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ARTICLE *in* ANALYTICAL CHEMISTRY · JUNE 2004

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# Detection of Femtomolar Concentrations of HF Using an SiO<sub>2</sub> Microcantilever

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**Femtomolar concentrations of hydrogen fluoride, a decomposition component of nerve agents, were detected using a SiO<sub>2</sub> microcantilever. The microcantilever underwent bending due to the reaction of HF with SiO<sub>2</sub>. The microcantilever deflection increased as the concentration of HF increased. Other acids, such as HCl, had no effect on the deflection of the cantilever. The mechanism of reaction-induced bending and the correlation of microcantilever deflection with the HF concentration are discussed. The deflection in response to HF of a commercially available silicon cantilever was also studied, and its response was compared with that of the SiO<sub>2</sub> cantilever. Much less bending amplitude and sensitivity were observed for the silicon cantilever.**

The threat posed by nerve agents has made them important targets for detection. Fluorine is a major component in many nerve agents, including sarin and soman. Nerve agents decompose quickly in alkaline conditions. After decomposition, the nerve agents release hydrogen fluoride or F<sup>−</sup> into the solution. Simultaneous identification of HF or F<sup>−</sup> and organophosphorus is a very helpful and reliable way to detect the existence of nerve agents. Furthermore, detection of HF is important itself because HF is highly toxic. Exposure to HF can cause injury through inhalation, direct contact, or ingestion. Airborne fluorides have caused more worldwide damage to domestic animals than any other air pollutant. HF is used industrially in large quantities throughout the United States (over 200 000 tons/year) and in a great number of applications across a broad range of industries (over 500 facilities).<sup>1,2</sup> HF serves as a major feedstock and source of the fluorine atom for the production of fluorinated compounds. Fluorocarbon manufacture consumes 63% of the total HF used. HF is also used as an alkylation catalyst for the production of gasoline blending components. Other uses include aluminum production and semiconductor applications.

Analytical methods employed currently to measure HF in an industrial environment include the infrared (IR) spectroscopic method,<sup>3,4</sup> electrochemical methods,<sup>5,6</sup> ion mobility spectrometry,<sup>7</sup>

interferometry,<sup>8,9</sup> and solid-state metal oxide or semiconductor gas sensor,<sup>10</sup> etc. The IR spectroscopic method requires instrumentation that is bulky, expensive, and complex and therefore not suited to the *field* analysis of multiple samples. Other sensing devices are excellent for real-time, in-field analysis of HF at part-per-million (ppm) level. They are appropriate for detection of leaking HF. However, the sensitivity of these systems is not sufficiently high for detecting and monitoring HF at part-per-billion or lower concentrations.

Recently, microcantilevers have been emerging as outstanding novel platforms for sensors with on-chip electronic circuitry and extreme sensitivity.<sup>12–22</sup> Selectivity of the microcantilever sensors has been achieved by modifying the microcantilevers with coatings or by covalently binding molecular recognition agents for identification of chemically specific species. The unique characteristic of microcantilevers is their ability to undergo bending due to molecular adsorption or a binding-induced change in surface tension. This bending is achieved by confining the adsorption to one side of the cantilever. Microcantilever bending occurs in both air and solution. Five methods (optical,<sup>23</sup> piezoresistive,<sup>24</sup> piezo-

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(1) Information can be found from EPA reports, Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units, at <http://www.epa.gov/ttn/oarpg/t3rc.html>.

(2) <http://www.fluoridealert.org> and references therein.

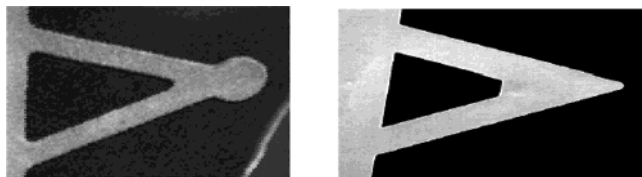
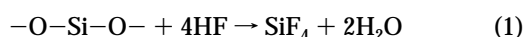


Figure 1. Scanning electron microscope pictures of a SiO<sub>2</sub> cantilever (left) and a silicon cantilever (right).

electric,<sup>25,26</sup> tunneling,<sup>27</sup> capacitive<sup>28</sup>) can be used for detection of cantilever motion.

