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LOW-COST HYDROGEN SENSORS: TECHNOLOGY MATURATION PROGRESS

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Abstract

We are developing a low-cost, solid-state hydrogen sensor to support the long-term goals of the Department of Energy (DOE) Hydrogen Program to encourage acceptance and commercialization of renewable energy-based technologies. Development of efficient production, storage, and utilization technologies brings with it the need to detect and pinpoint hydrogen leaks to protect people and equipment. The solid-state hydrogen sensor, developed at Oak Ridge National Laboratory (ORNL), is potentially well suited to meet cost and performance objectives for many of these applications. Under a cooperative research and development Agreement and license agreement, we are teaming with a private company, DCH Technology, Inc., to develop the sensor for specific market applications related to the use of hydrogen as an energy vector. This report describes our current efforts to optimize materials and sensor performance to reach the goals of low-cost fabrication and suitability for relevant application areas.

Introduction

The development and availability of low-cost hydrogen detectors will help speed the market acceptance of hydrogen as a safe and reliable energy vector. There are also many applications for low-cost hydrogen sensors in today's industrial and utility environments. Other sensor requirements include ruggedness, ease of deployment, and adaptability to many detector and alarm configurations. Many commercially available sensors designed for hydrogen detection are thought to be too expensive, and often they are not particularly selective for hydrogen gas, especially in the presence of other fuel vapors or automotive exhaust. Development of sensors that are hydrogen selective has been a more recent activity (Butler 1984, Benson et al. 1997, Hughes et al. 1992, Lauf et al. 1995, Lechuga et al. 1991), although few are available.

Workers at Oak Ridge National Laboratory (ORNL) demonstrated monolithic, resistive sensors that are inherently robust, selective to hydrogen, and easy to manufacture (Hoffheins and Lauf 1995). The sensor design, to the largest extent possible, uses traditional materials and fabrication methods because of obvious cost and reliability advantages. The ORNL sensor is composed of three electronic compositions that are separately screen-printed and fired onto an alumina substrate that measures 2.5 × 2.5 × 0.06 cm (Figure 1). Two of the compositions are standard electronic pastes, supplied by

DuPont Electronic Materials. Of those, one is a conductor and the other is a resistor encapsulant. The third composition is primarily composed of palladium metal, the key sensor component. Palladium easily forms a solid-state solution with hydrogen. DuPont developed this composition primarily for our application but is now a commercially available DuPont product (Felten 1994). In general, thick-film electronic materials are developed for use in reliable, high-temperature hybrid circuits and have an inherent ruggedness in challenging environmental conditions.

The sensing mechanism of the ORNL sensor relies on the reversible absorption of atomic hydrogen into and out of palladium metal, in proportion to the ambient partial pressure of hydrogen gas. The relationship of hydrogen and palladium is well known and characterized (Lewis 1967). Changes in hydrogen concentration in the palladium matrix lead to corresponding changes in the electrical resistance of the palladium, which can be easily measured. The sensor consists of four palladium resistors (or legs) that are arranged in a Wheatstone bridge configuration. Figure 1 depicts the sensor and its schematic representation. Two of the legs serve as reference resistors and are passivated with a thick-film resistor encapsulant to prevent entrance of hydrogen into the underlying palladium layer; thus, changes in the resistance of the palladium caused by temperature variation are compensated.

The sensor has been tested under a wide variety of conditions (Hoffheins et al. 1997). The technology was patented and licensed to DCH Technology, Inc., for the field of use encompassing hydrogen production, storage, and application as an energy vector. We continue to develop and refine design concepts and materials formulations.

Approach

During the previous year of this project, we prepared an assessment of sensor performance under various conditions of temperature and humidity for a range of hydrogen concentrations. The sensor performed successfully between a selected temperature range of 20 to 200°C and from 0 to 100% relative humidity. We began to study and analyze sensors that have failed under extreme conditions to better understand material limitations and possible approaches for improving the lifetime and stability. Preliminary results from tests of possible interference gases such as methane and propane were encouraging. During performance evaluations, we identified specific areas for improvement. These include stability of the materials over time, sensitivity and response to hydrogen, power consumption, and sensor packaging. Sensor material optimization is focused primarily on the palladium layer; however, the effectiveness of the passivation layer is also of interest. At the same time, we are exploring optimized materials and sensor layout designs to increase sensitivity and reduce power consumption over that of existing prototypes. This requires an iterative approach and close collaboration with our cooperative research and development agreement (CRADA) partner and thick-film materials suppliers.

