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A microcantilever-based alcohol vapor sensor-application and response model

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A recently developed microcantilever probe with integrated piezoresistive readout has been applied as a gas sensor. Resistors, sensitive to stress changes, are integrated on the flexible cantilevers. This makes it possible to monitor the cantilever deflection electrically and with an integrated reference cantilever background noise is subtracted directly in the measurement. A polymer coated cantilever has been exposed to vapors of various alcohols and the resulting cantilever response has been interpreted using a simple evaporation model. The model indicates that the cantilever response is a direct measure of the molecular concentration of alcohol vapor. On the basis of the model the detection limit of this cantilever-based sensor is determined to be below 10 ppm for alcohol vapor measurements. Furthermore, the time response of the cantilever can be used to distinguish between different alcohols due to a difference in the evaporation rates. © 2000 American Institute of Physics. [S0003-6951(00)02118-5]

Micromachined cantilevers are most commonly used for atomic force microscopy (AFM) imaging. Recently, micromachined cantilevers have been applied as very sensitive chemical sensors.[1–4] A reason for the interest in developing sensors based on this principle is the possibility of performing very local, high-resolution measurements. The principle is that changes in the surface stress or the temperature of a material on one side of the cantilever give rise to a cantilever deflection (a bimorph effect). Using this technique surface stress changes of 10^{-5} N/m[5] and temperature changes of 10^{-5} K[1] have been detected. Furthermore, a mass change of the cantilever causes a change in the resonant frequency of the cantilever. Mass changes down to 0.5 ng have been measured in this way.[6] The deflection of a cantilever is most commonly recorded optically by shining a laser beam onto the cantilever and monitoring the reflection of the laser beam (e.g., in AFM). This principle is very accurate, but for many applications it would be an advantage to have a more compact readout mechanism that requires less adjustment and alignment. A readout integrated on the probe would also greatly facilitate work in liquid. In order to reduce background noise, such as thermal drift and turbulence around the probe, a reference cantilever is crucial.[7]

We have recently developed micromachined cantilever probes with integrated piezoresistive readout and a built-in reference cantilever.[8] The probe includes two cantilevers and a full Wheatstone bridge placed on chip, shown in Fig. 1. When a voltage, V, is applied across the bridge, Fig. 1(a), the output voltage V_0 is given by $V_0 = 1/4 V \Delta R / R$. R is the resistance of the unstressed piezoresistors and ΔR is the difference between the resistance of the resistors placed on the cantilevers 2 and 3. The cantilevers are layered Si/SiO_2 beams with integrated poly-Si piezoresistors. The thickness of the beam is approximately 2 μm, the deflection sensitivity

is measured to be approximately $z^{-1} \Delta R / R = 10^{-6}$ nm^{-1}, and the surface stress sensitivity is $\sigma^{-1} \Delta R / R = 1.8 \times 10^{-4}$ (N/m)$^{-1}$.

Here we report the application of the probe as an alcohol vapor sensor.

In order to detect alcohol vapors, one side of one of the two cantilevers on the probe is coated with a polymer film. We have used a photoresist,[9] which contracts when it is exposed to alcohol vapor. The coating is performed manually with a glass capillary and a micromanipulator resulting in a polymer layer thickness of approximately 10 μm. Coating the cantilever with the polymer induces a stress change on the cantilever. This decreases the resistivity of the piezoresistor with approximately 10%, corresponding to a tensile stress in the polymer, but does not otherwise affect the electrical properties of the integrated measurement system. Figure 2 shows a scanning electron micrograph of the probe after coating.

The probe is placed in a measurement chamber, in which there is a controlled, constant flow of dry nitrogen. As the polymer coating is also sensitive to water vapor,[10] humidity levels were kept low and constant in all experiments, 3% ±0.5%. Liquid alcohol is led onto a ceramic substrate in the chamber approximately 2 cm from the probe using a syringe and Teflon tubing. The cantilever response, i.e., the change
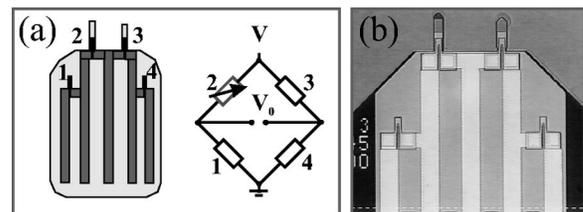

FIG. 1. Schematic drawing (a) and microscope image (b) of a micromachined cantilever probe with integrated piezoresistive readout. The cantilevers are 200 μm long, 50 μm wide, and approximately 2 μm thick.

