

Carbon Nanomaterial Polymer Composite ChemFET and Chemoresistors For Vapour Sensing

Dr James A. Covington and Prof Julian W. Gardner

*Sensors Research Laboratory
School of Engineering, University of Warwick, Coventry, CV4 7AL, UK
Tel: +44 (0) 2476 574494, Email: J.A.Covington@warwick.ac.uk*

Abstract. Carbon nanotubes (CNTs) have been proposed for a broad spectrum of applications, including chemical sensing. Here we report on an investigation of multi-walled CNTs (MWCNTs) as conductive filler for composite polymer sensing films. Such materials combine conductive fillers with an insulating polymer to produce a chemically sensitive, electrically conducting material. These polymer composites offer several important advantages for chemical sensing, including room temperature operation (hence ultra low power), a broad range of selectivities (due to the wide choice of available polymers), and low manufacturing cost. Our approach is to compare the sensing qualities of these composite films, in resistive and field-effect configurations, with existing carbon black polymer composites. Their responses to propanol and toluene vapour in air show that the carbon black resistive sensors outperform CNT sensors by a factor of four in response magnitude. Thus we conclude that for these vapours and using this sensor fabrication method, carbon black polymer composite films are preferable for chemical sensing than MWCNT polymer composites.

Keywords: Chemical Sensor, Composite Polymer, CNTs.

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INTRODUCTION

The use of carbon black (CB) as a conductive filler for chemical sensing has been widely reported [1,2]. In such a scheme, carbon nanoparticles are dispersed in an insulating polymer film. The resulting combination produces an electrically conducting material that changes its properties when exposed to a range of vapours. This is traditionally explained by a solvation and swelling effect where the polymer (solvent) expands when exposed to a vapour (solute), altering the nanoparticle dispersion (i.e. increasing the resistance in a chemo-resistive configuration or changing the average work function for a chemFET).

In addition to the use of CB/polymer composites, there have been significant efforts in using carbon nano-tubes (CNTs) for chemical sensing. This is by either using the CNTs on their own, in a resistive or FET configuration, or by combining the material with an insulating polymer in a resistive configuration [3,4].

Here we report on an investigation to compare the use of multiwalled (MW) CNTs / polymer composite materials for both chemFETs and chemoresistive devices and compare it with carbon black composite materials. Our aim is to determine whether CNTs give

any sensing advantage over the more traditional CB composites to test vapours.

EXPERIMENTAL METHODS

Here the two different types of chemical sensing devices are described, chemoresistive and chemFET.

Chemoresistive Device

The resistive device used in this study comprised of a silicon substrate (4.0 mm square), with a silicon nitride layer (200 nm thick), on to which a Ti/Au layer (10nm/250nm) had been deposited. The device was passivated with an additional 200 nm silicon nitride layer, with openings for bonding and sensor material deposition. The electrodes in the centre of the device were separated by a 50 μm gap and were 200 μm in length. The device was packaged onto a custom made PCB header for sensing material deposition and testing.

CHEMFET DEVICE

The chemFET substrate was fabricated using a standard silicon process at Southampton University (UK). Here an enhanced *n*-channel MOSFET was created from a *p*-doped silicon substrate, using standard silicon processing techniques. After oxidation, the polysilicon gate was exposed through dry etching. The active area was then defined using lithography and a portion of the polysilicon gate was etched away to expose the gate oxide. Thus two polysilicon electrodes either side of the exposed gate oxide remained to provide electrical contact to the sensing layer.

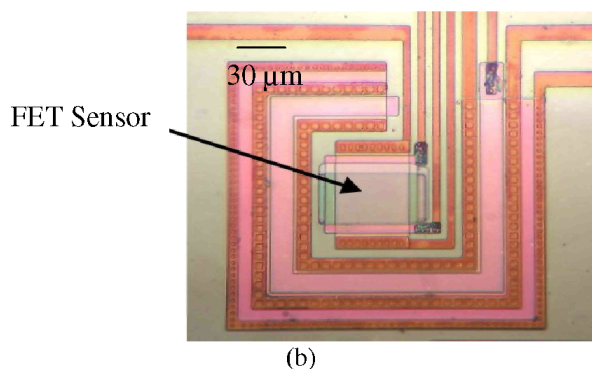
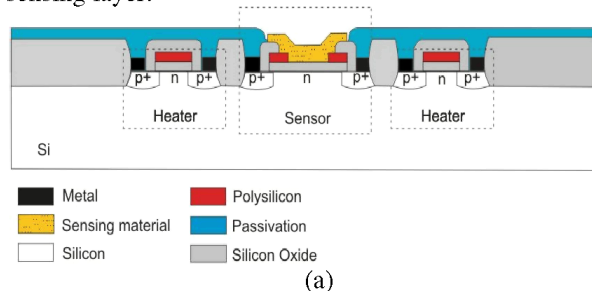


FIGURE 1. (a) Schematic and (b) photograph of the chemFET sensor.

