# Fast electrical detection of Hg(II) ions with AlGaN/GaN high electron mobility transistors

Hung-Ta Wang, B. S. Kang, T. F. Chancellor, Jr., T. P. Lele, Y. Tseng, and F. Ren[a)]
*Department of Chemical Engineering, University of Florida, Gainesville, Florida 32611*

S. J. Pearton
*Department of Materials Science and Engineering, University of Florida, Gainesville, Florida 32611*

W. J. Johnson, P. Rajagopal, J. C. Roberts, E. L. Piner, and K. J. Linthicum
*Nitronex Corporation, Durham, North Carolina 27703*

Bare Au gated and thioglycolic acid functionalized Au-gated AlGaN/GaN high electron mobility transistors (HEMTs) were used to detect mercury (II) ions. Fast detection of less than 5 s was achieved for thioglycolic acid functionalized sensors. This is the shortest response time ever reported for mercury detection. Thioglycolic acid functionalized Au-gated AlGaN/GaN HEMT based sensors showed 2.5 times larger response than bare Au-gated based sensors. The sensors were able to detect mercury (II) ion concentration as low as $10^{-7}M$. The sensors showed an excellent sensing selectivity of more than 100 for detecting mercury ions over sodium or magnesium ions. The dimensions of the active area of the sensor and the entire sensor chip are $50 \times 50~\mu m^2$ and $1 \times 5~mm^2$, respectively. Therefore, portable, fast response, and wireless based heavy metal ion detectors can be realized with AlGaN/GaN HEMT based sensors. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2764554]

Mercury (II) ($Hg^{2+}$) ion is one of the most environmentally important cations whose toxicity has long been recognized as a chronic environmental problem.[1–4] Mercury is released into the environment through a variety of courses including the combustion of fossil fuels, mining, volcanic emissions, and solid waste incineration. Mercury has attracted a great deal of attention around the world for its impact on wild life ecology and human health. Certain bacteria convert inorganic mercury $Hg^{2+}$ into neurotoxic organic-mercury compounds, which bioaccumulate through the plant, animals, and food chain and affect the entire ecosystem.[5–7]

It is highly desirable to develop sensitive and selective analytical methods for the quantitative detection of $Hg^{2+}$, which are applicable in a wide range of different sites and environments. Traditionally, there are several methods for heavy metal detection including spectroscopic (atomic absorption spectroscopy, Auger-electron spectroscopy, or inductively coupled plasma-Mass Spectrometry (ICP)-MS)) or electrochemical (ion selective electrodes or polarography); however, these methods are either expensive or not useful for detection on site, where hand-held portable devices could be invaluable for metal detections at low concentrations.[8–10] To date, a number of selective $Hg^{2+}$ ion sensors have been devised utilizing redox, chromogenic, or fluorogenic changes. Most of these systems display shortcomings in practical use, such as interference from other metal ions, delayed response to $Hg^{2+}$, and/or lack of water solubility.[11–14] Therefore, development of fast response and inexpensive methods for detection of bioavailable heavy metal concentrations is highly desirable.

GaN/AlGaN high electron mobility transistors (HEMTs) have been extremely useful for gas and liquid sensors for primarily two reasons: (1) they consist of a high electron

sheet carrier concentration channel induced by piezoelectric polarization of the strained AlGaN layer and (2) the carrier concentration strongly depends on the ambient.[15–19] For these reasons, nitride HEMTs are versatile devices that may be used for a variety of sensing applications.

In this letter, we report the detection of $Hg^{2+}$ with sensors fabricated with Au gated and thioglycolic acid functionalized Au-gated GaN/AlGaN HEMTs. We investigated a wide range of concentration from 10 $\mu$M to 10 nM. The temporal resolution of the device was quantified along with the limit of detection selectivity over sodium as well as magnesium and precision of measurements.

