For presentation at the International Conference on Microelectronic Test Structures (March 1996)

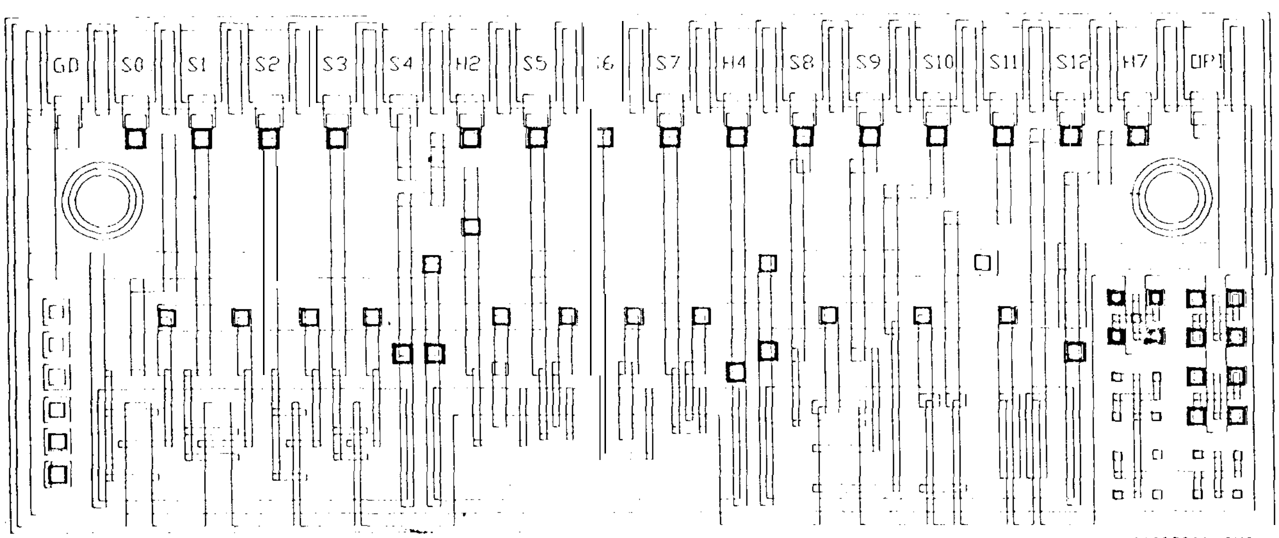
GAS SENSOR TEST CHIP

M. G. Buehler and M. A. Ryan

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, CA 91109

ABSTRACT: A new test chip has been developed to characterize conducting polymers used in gas sensors. The chip, a seven layer cofired alumina substrate with gold electrodes, contains 11 comb and U-bend test structures. The structures are designed to measure the sheet resistance, conduction anisotropy, and peripheral conduction of spin coated films that are not subsequently patterned. The resistance of the polypyrrole films change by a few percent in response to various alcohols. Results from the test chip revealed that the vapor response depends on electrode geometry.

INTRODUCTION: The use of organic polymers to detect gasses has been known [1] for several years to be an effective means for gas detection via conductivity changes. These chemoresistors offer significant advantages over other gas detectors in that they operate near room temperature and thus can be used in compact, low-power applications. This effort is directed at developing a gas monitor for the space station but it also has potential for those applications requiring personal gas exposure monitoring.



F i"1 e: GASS5821.DWG '

Figure 1. Gas sensor test chip 10 mm x 24 mm.

A polymer-based gas sensor is an array of polymer resistors where each chemoresistor has a different sensitivity to various gasses. The gas sensitivity of each polymer is determined by its polymerization and dopant characteristics [2]. The specific gas identification is made using pattern recognition techniques [3] applied to the response of the array to different gases.

At the current time the production of these sensors is limited by their lack of reproducibility. The first step in developing a gas sensor is to characterize the conductivity of the polymer films using a test chip shown in Fig 1. This chip was designed to measure various aspects of the conduction mechanisms such as sheet resistance, surface conduction, anisotropic conduction, and film non uniformity as well as contact resistance in order to identify reproducibility issues.