Recently, we have fabricated and characterized an SiO<sub>2</sub> microcantilever.<sup>29</sup> The SiO<sub>2</sub> microcantilever could be particularly useful for the detection of HF because of the characteristic reaction of HF with SiO<sub>2</sub>. HF selectively reacts with SiO<sub>2</sub> as shown in the following reaction, which has been widely used in the silicon industry.<sup>30</sup>



This is a very characteristic reaction. Several current commercial devices, such as the Shur-Shot HF detection system (Molecular Analytics Inc.), for HF measurement are also based on this reaction (either in air or in solution). Other acids, such as HCl and H<sub>2</sub>SO<sub>4</sub>, do not react with SiO<sub>2</sub>. We report here a highly sensitive SiO<sub>2</sub> microcantilever sensor for HF.

## EXPERIMENTAL SECTION

**Solvent and Materials.** In our experiments, we used a microcantilever fabricated in our laboratory<sup>29</sup> as well as commercially available silicon microcantilevers (Veeco Instruments) and SiO<sub>2</sub> (Figure 1). The dimensions of the V-shaped silicon microcantilevers were 180 μm in length, 25 μm in leg width, and 1 μm in thickness. One side of these cantilevers was covered with a thin film of chromium (3 nm) followed by a 20-nm layer of gold, both deposited by e-beam evaporation. On the uncoated side of the commercial microcantilever was silicon with a 12–19-Å-thick naturally grown SiO<sub>2</sub> layer, which is called “native oxide”.<sup>31</sup> The dimensions of the V-shaped SiO<sub>2</sub> microcantilevers were 200 μm in length, 25 μm in leg width, and 2 μm in thickness. One side of the SiO<sub>2</sub> cantilevers was covered with 3 nm of chromium/20 nm of gold as well.

The chemicals used in these experiments, including HF, KF, and HCl, were used as received from Aldrich. High-purity deionized water was obtained with a Milli-Q water system (Millipore). The pH of the deionized water was 6.90.

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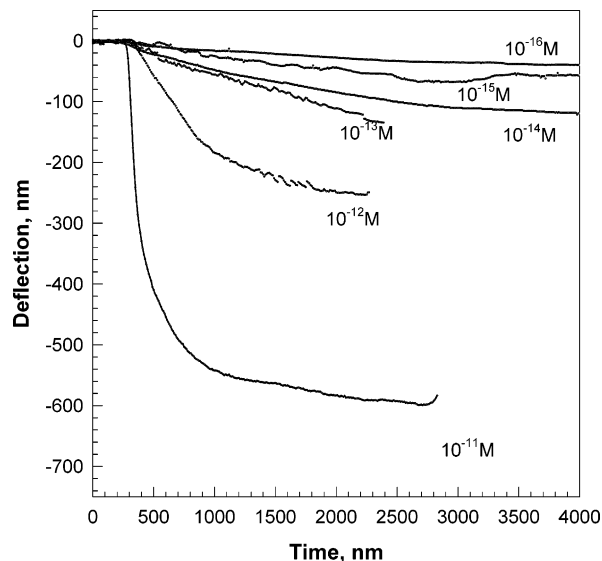


Figure 2. Bending response as a function of time, *t*, for SiO<sub>2</sub> microcantilevers after injection of different concentrations of HF solutions.

**Deflection Measurement.** The deflection experiments were performed in a flow-through glass cell (Digital Instruments) similar to those used in atomic force microscopy (AFM). The microcantilever was immersed in deionized water. Initially, the water was circulated through the cell using a syringe pump. A schematic diagram of the apparatus used in this study was previously reported.<sup>21</sup> Because a change in the flow rate would have created turbulence and thus would have induced noise in the cantilever bending signal, a constant flow rate of 4 mL/h was maintained during the entire experiment. Experimental solutions containing different concentrations of HF and the analytes of interest were injected directly into the slowly flowing fluid stream via a low-pressure injection port sample loop arrangement. This arrangement allowed for continuous exposure of the cantilever to the desired solution without disturbing the flow cell or changing the flow rate. Since the volume of the glass cell, including the tubing, was only 0.3 mL, a relatively fast replacement of the liquid in contact with the cantilever was achieved.

A new cantilever was used for each deflection measurement. Measurements were carried out by the optical beam deflection method. Cantilever bending was measured by monitoring the position of a laser beam reflected from the gold-coated side of the cantilever onto a four-quadrant AFM photodiode. We refer to bending toward the gold side as “bending up”; “bending down” refers to bending toward the uncoated side. The cantilever was immersed in deionized water until a stable baseline was obtained and the voltage of the position-sensitive detector was set as background corresponding to 0 nm.

