© 2008 Hung-Ta Wang
To my parents, my family.
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<th>Description</th>
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<tr>
<td>2DEG</td>
<td>Two Dimensional Electron Gas</td>
</tr>
<tr>
<td>AAS</td>
<td>Atomic Absorption Spectroscopy</td>
</tr>
<tr>
<td>AES</td>
<td>Auger Electron Spectroscopy</td>
</tr>
<tr>
<td>Ag</td>
<td>Silver</td>
</tr>
<tr>
<td>AKI</td>
<td>Acute Kidney Injury</td>
</tr>
<tr>
<td>Al</td>
<td>Aluminium</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>Aluminium oxide</td>
</tr>
<tr>
<td>AlGaN</td>
<td>Aluminum Gallium Nitride</td>
</tr>
<tr>
<td>Ar</td>
<td>Argon</td>
</tr>
<tr>
<td>ARF</td>
<td>Acute Renal Failure</td>
</tr>
<tr>
<td>As</td>
<td>Arsenic</td>
</tr>
<tr>
<td>Au</td>
<td>Gold</td>
</tr>
<tr>
<td>Cd</td>
<td>Cadmium</td>
</tr>
<tr>
<td>Cl$_2$</td>
<td>Chlorine</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon Nanotube</td>
</tr>
<tr>
<td>Cu</td>
<td>Copper</td>
</tr>
<tr>
<td>DNA</td>
<td>deoxyribonucleic acid</td>
</tr>
<tr>
<td>ELISA</td>
<td>enzyme-linked immunosorbent assay</td>
</tr>
<tr>
<td>FET</td>
<td>Field Effect Transistor</td>
</tr>
<tr>
<td>EL</td>
<td>electroluminescence</td>
</tr>
<tr>
<td>GaAs</td>
<td>Gallium Arsenide</td>
</tr>
<tr>
<td>GaN</td>
<td>Gallium Nitride</td>
</tr>
<tr>
<td>H$_2$</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>He</td>
<td>Helium</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>--------------</td>
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</tr>
<tr>
<td>HEMT</td>
<td>High Electron Mobility Transistor</td>
</tr>
<tr>
<td>Hg</td>
<td>Mercury</td>
</tr>
<tr>
<td>ICP</td>
<td>Inductively Coupled Plasma</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Inductively Coupled Plasma-Mass Spectrometry</td>
</tr>
<tr>
<td>In</td>
<td>Indium</td>
</tr>
<tr>
<td>In$_2$O$_3$</td>
<td>Indium(III) oxide</td>
</tr>
<tr>
<td>InGaAs</td>
<td>Indium Gallium Arsenide</td>
</tr>
<tr>
<td>InP</td>
<td>Indium Phosphide</td>
</tr>
<tr>
<td>ISE</td>
<td>Ion Selective Electrodes</td>
</tr>
<tr>
<td>I-V</td>
<td>Current-Voltage</td>
</tr>
<tr>
<td>IR</td>
<td>Infra Red</td>
</tr>
<tr>
<td>KIM-1</td>
<td>Kidney Injury Molecules-1</td>
</tr>
<tr>
<td>LD</td>
<td>Laser Diode</td>
</tr>
<tr>
<td>LED</td>
<td>Light Emitting Diode</td>
</tr>
<tr>
<td>LOD</td>
<td>Limit of Detection</td>
</tr>
<tr>
<td>MBE</td>
<td>Molecular Beam Epitaxy</td>
</tr>
<tr>
<td>Mg</td>
<td>Magnesium</td>
</tr>
<tr>
<td>MIS</td>
<td>Metal Insulator Semiconductor</td>
</tr>
<tr>
<td>MOCVD</td>
<td>Metal Organic Chemical Vapor Deposition</td>
</tr>
<tr>
<td>MOSFET</td>
<td>Metal Oxide Semiconductor Field Effect Transistor</td>
</tr>
<tr>
<td>MSFET/MESFET</td>
<td>Metal Semiconductor Field Effect Transistors</td>
</tr>
<tr>
<td>N$_2$</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Na</td>
<td>Sodium</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>ammonia</td>
</tr>
<tr>
<td>Ni</td>
<td>Nickel</td>
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NO$_2$: nitrogen dioxide

O$_2$: Oxygen

O$_3$: Ozone

Pb: Lead

PBS: Phosphate Buffered Saline

Pd: Palladium

PEI: polyethyleneimine

PEM: proton-exchange membrane

PIN diode: Positive-Intrinsic-Negative diode

PL: photoluminescence

PMMA: polymethyl methacrylate

ppb: parts per billion

ppm: parts-per-million

Pt: Platinum

RTA: Rapid Thermal Annealing

SiC: Silicon Carbide

SnO$_2$: Tin(IV) oxide

TE: Thermionic Emission

TFE: Thermionic Field Emission

Ti: Titanium

TiB$_2$: Titanium Boride

UV: Ultra Violent

XPS: X-ray Photoelectron Spectroscopy

XRR: X-ray reflectivity
Zn: Zinc
ZnO: Zinc Oxide
Pt-coated ZnO nanorods show a decrease of 8 % resistance upon exposure to 500 ppm hydrogen in room temperature. This is a factor of two larger than that obtained with Pd; approximately 95 % of the initial ZnO conductance was recovered within 20 s by exposing the nanorods to O2. This rapid and easy recoverability makes the ZnO nanorods suitable for ppm-level sensing at room temperature with low power consumption.

Pt-gated AlGaN/GaN based high electron mobility transistors (HEMTs) showed that Schottky diode operation provides large relative sensitivity over a narrow range around turn-on voltage; the differential designed Schottky diodes with AlGaN/GaN hetero-structure was shown to provide robust detection of 1 % H2 in air at 25 °C, which remove false alarms from ambient temperature variations; moreover, the use of TiB2-based Ohmic contacts on Pt-Schottky contacted AlGaN/GaN based hydrogen sensing diodes was shown to provide more stable operation.

Thioglycolic acid functionalized Au-gated AlGaN/GaN based HEMTs were used to detect mercury (II) ions. A fast detection (> 5 seconds) was achieved. This is the shortest response ever reported. 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 of detecting mercury ions over sodium, magnesium, and lead ions, but not copper.

AlGaN/GaN based HEMTs were used to detect kidney injury molecule-1 (KIM-1), an important biomarker for early kidney injury detection. The HEMT gate region was coated with KIM-1 antibodies and the HEMT source-drain current showed a clear dependence on the KIM-1 concentration in phosphate-buffered saline (PBS) solution. The limit of detection (LOD) was 1 ng/ml using a 20 µm × 50 µm gate sensing area. This approach shows a potential for both preclinical and clinical disease diagnosis with accurate, rapid, noninvasive, and high throughput capabilities.

The rest of this dissertation includes ZnO band edge electroluminescence from N⁺-implanted ZnO bulk, and the investigation of cryogenic gold Schottky contact on GaAs for enhancing device thermal stability.
CHAPTER 1
INTRODUCTION

1.1 Motivation

According to 2007 published “Sensors: A Global Strategic Business Report”, the global sensor market grows averagely at an annual rate of 4.5% between 2000 and 2008 and is expected to reach US $61.4 billion by 2010 [1]. The US $11.5 billion worth of chemical sensor market represents the largest segment of this global sensor market. This includes chemical detection in gas, chemical detection in liquid, flue gas and fire detection, liquid quality sensor, and biosensor. Semiconductor based sensor fabricated using the mature micro-fabrication techniques and/or novel nanotechnology is one of the major contestants in this market. Silicon based devices remain dominating due to their low cost, reproducible and controllable electronic behaviors, and abundant data of chemical treatment on silicon oxide or glass. However, they are unable to be operated at harsh environment, for instance, high temperature, high pressure, and corrosive ambient, so the application area is still limited. The two wide band-gap compound semiconductors, Gallium Nitride (GaN) and Zinc Oxide (ZnO), are very good alternative options to replace silicon because of many advantages, for example, highly chemical resistance, potential for high power operation, and blue and ultraviolet optoelectronic behaviors [2, 3]. A variety of sensors have been reported using GaN or ZnO materials, such as nanorod/wire, homo-structured thin film, and hetero-structured thin film based devices (diodes, transistors, surface acoustic wave devices, or electrochemical electrodes).

ZnO and GaN nanorods/wires are extremely attractive for sensing applications. In nature, 1-D nanostructures could dramatically enhance the sensitivity due to their high surface to volume ratio, Debye length comparable diameter, better crystallinity than 2-D thin film, and quantum effect [4, 5, 6]. In addition, for most of these applications, the nanorod/wire sensors have very
low power requirements and minimal weight. Combined with the native advantageous characteristics of ZnO and GaN, ZnO and GaN nanorods/wires are natural candidates for this type of sensing application.

GaN/AlGaN high electron mobility transistors (HEMTs) have been extremely useful for gas and liquid sensor 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 [7-9]. In addition, sensors fabricated from these wide band-gap semiconductors could be readily integrated with solar blind UV detectors or high temperature, high power electronics on the same chip. For these reasons, nitride HEMTs are versatile devices that may be used for a variety of sensing applications.

On the other hand, ZnO is an attractive candidate for Ultra Violent (UV) Light Emitting Diodes (LEDs) since it is an environmentally friendly material which is grown at low temperatures on cheap transparent substrates and has both a direct wide band gap of 3.3 eV and a very large exciton binding energy of 60 meV, important for robust light emission [10, 11]. Finally, it is important to increase Schottky barrier height in order to solve the reliability issues to compound semiconductor based HMETs. In particular, the gate reliability has been problematic. Increasing the Schottky barrier heights can improve the gate leakage current, gate-drain breakdown voltage, output resistance and power gain, and noise performance. Promising results engineering Schottky barrier heights have been demonstrated by cryogenic metal deposition at 77 K for GaAs, InP, and InGaAs [12, 13, 14].
1.2 Properties of GaN and ZnO

The properties of GaN and ZnO [2, 15, 16] are summarized and listed in Table 1-1. GaN can form either Wurtzite crystal structure with \( a=3.19\text{Å} \) and \( c=5.19 \text{Å} \) or Zinc Blende crystal structure with \( a=4.52 \text{Å} \) and \( c=4.5 \text{Å} \). Because of its large direct band-gap (\( E_g=3.5 \text{ eV} \)), high thermal stability, high electron mobility (1000 cm\(^2\)/V·s), and other physical properties, GaN and its alloys with Al and In have been the basic materials for short-wavelength optoelectronics, and high-power, high-temperature electronic devices and sensors. The energy gaps in these considered compounds (6.2, 3.4 and 1.9 eV for AlN, GaN and InN respectively) cover the whole visible spectrum and a large part of the UV range, as shown in Figure 1-1. At present, GaN based high-brightness blue and green light emitting diodes (LEDs) and low-power blue laser diodes (LDs) are commercially available. On the other hand, however, the development of GaN-based technology was, and still is, strongly limited by difficulties in obtaining large, high-quality crystals which could be used as substrates for epitaxial deposition of multilayer quantum structures necessary for devices [3, 17].

ZnO normally forms in the hexagonal wurtzite crystal structure with \( a=3.25 \text{Å} \) and \( c=5.20 \text{Å} \). The Zn atoms are tetrahedrally coordinated to four O atoms, where the Zn \( d \) electrons hybridize with the O \( p \) electrons. ZnO is also a direct band-gap semiconductor with \( E_g=3.4 \text{ eV} \). The band gap of ZnO, similar to GaN, can be tuned either up via Mg substitution or down via Cd substitution on the cation site, as shown in Figure 1-1. Substituting Mg on the Zn site in epitaxial films can increase the band gap to approximately 4.0 eV while still maintaining the wurtzite structure. The electron Hall mobility in ZnO single crystals is on the order of 200 cm\(^2\)/V·s at room temperature [18]. While the electron mobility is lower than that for GaN, ZnO has a higher theoretical saturation velocity. Electron doping in nominally undoped ZnO has been attributed to Zn interstitials, oxygen vacancies, or hydrogen [19-24]. The intrinsic defect levels that lead to \( n- \)
type doping lie approximately 0.01–0.05 eV below the conduction band. A strong room
temperature near-band-edge UV photoluminescence peak at ~3.2 eV is attributed to an exciton
state, as the exciton binding energy is on the order of 60meV [25]. In addition, visible emission
is also observed due to defect states. A blue-green emission, centered at around 500nm in
wavelength, has been explained within the context of transitions involving self-activated centers
formed by a doubly ionized zinc vacancy and an ionized interstitial Zn⁺ [26], oxygen vacancies
[27-30], donor–acceptor pair recombination involving an impurity acceptor [31], and/or
interstitial O [32-34].

Table 1-1 Physical properties of GaN and ZnO.

<table>
<thead>
<tr>
<th>Property</th>
<th>GaN</th>
<th>ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal structure</td>
<td>Wurtzite</td>
<td>Zinc Blende</td>
</tr>
<tr>
<td><em>Lattice constant (nm)</em></td>
<td>a₀</td>
<td>c₀</td>
</tr>
<tr>
<td></td>
<td>0.3189</td>
<td>0.5185</td>
</tr>
<tr>
<td></td>
<td>0.5185</td>
<td>0.45</td>
</tr>
<tr>
<td>a₀/c₀</td>
<td>1.6259</td>
<td>1.602</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>6.15</td>
<td>5.606</td>
</tr>
<tr>
<td><em>Thermal conductivity (W cm⁻¹°C⁻¹)</em></td>
<td>&gt;2.1</td>
<td>0.6, 1-1.2</td>
</tr>
<tr>
<td>a₀</td>
<td>5.59×10⁻⁶</td>
<td>-</td>
</tr>
<tr>
<td>c₀</td>
<td>3.17×10⁻⁶</td>
<td>-</td>
</tr>
<tr>
<td>Energy bandgap, E_g (eV)</td>
<td>3.51, direct</td>
<td>3.3, direct</td>
</tr>
<tr>
<td>Exciton binding energy (meV)</td>
<td>28</td>
<td>-</td>
</tr>
<tr>
<td><em>for n-type</em></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electron effective mass</td>
<td>0.2</td>
<td>-</td>
</tr>
<tr>
<td>Electron Hall mobility at 300K (cm²V⁻¹s⁻¹)</td>
<td>~1000</td>
<td>~1000</td>
</tr>
<tr>
<td><em>for p-type</em></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hole effective mass</td>
<td>0.8</td>
<td>-</td>
</tr>
<tr>
<td>Hole Hall mobility</td>
<td>≤ 200</td>
<td>≤ 350</td>
</tr>
<tr>
<td>Electron saturation velocity (10⁷ cm s⁻¹)</td>
<td>2-2.5</td>
<td>2.0</td>
</tr>
</tbody>
</table>

23
Figure 1-1 Energy band-gap of GaN and ZnO based compound semiconductors as a function of lattice constant.

1.3 Two Dimensional Electron Gas of AlGaN/GaN High Electron Mobility Transistor

AlGaN/GaN heterojunction has been shown to form a potential well and a two dimensional electron gas (2DEG) at the lower heterointerface, as show in Figure 1-2. The application of AlGaN/GaN 2DEG had accelerated the development of high voltage, high power operated microwave devices for use in broad band power amplifiers in wireless base station applications [35, 36, 37]. These devices are so called AlGaN/GaN high electron mobility transistor, or AlGaN/GaN HEMTs, well known for high electron mobility in the 2DEG channel, highest sheet carrier concentration among III-V material system, high saturation velocity, high breakdown voltage, and thermal stability.

