

**INTEGRATED MICRO-MACHINED
HYDROGEN GAS SENSOR**

FINAL REPORT

Frank DiMeo, Jr.

**ATMI, Inc.
7 Commerce Drive
Danbury, CT 06810
203-794-1100**

October 2, 2000

**PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY
Under Cooperative Agreement
No. DE-FG36-99GO10451**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Title: Integrated Micro-Machined Hydrogen Gas Sensor

Contractor: ATMI, Inc

Principal Investigator: Frank DiMeo, Jr.

INTRODUCTION..... 2

STATEMENT OF THE PROBLEM..... 3

 HYDROGEN SENSOR REQUIREMENTS..... 3

 EXISTING HYDROGEN SENSING TECHNOLOGY 4

PHASE I TECHNICAL APPROACH 5

 THE MICRO-MACHINED SENSOR PLATFORM..... 6

 MATERIALS SELECTION OF FUNCTIONAL SENSING MATERIALS 7

PHASE I PROGRESS AGAINST TECHNICAL TASKS 8

 MICROHOTPLATE SENSOR FABRICATION..... 8

 MICROHOTPLATE FUNCTIONALIZATION 9

 SENSOR RESPONSE TESTING 10

 SENSOR RESPONSE TESTING WITH HUMIDITY..... 17

 SENSOR LIFETIME TESTING 18

 ECONOMIC ANALYSIS..... 20

PHASE I SUMMARY AND CONCLUSIONS 20

PHASE II PROPOSAL..... 21

 PHASE II STATEMENT OF WORK..... 21

Phase II Technical Objectives 21

Phase II Tasks..... 21

Time Line and Schedule of Tasks..... 23

 PHASE II BUDGET REQUIREMENTS 24

 FACILITIES/EQUIPMENT 24

 PERSONNEL..... 26

RECEIVED

DEC 04 2000

OSTI

Introduction

The United States Department of Energy has been mandated by Congress to develop the critical technologies required for the implementation of hydrogen energy. These efforts have been aimed at all aspects of the hydrogen energy cycle: production, storage, transport and utilization. A common need to each of the areas is the ability to detect and monitor gaseous hydrogen. This is critical not only for health and human safety reasons, but also for the development of high efficiency hydrogen processes. Hydrogen gas sensors that can quickly and reliably detect hydrogen over a wide range of oxygen and moisture concentrations are not currently available, and must be developed in order to facilitate the transition to a hydrogen based energy economy.

This report details our recent progress in developing novel MEMS (Micro-Electro-Mechanical Systems) based hydrogen gas sensors. These sensors couple novel thin films as the active layer on a device structure known as a Micro-Hotplate. This coupling has resulted in a gas sensor that has several unique advantages in terms of speed, sensitivity, stability and amenability to large scale manufacture.

This Phase-I research effort was focused on achieving the following three objectives: 1) Investigation of sensor fabrication parameters and their effects on sensor performance. 2) Hydrogen response testing of these sensors in wet/dry and oxygen-containing/oxygen-deficient atmospheres. 3) Investigation of the long-term stability of these thin film materials and identification of limiting factors.

We have made substantial progress toward achieving each of these objectives, and highlights of our phase I results include the demonstration of signal responses with and without oxygen present, as well as in air with a high level of humidity. We have measured response times of <0.5 s to 1% H₂ in air, and shown the ability to detect concentrations of < 200 ppm. These results are extremely encouraging and suggest that this technology has substantial potential for meeting the needs of a hydrogen based economy

These achievements demonstrate the feasibility of using micro-hotplates structures in conjunction with palladium-coated metal-hydride films for sensing hydrogen in many of the environments required by a hydrogen based energy economy. Based on these findings, we propose to continue and expand the development of this technology in Phase II.

Statement of the Problem

"Hydrogen will join electricity in the 21st Century as a primary energy carrier in the nation's sustainable energy future".¹ This bold statement was made as part of the 1995 Hydrogen Vision Statement in a report by the Hydrogen Technology Advisory Panel (HTAP), and reflects the tremendous potential of hydrogen as an energy system. The abundance and versatility of hydrogen suggests that it can provide solutions to problems encountered with current fossil fuel energy systems, such as declining domestic supplies, air pollution, global warming, and national security.

Significant research and development efforts are currently underway to make the widespread use of hydrogen technically and economically feasible. These efforts are directed toward creating the basic building blocks of a hydrogen economy: production, storage, transport and utilization. An underlying need of each of these building blocks is the ability to detect and quantify the amount of hydrogen gas present. This is not only required for health and safety reasons, but will be required as a means of monitoring hydrogen based processes. For example, if hydrogen were to be introduced as an automobile fuel additive, a sensor would be needed to detect potential hydrogen gas leaks, as well as to monitor and provide feedback to regulate the air/fuel/hydrogen mixture.

Hydrogen Sensor Requirements

Hydrogen is the lightest and most abundant element in the universe, and as a gas, is odorless, colorless, and burns with a virtually invisible flame.² It has a lower explosive limit (LEL) of 4% in air, and an upper explosive limit of 75%. Although the safety record of the commercial hydrogen industry has been excellent, it is estimated that undetected leaks were involved in 40% of industrial hydrogen incidents that did occur.³ Emerging hydrogen based energy systems will require hydrogen sensors that are as ubiquitous as computer chips in our factories, homes, and in our cars. This means that the ability to produce large volumes of sensors at a low cost is paramount. It follows naturally that the same technology that has enabled

¹ Vision Statement, The Green Hydrogen Report; The 1995 Progress Report of the Secretary of Energy's Hydrogen Technical Advisory Panel, DOE/GO-10095-179 May 1995

² An effective odorant and luminant with minimal system and emission impact has not yet been developed.

³ "The Sourcebook for Hydrogen Applications", by the Hydrogen Research Institute and the National Renewable Energy Laboratory, 1998

computer chips to proliferate could be used to advantage for fabrication of hydrogen sensors: namely, solid state integrated circuit technology.

In order to support an effective hydrogen detection and monitoring system, the hydrogen sensor element must fulfill several requirements. It needs to be selective to hydrogen in a variety of atmospheres (including the oxygen-rich, high-humidity environments found in fuel cells). It must have a good signal to noise ratio and a large dynamic range. Speed of detection is a critical requirement to ensure rapid response to potentially hazardous leaks. Long lifetimes between calibrations are desirable in order to minimize maintenance. Low power consumption is requisite for use in portable instrumentation and personnel monitoring devices. Ultimately, these must all be achieved by a safe sensor element that is affordable to manufacture in large numbers, so that safe design principles, and not costs, are the deciding factor in the number and locations of detection points.

Existing Hydrogen Sensing Technology

There are a number of methods for the detection of hydrogen,³ ranging from the simple addition of odorants for human identification to the complexity of mass spectrometry. For continuous, multi-point applications, there are several general types of commercially available hydrogen sensors based upon electrical measurements (resistance) across a sensor material. The most popular is the "catalytic combustible" or "hot wire" sensor, consisting of two beads of resistive elements (Pt/Ir wire) arranged in a Wheatstone bridge configuration and heated to 600-800 °C. In the presence of a flammable gas, the heat of oxidation raises the temperature of one the bead and the associated heater element thus altering the Wheatstone bridge circuit. Unfortunately, in O₂ deficient environments or above the upper explosive limit, the oxidation process is quenched. Additionally, virtually all hydrocarbons have the same response. The sensor can also be contaminated by halogenated hydrocarbons or poisoned by silicones, lead and phosphorous.

A second H₂ sensor approach utilizes MOS (metal oxide semiconductor) technology, which consists of mixed iron, zinc and tin oxides heated to 150-350 °C. Oxygen atoms adsorb on MOS surface to create an equilibrium concentration of oxide ions in the surface layers. When certain target gases (CO, H₂S) or hydrocarbons encounter the sensor, they also adsorb on the surface of the MOS. This shifts the oxygen equilibrium, resulting in a decrease in resistance of the material, which can be detected. These sensors require frequent calibrations (every 3 months or less) and exhibit unacceptable response times (3-5 minutes) for rapid detection schemes. Again, a major drawback of the MOS sensor is a lack of specificity towards H₂. All volatile

organic compounds (e.g., pentane, toluene, acetone, etc.) as well as gases containing hydrogen (H₂S, ethylene) tend to react with the sensor materials. This type of sensor is also incompatible with halogenated vapors.

A third sensor is of the Gated Field Effect type. In this device, a field effect transistor (FET) like structure has a floating gate that is coated with a catalyst, typically palladium. As the catalytic gate adsorbs hydrogen, the potential of the gate changes, and modulates the conductance to the channel which is then measured. Although this device can be quite sensitive, it tends to saturate at low levels of hydrogen, making for it unsuitable for explosive limit detection.

