

Gas and vapour effects on the resistance fluctuation spectra of conducting polymer thin-film resistors

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Abstract

The effects of various vapours on the power spectrum of the resistance fluctuation of polypyrrole thin-film resistors were studied. An ultra-low noise amplifier and current source were built in order to detect the very low signal and bias the resistors. The samples were obtained by means of chemical vapour deposition on to oxidizing precursors. The method was successfully extended to *n*-methylpyrrole and thiophene polymerization.

Introduction

Conducting polymers with aromatic and hetero-aromatic units raised considerable interest in the last decade, mainly for their stability and ease of preparation. These materials exhibit promising properties suggesting applications in many fields [1-3].

Recently, it was found that the resistivity of many conducting polymers in this class is significantly influenced by the exposure to various gaseous chemical species [4-6]. In most cases, the phenomenon was characterized by good room temperature reversibility. Studies on this topic revealed that the response of conducting polymers to different gases is generally selective and varies from one polymer to another. On this basis, arrays of different conducting polymers were proposed as sensors capable of recognizing the presence of different gases and of discriminating between them [7].

The subject of this paper is to investigate the effects of exposure to gases on the resistance fluctuation power spectral density of polypyrrole (PPy) thin film resistors. The polymer films were grown by a chemical vapour deposition technique [8] which yielded good results, also for *n*-methylpyrrole and polythiophene polymerization. An advantage of this technique with respect to electrochemical procedures [9] is the possibility of defining the geometry of the films during deposition with micrometric resolution.

Resistance fluctuations are known to occur in most conducting media, with a power spectrum nearly proportional to $1/f^\gamma$ where f is the frequency and γ an

exponent in the range of 0.5 to 2. The voltage noise produced across resistors affected by resistance fluctuation is generally referred to as $1/f$ or 'flicker' noise. Reviews on this argument are given in refs. 10 and 11.

Flicker noise has been extensively studied in many solids [11, 12], including organic conductors [13, 14] in order to obtain information on charge transport-related phenomena. While a general interpretation of $1/f$ noise is still missing, trapping and detrapping of charge carriers seem to play a dominant role in many conductors [10]. Adsorption of gases on to the surface or into the bulk of conducting polymers is likely to affect the noise spectra through introduction or neutralization of electronic states, resulting in modifications of the trapping-rate distribution. This mechanism is not necessarily related to the cause of average resistance variations as supported by the experiments described in this paper.

Experimental

Conducting polymer thin films were grown by chemical vapour deposition (CVD) following an upgraded version of the technique described in ref. 8. The method consisted in introducing an oxidizing precursor into a Pyrex flask evacuated to about 10 Pa by a mechanical pump and then saturated with the monomer and water vapour at room temperature. Previous applications of this technique were limited to pyrrole polymerization [4, 8, 15]. Preliminary experiments dedicated to the deposition of poly(*n*-methylpyrrole) (Met-PPy) and polythiophene thin films (PTH) yielded encouraging results.

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Copper, gold and palladium chlorides were successfully used as precursors. Precursor preparation was accomplished by direct reaction of chlorine saturated with water vapour at room temperature with metal films (Au, Cu or Pd, 200–400 nm thick) evaporated on to oxidized silicon substrates. To improve adhesion, substrate temperature is set to 200 °C during evaporation. Patterning of the polymer films was possible by defining the geometry of the metal films with optical lithography. Some of the problems can be encountered during the chlorination step owing to the adsorption of water vapour, necessary to the reaction, on to the metal chloride causing loss of the pattern. This was found to be the major limiting factor to geometrical resolution especially when dealing with very hygroscopic metal salts (PdCl_2 , AuCl_3).

Typical polymerization times were in the range of 3 to 15 hours. Polymerization occurred according to the precursor geometry. Finally, the samples were rinsed in ethanol for 2 h and then dried in nitrogen.

The CVD technique was improved with respect to earlier versions [8, 15] by substituting the chemical procedure, previously adopted for chlorine production, with an electrolytic cell in order to achieve better reproducibility. A particular thermal cycle was also introduced, consisting in heating the samples to 80 °C for the first 5 min of polymerization and then decreasing the temperature to 35 °C; the latter temperature is maintained for the rest of deposition time. The initial heating was aimed to increase the polymerization rate, which was found to remain high even if the precursors are cooled to a temperature at which humidity and residual oxygen do not cause polymer degradation.

For the realization of samples dedicated to resistance fluctuation measurements, four probes of polymer structures were deposited; copper pads were evaporated through a metal mask in order to contact the polymer thin films. The samples were then encapsulated into metal cases and connections from the pads to the pins are accomplished with a wedge-bonding machine. A micrograph of the final structure is shown in Fig. 1.

