Chemical detection based on adsorption-induced and photoinduced stresses in microelectromechanical systems devices

P. G. Datskos[a)]
Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831-8039 and University of Tennessee, Knoxville, Tennessee 37996

S. Rajic
Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831-8039

M. J. Sepaniak, N. Lavrik, C. A. Tipple, and L. R. Senesac
University of Tennessee, Knoxville, Tennessee 37996

I. Datskou
EEG, Inc., Knoxville, Tennessee 37391

(Received 9 October 2000; accepted 29 May 2001)

The recent advent of microelectromechanical systems (MEMS) devices opened up possibilities for chemical detection. Microcantilevers respond to chemical stimuli by undergoing changes in their bending and resonance frequency when molecules adsorb on their surfaces. In our present studies, we extended this concept and studied changes in both the adsorption-induced stress and photoinduced stress as molecules adsorb on the surface of microcantilevers. We found that microcantilevers that have adsorbed molecules will undergo photoinduced bending that depends on the number of adsorbed molecules on the surface. Furthermore, when microcantilevers undergo photoinduced bending, molecules will adsorb on their surface differently. Depending on the photon wavelength used and microcantilever material, the microcantilever can be made to bend by expanding or contracting the irradiated surface. By coating the surface of the microcantilever with a thin chemical layer, chemical specificity for the target chemicals can be achieved. Chemical selectivity can also be altered by selecting appropriate photon wavelengths due to the introduction of surface states in semiconductor MEMS. In fact, choosing a handful of different photon wavelengths, tunable chemical selectivity can be achieved due to differentiated photoinduced response without the need for multiple chemical coatings. We present and discuss our results on MEMS interactions with two isomers of dimethylnaphthalene, tetrachloroethylene, trichloroethylene, diisopropyl methyl phosphonate, and trinitrotoluene. © *2001 American Vacuum Society.* [DOI: 10.1116/1.1387082]

I. INTRODUCTION

There is an increasing demand to perform rapid measurements of specific chemical species in minute quantities such as hazardous materials, explosives, drugs, chemical weapons, etc. In a similar manner to the way in which adoption of integrated circuit technologies revolutionized electronics, the sensor community needs simple, rugged, integrated sensor technologies that can serve as flexible, inexpensive building blocks for a nearly infinite variety of applications in compositional monitoring. Ideally, these modular sensors should be capable of detecting and identifying the presence and composition of specific analytes in the presence of a complex matrix, should provide virtually instantaneous response and recovery, and should require little or no end-user service.

Gravimetric chemical sensors achieve high chemical specificity due to chemically selective coatings.[1,2] Such coatings have been used in different types of gravimetric sensors to sorb various gaseous analytes. Mass produced microelectromechanical systems (MEMS) can serve this need for chemical detection. The MEMS devices employed in our studies for chemical detection are microcantilevers which are extremely sensitive to the adsorption of chemical analytes on their surface and responds via changes in their bending and resonance frequency.[3–9] In previous studies we have shown[8] that the minimum detectable mass can be two orders of magnitude smaller when the microcantilever bending is used as the chemical sensing mechanism instead of the resonance frequency change. Previous work has shown that atomic force microscopy microcantilever bending can be detected with extremely high sensitivity. Hansma[11] and Binnig[12] have demonstrated atomic force microscopy sensitivities of 10^{-11} N, corresponding to bending magnitudes of approximately 5×10^{-11} m. More recently, even smaller microcantilever deflections were measured with a resolution of 0.4×10^{-12} m.[13]

Our approaches are based on the fact that this photoinduced bending and adsorption-induced bending of microcantilevers depends on the amount of chemical analyte adsorbed on its surface. For the photoinduced bending in particular, for the same number of photons interacting with the microcantilever, its photoinduced bending will vary if the amount of molecular species adsorbed on its surfaces changes. Ear-

[a)]Electronic mail: pgd@ornl.gov

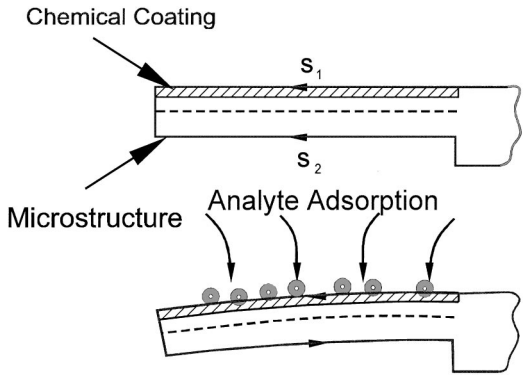

FIG. 1. Schematic diagram depicting the bending response of a microcantilever to chemical adsorption. Surface stresses s_1 and s_2 are balanced at equilibrium but become unequal and cause bending upon adsorption of analyte molecules. A force along the z direction is induced due to the differential surface stress, which causes the microcantilever to change its radius of curvature.

