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Polymeric resistive bridge gas sensor array driven by a standard cell CMOS current drive chip

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Abstract

Gas-sensitive micro-bridge devices, fabricated with four conducting polymer resistive elements, have been characterised using a standard cell Complementary Metal-Oxide Semiconductor (CMOS) current drive chip and precision linear analog interface circuitry. Poly(aniline) (PAN) types of polymers were used to create the four resistive elements, while two, opposite arms of the micro-bridge were passivated by a protective coating of either epoxy resin or nafion. The standard cell analog current drive chip was designed to supply currents in the micro-amp range through an array of six resistive polymer micro-bridge devices. The chip was fabricated using the Alcatel Mietec 2.4 μm CMOS process. It exhibits good d.c. stability, and a linear temperature coefficient of about -1.2×10^{-3}/°C. The chip can be driven in an a.c. as well as in a d.c. mode and gives a stable pulsed current source at frequencies of up to 10 kHz. The output voltages of all of the current-driven micro-bridges were observed to follow the Langmuir adsorption isotherm. The nafion-coated bridges exhibited a substantially reduced sensitivity to ambient humidity and, rather surprisingly, a *positive* temperature coefficient.

Keywords: Analogue CMOS chip; Current drive; Micro-bridge; Poly(aniline); Nafion; Ethanol vapour

1. Introduction

Arrays of conducting polymer resistors are of increasing interest in gas and odour sensing [1,2]. In order to reduce the effect of operating temperature on the base-line signal of discrete polymer sensors ($\approx10^{-2}$/°C), a silicon micro-bridge device was designed and fabricated at Warwick University with conducting polymer resistive elements on all four arms (two active) in a CMOS-compatible process [3,4]. In order to drive an array of six micro-bridges, an ASIC chip, which generates six constant reference currents, was designed at Southampton University. A constant current source was chosen over a constant voltage source because of the advantage that current driven bridges have less susceptibility to lead resistance, are easier to create, and have better linearity [5]. Preliminary tests have been conducted to investigate the long term stability, load effect and temperature dependence of the current reference. Voltage and current noise measurements were also performed using precision metal film load resistors. Further tests have been carried out with the ASIC chip as a part of a larger measurement system [4,6], in order to characterise the response of poly(aniline) (PAN) micro-bridges (with two active and two passive, epoxy resin or nafion-coated, elements) to ethanol at different temperatures and different humidities.

2. Chip design and fabrication

The current drive chip has been fabricated using the Alcatel Mietec 2.4 μm CMOS technology and, prior to fabrication, had been modelled using Cadence Analog Artist HSPICE interface. Fig. 1 shows the main part of its schematic diagram where Core cell High voltage range CUrrent Reference Cascode circuit (CHCURC) represents a standard Mietec current reference cell with improved power supply rejection; PPDR is the start-up circuit for the current reference and Core cell High voltage range CUrrent Mirror Cascode C type circuit (CHCUMCC) is the corresponding current mirror cell.

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Each CHCURC circuit delivers a typical current of 2 μA, while each current mirror has a current factor of 2. An input voltage, V_{DD}, for the ASIC chip should be set at 2.5 V. The normal operating voltage range of a CHCURC is 7–12 V. However, we operated the chip at + 2.5 V with the ground set to − 2.5 V to obtain the desired current. The output from each current mirror drives a polymer micro-bridge with a constant current of 16 μA, thus setting the bridge voltage at the suitable value according to the resistance of the polymer resistors. The chip also comprises of six independent analog switching circuits, and three operational amplifiers that could be used independently or in conjunction with the constant current reference part.

3. Chip characterisation

Initial tests were performed to investigate the stability of the current output of the chip in relation to the

