THE RESPONSE OF THE SANDIA ROBUST WIDE RANGE HYDROGEN SENSOR TO H_2-O_2 MIXTURES

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ABSTRACT

The Sandia Robust Hydrogen (SRH) sensor can detect partial pressures of H_2 over a wide range (~1 ppm to pure H_2) because it employs two different kinds of catalytic metal sensors. A Field Effect Transistor (FET) with a catalytic gate detects low H_2 concentrations and a resistor of the same metal is accurate for the higher concentrations. The use of Pd alloys with Ni preserves sensor reversibility by preventing the hydride phase transition under normal operating conditions. Mixing O_2 with H_2 does change the sensor signal under some conditions and comparison of the behavior of a pure Pd device with a Pd/Ni device is given. The H_2 concentration in flammable mixtures can be obtained, but an additional sensor is needed to measure the concentration of oxidant.

INTRODUCTION

The Sandia Robust Hydrogen (SRH) sensor was designed to solve a wide variety of hydrogen sensing problems in the military, space and commercial arenas. Batch fabrication can lead to large numbers of inexpensive, nearly identical sensors. This makes it feasible to deploy many point sensors in complex systems like rocket motors, semiconductor processing lines and petrochemical plants for safety and process control. The details of the design and fabrication in a standard CMOS silicon line have been reported [1]. This platform improves on the numerous other implementations in Si of Lundström's original field effect sensor concept [2] in two important ways: 1) a field effect transistor (FET) and resistor using the same thin film catalytic metal are on the same chip, along with the heater and temperature measuring p/n junction. 2) A series of Pd alloys with Ni have been developed that allow study of high H_2 partial pressures(pH_2's), up to pure H_2. One of the beneficial aspects of the Ni alloy is that the hydride phase transition requires much higher pH_2's; sensor reversibility depends on not going through the phase transition [3]. In this paper we will present the first reports of the data from SRH sensors comparing pure Pd with Pd/Ni metallizations for sensing mixtures of H_2 and O_2.

Over the years there have been a number of reports on the response of catalytic gate field effect devices to mixtures of H_2 and O_2 in both ultra high vacuum and laboratory air. Some of these studies have been reviewed by Lundström, et al. [2,4] and it has been found that the sensor response is a complicated function of the partial pressures of both H_2 and O_2. No single model predicts the behavior of all the experimental sensors, and there is a wide variation in the ratio of response to a given pH_2 with and without O_2 present among more or less "identical" sensors. In general the presence of high pO_2 causes the signal from a given pH_2 to become smaller.

The models all assume that H_2 molecules must dissociate into adsorbed hydrogen atoms (H_a) on the outer surface of the catalytic thin film. Dissociation is always the slow step in the response of the sensor to steps in pH_2. The H_a quickly comes into equilibrium with H in the bulk of the film and the field effect sensing sites on the inner metal/insulator interface. The isotherms for the bulk and interface are very different [3] so that the FET has a large response for low pH_2 and the resistor gives accurate values for high pH_2, notably in the range for explosive mixtures of H_2 (30 Torr).

When no O_2 is present, the gas phase pH_2 is in thermodynamic equilibrium with the surface, bulk and interface. However, the presence of O_2 leads to the water forming reaction on the catalyst surface. At low pH_2 and high pO_2 the chemical reaction causes both the FET and the resistor to give a reading indicating lower pH_2's . At pH_2's above about 6 Torr, our Pd/Ni sensors show little effect from a pO_2 of 140 Torr (the pure Pd devices are destroyed by these pH_2's, so no data is available). It is beyond the scope of this paper to validate a particular detailed model of H_2-O_2 reactions on Pd and Pd/Ni thin films. Rather we show the practical results of both kinds of catalytic sensor in laboratory environments. The response of the Pd/Ni sensor at the higher levels of pH_2 and pO_2 is given special attention.

