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The Final LDRD Report for the Project entitled: "Enhanced Analysis of Complex Gas Mixtures by Pattern Recognition of Microsensor Array Signals"

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Abstract:

Microsensors do not have the selectivity to chemical species available in large laboratory instruments. This project employed arrays of catalytically gated silicon microsensors with different catalysts to create data streams which can be analyzed by pattern recognition programs. One of the most significant accomplishments of the program was the demonstration of that mixtures of H_2 with the oxidants NO_x and O_2 could distinguished from one another by the use of different catalytic metals on the Sandia Robust Hydrogen (SRH) sensors and the newly developed pattern recognition algorithm. This sensor system could be used to identify explosive gas mixtures and analyze exhaust streams for pollution control.

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Introduction

Complex mixtures of gases and vapors present one of the most difficult analytical chemistry problems and in the real world there are many needs requiring real time knowledge about the concentrations of various species. Environmental hazards are one of the best known examples, but toxic and explosive gas mixtures can be present in a wide variety of DOE, DOD and civilian manufacturing sites as well as in the home. Laboratory analytical instruments can give the right answers when operated by skilled personnel, but are too large, power hungry and expensive for many applications and can not be installed on site for real time data.

Chemical microsensors are receiving considerable attention in the R&D community as potential solutions to many gas sensing problems. Some of them, for example the Sandia H_2 sensor, work very well when H_2 is the only gas which might be present and its concentration is the only unknown. However we and others have shown that other gases, including ethylene and formic acid will give "false" signals for H_2. Oxidants like O_2 can cause an incorrect concentration reading on the Sandia catalytic gate gas sensor. These other chemicals would be called "interferants" if the goal is to correctly measure the H_2 concentration. Microsensors often are not very selective in response, and when used in arrays this can have an advantage: if they respond to classes of compounds the arrays can give more valuable information than strictly selective sensors. In this project we have addressed this serious problem by combining two of Sandia's strengths: powerful new clustering algorithms and our catalytic gate sensor technology.

A pattern recognition scheme is required to infer the presence and concentrations of specific species from the collection of sensor array signals. We have recently developed a new data clustering technique which is directly applicable to this problem. Although many such clustering techniques exist, our technique has demonstrated the highest quality decision making results through the use of algorithms that mimic human perception of clusters in complex data sets. Use of this new technique will allow the development of a complete recognition system which is no longer limited by the clustering technique and achieves optimum performance with the available sensor films. The clustering technique will automatically evaluate which combinations of sensor signals and which regions in the sensor signal phase space are necessary and sufficient for recognition. The clustering results will then be directly incorporated into pattern recognition software.

In earlier work on catalytic gate field effect silicon gas sensors we reported on a comparison of pure Pd gates with Pd alloyed with Ag. Both sensors detect H_2 equally well, but mixtures of the two oxidants O_2 and/or NO_2 gave markedly different signals from the two sensors. We traced this difference to the basic mechanism of detection in this type of sensor: molecules which can be catalytically dissociated on a thin film catalyst to yield H atoms will produce a hydrogen-like response. However if oxidants are present the surface reactions between the oxidants and reductants will differ depending on the surface composition of the catalyst. There is a large body of literature on supported metal catalysts from the chemical processing industry and some of the information from that field can be used to guess which alloys will produce different reactions than others. For example, some reduction in oxidation rates on Pd/Ag vs. Pd is expected from the supported catalyst literature, but the effect of NO_2 was entirely unexpected. We now have field effect sensors with Pd alloys of Ni, Au and Cu, but only a few experiments on different gases have been performed. There is sufficient evidence that when data from several of these sensors is recorded during exposure to complex gas mixtures that the clustering techniques will allow us to "train" the array sensor output with known sets of concentrations . When "unknown" concentrations are introduced then the cluster algorithm will provide the best estimates of the individual concentrations of the gases.

Accomplishments on the LDRD Project.

