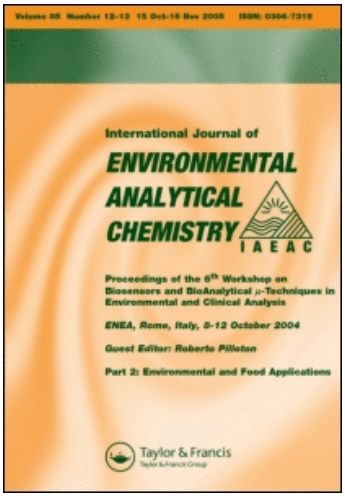

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Electrochemical sensors for heavy metals detection in liquid media

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Electrochemical sensors for heavy metals detection in liquid media

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The detection of very small concentrations of heavy metal traces in liquid food is important for quality-of-life control. The design and the experimental technology for an electrochemical sensor on silicon with application in these determinations are presented in this article. Its particularity consists in the integration of all three electrodes on the same chip: the reference electrode (RE), contraelectrode (CE) and the working electrode (WE); the last electrode, WE, is designed like an array of nanoelectrodes in order to enhance the active area and to improve the limit of detection. The voltammetric measurement results and calibration curves of the electrochemical sensor are presented.

Keywords: Nanoelectrode arrays; Cyclic voltammetry; Heavy metals

1. Introduction

The sensors designed for electrochemical measurements are very useful in trace metal determination due to the fact that they offer a good sensitivity and can be used for *in situ* analysis [1]. Two well-known voltammetric methods were used to determine the concentrations of different metallic ions in support electrolyte: cyclic voltammetry (CV) and square-wave voltammetry (SWV). The advantage of the SWV method in comparison with the CV method is that the background current is removed from the measurement and the limit of detection is improved to 10^{-9}.

2. Experimental

In the last few years it has been demonstrated that even infinitesimal amounts of heavy metal ions can affect the ecosystem or human life. The dimensions of normal electrodes used in electrochemistry are of the order of millimeters and their limit of sensitivity is in the range of 10^{-2}–10^{-3} M for different inorganic and organic species within solvents

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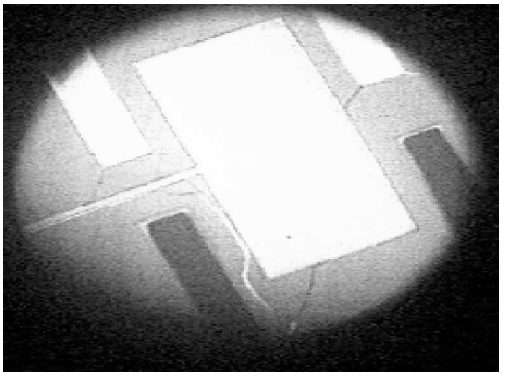

Figure 1. Layout of the integrated cell.

or electrolytes. Theoretical studies have demonstrated that the electrochemical measurements are mainly affected by the noise currents due to the potential drop in solutions iR_s, where i is the current through electrodes and R_s is the solution resistance between the reference electrode and the working electrode.

In order to minimize this parasitic effect, a new electrochemical system, with all three electrodes integrated on a single chip, was designed. The layout of the integrated cell is presented in figure 1. The main advantage is a smaller R_s value due to the smaller distance between electrodes.

It is also known [2] that the reduction of electrode surface area tends to decrease the quantity iR_s by reducing the current, i, so for improving the sensibility of electrochemical measurements, the electrode dimensions were reduced to microns and more recently to nanometers. The working electrode (WE) is the main part of the electrochemical cell and its sensitivity will determine the detection limit of the device. In order to maintain a measurable current output in the cell [3], we have designed the WE as an array of metal/dielectric/silicon nanoelectrodes with pyramidal shape which are connected in parallel; in this way, by adding these parallel currents results a better output current while a high signal/noise ratio is maintained.

We have designed different array structures in order to study the influence of the WE structure layout parameters: with two base areas, 8×8 and $8.2 \times 8.2\,\mu m^2$, two distances between structures, 12 and 24 μm, and three groups of electrodes in the array, 15×15; 30×30 and 60×60, respectively.

