Disposable microfabricated bismuth microelectrode arrays for trace metal analysis by stripping voltammetry

Christos Kokkinos\textsuperscript{a}, Anastasios Economou\textsuperscript{a,*}, Ioannis Raptis\textsuperscript{b}, Thanassis Speliotis\textsuperscript{c}

\textsuperscript{a}Department of Chemistry, University of Athens, Athens 157 71, Greece
\textsuperscript{b}Institute of Microelectronics, NCSR "Demokritos", Athens 153 10, Greece
\textsuperscript{c}Institute of Materials Science, NCSR "Demokritos", Athens 153 10, Greece

Abstract

This work reports the fabrication of disposable bismuth microelectrode arrays by a thin-film microengineering approach and their application in stripping voltammetry. The microelectrode array was fabricated by sputtering and photolithography and consisted of 625 bismuth microdisks 10 \( \mu \)m in radius with centre-to-centre separation of 200 \( \mu \)m. The detection of trace metals, by stripping voltammetry, was carried out in unstirred solutions containing low concentrations of supporting electrolyte. These sensors provided enhanced analytical characteristics compared to conventional bismuth-film electrodes (BiFEs).

© 2011 Published by Elsevier Ltd. Open access under CC BY-NC-ND license.

Keywords: bismuth electrodes; microelectrode arrays; stripping analysis; trace metals

1. Introduction

Microelectrodes, owing to their small size, provide several advantages as compared to conventional (macro-)electrodes, such as enhanced rates of mass-transport, decreased ohmic drop and increased signal-to-noise ratios [1,2]. Nevertheless, a major drawback in the use of single microelectrodes is that they give rise to extremely low currents. A way to deal with this problem is the use of arrays of microelectrodes, whereby multiple microelectrodes are operated in parallel [1,2]. Bismuth film electrodes (BiFEs) have gained importance in the field of electrochemical stripping analysis thanks to their advantageous

\* Corresponding author. Tel.: +30 210997728; fax: +30 2107274750.
E-mail address: aeconomo@chem.uoa.gr.
properties in stripping analysis with the low toxicity being their most attractive feature [3,4]. The most widely used approach for the preparation of bismuth film microelectrodes involves in situ or ex situ electrochemical plating by reduction of Bi(III) ions to metallic bismuth on a suitable supporting material [3,4]. A new methodology for the preparation of bismuth electrodes has been recently introduced based on thin-film microelectronic technology [5-7]. The application of this approach for the fabrication of bismuth film microelectrodes offers a series of advantages compared to traditional electroplating. In particular, a Bi(III) plating solution is not required, a conductive substrate is not necessary, the electrode geometry and the surface characteristics can be easily controlled and therefore the mass-production of inexpensive and disposable devices can be achieved in a reproducible fashion. In this work, a method for the fabrication of bismuth-film microdisk arrays is presented and the resulting devices were used for the analysis of Cd(II) and Pb(II) using anodic stripping voltammetry (ASV) in static solution.

2. Experimental

2.1. Instrumentation, chemicals

A home-made potentiostat was interfaced to a Pentium PC through a multi-function interface card (6025 E PCI, National Instruments, TX). Stripping voltammetry was carried out by a purpose-developed application programme in LabVIEW 7.1 (National Instruments). Experiments were carried out in a standard electrochemical cell incorporating a bismuth microelectrode array working electrode, a Ag/AgCl (sat. KCl) reference electrode and a Pt wire serving as the counter electrode.

All the chemicals were of analytical grade. Doubly-distilled water was used throughout. Working metal ion solutions were prepared from 1000 mg l⁻¹ atomic absorption standard solutions after appropriate dilution with water. The stock supporting electrolyte was 1 mol l⁻¹ acetate buffer (pH 4.5).

2.2. Fabrication of the sensors

The process for the fabrication of the bismuth microelectrode arrays is schematically illustrated in Fig. 1(a). Silicon wafers (3” in diameter, 500 μm in thickness) were covered with a layer of SiO₂ 1080 nm thick by means of wet thermal oxidation. Then, bismuth was sputtered on the wafer at a nominal thickness of 400 nm from a Bi target (99.9 % purity, Williams Advanced Materials, Buffalo, NY) at a constant current of 7 mA, using a thin film deposition system (CV401, Cooke Vacuum Products, South Norwalk, CT). The wafer was spin-coated at 7000 rpm for 1 min with a layer of AZ5214 photoresist (EZ-EM Materials) 1 μm thick followed by heating at 95 °C for 10 min. The mask (which was transparent except for the microelectrodes and the grip pad which were patterned as black areas) was attached firmly on the wafer and the wafer was illuminated with a Hg lamp (AZ210 Mega, UK) for 60 s, immersed in AZ726 MIF developer (EZ-EM Materials) for 90 s, washed with doubly distilled water and dried under nitrogen. Then, a layer of SiO₂ was sputtered on the wafer at a nominal thickness of 200 nm from a SiO₂ target (99.9 % purity, Williams Advanced Materials, Buffálo, NY) using a power of 200 W. In order to remove SiO₂ from the regions that were covered with photoresist (i.e the working and contact areas), the wafer was sonicated in acetone for 5 min (lift-off). Finally, the wafer was washed with acetone and isopropanol and dried under nitrogen. Fig. 1(b) illustrates a SEM image of a typical bismuth microelectrode array fabricated via the procedure described above.
3. Result and discussion

