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THE DETECTION OF MIXTURES OF NOx'S WITH HYDROGEN USING CATALYTIC METAL FILMS ON THE SANDIA ROBUST SENSOR WITH PATTERN RECOGNITION.

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SUMMARY

Microsensors often do not have the selectivity to chemical species available in large laboratory instruments. A new type of pattern recognition algorithm is used to classify mixtures of H_2 with NO_2 and O_2. The microsensors used are thin film catalytic metal field effect transistors and chemiresistors on the Sandia Robust Sensor platform. For this study pure Pd thin films and Pd/Ni alloys are shown to provide good classification of mixtures containing NO_2 from those containing O_2 or no oxidant.

INTRODUCTION

Since the discovery 20 years ago of the hydrogen sensitivity of palladium gated field effect structures by Lundström, et al [1], many variations on the basic thin film catalytic metal have appeared in the literature. It was found that various kinds of thin film structures produce sensitivity to hydrogen containing molecules and mixtures of oxidants with those reductants. Sensitivity to ammonia is achieved with several combinations of very thin metals (Pt) with thicker contact layers [2]. Ethanol and methanol have been done with pattern recognition of large area field effect structures with metal and temperature gradients and light response images [3]. CO can be selected by modified gate structures of Pd and Pt [4]. Suspended gate structures can detect vapors that enter the gap between the suspended gate material (which can be a conducting polymer or other metals) and the FET insulating surface [5]. In this paper we describe results obtained with combinations of catalytic alloys and the use of a new pattern recognition algorithm which had not previously been used with data from catalytic metal gas sensors.

EXPERIMENT

The Sandia Robust Hydrogen Sensor (SRH) provides a manufacturable electronic platform for a wide variety of catalytic alloys. The fabrication steps have been given previously [6], and the response to H_2-O_2 mixtures has also been detailed [7] The field effect transistor (FET) on the chip gives good information about low partial pressures of H_2 (pH_2), but its logarithmic response limits the accuracy at higher pH_2 values. The resistors made of the same catalytic alloy are not accurate at low values, but give a response that is roughly linear in the square root of pH_2 at higher pressures. However, the signal from a given pH_2 may change if an oxidizing agent is present, like O_2 or NO_x concentration of these reactants is high enough, flammable mixtures occur. Lower concentrations of NO_X are of interest for pollution control. We have found that mixtures of oxidizing and reducing agents do not always give the same sensor response on sensors with different catalytic alloys, for example pure Pd vs. alloys of Pd with Ni. We have used a five sensor array with the Sandia pattern recognition algorithm [8] to classify. H_2 mixtures with NO_2 vs. O_2. The five sensors include a pure Pd field effect transistor(FET) and resistor, a separate SRH Pd/Ni(9%) FET and resistor and a Nyad electrochemical oxygen sensor (commercial product). We have found that the Nyad sensor only responds to pO_2 and gives the correct value even with the highest pH_2 and the pNO_x values studied here (up to 200 ppm).

One of the tasks of the pattern recognition algorithm is to treat sensor array data with an arbitrary number of sensor inputs. Thus each of the five sensors described can be a sensor input, and each of the SRH sensors operating at a different temperature can be a sensor input. The algorithm decides how many sensor inputs are required to give a classification of the gas mixture seen by all the sensors.

RESULTS

As an example of classification, Fig. 1 shows how mixtures containing NO_2 can be distinguished from mixtures with O_2. or no oxidant at all (only H_2). This three dimensional plot only uses three of the sensor inputs, the Pd resistor (80°C), the Pd/Ni FET(80°C) and on the vertical axis, the oxygen sensor. The three classes chosen are 1) H_2 - open circles, 2) H_2 w/ O_2. - shaded circles, and 3) H_2 w/ NO_2 - solid circles. From the five sensor responses at 80°C, the group of three providing

