

## Thin Film Porous Membranes for Catalytic Sensors

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## Summary

This paper reports on new and surprising experimental data for catalytic film gas sensing resistors coated with nanoporous sol-gel films to impart selectivity and durability to the sensor structure. This work is the result of attempts to build selectivity and reactivity to the surface of a sensor by modifying it with a series of sol-gel layers. The initial sol-gel SiO<sub>2</sub> layer applied to the sensor surprisingly showed enhanced O<sub>2</sub> interaction with H<sub>2</sub> and reduced susceptibility to poisons such as H<sub>2</sub>S.

**Keywords:** gas sensor, sol-gel, Pd alloy

## Introduction

Nanoporous sol-gel based films are finding a wide variety of uses including gas separations and supports for heterogeneous catalysts [1]. The films can be formed by spin or dip coating, followed by relatively low temperature annealing. We are investigating the properties of these films as coatings for protection of catalytic film sensors and as the basis for a multilayer chemical sensor structure that contains catalytic layers for decomposing an analyte into easily detected molecules.

The basic design of the proposed sensor system is a catalyst layer, sandwiched between a top and bottom porous thin film SiO<sub>2</sub> membrane all of which are deposited on a chemical sensor surface. While work on producing modified catalytic sandwich are underway, we have found some very interesting results by the initial SiO<sub>2</sub> modifying layer.

In this report we will describe results for nanoporous films on a thin film catalytic hydrogen sensor. The first requirement for a coating is that it not severely degrade the hydrogen sensing performance compared to the uncoated sensor. All the porous coatings that we have tested pass molecular hydrogen easily and do not poison the catalyst surface where dissociation of molecular hydrogen to atomic H must occur for the sensor to operate. We had hoped that the nanoporous nature of the films would prevent other molecules from interfering with the molecular hydrogen signal. We obtained some interesting, unpredicted behavior in this regard, which shows that the mechanism of sensing hydrogen when mixed with other gases is not completely understood.

In particular, mixtures of H<sub>2</sub> and O<sub>2</sub> were studied because of the common occurrence of such mixtures. On bare catalytic surfaces O<sub>2</sub> competes with H<sub>2</sub> for adsorption sites, which usually causes the sensor to give a signal which would be characteristic of a lower partial pressure of H<sub>2</sub> in an inert atmosphere [2]. We had hoped that the nanoporous coating would reduce the concentration of O<sub>2</sub> and give a H<sub>2</sub> signal independent of O<sub>2</sub> partial pressure. This did not occur, and for some coatings, the catalytic activity of O<sub>2</sub> actually increased. Fortunately the effect is not so large as to completely obscure the H<sub>2</sub> signal.

We obtained very encouraging results when we compared poisoning of the Pd based catalyst sensors by H<sub>2</sub>S. The sol-gel coated sensors were unaffected by high concentrations of the poison, while bare sensors showed moderate to severe poisoning effects.

## Design and Fabrication:

The basic sensor investigated was a thin film meander line resistor of a Pd/Ni alloy which we have characterized as a molecular hydrogen sensor for a wide range of partial pressures [3]. The catalytic films are deposited through a shadow mask on device grade SiN on a Si wafer using a dual e-beam evaporator. The films were 100 nm thick and had 10 at. % Ni. An adhesion layer of Ti of 10 nm thickness is used for durability. The substrate temperature was maintained at room temperature during the deposition, and the pressure was  $(1 - 2) \times 10^{-6}$  Torr. The devices were annealed in a tube furnace using 2% H<sub>2</sub> in N<sub>2</sub> for 2 h at 350 C.

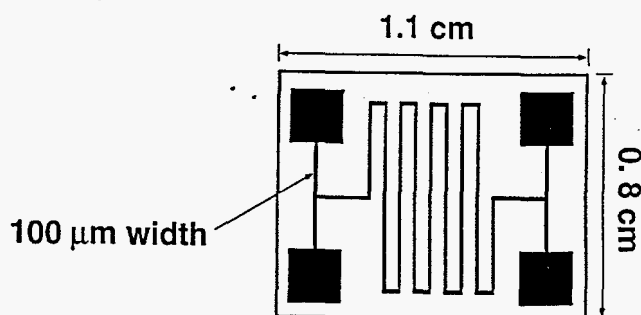


Fig. 1. Sensor pattern and dimensions on Si wafer.

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The mask design has four pads in the corners of a 1 cm<sup>2</sup> chip which can be used for a four terminal resistance measurement—using spring loaded pogo pins so that wire bonding is not required to obtain reliable resistance readings of the sensor films. The design is shown in Fig. 1.

Another advantage of this design is that the sensor can be removed and have other processing performed (such as, annealing or microscopy) with having to break permanent electrical connections.

