

# MEMS Chemical Gas Sensor

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**Abstract--** We have developed a miniature polymer-based chemical gas sensor array on silicon using micromachining technology. The sensors use conductive polymer – carbon black composite films, which swell reversibly and induce a resistance change upon exposure to a wide variety of gases. Using a SU-8 photoresist, we have constructed high aspect ratio wells which can contain the polymer – carbon black – solvent liquid volume present during deposition and allow the sensor film to be placed reproducibly in a specific and well-constrained area while reducing its overall size. Two sizes of wells,  $500 \times 600 \mu\text{m}$  and  $250 \times 250 \mu\text{m}$ , have been fabricated and tested. Six polymer – carbon black composite films were deposited into an array of sensor wells and exposed to three chemical gases at five concentration levels. The sensors were able to uniquely detect these gas vapors and demonstrated a linear response to the concentration levels. This design allows the integration of circuits to process the changes in resistance which will permit the realization of a completely integrated miniature gas sensor.

## 1. INTRODUCTION

The ability to monitor and detect various chemical gases is important to many applications. One example is environmental monitoring, such as determining the air quality inside a room or closed chamber and detecting the presence and concentration of toxic or otherwise dangerous gases that may come from spills and leaks [1]. Another broad application area is quality control and industrial monitoring, particularly in such industries as food processing, perfume, beverage, and other chemical products where complex vapor mixtures need to be analyzed and classified [2,3]. Monitoring and determining the constituents of a sample gas or environment involves collecting samples and analyzing them in complex and expensive laboratory analytical instrument such as a gas chromatograph-mass spectrometer (GC-MS). [1] Although GC-MS systems work very well, many applications need sensor systems that are smaller, more portable, cheaper, and even disposable.

## 2. SENSOR DEVICE

We have developed a miniature polymer-based chemical gas sensor array on silicon using micromachining technology. The sensors use conductive polymer – carbon black composite films, which have been shown to swell

reversibly upon exposure to gases [1,2]. This swelling induces a resistance change in the composite film. By depositing the film across two metal leads, this resistance change can be measured. Compared to conventional chemical sensors which use a specific receptor that selectively responds to a single analyte of interest [2], the polymer composite film is not specific to any one particular gas. However, when it is used in an array, with each sensor containing a different polymer composite film, gases and gas mixtures can be identified by the pattern of response of the array. This allows a much more general-purpose chemical gas sensor capable of broadly detecting and identifying various constituents.

### A. Design

Conductive polymer – carbon black composite films have been used as a sensing medium in several gas sensors or “electronic noses” [1,2]. They have been deposited on co-fired ceramic substrates [1] and on glass slides [2]. Most of these sensors have large-area composite film deposits ( $> \text{mm}^2$ ). During deposition, the composite film is dissolved into a solvent mixture, which evaporates and leaves behind the thin sensing film. We have designed micromachined reservoirs or wells to contain the large liquid volume present during deposition. The well allows the polymer – carbon black film to be placed reproducibly in a specific, well-constrained, and smaller area.

### B. Fabrication

The sensor array was fabricated on the surface of a silicon wafer by building high aspect ratio wells using thick-film photolithography. The starting material was a  $\langle 100 \rangle$ -silicon wafer coated with either silicon nitride or silicon dioxide. Gold was deposited by an e-beam evaporation system and patterned using a lift-off process into  $100\text{-}\mu\text{m}$ -wide leads which define the electrical contacts to the sensor. The wells were constructed on the surface of the wafer using a SU-8 photoresist (MicroChem Corp.). SU-8 is an epoxy-based negative imaging resist developed for thick-resist applications where high aspect ratios and resistance to harsh conditions are required. The SU-8 photoresist was patterned into  $200 \mu\text{m}$  thick square-ring wells with  $\sim 50 \mu\text{m}$  of the gold

leads exposed on opposite sides for contact with the polymer film. This fabrication process is shown in Figure 1. These wells can be post-processed onto silicon CMOS chips, which would allow for integration of on-chip electronics for measurement, signal processing, and analysis. The well sizes that we have fabricated and tested are  $500 \times 600 \mu\text{m}$  and  $250 \times 250 \mu\text{m}$ , shown in Figure 2.

