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Jetted Nanoparticle Chemical Sensor Circuits for Respirator End-of-Service-Life Detection

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Abstract

Gold nanoparticle chemiresistors, formed by ink-jetting onto spiral gold electrodes, are explored for use as respirator cartridge end-of-service-life indicators. Two 250 μm-diameter chemiresistors are connected electrically in a half-bridge circuit, with one capped as a reference. Output sensitivity is −123 μV/ppm for toluene. Breakthrough of 500 ppm toluene in a carbon cartridge simulator was demonstrated.

I. Introduction

Users of personal protective equipment have a need for inexpensive end-of-service-life indicators to inform them that the performance of their equipment has or soon will degrade, which may cause them to be exposed to harmful substances. A specific application is in respirator cartridges where a microsensor module would enable minimally invasive embedding into carbon packs. Analyte breakthrough detected at a sensor location embedded at some distance (e.g., 1 cm) from the pack inlet would indicate the cartridge is spent. Concentration levels of volatile organic compounds (VOCs) on the order of 1 ppm must be detectable in use where high flow, humidity and temperature fluctuations can be present. These requirements motivate integration of multiple sensors with preconcentrators and signal conditioning electronics. As an initial step towards this goal, approaches to create chemiresistors compatible with CMOS MEMS are currently being explored.

A large number of materials have been explored for chemiresistive sensing [1][2]. Our prior work was focused on semiconducting polythiophenes as chemical field-effect transistors [3]. Here, we present our progress on ink-jetted gold nanoparticle chemiresistive sensors, motivated by others' work on gold-thiolate nanoparticle chemiresistors [4][5].

II. Experimental Results

Gold nanoparticles protected with 1-octanethiol (C8) were synthesized by the single-phase method of Rowe *et al.* [6]. The 2 nm-diameter nanoparticles were mixed in 1,2,4-trichlorobenzene (TCB) at a 5 to 10 mg/ml concentration. The solution was loaded into a custom inkjet system with a 30 μm-diameter piezoelectric drop-on-demand jet nozzle (MicroFab Technologies, Plano, TX) that ejects drops on the order of 30 pl. The inkjet system includes computer vision calibration to position drops within 2 μm of targets [7]. The silicon device substrate is covered by a 1 μm-thick silicon dioxide layer. Spiral interdigitated 75 nm-thick gold electrodes on a thin Ti adhesion layer are patterned by a combination of ion milling and wet etching. The completed electrodes are 3 μm wide with 4 μm spacing, and span a diameter of 250 μm, as shown in Figure 1(a).

The inner 200 μm diameter of electrodes form the chemiresistor. The remaining 50 μm annular area surrounding the active electrodes houses electrically neutral "guard ring" electrodes. The guard rings ensure that splats cover the active electrodes and result in on-chip resistance matching to better than 10%.

Two example splats after drying are shown in Figure 1. The splat in (b) has an estimated film thickness of 1.5 μm. The deposited solvent puddle initially extends beyond the electrodes and later pulls back within the electrode boundary. The axi-symmetric and regular electrode layout ensures uniform surface tension effects. The TCB puddle takes several seconds to evaporate, allowing the nanoparticles precipitate into a thin film with minimal "coffee ring" effects. The jetted splats are dried in a vacuum oven at 40° for 4 hours.

The sensor output is generated from the half-bridge circuit, shown in Figure 2, to reject temperature

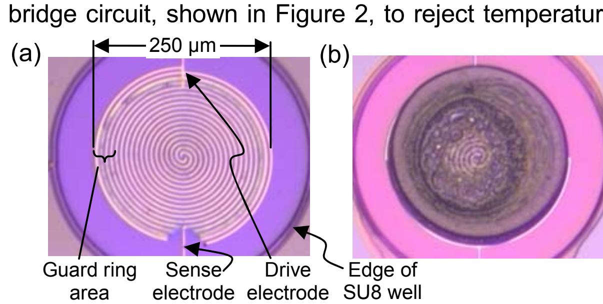

Figure 1. Spiral interdigitated electrode chemiresistors. (a) 15 drops. (b) 225 drops.

