ARTICLE IN PRESS

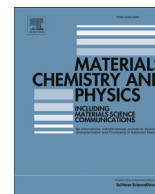Materials Chemistry and Physics xxx (2015) 1—7

Contents lists available at ScienceDirect

Materials Chemistry and Physics

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

Influence of the physical–chemical properties of polyaniline thin films on the final sensitivity of varied field effect sensors

Hugo José Nogueira Pedroza Dias Mello*, Tobias Heimfarth, Marcelo Mulato

Department of Physics, Faculty of Philosophy, Sciences and Letters at Ribeirão Preto, University of São Paulo — USP, Av. Bandeirantes 3900, Ribeirão Preto, SP 14040-901, Brazil

HIGHLIGHTS

- Electrodeposited polyaniline thin films were analyzed in two EGFET setups.
- Polymer protonation provided changeable sensitivities.
- Color and morphological variation confirm polymer aggregation and electrical changes.

ABSTRACT

We investigated the use of electrodeposited polyaniline (PANI) thin sensing films in pH sensors. Two configurations of the Extended Gate Field Effect Transistor (EGFET) sensor were studied: the Single EGFET (S-EGFET) and the Instrumental Amplifier EGFET (IA-EGFET) setups. The films were analyzed in both systems and the sensitivity and linearity of each sensor were compared. Initial sensitivities (70 −80 mV/pH) measured in the IA-EGFET were reduced due to polymer bulk protonation after a prior measurement in the S-EGFET system. Films with high amount of deposited polymer had their sensitivities least reduced. Bulk protonation occurred due to the step potential applied to the reference electrode in the S-EGFET system. These changes were also analyzed by scanning electron microscopy (SEM), visible reflectance spectroscopy and evaluation of CIE $L^*a^*b^*$ color scale. PANI pH EGFET sensors exhibited good linearity and stability that along with their high sensitivity, easy processing and low cost film production have large potential applications.

© 2015 Published by Elsevier B.V.

1. Introduction

The importance of chemical sensors comes from their capability to analyze several environments, detecting which substances are present and their quantities. They are composed of two connected components: the chemical recognition system and the physico-chemical transducer. Several studies have been focused on the development of new materials and improvement of chemical transducer structure. This contribution addresses both parts for potentiometric sensors based on FET (field effect transistor) structures.

The first ion-sensitive field effect transistor (ISFET) potentiometric sensor was fabricated by Bergveld. The device was based on metal-oxide-semiconductor field effect transistor (MOSFET)

technology. The component had its metal gate removed in order to expose the underlying insulator layer to the solution. This had the function of an ion selective electrode [1]. The extended-gate field effect transistor (EGFET) arose from a modification in the ISFET structure where the sensing membrane was separately fabricated and connected to the transistor's gate [2]. In this contribution, this sort of device will be called single EGFET (S-EGFET) [3]. Given that the configuration of such potentiometric sensors consists of a chemically-sensitive film connected to a high input impedance device, the further use of an operational amplifier led to the Instrumental Amplifier EGFET (IA-EGFET) system. The main difference between both systems is the need of a step change in the voltage applied to the reference electrode in the S-EGFET system, in order to overcome the S-EGFET's MOSFET threshold voltage. The potential must be high enough to ensure that the transistor is working on the linear region.

Several kinds of metal oxide materials have been used as ion-sensing films in EGFET sensors, such as SnO_2 [4], SnO_2:F (FTO) [5],

* Corresponding author.
  E-mail address: hugodiasmello@usp.br (H.J.N.P.D. Mello).

ZnO [6], V_2O_5/WO_3 [7], among others. Another interesting class of candidate materials is the conducting polymers (CP). Although polymers are historically seen as good electrical insulators, the discovery of polymers with semiconducting and conducting properties started a new subject of research because of the numerous technological possibilities [8,9]. CP shows pH sensitivity when acting as anion or cation exchangers. Consequently, potentiometric responses are possible [10].

Among the existing CP, polyaniline (PANI) is important due to its ease of synthesis, low cost monomer, tunable properties and environmental stability [11,12]. PANI has a variety of oxidation states that are both chemical (pH) and electrochemical dependent. The three existing forms of PANI are: leucoemeraldine (LEB, fully reduced) usually presenting yellow color, emeraldine base (EB, half reduced/half oxidized) in the blue color, and pernigranilina (PNB, fully oxidized) in the black color [11]. Each oxidation state can exist either in its base or protonated form (salt) [13]. The protonated form of the most common PANI state, the blue emeraldine base, is the green conducting emeraldine salt (ES) [11,14,15].

PANI sensitivity to pH comes from the pH's influence on the redox processes of the polymer [16]. The polymer can be protonated changing from EB to ES form, either by protonic acid or electrochemical doping. The protonation by protonic acid occurs in the quinoid rings (imine nitrogen groups) which presents a large affinity for charges [17], reaching an equilibrium between those groups and the protons in the contact medium [18]. This equilibrium generates a potentiometric response able to be measured.

