Thin Film Porous Membranes based on Sol-Gel Chemistry for Catalytic Sensors.

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ABSTRACT

Nanoporous sol-gel based films are finding a wide variety of uses including gas separations and supports for heterogeneous catalysts. The films can be formed by spin or dip coating, followed by relatively low temperature annealing [1]. We used several types of these films as coatings on the Pd alloy thin film sensors we had previously fabricated and studied [2]. The sol-gel films have little effect on the sensing response to H_2 alone. However, in the presence of other gases, the nanoporous film modifies the sensor behavior in several beneficial ways. 1) We have shown that the sol-gel coated sensors were only slightly poisoned by high concentrations of H_2S while uncoated sensors showed moderate to severe poisoning effects. 2) For a given partial pressure of H_2, the signal from the sensor is modified by the presence of O_2 and other oxidizing gases.

INTRODUCTION

Thin films of catalytically active materials have a long history of use as gas sensors. There are a variety of physical and chemical principles involved in the detection of the gas phase species [3]. The best known is the Taguchi type sensor where a thin film of a metal oxide semiconductor (often SnO_2) is "doped" with salts of catalytic metals like Pt and Pd. The detection of oxidizing and reducing gases occurs when the resistance of the thin films is changed in a background of normal O_2 concentration. The catalyst will promote the surface reaction between, for example, a hydrocarbon or H_2 and O_2 and the film resistance will drop because of the reduced oxygen coverage. Different catalytic metals produce relative changes in the sensitivity of the detection for different species to be detected and also affect the temperature dependence of the sensitivity. A large number of papers have been published on the sensitivity of these metal oxide sensors as a function of the type of materials and fabrication procedure; very large differences in sensor performance are found [3] and the differences in sensitivity for various species are used to build sensor arrays that can distinguish one chemical species from another using pattern recognition techniques. [3].

Another widely used catalytic metal based gas sensor is the combustible gas sensor, which again only works in a background of normal O_2 partial pressure. The principle is much more simple than the Taguchi sensor: the catalytic film is thermally isolated on a temperature sensor like a Pt wire, and the heat from the catalytic reaction of the combustible material (natural gas, many hydrocarbons, etc.) with O_2 is detected as a temperature rise, or a drop in power required to maintain constant temperature [3].

In this paper we discuss results for a different type of gas sensing resistor: thin films of Pd alloys that change resistance specifically in response to molecular hydrogen partial pressures. They work best when no oxidizing species like O_2 is present The catalysis in this type of sensor is the dissociation of molecular H_2 into atomic H on the surface of the Pd alloy and the quick absorption of H into the bulk of the metal film. The concentration of H in film is proportional to the external H_2 partial pressure and the resistance of the film is also proportional to the concentration of H in the metal lattice because of conduction electron scattering. Unlike the Taguchi sensor and the combustible gas sensor where the kinetics of reaction determine the size of the sensor response, these Pd alloy films are in thermodynamic equilibrium with the H_2 partial pressure which makes for a more stable a reproducible response. Although less well known and commercially limited, Pd type sensors have a considerable literature on the mechanism of response and performance [4].

Sensors that depend on gas phase heterogeneous catalysis all suffer from similar problems. The most serious is the poisoning of the catalyst, which usually means a large reduction in the chemical kinetic rates that the sensor depends on for speed and accuracy. Another closely related problem is the control of the relative rate constants for different reactions; this is important for obtaining selectivity in sensor arrays. In this digest paper we discuss the use of thin, deposited sol-gel films on the catalytic sensor films to protect against poisoning and to modify and stabilize catalytic reaction rates between species [5,6].

EXPERIMENTAL

DISCLAIMER

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 [2]. 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 sol-gel layers were dip coated onto the chips and annealed in a tube furnace under reducing conditions (2% H_2 /N_2) to produce a silica film. The SiO_2 films (referred to as A2**) are two-step acid catalyzed gels synthesized from silicon tetraethoxide, ethanol, water and HCl [1]. The details of the several different kinds of sol-gel layers that we have studied are given in [6]. The sensors have different catalytic properties when the sensor response to H_2/O_2 mixtures at 50°C is studied as a function of the higher annealing temperature of the sensor structure. In this digest paper we report on the effect of a 150°C anneal. The effect of other annealing temperatures will be reported in the full paper.

