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Sensors and Actuators B 121 (2007) 679–688
SENSORS AND ACTUATORS B CHEMICAL
www.elsevier.com/locate/snb

Integrated microfluidic gas sensor for detection of volatile organic compounds in water

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Received 19 January 2006; received in revised form 7 March 2006; accepted 9 March 2006
Available online 8 May 2006

Abstract

A polymer microfluidic system for monitoring of volatile organic compounds diluted in water is presented. The sensor platform employs silicon-based microhotplate gas sensors as active detection elements, using a silicon-in-plastic microfabrication technology to enable integration of individual sensor chips into a larger polymer microfluidic substrate. The fabrication process provides seamless fluidic and electrical interconnects between the silicon and polymer substrates. The chemical monitoring system is designed to sample a water source, extract solvent present within the aqueous sample into the vapor phase, and direct the solvent vapor past the integrated gas sensor for analysis. Design, fabrication, and characterization of a prototype system is described, and results from illustrative measurements performed using methanol, toluene, and 1,2-dichloroethane in water are presented.

Keywords: Integrated microfluidics; Microhotplate; Gas sensor; Volatile organic compounds; Water monitoring

1. Introduction

There is growing concern regarding the quality of water supplies, which are susceptible to both natural and man-made chemical contamination. Contamination by volatile organic compounds (VOCs) is of particular concern due to the potential of these compounds to cause significant negative effects on human health. Many VOCs produce serious health effects, such as liver or nervous system problems, reproductive difficulties, and increased risk of cancer [1]. The US Environmental Protection Agency (EPA) currently sets maximum contaminant levels for safe drinking water on 53 VOC contaminants.

While a variety of detection methods have been employed for water analysis, the gold standards are based on liquid or gas-phase chromatographic fractionation followed by mass spectrometry (LC/MS or GC/MS) [2,3]. However, these methods generally rely on labor-intensive sample collection and laboratory-based analysis, which limit the quality, quantity, and frequency of data collected. In addition, the integrity of off-site analyses can be compromised during sample collection, transport, and storage. These factors have led to a need to develop new technology for in situ VOC monitoring which is sensitive, selective, and compact, and with low power consumption for use in long-term monitoring applications.

Polymer absorption and metal–oxide–semiconductor sensors are viable candidates for use in VOC sensing systems based on their simplicity and robustness [4]. For example, researchers at Sandia National Laboratories have developed an in situ chemiresistor system for real-time detection of VOCs in soil and groundwater, which employs an array of polymer-based chemiresistors packaged in a waterproof but vapor permeable housing designed to protect the sensor from the water-saturated conditions [5]. Kohler et al. reported a test method which employs a commercial tin oxide semiconductor gas sensor element in an immersion probe behind a gas permeable membrane for identification and quantitative determination of volatile organic solvents in water using a five-component system of ethanol, toluene, benzene, acetone, and ethylacetate [6]. Ho et al. reported a surface acoustic

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[1] Certain commercial instruments and materials are identified to adequately specify the experimental procedure. In no case does such identification imply endorsement by the National Institute of Standards and Technology.

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doi:10.1016/j.snb.2006.03.023

wave sensor for in situ monitoring of VOCs which consists of a chemically adsorbent polymer film on a piezoelectric substrate [7], and a microscale gas chromatography system for biomedical and environmental monitoring applications was recently reported [8]. However, these devices rely on passive transport of gas from a water source, and do not support higher levels of integration for water delivery or vapor pressure control. Furthermore, the performance of these devices can be impacted by environmental temperature fluctuations, although localized sensor temperature control using microheaters has been proposed [5].

In the present work, we report the application of silicon-in-plastic microfabrication technology to the development of an integrated microfluidic gas sensor for the monitoring of VOCs in water supplies. Silicon-in-plastic fabrication provides the ability to use no more than the necessary silicon area, and thereby offers the potential to substantially reduce overall system fabrication costs, since the cost per unit area of silicon-based sensor fabrication is orders of magnitude higher than for the microfluidic substrate. The microfluidic system provides the required fluid routing, while offering several advantages for efficient solvent extraction such as large specific interface area, large ratio between interface area and channel volume, and short diffusion distance and time [9]. Furthermore, microfluidic systems can readily support integrated microheaters to control the liquid and vapor temperature, and thereby enhance the solvent concentration delivered to the gas sensor chip.

