MICRO-MACHINED THIN FILM HYDROGEN GAS SENSORS

Frank DiMeo, Jr., Ing-Shin Chen, Philip Chen, Jeffrey Neuner
Michele Stawasz, James Welch

ATMI, Inc. Danbury, Connecticut 06810
Email: fdimeo@atmi.com

A. Rohrl
ATMI Sensoric
Bonn, Germany

Abstract

The ability to detect gaseous hydrogen is of critical importance to acceptance and utilization of hydrogen as an energy carrier. Micro-machined gas sensors are a new generation of sensor technology combining existing integrated circuit fabrication technology with novel deposition and etching processing. This results in a new device structure, known as a “micro-hotplate”, which consists of an integrated hotplate on a suspended thermal isolation structure. This structure allows the sensor to operate at elevated temperatures, and provides a platform where the operating temperature can be rapidly changed to achieve desired response characteristics. ATMI has been developing novel thin film materials to function as hydrogen-selective active layers on top of micro-hotplate devices. This combination of micro-hotplate and novel active thin film materials has led to hydrogen sensors that demonstrate an array of highly desirable features, such as fast response speeds, low-level sensitivity, and amenability to mass production. These sensors are adaptable to a wide variety of sensing applications for a hydrogen-based energy economy, spanning from hydrogen based process monitoring to life safety protection.

This paper describes recent efforts and progress made in developing micro-hotplate based hydrogen gas sensors at ATMI. This progress includes designing the sensor geometry to reduce power consumption and investigating the cross sensitivity to several contaminant gases – carbon monoxide, hydrogen sulfide, and isopropyl alcohol. Portable signal conditioning hardware was developed to help study long-term operation stability. Future work will be directed towards continuous improvement of the fabrication process and the development of new application specific operational models.

Introduction

The reputation of hydrogen as the next generation energy delivery agent, supplementing electricity in use today, has been firmly established. This has been reinforced by recent coverage on a hydrogen-based energy economy from news media and professional trade magazines alike. For example, Paul M. Grant of Electric Power Research Institute, in a recent *The Industrial Physicist* column, observed the multifaceted use of hydrogen will play a crucial role in future communities where generation, storage, transportation, and utilization of hydrogen populates households and the landscape. The unfortunate events of September 11 provided an unanticipated but cogent argument for lessening dependence on fossil fuels as a national security priority.

While fuel cell cars often feature prominently in news media and are touted as evidence that hydrogen economy is just around the corner, it is generally recognized that building the infrastructure – not the vehicles – is *the* task to bring about the realization of hydrogen economy. For example, safe storage and delivery of hydrogen is a necessity that stands in line before public acceptance of using hydrogen, much like electricity today, as an energy medium. Electricity is a form of energy, and hydrogen is a matter. This fundamental difference calls for implementation of an entirely different infrastructure that is non-existent today. In fact, many of the technologies to build such an infrastructure are under development themselves, of which hydrogen sensor technology is one area of interest pertaining to this report.

The ability to detect and quantify the amount of gaseous hydrogen present is fundamental to all aspects of hydrogen processes. Unlike electricity, which is essentially confined to its carrier, hydrogen is a gaseous matter at atmospheric conditions and can escape from its containment to cause an explosion hazard. Hydrogen sensing is also required as a means of monitoring and controlling hydrogen-based processes used in, for example, fuel cells. Because the point-of-use nature of hydrogen-based energy economy, the demand for hydrogen sensors is very great in terms of quantity and variety because each application may have specific requirements for sensor characteristics. The quantity demand also translates into a requirement for low production cost so that needs, rather than costs, are the determining factor for sensor use.

Background on Micro-hotplate and Rare Earth Metals

Micromachined thin film hydrogen gas sensors developed at ATMI are built upon a micro-hotplate platform. Our embodiment of the micro-hotplate is a micromachined thermal isolation structure with an embedded polysilicon resistive heater where elevated temperature can be achieved with ease. The micro-hotplate layered stack is fabricated via a CMOS-compatible foundry process and has been described elsewhere (*e.g.*, Semancik, *et al.*, 2001). The as-received micro-hotplate platforms were subsequently etched at ATMI to create suspended thermal isolation structure.

A rare earth metal thin film overcoated with a palladium-based cap layer serves as the active sensing layer. The metal-insulator transition induced by hydrogenation of rare earth metals is a known phenomenon, and detection of hydrogen using rare earth metal hydride has been proposed as far back as 1973 (Toy and Phillips, 1973). However, the proposed approach was specific to steel industry and not adaptable for other applications. The recent discovery of spectacular changes in optical and electrical properties of *thin film* rare earth metals upon hydrogenation (Huiberts, *et al*, 1996) sparked great interest in these materials. We immediately recognized the technological advantages in using these novel thin film materials for hydrogen sensing (Bhandari and Baum, 1999; DiMeo and Bhandari, 2001). With the support of the DOE

Hydrogen Program, we have continued to develop micro-hotplate based hydrogen gas sensors incorporating rare earth metal coating as the active sensing layer.