Experimental

Sensor performance testing

In previous tests, a 9-V dc input voltage was used for the sensor excitation. We have also demonstrated sensor performance powered by a 9-V dc battery. Many commercial electronic interface products offer a 5-V dc supply for sensors and transducers. We tested the sensor at the lower voltage at various temperatures to compare the performance. A variety of sensor designs were tested to evaluate and compare sensor sensitivity and response time at three different temperatures (20, 40, and 60°C) and two input voltages (5-V dc and 9-V dc). The test configuration is shown in Figure 2.

The sensor was placed in a small test chamber inside a Tenny Junior Furnace (Model TJR). A thermocouple, attached to the back of the sensor substrate, continually measured sensor temperature. For all sensors tested, input power (HP 6205 dual dc power supply) was supplied across the passive legs of the sensor and output voltage was measured across the active legs. The gas flow to the sensor test chamber was controlled by two mass flow controllers (SEC-7330), one for air and one for 2% H_2 in dry air. Data acquisition and gas flow control was performed using a Dell laptop computer interfaced with a National Instruments DAQPad-MIO-16X2-50 (16-bit acquisition and control for the parallel port). National Instrument's LabView software was programmed to set test controls and acquire data. Temperature set points for the Tenny furnace were set manually using a Watlow Series 942 1/4 DIN ramping control.

The furnace temperature was initially set to 20°C with a sensor input voltage of 5-V dc. The test began by exposing sensors to 2% H_2 test gas for 3 minutes. The test gas was then turned off, and the test chamber was purged with air for 3 minutes. Readings were acquired every second and plotted (time in seconds vs. sensor output in volts).The test continued to alternate between 2% H_2 and air until a steady-state sensor response was observed. The same alternating 2 to 0% H_2 exposure cycles were performed at 40 and 60°C. The input voltage was then changed to 9-V dc and the same series of tests were performed.

Materials Optimization

Palladium composition modifications

During previous studies we noted that after many cycles of high hydrogen concentration cycling (10 to 30% H_2 in air), the palladium metallization swelled, cracked, and broke free from the underlying substrate. This volumetric expansion of the palladium matrix from hydrogen absorption has been noted (Lewis 1967) and some sensing approaches rely on this phenomenon. DuPont Electronics Materials formulated a new composition having a larger palladium particle size intended for better hydrogen cycling performance and improved fabrication results (Version 2). Both the original palladium composition and this new composition have a printed resistance that is too low for battery operation. A thick-film dielectric material (DuPont 5704) was mixed with the Version 2 DuPont palladium composition (4 parts palladium to 1 part dielectric by volume) to increase the printed electrical resistance and improve the adhesion of the layer to the alumina substrate. The dielectric material has a much higher percentage of glass particles, which decreases the conductivity of the palladium and at the same time adheres more strongly to the substrate.

Sensor design modifications

Another way to increase resistance of the printed palladium layer is to alter the geometry. The original sensor design used a serpentine pattern with a line width of 10 mil (250 μm). New sensors were fabricated using a line width of 5 mil (120 μm), which should at least double the printed resistance of the sensor. The Version 2 DuPont palladium composition was used for the serpentine pattern. The as-fired resistors (5 mil) measured 250 ohms, compared with 40 ohms for the 10-mil resistors. The dramatic increase in resistance was a consequence of reducing the thickness as well as the line width of the pattern.

Protective coating for palladium layer

Previous test results pointed to a slowing of sensor response over time. We suspect this is caused by adhesion of water vapor, oxygen, and other species that form a temporary barrier to hydrogen gas. Hydrogen-permeable protective coatings for the palladium layer were suggested to improve response time reliability. Among the candidates are SiO_2, Teflon™, thick-film dielectrics, acrylic, and silicone rubber. Teflon™ has been used in other hydrogen sensor work (Benson 1998). Thick-film dielectrics would be inherently compatible with existing sensor fabrication techniques. Silicone rubbers have very high permeabilities for H_2, approaching those for palladium. We are evaluating several of these materials.