lier work has shown that the absorption of photons by a solid results in temperature changes and thermal expansion which gives rise to acoustic waves at frequencies corresponding to the amplitude modulation of the probing photon beam.[14,15] It is known that the generation of ''free'' charge carriers (electrons and holes) via absorption of photons in a semiconductor results in a local mechanical strain.[14–18] It should be emphasized that this photoinduced strain is additional to the strain resulting from unequal thermal expansion of the semiconductor and metal. In fact, for the same power of photoirradiation, a gold-coated silicon microcantilever exhibits a photoinduced bending that is about four times larger than that due to thermally induced stress. In this work we extend the earlier concept of chemical detection and study changes in both the adsorption-induced stress and photoinduced stress as molecules adsorb on the surface of the microcantilevers. In earlier studies[10] we have demonstrated that micromechanical devices with various coatings respond sensitively to the presence of chemical analytes.

II. MOLECULAR ADSORPTION ON MICROCANTILEVERS

A. Chemical detection based on micromechanical adsorption-induced stress

The bending response of a microcantilever due to chemical adsorption is depicted in Fig. 1. As can be seen, surface stresses s_1 and s_2 are balanced at equilibrium but become unequal and cause bending upon adsorption of analyte molecules. As microcantilevers are stressed a change in the radius of curvature occurs which is given by[19–21]

$$\frac{1}{R}=\frac{6(1-\upsilon)}{Et^2}\Delta s, \tag{1}$$

where R is the radius of curvature of the microcantilever, t is the microcantilever thickness, υ is the Poisson's ratio, E is the Young's modulus, and $\Delta s(=\Delta s_1-\Delta s_2)$ is the surface differential stress. The surface differential stress Δs is proportional (at least to a first order approximation) to the number of adsorbed molecules and therefore to the total additional mass Δm_a, i.e.,

$$\Delta s=C_1\Delta m_a, \tag{2}$$

where C_1 is a proportionality constant that depends on the sticking coefficient of the adsorbed molecules; a typical value for C_1 is $\sim 10^{15}$ of dyn cm^{-1} g^{-1}. For a microcantilever with length l, the bending $z_{\max}[=l^2/(2R)]$, is related to the additional mass (and differential surface stress) through

$$z_{\max}=C_1\frac{3l^2(1-\upsilon)}{Et^2}\Delta m_a. \tag{3}$$

Therefore, measurement of the bending $z_{\max}$ allows the amount of adsorbed mass to be determined when the adsorption process is confined to only one side of the microcantilever. If one side of the microcantilever is relatively passive (i.e., nonadsorbing), the changes in Δs are caused primarily by the modulation of Gibbs surface free energy of the adsorbing side. In the case of a noble metal substrate and an organic modifying coating the change in bending is given by[22]

$$z_{\max}=\frac{3l^2(1-\upsilon)}{Et^2}\left(\sigma_{\text{sub}}-s_1-E_{\text{adh}}\frac{m_s}{M}-W_{\text{ster}}\right), \tag{4}$$

where σ_{sub} is the surface tension of the free substrate, E_{adh} is the binding energy per mole, m_s is the surface mass, M is the molar mass of the modifying material, and W_{ster} accounts for the energy of possible steric repulsive forces between molecules in the coating. In this case the surface tension of the free substrate is much greater than the surface tension of the coating.

Molecular adsorption can also induce changes in the spring constant, k, of the microcantilever which can be described as[6]

$$\Delta k=\frac{\pi^2 n}{4n_0}(\Delta s_1+\Delta s_2)=C_1\frac{\pi^2 n}{4n_0}\Delta m, \tag{5}$$

where the geometrical factor $n=0.24$ for a rectangular microcantilever and n_0 is another geometrical factor. Standard physical parameters for commercially available microcantilevers can be found in the literature.[23,24] Studies have shown[4] that a value of 0.38 N/m can be obtained for surface differential stress, Δs, as a result of exposure of a gold-coated microcantilever to chemical analytes. Thus, the magnitude of exposure can be related to the extent of the bending which, in turn, can be used as a sensitive way for chemical detection.

