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The Detection of Organophosphonates by Polymer Films on a Surface Acoustic Wave Device and a Micromirror Fiberoptic Sensor

R. C. HUGHES,* A. J. RICCO,
M. A. BUTLER AND K. B. PFEIFER

Microsensor Department 1315,
Sandia National Laboratories, Albuquerque, NM 87185

ABSTRACT

There is a need for sensitive detection of organophosphonates by inexpensive, portable instruments. Two kinds of chemical sensors, based on surface acoustic wave (SAW) devices and fiberoptic micromirrors, show promise for such sensing systems. Chemically sensitive coatings are required for detection, and data for thin films of the polymer polysiloxane are reported for both kinds of physical transducers. Both kinds of sensors are shown to be capable of detecting concentrations of diisopropylmethylphosphonate (DIMP) down to 1 ppm.

Index Entries: Organophosphates; SAW devices; fiberoptic micromirrors.

INTRODUCTION

Chemical microsensors represent a new set of technological solutions to chemical sensing problems that are not easy to solve with conventional analytical instrumentation. In a recent review article in *Science* (*1*) several of these new technologies were discussed, including sensors based on acoustic wave devices, fiber optics, miniature electrochemical cells, and

*Author to whom all correspondence and reprint requests should be addressed.

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silicon-based microelectronics. A basic theme in chemical microsensors is the interface between the chemical transducer element and the physical transducer, which results in a conversion for readout by modern electronic or electro-optic components. This article discusses how one kind of promising chemical transducer, a thin polymer film, can be used on two different kinds of physical transducers to achieve low-level detection of an important class of compounds, the organophosphonates.

Organophosphonates are closely related to chemical warfare agents, and are often either precursors or degradation products of the agents. Chemical microsensors for these species that are selective and sensitive provide a means for locating chemical-munition-producing factories, for protection from the agents, and monitoring them as toxic compounds in the environment. This article discusses the use of polysiloxane films for detecting two organophosphonates, diisopropylmethylphosphonate (DIMP) and dimethylmethylphosphonate (DMMP). These molecules both have the important carbon—phosphorous bond that often distinguishes chemical warfare agents from legitimate pesticides. These two compounds are liquids at room temperature and are safe to use in a normal chemistry laboratory with proper precautions. They have often been used as simulants for chemical warfare agents because they contain the carbon—phosphorous bond (*2,3*).

The authors show how different properties of the absorption of DIMP or DMMP are sensed when the film is used as a chemically sensitive coating on a surface acoustic wave (SAW) device vs a coating on a fiberoptic micromirror sensor.

EXPERIMENTAL

Surface Acoustic Wave Sensors

The techniques for constructing and reading out surface acoustic wave chemical sensors have been described in detail (*4*). The transduction technique involves the use of acoustic waves to detect the accumulation of species in or on a chemically sensitive film. The technique originated with the use of quartz resonators that were excited into thickness-shear resonance to monitor vacuum deposition of metals (*5*). The SAW device is operated in an oscillator configuration, with changes in oscillation frequency being simply related to the areal mass density accumulated on the crystal face. These devices have been coated with chemically sensitive films to produce gas and vapor detectors (*4*). The films discussed in this article are both a plasma-polymerized (1 μm thick as discussed in ref. [*4*]) and a spin-coated polysiloxane film about 0.3 to 0.5 μm thick. It was spun from a toluene-based solution containing 3–5% vinyl groups in the dimethylpolysiloxane. There was also $10^{-4}M$ benzoin, which acts as an initiator for a photopolymerization to toughen the film.

Polysiloxanes had been previously used to detect a variety of volatile organics, and have shown remarkable speed and reversibility compared to other polymer films (*4*). In addition, they do not respond strongly to water vapor. This is the first report of the use of polysiloxanes to detect organophosphonates.

Fiberoptic Micromirror Sensors

The micromirror fiberoptic sensor has also been described in detail elsewhere. It uses changes in the reflectivity of thin coatings on the end of an optical fiber (*6*). Using semitransparent metal films (100 Å thick), changes in reflectivity are observed from the chemisorption of submonolayer coverages of molecules on the metal surface. These changes reflect the nature of the chemisorption bond, as well as the optical properties of the chemisorbed atom or molecule. With a 50 μm diameter fiber core defining the size of the sensing area, the presence of $< 10^8$ mercury atoms has been detected using thin gold films (*7*). Similarly, the presence of less than one billion trichloroethylene (TCE) molecules has been detected by using a thin polymer coating on the end of the fiber (*8*). For this sensor, a plasma-polymerized tetrafluoroethylene film is deposited on the end of the fiber and forms a small optical cavity. The polymer absorbs the TCE and swells. The changes in dimensions of the optical cavity change its reflectivity. This article reports the first results of a polysiloxane polymer film deposited as a micromirror. The film was deposited in a plasma deposition system using hexamethyldisiloxane vapor with the procedure as described in ref. (*8*). The deposition rate was calculated to be on the order of 3–4 Å/s. The polymer film is 3940 Å thick and was deposited on top a 580 Å thick silicon film that aids in better adhesion to the fiber and gives higher reflectivity at the first interface through which the light must pass.