When wide band Al\textsubscript{x}Ga\textsubscript{1-x}N and narrow band GaN are brought into contact, thermal equilibrium align their respective Fermi levels (E\textsubscript{F}) that both conduction (E\textsubscript{c}) and valence (E\textsubscript{v}) band are bent and cause the GaN conduction band at the interface to drop below E\textsubscript{F}. Free
electrons will fill the triangular well and form 2DEG. From another viewpoint, as described by Ambacher et al., 2DEG is the compensation to a fixed sheet charge induced by both spontaneous polarization \( P_{SP} \) and piezoelectric or strain-induced polarization \( P_{PE} \) \([38, 39, 40]\). The spontaneous polarization for \( \text{Al}_x\text{Ga}_{1-x}\text{N} \) is,

\[
P_{SP}(x) = (-0.052x - 0.029) \ \text{C/m}^2,
\]

where the \( x \) is the Al concentration in \( \text{Al}_x\text{Ga}_{1-x}\text{N} \). In both AlN and GaN system, the spontaneous polarization is negative meaning that the spontaneous polarization is pointing toward substrate for Ga(Al)-face, and toward surface for N-face. The piezoelectric polarization can be calculated by,

\[
P_{PE} = e_{33}\gamma_z + e_{31}(\gamma_x + \gamma_y)
\]

where \( e_{33} \) and \( e_{31} \) are piezoelectric coefficients, \( \gamma_z = (c - c_0) / c_0 \) is the strain in c-axis,

\[
\gamma_x = \gamma_y = (a - a_0) / a_0
\]

is the in-plane strain that is assumed isotropic, and \( a, c \) are the lattice constants of the strained layer. Negative piezoelectric polarization represents that a GaN layer under compressive strain, and/or a AlGaN layer under tensile strain for Ga(Al)-face crystal.

For Ga-face AlGaN/GaN grown on \( c-\text{Al}_2\text{O}_3 \) substrate, tensile strain AlGaN layer contact with relaxed GaN layer and the spontaneous polarization and piezoelectric polarization align in parallel (Figure 1-3). The fixed charge induced by total polarization can be derived by,

\[
\sigma = P(bottom) - P(top) = P_{SP}(\text{GaN}) - [P_{SP}(\text{Al}_1\text{Ga}_{1-x}\text{N}) + P_{PE}(\text{Al}_1\text{Ga}_{1-x}\text{N})] \\
= [P_{SP}(\text{GaN}) - P_{SP}(\text{Al}_1\text{Ga}_{1-x}\text{N})] + [0 - P_{PE}(\text{Al}_1\text{Ga}_{1-x}\text{N})] \\
= \sigma(P_{SP}) + \sigma(P_{PE})
\]

The polarization induced sheet charge in this case is positive \( (+\sigma) \), and free electrons, therefore, tend to compensate it to form 2DEG at GaN interface with a sheet carrier concentration \( n_s \), which is expected to be,
\[ n_s(x) = \frac{\sigma(x)}{e} - \left( \frac{\varepsilon(x)}{d_\sigma e^2} \right) \left( e\phi_b(x) + E_F(x) - \Delta E_C(x) \right) \]  

(1-4)

where, \( \sigma(x) \) is piezoelectric polarization, \( \varepsilon(x) \) is the dielectric constant, \( d_\sigma \) is the AlGaN layer thickness, \( e\phi_b \) is the Schottky barrier of the gate contact on AlGaN, \( E_F \) is the Fermi level and \( \Delta E_C \) is the conduction band discontinuity between AlGaN and GaN. Because the spontaneous and piezoelectric polarization increase with Al concentration of AlGaN layer, the typical sheet carrier concentration could reach \( 1.6 \times 10^{13} \text{ cm}^{-2} \) for \( x = 0.3 \), in excess of other available III-V material systems.

Figure 1-2 Schematic diagram of normal AlGaN/GaN heterostructure with band diagram in the equilibrium state. 2DEG is located at the lower AlGaN/GaN interface.
1.4 Field-Effect Based Semiconductor Sensors

The idea for semiconductor sensor based on field-effect transistors (FETs) operation principle was first addressed by Bergveld who reported the use of metal-oxide-semiconductor field effect transistor (MOSFET), without incorporation of the regular gate electrode, for sodium ion and hydrogen ion detections in aqueous solution [41, 42]. In principle, for FET on p-type semiconductor (Figure 1-4), holes are injected from source electrode into the channel and collected at drain electrode. The conductance of this p-type channel can be tuned by a third gate electrode capacitively coupled through a thin dielectric layer: a positive gate voltage depletes carriers to cause a increase of space charge region underneath the gate electrode and reduces the conductance, while a negative gate voltage attracts carriers to compensate space charge region and leads an increase in conductance. Since the electric field resulting from binding of a charged species to the gate dielectric is analogous to applying a voltage using a gate electrode, the
potentiometric chemical signal can be measured by monitoring the conductance of the semiconductor channel that is field-effect sensitively modulated in a FET structure [43, 44]. The dependence of the conductance on gate voltage hence makes FETs natural candidates for electrical sensing of any binding of charged species. Thin film FET sensor had, however, constrained by limited sensitivity until the advent of one dimensional nanotubes, wires, and rods. Field-effect based semiconductor sensors made with those nanostructures have made a great impact, due to a dramatically increased surface to volume ratio with nanoscale diameter channel, that single molecule sensitivity might be possible.

The progress of nanostructure FET sensor recently has been accelerated by the successful surface functionalizations on semiconductor surface for selectivity detection purpose. For gas sensing, bare Carbon Nanotubes (CNTs) was reported that nitrogen dioxide (NO₂) and ammonia (NH₃) adsorptions result in reverse conductance responses because of the electron withdraw/donating mechanism[45]; The coating of amine group rich polymer, polyethyleneimine (PEI), on CNT causes an improved sensitivity and selectivity to NO₂ and other acidic gas, while the sulfonic acid group (-SO₃H) rich polymer, Nafion, obtaine NH₃ selective detection [46, 47]; Catalytic metal, Pt or Pd, coating made CNTs [48, 49] and Tin(IV) Oxide (SnO₂) nanowires [50] highly sensitive to hydrogen. For biosensing in aqueous solution, CNT have successfully detected specific proteins [51, 52, 53, 54] and glucose [51, 55, 56]; Si nanowires are able to detect protein [57, 58], deoxyribonucleic acid (DNA) [57, 59], drug [57, 60], and virus [57, 61]; Indium(III) oxide (In₂O₃) nanowires are also sensitive to protein [54] and DNA [62] though appropriate surface functionalizations. Table 1-2 is a summery of diverse chemical functionalization approaches applied to different nanostructure FET sensor for specific bio-
detections using selective bio-interaction, e.g. antigen-antibody reaction and DNA-DNA interaction.

<table>
<thead>
<tr>
<th>1-D nanomaterial</th>
<th>1st layer</th>
<th>2nd layer</th>
<th>3rd layer</th>
<th>4th layer</th>
<th>5th layer</th>
<th>sensing mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT (ref. 51, 52)</td>
<td>protein</td>
<td>protein</td>
<td>c-DNA</td>
<td>glucose</td>
<td>redox process</td>
<td></td>
</tr>
<tr>
<td>CNT (ref. 51, 52)</td>
<td>N-aliphatic molecules</td>
<td>©-biotin</td>
<td>protein</td>
<td>biotin-protein interaction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CNT (ref. 51, 52)</td>
<td>N-aliphatic molecules</td>
<td>©-protein</td>
<td>protein</td>
<td>antibody-antigen interaction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CNT (ref. 51, 53)</td>
<td>N-polymer(PEI)</td>
<td>©-biotin</td>
<td>protein</td>
<td>biotin-protein interaction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CNT (ref. 54)</td>
<td>©-phosphatic molecules</td>
<td>©-antibody</td>
<td>antigen</td>
<td>antibody-antigen interaction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CNT (ref. 51, 55, 56)</td>
<td>N-glucose oxidase</td>
<td>glucose</td>
<td>redox process</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si-NW (ref. 57, 58)</td>
<td>©-amine group</td>
<td>©-biotin</td>
<td>protein</td>
<td>biotin-protein interaction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si-NW (ref. 57, 59)</td>
<td>©-amine group</td>
<td>©-protein</td>
<td>©-biotin</td>
<td>c-DNA</td>
<td>DNA-DNA interaction</td>
<td></td>
</tr>
<tr>
<td>Si-NW (ref. 57, 60)</td>
<td>©-amine group</td>
<td>©-protein</td>
<td>drug</td>
<td>inhibitor reaction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si-NW (ref. 57, 61)</td>
<td>©-amine group</td>
<td>©-antibody</td>
<td>virus</td>
<td>antibody-virus interaction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>In$_2$O$_3$-NW (ref. 54)</td>
<td>©-phosphatic molecules</td>
<td>©-DNA</td>
<td>c-DNA</td>
<td>DNA-DNA interaction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>In$_2$O$_3$-NW (ref. 62)</td>
<td>©-phosphatic molecules</td>
<td>©-antibody</td>
<td>antigen</td>
<td>antibody-antigen interaction</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: © represents covalent functionalization; N represents covalent functionalization; highlighted final layer is the target analyte.

Figure 1-4 Cross section of a p-channel FET under positive $V_G$ and negative $V_G$. S, D, and G represent source, drain and gate electrodes respectively.
1.5 Dissertation Outline

The main objective of this work focuses on the design and fabrication of GaN and ZnO based sensing devices, and analysis of their sensitivity to hydrogen, heavy metal ions, and disease biomarkers. Chapter 1 reviews the material properties and recent sensor technologies combining field effect based devices with surface chemical functionalization. Chapter 2 illustrates details of fabrication and sensitivity measurement to hydrogen using catalytic metal coated multiple ZnO nanowires. Chapter 3 presents hydrogen detection using AlGaN/GaN HEMTs and Schottky diodes with the design of differential diodes and the use of TiB₂ based Ohmic contact. This is the extension for the previous work done by Dr. Byoung Sam Kang [63], toward practical applications. Chapter 4 focuses on the mercury ion detection using AlGaN/GaN HEMTs through a surface coating of carboxyl groups on gate region. Chapter 5 presents the detection of disease biomarker, kidney injury molecule-1 (KIM-1), using AlGaN/GaN HEMTs which are gate-coated with KIM-1 antibody.

The rest of this dissertation also includes ZnO band edge electroluminescence n⁻-implanted ZnO bulk (chapter 6), and investigation of cryogenic Schottky contact on GaAs regarding thermal stability and interfacial differences (chapter 7). Chapter 8 briefly summarizes a conclusion of above works and suggests future studies.
CHAPTER 2
HYDROGEN SENSOR USING MULTIPLE ZNO NANORODS

2.1 Background

There is a strong need to develop hydrogen sensors for use with proton-exchange membrane and solid oxide fuel cells for space craft and other long-term applications. A key requirement for these sensors is the ability to selectively detect hydrogen at room temperature with minimal power use and weight. Nanorods and nanotubes are potential candidates for this type of sensing. In the case of hydrogen sensing with carbon nanotubes (CNTs), several groups have reported that use of Pd doping or films or loading with Pd nanoparticles can functionalize the surface of nanotubes for catalytic dissociation of H₂ to atomic hydrogen [48, 49]. Of course, thin-film sensors of Si, GaAs, InP, SiC, and GaN with Pd contacts have been used previously as hydrogen sensors [64]. ZnO nanowires and nanorods have shown potential for use in gas, humidity, and chemical sensing [65, 66, 67]. The ability to make arrays of nanorods with large total surface area has been demonstrated with a number of different growth methods [5, 68–89] and a large variety of ZnO one-dimensional structures has been demonstrated [87]. The large surface area of the nanorods and bio-safe characteristics of ZnO makes them attractive for both chemical sensing and biomedical applications.

In this chapter, we demonstrate hydrogen detection use catalytic metal coated ZnO nanorod field effect based sensor. Section 2.2 presents a comparison of different metal coating layers on multiple ZnO nanorods for enhancing the sensitivity to detection of hydrogen at room temperature. Pt is found to be the most effective catalyst, followed by Pd. The resulting sensors are shown to be capable of detecting hydrogen in the range of ppm at room temperature using very small current and voltage requirements, and recovering quickly after the source of hydrogen is removed. In section 2.3, issues like quantifying the sensitivity, limit of detection (LOD) at
room temperature, power consumption of the sensors, and time response upon switching away from the H2-containing ambient are discussed in a Pd-coated multiple ZnO nanorod sensor. The sensors are also shown to detect ppm hydrogen at room temperature using <0.4 mW of power.

2.2 Detection of Hydrogen at Room Temperature with Catalyst-Coated ZnO Multiple Nanowires

ZnO nanorods were grown by nucleating on an Al2O3 substrate coated with Au islands [90]. For nominal Au film thicknesses of 20 Å, discontinuous Au islands are realized after annealing. The nanorods were deposited by molecular beam epitaxy (MBE) with a base pressure of 5×10^{-8} mbar using high-purity (99.9999 %) Zn metal and an O3/O2 plasma discharge as the source chemicals. The Zn pressure was varied between 4×10^{-6} and 2×10^{-7} mbar, while the beam pressure of the O3/O2 mixture was varied between 5×10^{-6} and 5×10^{-4} mbar. The growth time was ~2 h at 600 °C. The typical length of the resulting nanorods was 2–10µm, with typical diameters in the range of 30–150 nm. Figure 2-1 shows a scanning electronmicrograph of the as-grown rods. Selected area diffraction patterns showed the nanorods to be single crystalline. In some cases, the nanorods were coated with Pd, Pt, Au, Ni, Ag or Ti thin films (~100 Å thick) deposited by sputtering. Pd and Pt are known to be the most effective catalysts for dissociation of molecular hydrogen; Au was chosen to see if it could provide any enhancement in hydrogen sensitivity since it might potentially be used as an over-layer to prevent oxidation of the other metals, which are all significantly cheaper than Pd and Pt and were explored from the viewpoint of keeping the overall cost of the sensor fabrication as low as possible.

Contacts to the multiple nanorods were formed using a shadow mask and e-beam evaporation of Al/Ti/Au electrodes. The separation of the electrodes was ~300 µm. A schematic of the resulting sensor (left) and a picture of packaged sensor (right) are shown in Figure 2-2. Au
wires were bonded to the contact pad for current–voltage (I–V) measurements performed at 25 °C in a range of different ambients (N₂, O₂ or 10–500 ppm H₂ in N₂). Note that no currents were measured through the discontinuous Au islands and no thin film of ZnO on the sapphire substrate was observed with the growth condition for the nanorods. Therefore, the measured currents are due to transport through the nanorods themselves. The I–V characteristics of the multiple nanorods were linear with typical currents of 0.8 mA at an applied bias of 0.5 V.