The HEMT structures consisted of a 2 $\mu$m thick undoped GaN buffer and 250 Å thick undoped $Al_{0.25}Ga_{0.75}N$ cap layer. The epilayers were grown by metal-organic chemical vapor deposition on 100 mm (111) Si substrates at Nitronex Corporation. Mesa isolation was performed with an ICP etching with $Cl_2/Ar$ based discharges at −90 V dc self-bias, ICP power of 300 W at 2 MHz, and a process pressure of 5 mTorr. $50 \times 50~\mu m^2$ Ohmic contacts separated with gaps of 10, 20, and 50 $\mu$m consisted of e-beam deposited Ti/Al/Pt/Au patterned by lift-off and annealed at 850 °C and 45 s under flowing $N_2$ for source and drain metal contacts, and 5 nm thin gold film was deposited as gate metal to functionalize a self-assembled monolayer of thioglycolic acid. 500-nm-thick polymethyl methacrylate was used to encapsulate the source/drain regions, with only the gate region open to allow the liquid solutions to cross the surface by e-beam lithography. The source-drain current-voltage characteristics were measured at 25 °C using an Agilent 4156C parameter analyzer with the Au-gated region exposed to different concentrations of $Hg^{2+}$, $Mg^{2+}$, or $Na^+$ solutions. ac measurements were performed to prevent side electrochemical reactions with modulated 500 mV bias at 11 Hz.
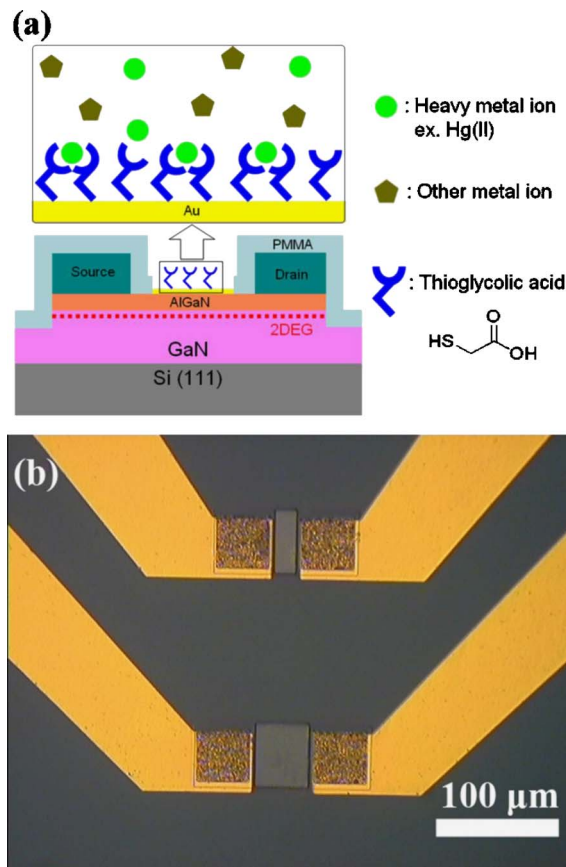
a)Electronic mail: fren@che.ufl.edu

**(a)**

FIG. 1. (Color online) (a) Schematic of AlGaN/GaN HEMT. The Au-coated gate area was functionalized with thioglycolic acid. (b) Plan view photomicrograph of a completed device with a 5 nm Au film in the gate region.



FIG. 2. Changes in HEMT drain-source current as results functionalizing Au gate with thioglycolic acid.