A number of sensors were sputtered with SiO_2. Sputtered composition was maintained close to stoichiometric proportions, although it was not measured. This material was chosen because it exhibits a somewhat greater H_2 permeability compared with other ceramic materials, especially in thin layers. In addition, it is a mature and available process. SiO_2 coatings are widely applied for their optical properties, electrical insulation, and resistance to physical and chemical attack. Its columnar microstructure, a consequence of sputtering, should enhance H_2 permeability. The coating thickness is in the range of 100 to 150 nm. Testing has begun, but results are not yet available.

Results and Discussion

Sensor operation

Sensor operation was evaluated at two input levels. Figure 3 shows the responses of one sensor to 2% H_2 (in air) cycles at 5-V dc and at 9-V dc for three temperatures. The H_2 gas cycle was 3 minutes (seconds 1 through 180 along the x axis of the chart). An air cycle followed (seconds 181 through 345 along the x axis). At 20°C, the sensor responses are similar, suggesting no significant difference in performance because of the excitation voltage. The time to reach 90% of full response is on the order of 1 minute. At the higher temperatures, the response is faster, about 30 seconds, and more level but the magnitude of the response is significantly diminished. Recovery times in air follow a similar pattern. It is known that as temperature increases palladium's solubility for hydrogen decreases.

For sensor applications that experience wide shifts in temperatures, temperature measurement may be incorporated in the sensor design and signal-conditioning electronics. In general, these results are preliminary and the data do not indicate that overall performance or sensitivity is limited.

Materials optimization

Palladium composition modifications

Thick-film materials, in general, are designed to be stable over time. Our thick-film application is somewhat unusual in that we are requiring the palladium composition to be "active" rather than "passive" to respond accordingly to changes in the ambient partial pressure of hydrogen. The material structure must accommodate rapid shifts in hydrogen absorption and desorption without becoming brittle. The electrical resistance of the fired pattern must be high enough to be easily measured and to prolong battery life. The material must also adhere well and reliably. These requirements, though not necessarily in conflict with each other, necessitate an iterative approach to arrive at the final design for the palladium composition.

Planned tasks include the following. (1) Modify the Version 2 DuPont composition with materials that increase the electrical resistance and possibly alter the fired structure to favor repeated reversible hydrogen absorption. (2) Reformulate the palladium compositions through the addition of alloying elements to reduce or eliminate phase changes and minimize volume expansion. This approach has been used successfully for a sensor developed at Sandia National Laboratories (Hughes et al. 1992). (3) Optimize the glass content required for adequate adhesion to the substrate. The glass also acts as an insulator and can increase the electrical resistance of the fired pattern. (4) Study palladium particle size and the effects of printing and firing on mechanical and absorption properties. We will also evaluate optimum printing geometries for measurement and power conservation. We have begun working in a number of these areas.

Sensors were fabricated with the Version 2 DuPont palladium plus DuPont 5704 dielectric compositions described earlier. One sensor (DT052) was cycled through many exposures to hydrogen from 0 to 4% in air. When compared with an unexposed sensor, DT053, from the same fabrication series, the metallization looks intact and similar in uniformity (Figure 4). Each of these sensors was scratched with a small, wooden dowel to test the brittleness and adhesion of the palladium metallization. There were no discernible differences between the sensors. The palladium layer for each was solid and held firmly to the substrate.

Sensors printed with the unmodified Version 2 DuPont using the narrower pattern were also tested. At 4% hydrogen in air, the sensors quickly peeled away from the substrate. Using different sensors, better results were obtained for tests with 2% hydrogen in air.

A comparison of three sensors with different palladium compositions is shown in Figure 5. Sensor DT052 shows the best sensitivity overall with a 150-mV output at 2% H_2. Sensor K0136 with Version 1 DuPont composition and Sensor DT227 with Version 2 DuPont composition exhibit similar sensitivity although the hydrogen exposure time for DT227 was 180 seconds instead of the 600 seconds used for the other two tests. Further tests of the modified composition used for DT052 will be required to verify the promising results of improved sensitivity and durability. A summary of results for the palladium compositions is shown in Table 1. Note that the modified composition called DT "C" also shows an improvement in power consumption over Version 1 (KS series). It is evident that reducing the line width will improve power consumption of the sensor. A next step will be to fabricate sensors with the modified palladium and use the finer line width pattern.

