GALLIUM NITRIDE INTEGRATED GAS/TEMPERATURE SENSORS FOR FUEL CELL SYSTEM MONITORING FOR HYDROGEN AND CARBON MONOXIDE

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Abstract

High-temperature electrical performance of thermally stable GaN-based MESFETs and MODFET sensors is presented. Data on Ti/Al ohmic contacts, with Cr(TiWN) /Au protection layers, to n-type GaN and Al$_{0.3}$Ga$_{0.7}$N grown by MBE is presented. Preliminary data is also presented on the current-voltage and capacitance-voltage characteristics of the gas sensing structure (Schottky contacts to both n-type GaN and Al$_{0.3}$Ga$_{0.7}$N). Electrical performance was measured from room temperature to 400°C.
Introduction

Need for Gas Sensors for Fuel Composition in Fuel Cell Systems

The electrodes in solid polymer electrolyte fuel cell systems require hydrogen fuel free from carbon monoxide (CO), otherwise the platinum electrodes are poisoned and fuel efficiency is degraded. Steam reforming of hydrocarbon fuels produces a mix of hydrogen, carbon dioxide and enough by-product CO to poison the electrodes. Preferential oxidation (PROX) of CO to reduce this contaminant is accomplished over a noble metal catalyst typically platinum by adding oxygen to the hydrogen fuel upstream of the PROX catalyst (Mann, et al 1993 and Krumpelt 1999). An inexpensive monitor to confirm the PROX catalyst efficiency and ultimately control the PROX system conditions is useful if not necessary to avoid the risk that PROX catalyst degradation could lead to reduced fuel efficiency or failure of the fuel cell due to contaminated hydrogen. Since the environment for a PROX monitor is rich in hydrogen, the problem is developing a sensor that can monitor carbon monoxide at high temperature without the sensor output being dominated by hydrogen or temperature. This proposal will cover preliminary research to prove this concept by fabricating and testing prototype sensors. The requirements for a prototype sensor include: successful high temperature operation (ca 100-400°C) and the resolution of CO (ca. 2-200 ppm) in the presence of hydrogen (ca 35-75%vol), oxygen, hydrocarbons and water vapor. Monitoring the concentration of hydrocarbons and reactive sulfur (H₂S) may also important in some systems (DOE 1999).

Science and Technology

We are exploring an approach combining the advantages of the sensing capabilities of the catalytic metal gate with a wide bandgap GaN semiconductor metal semiconductor field effect transistor (MESFET) and modulation doped field effect transistor (MODFET) transducers for high temperature measurement of carbon monoxide in hydrogen. The choice of the catalytic metals for the device is based on the metals used in FET detectors for lower temperature applications and based on data for metals used in the three-way automobile catalytic converter: platinum, palladium/silver and rhodium. The reasons for three different metals and the sensor architecture and materials is discussed later in the introduction.

GaN high temperature electronics background

GaN based devices and circuits have the potential to operate at 600°C or higher temperatures owing to the wide band gap (e.g. ~ 3.4 eV). The interface between the semiconductor and the first metallization layer is the most important for it controls the transport mechanism(s) in solid state devices. In a FET low resistance (ohmic) contacts are made for the source and drain regions. The FET is a switch, and current flows through these contacts when the switch is “turned on” (Sze 1983). The voltage applied to the gate metal in a MESFET or MODFET determines whether the switch is on or off. A large electrical impedance is typically sought for the gate contact as it is important that little or no current flows through the gate electrode. For GaN and other highly ionic semiconductors, evidence has suggested that electrical transport properties of metal to Group III-nitride contacts strongly depends on the difference between the work function of the metal and the electron affinity of the semiconductor (Sze 1983). In a GaN
MESFET or MODFET with metal contacting the semiconductor directly, the so called Schottky barrier is the electric field produced by the difference between the work function of the metal gate and the electron affinity of the semiconductor and any chemical interaction of the metal with the semiconductor that can change the resistivity of the material. Theory suggests that metals with lower work functions form ohmic contacts on n-GaN. In fact, Ti, Al, and Cr are common metals for ohmic contact to n-GaN. Similarly, metals with higher work function, such as Pt, Rh and PdAg are expected to form high impedance gate Schottky contacts to n-GaN.

