Talanta 117 (2013) 45–54

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Elaboration of ammonia gas sensors based on electrodeposited polypyrrole—Cobalt phthalocyanine hybrid films

Tilia Patois [a,b], Jean-Baptiste Sanchez [c], Franck Berger [c], Patrick Fievet [a], Olivier Segut [d], Virginie Moutarlier [a], Marcel Bouvet [e], Boris Lakard [a,*]

[a] Institut UTINAM, UMR CNRS 6213, University of Franche-Comté, 16 route de Gray, 25030 Besançon, France
[b] Institute of Condensed Matter and Nanosciences, Université Catholique de Louvain, Croix du Sud, 1/4, 1348 Louvain-la-Neuve, Belgium
[c] Laboratoire Chrono-Environnement, UMR CNRS 6249, University of Franche-Comté, 16 Route de Gray, 25030 Besançon, France
[d] Laboratoire MOLTECH-Anjou, UMR-CNRS 6200, Université d'Angers, 2 bd Lavoisier, 49045 Angers, France
[e] Institut de Chimie Moléculaire de l'Université de Bourgogne, UMR-CNRS 6302, University of Bourgogne, 9 avenue Alain Savary, 21078 Dijon, France

ARTICLE INFO

Article history:
Received 19 May 2013
Received in revised form
26 August 2013
Accepted 28 August 2013
Available online 31 August 2013

Keywords:
Gas sensors
Hybrid materials
Polypyrrole
Phthalocyanine
Electrochemistry
Ammonia

ABSTRACT

The electrochemical incorporation of a sulfonated cobalt phthalocyanine (sCoPc) in conducting polypyrrole (PPy) was done, in the presence or absence of $LiClO_4$, in order to use the resulting hybrid material for the sensing of ammonia. After electrochemical deposition, the morphological features and structural properties of polypyrrole/phthalocyanine hybrid films were investigated and compared to those of polypyrrole films. A gas sensor consisting in platinum microelectrodes arrays was fabricated using silicon microtechnologies, and the polypyrrole and polypyrrole/phthalocyanine films were electrochemically deposited on the platinum microelectrodes arrays of this gas sensor. When exposed to ammonia, polymer-based gas sensors exhibited a decrease in conductance due to the electron exchange between ammonia and sensitive polymer-based layer. The characteristics of the gas sensors (response time, response amplitude, reversibility) were studied for ammonia concentrations varying from 1 ppm to 100 ppm. Polypyrrole/phthalocyanine films exhibited a high sensitivity and low detection limit to ammonia as well as a fast and reproducible response at room temperature. The response to ammonia exposition of polypyrrole films was found to be strongly enhanced thanks to the incorporation of the phthalocyanine in the polypyrrole matrix.

1. Introduction

Since the conductive properties of oxidatively doped polyacetylenes was evidenced in the 1970s [1], π-conjugated polymers have been extensively studied. Amongst conducting polymers, polypyrrole (PPy) has been one of the most studied because of its easy deposition from aqueous and non-aqueous media using either chemical or electrochemical oxidation. Electrodeposited PPy films have already been used for many different applications. An interesting example of application concerns sensors where PPy films are used as sensitive layer. Thus, many kinds of PPy-based sensors have been developed including: pH sensors [2–5], chemical sensors for the detection of zinc ions [6], silver ions [7], copper ions [8] or nitrate ions [9], DNA biosensors [10–12] and enzymatic biosensors [13–15].

