Micro-gas-sensor with conducting polymers

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Abstract

In this paper design and fabrication of micro-gas-sensors, the deposition of four different poly(pyrrole) (PPY) thin films as chemoresistor in the micro-gas-sensors by electrochemical processing and chemical oxidation, and characterisation these films by FTIR, SEM, surface test instrument (WYKO NT2000) and optical microscopy, are reported. The effect of anions in PPY thin films, thickness and surface roughness of the PPY films on the response of micro-gas-sensors and the effect of ethanol vapour concentration on the response of polymer films have also been investigated. The experimental results show that a typical sensitivity to ethanol of ca. 5 µV/ppm was observed at 30 °C and the gas sensitivity of the integrated silicon planar micro-sensor depends on the counter ions in the PPY films, PPY film thickness and surface morphologies. The gas sensitive mechanism of the conducting PPY thin films is also discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Micro-gas-sensor; Conducting polymers; Poly(pyrrole) (PPY); Gas sensitivity

1. Introduction

Gas sensors have been manufactured as a commercial product for more than three decades in many applications. Recent advances in micro-technology and micro-machining techniques have led to integrate a gas sensor system (including gas-sensitive thin film, micro-heater, electrodes and wires) onto a silicon chip [1,2]. The performance of gas sensitive materials including MOS, ionic conductor and conducting polymers can be improved by control of the composition, morphology and increasing operating temperatures. Poly(pyrrole) (PPY) is one of the most promising candidates for use as an active component in many technological applications such as light emitting diodes (LEDs), solar cells, sensors and actuators. Currently there is a considerable interest in conducting polymer materials used in micro-gas-sensor [3,4], since they are expected to possess unique electronic functions, to operate around room temperature and devices based on molecules instead of bulk semiconductors. As a chemoresistor, however, there are three disadvantages to their use have been reported for some conducting polymers, such as PPY and polyaniline (PAN). Firstly, the specificity of an individual conducting polymer chemoresistor is poor, since these materials are sensitive to a wide range of vapours. Secondly, conducting polymer chemoresistors show a significant temperature coefficient of resistance of about -10^{-3} °C [5]. Third, a batch-to-batch

variation in resistance of about 35% has been found [6]. To solve the poor selectivity problem, gas sensor array and pattern recognition analysis has been widely used for the identification of odours or gases [7,8]. To reduce the effect of variations in batch conditions and operating temperature on the device base-line signal, a micro-bridge structure with four arms has also been constructed and tested. This is owing to quite many factors that influence the gas-sensitive properties of PPY-based polymers, much of the structure—property relationship still remains to be determined.

In this work the authors describe the design and fabrication of micro-gas-sensors used PPY as chemoresistor, the deposition and characterisation of PPY thin film in the micro-gas-sensors by electrochemical processing and chemical oxidation and by FTIR, SEM, surface test instrument (WYKO NT2000) and optical microscopy, are reported. The effect of anions in PPY thin films, thickness and surface roughness of the PPY films on the response of micro-gas-sensors and the effect of ethanol vapour concentration on the response of polymer films have also been investigated.

2. Experimental details

2.1. Device design and fabrication

Fig. 1 shows the cross-section view of the micro-gas-sensor structure. As shown in Fig. 1, the micro-gas-sensor is composed of PPY-sensing film, Pt micro-heater and Au electrodes on a stress free $SiN_x/SiO_2/SiN_x$ diaphragm. The micro-gas-sensor device has been designed using the

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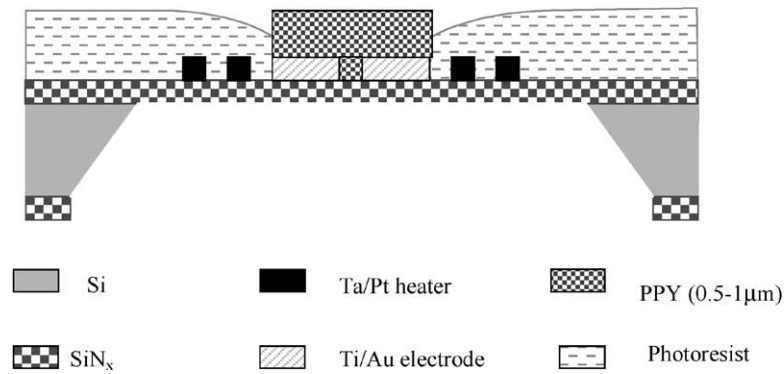*E-mail address:* q.fang@ee.ucl.ac.uk (Q. Fang).

