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Sensors and Actuators B 48 (1998) 289–295

SENSORS AND ACTUATORS B CHEMICAL

Response of a poly(pyrrole) resistive micro-bridge to ethanol vapour

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Abstract

In this paper the authors describe the behaviour of a silicon micro-bridge fabricated with four conducting polymer resistive elements (two active) in a CMOS-compatible process. The poly(pyrrole) (PPy) bridges were characterised using a precision analogue interface circuit with the constant-current drive and voltage off-set set by a Labview Virtual Instrument. The responses of eight polymer micro-bridges to ethanol vapour were recorded at different temperatures and humidity's. The output voltage of the bridge circuit followed the classical Langmuir adsorption isotherm in concentration and generally fell with increasing temperature and humidity. A typical bridge sensitivity to ethanol of ca. 30 μV/ppm was observed at room temperature with the linear temperature coefficient of the operation being relatively high at -2.8×10^{-2}/°C.

Keywords: Micro-bridge; Ethanol vapour; Poly(pyrrole)

1. Introduction

Conducting polymers resistors are of increasing interest in the fields of gas and odour sensing due to their ease of fabrication and ability to operate around room temperature [1,2]. Unfortunately, two disadvantages to their use have been reported namely some conducting polymers, such as polypyrrole (PPy) and polyaniline (PAN), not only have a significant batch-to-batch variation in resistance of ca. 35% [3] but also show a significant (null gas) temperature coefficient of resistance of ca. -10^{-3}/°C [1]. The authors have therefore constructed a bridge with all four arms made of a conducting polymer resistor in order to reduce the effect of variations in batch conditions and operating temperature on the device base-line signal. Clearly, the response of the bridge will still be temperature dependent due to the nature of the chemical sorption process.

2. Device fabrication

Two micro-bridge devices have been designed using the software package L-Edit (Tanner Tools) with four gas-sensitive elements on a 4 by 4 mm die, one bridge with a 10 μm inter-electrode gap and the other with a 50 μm inter-electrode gap. The geometry of the device is shown in Fig. 1. The fabrication process consisted of the thermal oxidation (100 nm) of a 3 in. silicon wafer, followed by the thermal evaporation of a 10 nm seeding layer of NiCr followed by 100 nm of Au. The metallisation layer was patterned using a positive resist (Shippley 1813) and conventional UV lithography to form the bridge tracks. Next, photoresist was spun down again, soft-baked and the windows opened up using a second mask but this time the resist was hard-baked and used as a passivation layer against aqueous electrolytic solutions. The 3 in. wafers were then diced using a diamond scribe and glued onto a custom-designed PCB header using a special epoxy resin that was compatible with the electrodeposition process of conducting polymers. Next, the four contact pads were ultrasonically wire-bonded contact to the gold-plated i.c. vertical pin header (Harwin Plc) which was soldered onto the PCB.

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0925-4005/98/$19.00
PII S0925-4005(98)00059-8

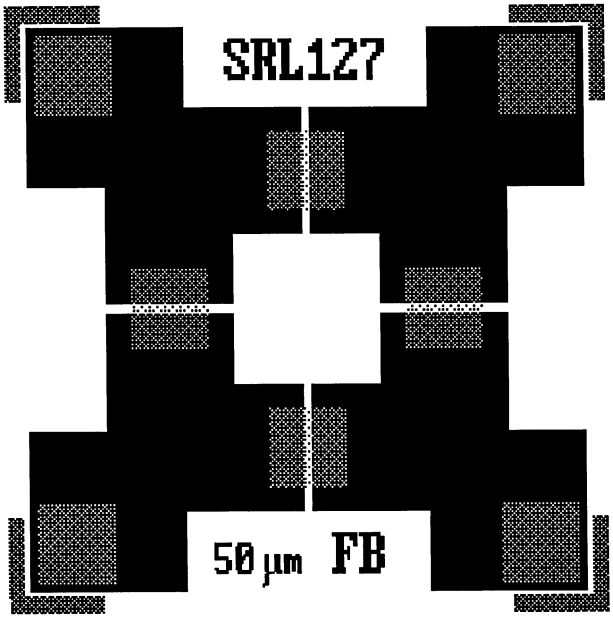

Fig. 1. Lay-out of silicon micro-bridge.

