

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

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Abstract

Experimental results indicate the Pt-GaN based MODFET gas sensors have exquisite sensitivity to hydrogen and fast response times at 450C. The sensor failed in less than two hours when heated to 750C. The results are discussed in terms of the need and work necessary to qualify the sensor for hydrogen safety and control applications and relieving the materials limitations on the sensor for higher temperature operations to open applications such as NOX measurement in combustion gas.

Introduction

Gas sensing and analysis based on gas adsorption on a catalytic metal surface has been extensively explored using chemically sensitive semiconductor devices (Lundstrom, 1989 and Spetz, 1992). Recent work on field effect devices using catalytic metal gates on silicon carbide substrates has been reviewed (Spetz 1997 and Tobias 1997) and suggests the promising application of the field effect technology for high temperature gas monitoring. The limited use of large bandgap semiconductors for volume electronic applications has resulted in limited sources for devices for sensor applications. It is reasonable therefore to examine other high bandgap semiconductors as potential sources for high temperature sensors. Other materials in the III-V group of compound semiconductors are a potential source.

The field effect technology using catalytic metal electrodes on a semiconductor exploits dissociative chemisorption (bond breaking). The detection of hydrogen was reported first by

Lundstrom (Lundstrom 1975) on a palladium gate field effect transistor (FET) on silicon. Later work demonstrated sensitivity to ethylene and carbon monoxide (Poteat 1983) hydrogen sulfide, propylene oxide, ethylene, formic acid, carbon monoxide and NO₂ (Hughes 1987). Hydrogen, carbon monoxide, ethylene and acetylene sensitivity has have been observed on metal-insulator-semiconductor (MIS) capacitors with electrodes of pure platinum and platinum and palladium compositions with small amounts (ca. 5-10%) of transition metals such as copper, silver, and chromium (Feinstein et al 1997 and Pyke 1993). High temperature operation of these devices has been limited by the silicon based FET to about 150C. Higher bandgap semiconductor FETs are being made and are expected to push the envelope. The report by this group of enhanced sensitivity to CO in hydrogen at temperatures above 100C to 150C on Pt gate GaN MODFET suggested greater performance and commercial opportunities for this technology when the operational limits of silicon devices were overcome (Pyke and Sadwick 2001). Reports on GaN Schottky diode sensors (Schalwig et al 2001) and prototype silicon carbide (SiC) FET based sensors show enhanced sensitivity at high temperature to combustion gases and the potential application of the technology to automotive exhaust gas monitoring. These and other sensor developments for automotive and aerospace applications have been recently reviewed (Mueller et al 2001).

There are two well-known hypotheses for how hydrogen and other gases are sensed by catalytically active metal electrodes on FET sensors. Both hypotheses concur the change in work function changes the population distribution of carriers in the semiconductor under the metal by changing the surface potential of the semiconductor. In the first model, molecular hydrogen dissociates on the catalytic metal forming two adsorbed hydrogen atoms. Depending on their solubility and diffusivity, hydrogen atoms penetrate the metal to reach the metal-insulator or metal-semiconductor interface. In this model, only hydrogen alters the surface potential of the semiconductor covered with a solid electrode. The steady state concentration of adsorbed hydrogen is mediated by reaction with other gases adsorbed on the surface affecting the hydrogen concentration at the metal-insulator or metal-semiconductor interface. Thus, gases impacting the concentration of hydrogen on a catalytic surface can be measured only indirectly through the effect they have on hydrogen concentration at the metal-insulator or metal-semiconductor interface. In the second model, a perforated or porous solid electrode adsorbs gas as in the first model, however it is proposed the electric field produced by hydrogen at the metal semiconductor interface changes the surface potential of the semiconductor without diffusion into the metal (Dobos 1990, Hedborg 1994 and Lundstrom 1996). The electric field results from adsorbed gas where the field lines are not blocked by metal film but perforations or pores allow the field to penetrate to the semiconductor changing the surface potential. A similar but more aggressive design to expose more of the metal surface facing the semiconductor used a suspended metal electrode (Cassidy 1986). By etching away a sacrificial metal layer deposited between the dielectric and the catalytic metal, a cavity is produced which is accessible to gas. Perforations in the suspended metal allow any gas to penetrate to the cavity and adsorb on the metal facing the semiconductor. In principle, nearly the total underside surface is available for any gas to be to adsorb and produce the dipole field and so influence the surface potential of the semiconductor. This concept was tested in product development, but the mechanical weakness of the suspended metal films and the residual stresses from the deposition process resulted in the loss of the gate and low production yield, and distortions in the suspended gate metals led to broad statistical performance distribution in the final product and its downfall as a commercial product. The additional manufacturing cost for correcting for the broad performance distribution completely outweighed the cost benefit from the microfabrication process. The materials combinations turn out to be the most critical barriers to product development with microelectronic sensors.