These new sensors incorporate novel rare earth metal coatings that react with hydrogen upon exposure, leading to a change in electrical resistance that scales with hydrogen concentration in the gas phase. The reaction is reversible and the reaction kinetics can be engineered by the micro-hotplate temperature. We have previously demonstrated fast speed of response (< 1 second), large signal range (120% resistance change at 0.25% H_2), and low-level sensitivity (< 200 ppm). During the past program year, we further exploited protective coatings for extended lifetime and detection of high-levels of hydrogen, demonstrated signal integrity in the presence of low-level contaminant gases, and developed signal-conditioning electronics as an evaluation aid for outside laboratories.

Experimental

Design and Fabrication

The sensor manufacture process flow includes several steps. The first step is *Micro-hotplate formation*. Micro-plate geometry design is performed at ATMI using commercial layout software and delivered to a commercial foundry for CMOS-compatible fabrication. The as-received silicon wafer dies are surface micromachined at ATMI to release the thermal isolation structure. The second step is *Sensing layer functionalization*. The dies are first patterned by photolithography. Deposition of active and passivation layers follows, and a liftoff step completes the pattern definition. Finally, the third and last step is *Device packaging*. The dies are diced and the resulting miniature sensors are individually packaged. In the past program year, we have focused on reducing the operating voltage and power consumption by modifying the heater resistance and micro-hotplate geometry.

Cross Sensitivity to Contaminant Gases

Sensor operation in the presence of several potential contaminant gases was examined. Potential contaminant gases tested include carbon monoxide, hydrogen sulfide, and isopropyl alcohol vapor. These are gases often present with hydrogen in many applications, and can lead to false signal readings or can cause device failure on sensors based on existing technology.

Long-term Sensor Performance

There are many inputs to the short- and long-term stability of theses sensors: design and fabrication of micro-hotplate platform, materials science of the functional layer, sensor packaging, to name a few. We sought to develop an understanding of these mechanisms and to feed this knowledge back for design/fabrication improvement. Engineering solutions and signal conditioning were also investigated as a means of extending sensor functional lifetimes.

Results

Micro-hotplate Geometry

The basic micro-hotplate geometry (Figure 1) can be tailored in many ways to accommodate desired heating characteristics. We have experimented with the polysilicon micro-heater resistance and platform size to reduce power consumption *and* operating voltage.

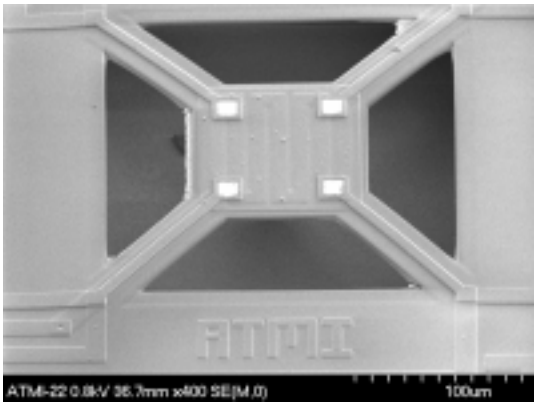

Figure 1 A SEM micrograph of a released micro-hotplate thermal isolation structure. The structure release is performed by dry etch of underlying silicon sacrificial layer. The micromachined platform is suspended by four supporting bridge legs. The bridge legs also contain embedded aluminum interconnects serving as electrical leads to route polysilicon micro-heater power and sensor signal.

Heater Resistance Scaling

The polysilicon micro-heater operates as a resistive heating element: Power = Voltage^2/Resistance. A smaller polysilicon resistance allows the same amount of heater power at a reduced operating voltage. Therefore, one can scale the polysilicon heater resistance according to a specified operating voltage and power. In the present study, we reduced the operating voltage from 9V to 5V by heater resistance scaling. Conversely, a larger heater power can be achieved at same operating voltage using a smaller heater resistance, allowing a larger operating temperature range.

Platform Geometry Scaling

Scaling the platform geometry is comparatively complex. A small platform size implies increased heating power density, which should allow reduced power consumption for a given operating temperature. The heater ramp-up should also be faster due to smaller thermal mass. However, the reduced sensing area, which is the platform coated with active layer, may lead to reduced sensor signal. In addition, one of the heat loss mechanisms is thermal conduction through supporting bridges, which does not scale with platform size. The small thermal mass also makes it more susceptible to loading of unheated ambient gas. It is therefore not clear, *a priori*, how the platform size will interact with overall power consumption. We have experimented with micro-hotplates of several configurations and succeeded in reducing the operating power from 12 mW to less than 5 mW, as shown in Figure 2.