TEST CHIP DEVELOPMENT: The development was guided by the limitation that the polymer films can not be patterned once applied via spin coating. The test chip was fabricated using a two-conductor thick film technology. The conducting polymer film coats the region between gold electrodes. The use of gold electrodes essentially eliminates the electrode-polymer contact resistance which is found with aluminum based electrodes [4]. The low-temperature (800°C) cofired ceramic substrates [5] are currently being fabricated using 125-μm linewidths and spaces and have seven screen printed layers. Bridge and van der Pauw resistor structures are not applicable, for the films can not be patterned once deposited.

The sensors, shown in Fig. 1, have one electrode connected to OPI, the Op Amp input shown in Fig. 2. The other electrode is connected to one of the sensor pins labeled SO to S12. The electrodes are covered by an insulating glassy layer except in the channel where the electrodes are exposed to the film.

The critical dimensions for the structures shown in Fig. 1 are listed in Tables 1 to 5 along with the number of squares, Ns, which is explained in a later section. The Comb Resistors, sensors SO to S3, are used to determine sheet and contact resistance. The U-bend Resistors, sensor S4 to S7, are used to determine sheet resistance. The Contact Resistor Structure, sensors S8 to S1O, is used to determine the sheet and contact resistance. The Serpentine Resistor, sensor S11, is used to determine the feasibility of such a design. The Isolation Resistor, sensor S12, is used 10 determine the degree of conductivity across the insulating glassy layer.

Table 1. Comb Resistor Dimensions

SENSOR	so	S1	S2	S3
L(mil)	4	1	4	1
W(mil)	4	4	1	1
N_S	0.5	0.125	2	0.5

Table 2. U-Bend Resistor Dimensions

SENSOR	S4	S5	S6	S7
L(mil)	2	1	2	1
W(mil)	2	2	4	1
N_S	0.243	0.164	0.164	0.243

Table 3. Contact Resistor Dimensions

SENSOR	S8	S9	S10
L(mil)	1	4	9
W(mil)	6	6	6
N_S	0.167	0.667	1.5

Table 4. Serpentine Resistor Dimensions

SENSOR	S11
L(mil)	24
W(mil)	1
N_S	24

Table 5. Isolation Resistor Dimensions

SENSOR	S12
L(mil)	3
W(mil)	12
N_S	0.25

The test chip has only 18 pins as seen in Fig. 1 allowing access to 11 chemoresistor test structures and 3 heaters used to control polymerization. The measurement circuitry, shown in Fig. 2, is used to sequentially place each chemoresistor in the feedback loop of an operational amplifier using multiplexing circuitry. The operational amplifier is a current to voltage converter where a constant current is driven through each chemoresistor. This approach allows ppm (parts per million changes in conductivity to be detected.

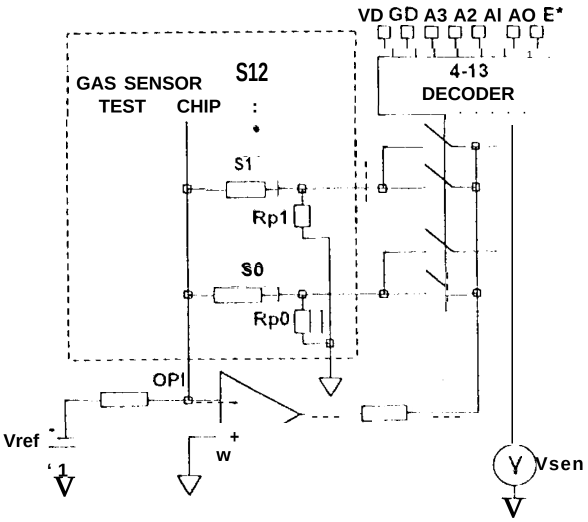


Figure 2. Gas sensor test chip and associated test circuitry where S0-S12 are chemoresistors and Rp0-Rp12 are peripheral resistors.

In designing the test chip, the following design principles were used to meet the design requirements which call for multisensing an array of chemoresistors:

a. Common bussing was used to conserve pins.
b. Kelvin voltage sensing was used in the surround circuitry to avoid analog switch resistor voltage drops.
c. Structure geometry variations were used to separate contact and sheet resistance.
d. Electrode guarding was used to eliminate leakage currents. This was accomplished by grounding all resistors except for the resistor under test.

