INTEGRATED CHEMIRESISTOR AND WORK FUNCTION MICROSENSOR ARRAY WITH CARBON BLACK/POLYMER COMPOSITE MATERIALS

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ABSTRACT

An array of chemically-sensitive field-effect transistors (CHEMFETs) that measure both work function and bulk resistance changes in thin films was used to detect volatile organic compounds. Carbon black/organic polymer composite films were deposited onto the CHEMFETs using an automated microdispensing method.

INTRODUCTION

Development of hybrid device arrays--those comprised of more than one sensor physical platform type--is an important technology for successful future applications of chemical sensors. Hybrid device arrays offer advantages over traditional sensor arrays because they introduce diversity by measuring different parameters of the sensing layers, as opposed to relying solely on the chemical diversity of the sensing elements. In theory, a low number of chemically diverse coatings deposited on different sensor platforms is sufficient to analyze a large number of chemical compounds.

In addition to increasing response information content, it is desirable to integrate different sensor platforms into a single device for cost and space efficiency reasons. We have fabricated chemically-sensitive field-effect transistors (CHEMFETs) which allow resistance and work function (WF) measurements on a single chemically sensitive layer [1]. In the work described here, carbon black/organic polymer composites were used as chemically sensitive coatings on these devices. Although carbon-loaded chemiresistors functioning via vapor-induced swelling have been previously demonstrated [2,3], the purpose of this work is to show the advantages of measuring both WF and electrical resistance.

We also show that composite materials can be successfully deposited onto the target sites of CHEMFETs by an automated microdispensing method [4]. In contrast to most traditional thin-film deposition techniques, microdispensing does not have to be combined with photolithographic or other patterning methods, because, typically, nanoliter volumes of materials are deposited only onto selected target locations.

EXPERIMENTAL DETAILS

The carbon black/polymer composite materials deposited on CHEMFETs are listed in Table 1. Graphitized carbon particles with a 27 - 30 nm diameter were used (Polysciences, Inc., Warrington, PA). Each polymer was dissolved in deionized water or toluene to yield a 2% weight/volume solution. To promote monodispersion of carbon particles, samples were agitated in an ultrasonic bath for several hours, followed by agitation with a point-source

ultrasonic processor, resulting in samples that were kinetically stable for several weeks.

Table 1. Composite films deposited on CHEMFETs.

Coating Code	Polymer	CL*	Solvent	Resistivity^1 [Ω-cm]
PVA-40-C	poly(vinyl-alcohol)	40	water	22 ± 4
PVA-50-C	poly(vinyl-alcohol)	50	water	1.0 ± 0.6
PVA-60-C	poly(vinyl-alcohol)	60	water	1.1 ± 0.3
PAAS-40-C	poly(acryl-amide-acrylic acid, Na$^+$ salt)	40	water	2.8 ± 0.8
EC-40-C	ethyl cellulose	40	toluene	3.1 ± 0.7

*CL - carbon loading of the solvent-free composite film, wt%,
^{1}Measured at 21°C and 38% RH.

Resistivities of the samples deposited on an insulating substrate were calculated from the sheet resistance (4-point probe) and thickness (contact profilometer).

Carbon black/polymer composites were deposited on CHEMFETs using an automated dispensing system (Model A402B, Asymtek, Carlsbad, CA) equipped with AV-500 targeting offset camera and DV-01 syringe valve bracket [4], using 30-Gauge stainless-steel needles. Prior to film deposition, the top Si_3N_4 surface of each CHEMFET chip was etched in buffered HF. The materials were microdispensed as lines ~ 400 μm wide by 600 μm long. Typically, less than 30 μL of the solution was sufficient both for the deposition tests on Si wafers and on several CHEMFET chips. On each chip, the same material was deposited on two CHEMFET gates.

