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Modification of micro-cantilever sensors with sol-gels to enhance performance and immobilize chemically selective phases

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Abstract

A chemical sensor based on the deflection of a surface modified silicon micro-cantilever is presented. A thin film of sol-gel was applied to one side of the micro-cantilever surface using a spin coating procedure. The sensor has been shown to give different responses to vapor phase analytes of varying chemical composition, as well as to varying concentrations of a given analyte. Ethanol, a highly polar molecule, exhibits a strong affinity for the polar sol-gel coating resulting in a large response; pentane, a non-polar hydrocarbon, shows very little response. The sol-gel coating has also been shown to function as a backbone for the immobilization of chemically selective phases on the cantilever surface. Reaction of the sol-gel film with chlorotriethoxysilane and subsequent capping of the remaining reactive surface silanols with hexamethyldisilizane increases the non-polar nature of the film. This results in an increase in the response of the sensor to non-polar analytes. The effects of film thickness and cantilever structure thickness on response were also investigated. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Micro-cantilever sensors; Sol-gels; Chemically selective phases

1. Introduction

Over the past 15 years, there has been an enormous interest in the development and applications of chemical sensors. For the period of 1994–1997, the field of chemical sensors experienced a 44% increase in the number of sensors developed [1]. Chemical sensors are often classified according to their mode of transduction into four major categories: electrochemical, optical, thermal sensitive, and mass sensitive sensors. Mass sensitive sensors, the category to which the chemical sensor presented in this work belongs, respond in proportion to the mass of analyte that interacts with the surface of the sensing element [2]. In recent years, much of the focus in chemical sensor development has been upon miniaturiza-

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tion of chemical sensors, including those employing micro-cantilevers as the sensing element. Micromachined cantilevers such as those used in atomic force microscopy (AFM) have been used for a variety of chemical sensing applications [3–10]. Adsorption of analyte onto the micro-cantilever surface can cause changes in the resonance frequency of the micro-cantilever due to a change in mass and/or the cantilever spring constant. Adsorption may also result in stress-induced bending of the micro-cantilever [6,11,12]. In this work, bending is monitored based on deflection of a laser beam that is reflected from the micro-cantilever surface onto a position sensitive detector.

Micro-cantilever chemical sensors have several advantages over other mass-sensitive chemical sensing techniques. These sensors have been shown to exhibit over two orders of magnitude greater absolute sensitivity compared to other currently available sensors [2,13,14] such as quartz crystal microbalances (QCM) [14], surface acoustic wave (SAW) devices [2,15], acoustic plate mode (APM) devices [15], chemiresitors [13], and flexural plate wave (FPW) oscillators [15]. This increase in sensitivity can be attributed largely to the extremely small size of the sensing element. With an active area of 10^{-5} cm^2, the micro-cantilevers used in this work have approximately five orders of magnitude smaller area than QCM, SAW, and FPW devices. The potential advantages of smaller size include faster response time, lower cost of fabrication, the possibility of sensor arrays with small overall dimensions, the ability to explore microenvironments, and improved portability for field applications.

To facilitate selective detection of diverse chemical analytes, a chemically selective layer can be deposited onto one side of the micro-cantilever to create a bimaterial actuator. Due to the difference in affinity of the two surfaces for the target analyte, a differential stress on the sides of the cantilever is achieved causing it to bend. A variety of coatings have been applied to the surface of micro-cantilevers to enhance the chemical sensitivity and selectivity of the sensor. Micro-cantilevers coated with polydimethylsiloxane [9] and thin films of polymeric chromatographic stationary phases [16] have been used for the detection of volatile organic compounds. Gold coatings have been used for the detection of alkanethiols [8]. A sensor for the detection of cesium metal ions based upon complexation with surface bound self-assembled monolayers of crown ethers has been developed [17]. Phosphoric acid and bovine skin gelatin have been used for the detection of water vapor [7]. An 'artificial nose' based on an array of silicon cantilevers coated with a variety of materials has been developed for the detection of hydrogen, primary alcohols, natural flavors, and water vapor [3,10]. Each of these coatings has been successful in enhancing the sensitivity of the chemical sensor; however, the level of selectivity achievable with chemically modified micro-cantilevers has not been established or investigated adequately.