Table 1. Comparison of palladium metallizations

Sensor series	KS	DT 1xx	DT 2xx	DT "C"
Sensor paste	DuPont, Ver. 1	DuPont, Ver. 2	DuPont, Ver. 2	80 vol% DuPont, Ver. 2 20 vol% DuPont 5704
Line width (mil)	10	10	5	10
Power consumption (mW)	400	600	100	250
Sensitivity at 2% H_2/air (mV)	100	Not tested	100	50-160
Durability (4% H_2 cycling)	Yes	Not tested	No	Yes

Sensor design and packaging

As we continue materials optimization, we will also be involved with DCH Technology to refine sensor layout and packaging design. A new sensor layout was designed to reduce the size of the sensor. The sensor patterns are printed on both sides of a square alumina substrate measuring 1.3 × 1.3 × 0.06 cm. This size is convenient for conventional and prototype sensor packages (Figure 6). The small size demands that the sensor patterns are narrower, which also reduces power consumption.

Thick-film designs are relatively simple to lay out and fabricate. In addition, small fabrication batches are economical. Many sensors can be printed and fired on a single substrate and then separated for individual packaging (Figure 7). (Our facility has the capability of screen-printing up to 3 × 3-in. substrates, but commercial manufacturers can produce circuits on much larger substrates.) Our goal is to complete as many of the fabrication steps as possible on large, unbroken substrates so that a high level of uniformity is maintained. This will also control fabrication costs by limiting the number of different process steps.

CRADA Partner Activities

DCH Technology has been conducting an economic evaluation to prepare the sensor for market acceptance in the emerging hydrogen energy based industries. The following activities describe recent efforts.

A market survey of acceptable cost/price thresholds in both hydrogen safety and process monitoring applications was completed. A product price strategy has been created for the new generation hydrogen sensors, and this provides a baseline for design and fabrication costs.

A continuing activity is the establishment of a working relationship with the insurance industry to ensure acceptance of new technology into the existing Standard Industrial Categories (SIC). This includes the creation of a joint venture on insurance for hydrogen project protection called the Renewable Energy Group.

The case for hydrogen sensors was presented to the DOE Hydrogen Source Book task force and the International Organization for Standardization Working Group No. 7. New generation sensors have been included in the dialog with the National Fire Protection Association update to standards. This is a continuing activity.

A series of agreements is now in place for beta testing of new generation hydrogen sensors into application areas most appropriate to the sensor attributes. Product development is under way that includes packaging, controls, interfaces, and integration into larger-scale systems. Staff from DCH and ORNL will be working more closely to tailor sensor design and performance to specific applications. Strategic marketing activities, including a prototype demonstration at the 1998 National Hydrogen Association meeting, have been accomplished and will continue in the future.

Future Work

Our plans are to continue materials and performance optimization for challenging target applications (high-temperature, humidity, and corrosive environments). We will evaluate sensor design and size along with various packaging and communication schemes for optimal acceptance by end users.

Conclusions

Our continuing evaluation of sensor performance points to the need to better understand the dynamics of the sensor's palladium metallization. We are planning to use infrared imaging technology to evaluate surface heating from catalytic effects. Other results include a need to further understand the effects of possible interferences such as combustible gases and automotive exhaust.

We continue testing to evaluate sensor material stability and durability. We have successfully tested a modified sensor metallization for repeated hydrogen cycling at low concentrations. We are working to optimize this composition regarding sensitivity and lower power consumption.

We continue to evaluate the interfering effects of adsorbed water and oxygen on sensor response. We are coating sensors with materials that block molecules and atoms larger than hydrogen gas.

A modified design for the sensor metallization was completed and is under evaluation. Preliminary results indicate that sensitivity is maintained and that power consumption is lower by a factor of four.

We demonstrated the current sensor prototypes at the 1998 National Hydrogen Association meeting. We showed that the sensor is easily compatible with commercial data acquisition hardware and software and ultimately with "smart sensor" plug and play concepts proposed in the IEEE 1451 standard.