CONCENTRATIONS OF VAPORS

The various concentrations of the vapors of both DIMP and DMMP were produced by flow controllers that could mix two gas streams: one flowed pure N_2 through a glass bubbler containing either pure DIMP or pure DMMP, and the other a dry N_2 stream. In the case of the fiberoptic micromirror, the fiber end was inserted into a Pyrex tube through which the mixed stream flowed. In the case of the acoustic wave device, a special RF-shielded fixture was used with fittings to allow the gas to flow over the SAW device surface. The bubblers were thermostatted at 25°C. The vapor pressure of DIMP was recently remeasured (*2*) and found it to be considerably higher at 25°C than some previous authors had reported: 0.7+/−0.2 torr. The DMMP vapor pressure has been reported to be 1 torr at 25°C (*9*). Using the flow controller method, concentrations of DIMP could be generated and measured down to a ratio of P/P_{sat} of 0.1%, which

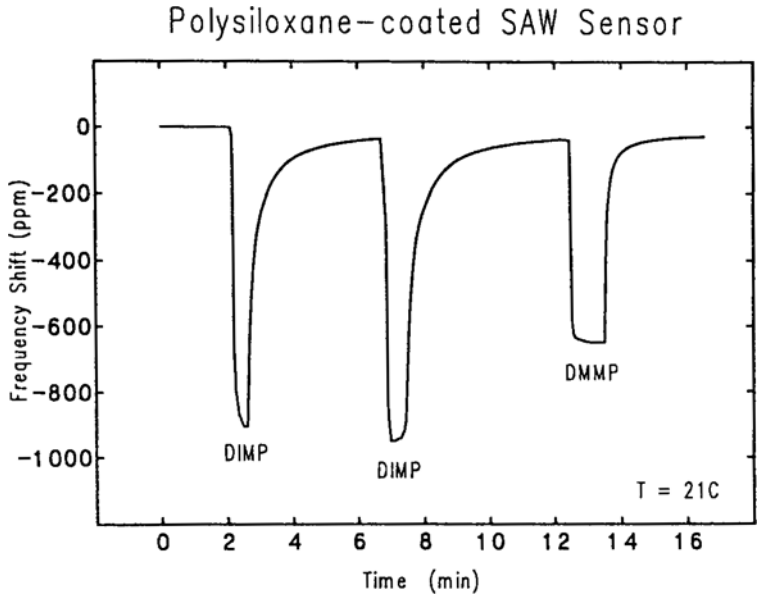

Fig. 1. The response of a SAW sensor with a polysiloxane coating to vapors of DIMP and DMMP. The vapors were drawn across the SAW device surface by a small pump, and the fast response is seen as a drop in frequency. The increase in frequency occurs when a scrubber is put in series with the pumped gas stream, and the DIMP and DMMP desorb.

corresponds to a concentration of about 1 ppm (all ppm values refer to moles of vapor per mole of air or N_2, assuming ideal gases).

RESULTS

SAW Sensors

Figure 1 shows the results of exposing the plasma-polymerized film on the SAW to vapors pulled from an open flask containing DIMP at 21°C. The frequency of the SAW, given in units of ppm, decreases very quickly on exposure, showing an increase in mass owing to DIMP molecules absorbing into the polymer film. The rapid increase in frequency corresponds to the point in time when a charcoal scrubber was switched in series with the gas flow. The scrubber removes all DIMP molecules from the flow, and the rapid increase in frequency back toward the baseline shows that the DIMP is desorbing readily from the film at 21°C. The concentration of DIMP was <1000 ppm in this case because of the dilution caused by pumping on the head space over the liquid in air. A second pulse of this concentration shows a similar fast response. The third pulse of vapor was from DMMP, which gives a smaller response even though the concentration is somewhat larger than the DIMP; note that DMMP

