

## NOVEL DUAL TRANSIENT TEMPERATURE MODULATION TECHNIQUE FOR MULTI-VAPOUR DETECTION

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### ABSTRACT

Here we present a novel signal processing technique for a square wave thermally-modulated carbon black/polymer composite chemoresistor. The technique consists of only two mathematical operations: summing the off-transient and on-transient conductance signals; and subtracting the steady-state conductance signal. A single carbon black/polyvinylpyrrolidone composite chemo-resistor was fabricated and used to demonstrate the validity of the technique. Classification of water, methanol and ethanol vapours was successfully performed using only the peak time of the resultant curves. Quantification of the different vapours was also possible using the height of the peaks, because it was linearly proportional to concentration. This technique does not require zero-gas calibration and thus is superior to previously reported methods.

### KEYWORDS

Carbon black/polymer composite, Gas sensor, Micro-hotplate, Temperature modulation

### INTRODUCTION

At present there is significant demand for low power, portable gas monitors, employing sensors that can detect multiple gases with suitable sensitivity and selectivity. Unfortunately, existing sensor technologies have yet to achieve these performance requirements.

Currently the most reliable way to analyse gases is by using analytical instruments (e.g. optical spectrometers, gas chromatographs and mass spectrometers) – although they are generally bulky and expensive. Therefore there has been considerable effort to reduce the size and cost of such instruments through miniaturization (e.g. [1]). However, only a limited degree of miniaturization has been achieved due to the nature of the parts to be replicated, e.g. high voltages, vacuum systems, pumps.

There are two other approaches to portable gas monitors: either constructing an array of gas sensors with different sensing materials [2] or thermally modulating a single gas sensor [3]. The feasibility of the first approach has already been proved [2]. However, the cost of developing and manufacturing 12 to 32 different types of chemical sensors is high and thus is not suitable for ubiquitous sensing. Regarding the second approach, previous research has been reported on the temperature modulation of metal oxide chemoresistors [3]. The

classification and quantification were successfully demonstrated but a major issue was identified: pre-calibration of the sensors is required for both single gases and their mixtures. This is because the response of metal oxide gas sensors is non-linear in gas concentration and thus a simple linear superposition of the responses for different gases is not generally possible [4]. Assuming that the classification and quantification of up to 5 different types of gases are needed (a reasonable assumption for an environmental gas monitor) pre-calibration has to be carried out for all the possible concentration combinations of those 5 gases, which makes commercialization difficult.

We recently proposed a gas sensing technique that employs a temperature-modulated change in electrical conductance of a carbon black/polymer composite sensor that enables a single sensor to identify (i.e. classify) different vapours [5]. However, this technique has two limitations: it is not always easy to identify the components when mixed, as the curves used are always monotonously increasing (or decreasing); and the technique requires measurement in a reference gas (e.g. clean air).

In this paper, a novel signal processing technique is proposed that overcomes these two limitations and thereby extends both its capability and application potential.

### THEORETICAL

Fig. 1 illustrates the concept of the technique. The temperature of the SOI CMOS micro-hotplate [6], onto which carbon black/polyvinylpyrrolidone (PVP) composite was deposited (Figs. 2 and 3), is switched between two temperatures  $T_1$  and  $T_2$  ( $T_1 < T_2$ ) in the presence of the vapour. Figs. 1 (a) and (b) show the conductance of the sensor during the off and on transients, which are expressed as follows:

(off-transient –  $T_2 \rightarrow T_1$ )

$$G_{T_1}(t) = G_{T_1, dry}(t) \left[ 1 - Nc_{vapour} \left[ K(T_1) - \frac{8}{\pi^2} \{K(T_1) - K(T_2)\} \right. \right. \quad (1a)$$

$$\left. \left. \sum_{m=1}^{\infty} \left[ \frac{1}{2m-1} \exp\left( -\frac{\pi(2m-1)^2 D_{T_1} t}{4h^2} \right) \right] \right] \right]$$

