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Detection of Fluorophosphonate Chemical Warfare Agents by Catalytic Hydrolysis with a Porous Silicon Interferometer

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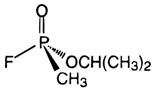
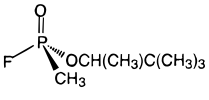
Porous silicon (PSi) has been investigated extensively since the discovery of its luminescence properties in 1990.[1] Prepared by electrochemical etching of a silicon substrate in HF, PSi presents a high surface area (a few hundred m^2/cm^3) which has shown to be useful for a variety of applications[2−4] including sensitive thin film chemical and biological sensors.[5,6]

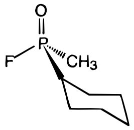
Rapid detection of sarin, soman and GF chemical warfare agents is currently of great interest. These compounds are highly toxic (death may follow one minute after direct ingestion of 0.01 mg per kg of body weight), and there are growing concerns about their use as chemical weapons for terrorist or war actions (in May 1995, terrorists released sarin gas in a Tokyo subway, killing 12 persons and injuring 5500). The main method currently used to detect nerve agents is based on a surface acoustic wave (SAW) device.[7,8] Other techniques using enzymes[9] have also been developed. Diisopropylfluorophosphonate (DFP) is a widely used simulant for the chemically similar nerve warfare agents sarin, soman, and GF.



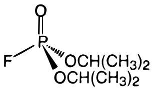
Sarin



Soman



GF



DFP

It has recently been demonstrated[10] that HF vapor can be detected with a surface oxidized PSi interferometer. Removal of the oxide layer as volatile $SiF_{4(g)}$ results in a decrease of the optical index of the film, which is recorded as a blue-shift of the Fabry−Pérot fringes. The aim of this work was to use the fact that the hydrolysis of the nerve agent simulant DFP produces HF gas (eq 1). Hydrolysis of nerve warfare agents has been widely investigated for decontamination applications in the past decades.[11] Fluorophosphonate esters hydrolyze spontaneously in air, but the hydrolysis rate can be increased substantially by chemical catalysts[12−15] or enzymes (eq 1).[16,17]

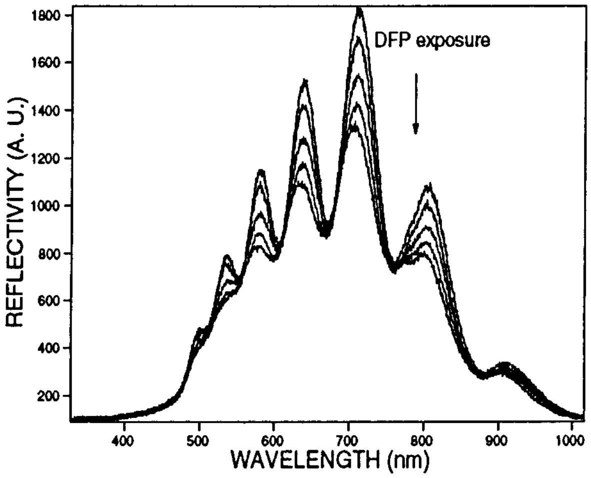
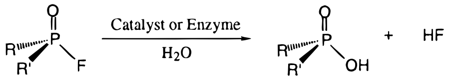


Figure 1. Reflectivity spectra of a PSi sample containing TMEDA-[Cu(II)] and CTABr surfactant were recorded every 5 min, in situ, under a flux of DFP in wet air. A blue-shift (15 nm) and decrease in fidelity of the Fabry-Pérot fringes are observable.



(1)

Chemical specificity in the detector is obtained by incorporating a catalyst in the interferometer thin film that selectively hydrolyzes P−F bonds. The catalysis event triggers an irreversible chemical reaction (the dissolution of SiO_2 by HF), so that the signal accumulates with every additional molecule recognized (eq 1). The nerve agent is detected by the shift to the blue and a decrease in intensity of the Fabry−Pérot interference fringes from the PSi interferometer.

The PSi thin films were prepared as described previously.[10] Incorporation of a copper hydrolysis catalyst was achieved by soaking the porous Si sample in an aqueous solution containing 0.01 M of tetramethylethylenediamine copper complex, TMEDA-[Cu(II)], and 1 wt % of the surfactant cetyltrimethylammonium bromide (CTABr). The sample was dried under vacuum, and placed in the exposure chamber fitted with transparent windows. The TMEDA[Cu(II)] complex was one of the first catalysts discovered for the hydrolysis of sarin,[12] and more recent studies have shown that added surfactant accelerates hydrolysis of nerve agents.[18] After catalyst incorporation, the samples were then exposed to a flux of DFP (partial pressure of 0.6 Torr or 800 ppm) in wet air. Figure 1 shows reflectivity spectra recorded every 5 min, in situ, while exposing the detector to the nerve agent simulant DFP. A decrease in fidelity and a blue-shift of the Fabry−Pérot interference fringes is observed. The blue-shift in the fringes requires a decrease in the optical index of the film. Such behavior is expected if silicon oxide is removed by HF gas produced by the hydrolysis reaction, as depicted in eq 2. The

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[1] Canham, L. T. *Appl. Phys. Lett.* **1990**, *57*, 1046.