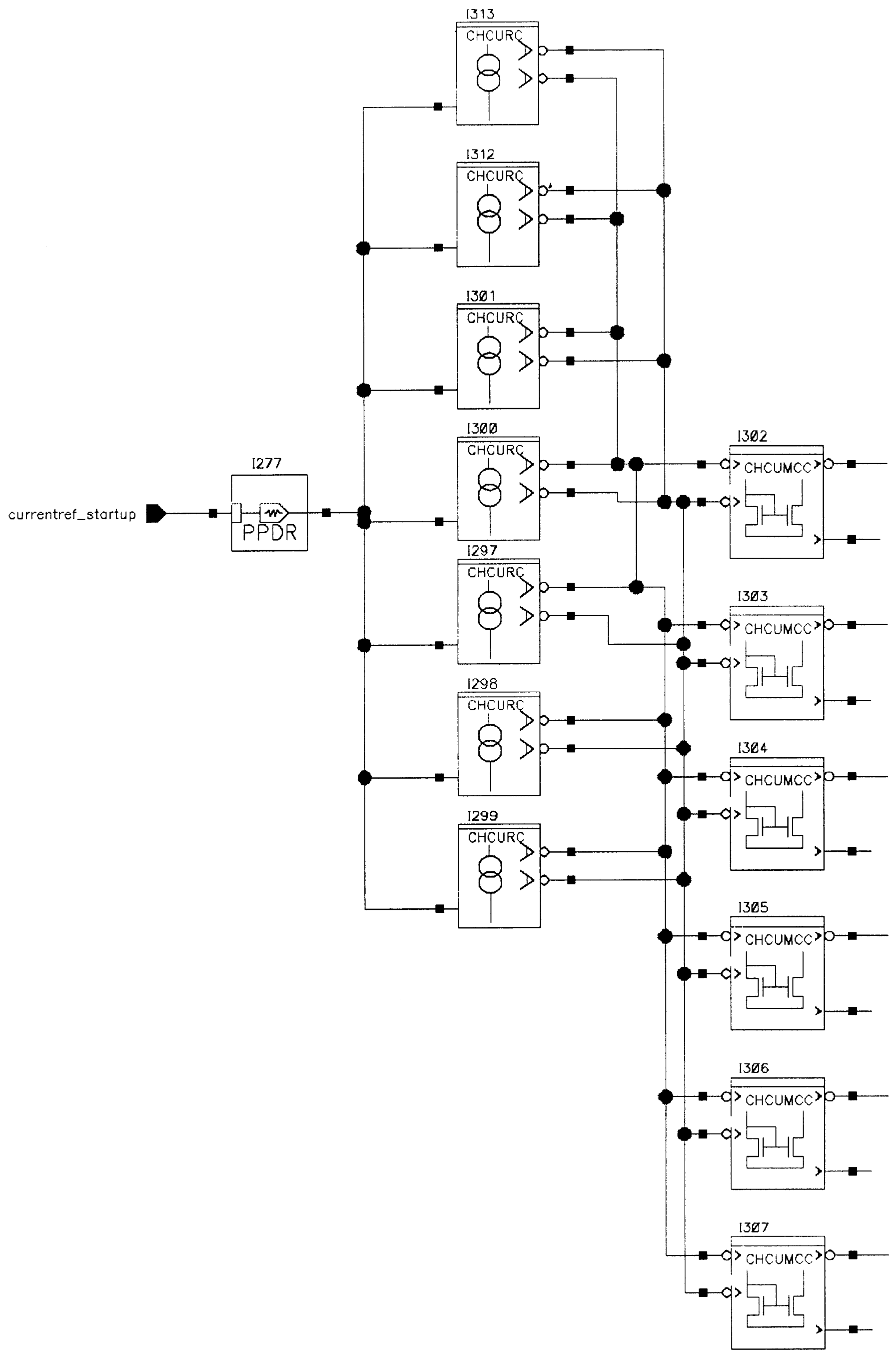

Fig. 1. Schematic of the Southampton-Warwick (SW) standard cell CMOS (ASIC) current drive chip.

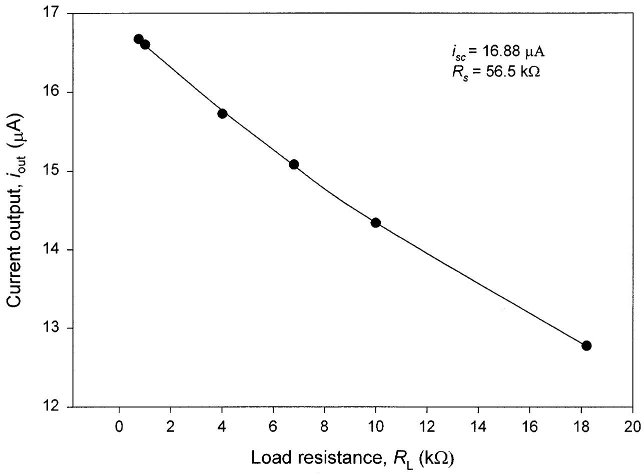

Fig. 2. Effect of load on the current mirror output of the SW ASIC chip.