(on-transient –  $T_1 \rightarrow T_2$ )

$$G_{T_2}(t) = G_{T_2,dry}(t) \left[ 1 - Nc_{vapour} \left[ K(T_2) - \frac{8}{\pi^2} \{K(T_2) - K(T_1)\} \cdot \sum_{m=1}^{\infty} \left[ \frac{1}{2m-1} \exp\left(-\frac{\pi(2m-1)^2 D_{T_2} t}{4h^2}\right) \right] \right] \right] \quad (1b)$$

where  $G$  is the sensor conductance,  $N$  a constant,  $c_{vapour}$  the concentration of vapour in the gas phase,  $K$  the partition coefficient,  $D$  the diffusion coefficient and  $h$  the thickness of the carbon black/polymer composite film. These equations can be obtained from equations (12) and (7) in [5]. The transient curve in Fig. 1 (a) has a larger time constant than Fig. 1 (b). This is because the transients in Figs. 1 (a) and (b) occur at different temperatures (when  $T_1 \neq T_2$ ) and the diffusion coefficient of the vapour molecules in the polymer depends on the temperature ( $D_{T1} < D_{T2}$ ).

Next, by simply summing the curves in Figs. 1 (a) and (b), we find the curve shown in Fig. 1 (c) with a peak which is formed due to the different time constants of the off and on transients. The mathematical expression of the curve is as follows:

$$\begin{aligned} G_s(t) &= G_{T_1}(t) + G_{T_2}(t) \\ &= [G_{T_1,dry}(t) \{1 - Nc_{vapour} K(T_1)\} + G_{T_2,dry}(t) \{1 - Nc_{vapour} K(T_2)\}] \\ &\quad + G_{T_1,dry}(t) Nc_{vapour} \frac{8}{\pi^2} \{K(T_1) - K(T_2)\} \\ &\quad \cdot \sum_{m=1}^{\infty} \left[ \frac{1}{2m-1} \exp\left(-\frac{\pi(2m-1)^2 D_{T_1} t}{4h^2}\right) \right] \\ &\quad - G_{T_2,dry}(t) Nc_{vapour} \frac{8}{\pi^2} \{K(T_1) - K(T_2)\} \\ &\quad \cdot \sum_{m=1}^{\infty} \left[ \frac{1}{2m-1} \exp\left(-\frac{\pi(2m-1)^2 D_{T_2} t}{4h^2}\right) \right] \end{aligned} \quad (1c)$$

It should also be noted that this summing step negates the zero gas transient, one of the limitations of the previous technique [5]. Then, by subtracting the curve in Fig. 1 (c) by the steady state conductance, we obtain the curve in Fig. 1 (d):

$$G_s(t) - G_s(\infty) = Bc_{vapour} \left[ G_{T_1,dry}(\infty) \cdot \sum_{m=1}^{\infty} \left[ \frac{1}{2m-1} \exp\left(-\frac{\pi(2m-1)^2 D_{T_1} t}{4h^2}\right) \right] \right. \\ \left. - G_{T_2,dry}(\infty) \cdot \sum_{m=1}^{\infty} \left[ \frac{1}{2m-1} \exp\left(-\frac{\pi(2m-1)^2 D_{T_2} t}{4h^2}\right) \right] \right] \quad (t \gg t_m) \quad (1d)$$

$$B \equiv N \frac{8}{\pi^2} \{K(T_1) - K(T_2)\} \quad (1e)$$

where  $t_m$  is the thermal response time of the micro-hotplate, and  $B$  is a constant. The peak time  $t_p$  of the resultant curve depends only upon the diffusion coefficients (assuming they are independent of concentration) at temperatures  $T_1$  and  $T_2$  and is thus specific to vapour class. The peak height  $G_p$  is proportional to vapour concentration and shows a linear response to the different vapours [7].