It was proposed that a simple fabrication technology [4, 5] based on standard processes was used in silicon device manufacturing systems. The technological steps used to realize the WE structures are as follows:

- The substrate material was a p-type (100) silicon wafer of 6–10 Ω cm resistivity.
- Si etching of pyramidal structures through a 0.6 μm silicon dioxide mask. After etching, the substrate was again oxidized to ensure the isolation between electrodes and the semiconducting Si substrate.
- Au or Pt thin films (100–300 nm thickness) as electrode material were deposited on the whole Si surface, by the evaporation method and by MOCVD respectively; the insulating material was SiO_2 or SiO_2/Si_3N_4 sandwich.
- A short UV exposition process was performed without any mask in order to release the metallic top of the electrodes.

- Finally, contact wires were bonded and the structures were isolated with siliconic resin.

Figure 2 presents an SEM image of the WE as a nanoelectrode array. From a technological point of view, the best base area for nanoelectrodes fabrication is 8 μm × 8 μm. In order to select the optimum number of electrodes [6] in an array we investigated the current response in voltammetric measurements and we observed that the best sensibility is obtained for a 900 nanoelectrodes array. The last studied parameter is the distance between electrodes in the array. Figure 3 presents the evolution of peak positions recorded by square-wave voltammetry measurements for two types of arrays, 900 nanoelectrodes with a distance of 12 μm between one-another, and 24 μm for a different Cu concentration in a 0.1 M HCl support electrolyte. The measured current is two orders magnitude higher for the NE array with bigger distances between two adjacent nanoelectrodes, and this result can be an effect of the diffusion regime characteristics [7, 8]. The electrochemically active area of the nanoelectrode arrays,

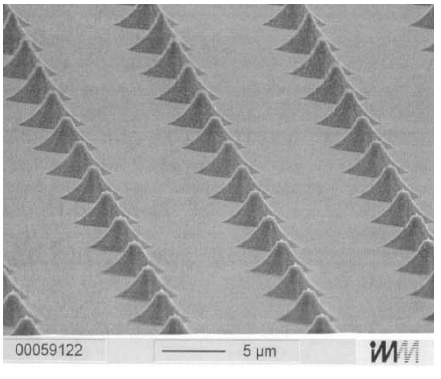

Figure 2. Detail of WE–SEM image of a nanoelectrode array.

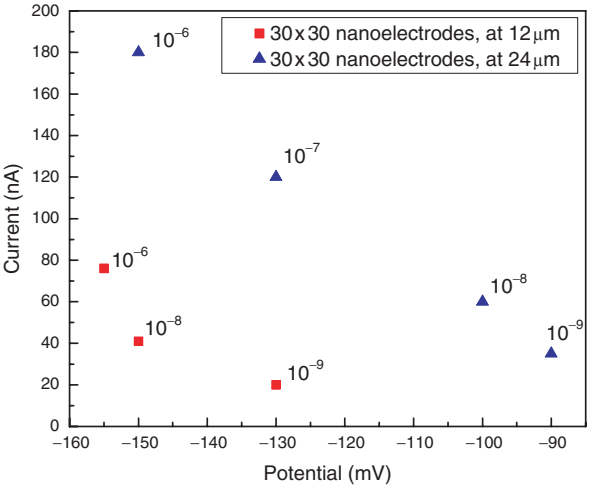

Figure 3. Evolution of peak position recorded for two types of nanoelectrode arrays at different Cu ion concentrations.

