

## **Gallium Nitride Integrated Gas/Temperature Sensors for Fuel Cell Systems**

*Steve Pyke (Primary Contact) and Larry W. Sadwick*

*Fluence*

*PO Box 1257*

*Sisters, OR 97759*

*Phone: (541) 390-9572; Fax: (810) 592-1523; E-mail: stevepyke@direcway.com*

*DOE Technology Development Manager: Neil Rossmeissl*

*Phone: (202) 586-8668; Fax: (202) 586-5860; E-mail: Neil.Rossmeissl@ee.doe.gov*

*Subcontractor: Larry W. Sadwick, Innosys, Salt Lake City, Utah*

### **Objectives**

- Fabricate gallium nitride (GaN) field effect transistor (FET) sensors to resolve and detect carbon monoxide in a background of varying hydrogen concentration and high water content at  $T > 250^{\circ}\text{C}$
- Develop method for resolving CO at 10 ppm from  $\text{H}_2$  interference
- Validate sensors and analysis in operational reformers

### **Technical Barriers**

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- B. Sensors
- K. Emissions and Environmental Issues
- L. Hydrogen Purification/Carbon Monoxide Cleanup

### **Approach**

- GaN and silicon carbide (SiC) are semiconductors with large band gaps and are an attractive option for high temperature electronic applications including gas monitoring
- Catalytic metals such as platinum, rhodium and palladium are good candidates for the gate metal in GaN FET sensors for CO detection
- The same metals are well known catalysts in the preferential oxidation (PROX) process for oxidizing trace amounts of CO by reaction with oxygen in excess  $\text{H}_2$
- Test GaN FET sensors in mixtures of  $\text{H}_2$  and CO for array analysis of CO
- Develop a simple analysis method for extracting CO concentration from background  $\text{H}_2$  effects

### **Accomplishments**

- Completed main effect testing of CO (0-80 ppm) and  $\text{H}_2$  (30-70%)
- Developed quantitative method for reliably detecting CO at 10 ppm in 30-70%  $\text{H}_2$

### **Future Directions**

- Determine consistency or reproducibility of calibration results in CO and  $\text{H}_2$
- Confirm higher fabrication yield by improved gate metal adhesion
- Complete testing of Rh and Zr gate metals

- Field test working hydrogen reforming processes to validate process control and analysis statistics
- Test in wet and dry hydrogen sources (ca H<sub>2</sub>O ~ 25%vol)
- PdAg abandoned in favor of Zr due to potential surface segregation of Ag and alloys in general leading to sensor drift

## **Introduction**

A low-cost sensor capable of resolving CO (1-100 ppm) in hydrogen (30-75%) and water vapor (25%) is needed but technically difficult to achieve. Platinum based sensors have been used for CO detection, but the cross-sensitivity of CO and hydrogen precludes their selective measurement of CO. Similar cross-sensitivity is expected for any single metal with a catalytic response to CO. A method is needed to resolve the CO in a background of varying hydrogen concentration. Arrays of inexpensive sensors have been proposed as a solution for when selectivity of an individual sensor is insufficient to reliably detect and measure the gas of interest. This project demonstrates how an array can be used for resolving the CO and hydrogen concentrations using two GaN FET sensors with a Pt and Rh gate metal and a two-component calibration matrix of 25 pairs of CO and hydrogen concentrations. The measurements of gate voltage at each of the 25 calibration points are used to compute a three-dimensional response surface. The intersection of the response surfaces for the different gate compositions is used to resolve and measure the concentrations of CO and hydrogen.

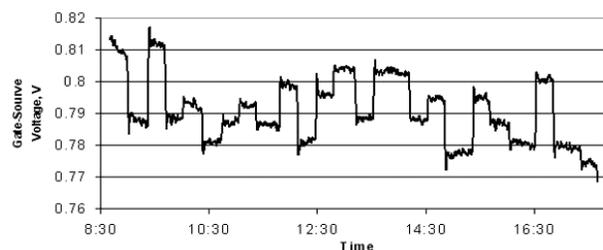
## **Approach**

Recent work on SiC FET sensors using catalytic metal gates has been reviewed (1) and suggests SiC FETs with metal gates are attractive candidates for high temperature gas monitoring. GaN based devices and circuits are also an attractive option for high temperature applications including gas monitoring. The effect of gas on GaN FETs with metal gates has been studied and reported (2). Catalytic metals such as platinum, rhodium and palladium are good candidates for the gate metal in GaN devices because they have been shown to form good Schottky barriers on n-GaN. These metals are also suggested for this application because each has shown catalytic activity in the preferential oxidation

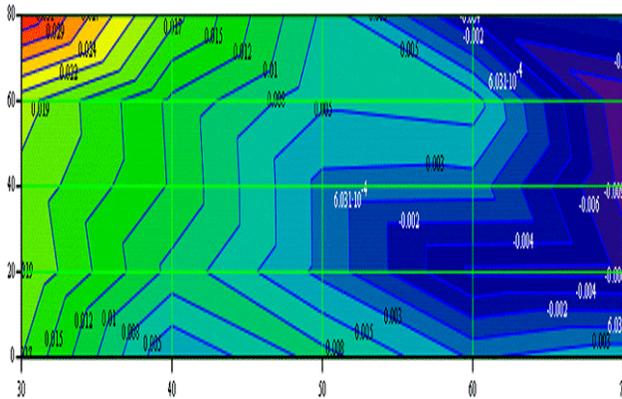
(PROX) process for oxidizing trace amounts of CO by reaction with oxygen in excess hydrogen.