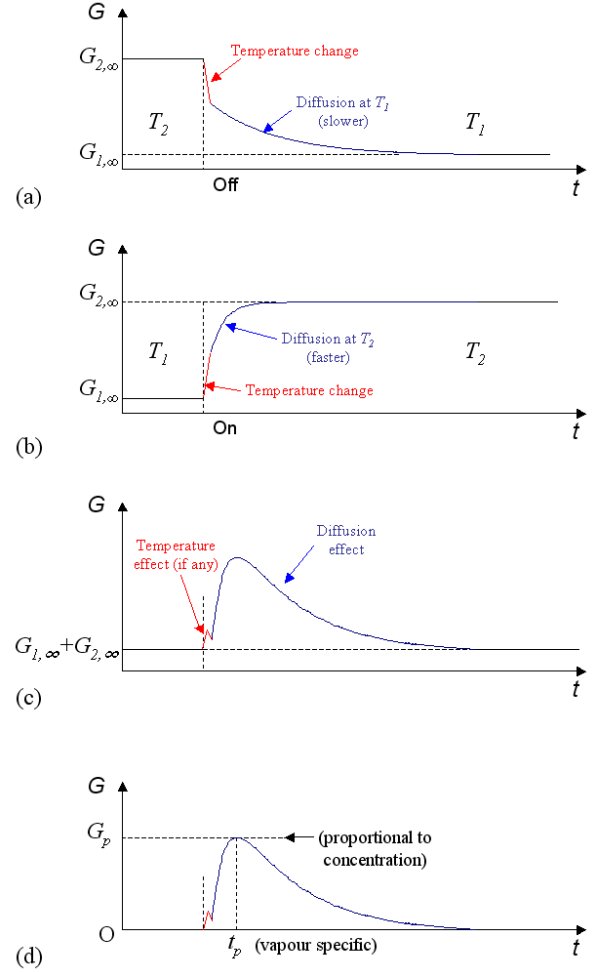


Figure 1: Conceptual explanation of the novel signal processing technique. (a) Sensor conductance ( $G$ ) for off-transient, (b) sensor conductance for on-transient, (c) sum of off and on transients, (d) final curve for classification and quantification.

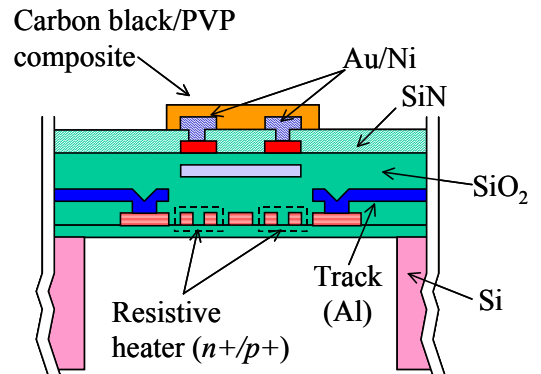


Figure 2: Schematic cross-section of a carbon black/PVP composite chemoresistor deposited on an SOI CMOS micro-hotplate.

## EXPERIMENTAL

Carbon black/polyvinylpyrrolidone (PVP) composite (20 wt % carbon black) was used as the sensing material. The material with powder form was used with a molecular weight of *ca.* 40,000, supplied by Sigma Aldrich (UK). The polymer has two atoms with strong electronegativity *i.e.* oxygen and nitrogen (electronegativity of oxygen and nitrogen atoms are 3.5 and 3.0 in Pauling's definition) [8]. Therefore, it is expected that the material has a larger sensitivity to polar vapours, such as alcohols than non-polar vapours. Carbon black nanospheres with a diameter of typically 50 - 80 nm (Black Pearls 2000) supplied by Cabot Corporation (USA) was used as the conductive filler material. PVP was dissolved in pure ethanol at 50 °C with the aid of a magnetic stirrer for 12 hours. Then 0.3 g carbon black was added and mixed with 20 ml of ethanol using a flask shaker (Griffin and George, UK) for 10 min. The mixture was deposited onto an SOI micro-hotplate by a commercial air brush (HB-BC or HP-CP Iwata, Japan) using a mechanical mask made by micro-stereolithography. The device was bonded on a 68 pin ceramic package and the resistance of the film was measured during deposition process to control the film thickness. The mask comprised two circular apertures with diameters of 400  $\mu\text{m}$ , and the distance between their centres was 1.0 mm. One hole defined the area of the sensing film on the chip, whilst the other was used to measure the thickness of the film. After deposition, the chips were baked at 50 °C for 24 hours in an oven to dry out the solvent. Finally, the sensors were exposed to the flow of dry air at 25 °C for 12 hours using an FIA (flow injection analysis) test station (described later).