The use of sol-gel materials for the development of chemical sensors and biosensors is of intense current interest [18–21]. In most applications, the sol-gel material functions as a porous support matrix in which analyte-sensitive species are entrapped [22]. The sol-gel process is attractive because gelation can occur at low temperatures which allows for the encapsulation of a variety of molecules that are temperature sensitive, including biological reagents [23,24]. A glucose sensor based on the entrapment of the protein glucose oxidase within a sol-gel matrix has been developed [25]. An optical sensor based on the entrapment of high pK_a dyes within a sol-gel matrix has been developed for the determination of pH in highly acidic and highly alkaline environments [26,27]. Raiteri et al. [28] have used thin films of sol-gel coated onto silicon nitride micro-cantilevers via a dip coating process to show the change in response of the micro-cantilever to different mixtures of ethanol and water. In the work presented herein, we modify and evaluate silicon micro-cantilevers with thin films of sol-gel. Thin films of sol-gel are deposited onto micro-cantilevers using a spin coating procedure. This method of film formation requires less equipment and is less expensive than conventional techniques such as CVD, evaporation, or sputtering [22]. We evaluate the effect of the sol-gel coating on the response of the micro-cantilever to analytes of

varying chemical composition. The ability to modify the selectivity of the micro-cantilevers by modifying the chemical nature of the surface of the sol-gel film by reaction with organosilanes is also studied. Sol-gel film thickness and micro-cantilever structure thickness are shown to influence response.

2. Experimental

2.1. Chemicals

All chemicals were used as received from the manufacturer. Reagent grade methanol, hydrochloric acid, sulfuric acid, hydrogen peroxide, and toluene were purchased from Fisher Scientific (Fair Lawn, NJ). Absolute ethanol was supplied by Aaper Alcohol and Chemical Co. (Shelbyville, KY). Tetramethoxysilane (TMOS), chlorodimethyloctadecylsilane (CDOS), and octadecyltriethoxysilane (OTEOS) were purchased from Aldrich Chemical Co. (Milwaukee, WI) and hexamethyldisilizane (HMDS) from Petrarch Research Systems (Bristol, PA).

2.2. Sol-gel film preparation

The sol solution from which the films were cast was prepared by adding 300 μl of TMOS to a mixture of 125 μl H_2O, 15 μl 0.01 M HCl, and 250 μl of methanol. After waiting 6 h to allow for crosslinking of the sol, thin films of sol-gel were created on V shaped, silicon micro-cantilevers (Park Scientific Instruments, Sunnyvale, CA) using a spin coating procedure. The 600 nm thick silicon micro-cantilevers had a 120 μm height, 90 μm base, and legs with a width of 26 μm. As supplied, the micro-cantilevers had a 50 nm coating of gold on the underneath side. Before deposition of the sol-gel film onto the topside of the micro-cantilever, they were cleaned by immersion in piranha solution (75% H_2SO_4, 25% H_2O_2) for 3 h. The sol was deposited onto the center of a spinning circular Teflon mount that secured the cantilevers in place. The mount was allowed to spin at a rate of 500 rpm for 5 s after deposition. The spin rate was then increased at 30 000 rpm s^{-1} to a final spin rate of 6000 rpm at which the spin rate was held constant for 2 min to evaporate all remaining solvent. After spin coating, the micro-cantilevers were placed in a 110°C oven for 12 h to cure the sol-gel coating. Finally, to remove any unwanted sol-gel from the underside of the micro-cantilever, the micro-cantilevers were soaked in aqua regia (75% HCl, 25% HNO_3) for 6 h. This mixture of hydrochloric and nitric acids is known to dissolve gold. By dissolving the gold coating from the underneath of the micro-cantilever, the aqua regia functioned to remove any sol-gel that may have coated the underneath of the micro-cantilever.

The thickness of the sol-gel films on the cantilever surfaces was determined by profilometry (Dektak 8000, Veeco/Sloan Technology, Santa Barbara, CA). Due to bending of the cantilever under the profilometer stylus, direct measurement of film thickness was not possible. Therefore, film thickness was measured on films cast onto silicon wafers under the same conditions used to apply the films to the micro-cantilevers. The thickness of the sol-gel films was determined to be between 50 and 100 nm. A scanning electron micrograph of a sol-gel coated micro-cantilever (Fig. 1) was obtained using a Hitachi S-800 Scanning Electron Microscope (Hitachi Instruments, Inc., San Jose, CA) located in the Division of Biology, Electron Microscopy Facility, University of Tennessee, Knoxville.