A schematic cross section of the device with $Hg^{2+}$ ions bound to thioglycolic acid functionalized on the gold gate region and plan view photomicrograph of a completed device is shown in Fig. 1. The thioglycolic acid, $HSCH_2COOH$, is an organic compound and contains both a thiol (mercaptan) and a carboxylic acid functional group. A self-assembled monolayer of thioglycolic acid molecule was adsorbed onto the gold gate due to a strong interaction between gold and the thiol group. The extra thioglycolic acid molecules were rinsed off with de-ionized (DI) water. An increase in the hydrophilicity of the treated surface by thioglycolic acid functionalization was confirmed by contact angle measurement which showed a change in contact angle from 58.4° to 16.2° after the surface treatment. x-ray photoemission spectroscopy and electrical measurements confirming a high surface coverage and Au–S bonding formation on the GaN surface and the results have been previously published.[19]

Unlike conventional semiconductor field effect transistors, there is no intentional dopant in the AlGaN/GaN HEMT structure. The electrons in the two-dimensional electron gas (2DEG) channel of the AlGaN/GaN HEMT are induced by piezoelectric and spontaneous polarization effects. This 2DEG is located at the interface between the GaN layer and AlGaN layer. There are positive countercharges at the AlGaN surface layer induced by the 2DEG. Any slight changes in the ambient of the AlGaN/GaN HEMT affect the surface charges of the AlGaN/GaN HEMT. These changes in the surface charge are transduced into a change in the concentration of the 2DEG in the AlGaN/GaN HEMTs.
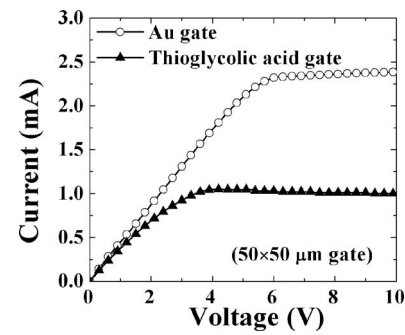
Based on this principle, we have demonstrated the use of appropriately functionalized AlGaN/GaN HEMTs as gas or liquid sensor. Figure 2 shows the drain *IV* curves of a bare Au gate AlGaN/GaN HEMT sensor and a thioglycolic acid functionalized AlGaN/GaN HEMT sensor. After the thioglycolic acid functionalization the drain current was reduced by more than 50%.

As shown in Fig. 3(a), the drain current of both sensors further reduced after exposure to different concentrations of $Hg^{2+}$ ion solutions. Being exposed to $10^{-5}M$ $Hg^{2+}$, the drain current reduced ~55% for the thioglycolic acid functionalized AlGaN/GaN HEMT sensors and bare Au-gate sensor had less than ~8% changes of the drain current. The mechanism of the drain current reduction for bare Au gate and thioglycolic acid functionalized AlGaN/GaN HEMT sensors was quite different. For the bare Au-gate devices, Au-mercury amalgam formed on the surface of the bare Au gates
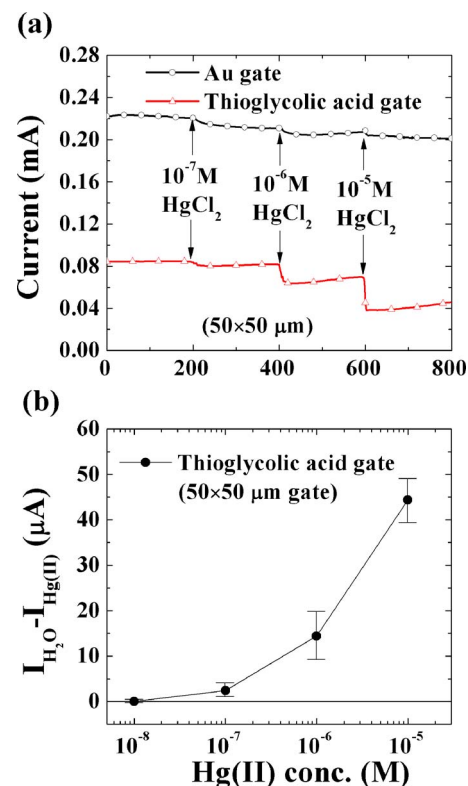