Two sensors were used here in the experimental work and they are referred to as PVP8 and PVP11. The resistances of the film were 1.91 and 13.65 k $\Omega$ , respectively, at 25 °C in the dry air environment in the FIA test station. The film thickness was measured to be *ca.* 6  $\mu\text{m}$  and 0.8  $\mu\text{m}$  for PVP8 and PVP11.

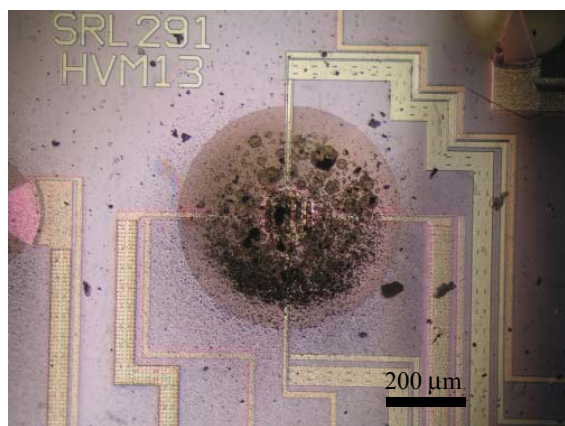


Figure 3: Photograph of a carbon black/PVP composite (thickness: 0.8  $\mu\text{m}$ , PVP11) chemoresistor deposited on an SOI CMOS micro-hotplate.

The devices were bonded onto ceramic packages and mounted in a temperature controlled stainless steel chamber with the controlled temperature of 25 °C in a fully automated FIA test station. The temperature of the carbon black/PVP composite film was controlled by applying a voltage to the micro-hotplate. The temperatures used in the experiments were 25 °C, 35 °C and 55 °C, which require operating voltages (and powers) of 0 V (0 mW), 0.78 V (0.8 mW) and 1.35 V (2.4 mW), respectively. The accuracy of the temperature modulation amplitude was  $\pm 0.3$  °C. The concentrations of water, methanol and ethanol vapours in the chamber were controlled independently with an error of *ca.* 5 %. A constant current of 10  $\mu\text{A}$  was applied to the carbon black/PVP composite film and the voltage was recorded every 10 ms.

Temperature modulation (between 25 °C and 55 °C) experiments of the device PVP11 were carried out in the presence of single vapours (water, methanol and ethanol) in air and the results processed using the new technique. The frequency of the square wave was 50 mHz for water and methanol and 1.67 mHz for ethanol, respectively.

The results are shown in Fig. 5. The curves for water and methanol vapour are averaged over 30 transients and those for ethanol vapour are over 3 transients. Each vapour is separated out clearly using the difference of their peaks in time (water: 50 ms, methanol: 1 s, ethanol 30 s). This is a reasonable result indicating that the species with the lowest molecular mass has the highest diffusion coefficient (molecular mass of water, methanol and ethanol are 18, 32 and 46, respectively [9]). The height of the peaks, shown in Fig. 5, increase with increasing vapour concentration. Fig. 6 plots the sensor response against concentration for all the test vapours (water, methanol and ethanol), and shows that the responses are linearly proportional to the concentrations, again as predicted by our theory.