Acknowledgments

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Figure Captions

Figure 1. Prototype hydrogen sensor, 1.5X actual size (left) and schematic representation (right).

Figure 2. Configuration for sensor testing.

Figure 3. Sensor response to 2% H_2/air for indicated input voltage and temperature.

Figure 4. Comparison of palladium metallizations for sensors DT052 (left) and DT053 (right) (magnification: 100X).

Figure 5. Comparison of sensor performance for three palladium compositions (2% H_2/air, 5-V sensor input).

Figure 6. Sensor packaging scenarios compatible with 1.3 X 1.3 cm sensor size.

Figure 7. The ORNL sensor can be mass-produced on large substrates and then be broken apart for individual packaging.

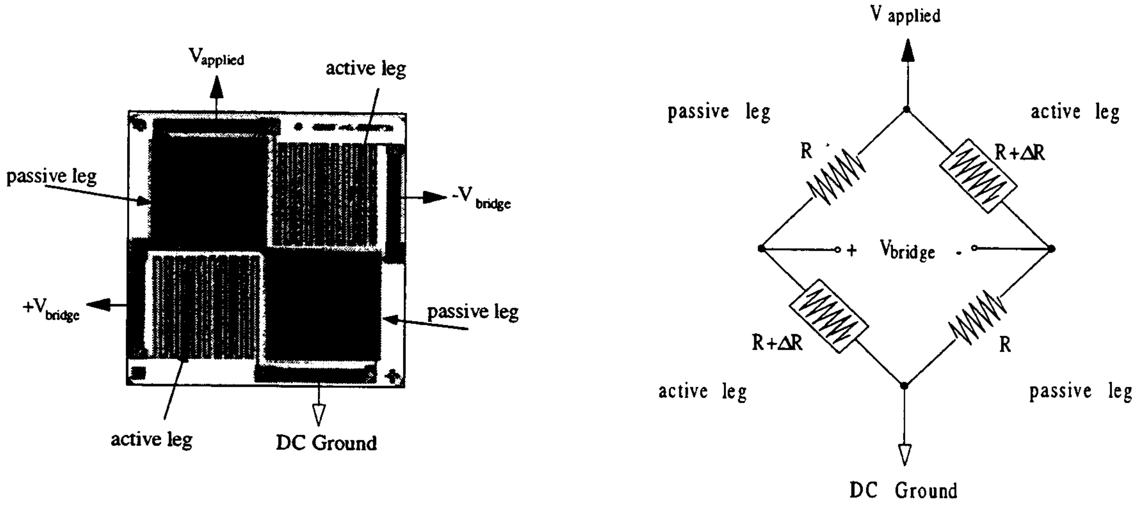

$V_{applied}$
active leg
passive leg
$-V_{bridge}$
$+V_{bridge}$
passive leg
active leg
DC Ground
V applied
passive leg
active leg
R
R+ΔR
+ Vbridge -
R+ΔR
R
active leg
passive leg
DC Ground