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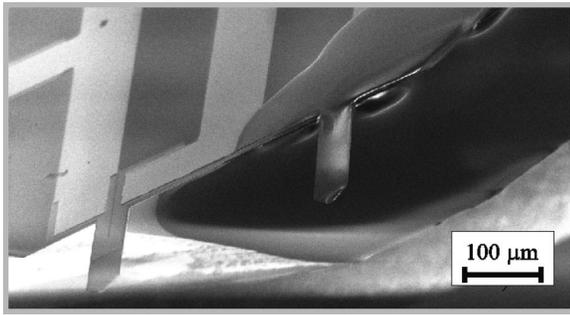
FIG. 2. Scanning electron micrograph of a piezoresistive micromachined cantilever. One side of one of the two cantilevers and part of the substrate have been coated with an approximately 10 μm thick polymer layer.

in resistivity of the resistor on the cantilever, induced by the stress change in the film, is monitored as the output voltage from the Wheatstone bridge.[11] With the combined effect of the reference cantilever and the on-chip Wheatstone bridge configuration, a total noise reduction of a factor 25 is obtained.

We have developed a simple model to interpret the gas measurements. The model describes the alcohol concentration in the measurement chamber as a function of time.

When a drop of liquid alcohol is injected into the chamber, the alcohol will evaporate and give rise to a time dependent concentration of alcohol vapor in the chamber, $n(t)$. The change in the molecular concentration of gaseous alcohol in the chamber is described by the rate of evaporation of the alcohol from the drop minus the flow rate out of the chamber, due to the constant throughflow of the carrier gas

$$\frac{dn}{dt} = \frac{1}{V}(Q_{AM} - nQ_0) = \frac{Q_{AM}}{V} - \frac{n}{\tau_0}, \tag{1}$$

where Q_{AM} is the molecular flow of alcohol from the evaporating drop, V is the volume of the chamber, Q_0 is the volumetric flow of the carrier gas, and $\tau_0 = V/Q_0$ is the residence time of the system. As the surface area of the droplet decreases the alcohol flow decreases.

To solve Eq. (1) we first find the time dependence of the molecular flow of alcohol, Q_{AM}, from the mass balance of the drop as it shrinks

$$dm/dt = -Q_{AM}M, \tag{2}$$

where m is the mass of the drop and M is the molecular mass of the alcohol.

We assume that the injected liquid alcohol forms a spherical drop and that Q_{AM} is diffusion limited in a boundary layer around the drop. At low vapor concentrations the diffusion coefficient, D, can be assumed to be concentration independent, and when the diffusive layer extends to distances far larger than the radius of the drop the mass loss rate, dm/dt, can be approximated with an expression due to Langmuir[12]

$$dm/dt \approx -4\pi D n_{eq} R_s M. \tag{3}$$

R_s is the radius of the surface of the drop and n_{eq} is the molecular alcohol concentration of saturated alcohol vapor with equilibrium vapor pressure $P_{eq} = n_{eq}kT$, where k is Boltzmann's constant and T is the absolute temperature. The diffusivity is calculated from $D = 1/3\lambda \bar{\nu}$, where $\bar{\nu}$ is the av-

erage molecular velocity in one direction and λ is the mean free path in air at ambient conditions ($\sim$70 nm). From kinetic gas theory $\bar{\nu}$ is given by $\bar{\nu} = \sqrt{8kT/\pi M}$.

The mass of the drop is $m = 4/3\pi_s^3\rho$, where ρ is the density of liquid alcohol, hence,

$$\frac{dm}{dt} = \frac{4}{3}\pi\rho \frac{dR_s^3}{dt}. \tag{4}$$

Combining Eqs. (3) and (4) we obtain a differential equation in R_s which has the solution

$$R_s^2 = R_0^2 - (2Dn_{eq}M/\rho)t. \tag{5}$$

R_0 is the initial radius of the drop and at $t_0 = R_0^2\rho/2DMn_{eq}$ the drop has completely evaporated. Using Eqs. (2) and (3) to express $Q_{AM} \approx 4\pi Dn_{eq}R_s$ and inserting the expression for R_s, given by Eq. (5), we obtain the time dependence of the molecular flow of alcohol

$$Q_{AM} = 4\pi R_0 Dn_{eq}\sqrt{1 - t/t_0} = Q_{A\,max}\sqrt{1 - t/t_0}. \tag{6}$$

With this relation we may finally solve Eq. (1) and obtain an expression for the time dependence of the molecular concentration of alcohol vapor in the chamber.