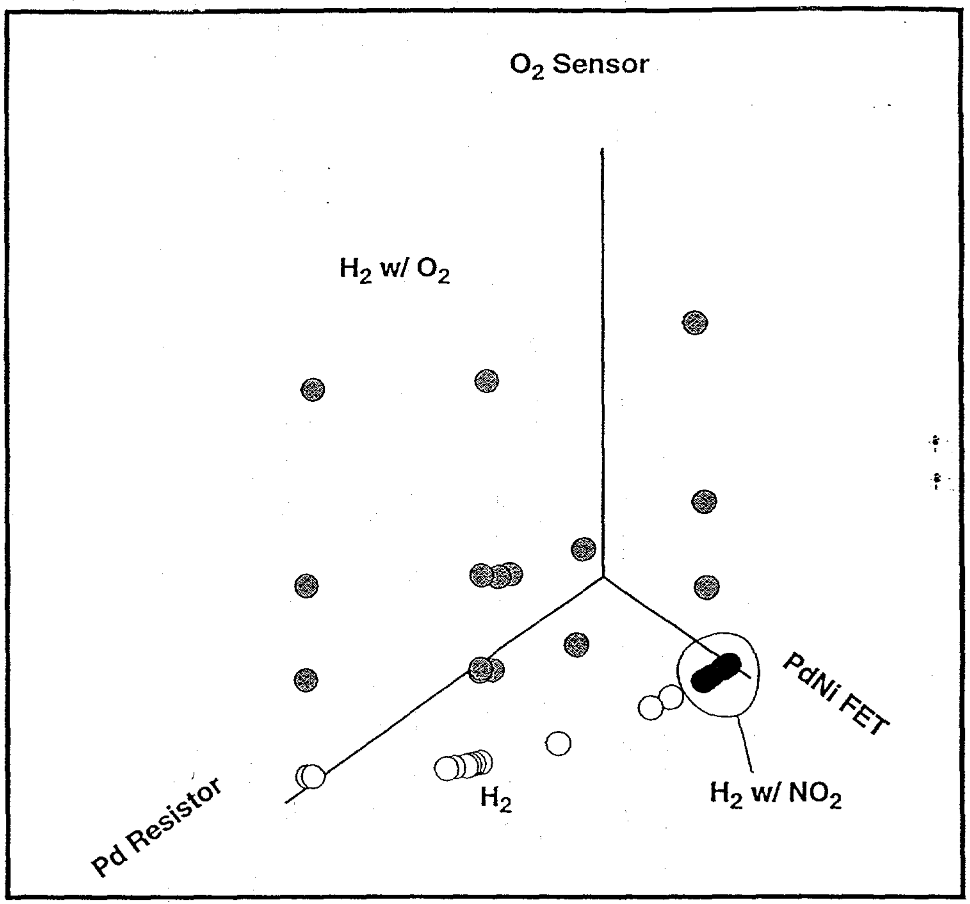

Figure 1. Three dimensional pattern recognition plot showing classification of mixtures. Each dot is for a specific mixture with the highest pO_2 (20%) and pH_2 (4%) appearing in the upper left hand corner. Note the grouping of all the pH_2 concentrations with NO_2 in the lower right hand corner.

the greatest class separation was chosen. The classification algorithm equalizes the maximum responses of each of the three sensors. Since the O_2. sensor separates O_2. concentrations exclusively, only the two remaining sensor responses are normalized to provide a vector response. The resulting spread of classes lie on a cylindrical surface with the O_2. sensor axis as the axis of rotation. The PdNi FET sensor and Pd Resistor sensor separate the different concentrations of H_2. This initial classification does not reveal the concentration of the various gases, but clusters them in a class; the solid circle cluster for H_2 /NO2 contains many different H_2 and NO_2 concentrations. Once classification (i.e. the presence of certain molecules) is performed, a separate algorithm can be used to estimate individual concentrations. In this way, flammable mixtures of H_2 and O_2. were distinguished from non-flammable mixtures, a very important application of the array technique.

The detailed response of the various catalytic metals to the gas mixtures has not been predictable from any theory of catalysis. The temperature dependence of the responses to both O_2. [7] and NO_2 were unexpected (but reproducible). The basic feature of the data that allows the classification is that the presence of small values of NO_2 blocks the signal from a given pH_2 on a pure Pd surface much more than on the Pd/Ni surface. As an example of this kind of data, Fig. 2 shows the response of the two kinds of catalytic resistors to a series of pulses of pH_2 and pNO_2. Each pulse lasts for 5 min. followed by 5 min. of purging with dry air. The upper trace is from the Pd resistor and it can be seen that a mixture of 5000 ppm

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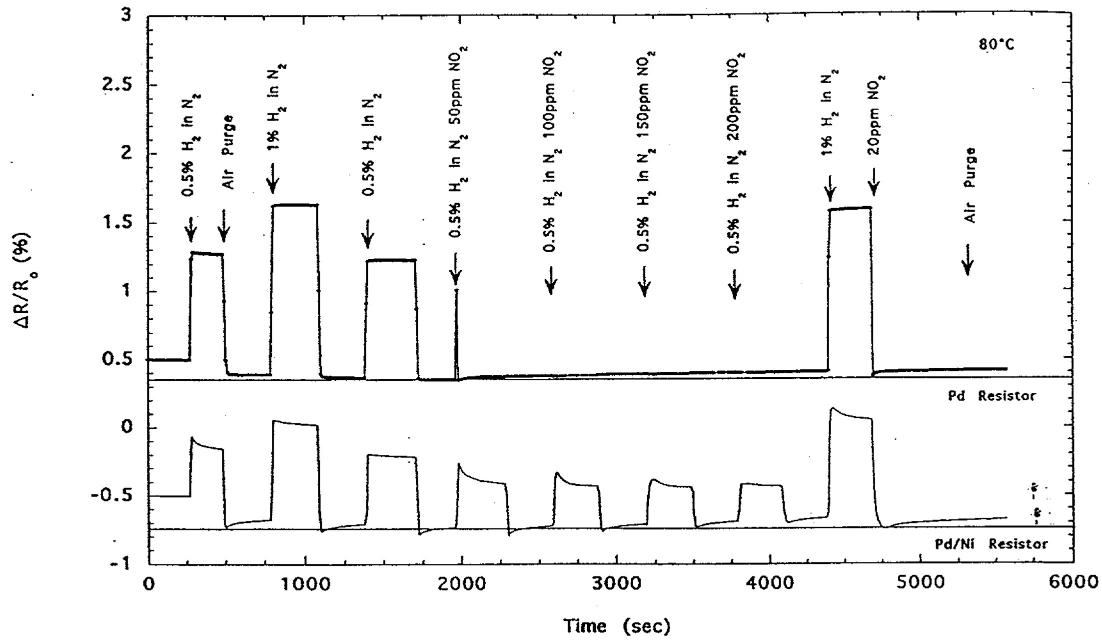