As with other semiconductor systems, especially compound semiconductor systems, the formation of an alloyed semiconductor/contact is usually the most straightforward method to achieve ohmic behavior. This is most certainly true for other group III-V semiconductors such as the well-studied and characterized GaAs semiconductor (Chern 2000). Almost all known, successful contacts to III-V semiconductors consist of bi-level to multi-level metallization schemes. Usually, chemical or thermal reactions, solid-state diffusion and interdiffusion, and/or other methods produce an alloy and possibly material damage that reduces the resistivity of the semiconductor and concomitantly the penetration depth of the barrier electric field region under the first metal layer.

**Gate Metal Adhesion and Barrier metals**

The adhesion of catalytic noble metals to GaN is typically improved with a metal or nitride intermediate layer, because the noble nature of the catalytic gate metals reduces the reactivity toward other materials and the strength of bonds otherwise made strong by alloying, compound formation, or intermetallic oxides or nitrides. The stresses inherent in the sputter deposited metal films often results in the noble metals lifting off the substrate. Temperature coefficients of expansion mismatch between the metal films and substrate exacerbate this problem, and mechanical reliability is an important consideration. Tungsten or titanium nitride or tantalum nitride are potential adhesion layers that also help prevent contamination and sensor drift caused by interdiffusion of the substrate components and metal films. Phase diagrams for the nine combinations of Pt, PdAg and Rh with TiWN, TiN and TaN are lacking. A priori calculations by (Niessen 1983) suggest a small enthalpic driving force for solvation of W and Ta by platinum and palladium but a zero or slightly positive enthalpy for solvation by rhodium. The enthalpic driving force for Ti solvation by any of these metals is expected to be smaller because of the size mismatch compared to W and Ta. The fact that Ta, W and Ti are nitrides further reduces the driving force for solid solutions and interdiffusion with the overlying catalytic metal layer, but the driving force for interdiffusion of TaN, WN and TiN with GaN is not well known.

**Catalytic gate FET sensor background**

The development of gas sensing and analysis using the well-known effect on surface potential of gas adsorption on a metal surface has been extensively explored using chemically sensitive semiconductor devices (Lundstrom 1989). Recent work on field effect devices using catalytic metal gates on silicon carbide substrates has been reviewed (Lundstrom 1996) and suggests the promising application of the field effect technology for monitoring the composition of automobile emissions and the efficiency of the catalytic converter.
The field effect technology using catalytic metal electrodes on a semiconductor exploits dissociative chemisorption on the surface. The effect of hydrogen was reported (Lundstrom 1975) on a palladium gate FET on silicon. Other work (Poteat 1983) demonstrated sensitivity to ethylene and carbon monoxide hydrogen sulfide, propylene oxide, ethylene, formic acid, carbon monoxide and NO\textsubscript{2}. More recently, hydrogen, carbon monoxide, ethylene and acetylene effects have been observed on metal-insulator-semiconductor (MIS) diodes with electrodes of pure platinum and platinum and palladium compositions with small amounts (ca. 5-10%) of transition metals such as copper (Feinstein 1998 and Pyke 1993). These electrodes were suspended above a silicon nitride/silicon dioxide barrier dielectric covering a silicon substrate.

The theory behind the effect, in a FET or diode sensor, is that hydrogen and other gases chemisorb on the catalytically active metal electrodes, and in the process yield a species which alters the surface component of the metal work function. The change in work function alters the population distribution of carriers in the semiconductor under the metal by changing the surface potential of the semiconductor. The consensus in the literature is that gases other than hydrogen cannot be detected directly on a solid electrode. Without a pathway for the molecules to penetrate to the metal insulator interface, the effect on the work function produced on the outside of the electrode (exposed to gas) does not influence the surface potential of the semiconductor. In the case where a solid electrode does show a response, it is usually in the presence of hydrogen. The catalytic interaction of gases adsorbed on the surface affects the steady state surface chemical composition changing the metal work function and surface potential of the semiconductor. Thus, it is thought gases reacting with hydrogen on a catalytic surface can be measured indirectly through the effect they have on hydrogen at the metal dielectric interface (Hughes 1987). The observations above on NO\textsubscript{2} and CO were explained in this way. The current hypothesis is gases that do not dissolve and diffuse through the metal can be detected only by sensors with a perforated or ultrathin porous catalytic metal electrode (Cassidy 1985, Dobos 1990, Hedborg 1994 and Lundstrom 1996), and perforations or pores must extend down through the metallic layer to the metal dielectric interface for electric field penetration of the semiconductor. The resulting surface potential distribution would have a two-dimensional fine structure depending on the morphology of the metal film, but the average surface potential will change with the adsorption of gas, and for a FET, the gate voltage will change accordingly.

