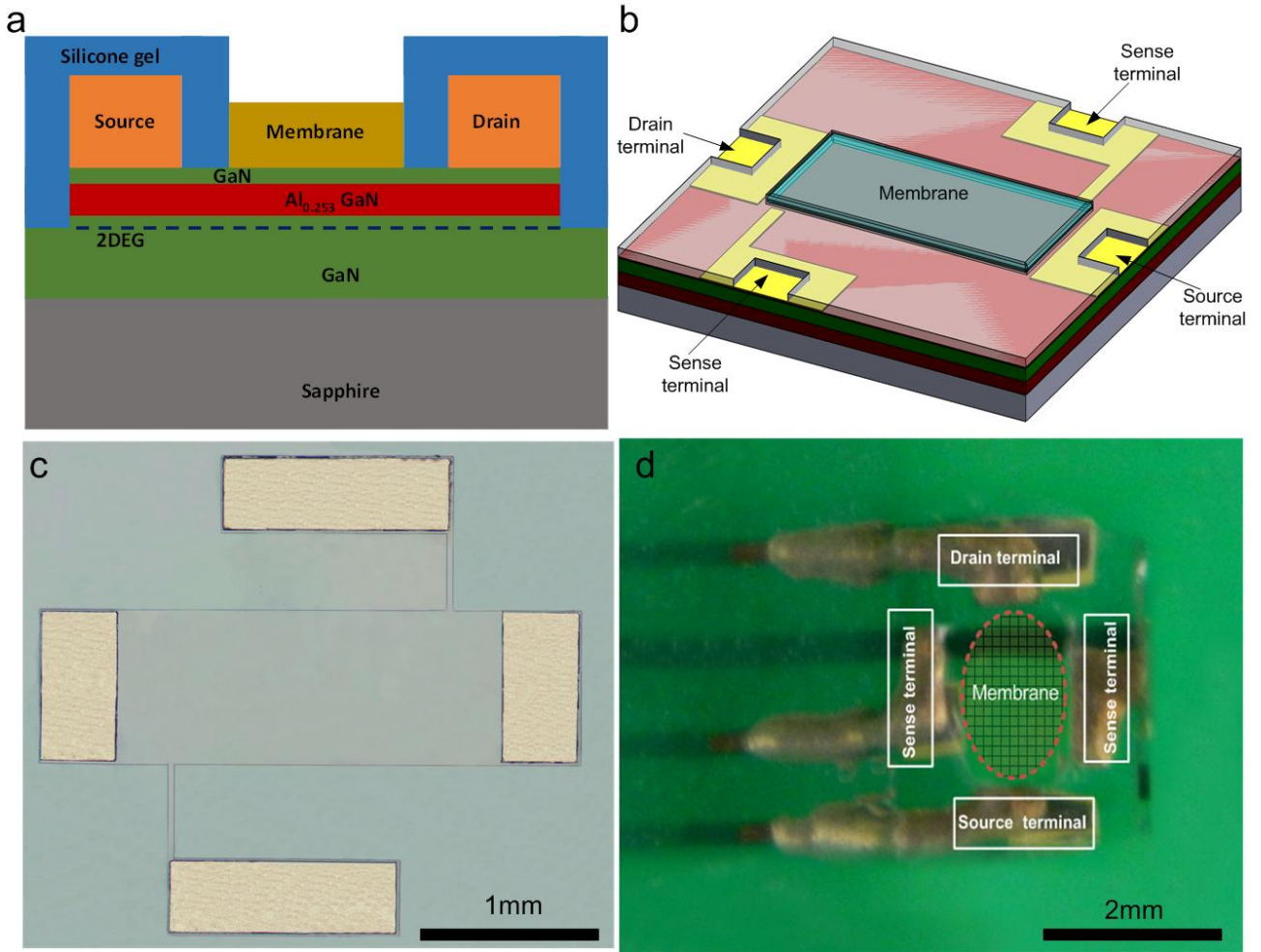


Figure 2: (a) A schematic of GaN-capped AlGaIn/GaN ISFET sensor cross-section with deposited membrane. (b) A schematic of the device showing the terminals and membrane. (c) An optical image of the sensor showing the contact and active area. (d) An optical image of the device after packaging.

#### 2.4 Sensor testing

For device sensor testing with  $\text{Hg}^{2+}$  ions, the membrane-coated device was conditioned by soaking in a  $10^{-2}$  M solution of acidified mercuric nitrate for 4 hours. The devices were then removed from this solution and were thoroughly rinsed with deionised water for 20 minutes.