The conducting polymers were grown across the inter-electrode gaps using a three electrode electrochemical cell. All four bridge terminals were shorted together to form the working electrode and the conducting polymers were grown from aqueous solutions. Table 1 summarises the type of micro-bridges fabricated, i.e. electrode gap and polymer system used, and also relates to the polymers analysed in Ref. [7]. Full details of the electrochemistry may be found elsewhere [3–5].

Table 1
Names of conducting polymers grown on micro-bridges with nominal electrode gap shown

Gap (μm)	Polymer	Abbreviation
10	Pyrrole/pentane sulfonate	PPy/PSA
10	Pyrrole/decane sulfonate	PPy/DSA
10	Aniline/pentane sulfonate	PAN/PSA
10	Aniline/decane sulfonate	PAN/PSA
50	Pyrrole/pentane sulfonate	PPy/PSA
50	Pyrrole/decane sulfonate	PPy/DSA
50	Aniline/pentane sulfonate	PAN/PSA
50	Aniline/decane sulfonate	PAN/DSA

A photograph of the polymeric micro-bridge is shown in Fig. 2 where the four black regions of conducting polymer are clearly visible and well-defined by the 500 μm square window in the resist. The epoxy resin coats all the bond pads and thus prevents accidental growth of the polymer onto the connecting wires.

Two opposite arms of the bridge were coated with epoxy resin, using a mechanical mask to act, as the dummy elements of the bridge. No change in resistance was observed during this coating process, although some longer term drift did occur which may be attributed to a difference in the humidity of the exposed and hermetically sealed polymer elements.

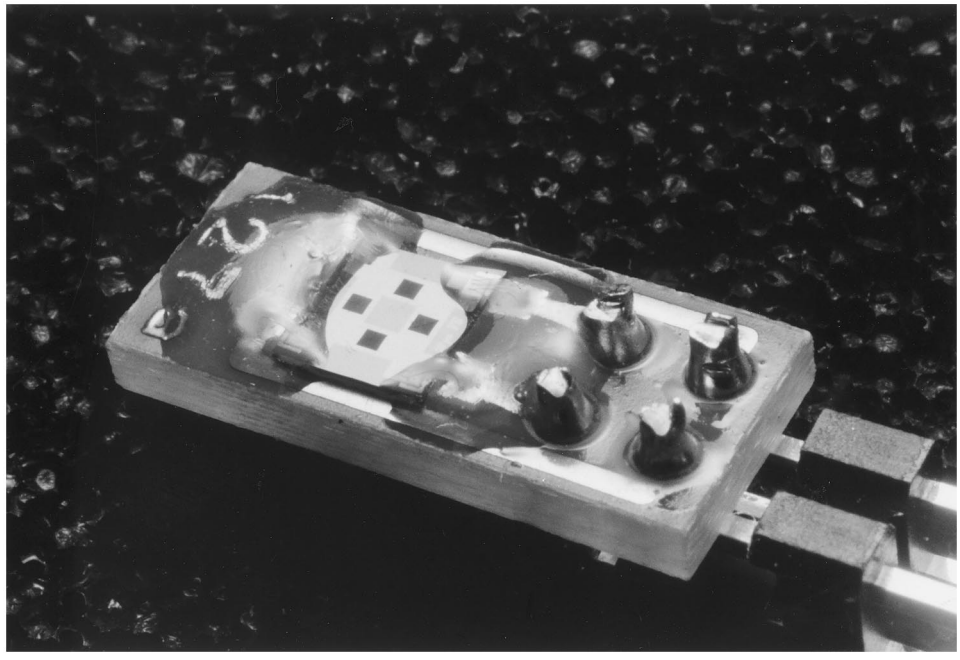

Fig. 2. Photograph of conducting polymer based resistive micro-bridge bonded into a PCB header with epoxy protection of gold bonding wires.