Owing to their large bandgap, the III-V nitrides are attractive for high temperature, high power electronics applications. For GaN and other highly ionic semiconductors, evidence has suggested that the Schottky barrier height of metal to III-nitride contacts strongly depend on the difference between the work function of the metal and the electron affinity of the semiconductors. Metals with lower work functions form ohmic contacts on n-GaN. This explains why Ti, Al, W, and Cr are chosen as ohmic contacts on n-GaN. Similarly, metals with higher work function, such as Pt, Ni, Pd, and Au are expected to form good Schottky barriers to n-GaN.

Platinum and palladium have been used in the catalytic metal FET before, and both metals are used in the three-way catalytic converter this product is designed to monitor. Rhodium was chosen, because of its use in the catalytic converter and selectivity to NO over O\textsubscript{2} in the catalytic oxidation of CO (Shelef 1994) and the probability that in a sensor, Rh will add some selectivity to the analysis of the exhaust gases. Each of these metals is refractory and as such do will not
sublime or corrode under the operational conditions of high temperature and exhaust gas exposure.

The adhesion of these catalytic metals to GaN is typically improved with a metal or nitride intermediate layer, because the unreactive nature of the catalytic gate metals with Pd a possible exception (Oelhafen 1983) makes the bond to other materials weak. The stresses inherent in the deposited metal films often result in the noble metals lifting off the substrate. Temperature coefficients of expansion mismatch between the metal films and substrate exacerbate this problem, and an adhesion metal layer is an important component in the design. In the case of one design for a suspended gate GasFET (Cassidy 1984) where a sacrificial metal is etched away from under the catalytic metal to form a metal bridge for gas access, compressive stress in the catalytic metal films (usually sputter deposited) caused the films to buckle when the sacrificial metal is etched away (Pyke 1993). At the very least, the buckling resulted in a gap capacitance that was highly variable and resulted in an unacceptably wide distribution in sensor performance.

Tungsten or titanium nitride or tantalum nitride are potential adhesion layers that also help prevent contamination and sensor drift caused by interdiffusion of the substrate components and metal films. At the high temperatures proposed for this work, a barrier is necessary to impede any potential alloying reactions of the catalytic metal with gallium. A priori calculations (Niessen 1983) suggest a small enthalpic driving force for solvation of W and Ta by platinum and palladium but a zero or slightly positive enthalpy for solvation by rhodium. Recent data suggests significant solvation of Pd by W. The enthalpic driving force for Ti solvation by any of these metals is expected to be smaller because of the size mismatch compared to W and Ta. The fact that Ta, W and Ti are nitrides further reduces the driving force for solid solutions and interdiffusion with the overlying catalytic metal layer. A small positive enthalpic contribution to solid solutions of the two metals has the corresponding potential detrimental effect of a mechanically unreliable combination. Our approach will be to deposit a thin layer (10-100 nm) of the barrier nitrides described above then an ultrathin film (5-20 nm) of the catalytic metal. Film formation is expected to give rise to island or clusters connected on the corners of the nanocrystallites for conduction but sufficiently separated to form a porous film and to relieve the intrinsic stress.

**Choice of Pt, Rh and PdAg as Catalytic Gate Materials**

Platinum and palladium were selected because each has shown sensitivity in the ppm range for ethylene, acetylene, CO. Both metals are PROX catalyst candidates, and both metals have been used in metal-semiconductor junctions on GaN. PdAg was selected, because the mechanical integrity is better than pure Pd at these hydrogen concentrations and because PdAg has been used successfully in hydrogen purification membranes. Rhodium was selected, because of its PROX catalytic activity and to help resolve the effects of the multiple gases in combination with platinum and palladium-silver. Each of these metals is expected to adsorb CO preferentially in the fuel stream just as in the PROX catalyst. The reaction of CO and hydrogen with oxygen on the surface of the catalyst produces a steady state surface composition that can be detected through the work function change of the catalyst. Our expectation is that with a higher affinity for CO, the three metals chosen for this work should show a higher resolution for changes involving CO and a more accurate and precise analysis in a parallel sensor array.
Experimental

