



# An impedimetric chemical sensor for determination of detergents residues

Andrey Bratov\*, Natalia Abramova, Andrey Ipatov, Angel Merlos

*Instituto de Microelectronica de Barcelona, Centro Nacional de Microelectronica (IMB-CNM, CSIC), Campus U.A.B., 08193 Bellaterra, Barcelona, Spain*

## ARTICLE INFO

### Article history:

Received 24 July 2012

Received in revised form

22 October 2012

Accepted 29 October 2012

Available online 10 November 2012

### Keywords:

Surfactants

Detergents

Interdigitated Electrode Array

Impedimetric sensor

## ABSTRACT

A new impedimetric sensor based on an interdigitated electrode array with electrode digits located at the bottom of microcapillaries formed in silicon dioxide is presented. Microcapillaries are opened at the top, so that in contact with an electrolyte solution the ac current flows close to the surface of the capillary wall from one electrode to another and is significantly affected by changes in the surface conductance at the SiO<sub>2</sub>/electrolyte interface. Adsorption of detergents on the sensor surface affects the charge distribution in the electrical double layer and thus the surface conductance. These changes are registered by measuring impedance. Effect of surface adsorption of ionic and non-ionic surfactants on the sensor impedance is studied. The sensor is shown to be able to measure commercial detergents residues in a tap water starting from 5 ppm even in solutions with high electrolyte conductivity.

© 2012 Elsevier B.V. All rights reserved.

## 1. Introduction

In a sustainable society there is a permanent demand of “green” environmentally friendly products among which are typical for any household washing and dish-washing machines. Modern machines use various sensor systems for controlling the washing process to make it energy efficient and water saving. However, there exists a need for sensors that can be used to measure detergents or surfactants residues [1,2]. Such a sensor could be helpful in reducing the number of rinsing cycles or reducing the amount of water used for rinsing, resulting in both saved water and energy. It also could guarantee safe levels of residue detergent in the washed laundry.

Modern detergents can comprise 20 or more ingredients [3] but all the formulations contain surfactants — molecules, which due to the combination of hydrophilic and hydrophobic moieties within the same molecule show amphiphilic character. This property gives surfactants ability to concentrate at interfaces. There is a large variety of surfactants that are generally classified according to their hydrophilic component as non-ionic, anionic, cationic, or amphoteric. Typical laundry or dishwash detergent formulations contain up to 35% of anionic detergents and 1–5% of non-ionic detergents [3,4]. Among anionic detergents the most commonly used are linear alkyl benzene sulfonates, and fatty alcohol ethoxylates are the most typical non-ionic surfactants in detergents formulations [3–5].

There are numerous analytical methods and techniques that may be used for chemical analysis of surfactants [4–8] that include infra red and nuclear magnetic resonance spectroscopy, spectrophotometry, high performance liquid chromatography (HPLC), ion chromatography and others. Measurements of ionic and non-ionic surfactants may be performed by titration using potentiometric sensors [6–10] or with biosensors [11–13]. However, all these methods require expensive laboratory equipment and qualified personal and are not suitable for in-line or at-line measurements.

To measure detergent concentration in washing machines optical systems based on surface-plasmon resonance (SPR) phenomenon have been proposed [14–16]. Optical methods of detection are quite expensive, so commonly to control the amount of detergent in the washing machines different sensors and systems based on measuring the conductivity of the washing liquid with a detergent are used [17,18]. A conventional conductivity sensor is formed by two metal electrodes. When a voltage is applied externally between two electrodes, an electric current is generated which corresponds to the conductivity of the washing liquid, which depends on the concentration of the detergent. Thus, the electric current value, which can also be converted to impedance, is used to measure the concentration of the detergent present.

Disadvantages of methods based on the conductivity measurement arise from the fact that conductivity of the washing water depends on the concentration of detergent in cases when the final concentration is high. In the rinse cycle, when the concentration of detergent decreases, the conductivity of the solution will depend on the conductivity of the water itself and not on the present detergent residues. Therefore, these methods are useful for dispensing and dosing the detergents, but not to control their residues.

\* Corresponding author. Tel.: +34 93 594 77 00; fax: +34 93 580 14 96.  
E-mail address: [Andrei.Bratov@imb-cnm.csic.es](mailto:Andrei.Bratov@imb-cnm.csic.es) (A. Bratov).

An interesting approach was proposed by a Swedish group which used voltammetric electronic tongue to determine amounts of detergents in process water from washing machines [2,19]. However, authors conclude that there are no ways to distinguish between supporting electrolytes or the anionic surfactant with the electronic tongue. Thus, for process control the simpler conductivity meter will perform equally well.

Earlier we have reported [20–23] a new impedimetric device that is very sensitive to the presence of charged molecules (e.g. antigens, DNA, large polycations and polyanions) at its surface and that may be used as a transducer for the development of different sensors and biosensors. The objective of the present work was to study the sensor response to the presence of surfactants in water solutions.