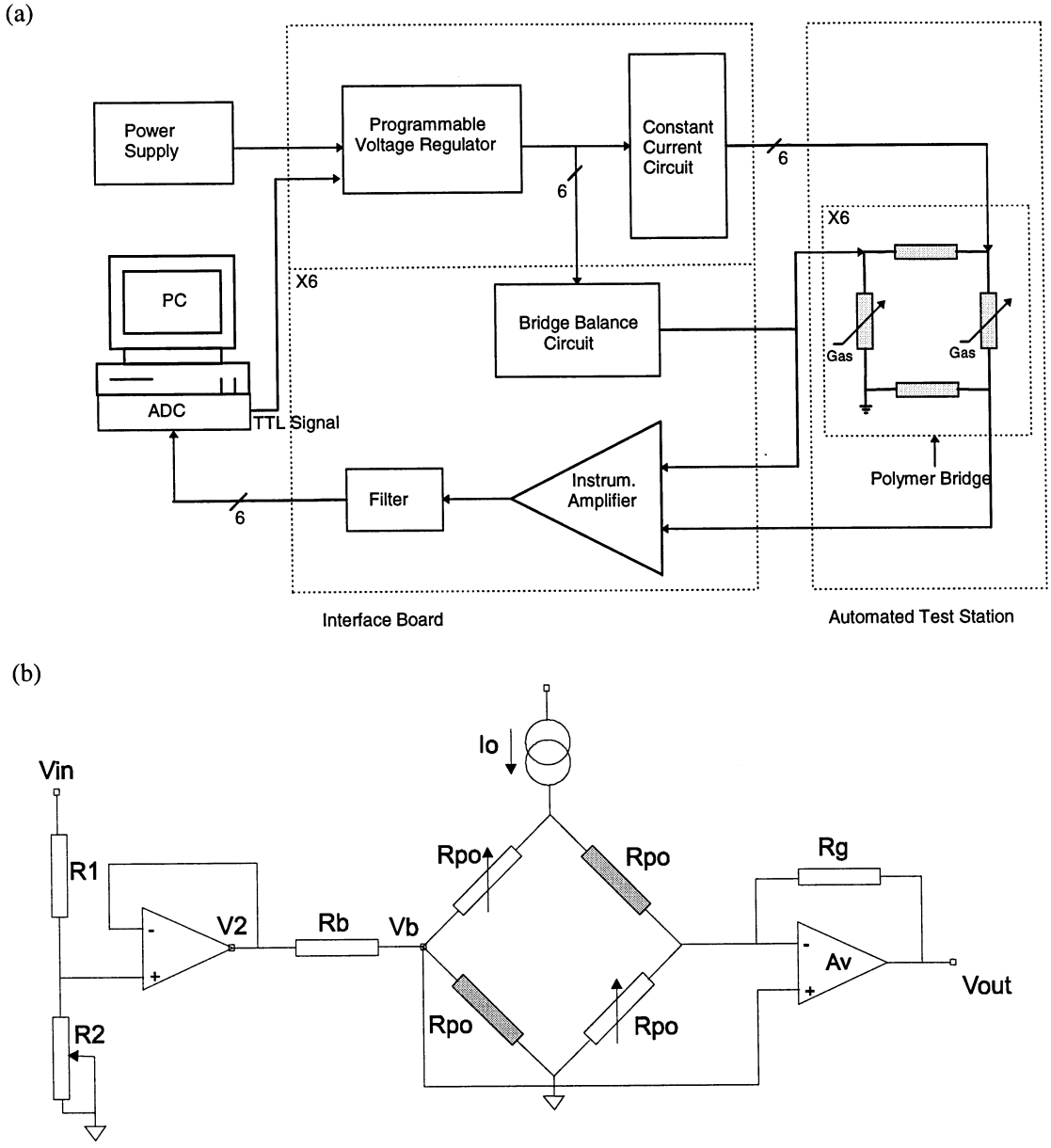

Fig. 3. (a) Schematic lay-out of bridge measurement system; (b) bridge interface circuit with constant-current I_o drive, programmable off-set or bias voltage V_b and gain A_v of output voltage V_{out}.

