

An embedded polymer piezoresistive microcantilever sensor

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Abstract

We have developed a new type of chemical microsensor based on piezoresistive microcantilever technology. In this embedded polymer microsensor, a piezoresistive microcantilever is partially “embedded” into a polymeric material. Swelling of the polymer upon analyte exposure is measured as a simple resistance change in the embedded cantilever. Arrays of these sensors, each employing a different polymeric material, provide for the identification of a wide range of chemical vapor analytes. Advantages of this system over previous “surface” piezoresistive microcantilever chemical sensors include enhanced mechanical simplicity (no mechanical approach necessary), greater resistance to shock or movement, and lower cost.

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1. Introduction

The need for portable, inexpensive and robust sensors capable of detecting chemical vapor analytes has never been greater. From the simple measurement of water vapor concentration to the detection of volatile organic compounds (VOCs) such as industrial solvents or environmentally important chemical vapors and chemical warfare agents, polymer-based microsensors have shown a great deal of promise [1–5]. In most of these polymer-based devices, the swelling of a common organic polymer material upon analyte exposure,

as the vapor molecules partition into the polymer matrix, is measured. The degree of swelling depends on the type of polymer as well as the analyte [5], with most common organic polymers swelling to some extent upon exposure to many different analytes. Sensing arrays incorporating several independent polymer-based sensors, each using a different polymer, may be used in conjunction with pattern recognition techniques to obtain a unique signature for a given analyte.

The accurate, precise measurement of polymer swelling in these sensors is one of the most important issues regarding the viability of these devices. Chemiresistor sensors incorporate conductive dopants or particles within the polymer itself to achieve this goal. Baseline conductivity for the composite material is established, which is

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dependent on the dopant/conductive particle concentration and distribution. During analyte exposure, polymer swelling produces a drop in the material conductivity as initial conductive pathways through the material are altered or disturbed. The most successful of these chemiresistor sensors utilizes carbon particles dispersed throughout the polymer material to produce a conductive polymer sensor [1]. There are some disadvantages inherent to this design, though. Exact ratios of carbon to polymer are needed to produce the largest responses, and the spatial distribution of the particles must be controlled precisely. Carbon particles may themselves absorb analyte vapors, and slowly release them into the surrounding polymer, resulting in slow recovery times or sensor drift [5]. Finally, the carbon/polymer composite is inherently metastable, which may result in the slow redistribution of the carbon within the polymer host [6].

Another method of measuring the tiny swelling of a polymer film is through the use of microcantilevers, such as those used in various scanning force microscope instruments. The “bending” of microcantilevers to produce a measurable signal in sensing devices has been successfully used in many types of devices [7–15]. For example, in a previous microsensor design by us a piezoresistive microcantilever was placed in direct contact atop a polymer film. Swelling of the film was directly measured as a resistance change as a result of the cantilever strain [10]. Here, we have improved on that design by partially “embedding” the piezoresistive microcantilever in the polymer layer. The resulting sensing unit is simple to fabricate, requires only an ohmmeter (or multiplexing/scanning ohmmeter in the case of a sensor array) for signal measurement, and is highly robust.

2. Experimental

In the original piezoresistive microcantilever design, an external mechanical approach mechanism is used to bring a piezoresistive cantilever into contact with the sensor (polymer) film [10]. The cantilevers used in our experiments are commer-

cially available from Veeco, Inc. These cantilevers are only 100–200 μm long, and about 50 μm wide. The cantilevers contain an internal channel of piezoresistive material, connected to two tiny external electrodes. The non-stressed resistance of these cantilevers is on the order of 2 k Ω , but changes rapidly and measurably in response to any bending of the cantilever. In fact, these cantilevers are sensitive enough to measure bending strains of only a few tens of \AA , with the stated sensitivity being $1 \times 10^{-6} \text{ nm}^{-1}$ fractional change in resistance. The nominal force constant is 1 N/m. Any swelling of the polymer material in contact with the cantilever tip will result in an immediate, easily measurable change in the cantilever channel resistance. This change will be in exact proportion to the amount of the vertical swelling, a simple ohmmeter is thus sufficient to record the sensing activity. A single sensor based on the above design would occupy only a tiny area. Because of this small size, large numbers of piezoresistive cantilever-based sensors could be incorporated onto a single substrate. Each could utilize a different active sensing material, and a single multiplexing or scanning ohmmeter could record the response of the sensor array. We have previously tested sensors based upon this principle, using the organic polymers poly(vinyl acetate) (PVA), poly(isobutylene) (PIB), and poly(ethylene vinyl acetate) (PEVA) [10]. These individual sensors were exposed to the analytes water vapor, ethanol, acetone, hexane and toluene, and a unique signature was obtained for each.