A fourth sensor is based on the resistivity changes that occur as a function of hydrogen content in Pd or Pd alloys. The solubility behavior of hydrogen in palladium and palladium alloys is well known, as is the concomitant change in resistivity. These types of devices however suffer from the fact that the magnitude of the change in resistance is typically small, on the order of 1-10% in pure hydrogen, and can be temperature sensitive. The small signal level can present a problem in electrically noisy environments.

Not yet commercially available, but promising, are fiber optic sensors. These are based on the detection of a change in transmissivity of a hydrogen-sensitive coating at the end of an optical fiber. Such an optical sensor could potentially be immune to electrical noise, but to date have been hindered by unacceptably slow response times.

Phase I Technical Approach

To meet the need for reliable, low cost hydrogen gas sensors designed for high unit volume manufacture, this program has focused on developing and demonstrating the use of micro-machined structures, known as micro-hotplates coupled with newly developed palladium-coated metal-hydride thin films.

Individually, the micro-hotplate device structure and palladium coated metal-hydride films have unique properties which will be discussed in detail in the sections that follow. This work has demonstrated some of the potential of coupling these properties to create a sensor platform for the safe detection of hydrogen gas that has the required selectivity, sensitivity and speed, and is inherently amenable to manufacturing.

The Micro-machined Sensor Platform

The micro-hotplate structure, developed at the National Institute of Standards and Technology (NIST) has been described in detail in the literature⁴. The structure is shown in Figure 1. In Figure 1a, a 4-element gas sensing array is shown. The light gray regions are SnO₂ thin films that have been deposited by chemical vapor deposition. Figure 1b is a schematic of an individual micro-hotplate structure which consists of a thermally isolated, suspended resistive heater, a thin film thermometer, and four contact pads for measuring the conductance of the active layer. Typical physical characteristics of these devices are listed in Table 1.

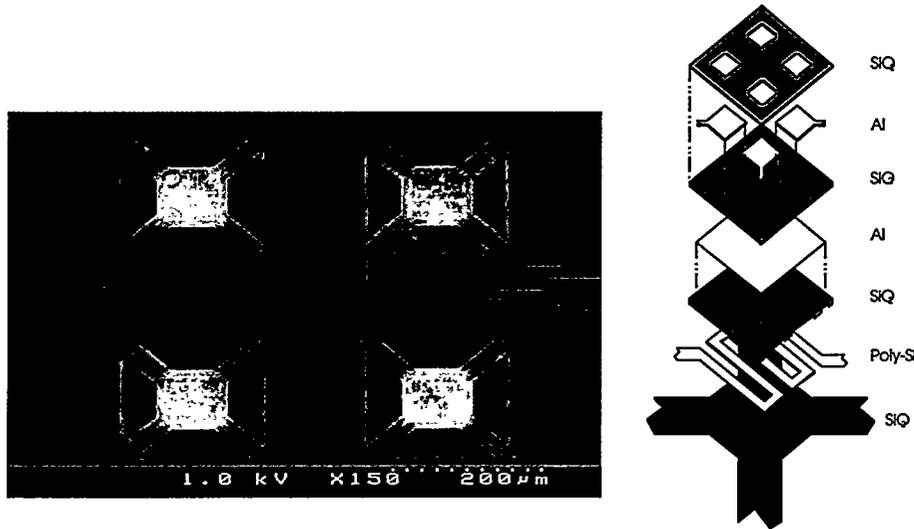


FIG. 1 a) SEM of a 4- element array of micro-hotplate gas sensors. Light gray areas are the SnO₂ thin film active layers that have been deposited by selected area CVD.⁵ b) Schematic drawing of the component CMOS layers of an individual micro-hotplate device.

⁴ R. E. Cavicchi, S. Semancik, M. Gaitan, and J. S. Suehle, USA Patent No. 5356756 (10/18/94). S. Semancik, R. E. Cavicchi, M. Gaitan, and J. S. Suehle, USA Patent No. 5345213 (9/6/94). S. Semancik, R. E. Cavicchi, M. Gaitan, and J. S. Suehle, USA Patent No. 5345213 (9/6/94). J. S. Suehle, R. E. Cavicchi, M. Gaitan, and S. Semancik, "Tin Oxide Gas Sensor fabricated using CMOS Micro-hotplates and In Situ Processing," *IEEE Electron Device Lett.* 14, 118-120 (1993). R. E. Cavicchi, J. S. Suehle, K. G. Kreider, M. Gaitan, and P. Chaparala, "Fast Temperature Programmed Sensing for Microhotplate Gas Sensors," *IEEE Electron Device Letters* 16, 286-288 (1995). R. E. Cavicchi, J. S. Suehle, K. G. Kreider, B. L. Shomaker, J. A. Small, M. Gaitan, and P. Chaparala, "Growth of SnO₂ films on micromachined hotplates," *Appl. Phys. Lett.* 66 (7), 812-814 (1995). R. E. Cavicchi, J. S. Suehle, K. G. Kreider, B. L. Shomaker, J. A. Small, M. Gaitan, and P. Chaparala, "Growth of SnO₂ films on micromachined hotplates," *Appl. Phys. Lett.* 66 (7), 812-814 (1995).

⁵ F. DiMeo Jr., S. Semancik, R. E. Cavicchi, J. S. Suehle, P. Chaparala, and N. H. Tea, "MOCVD of SnO₂ on silicon microhotplate arrays for use in gas sensing applications," *Mat. Res. Soc. Symp. Proc.* 415, 231-236 (1996).

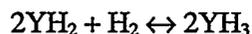
Table 1. Typical Micro-hotplate Physical Characteristics

Feature	Measure	Comment
Suspended Mass	~0.2 μg	Low thermal mass
Suspended Area	100 μm x 100 μm ,	Small size
Maximum Surface Temperature	550 $^{\circ}\text{C}$	High Temperature Operation
Thermal rise time, fall time	1-3ms, 3-4 ms	$> 10^5$ $^{\circ}/\text{s}$
Continuous-use Power Consumption	60 mW	Low Power Consumption

The basic design concept of the structure permits electrical measurements via the top contacts as a function of temperature, which is controlled using the embedded poly-silicon heater. The micro-machining step creates the suspended structure, which is thermally isolated from the substrate. This, together with the small thermal mass, enables extremely rapid heating and cooling while using minimal power. The micro-hotplate can then be used as a gas sensor by depositing a gas-reactive coating. The response of the gas-reactive coating is typically a function of the gas concentration, temperature and time. The rapid thermal response of the micro-hotplate permits the measurement of transient responses that cannot be realized by any other means. Since the devices envisioned for mass production use the same structure as the research device, the experimental results have the added benefit of being directly applicable to the final product.

Materials Selection of Functional Sensing Materials

Given the utility of the micro-hotplate platform, a critical step is the selection of a hydrogen specific reactive layer. We have chosen palladium coated yttrium thin films. The sensing mechanism of Pd-coated yttrium films is based on the reversible, hydrogen-induced transition from the metallic di-hydride compound to the semi-conducting tri-hydride compound.⁶ This is represented by the following equation involving yttrium:



The change in the electrical resistivity as the material goes from the di-hydride to the tri-hydride is the basis of the proposed sensors. Previously, Y, La, and other rare-earth hydride films were unusable due to the extreme oxophilic nature of these materials. It was recently reported

⁶ J.N. Huiberts, R. Griessen, J.H. Rector, R.J. Wijngaarden, J.P. Dekker, D.G. de Groot, N.J. Koeman, Nature 380 231(1996)

that thin films of these materials could be deposited by evaporation under ultra high vacuum, and capped with a protective Pd film.⁷ Hydrogen is known to diffuse readily through Pd, thus allowing the formation of the conducting hydride without the formation of the insulating oxide. Important issues are the speed of the response after exposure to hydrogen and of the recovery when the hydrogen is removed. In previous work at ATMI, we determined that slightly elevated temperatures were required to achieve improved response and recovery speeds. This suggested that the thermal abilities of micro-hotplates would be ideally suited for these materials.

Phase I Progress Against Technical Tasks

The Phase-I research effort was focused on achieving the following three objectives:

- 1) Investigation of sensor fabrication parameters such as layer thickness and composition, and their effects on sensor performance;
- 2) Hydrogen response testing of these sensors in wet/dry and oxygen-containing/oxygen-deficient atmospheres;
- 3) Investigation of the long term stability of these materials and identification of limiting factors.

To achieve these objectives, the following four tasks were identified: 1) Microhotplate Sensor Fabrication 2) Microhotplate Functionalization 3) Sensor Response Testing and 4) Sensor Lifetime Testing. The preparation of this project report was included as the fifth task.

