Sensors and Actuators B 210 (2015) 574–580

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Understanding the sensing mechanism of polyaniline resistive sensors. Effect of humidity on sensing of organic volatiles

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ARTICLE INFO

Article history:
Received 4 September 2014
Received in revised form 7 January 2015
Accepted 9 January 2015
Available online 17 January 2015

Keywords:
Resistive sensor
Humidity
Polyaniline

ABSTRACT

Polyaniline (PANI) is the oldest and potentially one of the most useful conducting polymers. Among other technological applications, PANI films have been extensively used as resistive sensors of volatile analytes. However, at present the mechanism underlying the resistivity changes of the films upon exposure to volatile substances is still unclear. In this work, we investigate different effects of the volatile absorption which can cause the changes polymer electrical resistance when it acts as resistive sensor. This model takes into account three major components: (i) changes in the electronic structure of the polymeric chains (ΔR_{ele}), (ii) variations in the electron hopping process (ΔR_{hop}) and (iii) changes in the ionic conductivity between chains due to changes in the dielectric medium between them (ΔR_{med}). Using two point probe resistivity, UV–visible spectroscopy, environmental ellipsometric porosimetry and atomic force microscopy we study the effect of volatiles on polyaniline films properties to improve the understanding on the mechanism of resistivity changes. Specifically, in the case of water absorption, the resistivity changes seem to be associated with dielectric medium changes and swelling effects (in the high humidity range). It is found that ambient humidity not only gives a resistive signal but also strongly affect the sensing of other volatiles (e.g. ethanol).

1. Introduction

The market of chemical sensors continues growing at a rapid rate, reflecting the wide range of possibilities of improving technological processes within the industrial, agricultural, military sector, among others [1–7]. Recent advances in polymer science and films preparation have made polymer films useful, practical and economical for wide range of sensing applications. Classical polymers are dielectric, so they have to be mixed with conducting materials (e.g. carbon particles) to build electric sensors based on changes of conductivity. However, pure conducting polymer films can be directly used in this kind of sensors. Among them, polyaniline (PANI) is one of the more interesting conducting polymers, which is a suitable material to produce chemical sensors, due to its processability, high sensitivity and low cost [8]. The development of efficient chemical sensors is challenging and a lot of work is in progress to explore new materials with improved sensing characteristics [9–14].

In the literature there are many research works about sensors built using conducting polymers. S.V. Bhoraskar et al. [15] reported the behavior of humidity sensors with polyaniline-based conducting polymers doped with different weak acidic, Lau et al. [16] described the use of polyaniline nanofibers as an humidity sensor. In both cases, PANI is the sensitive material used and the authors proposed that the humidity sensing mechanism can be explained on the basis of proton transfer mechanism. Kulkarni et al. [17] have also studied PANI and modified PANI as humidity sensors, and Varahramyan et al. [18] have shown that the use of layer-by-layer nano-assembly for deposition of ultrathin poly(anilinesulfonic acid) films in order to fabricate highly sensitive and fast responsive humidity sensors. However, none of these

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http://dx.doi.org/10.1016/j.snb.2015.01.029
0925-4005/

Table 1
Relationship between relative humidity and sulfuric acid concentration.

Concentration of sulphuric acid solutions (mol/l)	Relative humidity (%) at 20 °C
0.0	98.0
4.3	70.4
6.0	47.2
9.2	18.8
18.7	3.2

works have been focused on the interaction mechanism involved when the sensitive material is in contact with the analyte molecule.

Resistive PANI sensors have been applied in different fields [19]. The effect of humidity on the volatile's signal, described in the present communication, have to be taken into account in those applications.

In this paper we employ different techniques: two point probe, atomic force microscopy, UV–visible spectroscopy and environmental ellipsometric porosimetry to study the processes involved in the polymer–analyte interaction while the PANI changes its resistivity. Based on these results, we propose a model that explains the changes on the electrical resistance of the polymer when this acts as resistive sensor. The model takes into account three components: (i) the intrinsic resistivity of the polymeric chains due to electronic effects (ΔR_{ele}), (ii) the resistivity changes related to variations in the electron hopping process (ΔR_{hop}) and (iii) the resistivity changes due to modifications in the dielectric medium between the chains (ΔR_{med}). Moreover, we applied successfully the proposed model to explain how changes in ambient humidity alters PANI sensor readings when sensing butanol or ethanol.