Figure 1 shows (a) a schematic of the cross-structure of the FET device and (b) a microscope image of the active area of the FET before the sensing material was deposited.

Sensor Coatings

Three different recipes of MWCNT/Polymer and CB/Polymer were employed. Here the same weight of CNTs and CBs were used. Table 1 gives the details of these recipes. Note that 10 ml greater volume of toluene was used in depositing the CNT films. This is because the original recipe was too viscous for controlled air-brush deposition.

TABLE 1. Nano-material/polymer compositions.

Polymer (g)	CNT/CB (g)	Toluene (ml)
Poly(ethylene-co-vinyl acetate) / PEVA (1.2)	0.3	20 (CB) 30 (CNT)
Polycaprolactone / PCL - (1.2)	0.3	20 (CB) 30 (CNT)
Poly(Styrene-co-butadiene) / PSB - (1.2)	0.18	20 (CB) 30 (CNT)

The polymers were supplied by Sigma Aldrich (UK), the carbon black (Black Pearls 2000, Cabot Corporation, USA) and the CNTs from Nancyl (Belgium). The polymers were either in powder form or small crystals while the carbon black was supplied as nanospheres with diameters of typically 50 to 80 nm. The polymers were first dissolved with the aid of a magnetic stirrer in their respective solvent overnight at an elevated temperature (50 °C). Next, CB or CNT was added and the mixture sonicated for 10 min using a flask shaker (Griffin and George, UK). The mixture was then deposited onto the sensor electrodes using an airbrush (HP-BC Iwata, Japan) controlled by a micro-spraying system (RS precision liquid dispenser, UK). Before coating, the sensor substrate was mounted and wire-bonded on to a PCB header for monitoring the resistance whilst coating. This, in turn, was mounted onto an X-Y stage and aligned to an aluminium mask, containing a 1.0 mm hole. The device was coated multiple times until a resistance of around 5 kΩ was achieved. As stated above, Figure 2 shows the resistive sensor coated with a 3 μm ± 0.5 μm CB/PSB composite film.

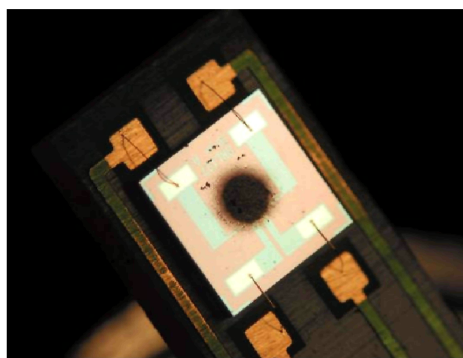


FIGURE 2. Coated resistive sensor.

SENSOR TESTING

The sensors were tested to six different concentrations of 1-propanol and toluene vapour in air using an automated testing station. In addition, two different humidities were used of 3500 PPM (Parts Per Million) and secondly at 9800 PPM. 3500 PPM corresponds to 10% relative humidity in air at a temperature of 20 °C and 9800 PPM corresponds to

40% relative humidity in air at 20 °C. Before testing, the sensors were left for 24 h in a Dri-block™ heater at (30 ± 1) °C to stabilize their baseline signals.

The sensors were driven at a constant current of 10 μA and the voltage drop across the sensors measured. In the case of the chemFET the gate and drain were shorted, thus the device was operated in the saturated region. In this case, with a constant current drive the change in output voltage is directly proportional to the change in threshold voltage. This is proportional to the change in the work function of the sensing material.

RESULTS

Figure 3 shows the transient responses of a CNT/PSB resistive, CB/PSB resistive and CNT/PSB chemFET sensors to six different concentrations of toluene vapour (1300, 1800, 2600, 5800, 8700 and 12400 PPM) in air (3500 PPM water).

