A Selective Organic Vapour Sensor based on Simultaneous Measurements of Changes of Mass and Resistance of a Poly(pyrrole) Thin Film

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Organic vapours such as primary alcohols are analysed qualitatively as well as quantitatively by simultaneously measuring the mass and resistance changes of a poly(pyrrole) thin film assembled in a gas sensor.

The use of organic conducting compounds as sensitive elements in gas sensors is of current interest. For example, conductive polymers[1-3] and molecular semiconductors[3-5] such as poly(pyrrole) (PP) and phthalocyanines have been investigated for use in chemical sensors, where gas concentrations are monitored by the resistance of the organic conductors used. Resistance change measurement has general application to various organic gases, although it has poor selectivity. A quartz crystal microbalance (QCM) technique is very useful for evaluating a mass increase due to adsorbed or deposited molecules on the quartz substrate.[6,7] Recently, a combination of mass (piezoelectric) and resistance (conductivity) measurements has been used to study the interaction of gas molecules with PP films.[8-11] Piezoelectric and conductivity measurements carried out on the separate polymer films are likely to be inaccurate.

Here, the resistance change (ΔR) and mass change (ΔM) of a PP film prepared on a QCM substrate are monitored simultaneously when the polymer film is exposed to organic vapours. Characterisation of a gas will be made possible by the measurement of $\Delta R/\Delta M$, and the gas concentration by ΔR or ΔM.

The substrate used in the QCM experiments was 1.4 cm diameter 6 MHz AT-cut quartz crystal plate (Leybold Inficon). On the one side of the crystal, a gold film electrode (150 nm) with a gap of 50 μm was prepared by vacuum deposition on the top of the pre-coated Cr layer (15 nm). On the opposite side, a gold film electrode (150 nm) was prepared so as to overlap the gold electrode on the other side (Fig. 1). The mass sensitive region is restricted to the overlap area (0.35 cm^2) between the two opposing gold electrodes. Resistance of the polymer film between the two gold electrodes having a 50 μm gap was measured by the ordinary two-electrode system.

The PP film was deposited electrochemically on the gold gap electrode from degassed MeCN containing 0.05 mol dm^{-3} pyrrole and 0.5 mol dm^{-3} tetraethylammonium tetrafluoroborate so as to cover the gap region.[12] The doped PP film
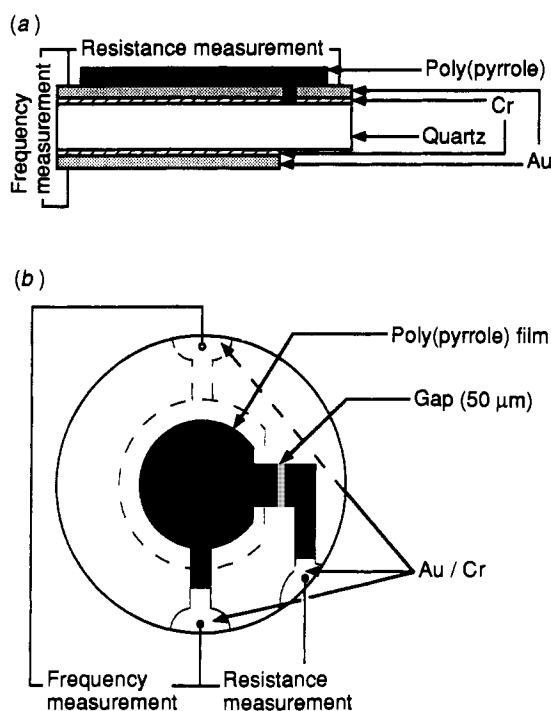

Fig. 1 Schematic illustrations for the gas sensor chip: (a) side view; (b) top view
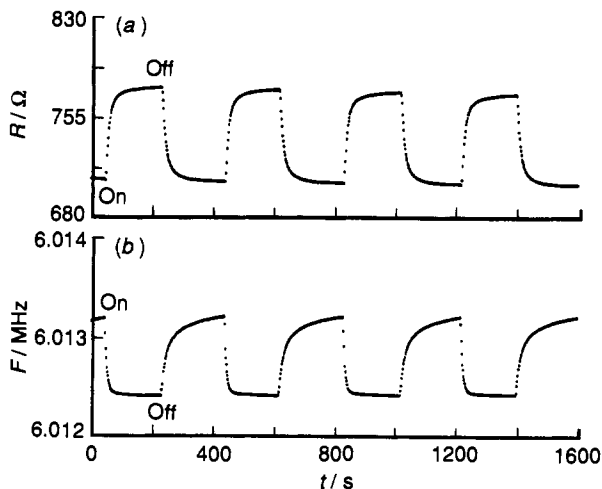