## 2. Experimental section

### 2.1. Microcapillary device design and fabrication

As presented earlier [21–23], the device was fabricated using conventional microelectronic techniques. Silicon wafer covered with a thermally grown silicon dioxide layer of 2500 nm was used as a substrate. A 230 nm thick layer of tantalum silicide ( $\text{TaSi}_2$ ), which is a highly conductive material, is deposited by magnetron sputtering. The first photolithographic step defines collector bars and digits of two electrodes. The patterning is done by a reactive ion etching technique. This results in an interdigitated electrode array (IDEA) with 216 digits of 3  $\mu\text{m}$  width and 3  $\mu\text{m}$  gap between the adjacent electrode digits. The electrode digits are 1.5 mm long and the aperture between the adjacent digits is 1.4 mm.

To form the contact pads 1  $\mu\text{m}$  of aluminum is deposited and patterned using standard photolithographic and etching steps leaving metal only at extremes of the two collector bars.

In the final step the wafer with formed IDEA devices is covered with a 4  $\mu\text{m}$  thick silicon oxide layer deposited by a low pressure chemical vapor deposition (LPCVD). This material is virtually the  $\text{SiO}_2$  but with a lower density compared to thermally grown silicon oxide or quartz. Photolithography is used to define the trenches to be opened in the oxide layer over the electrodes digits and over contact pads. These zones are opened by deep reactive ion etching (DRIE), which permits to obtain nearly vertical walls. In this way capillaries are formed in silicon dioxide over the electrode digits. The capillaries over each electrode digit are 3  $\mu\text{m}$  wide, 4  $\mu\text{m}$  high, 1.5 mm long and are opened at their top. Fabricated device is schematically presented in Fig. 1A.

After being cut from the wafer the sensors are glued to a printed circuit board (PCB) substrate with copper leads and are

wire bonded for electrical connections. Contact pads and wires were encapsulated using epoxy resin.

### 2.2. Impedance measurements

Characterization of sensors was performed by impedance measurements in a 100 Hz–1000 kHz frequency range with a 25 mV (amplitude) voltage excitation using QuadTech 7600 Plus precision LCR meter. Z-Plot/Z-View software package (Scribner Associates, Southern Pines, NC, USA) was used for impedance data treatment and an electrical equivalent circuit fitting. Measurements were performed by immersing sensors into a beaker with 10 mL of a test solution. Concentration of the solution components was changed by adding a known volume of prepared stock solutions. All experiments were carried out at controlled temperature of  $25 \pm 0.5$  °C in a thermostatic laboratory environment. At least two identical sensors of each type were tested in the experiments.

The conductivity of test solutions was controlled with a commercial conductimeter EC-Meter GLP 31+ (Crison).

### 2.3. Chemicals

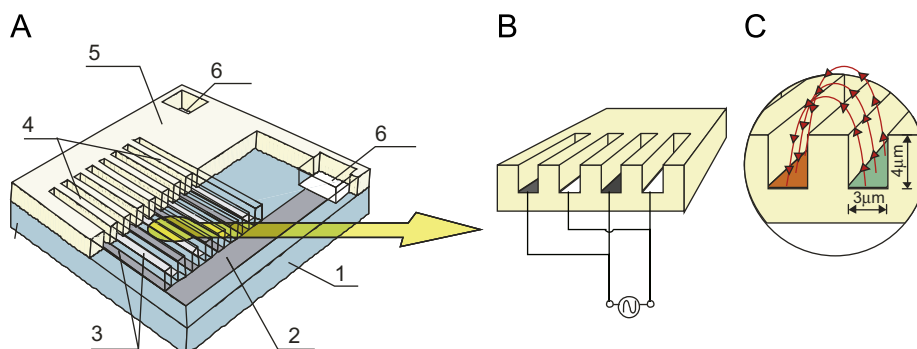
As an ionic surfactant sodium dodecyl benzene sulfonate (NaDBS) from Sigma-Aldrich was used. Decaethylene glycol monododecyl ether (polyoxyethylene 10 lauryl ether, C12E10, Sigma-Aldrich) was used as a non-ionic surfactant. Commercial detergents were purchased at a local supermarket.

Test solutions were prepared using deionised water and analytical grade chemicals. In experiments with commercial detergents tap water was used to prepare detergent solutions.

## 3. Results and discussion

### 3.1. Physical model of the device and its equivalent electrical circuit

When a tangential electric field is applied at the solid/solution interface, due to a higher concentration of ions within the electrical double layer (EDL), the local electric current can be higher than that typical of the bulk electrolyte solution. For a long time it was considered that surface conductivity is associated only with migration of ions accumulated within diffuse part of the EDL. Accumulated experimental evidence obliged to revise the EDL model of the solid/liquid interface [24,25] and to assume that under electric potential gradient part of ions which can migrate under the electric field is located in a stagnant layer of EDL. The current density in both surface layers is determined by concentration and mobility of ions. It may be noted that ion mobility



**Fig. 1.** (A) Design of the studied device with microcapillaries on its surface (1—isolating substrate, 2—electrode collector bar, 3—electrode digits, 4—microcapillaries opened over electrode digits, 5—silicon dioxide cover layer, 6—contact pads). (B) Electrical connection scheme. (C) Electrical field lines passing over the barrier separating two electrode digits are shown.

Download English Version:

<https://daneshyari.com/en/article/7683827>

Download Persian Version:

<https://daneshyari.com/article/7683827>

[Daneshyari.com](https://daneshyari.com)