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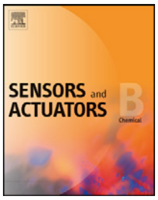

Nitrate ion detection using AlGaN/GaN heterostructure-based devices without a reference electrode

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ABSTRACT

AlGaN/GaN heterostructure-based devices can be engineered through heterostructure design to have a high transconductance near zero gate–drain voltage, potentially enabling high sensitivity, reference electrode free, ion sensing. As a proof of concept, these devices were coated with a PVC-based membrane containing a plasticizer and an ionophore to detect nitrate ions in solution. The sensor response is measured as a change in conductivity across two contacts using a Kelvin probe (or four-contact) geometry, with the current between the two outer contacts kept constant. We show that this sensor for nitrate is sensitive and stable with a rapid response time (i.e. less than 60 s). The detection limit remains consistently low over multiple runs/days. In a 0.1 M KH_2PO_4 ion buffer, a detection limit of less than 1×10^{-6} M and a linear response range of 10^{-6}–10^{-3} M were achieved. Furthermore, detection limits of approximately 10^{-6} M and 10^{-4} M in 0.1 M K_2SO_4 and 0.1 M KCl ion buffers, respectively, were demonstrated. In a 0.1 M KH_2PO_4 ion buffer, there was minimal change in sensor response upon addition of KOH increasing the pH from approximately 4–11. As a control, devices without a PVC membrane coating were tested under identical conditions and exhibited negligible response to nitrate ion exposure. Furthermore, using transistor theory, we show that the apparent gate response is near-Nenrstian under a variety of conditions. The success of this study paves the way for extending this technology to selectively sensing multiple ions in water through incorporation of the appropriate polymer based membranes on arrays of devices.

1. Introduction

Ion sensors for aqueous solutions are a critical monitoring component in a wide variety of industries including agricultural, water, medical (clinical analysis) and environmental monitoring, to name a few. However, most conventional sensors suffer from a combination of factors such as poor selectivity and/or sensitivity, limited scope of detectable analytes, short device lifetimes, high cost and bulkiness [1]. Ion-selective electrodes are important low-cost water testing tools that have been used extensively for many years to detect a wide variety of ions [2]. However, they require careful and regular calibration and must be used in conjunction with a reference electrode, which has its own stability and bulkiness issues.

Bergveld reported that the chemical responsiveness of the gate metal oxide layer of a Si-based field-effect transistor could be used to modulate the conduction properties of the source–drain channel giving rise to a chemical sensor [3]. Unfortunately such devices typically require a reference electrode in order to bias the gate of the transistor beyond the threshold voltage, to allow majority carriers to travel through the conductive channel [4]. On-chip miniaturised Ag/AgCl reference electrodes have been designed and tested, but their fabrication is typically complex and electrode solution leakage remains a serious issue compromising sensor accuracy and device lifetime [5]. A simpler solution for biasing the transistor is to add an on-chip noble metal (e.g. gold) contact/electrode, but this addition alone is not adequate as the metal/electrolyte interface potential is not stable. A reference field-effect transistor (REFET), which has a chemically passivated gate surface and is insensitive to changes in solution composition, can be used in conjunction with the ion selective field effect transistor (ISFET) device to compensate for these changes in interfacial potential [6]. However, despite many attempts, this method also suffers from chemical instability and drift [7]. Si-based transistors can be heavily doped resulting in a “normally-on” state possibly precluding the necessity for a

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reference electrode, but heavy doping results in decreased device performance (e.g. poor electron mobility) and increased manufacturing costs.

AlGaN/GaN high electron mobility transistors (HEMTs) are an attractive alternative to Si-based transistors, with higher device transconductance, vastly improved chemical stability and diminished charging effects [8,9]. The high electron mobility and transconductance are the result of a 2-dimensional electron gas layer (2DEG) that forms at the AlGaN/GaN interface. The conductivity of this 2DEG layer is sensitive to charges on the surface, thus forming the basis for an ion sensor. AlGaN/GaN devices with various capping layers (such as native or deposited oxides) have been shown to be effective pH sensors [10,11]. It has recently been shown that with an ultrathin GaN/AlGaN/GaN device that a reference electrode is not necessary to achieve very sensitive measurements of solution pH [12]. In other reports it has been shown that for uncapped reference electrode free AlGaN/GaN device measurements the device sensitivity is towards negative ions (i.e. chloride) and not exclusively changes in pH [13].

