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FOR THE FUTURE**

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Determination of Trace Heavy Metals by Anodic Stripping Voltammetry at Mercury-plated Silicon Microelectrodes

ABSTRACT

High conductive p- or n-type silicon substrates have been investigated as a support for mercury electroplating. The influence of many parameters, including concentration of the plating solution, plating potential, the kind and concentration of supporting electrolyte on mercury plating has been studied. We have investigated the influence of different electrolytes (acetate buffer, KNO_3 and HClO_4) as well as the effect of a small quantity of BHF (0.2%) added to each electrolyte on mercury plating. The best mercury hemispheres were formed on p-type of silicon in 0.1 mol/L HClO_4 . The stripping current response of trace heavy metals (Cu(II), Pb(II) and Cd(II)) on mercury plated silicon microelectrode array has been demonstrated by square wave anodic stripping voltammetry (SWASV).

INTRODUCTION

Mercury-film electrodes prepared by coating a suitable substrate with a thin layer of metallic mercury have proved to be a powerful tool for heavy metals analysis by anodic stripping voltammetry (ASV). Toxic metals (Cu, Cd, Pb) can simultaneously be determined for concentration levels down to sub-ppb [1]. The high sensitivity and low detection limits are mainly given by the first step involving preconcentration of the analyte species in mercury, which is carried out under a fixed reduction potential for a predetermined time. In the second, stripping step, the accumulated species are stripped from mercury into the solution by reoxidation. The stripping current peaks are proportional to the concentration of the species in the analyte. The choice of the electrode material for sensor construction onto which mercury is deposited is crucial. Different materials such as Ag, Au, Pt, glassy carbon or Ir have been used in voltammetric sensors as a support for mercury-film formation. Especially, iridium is favourable at present because of its good wettability, chemical and mechanical resistivity and low solubility in mercury [2]. In this work, high conductive silicon has been investigated as a support for mercury electroplating. The influence of many parameters, including the concentration of the plating solution, plating potential, the kind and

concentration of supporting electrolyte on mercury formation on different silicon substrates has been investigated. The stripping current response of trace heavy metals on mercury plated silicon microelectrode array has been demonstrated.

EXPERIMENTAL

A voltammetric sensor has been fabricated very simply by the standard silicon technology (Fig. 1). The sensor consists of 50 000 silicon disc-shaped microelectrodes with disc diameter of 2 μm each and interelectrode spacing 20 μm . A detail of photolithographically patterned microelectrode array is shown in Fig. 2.

High conductive (0.008 - 0.024 Ωcm) p- or n-type silicon substrates have been investigated as a support for mercury electroplating. Mercury (II) nitrate dissolved in a supporting electrolyte was used for mercury electroplating under constant reducing potential at a constant stirring rate. All solutions including trace metals (Cu, Pb and Cd) and electrolytes were prepared from analytical grade chemicals in deionized water. A three-electrode arrangement was used in all

experiments. As a reference, a home-made $\text{Ag}/\text{AgCl}/\text{agar Cl}^-$ (3 mol/L)/ agar NO_3^- (1 mol/L) electrode and, as a counter electrode, a platinum wire were used. Preplated mercury has to be renewed after every measurement in concentrated nitric acid. The native oxide on the silicon surface was removed by dipping the sample into diluted

