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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 10⁻³ N/m² and temperature changes of 10⁻³ K1 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 V₀ is given by V₀ = 1/4VRΔR/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/SiO₂ beams with integrated poly-Si piezoresistors. The thickness of the beam is approximately 2 μm, the deflection sensitivity is measured to be approximately z⁻¹ΔR/R = 10⁻⁶ nm⁻¹, and the surface stress sensitivity is σ⁻¹ΔR/R = 1.8 × 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.
molecular alcohol concentration of saturated alcohol vapor
tion in the measurement chamber as a function of time.
measurements. The model describes the alcohol concentra-
tained.
configuration, a total noise reduction of a factor 25 is ob-
tained.
We have developed a simple model to interpret the gas
measurements. The model describes the alcohol concentra-
chamber as a function of time.
When a drop of liquid alcohol is injected into the cham-
er, the alcohol will evaporate and give rise to a time de-
pendent concentration of alcohol vapor in the chamber, \( n(t) \). The change in the molecular concentration of gaseous al-
hol 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
\[
\frac{dn}{dt} = \frac{1}{V} (Q_{AM} - nQ_0) = \frac{Q_{AM}}{V} \frac{n}{\tau_0},
\]
where \( Q_{AM} \) is the molecular flow of alcohol from the evapo-
ating drop, \( V \) is the volume of the chamber, \( Q_0 \) is the vol-
metric 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 de-
creases 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
\[
dm/dt = \frac{4}{3} \pi \rho \frac{dR_s^3}{dt}.
\]

Combining Eqs. (3) and (4) we obtain a differential
expression for the time dependence of the molecular flow of alcohol
\[
Q_{AM} = 4 \pi R_0 D n_{eq} \sqrt{1 - tr_{0}} = Q_{Amax} \sqrt{1 - tr_{0}}.
\]

This integral cannot be solved analytically, however, it is
easily evaluated numerically. For \( t \geq t_0 \) the drop has evapo-
rated, \( Q_{AM} = 0 \), and with \( n(0) = 0 \) we obtain
\[
n(t) = Q_{Amax}/Q_0 \times \exp(-t/t_0) \int_0^{1/t_0} \exp(u) \sqrt{1 - u \tau_0/t_0} \ du; \quad t \leq t_0.
\]

With our piezoresistive probe we have measured the re-
sponse 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-\( \mu \)-thick polymer
layer. As the amount of ethanol is increased, the maximum
of the cantilever signal increases and the size it takes for the
signal to reach its maximum value also increases. The mea-
surements have been plotted together with the alcohol evapo-
ration model, Eqs. (7) and (8), in terms of the partial pressure
of alcohol in the chamber (Fig. 3, smooth lines, and right
axis). It is seen that there is a good agreement between the
experiment and the model. Thus, for 20 \( \mu \)l of liquid ethanol
the maximum vapor pressure of alcohol is approximately 7
Pa. The good agreement between experiment and model sug-
gest that we are not detecting the diffusion of alcohol in the
resist film. Rather, on the time scale of the experiment, the

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 \( \mu \) thick polymer layer.
The 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 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 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. 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.

9. AZ 5200 E, Hoechst Celanese Corp., Chatham, NJ 07928.
10. For the measurements presented here we have used a measurement chamber of 30 l and a nitrogen flow of 10 l/min. The bridge supply voltage is 4 V.
12. The parameters used in the model in Fig. 3 are: \( V = 3.01 \), \( Q_0 = 10 \) l/min, \( p_{\text{eq}} = 9 \times 10^4 \) Pa, \( \rho = 785 \) kg/m\(^3\), and \( M = 46 \times 1.66 \times 10^{-27} \) kg.
13. For ethanol the values are the same as earlier. For methanol: \( p_{\text{eq}} = 19.7 \times 10^4 \) Pa, \( \rho = 791 \) kg/m\(^3\), and \( M = 32 \times 1.66 \times 10^{-27} \) kg. For 2-propanol: \( p_{\text{eq}} = 78 \times 10^4 \) Pa, \( \rho = 785 \) kg/m\(^3\), and \( M = 60 \times 1.66 \times 10^{-27} \) kg.