The sol-gel layers were dip coated onto the chips and annealed in a tube furnace under reducing conditions (2% H<sub>2</sub> /N<sub>2</sub>) to produce a silica film. The SiO<sub>2</sub> films (referred to as A2\*\*) are a two-step acid catalyzed gels synthesized from silicon tetraethoxide, ethanol, water and HCl [1]. We found that we are unable to use the normal calcining process for these films which is in air at 400 to 550 C. These temperatures with O<sub>2</sub> cause oxidation and delamination of our thin film sensors. Instead our drying and annealing of the coated sensors was done in a reducing atmosphere (2% H<sub>2</sub> in N<sub>2</sub>) at temperatures from 50 C to 400 C. While these films have an obviously glassy appearance under a microscope, we do not know whether their nanostructure is the same and have the same sorption and permeation properties as films reported in [1].

## Results

The sensors were mounted in fixture wherein six sensors were exposed to gas mixtures at the same time and their four-terminal resistances can be sequentially measured in about 10 seconds. The fixture is in an oven which is inside a large hood so that toxic and corrosive gases can be tested. The sensors can be maintained at any temperature between about 25 C and 110 C in the oven for data acquisition. The gas flows are kept at one Standard Liter per Minute (SLM) by a bank of flow controllers in the hood. The sensors are tested by pulses of H<sub>2</sub> mixed with N<sub>2</sub> or other gases so that both the transient and steady state responses can be monitored.

**H<sub>2</sub> / O<sub>2</sub> Sensing:** Fig. 2 shows the responses of three different sensors to pulses of H<sub>2</sub> and H<sub>2</sub> mixed with O<sub>2</sub>. Sensor HTR 16.3 has the sol-gel coating. The sensor temperatures during measurement are all 80 C, and HTR 16.3 and HTR 9.4 had both received the same 150C anneal in a separate tube furnace. HTR9.3 is left in the test fixture as a control. It can be seen that there is little difference in the time response of the coated sensor vs. uncoated. The steady state response is normalized in units of  $\Delta R/R_0$  where  $R_0$  is the base resistance at the temperature of the sensor. The difference in the magnitude of the steady state response is typical of sensors of this type; the fact that the coated sensor has a slightly larger signal is probably not significant.

However the difference in response to mixtures of H<sub>2</sub> and O<sub>2</sub> is quite significant. We show two different partial pressures of O<sub>2</sub> while holding the partial pressure of H<sub>2</sub> constant during the pulses.

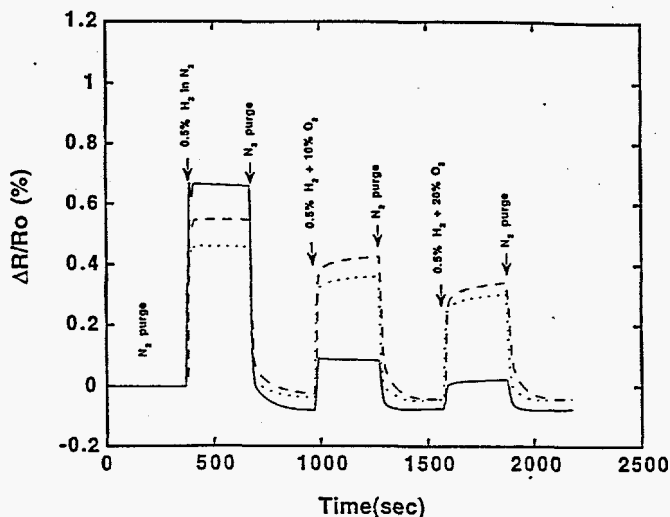


Fig. 2 The resistance change of three Pd/Ni sensors to pulses of the mixtures indicated. Flow rate is always one. SLM, with N<sub>2</sub> as the make-up gas. Sensor HTR 16.3 has the silica coating. The sensor temperatures are all 80 C, and sensors 16.3 and 9.4 had both received a 150 C anneal.

The ratio of the response with no O<sub>2</sub> present and with excess O<sub>2</sub> (e. g. 20%) was surprising. We had hoped that the very small pores in the A2\*\* silica would reduce the concentration of O<sub>2</sub> reaching the catalytic sites on the Pd/Ni surface, resulting in a signal independent of O<sub>2</sub> partial pressure. Not only did this not occur, but the signal on the 16.3 (coated) sensor is smaller than on the uncoated sensors. One would expect this result for a very clean catalyst surface in an ultra high vacuum when there is an excess of O<sub>2</sub> (i.e. more O<sub>2</sub> than necessary to react with all the H<sub>2</sub>). The result of "enhanced" catalysis of the H<sub>2</sub>-O<sub>2</sub> reaction as shown in Fig.2 is reproducible on the same sensor if there are no further high temperature anneals. However, the same coated sensor annealed at temperatures from 250 C to 400 C shows results very similar to the uncoated sensors as far as the H<sub>2</sub>-O<sub>2</sub> mixture is concerned. We were not able to find an annealing protocol that would exclude O<sub>2</sub> from the reaction and give an H<sub>2</sub> signal independent of O<sub>2</sub> partial pressure.