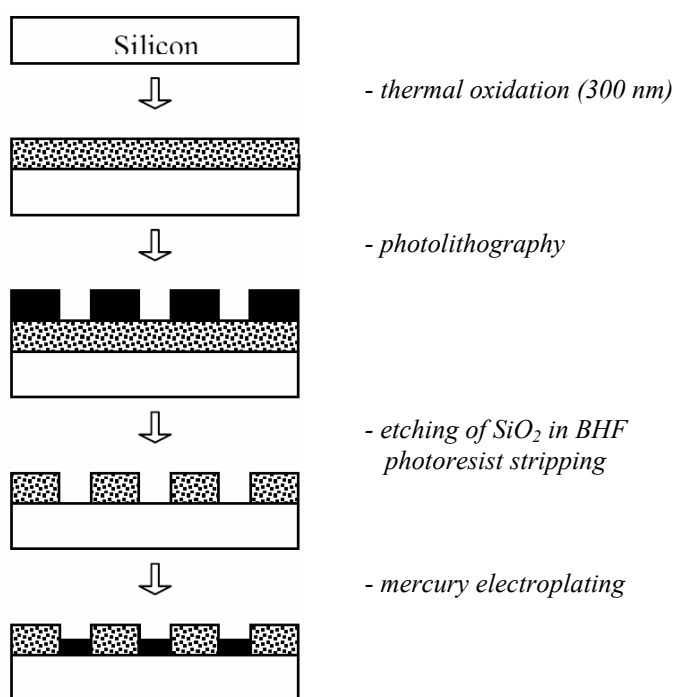


Fig. 1: Fabrication process of the silicon based mercury microelectrode array

buffered hydrofluoric acid (BHF) in volume ratio 1:20 with water immediately before plating. The mercury deposit was examined by optical microscope (Jenapol, C.Zeiss). Cyclic voltammetry (CV) was used to characterize and condition the microelectrode array. Square wave voltammetry (SWV) with $E_{\text{step}} = 5 \text{ mV}$, $E_{\text{pulse}} = 25 \text{ mV}$ and frequency 25 Hz was used to record the stripping current responses. All voltammetric experiments were performed with an Electrochemical Sensor Interface (PalmSens, Palm Instruments BV) in combination with a personal computer.

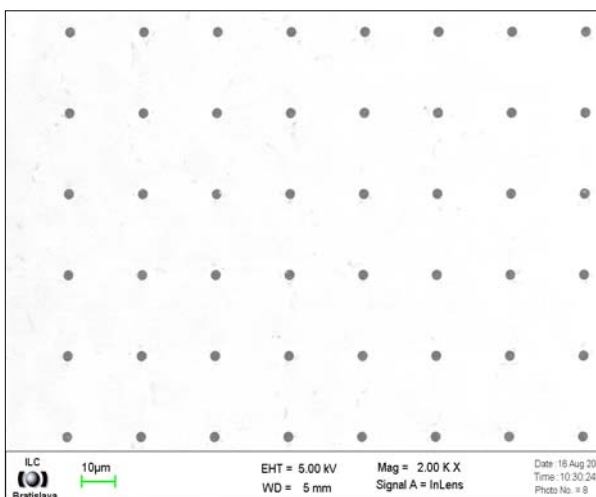


Fig. 2. Detail of the silicon disc-shaped microelectrode array

RESULTS AND DISCUSSION

Characterization of the silicon microelectrode array

In anodic stripping voltammetry on preplated mercury it is very important to select a supporting electrode material with solubility in mercury as low as possible [3]. The

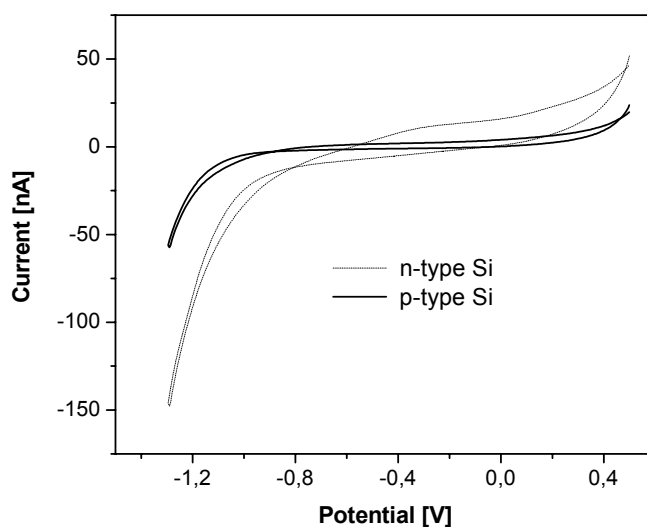


Fig. 3: Cyclic voltammograms of different silicon microelectrodes in 0.1 mol/L acetate buffer; scan rate 50 mV/s