We have made substantial progress toward achieving each of these objectives and our results are described in detail below.

Microhotplate Sensor Fabrication

A major attribute of micro-hotplates is that the basic structure of the device can be readily produced today by commercial foundries, produced in the following manner. Computer aided designs are submitted electronically to a commercial foundry for fabrication. The fabricated chips are etched to preferentially remove exposed silicon and form the suspended micro-bridge. After this process, the gas sensing elements are functionalized by the deposition of the active layer(s), typically by either physical or chemical vapor deposition. Previously fabricated chips have contained 4 devices per array, but this is easily be varied from 1, 2 to 9, 16 or more.

Ease of fabrication is an important concern for the successful commercialization of these devices. As noted above, the distinguishing feature of this design is that it is realized through a

⁷ ibid

commercially available complementary metal oxide semiconductor (CMOS) process. The use of a CMOS compatible process significantly lowers the barrier to manufacturing and commercializing these devices, because the infrastructure for volume production is currently in place. Furthermore, it also provides a straightforward means of increasing device functionality by incorporating on-board integrated circuitry, such as amplifiers and multiplexers to the sensor chip. It is also envisioned that these sensors could be integrated with additional chemical, temperature, pressure, and thermal conductivity sensors to provide a complete picture of the chemical state.

In this work, three types of micro-hotplates were used, varying primarily in size and electrical contact pad placement, as shown in Figure 2.

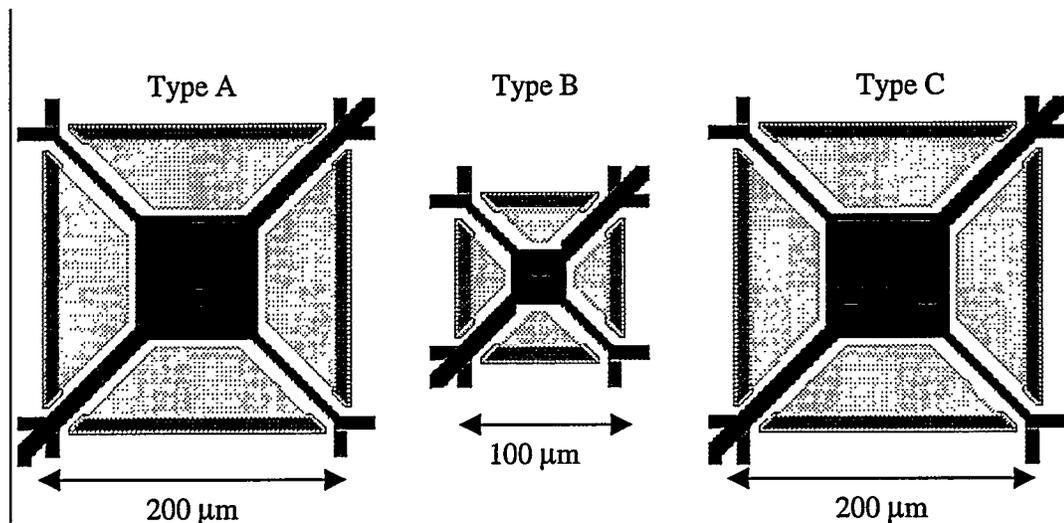


Figure 2. The three microhotplate designs investigated in this work.

Microhotplate Functionalization

The designs shown in Figure 2 were fabricated using a 2.0 micron CMOS process, and were functionalized with hydrogen sensitive layers. (Additional designs were fabricated using an alternate process, and these will be functionalized in phase II of this project). Functionalization consisted of using a physical vapor deposition process to deposit the thin film layers on the microhotplate devices, and then subsequently device packaging. Several types of functional coatings were used in order to investigate the effect of coating composition on sensor performance.

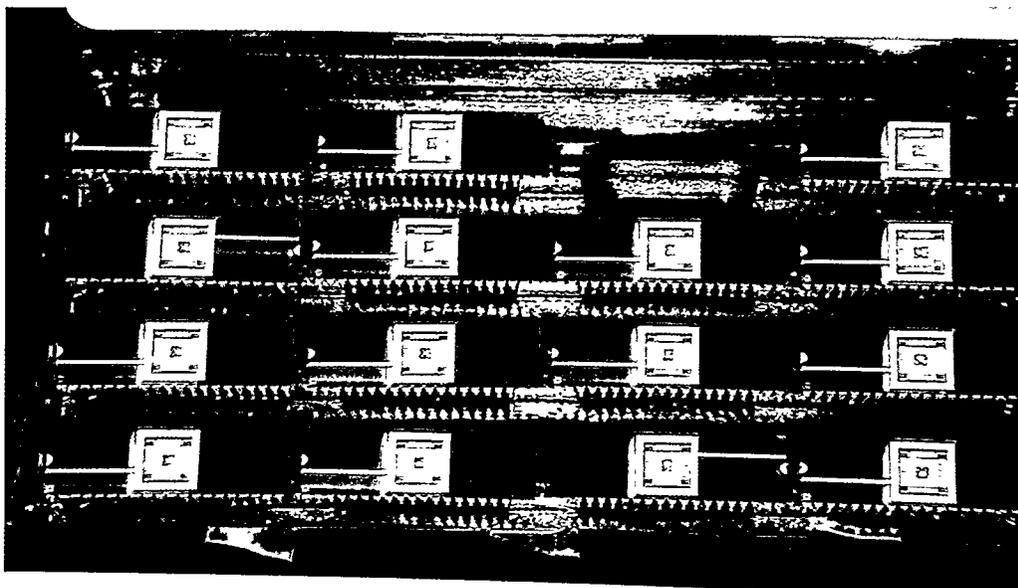


Figure 3. Optical photograph of functionalized and packaged microhotplate hydrogen gas sensors.

Sensor Response Testing

The sensor response testing task consisted of two subtasks: a) the design and construction of the response testing experimental set up and b) use of this setup to measure the performance of gas sensors. Measuring the speed of response to H_2 of the gas sensors was a primary design consideration for both the data collection system and the gas handling manifold. For the data collection, we constructed an automated system based on an HP 34970A DMM data logger with an HP 34902A scanning card. This system is capable of a scanning speed of 250 channels/s. In order to achieve fast gas switching speeds, the gas handling manifold used low volume gas chromatography valves in combination with 1/8" tubing and a small test chamber size. A schematic diagram of the system and a photograph are shown in Figure 4 and in Figure 5, respectively. Two types of ambient gas were used, clean dry air, and nitrogen. The clean dry air was obtained using triple filtered compressed air that was passed through a membrane drier, with a dewpoint specification of $-40^{\circ}C$. Nitrogen was taken from ATMI facility liquid nitrogen system, and transported through the house N_2 system. As a test gas, Grade 5.0 hydrogen was used and blended with the air using mass flow controllers with ranges of 10 and 5000 sccm respectively. For the humidity experiments, the clean dry air was passed through a temperature controlled water saturation system. This fully saturated stream was then diluted with a known amount of dry air.

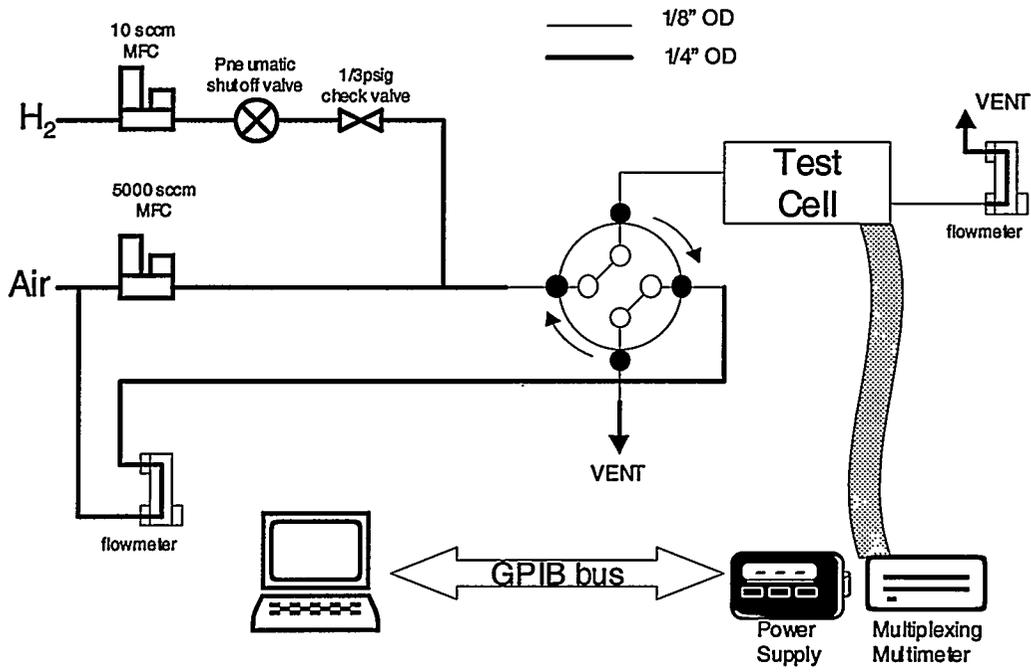


Figure 4. Schematic diagram of the automated data collection system and the gas handling manifold.



