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Vapour and gas sensing by noise measurements on polymeri(balanced bridge microstructures

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Abstract

A procedure for depositing and patterning thin polypyrrole films is described. Geometrical resolution tests are pres(showing that lines with submicrometric width can be produced by means of this technique. Noise measurements perfo on balanced polypyrrole thin-film microbridges are presented. The measurements are aimed to study the effects of exp(to gaseous species on the spectral density of the resistance fluctuations. The use of balanced structures permits the e: of d.c. voltage transients and drift on the measured power spectra to be reduced.

Keywords: Gas sensors; Microstructures; Polymers; Vapour sensors

1. Introduction

In the field of chemical sensing of gases and vapours, conducting polymers may play a relevant role due to their original and robust transducing mechanisms. In fact many species of conducting polymers were found to exhibit conductivity variations when exposed to gases or vapours [1–3]. This phenomenon suggested possible applications to new gas sensors for industrial, biomedical and environmental control. Recently arrays of different polymers were proposed as devices capable of discriminating different gaseous mixtures [4,5].

However, in order to propose conducting polymer-based sensors, two key problems should be addressed: (i) the immunity of the transduced signal to possible interferences (e.g., thermal variations); (ii) the preparation of the material in specific patterns with procedures fully compatible with microelectronic industrial processes in view of the design of integrated silicon–polymer devices.

In a previous paper, we proposed [6] a technological approach to the chemical deposition of conducting polymers from the vapor phase which is silicon compatible and, after successive improvements, now permits the realization of micrometric structures.

As far as the transduced signal is concerned, average resistance variations, induced by changes of gas and vapor concentrations, are mostly used. Recently we presented experiments performed on polypyrrole (PPy) thin-film resistors [7], demonstrating that exposure to vapours also causes modifications in the power spectral density of the random resistance fluctuations. Vap induced variations of the spectra were reversible independent of the corresponding average resist variations.

In this paper resistance-fluctuation measuremen polypyrrole balanced bridge structures are descri The use of balanced bridges instead of single resi allowed us to reduce the effects of the d.c. vol transients on the measured spectra, which, there included only contributions from random fluctuat

The bridges were realized by patterning PPy films grown by means of a chemical-vapour depos technique.

2. Sample preparation

Polypyrrole thin films of thickness from 0.4 to 2 were deposited onto oxidized silicon substrates ι a procedure similar to that described in Refs. [6,7 a first step, copper thin films were evaporated o: sputtered onto the substrates and patterning of films was performed by means of UV or electron-b lithography. Then, the copper films were convert $CuCl_2$ thin films by exposure to a mixture of chl(and water vapour. During this step, the $CuCl_2$ formed maintained the original geometry of the co films. The polymer deposition was accomplishe introducing the substrates with the precursors ir reaction chamber saturated with monomer and eth vapours. Typical polymerization times were of the c

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of 15 h. In order to eliminate any residual amount of copper salt, the films were rinsed in ethanol for several hours and then dried in nitrogen.

The procedure used to convert copper films into $CuCl_2$ films was improved to obtain higher resolution and reproducibility. Instead of carrying out the reaction at room temperature as in Ref. [7], the chlorine/water-vapour mixture was heated to 200 °C before introducing the copper films into the reactor. This completely eliminated the problem of the hygroscopicity of the forming $CuCl_2$ films. It was found that 30 min were sufficient to convert copper films of thickness up to 0.2 μm; slow cooling of the samples before introducing them into the polymerization chamber was needed to avoid cracking of the films.

In order to check the resolution limit of the patterning procedure, electron-beam lithography (and lift off) was used to define copper lines with decreasing width from 4 to 0.5 μm. The above-described steps of chlorine exposure and pyrrole polymerization were performed on these test patterns. A typical result is shown in Fig. 1, where a scanning electron micrograph is presented: the resolution limit of the polypyrrole line we obtained was 0.8 μm. The reproducibility of the test was satisfactory, so the method was exploited to deposit more complicated polypyrrole structures. The sensing structures we deposited were balanced resistor bridges with dimensions ranging from 800 μm$\times$800 μm to 100 μm$\times$100 μm. Fig. 2 shows polymeric bridges with different magnifications.

To complete the device structure, contacts to the polypyrrole lines connected to the four vertices of the bridge were accomplished by means of evaporated copper pads, which were then wedge bonded to the terminals of a standard IC package.