Experiments using sensor arrays

During the first year of the project an apparatus was constructed to control multiple gas flows and acquire data from 9 sensors simultaneously. Circuit boards for controlling the on-chip temperature and two catalytic gate sensors per chip was made functional and the first data streams were delivered for pattern recognition. There were five chemical sensors being monitored almost simultaneously by a Keithley data logger/voltmeter. Up to 9 channels of data can be sent to a Mac running LabView. The flow controllers delivering the gas mixtures are also controlled from LabView. The five sensors used are on three platforms: Two Sandia Robust sensors, one with Pd metal and the other with Pd/Ni metal. The details of the performance of the Sandia Robust Hydrogen (SRH) sensor are given in Appendix D in a paper entitled: "Gas Sensor Technology at Sandia National Labs: Catalytic Gate, Surface Acoustic Wave and Fiber Optic Devices". The oxygen sensor is a commercial Nyad. Gas flows past all three sensor platforms. The on-chip temperature for the two robust chips is also in the data stream.

In this particular case we were trying to analyze for explosive vs. non-explosive mixtures of O_2 and H_2 which is an extremely important problem for the DOE in radioactive mixed waste among other industrial and military situations. The first indications are that we can get a very accurate picture of the mixtures around the Lower Explosive Limit (4% H_2 and 20% O_2) A detailed discussion of this topic is found in Appendix B in a paper entitled: "The Response Of The Sandia Robust Wide Range Hydrogen Sensor To H_2 -O_2 Mixtures".

Pattern recognition methods

We successfully accomplished the key pattern recognition milestone for FY93: with an extension of our 2-d clustering technique to treat pattern recognition of sensor array data with arbitrary numbers of sensor inputs. We have implemented this sensor pattern recognition code in C on a SPARC 10 workstation. The method was debugged and tested on published sensor array data and on a famous data set from the pattern recognition literature (the Fisher IRIS data). We find that the method provides good classification performance in these cases, and also provides information which is not available or reliable from other techniques (e.g. automatically identifying outlier points and points which overlap with more than one class). We also verified that our method provides an automated tool for comparing the effectiveness of alternative sets of candidate sensors in an array.

We have also developed code to automatically extract the n-dimensional data points of interest from the continuous stream of microsensor data. The code treats the output of each device at each operating temperature as a distinct dimension, and one n-dimensional point is collected for each distinct set of gas mixtures. We collected a sufficiently large set of n-dimensional points on H_2 and O_2 mixtures to complete our first pattern recognition analysis on Sandia-generated array data. The details of the pattern recognition algorithm and its method of implementation for sets of sensor data is given in Appendix E in a paper entitled: "Clustering-Based Pattern Recognition Applied to Chemical Recognition Using SAW Array Signals".

We have also generated macros for the graphics package TecPlot to automatically display, reorient and animate 3-d subsets of the data. The graphics also can show the pattern recognition decisions for each point. This will be used to illustrate and allow visual verification of our method.

Detection of mixtures of H_2 with NO_x's and Oxygen

The Sandia Robust Hydrogen Sensor provides a manufacturable electronic platform for a wide variety of catalytic alloys. For sensing of H_2 alone, an alloy of Pd with Ni allows detection over a very wide range, from about 1 ppm to pure H_2. However, the signal from H_2 may change if an oxidizing agent is present, like O_2 or NO_x. If the concentration of these reactants is high enough, flammable mixtures occur. Lower concentrations of NO_x are of interest for pollution control. A significant accomplishment during FY94 was the use of a five sensor array with the pattern recognition algorithm 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 Pd/Ni(9%) FET and resistor and a Nyad oxygen sensor (commercial product). One of the tasks of the pattern recognition algorithm developed at Sandia 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 robust 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. As an example of classification, mixtures containing NO_2 can be distinguished from mixtures with O_2 or no oxidant at all (only H_2). The details are given in the paper in Appendix A entitled: "The Detection of Mixtures of NOx's with Hydrogen using Catalytic Metal Films on the Sandia Robust Sensor with Pattern Recognition" 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/NO_2 contains many different H_2 and N_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 and NO_2 were unexpected (but reproducible). 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.