## RESULTS AND DISCUSSION

When solutions containing various concentrations of HF were injected into the fluid cell, the microcantilever bent down (toward the uncoated SiO<sub>2</sub> side) with different amplitudes as shown in Figure 2. Deflection increased as the concentration of HF increased. For each measurement, a 2.0-mL aliquot of HF solution was injected into the fluid cell. It took 30 min for the injected HF solution to flow through the fluid cell, at which time the deionized

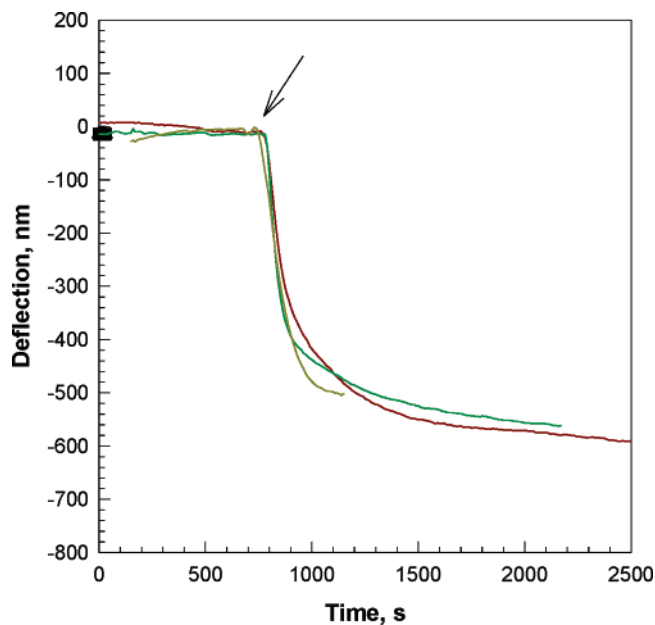


Figure 3. Reproducibility of the response of three independent  $\text{SiO}_2$  microcantilevers exposed to a solution of  $10^{-11}$  M HF. The injection point is indicated with an arrow.

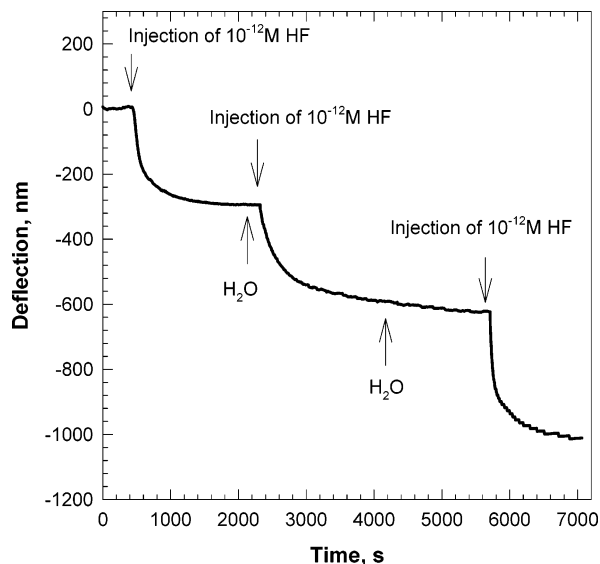


Figure 4. Reproducibility of the response of a  $\text{SiO}_2$  microcantilevers upon repetitive injection of a solution of  $10^{-12}$  M HF. The injection points are indicated with arrows.

water was circulated back into it. While the concentration of HF was constant in this 40-min window, the microcantilever deflection rate gradually decreased. This decrease may be due to the diffusion control of the reaction. Both HF consumption and  $\text{SiF}_4$  accumulation near the  $\text{SiO}_2$  surface could decrease the reaction rate.

Exposure of the  $10^{-11}$  M solution of HF to two new  $\text{SiO}_2$  microcantilevers fabricated using the same procedure caused similar deflection amplitudes and bending rates, as shown in Figure 3. The standard error was within 5%, indicating good cantilever-to-cantilever reproducibility. The repetitive injection of HF to the same cantilever also showed reproducible cantilever deflections (Figure 4).