3. Interface circuitry

The general lay-out of polymer bridge and interface circuitry is shown in Fig. 3(a). A programmable micro-power voltage regulator (MAX666, MAXIM) was used to generate a pulsed supply of 0–10 V at a frequency of 1 Hz to drive both the constant-current source and the bridge bias circuitry. The constant current circuitry provides six outputs I_o for driving six resistance bridges. The three terminal adjustable constant current source ICS (LM334, National Semiconductor) were used to generate 20 μA output current each, thus setting the bridge voltage at the suitable value according to the resistance of polymers. This d.c. voltage V_{po} was typically between 30 and 240 mV. Higher values ($V_{po} \gg 100$ mV) can lead to a permanent change in the polymer resistance. An additional resistor and a diode were added to the standard LM334 configuration in order to cancel its temperature-dependent characteristic. The balancing of the bridge was carried out by a variable voltage source through a series resistor to provide the current, this way enforcing the null condition.

Fig. 3(b) shows a part of the circuitry used for balancing the bridge devices. The simple circuitry comprises of a voltage follower (OPA177, Burr-Brown), high precision trimmer (3299W Series, Bourns) and a resistor for voltage range and resolution regulation. A

bias voltage V_b was applied to one of the bridge midpoints for balancing any differences between the chemoresistors base-line resistances. Values of the resistors were different for each channel depending on the base-line resistance of the particular device. The output of the bridge was connected to an instrumentation amplifier (INA 114, Burr-Brown). The internal gain was set by an external reference resistor and for most of the devices it was set at the value of 500. The output of the instrumentation amplifier V_{out} was connected to an active second order filter comprising precision instrumentation amplifier OPA177 and two sets of resistor-capacitor arrangements. The component values were chosen to produce a bandwidth of 10 kHz. Finally, an LM35DZ (National Semiconductors) temperature i.c. was used to monitor the temperature of the interface electronics and thus test its temperature-stability. A virtual instrument (VI) has been written using Labview software (National Instruments) to record the deflection voltage of the bridge circuit and the voltage from the temperature i.c. via a PC–LPM–16 12-bit (National Instruments) ADC card.

4. Experiments

The response of the polymer micro-bridges to ethanol vapour was tested in an automated mass flow system which is described elsewhere [6]. Several tests were carried out on three different temperatures:

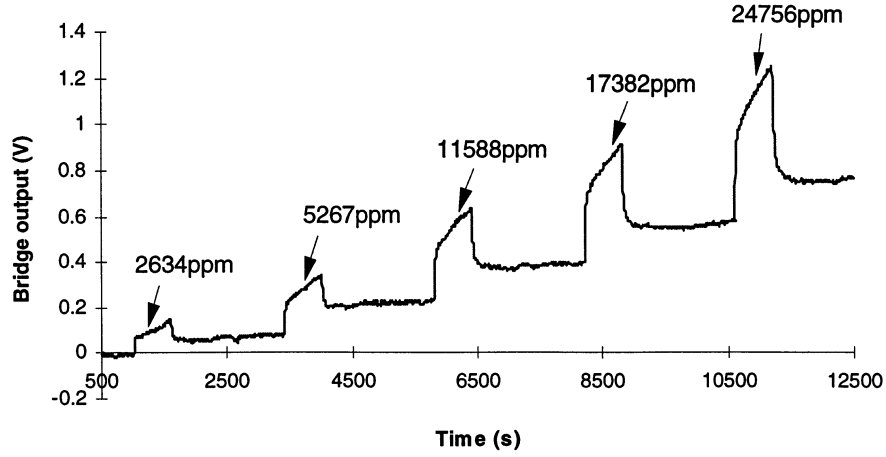

Fig. 4. Typical response of a poly(pyrrole) micro-bridge to pulses of ethanol vapour at a fixed humidity and temperature.

