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Disposable microfabricated 3-electrode electrochemical devices with integrated antimony working electrode for stripping voltammetric determination of selected trace metals

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ABSTRACT

This work reports the fabrication of novel 3-electrode integrated devices featuring an Sb-film working electrode and Ag and Pt planar strips serving as the reference and counter electrodes, respectively. The deposition of the metal layers was carried out by sputtering of the respective metals on an oxidized silicon substrate, while the electrodes were patterned via a metal mask and isolated using a simple photolithographic step. The utility of these devices was tested for the simultaneous trace determination of Pb(II) and Tl(I) by square-wave anodic stripping voltammetry (SWASV) in strong acidic medium (0.05 mol L^{-1} phosphoric acid) in which the antimony sensor exhibited advantageous electroanalytical performance. The limits of detection were 0.7 $\mu g\,L^{-1}$ for Pb(II) and 0.9 $\mu g\,L^{-1}$ for Tl(I), and the within-sensor reproducibility was 3.2% for Pb(II) and 3.9% for Tl(I) at the 20 $\mu g\,L^{-1}$ level ($n = 12$). The applicability of these novel sensors was demonstrated for the analysis of a spiked mineral water sample.

1. Introduction

Among different electrochemical techniques, stripping voltammetry plays an important role and has long been recognized as one of the most powerful tool in trace and ultratrace analysis of heavy metals and some organic compounds, due to its exceptional sensitivity in conjunction with different electrode materials [1]. Mercury, in the form of either the hanging mercury drop electrode (HMDE) or the mercury-film electrode (MFE), has been the commonest electrode material in electroanalysis. However, the drawback of metallic mercury and the mercury salts is their toxicity [2]. In the search for less toxic electrode materials, bismuth has been shown to be one of the most promising, as demonstrated in recent comprehensive reviews [3,4].

The antimony-film electrode (SbFE) was introduced in 2007 offering some attractive characteristics in electrochemical stripping analysis [5]. Its main advantage in comparison to the bismuth-film electrode (BiFE) is its favorable performance in strong acidic media [6,7]. The commonest approach for the fabrication of SbFEs involves in situ [5–15] or ex situ [16] electrochemical plating by reduction of Sb(III) to metallic Sb at a suitable support material. Additionally, Sb-modified electrodes have been reported including a macroporous SbFE [17], an antimony modified boron-doped diamond electrode [18], an antimony powder-modified carbon paste electrode [19] and some antimony-precursor modified electrodes [20,21].

Recently, an alternative microfabrication approach for the preparation of metal-film electrodes has been proposed, based on the formation of a thin metal film on a silicon substrate by sputtering [22,23]. This methodology offers several advantages compared to electroplating since neither a plating solution nor a conductive substrate are required (resulting in a simpler, shorter and low-cost fabrication procedure), complications associated with the composition and the pH of the plating solution are avoided, reproducible surface area and morphology of the electrodes are ensured and, finally, there is increase scope toward the mass-production of inexpensive and disposable devices with small size and with a variety of configurations.

This work reports the fabrication of miniaturized integrated devices featuring metal-film electrodes (a Sb-film working electrode, a Ag-film reference electrode and a Pt-film counter electrode) by a thin-film microengineering approach. The integration of all three electrodes in a single package is ideal for on-site and field analysis that requires miniaturized and simple instrumentation. The microfabricated devices were tested for the simultaneous determination of Pb(II) and Tl(I) at trace levels by anodic stripping voltammetry (ASV) and the method developed was successfully applied to the analysis of a spiked mineral water sample.

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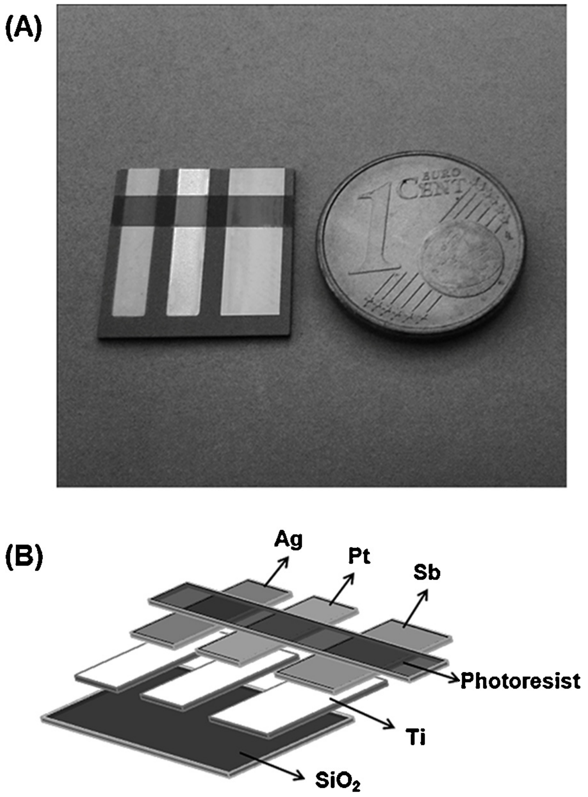

Fig. 1. (A) Photograph of the microfabricated device and (B) steps for the microfabrication of the Sb device.