## **Results**

Device characterization, architecture, control electronics, the calibration system and chemical analysis of the metal gate GaN FET sensors used in this study are described in the DOE reports in Reference 2. The time history of responses of the Pt sensor is shown in Figure 1. Figures 2 and 3 show the response surfaces for a Pt and Rh gate GaN MODFET sensor. The contours of constant gate voltage were mapped using MathCAD from measurements at 25 ppm CO and hydrogen concentration pairs in the range required for the application above. The plots are a two-dimensional representation of a three-dimensional surface. A single measurement of gate voltage for either of the different sensors could indicate any combination of CO and hydrogen along a constant voltage contour. CO and hydrogen are resolved by the combined measurement using sensors with sufficiently different response surfaces. For an unknown blend of CO and hydrogen, the gases are resolved and concentrations determined from where the contours



**Figure 1.** Typical Calibration Run (Twenty-five calibration pairs of CO and H<sub>2</sub> are delivered to the sensor in random order pair presentation to minimize systematic error. There are three source gases: CO in H<sub>2</sub> (1000 ppm), H<sub>2</sub> and N<sub>2</sub>, with a total flow = 1356 cm<sup>3</sup>/min at T = 250°C and P = 1 atm. The system limited response time = 15 sec to 90% of full scale.)



**Figure 2.** Pt Response Surface at 250°C (Mapping is a fit to the calibration data. Calibration pairs are at grid intersections. Contour spacing is 1 standard deviation.)

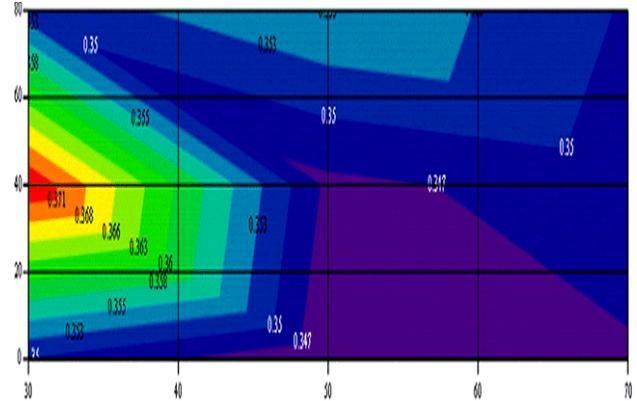
computed for the Pt and Rh sensors intersect. These data suggest the detection of CO at 10 ppm is possible over most of the range.

### **Conclusions**

Laboratory results confirm arrays of GaN FET sensors can be used to detect the contamination of as little as 10 ppm CO in H<sub>2</sub> fuels used in proton exchange membrane fuel cells. These sensor arrays can operate in temperatures exceeding 250°C, thus eliminating the need for water separation before analysis.

### **References**

1. A.L. Spetz, L. Uneus, H. Svenningstorp, P. Tobias, L.G. Ekedahl, O. Larsson, A. Goras, S. Savage, C. Harris, P. Martensson, R. Wigren, P. Salomonsson, B. Haggendahl, P. Ljung, M. Mattsson and I. Lundstrom, *Physica Stat. Solidi A – Applied Research*, 185, 15-25 (2001).



**Figure 3.** Rh Response Surface at 250°C (Closer spacings improve precision. 90° crossing angles for contours from different sensors improve accuracy. Straighter contours improve accuracy. Single crossings increase confidence.)

2. Y. Kokubun, T. Seto and S. Nakagomi, *Jpn. J. Appl. Phys.*, 40, L663-L665 (2001). J. Schalwig, G. Muller, M. Eickhoff, O. Ambacher and M. Stutzman, *Sensors and Actuators B-Chemical*, 87, 425-430 (2002). B.P. Luther, S.D. Wolter and S.E. Mohny, *Sensors and Actuators B*, 56, 164 (1999). S.C. Pyke and L. Sadwick, DOE Report, <http://www.eere.energy.gov/hydrogenandfuelcells/pdfs/32405b16.pdf>, 2002. S.C. Pyke and L. Sadwick, DOE Report, <http://www.eere.energy.gov/hydrogenandfuelcells/pdfs/30535ay.pdf>, 2001. And S.C. Pyke, J-H. Chern, J. Hwu and L. Sadwick, DOE Report, <http://www.eere.energy.gov/hydrogenandfuelcells/pdfs/28890ii.pdf>, 2000.

### **Special Recognitions & Awards/Patents Issued**

1. Invited paper to be presented at “High Band Gap Material FET Chemical Sensors”, IEEE Sensors 2003, Toronto, October 21-24, 2003.