EXPERIMENT

A photograph of the SRH sensor is seen in Fig.1. The die size is approximately 270 by 120 mils. The large Al metallizations at both ends are power MOSFETs for heating the chip. The use of MOSFETs allows lower power consumption in the control circuits than resistive heaters. There are nine diodes for use as temperature sensors and ESD (electrostatic discharge) protection circuitry. The 6 pairs of catalytic gated FET's are in the center of the die. In practice only one FET is bonded out and no significant performance differences were observed with the different FET designs. The meander line H_2 sensing resistor can be seen in the lower middle of the chip. The catalytic gates and resistors are deposited in a sputtering process as the last step in the wafer fabrication. The sputter target for the Pd/Ni sensors has 9% (atomic) Ni. For both the Pd and Pd/Ni sensors the metallizations are 0.1 microns thick and the 20 micron wide meander line gives the Pd/Ni resistor about 1000 ohms base resistance. More fabrication details are given in Ref. [1].

A printed circuit board with the analog control circuit and signal processing is used for each sensor. The analog signals from the sensor read-out circuits are digitized and sampled by a LabVIEW

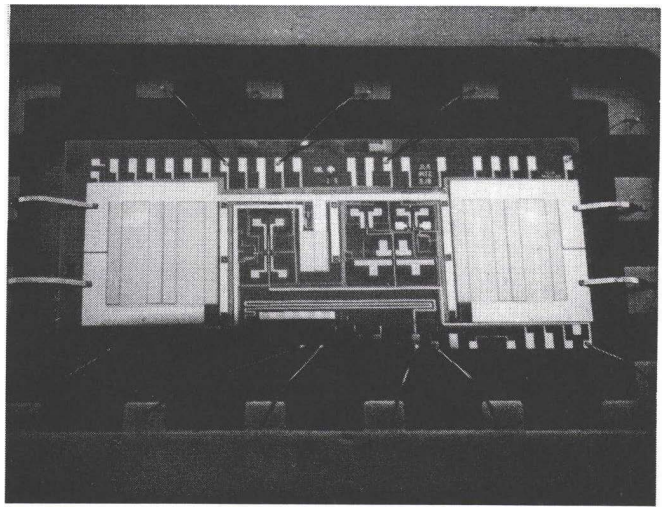

Fig. 1. A photograph of the SRH sensor mounted in a 16 pin DIP package. The die size is approximately 270 by 120 mils. The large Al metallizations at both ends are power MOSFETs for heating the chip. The 6 pairs of catalytic gated FET's are in the center of the die. The meander line H_2 sensing resistor can be seen in the lower middle of the chip.

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program. The data was obtained with a previously described Gas Sensor Test Bed [3], using a manifold that has fixtures for separate sensors in series with the flow of the mixtures. These experiments had one Pd SRH and one Pd/Ni(9%) SRH along with a commercial fuel cell oxygen sensor (Nyad, Inc., Concord, CA, model OS-2) in series. The flow rate for the data shown in this paper was held at one Standard Liter per Minute (SLM). Using a flow rate a factor of five lower did not change the signals for mixtures of H_2 and O_2. The atmospheric pressure in the laboratory is about 630 Torr; the back pressure due to the flow is only a few Torr, less than daily variations in pressure. The partial pressures given in this paper are either in % (because of common usage) or Torr.

RESULTS

Fig. 2a and 2b show typical data for one of the sensors, the Pd/Ni metallized device. In this case the device operating temperature was 80°C and the test protocol requires a 140°C anneal in synthetic air for 15 minutes in order to zero the FET before each series of test mixture pulses. The signal processing circuit [1] for reading the threshold voltage of the FET allows the analog output voltage to be zeroed with a potentiometer. Therefore the signal is proportional to the FET threshold voltage but is offset from the actual voltage. Each pulse of a gas mixture is followed by a "purge" or anneal in synthetic air.