Data obtained with different sensor temperatures is effectively a new sensor since the response to a given mixtures may be different at different temperatures. In this way a training set with 12 sensors was obtained. The Sandia pattern recognition algorithm was able to use the training set to cluster mixtures containing H_2/NO as distinct from H_2/NO_2, H_2/O_2 and H_2 alone. Once this important task has been accomplished, an unknown gas sample can then have the individual molecular concentrations determined from the training set. It was found that mixtures with N_2O could not be clustered as different from

H_2 alone because there is apparently no catalytic reaction. However in later experiments, a new combustible gas sensor was added to the array and with it the N_2O mixtures could also be classified.

Detection of Other Molecules

The focus of the project was mainly on mixtures of H_2 with oxidizing agents. This is perceived as the type of problem that will have the most practical utility in the near future. The mechanism of detection involves the dissociation of molecular H_2 into adsorbed atomic H on the surface of the catalyst film. Our model for the action of the oxidants is that they compete for these surface sites and reduce the coverage of H and thereby reduce the signal from the sensor for a given partial pressure of H_2. However we have found that other molecules can give a sensor signal with no H_2 present and a few of these were studied in the project to see if training sets could be developed to distinguish them from H_2 containing mixtures.

Carbon Monoxide

There is a rapidly developing market for detecting lethal levels of CO in the home market. While there is no hydrogen in the CO molecule, at high temperatures it undergoes a reaction with water (relative humidity) to form H_2 and CO_2. This is a the famous "water-gas-shift" reaction. We attempted to use this reaction to detect CO using the SRH sensors in our array. While we did obtain a response for sensor temperatures in the 150 to 200C range, we did not get a consistent and reproducible response for the low (10-100 ppm CO) concentrations that would be of use in the safety market. Since the specific catalytic powders for the water-gas-shift reaction are well known, it is possible that a small reactor could be designed as part of a micro-total analytical system (lab-on-a-chip) where all the CO could be converted to H_2 in a step before the gas reached the SRH sensor. This would be a future project and issues like changes in relative humidity and oxygen interference would have to be addressed.

Formic Acid

Formic acid is a small molecule (CH_2O_2) that is widely used in the chemical industry. It is thermodynamically unstable and is known to decompose into H_2 and CO_2 on selected catalysts. We found that we could detect low concentrations of formic acid with both Pd and Pd/Ni SRH sensors. The decomposition appears to be more facile on Pd than on Pd/Ni(10%) and the pattern recognition was fairly successful in distinguishing gas streams of formic acid from H_2. There were experimental problems associated with formic acid induced baseline drift sensitivity to changes in relative humidity (RH) and scatter in the responses of given SRH sensors to repeated exposures over a period of time. These changes in baseline and sensitivity create problems for any training set of data that can not be recalibrated from time to time. If a customer for the formic acid detection appeared, a more extensive study of sensor operating temperatures and selective coatings would have to be undertaken to provide accurate information.

Ethylene Oxide

Ethylene oxide (C_2H_4O) is a small molecule used to sterilize surgical instruments and other biomedical products and as a fumigant. It is highly toxic to humans and there is a market for detecting low concentrations for safety in handling. We found that we could detect higher concentrations of ethylene oxide (> 1000 ppm), but not the 1 ppm that would be necessary for a safety warning device. Since it is a relatively unstable molecule we had hoped that it would readily decompose on our SRH catalysts. The Pd and Pd/Ni versions did not work as well as needed and a search for better catalyst systems would be required to meet this market's requirements.

Conclusions, Work for the Future and Lessons Learned.

This LDRD has led to important discoveries about how to monitor explosive and toxic gas mixtures that exist in the real world, for example, in the radioactive mixed waste storage tanks at Hanford. A sensor array consisting of SRH sensors with two kinds of catalytic metal, Pd and Pd/Ni combined with a miniature oxygen sensor and the Sandia combustible gas sensor could be used now a many applications when combined with data acquisition using the Sandia pattern recognition software. Improvements in the accuracy of the identification of different classes of mixtures can be made by reducing the baseline drift and sensitivity drift of the SRH sensors. We have already made improvements in this area by selective anneals of the catalytic metal films.