GaN High Temperature Electronics

Owing to their wide bandgap, the III-V nitrides are attractive for high temperature, high power electronics applications. Forming low contact resistivity, thermal stable and uniform ohmic contacts constitutes a major obstacle for wide band gap materials such as GaN with a band gap about 3.4eV, is therefore, receiving increased attention. GaN-based devices and circuits have the potential to operate at 600C or higher temperatures. 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. It is fairly easy for metals with lower work functions to 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, Rh and PdAg are expected to form good Schottky barriers (necessary for high impedance contact and low leakage current) to n-GaN.

Low Resistance Contacts to the Source and Drain

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. Almost all known, successful contacts to III-V semiconductors consist of bi-level to multi-level metallization schemes. The interface between the semiconductor and the first metallization layer is the most important for it controls the transport mechanism(s). Usually, chemical or thermal reactions, solid-state diffusion and interdiffusion, and/or other methods produce mixing due, possibly to material damage (i.e., ion mixing and ion implantation). The key is to find some species, usually an element, that reacts with the respective substitutional dopant and either the group III or group V element to form an alloy of variable composition such that transitions occur from semiconducting to semimetallic to metallic. This type of contact, essentially, forms a tunneling ohmic contact with linear I-V characteristics. An example of this is the Au-Ge-Ni ohmic contact to n-type GaAs.

Among the several metals studied for ohmic contacts on n-GaN, Pd/Al and Ti/Al were found to have the lowest specific contact resistances. The formation of Pd/Al on n-GaN has been reported (Ping 1996), whose specific contact resistance was found to be 1.2×10^{-5} ohm-cm² upon annealing at 650C for 30 seconds. A significant improvement with Ti/Al on n-GaN was obtained (Lin 1994), who employed a Ti/Al bilayer deposited by e-beam evaporation followed by rapid thermal annealing (RTA) at 900C for 30 sec in N₂ ambient. A specific contact resistance of 8×10^{-6} ohm-cm² was reported. A metallization scheme involving Ti/Al based composites, namely Ti/Al/Ni/Au (150Å/2200Å/400Å/500Å) preceded by a reactive ion etching (RIE) process which most likely rendered the surface highly n-type was reported (Fan 1996). After annealing at 900C for 30s, specific contact resistance of 1×10^{-7} ohm cm² for a doping level of 4×10^{17} cm⁻³ was obtained. Unfortunately, Au reacted with GaN during the annealing.

Lin et al. found specific contact resistance of Ti/Al metallization suffered from Ga outdiffusion and subsequent reaction with Al rendering the surface metal discontinuous and increasing its resistance. A second sequence of Ti/Al was added (Wu 1995) following the annealing step, to minimize the high resistivity problem. Specific contact resistance was lowered to $\sim 3 \times 10^{-6}$ ohm-cm².

Pt, Rh and PdAg Catalytic Gate Materials

Platinum and palladium were selected because each has shown sensitivity in the ppm range for ethylene, acetylene and carbon monoxide. Both metals are also PROX catalyst candidates, and both metals have been used as Schottky junctions on GaN. PdAg was selected, because the mechanical integrity is better than pure Pd at these hydrogen concentrations. Rhodium was selected, because of its PROX catalytic activity and to help resolve the effects of the multiple gases in combination with platinum and PdAg. Each of these metals is expected to adsorb CO preferentially in the fuel stream just as in the PROX catalyst. It was surmised the reaction of CO and hydrogen with oxygen on the surface of the catalyst produces a steady state surface composition detectable through the work function change of the catalyst. The higher affinity for CO in preferential catalysis also suggests the three metals have sufficient selectivity for CO over H₂ to detect carbon monoxide in the presence of a great excess of hydrogen

Experimental

Fabrication

We have successfully fabricated Schottky contacts using platinum, palladium/silver and rhodium by e-beam evaporation. E-beam evaporation typically produces films with the least amount of residual stress, but the process is typically followed with annealing so that the mechanical contact is strengthened by interdiffusion of the metal with the GaN. The gate metals were evaporated onto a variant of the MESFET called a MODFET for modulation-doping-field-effect-transistor. The architecture is shown in Figure 1. The source and drain contact metallization was sputtered Ti-Al on n-GaN which has been demonstrated to maintain low resistance when exposed to air at 500C.