Fig. 2a shows the FET results for two sets of pH_2 concentrations, 0.05% (500 ppm) and 4%, for a series of increasing pO_2's, 5%, 10%, and 20%. The last mixture is at the Lower Explosive Limit (LEL) for H_2-O_2 mixtures. Each data point is 10 seconds apart. The FET threshold voltage goes in a negative direction when exposed to H_2. It can be seen that the air purge at 80°C does not return the sensor reading to zero in the few minutes allotted in these experiments. That is the reason that the voltage at time zero is also not zero; there were other sets of pulses before the selected ones shown. There are some deeply adsorbed H_a's that require a longer or higher temperature purge for removal. For the pulses with 4% pH_2 the small effect of pO_2 mentioned above can be seen.

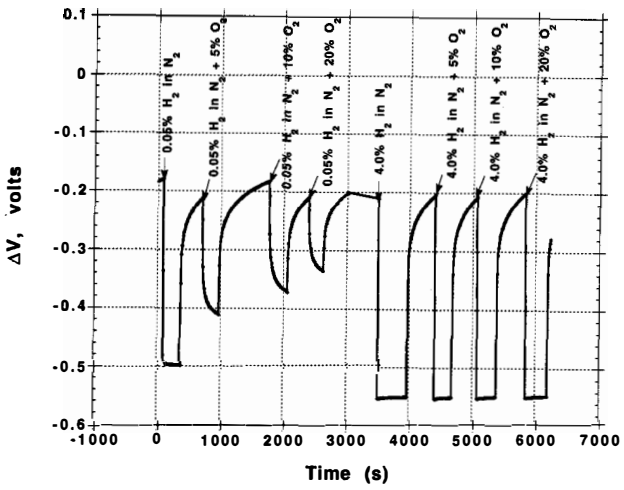

Fig. 2a. Pd/Ni FET operating at 80°C and exposed to several pulses of H_2-O_2 mixtures. The zero is defined as the FET threshold voltage after a 140°C anneal in air. H_2 causes the threshold voltage to move in the negative direction. Each pulse labeled in the Fig. is followed by a dry air purge before the next mixture is selected. Data points are 10 sec apart. The last pulse, with 4% pH_2 (25 Torr) and 20% O_2 (130 Torr), is at the lower explosive limit (LEL) for H_2-O_2 mixtures.

Fig. 2b shows the signal from the resistor on the same chip taken at the same time. The zero for the resistor was also set after the 140°C anneal and the pulses of H_2 before the sets shown have established a new baseline at a slightly negative value. This is a repeatable phenomenon for these resistor sensors. H dissolved in the bulk of the metal film increases the resistance because of increased electron scattering. The 0.05%(500 ppm) pH_2 pulse gives a very small signal, about 0.3 in units of % change in resistance over base resistance. Adding pO_2 reduces the signal to close to zero. The isotherm for the bulk concentration of H follows a ~$(pH_2)^{0.5}$ relation [3] and so the signal for 4% pH_2 is much larger. The result of adding a pO_2 of 20% (120 Torr) is a small reduction in signal. The fact that this mixture is at the lower explosive limit has little effect on the trend of the data; the temperature of the sensor is too low to support true combustion. The "error" in reading the pH_2 level without knowledge of the pO_2 level in this case is about 20% (i.e. the signal for the last pulse would correspond to 20 Torr instead of 25 Torr pH_2). Data taken with a higher pH_2, 252 Torr, shows no difference between pO_2=0 and 120 Torr.

The Nyad O_2 sensor gives accurate readings of the pO_2 even in the presence of H_2. Data has been taken up to 252 Torr pH_2 for 130 Torr of pO_2.