B. Chemical detection based on micromechanical photoinduced stress

It is known that microcantilevers undergo bending following the absorption of photons.[14–17] Figure 2 schematically presents the bending process of a rectangular semiconductor

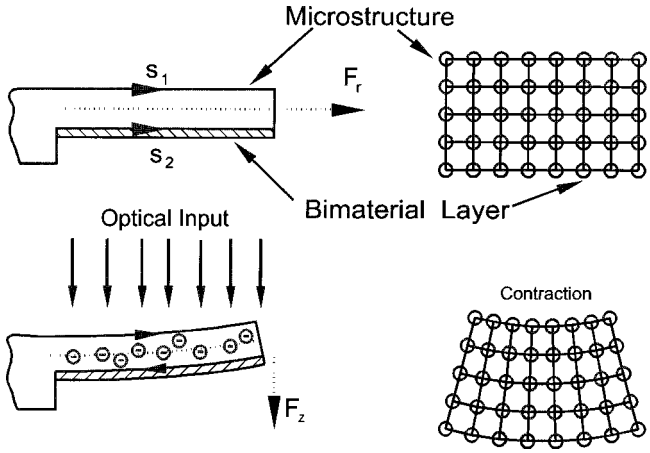

FIG. 2. Schematic diagram showing the bending process of a semiconductor microcantilever exposed to photons. Surface stresses s_1 and s_2 are balanced at equilibrium. Also depicted is the accompanied expansion of the semiconductor lattice following the generation of electron pairs.

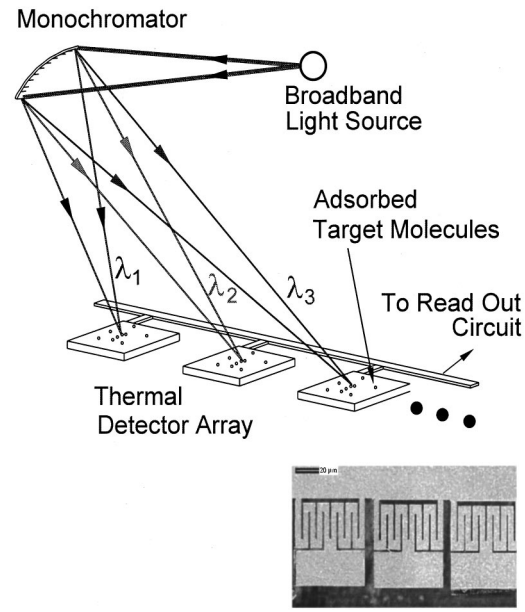

FIG. 3. Schematic representation of the principle of the microcalorimetric spectroscopy technique. Photons of different wavelength irradiate different thermal detectors configured as a linear array. Molecules adsorbed on the surface of the thermal detector elements absorb photons and a photothermal spectrum is obtained.

bar of thickness t, length l, and energy band gap ϵ_g, exposed to photons. The bending of a microcantilever, as has been discussed in earlier studies[22] is expressed as

$$z_{\max} \approx \frac{(1-\upsilon)l^2}{t}\left(\eta \frac{\lambda}{hc}\frac{d\epsilon_g}{dP}\frac{1}{lwt} + \frac{3\alpha}{mc_p}\right)\tau_L \Phi_e, \tag{6}$$

where υ is Poisson's ratio, $d\epsilon_g/dP$ is the pressure dependence of the energy band gap, α is the coefficient of thermal expansion, Φ_e is the radiant power absorbed by a semiconductor microcantilever, η is the quantum efficiency, h ($=6.625\times10^{-34}$ J s) is Planck's constant, c ($=3\times10^8$ m s^{-1}) is the speed of light, m, c_p are, respectively, the microcantilever mass and the heat capacity, and τ_L is the lifetime of the carriers in the semiconductor.

Microcantilevers that have adsorbed molecules will undergo photoinduced bending that depends on the number of adsorbed molecules on the surface; on the other hand, microcantilevers that have undergone photoinduced bending will adsorb guest molecules differently. This is important in cases where the photoinduced stresses can be used to counter adsorption induced stresses and thus increase the dynamic range. Depending on the photon wavelength and microcantilever material, the microcantilever can be made to bend by expanding or contracting a surface layer on one of its sides. Coating the surface of the microcantilever with a different material can provide chemical specificity for the target chemicals. However, by choosing a handful of different laser diode wavelengths an increase in the chemical selectivity can be achieved due to the differentiated photoinduced response without the need for different surface coatings; due to the lack of appropriate diode lasers a broadband source and a monochromator can be used instead. One can also obtain a photothermal spectrum by exposing microcantilevers to photons with different wavelengths. In this case the chemical detection is based on the ability to detect small changes in the temperature of the microcantilevers due to interaction of the adsorbate with the probing photons.

When the photoinduced bending is used as the detection method, the chemical coating does not have to be restricted to only one surface as in commonly used micromechanical-based chemical sensors.[4,5,7,9,10,25–28] Coating both sides with a chemically sensitive layer will essentially increase the effective area available for adsorption of analytes. Since these microcantilevers are also very sensitive temperature sensors, care should be taken to account for bending due to heat dissipation. One approach would be to employ reference microcantilevers that are not exposed to analytes and perform differential measurements. The actual photoinduced bending of microcantilevers exposed to chemical analytes can be measured with a number of techniques originally developed for scanning force microscopy.