voltage supply of the chip and also to investigate its long term stability. A programmable micropower voltage regulator (MAX666, Maxim) was used to generate the voltage supply for the chip in the range of 2–10 V with increments of 0.5 V. Each current mirror output of the ASIC chip was connected to a 1 kΩ precision metal film load resistor. Voltages across the resistors were measured using a M810 (Precision Gold) multimeter calibrated against a Knick 5252 d.c. voltage calibrator. It was apparent that there was an increase in the voltage across, and therefore an increase in current through the resistors, with an increase of V_{DD}. For a given chip supply range of 2–10 V, the current output exhibited change from 8.4 to 78.5 μA. This effect was even observed in the operating range of 7–12 V and so cannot be attributed to a simple saturation effect. Although such dependence of the current output on the input of the chip is undesirable, this was not considered a disadvantage because a high voltage regulation for the power supply could always be provided. For the long term stability test, the programmable voltage regulator was set at +2.5 V and voltages across six precision load resistors connected to six current outputs of the chip were monitored for 24 h. A virtual instrument (VI) written using Labview software (National Instruments) was used to control and record the data during the test via a PC-LPM-16 12-bit (National Instrument) card. Although the measurements were slightly limited by the accuracy (±1.0 LSB typical) and the noise level (0.3 LSB rms) of the data acquisition card, current reference outputs have exhibited good stability (< 0.7%/day).

The effect of a load resistor on the current output was also investigated. The programmable voltage regulator was again set at +2.5 V and current from the ASIC current mirror was passed in sequence through the set of precision metal film resistors of 0.75, 1.00, 4.02, 6.81, 10 and 18.2 kΩ. Fig. 2 shows a typical effect of the resistive load on the current reference. Voltages across the load resistors and calculated current values were used to determine the Norton short-circuit current and source resistance from the equation

$$i_{out} = \frac{R_s}{(R_s + R_L)} i_{sc} \quad (1)$$

where i_{out} is current through the load resistor, R_L is resistance of the load, and i_{sc} and R_s are equivalent source current and resistance, respectively. Values for i_{sc} and R_s were found to be 16.88 μA and 56.5 kΩ by fitting the model to the experimental data (see Fig. 2).

In order to investigate the temperature dependence of the current output, the same set-up as before was used: i.e. +2.5 V voltage supply and six current outputs connected to six 1 kΩ precision load resistors. The ASIC chip was isolated and placed in a Dri-Block® heater (Techne Ltd) in order to minimise the influence of other components on its temperature characteristic. Values of current outputs were recorded at seven different temperatures (±0.05°C): 24.3, 30.6, 34.8, 41.5, 46.7, 51.5 and 56.3°C. Fig. 3 shows a typical plot of the temperature dependence of the current source. Test results are represented by symbols while the line represents a model based on the assumption that simple polynomial temperature dependence of current output could be employed:

$$\Delta i_{out} = \Delta i_0(1 + \alpha T + \beta T^2) \quad (2)$$

where i_{out} is change in current output in μA at temperature T, Δi_0 is change at 0°C, and α and β are linear and quadratic temperature coefficients with units of °C^{-1} and °C^{-2}, respectively. The temperature coefficients α and β were calculated for all six current outputs and it was observed that the temperature dependence for all of them is approximately linear with a linear coefficient of $\approx 1.2 \times 10^{-3}$/°C. Thus, the temperature coefficient of the current chip is negligible compared to the temperature coefficient of the *response* from a polymer micro-bridge [4], namely $\sim 10^{-2}$/°C.

4. Noise measurements

The noise measurements were carried out using an Hewlett-Packard HP 35660A dynamic signal analyser with the same circuit as before in which constant current was passed through precision metal film load resistors. Noise spectra have been taken from a number of different precision resistors: 0.75, 1.00, 5.11, 6.81 and 10.0 kΩ. Noise measurements were made over a frequency range of 15 mHz to 3.2 kHz and results were as expected. Fig. 4 shows the effect of load on the noise voltage at a frequency of 16 Hz—a value close to the frequency at which the chip would be operated in a gas sensor array. It can be seen that the noise level increases with an increase of the load. Measurements were also taken from the load resistor of 1 kΩ, changing the voltage supply V_{DD} of the chip in the range of + 2–10 V. An increase in noise with an increase of supply voltage, and therefore an increase of the current output, was also observed.

5. Experiments and results

The current drive CMOS ASIC chip was used in a set of experiments to drive an array of six polymer resistive micro-bridges. The input voltage, V_{DD}, for the chip was set at 2.5 V thus setting the voltages across six bridges at 5, 9, 10, 12, 22 and 44 mV depending on the