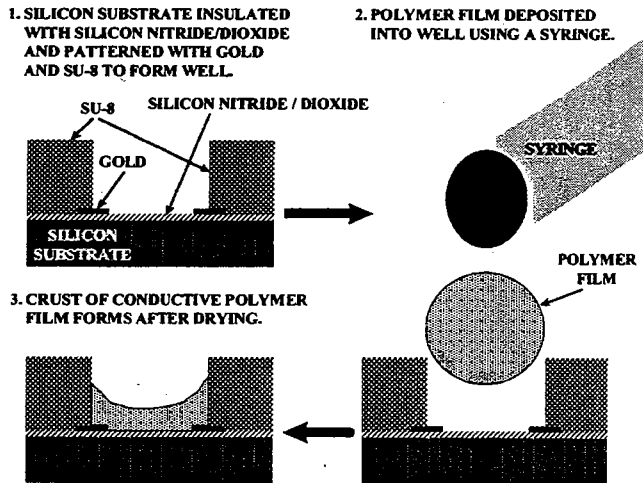


Figure 1: Fabrication of the gas sensor on the silicon surface using SU-8 photoresist.

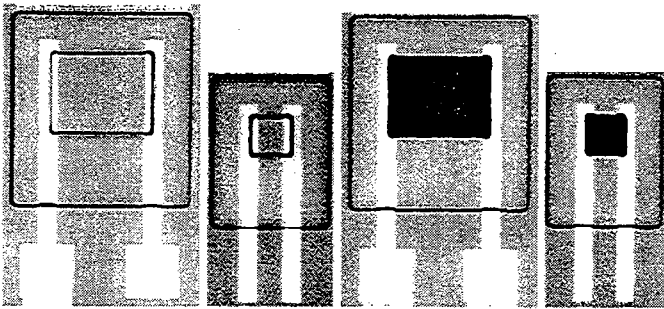


Figure 2:  $200 \mu\text{m}$  high SU-8 square ring on silicon surface forming  $500 \times 600 \mu\text{m}$  and  $250 \times 250 \mu\text{m}$  wells in the middle with gold leads on each side (left two images) before and (right two images) after polymer deposition.

### C. Composite Film Deposition

The polymer – carbon black composite film was deposited into the well using an automated syringe (Nanojet II by Drummond Scientific Comp.) which is capable of reproducibly injecting nanoliter volumes. The tip of the syringe is a disposable, pulled-glass capillary with a  $10 \mu\text{m}$  diameter. The tip was changed between the deposition of different polymer composite films. In general, the polymer was first dissolved in a solvent or solvent mixture and agitated in an ultrasonic bath. [1,2] Once the polymer had fully dissolved, carbon black was added to the solution and

sonicated further to promote uniform dispersion. Depending on the height of the wells, approximately 50 nl was injected into the  $500 \times 600 \mu\text{m}$  wells and 12 nl was injected into the  $250 \times 250 \mu\text{m}$  wells. After depositing the film solution, the solvents would immediately start to evaporate and within minutes, a polymer – carbon black residue crust was left between the two metal leads on each side of the well. The resistance of the film was measured and adjusted by additional injections of the composite film solution. The targeted resistance for these films was between 5 - 30 k $\Omega$ .

## 3. EXPERIMENT

The sensor array was evaluated by exposing it to several chemical gas vapors in a closed and controlled gas flow system. The micromachined gas sensor array was custom packaged and placed in a sealed chamber within the gas flow system and connected to a data acquisition system.

Six polymer – carbon black films were used to evaluate the sensor array which were: styrene/butadiene, aba block copolymer; poly (ethyl methacrylate); polyisoprene, chlorinated; styrene/ethylene/butylene aba block copolymer; polypropylene, isotactic, chlorinated; polyepichlorohydrin. The polymers were dissolved in toluene.

Three different chemical gas vapors at five concentration levels for each were used. Each gas sample was repeated five times sequentially. The gas vapors were methanol, methyl ethyl ketone, and methylene chloride. The concentration levels tested were 2,000, 4,000, 6,000, 8,000 ppm, and at the saturated vapor pressure for the gas. The gas was turned on for 4 min. and then turned off for 10 min.

## 4. RESULTS

The response of the sensors was measured as a percentage change in resistance divided by the baseline resistance. Figure 3 shows the time-domain response of the polyepichlorohydrin film when exposed to five concentrations of methanol vapor. The baseline to peak heights, representing the response of the sensor to the sample chemical vapor, are extracted from this series of data. Figure 4 shows the responses of four of the polymer – carbon black films when exposed to the three sample chemical vapors each at 8000 ppm. Each of the polymer sensor films responded differently to each of the gas vapors. By integrating the responses from the sensor array, a unique pattern or signature is produced for each chemical gas vapor as shown in Fig. 5. The response of the polymer – carbon black sensors increases proportionally as the concentration of the gas vapor increases. Figure 6 shows the linearity of the response of six polymer sensors with concentration ranging

from 2,000 to 10,000 ppm. Thus, using pattern recognition techniques such as principle component analysis (PCA), data clustering, or artificial neural networks, the identity of the gas vapor and its concentration can be determined from the response of the sensor array.