Figure 2-3 shows the time dependence of relative resistance change of either metal-coated or uncoated multiple ZnO nanorods as the gas ambient is switched from N₂ to 500 ppm of H₂ in air and then back to N₂ as time proceeds. These were measured at a bias voltage of 0.5 V. The first point of note is that there is a strong increase (by approximately a factor of five) in the response of the Pt-coated nanorods to hydrogen relative to the uncoated devices. The maximum response was ~8 %. There is also a strong enhancement in response with Pd coatings, but the other metals produce little or no change. This is consistent with the known catalytic properties of these metals for hydrogen dissociation. Pd has a higher permeability than Pt but the solubility of H₂ is larger in the former [91]. Moreover, studies of the bonding of H to Ni, Pd and Pt surfaces have shown that the adsorption energy is lowest on Pt [92].

There was no response of either type of nanorod to the presence of O₂ in the ambient at room temperature. Once the hydrogen is removed from the ambient, the recovery of the initial resistance is rapid (≪20 s). By sharp contrast, upon introduction of the hydrogen, the effective nanorod resistance continues to change for periods of >15 min. This suggests that the kinetics of the chemisorption of molecular hydrogen onto the metal and its dissociation to atomic hydrogen are the rate-limiting steps in the resulting change in conductance of ZnO [88]. The gas-sensing mechanisms suggested in the past include the desorption of adsorbed surface hydrogen and grain boundaries in poly-ZnO [93],
exchange of charges between adsorbed gas species and the ZnO surface leading to changes in depletion depth [94] and changes in surface or grain-boundary conduction by gas adsorption/desorption [95]. Finally, Figure 2-3 shows an incubation time for response of the sensors to hydrogen. This could be due to some of the Pd (or Pt) becoming covered with native oxide, which is removed by exposure to hydrogen. A potential solution is to use a bi-layer deposition of the Pt/Pd followed by a very thin Au layer to protect the Pd from oxidation. However, this adds to the complexity and cost of the process and, since the Pd is not a continuous film, the optimum coverage of Au would need to be determined. We should also point out that the I–V characteristics were the same when measured in vacuum as in air, indicating that the sensors are not sensitive to humidity.

The power requirements for the sensors were very low. Figure 2-4 shows the I–V characteristics measured at 25 °C in both a pure N2 ambient and after 15 min in a 500 ppm H2 in N2 ambient. Under these conditions, the resistance response is 8 % and is achieved for a power requirement of only 0.4 mW. This compares well with competing nanotechnologies for hydrogen detection such as Pd-loaded carbon nanotubes [48, 49]. Moreover, the 8 % response compares very well to the existing SiC-based sensors, which operate at temperatures >100 °C through an on-chip heater in order to enhance the hydrogen dissociation efficiency [64]. Figure 2-5 shows the sensors can detect 100 ppm H2.

In conclusion, Pt-coated ZnO nanorods appear well suited to detection of ppm concentrations of hydrogen at room temperature. The recovery characteristics are fast upon removal of hydrogen from the ambient. The ZnO nanorods can be placed on cheap transparent substrates such as glass, making them attractive for low-cost sensing applications, and can operate at very low power conditions. Of course, there are many issues still to be addressed, in
particular regarding the reliability and long-term reproducibility of the sensor response before it can be considered for space-flight applications. In addition, the slow response of the sensors at room temperature is a major issue in some applications.

Figure 2-1 Scanning electron micrograph of ZnO multiple nanorods
Figure 2-2 Schematic of contact geometry for multiple nanorod gas sensor (left) and a picture of packaged sensor (right).

Figure 2-3 Time dependence of relative resistance response of metal coated multiple ZnO nanorods as the gas ambient is switched from N$_2$ to 500 ppm of H$_2$ in air as time proceeds. There was no response to O$_2$.
Figure 2-4 I–V characteristic of Pt-coated nanowires in air and after 15 min in 500 ppm of H₂ in air.

Figure 2-5 Time dependence of resistance change of Pt-coated multiple ZnO nanorods as the gas ambient is switched from N₂ to various concentrations of H₂ in air (10–500 ppm) and then back to N₂.
2.3 Hydrogen Sensing Using Pd-Coated ZnO Multiple Nanowires

The device fabrication details are as described in section 2.2. Figure 2-6 shows the time dependence of resistance of either Pd-coated or uncoated multiple ZnO nanorods as the gas ambient is switched from N$_2$ to various concentrations of H$_2$ in air (10–500 ppm) as time proceeds. There are several aspects of the data. First, there is a strong increase (approximately a factor of 5) in the response of the Pd-coated nanorods to hydrogen relative to the uncoated devices. The addition of the Pd appears to be effective in catalytic dissociation of the H$_2$ to atomic hydrogen. Second, there was no response of either type of nanorod to the presence of O$_2$ in the ambient at room temperature. Third, the effective conductivity of the Pd-coated nanorods is higher due to the presence of the metal. Fourth, the recovery of the initial resistance is rapid (<20 s) upon removal of the hydrogen from the ambient, while the nanorod resistance is still changing at least 15 min after the introduction of the hydrogen. The reversible chemisorption of reactive gases at the surface of metal oxides such as ZnO can produce a large and reversible variation in the conductance of the material [93]. Fifth, the relative response of Pd-coated nanorods is a function of H$_2$ concentration in N$_2$. The Pd-coated nanorods detected hydrogen down to <10 ppm, with relative responses of >2.6 % at 10 ppm and >4.2 % at 500 ppm H$_2$ in N$_2$ after a 10 min exposure, as shown in Figure 2-7. By comparison, the uncoated devices showed relative resistance changes of ~0.25 % for 500 ppm H$_2$ in N$_2$ after a 10 min exposure, and the results were not consistent for lower concentrations. The gas-sensing mechanisms suggested in the past include the desorption of adsorbed surface hydrogen and grain boundaries in poly-ZnO [94], exchange of charges between adsorbed gas species and the ZnO surface leading to changes in depletion depth [89] and changes in surface or grain boundary conduction by gas adsorption/desorption [95]. The detection mechanism is still not firmly established in these
devices and needs further study. It should be remembered that hydrogen introduces a shallow donor state in ZnO and this change in near-surface conductivity may also play a role.

Figure 2-8 shows the time dependence of relative resistance change of Pd-coated multiple ZnO nanorods as the gas ambient is switched from vacuum to N₂, oxygen or various concentrations of H₂ in air (10–500 ppm) and then back to air. These data confirm the absence of sensitivity to O₂. The resistance change during the exposure to hydrogen was slower in the beginning and the rate resistance change reached maximum at 1.5 min of the exposure time. This could be due to some of the Pd becoming covered with native oxide, which is removed by exposure to hydrogen. Since the available surface Pd for catalytic chemical absorption of hydrogen increased after the removal of oxide, the rate of resistance change increased. However, the Pd surface gradually saturated with the hydrogen and the rate of resistance change decreased. When the gas ambient switched from hydrogen to air, the oxygen reacted with hydrogen right away, with the resistance of the nanorods changed back to the original value instantly. Moreover, the data were recorded at a power level of ~ 0.4 mW, which is low even in comparison with CNTs [48, 49]. This is attractive for long-term hydrogen sensing applications.

Figure 2-9 shows the Arrhenius plot of nanorod resistance change rate. The rate of resistance change for the nanorods exposed to the 500 ppm H₂ in N₂ was measured at different temperatures. An activation energy of 12 KJ/mole was calculated from the slope of the Arrhenius plot. This value is larger than that of a typical diffusion process. Therefore, the dominant mechanism for this sensing process is more likely to be the chemisorption of hydrogen on the Pd surface.

In conclusion, Pd-coated ZnO nanorods appear well suited to detection of ppm concentrations of hydrogen at room temperature. The recovery characteristics are fast upon
removal of hydrogen from the ambient. The ZnO nanorods can be placed on cheap transparent substrates such as glass, making them attractive for low-cost sensing applications and operate at very low power conditions.

Figure 2-6 Time dependence of resistance of either Pd-coated or uncoated multiple ZnO nanorods as the gas ambient is switched from N\textsubscript{2} to various concentrations of H\textsubscript{2} in air (10–500 ppm) as time proceeds. There was no response to O\textsubscript{2}. 
Figure 2-7 Relative response of Pd-coated nanorods as a function of H$_2$ concentration in N$_2$.

Figure 2-8 Time dependence of relative resistance of Pd-coated multiple ZnO nanorods as the gas ambient is switched from N$_2$ to oxygen or various concentrations of H$_2$ in air (10–500 ppm) and then back to N$_2$. 
Figure 2-9 Arrhenius plot of rate of resistance change after exposure to 500 ppm H$_2$ in N$_2$. 

![Arrhenius plot](image.png)

- Adsorption curve
- Arrhenius fitting

Slope = -1420.00457
Activation energy (E) = 11.805 kJ/mol

Room T
CHAPTER 3
HYDROGEN SENSOR USING ALGAN/GAN SCHOTTKY DIODE AND HIGH ELECTRON MOBILITY TRANSISTOR

3.1 Background

There is great current interest in detection of hydrogen sensors for use in hydrogen-fueled automobiles and with proton-exchange membrane (PEM) and solid oxide fuel cells for spacecraft and other long-term sensing applications. These sensors are required to selectively detect hydrogen near room temperature with minimal power consumption and weight and with a low rate of false alarms. Due to their low intrinsic carrier concentrations, wide bandgap semiconductor sensors based on GaN or SiC can be operated at lower current levels than conventional Si-based devices and offer the capability of detection to ~600 °C [8, 96-117]. The ability of electronic devices fabricated in these materials to function in high temperature, high power and high flux/energy radiation conditions enable performance enhancements in a wide variety of spacecraft, satellite, homeland defense, mining, automobile, nuclear power, and radar applications.

AlGaN/GaN high electron mobility transistors (HEMTs) show promising performance for use in broad-band power amplifiers in base station applications due to the high sheet carrier concentration, electron mobility in the two dimensional electron gas (2DEG) channel and high saturation velocity. The high electron sheet carrier concentration of nitride HEMTs is induced by piezoelectric polarization of the strained AlGaN layer and spontaneous polarization is very large in wurtzite III-nitrides. This provides an increased sensitivity relative to simple Schottky diodes fabricated on GaN layers [8, 99-117]. An additional attractive attribute of AlGaN/ GaN diodes is the fact that gas sensors based on this material could be integrated with high-temperature electronic devices on the same chip. The advantages of GaN over SiC for sensing include the presence of the polarization-induced charge, the availability of a heterostructure and the more
rapid pace of device technology development for GaN which borrows from the commercialized light-emitting diode and laser diode businesses.

Section 3.2 discusses a comparison of two modes of operation for the detection of hydrogen with AlGaN/GaN HEMTs, namely through monitoring changes in either the drain-source current at different gate biases or in the gate current at zero drain-source bias. These correspond to a comparison of Schottky diode versus field effect transistor (FET) operation. The FET mode of operation provides much higher current changes but the diode mode shows a higher relative sensitivity over a limited range of forward biases. Section 3.3 reports on the use of a differential pair of AlGaN/GaN HEMT diodes for hydrogen sensing near room temperature. This configuration provides a built-in control diode to reduce false alarms due to temperature swings or voltage transients. We demonstrate fast response of the diodes to 1 % H₂ in air.

Section 3.3 shows that use of Ti/Al/TiB₂/Ti/Au Ohmic contacts on AlGaN/GaN HEMT diodes produces less noise in the gate current of the sensor at fixed forward bias voltage compared to conventional Ti/Al/Ni/Au contacts. This is attractive for reducing false alarms and reducing the ultimate detection threshold of the sensors.

3.2 Comparison of Gate and Drain Current Detection of Hydrogen at Room Temperature with AlGaN/GaN High Electron Mobility Transistor

The HEMT layer structures were grown on c-plane Al₂O₃ substrates by Metal Organic Chemical Vapor Deposition (MOCVD). The layer structure included an initial 2μm thick undoped GaN buffer followed by a 35 nm thick unintentionally doped Al₀.₂₈Ga₀.₇₂N layer. The sheet carrier concentration was ~1×10¹³ cm⁻² with a mobility of 980 cm²/V·s at room temperature. Mesa isolation was achieved by using an inductively coupled plasma system with Ar/Cl₂ based discharges. The Ohmic contacts were formed by lift-off of e-beam deposited Ti
(200 Å)/Al (800 Å)/Pt (400 Å)/Au (800 Å). The contacts were annealed at 850 °C for 45 sec under a flowing N₂ ambient in a Heatpulse 610T system. A 200 Å thick circular Pt Schottky contact was deposited for the gate metal. The final step was deposition of e-beam evaporated Ti/Au (200 Å/2000 Å) interconnection contacts. The gate dimension of the device was 1×50 µm². The devices were bonded to electrical feed-through and exposed to either pure N₂ or 500 ppm H₂ in N₂ ambient in an environmental chamber in which the gases were introduced through electronic mass flow controllers.

Figure 3-1 shows the HEMT drain-source current-voltage (I_{DS}-V_{DS}) characteristics (top) and the transfer characteristics (bottom) at 25 °C measured in both the pure N₂ and the 500 ppm H₂ in N₂ ambients. The increase in drain current at each applied gate voltage current is consistent with the hydrogen molecules dissociating into atoms through the catalytic action of the Pt gate contact and diffusing to the Pt/AlGaN interface where it screens some of the piezo-induced channel charge [118]. Previous measurements have shown an effective decrease in the effective barrier height of Pt on GaN by 30~60 meV by introduction of hydrogen into a N₂ ambient [103]. This data represents the FET mode of operation for hydrogen gas sensing. The transconductance of the HEMT also increases slightly when measured in the hydrogen-containing ambient due to the increase in effective channel charge, as shown at the bottom of Figure 3-1.

Figure 3-2 shows the gate I-V characteristics at 0 V I_{DS} measured at 25 °C under pure N₂ ambient or in a 500 ppm H₂ in N₂ ambient. Both the forward and reverse currents increase due to the reduction in barrier height. This data represents the Schottky diode mode of operation for hydrogen gas sensing.

Figure 3-3 shows the change in drain-source or gate currents as a function of gate voltage (top) and percentage change in these currents (bottom) for measurement under pure N₂ ambient
or in a 500 ppm H₂ in N₂ ambient. The FET mode of operation (monitoring of change in drain-source current) shows a much larger signal over a broad range of gate voltage. By sharp contrast, the diode mode of detection shows a large relative change in current only at high forward gate biases. This shows the advantage of using the 3-terminal device structure, with its attendant current gain. The percentage change in both drain-source and gate currents when the hydrogen is introduced into the measurement ambient are shown at the bottom of Figure 3-3. The relative change can be much larger in the diode mode of operation at small forward bias (~1 V) due to the lower baseline current. At higher forward bias the effects of series resistance dominate the current both in N₂ and H₂-containing ambients.