The resistance fluctuations were characterized by biasing the samples with a constant current and measuring the power spectral density (PSD) of the fluctuation of the voltage across the potentiometric terminals. The system used for the measurements is schematically described in Fig. 2. The circuit is composed of the operational amplifier IC1 (TCL2201), the resistor R and the battery E . It is a current source supplying current $I_0 = E/R$ to the sample.

The current is used to transform resistance fluctuations into voltage fluctuations across the potentiometric contacts (V1 and V2 in Fig. 2). The latter constitutes the signal which is fed to an ultra-low noise amplifier (ULNA). Signal amplification is required as voltage

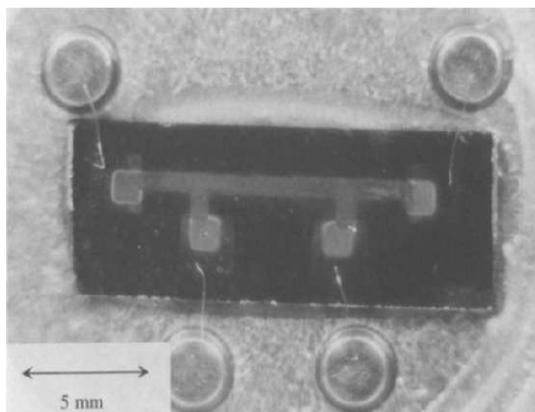


Fig. 1. Microphotograph of a polypyrrole thin-film resistor. The copper pads with bonding are visible.

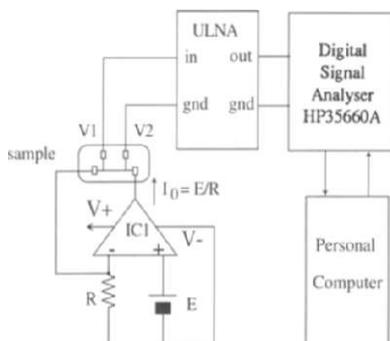


Fig. 2. Block diagram of the experimental apparatus used for the resistance fluctuation measurements. The current source consisting of the operational amplifier IC1 (TCL2201), the battery E and the low noise resistor R supplies the current bias $I_0 = E/R$ to the sample. The ULNA is an ultra-low noise amplifier.

fluctuations in PPy films were too small to permit direct processing by commercial signal analysers. The ULNA was devised to provide 67 dB amplification with very low noise at low frequencies. The low frequency rolloff was set at 7 mHz by internal a.c. coupling in order to discard the d.c. component of the signal. The structure and performances of the amplifier were similar to those described in ref. 16. The output of the ULNA is fed to the HP 35660 digital signal analyser, controlled by a personal computer. The amplifier and the current generator had separate power supplies consisting of lead/acid sealed batteries; both were enclosed in a copper box and placed into a metal box to provide electrical and magnetical shielding. The bias current and then the d.c. voltage across the sample were established by giving an appropriate value to the low noise resistor R .

The background noise of the system is the sum of two contributions: (i) Johnson noise from resistor R

and the sample, and (ii) noise from the current generator.

The spectral density of the total background noise, S_N , is given by:

$$S_N(f) = 4kTR_{4C} \left(\frac{R_{4C}}{R} + \frac{R_v}{R_{4C}} \right) + S_1(f) \frac{V_0^2}{E^2} \quad (1)$$

where R_{4C} is the resistance of the sample measured by the four probes procedure, R_v the resistance measured between the potentiometric contacts (including the resistance of contacts), V_0 the d.c. component of the voltage across the potentiometric contacts of the sample, $S_1(f)$ the input noise voltage spectral density of IC1, T the absolute temperature and k the Boltzmann constant. The contribution of the background noise of the ULNA was found to be negligible in any experimental condition.

$S_1(f)$ was measured and the result was utilized to implement a procedure on the personal computer for the subtraction of the background noise from the measured data using eqn. (1). The procedure yielded reliable results in frequency intervals where, in the worst case, the signal was at least not smaller than the background noise.

Results

Polypyrrole and poly(*n*-methylpolypyrrole) thin films were grown from copper, palladium and gold chloride precursors. Thiophene polymerization could be accomplished only from gold precursors because of the higher oxidation potential of the monomer. The thickness of the films, measured with a profilometer, ranged from 1 to 4 μm . PPy-film conductivity was in the interval $1\text{--}10 \Omega^{-1} \text{cm}^{-1}$; results of three orders of magnitude lower were found for Met-PPy and PTH films.