RESULTS AND DISCUSSION

A comparison of the sensor response of a coated and uncoated Pd/Ni thin film sensor is given in Fig. 1.

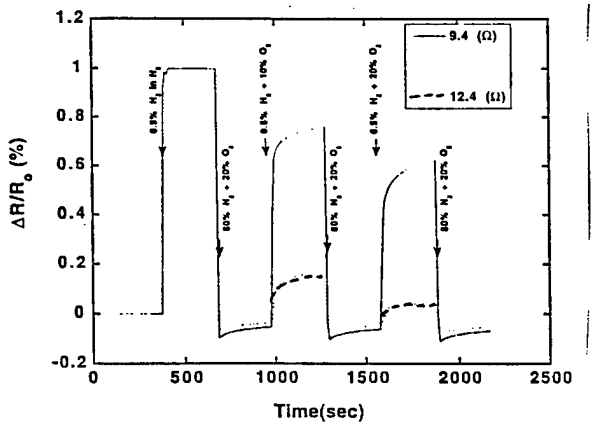

Fig. 1 Sensor responses to H_2 and O_2.

The peak response for either sensor to a pulse of 0.5% H_2 has been normalized to unity for purposes of comparison when O_2 is mixed with the H_2. The speed of response is close to the same for both the uncoated and coated sensor films; both take only a few seconds to reach full response. The purge in synthetic air is also very fast, but shows a small undershoot in resistance value which recovers in time to the initial baseline. The subsequent pulses with two different O_2 concentrations shows the large difference in response between the coated (labeled 12.4) and uncoated sensor (9.4) for the mixtures.

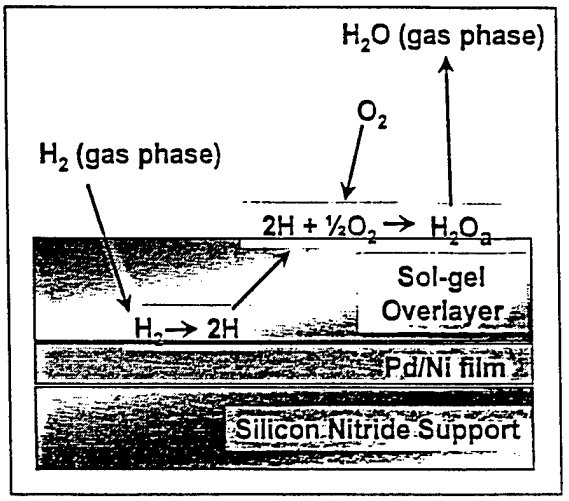

Fig. 2 Cartoon of sensor structure and reactions of H_2 and O_2.

A hypothesis for the effect of the film overlayer is given in the cartoon of Fig. 2. Molecular hydrogen easily passes through the 100 nm thick sol-gel film. The fast response of the coated sensor to H_2 alone shows that the catalytic sites on the Pd are not poisoned by the SiO_2 layer. However, the small response in the presence of 20% O_2 indicates that a fast water forming reaction between atomic H and the O_2 is occurring on the outer surface of the sol-gel film where the O_2 concentration is very high. This reaction is apparently more efficient than that on a uncoated film, which is an unexpected result.

We recently reported that similar sol-gel films provide protection against catalyst poisoning by H_2S [5,6]. The hypothesis based on Fig. 2 is that the H_2S molecule must reach the Pd metal sites to cause the poisoning by chemically bonding to Pd atoms. With the sol-gel film in place, the H2S can not reach the Pd atoms, but the H atoms can come to the outer surface to do reactions like the water formation.

We can use the difference in the reaction rates between the uncoated and coated sensor to make an independent determination of unknown concentrations of H_2 and O_2.