Fig. 1. Schematic of cross-section view of the PPY micro-gas-sensor structure.

software package L-Edit^{TM} (Tanner Tools Ltd.) on a 4 mm × 4 mm die with a 10 μm inter-electrode gap. The geometry of the device is shown in Fig. 2. The fabrication process consisted of a thin $Si_xO_yN_z$ (200 nm) on a 3 in., 350 μm thick, double-side polished silicon (1 0 0) wafer, followed by the thermal evaporation of a 10 nm seeding layer of Ti followed by 100 nm Au. The $Si_xO_yN_z$ was deposited by LPCVD using controlled flow-rate of dichlorosilane, NH_3 and N_2O. The metallisation layers were patterned using a positive resist and conventional UV lithography to form passivation layer. The photoresist was hardbaked for 1 h at 180 °C after developing. Then a timed KOH anisotropic silicon back-etch was used to produce a membrane structure and snap grooves. The membrane structure is composed of a thin silicon oxynitride ($Si_xO_yN_z$) layer on a thin layer of silicon, which was used to strengthen the structure. The 3 in. wafer was then diced using a diamond scriber and glued onto a custom-designed PCB header using a special epoxy resin that was compatible with the electrochemical deposition process of conducting polymers. Next, the four contact pads were ultrasonically wirebonded contact to the gold-plated vertical pin header that was soldered onto the PCB.

2.2. Deposition of the PPY thin films

The PPY thin films were grown across the inter-electrode gaps using a three-electrode electrochemical cell. To electrochemically deposit a PPY thin film the pyrrole monomer (freshly distillate or filtered using ultra fine Al_2O_3 (size <1.0 μm)) is dissolved in an appropriate solvent. A large excess of a species that dissociates to form ions is added to the solution to ensure that the solution is sufficiently ionically conducting and to supply a counter ion, which is used to dope the growing polymer. Two different methods have been employed to deposit PPY, namely, cyclic voltammetry and potentiostatic method. The thickness of the film can be estimated from the total charge passed. The growth across inter-electrode gaps on the micro-gas-sensor designs is achieved by applying the same potential to both electrodes. So that the PPY films grow at equal rates on each electrode and can be across the inter-electrode gap from both sides. In order to ensure uniform and good adhesion PPY film growth on the micro-gas-sensor, it is essential that the Au electrodes be cleaned electrochemically prior to polymer deposition. This process involves cycling the Au electrode potential three times between −0.3 and 1.8 V at a sweep rate
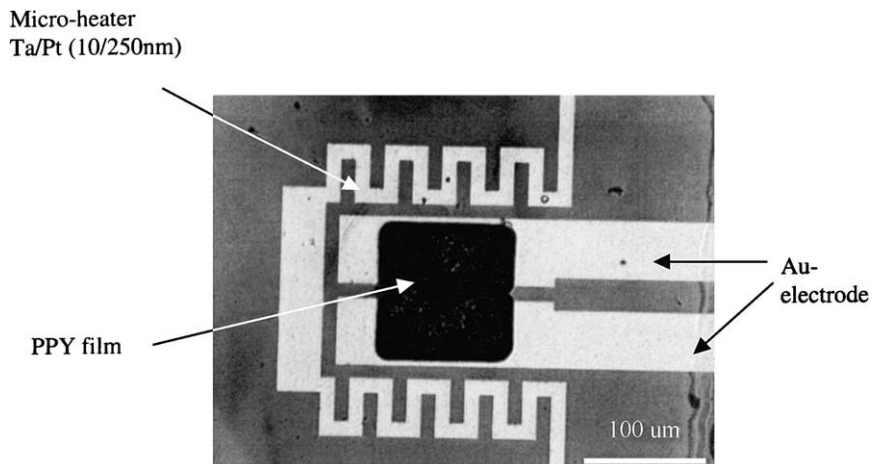

Fig. 2. Geometry of the PPY micro-gas-sensor.

