



Short communication

Tin-film mini-sensors fabricated by a thin-layer microelectronic approach for stripping voltammetric determination of trace metals

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ARTICLE INFO

Article history:

Received 26 October 2013

Received in revised form 14 November 2013

Accepted 18 November 2013

Available online 22 November 2013

Keywords:

Tin-film electrode

Trace metals

Stripping voltammetry

Sputtering

Photolithography

ABSTRACT

This work describes a novel type of disposable microfabricated tin-film electrode (SnFE) suitable for trace metal analysis by stripping voltammetry. The tin sensors were fabricated by sputtering of metallic tin on an oxidized silicon chip with the exact geometry of the sensors defined by photolithography. The resulting sensors were characterized by optical and electrochemical techniques. The SnFEs were tested for the simultaneous determination of Zn(II) and Cd(II) by square-wave anodic stripping voltammetry (SWASV) and of Co(II) by square-wave adsorptive stripping voltammetry (SWAdSV) in the presence of dissolved oxygen. The limits of detection were $0.7 \mu\text{g L}^{-1}$ of Cd(II), $1.1 \mu\text{g L}^{-1}$ of Zn(II) and $0.6 \mu\text{g L}^{-1}$ of Co(II). The within-sensor reproducibility was 3.4% for Cd(II) and 4.5% for Zn(II) at the $10 \mu\text{g L}^{-1}$ level ($n = 8$) and 3.2% for Co(II) at the $8 \mu\text{g L}^{-1}$ level ($n = 8$). The tin-film sensors are disposable, sensitive, environmentally friendly and readily mass-produced; therefore, they can serve as alternative to conventional electroplated metal-film electrodes for stripping voltammetric analysis.

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1. Introduction

For many years, mercury film electrodes (MFEs) have been the transducers of choice for sensitive stripping voltammetric determination of trace metals owing to the advantageous electroanalytical properties of mercury [1]. In view of the concerns over the toxicity of mercury [2], the development of alternative mercury-free electrodes has been the focus of intense research. The bismuth-film electrode (BiFE) was the first such "green sensor" [3,4] which was later complemented by the antimony-film electrode (SbFE) [5–7]. Bismuth and antimony exhibit relatively low toxicity and satisfactory electroanalytical properties and, thus, the respective electrodes can serve as mercury-free transducers in stripping voltammetry [3–7].

The tin-film electrode (SnFE) is the latest addition in this arsenal of new metal-film sensors with low toxicity and its electroanalytical performance is still under preliminary investigation with promising results [8–13]. Existing SnFEs have been fabricated only by in situ electroplating protocol (i.e. reduction of Sn(II) added in the sample solution to metallic tin) on various forms of carbon (glassy carbon, carbon nanotubes carbon paste) [8–12] or gold nanoparticles [13]. These SnFEs have been exclusively applied to anodic stripping voltammetric (ASV) determination of trace heavy metals. On the other hand, no attempt has been made so far to utilize SnFEs for adsorptive stripping voltammetry (AdSV).

In this work, we report a novel type of SnFE fabricated using a microengineering thin-layer methodology based on a combination of sputtering and photolithography. This microfabrication approach successfully addresses the main problems of in situ electroplating, namely the need for a Sn(II) plating solution, the requirement for a conductive substrate, the restrictions regarding the pH of the solution (to avoid hydrolysis of Sn(II)) and the dependence of the structure of the tin deposit on the electroplating conditions. Additionally, the use of microengineering technology enables mass-production of reproducible, inexpensive and disposable sensors with the desirable size and configuration. The scope of the microfabricated SnFEs for stripping analysis was demonstrated for the simultaneous determination of Zn(II) and Cd(II) by ASV and of Co(II) by AdSV in the presence of oxygen and their performance was compared to the benchmark BiFEs.

2. Experimental

2.1. Reagents – instrumentation

All the chemicals were of analytical grade (Darmstadt, Germany) and doubly-distilled water was used throughout. Working metal ion solutions were prepared from 1000 mg L^{-1} atomic absorption standard after appropriate dilution with doubly-distilled water. The stock solutions used in different stages of the analysis were 0.1 mol L^{-1} acetate buffer (pH 4.5), 0.1 mol L^{-1} ammonia buffer (pH 9.2) and 0.05 mol L^{-1} phosphoric acid. A 0.1 mol L^{-1} solution of dimethylglyoxime (DMG) was prepared by dissolving the appropriate amount of the

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solid compound in absolute ethanol. A 0.01 mol L^{-1} stock solution of $\text{K}_4[\text{Fe}(\text{CN})_6]$ was prepared in water. All electrochemical experiments were carried out with an electrochemical analyzer PGSTAT101 (Metrohm Autolab, Utrecht, The Netherlands) connected to a personal computer. Baseline correction of the resulting voltammogram was performed using the NOVA 1.8 software (Metrohm Autolab). Measurements were performed in a standard glass voltammetric

cell equipped with a Ag/AgCl (sat. KCl) reference electrode and a Pt wire auxiliary electrode. The morphology of the tin deposit was observed with an atomic force microscope (SPM SMENA, NTMDT Co., Moscow, Russia) and an X-ray diffractometer (Siemens D500, Bruker GmbH, Karlsruhe, Germany) using the Ni-filtered Cu K α radiation line. The tin and silica oxide targets were of 99.9% purity (Williams Advanced Materials, Buffalo, NY).