[2] Motohashi, A.; Kawakami, M.; Aoyagi, H.; Kinoshita, A.; Satou, A. *Jpn. J. Appl. Phys.* **1995**, *34*, 5840−5843.

[3] Harper, J. Ph.D. Thesis, University of California, San Diego, 1996.

[4] Schoning, M. J.; Crott, M.; Ronkel, F.; Thust, M.; Schultze, J. W.; Kordos, P.; Luth, H. *Electrochim. Acta* **1997**, *42*, 3185−3193.

[5] Lin, V. S.; Motesharei, K.; Dancil, K. S.; Sailor, M. J.; Ghadiri, M. R. *Science* **1997**, *278*, 840−843.

[6] Dancil, K.-P. S.; Greiner, D. P.; Sailor, M. J. *J. Am. Chem. Soc.* **1999**, *121*, 7925−7930.

[7] Nieuwenhuizen, M. S.; Harteveld, J. L. N. *Sens. Actuators B* **1997**, *B40*, 167−73.

[8] Williams, D.; Pappas, G. *Field Anal. Chem. Technol.* **1999**, *3*, 45−53.

[9] LeJeune, K. E.; Wild, J. R.; Russell, A. J. *Nature* **1998**, *395*, 27−28.

[10] Letant, S.; Sailor, M. J. *Adv. Mater.* **2000**, *12*, 355−359.

[11] Yang, Y.-C.; Baker, J. A.; Ward, J. R. *Chem. Rev.* **1992**, *92*, 1729−1743.

[12] Courtney, R. C.; Gustafson, R. L.; Westerback, S. J.; Hyytiainen, H.; Chaberek, S. C., Jr.; Martell, A. E. *J. Am. Chem. Soc.* **1957**, *79*, 3030−3037.

[13] Gustafson, R. L.; Martell, A. E. *J. Am. Chem. Soc.* **1962**, *84*, 2309−2316.

[14] Epstein, J.; Bauer, V. E.; Saxe, M.; Demek, M. M. *J. Am. Chem. Soc.* **1956**, *78*, 4068−4071.

[15] Epstein, J. *Science* **1970**, *170*, 1396−1398.

[16] Czafranic, L. L.; Cheng, T.-C.; Rastogi, V. K.; Defrank, J. J.; Sawiris, G. P. *Enzyme Eng. XIV* **1998**, *846*, 253−258.

[17] Defrank, J. J.; Beaudry, W. T.; Cheng, T.-C.; Harvey, S. P.; Struop, A. N. *Chem. Biol. Interact.* **1993**, *87*, 141−148.

[18] Blasko, A.; Bunton, C. A.; Hong, Y. S.; Mhala, M. M.; Moffatt, J. R.; Wright, S. *J. Phys. Org. Chem.* **1991**, *4*, 618−628.

10.1021/ja0006200 CCC: $19.00

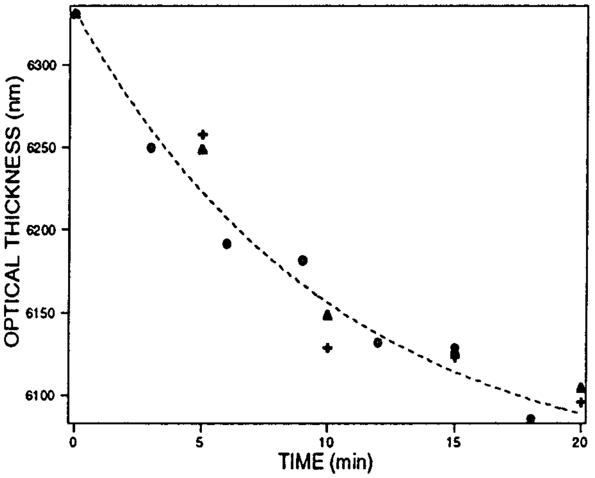

Figure 2. Behavior of the effective optical thickness of PSi thin films versus time upon DFP exposure. This plot shows experimental points obtained in three replicate experiments performed with samples prepared as indicated in Figure 1. The dotted line is the exponential fit $OT = a + b\ \exp(-kt)$, with *OT* the optical thickness and *t* the time. The fitting parameters are: $a = 6046$ nm, $b = 285$ nm and $k = 0.1$ min^{-1}. The data are shifted along the *y* axis (by from 0 to 60 nm) such that they all begin at an optical thickness of 6331 nm.