Polypyrrole has also been used as active layer for gas sensors and it has been demonstrated that polypyrrole is a promising material for this application. Indeed polypyrrole-based gas sensors are interesting for environmental pollution monitoring because, upon exposure to vapor, the polymer shows rapid conductivity changes, which are generally reversible at room temperature. These characteristics are interesting since most of the commercially-available sensors, usually based on metal oxides, work at high temperatures (300–400 °C). In particular, several authors developed polypyrrole-based ammonia gas sensors and tried to optimize the stability, sensitivity and response time of the gas sensors. These studies demonstrated the influence of electropolymerization parameters including: initial conductivity [16], doping anions [16–18], electrodeposition potential [18], pyrrole and anion concentration [18]. Other studies have tried to combine polypyrrole with another material to improve the detection abilities of the ammonia gas sensors. This is the case of Bai et al. [19] who electrochemically co-polymerized polypyrrole and sulfonated polyaniline to obtain an ammonia sensor which was efficient for concentrations higher than 20 ppm. Other authors have synthesized hybrid materials composed of polypyrrole and carbon materials such as graphite and graphite oxide [20] or single-walled carbon nanotubes [21], and also hybrid materials composed of polypyrrole and metal oxides such as ZnO [22] or TiO_2 particles [23]. Another

* Corresponding author. Tel.: +33 3 81 66 20 46.
E-mail address: boris.lakard@univ-fcomte.fr (B. Lakard).

0039-9140/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2013.08.047

alternative consists in incorporating organic molecules into the polypyrrole matrix. Indeed, it is expected that the combination of molecular compounds and conducting polymer films creates synergetic effects between the two components. For example the preparation of hybrid materials has already been achieved by combining polypyrrole with cyclodextrines [24–26], metal porphyrins [27–29] or metal phthalocyanines [30,31]. In particular, the works from Radhakrishnan et al. [30] and from Tiwari et al. [31] have shown that it is possible to obtain a hybrid material by electrochemical polymerization from an electrolyte containing pyrrole and copper phthalocyanine. It must also be noticed that metal phthalocyanines are very interesting for applications in the field of chemical sensors since they have already been successfully used as sensitive layers of gas sensors [31–35]. Furthermore, the study from Tiwari et al. is particularly interesting since the electrosynthesized polypyrrole/copper phthalocyanine material was successfully tested as sensitive film of a gas sensor for the selective detection of a nerve gas simulant dimethyl methyl phosphonate (DMMP). In particular, the sensor was unaffected by the interfering vapors like ethanol, benzene, toluene and hexane even at high concentration, which makes it more suitable for DMMP sensing in presence of them. In a previous study we have also shown that a polypyrrole/phthalocyanine film can respond to ammonia concentration changes whatever the relative humidity rate, in contrast to traditional gas sensors based on phthalocyanines [36].

In this context, the present work aimed at electrosynthesizing hybrid materials from electrolytic aqueous solutions containing pyrrole, sulfonated copper phthalocyanine and lithium perchlorate (for only some of them). After characterization, these hybrid materials were deposited on platinum microstructured electrode arrays and tested as sensitive layers of chemiresistive gas sensors. More precisely, the conductance changes of PPy/sCoPc-based sensors were measured during their exposition to different ammonia concentrations, leading to the determination of their characteristics (response time, sensitivity, reproducibility, kinetics).

2. Experimental

2.1. Microfabrication

Silicon microtechnologies were used to fabricate microsystems in a clean room. The design of the microsystems consisted in two interdigitated platinum microelectrode arrays deposited on an insulating SiO_2 wafer (Fig. 1). Each array was composed of 50 microelectrodes measuring 100 μm wide and 9896 μm long. This microsystem geometry was chosen because it allowed for the measurement of conductivity changes between the 2 arrays and because it optimized the signal delivered. The objective was to electrodeposit PPy/sCoPc films both on the conductive microelectrode arrays and across the insulating gap separating the microelectrodes of the sensor.

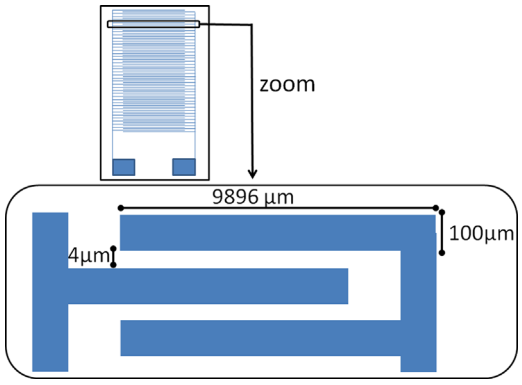

Fig. 1. Schematic drawing of the microsystem.