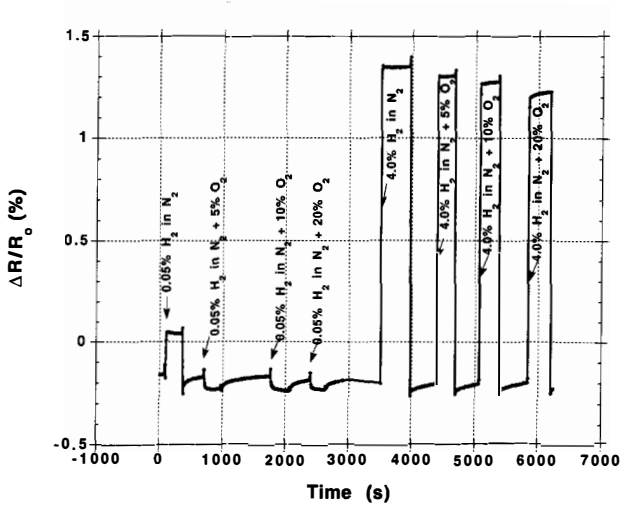

Fig. 2b. The Pd/Ni resistor data on the same sensor as for Fig. 2a taken at the same time. The value of zero is defined after the 140°C anneal and several H_2 exposures prior to the data shown here establish a new "zero" value for the resistor.

Figs. 3 and 4 show the steady state signals from both the Pd and Pd/Ni SRH FET sensors including the data from Fig. 2. The threshold voltage shifts, ΔV, in Figs. 3 and 4 were computed using the zero annealed value and the sign was changed to give consistent positive signals. The data for three temperatures is given for both pO_2 equal to zero and 20%. These data emphasize the fact that the ratio of the signals with and without O_2 are remarkably independent of temperature. The lines connecting the data points are guides to the eye. The thick dashed line in Fig. 3 is from a model described in the Discussion section.

Figs. 5 and 6 show the steady state signals from both the Pd and P/Ni resistor sensors including the data from Fig 2b. The signal is measured from the purge value in air to the steady state value. The resistance changes at a given pH_2 are quite temperature dependent because the solubility of H in the films decreases with increasing temperature. In order to show the temperature dependence of the O_2 effect, the data without O_2 at 80°C and 110°C have been normalized to the 50°C data by the following solubility constants: 1.5 times all

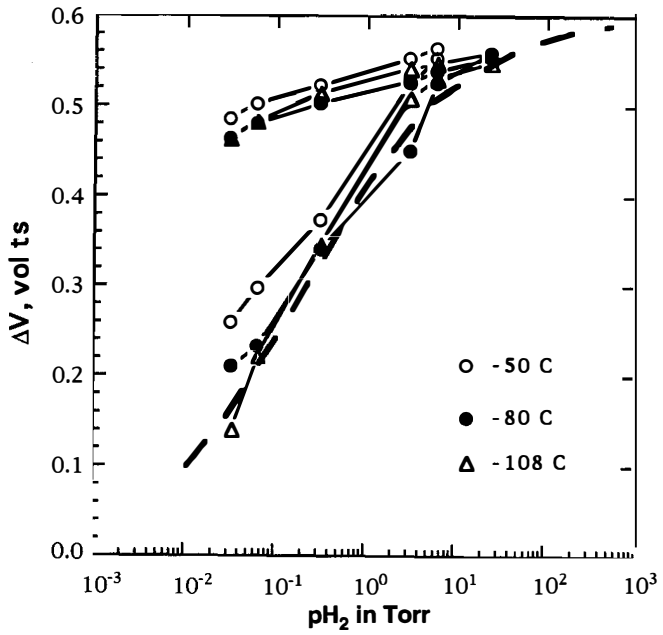

Fig. 3. The Pd/Ni FET threshold voltage shifts at the three indicated temperatures. The top three sets are the isotherms in N_2, while the lower curves are in 20% O_2. The zero value is defined after a purge in air at 140°C.