To separate volumetric flasks, an appropriate amount of  $\text{Hg}(\text{NO}_3)_2$  (to achieve  $10^{-8}$  M to  $10^{-4}$  M, in 10-fold increments) and an appropriate amount of  $\text{KNO}_3$ ,  $\text{Pb}(\text{NO}_3)_2$  or  $\text{Cd}(\text{NO}_3)_2$  was added (acting as interfering ions at a concentration of  $10^{-2}$  M for each of the different salts).

To prevent spontaneous formation of insoluble  $\text{Hg}(\text{OH})_2$  when  $\text{Hg}(\text{NO}_3)_2$  is added to water, small volumes of concentrated nitric acid were added to both the ionic strength buffer solution as well as  $\text{Hg}^{2+}$  analyte solution to achieve a measured pH of 2.8. Mercury nitrate added to water is soluble but it immediately forms insoluble mercury hydroxide if the pH is not kept low. A fixed pH value of 2.8 was therefore used to prevent the formation of any mercury hydroxide.

All the experiments were performed in a dark room environment to avoid the effects of light on the AlGaIn/GaN device conductivity [7].

### 3. Results and discussion

Starting with the lowest concentration  $10^{-8}$  M and  $\text{KNO}_3$  as the interfering ion, the device was placed in the solution and allowed to equilibrate for approximately 30 minutes and then immediately dipped into the solution with next highest concentration. Figure 3 shows the sensor response during this series of experiments. The sharp peak at the start of each step is due to the few seconds that the sensor is not in the solution while changing the solutions. After dipping into the highest concentration solution ( $10^{-4}$  M) and rinsing, the process was then repeated in reverse back to the lowest concentration. The results show a decrease in sensor voltage with increase in the concentration of  $\text{Hg}^{2+}$  ions presumably due to an increase in captured  $\text{Hg}^{2+}$  ions (positive charge at the surface) increasing the electron density of the 2DEG channel, increasing the 2DEG channel conductivity and therefore inducing a smaller voltage potential at a fixed 100  $\mu\text{A}$  channel current level. It is also clear from Figure 3 that the sensing behaviour of the membrane remained unchanged whether the measurements were made either moving from low to high concentrations or vice versa.