Figure 1

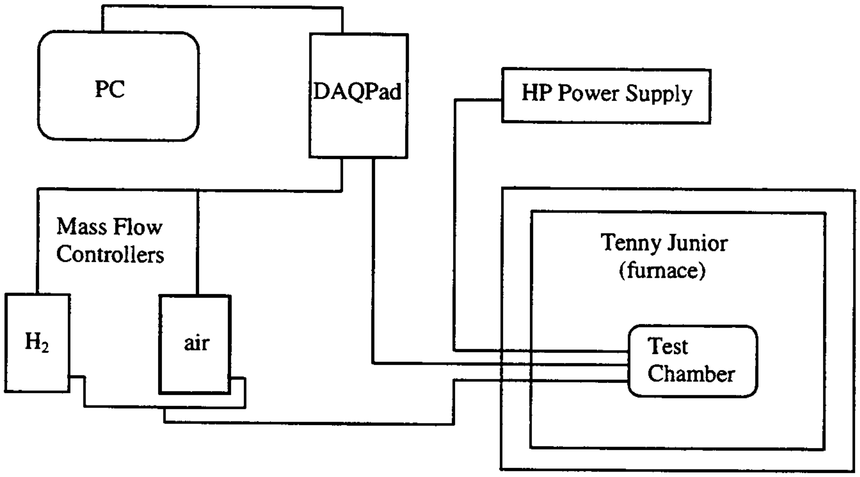
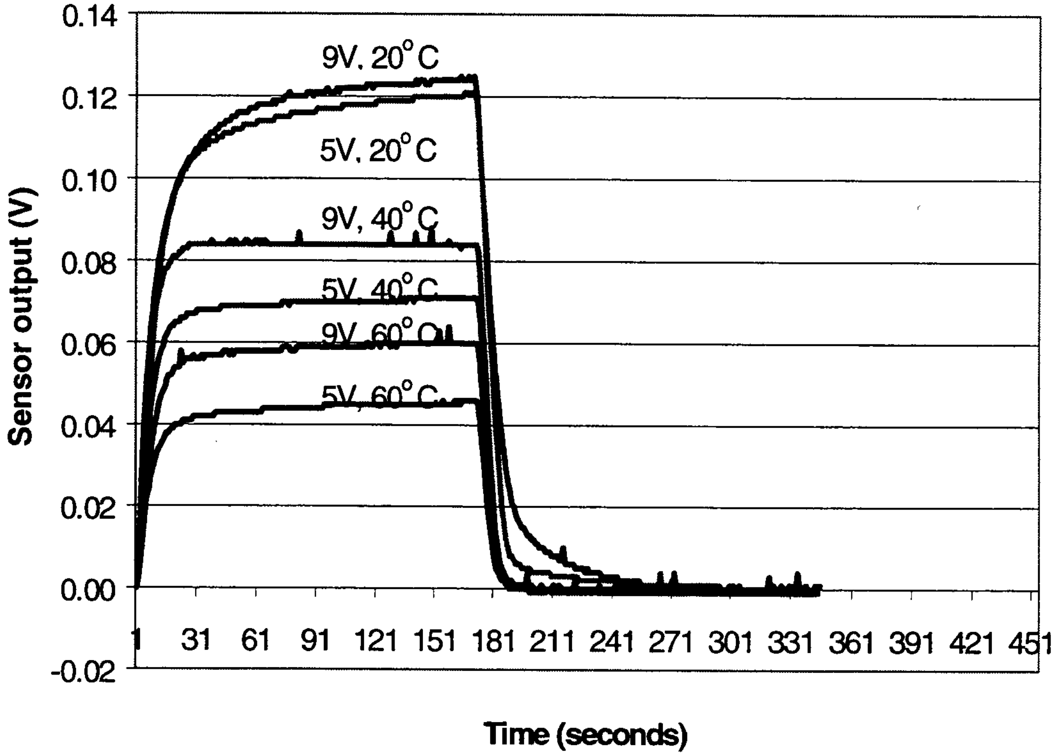

PC
DAQPad
HP Power Supply
Mass Flow Controllers
H_2
air
Tenny Junior (furnace)
Test Chamber

Figure 2.



0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
Sensor output (V)
1
31
61
91
121
151
181
211
241
271
301
331
361
391
421
451
Time (seconds)
9V, 20°C
5V, 20°C
9V, 40°C
5V, 40°C
9V, 60°C
5V, 60°C