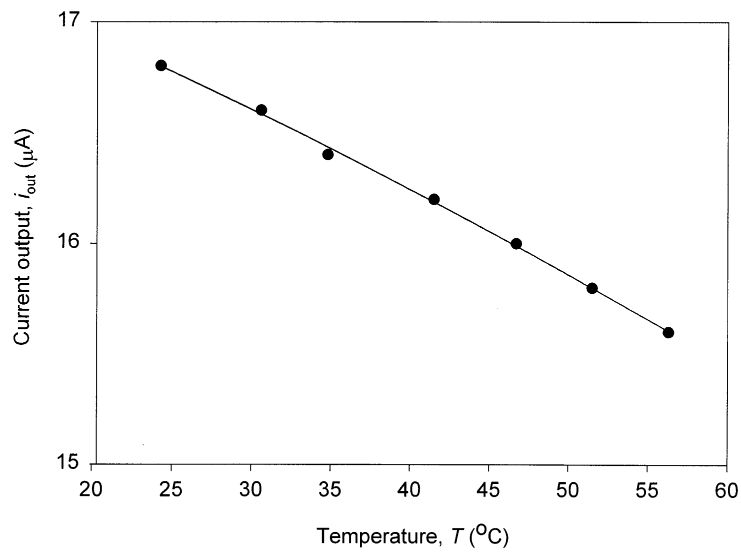

Fig. 3. Effect of temperature on the current mirror of the SW ASIC chip.

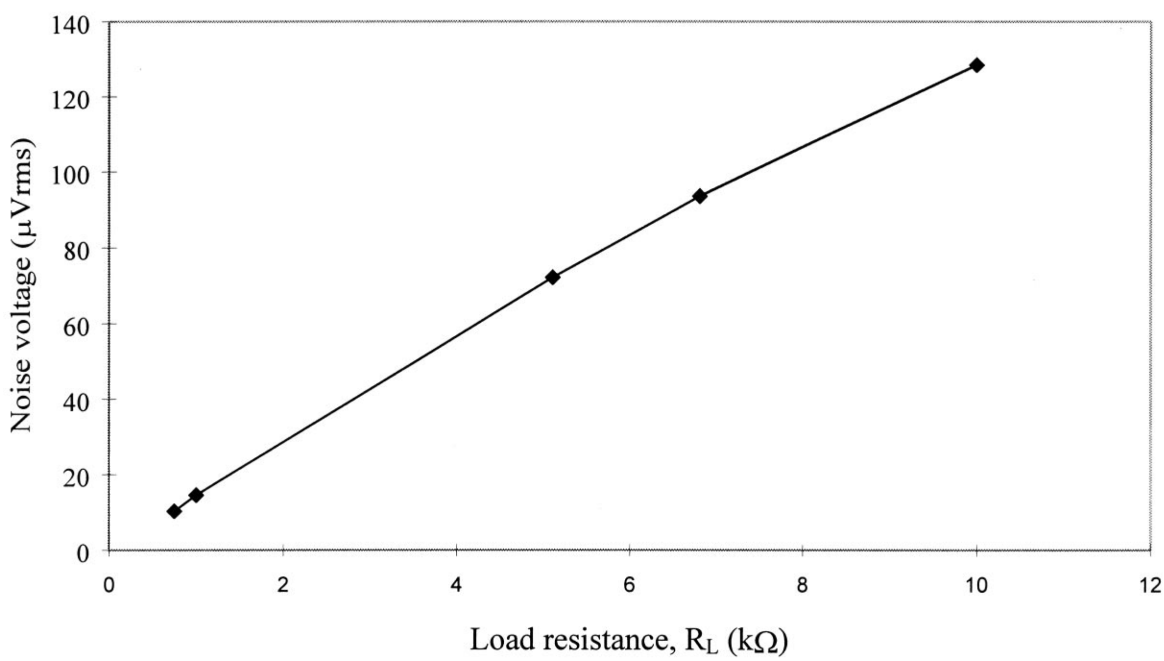

Fig. 4. Typical noise voltage measured at a frequency of 16 Hz for different precision load resistors.