C. Microcalorimetric spectroscopy detection

Photomechanical chemical detection can also be enhanced using microcalorimetric spectroscopy.[29] Figure 3 shows the concept of microcalorimetric spectroscopy. This spectroscopic technique relies on measurement of minute changes of a micromechanical structure as a function of probing wavelength. We have applied this technique to the detection of diisopropyl methyl phosphonate (DIMP) and trinitrotoluene (TNT). During the detection process the sample is allowed to adsorb onto the coated surface of a femtojoule sensitive micromechanical structure (or microcantilever). The surface of the device will be coated with an appropriate chemical layer which preferentially adsorbs a category of chemicals similar to the target analytes. The chemical sensing is accomplished in three steps. First, vapors from the sample are drawn into contact with the device surface. As the sampling continues, molecules adsorb on the device surface

as shown in Fig. 3. Changes resulting from the initial adsorption of molecules are detected as changes in the adsorption-induced bending of the device. This provides a kind of extremely sensitive ''trigger'' as to when molecules have adsorbed on the surface but provides little information about the identity of the unknown chemical. Next, a photothermal signature is obtained for the adsorbed chemicals by scanning a broadband wavelength region with the aid of a monochromator/microspectrometer across a linear array of such micromechanical devices. For the wavelengths at which the adsorbed chemical absorbs photons, the temperature of those particular microstructures will rise in proportion to the number of molecules present on the surface. Since different devices will be exposed to different wavelengths, a unique photothermal spectrum can be obtained. The detection sensitivity and resolution depends on a number of parameters such as the sensitivity of the device, quality of the optical system, and the density and number of devices used. When a two-dimensional device array is employed, a multichannel spectrum can be obtained if multiple adjacent rows of micromechanical devices are coated with different chemically sensitive materials. Thus, both a sensitive and selective sensing technique can be developed that can detect different families of chemical species simultaneously.

III. EXPERIMENT

In our approach the transduction mechanism is based on the bending of microcantilevers. Bending of microcantilevers can readily be determined by a number of means (optical,[30] capacitive,[31] electron tunneling,[30] and piezoresistive methods).[30,32] In this work, we used optical readout techniques. The approach used was adapted from standard atomic force microscopy imaging systems. The experimental setup is described in detail elsewhere.[8,27] Microcantilevers were placed into a measurement cell and N_2 gas was used as the carrier gas. Analyte molecules diluted in nitrogen were delivered into the cell through a four-way valve, which enabled switching between the analyte/N_2 mixture and the pure carrier gas. A syringe pump was used to inject saturated analyte vapors into a flow system at a controllable rate. The ratio of the analyte injection rate to a total flow rate defined the degree of analyte dilution. The total flow rate was measured at the cell outlet using a mass flow meter. Headspace analyte concentrations were determined using GC–MS.

The microcantilevers used in our studies were chemically modified using two procedures. The first type of coating used was a gold coated (on one side) silicon nitride microcantilever which was modified using thiol-derivatized β-cyclodextrin. For our present experiments, the microcantilevers were immersed in a 1 mM solution of per-6-thio-β-cyclodextrin in DMSO/H_2O(3:2) for 18 h. The microcantilevers were subsequently rinsed with the DMSO/H_2O mixture. The second type of chemically selective coatings are thermally evaporated films of calixarene derivatives. Many of calix[*n*]arene derivatives can readily be deposited on solid substrates using thermal evaporation in vacuum. We have selected calix[4]arene because of its high affinity to smaller molecules of chlorinated nonaromatic organic solvents. 4-tert-butylcalix[4]arenes (Acros Organics) was evaporated onto SiN_x microcantilevers using a Cooke 200 evaporator equipped with a resistance heater, a quartz crucible and a quartz-crystal microbalance thickness monitor. A deposition rate of 0.02–0.05 nm/s was maintained until the desired thickness was obtained.

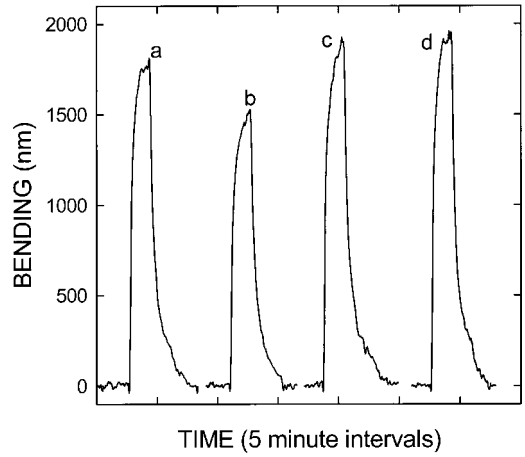

FIG. 4. Bending response of β-cyclodextrin modified microcantilevers to (a) 196.6 ppb of 1,8-dimethylnaphthalene, (b) 83.0 ppb 2,7-dimethylnaphthalene, (c) 201.8 ppm tetrachloroethylene, and (d) 680.2 ppm trichloroethylene.