solubility of silicon in mercury is 0.001% [3], which is lower than for frequently used metals in this field such as Au, Ag or Pt, but higher than for Ir. For optimal electroplating of mercury, an electrode material with a great potential window is required. In Fig. 3, cyclic voltammograms are shown in acetate buffer (pH 4) recorded for p- and n-type silicon. From the current curves it is evident that p-type of silicon is more suitable for mercury plating. Intensive hydrogen gas evolution started at approximately -1 V.

Mercury electroplating

The quality of a mercury plated microelectrode greatly influences the sensitivity of anodic stripping voltammetry. A lot of parameters have an influence on the formation of the mercury deposit including plating solution, plating potential and time, etc. In our preliminary experiments, plating solutions consisting of 0.1 mol/L acetate buffer (pH 4) with different contents of Hg (II) (1×10^{-4} , 1×10^{-3} and 1×10^{-2} mol/L) were used. We

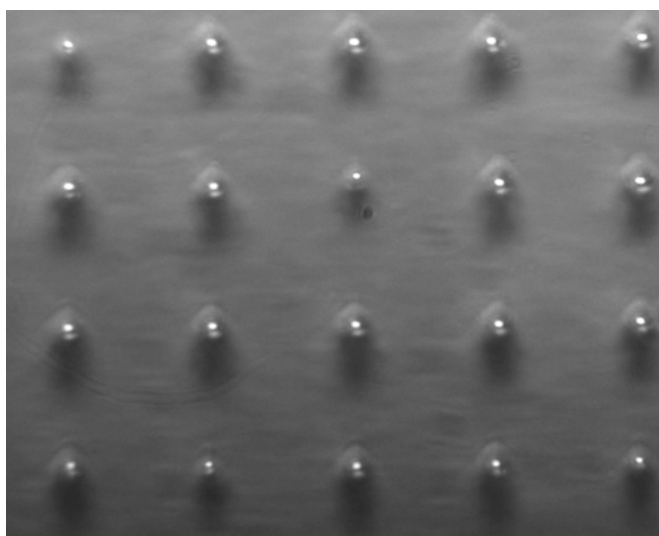


Fig. 4: Detail of silicon (p-type) microelectrode array preplated by mercury hemispheres

obtained the best results in the solution with concentration of Hg (II) 1×10^{-3} mol/L. Almost no mercury was deposited in the solution with 1×10^{-4} mol/L concentration. As far as the plating potential is concerned, a typical value of -1.3 V vs Ag/AgCl/Cl⁻ for deposition of metals (Cu, Pb, Cd, Zn) was insufficient for a silicon substrate. We had to

combine two deposition steps, the first step at -2 V (for 2 min) followed by the second one at -1.3 V for 2 min. High hydrogen gas evolution at -2 V probably disturbed the diffusion layer and thereby it improved the condition for more homogeneous growth of mercury at -1.3 V. When we started the deposition from -1.3 V, only small mercury drops were irregularly formed on silicon discs. It was not possible to cover the silicon surface completely even if the deposition time was prolonged. A detail of mercury hemispheres grown on the silicon microelectrode array is shown in Fig. 4. We have to note that no attempt to cover the silicon surface by a true mercury film at a constant deposition potential was successful.