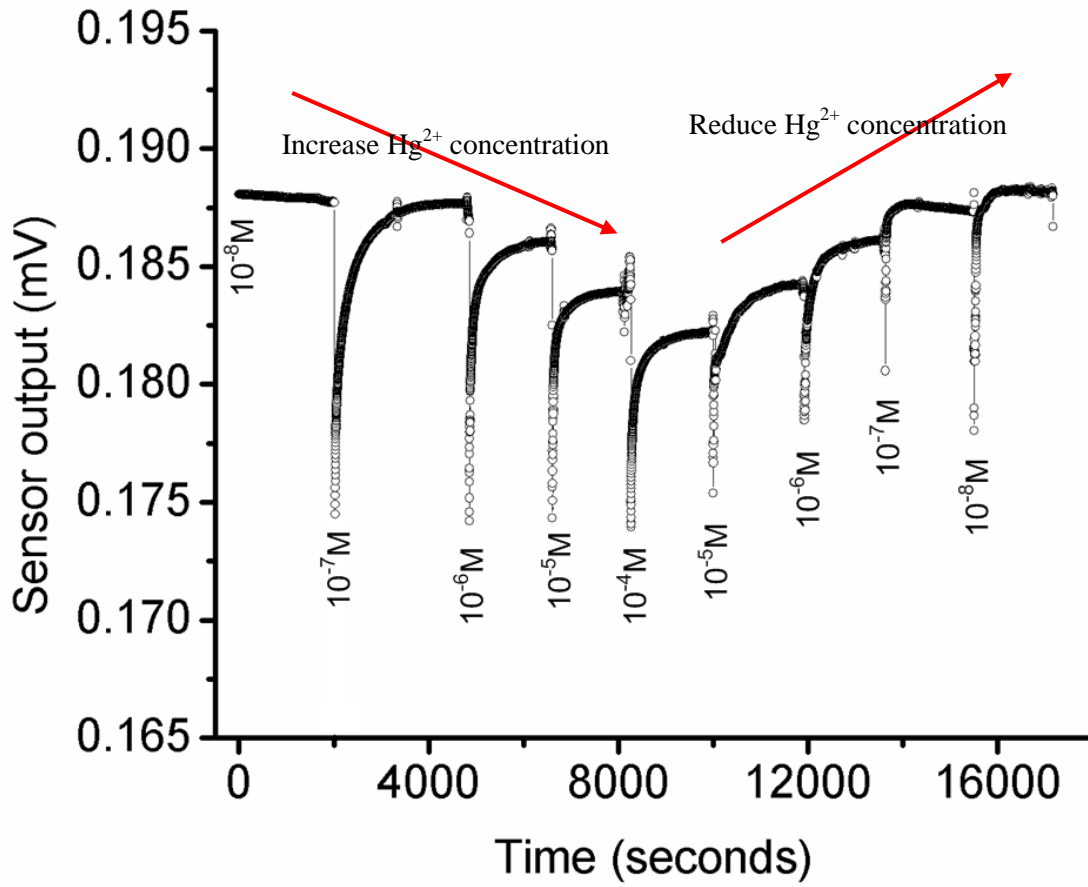


Figure 3: Time dependent response after exposure to beakers containing different concentrations of  $\text{Hg}(\text{NO}_3)_2$  at a  $10^{-2}\text{M}$   $\text{KNO}_3$  concentration and a constant pH value of 2.8.

Figure 4 is a plot of the equilibrium sensor output versus  $\text{Hg}^{2+}$  concentrations in a  $10^{-2}\text{M}$   $\text{KNO}_3$  ion buffer solution at constant pH value of 2.8 for multiple runs conducted at intervals of 10 days. The error bars given in Figure 4 are generated from the variation between 3 consecutive experiments on the same day for each run. As shown in this figure, a linear response range between  $10^{-8}\text{M}$ - $10^{-4}\text{M}$  was achieved. The  $\text{Hg}^{2+}$  ion detection limit of the AlGaIn/GaN device is approximately  $10^{-8}\text{M}$  which is lower than the reported detection limit of  $10^{-7}\text{M}$  for the thioglycolic acid monolayer functionalised AlGaIn/GaN HEMT devices [10,15,16]. The best reported detection limit for most of the traditional PVC-electrode-based sensors and other portable ion sensors are on the order of  $10^{-7}\text{M}$  [2, 6, 19].

The results for different runs show that despite the small measurement variability in sensor output over time (due to different factors such as effect of light, temperature, solution concentration etc.), the  $\text{Hg}^{2+}$  detection limit and the linear detection range remain approximately the same. This suggests that with appropriate calibration, the sensors can be used for at least 50 days for analytical determination of  $\text{Hg}^{2+}$  concentrations without any considerable divergence in response.