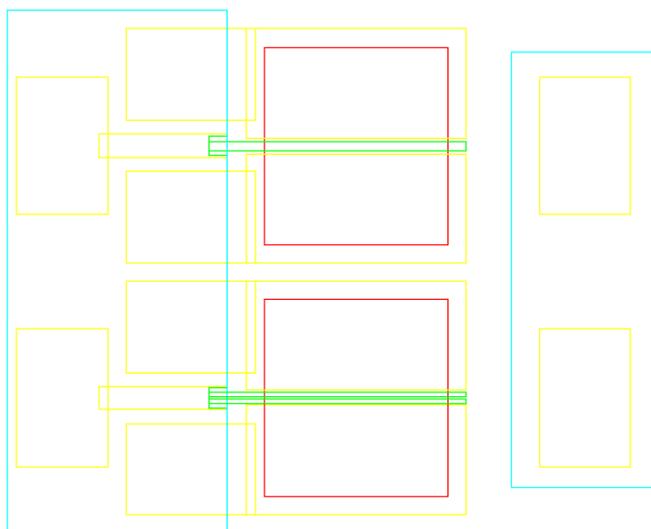


Figure 1: FET Sensor Architecture showing two FETs. The gates are represented by the green strips. Each gate is bounded by a yellow boundary representing the source and drain ohmic contact.

Two gate designs (single and dual strips) were fabricated. The collocation of the single and dual gate on the wafer makes for the closest match in electrical properties for the most accurate comparison of the gas effect.

Sensor Electronics

Sensor electronics were designed to operate FET sensors at a constant source drain current. As changes in the gate voltage due to gas exposure change the source drain current, a feedback voltage equal and opposite to the gas effect is applied to the gate. This is important, because the field gradient between the gate metal and the GaN can cause migration of charged species which result in long term changes in the baseline electrical properties of the device. The potential for long-term drift (field driven ionic migration) is reduced if the field remains constant. The circuit elements in the block diagram in Figure 2 were designed to achieve this objective.

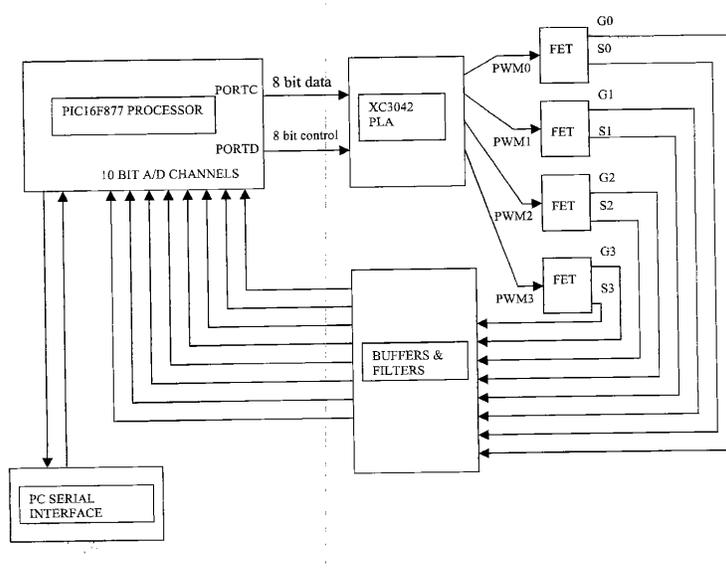


Figure 2: Block diagram of the constant current constant voltage sensor drive circuit.

The circuit is programmed through a serial connection using the terminal program on a PC. The drain source voltage is a constant 14V. The unit searches for the gate voltage to achieve the programmed source drain current. When the unit finds this gate voltage, it maintains each sensor so that only external changes to the gate voltage or source drain current cause the output voltage to the gate metal to change. A positive control lock is indicated by lighted LEDs on the front panel of the controller for each of the sensors under control.