We have found a strong influence of the electrolyte on mercury plating. We have investigated different electrolytes such as 0.1 mol/L acetate buffer (pH 4), 0.1 mol/L KNO_3 (acidified by HNO_3 to pH 2.5) and 0.1 mol/L HClO_4 . We also investigated the effect of a small quantity of BHF (0.2%) added to each electrolyte in order to keep the silicon surface without oxide all the time. The values of the mercury reoxidation current peak in dependence on electrolyte with and without BHF addition are summarized in Tab. 1. One can see a strong effect of BHF in electrolyte on the mercury reoxidation current for p-type Si. We assume that the presence of the BHF in electrolytes caused

Tab. 1: Influence of the electrolytes on mercury plating condition at concentration of Hg(II) 1×10^{-3} mol/L

Electrolyte (0.1 mol/L)	Hg reoxidation peak [μA]	
	<i>p-Si</i>	<i>n-Si</i>
Acetate	7	12
Acetate + BHF	16	11
KNO_3	75	50
KNO_3 + BHF	220	37
HClO_4	40	15
HClO_4 + BHF	600	11

that a thin oxide layer on silicon was etched permanently, while for electrolytes without BHF the oxide layer remained. This oxide barrier behaviour is probably very sensitive to the Si-Hg interface. We can conclude that the best mercury hemispheres were formed

on p-type of silicon in 0.1 mol/L HClO₄. Hg reoxidation peak appeared at +380 mV. In the case of n-type of silicon, the deposit was unstable; most of mercury hemispheres or spheres were moved away from the microelectrodes towards the insulator layer. Usually only a few microelectrodes were covered by mercury. Moreover, no effect of BHF addition on mercury plating was observed.

Determination of heavy metals

A mercury-plated silicon microelectrode array prepared in a solution of 1 mmol/L Hg(II) in 0.1 mol/L HClO₄ with BHF (0.2%) was used in ex-situ determination of Cu(II), Pb(II) and Cd(II). In Fig. 5, the current response is shown for concentration of heavy metals 3.3×10^{-8} mol/L obtained by square wave voltammetry.

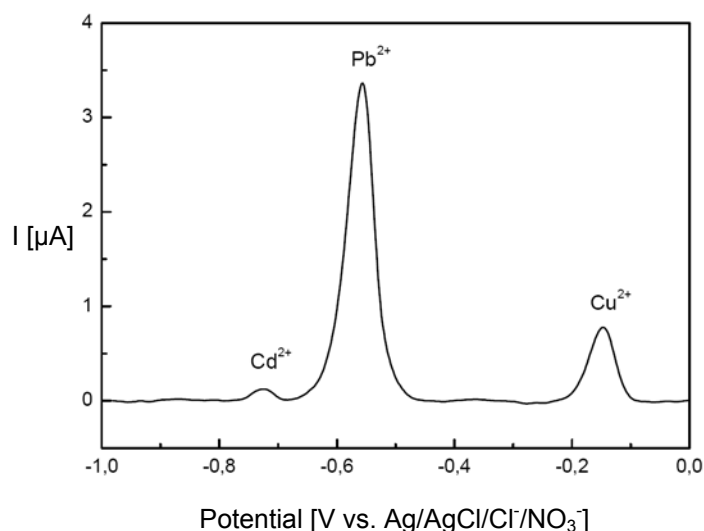


Fig. 5: Square-wave voltammogram for 3.3×10^{-8} mol/L of heavy metals in 0.1 mol/L KNO₃; SWASV was carried out for preconcentration potential of -1V for 120 s

CONCLUSIONS

In this work, high conductive (0.008 - 0.024 Ωcm) p- or n-type silicon substrates have been investigated as a support for mercury electroplating. The influence of many parameters, including the concentration of the plating solution, plating potential, kind and concentration of the supporting electrolyte on mercury plating has been studied. We had to start mercury plating at -2 V (for 2 min) and proceed at -1.3 V for 2 min in order to

form mercury hemispheres. We have investigated the influence of different electrolytes (acetate buffer, KNO_3 and HClO_4) as well as the effect of a small quantity of BHF (0.2%) added to each electrolyte in order to keep the silicon surface without oxide on mercury plating. The best mercury hemispheres were formed on p-type of silicon in 0.1 mol/L HClO_4 . The stripping current response of trace heavy metals (Cu(II), Pb(II) and Cd(II) in concentration 3.3×10^{-8} mol/L of each) on mercury plated silicon microelectrode array has been demonstrated by SWASV.

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