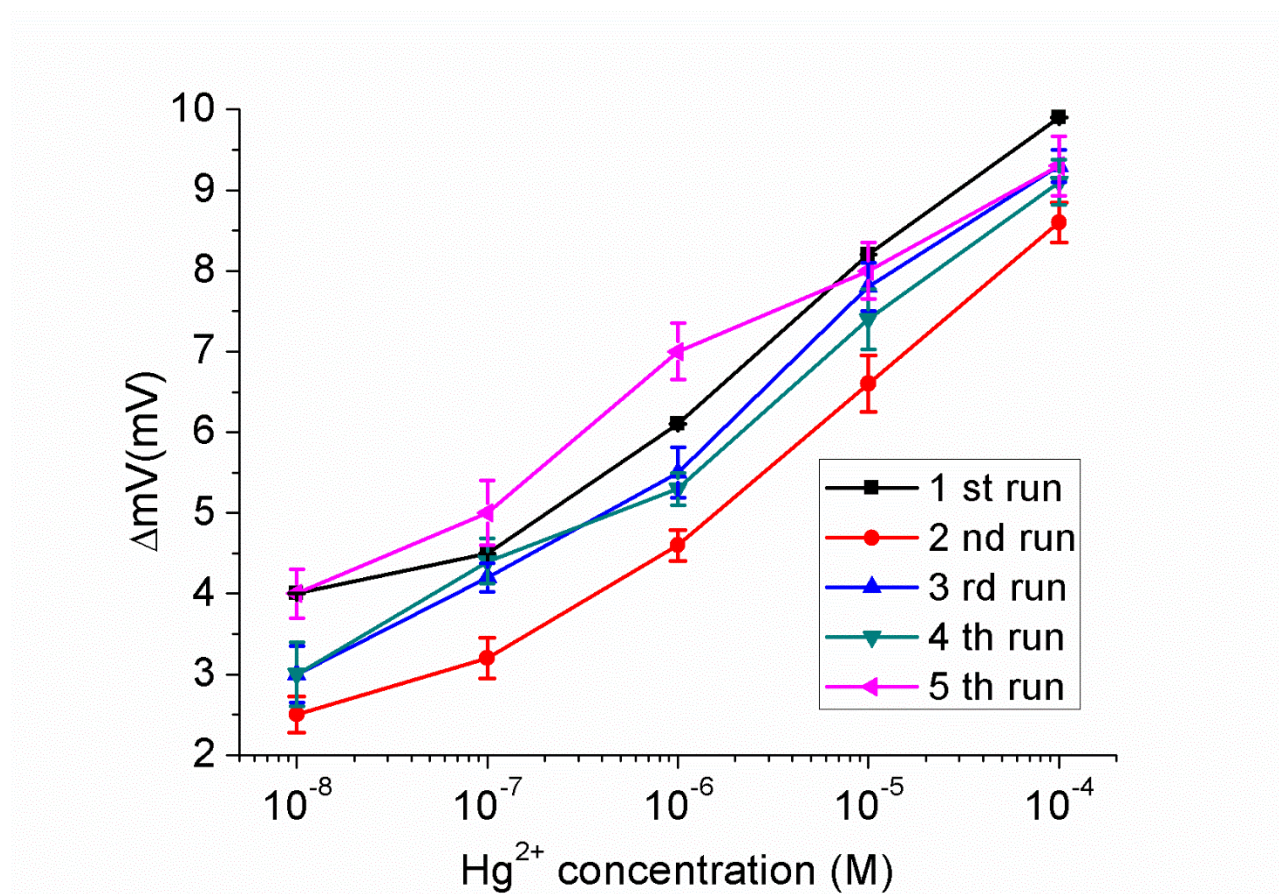


Figure 4: Equilibrium of potential response ( $\Delta\text{mV} = V_{\text{after Hg}^{2+} \text{ added}} - V_{\text{before Hg}^{2+} \text{ added}}$ ) as a function of  $\text{Hg}^{2+}$  concentration in a  $10^{-2}$  M  $\text{KNO}_3$  ionic strength buffer solution at constant pH value of 2.8 with intervals of 10 days between each experiment.

Figure 5 is a plot of the equilibrium sensor output versus  $\text{Hg}^{2+}$  concentration in various ionic strength buffer solutions at a constant pH value of 2.8, including the data from the 1<sup>st</sup> run in a  $10^{-2}$  M  $\text{KNO}_3$  ionic strength buffer solution as given in Figure 4. For comparison, the response in non-ionic strength buffered solution ( $\text{HNO}_3$  only) is also given. Detection

limits of approximately  $10^{-7}$  M and  $10^{-6}$  M in  $10^{-2}$  M  $\text{Cd}(\text{NO}_3)_2$  and  $10^{-2}$  M  $\text{Pb}(\text{NO}_3)_2$  ion buffers were achieved, respectively. It is apparent that the sensor performance (detection limit and linear range) in the presence of other heavy metal ions such as  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  significantly reduces, presumably due to a similar ionophore binding mechanism for the various heavy metals. Detection limits and linear range for the different ionic strength buffer experiments are summarised in Table 1.