SAMPLE PREPARATION: Test chips were coated with films of polypyrrole (PPY). The PPY was prepared by dissolving 1.5×10^{-3} moles pyrrole in 4 mL tetrahydrofuran (THF), 7.5×10^{-4} moles phosphomolybdic acid in 4 mL THF, and mixing equal volumes of the two solutions. Polymerization began immediately as evidenced by a color change. The polymer was allowed to form for - 15 minutes. A barrier tape was placed between the active electrodes and the connecting pins to prevent the solution from wicking to the pins. The solution was pipetted onto the test chip and spun for several seconds at 1500 rpm. The PPY was allowed to polymerize on the chip for a period of 30 minutes. During this time the resistance of each chemoresistor was monitored and found to be in the MΩ range.

Chips were then rinsed in MeOH to remove unreacted pyrrole, excess THF, and excess acid, leaving an insoluble film of PPY. After removing non-conductive excess reactant and solvent, the resistance of the PPY films dropped by two orders of magnitude.

ELECTRICAL TESTS: The resistance for chemoresistors found on Chip 13 is shown in Fig. 3. The resistors have a linear IV characteristic. The measured sensor resistance, R_m, was plotted against the number of squares, Ns. The resistance is given by $R = R_S \cdot N_S$ where Rs is the sheet resistance. For the Comb Resistors, SO to S3:

$$Ns = L/2W \qquad (1)$$

where L is the channel length and W is the channel width. For the U-bend Resistors, S4 to S7 [6]:

$$Ns = 1/(2.111 + 2W/L) \qquad (2)$$

This equation was derived from the U-bend resistor shown by Hall [6] in his Fig. 47. For the contact resistor test structure:

$$R = \rho_C/W + R_S \cdot N_S \qquad (3)$$

where ρ_C is the contact resistance and Ns = L/W.

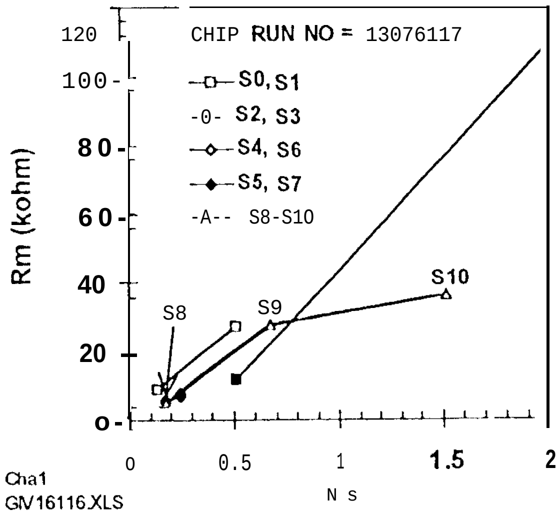


Figure 3. Measured resistor values from eleven chemoresistors found on Chip 13 showing the variation in resistance as a function of the number of squares, Ns.

From the slope of the results shown in Fig. 3, the sheet resistance is about 50 kQ/11, Since the curves intercept close to the origin the the contact resistance is small. These results are difficult to evaluate in detail because the film appears to vary in thickness. This is evident in the nonlinear behavior of Contact Resistor, sensors S8 to S1O, represented by triangles in Fig. 3. From the figure it is evident that the sheet resistance is higher between S8 and S9 than between S8 and S1O. This can be explained by a thicker hence more conducting film near the edge of the chip.

GAS RESPONSE: The percent resistance change of chemoresistors to methanol (MeOH), ethanol (EtOH), 2-propanol (PrOH), and water (HOH) is shown in Figs. 4 to 8 where the initial resistance is given in the key in kΩ. During tests, the sensor was exposed to a saturated atmosphere of each compound and to air between exposures.

The gas response for Chip 13 is shown in Figs. 4 and 5. In Fig. 4, the response for

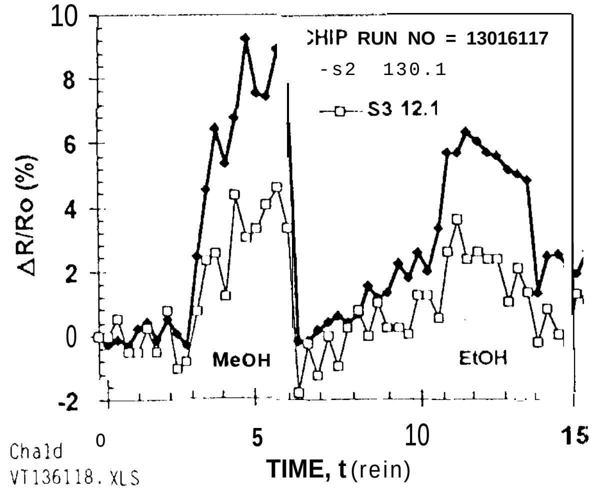


Figure 4. Comb resistor response to methanol (MeOH) and ethanol (EtOH) for Chip 13. The EtOH response shows a characteristic declining behavior during exposure.