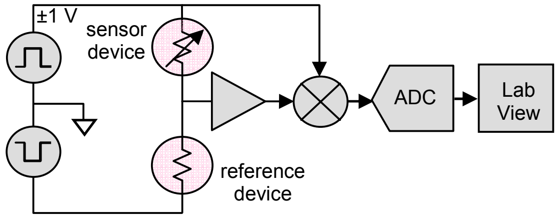

Figure 2. Sensor circuit diagram.

disturbances to a first order. The reference chemiresistor is covered with a glass cap attached with a low-outgassing polyurethane adhesive. The voltage divider is driven by balanced square-wave modulation that changes from +1 V to −1V every 5 s. The voltage signal is detected using a high-impedance input preamplifier, demodulated and converted to digital format (ADC) through LabView control on a PC.

A typical silicon chip, shown in Figure 3, comprises three chemiresistive voltage dividers with capped reference devices. The seven bond pads on the chip route the two drive voltages, the three sensor outputs, V_{s1}, V_{s2}, and V_{s3}, and two leads to a gold resistive temperature device (RTD). The chip is patterned with 40 µm-thick SU-8 epoxy to form wells around the devices and to act as interconnect passivation.

Figure 4 shows a typical pulse response exposed to various organic solvents with a VICI M6 micro-dispensing pump in 32 L/min air flow. The devices have a high sensitivity of −123 µV/ppm toluene and low sensitivity of −2 µV/ppm methanol. Sensitivity matches to within 10% on-chip. Figure 5 is a breakthrough curve for a sensor embedded in a carbon pack simulating a cartridge. Conditions were 32 L/min air flow, 23% RH and 500 ppm toluene.

III. Conclusions

Use of TCB and axi-symmetric electrodes in drop-on-demand jet deposition of nanoparticles leads to well controlled diameter of the splats. The thin-film nanoparticle sensors must be augmented with other devices that are more sensitive to alcohol vapors, such as polythiophene chemiresistors. The voltage divider configuration for readout does not completely eliminate thermal effects, possibly due to the different environment of the sensor and reference devices. Improved nanoparticle resolution beyond 10 ppm, will require the addition of preconcentrators.

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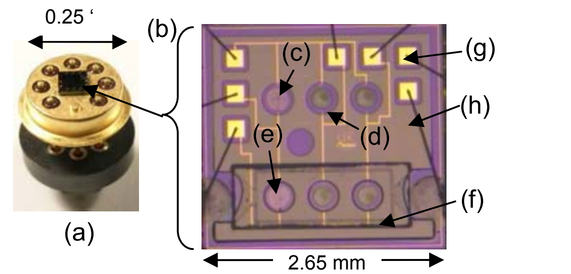

Figure 3. Silicon sensor chip with three chemiresistive half-bridge circuits. (a) TO-5 package. (b) Chip. (c) Sensor device. (d) Edge of SU-8 well. (e) Reference device under glass cap. (f) Arathane around glass cap. (g) Bondpad and bondwire. (h) RTD location.

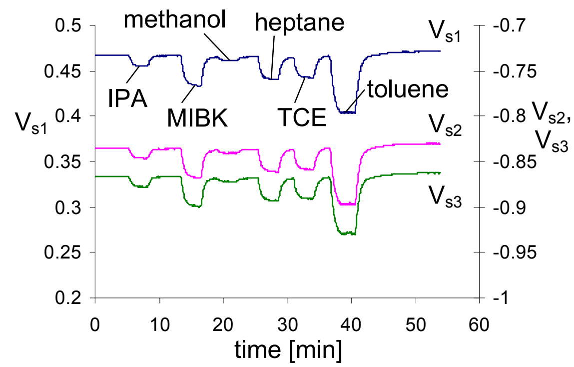

Figure 4. Pulse response of jetted gold nanoparticle sensors to six VOCs. Pulses are 500 ppm except methanol at 2000 ppm and MIBK at 200 ppm.

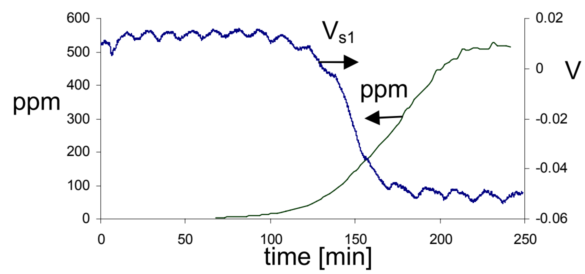

Figure 5. Cartridge breakthrough curve.

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