During this project, we were surprised by the vast quantity of sensor data that is required to make an adequate training set for the pattern recognition. Any customer for this kind of system has to be aware of the calibration requirements that are necessary to keep a system in the field giving accurate output information.

We also found that development of different catalyst films for the SRH sensor is very expensive if the full microelectronic fabrication process is used. This occurs because most modern fabs use six inch diameter wafers or larger and so thousands of sensors are fabricated in one run. But variations in the catalyst film can not be made by carving up the six inch wafer before film deposition for processing reasons. This means that very large area targets have to be used that cost $15K or more for each type of catalyst (i.e. for each different percentage Ni in a Pd/Ni system). This is cost effective for a large run sensors where many of the same type will be sold, but it is prohibitively expensive for development studies. We have designed simple mask sets for photolithographic fabrication of small lots of metal-insulator-semiconductor (MIS) capacitors. Using our dual e-beam evaporator, explorations of many binary metal catalysts will be possible in a cost effective manner in the future.

In conclusion, we have achieved the important goals of the project and along the way have learned a significant amount about the basic mechanisms of operation of the catalytic metal thin film sensors and about the properties of pattern recognition algorithms. The knowledge gained in this project forms the basis for technological solutions to many chemical sensing problems in defense, commercial and consumer markets.

Acknowledgments.

We gratefully acknowledge the technical assistance of Mark Jenkins and Dan Moreno in data acquisition and sensor test bed development. John Bartholomew and Rubel Martinez contributed significantly to the development of the pattern recognition algorithms. The work was funded by the LDRD program on case 3505.180.

Appendix A:

A reprint of a publication entitled: "The Detection of Mixtures of NOx's with Hydrogen using Catalytic Metal Films on the Sandia Robust Sesnor with Pattern Recognition" R. C. Hughes, G. C. Osbourn, J. W. Bartholomew and J. L. Rodriguez, Technical Digest, Transducers '95 (Stockholm, Sweden, June 25-29 1995) pp. 730-733. SAND943162C

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Appendix B:

A reprint of a publication entitled: "The Response Of The Sandia Robust Wide Range Hydrogen Sensor To H_2 -O_2 Mixtures.", R. C. Hughes, D. J. Moreno, M. W. Jenkins, and J. L. Rodriguez, Technical Digest, Solid State Sensor and Actuator Workshop (Hilton Head Island, South Carolina, June 13-16, 1994). pp. 57-60. SAND94-0047A

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Appendix C: Project Related Information

Number of patent disclosures: (where the invention was at least in part attributable to LDRD support)	2
Number of patent applications: (where the invention was at least in part attributable to LDRD support)	1
Number of patents: (where the invention was at least in part attributable to LDRD support)	0
Number of copyrights on computer software: (where the code was at least in part attributable to LDRD support)	0
Number of students: (if any) supported by the project	0
Number of post docs: (if any) supported by the project	1
Number of permanent technical or scientific staff hired: (if any) supported by the project	0
Number of awards (and their names): by organizations outside the laboratory to an individual or team attributed at least in part to LDRD support	R&D 100 Award for Sensor Technology
Number of new non-LDRD funded projects: their amounts and source of funding	INUMM is a new $8M per year DP program for integrating sensors and data analysis for monitoring nuclear material; this LDRD provided much basic information about how to do it.

Appendix D:

A reprint of a publication entitled: "Gas Sensor Technology at Sandia National Labs: Catalytic Gate, Surface Acoustic Wave and Fiber Optic Devices", Robert C. Hughes, D. J. Mareno, M. W. Jenkins, and J. L. Rodriguez, NIST Workshop on Gas Sensors: Strategies for Future Technologes, in Gaithersburg, Maryland Sept. 8-9, 1993. NIST special Pub. 865 pp. 47-52. SAND93-1954C

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Appendix E:

A reprint of a publication entitled: "Clustering-Based Pattern Recognition Applied to Chemical Recognition Using SAW Array Signals", G. C. Osbourn, J. W. Bartholomew, G. C. Frye, and A. J. Ricco, Technical Digest, Solid State Sensor and Actuator Workshop (Hilton Head Island, South Carolina, June 13-16, 1994) pp.193-196.

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