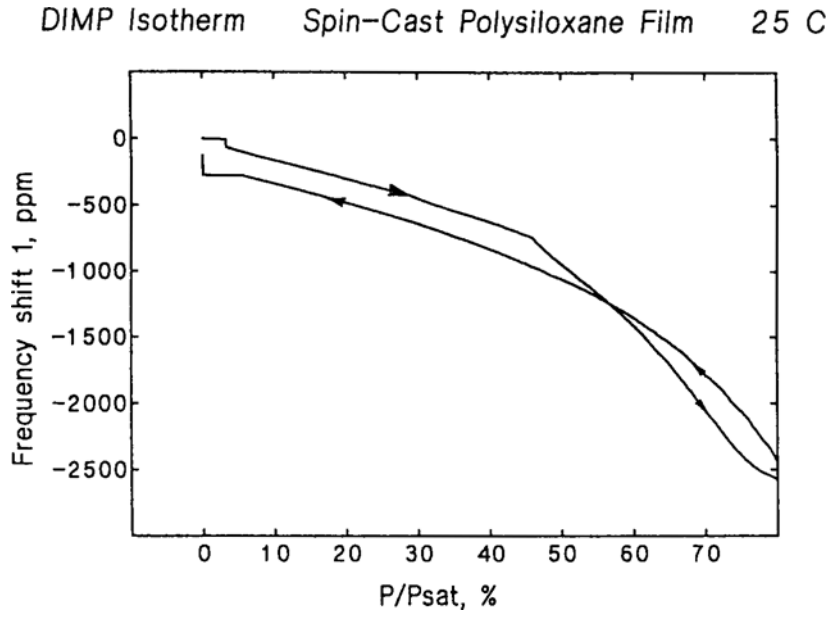

Fig. 2. The isothermal response at 25°C for DIMP on a spin-cast polysiloxane surface. The curve with the arrow pointing to the right is for increasing pressure, defined as P/P_{sat}, the fraction of the saturated vapor pressure. The curve with the left-pointing arrow is for the desorption cycle. A decrease in oscillator frequency, given in units of ppm, indicates increasing mass loading. The smallest increment in pressure is 3% and can be seen as a step in the absorption curve.

has a mol wt that is 69% of DIMP's mol wt. These experiments were performed using a portable sensor system known as the PAWS (Portable Acoustic Wave Sensor) (4). The SAW device and much of the electronics have been packaged in a compact box that also contains a small pump to bring in air samples and a three-way valve that allows the sample stream to be cleaned in the charcoal scrubber mentioned above.

The polysiloxane film in the PAWS box showed that it is a very good absorbing film for both DIMP and DMMP, appears not to have a permanent chemical reaction, and that the phosponates are easily absorbed and desorbed at 21°C. To learn more about the detailed sensitivity of polysiloxane films, the spin-cast version of the film (about 0.5 micron thickness) was chosen and the flow-control system described above was used to give lower and more precise values of the DIMP concentration. Figure 2 shows the isotherm at 25°C for DIMP with N_2 as the carrier gas. The step from pure N_2 to the lowest concentration (P/P_{sat} of 3%) is easily observable, but because of the linear scale of the graph, it appears quite small. The ramp for increasing partial pressure is indicated by the arrows pointing to the right. A computer-controlled flow controller system was used to ramp the partial pressures, and a complete run from P/P_{sat} of

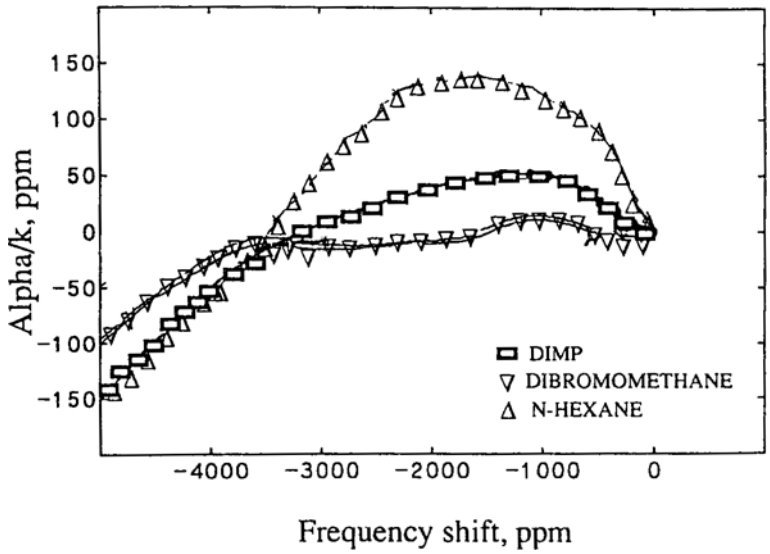

Fig. 3. Dual output data from a SAW device for DIMP and two solvents, *n*-hexane and dibromomethane. Each data point, moving from right to left, corresponds to a step increase in the P/P_{sat}. The unique signature of each compound allows molecular identification and determination of the concentration.