In the photomechanical studies we used micromechanical structures as photon detectors.[33,34] These photon detectors were exposed to photons from a laser source or to infrared (IR) radiation from a spectrometer prior to any exposure to chemicals and their thermal response was recorded as a function of photon wavelength. The wavelength region (2.5–14.5 μm) attainable with our spectrometer (Foxboro Miran-80 IR spectrometer) was divided into three regions: (i) 2.5–4.5, (ii) 4.5–8.0, and (iii) 8.0–14.5 μm. The thermal detectors were then exposed to chemical analytes and a new thermal response was recorded as a function of photon wavelength. The increase in thermal response of the detector at particular wavelengths was attributed to the absorption of photons by the molecules adsorbed on the thermal detector surface. All measurements were conducted at ambient temperature and atmospheric pressure.

IV. RESULTS AND DISCUSSION

A. Adsorption-induced studies

1. β-Cyclodectrin coatings

β-cyclodextrin modified microcantilevers were placed in the flow cell and exposed to analyte vapors. Figure 4 shows typical responses of the β-cyclodextrin modified microcantilever to vapors of a series of organic compounds. Exposure of the functionalized surface to the analyte for 2 min was followed by purging the cell with pure carrier gas for 5–10 min. Diluted vapor of each of the selected analytes was used in order to obtain the responses shown in Fig. 4. Diluted vapors of 1,8-dimethylnapthalene (1,8-DMN) and 2,7-

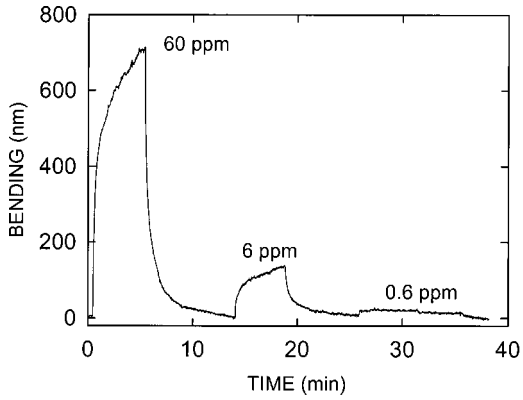

FIG. 5. Bending response of calix[4]arene coated silicon microcantilevers to TCE.

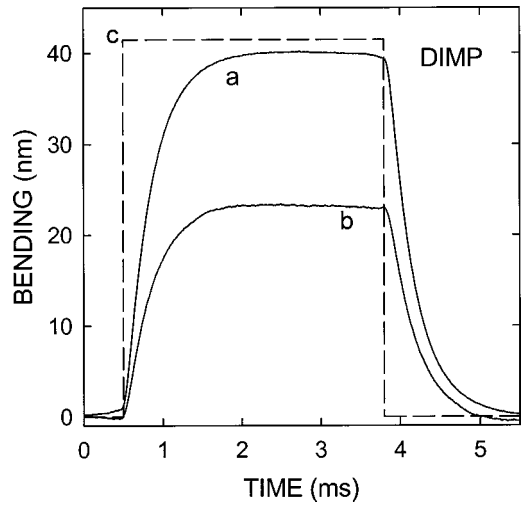

FIG. 6. Photoindcued bending of (a) a gold-coated microcantilever with no analytes adsorbed, and (b) same microcantilever as before but exposed to DIMP. The dashed curve (c) shows the amount of time the microcantilever was exposed to photons that caused the photoinduced bending observed. During the exposure time no measurable change in the resonance frequency was observed.