Figure 5. Photograph of the automated data collection system and gas handling manifold.

The measured response of these gas sensors is the change in resistance that occurs in the active layer film stack when exposed to hydrogen, where the resistance of the film increases with

increasing hydrogen concentration. Based on the design flexibility of the micro-hotplate, the resistance of these films can be measured in either a 2-wire or a 4-wire configuration

Figure 6 shows the resistive response of a micro-hotplate based H_2 gas sensor. The measurement was made in a 2-wire configuration, and the micro-hotplate was held at an elevated temperature by passing current (< 5 mA) through the embedded polysilicon heater. In this experiment, the sensor was cyclically exposed 10 times to 0.25% H_2 in dry air. Figure 7 focuses on the transition of one particular cycle with an expanded scale. From this figure, a rise time of < 0.44 s was measured. It should also be noted that the magnitude of the response was greater than 120%. This can be compared with the typical change in response of palladium alloy resistors, which is on the order of 10% when exposed to 1 atm of H_2 .⁸ Both the magnitude and speed of response measured here are significant achievements for this technology, and provide a strong motivation for continued development.

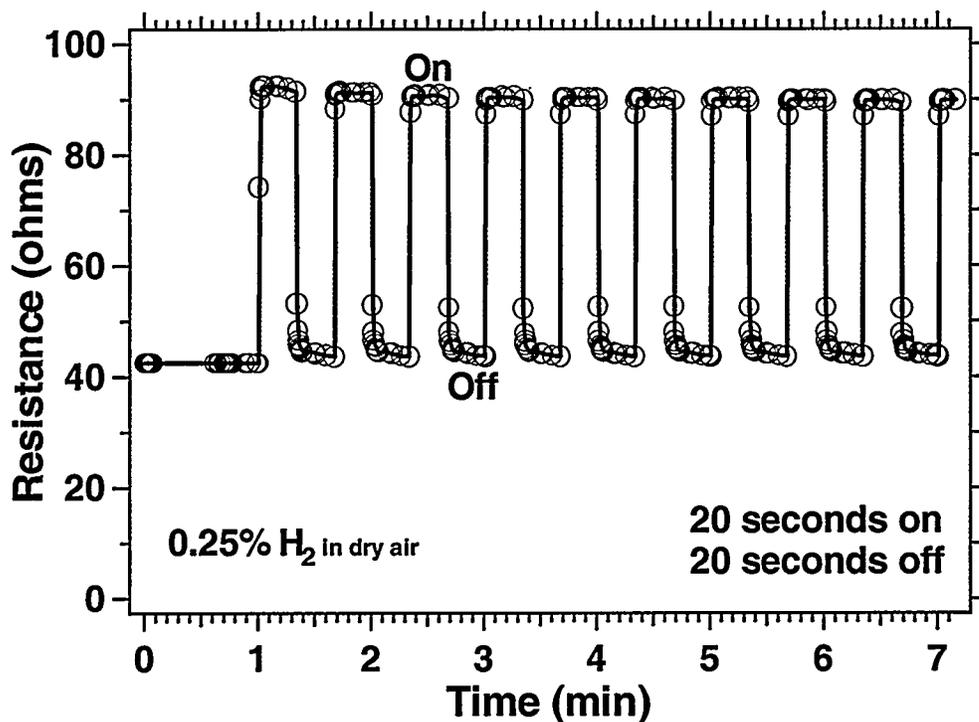


Figure 6. Resistive response of a microhotplate based H_2 gas sensor to repeated exposure to 0.25% H_2 in air. The magnitude of response is greater than 120% of the pre-exposure baseline.

⁸ Hunter, G. W. (1996). PdTi Metal Alloy as a hydrogen or hydrocarbon sensitive metal. US 5520753

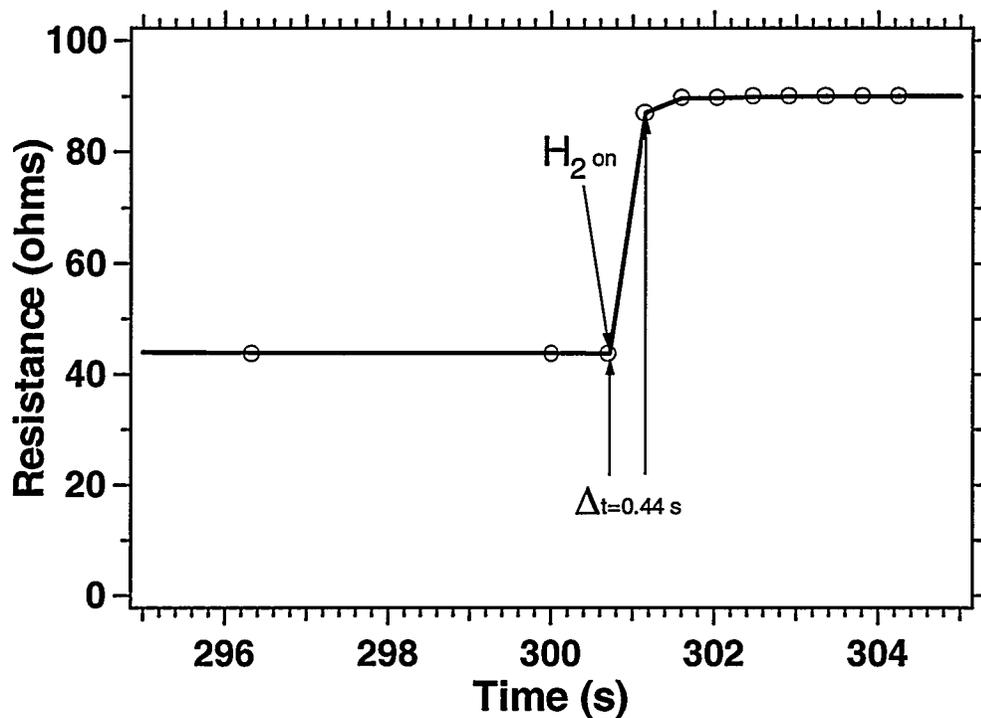


Figure 7. Expanded scale plot of the resistive response of a microhotplate based H_2 gas sensor to exposure to 0.25% H_2 in air, with a demonstrated speed of response < 0.5 sec.

Figure 8 shows the response of a similar microhotplate to different concentrations of H_2 . In this experiment, the initial concentration was 1%, and it was decreased by a factor of 2 with each step until a final concentration of ~0.01% (150 ppm) was reached. The sensor was exposed two times at each concentration. The exposure time was 300 s and the time between exposures was also 300 s. The sensor exhibited detectable responses to nearly two orders of magnitude of H_2 concentration, to levels as low as 150 ppm. The temperature of the hotplate was held constant in this experiment. It is highly likely that the minimum detectable gas concentration can be further improved by optimizing the operation conditions at lower H_2 concentrations. Figure 9 is a plot of the responses from Figure 8 as a function of H_2 concentration. For this plot, the response was taken as the absolute change in resistance as measured from the beginning baseline resistance. The H_2 concentration is plotted on a logarithmic axis, and shows that the response does not follow a simple dependence on the H_2 concentration. The reasons for the behavior of the resistivity as a function of H_2 are not currently well understood. One factor influencing the behavior of the curve in Figure 9 is the fact that at the lower H_2 concentrations, the films response does not appear to have come to equilibrium within the exposure time. In addition to this, the

influence of contact resistance in a two-probe configuration should be considered. Further testing is required to obtain a more accurate understanding of this behavior.

Stability is an important requirement of any type of sensor. To begin the investigation in this area, the resistance as a function of time without H₂ exposure was examined for a period of several days in dry air, as shown in the top panel of Figure 10. There was no flow over the sensor at this time. During the first day or so there is a small steady reduction in resistance, which eventually leveled out. This small drift was on the order of an ohm, which represents hydrogen in the sub-200 ppm range, and may either be due to hydrogen outgassing from the sensing film, or from the chamber wall. After this, the resistance reached steady state, with a standard deviation of ~0.05 ohms. This resulted in a signal to noise ratio of ~1200 (average value/standard deviation). The middle panel of Figure 10 shows the power consumed by the polysilicon heater element of the microhotplate over the same time frame, which is expected to be representative of the operating temperature. There appeared to be a cyclical variation in the power, which has a ~24 hour period, i.e. a day/night difference. When the resistance is multiplied by the power consumed, which, to first order, compensates for temperature, the variation is much reduced. The signal to noise now increases to nearly 3000, and a jump in resistance on day 6, which was lost in the noise, becomes noticeable. The result is an excellent demonstration of synergy of the microhotplate device structure and the hydride thin films. By using the thermal properties of the hotplate, the resistance noise level of the thin film can be greatly improved. This in turn allows improved hydrogen detection, both in terms of lower limit detection levels, as well as long term stability.