The noise level of the sensor output is about ± 20 mV. While the control loop timing and precision of the circuit are the most probable cause for the noise, some of this noise could be due to the heating source, pressure fluctuations or incomplete mixing of the gas. Material changes to the composition or structure of the sensor can be ruled out, because the noise does not vary with temperature. Solid-state processes are typically highly temperature activated and very temperature dependent. However, sufficient signal to noise was available in the testing to measure significant sensitivity to H₂ and CO in the concentration range of interest.

Gas Testing

Testing in gas was done with the sensor sealed in a quartz chamber. The sensor was heated by infrared radiation from a 600W quartz halogen lamp, and the temperature controlled by a thermocouple measurement on the top surface of the glass substrate next to the sensor die. Lamp current switching was accomplished by a solid state relay Model no. SSRDUAL240DC40, Omega, Stamford, CT under the control of a CN4800 Fuzzy Logic Controller also from Omega. A thermocouple (J-type) was bonded to top of the glass sensor package. The thermocouple voltage was input to the CN4800 controller to maintain a constant temperature. Temperature fluctuations measured by the TC were $\pm 1^\circ\text{C}$.

The concentrations of the gas components were determined by switching open solenoid valves for precisely timed short periods. The source gases at the solenoid valves were UHP N_2 , UHP H_2 , 35% H_2 (balance N_2), CO (2000ppm in 35% H_2 (balance N_2)) and CO (500ppm in nitrogen). The valves were opened sequentially under the control of microprocessor and a timing schedule programmed and delivered via serial interface from a PC. The gas pulses from the sources enter a mixing chamber (~0.3l) filled with glass beads to force turbulent flow and keep dead volume to a minimum. The gas stream then enters the quartz chamber and is subsequently diluted with large volumes of air and exhausted. Flow rates are balanced for the sources so that each delivers 1.5l/m when the valve is opened. The mix concentration is completely variable over range of about a hundred and depends strongly on the dead volume of the delivery system.

Data was obtained by polling up to four sensor gate voltages and four source voltages using a CIO-DAS16/Jr data acquisition board for the PC from Computerboards, Middleboro, MA. Data was logged to a text file by a program called Vlogger. The text files were imported into Microsoft Excel, give names corresponding to the date and time of the last entry in the file and charted. We used two standard charts for data analysis. The first was an x-y plot of gate voltage versus time. The second chart was a x-y plot of gate voltage versus H_2 or CO concentration.

Results

The sensor used for the high temperature experiments reported here is shown in Figure 3 prior to exposure to testing temperatures greater than 150C. The bonding pads are evaporated films of gold on both the GaN sensor die and on the glass substrate. Gold wires (1mil) interconnect the sensor pad with the larger pads on the substrate. The dimensions of the features above were measured from SEM and TEM photographs and are listed in Table 1.

Results for Hydrogen and High Temperature Stability

The results reported previously were at constant hydrogen concentration (35%) since the source gas was CO and O_2 each diluted into premixed H_2/N_2 prepared by Scott Specialty Gas. The CO dependence was determined by varying the ratio of two source gases at 35% H_2 – one with 2000ppm CO and one without. In this way, we could confirm the CO dependence without having to control the H_2 concentration. The data demonstrated a CO sensitivity that increased with increasing temperature as shown (Pyke and Sadwick 2000), but it did not reveal the interference effect of changes in H_2 concentration.

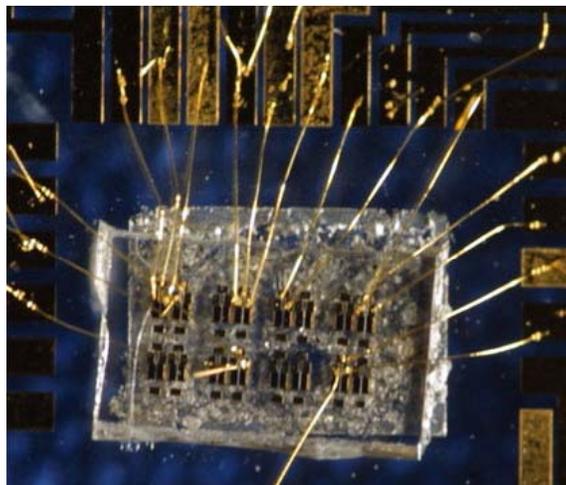


Figure 3: Shown is the Pt-Right sensor (Pt-R in data files). The source and drain (ohmic) contacts are the long black rectangles. The Pt gate is barely visible as a light line between the source and drain.

