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A major research effort has been devoted over the years for the development of chemical sensors for the detection of chemical and explosive vapors. However, the deployment of such chemical sensors will require the use of multiple sensors (probably tens of sensors) in a sensor package to achieve selective detection. In order to keep the overall detector unit small, miniature sensors with sufficient sensitivity of detection will be needed. We report sensitive detection of dimethyl methylphosphonate (DMMP), a stimulant for the nerve agents, using a miniature sensor unit based on piezoresistive microcantilevers. The sensor can detect parts-per-trillion concentrations of DMMP within 10 s exposure times. The small size of the sensor makes it ideally suited for electronic nose applications. © *2007 American Institute of Physics.* [DOI: 10.1063/1.2735841]

A wide variety of chemical sensor platforms, including surface acoustic wave (SAW), quartz crystal microbalance (QCM), metal oxide, conductive polymer, and microcantilever sensors, are being explored for the detection of chemical and explosive vapors.[1,2] Most of the effort so far has been devoted to the development of suitable chemical coatings for sensitive detection of different chemical and explosive vapors. However, such individual coatings are not selective for a particular analyte. In order to develop an actual detector unit that can unambiguously detect a particular vapor, selective detection of such vapors is needed to be achieved. The proposed "electronic nose"[3] involves the use of multiple sensors (with different coatings) in an approach similar to the biological olfactory system. The olfactory receptors are not highly selective toward specific odorants; each receptor responds to multiple odorants, and many receptors respond to any given odorant.[4] Pattern recognition techniques, including those based on artificial neural networks (inspired by the biological olfactory systems), are being investigated for analyzing the data from sensor arrays to identify the presence of target analytes in a given vapor mixture.

The drive behind the electronic noses is that they are expected to be smaller and much less expensive compared to the established detectors based on gas chromatography, mass spectrometry, or ion mobility spectrometry and are also expected to be easy to use. All these features make this approach attractive for a variety of applications including war on terrorism and environmental monitoring.[5] In order for the electronic nose concept to be viable, the sensors should have high sensitivity, detection in short times, fast recovery, and require long term stability of the chemical coatings used on the sensors, just as for the biological nose.

The ability to selectively detect certain analyte(s) in complex mixtures requires the use of multiple sensors in the sensor array. Therefore, a microelectromechanical system (MEMS)-based sensor platform, such as microcantilevers, is ideally suited since hundreds of individual sensors can be incorporated in a small area on the order of 1 cm^2.[5] However, just having a miniature sensor is not enough, since the detection circuitry can be large.

Previously, we developed a nonselective handheld sensor unit that had the ability to detect low concentrations of explosive vapors.[6] In that sensor unit, the flow cell containing a pair of microcantilevers and the detection electronics required an area of roughly 100 cm^2. We have recently developed a sensor package that is roughly an order of magnitude smaller. In this Note, we report the sensitive detection of dimethyl methylphosphonate (DMMP) vapors using this miniature sensor unit.

The sensor package is shown in Fig. 1. The miniature flow cell containing the microcantilever sensors is located at the right on the circuit board in the figure. The circuit board contains the Wheatstone bridge circuit and all the required electronics. A commercially available universal serial bus (USB) adapter (not shown in the figure) allows the sensor to be connected to a laptop or a desktop computer using a USB cable. Therefore, a data acquisition card is not needed in the computer. In the future, this USB-adapter circuit may be incorporated on the sensor board with the flow cell. It will also be possible to incorporate telemetry on the sensor board, thus making remote sensing possible.

The flow cell contained a microcantilever chip with four piezoresistive microcantilevers fabricated with epoxy-based photoresist SU-8 which is highly chemically resistant and
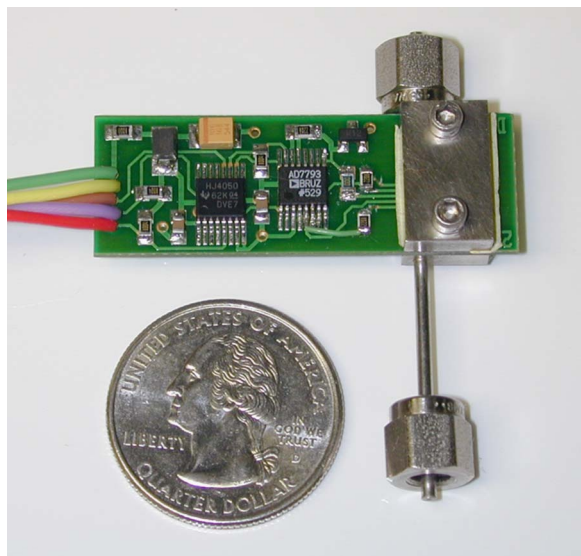
FIG. 1. (Color online) The sensor board with the flow cell is roughly 4 $\times$ 2 cm^2 disregarding the vapor inlet and outlet tubing. A US quarter-dollar coin is also shown for size comparison. Using a commercially available USB adapter, the sensor board can be connected to a personal computer (PC) or a laptop computer with a USB cable for data acquisition and display.