Fabrication

GaN-MESFET and MODFET structures were grown on sapphire substrates using MBE. The cross sections of these two structures are illustrated in Figure 1. All structures had a buffer layer consisting of a 20 nm AlN layer on a sapphire substrate, followed by a 3 µm unintentionally-doped GaN layer. The active layers were then grown on the 3 µm-thick GaN layer. The MESFET consisted of 100 nm thick, 1×10^{17} cm^{-3} Si-doped channel thinned from an originally 2 µm layer and without a n++ capping layer. The MODFET had a 20 nm thick, Si-doped AlGaN epilayer with an Al composition of 30% and a 1 µm thick, undoped GaN channel layer. The sheet carrier concentration and Hall mobility were measured as 1.3×10^{12} cm^{-2} and 960 cm/Vsec, respectively. All FETs were fabricated with a source-drain spacing of 6 µm. The gate length was 2 µm and the width varied from 100 µm to 200 µm. The wafer was first covered with a 200 nm-thick, sputtered, Ti layer as the mask prior to the photolithography. Processing steps were similar to that have been described for GaAs-based devices. The major difference in processing between the GaN-based devices and GaAs-based devices is that the wet etching was ruled out in the former case.

![Fig.1 GaN FET cross-section (a) Si-doped MESFET and (b) AlGaN/GaN MODFET.](image)

The trench etching for device isolation was carried out by reactive ion etching (RIE) using Cl plasma. The final depth of the mesa is close to 2 µm. The Ti mask is then removed in HF solution and contact windows were exposed. The wafer received plasma etching for 30 sec in CF₄ and Ar plasma. Then, the Ti-Al ohmic contacts were deposited using e-beam evaporation. For MESFET, TiPtAu gate contacts were deposited by sputtering, while Pt gate was used for MODFET structure. The annealing condition was optimized at 600°C for 5 min in forming gas (10%vol H₂ in N₂) ambient.
Electrical Measurements

All the current-voltage (I-V) measurements were conducted using a test system comprised of a HP 4145B parameter analyzer, a Micromanipulator HSM hot stage and chuck controller, and an IBM PC compatible computer. The data was acquired via an IEEE 488 HPIB data bus and stored electronically for further analysis. The capacitance-voltage characteristics were obtained with an EG&G PAR 410/4108 CV system also controlled by the PC. If the slope of the $C^{-2}$ vs $V$ plot obtained is linear, one can obtain an independent measurement of barrier height using the method of least squares fit, from the intercept of the voltage axis $V_{int}$ through the use of the relationship (Goodman 1999)

$$\phi_b = V_{int} + \phi_o + kT/q$$

where $\phi_o = (kT/q)ln(N_c/n)$ can be determined from the donor density which in turn can be calculated from the slope of the $C^{-2}$ vs $V$ plot. The density of states in conduction band of Al$_x$Ga$_{1-x}$As can be found in (Missous 1990)

Results

Ohmic Contacts

We have found that Cr/TiW/Ti-Al and Cr/Ti-Al to n-GaN are both suitable ohmic contact systems to n-GaN for prolonged use in air ambients to temperatures of at least 500°C. We chose Cr as a capping layer to protect the Ti-Al ohmic contacts since TiW intended to oxidize during the aging tests. The Cr cap layer has a high electrical conductivity and high thermal resistance to oxidation and also does not diffuse through the TiW layer. A final layer of Au (Cr acts as a blocking layer to interdiffusion) improves the chemical and oxidation resistance of the contacts and is amenable standard packaging techniques and equipment. Considering the work function effect on the Schottky barrier height, the contact resistance is not expected to degrade much in case of further diffusion of Cr from the capping layer to the interface between GaN and Ti-Al because of the low work function of Cr. The specific contact resistance was $2.0 \times 10^{-6}$ Ohm-cm$^2$ and remained unchanged after annealing in air at 350°C for over 120 hours.
**GaN MESFET with TiPtAu Gate**

Figure 2 shows poor transistor performance. The ideal curve should rise steeply and then be insensitive to $V_{ds}$. The inflection point (e.g. typically $V_{ds}$~1-2V) is called the pinch off voltage.