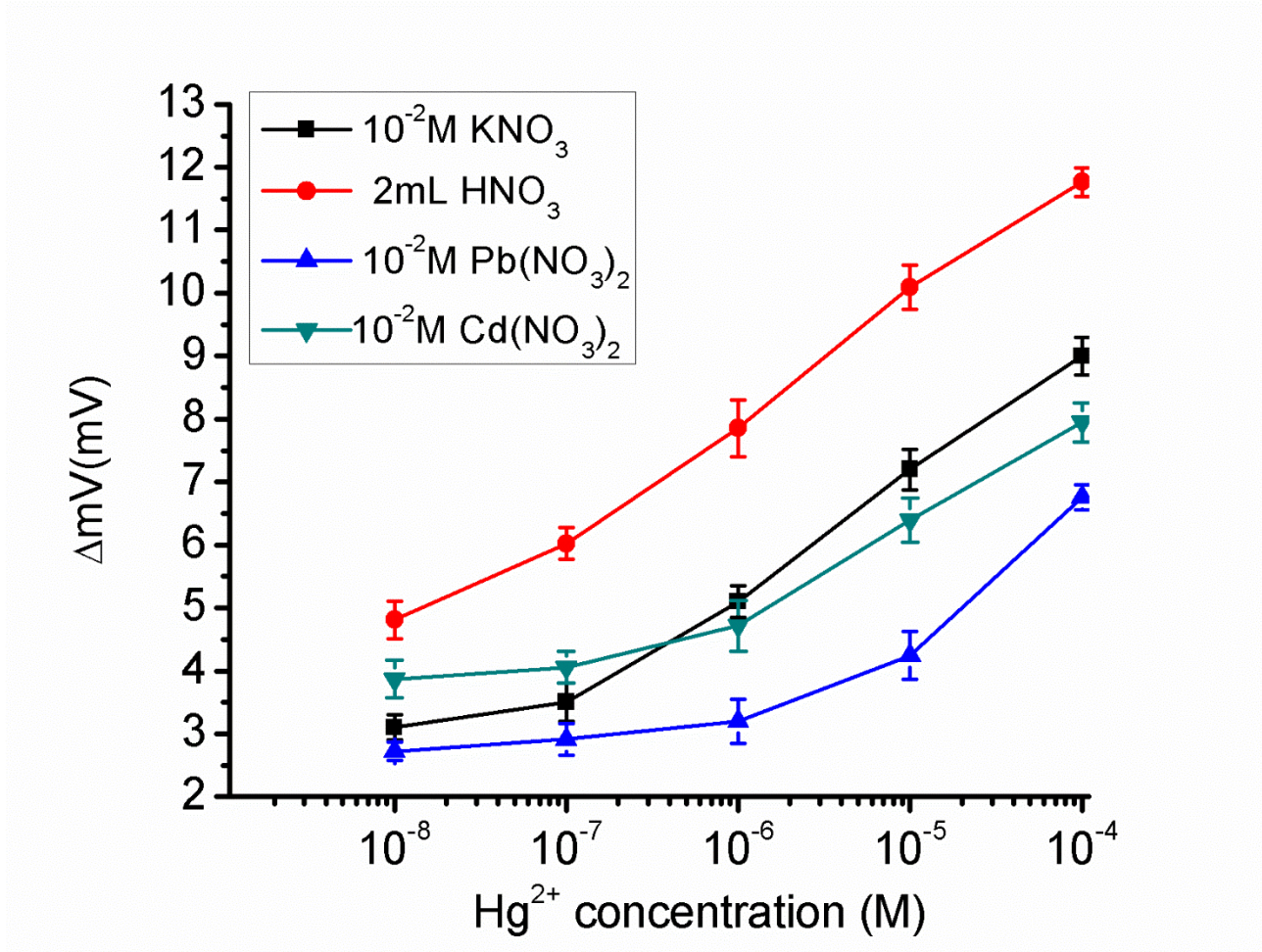


Figure 5: Plot of equilibrium sensor response ( $\Delta\text{mV} = V_{\text{after Hg}^{2+} \text{ added}} - V_{\text{before Hg}^{2+} \text{ added}}$ ) versus  $\text{Hg}^{2+}$  concentration in  $10^{-2}$  M of  $\text{KNO}_3$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Cd}(\text{NO}_3)_2$  with addition of  $\text{Hg}(\text{NO}_3)_2$  solution at constant pH value of 2.8.

These devices are operated without a metal gate or reference electrode. To extract the selectivity of the devices from the response data requires plotting the effective gate voltage as a function of concentration. The effective gate voltage can be obtained by considering the  $I_D$ - $V_D$ - $V_G$  relationship for the HEMT under the conditions of operation.

The behaviour of field effect transistors operating in the non-saturated (triode) regime can be described by:

$$I_D = \mu C \frac{W}{L} V_{SD} \left( (V_G - V_T) - \frac{1}{2} V_{SD} \right) \quad (1)$$

where  $I_D$  is the drain current,  $\mu$  is the channel electron mobility,  $C$  is the capacitance density of the gate,  $W$  is the channel width,  $L$  is the channel length,  $V_{SD}$  is the source-drain voltage,  $V_G$  is the gate voltage and  $V_T$  is the threshold voltage. Under typical sensor operating conditions, corresponding to effective gate potential sufficiently above the channel's threshold voltage and at current levels that lead to very small drain voltages, the drain voltage is such that  $V_{SD} \ll V_G - V_T$ , hence Eq. (1) can be approximated as:

$$I_D \approx \mu C \frac{W}{L} V_{SD} (V_G - V_T) \quad (2)$$

In Si-based ISFETs when used to detect ionic concentration,  $I_D$  and  $V_{SD}$  are usually chosen for operation in the linear (or triode) region and kept constant using a feedback loop to adjust the potential applied to a reference electrode as the membrane potential varies with ion concentration. It is the change in the potential applied to the reference electrode that results in the Nernstian response that is often observed for Si-based ISFETs and other reported AlGaIn/GaN-based sensors. In this work, the current level is also optimised to ensure that the device operates in the linear regime (triode or ohmic region), however no reference electrode is employed. The source-drain current level was kept constant, whilst the channel conductivity is monitored through direct measurement of the resulting  $V_{SD}$  potential developed. Thus, this characterisation scheme enables the measurement of changes in channel conductivity induced by changes in the effective surface gate potential arising from exposure to different ion concentrations. Rearranging

Eq. (2) shows that, with a constant current, the measured conductivity is proportional to the gate voltage:

$$\sigma \approx \frac{(V_G - V_T) \mu C W}{L} \quad (3)$$

in which the capacitance of the dielectric layer (i.e., AlGa<sub>N</sub> and Ga<sub>N</sub> cap) is given by

$$C = \frac{\epsilon_0 \epsilon_{material}}{d} \quad (4)$$

where  $C$  corresponds to the series combination of  $C_{AlGaN}$  and  $C_{GaN}$ ; the static dielectric constant for the AlGa<sub>N</sub> layer is modelled empirically with respect to Al mole fraction ( $x$ ) using the relation.

$$\epsilon_{material}(X) = -0.5x + 9.5 \quad (5)$$

The devices in this study had an AlN mole fraction of  $x = 0.23$  in the AlGa<sub>N</sub> layer, and had thicknesses of  $d_{AlGaN} = 12nm$  and  $d_{GaN} = 2nm$ , resulting in a total combined capacitance of  $5.94mF/m^2$ . The sensors had a channel width of  $W = 1mm$ , channel length of  $L = 2mm$ , with a measured Hall electron mobility of  $\mu = 1785 \times \frac{10^{-4}m^2}{V} s$ .

Substituting these values into into Eq. (3), and rearranging, leads to a relationship between change in conductivity and change in apparent gate voltage:

$$V_G - V_T(mV) = \frac{\sigma(\mu S)}{0.530} \quad (6)$$

Thus a linear relationship exists between conductivity and gate voltage for the transistor device when biased to operate in under uniform channel conditions (or ohmic region). By

using Eq. (6), the equilibrium potential data in Figure 5 can be expressed in terms of  $V_G - V_T$ , as shown in Figure 6.

For potentiometric sensors operated with a reference electrode, the relationship between gate voltage and potentiometric response follows the Nikolski-Eisenman equation:

$$V_G - V_T = E_0 - R \log(a_{mercury} + S a_{ion buffer}) \quad (7)$$

where  $E_0$  is a device constant,  $R$  is the potentiometric response slope,  $S$  is the selectivity coefficient and  $a$  is the activity coefficient. For a divalent cation such as  $Hg^{2+}$ , the slope (i.e. the  $R$  value) is expected to be  $29.6 \text{ mV}$  per decade in ion concentration at room temperature. The data in Figure 6 to was fitted to Eq. (7) to obtain a potentiometric response slope equivalent to that measured using standard ISFET configuration with a reference electrode. The extracted slope for each data set is given in Table 1. It can be seen that near-Nernstian behaviour of the sensor is confirmed. The selectivity coefficients can also be obtained from Figure 6 and these are also given in Table 1. Using the PVC-based membrane, the devices exhibited an approximately 2000, 40000 and 150000-fold selectivity for  $Hg^{2+}$  over  $Pb^{2+}$ ,  $Cd^{2+}$  and  $K^+$ , respectively. For  $Pb^{2+}$ , these PVC membrane-coated device results compare favourably with the 100-fold selectivity reported for thioglycolic acid monolayer functionalised AlGaIn/GaN devices [16]. The selectivity results of the AlGaIn/GaN device as given in Table 1 also compare favourably with an electrochemical cell ion selective electrode using the same membrane formulation used here (i.e. 35, 16, 32-fold selectivity for  $Hg^{2+}$  over  $K^+$ ,  $Cd^{2+}$  and  $Pb^{2+}$ , respectively)[18].