Figure 3-4 shows some of the recovery characteristics of the HEMTs upon multiple cycling of the ambient from N₂ to 500 ppm H₂ in N₂ and back again. The sensors show good recyclability and recovery in both modes of operation. Once again the change in drain-source current is much larger in the FET mode. The initial response to hydrogen in both cases is rapid (<5 sec), while the recovery back to the N₂ ambient value takes much longer (100-200 secs) because of the mass transport characteristics of gas in our test chamber. From the fast initial response of the sensors in both modes, the effective diffusivity of the atomic hydrogen through the Pt is >4×10⁻¹³ cm²/V·s at 25 °C. This is only an estimate, since the response time includes the gas flow dynamics of the gas into the test chamber, the dissociation of the molecular hydrogen and the diffusion to the Pt/AlGaN interface of the atomic hydrogen.

In conclusion, Pt/AlGaN/GaN HEMTs operated in either a diode mode or in an FET mode show the ability to detect 500 ppm H₂ in N₂ at room temperature. The FET mode provides a larger total current change with introduction of hydrogen into the ambient, but the diode mode shows a higher relative sensitivity over a limited range of forward biases.
Figure 3-1 $I_{DS}-V_{DS}$ characteristics (top) and transfer characteristics (bottom) of Pt-gated HEMT measured at 25 °C under pure N$_2$ ambient or in a 500 ppm H$_2$ in N$_2$ ambient.
Figure 3-2 Gate I-V characteristics at 0 V $I_{DS}$ measured at 25 °C under pure $N_2$ ambient or in a 500 ppm $H_2$ in $N_2$ ambient.
Figure 3-3 Change in drain-source or gate currents as a function of gate voltage (top), and percentage changes in these currents (bottom) for measurement under pure N₂ ambient or in a 500 ppm H₂ in N₂ ambient.
Figure 3-4 Time dependence of drain-source (top) or gate current (bottom) when switching from pure N₂ ambient to a 500 ppm H₂ in N₂ ambient and back again.
3.3 Robust Detection of Hydrogen Using Differential AlGaN/GaN High Electron Mobility Sensing Diode

A maskset was designed for fabricating differential diodes to eliminate the temperature effect on the diode characteristics. Schottky contacts of 100 Å Pt for the active diode and Ti (200 Å)/Au (1200 Å) for the reference diodes were deposited by e-beam evaporation. Details of device fabrication are as described in Section 3.2. Figure 3-5 shows an optical microscope image of the completed devices. The devices were bonded to an electrical feed-through and exposed to a 1 % H₂ ambient in an environmental chamber.

Figure 3-6 shows the absolute and differential forward current-voltage (I-V) characteristics at 25 °C of the HEMT active (top) and reference (bottom) diodes, both in air and in a 1 % H₂ in air atmosphere. For the active diode, the current increases upon introduction of the H₂, through a lowering of the effective barrier height. The H₂ catalytically decomposes on the Pt metallization and diffuses rapidly to the interface where it forms a dipole layer [117]. The differential change in forward current upon introduction of the hydrogen into the ambient is ~1-4 mA over the voltage range examined and peaks at low bias. This is roughly double the detection sensitivity of comparable GaN Schottky gas sensors tested under the same conditions, confirming that the HEMT based diode has advantages for applications requiring the ability to detect hydrogen even at room temperature.

As the detection temperature is increased to 50 °C, the differential current response of the HEMT diode pair was almost constant over a wide range of voltages due to more efficient cracking of the hydrogen on the metal contact, as shown in Figure 3-7. The maximum differential current is similar to that at 25 °C, but the voltage control to achieve maximum detection sensitivity for hydrogen is not as important at 50 °C.
To test the time response of the HEMT diode sensors, the 1 % H₂ ambient was switched into the chamber through a mass flow controller for 200 seconds and then switched back to air. Figure 3-8 shows the time dependence of forward current for the active and reference diodes at a fixed bias of 2.5 V under these conditions. The response of the sensor is rapid (<1 sec based on a series of switching tests). Upon switching out of the hydrogen–containing ambient, the forward current decays exponentially back to its initial value. This time constant is determined by the volume of the test chamber and the flow rate of the input gases and is not limited by the response of the HEMT diode itself. Note that the use of the differential pair geometry removes false alarms due to changes in ambient temperature or voltage drifts.

In conclusion, AlGaN/GaN HEMT differential sensing diodes appear well-suited to hydrogen detection applications and suggest that integrated chips involving gas sensors and HEMT-based circuitry for off-chip communication are feasible in the AlGaN/GaN system. Future work will involve design and fabrication of an integrated sensor chip with GaN HEMT amplifier and transmitter.

Figure 3-5 Microscopic images of differential sensing diodes. The opening of the active diode was deposited with 10 nm of Pt, and the reference diode was deposited with Ti/Au.
Figure 3-6 Absolute (a) and differential (b) current of HEMT diode measured at 25 °C.
Figure 3-7 Absolute (a) and differential (b) current of HEMT diode measured at 50 °C.
3.4 Stable Hydrogen Sensors from AlGaN/GaN Heterostructure Diodes with TiB$_2$-Based Ohmic Contacts

We compared two types of Ohmic contacts formed by sputter deposition and lift-off, i.e. Ti (200 Å)/Al (1000 Å)/Pt (600 Å)/Au (800 Å) or Ti (200 Å)/Al (1000 Å)/TiB$_2$ (400 Å)/Ti (200 Å)/Au (800 Å). All of the metals were deposited by Ar plasma-assisted rf sputtering at pressures of 15-40 mTorr and rf (13.56 MHz) powers of 200-250 W. Other details of device fabrication are as described in Section 3.2. Figure 3-9 shows a schematic of a completed device. The device was bonded to an electrical feed-through and exposed to a 1 % H$_2$ ambient in an environmental chamber.

Figure 3-10 shows the linear (top) and log scale (bottom) forward current-voltage (I-V) characteristics at 25 °C of the HEMT active (ie. Pt-gate) diode, both in air and in a 1 % H$_2$ in air atmosphere. For these diodes, the current increases upon introduction of the H$_2$, through a
lowering of the effective barrier height. The H$_2$ catalytically decomposes on the Pt metallization and diffuses rapidly to the interface where it forms a dipole layer [117]. The differential change in forward current upon introduction of the hydrogen into the ambient is $\sim$1 mA over the voltage range examined. By sharp contrast, the passive diodes with Ti/Au gates showed no difference in current when measured in H$_2$-containing ambients.

Figure 3-11 shows the time dependence of forward current for the active diodes at a fixed bias of 1.5 V as the 1 % H$_2$ ambient was switched into the chamber through a mass flow controller for 200 seconds and then switched back to air. The response of the sensor is rapid (<1 sec based on a series of switching tests). The decay time of the forward current back to its initial value is a function of the volume of the test chamber and the flow rate of the input gases and is not limited by the response of the HEMT diode itself. As we have previously noted, the use of the differential pair geometry removes false alarms due to changes in ambient temperature or voltage drifts [119].

The TiB$_2$-based Ohmic contact devices showed much more stable forward currents at fixed bias than their conventional counterparts. Figure 3-12 shows the time dependence of forward current at 1.5 V gate bias for devices with both types of Ohmic contacts. These tests were carried out in the field, where temperature and humidity were not controlled. There are several features of note. First, the current is much higher in the diodes with TiB$_2$–based contacts because of their lower contact resistance ($1.6 \times 10^{-6} \, \Omega \cdot \text{cm}^2$ vs $7.5 \times 10^{-6} \, \Omega \cdot \text{cm}^2$ for the conventional Ti/Al/Pt/Au). Second, there is much better stability of the devices with TiB$_2$–based contacts. There is much less temperature dependence to the contact resistance of the boride contacts and this translates to less variation in gate current as the temperature cycles from day to night. We know from previous results that the TiB$_2$ is an effective diffusion barrier and prevents degradation of the
contact morphology [120]. We expect that the AlGaN/Ti interface is therefore more uniform with the TiB$_2$ overlayer and this translates to less noise in the current at fixed voltage. Note that this leads to a lower threshold for hydrogen detection.

In conclusion, Pt-gated AlGaN/GaN HEMT diodes show greatly improved current stability under field conditions with use of Ti/Al/TiB$_2$/Ti/Au contacts replacing the more conventional Ti/Al/Pt/Au. Combined with the superior thermal stability of these boride-based contacts, this metallization system appears attractive for sensors for long-term monitoring applications.

Figure 3-9 Schematic of HEMT diode hydrogen sensor using either conventional or TiB$_2$-based Ohmic contacts.
Figure 3-10 I-V characteristics in linear (a) or log (b) form of Pt-gated diode measured in air or 1% hydrogen ambient at 25 °C.
Figure 3-11 Time-dependence of current test biased by 1.5 V of Pt-gated diode as the ambient is switched from air to 1% hydrogen and back to air.

Figure 3-12 Variation in forward current at fixed bias for diodes with boride-based Ohmic contacts (top) or conventional Ohmic contacts (bottom) as a function of time under field conditions where the temperature increases during the day and decreases at night.
CHAPTER 4
MERCURY ION SENSOR USING ALGAN/GAN HIGH ELECTRON MOBILITY TRANSISTOR

4.1 Background

The toxicity of heavy metal ions, including mercury(II) (Hg$^{2+}$), lead(II) (Pb$^{2+}$), copper(II) (Cu$^{2+}$), and zinc(II) (Zn$^{2+}$) has long been recognized as a chronic environmental problem [121-125]. In particular, 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 neuro-toxic organic-mercury compounds, which bio-accumulate through the plant, animals, and can food chain and affect the entire eco-system [126, 127].

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 (AAS), Auger electron spectroscopy (AES), or inductively coupled plasma-Mass Spectrometry (ICP-MS)), or electrochemical (ion selective electrodes (ISE) 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 [128-130]. 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 [131-134]. 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 also shown promise for gas and liquid sensor applications due to primarily two reasons: 1) they consist of a high electron sheet carrier concentration channel induced by both piezoelectric polarization of the strained AlGaN layer and the difference in spontaneous polarization between AlGaN and GaN. Unlike conventional semiconductor field effect transistors, there is no intentional dopant in the AlGaN/GaN HEMT structure. 2) the electrons in the two-dimensional electron gas (2DEG) channel are located at the lower interface between the AlGaN layer and GaN layer. The electron carrier concentration in 2DEG strongly depends on the ambient [7-9, 135-139]. We have recently exploited these properties to detect a variety of species in gases and liquids using appropriately functionalized AlGaN/GaN HEMTs [135-139]. For these reasons, nitride HEMTs are versatile devices that may be used for a variety of sensing applications.

Section 4.2 presents 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 µM to 10 nM. The temporal resolution of the device was quantified, along with limit of detection selectivity over sodium as well as magnesium and precision of measurements. Section 4.3 illustrates the detection of Hg$^{2+}$ and Cu$^{2+}$ ions with sensors fabricated with Au-gated and thioglycolic acid functionalized Au-gated GaN/AlGaN HEMTs. We investigated a wide range of concentration from 10 µM to 10 nM. The temporal resolution of the device was quantified, along with limit of detection and selectivity over sodium, magnesium and lead ions. The recyclability of the sensors between measurements was also explored.
4.2 Fast Electrical Detection of Hg(II) Ions with AlGaN/GaN High Electron Mobility Transistors

The HEMT structures consisted of a 2 μm thick undoped GaN buffer and 250 Å thick undoped Al$_{0.25}$Ga$_{0.75}$N cap layer. The epi-layers were grown by metal-organic chemical vapor deposition on 100 mm (111) Si substrates at Nitronex Corporation. Mesa isolation was performed with an Inductively Coupled Plasma (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. 50×50 µm$^2$ Ohmic contacts separated with gaps of 10, 20, and 50 µm consisted of e-beam deposited Ti/Al/Pt/Au patterned by lift-off and annealed at 850 ºC, 45 sec 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 (PMMA) 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 ºC 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 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 Figure 4-1. The thioglycolic acid, HSCH$_2$COOH, 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 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 (Figure 4-2) which showed a change in contact angle from 58.4° to 16.2° after the surface treatment. X-ray Photoelectron Spectroscopy (XPS) and electrical measurements confirming a high surface coverage and Au-S bonding formation on the GaN surface and the results have been previously published [139].

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 counter charges 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 mercury ion (Hg^{2+}) sensors.

As shown in Figure 4-3(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 when the Au-gate electrode 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 4-3(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 seconds for the drain to reach steady state. However, the drain current required 30-55 seconds to reach steady state, when the sensor was exposed to the less concentrated Hg^{2+} ion solutions.

A less than 5 second 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 carboxylic acid functional group toward the solution [140]. 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 [141]. The difference of drain current for the device exposed to different Hg^{2+} ion concentration to the DI water is illustrated in Figure 4-3(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 billion). The thioglycolic acid functionalized sensor also showed excellent sensing selectivity (over 100 times higher selectivity) over Na^{+} and Mg^{2+} ions, as illustrated in Figure 4-4.

Since our sensor chip is very compact (1 mm × 5 mm) and operates at extremely low power (8 µW based on 0.5 V of drain voltage and 80 µA of drain current operated at 11 Hz), it can be integrated with a commercial 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.

Figure 4-1 (a) 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.

Figure 4-2 Photographs of contact angle of water drop on the surface of bare Au (left) and thioglycolic acid functionalized Au (right).
Figure 4-3 (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.
4.3 Selective Detection of Hg(II) Ions from Cu(II) and Pb(II) Using AlGaN/GaN High Electron Mobility Transistors

The HEMT structures consisted of a 2 μm thick undoped GaN buffer and 250 Å thick undoped Al$_{0.25}$Ga$_{0.75}$N cap layer. The epi-layers were grown by molecular beam epitaxy system on 2” sapphire substrates at SVT Associates. Details of the device fabrication are as described in Section 4.2. 5-nm thin gold film was deposited as gate metal for two set of samples. One was for the bare Au-gate sensor and the other was for functionalizing a self-assembled monolayer of thioglycolic acid on the Au-gate. An increase in the hydrophilicity of the treated surface by thioglycolic acid functionalization was confirmed by contact angle measurement as well. A schematic cross-section of the device with Hg$^{2+}$ ions bound to thioglycolic acid functionalized on the gold gate region is as shown in Figure 4-1(a). 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\textsuperscript{2+}, Cu\textsuperscript{2+}, Pb\textsuperscript{2+}, Mg\textsuperscript{2+} or Na\textsuperscript{+} solutions. AC measurements were performed to prevent side electrochemical reactions with modulated 500 mV bias at 11 Hz.