biocompatible.[7] Therefore, it is becoming widely used in micromechanical and microfluidic devices, not only as a photoresist but also as the constitutional material of the device. Furthermore, due to the low Young's modulus of SU-8, a high sensitivity can be obtained. The fabrication procedure and the characteristics of the SU-8 microcantilevers used in this study have been discussed in detail.[7] One surface of each of the four microcantilevers on the chip was coated with a 2 nm Ti adhesion layer and a 20 nm gold layer. Only two of the microcantilevers on a chip were used in the present study, where a 4-mercaptobenzoic acid (4-MBA) self-assembled monolayer (SAM) was applied to the gold surface of one microcantilever, with the other gold-coated cantilever used as a reference. The selective application of the 4-MBA SAM coating on only one microcantilever was achieved by placing a drop of the SAM solution on one gold-coated microcantilever by the use of a capillary tube mounted on a micromanipulator and a stereo microscope. The relative bending of the 4-MBA SAM coated cantilever with respect to a gold-coated reference cantilever was monitored using a Wheatstone bridge circuit.[6,7]

Organophosphates are found as major components in chemical warfare agents such as tabun (GA), sarin (GB), and

VX.[8] Recently, possibly due to concern about possible terrorist attacks, a number of reports have appeared on the detection of the organophosphonate DMMP using a variety of chemical sensor platforms: metal oxide sensors,[9,10] carbon nanotube sensors,[11,12] SAW sensors,[13] and microcantilever sensors.[14,15] While some of the required features for an electronic nose are satisfied according to these reports, most of them do not satisfy all the requirements [in particular, high sensitivity at low parts-per-trillion (ppt) concentrations, detection in several seconds, and reversible within a few minutes] simultaneously.

In this Note, we report fast, sensitive, and reversible detection of DMMP at low ppt concentrations using a self-assembled monolayer (SAM) coating. The stability of coatings used on the sensors is quite important for electronic noses, since the repeated application of a "trained" neural net over long periods will be possible only if the sensor response is repeatable. SAM coatings can be applied with simple procedures and are extremely stable, thus providing repeatable responses over long periods (we have been using some for over three years). Thus, this sensor meets the requirements for use in an electronic nose. Furthermore, we used a sensor unit that is truly miniature and which can be used to accommodate hundreds of individual sensors in the future for selective detection, without making the size of the sensor package large.

Bertilsson *et al.*[16] has conducted a detailed investigation of the adsorption of DMMP on three SAM coatings with respective tail groups of –OH, –CH$_3$, and –COOH prepared by the self-assembly of alkanethiols (SHCH$_2$)$_m$X ($X=-$OH, –CH$_3$, –COOH) on gold. The –COOH-terminated surface [obtained with SH(CH$_2$)$_{15}$COOH coating] yielded the highest response from DMMP, while the –CH$_3$-terminated surface [obtained with SH(CH$_2$)$_{15}$CH$_3$ coating] yielded the lowest response.[16]