Table 1: Dimensions as measured from SEM and TEM photographs

	Single Gate		Dual Gate		No Gate
	Design	Actual	Design	Actual	Design
Gate Length	200 μm	200 μm	200 μm	200 μm	200 μm
Ohmic Contacts	20000 μm^2		20000 μm^2		20000 μm^2
Gate Metal Width	10 μm	8.6 μm	2x5 μm	2x4.25 μm	n/a
Gate Metal Area	2000 μm^2	1920 μm^2	2000 μm^2	1900 μm^2	n/a
Drain-Gate	3~4 μm	5 μm	2 μm	3.5 μm , 3.7 μm	n/a
Drain-Source	17 μm	18.7 μm	17 μm	18.7 μm	17 μm
Intergate spacing	n/a		3 μm	3.1 μm	n/a
Gate Area Exposed	1400 μm^2	2030 μm^2	1400 μm^2	2050 μm^2	3400 μm^2

We report here on the response of the platinum gate in hydrogen and on the failure of the sensor at 750C. The Pt gate response to H₂ shown in Figure 4.

The sensor shows a response time of <20sec to 90% of full scale in a change from 0-100% H₂. It is likely this is a time constant for the system response limited by flow rate and volume of gas in the delivery system. The relatively slow recovery is due to the log aspect of the sensitivity. The sensor is likely to have a much faster response time at this temperature.

The concentration dependence or isotherm is shown below and fits a logarithmic response. The voltage recovery in Figure 5 suggests the H₂ in the delivery system is still being purged by the N₂ flow and is not due to sensor recovery.

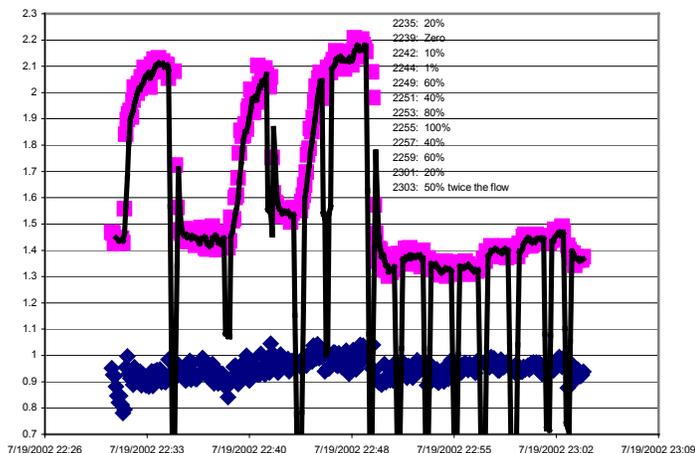


Figure 4: Pt-R sensor 2 response to H₂ from 0-100% at 450C.

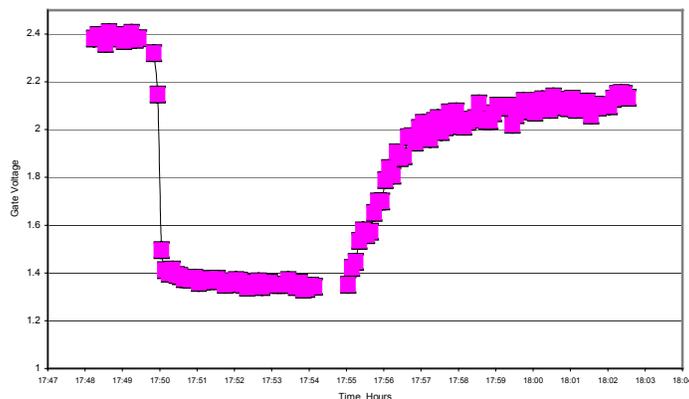


Figure 5: Response of Pt-R sensor 2 to 100% H₂ followed by a reduction to 0% at 450C.

The sensor was taken from 150C to higher temperatures in 100C increments to test for drift and temperature activated processes that would indicate the degradation or failure of the electrical contacts. The background gas for this test was simulated automobile exhaust consisting of 2% O₂, 10% CO₂, 100ppm CO, 100ppm NO and the balance N₂. The output was constant when the gas concentration and temperature was constant until 650C where a positive drift in gate voltage was observed. About two hours after moving the sensor to 750C, the gate voltage lock failed indicating the inability of the electronics to find a gate voltage to sustain a drain current of 200 μ A. There was no drain current from 10 μ A-1mA that could be sustained by a gate voltage ranging from 0.1-9.5V. The damage to the sensor and package is shown in a comparison of the sensor before and after heating in Figure 6 below.