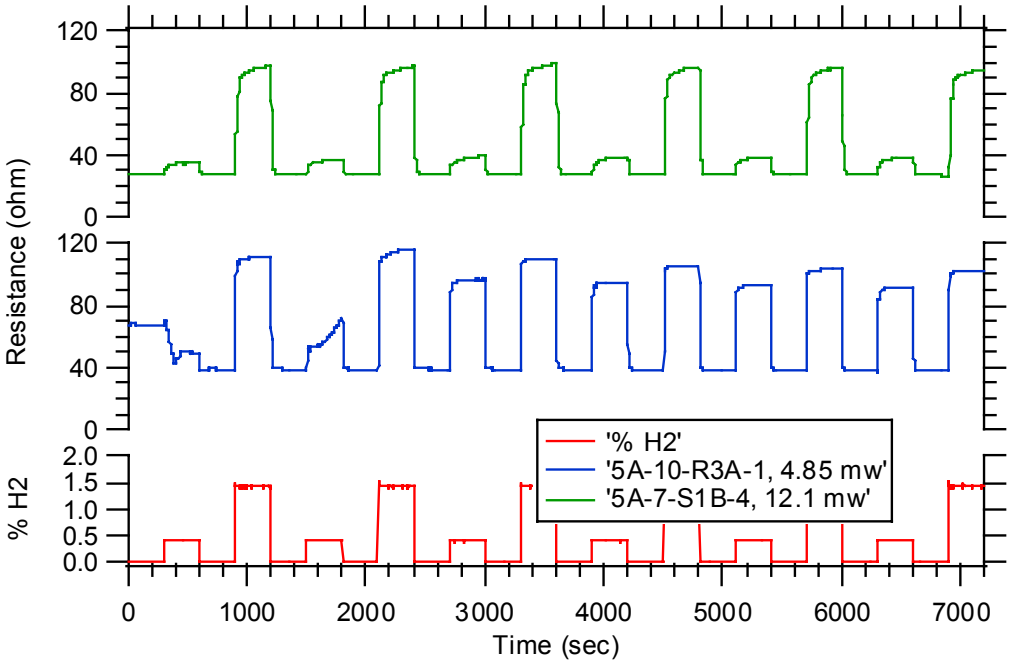

Figure 2 Responses of two sensors of different designs. A low operating power is achieved when the sensor is optimized for reduced power consumption.

Micro-hotplate Surface Pre-treatment

Previously we have observed sensors with a wide range of resistance values ranging from a few ohms for 4-wire configurations in 40-pin packages to several hundreds ohms for 2-wire configurations on 8-pin packages. The higher resistance for sensors with a 2-wire configuration is attributed to high contact resistance between the sensing layer and the underlying aluminum interconnect, probably due to aluminum oxidation prior to sensing layer deposition. Our efforts have centered on an optically based surface treatment process, which has lowered the contact resistance and improved the yield to a usable value, although there remains room for improvement in this area.

Sensing Layer Stack Functionalization

The functionalization step of this process involves applying a sensing layer stack to the surface of the micro-hotplate platform. For the purposes of this report, the stack can be thought to consist of three layers from bottom up: a rare earth metal hydride based thin film, a palladium-based cap layer and, when employed, an additional proprietary barrier layer.

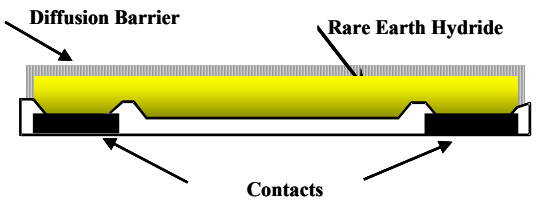

Figure 3 Schematic of functional layer stack on a micro-hotplate platform. The stack is made up by two or more layers of various functionality.

Protection of Palladium-based Cap Layer

We have learned from previous studies that gradual oxidation of the rare earth sensing film is a potential signal degradation pathway. A palladium-based cap layer is utilized to deter oxygen diffusion from air ambient. Repeated hydrogen exposure of the palladium-based cap layer, however, may cycle the cap layer between α and β phases of palladium hydride, which occurs at about 2% H_2 concentration. The volume change associated with this phase transformation may lead to formation of micro-cracks and cause the cap layer to lose its protective functionality. We have investigated the stabilization of the cap layer through alloying, as it is well known that phase transformation in palladium can be suppressed by such methods. Alloying of palladium cap layer, however, tends to reduce the sensor reaction and recovery rates, as the alloying elements are not as permeable to hydrogen as palladium. Alternatively, it was found that improved thin film processing could produce sensors with an unalloyed cap layer that perform reliably when exposed to H_2 at concentration up to 3.4% in air (Figure 4).