The apparatus used in the present study is shown in Fig. 2. A DMMP permeation tube that was estimated at 0.25 ng/min at 30 °C (from VICI Metronics, Inc.) was used to generate the DMMP vapor. The permeation tube was located in a permeation tube holder that was immersed in a heated/refrigerated circulator that was maintained at 30 °C. The glass beads in the permeation tube helped thermalize the carrier gas quickly. The permeation tube holder and the glass beads were also purchased from VICI Metronics, Inc. Flushing of the DMMP generator for several days was required to achieve a constant rate of delivery of DMMP from the permeation tube, since initially there is some DMMP on the
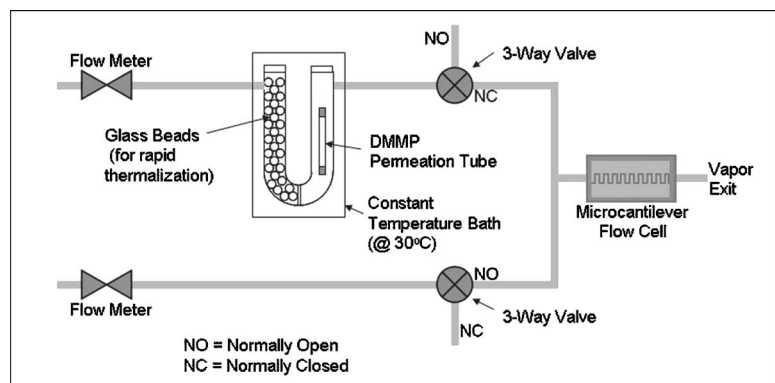

FIG. 2. A schematic diagram of the apparatus. Helium flow through the three-way valve at the bottom of the figure provided the base line for the sensor signal. A pulse of DMMP vapor was delivered to the flow cell by simultaneously activating both three-way valves which are controlled by the data acquisition computer.
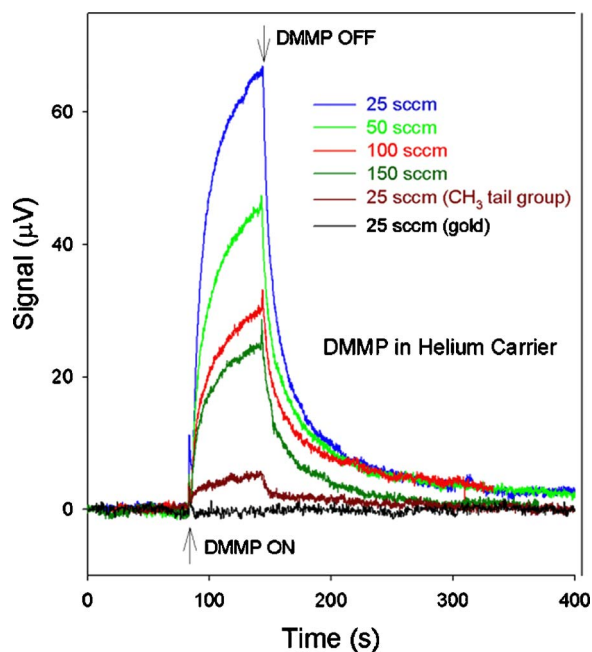
FIG. 3. (Color online) The response of a 4-mercaptobenzoic acid (4-MBA)-coated cantilever to a 1 min long pulse of DMMP at flow rates of 25, 50, 100, and 150 SCCM (in all cases, the amount of DMMP injected to the vapor stream is 0.25 ng/min). Response for a cantilever coated with the SH(CH$_2$)$_{11}$CH$_3$ coating at a flow rate of 25 SCCM is also shown, which is an order of magnitude smaller compared to the data for the 4-MBA chip at 25 SCCM. The flat trace at the bottom was obtained when a cantilever with just the gold coating was exposed to the same DMMP stream at 25 SCCM flow rate (in all cases, the signal shown is the differential signal with respect to a gold-coated cantilever on the same cantilever chip). These data were taken after purging the generator for several days.
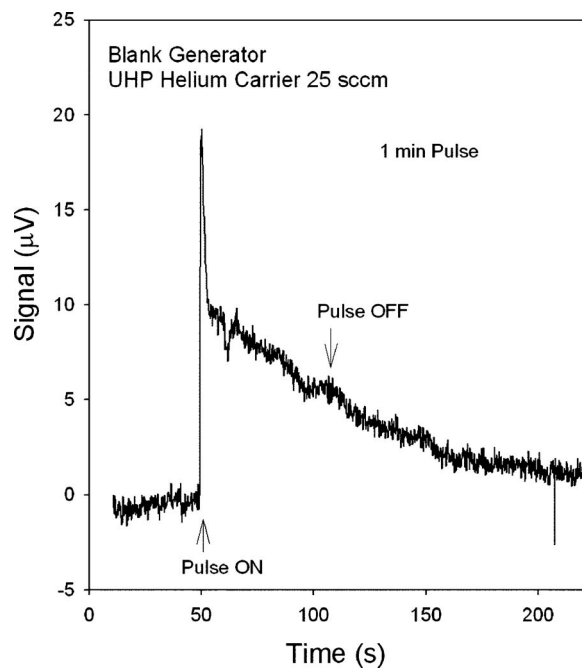