**Poisoning by H<sub>2</sub>S:** It is well known that many sulfur containing compound act as poisons for catalysts. In chemical process catalysts poisoning will show up as a drop in yield of the desired chemical product. In a catalytic converter on a car it will show up as an increase of undesirable pollutants in the car exhaust. In catalytic sensors like the Pd/Ni resistors under discussion here it shows up as

a slow response to pulse of  $H_2$  of a given partial pressure. The usual model is that the sulfur compound decomposes on the Pd surface and forms a strong Pd-S bond which blocks further catalytic activity on that site. We performed tests to determine the amount of protection the A2\*\* sol imparts to the Pd/Ni surface against poisoning by  $H_2S$ . Six sensors were tested at the same time. The sensor temperatures were held at 34 C in the oven in our hood. Two of the sensors were sol-gel coated

### Sol-gel Coated Sensor (16.1)

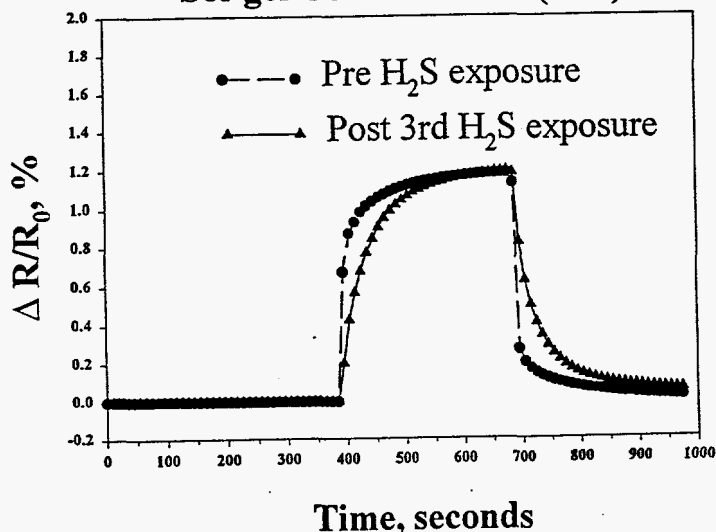


Fig. 3 Pre and post poisoning signals from HTR 16.1.

and had been annealed at temperatures up to 400 C in 2%  $H_2/N_2$  and had undergone a large number of tests with  $H_2-O_2$  mixtures. A third sensor in the group of identical sensors was an uncoated meander line sensor, 9.3, our control sensor from Fig. 2.

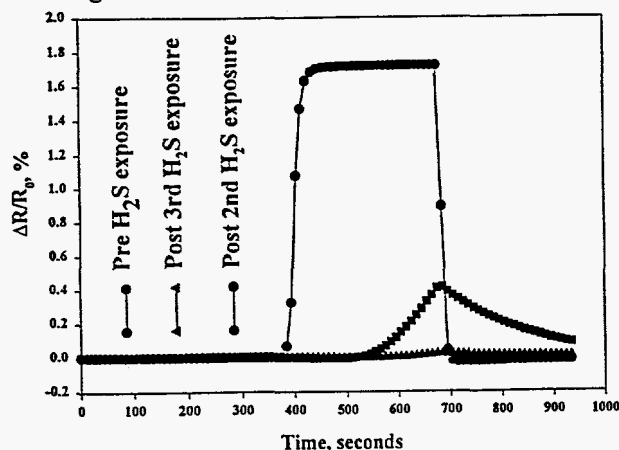


Fig. 4 Pre and post poisoning from WRS sensor.

The other three sensors were of a design called "Wide Range Sensor" (WRS), in which the resistors are formed from a photolithography process along with a heater and temperature sensor on the same substrate. The Pd/Ni metallurgy was the

same as on the other sensors, the only difference being the processing of photolithography vs. shadow mask a geometry. All six sensors were exposed to a test pulse of 0.5%  $H_2$  as in our earlier tests, followed by a purge of synthetic air. Then all six sensors were exposed to 1000 ppm of  $H_2S$  in  $N_2$  at 34 C in three separate tests. For the sensor shown in Fig. 3, the exposure was for 30 minutes. The sensors were then re-tested by a pulse of 0.5%  $H_2$  followed by the purge.