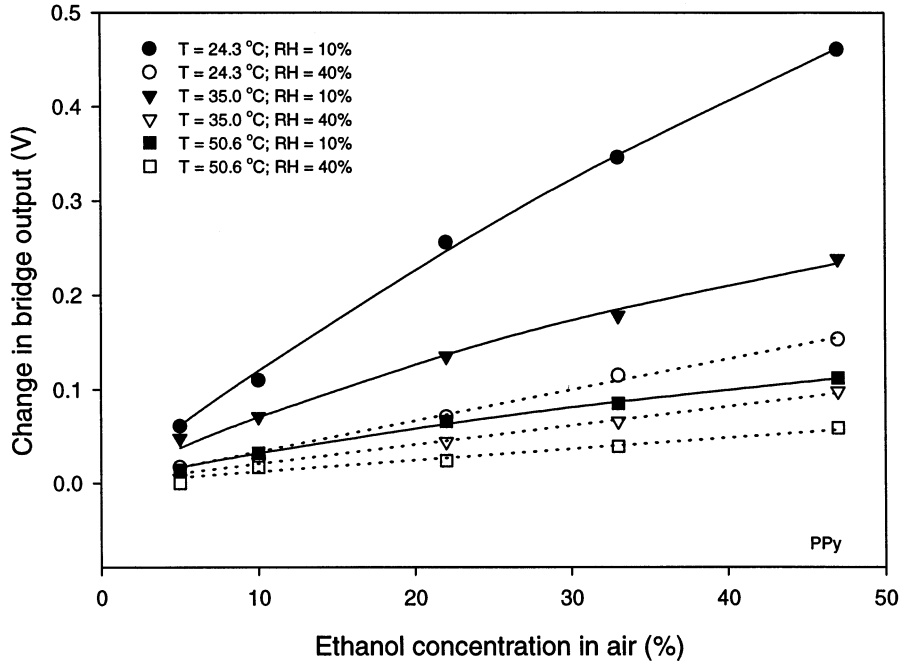

Fig. 5. Effect of ethanol concentration on the response of a poly(pyrrole) micro-bridge. A Langmuir model has been fitted to the experimental data at different temperatures and humidities (—) 10% r.h.; (– – – –) 40% r.h.

Table 2
Values of the Langmuir coefficients computed from experimental runs carried out on PPy/PSA with an r.h. for 10%

Device no.	T(°C)	a(V)	$b(10^{-3}/\%)$	Mean and standard deviation
1	24.3	2.00	6.35	
2	24.3	1.54	7.76	$a = (2.15 \pm 0.56)$V
3	24.3	2.17	6.41	$b = (6.93 \pm 0.7) \times 10^{-3}/\%$
4	24.3	2.89	7.21	
1	35.0	0.62	12.83	
2	35.0	0.98	7.18	$a = (120 \pm 0.77)$V
3	35.0	0.87	10.29	$b = (8.92 \pm 3.3) \times 10^{-3}/\%$
4	35.0	2.34	5.38	
1	50.6	0.34	10.31	
2	50.6	0.24	14.91	$a = (0.33 \pm 0.11)$V
3	50.6	0.27	15.62	$b = (13.59 \pm 2.3) \times 10^{-3}/\%$
4	50.6	0.48	13.52	

The ethanol concentrations are expressed in units of % in air.

1. 24.3°C at 7.64 and 30.6% relative humidity;
2. 35.0°C at 3.65 and 14.6% relative humidity;
3. 50.5°C at 1.62 and 6.49% relative humidity.

Prior to the test, the micro-bridges were allowed 24 h to stabilise at each temperature. An exposure time of 60 min to a certain relative humidity was found to be sufficient in order to establish stable base-line resistance which was followed by the balancing of the devices. After the balancing procedure, micro-bridges were exposed to 2630, 5720, 11600, 17400 and 24800 ppm of ethanol in air at three temperatures and at two relative humidity's for each temperature. An exposure time of 10 min to a certain concentration of ethanol was followed by 30 min recovery time before the next exposure. These times were required due to relatively large dead-volumes in the wetware pipe-work.

5. Results

Fig. 4 shows the typical response of the 10 μm PPy/PSA micro-bridge to 2630, 5270, 11600, 17400 and 24800 ppm of ethanol in air at 7.67% r.h. and 24.3°C. An optimum bridge sensitivity of ca. 30 μV/ppm was found under these conditions. The micro-bridges demonstrated a negligible drift during the exposure to a constant humidity. However, during the ethanol exposure a significant long term effect was exhibited by the polymer micro-bridges. Previous research carried out on the effects of ethanol vapour on the response of PPy/PSA [3–5] shows that the polymers demonstrate a reversible response with negligible long term effects to this type of organic compound. This would seem to indicate that the alteration of the base-line characteristic of the bridge is due to some interaction between the epoxy coating used to passivate two arms of the bridge and the ethanol. Further research into the area of inert polymer coatings is required.