FIG. 4. The response of a 4-mercaptobenzoic acid (4-MBA)-coated cantilever to a 1 min long pulse from the "blank generator" kept at 30 °C and at a flow rate of 25 SCCM. The blank generator was purged only for a day, so this small signal is probably due to the leftover water vapor.

walls of the permeation tube due to constant permeation of DMMP. Initially, when the generator was first attached to the apparatus, a significantly larger signal was observed due to this extra DMMP and also possibly due to water vapor desorbing from the walls of the permeation tube holder and other tubings in the apparatus. This signal decayed over time and reached a plateau after 2–3 days. After that, the signal levels did not vary significantly from day to day. The data presented in this article were taken after the generator was purged for several days.

During the experiment, two computer-controlled three-way valves were used to switch between helium and DMMP in helium delivered to the flow cell at the given flow rate. Therefore, the flow rate through the microcantilever flow cell was maintained at the given flow rate during the whole experiment, and thus microcantilever bending due to change in flow was avoided.

The response of the sensor to a pulse of DMMP vapor of 1 min duration at different flow rates is shown in Fig. 3. The estimated concentrations of the DMMP vapor varied from 2 ppb at 25 SCCM (SCCM denotes cubic centimeter per minute at STP) to ≈0.33 ppb at 150 SCCM. Even though the range of concentration levels changed by a factor of 6, the signal dropped only a factor of ≈3 when the flow rate increased from 25 to 150 SCCM. Regardless of the flow rate, 0.25 ng/min is expected to be delivered to the flow cell. In order to compare with the data of Bertilsson *et al.*,[16] a cantilever on a separate chip was coated with SH(CH$_2$)$_{11}$CH$_3$. The response of that cantilever to a 1 min

pulse of DMMP at a flow rate of 25 SCCM is also shown in Fig. 3. Consistent with the results of Bertilsson *et al.*,[16] that response is much weaker compared to the response of the 4-MBA coated cantilever under the same conditions. Finally, the response of a gold-coated cantilever (with respect to another gold-coated cantilever) at 25 SCCM flow rate is shown. As expected, there is no signal with this combination.

Since the 4-MBA coating is quite sensitive to water vapor, it is important to verify that the observed signal is not due to trace water vapor. A control experiment was conducted with the DMMP permeation tube removed from the permeation tube holder (with everything else kept the same). The "signal" due to a 1 min pulse with the blank generator at a flow rate of 25 SCCM is shown in Fig. 4. We let the "blank generator" purge with helium only for 1 day (overnight), so this small signal is likely to be due to leftover water vapor on the walls of the permeation tube holder. The signal of Fig. 4 for the blank generator is to be compared with the 25 SCCM data set in Fig. 3 for the DMMP vapor stream.

The rapidity with which the DMMP vapor can be detected at low concentrations and the relatively fast relaxation of the cantilever when the DMMP vapor is turned off can be seen in Fig. 5. When the DMMP vapor is turned on for 10 s, ≈20 μV deflection signal is observed; after the vapor stream is turned off, the cantilever relaxed back almost to the original position within 60 s. The noise level (three times the standard deviation of the background) for the data of Fig. 3 is ≈1.1 μV, and thus the signal-to-noise ratio (S/N) is about 18; i.e., the detection limit for 10 s pulses is ≈30 ppt.