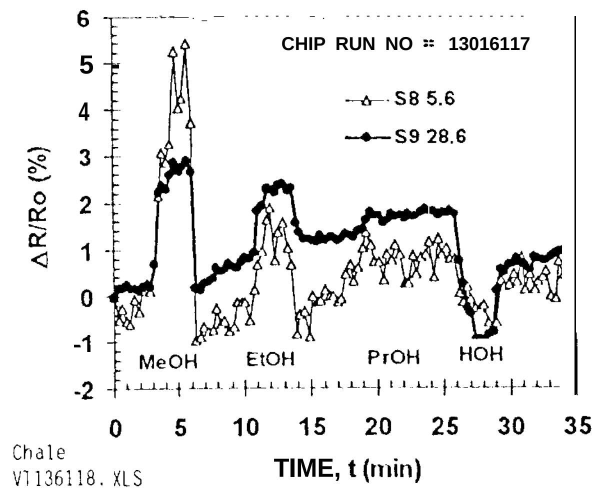


Figure 5. Contact resistor response to methanol (MeOH), ethanol (EtOH), propanol (PrOH), and water (HOH) for Chip 13. The sensors have a positive response to the alcohols and a negative response to water.

sensors S2 and S3 indicates that the resistances change by nearly 10 percent where the MeOH has the greatest effect. The response to EtOH shows a declining characteristic during exposure. This behavior has been seen in other chips as explained below.

The response shown in Fig. 5 represents a sequential exposure to four vapors for sensors S8 and S9. Notice that the alcohol response is always positive; whereas, the water response is negative. This response also has a very low noise behavior when compared to the response of sensor S8. This low noise behavior is essential to ppm gas detection where ppm resistance changes are expected.

In Figs. 6 to 8, the gas response of Chip 10 is shown for all sensors for MeOH, EtOH, and PrOH. Note that the magnitude of the

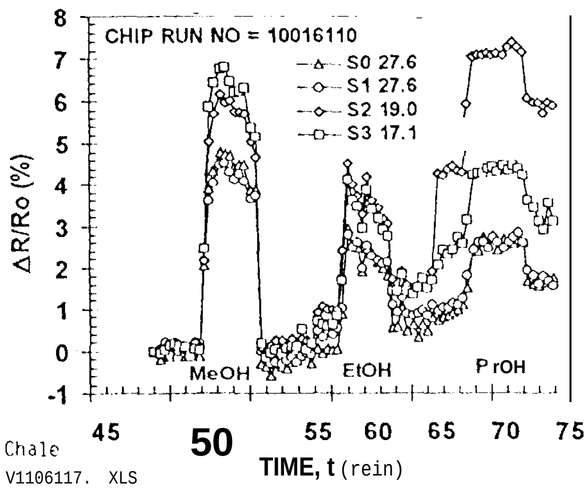


Figure 6. Comb Resistors, SO to S3, found on Chip 10 respond to methanol (MeOH), ethanol (EtOH), and propanol (PrOH).

resistance change is inversely proportional to the molecular weight of the vapor. The sensors have a time response that is less than the 15 second sampling period. The curves also have a characteristic shape that depends on the vapor identity. That is, the MeOH response has a relatively slow rise and fall during exposure. The EtOH response has a declining behavior during exposure and exhibits a unique dip. The PrOH response shows a flat top behavior.