Extensive research carried out on the conducting polymer based gas sensors [3–5] has shown that the resistance of PPy/PSA rises by a few percents when exposed to the ethanol. The change in resistance follows the Langmuir adsorption isotherm [5,7]. So the authors would expect the output voltage V_{out} of a constant-current I_o driven resistance bridge with two active arms to be directly proportional to the change of the polymer resistor $\Delta R_{po,}$ namely

$$V_{out} = 500 V_b \approx \frac{I_o}{2} \Delta R_{po} \approx a\left(\frac{bC}{1+bC}\right) \quad (1)$$

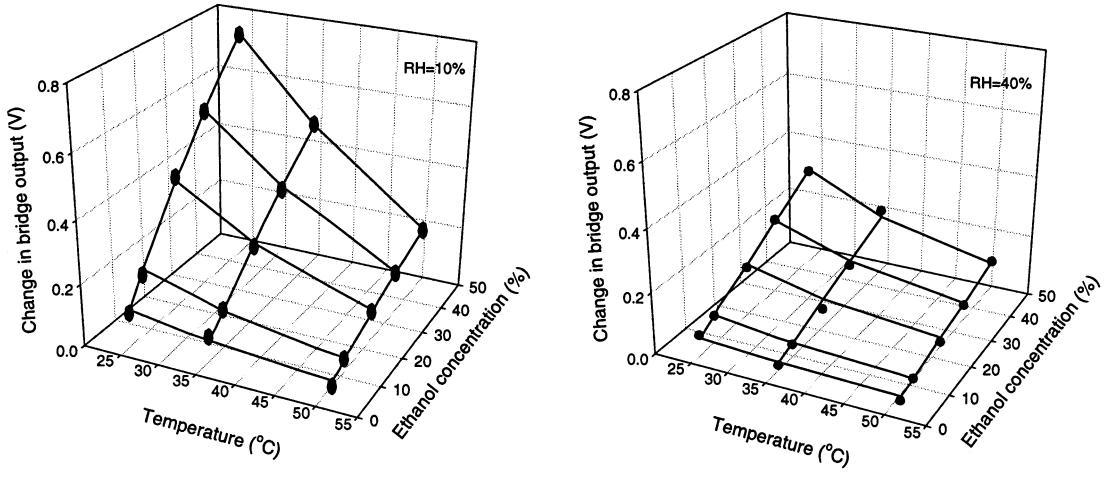

Fig. 6. 3-D plots showing the typical response of a poly(pyrrole) micro-bridge to ethanol at different temperatures for two different humidities.

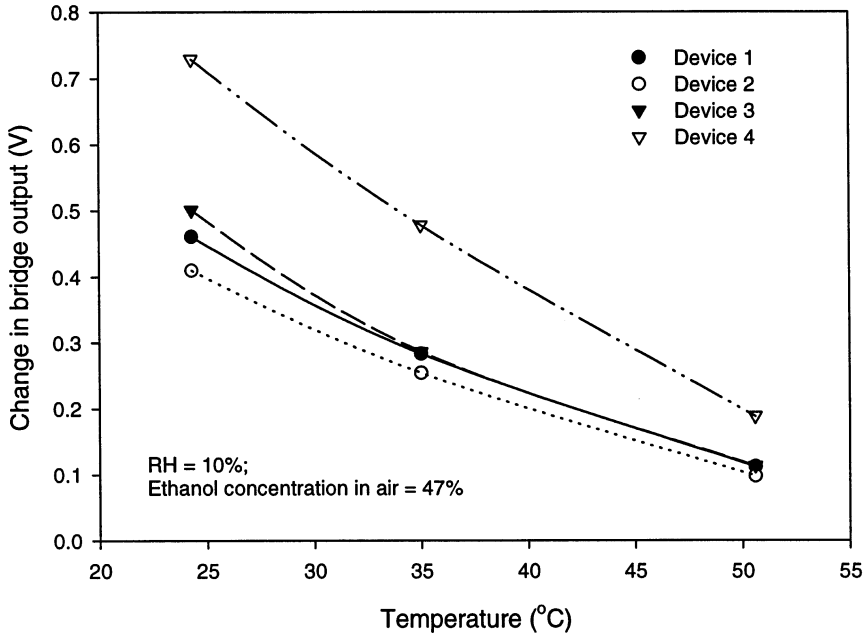

Fig. 7. Effect of temperature on the output of a poly(pyrrole) bridge. A second order model has been fitted to the experimental data for each of the four devices.

where a and b are constants in the Langmuir model and C is the concentration of the ethanol vapour in air.