The dual-gate CHEMFETs with SiO_2/Si_3N_4 gate insulators were fabricated at the University of Utah [1]. On both sides of each CHEMFET channel, two parallel Au-plated Pt lines ~ 165 μm apart were formed to allow resistance measurement. Carbon black/polymer composites were deposited onto the Si_3N_4 surface over the channel area (20 x 400 μm) and on the Au-plated Pt lines, thereby forming the dual-use transistor gate/chemiresistor films (Fig. 1). Length of the electrode pair in contact with the coating was ~ 500 μm. CHEMFET chips with deposited films were attached to 16-pin TO-8 headers and wirebonded. Thickness profiles of carbon black/polymer composites were investigated with a Zygo NewView 200 non-contact profilometer. Headers with mounted CHEMFET chips were placed in a temperature-controlled stainless-steel flow cell [5]. Current-voltage

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characteristics of the composite films were measured with a Hewlett-Packard 4142 modular DC Source/Monitor.

An automated vapor-generating/mixing system provided dilutions of isooctane (IOC), acetonitrile (ACN), isopropyl alcohol (IPA), methyl isobutyl ketone (MIK), and water vapor in nitrogen at a flowrate of 100 sccm. Sensors were exposed for 20 min each to six concentrations of each organic vapor, separated by 20-minute N_2 exposures.

Both WF [5] and DC resistance measurements were obtained with multichannel instrumentation. WF changes were deduced by measuring the gate voltage (applied to the coating) necessary to maintain a preset drain-source current. The resistance changes of the films were measured across the width of the coating with HP 34401 multimeters in two-probe, constant-current mode (500 nA or 5 µA). Maximum voltage applied to coatings was ~ 2 V. The data-acquisition sampling period was 10 s. The sensors were maintained above the room temperature at 35°C during all measurements.

RESULTS AND DISCUSSION

A photograph of a carbon black/polymer composite microdispensed on a CHEMFET chip is shown in Fig. 2a. The composite film overlaps the gate electrodes and completely covers the channel area, critical for proper device operation. A significant advantage of automated microdispensing is that the deposition is localized, but a drawback is that the thickness uniformity across the film is difficult to control. Fig. 2b. shows a 3-D surface profile of one of the films. The thickness of PVA-60-C is greatest around the perimeter, a source of potential problems for resistance measurements: because the electrodes contact both the thick perimeter section and the thin middle area, the thick edge can adversely affect resistance response time. In contrast, WF response time is not affected because the thick edges are completely outside the transistor channel region. We note that edge effects can be eliminated by burying the electrodes under the perimeter in an electrically insulating film while leaving them exposed in the middle area, where the thickness of the composite material is relatively uniform.

Prior to vapor-exposure experiments, current-voltage characteristics of the composite films on CHEMFETs were measured, and all were found to be ohmic, justifying measurement of resistance changes in constant-current mode. We found resistances measured in N_2 and synthetic air to be very similar, indicating a minimal effect of oxygen. Comparison of the resistivity values in Table 1 with resistances measured on the coated CHEMFETs suggests that the average thickness of EC-40-C on a CHEMFET is approximately ten times less than that of PAAS-40-C.

When carbon black/polymer composites are exposed to a vapor, analyte molecules can adsorb on the surface of the composite material, absorb in the polymer, adsorb on the surface of carbon particles, and adsorb at the composite material/substrate interface. Vapor-induced polymer swelling and the resulting increase in the average spacing between conductive carbon particles is the predominant response mechanism for the resistance changes [2,3]. The effect of the composite material/vapor interaction on the transistor threshold voltage shift (ΔV_t) is more complex. We believe ΔV_t is controlled through chemical modulation of the WF by the adsorption of analyte molecules on the surface of carbon particles. However, other effects, such as the analyte-induced

change of the polymer dielectric constant, or increased distance of the carbon particles from the Si_3N_4 surface, can also play a role.

Fig. 3 shows the resistance and WF responses of one of the composite materials, PVA-50-C, upon exposure to acetonitrile vapor. Two differences between the resistance and WF responses are notable. First, the WF response for this particular material and analyte is faster than the resistance response, perhaps a consequence of the thicker edge region of the film being probed by the resistance measurement but not by the WF. Second, the WF response is approximately logarithmic while the resistance response is linear. This trend is more clear in Fig. 4, which shows the response of PVA-50-C for acetonitrile as well as four other vapors. The linearity of the resistance effect is suggestive of a linear relationship between dissolved analyte and vapor concentrations, coupled with a linear dependence of resistance upon polymer swelling (over the range of concentrations examined). The logarithmic concentration dependence of the WF is likely a consequence of the dependence of the change in carbon-particle surface WF upon the number of adsorbate molecules, convoluted with the adsorption isotherm for the adsorbate on carbon particles.