In the current design, the mechanical approach mechanism is eliminated (Fig. 1). The polymer, in liquid form, is deposited directly around the tip end of the cantilever, covering approximately $\frac{1}{3}$ to $\frac{1}{2}$ of the cantilever length. For these experiments, the polymer used was lithium perchlorate doped poly(ethylene oxide) (PEO). For the liquid polymer preparation, a 10:1 polymer powder to solvent ratio was used, and the dopant level was also set to a 10:1 ratio. The polymer was allowed to dry for 24 h, after which testing of the sensor could begin. Fig. 2 is a photo of a single sensor element. The analytes used in this study included water vapor, toluene, acetone, hexane and ethanol. The analyte exposure apparatus was

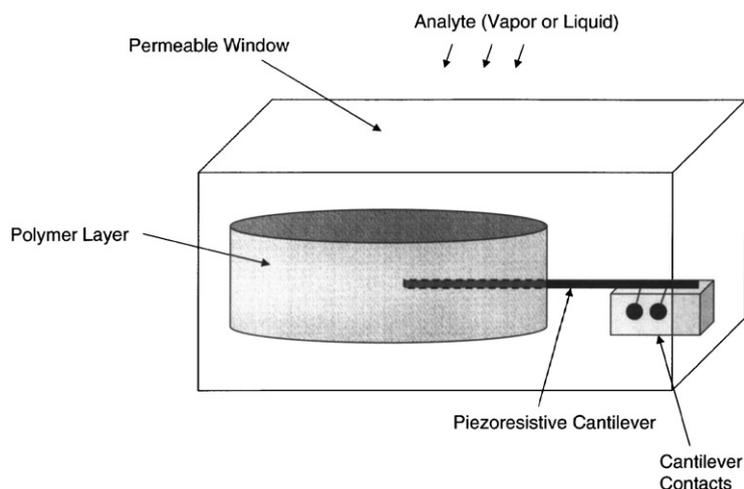


Fig. 1. Embedded polymer piezoresistive microcantilever sensor. Approximately $\frac{1}{2}$ of the cantilever length is embedded directly into the polymer sensing layer. In this new design, no mechanical tip-polymer approach mechanism is necessary.

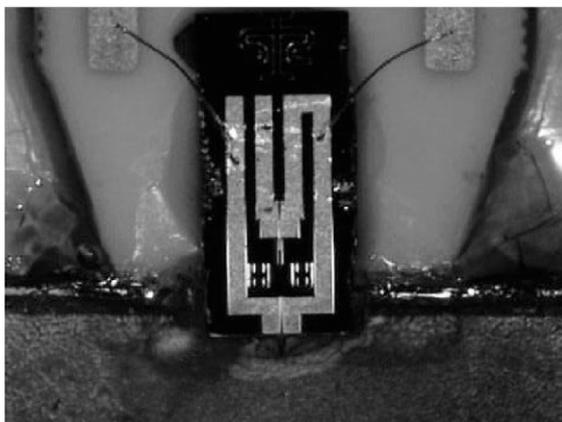


Fig. 2. Photograph of embedded polymer piezoresistive microcantilever sensor.

similar to that used in the previous study [10], and all gases were set at a 50% saturation level with respect to dry nitrogen.

3. Results and discussion

The embedded sensors required no vibration isolation, and could be handled and moved about with no adverse effects. The PEO polymer-based sensor exhibited maximum sensitivity to water

vapor. Prior to testing, the sensor was subjected to 4 h of dry nitrogen flow. Sensor output after this initial period indicated all changes owing to loss of water molecules had been reduced by approximately 97%. For all subsequent analyte measurements, a 15 s exposure to the analyte was performed, followed by a 185 s recovery period. During recovery periods, only dry nitrogen was passed over the sensor. Some residual water vapor partitioning into or out of the polymer did occur over longer periods of time, resulting in a small amount of sensor drift for the analytes acetone and hexane. This drift may also be attributable to some residual water vapor within the experimental apparatus.

In Fig. 3, the sensor response to 50% water vapor, toluene, ethanol, acetone, and hexane is indicated. Looking first at the water vapor response, in all five analyte cycles, the initial response to the water vapor is large and rapid, with a 15–17 Ω cantilever response. The recovery times are slower, taking nearly the entire 185 s period to return to the initial baseline resistance reading. Some of the lag in response time may be due to the volume of the experimental apparatus surrounding the sensor (approximately 2 l). For future designs, an array using three or more different polymers as active sensing layers may be needed to decouple the large water vapor

response from that of other analytes. This could be accomplished using pattern recognition techniques for each desired analyte, with known patterns in memory for a variety of humidity levels. Additionally, in an earlier study, the polymer poly (isobutylene) (PIB) showed little or no response to water vapor [10], while responding to a variety of other vapors. A pattern recognition algorithm for an array of polymer-based sensors containing this polymer should be able to eliminate or accommodate any large water vapor effects.