Figure 4-5 shows the change in drain current of a bare Au-gated AlGaN/GaN HEMT sensor and a thioglycolic acid functionalized AlGaN/GaN HEMT sensor exposed to 10\textsuperscript{-5} M Hg\textsuperscript{2+} ion solutions as compared to exposed to DI water. The drain current of both sensors decreased after exposure to Hg\textsuperscript{2+} ion solutions. The drain current reduction of the thioglycolic acid functionalized AlGaN/GaN HEMT sensors was almost 80 % more than that of the bare Au-gate sensor. The mechanism of the drain current reduction for bare Au-gate and thioglycolic acid functionalized AlGaN/GaN HEMT sensors is probably quite different. For the thioglycolic acid functionalized AlGaN/GaN HEMT, the thioglycolic acid molecules on the Au surface align vertically with carboxylic acid functional group toward the solution [140]. The carboxylic acid functional group of the adjacent thioglycolic acid molecules probably forms chelates (R-COO'(Hg\textsuperscript{2+})OOC-R) with the Hg\textsuperscript{2+} ions. If the chelates are indeed forming, one would expect the charges of trapped Hg\textsuperscript{2+} ion in the R-COO'(Hg\textsuperscript{2+})OOC-R to change the polarity of the thioglycolic acid molecules. This is probably why the drain current changes in response to mercury ions. A similar type of surface functionalization was used by Chang et. al. and the detection performed with gold-nanoparticle-based fluorescence[141], but the detection time is longer than the nitride HEMT based sensor. Because Hg\textsuperscript{2+} ions were used in our experiments, we do not expect an Au-mercury amalgam to form on the bare Au-surface. The detailed mechanism for mercury ion induced reduction in drain current of the Au-gate device is not clear and currently under further investigation.
**Figure 4-6** shows time dependence of the drain current for the two types of sensors for detecting Hg$^{2+}$, Cu$^{2+}$, and Pb$^{2+}$ ions. Both type of sensors showed very short response time (less than 5 seconds), when exposed to Hg$^{2+}$ ion solution. The limits of detection for Hg$^{2+}$ ion detection for the bare Au-gate and thioglycolic acid functionalized sensor were $10^{-6}$ and $10^{-7}$ M, respectively. Neither sensor could detect Pb$^{2+}$ ions. For the Cu$^{2+}$ ions, the detection limit of the thioglycolic acid functionalized sensor was around $10^{-7}$ M. However, the bare Au-gate could not detect the Cu$^{2+}$ ions as shown in **Figure 4-6**. **Figure 4-7** shows the drain current changes in response to Hg$^{2+}$ and Cu$^{2+}$ ions as a function of the ion concentration for the two different surfaces. The difference in the response between the bare Au-gate and the thioglycolic acid functionalized sensor offers the possibility for selective detection for Hg$^{2+}$ and Cu$^{2+}$ ions presented in a single solution with a sensor chip containing both type of sensors, as shown in **Figure 4-8**. The dimension of the active area of the AlGaN/GaN HEMT sensor is less than 50 µm × 50 µm, and the sensors can be fabricated as an array of individual sensors. The fabrication of both sensors is identical except for the thioglycolic acid functionalized sensor, which has an additional functionalization step. This step can be accomplished with micro-inkjet system to locally functionalize surfaces. The bare Au-gate and thioglycolic acid functionalized sensors also showed excellent sensing selectivity (over 100 times higher selectivity) over Na$^{+}$ and Mg$^{2+}$ ions. As illustrated in **Figure 4-9**, there was almost no detection of Na$^{+}$ and Mg$^{2+}$ ions for both types of sensors with 0.1 M concentrations.

Most semiconductor based chemical sensors are not reusable. The bare Au-gate and thioglycolic acid functionalized sensors showed very good recyclability, as shown in **Figure 4-10**. After a simple rinse with DI water, the sensors can be reused for Hg$^{2+}$ ion detection repeatedly and the responses to different ionic solutions remain unchanged. The stability of
thioglycolic acid functionalized Au surface is affected by several factors, like oxygen level, light, initial packing quality, chain length, and terminal functional group [142, 143]. Our devices have been stored in nitrogen ambient and repeatedly used over a couple of weeks. The long term stability of the thioglycolic acid functionalized Au surface is under investigation.

The current sensor operates at 0.5 V of drain voltage and 2 mA of drain current. However, the operation voltage and device size can be further reduced to minimize the power consumption to μW range. The sensor can be integrated with a commercial available hand-held wireless transmitter to realize a portable, fast response and high sensitivity Hg$^{2+}$ and Cu$^{2+}$ ion detector.

In summary, we have demonstrated bared Au-gate and thioglycolic acid functionalized AlGaN/GaN HEMT sensors to heavy ion detections. The bare Au-gate sensor was sensitive to Hg$^{2+}$ and thioglycolic acid functionalized sensors could detect both Hg$^{2+}$ and Cu$^{2+}$ ions. By fabricating an array of the sensors on a single chip and selectively functionalizing some sensors with thioglycolic acid, a multi-functional specific detector can be fabricated. Such a sensor array can be used to detect quantitatively Hg$^{2+}$ ions in Cu$^{2+}$ ion solution or Cu$^{2+}$ ions in Hg$^{2+}$ ion solution. Both bare Au-gate and thioglycolic acid functionalized sensor can be repeatedly used after a simple DI water rinse.
Figure 4-5 Changes in HEMT drain-source current for bare Au-gate and Au-gate with thioglycolic acid functionalization exposed to $10^{-5}$ M Hg$^{2+}$ ion solutions.

Figure 4-6 (a) Time dependent response of the drain current as a function of Hg$^{2+}$, Cu$^{2+}$, Pb$^{2+}$ ion concentrations for bare Au-gate AlGaN/GaN HEMT sensor. (b) Time dependent response of the drain current as a function of Hg$^{2+}$, Cu$^{2+}$, Pb$^{2+}$ ion concentrations for thioglycolic acid functionalized Au-gate AlGaN/GaN HEMT sensor.
Figure 4-7 Drain current changes in response to Hg^{2+} and Cu^{2+} ions as a function of the ion concentration for (a) the bare Au-gate and (b) the thioglycolic acid functionalized Au-gate AlGaN/GaN HEMT sensor.

Figure 4-8 Plan view photograph of a multiple cell AlGaN/GaN HEMT sensors.
Figure 4-9 Time dependent change in the drain current in response to Na$^+$ and Mg$^{2+}$ with bare Au-gate and thioglycolic acid functionalized Au-gate HEMT sensor.

Figure 4-10 Recyclability for (a) the bare Au-gate, and (b) the thioglycolic acid functionalized Au-gate surface.
CHAPTER 5
DISEASE BIOMARKER SENSOR USING ALGAN/GAN HIGH ELECTRON MOBILITY TRANSISTOR

5.1 Background

Disease diagnosis by detecting specific biomarkers (functional or structural abnormal enzyme, low molecular weight proteins, or antigen) in blood, urine, saliva, or tissue samples has been established into several approaches including enzyme-linked immunsorbent assay (ELISA), particle-based flow cytometric assays, electrochemical measurements based on impedance and capacitance, electrical measurement of microcantilever resonant frequency change, and conductance measurement of semiconductor nanostuctures. ELISA possess a major limitation that only one analyte will be measured at one time [144, 145]. Particle-based assay opens a spotlight for multiple detections by using multiple beads but the whole detection process over than 2 hours is not practical to bedside detecting [146]. Electrochemical devices have attracted attention due to their low cost and simplicity, but significant improvements in their sensitivities are still needed for use with clinical samples [147, 148]. Microcantilever capable for detecting concentration as low as 10 pg/ml, unfortunately, suffers from an undesirable resonant frequency change due to viscosity of the medium and cantilever damping in the solution environment [149, 150]. Nanomaterial devices so far have provided the best option toward fast, label-free, sensitive, selective, and multiple detections for both preclinical and clinical applications. Examples of electrical measurements of semiconductor devices include carbon nanotubes for lupus erythematosus antigen detection [151], compound semiconducting nanowires, In$_2$O$_3$ nanowires, for prostate-specific antigen detection[152], and silicon nanowire array detecting prostate-specific antigen, carcinoembryonic antigen, and mucin-1 in serum for diagnosis of prostate cancer [153-156]. Recently, AlGaN/GaN high electron mobility transistors (HEMTs) have
shown promise for such applications due to a high electron sheet carrier concentration channel induced by both piezoelectric polarization and spontaneous polarization [7, 8, 135-139, 157].

Acute Kidney Injury (AKI) or Acute Renal Failure (ARF) is one of the most common and serious medical complications that is closely associated with high mortality [158-160]. Despite the improvements in dialysis and kidney transplantation techniques over the past two decades, the high mortality rate has remained. The AKI diagnosis by detecting the urinary biomarker, kidney injury molecule-1 or KIM-1 (a specific sensitive AKI biomarker) [161], have been proved with enzyme-linked immunsorbent assay (ELISA) technology [145]. Most state-of-art testing methods for kidney injury disease biomarkers have limitations due to the laboratory-oriented nature of the measurements requiring sample transportation, time consuming analysis and high cost of detection. In this chapter, we report the detection of KIM-1 with KIM-1 antibody functionalized Au-gated GaN/AlGaN HEMTs (Section 5.2). We quantified the sensitivity of the HEMT sensor and the temporal resolution, along with the limit of detection (LOD) and selectivity.

5.2 Kidney Injury Molecule-1 Detection Using AlGaN/GaN High Electron Mobility Transistors

The HEMT structures consisted of a 2 μm thick undoped GaN buffer and 250 Å thick undoped Al$_{0.25}$Ga$_{0.75}$N cap layer. The epi-layers were grown by metal-organic chemical vapor deposition on 100 mm (111) Si substrates. Mesa isolation was performed with Inductively Coupled Plasma (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 × 50 µm$^2$ Ohmic contacts separated with gaps of 20 µm consisted of e-beam deposited Ti/Al/Pt/Au patterned by lift-off and annealed at 850 ºC for 45 sec under flowing N$_2$. 5 nm thin gold film was deposited as gate metal to
functionalize a self-assembled monolayer of thioglycolic acid. 500-nm-thick polymethyl methacrylate (PMMA) was used to encapsulate the source/drain regions, with only the gate region opened using e-beam lithography. A plan view photomicrograph of a completed device is shown in Figure 5-1(a).

Before thioglycolic acid coating, the sample was exposed to UV ozone for 5 mins to clean surface contamination. The thioglycolic acid, HSCH₂COOH, is an organic compound and contains functional groups of a thiol (mercaptan) and a carboxylic acid functional group. A self-assembled monolayer of thioglycolic acid molecule was adsorbed onto the Au-gate due to strong interaction between gold and the thiol-group. The extra thioglycolic acid molecules were rinsed off with de-ionized water. An increase in the hydrophilicity of the treated surface by thioglycolic acid functionalization was confirmed by contact angle measurements which showed a change in contact angle from 58.4° to 16.2° after the surface treatment. The sample was treated with monoclonal anti rat KIM-1 antibody in a solution of 10 mM phosphate-buffered saline (PBS) buffer solution containing 4 mM sodium cyano-borohydride, pH 8.8 at room temperature for 2 hours. This antibody immobilization is based on a strong reaction between carboxyl group on thioglycolic acid and amine group on KIM-1 antibody. Excess KIM-1 antibodies were washed off by PBS buffer and the unreacted surface carboxyl groups were passivated by a blocking solution of 100 mM ethanolamine in 10 mM phosphate buffer pH 8.8. Figure 5-1(b) shows a schematic device cross section with thioglycolic acid followed by KIM-1 antibody coating. The source-drain current-voltage characteristics were measured at 25 °C using an Agilent 4156C parameter analyzer with the KIM-1 antibody functionalized Au-gated region exposed to different concentrations of KIM-1/PBS buffer. AC measurements were performed to prevent side electrochemical reactions with modulated 500 mV bias at 11 Hz.
The electrical properties of the devices, source and drain current ($I_{DS}$) vs. voltage ($V_{DS}$), were measured in PBS buffer and 100 ng/ml KIM-1 in PBS buffer, as shown in Figure 5-2. There is a clear conductance decrease with KIM-1 exposure and this suggests that through the selective binding of KIM-1 with antibody, there are charges accumulated at the surface and these surface charges are transduced into a change in the carrier concentration of AlGaN/GaN 2DEG, leading to the obvious decrease in the conductance of the device after KIM-1 exposure.

Figure 5-3 shows the time dependent source-drain current signal with constant bias of 500 mV for KIM-1 detection in PBS buffer solution. No current change can be seen with the addition of buffer solution around 50 sec. This stability is important to exclude possible noise from the mechanical change of the buffer solution. By sharp contrast, the current change showed a rapid response in less than 20 seconds when target 1 ng/ml KIM-1 was switched to the surface at 150 sec. The abrupt current change due to the exposure of KIM-1 in a buffer solution stabilized after the KIM-1 thoroughly diffused into buffer to reach a steady state. 10 ng/ml KIM-1 was then applied at 350 sec and it was accompanied with a larger signal correlated to the higher KIM-1 concentration. Further real time tests were carried out to explore the limit of detection of KIM-1 antibody (Figure 5-4). The device was exposed to 10 pg/ml, 100 pg/ml, 1ng/ml, 10ng/ml, and 100ng/ml individually and each concentration was repeated five times to obtain the standard deviation of source-drain current response for each concentration. The limit of detection of this device was 1ng/ml KIM-1 in PBS buffer solution and the source-drain current change is nonlinearly proportional to KIM-1 concentration. Between each test, the device was rinsed with a wash buffer of 10 μM phosphate buffer solution containing 10 μM KCl with pH 6 to strip the antibody from the antigen. These results suggest that our HEMTs are compatible with AKI biomarker, KIM-1, are very sensitive compared to nano-devices [151-156] and are useful for
preclinical and clinical applications. Similar surface modifications can be applied for detecting other important disease biomarkers and a compact disease diagnosis array can be realized for multiplex disease analysis.

In summary, we have shown that the Au-gated region of an AlGaN/GaN HEMT structure can be functionalized with KIM-1 (a kidney injury disease biomarker) antibody for the detection of KIM-1 with a limit of detection of 1 ng/ml in PBS buffer. This electronic detection of disease biomarker is a significant step towards a compact sensor chip, which can be integrated with a commercial available hand-held wireless transmitter to realize a portable, fast and high sensitive device for multiple disease diagnosis.
Figure 5-1 (a) Plan view photomicrograph of a completed device with a 5 nm Au film on the gate region. (b) schematic device cross section. The Au-coated gate area was functionalized with KIM-1 antibody on thioglycolic acid.
Figure 5-2 $I_{DS}$-$V_{DS}$ characteristics of HEMT in both PBS buffer and 100 ng/ml KIM-1.