While the drop is evaporating, $Q_{AM} > 0$ and $t \leq t_0$, and with $n(0) = 0$ we obtain

$$n(t) = Q_{A\,max}/Q_0$$
$$\times \exp(-t/\tau_0) \int_0^{1/\tau_0} \exp(u)\sqrt{1 - u\tau_0/t_0}\,du; \quad t \leq t_0. \tag{7}$$

This integral cannot be solved analytically, however, it is easily evaluated numerically. For $t \geq t_0$ the drop has evaporated, $Q_{AM} = 0$, and with the initial condition $n = n(t_0)$ the solution to Eq. (1) is

$$n(t) = n(t_0)\exp(-(t - t_0)/\tau_0); \quad t \geq t_0. \tag{8}$$

Equations (7) and (8) describe the concentration of gaseous alcohol in the chamber as a function of time during and after the alcohol evaporation. Note that the model contains no fitting parameters.

With our piezoresistive probe we have measured the response of the resist coated cantilever to different amounts of the same alcohol and to the same amount of three different alcohols. In Fig. 3 the measured time response, due to the stress change in the film, is plotted for five different amounts of ethanol. The response is reproducible to better than 10%. A change of the signal of 0.1 mV corresponds to a stress change of $\sim$0.05 MPa assuming a 10-μm-thick polymer layer. As the amount of ethanol is increased, the maximum of the cantilever signal increases and the time it takes for the signal to reach its maximum value also increases. The measurements have been plotted together with the alcohol evaporation model, Eqs. (7) and (8), in terms of the partial pressure of alcohol in the chamber (Fig. 3, smooth lines, and right axis).[13] It is seen that there is a good agreement between the experiment and the model. Thus, for 20 μl of liquid ethanol the maximum vapor pressure of alcohol is approximately 7 Pa. The good agreement between experiment and model suggest that we are not detecting the diffusion of alcohol in the resist film. Rather, on the time scale of the experiment, the
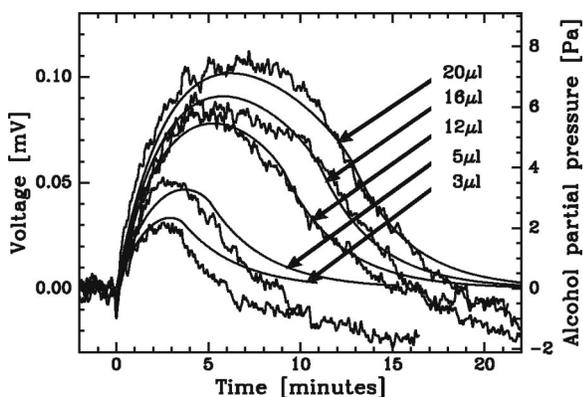
FIG. 3. The reaction of a resist coated cantilever to different amounts of ethanol. The smooth curves are the concentration curves calculated from the model, Eqs. (7) and (8), for alcohol evaporation.

resist seems to respond instantaneously to the alcohol concentration. The cantilever deflection can therefore be interpreted as a direct measure of the alcohol concentration in the chamber. From Fig. 3 it is seen that a change in alcohol partial pressure of 1 Pa, corresponding to a sensitivity of 10 ppm, is easily resolved. Measurements suggest that the sensitivity increases with the thickness of the polymer coating. In the tail of the measurements there is a discrepancy between the model and the experiment. The measured response does not directly stabilize at zero but continues to decrease, corresponding to a swelling of the polymer. This might indeed be due to more complex chemical processes in the film. Full reversibility is reached after about an hour, when the signal returns to zero.

When injecting the same amount of different alcohols, Fig. 4, different cantilever responses are observed, as also reported in Ref. 7. Measurements are presented on 16 μl of methanol, ethanol, and propanol. Methanol, which has the lowest molecular mass and the highest vapor pressure, gives rise to the fastest and largest cantilever response. The response to ethanol and propanol are similar and the maximum response is about half that of methanol. With the different
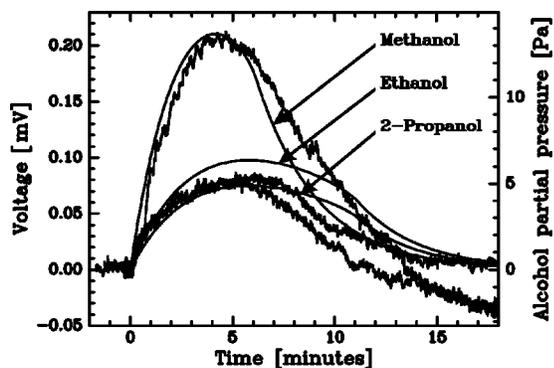