The sensors have a characteristic response which depends on electrode geometry. For instance, the Comb Resistor response is always greatest for S2 and least for SO. The sensor S2 has a narrow conduction channel; where SO has

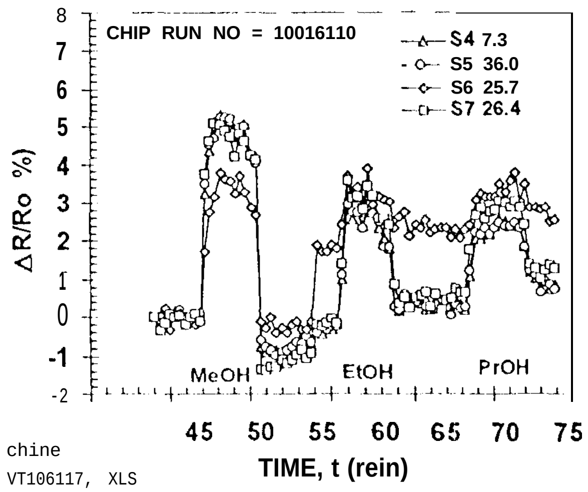


Figure 7. U-Bend Resistors, S4 to S7, found on Chip 10 respond to methanol (MeOH), ethanol (EtOH), and propanol (PrOH).

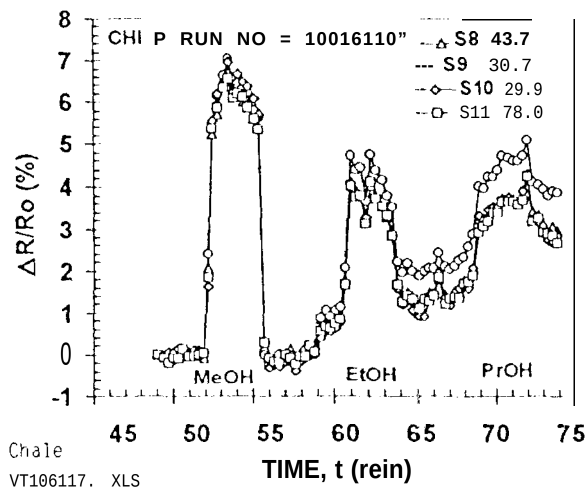


Figure 8. Contact Resistors, S8 to S1O, and Serpentine Resistor, S11, found on Chip 10 respond to methanol (MeOH), ethanol (EtOH), and propanol (PrOH).

a wider conduction channel. That is, 2W/L is 0.5 for S2; whereas, for S0 it is 2. It is possible that the proximity of the conducting channel to the insulating walls, enhances vapor adsorption in S2. The U-bend Resistors, however, seem to have a more uniform behavior. This may be due to the lack of insulating walls in the vacinity of these structures.

CONCLUSION: The change in sensor resistance is determined by the molecular weight of the vapor type and resistor geometry. Also the vapor response is unique for the vapors used in this effort. To our knowledge this is the first observation of the influence of resistor geometry on sensor response. This demonstrates the utility of using the test chip for rapid sensor development.

ACKNOWLEDGMENTS: This research was carried out by the Center for Space Microelectronic Technology, Jet Propulsion Laboratory, California Institute of Technology, and was sponsored by NASA/OSAT. The assistance of Dennis Martin, Halcyon Microelectronics, Inc., Irwindale, CA in the design and fabrication of the test chip are gratefully acknowledged. The authors are appreciative of the discussions and many good ideas of Roger Williams, JPL and Anthony Kim, UCLA. File: GAS#6325.doc

REFERENCES:

1. J. W. Gardner, "Microsensors, Principles and Applications," J. Wiley & Sons (Chichester, England, 1994)

2. M. S. Freund and N. S. Lewis, "A chemically diverse conducting polymer-based "electronic nose''," Proceedings of the National Academy. Science, Vol. 92, 2652-2656 (March 1995).

3. J. W. Gardner and P. N. Bartlett, "Performance definition anti Standardisation of electronic noses," The 8th International Conference on Solid-State Sensors and Actuators and Eurosensors IX, Stockholm, Sweden, 671-674 (June 1995)

4. W. H. Ko, et. al. "Phthalocyanine L-B Film Gas sensors," Sensor and Materials, vol. 239-55 (1990).

5. D. A, Deane and P. D. Franzon, eds. "Multichip Module Technologies and Alternatives: The Basics," Van Nostrand Reinhold (New York, 1993).

6. P. M. Hill, "Resistance Calculations for Thin Film Patterns," Thin Solid Films, Vol. 1, 277-295 (1 967/68).