Figure 5-3 Time dependent current signal when exposing the HEMT to 1 ng/ml and 10 ng/ml KIM-1 in PBS buffer.
Figure 5-4 Current change in HEMT as a function of KIM-1 concentration.
ZnO is attracting renewed interest for use in blue/UV light-emitting diodes (LEDs) and photodetectors with potential advantages over the III-nitride system due to the higher exciton binding energy, availability of high quality bulk substrates and ease of wet etching [162-166]. The reports of ZnO metal-insulator-semiconductor (MIS) electroluminescent diodes go back to the 1970’s, with most of the emission being due to defect bands in the blue/green and infra-red (IR) [167-171]. However, in some cases, small band-edge emission was observed at low temperatures [171], with little understanding of the origin of the holes in these n-type ZnO structures. Generally, no electroluminescence was observed in these devices in the reverse bias or without the i-layer. More recently, a number of groups have reported hybrid heterojunction LEDs using n-type ZnO deposited on top of p-type layers of GaN, AlGaN or conducting oxides [165, 166, 172-175]. Homojunction ZnO LEDs have been reported by Tsukazaki [176, 177] who used temperature modulation epitaxy for p-type doping of ZnO using N as dopant and fabricated a p-ZnO/i-ZnO/n-ZnO LED on a ScAlMgO₄ substrate. Most of the emission consisted of bands at 420 and 500 nm, with a small shoulder at 395 nm assigned to radiative recombination in the p-ZnO through donor-acceptor pair transitions. Another homojunction ZnO LEDs have also been recently reported by Jae-Hong [178, 179] who used rf sputtering technique for P dopant p-type ZnO and fabricated p-ZnO/n-ZnO LED. The emission consisted of a near band edge emission at 380nm and broad deep level emission at approximately 640 nm. With p-ZnO/barrier-MgZnO/n-ZnO/b-MgZnO/n-ZnO structure, carrier combination process is confined in high quality n-type ZnO thin film and the defect related emission at 640 nm is removed. In addition, it has been suggested that semiconducting nanowires may offer additional advantages for light emission due
to the increased junction area, reduced temperature sensitivity, enhanced polarization
dependence of reflectivity and improved carrier confinement in 1-D nanostructures [180-181].

In this chapter, we demonstrate that N⁺ implantation into bulk single-crystal ZnO substrates can be used to achieve bandedge electroluminescence (EL) in simple diode structures. The mechanism for bandedge EL is most likely hole creation by impact ionization in the MIS structure.

6.2 Band-Edge Electroluminescence from N⁺-Implanted Bulk ZnO

There have also been recent breakthroughs in the understanding of damage creation and annealing in ion implanted ZnO [182-189] and reports of p-type doping using As implantation at low temperatures, followed by multiple step annealing [190]. Ion implantation is an attractive process for low-cost, high throughput device manufacturing and in this section we show that N⁺ implantation into bulk single-crystal ZnO substrates can be used to achieve bandedge electroluminescence (EL) in simple diode structures. The mechanism for bandedge EL is most likely hole creation by impact ionization in the MIS structure.

The ZnO samples were (0001) undoped grade I quality bulk, single-crystal ZnO crystals from Cermet. They were epiready with one-side-Zn-face-polished by the manufacturer. The room temperature electron concentration and mobility established by van der Pauw measurements were 10¹⁷ cm⁻³ and 190 cm²/V·s, respectively. Ion implantation was performed at 300K with N⁺ ions of energy 5 keV (dose of 1.5×10¹³ cm⁻²), 20 keV (dose of 5×10¹³ cm⁻²) plus 50 keV (dose of 1.3×10¹⁴ cm⁻²) and 130 keV (dose of 3.5×10¹⁴ cm⁻²), followed by rapid thermal annealing (RTA) for 2 mins under a flowing O₂ ambient. We also annealed some of the samples in either a conventional tube furnace or a pulsed laser deposition chamber under O₂ ambients for 45 mins, with the same basic trends observed in diode behavior as for the RTA processed
devices. The backside of the substrates was deposited with full area contacts of e-beam deposited Ti (20 nm)/Au (200 nm) annealed at 400 °C [191]. Circular front-side contacts of Ni (20 nm)/Au (80 nm) with diameter 200 μm were deposited by e-beam evaporation and patterned by lithography and lift-off. A schematic of the completed diodes is shown in Figure 6-1. The current-voltage (I-V) characteristics were measured at 300 K using a probe station and Agilent 4145B parameter analyzer. The EL spectrum and output power from the structures were measured using a spectrometer and Si photodiode, respectively while the photoluminescence (PL) was excited with a He-Cd laser.

Figure 6-2 shows the I-V characteristics from the implanted structures as a function of post-implant RTA temperature under an O2 ambient for 2 mins. The I-Vs are characteristic of back-to-back diodes for low anneal temperatures and transition to Schottky-diode like-behavior at the highest anneal temperature. Note that for anneals at 800 °C the behavior might be misinterpreted as that from a pn junction because the forward turn-on voltage is that expected from a material with bandgap around 3 eV but this is misleading if not considered in the context of all the data. Thus we do not believe that we create a p-type region by activation of the implanted N acceptors. This is consistent with our relatively low dose, the large ionization energy of the N and the residual n-type background of the substrate. With all of these considerations, it is not likely we have converted the implanted region to p-type conductivity.

Figure 6-3 shows room temperature PL from the bulk ZnO before and after N⁺ implantation and annealing at 800 °C for 2 mins (top) and EL from MIS diode at room temperature and 120 K (bottom). The unimplanted ZnO shows strong band-edge (~380 nm) PL, whereas after implantation and annealing the intensity of this transition is decreased and deep level-related emission peaked at >600 nm is introduced. This is expected, since the annealing of
point defects will not be complete for 600 °C anneals [182-185] and most of the small band-edge peak may actually come from the undamaged ZnO underneath the implanted region. In the EL spectrum, we did not observe any band-edge emission at room temperature, but at lower temperatures (120 K), there is a small peak shifted to higher wavelengths. This is similar to the results previously in ZnO MIS diodes [171] and to the EL spectra reported for the ZnO Positive-Intrinsic-Negative (PIN) homojunction diodes. The band-edge emission from our diodes was absent for higher annealing temperatures, although the deep level emission was still present. This is also consistent with our diodes being MIS structures and not pn junctions.

Figure 6-4 shows I-V characteristics and forward bias current dependence of integrated EL intensity measured by a Si photodiode from a structure annealed at 800 °C. The device shows an apparent threshold of about 4.5 V and the forward current above this threshold is limited by a series resistance of about 25 Ω, much lower than reported for the LEDs grown on insulating oxide substrates [176, 177]. The EL intensity increases almost linearly with drive current above threshold. Figure 6-5 (top) shows an optical microscope image of the light emitted from a single device whereas the bottom of the figure shows a photograph of a device under bias in the light and dark. The diodes emit a yellowish light due to the dominance of the deep level emission. We would expect a more uniform emission if we add a transparent conducting layer on the implanted layer to obtain improved current spreading.

Given that we do not believe the N⁺ implanted region is p-type, then the origin of the holes needed for observation of the band-edge EL needs to be established. Mahan et al. [192] in presenting a theory to explain the conduction in ZnO-based metal-oxide varistors suggested that holes could be created by impact ionization during biasing. Direct evidence of the production of holes in forward-biased ZnO varistors was later reported by Pike et al. [193], with the detection
of band-edge EL in addition to the broad sub-bandgap luminescence peaked near 600 nm. We therefore suggest that the role of the N$^+$ implantation and subsequent anneal in our samples is to create a resistive layer [182-185] that leads to the realization of an MIS diode upon metallization. It is important that such effects are accounted for in any pn junction ZnO LEDs where the low hole density and propensity for p-layers in ZnO to exhibit unstable conductivity [194] may lead to misinterpretation of the device results.

In conclusion, band-edge and yellow EL has been obtained from N$^+$-implanted bulk ZnO diodes similar to that observed in MIS diodes. Future work on acceptor implantation should focus on achieving p-type conductivity in the ZnO so that true injection LEDs may be realized.

Figure 6-1 Schematic of ZnO MIS diode formed by N$^+$ implantation into a bulk single crystal substrate.
Figure 6-2 I-V characteristics as a function of post-implant annealing temperature under an O₂ ambient for 2 mins.
Figure 6-3 Room temperature PL from ZnO before and after N$^+$ implantation and annealing at 800 °C for 2 mins (top) and EL from MIS diode at room temperature and 120 K (bottom).
Figure 6-4 I-V characteristics and forward bias current dependence of integrated EL intensity from an MIS diode annealed at 800 °C. The EL intensity was measured by a Si photodiode.

Figure 6-5 Optical microscope image of the emission from the diode in the dark (top) and photos of the diode under bias from the probe contact taken both in the light and dark (bottom).
CHAPTER 7
INCREASING SCHOTTKY BARRIER HEIGHT WITH CRYOGENIC METAL DEPOSITION

7.1 Background

There is no established gate oxide for III-V compound semiconductors and therefore all field effect transistors (FETs) in GaAs [195] and GaN [196-201] are based on metal Schottky gates. This has some advantages in terms of switching speed because of the low parasitic capacitance of metal-semiconductor FETs (MESFETs) but is less thermally stable than the metal-oxide-semiconductor FET (MOSFET) approach. Another significant drawback is the limited range of barrier heights available, especially for metals on GaAs, where surface Fermi level pinning generally limits the barrier height to ~0.72 eV [195]. Higher barrier heights would enable larger gate-drain breakdown voltage, output resistance and power gain and lower gate leakage current and noise in GaAs MESFETs. There have been a number of reports of enhancing barrier heights on III-V semiconductors by use of cryogenic temperatures during the gate metal deposition. Metal films deposited at cryogenic temperatures have been shown to enhance Schottky barrier heights on InP, GaAs, InGaAs and some II-VI compounds [12, 13, 202-204].

The barrier height enhancements have been as high as 0.5 eV relative to those deposited at room temperature. The mechanism for the barrier height enhancement is still not firmly established. In the case of Au contacts on InP [204], room temperature deposition produced an ideality factor of 1.02 nearly independent of temperature and the current transport was controlled by thermionic emission (TE). For the case of cryogenic deposition, the ideality factor was increased and the current transport was controlled by thermionic field emission (TFE) [204]. The barrier height enhancement and the difference in transport mechanism was attributed to the formation of an amorphous-like structure at the cryogenic diode interface. This amorphous layer was suggested to act as an insulator to create a metal-insulator-semiconductor (MIS)-like structure [204].
However, others have disputed this interpretation and suggested the results were due to an inhomogeneous Schottky barrier height in the diodes due to a dependence of the local interface dipole on the local interface structure [205].

This chapter mainly examines the effect of cryogenic deposition temperatures on the properties of Au Schottky contacts on n-type GaAs. Section 7.2 presents the role of deposition temperature on the electrical properties of Au/GaAs diodes. We find the barrier height is increased by cryogenic deposition and the interfacial roughness is decreased. Section 7.3 examines the effect of post-deposition annealing temperature on the barrier height and reverse breakdown voltage of Au/n-GaAs diodes deposited at either 77 or 300K. The barrier height is increased by cryogenic deposition and remains higher throughout the annealing temperature range up to 300 °C. The reverse breakdown voltage is also increased by the low temperature Au deposition. Finally, section 7.4 reports on X-ray reflectivity (XRR) studies of the interface between Au deposited on n-GaAs at either 77 K or 300 K, followed by post-deposition annealing at temperatures up to 300 °C, for comparing with the results in section 7.2 and 7.3. The barrier height is increased by ~0.09 eV by cryogenic deposition relative to the room temperature deposition value of 0.73 eV. This is accompanied by a smoother metal surface, while the metal/GaAs interfacial roughness is similar. As the diodes are annealed to 300 °C, the barrier height enhancement disappears; the Au/GaAs interfaces continue to show the same degree of roughness while the metal surface becomes rougher. Other metals such as Pt, Ti, Pd and Ni were also examined for barrier height enhancement.
7.2 Improved Au Schottky Contacts on GaAs Using Cryogenic Metal Deposition

An evaporator system with a load-lock and five pockets for different metals was used in these experiments. The load-lock maintained the background pressure in the metal deposition chamber in the range of $10^{10}$ Torr. The background pressure of a typical commercial evaporator is in the range of low $10^{-7}$ to high $10^{-8}$ Torr and the theoretical monolayer formation time in this vacuum environment is around 1 minute. With MBE-like background pressures, the rate of gas molecule impingement on a sample surface is significantly reduced and the theoretical monolayer formation time is extended to approximately an hour or two. In comparison to conventional evaporation techniques, this system results in enhanced integrity of the semiconductor surface before metal deposition. Front-side contacts of 1000 Å thick Au were deposited at 77 K or 300 K onto n-GaAs (n~10¹⁷ cm⁻³) substrates with full area back Au/Ge/Ni/Au contacts that had been alloyed at 400 °C for 3 mins. Prior to insertion in the evaporator, the samples were cleaned in 3:1:50 of HNO₃: HF: H₂O for 1 min. The Au contacts ranged in diameter from 200-800 μm and were patterned by lift-off of photoresist. The current-voltage (I-V) characteristics of the resulting diodes were measured on an Agilent 4156C parameter analyzer. The barrier height, $\phi_b$, and diode ideality factor, $n$, were extracted from the relation for the thermionic emission over a barrier [206],

$$J_F = A^* T^2 \exp\left(-\frac{e\phi_b}{kT}\right) \exp\left(\frac{eV}{nkT}\right)$$

(7-1)

where $J_F$ is the forward current density, $A^*$ is the Richardson’s constant for n-GaAs, $T$ is the absolute temperature, $e$ is the electronic charge, $k$ is Boltzmann’s constant, and $V$ is the applied voltage. In addition, the surface and interfacial roughness of thin Au films (~100 Å) deposited on GaAs substrates was examined by X-Ray Reflectivity (XRR).
Figure 7-1 shows I-V characteristics of Au/GaAs Schottky diodes deposited at either 77 K (▲) or 300 K (○) with 200 μm (left) or 800 μm (right) in contact diameter. An expanded view of the forward voltage part of the curves is shown at the bottom of the figure. There is a clear decrease in both reverse and forward bias current for the diodes with Au deposited at 77 K, consistent with an increase in the effective Schottky barrier height. It has been reported that the crystal structure and grain size of the low temperature deposited metal are different from metals deposited at room temperature.

The changes in electrical behavior were consistent both spatially within a 2” wafer and for different contact diameters. Figure 7-2 shows the forward current densities as a function of bias for diodes of different diameter, deposited at either 77 or 300 K. The Schottky barrier height enhancement by deposition at cryogenic temperatures is thought in part to result from the minimized interaction between the metal and semiconductor during the metal deposition. The stability of the metal-semiconductor interface and the stability of the small grain size metal contact are important for device reliability. Typically after the gate metallization step, the device is encapsulated by a SiNx dielectric for packaging. This dielectric is deposited by PECVD and the temperature that the substrate is exposed to is 200-300 °C. At these temperatures, it is desirable that interface diffusion and grain growth be minimized. Table 7-1 lists the common metals used for Schottky contacts on GaAs and their melting temperatures. A recognized measure for the onset of grain growth is 0.4 T_{melt}. As indicated in the table, contacts of Ti, Pt, and Pd should not recrystallize at PECVD deposition temperatures and therefore these may be more effective choices for actual GaAs devices. For significant interfacial diffusion to take place, the constituents of either the semiconductor or the metal contact must become mobile and form a solid solution. The contact metals of Ti, Pt, and Pd have little diffusion below 0.4 T_{melt}. 