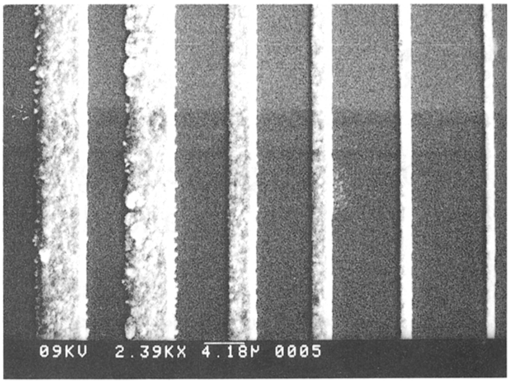

Fig. 1. Scanning electron micrograph of a series of polypyrrole lines ranging from 5 to 0.8 μm in width.

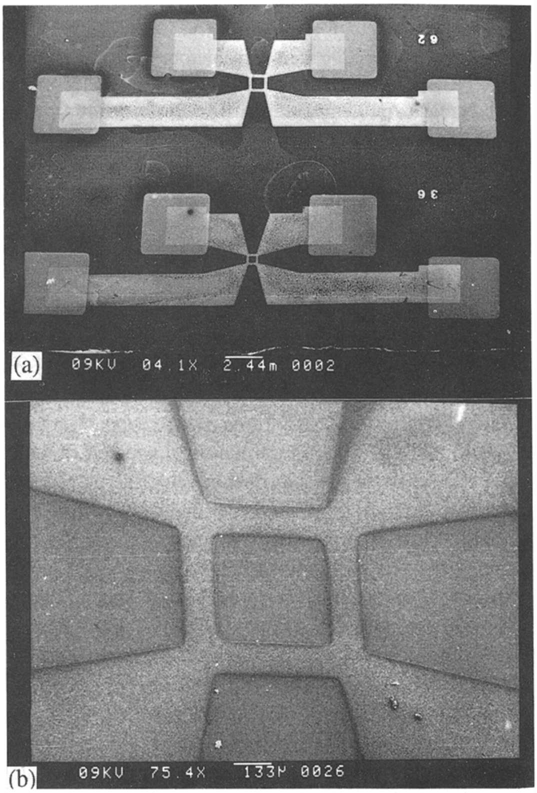

Fig. 2. Scanning electron micrographs of two microbridge structures (upper picture) and detail of the bridge (lower picture).

3. Results and discussion

Noise measurements are typically performed by biasing two or four resistor terminals with a constant current and measuring the fluctuations of the voltage across the resistors themselves. Voltage fluctuations are characterized through their power spectral density (PSD). In macroscopic resistors, voltage fluctuations contain two components, namely the Johnson noise (dependent only on the resistance of the sample) and the excess noise. The latter can be considered as the result of random resistance fluctuations around the average resistance. The excess noise is present in all conductors and shows a strong dependence on the type of material. A detailed study of noise in polypyrrole resistors is given in Ref. [9]. Effects of the exposure to gaseous chemical species on the excess noise were reported for different conductors [10,11]. As for polypyrrole resistors, we found that some organic vapours such as methanol and ethanol cause large and reversible changes in the noise spectra [7].

The need to separate the excess noise from the Johnson noise leads to performing the measurements at low frequency where the excess noise is higher [8]. The unexpectedly low noise level found in polypyrrole resistors forced us to focus on the range 0.03–6.25 Hz. In this frequency interval, average resistance variations due to temperature variations, aging-induced drift and exposure to gases generate d.c. voltage changes that cannot be distinguished from the required signal.

The particular structure of the samples described in this work was devised to permit accurate low-frequency noise measurements even in the presence of these sources of interference.

In fact, in a balanced structure the effects of average resistance variations (affecting all the elements of the bridge in approximately the same way) cancel each other, while random resistance fluctuations, because of their local nature, unbalance the bridge, producing output voltage fluctuations.

The block diagram of the apparatus used to perform the resistance-fluctuation measurements is shown in Fig. 3. The low-noise current source and the ultra-low-noise amplifier (ULNA) were the same as in Ref. [7]. The current was fed to a pair of opposite bridge vertices and the voltage fluctuations were detected at the other pair of vertices. The amplified signal was fed to a digital signal analyser (HP35660A).

The *I–V* dependence of the polypyrrole samples was linear in the whole range of imposed current density. This permitted the bridges to be modelled by means of a simple resistor network. In Fig. 4 the equivalent electrical circuit of the samples is shown; the four resistors on the arms of the bridge were considered to be identical and their resistance was indicated with *R*, whereas *R*A1, *R*A2, *R*V1 and *R*V2 represent the resistance of the connections. Each resistor can be considered as a series of an ideal (noise-free) resistor and a noise voltage generator, accounting for thermal noise (Johnson noise) and for the excess noise produced by random resistance fluctuations [8].