Control experiments were performed by exposing an  $\text{SiO}_2$  microcantilever to a  $10^{-5}$  M solution of HCl. No deflection of the

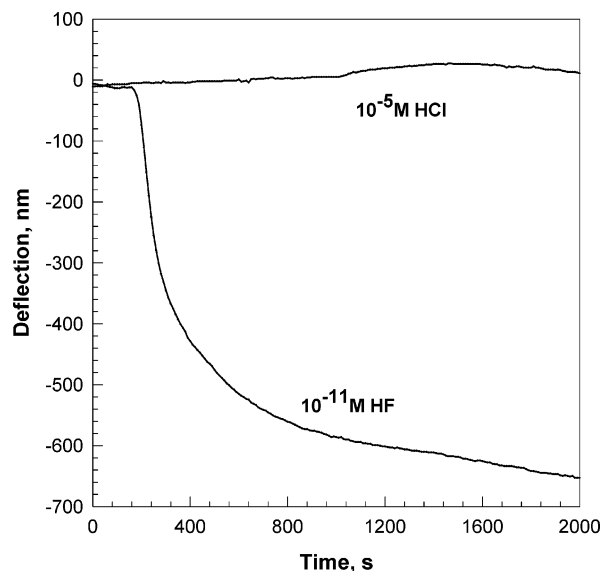


Figure 5. Bending responses as a function of time,  $t$ , for two  $\text{SiO}_2$  microcantilevers after injection of a  $10^{-11}$  M HF solution and a  $10^{-5}$  M HCl solution, respectively. The microcantilevers were preequilibrated in the water before injection of the HF and HCl solutions.

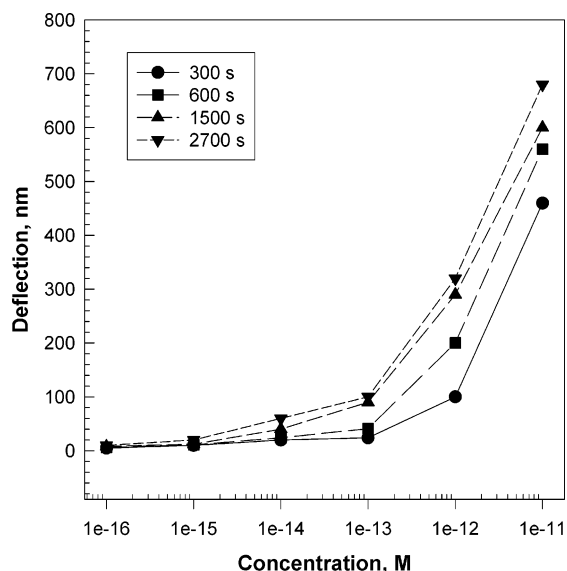


Figure 6. Deflection amplitude of a  $\text{SiO}_2$  cantilever as a function of the concentration of HF.

cantilever was observed (see Figure 5). In addition, stability experiments were conducted on microcantilevers after 5 months of storage in air. The deflection of the stored cantilevers showed a profile and bending amplitude similar to those in Figure 2.

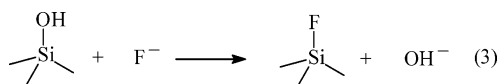
Figure 6 is a plot of the deflection amplitudes recorded at specific times after injection (300, 600, 1500, and 2700 s) versus the concentration of HF. The plot shows that this microcantilever can be used for the detection of HF at concentrations as low as  $10^{-16}$  M. Better sensitivity can be achieved with increased exposure time after injection. The maximum HF concentration in our experiments was at  $10^{-11}$  M; the effects of differences in ionic strength and pH at different HF concentrations can be neglected.

On the basis of our observations, we concluded that the microcantilever deflection was due to a reaction between the surface oxide layer of the microcantilever and HF as shown in eq 1.

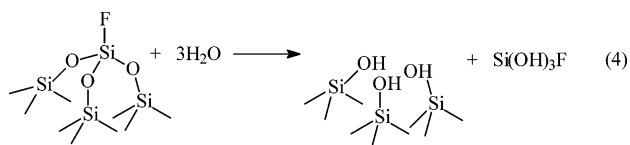
In silicon chemistry, it was widely understood, based on empirical results, that the SiO<sub>2</sub> etching rate is direct proportional to the concentration of HF.