dimethylnaphthalene (2,7-DMN) caused responses shown in Fig. 4 by curves (a) and (b), respectively. The next two responses [curves (c) and (d) in Fig. 4] were caused by diluted vapors of tetrachloroethylene (TCE) and trichloroethylene (TRCE). The differences in magnitudes of the responses reflect the coated microcantilever selectivity. The higher magnitude of the response to 1,8-DMN as compared to 2,7-DMN correlates well with the model of inclusion complexes of β-cyclodextrin and different DMN isomers. The 1,8-DMN molecule is less elongated than 2,7-DMN and thus causes the cyclodextrin to distort more upon complexation. The sensitivities of 1,8-DMN and 2,7-DMN were determined to be 11.2 and 22.0 nm deflection per parts per billion, respectively. Comparison of the responses to TCE and TRCE [curves (c) and (d) in Fig. 4] reveals lower sensitivity of the β-cyclodextrin modified microcantilevers to these chlorinated compounds. The lower sensitivity can be explained by the fact that the molecules of TCE and TRCE are smaller than the β-cyclodextrin cavity and their complexation is less favorable than in the case of the DMNs. The deflection sensitivities of β-cyclodextrin modified microcantilevers to TCE and TRCE were determined to be 11.5 and 3.4 nm per parts per million, respectively. We estimated respective limits of detection (LOD) using linear regressions of the calibration plots obtained for each analyte. A concentration at which the extrapolated response exceeds the noise level three times was accepted as a value of LOD. A typical noise level of the monitored microcantilever deflection was 20 nm. The calculated LODs for 1,8-DMN, 2,7-DMN, TCE, and TRCE were determined to be 5.3, 2.7 ppb, 5.2, and 17.5 ppm, respectively.

2. Evaporated calixarene coatings

Microcantilevers with 75 nm calixarene coatings were investigated for their response to TCE. The responses of the microcantilevers to TCE were measured in 1 ml flow cell. Figure 5 shows typical responses obtained with calix[4]arene coated Si microcantilevers in the presence of TCE. Each response in Fig. 5 was induced by switching the cell to a flow of TCE/N_2 mixture for 10 min. A constant gas flow of 3 ± 0.5 ml min^{-1} was maintained during the experiment. Using a linear regression of the obtained calibration plot and the value of measured noise level (20 nm) the LOD for TCE was approximated to be 1.1 ppm.

B. Photoinduced chemical response

We used gold-coated microcantilevers to investigate photomechanical chemical sensing and study the effect of molecular adsorption on the photoinduced bending of microcantilevers. We found that depending on the photon wavelength and microcantilever material, the bending can be in either direction. In our studies, we have measured these effects for DIMP, TNT, ethanol, and toluene adsorbing on the surface. However, only results for DIMP and TNT will be presented here.

1. DIMP

We used DIMP which has a vapor pressure of ~700 mTorr at 25 °C. DIMP is a phosphorous containing organic chemical which is used as a model for chemical warfare agents. A number of gravimetric based transducers have been used previously as platforms for detecting analogous phosphorous organic compounds. An earlier study[35] has used a surface acoustic wave device with scanning Auger microscopies to achieve selectivity and reversibility. In the present studies we exposed DIMP directly to gold-coated microcantilevers both for simplicity and because gold reflects most of the incoming IR energy minimizing direct heating of the substrate. We measured the photoinduced bending of a gold-coated Si microcantilever exposed (Si side) to a 790 nm diode laser and obtained the photomechanical response shown in Fig. 6 by curve (a). We subsequently exposed the gold-coated microcantilever to DIMP. Following the adsorption of DIMP molecules, the microcantilever was exposed to photons using a diode laser (790 nm, and same intensity as before) and again measured the photo-

induced bending shown by curve (b) in Fig. 6. During the exposure of the microcantilever to DIMP, we did not detect any changes in the resonance frequency (<0.1 Hz) of the microcantilever, which puts a limit on the adsorbed mass of less than 1×10^{-9} g/cm^2.

We also obtained the photothermal response of a microcantilever thermal detector from 8.0 to 14.5 μm with DIMP molecules adsorbed on its surface. The photothermal spectrum was obtained with about one monolayer of coverage on the surface. The peaks in the photothermal spectrum of DIMP correspond well with the absorption peaks in the IR spectrum of DIMP. Since DIMP molecules absorb photons at these wavelengths, their internal energy increases as molecules populated higher vibrational levels. The internal energy of each DIMP molecule is dissipated either by radiation, convection or conduction to the gold substrate. It is the heat of conduction from the ''hot'' molecules to the gold substrate of the microcantilever that increases its temperature causing it to bend. Our present results demonstrate that it is possible to detect less than a submonolayer of DIMP coverage using microcalorimetric spectroscopy.