A composite of the pre and post signals from HTR 16.1, a coated sensor, is shown in Fig. 3. Little effect from the  $H_2S$  is noted. Fig. 4 shows the large effect on one of the WRS sensors, where virtually no response can be seen from the third  $H_2S$  treatment. The small signal from the shorter second treatment is also shown. It has the interesting characteristic of a long "induction" period of no response, followed by a slow response. The bare sensors could be rejuvenated by annealing in air above 100 C for > 60 min.; The S compounds are probably burned off. Fig. 5 shows the poisoning effect on 9.3. It is not as marked as for the three WRS sensors, but is notable nevertheless. The coated sensor HTR 15.3 also showed little effect from the  $H_2S$  under the conditions used here.

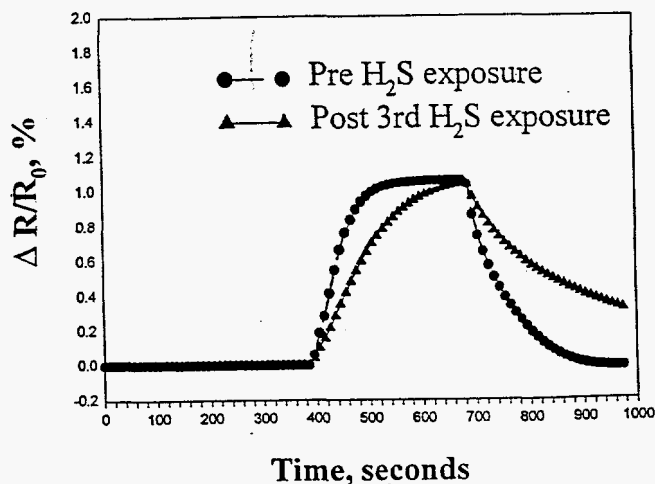


Fig. 5 Pre and post poisoning from uncoated sensor HTR 9.3.

### Discussion

The experimental results for sensing on the coated Pd/Ni films requires an updated model for the mechanism of sensing [2]. A body of work by Maier et al., over the last few years [4,5] presents the hypothesis that silica layers over catalysts, like Pt, do not destroy catalytic behavior. Molecular hydrogen must diffuse through the silica to the Pd/Ni surface and dissociate into atomic H. The generated atomic hydrogen can migrate from the catalyst surface through the silica glass and perform catalytic chemistry at

the gas-solid interface. This phenomenon is sometimes called the "spill-over" effect, where active H can appear in locations physically separate from the catalyst atoms. Thus our results indicate that the steady state coverage on H<sub>2</sub> on the Pd/Ni surface (which is in equilibrium with the bulk concentration of H and causes the resistance change) is strongly influenced by reactions with O<sub>2</sub>, 100 nm from that surface. The concentration profile of atomic H in the silica film resulting from the H<sub>2</sub>-O<sub>2</sub> reaction must then be reflected on the surface coverage of the atomic H on the Pd/Ni surface. This in turn must influence the steady state concentration of absorbed H in the bulk of the Pd/Ni film, producing the signals shown in Fig. 2. The poison resistance effect must stem from the inability of the H<sub>2</sub>S molecule to diffuse through the silica film and block the Pd sites. This effect in active hydrogenation catalysts has been demonstrated by Maier and co-workers [5].

### Conclusion

Modifying the surface of the sensor with a SiO<sub>2</sub> layer has enhanced the O<sub>2</sub> interaction with H<sub>2</sub> of the sensor and reduced its susceptibility to poisoning from H<sub>2</sub>S. From a sensor performance standpoint, this is a very encouraging result. Sensors are often required to operate in chemically hostile environments for extended periods of time. A coating which imparts poison resistance and protects the catalytic film from other hazards like condensed water and dust, while not degrading the performance for detecting hydrogen, is a great improvement.

While we have not yet achieved the goal of blocking O<sub>2</sub> from catalytic activity, it may be that the "spill over" effect will prevent us from achieving independence from any of the oxidants. This remains to be tested in future experiments.

A positive result from the data in Fig. 2 is that the large difference in response of the coated and uncoated films allowed us to employ a pattern recognition scheme [6] to classify mixtures of H<sub>2</sub> and O<sub>2</sub> and to actually extract the individual H<sub>2</sub> and O<sub>2</sub> concentrations in cases where both are unknown. Data was taken on many more concentrations than shown in Fig. 2 and these results with the pattern recognition will be reported in a later publication.

The basic design of the proposed sensor system is a catalyst layer, sandwiched between a top and bottom porous thin film membrane all of which are deposited on a chemical sensor surface. These results also show that thick sol-gel coatings on Pd/Ni films do not destroy the sensor's ability to detect hydrogen. Addition of the double alkoxide catalytic layer as a [NaTi(OR)<sub>5</sub>] which can be ion exchanged to form a RhTi catalyst has already been demonstrated. Work is

currently underway to investigate the catalytic decomposition of a wide variety of organic species and further production of H<sub>2</sub> selective membranes.

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