2. Experimental

2.1. Chemicals and reagents

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 solution was 0.5 mol L^{-1} phosphoric acid. A 0.01 mol L^{-1} stock solution of $K_4[Fe(CN)_6]$ and a 2 mmol L^{-1} stock solution of the disodium salt of EDTA were prepared in water.

2.2. Fabrication of the sensors

A schematic diagram of the fabrication of a sensor is illustrated in Fig. 1. A metallic plate manufactured by a thin sheet of aluminum and featuring slots for the three electrodes was used as a metal mask to define the planar geometry of the electrodes. Silicon wafers (3″ in diameter, 500 μm in thickness) were covered with a layer of SiO_2 1080 nm thick by means of wet thermal oxidation. The metal mask was attached firmly on the wafer and Ti was first sputtered on the wafer areas to a thickness of 5 nm. This layer was found to be necessary for better adhesion of the metallic films on the wafer. Then, the three electrodes were formed by successively sputtering of each metal in the order: Ag (800 nm), Pt (400 nm) and Sb (400 nm) on the wafer at the respective slots by covering the other two slots with a plastic sheet. Then the wafer was spin-coated at 4000 rpm for 1 min with HMDS (hexamethyldisilazane, BASF VILSI Selectipur) followed by heating at 95 °C for 10 min. Next, the wafer was spin-coated at 7000 rpm for 1 min with a layer of AZ5214 photoresist (EZ-EM Materials) and heated at 95 °C for 10 min. The photoresist mask 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. As a final step, the wafer was heated at 150 °C for 15 min. The final dimension of the planar electrodes were (length × width, in mm): WE 5 × 5; CE 3 × 5; RE 3 × 5. A photograph of the complete sensor is shown in Fig. 1(A). It must be mentioned that the goal of the addition of HMDS and the final step of heating was to enhance the mechanical stability of the insulator layer and prolong the life-time of the sensor, making it suitable for extended use. Microfabricated bismuth sensors used for comparative studies were fabricated according to our previous work [23].

Before use, the sensor was immersed into a 0.1 mol L^{-1} KCl solution and the Ag and Pt electrodes were connected to the anode and cathode, respectively, of a power supply. An anodic current of 1 mA was applied for 10 s in order to cover the Ag electrode with AgCl.

2.3. Apparatus

All electrochemical experiments were carried out with an electrochemical analyzer PGSTAT101 (Metrohm Autolab, Utrecht, The Netherlands) connected to a personal computer. Control of the potentiostat, data acquisition and data manipulation was performed with the NOVA 1.8 software (Metrohm Autolab). The morphology of the antimony and bismuth deposits was observed with an atomic force microscope (SPM SMENA, NT-MDT Co., Moscow, Russia). The thin film deposition system was the CV401 (Cooke Vacuum Products, South Norwalk, CT) and the metal targets were 99.9% purity (Williams Advanced Materials, Buffalo, NY).

2.4. Sample preparation

18.0 mL of a mineral water sample was acidified with 2.0 mL of 0.5 mol L^{-1} phosphoric acid, the solution was spiked with 5 μg L^{-1} of Pb(II) and 10 μg L^{-1} Tl(I) and the solution was subjected to analysis as described in the next section with no further treatment.

2.5. Measurement procedure

The sensor was immersed in the sample solution and electrolytic preconcentration of Pb(II) and Tl(I) was carried out at −1.20 V for a predefined time period in stirred solution. After the accumulation, the stirring was stopped, the solution was allowed to settle for 10 s and a SW voltammetric scan was applied to the working electrode from −1.10 V to −0.20 V, while the voltammogram was recorded. Then, the electrode was cleaned from traces of remaining target metals for 20 s at −0.20 V. Quantification was performed by standard additions of Pb(II) and Tl(I).

3. Results and discussion

3.1. Optical and electrochemical characterization of the antimony working electrode

Macroscopic inspection of the sputtered Sb-film showed a grayish, mirror-like surface of the antimony deposit. However, inspection by AFM (Fig. 2(A)) revealed that the fine structure of the Sb coating was coarse, with average roughness of a few nanometers which is similar to sputtered Pt and Ag layers. On the contrary, the bismuth film surface exhibited a much coarser surface morphology characterized by significantly higher average roughness (Fig. 2(B)). This is corroborated by earlier work indicating that the roughness of the sputtered film surface depends on the melting point of each metal: deposits of metals with lower melting point have higher average roughness (melting points for Sb ~630 °C and for Bi ~271 °C) [24].

Since previous studies have demonstrated the suitability of the SbFE for ASV measurements of metal ions in relatively strong acidic