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Sensors and Actuators B 129 (2008) 241–245
SENSORS AND ACTUATORS B CHEMICAL
www.elsevier.com/locate/snb

Al_2O_3-coated microcantilevers for detection of moisture at ppm level

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Received 6 May 2007; received in revised form 1 August 2007; accepted 2 August 2007
Available online 14 August 2007

Abstract

We have demonstrated that the Al_2O_3-modified microcantilevers (MCLs) can be used to detect low level of moisture. The detection limit for moisture in nitrogen was 10 ppm. The MCLs' response time to moisture was less than 3 min. The sensors were stable for months stored under ambient conditions. The bending amplitudes were proportional to the moisture level and temperature, and the detection of moisture was not affected by alcohols in the environment.

Keywords: Microcantilever; Sensors; Moisture; Natural gas; Aluminum oxide; Al_2O_3

1. Introduction

Natural gas, a combustible mixture of hydrocarbon gases, is a vital component of the world supply of energy. Raw natural gas contains water vapor, hydrogen sulfide, alcohol, carbon dioxide, etc., which need to be removed before the natural gas enters the pipeline. Water vapor is typically removed by a dehydrating agent such as glycol that absorbs water vapor from the gas stream. After dehydrating process, industrial gas manufacturers monitor moisture content to meet industry specifications for pure, dry gas. Excess amounts of water vapor will not only lower the burning efficiency, but also corrode the pipeline. The moisture was controlled down to the parts-per-million (ppm) to billion (ppb) level and monitored by moisture meters.

Current techniques to measure water vapor content include cooled (chilled) mirrors, electrolytic cells, oscillating crystals, infrared absorption, metal oxide or polymer capacitive films, etc. [1,2]. The prices range from a couple of thousand to tens of thousands US dollars. Besides these devices, length-of-stain tubes occupy the low end of technology. These detector tubes are quick, cost-effective, and convenient to operate, but the trade-off is its low accuracy.

Each device has their advantages and disadvantages. The optical devices suffer from higher cost and interference from alcohols although they are the only devices that can handle high corrosive gases since these devices do not directly contact with gases. In general, other devices are less sensitive than optical devices, but more cost-effective. With advances in material and microelectronic technology moving rapidly, manufacturers are finding ways to overcome disadvantages inherent in these sensors. Furthermore, research on new systems is also undergoing.

Advances in the field of micro-electro-mechanical systems (MEMS) now offer unique opportunities to design sensitive and cost-effective analytical methods. Recently, microcantilevers (MCLs) have been proven to be an attractive platform for sensors with on-chip electronic circuitry and extreme sensitivity [3,4]. Because the micromechanical aspects of the MCL can be integrated with on-chip electronic circuitry, it provided an outstanding platform for chemical [5,6] and biological sensors [7,8]. Extremely sensitive chemical vapor sensors based on MCLs have been demonstrated using selective coatings on the MCLs.

MCLs undergo bending due to molecular adsorption by confining the adsorption to one side of the cantilever. Adsorption or intercalation of the analyte will markedly change the surface characteristics of the MCL, and results in the bending of the MCL. Using Stoney's formula [9], the radius of curvature of bending of the MCL due to adsorption can be written as

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

where R is the radius of curvature for the MCL, ν and E are Poisson's ratio and Young's modulus for the substrate, respectively, t the thickness of the MCL, and δs is the film stress.

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doi:10.1016/j.snb.2007.08.019

MCL-based moisture sensors have been developed using SiO_2, Si_3N_4, and polymer coatings [10–13]. However, these sensors are not sensitive enough for ppm level moisture detection. Furthermore, sensors developed by these sensing materials were affected by alcohols existed in the background.

Aluminum oxide (Al_2O_3), on the other hands, has been demonstrated highly selective for moisture measurement [14–16] and an excellent material for measurement of moisture in most industrial gases. It is anticipated that the adsorption of water molecules on the Al_2O_3 thin film will result in the tensile force on the Al_2O_3 film that will deflect a MCL modified by the Al_2O_3 film. In this paper, we report the sensitivity, temperature effects, and selectivity of Al_2O_3-modified MCLs for low level moisture detection.

2. Experimental

2.1. Materials

In our experiments, we used commercially available silicon MCLs (Veeco Instruments, Santa Barbara, CA). The dimensions of the V-shaped silicon MCLs were 180 μm in length, 25 μm in leg width, and 1 μm in thickness. One side of these MCLs were covered with a thin film of chromium (3 nm) and followed by a 20 nm layer of gold, both deposited by e-beam evaporation. Another side of MCL was deposited by a layer of 100 nm thick aluminium (Al). The Al film was oxidized by oxygen in a high vacuum chamber while oxygen gas flowing through at 100 °C. In comparison with conventionally direct deposition of Al_2O_3, oxygen oxidation provides a way to obtain compact thin oxide layers. Ethanol was used in experiments where alcohols were mentioned.