Fig. 3 shows a plot of the actual responses from the two sensors shown in Fig. 1 against each other to a wide variety of H_2 and O_2 concentrations (including the ones shown in Fig. 1). The top curve shows the responses to H_2 alone (solid dots as shown in

legend). Addition of the various levels of O_2 concentrations gives a string of points for each H_2 concentration. A new gas sample with an unknown concentration of both species can be analyzed by placing the new pair of responses on the graph and interpolating the concentrations from the two nearest known responses in the graph. There are some points in Fig. 3 that are repeats of the same concentrations and the repeatability can be seen in the spread of those points.

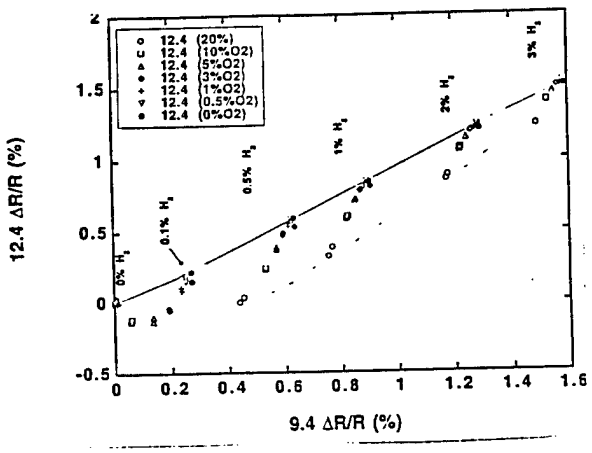

Fig. 3 Responses of a coated and uncoated sensor plotted against one another for a large number of H_2 and O_2 concentrations.

It can be seen that the accuracy in determination of the H_2 concentration is much higher than for the O_2 concentration, particularly for the lower O_2 concentrations, 0 to 1%. However the accuracy is good enough to give a warning that the H_2 and O_2 concentrations are approaching explosive levels. (any concentrations below 4% H_2 and 20% O_2 are non-explosive).

CONCLUSIONS

We have shown that nano-porous sol-gel based films have several important beneficial effects on gas sensors that rely on gas-solid catalysis for their operation. The films can protect the catalyst surface atoms from poisoning by species like H_2S. The films can also modify the catalytic reaction rates of important reactions like the H_2-O_2 water forming reaction. This effect was exploited to show that a two sensor array can the determination of unknown H_2 and O_2 concentrations over an important range near the explosive limits. These films may also show beneficial effects on other kinds of catalyst based gas sensors, like the Taguchi and combustible gas sensor. Many experiments remain to be done to show the full potential of these thin, nanoporous films.

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REFERENCES

[1] C. J Brinker, S. Wallace, N. Raman, R. Sehgal, J. Samuel and S. M. Contakes, "Sol-gel Processing of Amorphous Nanoporous Silicas: Thin Films and Bulk", in *Access in Nanoporous Materials,* T. J. Pinnavaia and M. F. Thorpe, Eds. Plenum Press, NY, 1995.

[2] "Sensors for detecting molecular hydrogen based on Pd metal alloys", R. C. Thomas and R. C. Hughes JECS 144, 3245-3249 (1997)

[3] *Techniques and Mechanisms in Gas Sensing*, P. T. Moseley, J. O. W. Norris, and D. E. Williams, Eds., IOP Publishing (Adam Hilger Series on Sensors), Bristol, England (1991).

[4] I. Lundstom, M. Armgarth and L.-G Peterson, CRC Crit. Rev. Solid State Mater. Sci., 15, 210 (1989)

[5] "Thin Film Porous Membranes for Catalytic Sensors", R. C. Hughes*, T. J. Boyle*, T. J. Gardner*, C. J. Brinker* and Ross Thomas**
Technical Digest, Transducers '97, IEEE, New York (1997), page 581

[6] T. J. Boyle, T. J. Gardner, R. C. Hughes, C. J. Brinker and A. G. Sault, " Catalytic Membrane Sensors. A Thin Film Modified H_2 Resistive Sensor for Multi-Molecular Detection." to be published in Comments on Inorganic Chemistry.

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