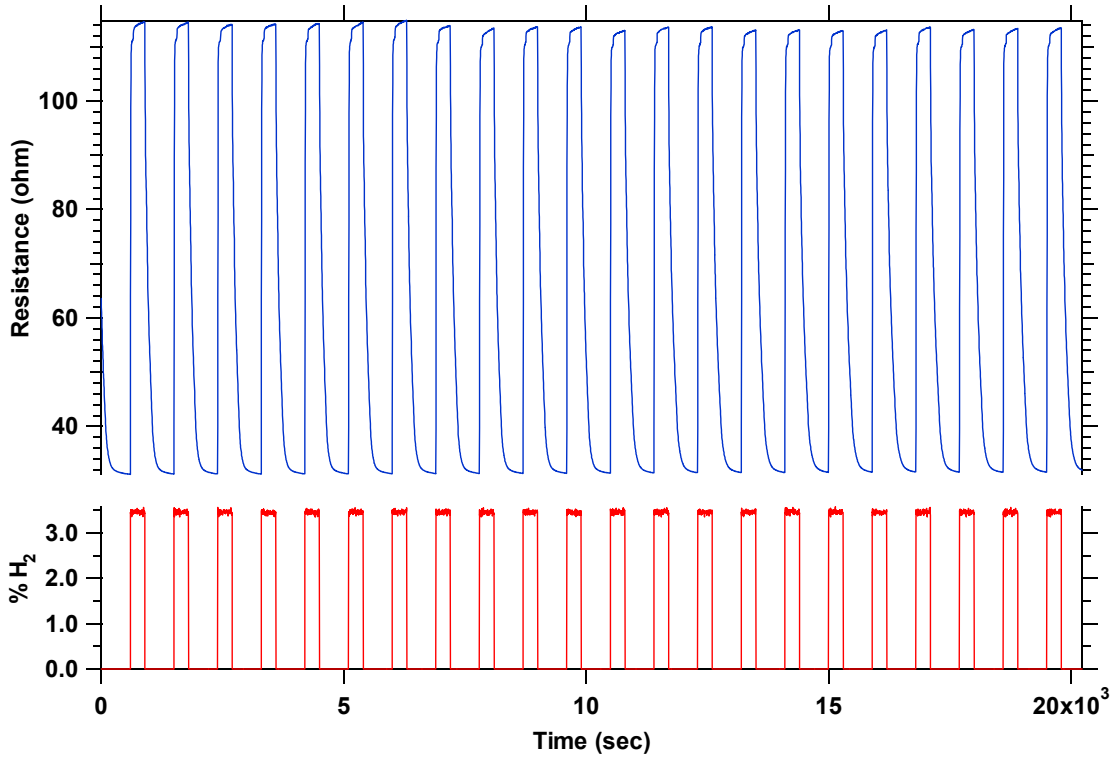

Figure 4 Response of a sensor repeatedly exposed to 3.4% H_2.

The use of an additional diffusion barrier was conceived of as a potential solution to exposure to concentration levels above the LEL. We have developed several proprietary methods that permit this barrier layer to be specifically engineered for the desired performance characteristics. A sensor with this additional barrier was subjected to high concentrations of hydrogen and the response is shown in Figure 5. It is seen that the modified sensor requires slightly higher operating powers but displays an acceptable speed of response for up to 30% H_2 exposures.

