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Sensors and Actuators B 116 (2006) 130–134

SENSORS AND ACTUATORS B CHEMICAL

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Multi-sensor array used as an "electronic tongue" for mineral water analysis

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Received 10 July 2005; received in revised form 8 September 2005; accepted 7 December 2005
Available online 19 April 2006

Abstract

An "electronic tongue" based on a monolithically integrated array of chemical sensors is presented. The device is composed by six independent ion selective field effect transistors (ISFETs), an interdigitated platinum electrode (IDS) and a silicon diode used as a temperature sensor. K^+, Na^+, Ca^{2+} and Cl^- ISFET based sensors were obtained by depositing different photocurable membranes onto their gates. IDS was used to measure conductivity and redox potential. The multi-sensor was used to classify 13 different brands of mineral water. Several pattern recognition methods such as hierarchical clustering analysis (HCA) and principal component analysis (PCA) were applied to the multi-sensor output data sets. They showed the possibility of this electronic tongue to distinguish well between different classes (HCA) as well as different brands (PCA) of waters. Eventually, soft independent modelling class analogy (SIMCA) algorithm was used to construct the classification model based on experimental data sets. The model applied to the test data provided a 100% correct prediction of the water brand, giving possibility to perform fast and cheap classification or quality analyses.

Keywords: ISFET; Multisensor; Electronic tongue; Water analysis

1. Introduction

In recent decades, the interest in quality control of food, water, products for human use and anything that could have adverse effects on the environment or human health has increased considerably. Ideally, this control should be performed in real time and "in-line". To date one of the best approaches to this is provided by use of chemical sensor arrays with posterior multivariate analysis of their response. When the analysis is performed in a gas phase the device is called "electronic nose". By analogy, the so-called "electronic tongue" is often referred to analysis performed in wet environments.

The response of an electronic tongue is provided by an array of sensors detecting various components in liquid samples. The output data is treated subsequently with some kind of a multivariate analysis technique. Commonly an electronic tongue is not an integrated sensor array on some substrate, but rather comprises a set of individual sensors measuring simultaneously [1]. One of the most important drawbacks of the electronic tongues reported until now is that normally they are composed by the same type of sensors, either potentiometric [2–4], voltammetric sensors [5–7] or interdigitated electrodes [8]. This implies a limited amount of data that can be obtained within the analysis. Signals coming from a sensor array measuring in different samples are treated using pattern recognition techniques, such as the principal component analysis (PCA), the K-nearest neighbor (KNN) and most popular in recent years, the artificial neural networks (ANN) and the fuzzy neural network [9,10].

The innovation presented in this work is the development and application of a chemical multi-sensor array fabricated by monolithic integration of different electrochemical sensors using BESOI (bond and etch back silicon on insulator) wafers. The array consists of six ion selective field effect transistors (ISFETs) with polymeric membranes sensitive to different ions, a diode used as a temperature sensor and an interdigitated platinum electrode (IDS) used to measure the conductivity and the RedOx potential. Different pattern recognition methods, HCA (hierarchical clustering analysis), PCA, and SIMCA (soft independent modelling of class analogy) were used to classify 13 different brands of bottled mineral water. Multivariate factor based PLS

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0925-4005/$ – see front matter
doi:10.1016/j.snb.2005.12.063

(partial least squares) regression was used to estimate the ion concentrations using the whole set of data obtained from sensors.

This work may be regarded as a preliminary task to demonstrate the feasibility of this sensor array as an electronic tongue.

2. Experimental

2.1. Apparatus and devices

The multisensor is integrated in one chip 20.71 mm × 8.00 mm size combining NMOS and thin film technology. BESOI wafers used are formed by three layers, a lower thick silicon substrate, an intermediate silicon oxide layer, and an upper thin silicon layer used to form semiconductor devices. The developed technology [11] permits to isolate electrically sensors one from each other to guarantee their independent functioning.

After fabrication of the ISFET sensors and the diode of the array, platinum interdigitated electrodes are formed by deposition of a thin layer of platinum and subsequent lift-off process. E-beam process used to deposit Pt resulted in a considerable damage of ISFET devices affecting their threshold voltage and introducing build-in charge into the gate insulator. These problems were resolved by a special annealing process described elsewhere [11].