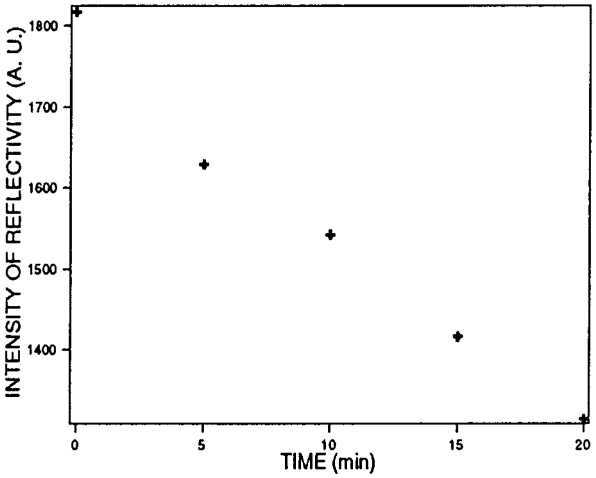

Figure 3. Behavior of the intensity of the spectral fringe occurring at 710 nm versus time of DFP exposure, taken from Figure 1.

experiment was repeated three times under identical experimental conditions with comparable results. A control experiment was performed in which a sample was only exposed to a flux of wet air. No detectable change in the reflectivity pattern was observed during a 1 h exposure period.

$$4HF + SiO_2 \rightarrow SiF_{4(g)} + 2H_2O \tag{2}$$

The decrease in optical thickness (obtained from a Fourier transform of the interferogram) of three samples exposed to DFP gas (Figure 2) appears to be exponential. This observed decrease in detector response with exposure time is attributed to catalyst deactivation. The activity of copper catalysts toward phosphate ester hydrolysis has previously been shown to be strongly dependent on pH, with the catalyst activity decreasing significantly below pH 6.0.[19,20] Data were recorded for 20 min, although a measurable modification of the optical thickness (2%) is detected after 5 min of exposure (Figure 2).

Control experiments on samples containing neither catalyst nor surfactant and samples containing only surfactant were also performed. An oxidized PSi sample containing neither catalyst nor surfactant leads to no detectable change in the interference pattern during a 20 min exposure to DFP vapor. A sample containing only surfactant exhibits a small blue-shift corresponding to a decrease of 0.1% of the optical thickness in 20 min. When the sample matrix contains both surfactant and copper catalyst (Figures 1 and 2), the decrease of the optical thickness over the same period of time is increased 40-fold. Thus, specificity for detection can be achieved by use of a reference PSi sample not containing surfactant and catalyst. A signal will only be detected for compounds in the vapor that are converted into HF through catalytic hydrolysis. Previous studies have shown that the porous Si interferometer is insensitive to other mineral acids, water, and organic solvent vapors.[10,21]

Figure 3 shows the behavior of the intensity of the reflectivity fringes at a fixed wavelength during DFP exposure. The decrease of this parameter after 5 min of gas exposure is about 10%, which is 5 times more sensitive than the modification of the optical thickness. The intensity of reflectivity depends on the reflection coefficients at the PSi/air and PSi/Si substrate interfaces. A decrease in the optical index of the film due to removal of oxide should induce both a blue-shift and a decrease in fidelity of the Fabry−Pérot fringes. However, the relative loss in fringe intensity is more than 5 times larger than the relative decrease in the optical index. This cannot be accounted for in a simple effective medium model and implies that the predominant change in the refractive index occurs at the surface of the porous layer. Scanning electron microscopy and energy-dispersive X-ray analysis show copper-containing catalyst crystallites segregated on the surface of the PSi film.

The second method for catalyst incorporation involved covalently linking a modified Cu catalyst to the PSi surface by refluxing PSi in a 100 mM solution of the *N,N,N′*-trimethyl-*N′*-propyldimethylmethoxysilylethylenediamine dissolved in toluene for 12 h. After derivatization the PSi sample was rinsed with toluene, methanol, and water several times, respectively, and soaked in an aqueous solution of 0.01 M $Cu(NO_3)_2$ for 2 h. The treated sample was washed with water several times and dried under vacuum. Upon exposure of DFP, no significant modification of optical thickness and intensity of the reflectivity fringes were observed. A PSi thin film was also covalently modified as described above, soaked in 0.01 M $Cu(NO_3)_2$ and soaked in 0.01 M aqueous solution of the CTABr before exposure to a flux of DFP in wet air for 10 min. This surface-attached catalyst shows no detectable modification of optical thickness, but it displays a 39% decrease of the intensity of the reflectivity fringes. This result further indicates that the predominant chemical reaction may be occurring on the surface of PSi rather than deep in the porous layer. Such behavior could arise from simple diffusive constraints or from an inhomogeneous distribution of catalyst in the porous matrix. Although it appears to be more sensitive, measurement of fringe intensity was not as reproducible as measurement of the blue-shift of the Fabry-Pérot fringes. Recording both parameters constitutes the most efficient configuration for a device.

In summary, the detection of a fluorophosphonate nerve CW agent can be achieved with an oxidized porous silicon interferometer film containing a copper(II) hydrolysis catalyst and surfactant. Hydrolysis of the nerve agent produces HF gas, which removes the silicon oxide as $SiF_{4(g)}$ and induces both a blue-shift and a decrease in intensity of the Fabry−Pérot fringes. Significant changes in these two parameters are detected after 5 min of DFP vapor (800 ppm) exposure.

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(19) Morrow, J. R.; Trogler, W. C. *Inorg. Chem.* **1988**, *27*, 3387−3394.
(20) Morrow, J. R.; Trogler, W. C. *Inorg. Chem.* **1989**, *28*, 2330−2333.
(21) Content, S.; Trogler, W. C.; Sailor, M. J. *Chem. Eur. J.* **1999**, in press.