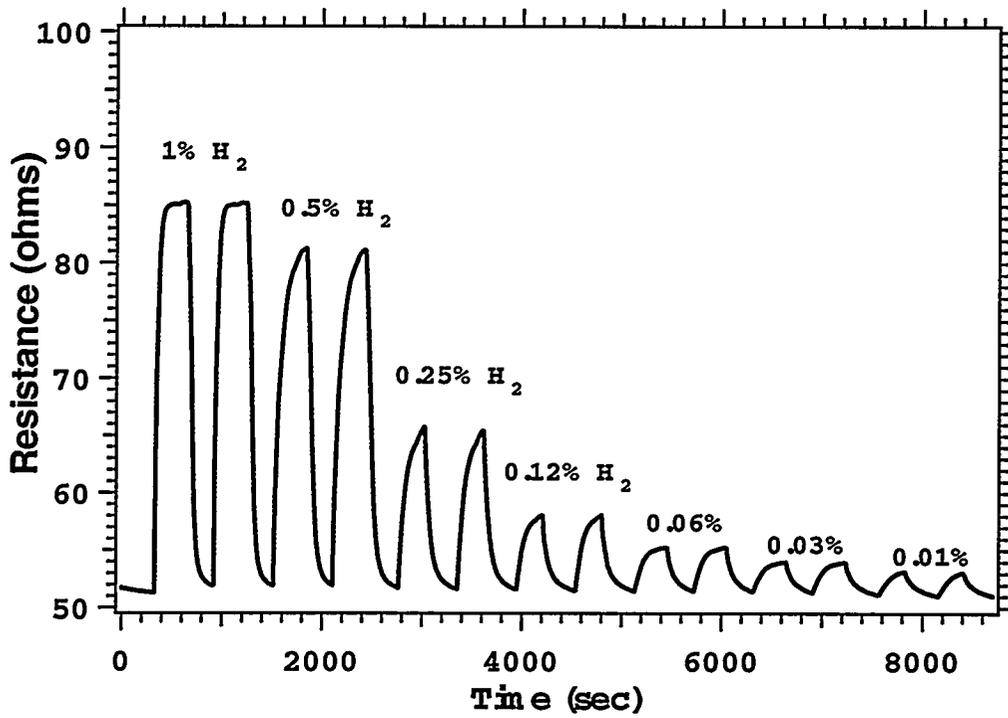


Figure 8. Resistive response of a microhotplate based H₂ gas sensor to concentrations of H₂ in air ranging from 1% to 0.01%.

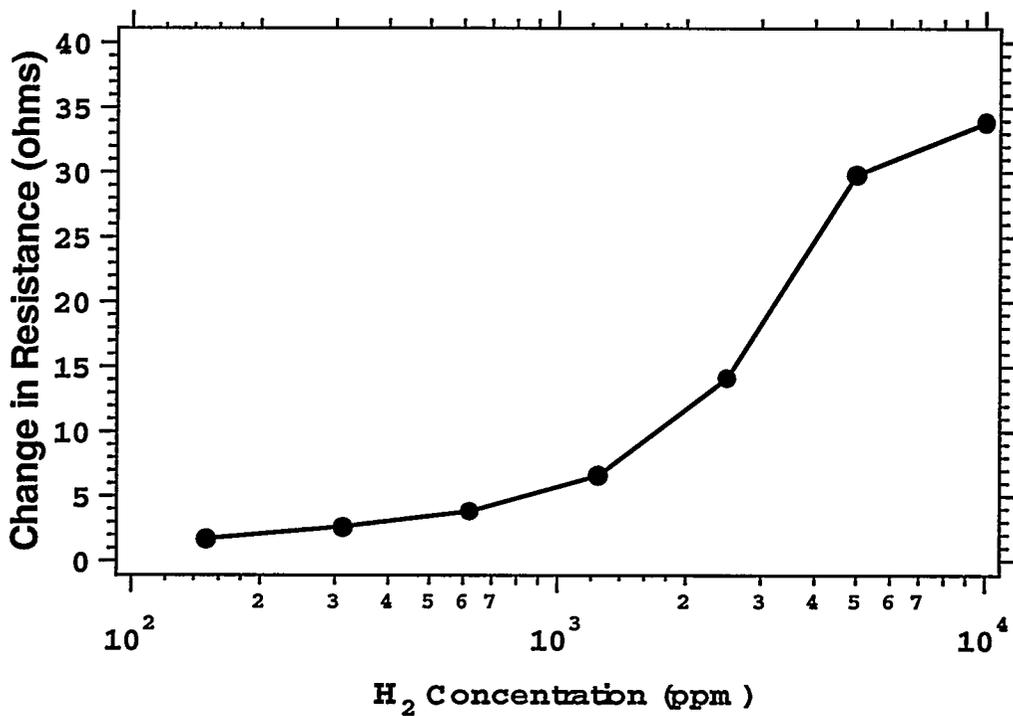


Figure 9. The resistive response from the previous figure, plotted as function of H₂ gas concentration

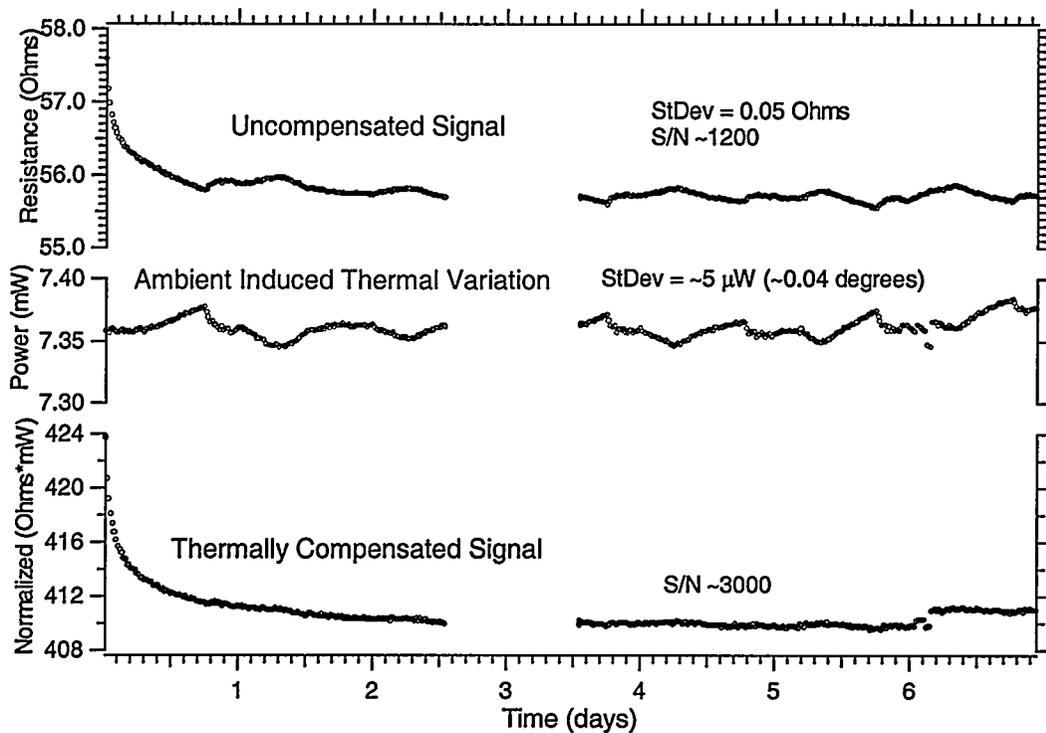


Figure 10. Stability results over a 7 day time frame. Top: H₂ sensor resistance in air. Middle: Measured poly silicon heater power. Bottom: Normalized sensor response (Resistance x Heater Power).