Figures 4, 5 and 6 show the steady state isotherms of resistive and chemFET devices coated with CNTs and CB polymer composite films to toluene vapour in air. Here the water concentration was set at 3500 PPM. The data are displayed comparing the same polymer film, instead of device configuration for ease of comparison.

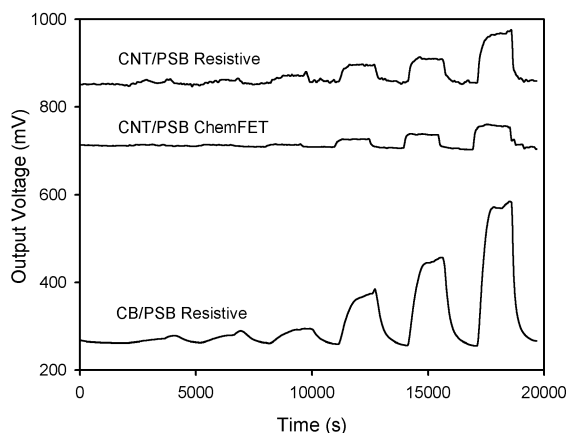


FIGURE 3. Transient responses of CB and CNT polymer composites to pulses of toluene vapour in air. Response times (t_{90}): CB/res - 375 s, CNT/Res - 35 s, CNT/FET - 260 s.

The data in figures 4 to 6 are plotted against the fractional response as defined by:

$$\text{Fractional Response} = (R_i - R_f) / R_i$$

Where R_i is the initial resistance, without vapour, R_f is the steady state resistance when exposed to a vapour. For the ChemFET sensors, the resistances R_i and R_f are replaced with the initial and steady state drain-source voltages. This pre-processing algorithm has been

employed both to reduce signal noise and make the sensors more comparable.

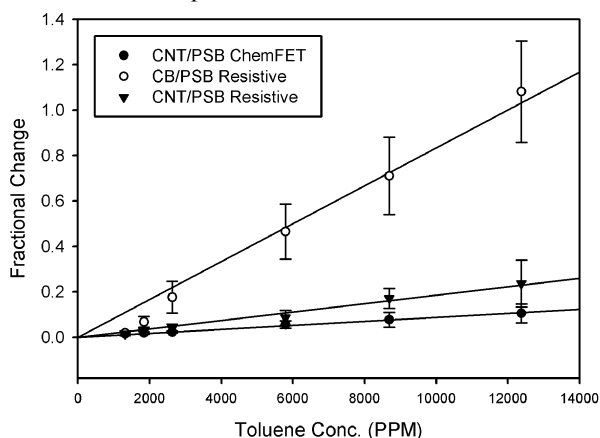


FIGURE 4. Response of sensors using PSB composite films to toluene vapour in air.

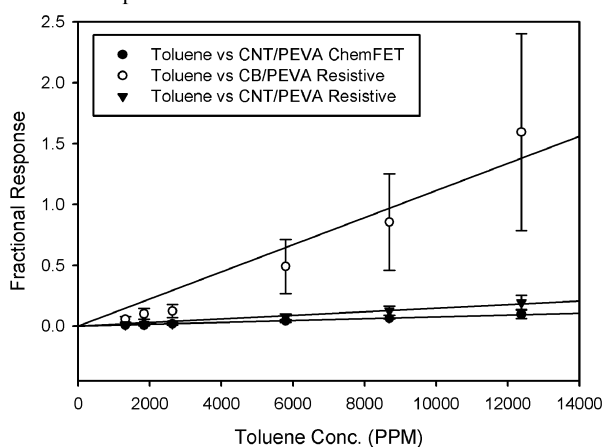


FIGURE 5. Response of sensors using PEVA composite films to toluene vapour in air.

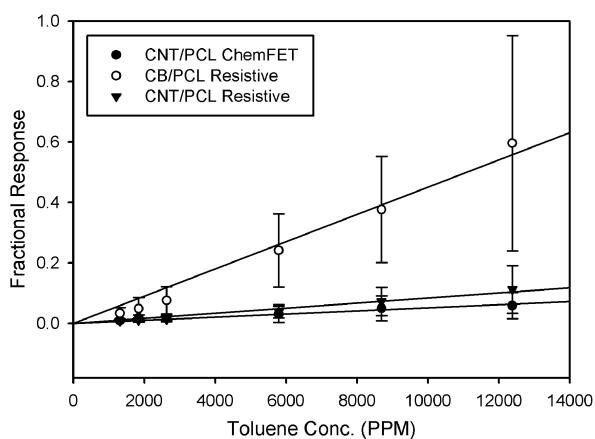


FIGURE 6. Response of sensors using PCL composite films to toluene vapour in air.