In square arrays of circular disk microelectrodes, the ratio $d/R_b$ (where $d$ is the inter-electrode spacing and $R_b$ is the individual electrodes’ radius) is a critical parameter that defines the diffusion profiles of the electro-active substance to the surface of the electrodes [1,2]. When the individual electrodes in the array are sufficiently separated (the ratio $d/R_b$ is large) each microelectrode experiences its own (radial) diffusion regime and behaves like an isolated microelectrode. At the other extreme, when the inter-electrode distance in the array is not sufficiently large (the ratio $d/R_b$ is small), the individual microelectrodes experience completely overlapping diffusion regimes such that one dimensional diffusion predominates. In the literature, values of $d/R_b$ of at least 10 are recommended, in order for the array to behave like an ensemble of ideal microelectrodes [8]. Under these conditions, the preconcentration step can be performed in quiescent solution in stripping analysis. Therefore, in this work, bismuth microdisk arrays 10 μm in radius with centre-to-centre separation of 200 μm were exploited to carry out the analysis in unstirred solutions.

Fig. 2 illustrate stripping voltammograms and calibration graph for the determination of Pb(II) and Cd(II) in standard solution. The limits of detection (calculated as LOD=$3\sigma_b/S$, where $\sigma_b$ and $S$ are the standard deviation of the intercept and the slope of the calibration plot, respectively) were 3.4 μg l$^{-1}$ for Pb(II) and 6.7 μg l$^{-1}$ for Cd(II). On average, 8-10 consecutive preconcentration/stripping cycles (equivalent to 15-20 min of operation) could be performed with each bismuth microelectrode array without statistically significant change in sensitivity.

4. Conclusion

In this work we have described the fabrication of bismuth microdisk arrays and their utility in stripping analysis. The sensors were fabricated by a multistep microfabrication approach combining sputtering for the deposition of the bismuth layer and the insulator on the surface of a silicon wafer and
photolithography for the definition of the geometry of the sensing and grip areas. The measurements were carried out in unstirred solutions demonstrating the enhanced analytical characteristics of these devices.

The sensors are mercury-free and environmentally-friendly, disposable, easy and inexpensive to mass-produce in a reproducible manner and they can be easily used for on-site analysis in combination with micro-total analysis systems (μ-TAS).

![Square-wave stripping voltammograms in static solution on a bismuth microelectrode array for increasing concentrations of Pb(II) and Cd(II) after preconcentration for 120s. From below: blank and nine successive additions of 10 μg l⁻¹ Pb(II) and Cd(II) (the calibration graph is shown as the inset (●-Pb, ○-Cd)).](image)

References

[1] Daniele S, Baldo MA, Bragato C. Recent developments in stripping analysis on microelectrodes. *Curr Anal Chem* 2008; 4: 215-228.

[2] Beni V, Arrigan DWM. Microelectrode arrays and microfabricated devices in electrochemical stripping analysis. *Curr Anal Chem* 2008;4: 229-241.

[3] Economou A. Bismuth-film electrodes: Recent developments and potentialities for electroanalysis. *TrAC* 2005; 24: 334-340.

[4] Kokkinos C, Economou A. Stripping analysis at bismuth-based electrodes. *Curr Anal Chem* 2008;4:183-190.

[5] Zou Z, Jang A, MacKnight E, Wu PA, Do J, Bishop PL, Ahn CH. Environmentally friendly disposable sensors with microfabricated on-chip planar bismuth electrode for in situ heavy metal ions measurement. *Sens Actuat B* 2008; 134:18-24.

[6] Kokkinos C, Raptis I, Economou A, Speliotis T. Determination of trace Tl(I) by anodic stripping voltammetry on novel disposable microfabricated bismuth-film sensors. *Electroanalysis* 2010; 22: 2359-2365.

[7] Kokkinos C, Economou A, Raptis I, Speliotis T. Disposable lithographically fabricated bismuth microelectrode arrays for stripping voltammetric detection of trace metals. *Electrochem Commun* 2011; 13:391-395.

[8] Xie X, Stueben D, Berner Z. The application of microelectrodes for the measurements of trace metals in water. *Anal Lett* 2005; 38: 2281-2300.