In addition to detecting hydrogen in oxygen containing environments, there is also a need to detect hydrogen in inert environments. Figure 11 shows the response of a microhotplate to 1% hydrogen in a background of nitrogen. As in the case in air, there is a substantial response (>50%) by the film to the presence of hydrogen. The most significant differences when responding in an oxygen free environment are that the response time is somewhat slower, ($T_{90} \sim 60$ s) and the recovery level does not return to the pre-exposure value. This is consistent with our understanding of the surface chemistry, i.e. without oxygen present, there is less driving force for the extraction of hydrogen from the film. We believe this can be substantially improved through the use of higher temperatures, but this has not been thoroughly investigated yet. Figure 11 also clearly shows the stages of hydride formation. Upon the first exposure to hydrogen, the resistance actually decreases with the formation of the dihydride, and subsequently increases. This is quite typical behavior, and is easily dealt with preconditioning each sensor to hydrogen before use.

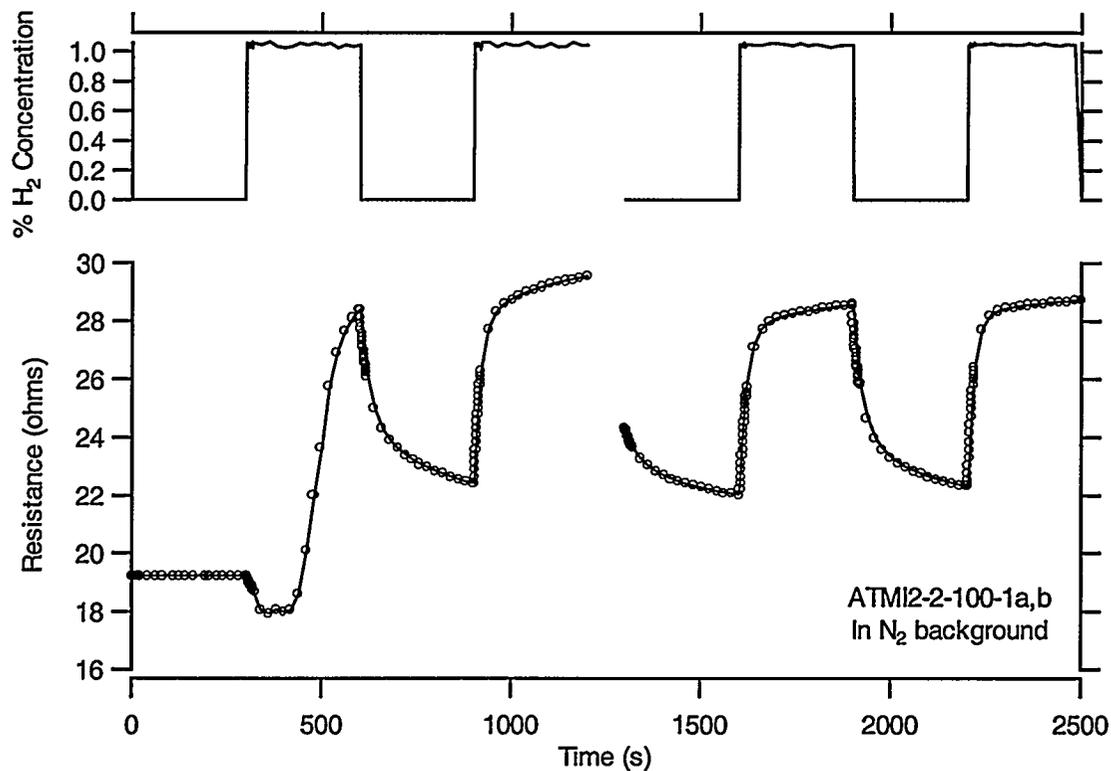


Figure 11. The resistance response of a microhotplate gas sensor when exposed to hydrogen in a background of nitrogen. Note the incomplete recovery when the hydrogen is removed, as well as the slower recovery time. The first exposure of the sensor results in the formation of YH_2 , and decrease in resistance. With continued exposure the resistance increases. With subsequent exposures, the response behaves more regularly.

Sensor Response Testing with Humidity

An important issues for any hydrogen sensor technology is its ability to work in variable humidity environments. Figure 12 shows the results of testing the micro-hotplate sensor in a humid ambient. In this test the clean dry air was passed through a high surface area humidifier, which resulted in an ambient gas near 100 % relative humidity at room temperature. The microhotplate was then exposed to 1% H_2 and, as can be seen in the figure, had a response similar to that observed in other sensors. This is an extremely important result as it indicates that this sensor may be compatible with the high humidity environment found inside of membrane based fuel cells.

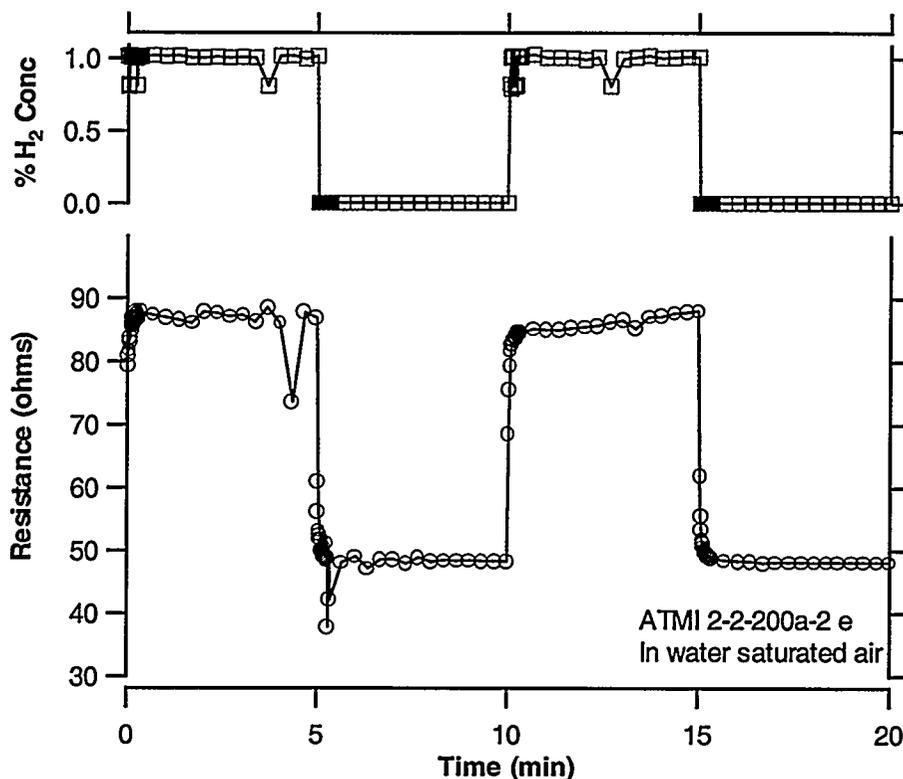


Figure 12. The resistance response of a micro-hotplate gas sensor when exposed to 1% H₂ in a humid air environment. Note deviations from the hydrogen mass flow set point are detected by the sensor a short time later.

Sensor Lifetime Testing

The long term behavior of this sensor is an extremely vital consideration, and the investigation of this behavior was initiated in phase I of this program. An important question to answer is how long will it take for the sensor to drift to an alarm condition without hydrogen present. To test this, the circuit in Figure 13 was designed and constructed. This circuit was set up to data log a sensor running at typical operating temperatures while operating in an open room air environment. The circuit uses a programmable IC (PIC) to both measure voltage levels as well as communicate via a RS232 protocol. (The resultant recorded data is in the form of unscaled bits.) The results of a 10 day trial run are shown in Figure 14. In the top panel shows the collected signal compared to the scale of 1/10th of the lower explosive limit (LEL) of hydrogen, where it looks quite flat. The bottom panel is an expanded scale of the signal of the top panel. A linear extrapolation of this data indicates that it will take ~560 days before this will drift past the 1/10th LEL level, and ~1400 days before passing the 1/4 LEL level. This suggests that the current sensor

can go 18 months without calibration, and we believe that with continued development this can be extended to 3 years. In Phase II, this type of test will be conducted over even longer time frames, and on multiple samples to validate these extrapolations, and determine areas of improvement. There are also a number of fabrication paths that can be explored to extend the overall lifetime. For example, multiple sensors can be used sequentially to double or quadruple this lifetime.