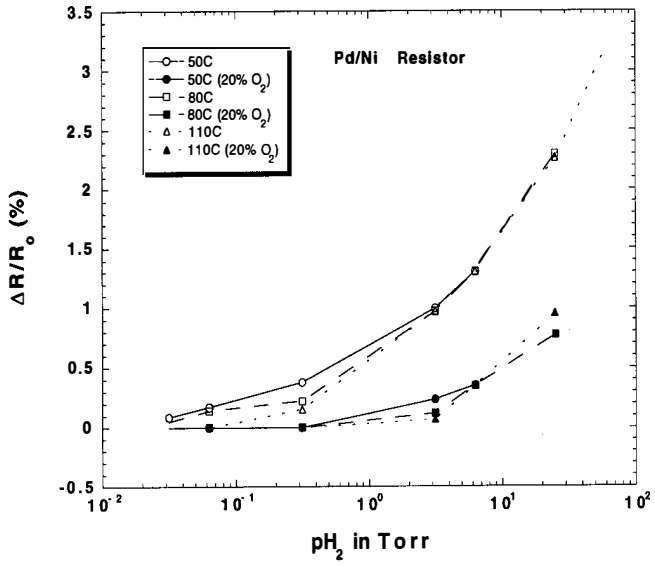

Fig. 5. The signals from the Pd/Ni resistor taken at the same time and on the same chip as Fig. 3. Examples of some of the data are seen in Fig. 2b. The temperature dependence due to H solubility has been normalized to show the lack of temperature dependence of the mixture signals. The lower data are for the mixtures with 20% O_2.

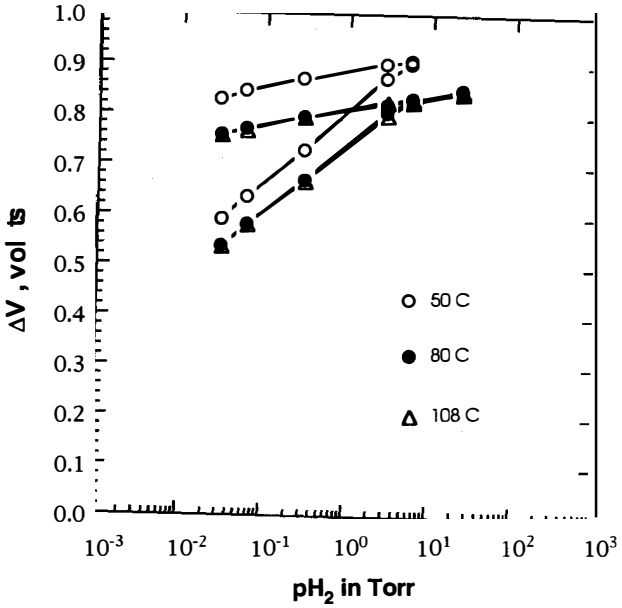

Fig. 4. Pd FET data at three temperatures. The top three sets are the isotherms in N_2, while the lower curves have 20% O_2. The zero value is defined after a purge at 140°C in air.

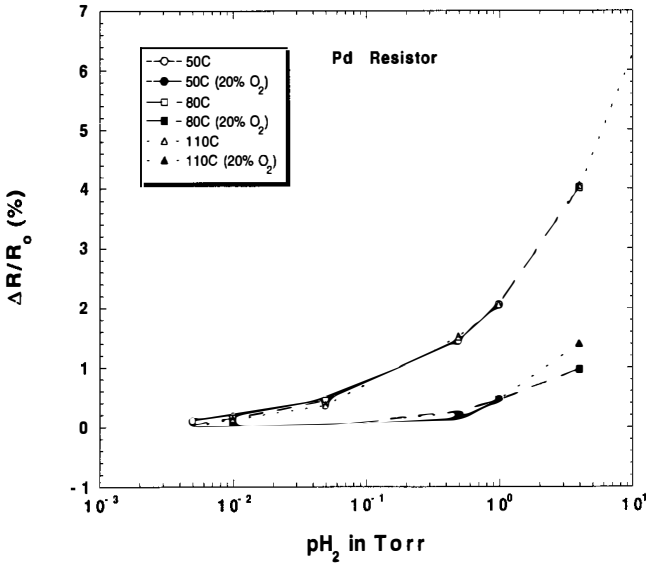

Fig. 6. The signals from the Pd resistor taken at the same time and on the same chip as Fig. 4. The temperature dependence due to H solubility has been normalized to show the lack of temperature dependence of the mixture signals. The lower data are for the mixtures with 20% O_2.

the 80°C data and 2 times all the 110°C data. All the steady state signal data with 20% O_2 were normalized to the 110°C data for clarity. The intent of plotting the data in this fashion is to emphasize that the same lack of temperature dependence of the pO_2 effect shows up in both the FET data and the resistor data.