The ability to detect low concentrations of analytes in tens of seconds is critically important for an electronic nose (it takes less than a second for a trained neural net to analyze a data set). The achievement of sufficient selectivity with a sensor array is likely to require the use of multiple individual
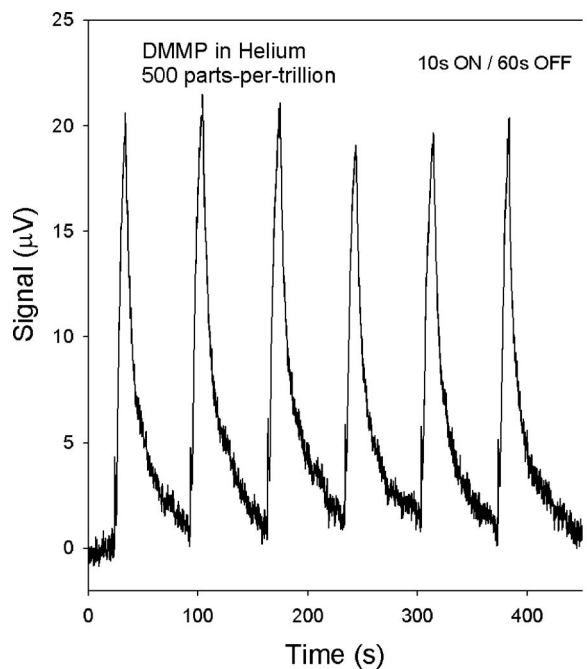
FIG. 5. The response of a 4-mercaptobenzoic acid (4-MBA)-coated cantilever to the periodic turning on (10 s) and off (60 s) of a DMMP stream of 0.5 ppb concentration in helium. Since the signal-to-noise ratio is ≈ 18, the detection limit at this fast detection rate is ≈ 30 ppt.

sensors in the sensor array (the biological nose has thousands of individual sensors called cilia, which are of size comparable to the microcantilevers). Unlike many other miniature sensor platforms such as SAW or QCM, the microcantilevers are true MEMS sensors, and it is possible to accommodate hundreds of sensors on a 1 cm^2 chip. Furthermore, as we illustrate here, a simple detection circuitry can be assembled on a miniature circuit board to monitor the signals from the microcantilever sensors. Therefore, the size of the circuit board can be kept small. Thus, selectivity for complex mix-

tures could be achieved without making the sensor package large. We are currently conducting research on the selective detection of individual vapors in vapor mixtures using an array of microcantilever sensors with the use of an artificial neural network for pattern recognition.

[1] K. J. Albert, N. S. Lewis, C. L. Schauer, G. A. Solzing, S. E. Stitzel, T. P. Vaid, and D. R. Walt, Chem. Rev. (Washington, D.C.) **100**, 2595 (2000).
[2] J. W. Gardner and P. N. Bartlett, *Electronic Noses: Principles and Applications* (Oxford University Press, Oxford, 1999).
[3] K. Persaud and G. H. Dodd, Nature (London) **299**, 352 (1982).
[4] I. Gaillard, S. Rouquier, and D. Giorgi, Cell. Mol. Life Sci. **61**, 456 (2004).
[5] L. A. Pinnaduwage, H. F. Ji, and T. Thundat, IEEE Sens. J. **5**, 774 (2005).
[6] L. A. Pinnaduwage *et al.*, Rev. Sci. Instrum. **75**, 4554 (2004).
[7] A. Johansson, M. Calleja, P. A. Rasmussen, and A. Boisen, Sens. Actuators, A **123–124**, 111 (2005).
[8] *Chemical Warfare Agents: Toxicity at Lower Levels* (CRC, Boca Raton, FL, 2000).
[9] A. A. Tomchenko, G. P. Harmer, and B. T. Marquis, Sens. Actuators B **108**, 41 (2005).
[10] C. Yu, Q. Hao, S. Saha, and L. Shi, Appl. Phys. Lett. **86**, 063101 (2005).
[11] K. Cattanach, R. D. Kulkarni, M. Kozlov, and S. K. Manohar, Nanotechnology **17**, 4123 (2006).
[12] J. P. Novak, E. S. Snow, E. J. Houser, D. Park, J. L. Stepnowski, and R. A. McGill, Appl. Phys. Lett. **83**, 4026 (2003).
[13] C. Zimmermann, P. Mazein, D. Rebiere, C. Dejous, J. Pistre, and R. Planade, IEEE Sens. J. **4**, 479 (2004).
[14] I. Voiculescu, M. E. Zaghloul, R. A. McGill, E. J. Houser, and G. K. Fedder, IEEE Sens. J. **5**, 641 (2005).
[15] Q. Zhao, Q. Zhu, W. Y. Shih, and W. Shih, Sens. Actuators B **117**, 74 (2006).
[16] L. Bertilsson, K. Potje-Kamloth, H. D. Liess, and B. Liedberg, Langmuir **15**, 1128 (1999).