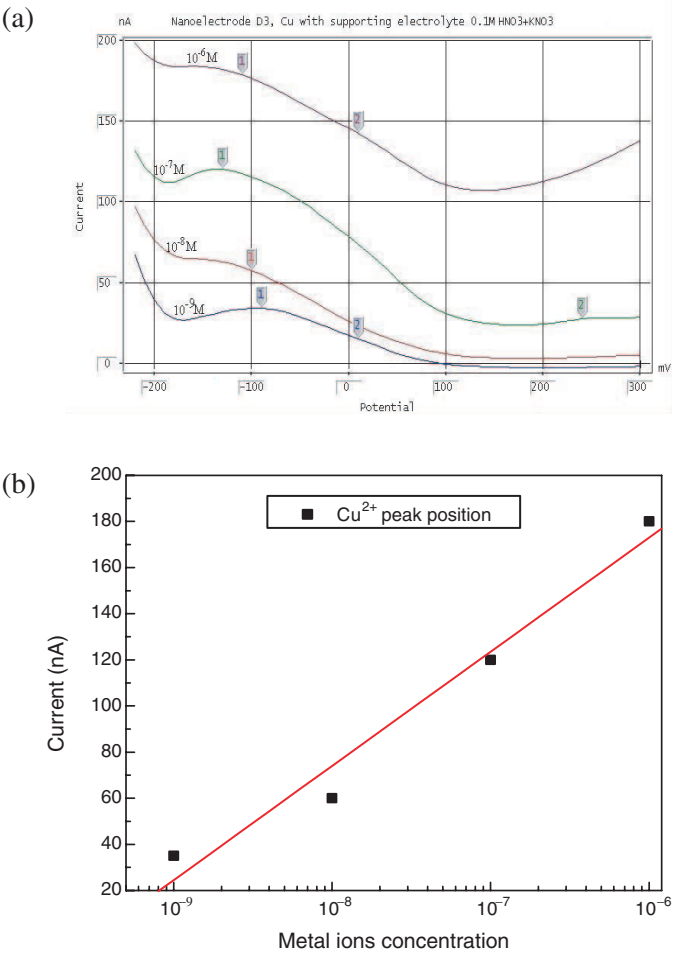

Figure 4. (a) Determination by square-wave voltammetry (SWV) of Cu^{2+} concentrations in support electrolit (b) Calibration curve for Cu^{2+} ions resulted from voltammograms with 30×30 nanoelectrodes arrays.

and also the measured faradaic current, depend both on electrode size and array geometry: for small distances between electrodes an overlapping regime appears and diffusion of electroactive species from electrolit to the electrode surface will be linear, and the NE array will act like a macroelectrode which imply a diminishing current response.

The nanoelectrode arrays as working electrodes were calibrated for Cd^{2+}, Pb^{2+}, Fe^{2+} and Cu^{2+} detection; the calibration curves allow the interpolation of the results for determination of metallic ion concentrations in different solutions. Figure 4(a) presents the results obtained by square-wave voltammetry measurements in a 0.1 M HCl support electrolyte with different concentration of Cu^{2+}. Figure 4(b) presents a WE with an array of 30×30 nanoelectrodes and calibration curves for Cu^{2+} resulting from corresponding voltammograms. The observation is that it presents a good linearity between peak currents and ion concentrations.

3. Conclusions

The electrochemical sensor based on nanoelectrode arrays as a working electrode presents an improved sensitivity compared with macro- or microelectrode sensors. Another important advantage is that a small sample volume is required by reducing sensor dimensions. The impurity detection limit is lower in square-wave voltammetry than in cyclic voltammetry measurements. A good linearity of the calibration curves was obtained; calibration curves allow the interpolation of the results for different concentrations of metallic ions. A new electrochemical cell structure with all three electrodes integrated on the same silicon chip was designed.

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References

[1] K.-S. Yun, H.-J. Kim, S. Joo, J. Kwak, E. Yoon. *Jpn. J. Appl. Phys.*, **39**, 7159 (2000).
[2] C.A. Amatore. In *Physical Electrochemistry*, I. Rubinstein (Ed.), Marcel Dekker, NY, USA, pp. 131–208 (1995).
[3] W.E. Morf, N.E. de Rooij. *Sensors & Actuators B*, **44**, 538 (1997).
[4] I. Kleps, A. Angelescu, M. Avram, M. Miu, M. Simion. *Microelectron. Eng.*, **61–62**, 675 (2002).
[5] I. Kleps, A. Angelescu, M. Miu, M. Avram, M. Simion. *Mater. Sci. and Eng.*, **C19**, 219 (2002).
[6] B. Brunetti, P. Ugo, L.M. Moretto, C.R. Martin. *Journal of Electroanalytical Chemistry*, **491**, 166 (2000).
[7] I. Kleps, A. Angelescu, M. Miu, M. Simion. NATO Science Series. In *Mathematics, Physics and Chemistry*, Thomas Tsakalakos (Ed.), Vol. 128, pp. 639–649 (2001).
[8] J.C. Hulteen, V.P. Menon, C.R. Martin. *J. Chem. Soc., Faraday Trans.*, **92**, 1029 (1996).