Table 1
Summary of the polymer system and PPY film deposition method used

Sample number	Polymer system	Abbreviation	Deposition method used
MGS-1	Poly(pyrrole)/decane sulfonate	PPY/DSA	Electrochemically
MGS-2	Poly(pyrrole)/1-butane sulfonete	PPY/BSA	Electrochemically
MGS-3	Poly(pyrrole)/FeCl$_3$	PPY/FeCl$_3$	Chemical oxidation
MGS-4	Poly(pyrrole)/methylphosphonic acid	PPY/MPA	Electrochemically

100 mV/s in 1 M sulphuric acid. Full details of the electro-chemistry may be found elsewhere [9–11]. Apart from electrochemical deposition, as a comparison, the PPY thin film from a chemical oxidation with FeCl$_3$ as an oxidant was also employed in the micro-gas-sensor device. This method consists of mixed fresh distillate pyrrole monomer with de-ion water and 0.02 M FeCl$_3$ solution, then spin-coated onto the cleaned inter-electrodes. Table 1 summarises the polymer system and PPY film deposition method used. The counter ions used in PPY films that are at present work being investigated are decane sulfonate (DSA), 1-butane sulfonete (BSA), methylphosphonic acid (MPA) and FeCl$_3$.

2.3. Test system and condition

The response of the micro-gas-sensor with PPY thin films as chemoresistor to ethanol vapour was tested in an auto-mated mass flow system which is described elsewhere [6,12,13]. Previous research shows that the response (output voltage) of the PPY micro-gas-sensor followed in ethanol concentration and generally fell with increasing temperature and humidity, and linear thermal coefficient of ca. -10^{-3} °C has determined by several tests [12]. In this work experiments at a fixed temperature of 30 °C and relative humidity from 10 to 33% were carried out, focusing on the effect of counter ion, morphology of the PPY thin films in the micro-gas-sensors on the response to ethanol vapour.

The four micro-gas-sensors were placed in a sensor chamber, which then put in a dri-block heater (Techne Ltd.). Prior to the tests, the temperature stabilisation time for the micro-gas-sensors at 30 °C was 24 h. An exposure time of 60 min to equivalent of 40% relative humidity at 20 °C was found to be sufficient to establish stable base-line resistance which by the balancing of the devices. After the balancing procedure, micro-gas-sensors were exposed to 2265, 3732, 5331, 11 729, 17 593 and 25 058 ppm of etha-nol in air at 30 °C for four relative humidity. An exposure time of 10 min to a certain concentration of ethanol was followed by 30 min recovery time before the next exposure.

3. Results and discussion

A typical response of PPY/BSA micro-gas-sensor to 2265, 3732, 5331, 11 729, 17 593 and 25 058 ppm of etha-nol in air at 30 °C and 22% RH is shown in Fig. 3. An optimum sensitivity of ca. 5 μV/ppm was found under these
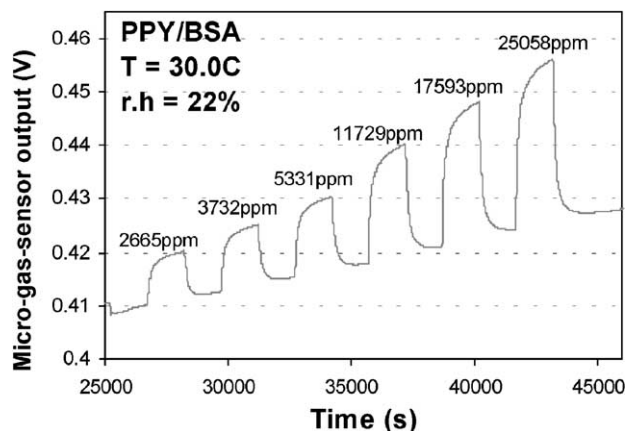
Fig. 3. Typical response of a PPY micro-gas-sensor to pulses of ethanol vapour at a fixed temperature and relative humidity.

conditions, although from the Fig. 3 it is evident that after 10 min of exposure to ethanol the micro-gas-sensor still responding. A higher optimum sensitivity would be achieved if the exposure time was extended, but the auto-mated mass flow system kept the exposure time of 10 min during this work for comparison purposes.