0–80% and back took 12 h. The slow ramp and small steps were to ensure equilibrium between steps. The negative shift in frequency corresponds to an increase in mass absorbed by the polysiloxane film, and the size of the signal is comparable to that obtained in Fig. 1 for similar concentrations.

The results in Fig. 2 show that the polysiloxane film is quite sensitive to low concentrations of DIMP, but the question remains of distinguishing DIMP or DMMP from other common molecules in the environment. The dual output method, developed at Sandia (4), allows some discrimination. The details of the method are given in ref. (4), but basically it involves the measurement of the attenuation response of the film at the same time that the frequency shifts are measured. This provides two values for the response of the film for each partial pressure (concentration) of the vapor to be measured. In ref. (4) it was shown that this method allowed several chlorinated hydrocarbons to be distinguished from solvents like *n*-hexane. Figure 3 shows a comparison of the response for DIMP and two solvents with widely different liquid densities: *n*-hexane and dibromomethane. Each data point for each vapor corresponds to an increase in pressure moving from right to left. The actual partial pressures for DIMP can be obtained by comparison with the data in Fig. 2 for the frequency shifts. The P/P_{sat} values for the other molecules are comparable. The difference in attenuation response at a given frequency shift would allow the user to decide if the signals were owing to DIMP vapor or one of the others. Data for a number of other volatile organics for polysiloxanes have been measured (4).

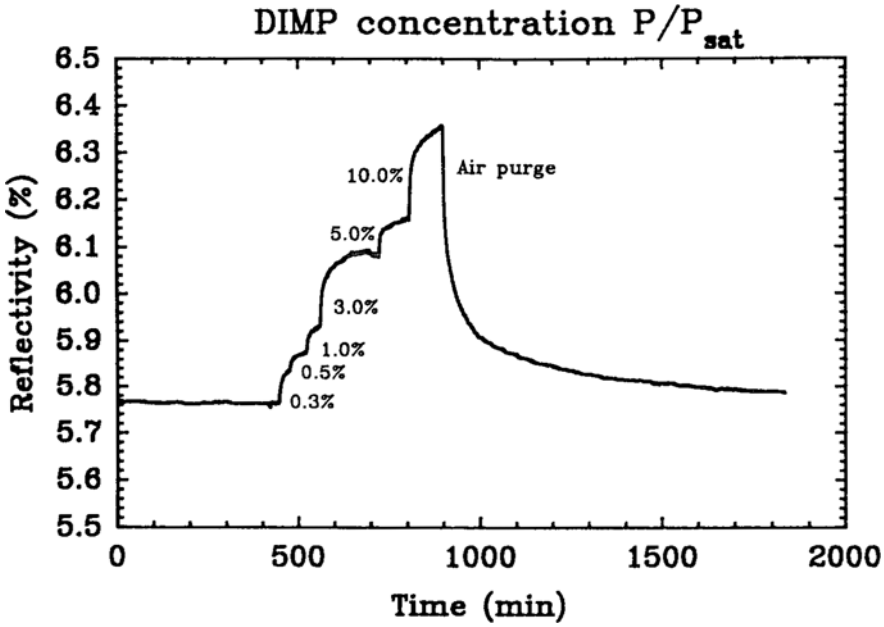

Fig. 4. The change in reflectivity of a micromirror fabricated from a polysiloxane film. The baseline drift in air is seen up to the point where 0.3% P/P_{sat} of DIMP is introduced. The subsequent steps in P/P_{sat} are indicated in the figure, followed by a purge in dry air.

Fiber-Optic Micromirror Sensor

The fiber-optic micromirror coated with a plasma-polymerized film of polysiloxane also responds to low concentrations of DIMP. Figure 4 shows the isothermal response of the reflectivity at 23°C for six increasing values of P/P_{sat}. Part of the time to reach steady state at each value is owing to the low flow rates and the time for the new P/P_{sat} to be established. The flow rates are typically 100 mL/min. The increase in reflectivity with increasing partial pressure is expected for absorption of the DIMP, which causes an increase in the polymer film thickness. Figure 5 shows the change in reflectivity as a function of P/P_{sat} on a log-log plot for clarity. The dynamic range of the micromirror sensor for DIMP is seen to be quite large. The closed circles and open triangles are from two separate runs of increasing P/P_{sat} similar to the run shown in Fig. 4. The repeatability is very good at the higher pressures. The lowest concentration of DIMP that could be detected was about 1 ppm in N_2.