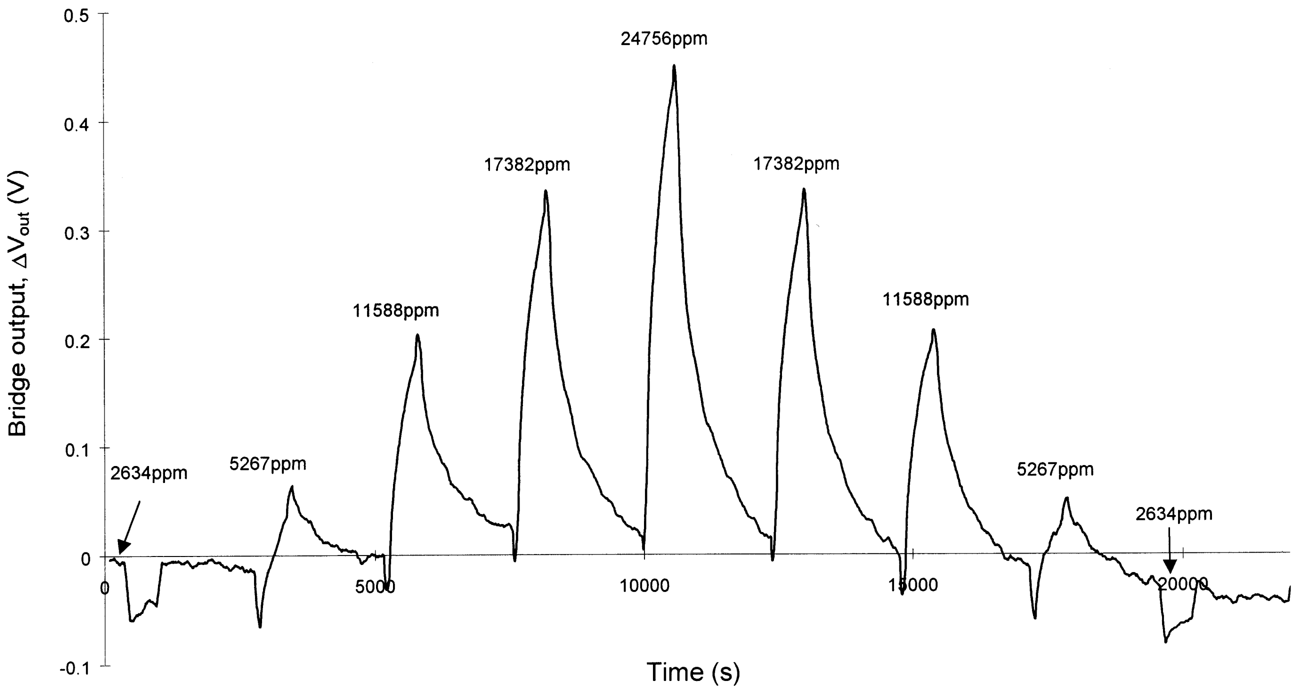

Fig. 5. Typical response of a PAN micro-bridge to pulses of ethanol vapour at a fixed humidity and temperature.

resistance of the polymer resistors. The response of six current driven PAN devices to ethanol vapour was tested in an automated mass flow system [7]. The general lay-out of polymer micro-bridge and interface circuitry is described elsewhere [4,6]. The two passive arms of the bridge were created through the coating of conducting polymers with epoxy resin or nafion (which offers the potential for common mode rejection of humidity signals). Previous research shows that the response of resistive sensors to humidity can be significant ($\sim 10^{-2}$/%rh) and equilibration slow [8]. In these experiments an initial assumption was made that the effect of humidity upon the response and temperature sensitivity could be reduced by coating two arms of the micro-bridge with a water-permeable nafion film.

Several tests were carried out following the procedure similar to one described elsewhere for characterisation of poly(pyrrole) (PPy) devices [4]. The responses of six polymer micro-bridges were recorded at three different temperatures:

1. 25.6°C at 8.1 and 32% relative humidity;
2. 35°C at 4.7 and 18.8% relative humidity; and
3. 49.2°C at 8.9% relative humidity.

The sensor chamber with six polymer bridges was placed in a Dri-Block™ heater (Techne Ltd). Prior to the tests stabilisation time for the devices at each temperature was 24 h. An exposure time of 60 min to equivalent of 40% relative humidity at 20°C was found to be sufficient in order to establish stable base-line resistance which was followed by the balancing of the bridge devices. In the case equivalent of 10% relative humidity at 20°C exposure time had to be extended to 120 min or more. During the tests micro-bridges were exposed to 2630, 5720, 11600, 17400 and 24800 ppm of ethanol vapour in air at three temperatures and at two relative humidities for most temperatures. An exposure time of 10 min to a certain concentration of ethanol was followed by 30 min recovery time before the next exposure.

A typical response of the 10 μm PAN/PSA (poly(aniline)/pentane sulphonate) micro-bridge to 2630, 5270, 11600, 17400 and 24800 ppm of ethanol in the air at 9% r.h. and 49.2°C is shown in Fig. 5. Previous research conducted on the effects of ethanol vapour on the response of epoxy-coated PPy/PSA (poly(pyrrole)/pentane sulphonate) micro-bridge devices [4] shows that devices demonstrate a negligible drift during the exposure to a constant humidity but they exhibit significant long term effect during the ethanol exposure. Fig. 5 indicates that in the case of PAN micro-bridges, with two nafion coated arms, such long term effect is almost completely eliminated. A relative bridge sensitivity of ≈ 25 μV/ppm was found under given test conditions, although from the Fig. 5 it is evident that after 10 min of exposure to ethanol the devices were still responding. A significantly higher optimum sensitivity would be achieved if the exposure time was extended, but during these experiments it was kept at 10 min for comparison purposes.