2.3. Modification of sol-gel film

In some cases, the sol-gel films were treated with organosilanes. In the first attempt, the sol-gel coated micro-cantilever was immersed in a 5% w/w solution of (CDOS) in absolute ethanol with gentle heat. The micro-cantilever was allowed to remain in solution for 25 min, then was removed and rinsed thoroughly with absolute ethanol. In an attempt to increase the amount of bonded phase on the sol-gel film surface, a second sol-gel coated micro-cantilever was immersed in a 5% w/w solution of OTEOS in toluene for 2.5 h at 90°C. The micro-cantilever was then removed from solution and rinsed with toluene followed by absolute ethanol. To cap the remaining reactive

silanols, the microcantilever was placed in a 3% w/w solution of HMDS in toluene for 1 h. The solution was kept at 110°C. The micro-cantilever was removed and rinsed with toluene and absolute ethanol.

The effect of sol-gel film thickness on cantilever response is discussed within this work. The sol-gel film was thinned using a focused ion (Ga ion) beam milling (FIB) machine (FIB 200, FEI Co., Hillsboro, OR). FIB was also used to determine the effect of micro-cantilever structure thickness on sensor response.

2.4. Optical instrumentation

The micro-cantilevers were mounted into an optical system similar to that used for atomic force microscopy. A block diagram of the optical setup is shown in Fig. 2. A 5 mW diode laser (Coherent Laser Corp., Auburn, CA) operating at 635 nm was spatially filtered and focused onto the tip of the micro-cantilever using a video microscope to visualize the process. The reflected beam was focused using a bi-convex lens onto a position-sensitive photodiode detector built in house. Deflection of the cantilever was measured using the output of the position-sensitive detector that corresponded to vertical laser beam deflection. The amplified voltage from the position-sensitive detector was monitored using a lock-in amplifier (Stanford Research Systems, Sunnyvale, CA). The signals in this work are reported in voltage output of the detector. The relationship between cantilever displacement and output voltage was not determined. For a typical optical configuration used in these studies, the conversion between deflection of the cantilever tip and detector voltage is roughly 80 nm V^{-1} [16,29]. However, changes in optical alignment over the course of this work resulted in considerable variation in the deflection-to-voltage factor. Nevertheless, the alignment was constant for each individual study presented herein.

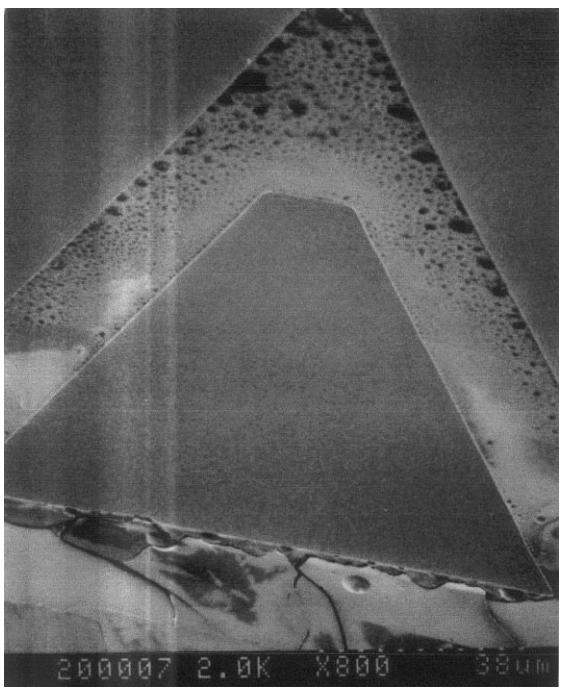


Fig. 1. Scanning electron micrograph of a sol-gel coated micro-cantilever at a magnification of 800 × . The image was obtained at a beam energy of 2 keV with a working distance of 6 mm.

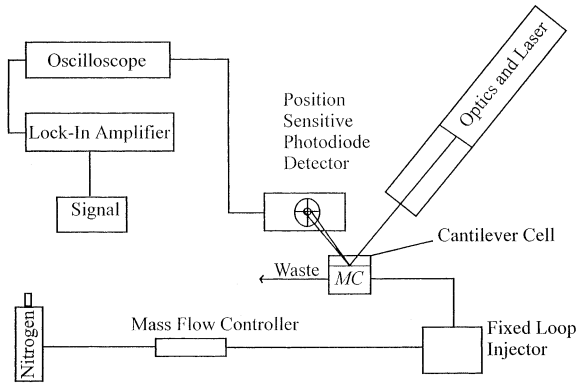


Fig. 2. Block diagram of optical setup.