Fig. 4 shows that the change in output voltages (refer-enced to off-set voltage) for PPY micro-gas-sensors with four counter ions when exposed to ethanol. The output voltage of a constant-current I_0 driven resistance is directly proportional to the change of the polymer resistor. This was expected that the response (output voltage) of four types of PPY micro-gas-sensor increased with ethanol concentration
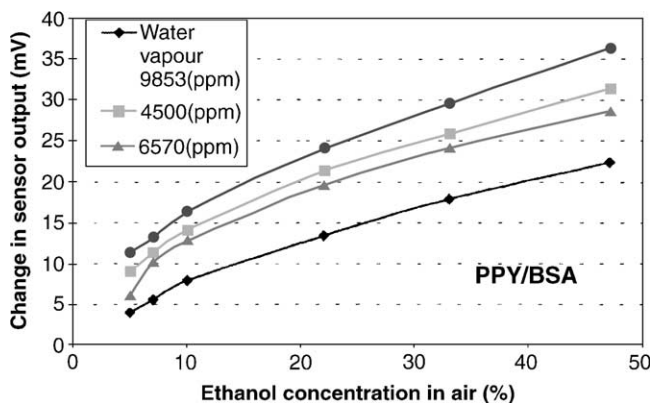
Fig. 4. Ethanol vapour response of micro-gas-sensors with PPY/BSA chemoresistors At 30 °C and relative humidity of 10% (3000 ppm), 15% (4500 ppm), 22% (6570 ppm) and 33% (9853 ppm).
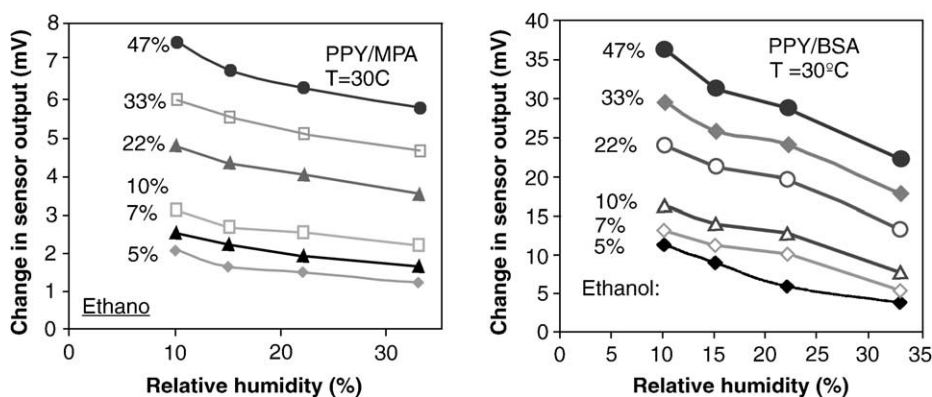
Fig. 5. Effects of relative humidity and ethanol concentration on the response of PPY films with two different counter ions (BSA and MPA) at 30 °C and of 15%.

and generally fell with increasing relative humidity (see Fig. 5). Extensive research carried out on the conducting polymer based gas sensors has shown that the resistance of poly(pyrrole)/pentane sulphonate (PPY/PSA) rises by a few percents when exposed to ethanol vapour. The change in resistance follows the Langmuir adsorption isotherm [9,13,14]. In Fig. 4 our test results show that in the cases of four PPY polymer-based micro-gas-sensors, the change in sensor output did follows the Langmuir adsorption isotherm. When the ethanol concentration in air is smaller than 10%, the output voltage V_{out} is described nearly as a linear relationship with the concentration of ethanol vapour in air, C:

$$V_{out} \not\subset aC \qquad (1)$$

When the ethanol concentration in air is greater than 10%, the output voltage V_{out} is described as follows:

$$V_{out} \not\subset a\left(\frac{bC}{1+bC}\right) \qquad (2)$$

where a and b are constants in the Langmuir model.