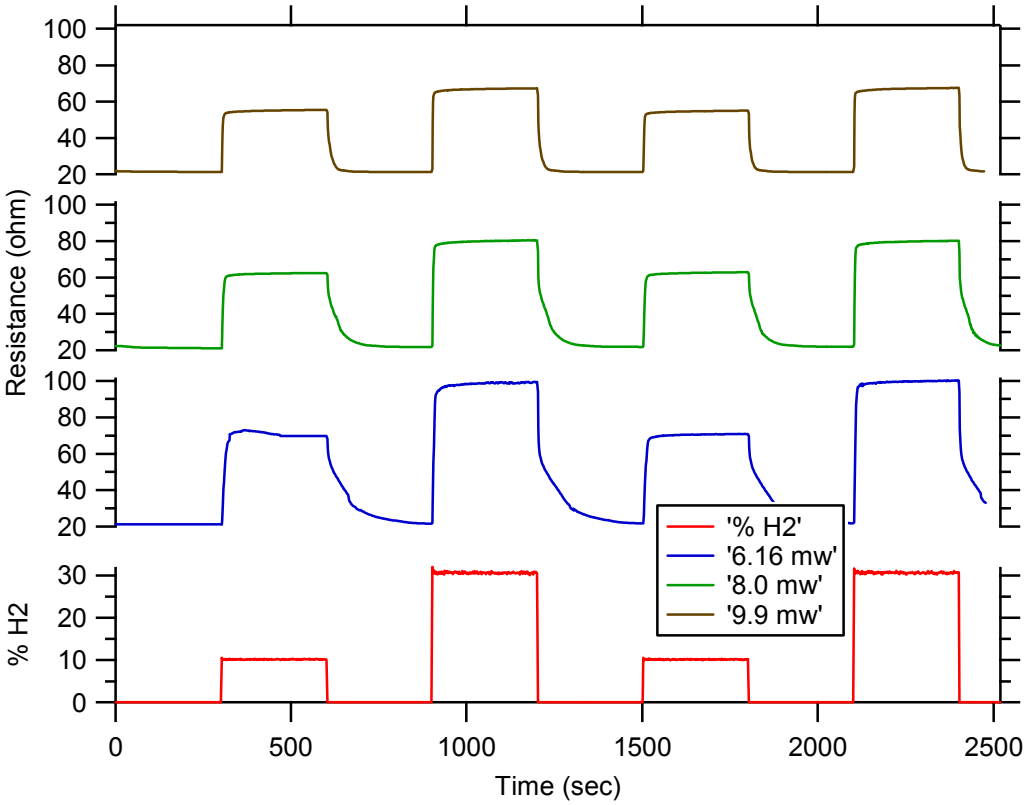

Figure 5 Responses of a barrier-coated sensor at 10% and 30% H_2 concentrations in air at three operating powers.

Cross-sensitivity to Contaminant Gases

To obtain a baseline of sensor performance in the presence of contaminant gases, sensors without cap layer alloying or additional barrier layers were exposed to low-level contaminant gases in air. The first experiment was performed without hydrogen in the gas stream. Dry air was used as the purge gas during the OFF cycle, and low-level contaminant gas – 100 ppm CO, 20 ppm H_2S, or 600 ppm IPA – was blended in air during the ON cycle. A set of representative data is shown in Figure 6. *The sensors did not respond to the presence of the contaminant test gas in the absence of hydrogen.*

The next experiment was performed with hydrogen in the gas stream during the ON cycle. Dry air was used as the purge gas during the OFF cycle, and low-level contaminant gas – 100 ppm CO, 20 ppm H_2S, or 600 ppm IPA – was blended with 0.5% H_2 during the ON cycle. A set of representative data is shown in Figure 7. The first, third, fifth, and the last subsets of data were collected with 0.5% H_2 in dry air (*i.e.*, no contaminant gas), bracketing data collected with the presence of contaminant gas and providing a reference background. The sensors *did* respond to the presence of the contaminant test gas, albeit in unexpected ways.

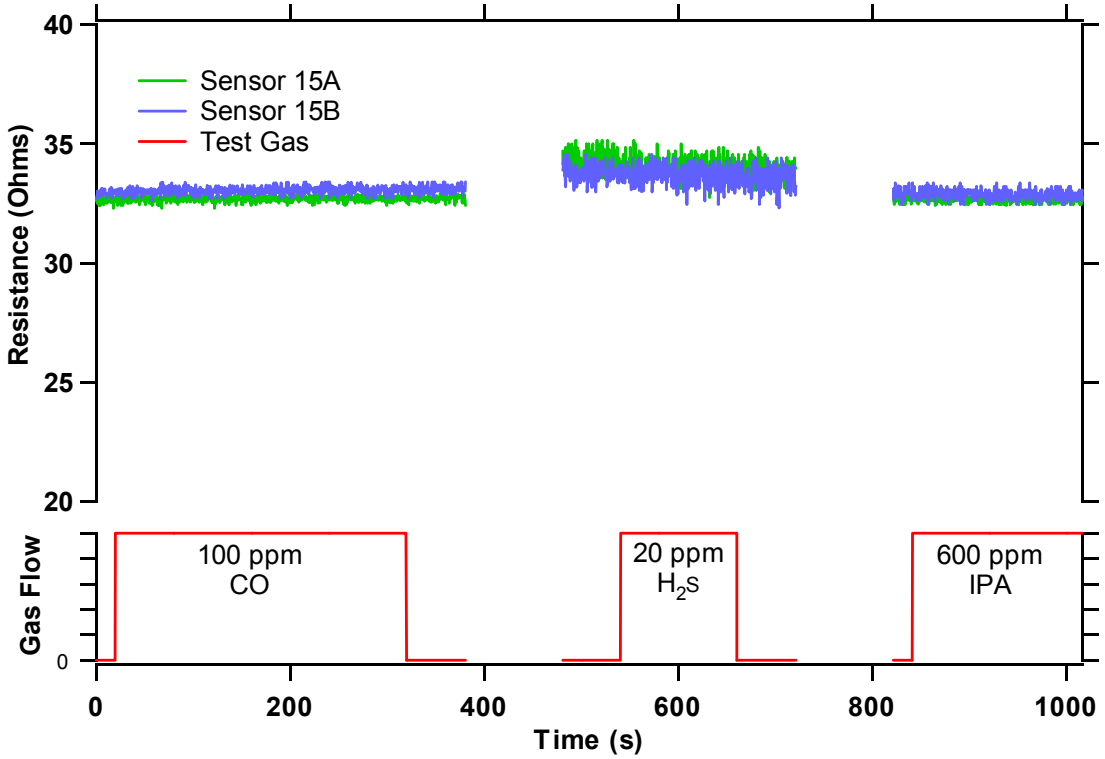

Figure 6 Responses of a sensor in the presence of 100 ppm CO, 20 ppm H_2S, or 600 ppm IPA in air. The purge gas is dry air.