Samples were created from headspace above analyte solutions developed in 40 ml headspace vials that were fitted with Teflon septa. Prior to the development of analyte headspace, the vial headspace was purged with nitrogen to ensure that the analyte and the nitrogen carrier gas were the only components to enter the flow cell. Sampling and subsequent injection into the fixed loop injector was accomplished using a gas-tight syringe. For preparation of different analyte vapor concentrations, the analyte vapor was diluted with nitrogen within the sampling syringe.

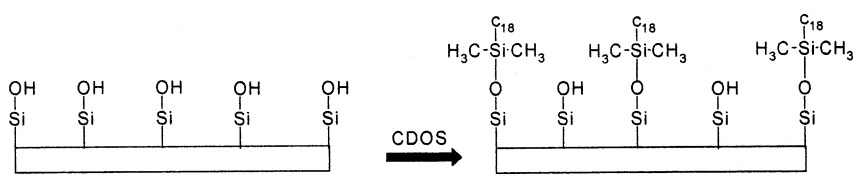
A 3 ml flow cell was mounted over the micro-cantilever to allow for the flow of gaseous analytes across its surface. A constant flow of ultra high purity nitrogen at a rate of 1.0 ml min^{-1} was achieved using a digital mass flow controller (MKS Instruments, Inc., Andover, MD). Nitrogen flow was directed first through a 1 ml fixed loop sample injection valve (Model 5020, Rheodyne, Inc., Cotati, CA) and then through the flow cell. Transient signals due to cantilever bending were observed upon injection of headspace samples. Considerable dilution of the sample occurred due to the large volume and flow configuration of the flow cell, which was not designed for optimum sensitivity. The flow injection system would not be needed for actual sensing work but facilitated rapid evaluation of the effects of modifying the surface of the cantilevers with sol-gel in these laboratory experiments.

3. Results and discussion

The sol-gel coating applied to the micro-cantilever surface serves to enhance the sensitivity of the sensor by creating an adsorptive coating, increase the binding capacity by introducing a mesoporous-structured surface, and provide a reactive surface for the covalent attachment of a variety of analyte binding reagent phases. A primary goal of this work was to develop a chemical sensor based on sol-gel coated micro-cantilevers that would be capable of distinguishing between vapor phase analytes of varying chemical composition, as well as to varying concentrations of a given analyte. The sol-gel film on the micro-cantilever surface allows for modification of the selectivity of the sensor by immobilizing chemically selective phases on the sol-gel backbone. By altering the chemical nature of the phase bonded to the sol-gel matrix, the selectivity of the sensor can be tailored for a certain class of compounds. The following analytes, all monitored in the vapor phase, and potential modes of molecular interaction with the sol-gel film were employed: ethanol (very weakly acidic compound with strong H-bonding capabilities), aniline (aromatic weakly basic compound with H-bonding capabilities), toluene (aromatic system with high polarizability), and pentane (very non-polar compound, dispersive interactions only).

The responses of a sol-gel coated micro-cantilever to these analytes are quite different as illustrated in Fig. 3. Because the gaseous analytes have different vapor pressures, their headspace concentrations were determined by GC/MS. The response factors (signal/concentration) relative to toluene set to 1.0 appear in Table 1. These factors are specific for the flow injection analyte delivery system employed. The sharp increase in signals seen in Fig. 3 is due to the adsorption of analyte onto the sol-gel film surface. Due to the polar nature of the sol-gel film, the response of the sensor to polar and polarizable analytes is much greater than the response to non-polar analytes. Also, the desorption of the polar or polarizable analytes from the film is relatively slow due to the affinity of the polar sol-gel film for the analytes. Pentane, a non-polar hydrocarbon, shows little affinity for the sol-gel film and completely desorbs in a short period of time. The reproducibility of peak responses is currently limited by the crude method of preparing these gas phase samples and is generally about 10%.

Perhaps the most desirable feature in an effective sensor is the ability to target a certain analyte or class of compounds. In an effort to alter the selectivity of sol-gel modified cantilevers, the polarity of the gel was modified by treating with organosilanes. Initially, the film was treated with CDOS as described above. This reagent reacts with the sol-gel film surface in the following manner:



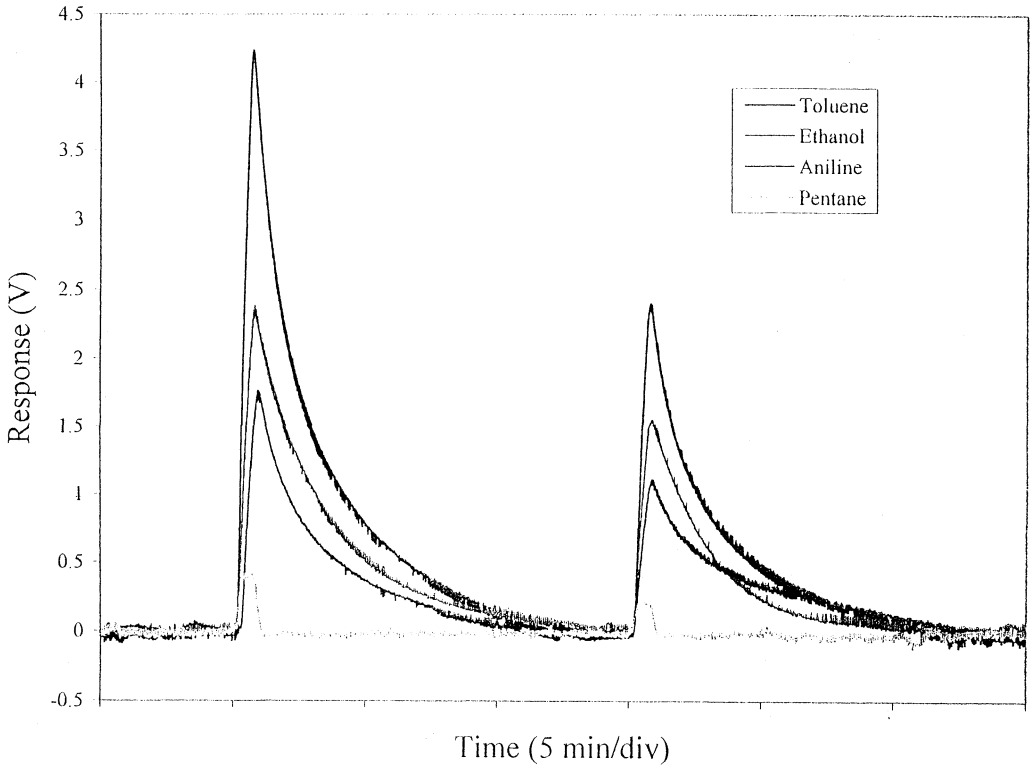


Fig. 3. Response of sol-gel coated micro-cantilever to toluene, ethanol, aniline, and pentane in order of decreasing sensor response at injected concentrations of 100 and 50% of the developed neat headspace, respectively.

The addition of non-polar C_{18} chains to the surface of the sol-gel film should enhance the response of the chemical sensor to non-polar analytes. However, the amount of bonded phase attached to the silanol groups (Si–OH) of the sol gel is limited by steric effects. In one report, at least half of the original silanols are still present on the sol-gel film surface after reaction [30]. These remaining surface silanols can interact with analytes and contribute to the adsorptive properties of the chemical sensor. Therefore, the sensor maintains some of its polar nature. Fig. 4 shows the response of the sensor to the test analytes both before and after surface modification with CDOS. The signal for pentane after modification is more than twice the signal obtained from the native sol-gel coating. The desorption rate for pentane also increases (not shown). The presence of the non-polar alkyl chains on the sol-gel film surface caused the signals for toluene and aniline to dramatically decrease. The relatively constant signal for ethanol may be due to the affinity of the short alkyl group for the bonded phase, as well as the ability of the hydroxy group to hydrogen bond with the oxygens of the siloxane bonds.

While the surface coverage obtainable with monofunctional silanes is limited by steric hindrance, the reaction of multifunctional silanes results in a significantly higher content of bonded phase [30]. Also, the presence of water on the surface of the sol-gel can result in the formation

Table 1
Headspace concentrations and sensor response relative to toluene

	Headspace concentration (M)	Response relative to toluene
Toluene	1.02×10^{-4}	1.0
Aniline	6.40×10^{-6}	7.2
Ethanol	1.35×10^{-4}	0.51
Pentane	1.74×10^{-3}	6.2×10^{-3}

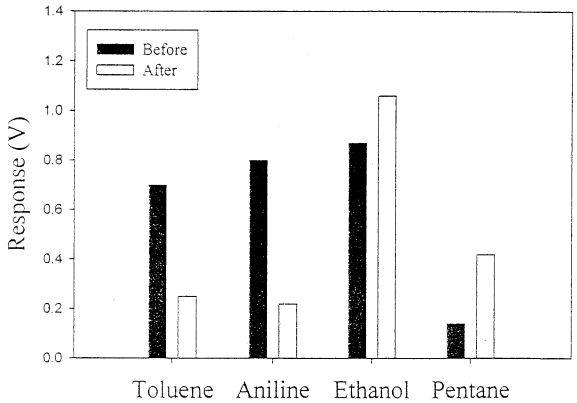


Fig. 4. Sensor response to the test analytes both before (native sol-gel coating) and after treatment with CDOS.