Fig. 6 shows that the change in PAN micro-bridge output voltage ΔV_{out}, when exposed to ethanol, (referenced to off-set voltage) follows the Langmuir adsorption isotherm. This was expected considering that the

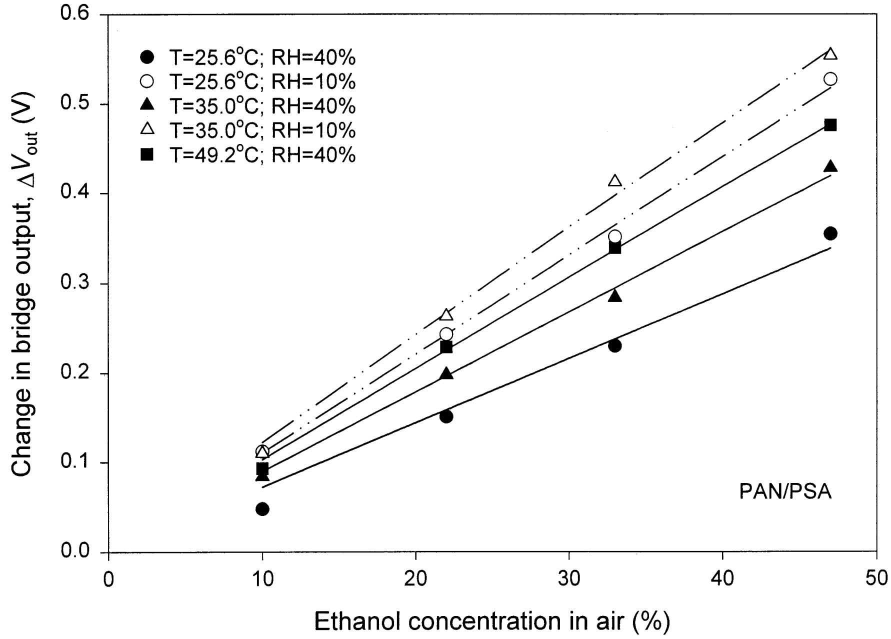

Fig. 6. Effect of ethanol concentration on the response of a PAN micro-bridge with the Langmuir model (lines) fitted to the experimental data (symbols). Absolute humidity set at 20°C to 10% and 40% r.h.

change in conductance of individual PAN/PSA polymers follows the same model. The output voltage V_{out} of a constant-current I_0 driven resistance bridge with two active arms is directly proportional to the change of the polymer resistor ΔR_{po} [4]:

$$V_{out} = 500V_b \approx \frac{I_0}{2}\Delta R_{po} \approx a\left(\frac{bC}{1+bC}\right) \tag{3}$$

where 500 is the gain of the interface circuit on the bridge output V_b, a and b are constants in the Langmuir model and C is the concentration of the ethanol vapour in the air. In Fig. 6, test results are represented by symbols, while lines represent models based on the Langmuir isotherm. Values for a and b are found by fitting the models to the experimental data and some of their typical values are shown in Table 1.

Fig. 7 shows a typical nafion-coated PAN micro-bridge response to different concentrations of ethanol at different temperatures and at constant absolute humidity. Experimental data are shown as symbols, while lines represent the model based on the following simple, empirical polynomial temperature dependence of the bridge response [4]:

$$\Delta V_{out} = \Delta V_0(1+\alpha T+\beta T^2) \tag{4}$$

where ΔV_{out} is the change in bridge circuit output in volts at temperature T and ΔV_0 is the change at 0°C to ethanol vapour, α and β are temperature coefficients with units of $°C^{-1}$ and $°C^{-2}$, respectively. Typical values for these coefficients at different concentrations of ethanol and at 40% r.h. are presented in Table 2.

Unexpectedly, a positive temperature coefficient was observed for the nafion-coated PAN micro-bridge (see Fig. 7), because previous research carried out on conducting polymer based gas sensors [8–10] has always shown that the response of a polymer resistor generally falls with increasing temperature. The nafion coating has thus reversed the behaviour with an increased response at higher temperatures. This effect has now been confirmed on individual nafion-coated resistive polymers [11] as well as for nafion-coated micro-bridges. This phenomenon is shown in Fig. 8 in a form of a 3D plot of uncoated PAN resistor response (Fig. 8a) and nafion-coated PAN resistive bridge response (Fig. 8b) to different concentrations of ethanol at different temperatures and different humidities. In Fig. 9 it could also be seen this significant change in the effect of temperature upon the response of an epoxy resin coated PPy (Fig. 9a) and a nafion coated PAN (Fig. 9b) micro-bridges. The epoxy resin coated micro-bridge exhibits the decrease in the response to ethanol with the increase of temperature, while in the case of nafion