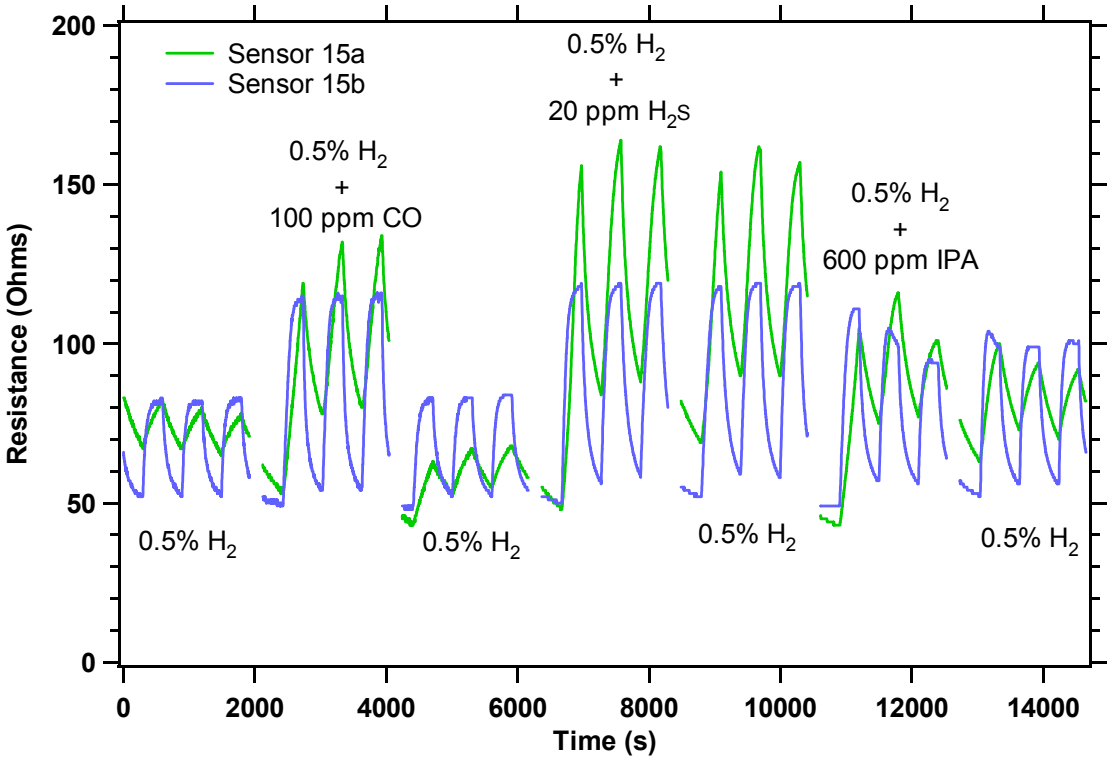

Figure 7 Responses of a sensor to 0.5% H_2 in the presence of 100 ppm CO, 20 ppm H_2S, or 600 ppm IPA in air. The purge gas is dry air.

The sensor exhibited enhanced response (*i.e.*, resistance) to 0.5% H_2 in the presence of 100 ppm CO. Since CO does not contain any hydrogen and the sensor does not respond to CO in the absence of hydrogen, it is postulated that the presence of CO modifies the catalytic dissociation of hydrogen molecules on the palladium-based cap layer (Fornander, *et al.*, 1999). The signal interference due to the presence of H_2S may follow a similar argument. The reactions are more complicated because hydrogen is a constituent element of H_2S, and sulfur has multiple oxidation states and thus many possible reaction paths. Sulfur is also well known to poison the catalytic properties of the palladium surface (Wilke and Scheffler, 1995). It is nevertheless noticed that H_2S acts *positively* to enhance the sensor signal, and the interference may be recoverable. The IPA result was mixed, seemingly affected by the lingering effect of the previous exposure to H_2S. These enhancement effects are very interesting and remain under investigation.

These cross-sensitivity studies have begun to provide significant insight into the sensing mechanisms and potential ways of improvements. Another important result is that, despite varied signal strength, *the sensor remains functional during and after repeated exposure to any of these contaminant gases*, faithfully providing a signal indicating the presence of hydrogen during the ON cycle.