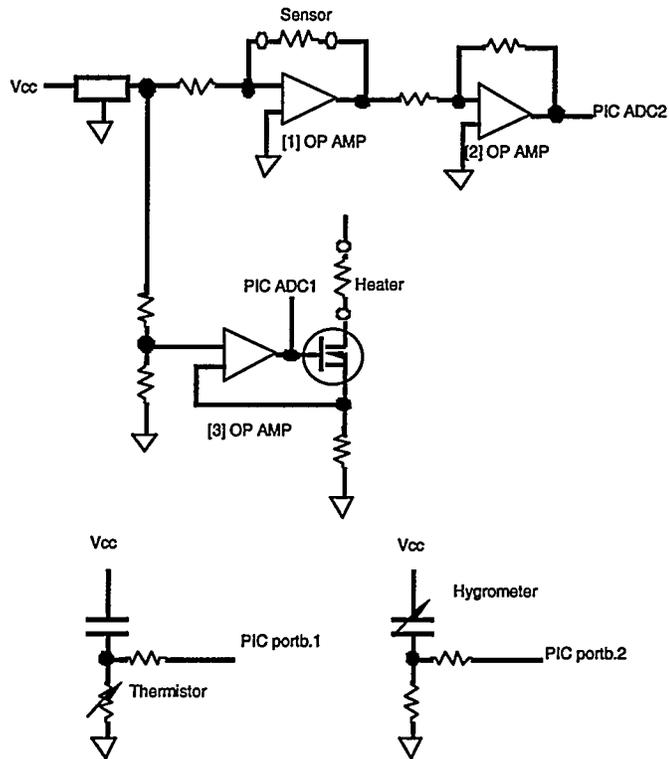


Figure 13. Electrical schematics for long term room air experiments

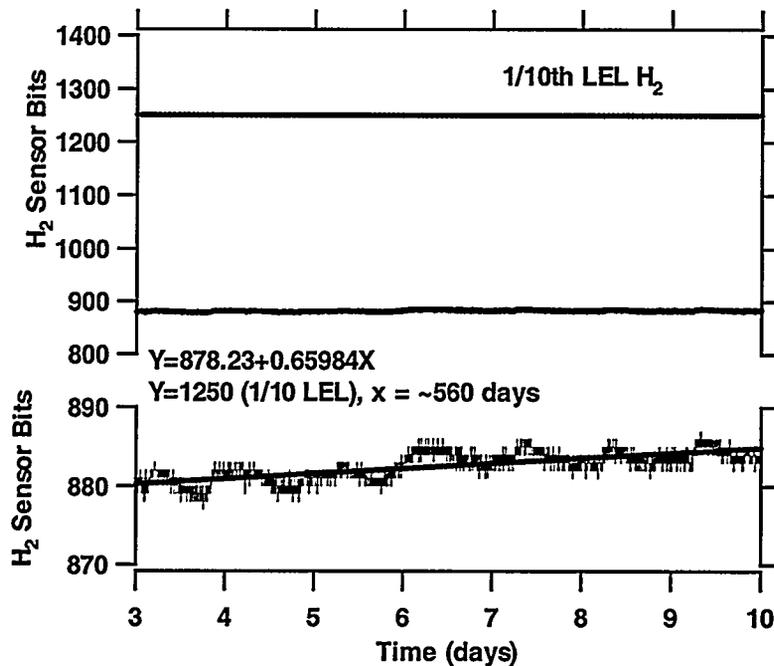


Figure 14. Time dependent signal for a sensor operating in room air. The extrapolated time to exceed the 1/10th LEL of H₂ is ~560 days.

Economic Analysis

A significant advantage to the microhotplate based approach for H₂ gas sensing is that it is based on commercially available semiconductor processing technology, which is readily accessible through a number of integrated chip foundry facilities. The small size and simplicity of the microhotplate device can further leverage this advantage, and we estimate that more than 1 million devices could be produced on a single lot of 25 six-inch wafers. Our analysis further indicates that at these quantities, the final device cost becomes dominated by the packaging, which accounts for nearly 90% of the total cost.

Phase I Summary and Conclusions

In phase I, we have developed novel thin films in conjunction with micro-hotplate devices to produce H₂ gas sensors. This combination has proven to be extremely effective and impressive sensing characteristics have been measured. In phase I, we have demonstrated signal responses with and without oxygen present, as well as in air with a high level of humidity. We have measured response times of <0.5 s to 1% H₂ in air, and shown the ability to detect concentrations of < 200 ppm. We believe that these results indicate that the combination of metal hydride thin film and micro-hotplate device structures have substantial potential for satisfying the

needs of a hydrogen based economy, and conclude that these results support further development of this technology.

Phase II Proposal

Based on the success of our phase I investigations, we propose to continue the development and evaluation of the Micro-Machined Hydrogen Gas Sensor. We have demonstrated that the concept of coupling the micro-machined device known as a micro-hotplate with novel thin films results in an effective hydrogen gas sensor in both oxygen containing and oxygen free environments. There remain a number of issues to be addressed, however, including device optimization, resiliency to potential contaminants and poisons, and long term operational stability. These issues will be addressed in Phase II of this program, as described in the following section.

Phase II Statement of Work

Phase II Technical Objectives

Phase II of this program will be focused on achieving the following three objectives

- 1) The optimization of Micro-hotplate based H₂ sensor design and fabrication processes.
- 2) The investigation of potential sensor cross sensitivities and degradation mechanisms.
- 3) The demonstration of an extrapolated sensor life time > 3 years.

Phase II Tasks

In order to efficiently achieve these objectives, the following three task have been identified: 1) Sensor Design and Fabrication 2) Short Term Response Testing 3) Long Term Behavior Investigation. The preparation of the project report has been included as a fourth task. Each task is described in detail below.

Sensor Design and Fabrication

In the first year of this project, (Phase I) we produced micro-hotplate based gas sensors, using palladium coated metal hydrides as the hydrogen selective active layer. Sensor device processing consisted of several steps: CAD design, CMOS fabrication, active layer functionalization, and packaging. In year two, we will continue to build on the work of year one, and concentrate on the optimization of device design as well of the device processing. In the

design optimization, we will minimize the device size and power consumption, while process optimization will concentrate on maximizing device yield, and uniformity. Each optimization will also use feedback from the sensor response testing in the following tasks.

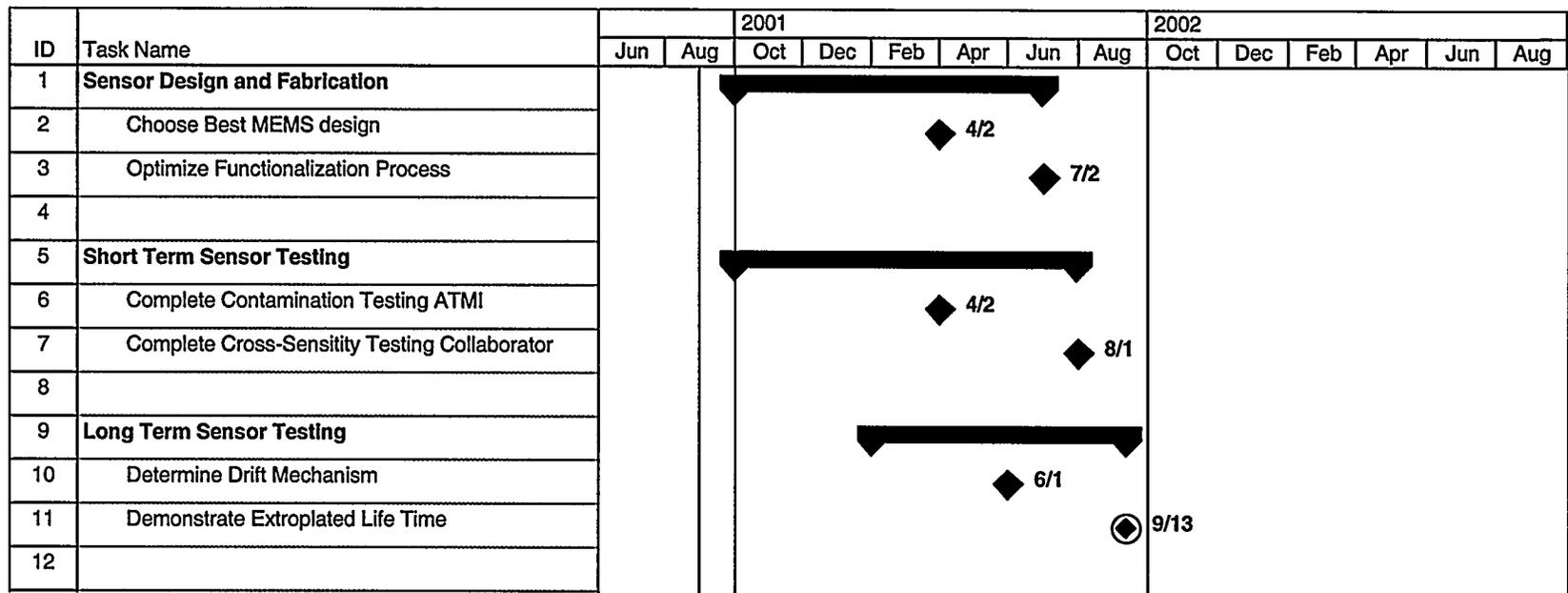
Short Term Response Testing

The sensors produced in the first year were successfully tested in a fully automated gas sensing manifold, specifically designed and constructed for this project. In year two, we will continue to use this manifold to test for the effect of potential contaminant/poisoning gases on sensor performance as well as environmental temperature effects. Potential contaminant gases of interest will include: hydrogen sulfide, sulfur dioxide, benzene, and other types of hydrocarbons such as aldehydes and ketones. Portions of the cross sensitivity, contamination and environmental studies will be performed through a collaboration with an outside industrial laboratory partner.