Fig. 2 Simultaneous conductivity and frequency responses of the PP film to MeOH vapour: (a) conductivity change; (b) frequency change
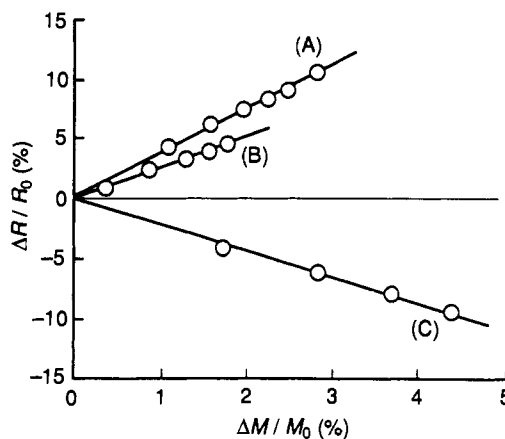

Fig. 3 Plots of the relative resistance change as a function of the relative mass change for the PP film: (A) acetone; (B) MeOH; (C) H$_2$O

Table 1 Sensitivity of the poly(pyrrole) sensor for alcohol vapours

Alcohol	$(\Delta R/R_0)/(\Delta M/M_0)$	$(\Delta R/R_0)/(N_{ad}/M_0)$ per g
MeOH	2.6	1.4×10^{-22}
EtOH	2.2	1.5×10^{-22}
PrOH	1.7	1.7×10^{-22}
BuOH	1.0	1.3×10^{-22}

prepared was washed thoroughly with MeCN, dried for 2 h at 80 °C in a vacuum, and preserved on silcia gel under vacuum. Organic vapours were introduced into the analytical cell (200 cm^3) by injection or using a flow system.

Fig. 2 shows the simultaneous change of conductivity and frequency obtained with the PP film sensor when nitrogen gas half-saturated with methanol or dry pure nitrogen gas was introduced into the cell. The changes are reversible. The time to reach 95% of the plateau response is estimated to be 60 s for the resistance change and 28 s for the frequency change. These response times are almost the same as those reported elsewhere.[11]

Fig. 3 shows typical plots of the relative resistance change ($\Delta R/R_0$) and the relative mass change ($\Delta M/M_0$) observed with the PP film exposed to various concentrations of organic vapours, where R_0 and M_0 are the initial resistance and the initial mass of the polymer film respectively. The relative values are used in order to cancel the discrepancy due to the difference in thickness of the polymer films studied. For all the samples, straight lines passing through the origin are obtained. The slopes ($\Delta R/R_0$)/($\Delta M/M_0$) were 3.7, 2.7 and -2.2 for acetone, MeOH and water, respectively. The quantitative analysis of these vapours can also be readily achieved by the $\Delta R/R_0$ or $\Delta M/M_0$ value. The amount of adsorbed molecules per unit area for the PP film equilibrated with vapours of the same partial pressure was found to increase in the order of MeOH, acetone and H_2O. For example, at a partial pressure of 11 mmHg, $\Delta M/M_0$ values were 0.9, 1.1 and 4.5% for MeOH, acetone and H_2O respectively. It is known that the resistance of the electrochemically synthesized PP film increases when electron-donating molecules are incorporated into the PP film.[13,14] On this basis, the positive slopes for MeOH and acetone indicate their electron-donating properties.

Similar measurements were made with a series of primary alcohols (MeOH, EtOH, propan-1-ol, butan-1-ol) by using the present system (Table 1). The ratio of $\Delta R/R_0$ to N_{ad}/M_0 shows the relative resistance change per adsorbed molecule, where N_{ad} is the number of alcohol molecules adsorbed on the PP film. The ($\Delta R/R_0$)/(N_{ad}/M_0) values for the primary alcohols examined are in good agreement with each other, whereas ($\Delta R/R_0$)/($\Delta M/M_0$) decreases with the increase in molecular mass of the alcohol. This implies that one OH group gives rise to a similar effect on the conductivity of the PP film. In other words, the OH group effect is almost independent of the alkyl groups in the alcohol molecules.

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