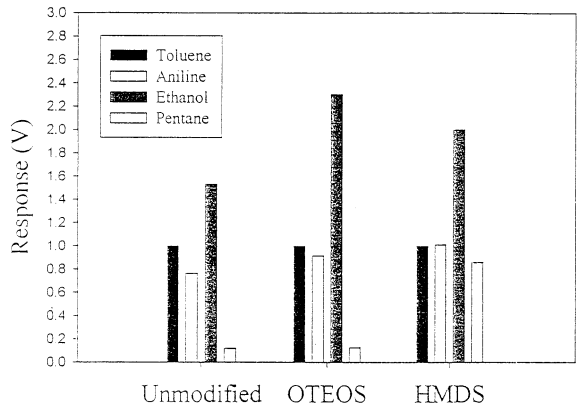
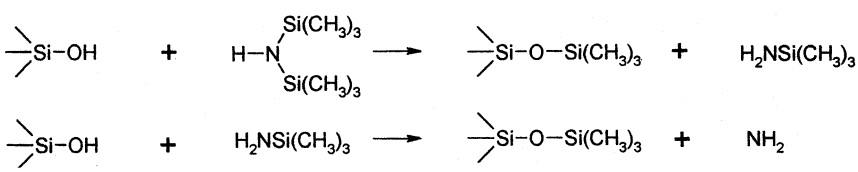


Fig. 5. Sensor response to the test analytes for native sol-gel coating (unmodified), coating reacted with OTEOS, final end-capped surface modified coating after reaction with HMDS. Each response is normalized to the response of the native sol-gel coating to toluene.

of additional silanols and thus increase the amount of bonded phase substantially [30]. In an attempt to increase the amount of bonded phase on the surface of the sol-gel film, the micro-cantilever was immersed in boiling deionized water for 30 min before modification of the sol-gel film. The micro-cantilever was then treated with OTEOS. This reagent with three reactive ethoxy groups functions to increase the non-polar nature of the sol-gel film by building a polymer-like matrix that contains non-polar C_{18} chains. The micro-cantilever was subsequently placed in HMDS, a reagent often used in column preparation in liquid chromatography to 'cap' remaining reactive silanols [30,31]. This reagent reacts with the unreacted silanols on the sol-gel film surface, as well as the silanols produced from the OTEOS, according to the following reactions:



The end result is the replacement of silanols with $Si(CH_3)_3$. The response of the sensor to analytes on the native sol-gel coating, the coating treated with OTEOS, and the final end-capped coating are shown in Fig. 5. The increase in signal for ethanol following the treatment of the sol-gel surface with OTEOS is possibly due to the increase in the number of silanol binding sites created by the polymerization reaction. The signal for pentane remained relatively constant following this treatment. After capping the remaining reactive silanols with HMDS, the signal for pentane increased nearly fivefold. This indicates a much less polar sol-gel surface.

The micro-cantilever chemical sensor is also capable of providing quantitative information by differentiating between varying concentrations of a given analyte. By diluting analyte headspace within the gas-tight sampling syringe with nitrogen, calibration plots were obtained for the test analytes on the native sol-gel coating as shown in Fig. 6. The response of the micro-cantilever decreased with decreasing concentration. The calibration plots for pentane are shown for the native sol-gel coating and the surface modified coating. A linear calibration plot for pentane was unattainable for the native sol-gel coating. After