2. Fabrication

2.1. Silicon-in-plastic fabrication

The fabrication process developed for integrating bare gas sensor chips into a polymer microfluidic substrate is depicted in Fig. 1. The silicon-in-plastic process used in this work is a modified version of a procedure previously reported by our group for seamlessly integrating silicon components into polymer microfluidic systems [10,11]. A round hole 3 mm in diameter is first milled through a 1.5 mm thick polycarbonate (PC) substrate. A microhotplate gas sensor chip is next placed face down on a flat layer of partially cured polydimethylsiloxane (PDMS, Sylgard 184; Dow Corning, Midland, MI). The PC substrate is aligned over the chip and placed onto the PDMS with the chip centered inside the milled hole. The PDMS forms a co-planar seal against the surface of the chip and PC substrate. The assembly is placed in a vacuum chamber and the milled hole is filled with epoxy (353ND; Epoxy Technology, Billerica, MA). Casting of the epoxy in vacuum prevents air bubbles from being trapped at the edge of the chip. After the epoxy is cured for 12 h at room temperature, followed by 12 h at 50 °C, the PDMS layer is removed. The epoxy serves to secure the chip within the PC substrate, while leveling the chip face to within 1 μm of the PC surface.

Although the epoxy layer can level the silicon chip and PC surfaces, small gaps can form at the silicon/epoxy/PC interfaces due to thermal mismatch and epoxy shrinkage during curing. These gaps, which are typically on the order of several microns deep, can cause several problems when forming metal interconnects between the PC substrate and on-chip bond pads. First, the sidewall of the bare gas sensor die is exposed semiconducting silicon, and deposited metal which touches the sidewall can potentially shunt the active area contact to ground. Second, open circuits can form due to incomplete metal coverage over the gap. To overcome these problems, a 6 μm layer of parylene C is deposited to passivate the sidewalls and bridge small gaps prior to metal deposition. Parylene C covering the bondpads and microhotplates of the gas sensor is removed by oxygen plasma etching using a Cr/Au mask. After the parylene layer is patterned, the mask metals are stripped, and new Cr (20 nm) and Au (500 nm) layers are deposited and patterned to provide interconnections from the bondpads on the gas sensor to connection pads on the PC substrate. Although not demonstrated here, the Cr/Au lines on the PC substrate may also be patterned during this step to form integrated microheaters for temperature and vapor pressure control. Finally, conductive epoxy is applied at the connection pads to provide electrical access to the system. A photograph of a typical device fabricated using this approach is shown in Fig. 2.

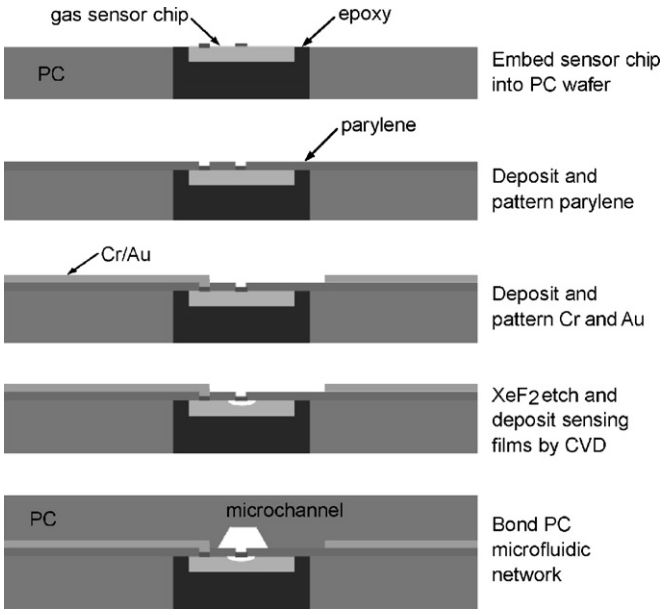

Fig. 1. Fabrication process for the integrated microfluidic gas sensing system. The upper and middle microchannels in the PC layer are not depicted in this schematic.

2.2. Sensing film formation

The integrated sensor array platforms used in this work are four-element microhotplate gas sensor chips designed by NIST researchers [12] and fabricated at MIT Lincoln Laboratory. Each chip is 1.6 mm square and contains a 2 × 2 array of four microhotplates. Each microhotplate is an individual gas sensor which consists of a polysilicon resistor for heating, a semiconducting SnO_2 sensing film, and metal contacts to the SnO_2 for measuring the conductivity of the sensing film. A single microhotplate element is illustrated in Fig. 3. The most obvious features are the suspended plate, four support beams, and the etch pit. The