$$\text{etching rate} = k[\text{HF}] \quad (2)$$

When a 49% HF solution is used, the etching rate of silicon oxide is  $\sim 165$  nm/min.<sup>32</sup> According to eq 2, at the highest HF concentration ( $10^{-11}$  M) used in our experiments, the etching rate was  $\sim 7 \times 10^{-11}$  nm/min. After 30-min exposure to HF,  $\sim 2 \times 10^{-9}$  nm of SiO<sub>2</sub> layer of the cantilever was etched off; i.e., only a small amount of surface SiO<sub>2</sub> reacted with HF. It is noted that these calculated results may not be accurate because of the lack of literature reports on the etching rate at low HF concentrations. However, in general, these data suggested that the HF/SiO<sub>2</sub> reaction on the microcantilever surface occurred at the molecular level and the reaction intermediate played major roles in microcantilever bending in our experimental conditions. At pH 7 and low HF concentrations, HF exists mainly in the form of fluoride (F<sup>-</sup>). The initiating reaction is the fluoride absorption at the surface silicon atom through a process of inner-sphere surface complexation:<sup>33</sup>



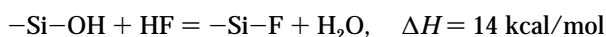
and the Si-F bond polarizes the underlying Si-O bonds, leading to the release of silicon atoms from the surface.



Based on these reaction models, the microcantilever downward bending is due to the replacement of Si-OH by Si-F (the Si-F moiety is smaller than Si-OH group) and the detachment of Si atoms from the surface that shrank the silicon surface of the microcantilevers after HF exposure.

It is noteworthy to discuss the temperature effect on microcantilever bending. Based on our experiences, in general, the temperature changes due to chemical interactions between analytes in solutions and molecules on the microcantilevers can be neglected. This is mainly because the local heat generated by interactions can be quickly released in solutions, especially in a continuous flow system. Furthermore, the chemical interactions on the cantilever surface normally do not cause enough heat to bend the cantilever.

For the first SiO<sub>2</sub> etching step, the reaction is endothermic



Since only a small amount of -Si-OH on the surface reacted with HF, the heat absorbed from the environment was negligible.

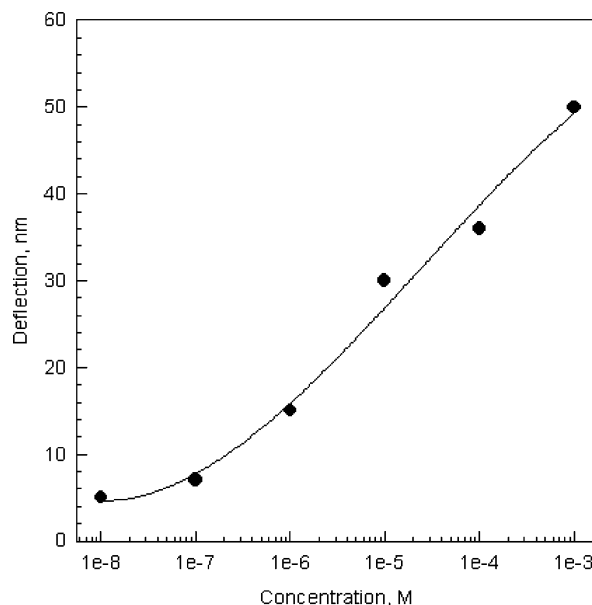


Figure 7. Deflection amplitude of a silicon cantilever as a function of the concentrations of HF.

The deflection response to HF of commercially available silicon cantilevers was also studied and was compared with that of the SiO<sub>2</sub> cantilevers. Normally, a 12–19-Å thickness of SiO<sub>2</sub> grows naturally on the silicon surface and thus provides a reactant for HF. However, much less bending amplitude and sensitivity were observed for the silicon cantilevers, as shown in Figure 7. The main cause of these results could be the larger spring constants of the silicon material (155.8 GPa) than that of SiO<sub>2</sub> (76.5–97.2 GPa). Materials that have smaller spring constants respond more sensitively than those who have larger spring constants upon surface stress changes.

## CONCLUSIONS

Our results showed that molecular-level chemical reaction or etching can be converted into nanoscale micromechanical bending. Based on this concept, an SiO<sub>2</sub> cantilever can be used to selectively detect HF at concentrations as low as  $10^{-16}$  M because of the reaction of HF with SiO<sub>2</sub>. The sensitivity for detection of HF using a simple SiO<sub>2</sub> cantilever was much higher than that of any current detection methods.

## ACKNOWLEDGMENT

This work was supported by the Board of Regents Support Fund under Contract LEQSF(2001-04)-RD-A-16, the Center for Entrepreneurship and Information Technology (CEnIT) Research Seed Grant of Louisiana Tech, and the U.S. Department of Energy (DOE), Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, Environmental Management Science Program, under Contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated for DOE by UT-Battelle, LLC.

Received for review September 28, 2003. Accepted February 3, 2004.

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