Consequently, the insulating gap between the neighboring electrodes had to be narrow enough, around 4 μm, to allow the PPy/sCoPc film to form a coating on the insulated gap and to electronically connect the two microelectrode arrays by polymer pathway.

The 4″ silicon wafers used in this study were 100-oriented, 500 μm thick, p-type doped and had a resistivity of 1 Ω cm^{-1} to 10 Ω cm^{-1}. They were thermally wet-oxidized, at 1200 °C in water vapour flux during 12 h to produce a 1.4 μm thick SiO_2 layer. In order to fabricate microsystems with this geometry, a Cr/Glass mask for lithography was designed using Cadence conception software, and it was fabricated using a Heidelberg DWL 250 optical pattern generator. Wafers and mask were pre-cleaned for 10 min in a mixture of H_2SO_4 (50 mL) and H_2O_2 (30 mL) to remove organic residues that contaminate their surface. Then, the wafer was dried under a N_2 stream and placed on a hot plate (Prazitherm) for 10 min at 120 °C. A layer of negative photoresist (AZ 5214, from Clariant) was spin-coated on the silicon wafer using a 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, after alignment of the mask, 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}. The last step of the photolithography process was the development of the wafer by immersion in AZ 726 developer for 1 min. The correct development of the resist and the appearance of the pattern were checked using an optical microscope before starting the deposition of metallic layers by sputtering to obtain conductive microelectrode arrays. Magnetron sputtering was done using a Plassys MP 500 system in a vacuum chamber pumped down to 3.10^{-6} mbar with primary rotating oil pump and secondary cryogenic CTI8 pump. The sputtering process started with an etching run (sputtering parameters: time: 1 min, pressure: 7.10^{-3} mbar with Ar gas, power: 250 W), followed by the deposition of a 30 nm adhesion layer of pure titanium (15 s at 1 A, 7.10^{-3} mbar with Ar gas, 150 W), and a 150 nm layer of pure platinum (1 min at 0.6 A, 7.10^{-3} mbar with Ar gas, 150 W). The dissolution of the remaining resist was finally done in acetone with ultrasonic waves, and the final microsystems composed of Ti/Pt microelectrodes arrays were controlled using an Olympus optical microscope.

2.2. Electrochemistry and surface analysis

Pyrrole was from ACROS (99% pure) and was distilled under reduced pressure before use. Lithium perchlorate was from Sigma Aldrich and used as electrolytic salt. A mixture of *n*-sulfonated cobalt phthalocyanines (sCoPc), known as $Co[(SO_3Na)_{2.3}Pc]$, was supplied by Europthal company as additive 8020 and used as molecular material. Some electrolytes were composed of 0.1 M pyrrole in an aqueous solution of 0.1 M $LiClO_4$. Other electrolytes were composed of pyrrole (0.1 M) and sulfonated cobalt phthalocyanine (0.05 M) with or without 0.5 M $LiClO_4$. These different electrolytes were electrochemically oxidized in order to deposit a thin solid film on array-patterned substrate. Electrochemical experiments were performed with a PGZ 100 potentiostat (Tacussel-Radiometer Analytical SA-France) controlled by the VoltaMaster 4 software. A standard three-electrode set-up was used to perform electrochemical experiments. A Saturated Calomel Electrode (SCE) and a platinum sheet were used as reference electrode and counter-electrode, respectively. The working electrode used was either a platinum wire for studying the electrochemical behaviour of the electrolytes or a Fluorine doped Tin Oxide (FTO) substrate (from Balzer, R=120 Ω, thickness: 2 mm) for surface analysis or both electrode arrays of microsystem to serve as gas sensor. All electrochemical experiments were carried out at room temperature (293 K).