The effect of carbon loading on the relative change of resistance for PVA is illustrated in Fig. 5. Since the resistance varies approximately linearly with concentration, each point represents a slope. The sensitivity for isooctane (a very nonpolar analyte) is independent of carbon loading, but for water and acetonitrile (the most polar, highest dielectric analytes), the sensitivity decreases with increasing carbon loading, while for isopropyl alcohol and methyl isobutyl ketone (moderate polarity/dielectric constant), the sensitivity increases. This interesting feature could be exploited to increase selectivity.

Figs. 6 and 7 show the resistance and WF response patterns of all five tested composite materials to five vapors. Resistance responses are either zero or positive, consistent with vapor-induced swelling. WF responses are mostly negative, consistent with the analytes being net electron donors to the carbon particles. For PVA, the responses decrease with increasing carbon loading for all vapors with the exception of isooctane.

CONCLUSIONS

The hybrid sensor array resolves all of the vapors at each of several concentrations reasonably well, which would not be possible using only the resistance or WF response alone. This demonstrates the advantage of the dual-mode measurement platform. Detail data analysis is necessary to quantitatively evaluate discrimination among vapors.

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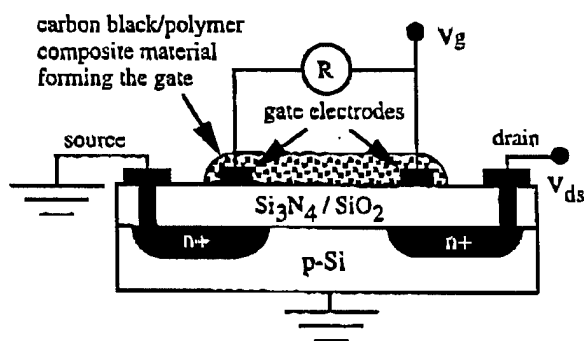
Fig. 1 Device cross section.
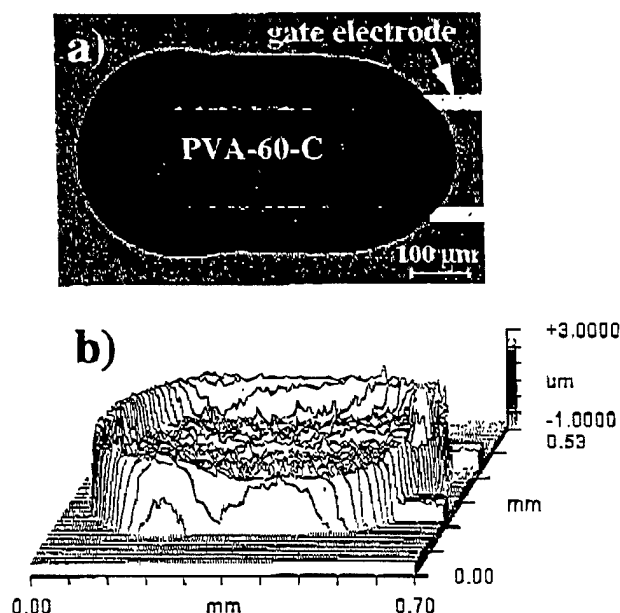
Figure 2. PVA-60-C microdispensed on a CHEMFET chip. a) Photograph of a gate. b) 3D surface profile of the same gate determined by non-contact profilometry.
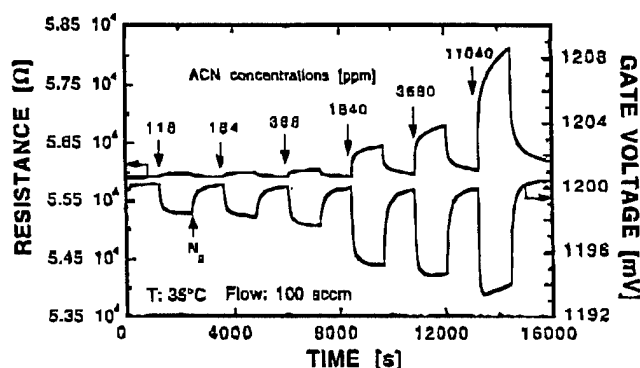
Figure 3. Resistance and work function responses of PVA-50-C to acetonitrile.
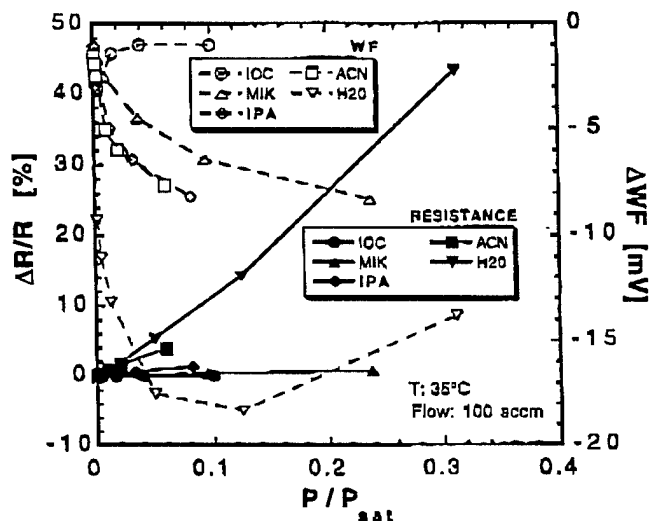
Figure 4. Calibration curves of PVA-50-C for isooctane, methyl isobutyl ketone, isopropyl alcohol, acetonitrile, and water.
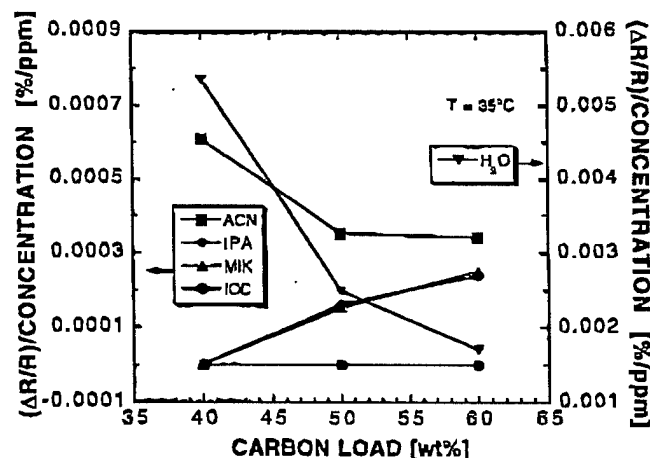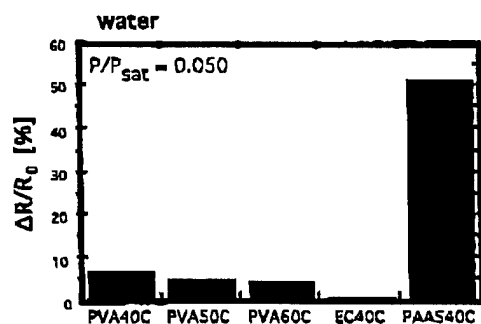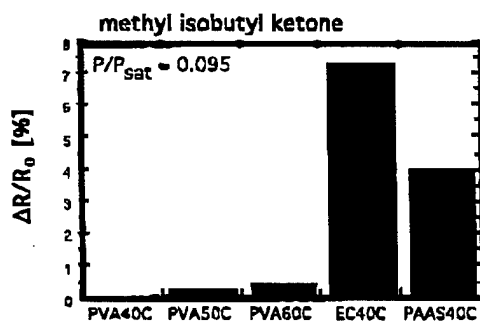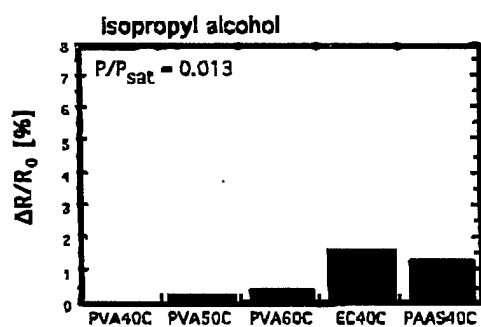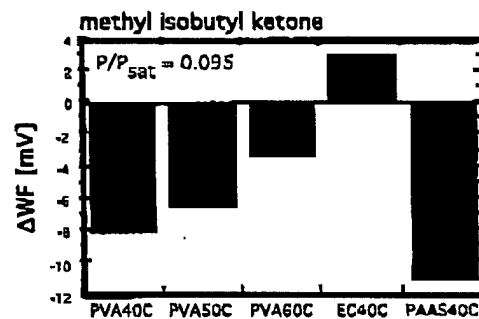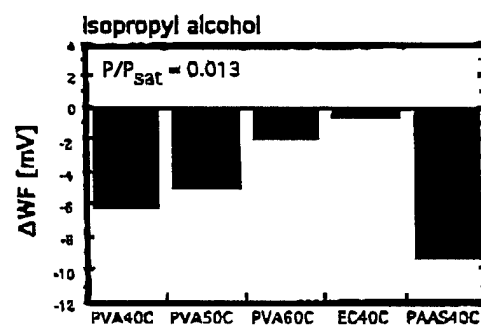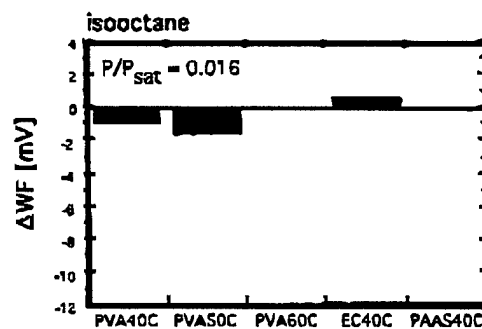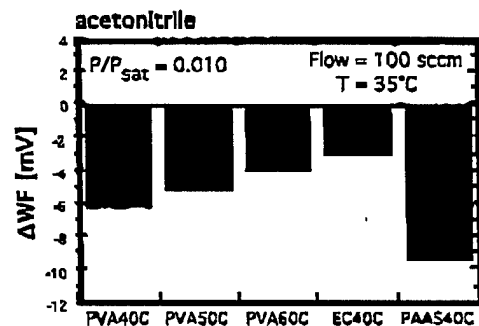