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The origin of the reverse current can be examined by looking at the dependence of current on perimeter/area ratio. Figure 7-3 shows reverse current at -4 V for diodes deposited at either 77 or 300 K, as a function of either contact diameter (top) or area (bottom). The reverse current was proportional to both the perimeter and area of the rectifying contact, suggesting that both surface and bulk contributions are present in this voltage range. Therefore, low temperature deposition does not seem to reduce Fermi level pinning by surface states in GaAs. Table 7-2 gives a summary of the electrical properties of the diodes. The main differences are an effective increase in barrier height of 10-13% for cryogenic deposition, from a mean value of 0.73 eV for room temperature deposition to a mean value of 0.82 eV for 77 K deposition. However, it should also be noted that the ideality factors were larger for the low temperature diodes, perhaps suggesting the presence of interfacial contamination gettered to the cold surface during the pump-down and initial stages of deposition. This could be improved by including gettering sources such as tungsten filaments within the chamber during evaporation. It has been proposed that these low temperature contacts could be governed by the lack of a thermally diffused interfacial layer, geometry differences due to reduced metal clustering, or strain imposed on the interface caused by thermal expansion differences between the metal and substrate, or some combination of the three. TEM and XPS studies by D. S. Cammack et. al support the assertion of increased barrier heights due to an interfacial layer differences [207]. Their TEM study of low temperature deposited contacts showed a more abrupt metal-semiconductor interface, than room temperature contacts.

All of the diodes showed excellent stability under forward bias aging. Figure 7-4 shows the time dependence of forward bias at a current of 10 mA for diodes deposited at either 77 or 300 K, with no evidence of drift due to trapping effects. There was also no apparent difference in
contact morphology at low resolution. Figure 7-5 shows optical microscope images of Au contacts deposited at 77 K (left) or 300 K (right), with both exhibiting excellent morphology. Cryogenic metal deposition also reduces the resistivity, of very thin films, four or five orders of magnitude compared to contacts deposited at room temperature [208]. By limiting surface diffusion, atoms deposited on cryogenically cooled substrates tend to stay close to where they impinge on the substrate surface. Conversely, room temperature deposited atoms are more likely to re-evaporate or diffuse along the surface. Diffusion can lead to clustering, and eventually coalescence leaving voids on the substrate [12]. The lack of temperature related diffusion at 77 K causes the cryogenic metal film to become continuous at lower film thicknesses than films deposited at room temperature. As metal thickness increases, room temperature films experience secondary nucleation, and the voids fill. Void filling makes the room temperature films more continuous, while the larger kinetic energy of room temperature deposited makes these atoms more likely to form regular crystal lattices than low temperature films. The increased continuity of room temperature films coupled with better crystal quality lead to a cross over, where the room temperature films then have lower resistances than comparable thickness cryogenic films. The lack of temperature related lateral surface diffusion of metal deposited at 77 K implies that cryogenic metal deposition may also be used to enhance the adhesion of refractory metals (such as molybdenum). The adhesion of such metals limits their application at short gate lengths. Successful use of refractory metals at short gate lengths may enhance the reliability of devices at elevated temperatures.

Figure 7-6 shows XRR of thin (~100 Å) Au layers of GaAs for the two different deposition temperatures, and the associated Au surface roughness and Au/GaAs interfacial roughness derived from the XRR. The Au surface is clearly smoother for low temperature deposition when
measured by this higher resolution technique. There is also a slight decrease in metal/GaAs interfacial roughness with cryogenic deposition, suggesting less diffusion of the initially deposited Au atoms, as discussed above. Details of XRR results are discussed in section 7.4.

In conclusion, the results of this study are summarized as follows:

- The use of low temperature deposition of Au on n-GaAs produces an increase in Schottky barrier height of 10-13 % relative to conventional room temperature deposition.
- The improved barrier height is accompanied by a smoother Au surface and more abrupt interface between the Au and the underlying GaAs.
- Additional work is needed to determine the origin of the increased ideality factors in low temperature diodes.

<table>
<thead>
<tr>
<th>Melting Temp. (°C)</th>
<th>Recrystallization Temp. 0.4T_melt (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>660</td>
</tr>
<tr>
<td>Gold</td>
<td>1064</td>
</tr>
<tr>
<td>Indium</td>
<td>156</td>
</tr>
<tr>
<td>Nickel</td>
<td>1453</td>
</tr>
<tr>
<td>Palladium</td>
<td>1552</td>
</tr>
<tr>
<td>Platinum</td>
<td>1769</td>
</tr>
<tr>
<td>Titanium</td>
<td>1668</td>
</tr>
</tbody>
</table>

Table 7-2 Summary of Au/GaAs diode characteristics for deposition of the Au at either 77 K or 300 K

<table>
<thead>
<tr>
<th>slope</th>
<th>J(A, intercept)</th>
<th>Diameter (μm)</th>
<th>R(cm)</th>
<th>J_s(A/cm²)</th>
<th>n</th>
<th>barrier height</th>
<th>dΦ</th>
<th>dΦ%</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 K</td>
<td></td>
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<td></td>
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<td>0.73</td>
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<td>400</td>
<td>0.02</td>
<td>2.27x10^-7</td>
<td>1.17</td>
<td>0.73</td>
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<tr>
<td>14.23</td>
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<td>800</td>
<td>0.04</td>
<td>1.91x10^-7</td>
<td>1.17</td>
<td>0.73</td>
<td></td>
<td></td>
</tr>
<tr>
<td>77 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.66</td>
<td>1.6x10^-12</td>
<td>200</td>
<td>0.01</td>
<td>5.27x10^-9</td>
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<td>0.83</td>
<td>0.097</td>
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</tr>
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<td>400</td>
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<td>8.18x10^-9</td>
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<tr>
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<td>1.02x10^-8</td>
<td>1.51</td>
<td>0.81</td>
<td>0.076</td>
<td>10.3</td>
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Figure 7-1 I-V characteristics of Au/GaAs Schottky diodes deposited at either 77 K(▲) or 300 K(○) for both 200 μm dia.(left) and 800 μm dia.(right) contact. An expanded view of the forward voltage part of the curves is shown at bottom.

Figure 7-2 Forward current densities as a function of bias for diodes of different diameter deposited at either 77 or 300 K.
Figure 7-3 Reverse current at -4 V for diodes deposited at either 77 or 300 K, as a function of either contact diameter (top) or area (bottom).

Figure 7-4 Time dependence of forward bias at a current of 10 mA for diodes deposited at either 77 or 300 K.
Figure 7-5 Optical microscope images of Au contacts deposited at 77 K (left) or 300 K (right).

Figure 7-6 XRR of thin (~90 Å) Au layers of GaAs for the two different deposition temperatures and the associated Au surface roughness and Au/GaAs interfacial roughness derived from the XRR.
7.3 Thermal Stability of Au Schottky Diodes on GaAs Deposited at Either 77 K or 300 K

The devices used for this study are those reported in section 7.2. The I-V’s were obtained as a function of post-deposition annealing temperature (up to 300 °C, 30 minutes anneals under air ambient). The Schottky barrier height, \( \phi_b \), and diode ideality factor, \( n \), were extracted from the relation for the thermionic emission (eq. 7-1) as well. Figure 7-7 shows I-V characteristics of 400 µm diameter diodes deposited at either 300 K (left) or 77 K (right), as a function of post-deposition annealing temperature. The diodes deposited at low temperature have reverse current densities approximately two orders of magnitude lower than those deposited at room temperature. The respective barrier heights extracted from the forward I-V characteristics were 0.73 eV for the room temperature diodes and 0.82 eV for the low temperature samples. Both types of diodes show increases in reverse current density after annealing at 200 °C or higher, with very significant increases after 300 °C anneals. The forward I-V characteristics as a function of annealing temperature are shown in more detail in Figure 7-8. Note that while both diode types show a deterioration in rectifying behavior, the samples with low temperature deposited contacts still retain lower current densities at all annealing conditions. The forward turn-on voltage for rectifiers is given by [206],

\[
V_F = \frac{n k T}{e} \ln \left( \frac{J_F}{A^{**} T^2} \right) + n \Phi_b + R_{ON} \cdot J_F
\]  

(7-2)

where \( k \) is Boltzmann’s constant, \( T \) is the absolute temperature, \( e \) is the electronic charge, \( A^{**} \) is Richardson’s constant and \( R_{ON} \) the on-state resistance. Thus the observed increase in turn-on voltage is also consistent as resulting from a larger barrier height. The on/off ratio of the diodes was \(~10^4\) at 1 V/-4 V for the low temperature deposited devices and \(~10^2\) for the room temperature diodes.
Figure 7-9 shows the Schottky barrier height as a function of annealing temperature for diodes deposited at either 77 or 300 K. The enhancement in barrier height of ~0.09 eV between the two types of diodes is retained over the entire annealing temperature range investigated. After annealing at 200 °C, the low temperature diodes exhibit a barrier height of 0.53 eV, compared to 0.44 eV for the comparable room temperature deposited diode. Note the ideality factor for the low temperature diodes was always larger than those for the room temperature devices. For example, the as-deposited diodes showed a value of 1.17 for the room temperature devices and 1.43 for the cryogenic diodes. This would be consistent with the presence of an interfacial layer that produces more of an MIS behavior than a true Schottky contact.

In the case of breakdown being initiated in the bulk, the reverse breakdown voltage of a diode $V_B$ can be expressed as \[ V_B = \frac{eN_D W_B^2}{2\epsilon} \] where $N_D$ is the doping on the epilayer, $W_B$ is the depletion depth at breakdown and $\epsilon$ is the dielectric constant of GaAs. Figure 7-10 shows the reverse leakage current (at -4 V) on two different scales as a function of annealing temperature for diodes deposited at either 77 or 300 K. We defined the breakdown voltage as the reverse bias needed to reach a current of 100 $\mu$A·cm$^{-2}$. These values are shown as a function of anneal temperature in Figure 7-11. There is roughly a 50% increase in $V_B$ for the diodes deposited at 77 K as a result of the increased barrier height. Previous electron microscopy and chemical bonding studies are supportive of interfacial layer differences being the cause of the differences in barrier height, with a more abrupt metal-semiconductor interface for low temperature deposited contacts [207].

Au rectifying contacts deposited at 77 K on n-GaAs show an enhancement in barrier height of ~12% over their value for room temperature deposition (0.73 eV). This enhancement persists
to annealing temperatures of 200 °C, while annealing at 300 °C produces a severe degradation in rectifying behavior for both types of diodes. The increase in barrier height translates to a decrease in reverse current density of several orders of magnitude for Au/GaAs diodes deposited at 77 K. This process is a relatively simple one with many potential advantages in the dc performance of GaAs MESFETs.

Figure 7-7 I-V characteristics of 400 μm diameter diodes deposited at either 300 K (left) or 77 K (right), as a function of post-deposition annealing temperature.

Figure 7-8 Forward I-V characteristics of 400 μm diameter diodes deposited at either 300 K (left) or 77 K (right), as a function of post-deposition annealing temperature.
Figure 7-9 Schottky barrier height as a function of annealing temperature for diodes deposited at either 77 or 300 K.

Figure 7-10 Reverse leakage current (@ -4 V) on two different scales as a function of annealing temperature for diodes deposited at either 77 or 300 K.
7.4 Interfacial Differences in Enhanced Schottky Barrier Height Au/n-GaAs Diodes Deposited at 77 K

100 Å thick Au films deposited at 77 K or 300 K, followed by post-deposition annealing at temperatures up to 300 °C, were used in this X-Ray Reflectivity (XRR) study. We interest in interfacial differences of 77 K and 330 K deposited Au on n-GaAs substrate before and after thermal treatment, which correlate with Au/n-GaAs diode characteristics and thermal behaviors as discussed in section 7.2 and 7.3. In addition, front-side contacts of 1000 Å thick Au, Pt, Ni, Pd or Ni were deposited at 77 K or 300 K onto n-GaAs (n ~10^{17} cm^{-3}) substrates to examine their individual barrier height enhancements.

As shown in Figure 7-1 (top), the diodes deposited at low temperature have reverse current densities approximately two orders of magnitude lower than those deposited at room temperature. The respective barrier heights extracted from the forward I-V characteristics (Figure 7-1, bottom) were 0.73 eV for the room temperature diodes and 0.82 eV for the low temperature
samples. Similar measurements were performed for the diodes deposited with Ni, Pt, Pd or Ti at 77 K or 300 K. Table 7-3 shows a summary of the extracted barrier heights for all the metals examined. Only Au, Pd and Ni showed any significant change in barrier height for cryogenic metal deposition. Note also that we observed cracking and peeling of the metal in the case of Pt, Pd and Ni, leaving Au as the only metal that showed an enhancement in barrier height and good adhesion to the GaAs. Optical micrographs of the Ti and Au diodes deposited at different temperatures are shown in Figure 7-12 as an example of a situation where the metal (Ti in this case) peels off when deposited at low temperature.

Figure 7-13 shows the XRR spectra from 77 K Au/GaAs diodes as a function of post-deposition anneal temperature. From this data, it is possible to deconvolute the interfacial roughness between the Au and GaAs and also the metal roughness at the air interface. To make the differences in the spectra more obvious, Figure 7-14 shows the XRR spectra from Au/GaAs diodes deposited at either 77 K or 300 K before (left) or after (right) annealing at 300 °C. Two things are obvious from this data, firstly, there is a clear difference between the samples deposited at different temperatures and secondly, the effect of the 300 °C annealing is to wash out these differences.

Figure 7-15 shows the interfacial Au/GaAs roughness and metal/air roughness data derived from the XRR spectra for samples deposited at either 300 K(left) or 77 K(right) as a function of post-deposition annealing temperature. The interfacial roughness in the room temperature deposited diodes is basically constant with anneal temperature, whereas that for the cryogenic diodes is initially smoother but roughens with annealing, reaching a similar value to that in the room temperature diodes (Figure 7-16). By contrast, the metal/air roughness improves above 200
C in the room temperature diodes, but worsens with annealing in the 77 K diodes. Note that the metal is initially smoother on the low temperature diodes (Figure 7-16).