Some limited previous studies have been undertaken into functionalisation towards specific ion detection. A PVC-based membrane incorporating bis(2-ethylhexyl) sebacate as a plasticizer and nonactin as an ammonium ionophore was coated onto an AlGaN/GaN device, resulting in an ammonium ion sensor using traditional ISFET configuration with a reference electrode [14]. Using an Ag/AgCl reference electrode and a feedback circuit to vary the gate bias (sensor response) to maintain a constant drain current ($I_{DS} = 2320\ \mu A$) at a constant drain–source voltage ($V_{DS} = 1000$ mV), a stable near-Nernstian response was observed and the sensitivity and selectivity were comparable to traditional ammonium ion selective electrodes. InN gated AlGaN/GaN devices have demonstrated sensitivity towards chloride ions and selectivity against Na^+, Mg^{2+} and H^+ [15]. Wang et al. have demonstrated sensitive and selective detection of Hg^{2+} ions with thioglycolic acid monolayer functionalized AlGaN/GaN devices [16,17]. In this paper, we demonstrate the possibility of extending this concept to the wide selection of ion selective PVC-based membranes [18–20] and demonstrate for polymer-functionalised AlGaN/GaN devices a reference electrode is not required for selective and sensitive ion detection.

2. Experimental

2.1. Materials

Tetradodecylammonium bromide, high molecular weight polyvinyl chloride and 2-nitrophenyl octyl ether and tetrahydrofuran were purchased from Sigma–Aldrich and used without further purification. Analytical grade potassium nitrate, potassium dihydrogen phosphate, potassium sulfate and potassium chloride were purchased from Chem Supply (Australia) and used without further purification in sensor testing as a dissolved salt in distilled water.

2.2. Nitrate selective membrane

For performance comparison with a Si-based ISFET device for nitrate detection, we utilized an optimized membrane formulation (10 mg of tetradodecylammonium bromide, 660 mg of 2-nitrophenyloctyl ether and 330 mg of high molecular weight polyvinyl chloride dissolved in 10 mL THF) to coat our own device [21].

2.3. Device construction and operation

For this study we used an AlGaN/GaN wafer having an Al fraction $x(\mathrm{Al}) = 23\%$ and AlGaN layer thickness of 12 nm, grown using MOCVD. The wafer was capped with a 2 nm GaN layer to improve the electrochemical stability of the device. The four-contact devices were fabricated using standard semiconductor fabrication (lithography and plasma etching) processes with thermally deposited Al/Cr/Au contacts (20, 50 and 300 nm thickness, respectively). The membrane solution was drop cast onto the active sensing area of the devices resulting in a 15 μm thick membrane (thickness was measured with a stylus profilometer) and allowed to thoroughly dry before device packaging and testing. Kelvin probe geometry (see Fig. 1) was used to measure the conductivity across the sense terminals at an operating current of 100 μA across the source/drain terminals.

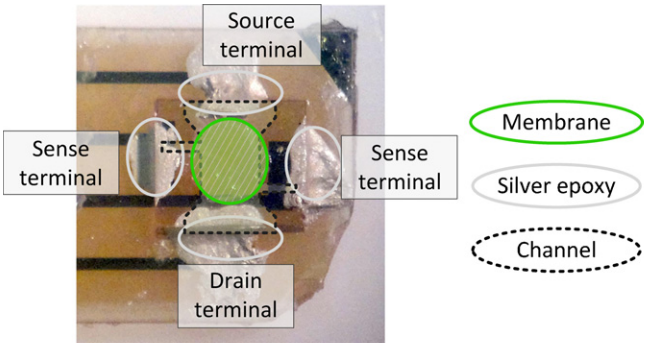

Fig. 1. Image with overlying schematic of sensor device layout.

2.4. Sensor testing

For testing the device response towards nitrate ions, the devices were first soaked in a 10^{-3} M KNO_3 solution for 30 min to exchange the bromide ions in the ionophore with nitrate ions. This step was followed by thorough rinsing with water and soaking in de-ionized water for 30 min. The devices were then equilibrated in 500 mL of an ion buffer solution (0.1 M KH_2PO_4, 0.1 M K_2SO_4 or 0.1 M KCl in de-ionised water) until a sufficiently stable baseline was obtained (typically 30–120 min). This step was followed by sequential additions of 1.0 μL, 10 μL, 100 μL, 1000 μL, 10 mL and 100 mL of 10^{-1} M KNO_3 solution at 30 min intervals while continuously stirring (low speed) the solution and monitoring the voltage across the sense terminals. For testing the device response towards changing pH, the membrane was equilibrated with 0.1 M KH_2PO_4 for 30 min. 5 M KOH in water was added sequentially (with sufficient time for equilibration between each addition) to vary the pH stepwise from approx. 4.0–11.0. The testing solution pH was measured independently using a calibrated pH metre. The error bars for the reported equilibrium sensor responses are determined by calculating the standard deviation of the response time series.

3. Results and discussion

Fig. 2 shows a sensor response vs. time profile as nitrate was added to a 0.1 M KH_2PO_4 ion buffer solution. For a 15 μm thick film, the response time was less than 60 s after each addition of nitrate and the response was stable with a rms noise level of less than 0.3 μS. There was a modest downward drift in response after each addition (particularly at higher concentrations) which is attributed to solution mixing and membrane equilibration. Fig. 3 gives a plot of the equilibrium response vs. NO_3-concentration in 0.1 M KH_2PO_4 ion buffer for runs conducted on four different days. Though there was some measurement variability in the response behaviour between runs on separate days, the nitrate detection limit and linear range remained approximately the same. This suggests that like most ion selective measurements, sensor calibration with