2. TNT

Micromechanical Si structures were exposed to TNT. TNT is solid at room temperature, has very low vapor pressure (10^{-6} Torr) and its detection under ambient conditions presents a challenge. In our studies, we exposed gold-coated Si microcantilevers to TNT molecules in order to investigate the effect of photoinduced stress. Because of the very low vapor pressure a minute quantity of TNT molecules could be adsorbed on the surface. Consequently, a very small adsorption-induced stress was expected. In fact, we found no measurable response to TNT due to any adsorption-induced stresses alone. Using a 10 mW HeNe laser, we measured the photoinduced stress both before and after exposure to TNT. The exposure of the gold-coated microcantilever to TNT was provided by placing less than 5 mg of TNT into the chamber housing the microcantilever. Afterwards, the sample was removed from the chamber and the measurements of photoinduced stresses were carried out again. The photoinduced response of the microcantilever prior to exposure to TNT and after exposure to TNT shows that the photoinduced bending depends on the presence of TNT molecules on the surface. Since Si contracts when exposed to 633 nm photons, the photoinduced bending decreases as more TNT molecules adsorb on the surface of our detector. We attribute our findings to changes in the surface states of the gold-coated microcantilever due to adsorption of TNT molecules.

We also studied thermal responses of micromechanical thermal detectors with TNT molecules adsorbed on their surface. In analogy to the previous experiments, TNT was placed in a chamber containing a platinum coated micromechanical thermal detector allowing the adsorption of TNT molecules on its surface. TNT was subsequently removed from the chamber and the thermal detector was exposed to IR radiation. In Fig. 7 we plotted the thermal response of the detector (exposed to TNT vapor) from 2.5 to 14.5 μm with

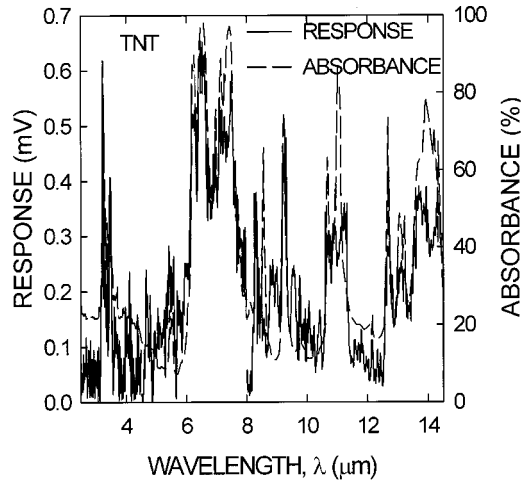

FIG. 7. TNT photothermal spectrum from 2.5 to 14.5 μm obtained using a micromechanical thermal detector with molecules adsorbed on its surface (solid curve). Also plotted is the IR spectrum of TNT (dashed curve).

TNT molecules adsorbed on its surface. As can be seen in Fig. 7, the photothermal spectrum of the adsorbed TNT exhibits a number of peaks in this wavelength region. These peaks correspond to infrared absorption peaks of TNT vapor. In order to estimate the number of TNT molecules adsorbed on the surface, we measured the resonance frequency of the structure before it was exposed to TNT molecules. However, we observed no measurable change in resonance frequency after TNT molecules adsorbed on the structure's surface. We estimated that the resonance frequency shift was less than 0.01 Hz, which defines an upper limit of the adsorbed mass of TNT to be less than 10^{-16} g or fewer than 3×10^{7} of adsorbed molecules.

V. CONCLUSIONS

The results of the present work demonstrate that photomechanical chemical sensors represent an important development in micromechanical chemical detection technology, and can be expected to provide the basis for considerable further development. For example, vastly improved micromechanical chemical detectors could be produced by making relatively simple changes in the materials and geometries used in microcantilever fabrication. While the optical readout method used in the present studies is useful with single element designs, practical implementation of microcantilever arrays may require the use of other readout methods, such as piezoresistance or capacitance. Fortunately, the present microcantilever technology is compatible with a variety of readout methods and also affords tremendous flexibility to potential system designers. We also have demonstrated that microcantilevers with various chemical coatings respond sensitively to the presence of chemical analytes. Earlier studies have demonstrated that the mass sensitivities of the frequency variation of microcantilevers can compete with those of other gravimetric chemical sensors. Monitoring the bending of microcantilevers can provide an attractive alternative to detect gas-phase analytes. We have measured the

adsorption-induced and photoninduced bending of microcantilevers exposed to small concentrations of analytes. We believe that the detection limits can be extended to sensitivities below parts per trillion by varying the coating and microcantilever properties.

ACKNOWLEDGMENTS

This work was supported by EMSP and the Laboratory Director's Research and Development Program of Oak Ridge National Laboratory. Oak Ridge National Laboratory is operated for the U.S. Department of Energy by Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Department of Energy under Contract No. DE-AC05-00OR22725. The work performed by EEG, Inc. was supported by DARPA Contract No. DAAH01-00-C-R223 and the National Science Foundation.

Presented at the 47th AVS International Symposium, Boston, MA, 2–6 October 2000.