Figure 5. The effect of carbon load on the relative change of resistance for poly(vinyl alcohol).
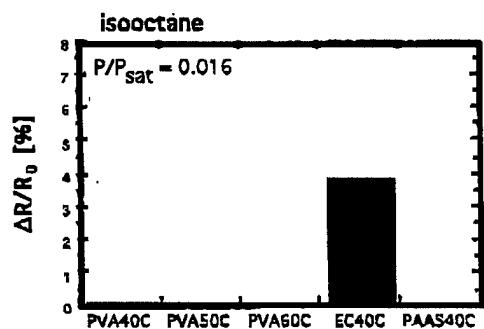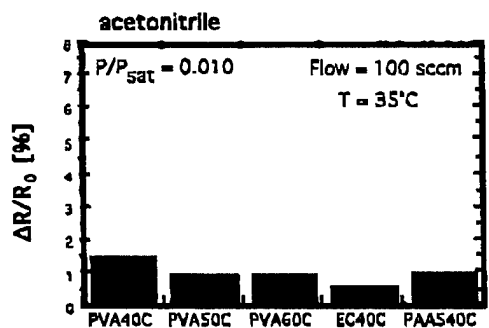
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Figure 6. Resistance response patterns
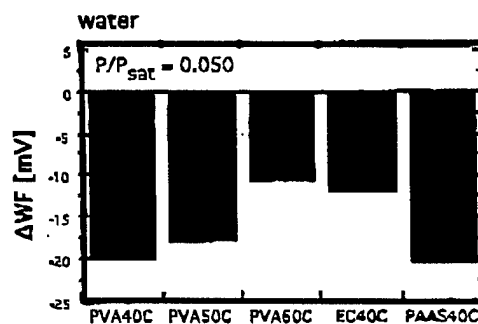
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Figure 7. Work function response patterns

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