The black source and drain contacts have faded suggesting an oxidation of the TiAl contact. The wire bonds have survived. The glass substrate softened and warped – cracking in three places.

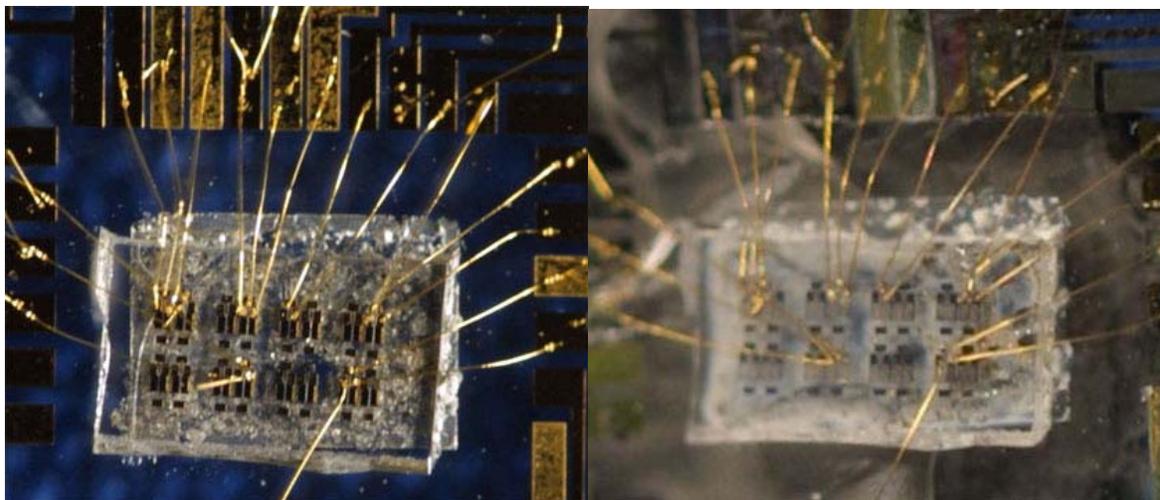


Figure 6: Pt-R as delivered on the left. Heat damaged sensor on the right.

Conclusions

The conclusions we draw are:

1. the Pt gate is very sensitive to H₂.
2. the response to CO would be confounded by changing H₂ in the range of 30-75% expected for the H₂ product gas of reformers.
3. the damage to the sensor above 650C is mainly to the glass substrate/package and also apparently to the contact metallization covering the source and drain regions.

The hydrogen response suggests this sensor would be a candidate for hydrogen safety and even control applications. The response time is probably much faster than that suggested by the data in Figure 5. The noise level of $\pm 20\text{mV}$ can be reduced to 1mV thereby reducing the measurement uncertainty. At 20mV, the uncertainty in the H₂ concentration measurement would be about 40%. This would be acceptable for safety purposes where the difference between 1%vol and 1.4% and even two standard deviations error at 1.8% would still be acceptable. The alarm would be well below the explosive limit for H₂ in air (4%vol). For control purposes a 40% error would be too high. The voltage error due to hydrogen calculates to be 55mV for a change in H₂ from 30-75%, and conclusions we may draw on the usefulness of this technology for measuring small amounts of CO in H₂ will have to be weighed by this fact. The true response time and the accuracy and precision of the hydrogen measurement will be two of the objectives in the work proposed for next year.

The failure of the package and perhaps the sensor started with a positive drift at 650C and proceeded rapidly to complete failure at 750C. While the damage to the package was dramatic, the packaging can be replaced by refractory packaging substrates such as sintered aluminum oxide or aluminum nitride. The wire bonds appeared to withstand the heat and at the very least did not separate from any of the sensor bonding pads. The contact degradation apparent in the discoloration of the TiAl source and drain contact metallization suggests this should be the major focus in the developing the technology other than the focus on performance.

Data indicate the contact is stable in air at 500C, but it may not last at 750C. The sensor for fuel cell applications may not need to be built for even 500C, but for many of the high volume sensor

products for which this sensor could be applied, the ability to withstand temperatures much higher than 500C will be an important milestone. One such application is the need to detect NOX downstream from SCR scrubbing systems soon to be part of the emissions control system in low-emission vehicles.

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