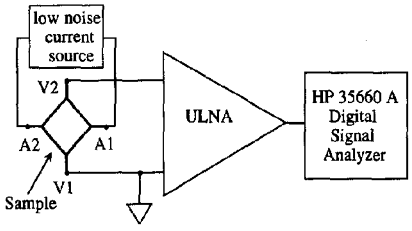

Fig. 3. Block diagram of the measurement system.

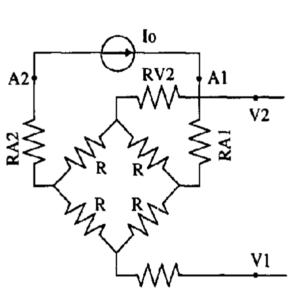

Fig. 4. Equivalent electrical circuit of the samples.

It can easily be shown that, if the noise generators of all the resistors are independent, the PSD of the output voltage (terminals V1, V2) $S_{v0}(f)$ is given by

$$S_{v0}(f) = S_{vR}(f) + 4k_b T R_V \quad (1)$$

where $S_{vR}(f)$ is the PSD of the excess noise voltage generator of one of the four resistors of the bridge (supposed to be identical), and $4k_b T R_V$ is the thermal noise associated with the resistance $R_V = R + R\mathrm{V1} + R\mathrm{V2}$ measured between the output terminals V1, V2. According to Eq. (1), the PSD of the excess noise measured between terminals V1 and V2 is the same as that generated by each arm of the bridge. Eq. (1) was exploited to set up an automatic procedure on the computer for extracting the required quantity, S_{vR}, from the power spectrum of the voltage measured at the output of the bridge.

In Fig. 5 the transient of the output d.c. voltage during exposure to methanol vapour is presented for a polypyrrole bridge and for a polypyrrole resistor similar to those described in Ref. [7]. The bias currents were such that the initial d.c. voltage across the resistor and each arm of the bridge were the same (3.8 V). As shown in Fig. 5, the bridge structure proved to be very effective in reducing the drift of the d.c. voltage. It should be observed that such a good result could be obtained thanks to the reliable deposition procedure, which permitted us to build really balanced polypyrrole bridges. This allowed us to assert that the measured noise spectral density variations induced by exposure to gases were due only to variations of the excess noise. The results of Ref. [7] were reliably confirmed by means of the bridge structures. In Fig. 6 the noise spectral density measured in nitrogen saturated with methanol (solid line) is compared with the spectra in dry nitrogen measured before (dotted line) and after (dashed line) exposure to the vapour. The response was marked by good reversibility and sensitivity. Exposure to vapours of iso-propanol, butanol, acetic acid, acetonitrile and

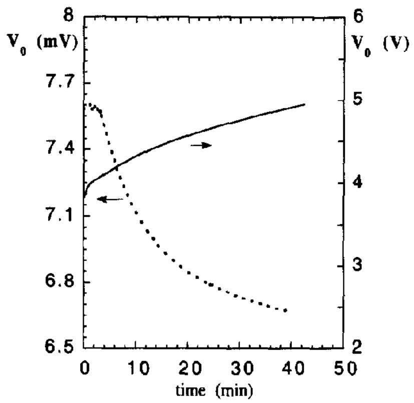

Fig. 5. Transient of the d.c. voltage after exposure to methanol for a bridge (dotted line) and a resistor (solid line).

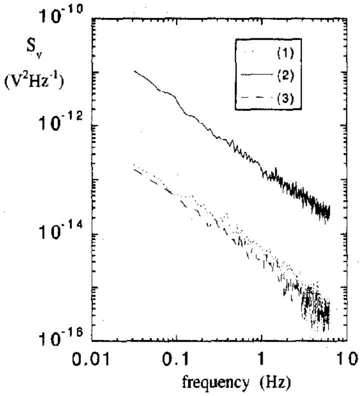

Fig. 6. Spectra measured in pure N_2 (1), N_2 saturated with methanol (2) and pure N_2 after the exposure to methanol.

acetone did not affect the spectra, though it caused average resistance variations. This suggests that resistance-fluctuation measurements could be employed in addition to average resistance monitoring in order to improve the selectivity of polypyrrole-based gas sensors.

4. Conclusions

The patterning technique we previously proposed was upgraded in order to improve the geometrical resolution. Test patterns with lines down to 0.8 μm wide were obtained with good reproducibility. This method of polypyrrole deposition is suitable for building more complicated sensing-oriented structures as balanced microbridges. Measurements of gas/vapour-induced variations of the excess noise power spectrum were performed on these devices, confirming the good selectivity and reversibility already found using single resistors [7]. The initial transients of the output d.c. component (after gas/vapour concentration changes), during which it is impossible to perform noise measurements, were drastically reduced using microbridge structures. The balanced structure of the samples was also effective in reducing effects due to aging and temperature variations.

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