However, the change in sensor output of PPY/MPA and PPY/DSA device in ethanol vapour is only a few millivoltages, while that of PPY/BSA and PPY/FeCl$_3$ is from 10 to 30 mV. Furthermore, the sensitivity of device demonstrates a significant different in ethanol vapour for four PPY micro-gas-sensors at 30 °C and relative humidity of 15%, shown in Fig. 6. Langmuir adsorption isotherm is an ideal model based on an assumption of mono-layer of absorbed molecules on the surface of solid. However, some cases involve absorption of multi-molecule-layer, although their absorption behaviours are following the Langmuir adsorption isotherm, such as some meseporous surface. The experimental results from Figs. 4–6 would seem to indicate that morphology of PPY thin film might play an important role for understanding the results and mechanism of response to ethanol vapour. Fig. 7 shows the surface of four PPY thin films used in micro-gas-sensors (1000×). The surface PPY/MPA and PPY/DSA looks smooth and less porous, while surface of PPY/BPA is distributed with many uniform

micro-particle (500 nm) and surface of PPY/FeCl$_3$ is quite porous. It is noted that PPY/FeCl$_3$ thin film is deposited by chemical oxidation and spin-coated, which has less adhesion on the inter-electrode, comparing to the PPY deposited using electrochemical method. A surface test instrument (WYKO NT2000) determined the thickness and surface roughness of the PPY films. Experimental data of four PPY micro-gas-sensors with various counter ions are presented in Table 2. As well known, in its oxidised state PPY exists as a polycation. The charge on the polymer is balanced by doping the film during electrochemical preparation. As a result the electrical characteristics, gas-sensing properties and structure of the final polymer depends on the choice of monomer and on the counter ions [10]. The poor response to ethanol vapour of PPY/MPA and PPY/DSA device in our experiments may be arise from the thicker and smoother surface of these films. PPY/BSA device with the best response to ethanol vapour in our tests has thinner film and its surface roughness is double for that of PPY/DSA, and 15 times bigger than PPY/MPA. Further research into the area of
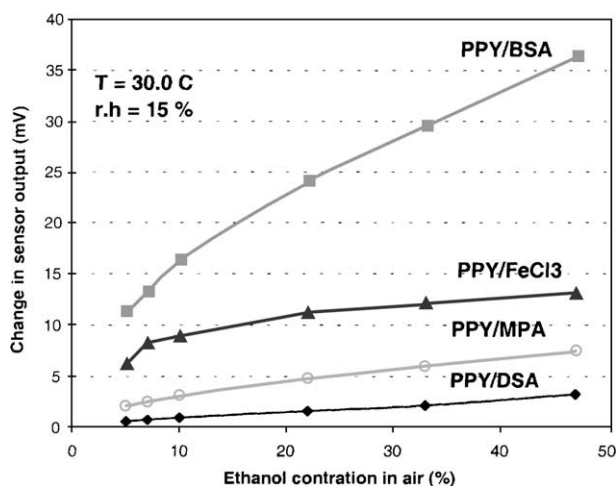