Extended Lifetime Testing

An additional automated gas manifold was built to examine sensor characteristics over a prolonged period. A set of representative data collected over a seven-day period is shown Figure 8. The gaps surrounding Day 4 indicates a time when the manifold was turned off (*i.e.*, stagnant condition). The total number of cycles was 156. Each cycle was one hour long, and was made up with a 10-minute exposure of 1% H_2 followed by dry air purge. As can be seen, the response increased gradually during the first two days and subsequently leveled off, suggesting a break-in behavior. The undulation of the subsequent response shows an approximately 24-hour period and is attributed to variations in ambient temperature. The result indicates that the sensor operates under both purging and stagnant conditions with expected responsitivity.

A subsequent experiment was carried out where a sensor was connected to the gas manifold and exposed to hydrogen over a three-month period. The temporal sequence of the gas stream included a 24-hour dry air purge followed by a 10-minute exposure to 1% H_2. Figure 9 shows the long-term test results. The sensor remains fully functional after approximately three months of repeated exposure to 1% H_2. This observation, while not providing a direct measure of sensor lifetime, is very encouraging. It appears, however, that long-term systemic fluctuations and sensor signal drift will require continued examination in order to further extend the lifetime of these sensors.

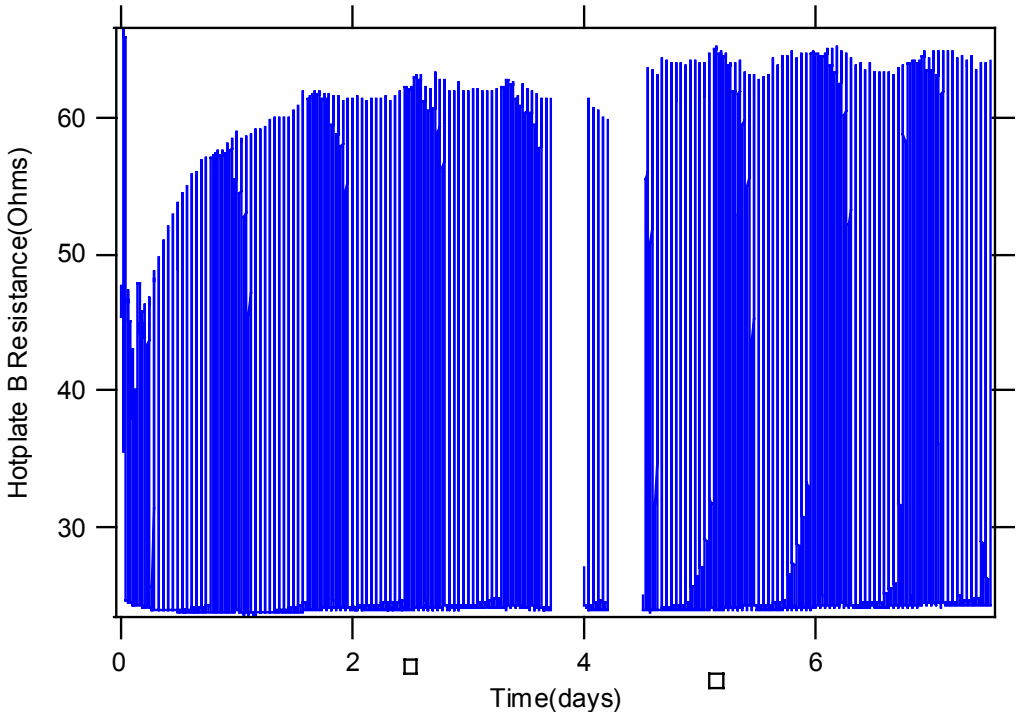

Figure 8 Responses of a sensor under repeated exposure to 1% H_2 in dry air across a 7-day period.