Thin metal lines with width in descending order were employed for precursor preparation in order to find the geometrical resolution limit of the technique. Preliminary experiments demonstrated that PPy lines with a width down to 4 μm can be obtained starting from copper thin films. The use of the electrochemical cell for chlorine production permitted a better control of water absorption on to the precursors, thus improving geometrical resolution. This procedure was not sufficient to overcome gold and palladium chloride hygroscopicity. Better results could be achieved by means of granular metal precursors as described in refs. 4 and 15.

Ageing and resistance fluctuation experiments were performed on PPy samples with the geometry of Fig. 1. All the samples were grown from copper chloride precursors. Figure 3 shows the resistance increase after deposition exhibited by two samples maintained in

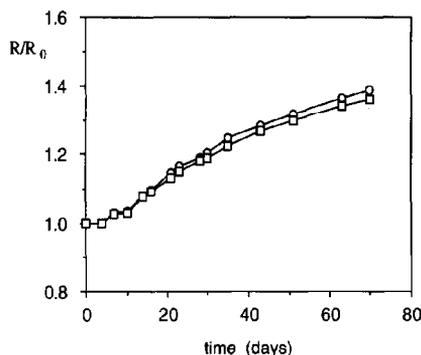


Fig. 3. Plot of the normalized resistance of two PPy thin-film resistors as a function of time after deposition. The two samples were few millimeters apart on the same substrate and were encapsulated in the same case.

nitrogen at room temperature. The resistances are normalized to the initial values. The two samples were a few millimeters apart on the same substrate and encapsulated in the same case. It should be observed that the two plots have a quite similar behaviour. This property could be exploited to overcome the problem of ageing in gas-sensor application by associating a reference duplicate to any active element kept in a controlled atmosphere.

The resistance fluctuation measurements were devoted to investigating the effects of the exposure to the vapour of several organic liquids. Each experiment consisted in measuring the power spectra in two different conditions, namely in dry nitrogen and in nitrogen saturated with water vapour under test. In the case of significant response the spectrum in dry nitrogen after exposure was also measured in order to test reversibility. The frequency range of 0.015 to 200 Hz was investigated. Results in the range of 0.015 to 6 Hz are presented. In this frequency interval the signal to background noise ratio was still high enough to permit a reliable signal recovering by the procedure described in the previous section.

Organic vapours cause significant resistance variations in PPy resistors [4]. This phenomenon was monitored by reading the voltage across the sample through a digital multimeter. The noise measurements were started only when the voltage, i.e., the resistance, was stable in order to rule out interference due to resistance drift. The biasing current was chosen so that the initial d.c. voltage was 2 V; the current was then maintained constant for the whole experiment.

In Fig. 4 the results of the exposure to ethanol are presented. The solid line, curve (1), is the spectrum before exposure. Large variations in shape and magnitude can be observed in the spectra during exposure to saturated ethanol vapours, represented by curves (2) and (3) taken 1 and 2 h after the commencement of the exposure, respectively. Reversibility was not

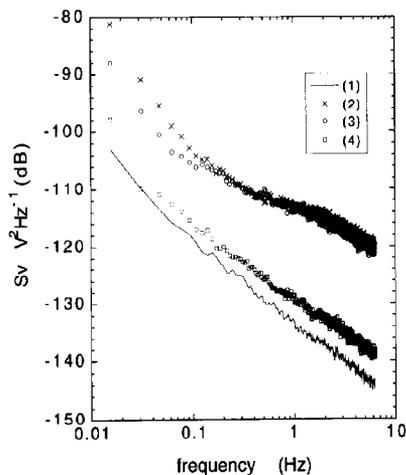


Fig. 4. Spectral densities of the voltage fluctuations across a constant-current biased PPy sample. Curve (1) is measured in dry nitrogen, curves (2) and (3) are measured in nitrogen saturated with ethanol vapours, 1 and 2 h after beginning of exposure, respectively. Curve (4) was measured in nitrogen 15 h after the end of exposure to ethanol.

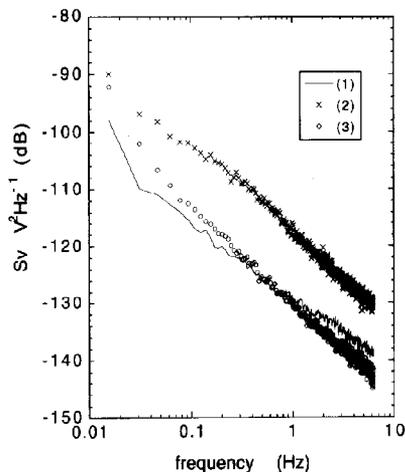


Fig. 5. Spectral densities of the voltage fluctuations across a constant-current biased PPy sample in (1) pure nitrogen, (2) nitrogen saturated with methanol vapours and (3) in nitrogen 15 h after the end of exposure to methanol.

perfect, as shown by curve (4) measured in dry nitrogen 15 h after the end of exposure.