![Current-voltage characteristics at 300°C for a representative GaN MESFET with a TiPtAu gate](image)

**Fig. 2:** Current-voltage characteristics at 300°C for a representative GaN MESFET with a TiPtAu gate

This can be explained on the basis or severe leakage currents between the gate electrode and the buffer layer shown by the $I_g$-$V_g$ characteristics as a function of temperature of the gate diode are shown in Figure 3. The weak rectifying property (low ratio of forward to reverse current) of the gate diode is ascribed to the defects in the doped-GaN layer, which is close to the buffer layer. It is well known that the threading dislocations may have a high density in or near the channel that may provide leakage paths at elevated temperatures. It is worth pointing out that the GaN structure was grown ~4 years ago and the material properties for GaN-based semiconductors were not as good compared to that of currently grown ones and had considerably more defects.

![Current voltage plot of a representative TiPtAu/n-GaN diode as a function of temperatures](image)

**Fig. 3:** Current voltage plot of a representative TiPtAu/n-GaN diode as a function of temperatures.
**AlGaN/GaN Modulation Doped Field Effect Transistor (MODFET)**

Figure 4 shows the characteristic $I_d$-$V_{ds}$ curves for a representative MODFET. The current when the channel was fully open was 33 mA and the breakage voltage was ~70 V (not shown in the figure). Self-heating was observed in this type of device as reflected by the decrease in drain current with respect to increased drain voltage. Another reason for such behavior is, at higher fields, the electron mobility is reduced due to the scattering of electrons (Bykovski 1997 and Asbeck 1997).

![I_d-V_ds curve for a representative Pt gate AlGaN/GaN MODFET at 35°C](image)

**Fig. 4: $I_{ds}$-$V_{ds}$ for a representative Pt gate AlGaN/GaN MODFET at 35°C**

The elevated temperature characteristic curves of representative MODFETs still show the ideal shape as shown in Figs.5 and 6 for temperatures of 300°C and 400°C, respectively. The current ratios of gate leakage to total drain leakage at $V_{ds} = 5$V and $V_{gs} = -2$V at 300°C and 400°C are 22.4 $\mu$A/48 $\mu$A and 271 $\mu$A/225 $\mu$A, respectively.
Fig. 5: $I_{ds}$-$V_{ds}$ for a representative Pt gate AlGaN/GaN MODFET at 300°C

Fig. 5: $I_{ds}$-$V_{ds}$ for a representative Pt gate AlGaN/GaN MODFET at 400°C
Discussion and Conclusions

While Figure 5 and 6 show the ideal shape gate leakage current has to be reduced for a sensitive FET detection circuit. The fact that the gate current became the dominate leakage source is not surprising because the barrier height characterized from forward I-V curves and $1/C^2$ vs $V$ plots for the gate diode at 35°C was ~1.0 eV. This is not sufficient to eliminate gate leakage at temperature higher than 350°C as been shown in all GaAs-based devices studied (Chern 2000).

Typical control and signal processing circuitry might try to maintain the $I_{ds}$ by controlling the $V_g$. If gate leakage is a significant load and thermally generated, the chemical effect on $V_g$ would be confounded by temperature. This leakage load depends exponentially on temperature and could easily dominate the relatively small (e.g 100mV-700mV) changes due to a chemical effect on $V_g$. Reducing the gate leakage current in the FET structure is necessary and should be the focus achieving sensitive and cost effective high-temperature sensing applications for GaN catalytic gate FET sensors using traditional signal processing. The barrier height may be improved by choosing metals having a large work function. Pt is already among the highest work function metals. Rh and Pd/Ag have slightly smaller work functions, however comparisons of the differences in electron affinity and work functions have yielded crude correlations at best (Sze, 1981). There is a need for a more accurate picture of the Schottky barrier height dependence on the metal work function and the relatively unknown chemical effect of the metal on the semiconductor electrical properties. An insulating layer between the metal and semiconductor is another way to reduce the gate leakage current. The AlGaN layer in the MODFET structure has this effect, and the performance comparison above suggests improvement consistent with this hypothesis. If this can be done with additional nitride or insulating oxide without adversely affecting the transconductance of the source drain channel, the layer could also have the effect of chemical passivation of the semiconductor in more aggressive chemical environments. These issues will be addressed in further work pending demonstration of the ability to detect and measure carbon monoxide in a hydrogen ambient.

In conclusion, using wide band-gap semiconductors such as AlGaN reduces the substrate leakage current at elevated temperatures and makes high temperature sensors based on GaN within reach of near term development. For this potential to be realized, defect levels must be reduced, and improvement of semi-insulating buffers and Schottky contacts is needed to optimize high temperature operation.

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REFERENCES