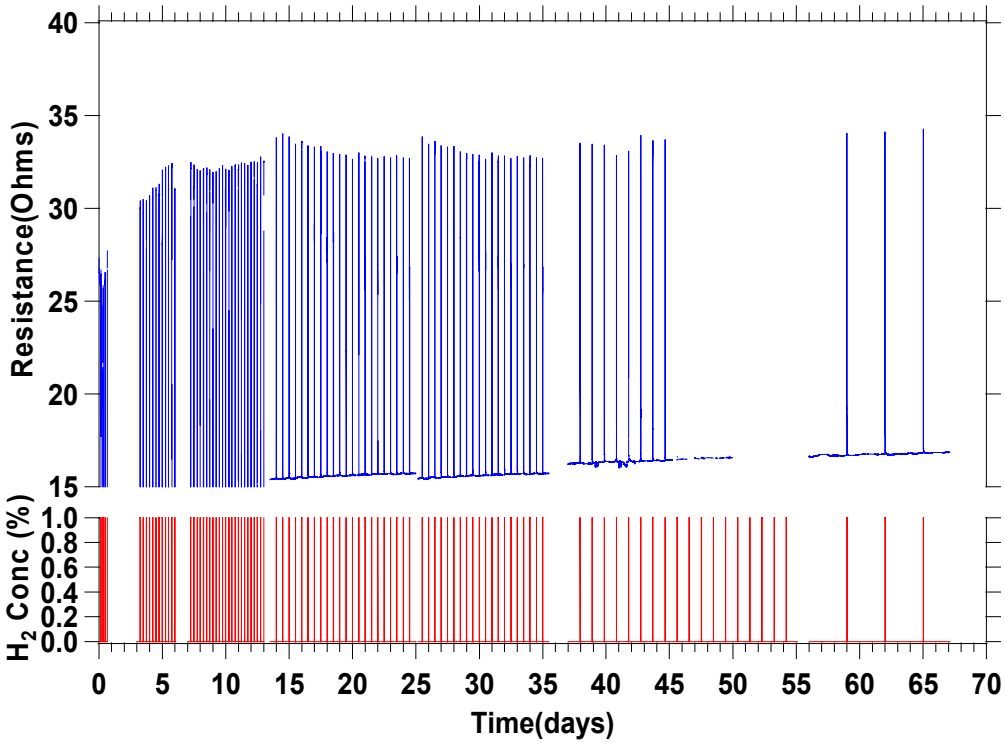

Figure 9 Responses of a sensor under repeated exposure to 1% H_2 across a three-month period.

Conclusions

We have successfully demonstrated a novel hydrogen gas sensing technology based on the combination of a micro-hotplate platform and rare earth metal hydrides and continue to develop this technology. These sensors showcase scalable operating voltage, low power requirement (~ 5 mW), and ability to operate at high-levels of hydrogen exposure (up to 30% H_2). They do not respond to common contaminant gases in the absence of hydrogen and therefore will not falsely alarm. They remain functional after repeated exposure to contaminant gases but do exhibit enhanced response in the presence of contaminant gases. This may have potential as a means to increase sensitivity to hazardous situations. Continuous sensor operation with repeated hydrogen challenges has been demonstrated for up to a three-month period, showing no indication of an intrinsic failure mechanism upon normal test conditions. The unique combination of these desirable features suggests that this technology has substantial potential for meeting the diverse sensing requirements of a wide variety of applications in a hydrogen-based energy economy.

Future Work

To date, we have observed a relatively low process yield and uniformity of sensor characteristics. We have performed a preliminary process analysis and identified several areas for focus, and have begun to deploy statistical process control techniques for continuous process improvement. Detection of hydrogen using rare earth metal hydride relies on a novel metal-insulator transformation that is not fully understood. The micro-hotplate structure provides a unique platform to study transient and steady state behaviors of these materials as a function of temperature, surface chemistry, and hydrogen partial pressure. Understanding these behaviors will enable us to gain deeper insights into the hydrogen sensing mechanism and feed the information back to design improvement. Lastly, packaging and signal conditioning issues need to be resolved to make these sensors user friendly and aid outside laboratories in evaluating their performance.

Acknowledgements

The contributions of Ed Hutchins of ATMI in the fabrication of the gas-testing manifold are gratefully acknowledged. Conversations with Glenn Tom, Steve Lurcott, and Peter Koller of ATMI and with NIST researchers, Steve Semancik, Dick Cavicchi, and John Suehle are also gratefully acknowledged. This work, performed at ATMI, was supported in part by the U.S. Department of Energy, under contract #DE-FC36-99GO10451. This support, however, does not constitute an endorsement by the DOE of the views expressed in this article.

References

G. Bhandari and T.H. Baum, “Hydrogen sensor utilizing rare earth metal thin film detection element,” U.S. Patent 6,006,582 (1999).

F. DiMeo and G. Bhandari, “Micro-machined thin film hydrogen gas sensor, and method of making and using the same,” U.S. Patent 6,65,222 (2001).

H. Fornander, L.-G. Ekedahl, and H. Dannetun, “Oxidation of carbon monoxide and deuterium on a Pd(100) film,” *Catalysis Letters* **59**, 107 (1999).

J.N. Huiberts, R. Griessen, J.H. Rector, R.J. Wijngaarden, J.P. Dekker, D.G. de Groot, N.J. Koeman, "Yttrium and lanthanum hydride films with switchable optical properties," *Nature* **380**, 231 (1996).

S. Semancik, R.E. Cavicchi, M.C. Wheeler, J.E. Tiffany, G.E. Poirier, R.M. Walton, J.S. Suehle, B. Panchapakesan, D.L. DeVoe, "Microhotplate platforms for chemical sensor research," *Sensors and Actuators* **B 77**, 579-591 (2001).

S.M. Toy and A. Phillips, "Rare earth hydrogen detector," U.S. Patent 3,732,076 (1973) S.M. Toy, "Hydrogen detection means," U.S. Patent 3,768,975 (1973).

S. Wilke and M. Scheffler, "Poisoning of Pd(100) for the dissociation of H_2: a theoretical study of co-adsorption of hydrogen and sulfur," *Surface Science* **329**, L605 (1995).