DISCUSSION

Polymer films have been employed for chemical detection on both SAW and fiberoptic micromirrors for a number of applications, but this is

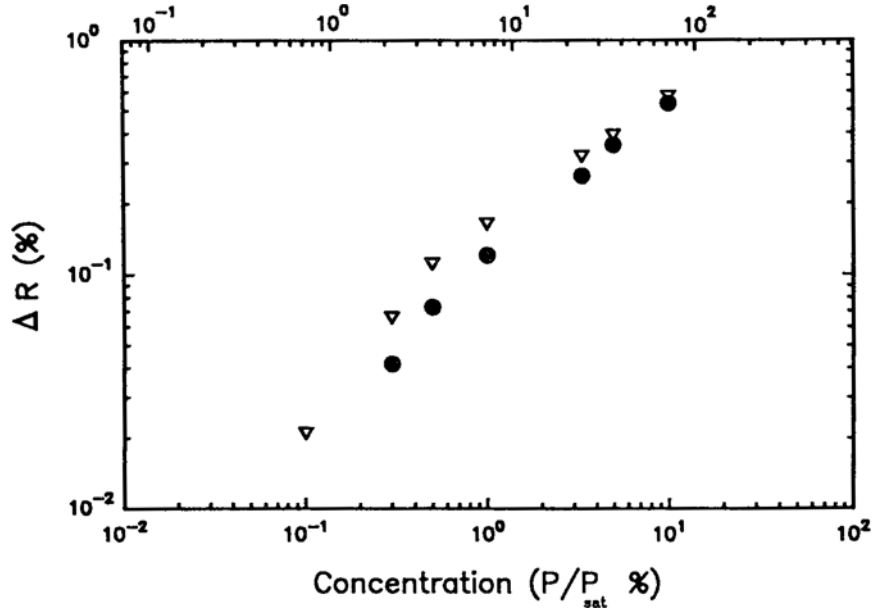

Fig. 5. Data from two runs similar to the one shown in Fig. 4. The change in reflectivity is given as a function of P/P_{sat} on a log-log plot. The closed circle and the open triangles indicate two separate runs with an air purge in between. The lowest observed concentration is about 1 ppm of DIMP.

the first report on a comparison of the same kind of polymer on both physical transducers for the same molecular species. In principle, the absorption and desorption mechanisms for DIMP and DMMP in polysiloxanes are independent of the physical transducer. The desorption data indicate that the organophosphonates are not chemically reacting with the polymer. The increase in mass seen in the frequency shift in Figs. 1 and 2 shows that the DIMP molecules have an affinity for the polysiloxane and are preferentially partitioning out of the gas phase into the polymer film. The change in attenuation that accompanies the mass accumulation shows that the viscoelastic properties of the polysiloxane are altered by the plasticizing action that occurs when the DIMP molecules insert between the polymer chains. The differences in mass loading and plasticizing action among different molecules are what allow the discrimination seen in Fig. 3.

The changes in reflectivity seen in the fiber-optic micromirror indicate that the DIMP molecules are swelling the film and changing its thickness. There is no comparable dual measurement that can be made with the fiber-optic micromirror to obtain better discrimination between DIMP and other molecules.

In summary, both physical transducers allow sensitive measurement of organophosphonates when using polysiloxane films as the chemical transducer. They both can detect concentrations as low as 1 ppm. The SAW sensor has the advantage that the dual output method allows some

discrimination between DIMP and other common solvents. However, if the vapors are mixed, there is no way to obtain the concentrations of each species with a single polymer film. An array of SAW sensors with different coatings could be used along with pattern recognition algorithms to distinguish both the identity and concentration of several species. Work on such arrays is proceeding in the authors' laboratory. Fiber-optic micromirrors offer extremely small sensors, which can be placed a long distance from the measuring electronics. They offer considerable immunity from electromagnetic interference and can provide sensing in regions where electrical wiring is undesirable. The total system weight for an array of fiber-optic micromirrors with different selective coatings is likely to be considerably less than the same number of SAW sensors. The selection of the most appropriate physical transducer system for a given application in the detection of organophosphonates will depend on these factors and others as the chemical sensing technology is developed.

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