The correlation of electrical and x-ray data clearly shows that the enhanced barrier height is associated with a smoother Au/GaAs interface and that post-deposition annealing of the cryogenic diodes roughens this interface to a value similar to that of diodes deposited at room temperature while at the same time reducing the Schottky barrier height back to the values obtained on the room temperature diodes annealed under the same conditions. Previous electron microscopy and chemical bonding studies are also supportive of interfacial layer differences being the cause of the differences in barrier height, with a more abrupt metal-semiconductor interface for low temperature deposited contacts [207]. There are still many issues to be resolved, for example, why only certain metals exhibit the increased barrier height when deposited at low temperatures. This may be related to the crystal structure and grain size of the particular metal layers on GaAs obtained at different deposition temperatures. The melting temperature of Au (1064 °C) is well below that of the other metals studied here (1453 °C for Ni, 1552 °C for Pd, 1769 °C for Pt, and 1668 °C for Ti) and thus the recrystallization (onset of grain growth) temperature will also be lower, since this is typically about 40 % of the melting temperature. It is desirable that that interface diffusion and grain growth be minimized during encapsulation of the GaAs device by a SiNx dielectric for packaging. This dielectric is deposited by PECVD and the temperature that the substrate is exposed to is 200-300 °C. For significant interfacial diffusion to take place, the constituents of either the semiconductor or the metal contact must become mobile and form a solid solution. The contact metals studied here should have little diffusion below 0.4T_melt.
The results of our study may be summarized as follows:

- The deposition of Au at low temperatures produces an increase in barrier height from 0.73 eV to 0.82 eV. Ni shows an even larger enhancement, but the metal contact in that case shows cracking and peeling.

- No significant enhancement in barrier height was observed for low temperature deposited Pt and Ti.

- The improved barrier height in the case of Au is accompanied by a sharper metal/GaAs interface. As the samples are annealed to 300 °C, this interface roughens to the same value as in room temperature deposited diodes and the enhancement in barrier height disappears.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Cracks at 77K</th>
<th>Φ(300K)(eV)</th>
<th>Φ(77K)(eV)</th>
<th>dΦ(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
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<td>0.73</td>
<td>0.82</td>
<td>12</td>
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<tr>
<td>Pt</td>
<td>Yes</td>
<td>0.79</td>
<td>0.79</td>
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</tr>
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<td>Ti</td>
<td>No</td>
<td>0.69</td>
<td>0.71</td>
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<tr>
<td>Pd</td>
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<td>0.81</td>
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<tr>
<td>Ni</td>
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<td>0.67</td>
<td>0.79</td>
<td>18</td>
</tr>
</tbody>
</table>
Figure 7-12 Optical micrograph images of Ti deposited at either 77 K (top left) or 300 K (top right) and Au at 77 K (bottom left) or 300 K (bottom right) on GaAs.

Figure 7-13 XRR spectra from 77 K Au/GaAs diodes as a function of post-deposition annealing temperature.
Figure 7-14 XRR spectra from Au/GaAs diodes deposited at either 77 K or 300 K before (left) or after (right) annealing at 300 °C.

Figure 7-15 Interfacial Au/GaAs roughness and metal/air roughness data derived from the XRR spectra for samples deposited at either 300 K (left) or 77 K (right), as a function of annealing temperature.
Figure 7-16 Comparison of metal roughness (left) and metal-semiconductor interfacial roughness (right) for the two types of diodes as a function
CHAPTER 8
SUMMARY AND FUTURE WORK

8.1 Hydrogen Sensor Using Multiple ZnO Nanorods

A variety of different metal catalyst cluster coatings (Pt, Pd, Au, Ag, Ti, and Ni) deposited on multiple ZnO nanorods were compared for their effectiveness in enhancing sensitivity for detecting hydrogen at room temperature. The metal cluster coated nanorods were biased at 0.5 V and power levels for these diode sensors were ~0.4 mW. Pt-coated nanorods showed an increase of conductance up to 8 % in room temperature upon exposure to 500 ppm hydrogen in N2. This is a factor of two larger than that obtained with Pd, and more than an order of magnitude larger than that achieved with the remaining metals. Pt-coated ZnO nanorods easily detected hydrogen down to 100 ppm, with 4 % increase of conductance at this concentration after 10 min exposure. It took a few minutes for the nanorods to return to their original conductance after switching hydrogen off and back to air. The slow response at room temperature is a drawback in some applications, but the sensors do offer low power operation and very good detection sensitivity.

The sensitivity for detecting hydrogen using multiple ZnO nanorods with cluster coating of Pd on the surface is further investigated with different hydrogen concentrations. The nanorods show changes of conductance upon exposure to hydrogen concentrations of 10-500 ppm balanced with N2 approximately a factor of five larger than without Pd. Pd-coated ZnO nanorods detected hydrogen down to ~10 ppm, with a increase of conductance >2.6 % at 10 ppm and >4.2 % at 500 ppm H2 in N2 after 10 min exposure. The nanorods had no response to O2 at room temperature. As opposed to the slow recovery for Pt coated nanorods, Pd coated nanorods showed a much quicker recovery time upon switching the ambient from hydrogen to either air or pure O2, for which approximately 95 % of the initial ZnO conductance after exposure to hydrogen was recovered within 20 s. This rapid and easy recoverability make the Pd-coated
nanorods suitable for practical applications in hydrogen selective sensing at ppm levels at room temperature with \( \sim 0.4 \) mW power consumption.

In conclusion, both Pt-coated and Pd-coated ZnO nanorods appear well suited to detection of ppm concentrations of hydrogen at room temperature. Pd coated nanorods showed better recovery characteristics. The ZnO nanorods can be placed on cheap transparent substrates such as glass, making them attractive for low-cost sensing applications, and can also operate at very low power conditions. Of course, there are many issues still to be addressed, in particular regarding the reliability and long-term reproducibility of the sensor response before it can be considered for space-flight applications. In addition, the slow response of the Pt coated sensors at room temperature is a major issue in some applications.

8.2 Hydrogen Sensor Using AlGaN/GaN Schottky Diode and High Electron Mobility Transistor

Pt-gated AlGaN/GaN high electron mobility transistors can be used as room temperature hydrogen gas sensors at hydrogen concentrations as low as 100 ppm. A comparison of the changes in drain and gate current-voltage (I-V) characteristics with introduction of 500 ppm \( H_2 \) into the measurement ambient shows that monitoring the change in drain-source current (FET mode) provides a wider gate voltage operation range for maximum detection sensitivity and higher total current change than measuring the change in gate current (Schottky diode mode). However, over a narrow gate voltage range, the relative sensitivity of detection by monitoring gate current changes (Schottky diode mode) is up to an order of magnitude larger than that of drain-source current changes (FET mode). In both cases, the changes are fully reversible in \( \sim 2-3 \) mins at 25\(^\circ\) C upon removal of the hydrogen from the ambient. These Pt/AlGaN/GaN HEMTs operated in either a diode mode or in an FET mode show the ability to detect 500 ppm \( H_2 \) in \( N_2 \)
at room temperature. The FET mode provides a larger total current change with introduction of hydrogen into the ambient, but the diode mode shows a higher relative sensitivity over a limited range of forward biases.

The design of AlGaN/GaN differential sensing diodes is shown to provide robust detection of 1% H₂ in air at 25 °C. The active device in the differential pair is coated with 10 nm of Pt to enhance catalytic dissociation of molecular hydrogen, while the reference diode is coated with Ti/Au. The active diode in the pair shows an increase in forward current of several mA at a bias voltage of 2.5 V when exposed to 1% H₂ in air. The use of the differential pair removes false alarms due to ambient temperature variations. These AlGaN/GaN HEMT differential sensing diodes appear well-suited to hydrogen detection applications.

The use of TiB₂-based Ohmic contacts (Ti/Al/TiB₂/Ti/Au) on Pt-Schottky contact AlGaN/GaN heterostructure hydrogen sensing diodes is shown to provide very stable operation for detection of 1% H₂ in air under field conditions where temperature is allowed to vary. By contrast, the use of more conventional Ti/Al/Pt/Au Ohmic contacts led to higher background variations in current that affect the ultimate detection threshold of the sensors. Combined with the superior thermal stability of these boride-based contacts, this metallization system appears attractive for sensors of long-term monitoring applications.

In conclusion, combined with a differential pair geometry that compares current from an active diode with Pt Schottky contact and a passive diode with Ti/Au Schottky contact, the more stable TiB₂-based Ohmic contacts reduce false alarms due to ambient temperature changes, and suggest that integrated chips involving gas sensors and HEMT-based circuitry for off-chip communication are feasible in the AlGaN/GaN system. Future work will involve design and fabrication of an integrated sensor chip with GaN HEMT amplifier and transmitter.
8.3 Mercury Ion Sensor Using AlGaN/GaN High Electron Mobility Transistor

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 seconds 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.

Bare Au-gated and thioglycolic acid functionalized Au-gated AlGaN/GaN HEMTs were further used to detect both mercury(II) and copper(II) ions. The bare Au-gate sensor was only sensitive to Hg$^{2+}$, and thioglycolic acid functionalized sensors could detect both Hg$^{2+}$ and Cu$^{2+}$ ions. Both surfaces had a selectivity of approximately a hundred-fold over other contaminating ions of sodium, magnesium and lead. Both bare Au-gate and thioglycolic acid functionalized sensor can also be repeatedly used after a simple DI water rinse. By fabricating an array of the sensors on a single chip and selectively functionalizing some sensors with thioglycolic acid, a multi-functional specific detector can be fabricated. Such a sensor array can be used to detect quantitatively Hg$^{2+}$ ions in Cu$^{2+}$ ion solution or Cu$^{2+}$ ions in Hg$^{2+}$ ion solution. The dimensions of the active area of the sensor and the entire sensor chip are 50 µm × 50 µm and 1 mm × 5 mm, respectively. Our results show that portable, selective, and fast Cu$^{2+}$ and Hg$^{2+}$ sensors can be realized by combining bare Au-gated and thioglycolic acid-functionalized surface in one sensor.
8.4 Disease Biomarker Sensor Using AlGaN/GaN High Electron Mobility Transistor

AlGaN/GaN high electron mobility transistors (HEMTs) were used to detect kidney injury molecule-1 (KIM-1), an important biomarker for early kidney injury detection. The gate region consisted of 5 nm gold deposited onto the AlGaN surface. The gold was conjugated to highly specific KIM-1 antibodies through a self-assembled monolayer of thioglycolic acid. The HEMT source-drain current showed a clear dependence on the KIM-1 concentration in phosphate buffered saline solution. The limit of detection was 1 ng/ml using a 20 µm × 50 µm gate sensing area. This electronic detection of disease biomarker is a significant step towards a compact sensor chip, which can be integrated with a commercial available hand-held wireless transmitter to realize a portable, fast and high sensitive device for multiple disease diagnosis. Our approach shows potential for both preclinical and clinical disease diagnosis with accurate, rapid, noninvasive, and high throughput capabilities.

8.5 ZnO Based Light Emitting Diode

N⁺ ion implantation at moderate doses (10^{13}-10^{14} cm^{-2}) into nominally undoped (n ~10^{17} cm^{-3}) bulk single crystal ZnO substrates followed by annealing in the range 600-950 °C was used to fabricate diodes that show band-edge electroluminescence at 120 K (~390 nm) under forward bias conditions. The current-voltage (I-V) behaviors of the diodes are characteristics of metal-insulator-semiconductor (MIS) devices but not p-n junctions, and suggest the implantation creates a more resistive region in the n-ZnO in which holes are created by impact ionization during biasing, similar to the case of electroluminescence in ZnO varistors. The series resistance is only 25 Ω due to the use of the conducting ZnO substrate. We demonstrated that band-edge and yellow EL could be obtained from N⁺-implanted bulk ZnO diodes similar to that observed in
MIS diodes. Future work on acceptor implantation should focus on achieving p-type conductivity in the ZnO so that true injection LEDs may be realized.

**8.6 Increasing Schottky Barrier Height with Cryogenic Metal Deposition**

The use of low temperatures (~77 K) during Au Schottky contact deposition onto n-GaAs produces an increase in barrier height from 0.73 eV for room temperature diodes to 0.82 eV. The increase in barrier height translates to a decrease in reverse current density of several orders of magnitude for Au/GaAs diodes deposited at 77 K. The reverse breakdown voltage of low temperature deposited diodes was ~50 % larger than conventional Au/GaAs diodes. There is no evidence of drift in the forward current in either type of diode, and the low temperature deposited samples show smoother Au layers and more abrupt Au/GaAs interfaces as determined by X-Ray Reflectivity measurements. Both types of diodes show surface and bulk contributions to the reverse bias current. The ideality factor of the cryogenically processed devices (~1.43) was higher than for room temperature diodes (~1.17) and it may result from contaminants gettered to the cold GaAs surface. Not all Schottky metals show this enhancement; for example Pt and Ti do not show any significant change in barrier height whereas Au, Pd and Ni show increases between 7-18 %.

The enhancement of ~0.09 eV (a 12 % increase) in Schottky barrier height for Au deposited at cryogenic temperatures on n-type GaAs relative to conventional deposition at 300 K is shown to persist for annealing temperatures up to 200 °C. At higher anneal temperatures (300 °C), both types of diodes show a severe deterioration in rectifying behavior. We used X-Ray Reflectivity to show that the main difference between Au deposited at 77 K and room temperature is a decreased interfacial roughness between the Au and GaAs. As the diodes are annealed to 300 °C both the difference in barrier height and interfacial roughness is lost. This is a
simple method has many potentials for improving the performance of GaAs metal semiconductor field effect transistors (MESFETs).

The results of our study may be summarized as follows:

- The use of low temperature deposition of Au on n-GaAs produces an increase in Schottky barrier height of 10-13 % relative to conventional room temperature deposition.
- The improved barrier height is accompanied by a smoother Au surface, and more abrupt interface between the Au and the underlying GaAs.
- Additional work is needed to determine the origin of the increased ideality factors in low temperature diodes.
- Ni shows an even larger enhancement, but the metal contact in that case shows cracking and peeling.
- No significant enhancement in barrier height was observed for low temperature deposited Pt and Ti.
- The improved barrier height in the case of Au is accompanied by a sharper metal/GaAs interface. As the samples are annealed to 300 °C, this interface roughens to the same value as in room temperature deposited diodes, and the enhancement in barrier height disappears.
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BIOGRAPHICAL SKETCH

Hung-Ta Wang was born in Nantou, Taiwan, in 1977. He received both the bachelor and the master degrees in the Department of Chemical Engineering of National Cheng Kung University, Tainan, Taiwan, in 1999 and 2001 respectively. He attended Taiwan Army for the mandatory training and service, and served as vice company commander with the position of 1st lieutenant officer from 2001 to 2003. After military service, he worked for Taiwan Semiconductor Manufacturing Company (TSMC) as a process integration engineer monitoring front-end process until 2004.

In 2004 Fall, he was enrolled in the Ph.D. program of the Department of Chemical Engineering of the University of Florida. He was under the guidance of Professor Fan Ren studying wide bandgap semiconductor chemical/bio sensors, light emitting diodes, as well as high speed devices. He earned his Doctor of Philosophy degree from the Chemical Engineering Department of the University of Florida in May 2008 with 2 filed patents, 32 SCI journal publications in highly recognized journals (*Applied Physics Letters*, *Nanotechnology*, *Journal of Electronic Materials*, *Applied Surface Science*, *Electrochemical and Solid-State Letters*, etc.), and 8 international conference oral presentations.