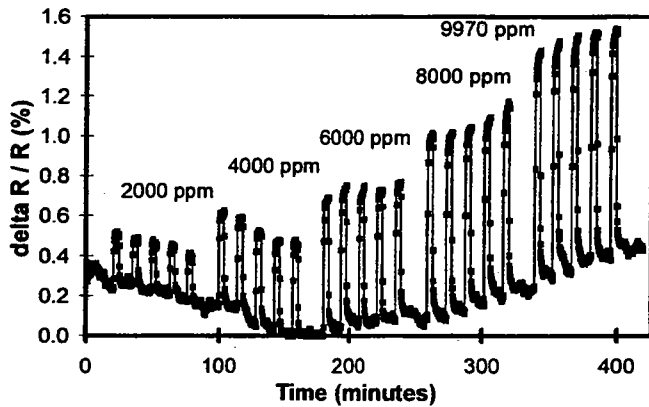


Figure 3: Time-domain response of polyepichlorohydrin sensor film when exposed to 5 concentrations of methanol.

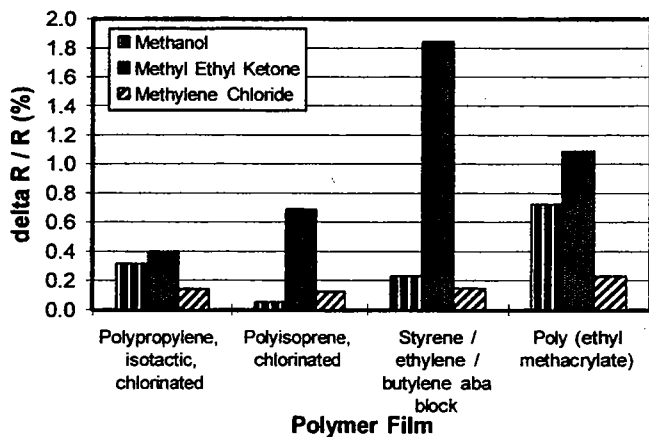


Figure 4: Responses of four polymer-carbon black sensor films when exposed to three gases at 8000 ppm.

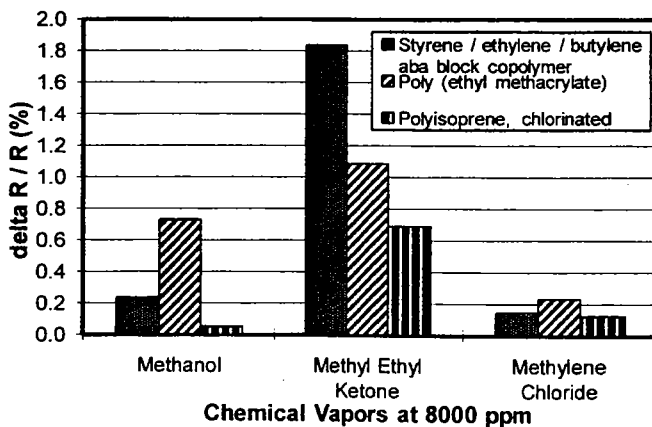


Figure 5: Pattern responses to three gases.

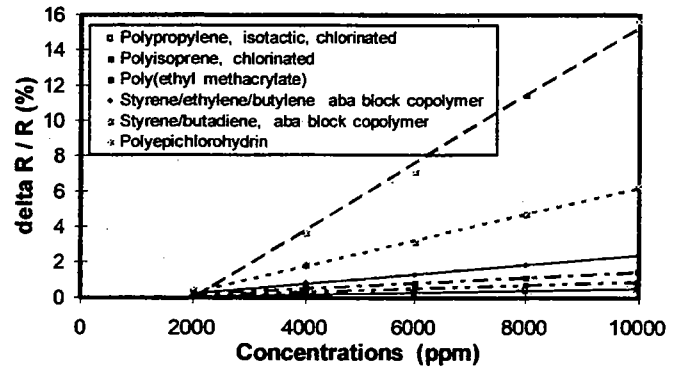


Figure 6: Response of six polymer sensors to increasing concentrations of methyl ethyl ketone.

## 5. CONCLUSIONS

An arrays of different polymer-carbon black composite films, whose resistances change uniquely with gas species and proportionally with vapor concentration, can be used effectively as a chemical gas sensor. Micromachining technologies can be used to miniaturize the sensor. Specifically, SU-8 photoresist can be patterned into 200  $\mu\text{m}$  high wells ranging in size from 500 $\times$ 600  $\mu\text{m}$  to 250 $\times$ 250  $\mu\text{m}$  which can precisely contain the large liquid volume present during deposition of the composite films. The design of this array of wells is compatible with silicon IC's and would permit the realization of a completely integrated miniature gas sensor.

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