FIG. 3. (Color online) (a) Time dependent response of the drain current for bare Au-gate AlGaN/GaN HEMT sensor and thioglycolic acid functionalized Au-gate HEMT sensor. (b) Drain current of a thioglycolic acid functionalized Au-gate HEMT sensor as a function of the $Hg^{2+}$ ion concentration.
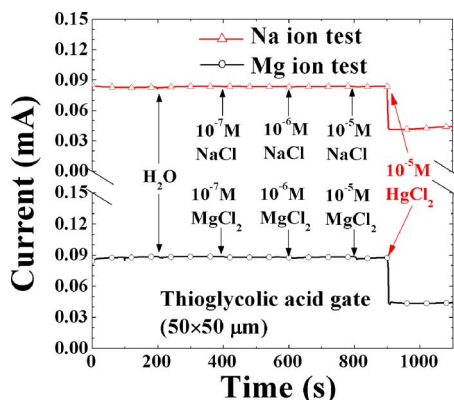
FIG. 4. (Color online) Time dependent response of the drain current for detecting Na$^+$, Mg$^{2+}$, or Hg$^{2+}$ with a thioglycolic acid functionalized Au-gate HEMT sensor.

when the Au-gate electrode is exposed to Hg$^{2+}$ ion solution. The formation rate of the Au-mercury amalgam depended on the solution temperature and the concentration of the Hg$^{2+}$ ion solution. Figure 3(a) also shows the time dependence of the drain current for the two types of sensors. For the higher Hg$^{2+}$ ion concentration solution, $10^{-5}M$, the bare Au-gate based sensor took less than 15 s for the drain to reach steady state. However, the drain current required 30–55 s to reach steady state, when the sensor was exposed to the less concentrated Hg$^{2+}$ ion solutions.

A less than 5 s response time was obtained for the thioglycolic acid functionalized AlGaN/GaN HEMT sensors, when the sensor was exposed to the $10^{-5}M$ of the Hg$^{2+}$ ion solution. This is the shortest response time of Hg$^{2+}$ ion detection ever reported. For the thioglycolic acid functionalized AlGaN/GaN HEMT, the thioglycolic acid molecules on the Au surface align vertically with the carboxylic acid functional group toward the solution.[19] The carboxylic acid functional group of the adjacent thioglycolic acid molecules form chelates of $R-COO^-(Hg^{2+})^-OOC-R$ with Hg$^{2+}$ ion, when the sensors are exposed to the Hg$^{2+}$ ion solution. The charges of trapped Hg$^{2+}$ ion in the $R-COO^-(Hg^{2+})^-OOC-R$ chelates changed the polarity of the thioglycolic acid molecules, which were bonded to the Au gate through–S–Au bonds. This is why the drain current changes in response to mercury ions. Similar surface functionalization was used by Chang *et al.* and the fluorescence was use for the detections.[20] The difference of drain current for the device exposed to different Hg$^{2+}$ ion concentration to the DI water is illustrated in Fig. 3(b). The Hg$^{2+}$ ion concentration detection limit for the thioglycolic acid functionalized sensor is $10^{-7}M$ which is approximately equivalent to 27 ppb (parts per $10^9$). The thioglycolic acid functionalized sensor also showed excellent sensing selectivity (over 100 times higher selectivity) over Na$^+$ and Mg$^{2+}$ ions, as illustrated in Fig. 4.

Since our sensor chip is very compact ($1 \times 5$ mm$^2$) and operates at extremely low power (8 $\mu$W based on 0.5 V of drain voltage and 80 $\mu$A of drain current operated at 11 Hz), it can be integrated with a commercially available hand-held wireless transmitter to realize a portable, fast response, and high sensitivity Hg$^{2+}$ ion detector.

In summary, we have demonstrated AlGaN/GaN HEMT to be an excellent Hg$^{2+}$ ion sensor through a chemical modification on the Au-gate surface. The thioglycolic acid functionalized Au-gate based sensor showed good sensitivity and shortest response time ever reported. The sensor also showed excellent detection selectivity over Na$^+$ and Mg$^{2+}$ ions.

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