[1]J. Janata, M. Josowicz, and D. M. Devaney, Anal. Chem. **66**, R207 (1994).
[2]J. W. Grate, S. L. Rose-Pehrsson, D. L. Venezky, M. M. Klusty, and H. H. Wohltjen, Anal. Chem. **65**, 1868 (1993).
[3]J. Brugger, N. Blanc, P. Renaud, and N. F. de Rooji, Sens. Actuators A **43**, 339 (1994).
[4]E. A. Wachter and T. Thundat, Rev. Sci. Instrum. **66**, 3662 (1995).
[5]T. Thundat, G. Y. Chen, R. J. Warmack, D. R. Allison, and E. A. Wachter, Anal. Chem. **67**, 519 (1995).
[6]G. Y. Chen, T. Thundat, E. A. Wachter, and R. J. Warmack, J. Appl. Phys. **77**, 3618 (1995).
[7]M. K. Baller *et al.*, Ultramicroscopy **82**, 1 (2000).
[8]P. G. Datskos and I. Sauers, Sens. Actuators B **3016**, 1 (2000).
[9]H. P. Lang *et al.*, Anal. Chim. Acta **393**, 59 (1999).
[10]T. Betts, C. Tipple, M. Sepaniak, and P. G. Datskos, Anal. Chim. Acta **422**, 89 (2000).
[11]J. H. Hoh, J. P. Cleveland, C. B. Prater, J.-P. Revel, and P. K. Hansma, J. Am. Chem. Soc. **114**, 4917 (1992).
[12]F. Ohnesorge and G. Binnig, Science **260**, 1451 (1993).
[13]J. Varesi, J. Lai, T. Perazzo, Z. Shi, and A. Majumdar, Appl. Phys. Lett. **71**, 306 (1997).
[14]R. G. Stearns and G. S. Kino, Appl. Phys. Lett. **47**, 1048 (1985).
[15]P. G. Datskos, S. Rajic, and I. Datskou, Appl. Phys. Lett. **73**, 2319 (1998).
[16]T. Figielski, Phys. Status Solidi **1**, 306 (1961).
[17]P. G. Datskos, S. Rajic, C. M. Egert, and I. Datskou, Proc. SPIE **3698**, 151 (1999).
[18]H. K. Wickramasinghe, R. C. Bray, V. Jipson, C. F. Quate, and J. R. Salcedo, Appl. Phys. Lett. **33**, 923 (1978).
[19]F. J. von Preissig, J. Appl. Phys. **66**, 4262 (1989).
[20]S. Tomishenko, *Theory of Plates and Shells* (McGraw-Hill, New York, 1940).
[21]G. G. Stoney, Proc. R. Soc. London, Ser. A **82**, 172 (1909).
[22]P. G. Datskos, M. J. Sepaniak, C. A. Tipple, and N. Lavrik, Sens. Actuators B **76**, 393 (2001).
[23]Park Scientific Instruments, Sunnyvale, CA.
[24]Digital Instruments, Santa Barbara, CA.
[25]T. Thundat, E. A. Wachter, S. L. Sharp, and R. J. Warmack, Appl. Phys. Lett. **66**, 695 (1995).
[26]T. Thundat, P. I. Oden, P. G. Datskos, G. Y. Chen, and R. J. Warmack, presented at The 16th Warner Brandt Workshop on Charged Particle Penetration Phenomena, Oak Ridge, TN, 1996.
[27]H. P. Lang *et al.*, Appl. Phys. Lett. **72**, 383 (1998).
[28]C. L. Britton, Jr., R. L. Jones, P. I. Oden, Z. Hu, R. J. Warmack, S. F. Smith, W. L. Bryan, and J. M. Rochelle, Ultramicroscopy **82**, 17 (2000).
[29]P. G. Datskos, S. Rajic, C. M. Egert, and I. Datskou, presented at the 3rd International Symposium on Technology and Mine Problems, Monterey, CA, 6–9 April 1998.
[30]D. Sarid, *Scanning Force Microscopy with Applications to Electric, Magnetic, and Atomic Forces* (Oxford University Press, New York, 1991).
[31]T. Göddenhenrich, H. Lemke, U. Hartmann, and C. Heiden, J. Vac. Sci. Technol. A **8**, 383 (1990).
[32]M. Tortonese, H. Yamada, R. C. Barrett, and C. F. Quate, presented at The IEEE Proceedings of Transducers '91, 1991.
[33]P. I. Oden, P. G. Datskos, T. Thundat, and R. J. Warmack, Appl. Phys. Lett. **69**, 3277 (1996).
[34]P. G. Datskos, P. I. Oden, E. A. Wachter, T. Thundat, and R. J. Warmack, Appl. Phys. Lett. **69**, 2986 (1996).
[35]L. J. Kepley and R. M. Crooks, Anal. Chem. **64**, 3191 (1992).