Figure 2. Resistor responses to 5 min. pulses starting with air. The top data is for the Pd resistor and bottom is for the Pd/Ni resistor. The baselines have been offset for clarity; the first 5 min. establishes the baseline, which is the resistance after a 15 minute purge at 140°C in air.

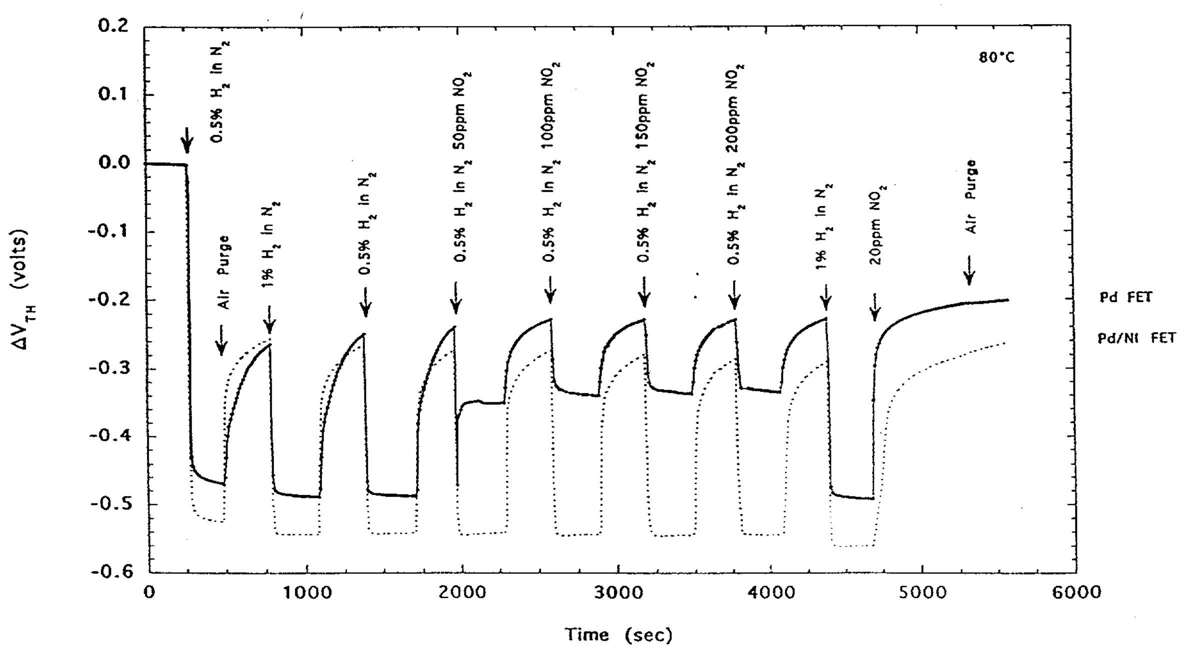

Figure 3. Pd/Ni and Pd FETs operating at 80°C; the individual data points at 10 second intervals are shown for the Pd FET and a dashed line through the points for the Pd/Ni FET. Five minute pulses of H_2 mixtures alternate with 5 minutes of dry air. The introduction of each new mixture is indicated by the arrow. The data were taken at the same time as those for the resistors in Fig. 2.The zero is defined as the FET threshold voltage after a 15 minute purge at 140°C in air; all H_2 containing mixtures cause the threshold voltage to move in a negative direction. In a routine run for use in the pattern recognition algorithm calibration pulses of H_2 are given before and after exposures to mixtures with NO_2 to make sure that the calibration of the sensor holds after exposure to NO_2.

pH_2 with 100 ppm pNO_2 gives no response, while the Pd/Ni resistor gives a reduced (from no NO_2) but easily measured response. Calibration pulses before and after the run, shown in the Fig. establish that the Pd sensor is still operating normally when no NO_2 is present. Fig. 3 shows the response of the two FETs during the same run. The suppression of the signal on the Pd FET when NO_2 is present is consistant with the signal from the Pd resistor.

CONCLUSIONS

The training set for the pattern recognition comes from many such pulses for different gas concentrations and sensor temperatures. This means that a considerable experimental data base must be obtained on a wide variety of gases, concentrations, sensor alloy compositions and temperatures. The data base will allow the algorithm to be used effectively in an ever wider number of commercial, industrial and military applications, and may also allow us to model the behavior of the sensor responses to enhance the predictive power to ranges of mixtures not tested.

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