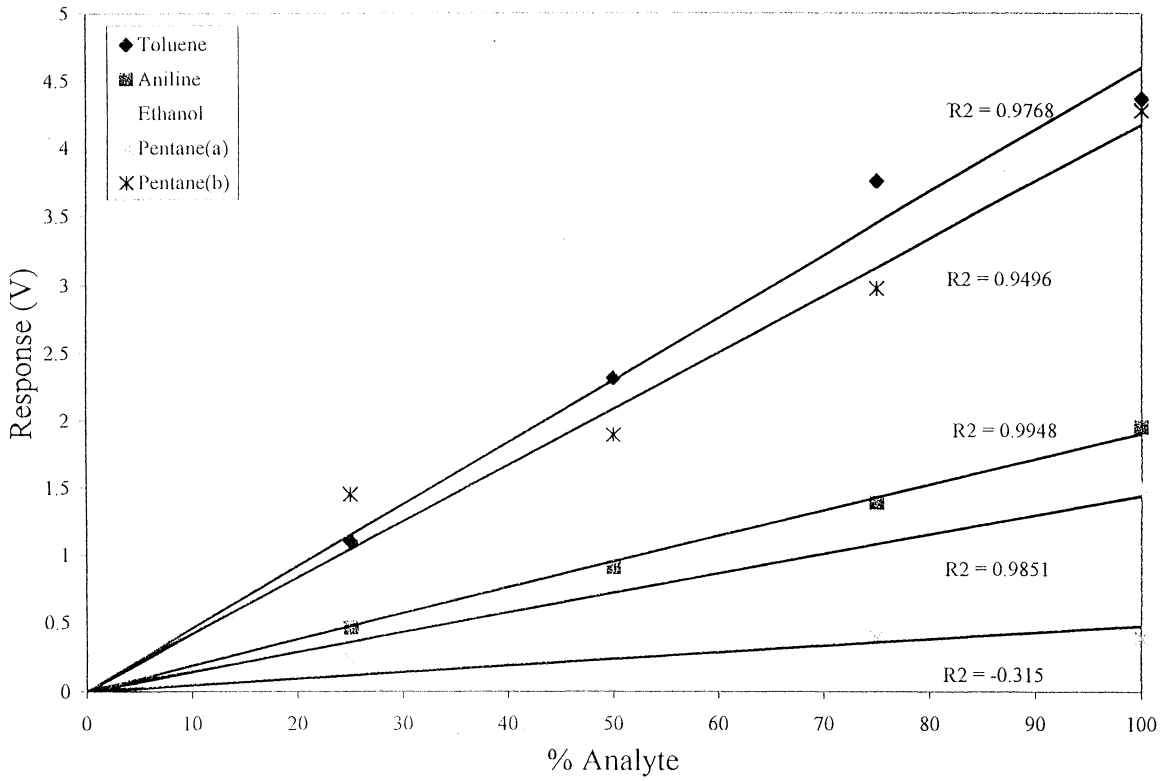


Fig. 6. Calibration plots for the native sol-gel coating exposed to the test analytes.

removing the high frequency baseline noise with a 250-point square polynomial fit, the limits of detection ($S/N = 2$) range from 550 μg l^{-1} for pentane down to 1.4 μg l^{-1} for aniline.

The effect of sol-gel film thickness on micro-cantilever response was also investigated. Bending occurs because of analyte-induced, differential stress between the bare silicon and sol-gel coated sides of the legs of the cantilever. The thickness of the silicon legs of the micro-cantilever was held constant at 560 nm and FIB was used to decrease the thickness of the totally porous sol-gel film. The depth of material removed (d) was determined according to the following equation:

$$d = \frac{(t)(I)(S_r)}{(l)(w)}$$

where t is the time exposed to focused-ion beam (s); I is the beam current (nA); S_r is the sputtering rate for SiO_2 (μm^3 nC^{-1}); l is the length of the area removed (μm); and w is the width of the area removed (μm).

An area 27 μm by 130 μm was milled on each leg for 130 s using a beam current of 2.7 nA. The sputtering rate for the sol-gel was assumed to be 0.20 μm^3 nC^{-1}, the sputtering rate for SiO_2 (Ion Tech, Inc., Fort Collins, CO). Under the stated conditions, the depth of material removed was roughly 20 nm. The initial film thickness was estimated by profilometry to be ~50 nm. After exposing the micro-cantilever to toluene vapor at the initial film thickness, the sol-gel film on the legs was thinned in increments of ~20 nm. Fig. 7 shows the response of the micro-cantilever at varying sol-gel film thickness. The response of the sensor dramatically decreased after the first milling and noticeably after the second milling. No noticeable change was observed in the sensor response between the second and third millings. This may indicate that the sol-gel film had been

nearly completely removed and also supports the preliminary estimate of the initial sol-gel film thickness. It should be noted that both SEM (Fig. 1) and profilometry experiments indicate the sol-gel surface is rough (thickness is not uniform). Fig. 1 also provides evidence that the sol-gel thickness on the legs decreases (at least for the one shown) as one moves from the base toward the pad of the cantilever. The lighter and darker features on the micrograph correspond to thicker and thinner layers of sol-gel, respectively.