2. Materials and methods

2.1. Sensor fabrication

The resistive sensor was made using a polymeric inert support (polyester woven cloth) covered with PANI as a sensitive material. To study the main processes involved in the characteristic response of the PANI, different supports were used, such as polypropylene (PP), polyethylene (PE) or gold slides (emf®). The conducting polymer was deposited onto these supports by in situ polymerization, which involves chemical oxidation of aniline (0.1 M) in HCl (0.1 M) with ammonium persulphate (equimolar to aniline) at 0 °C. This procedure has been previously described in detail in literature [20–22]. The polymerization reaction was performed in a glass vessel reactor with 400 ml of capacity, and cooled with an ice-water bath at 0 °C. The reaction temperature was measured using a thermocouple (Hanna Instruments) with an accuracy of 0.1 °C. After the polymerization, PANI covered supports were washed with HCl 1 M and dried at ambient conditions.

Once the sensitive material onto polyester woven cloth was dry, a piece of 1.5 cm × 1 cm was cut and then electrically contacted. The sensors supported on PE and PP were cut into 0.5 cm × 1 cm pieces.

2.2. Control of ambient humidity

To control the relative humidity (RH), different solutions of sulphuric acid were used [23]. The RH and the equilibrium vapour pressure used for the present experiments are given in Table 1.

2.3. PANI film characterization

2.3.1. UV–visible spectroscopy

UV–visible spectra of the PANI films deposited onto PP commercial films were measured in transmission mode using a HP 8452 UV–visible Spectrophotometer. Films were placed inside a stoppered quartz cell and the RH inside the cell was stabilized with aqueous solution of sulfuric acid (see Table 1).

2.3.2. Scanning electron microscopy (SEM)

The polymer was deposited onto polyester woven cloth by in situ polymerization and then the morphology of the films was studied using a Carl Zeiss EVO MA 10 low vacuum scanning electron microscope.

2.3.3. Fourier transform infrared spectroscopy (FTIR)

FITR spectra were obtained using a Bruker Tensor 27 FTIR spectrometer with a resolution of 4 cm^{-1}. The spectrum of the conductive polymer supported onto PE was obtained in transmission mode. The PE film was pretreated with sulfochromic solution to produce hydrophilic groups on the film surface before polymerization.

2.3.4. Environmental ellipsometric porosimetry (EEP)

EEP technique, first reported by Baklanov [24] is a very powerful technique for studying the evolution of thickness and refractive index of supported thin films at different humidity conditions. The experimental device is based on the coupling of a pressure controlled chamber and a variable angle spectroscopic ellipsometer. Film thickness and refractive index values were obtained from the ellipsometric parameters φ and Δ [25] under nitrogen flux with a variable water content, reaching RH values from 0 to 90%. This technique is usually used to study porous oxide films [26] but can be adapted to evaluate polymer swelling [27]. EEP measurements were performed using a SOPRA GES5A spectroscopic ellipsometer.

To model the ellipsometric signal, the Cauchy model and two Lorentz peaks were used. The refractive index n and $k(\lambda)$ values reported by Barbero et al. [28] for this material were used as seeds. The refractive index curves obtained can be found in the Supplementary Information (Fig. S1). The initial thickness of the used polymeric film was 150 nm, which was measured using an Atomic Force Microscopy Agilent 5500.

2.3.5. Atomic force microscopy (AFM)

AFM measurements were made with an Agilent 5420 AFM/STM microscope in contact mode with a commercial Point Probe® Plus Contact/Tapping Mode (constant force of 6 N m^{-1}, 156 Hz) It allowed the determination of the change in thickness of the PANI film as it passes from a protonated state to a deprotonated state. The polymer was deposited onto a gold slide by in situ polymerization. Then, a single laser pulse (532 nm, 350 mJ/cm^2, 6 ns pulse width) was used to remove a part of polymeric material and a circular hole was made on the polymeric film. Fig. 1 shows a covered and an uncovered area. The height changes suffered by the polymeric film after being exposed to acid and basic solutions were measured.

2.3.6. Conductometric response of the sensors

To study the effects of humidity on sensor response, the sensor was placed on the top of different closed Erlenmeyers (250 ml). The RH value in each Erlenmeyer was obtained using sulphuric acid solutions at 20 °C, as previously described. The sensor was placed for 20 min on the top of Erlenmeyer with the lowest humidity. Then, the sensor was changed to the sample flask (ethanol, butanol, etc.) for 20 min and the electrical response was recorded. In this static set-up, the equilibrium conditions are achieved. After that, the sensor was placed for 20 min in the second Erlenmeyer that contained 18.8% RH, and then was changed again for 20 min to the sample flask and so on.

The sensor response was measured with a multimeter (Kaiser, VA 40B). The two probe method was used to perform the