The encapsulation process, performed with a photocured polymer layer [12], is facilitated due to the on-chip electrical isolation of all the devices of the multi-sensor. For this reason it requires only to cover the contact pads of the chip and conducting lines of the PCB substrate.

The final step of multisensor fabrication is the deposition of different photocurable polyurethane membranes sensitive to K^+, Na^+, Ca^{2+}, and Cl^- ions over the ISFET gates. Preparation and deposition of these membranes are reported elsewhere [13–16].

Encapsulated multi-sensor chip with deposited ion-selective membranes is presented in Fig. 1.

A specially set-up for sensor control through computer was designed. It consists on a six-channel ISFET-meter working in a constant drain current/constant drain voltage mode. ISFET sensors were biased through the double junction Ag/AgCl reference electrode immersed into the test solution. A special module for measuring the impedance of the interdigitated electrode array at fixed frequency was used to control the conductivity of solutions.

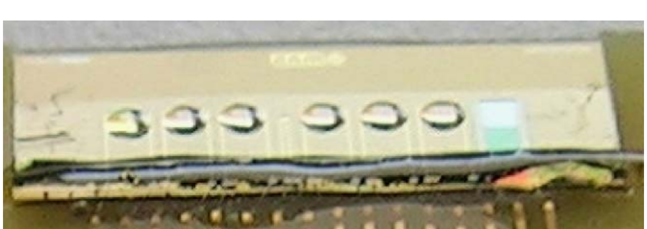

Fig. 1. The photograph of the chemical multi-sensor array.

2.2. Reagents and solutions

ISFETs with photocurable membranes were tested and characterised for their sensitivity, selectivity, stability and lifetime. It is important to emphasize that all parameters were the same as for conventional ISFETs [13–16] except for the lifetime of the polymer membrane that was reduced to 1 month of constant contact with a solution due to thinner membranes obtained in case of the array.

Along with mentioned ions, pH, conductivity and RedOx potential values of water samples were controlled. pH was measured by one of the ISFETs with a silicon nitride gate. RedOx potential and conductivity were measured using the platinum interdigitated electrodes. The former by measuring the platinum electrode potential versus a reference electrode and the later by measuring the impedance between two interdigitated electrodes.

Thirteen different brands of bottled mineral water were analysed. Among those were highly mineralised waters (Vichy Catalan, Vichy Célestins, Malavella), waters with elevated hardness (Ca^{2+} and Mg^{2+} content) (Peñaclara, Zambra), low mineralised waters (Font d'Or, Font Vella, Solan de Cabras, Fuente Liviana, Viladrau, Evian) and waters with very low chloride and bicarbonate content (Lanjaron, San Vicente). The test cycle for each water sample consisted in two steps: firstly the measurement was performed in a water sample and then in a reference solution. This reference solution was prepared from chloride salts and contained all the mentioned cations in concentrations close to mean values of corresponding ions reported for the commercial bottled waters [17]. In total the water samples were measured three times one by one giving three independent data sets. Values of ion concentrations and the number of total dissolved solids (TDS) are presented in Table 1.

Multi-sensor responses measured in each water sample were analysed by HCA and PCA. The data set was divided into two "training" sets used to construct the SIMCA classification model and the PLS (partial least squares) regression one, and the "test" set used for model validation. All of this data treatment was performed using the commercial software package Pirouette 3.02.

3. Results and discussion

Before introducing each data set into the pattern recognition software it was transformed in the following way. As an output value for each sensor in each water sample the difference between signals obtained in the sample and the reference solution was taken. This procedure avoids any possible drift of the sensor response with time.

Fig. 2 presents the results obtained by HCA analysis. In the dendogram five main clusters of mineral waters can be distinguished. Their principal differences are the nominal number of total dissolved solids and their water hardness. With these results it can be concluded that measured parameters are sufficient to distinguish at least between different classes of mineral waters.

Fig. 3 shows the results of PCA analysis of three experimental data sets. It is clearly seen that waters with similar characteristics are located in nearby space regions. Referring to the notation in the figure we may distinguish: I—highly mineralised waters,