Table 1
Values of the Langmuir coefficients computed from experimental data obtained at different temperatures and different absolute humidities (r.h. set at 20°C)

T (°C)	R.H. (%)	a (V)	b (10^{-4}/%)
25.6	40	67.13	1.08
35.0	40	75.85	1.18
49.2	40	27.78	3.72
25.6	10	110.00	1.01
35.0	10	16.88	7.30

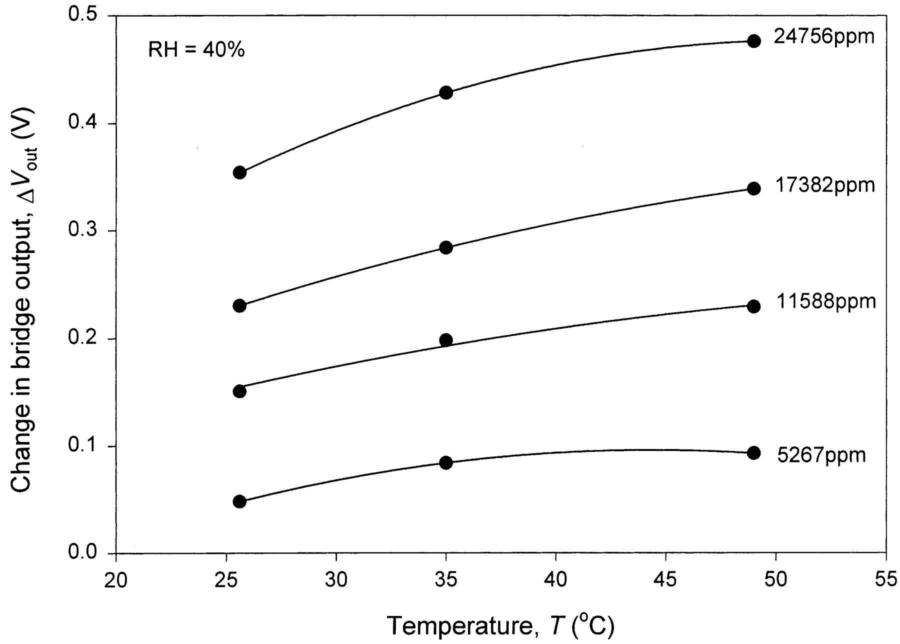

Fig. 7. Typical PAN micro-bridge response to different concentrations of ethanol a constant absolute humidity equivalent to 40% r.h. at 20°C. A second order model has been fitted to the experimental data for each concentration.