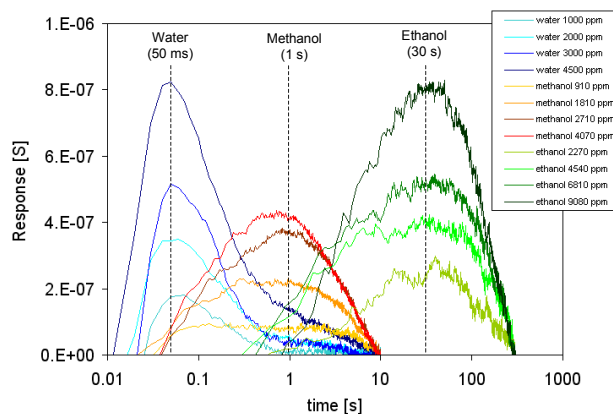


Figure 4: Dynamical response signatures of sensor PVP11 to water, methanol and ethanol vapours at different concentrations. The temperature was stepped between 25 °C and 55 °C. The frequency was 50 mHz for water and methanol, and 1.67 mHz for ethanol.

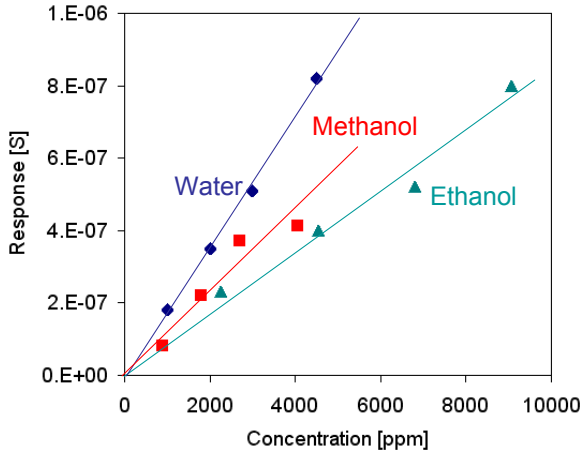


Figure 5: Concentration dependence of peak signature responses of sensor PVP11 in water, methanol and ethanol vapours in air.

Next, temperature modulation (between 25 °C and 35 °C) experiments of the devices PVP8 and PVP11 were performed in the presence of different concentrations of water vapour in order to investigate the effect of film thickness. The frequency of the square wave used was 10 mHz and the results processed using the new technique. Fig. 6 shows the results. The curves are the averages of 30 transients. The thicker film has a  $60 \times$  greater peak time (3 s) than the thinner film (50 ms). The result is reasonable, when considering the error in film thickness, because the peak time should be proportional to the square of the ratio of thickness (i.e.  $(6/0.8)^2 = 56$ ).

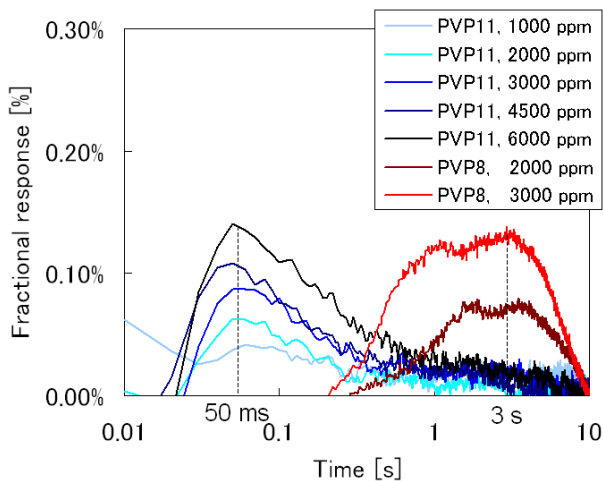


Figure 5: Fractional responses against time for thin (left) and thick (right) film PVP sensors.

## CONCLUSIONS

In conclusion, a novel signal processing technique has been proposed for a single carbon black/polymer composite vapour sensor. The peak of the resultant characteristic curve can be used to quantify multi-vapour mixtures without the

need for zero gas calibration or reference point. We believe that a low-power SOI CMOS micro-hotplate sensor combined with this signal processing technique could lead to a new generation of low-cost chip based analytical instruments with an embedded micro-controller or FPGA.

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