Figure 3

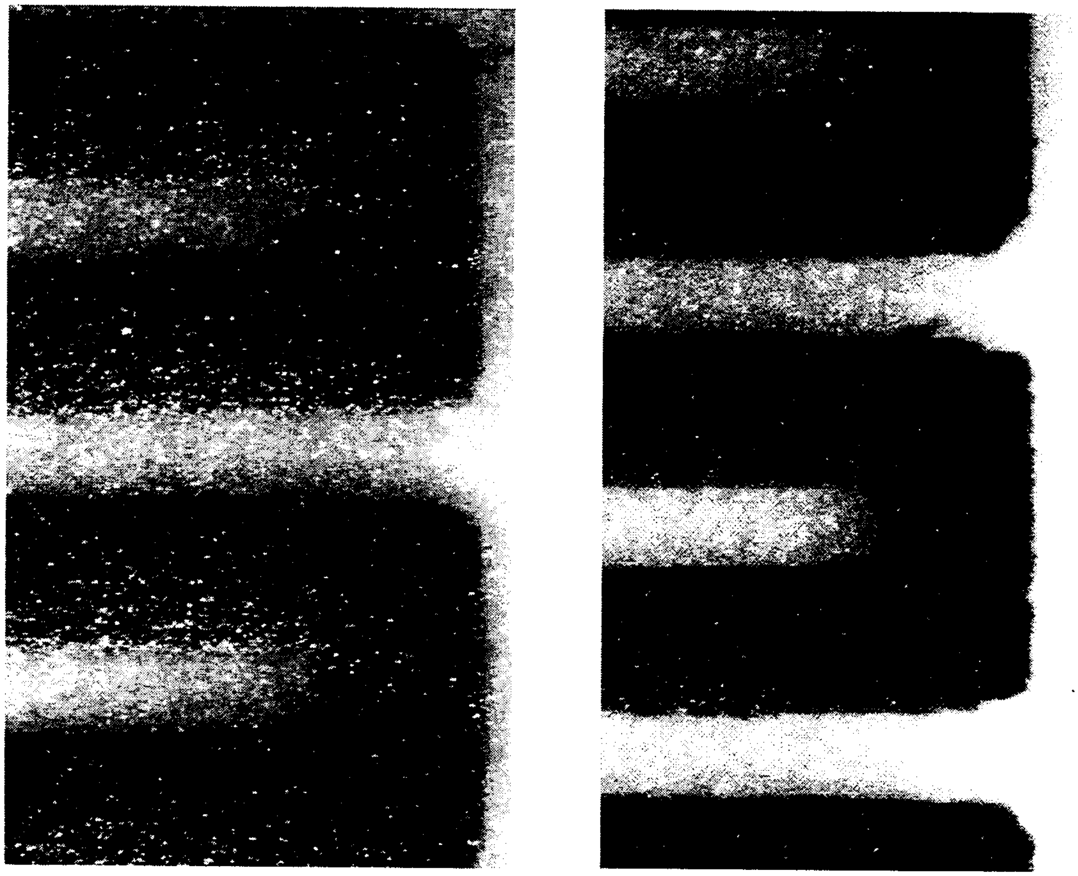


Figure 4.

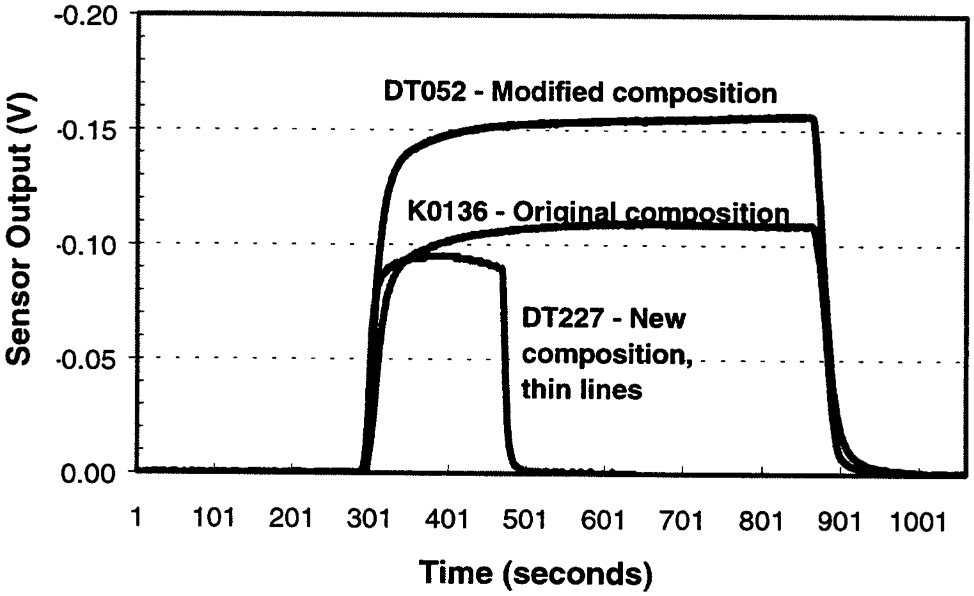

-0.20
-0.15
-0.10
-0.05
0.00
Sensor Output (V)
DT052 - Modified composition
K0136 - Original composition
DT227 - New composition, thin lines
1
101
201
301
401
501
601
701
801
901
1001
Time (seconds)

Figure 5.