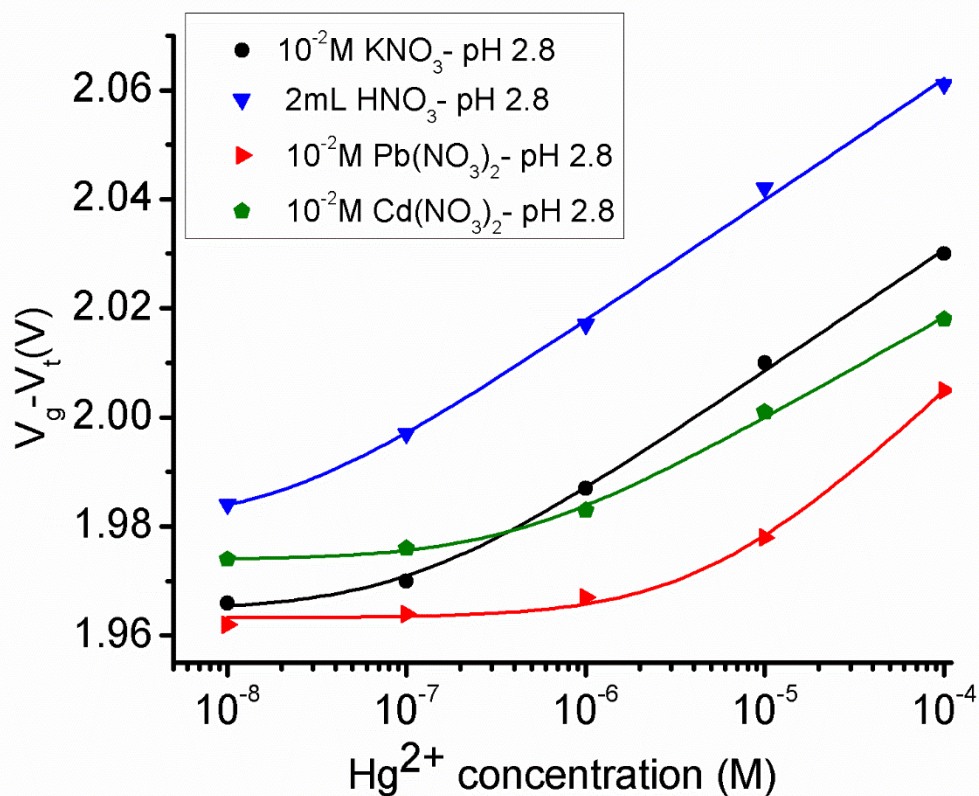


Figure 6: Plot of equilibrium sensor output as a function of mercury concentration in  $10^{-2}$  M  $\text{KNO}_3$ ,  $\text{Pb(NO}_3)_2$ ,  $\text{Cd(NO}_3)_2$  with additional  $\text{Hg(NO}_3)_2$  solution at constant pH value of 2.8 and the non-linear least squares fit of this data to the Nikolski-Eisenman equation (equation (7)).

Table 1: Sensor performance in different ionic strength buffer solutions as measured by selectivity coefficient and response slope (extracted by fitting to the Nikolski–Eisenman equation), linear response range and lower detection limit.

Ionic strength buffer solution	Selectivity coefficient K	Selectivity coefficient K (Ref. [18])	Response slope (mV/ $\log_{10}[\text{Hg}^{2+}]$ )	Linear range (M)	Detection limit (M)
$\text{HNO}_3$	3.77E-6	7E-2	0.023	$10^{-8}$ - $10^{-4}$	$10^{-8}$
$\text{KNO}_3+\text{HNO}_3$	6.38E-6	6.3E-2	0.021	$10^{-7}$ - $10^{-4}$	$10^{-8}$
$\text{Pb(NO}_3)_2+\text{HNO}_3$	4.84E-4	7.9E-2	0.026	$10^{-5}$ - $10^{-4}$	$10^{-6}$
$\text{Cd(NO}_3)_2+\text{HNO}_3$	2.39E-5	3.2E-2	0.019	$10^{-6}$ - $10^{-4}$	$10^{-7}$