PANI in sensors are widely studied, with some examples found in [11,19,20]. PANI is a polyelectrochromic material, which means it is a material that presents different colors for different oxidation states. Electrochromic materials can be used as optical sensor, organic light emitting diode (OLED), and others [21]. This property is also addressed in this paper aiming the spectral characterization of PANI, since its color will change according to the environmental pH in which it is exposed.

PANI films have been prepared in chemical, electrochemical, template, plasma and photo methods. In the potentiodynamic method, used also in this work, the film is grown by repeated cycling the potential over a specific range, period of time with constant scan rate, selected to induce polymerization [22].

PANI films have been used in FET sensors [23]. The films were deposited onto gold (Au) substrates with sensitivity around 58 mV/pH and small drift. However, a study about the differences in the operating procedures of S-EGFET and IA-EGFET systems on PANI films is still needed. The S-EGFET system is capable to change PANI's properties and the variation of PANI state might lead to undesired and misleading changes in sensitivity.

2. Material and methods

2.1. Materials

Fluorine-doped tin oxide (FTO) films deposited on glass substrates were obtained from Sigma−Aldrich. The samples had a surface area of 1×2.5 cm^2 and sheet resistance of 10 Ω cm^{-2}. The samples were chosen due to their well-known properties, which include time stability, sensitivity and performance as pH sensors [5]. The films were cleaned with de-ionized water followed by acetone using the ultra-sonication method in order to remove contaminants from the surface. Aniline ($C_6H_5NH_2$) was supplied by Vetec Brazil.

2.2. Preparation of PANI films

An acidic aqueous solution was prepared containing 0.1 M of aniline and 1.0 M of hydrochloric acid (HCl). The solution was deoxygenated by bubbling N_2 for 15 min [24]. The electrodeposition process was described for Bi_2Te_3 thin films in [25], and for PANI films in [26] and [27]. A platinum inert electrode was used as anode and FTO was used as cathode. Cycling the potential is advantageous to produce good homogeneity, strong adhesion to the substrate, and chemical stability [28]. Films were produced for sensor measurement and characterization according to: i) in the first set of films the voltage varied from − 0.2 V to a maximum potential (P) ranging from 0.8 V up to 2.0 V across the electrodes, during 15 min; and ii) in the second set of films the deposition time (T) was varied from 15 min up to 90 min, for a fixed maximum potential of 0.8 V. Scan rate was set to 50 mV/s and samples are identified according to the following scheme: P(maximum potential x10)T(deposition time).

According to cross section scanning electron microscopy measurements, all samples have a thickness below 200 nm, as already reported by others [28]. The finished PANI/FTO films were carefully washed in de-ionized water and dried. During washing, the polymer changed from green to blue as a consequence of the erosion of counter ions and protons [29]. All experiments were performed at room temperature.

2.3. Sensors measurements

Electrical contacts to the samples were made using pressured planar Cu pads (1×0.5 cm^2). An Ag/AgCl reference electrode was dipped into the pH buffer solution to define its electric potential. Sensors' pH sensitivity (S) and linearity (L) were measured in the pH buffer range from 2 to 8. The data were recorded 60 s after biasing the system. The films were carefully washed in de-ionized water in between each measurement.

A CA3140 Op-Amp was chosen for the IA-EGFET measurement system and unity gain was chosen because amplification is not needed. The sensing film was connected to the principal input stage. The contrast input stage was grounded. For this configuration the reference electrode is also connected to the ground, as shown in Fig. 1(a). The positive charge equilibrium between PANI sensing film and the solution determines the measured potentiometric values for each pH.

The pH sensitivity was also measured using the S-EGFET system, shown in Fig. 1(b) and detailed in [5]. The S-EGFET used a commercial CD4007 MOSFET. The sensing film dipped into the pH buffer solution is connected to the transistor gate. A step change in voltage (5 V) is applied to the reference electrode (V_{REF}) for MOSFET triggering. The source-drain contacts (V_{DS}) is also biased at 5 V, while the source-drain current (I_{DS}) is measured, for each pH. The potentiometric values were obtained converting the I_{DS} current to potential values using the transistor equation. The sensor's linearity was obtained from the coefficient of determination (R^2) of fitted curves. The linearity parameter L is calculated by R^2 times 100.

The sensor's stability was evaluated by measuring the output voltage for varied buffer solutions according to a pH sequence 5-2-5-8-5. For each pH buffer the measurement was performed during 20 s. The total cycle was repeated three times. The cycled measurements evaluate whether the PANI oxidation states remain constant in time after a sequence of experiments.

2.4. Characterization

The morphology of the final samples was studied using scanning electron microscopy (SEM). A ZEISS microscope EVO 50 model operating at 20 kV was used. A thin gold coating (≈ 20 Å) was applied to the samples by means of a Sputter Coater − Balzers SCD 050.