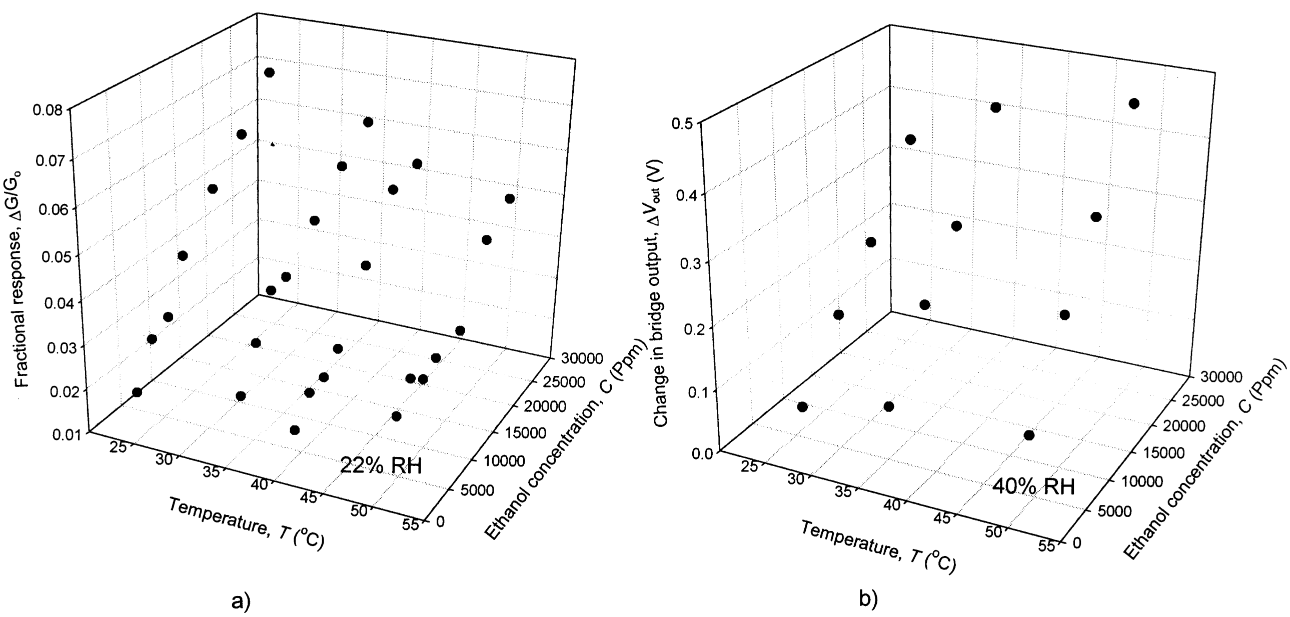

Fig. 8. 3-D plots showing the response of an uncoated PAN device (a), and a nafion-coated PAN micro-bridge to ethanol at different temperatures (b).

Table 2
Temperature coefficients for the response of PAN micro-bridge to four concentrations of ethanol at constant absolute humidity

Ethanol concentration (ppm)	ΔV_0 (10^{-2} V)	α (°C^{-1})	β (10^{-3}/°C^2)
5267	−17	−0.07	0.79
11 588	0.12	5.98	−46
17 382	1.3	0.78	−5.79
24 756	−1.8	−1.10	11

coated device a reversed effect is apparent. This is a very important observation and it requires further investigation.

6. Conclusion

A current drive CMOS ASIC chip has been designed and fabricated to drive an array of six polymer resistive micro-bridges. The micro-bridges are easy to produce in

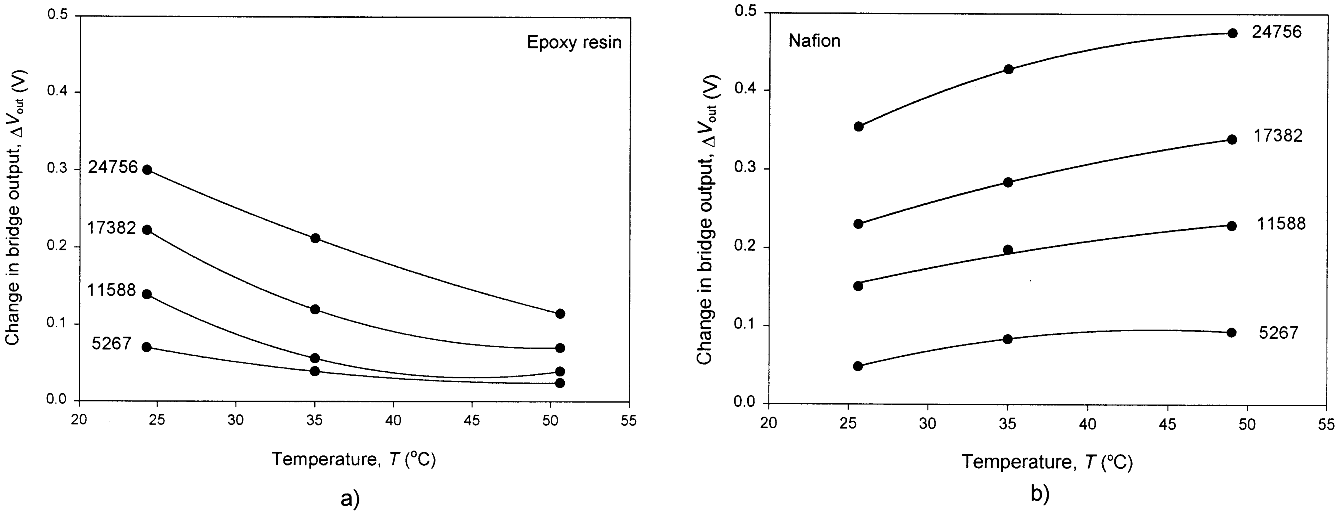

Fig. 9. Effect of temperature on the response of an epoxy resin coated PPy micro-bridge (a) and a nafion-coated PAN micro-bridge (b) at different ethanol concentrations. All measurements were taken at 40% r.h.

a CMOS-compatible process and this work is one of the first steps towards the integration of the gas sensors and CMOS circuits to make a smart sensor array device. The chip was found to be a poor constant current source because of its supply-voltage dependence but it showed reasonable stability and was useful in characterising our polymer micro-bridges. Although the temperature sensitivity of the polymer element currently exceeds that of the CMOS chip, temperature compensation of the complete bridge circuit is desirable and could be integrated into a single CMOS chip. The nafion-coated PAN micro-bridges have shown negligible long term effect during the exposure to ethanol and their response followed the Langmuir isotherm. Furthermore, they have shown an increase in response with an increase in temperature—the opposite behaviour to uncoated or epoxy-coated elements. These results could have significant implication for the practical use of conducting polymers within hand-held gas monitors.

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