Fig. 5 shows that in the case of the polymer-based micro-bridges, the change in bridge output ΔV_{out} (referenced to off-set voltage) did indeed follow the Langmuir isotherm as the change in resistance of individual PPy/PSA polymers. In Fig. 5 test results are represented by symbols, while lines represent models based on Langmuir isotherm. Constants a and b are calculated for four different devices and at three different temperatures based on experimental results. Calculated values are presented in Table 2.

Fig. 6 shows a typical 3D plot of micro-bridge response to different concentrations of ethanol at different temperatures and humidity's. From this plot an apparent temperature and humidity dependence of the output is clearly seen. Namely, the micro-bridge response decreases with the increase of both relative humidity and temperature. A simple, empirical polynomial temperature dependence of the response to ethanol has been employed:

$$\Delta V_{out} = \Delta V_o(1 + \alpha T + \beta T^2) \quad (2)$$

where ΔV_{out} is the change in bridge circuit output in volts at temperature T and ΔV_o is the change at 0°C to ethanol vapour, α and β are temperature coefficients with units of $°C^{-1}$ and $°C^{-2}$, respectively.

Finally, Fig. 7 shows a typical micro-bridge response to 24800 ppm of ethanol at 10% r.h. at different temperatures. Experimental data are shown as symbols, while lines represent models based on the above equation. Temperature coefficients α and β are calculated for four devices at five different concentrations at both 10 and 40% r.h. Typical results are shown in Table 3. The bridge output falls approximately linearly with increasing temperature and the linear coefficient α has a value of ca. -3×10^{-2}/°C for PPy.

6. Conclusions

The authors have fabricated silicon micro-bridges with a conducting polymer as the resistive elements. The bridges have a reduced zero-gas sensitivity, and respond to ethanol vapour following the Langmuir isotherm. The static sensitivity of the bridge to ethanol vapour is given by the product ab. In conclusion, a PPy/PSA micro-bridge was found to possess a typical sensitivity of ca. 30 μV/ppm to ethanol vapour that fell with increasing humidity and temperature. PAN micro-bridges were observed to have a significantly higher sensitivity to both ethanol vapour and water vapour.

Micro-bridges possessing a 50 μm gap were found, as expected, to have a higher base-line resistance but comparable sensitivity. They are preferable in that geometric errors due to the wet-etch processes are considerable smaller [8] and the nominal polymer resistances R_{po} in the kilo-ohm range. The micro-bridge is relatively simple to produce and can be integrated with CMOS circuitry. A look-up table may be used to store the values of the coefficients a, b, α and β and thus compensate for the temperature and humidity sensitivity of the bridge output. Furthermore, the CMOS circuit would need to null regularly the polymer bridge

Table 3
Temperature coefficients for the response of PPy micro-bridges to 47% ethanol vapour at 10 and 40% r.h.

Device no.	R.H. (%)	ΔV_o(V)	α (10^{-3})/°C	β (10^{-5}/°C^2)	Thermal model parameters
1	10	1.049	−28.1	20.6	
2	10	0.912	−27.3	19.1	$\Delta V_o = (1.175 \pm 0.242)$ V
3	10	1.280	−31.5	26.7	$\alpha = (-27.6 \pm 3.2) \times 10^{-3}$/°C
4	10	1.456	−23.6	12.7	$\beta = (19.8 \pm 3.2) \times 10^{-5}$/°C
1	40	0.363	−30.5	27.6	
2	40	0.341	−30.4	26.3	$\Delta V_o = (0.410 \pm 0.104)$ V
3	40	0.371	−28.0	23.0	$\alpha = (-27.9 \pm 3.7) \times 10^{-3}$/°C
4	40	0.565	−22.6	13.5	$\beta = (22.6 \pm 6.37) \times 10^{-5}$/°C^2

because of changes in the relative humidity seen by the active and passive arms or any long-term drift.

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