2.2. Gas system

Instead of natural gas, dry nitrogen was used as the carrier gas for sensing validation. This is reasonable and convenient since alkanes do not interact with Al_2O_3. Dry nitrogen was passed through a gas bubbler containing distilled water used to generate wet gas. Dual stage gas regulators for wet and dry gases controlled the gas flow into a gas mixing setup. The desired moisture level was obtained by controlled mixing of the dry and wet gases. The magnetic heater and thermometer as well as a water-bath provide the temperature control of the vapor generation system. The moisture level of the final mixture was measured using a Meeco Waterboy moisture meter (Warrington, PA) with a range of 1 ppm to 5000 ppm and an accuracy of ±5%. The flow rate of the gas inside the cell was 100 mL/min. For experiments at temperatures of 30–50 °C, a heated water-bath was used to maintain the gas temperature. The volume of the sample glass cell including the plumbing was 0.5 cm^3, thus ensuring fast exchange of gases. Typically 10–20 min will be needed to stabilize the cantilevers to reach a stable baseline prior to the measurement.

2.3. Deflection measurement

A MCL is placed in a flow-through glass cell (Veeco Instruments, Santa Barbara, CA) and dry nitrogen gas was passed through the cell at a constant 100 mL/min flow rate during each experiment. When the stable baseline was reached the moisture gas was switched in for testing. The flow rate is relatively high and the gas is expected to flow through the flow cell within 1 s.

The bending of the MCL was measured by monitoring the position of a laser beam reflected from the gold-coated side of the MCL onto a four-quadrant atomic force microscope (AFM) photodiode. We define bending toward the gold side as "upward bending"; "downward bending" refers to bending toward the Al_2O_3 side. When the adsorption occurs on the Al_2O_3 surface, in general, the upward bending is caused by repulsion or expansion of molecules on the Al_2O_3 surface, which is so called compressive stress.

3. Results and discussions

3.1. Detection limit

Fig. 1 compares the bending response of the modified MCL to various moisture levels in nitrogen at a 100 mL/min flow rate. The moisture gas was switched in at the marked time. The MCLs underwent upward bending and the maximum deflection amplitude depended on the concentration of moisture. After approximately 3 min, the dry nitrogen was switched back through the fluid cell, and the MCL bent downward back to their original positions. Fig. 1 insert shows the reproducible response of the MCL to 30 ppm level of moisture.

The sensing was independent of the aluminum thickness. The adsorption follows a Langmuir model (Fig. 2). The rate of formation of a fraction of a monolayer, θ, is proportional to the concentration of water molecules and to the fraction of the surface remaining free of adsorbate, $1-\theta$. Thus, the cantilever bending versus time follows the relationship [3]

$$\Delta Z = \left(\frac{3(1-\upsilon)L^2}{ET^2}\right)\delta s \propto 1-\exp(-kt) \qquad (2)$$

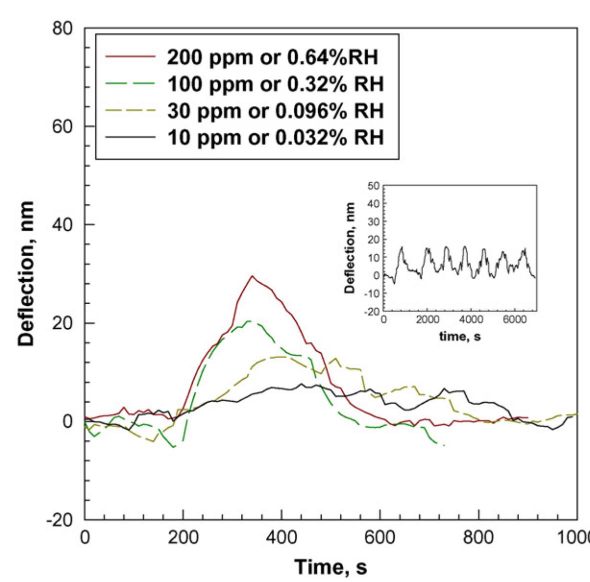

Fig. 1. Deflection of Al_2O_3-modified MCLs vs. time at various moisture levels in nitrogen at 30 °C. The gas flow rate was 100 mL/min. Inset: deflection of the MCLs vs. time after repetitive exposure to 30 ppm moisture in nitrogen.