The micro-cantilever structure thickness also has an effect on the response of the sensor. The initial thickness of the micro-cantilevers as received from the manufacturer is 600 nm. The legs of the sol-gel coated micro-cantilever were thinned in increments of 80 nm according to the same equation used above to determine the amount of sol-gel material removed. The S_r for silicon is 0.15 μ^3 nC^{-1}. As the legs were thinned, the response of the sensor increased steadily at a rate of $\sim 0.2\%$ per nm of thinning down to a thickness of 300 nm. This trend is consistent with prior studies involving micro-cantilevers modified with GC polysilane phases [16].

4. Conclusion

In the work presented, we have shown that sol-gel coatings can substantially influence the response characteristics of micro-cantilevers. Immobilization of chemically selective phases on the surface of sol-gel films provides a method for altering the selectivity of micro-cantilever chemical sensors. There are a variety of organosilanes that may serve to achieve this purpose. Ideally, an array of cantilevers, each coated with a sol-gel film modified with an organosilane specific for a class of compounds, could be used to identify the

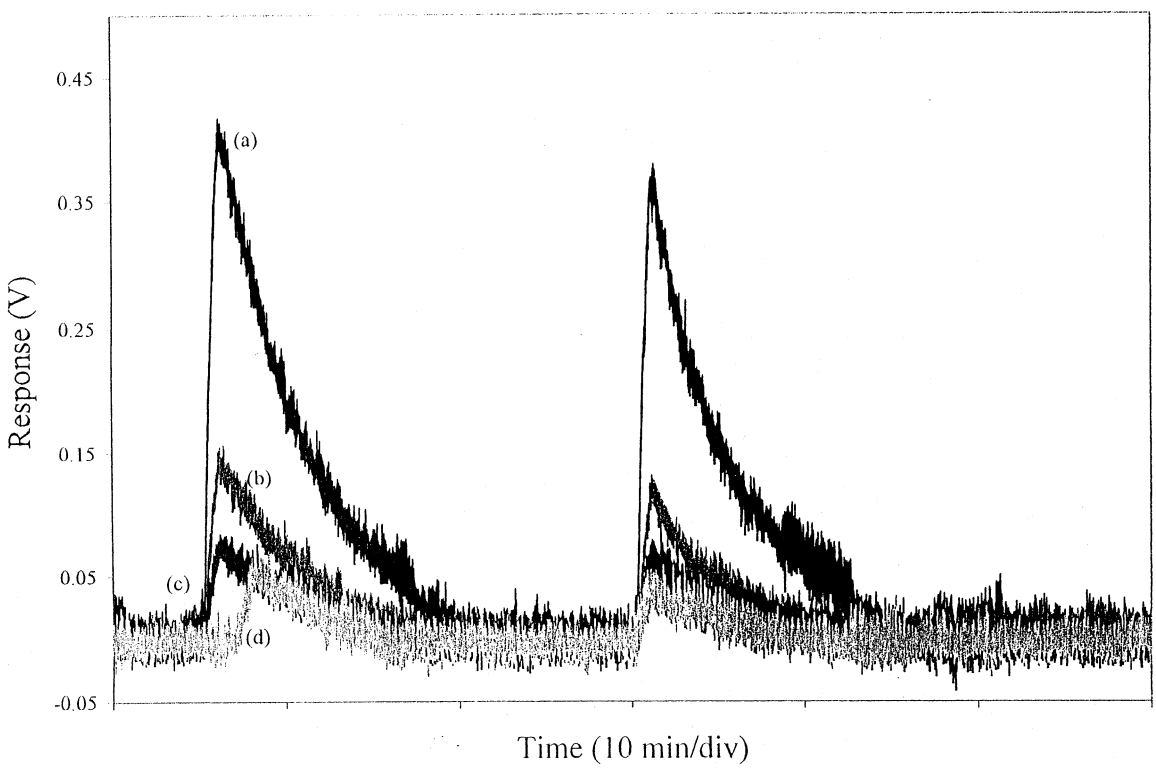


Fig. 7. Sensor response to toluene at varying sol-gel film thickness (a) initial film thickness; (b) after first milling; (c) after second milling; and (d) after third milling.

chemical nature of an unknown analyte. Also, the use of sol-gel matrices for the entrapment of analyte-sensitive species could provide a means for the development of micro-cantilever sensors for a wide variety of analytes.

Acknowledgements

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