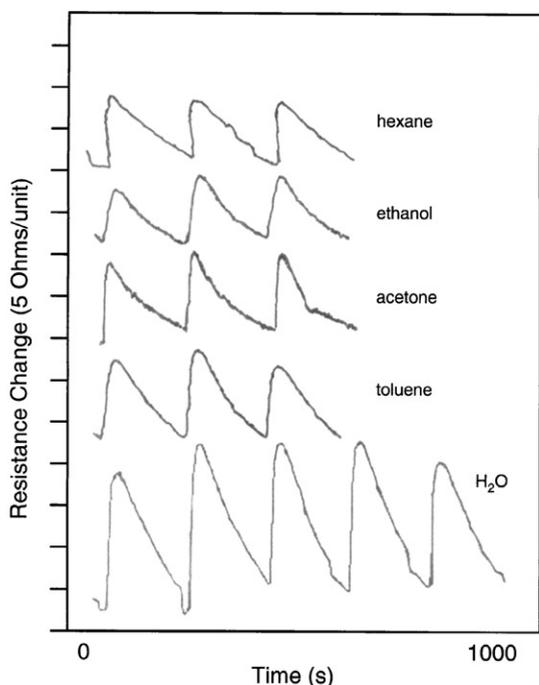


Fig. 3. Sensor response to exposure to 50% water vapor, toluene, acetone, ethanol, and hexane. 15 s exposure times were followed by 185 s recovery times for five complete cycles. The measured response to toluene was unusually large based on solubility parameter arguments alone, and may be the result of lithium perchlorate doping in the polymer.

In Fig. 3, the responses in order from smallest to greatest are hexane, ethanol, acetone and toluene (excluding water vapor). As previously mentioned, the ethanol and hexane responses show small drifts, upward for ethanol, and downward in resistance for hexane. These drifts were essentially random, occurring for all of the analytes except water vapor over at least one experimental run out of three for each analyte. Owing to the high sensitivity of the PEO sensor to water vapor, and the lack of any long-term drift in any of the water vapor trials, we believe that all of the observed drifts are due to spurious or residual water vapor in our experimental apparatus. Also, similar to the case for pure water vapor exposure, the response time for all of the analytes is very rapid, almost instantly, while the recovery times are much slower (about 185 s).

Much of the behavior of the PEO sensor to a given analyte may be explained in terms of the solubility parameters of the polymer and the analyte vapors. The solubility parameter of PEO is $22.7 \text{ MPa}^{1/2}$. A table of solubility parameters for the analytes used in this set of experiments is shown in Table 1. In general, for the partitioning of organic molecules into an organic host, we expect the greatest degree of partitioning to occur when the organic analyte solubility parameter most closely matches the host solubility parameter. Excluding water vapor, this pattern is followed in the current experiments with the exception of toluene, which should have exhibited a smaller response, between that of ethanol and hexane. This anomaly, along with the large response measured for water vapor exposure, is most likely due to the lithium perchlorate introduced into the PEO as a dopant. Also, the sensor response is measured in terms of polymer expansion, owing to the incorporation of the analyte molecules into the polymer matrix. The chemical bonding or

Table 1
Solubility parameters for the analytes used in this experiment

	H ₂ O vapor	Hexane	Toluene	Ethanol	Acetone
Solubility parameter ($\text{MPa}^{1/2}$)	48.0	16.7	18.2	26	20.5

Note: The solubility parameter of PEO is $22.7 \text{ MPa}^{1/2}$.

chemical activity of one analyte molecule may differ somewhat from one molecular species to another within the polymer matrix. The volume expansion of the polymer may depend upon the number of analyte molecules accommodated, as well as the precise chemical interaction between the polymer and the analyte. Further experiments are currently underway using embedded polymer sensors with other polymers, including pure PEO, PVA, PEVA and PIB.

4. Conclusions

The embedded polymer piezoresistive microcantilever sensor represents a marked improvement over standard piezoresistive (polymer) sensors. These new devices may be constructed easily and inexpensively. They require no initial mechanical approach mechanism, and no subsequent mechanical adjustment. The response of these devices (change in resistance) is large, owing to the relatively thick polymer layer used, and there are no adhesion problems associated with coating the cantilever with a precise polymer layer. The use of a Wheatstone bridge configuration to further improve signal/noise, however, may also improve this design [15]. After assembly, they are highly robust, and may be transported and handled with no adverse effects. Arrays of individual sensing units, using a number of different common organic polymers in the sensing layers, may be combined into sensing arrays. These arrays could provide for unique identification of a wide variety of vapor analytes. Further work on these devices may include chemiresistor/cantilever “hybrid” sensors, combining microcantilever-based sensing with chemiresistor (impedance) sensing, in order to further improve analyte selectivity.

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