DISCUSSION

The models for the effect of pO_2 on the signal from a given pH_2 mostly differ in assumptions about chemical reaction rate constants between species adsorbed on the catalyst surface. Since there are many possible species and values for the rate constants which are difficult to measure, it has been hard to "prove" one model over another. A particularly simple model given by Lundström [4] assumes that O_2 reacts directly with H_a and a steady state solution to the kinetic equations gives:

$$\Delta V/(\Delta V_0-\Delta V) = A/B\ (pH_2/pO_2)^{0.5}$$

where ΔV is the measured FET threshold voltage shift, ΔV_0 is the maximum shift seen at very high pH_2, A is a rate constant for H_2 dissociation and B is a rate constant for the O_2 reaction. The data in Figs. 3 and 4 with pO_2 can be fit fairly well with this equation. The dashed thick line in Fig. 3 shows one theory curve for a value of A/B.On a semilog plot like this different values of the A/B ratio simply translate the theory curve along the x axis. The lack of temperature dependence in the data can be rationalized by assuming that the rate constants A and B both have the same activation energy.

For pH_2's lower than about 1 Torr, there is an obvious difference in the pO_2 effect between Pd and Pd/Ni in Figs. 3 and 4. This difference can be used in a pattern recognition scheme to obtain values for unknown pH_2 and pO_2 values. One such scheme was given in Ref. [5] using Pd/Ag and Pd tunnel diode sensors. So far this procedure has not proven to be very reliable because different sensors, which should be close to identical, give different A/B ratios depending on the cleanliness of the catalytic surface and other undefined conditions [4].

In addition, all the pattern recognition schemes fail for high pH_2 where there is no effect on the sensor signal from pO_2. The Nyad O_2 sensor was shown to provide accurate pO_2 values even in the presence of high pH_2, up to 252 Torr. There are many potential users who wish to know the pH_2 as accurately as possible in order to know if an explosive mixture exists. Combining an SRH and fuel cell pO_2 sensor is one way to solve the problem, although other oxidizing gases, like N_2O, will also form explosive mixtures with H_2. Another solution would be to use a combustible gas sensor of the pellistor type to diagnose explosive mixtures. A silicon micromachined pellistor filament could be integrated with the SRH sensor, and although the pellistor technology is notoriously difficult to maintain in calibration, useful information about potentially flammable mixtures could be obtained.

In summary, we have shown that both the Pd and Pd/Ni gated SRH-FET structures respond to H_2-O_2 mixtures in a similar fashion to other field effect Pd devices reported in the literature [2,4]. The FETs can sense the presence of H_2 reliably down to about 10 ppm (~10 milliTorr) in air, but the exact concentration will be undetermined unless the pO_2 is known from other measurements (or if the sensor in outdoors and it can be assumed that pO_2~20%). The Pd/Ni FET gives reversible measurements of pH_2 up to pure H_2 as long as the sensor chip temperature is >50°C.

The resistor sensors do not give reliable readings for less than about 1 Torr pH_2 in air, although for pO_2=0, they can sense pH_2 to quite low levels. This behavior can be easily understood if it is assumed that the bulk concentration of H follows the same equilibrium relationship to H_a with or without O_2 present. The Pd/Ni resistor gives accurate readings of pH_2 above ~10 Torr, in particular around the LEL for H_2 of 30 Torr. We are investigating other alloys of Pd with the intent of finding one that is so sensitive to pO_2 that pattern recognition can be used to determine both pH_2 and pO_2 at high pO_2 levels.

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