FIG. 4. The reaction of a resist coated cantilever to 16 μl of three different alcohols. The smooth curves are calculated from the model, Eqs. (7) and (8), for alcohol evaporation.

alcohol masses and vapor pressures inserted in the evaporation model (Fig. 4, smooth curve)[14] a good agreement with the measurements is again observed. Thus, the resist coated cantilever seems to react identically to the different alcohols and simply monitors the concentration of alcohol vapor in the chamber. Different alcohols can therefore be detected by this technique due to their different evaporation rates and not because of different diffusion behaviors or chemical reactions in the resist film.[7] The timescale for alcohol diffusion in a 10 μm resist film is expected to be in the subsecond range.[15] Hence, in order to study diffusion in the resist and not in the flow chamber, the response time of the measuring system must be considerably reduced. The response time can be tuned by for example changing the volume of the measuring chamber and the flow rate of the carrier gas, which determine the system residence time.

In conclusion, the developed micromachined cantilever probe with integrated piezoresistive readout and built-in reference cantilever has a good design for cantilever-based sensor applications. The probe has been used to investigate the response of a resist coated cantilever to alcohol vapor. A simple evaporation model describes well the observed cantilever response, and we conclude that the cantilever-based sensor is monitoring the instantaneous alcohol concentration in the measuring chamber. The response also discriminates between different alcohols, not because of differences in diffusive behavior in the polymer film but due to differences in the evaporation rates of the alcohols.

[1] J. K. Gimzewski, Ch. Gerber, E. Meyer, and R. R. Schlittler, Chem. Phys. Lett. **217**, 589 (1994).

[2] J. R. Barnes, R. J. Stephenson, M. E. Welland, C. Gerber, and J. K. Gimzewski, Nature (London) **372**, 79 (1994).

[3] T. Thundat, E. A. Wachter, S. L. Sharp, and R. J. Warmack, Appl. Phys. Lett. **66**, 1695 (1995).

[4] R. Berger, E. Delamarche, H. P. Lang, C. Gerber, J. K. Gimzewski, E. Meyer, and H.-J. Güntherodt, Science **276**, 2021 (1997).

[5] S. J. O'Shea, M. E. Welland, T. A. Brunt, A. R. Ramadan, and T. Rayment, J. Vac. Sci. Technol. B **14**, 1383 (1996).

[6] J. P. Cleveland, S. Manne, D. Bocek, and P. K. Hansma, Rev. Sci. Instrum. **64**, 403 (1993).

[7] H. P. Lang, R. Berger, F. Battiston, J.-P. Ramseyer, E. Meyer, C. Andreoli, J. Brugger, P. Vettiger, M. Despont, T. Mezzacasa, L. Scandella, H.-J. Güntherodt Ch. Gerber, and J. K. Gimzewski, Appl. Phys. A: Mater. Sci. Process. **66**, S61 (1998).

[8] J. Thaysen, A. Boisen, O. Hansen, and S. Bouwstra, Digest of Technical Papers, Transducers '99, 10th International Conference on Solid State Sensors and Actuators, Sendai, Japan 7–10 June 1999, pp. 1852–1855.

[9] AZ 5200 E, Hoechst Celanese Corp., Chatham, NJ 07928.

[10] A. Boisen, J. Thaysen, H. Jensenius, and O. Hansen, Ultramicroscopy **82**, 11 (2000).

[11] For the measurements presented here we have used a measurement chamber of 30 I and a nitrogen flow of 10 l/min. The bridge supply voltage is 4 V.

[12] I. Langmuir, Phys. Rev. **12**, 368 (1918).

[13] The parameters used in the model in Fig. 3 are: $V=30$ l, $Q_0=10$ l/min, $p_{eq}=9 \times 10^3$ Pa, $\rho=785$ kg/m^3, and $M=46 \times 1.66 \times 10^{-27}$ kg.

[14] For ethanol the values are the same as earlier. For methanol: $p_{eq}=19.7 \times 10^3$ Pa, $\rho=791$ kg/m^3, and $M=32 \times 1.66 \times 10^{-27}$ kg. For 2-propanol: $p_{eq}=78 \times 10^3$ Pa, $\rho=785$ kg/m^3, and $M=60 \times 1.66 \times 10^{-27}$ kg.

[15] R. K. Traeger, 26th Electronics Components Conference, IEEE, San Fransisco, California (1976), pp. 361–367.