Fig. 6. Effect of ethanol concentration on the response of PPY films with different counter ions (BSA, DSA, MPA and FeCl$_3$) at 30 °C and relative humidity of 15%.
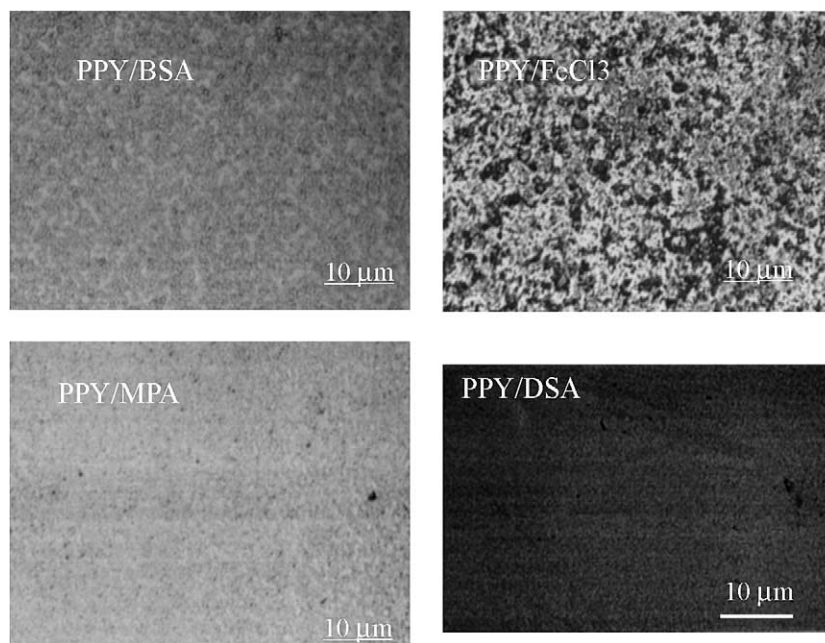
Fig. 7. Surface morphologies of PPY films with different counter ions (BSA, DSA, MPA and FeCl$_3$).

Table 2
Experimental data of micro-gas-sensors with various counter ions

	Sample			
	MGS-1	MGS-2	MGS-3	MGS-4
Chemical composition	PPY/DSA	PPY/BSA	PPY/FeCl$_3$	PPY/MPA
Deposition technique	EC[a]	EC	Chemical oxidation	EC
Thickness (μm)	2.8	1.5	1.8	2.5
Surface roughness, R_a (nm)	592.6	1010.2	723.5	71.8
Surface resistance (kΩ/cm)	2.07	6.20	7.14	1.36
Maximum sensitivity to ethanol vapour (μV/ppm)	0.26	5.01	2.74	0.92

[a] Electrochemical deposition.

morphology effect of conducting polymers on odours or gases response.

The understanding and material characteristics of gas-sensitive such as MOS is at quite an advanced level, however, this is not the case for conducting polymers which have only emerged in the last few years as a gas-sensitive material. Langmuir adsorption isotherm has been empirically shown to be a good description. Researchers to discover a correlation with the empirical models are investigating several possible theoretical mechanisms. The theoretical explanations have envisaged swelling of the polymer, interaction between the gas molecules and the charge carriers on the polymer chain, gas molecule/counter ion interactions and the oxidation or reduction of the polymer by the gas. Bartlett and Gardner [1] have suggested five possible mechanisms, which might contribute to the overall, observed gas-sensitivity of a conducting polymer chemoresistor. The variability in material characteristics caused by varying the deposition conditions required a large number of devices with PPY thin films for characterisation purposes.

Once a better understanding of the gas-sensing mechanisms has been established, the sensor performance can be improved by exploiting the high degree of property control with the electrochemical deposition conditions.

4. Conclusions

Four different electrochemically and chemically prepared resistive conducting polymer micro-gas-sensors have been designed and fabricated. The deposition of the four different PPY thin films and characterisation these films by FTIR, SEM, surface test instrument (WYKO NT2000) and optical microscopy, are reported. The response of four different electrochemically and chemically prepared resistive conducting polymer sensors to ethanol vapour has been investigated. The effect of anions in PPY thin films, thickness and surface roughness of the PPY films on the response of micro-gas-sensors and the effect of ethanol vapour concentration on the response of polymer films have also been

investigated. The experimental results show that a typical sensitivity to ethanol of ca. 5 μV/ppm was observed at 30 °C and the gas sensitivity of the integrated silicon planar microsensor depends on the counter ions in the PPY films, PPY film thickness and surface morphologies. A model is developed relating the effect of the anions in PPY thin films, thickness and surface roughness of the PPY films on the response of micro-gas-sensors, which is compared with experimental results gathered when exposing the sensors to different concentrations of ethanol vapour in air at different relative humidities.

Acknowledgements

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Biographies

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