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Ammonia gas sensors based on polypyrrole films: Influence of electrodeposition parameters

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ABSTRACT

A gas sensor consisting in polypyrrole films electrochemically deposited on microelectrodes arrays was fabricated using silicon microtechnologies. Polypyrrole was electrodeposited on platinum microelectrodes using four different electrodeposition potentials, five counter-ions and three salt concentrations to assess the effects of these parameters on the sensing properties of polypyrrole films. The change in conductance of thin polymer layers, due to adsorption of ammonia gas, was used as a sensor signal. The behaviors of the polymer-based gas sensors, including response time, response amplitude, reproducibility and reversibility, to various ammonia gas concentrations ranging from 1 to 100 ppm were investigated. The experimental results showed that these ammonia gas sensors were efficient since they were sensitive to ammonia, and since their response was fast and reproducible at room temperature. The most efficient ammonia gas sensor was obtained with a 248 nm-thick polypyrrole film electrosynthesized from 0.1 M pyrrole and 0.1 M $LiClO_4$ under an electrodeposition potential of +2.0 V/SCE.

1. Introduction

Since polyacetylene was first shown to have high electrical conductivities when properly doped [1,2], π-conjugated polymers have been studied extensively, and subsequently, used in various applications such as: field effect transistors [3,4], solar cells [5,6], electrocatalysis [7,8], protection against corrosion [9,10], (bio)sensors [11–13] or cell culture [14–17]. Among the various conducting polymers, polypyrrole (PPy) stays one of the most studied because of its easy deposition from aqueous and non-aqueous media, its adherence to many types of substrates, its high electronical conductivity and its stability in air and aqueous media. The simplicity of preparation and the possibility to control experimental conditions by electrochemical techniques make it the most employed way. Moreover, it is now well-known that many chemical or physical properties of electrodeposited polypyrrole can be strongly varied by modifying the electropolymerization parameters including: solvent [18–21], current density [22], pH [23], temperature [24], pyrrole concentration [25–27], electrodeposition potential [26–28], counter-ion [19,26,27,29–31] and its concentration [32]. Furthermore, it has already been demonstrated that electrochemical polymerization conditions, particularly counter-ion type, can strongly affect the conductivity of polypyrrole films [27,30]. Indeed, large organic counter-ions induce higher conductivity in PPy films, because they are more efficient space fillers and produce isotropic polymers with higher crystallinity than those incorporating small inorganic species [27,30]. This is of importance since the initial conductivity of the polymer film is supposed to impact on the gas sensitivity of the polymer film to ammonia gas [33]. The morphological features of polypyrrole films also strongly modify their properties. For example, polypyrrole films prepared by Kaynak [32], in solutions with high concentration of *p*-toluenesulfonic acid, exhibited a higher roughness than those elaborated in less concentrated solutions. The nature of the counter-ions can also influence the polypyrrole's film morphology as shown by Fang et al. [34]. Indeed, they observed that the use of different counter-ions led to polymer films with very different roughness and morphology. Furthermore, both roughness and morphology of the films greatly influenced the response of the polypyrrole films to ethanol vapor when used as sensor's sensitive layer. Our research group has also studied the effect of counter-ion's type, pyrrole concentration and electrodeposition potential on the conductivity [27] and morphological features of polypyrrole films [26]. Concerning the conductivity [27], it was shown that: (i) increasing the pyrrole concentration increased the film conductivity, (ii) the highest conductivity was obtained for an electrodeposition potential similar to pyrrole oxidation peak's, (iii) biggest counter-ions, such as *p*-toluenesulfonate or

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1-naphthalenesulfonate, led to the highest conductivity. Concerning the morphological features [26], the roughness of the films was proved to be very dependent on the counter-ion type since the biggest anions led to very flat surfaces having a small roughness and a high homogeneity. On the contrary, the smallest anions tested or the use of a high electrodeposition potential led to high roughness. Since the electropolymerization conditions strongly influence the properties of polypyrrole films, it can be supposed that they also influence the gas detection efficiency of the polymer films, even if the influence of polymerization parameters on the gas detection efficiency of conducting polymer-based sensors has received little attention in the literature until now.

In this context, the present work aims at investigating the influence of the electropolymerization parameters on the gas detection efficiency of polypyrrole-based sensors and at studying the correlation between conductivity or morphological features of the polypyrrole films and their gas detection efficiency. That is why polypyrrole films were electropolymerized at electrodeposition potentials varying from +0.7 to +2.0 V/SCE, with 5 counter-ions of different sizes: *p*-toluenesulfonate (TsO^-), naphtalenesulfonate (NS^-), nitrate, tetrafluoroborate, and perchlorate anions, and at salt concentration varying from 0.01 to 0.5 M. These various polypyrrole films were electrodeposited on microsystems fabricated using silicon microtechnology. The so-obtained gas sensors consisted of platinum microstructured electrode arrays. The polymer films were deposited on these microelectrodes and also across the insulating gap separating the microelectrodes of the sensor since the insulating gap between the neighboring electrodes was close enough, around 4 μm, to allow the polymer film to coat the insulated gap and to connect microelectrodes. Then, these polypyrrole-based chemiresistors were tested for ammonia gas sensing. In particular, their response, in terms of conductance changes when exposed to different ammonia concentration, was studied.