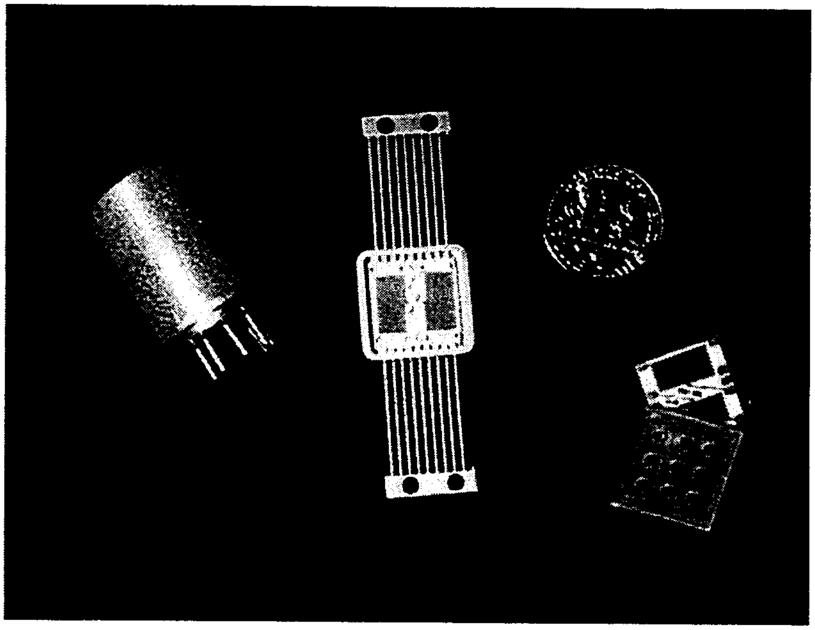


Figure 6.

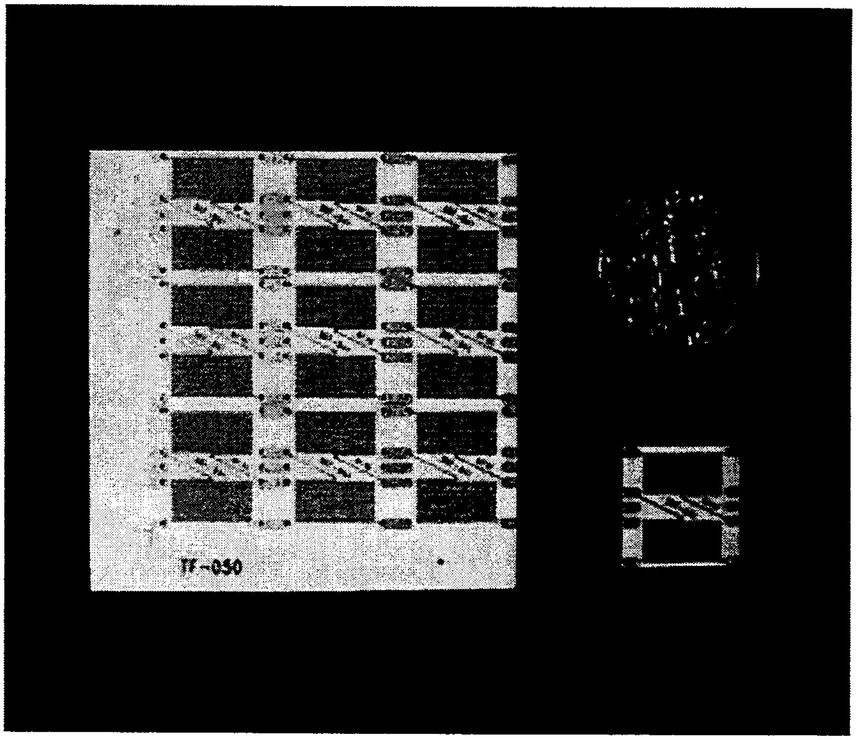


Figure 7.