From this data and tests performed using 1-propanol and toluene vapour in air, we can define the sensitivity of each sensor type and sensing material. This is shown table 2 below.

TABLE 2. Sensitivity values in fractional response to toluene and 1-propanol vapour in air.

Sensor	Toluene $\times 10^{-6}$ /PPM	1-Propanol
CNT/PEVA FET	7.8 ± 2.8	2.4 ± 0.7
CNT/PCL FET	4.7 ± 3.5	3.5 ± 1.7
CNT/PSB FET	8.5 ± 3.4	3.3 ± 0.9
CB/PEVA Res	128.7 ± 65.4	11.6 ± 4.9
CB/PCL Res	48.1 ± 28.8	9.6 ± 3.9
CB/PSB Res	84.7 ± 18.0	4.2 ± 2.1
CNT/PEVA Res	15.7 ± 4.8	2.1 ± 0.3
CNT/PCL Res	9.0 ± 6.4	3.4 ± 1.8
CNT/PSB Res	19.1 ± 8.3	7.5 ± 7.3

In addition, to considering response to vapours, we have also considered the effect of water concentration on the magnitude of response. An example of this effect is shown in figure 7. Here the fractional response to different concentrations of toluene vapour is plotted with two different water concentrations. Results show that the magnitude of the response decreases with increasing water concentration. This was found for all the sensors and composite films tested.

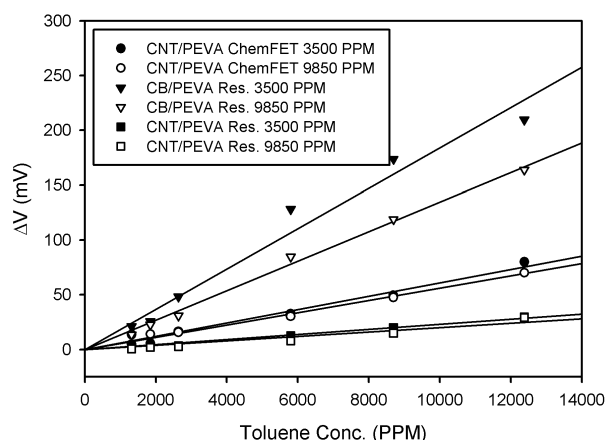


FIGURE 7. Effect of water concentration on the magnitude of the steady state response.

DISCUSSION

The results show that MWCNT FET and resistive sensors respond to simple organic vapours. We observed in these experiments that the carbon black resistive sensors had a larger response to these vapour concentrations than the CNT based resistive or chemFET devices; independent of the polymer used. We believe this reduced performance could possibly be due to nanoparticles clumping within the polymer; thus the swelling effect would not change the conduction path through these coagulated areas. Furthermore, multi-wall CNTs were used in our experiments. These are longer and wider than, for example, single wall CNTs. Thus it is possible that

they are forming networks through the material (like a mesh), that restricts the expansion of the polymer. It might be possible to get a better response profile from these composites by using single walled CNTs. The carbon black is made of nanospheres, and so might not be as susceptible to these issues. However, it is possible and probably necessary to functionalise the CNTs to improve their sensing characteristics for main stream use.

Furthermore, we have observed a strong water dependence of these films. This is not surprising as similar effects have been seen with these polymers. In these cases we believe there is competition for absorption sites on the polymer between the water and the test analyte, though it is interesting to note that toluene, a non-polar molecule, suffers the same reduction in response magnitude as 1-propanol.

CONCLUSIONS

Here we report on a comparison between carbon black and MWCNTs as the conductive filler for polymer composite vapour sensors. We have fabricated both resistive and chemFET sensors with three different polymers combined with carbon black nanospheres and carbon nanotubes. These sensors have been tested to different concentrations of toluene vapour and 1-propanol vapour in air. Results show that the carbon black resistive sensors outperform the CNT and chemFET sensors by a considerable margin. We believe that the CNTs are restricting the swelling of the polymers. Furthermore, we have tested the water dependence of these sensors and we have found that increased water concentration reduces the steady state response. We believe that the low sensitivity of CNT sensors may be addressed by using single wall CNTs and functionalising the CNT to improve selectivity.

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