2. Experimental

2.1. Microsystems fabrication

The elaboration of the gas sensors began with the microsystems fabrication using lift-off process that consists in a photolithography followed by a cathodic sputtering to obtain platinum patterns deposited on 4″ silicon wafers. To make the desired pattern, consisted of two interdigitated microelectrodes combs, it was necessary to fabricate a Cr/Glass mask for lithography. This mask was designed using Cadence conception software, and it was fabricated using a Heidelberg DWL 250 optical pattern generator. Silicon wafers used in this study were 100-oriented, 500 μm thick, p-type doped and had a resistivity of 1–10 $\Omega\,cm^{-1}$. They were thermally wet-oxidized, at 1200 °C in water vapor flux during 12 h, in order to produce a 1.4 μm thick SiO_2 layer. Wafers and mask were precleaned with a solution containing 50 mL of H_2SO_4 and 30 mL of H_2O_2. This step was necessary to remove organic residues at the surface in order to start process in better conditions. Then, the wafer was dried and placed on a hot plate (Prazitherm) for 10 min at 120 °C. Next, a layer of negative photoresist (AZ 5214, from Clariant) was deposited by spin-coating thanks to an RC8-Karlsuss spin coater (30 s at a rotation speed of 3000 rpm). Wafer was again placed on the hot plate for 150 s at 120 °C, before the photoresist was exposed, with the mask at the right position after alignment, to an UV radiation flux of 36 $mJ\,cm^{-2}$ delivered by a double-sided EVG 620 aligner. After 2 min at 120 °C on the hot plate, the wafer was exposed, without the mask, to an additional UV dose of 210 $mJ\,cm^{-2}$. Therefore, the pattern drawn on the mask was transferred to the resist, which was then developed, by immersion in AZ 726 developer for 1 min, to reveal the pattern. At the end of the negative photolithography process, optical microscopy was used to ensure the correct development of the resist, and a Fogale-Microsurf 3D profilometer was used to control the thickness of the deposited layer (1.4 μm). Then, with magnetron sputtering Plassys MP 500 system, it was possible to realize the electrode layer. The vacuum chamber was first pumped down to 3×10^{-6} mbar with primary rotating oil pump and secondary cryogenic CTI8 pump. Before the depositing step, and in order to increase the adhesion of the layer, 1 min of etching run at a pressure of 7×10^{-3} mbar with argon gas and 250 W of RF power was performed. Then, a thin adhesion of pure titanium layer (30 nm) was sputtered to improve the adhesion of the platinum layer. The deposition of a pure platinum layer (150 nm) was then achieved to realize the electrode system of the sensors. Sputtering deposition parameters were as follows: sputtering pressure (Ar): 7×10^{-3} mbar, power: 150 W with DC Huttinguer generator, deposition time: 15 s at 1 A for the Ti layer and 1 min at 0.6 A for the Pt layer. The last step was the dissolution of the remaining resist in acetone with ultrasonic bath. The final optical control was done to eliminate microsystems containing some defects. The sensor geometry, consisting of two interdigitated microelectrodes combs (Fig. 1a), was chosen because it allows to measure conductivity changes between the 2 combs, optimizes the signal delivered by the sensor, and allows the electrodeposition of the polymer both on the combs and in the gap between the 2 combs. Each microelectrode comb was composed of 50 bands measuring 100 μm wide and 9996 μm long. The gap between the two combs was 4 μm so that the polymer can be deposited in this gap and can inter-connect the two combs (Fig. 1b and c).

2.2. Electrochemistry

Electropolymerization of polypyrrole films was performed with a PGZ 100 potentiostat (Tacussel-Radiometer Analytical SA-France) controlled by using the VoltaMaster 4 software. A standard three-electrode electrochemical set-up was used. The reference electrode was a Saturated Calomel Electrode (SCE) and the counter-electrode was a platinum sheet. The working electrode was the platinum combs of the microsystem. All electrochemical experiments were carried out at room temperature (293 K). Pyrrole was from ACROS (article 15771 1000, 99% pure) and was distilled under reduced pressure before use. All salts were from Sigma Aldrich and were used as received: lithium perchlorate ($LiClO_4$), sodium nitrate ($NaNO_3$), sodium *p*-toluenesulfonate (NaTsO), sodium tetrafluoroborate ($NaBF_4$), sodium perchlorate ($NaClO_4$) and sodium naphtalenesulfonate (NaNS). Chronocoulometry was used in order to coat all platinum combs with a polypyrrole film of ~250 nm. Thus an electrodeposition potential of +1 V/SCE was applied until reaching a total electric charge density of 99.2 $mC\,cm^{-2}$, corresponding to a polypyrrole thickness of 248 nm, according to the Faraday's law [26,27]. However, since the charge efficiency of the pyrrole electropolymerization could be different at various electrodeposition potentials, the polymer film thickness could be slightly different even if the total electric charge density was the same for all experiments. Furthermore, Faraday's law was used to determine polypyrrole film thickness rather than measurements performed by optical profilometry or by SEM because Faraday's law allowed obtaining the average thickness of the polymer films when profilometry led only to local measurements of the thickness even if it gave additional information about the sample roughness.

Glow Discharge Optical Emission Spectrometry measurements were done to confirm the presence of dopants inside the polypyrrole film or/and on its surface using a GD Profiler HORIBA Jobin Yvon.