Smaller response but better reversibility were found with methanol vapours. In Fig. 5, the solid line (1) and curve (3) were obtained in dry nitrogen before and after exposure to methanol, respectively. Curve (2) is taken in nitrogen saturated with methanol. A singular change in the slope of the spectrum can be observed as a permanent result of exposure.

Experiments carried out with acetone, isopropanol and water vapour showed significantly minor response.

The results are summarized in Fig. 6 where solid lines represent the spectra before exposure and data plots those during exposure.

The meaning of Fig. 6 is the following. Spectra relative to the same test (for instance the two spectra measured before and during exposure to acetone) were translated in terms of the same amount along the y-axis. This was done in order to combine the results of three different experiments in the same Figure. If the spectra were not translated, they would have been superimposed making the picture difficult to understand. Therefore, no comparison can be made between the three spectra of Fig. 6 measured in pure nitrogen. Meaningful comparisons are possible only between each couple of spectra, that is between each spectrum in nitrogen (solid lines) and the corresponding spectrum during exposure (data plots). Response to water vapour (33 %) and saturated acetone vapour were apparently negligible, while a slope modification can be detected as a result of exposure to isopropanol.

Except for the test with water vapour, all results of Figs. 4 to 6 regard the same sample. Experiments performed on other samples substantially confirm the typical responses presented in this work.

Variations of the d.c. voltage across the sample during the experiments never exceeded 20% of the initial value (2 V). Effects on the spectrum can be estimated considering that the PSD of voltage noise caused by resistance fluctuations is proportional to the square of the d.c. voltage [10]. Therefore, increases in d.c. voltages

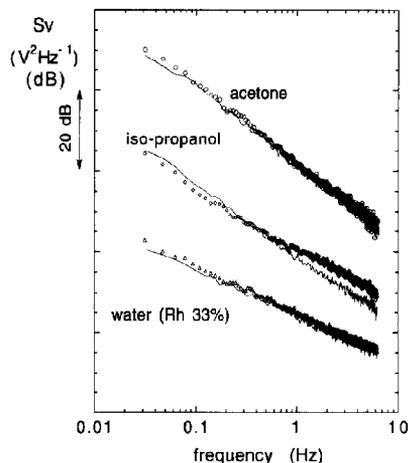


Fig. 6. Effects of exposure to acetone, water (33%) and isopropanol vapours on the spectral densities of the voltage fluctuations across constant-current PPy samples. The spectra in dry nitrogen before exposure are represented by solid lines; data dots represent the spectra during exposure to the vapour under test. Curves relative to the same experiments are translated in terms of the same amount along the y-axis to improve clarity, therefore comparisons of the curves can be made only between each couple of spectra, i.e., before and during exposure to the gas.

can account only for a small part (<1.6 dB) of the noise magnitude increase induced by ethanol and methanol vapours. In addition, resistance and, consequently, d.c. voltage increase exhibited upon exposure to water vapour [4] did not result in significant increase in the spectral density.

It is interesting to observe that the response of resistance fluctuation power spectrum is not a replica of that of the average resistance [4, 6]. Large response to ethanol and methanol were found in both cases, whereas insensitivity to acetone and water vapours was a peculiar characteristic of the noise measurements. Therefore, combination of average resistance measurements with resistance fluctuation measurements would permit one to obtain more information from the same sensor about the interacting chemical species.

Conclusions

A previously described chemical vapour deposition technique for PPy thin-film growth was improved and extended to the polymerization of n-methylpyrrole and thiophene monomers. The method proved to be suitable for the deposition of narrow PPy lines with a width down to 4 μm . PPy resistors designed for four probes resistance measurements were fabricated in order to characterize the influence of gases on the resistance fluctuation spectral density of PPy. Experiments with various vapours revealed that the magnitude of resistance fluctuations power spectra magnitude increases significantly as a result of exposure to ethanol and methanol vapours. Minor or negligible changes in the spectra were caused by acetone, water and isopropanol vapours even when significant variations of the average resistance were detected. Therefore, fluctuations measurements to be combined with simple resistance monitoring could improve gas recognition capability of conducting polymer sensors.

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