Long Term Behavior Investigation

The long term stability and behavior of the sensor is an important consideration for most potential applications. In year one, we began the investigation of the stability of these devices and will continue these experiments in year two. In year two we will perform experiments to develop an understanding of potential drift mechanisms of these devices and the effect operating conditions have on these mechanisms. This task will tie in closely with the tasks above, and the ultimate goal of this will be to demonstrate an extrapolated lifetime of 3 years.

Time Line and Schedule of Tasks



Phase II Budget Requirements

In order to complete the above tasks and achieve the phase II Objectives, we are requesting \$300,000 in funding from DOE, and have secured \$75,000 of in kind cost share from our collaboration partner.

Facilities/Equipment

The facilities that will be used in this program have been described in detail in the phase I proposal, but are summarized briefly below, as are several new additions to our resources.

ATMI's corporate research and development facilities are located at 7 Commerce Drive, Danbury, CT. Housed within a 73,000 square foot building are laboratories and production capability serving ATMI's three primary business units: semiconductor environmental equipment, semiconductor materials, and high performance semiconductor devices based on novel materials. The company's capabilities are unique in that it can iteratively perform the entire semiconductor fabrication process on site, including: wafer fabrication, thin film precursor fabrication, semiconductor thin film growth and analysis and electronic device fabrication (800 sq. ft. clean room) and characterization. ATMI also has routine access to the facilities of the Yale University Center for Microelectronics and Structures and cooperative arrangements that provide access to laboratories at Cornell, Harvard, and Princeton Universities. ATMI, Inc., is in compliance with all federal, Connecticut, and local Danbury environmental laws and regulations for, but not limited to, airborne emission, waterborne effluents, external radiation levels, outdoor noise, solid and bulk waste disposal practices, and handling and storage of toxic and hazardous materials.

Microscopy facilities

ATMI possesses a full suite of microscopy capability, including optical, scanning electron, and atomic force instruments. Optical microscopy is conducted using either an Olympus Stereomicroscope or an Olympus reflected light microscope. SEM analysis is performed on a JEOL JSM-5800 scanning electron microscope, with 3.5 nm resolution, accelerating voltages from 0.3 – 30 kV. The JEOL JSM-5800 SEM is also equipped with a PGT IMIX-PC electron dispersive spectroscopy (EDS) system for semi-quantitative elemental analysis with 115eV resolution. ATMI has a Digital Instruments Dimension 3000 atomic force microscope (AFM) with a 0.5 Angstrom height resolution. The AFM is capable of contact, non-contact, and tapping modes, and wafers up to 8" in diameter can be analyzed and automatically stepped and mapped.

Structural and Compositional Analysis Facilities

The x-ray diffraction facility has a Rigaku D/Max-3HFX X-ray diffractometer configured by the factory with horizontal goniometer/Eulerian cradle/thin film optics. There is also a Bede 200 high resolution double crystal x-ray diffractometer with a 2-bounce channel cut collimator. A Rigaku 3613 wavelength dispersive x-ray fluorescence spectrometer is used for quantitative composition and thickness analysis of multilayer thin film samples up to four layers on substrates up to 6" in diameter.

Device Fabrication and Characterization Laboratories

The ATMI Device Fabrication Laboratory is equipped with three laminar flow fume hoods. Two reactive ion etching systems allow etching using either non-corrosive gases in a standard system or corrosive gases in a load-locked system. The first system is a PlasmaLab μ P reactive ion etching reactor equipped with a 300W rf supply and capable of a dc bias up to 1 kV. The second RIE system is a PlasmaTherm Shuttlelock 700 series reactive ion etch system capable of etching one 10" substrate or fourteen 2" substrates simultaneously. A Cobilt Mask Aligner which can be used in UV contact mode as well as Karl Susse UV and deep UV aligner which can be used in both contact and proximity modes are used for exposing resists. A Tegal 415 plasma etcher equipped with temperature control and a 300W rf power supply is used for dry-ashing resists. Metallization structures are deposited with an Airco Temescal multi-crucible single gun e-beam evaporation system or a Kurt J. Lesker Torus sputtering unit. Film thicknesses are measured in a Dektak IIA profilometer or a Perkin Elmer 1600 FTIR. Device packaging equipment includes a SEC 2800 scribing unit with automatic X-Y indexing for dicing of wafers and a K&S wire bonder equipped with heated tip and capable of ball or wedge bonds.

Micromachining Facility

ATMI has built an automated vapor phase XeF_2 etching system to selectively etch silicon for micro-machining applications. It consists of a stainless steel high vacuum chamber capable of handling 3 inch substrates. Solid XeF_2 is held in a steel crucible, where it sublimates to provide the reactive species to remove exposed silicon. The process may be operated in either continuous or pulsed modes.

ATMI is expecting to add laser micromachining to this facility in Q4 of 2000 with the acquisition of a QuikLaze[™] system from New Wave Research. This system will be used for cutting through a number of different materials, and will greatly expand our capability for rapidly prototyping MEMS device structures.

Personnel

This proposal will be carried out at the laboratories of Advanced Technology Materials, Inc. (ATMI) in Danbury CT. The principal Investigator will be **Dr. Frank DiMeo, Jr.** of ATMI. Dr. DiMeo has extensive experience in MOCVD of novel materials, and of particular relevance to this proposal, significant experience with micromachined gas sensors. He completed his Ph.D. research on the growth and characterization of BiSrCaCuO superconducting thin films at Northwestern University in 1995. He then went on to a National Research Council post-doctoral position at NIST, where he worked on micro-hotplate gas sensors. Since joining ATMI, Dr. DiMeo's research has focused on MEMS processing, MEMS based gas-sensor development, and metal hydride thin film materials development, as well as the development of high dielectric BaSrTiO₃ thin films for cryogenic applications.

Ing-Shen (Barry) Chen, PhD, will work with Dr. DiMeo in the design, characterization and testing of the micro-hotplate based sensors as well as development of ancillary detection circuitry. Dr. Chen has extensive experience in the area of thin film processing, as well as in the area of MEMS development and processing. His research career at ATMI has involved developing processing integration techniques for lead based ferro-electric thin film for both IC and MEMS based applications. In addition, Dr. Chen has been responsible for several major control-software development projects for both deposition and characterization tools.

FRANK DiMEO JR.

EDUCATION

Ph.D., Materials Science and Engineering, Northwestern University, Evanston IL, 1995
B.S.E. Electrical Engineering and Materials Science and Engineering, University of Pennsylvania, Philadelphia PA, 1989

EXPERIENCE

1997-present

Advanced Technology Materials, Inc. Danbury, CT

Senior Research Scientist, Ventures Division

Primary investigator for metal hydride materials and advanced MEMS based sensor development. Responsible for developing CVD processes to deposit BaSrTiO₃ oxide thin film materials for use in cryogenic capacitors. Developed methods to etch noble metal electrodes for ferroelectric applications.

1995 - 1997

Nat'l Inst. of Standards and Technology, Gaithersburg, MD

National Research Council Research Associate, Process Measurements

Division of the Chemical Science and Technology Laboratory.

Developed selected area CVD process for the deposition of SnO₂, ZnO and Pt film on microhotplates. Developed *in situ* SEM analysis technique for the observation of morphological changes in Pt films during high temperature annealing.

ING-SHIN CHEN

EDUCATION

Ph.D. in Electrical Engineering, Pennsylvania State University, University Park, 6/95
M.S.E. in Electrical Engineering, University of Michigan, Ann Arbor, 8/91

EXPERIENCE

1995-present

Advanced Technology Materials, Inc. Danbury, CT

Senior Research Scientist, Ventures Division

Responsible for research and development in the area of ferroelectric oxide thin films using MOCVD. Developing low temperature deposition processes for pyroelectric and piezoelectric Pb-based ferroelectrics on MEMS structures. Also investigating novel high permittivity SrTiO₃ thin films for and low polarization ferroelectrics for FET gate applications. Extensive experience in the development of complex computer control systems, including the data collection system currently used in the H₂ gas sensor project.

6/95-12/95

Pennsylvania State University, State College, PA

Postdoctoral Researcher, Electrical Engineering

Developed control and data reduction packages for PECVD tool equipped with a real-time spectroscopic ellipsometer. Investigated high efficiency amorphous silicon alloys-based solar cells.