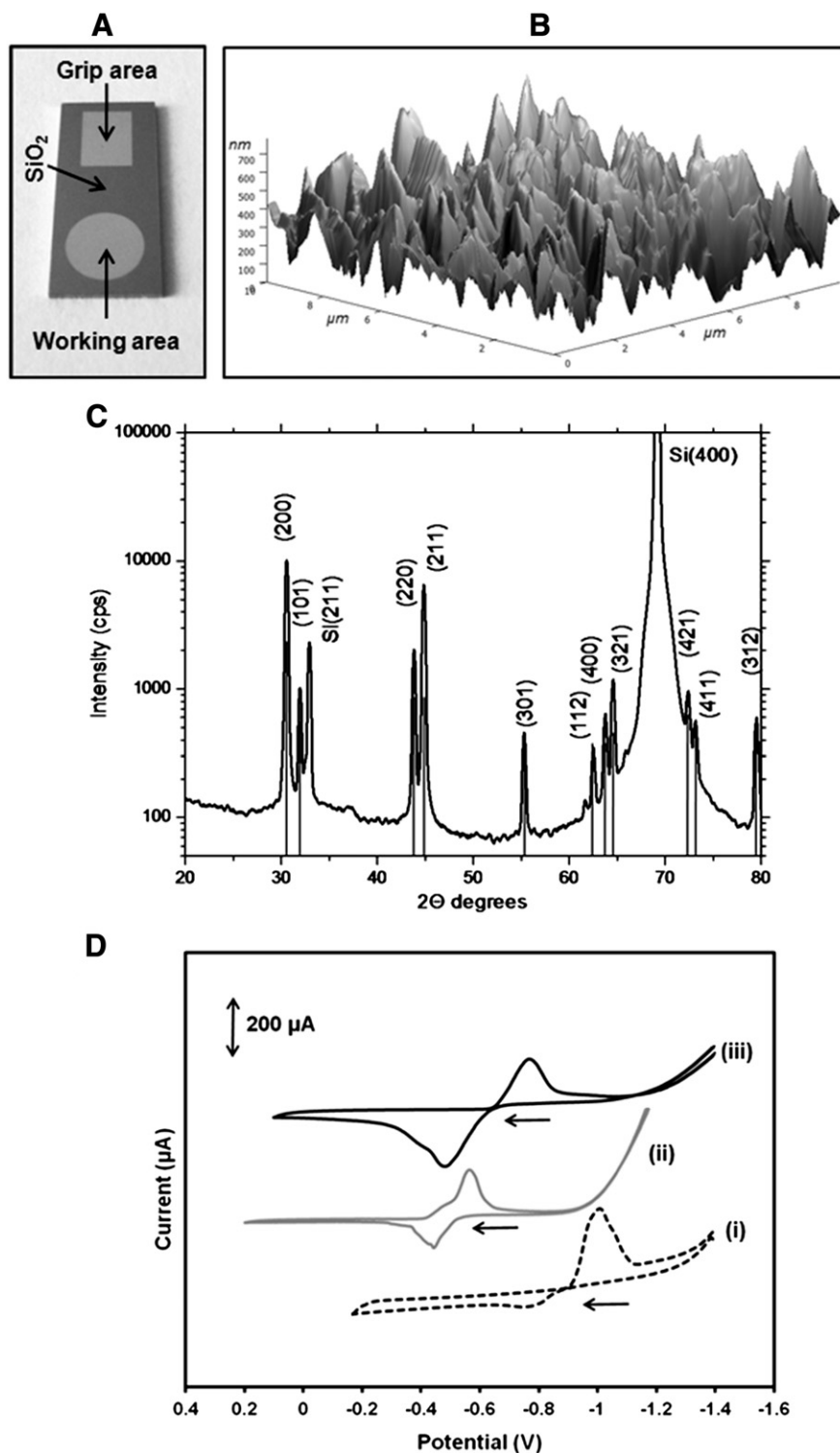


Fig. 1. (A). Photograph of the tin sensor. (B). AFM image of the sputtered SnFE surface. (C). XRD spectrum of the sputtered SnFE (lines correspond to maxima of the XRD spectrum of powdered tin). (D). Cyclic voltammograms of the sputtered SnFE in: (i) 0.1 mol L^{-1} ammonia buffer (pH 9.2); (ii) 0.05 mol L^{-1} phosphoric acid, and; (iii) 0.1 mol L^{-1} acetate buffer (pH 4.5). Scan rate: 100 mV s^{-1} .

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