Finally, we performed X-ray photoelectron spectroscopy (XPS) to investigate the membrane behaviour after exposure to  $\text{Hg}^{2+}$  solutions and subsequent rinsing with de-ionized water. For these experiments 15  $\mu\text{m}$  membranes were deposited on a GaN wafer and various controlled experiments were performed (before exposure to  $\text{Hg}(\text{NO}_3)_2$ , after immersion in  $10^{-2}$  M  $\text{Hg}(\text{NO}_3)_2$  for 7 hours without subsequent rinsing and after immersion in  $\text{Hg}(\text{NO}_3)_2$  for 7 hours and subsequent rinsing with de-ionized water). These experiments confirmed the binding of mercury atoms to the membrane when exposed to  $\text{Hg}^{2+}$  and their subsequent removal after rinsing with de-ionized water. A distinctive peak at 102.5 eV was also observed for all cases which is likely due to silicon contamination in the membrane composition.

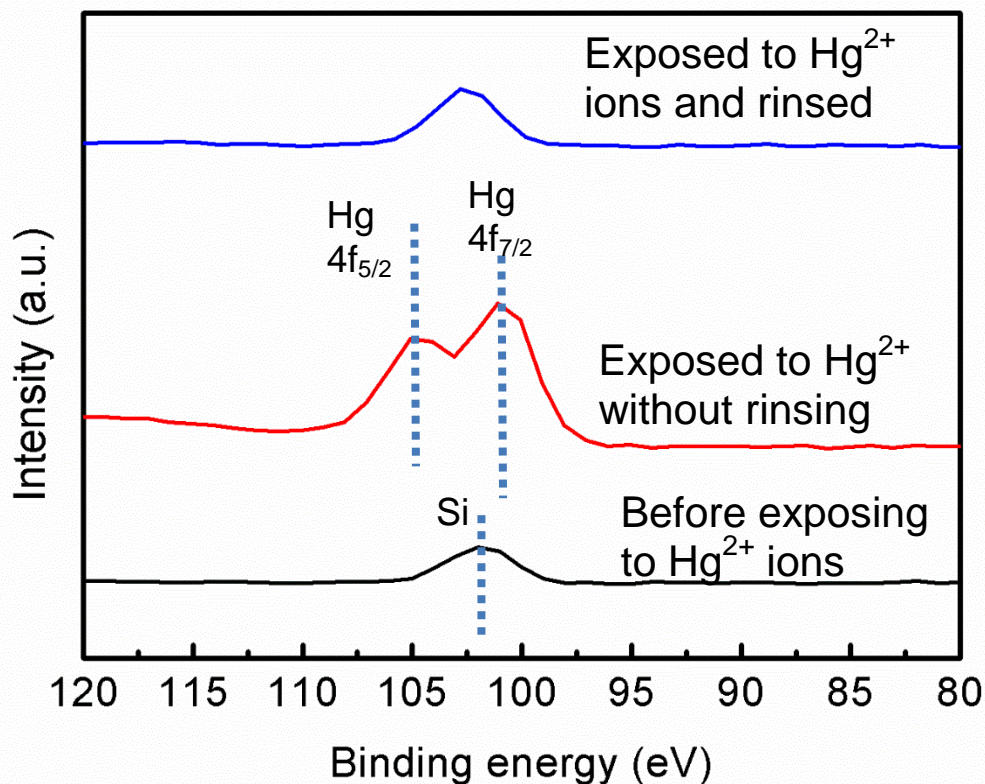


Figure 7: X-ray photoelectron spectroscopy results for the membrane-coated GaN (I) before being exposed to  $\text{Hg}^{2+}$ , after being immersed in  $10^{-2}$  M  $\text{Hg}(\text{NO}_3)_2$  solution for 7 hours without rinsing (III), after immersion in  $10^{-2}$  M  $\text{Hg}(\text{NO}_3)_2$  solution for 7 hours and subsequent rinsing with de-ionized water.



#### **4. Conclusion**

In this work we have demonstrated that an AlGaIn/GaN device without a reference electrode can be used as a mercury sensor when applying the appropriate ion selective membrane. The proposed device shows a better performance in terms of selectivity and sensitivity as compared to published results for an electrochemical cell ion selective electrode using the same membrane and for AlGaIn/GaN devices with other forms of functionalisation. Without the necessity of a reference electrode, these devices suggest greater opportunities for integration and miniaturisation, while lowering the manufacturing cost of the ISFET device. Furthermore, by use of different ionophores an array of sensors can be integrated on a single chip to detect various analytes. Subsequently, by using statistical analysis of the array, both sensitivity and selectivity of analytes can be improved.

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