Nanomolar Trace Metal Analysis of Copper at Gold Microband Arrays

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Abstract. This paper describes the fabrication and electrochemical characterization of gold microband electrode arrays designated as a highly sensitive sensor for trace metal detection of copper in drinking water samples. Gold microband electrodes have been routinely fabricated by standard photolithographic methods. Electrochemical characterization were conducted in 0.1 M H$_2$SO$_4$ and found to display characteristic gold oxide formation and reduction peaks. The advantages of gold microband electrodes as trace metal sensors over currently used methods have been investigated by employing under potential deposition anodic stripping voltammetry (UPD-ASV) in Cu$^{2+}$ nanomolar concentrations. Linear correlations were observed for increasing Cu$^{2+}$ concentrations from which the concentration of an unknown sample of drinking water was estimated. The results obtained for the estimation of the unknown trace copper concentration in drinking was in good agreement with expected values.

1. Introduction

The development of robust and reliable sensors with lower detection limits is of increasing importance in analytical chemistry, for both biological and chemical sensing applications. To this end, electrochemical based sensors are being increasingly investigated, due to key advantages such as high sensitivity, selectively, low operating voltages, portability, accuracy and low production costs [1]. Further enhancements arise the dimensions of the sensor electrode are scaled down to ultra micro regimes. At ultra-microelectrodes, i.e. with radii less than 25 μm, radial diffusion profiles of analytes begin to dominate causing increased current densities, mass transport, and increased Faradaic to capacitive current ratios [1-4]. In this manner the application of ultramicroelectrodes as sensors allow increased sensitivity in detection of target analytes, for instance in biologically important molecules (hydrogen peroxide, glucose) [2, 5] and environmental analytes (heavy metals) [6, 7].

Toxicity associated with heavy metals is driving the need for detection of trace metals in a variety of media, such as food and drinking water and is as such a concern no longer restricted to environmental assays. Metals such as lead, zinc, cadmium and copper can cause chronic toxicity to children at relatively low doses (e.g. 8 mg/L for copper). A key concern therefore, is the use of copper pipes for the supply of potable water in domestic urban settings. In this regard, the current EU standard maximum concentration of copper in drinking (tap) water is 2 mg/L (2 ppm) [8]. Current approaches to copper detection involve spectroscopic methods with complex wet chemical sample pre-treatment requirements. These approaches are both costly and time consuming and are restricted

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to laboratory settings with qualified personnel. It is therefore important to develop new robust copper
detection methodologies which may be performed by unskilled personnel at remote locations with
high sensitivity. One approach is the application of electrochemical techniques where a voltage is
applied to an electrode immersed in an acidified sample of interest for a given time interval. By
judicious choice of voltage (versus a reference electrode) copper is selectively plated out of solution
onto the working electrode thereby eliminating the requirement for sample pre-treatment such as
reaction with complex agents e.g. EDTA (Ethylenediaminetetraacetic acid). While traditional
electrochemical analysis of these heavy metals have been conducted at mercury electrodes [9, 10]
due to the fast electrode kinetics), research on detection of metallic analytes at solid-state or noble
metal electrodes has achieved increasing popularity, due to increased sensitivity and low limits of
detection achievable by anodic stripping voltammetry techniques [9].

At noble metal electrodes, cyclic voltammograms (CVs) exhibit two reduction and two oxidation
peaks in the presence of a metallic analyte, one arising from bulk (i.e. multilayer) deposition and
oxidation and the other associated with under potential (i.e. single monolayer) deposition and
oxidation peak. Deposition of the metallic analytes at an under-potential combined with anodic
stripping voltammetry (UPD-ASV) of the monolayer provides a highly sensitive method of analysis
for trace concentrations of metals at nanomolar concentrations [9]. In this work, determination of
copper employing UPD-ASV at gold microband electrode arrays is presented. UPD involves the
pre-concentration of a monolayer of a metallic ion, in our case copper ions, by the application of a lower
potential than would be thermodynamically optimal for bulk deposition. This step is then
immediately followed by the oxidation of this monolayer via a potential sweep method such as linear
voltammetry, from which the amount deposited can be determined. Thus UPD-ASV consists
of two consecutive steps relying on key parameters that are the deposition potential, deposition time
and stripping potential range of the monolayer. Detection of copper at concentrations as low as 10
nM was easily achievable.

2. Experimental

2.1. Gold Microband Electrode Fabrication:
Gold microband electrodes were fabricated using standard optical lithography, metal deposition and
lift-off techniques on silicon substrates comprising a ~300 nm thermally grown silicon dioxide layer.
Microband structures and overlaid metal interconnection tracks were patterned on Microposit LOR
10A Lift-off resist ~ 500 nm thick, followed by metal evaporation (Ti/Au 10/200 nm) and lift-off.
Silicon Nitride (500 nm) was then blanket deposited onto the devices as passivation layer to prevent
unwanted electrochemical reactions occurring at these metal interconnects. Finally trenches were
opened in this passivation layer to expose the microband electrode arrays allowing subsequent contact
with an electrolytic solution.

2.2. Microband Characterization:
Optical micrographs were acquired using a calibrated microscope (Axioskop II, Carl Zeiss Ltd.)
equipped with a charge-coupled detector camera (CCD; DEI-750, Optronics).

2.3. Electroanalysis at Gold Microband Electrodes:
Prior to electrochemical experiments, microband array electrodes were cleaned in pure ethanol
(Sigma-Aldrich) followed by thoroughly rinsing with deionized water. All electrochemical studies
were performed using a CHI760a Electrochemical Analyzer and Faraday Cage CHI200b (CH
Instruments) connected to a PC. Experiments were performed in a three-electrode cell configuration
employing an array of microbands as working electrodes, with gold counter and Ag wire reference
electrodes (Sigma-Aldrich). Cyclic voltammetry was conducted in 0.1 M sulphuric acid in the
voltage range of -0.9V to 1.5V at a scan rate of 5V.s⁻¹. A range of copper sulfate standards in 0.1 M
sulphuric acid were prepared using copper sulphate CuSO₄ (Sigma-Aldrich). All solutions were
prepared with deionized water; 18.2 MΩ cm (ELGA Pure Lab Ultra). All glassware was cleaned and rinsed in DI water prior to all measurements.

3. Results and Discussion:
3.1. Gold Microband Structural characterization:
Gold microband array electrodes were fabricated using photolithography process at silicon wafer substrates bearing a 300 nm layer of thermally grown silicon dioxide, see experimental section. Standard optical lithography was employed to overlay electrical contacts and interconnection tracks onto microband arrays, followed by metal deposition and liftoff. Unwanted electrochemical reactions occurring between metal interconnection tracks and electrochemically active species were prevented by the presence of the silicon nitride layer. A lithographically patterned trench (~30 x 30 μm) was selectively opened in the insulating silicon nitride layer directly above the microband array to allow exclusive exposure of the microband array to the electrochemically active species. Following device fabrication, microband electrodes were characterized using optical microscopy. Figure 1 shows an optical micrograph of a fully fabricated microband array device, with interconnections and silicon nitride passivation. Microband electrodes of width ~2 μm were routinely fabricated.

![Figure 1: An optical micrograph of a fully integrated and passivated microband electrode array.](image)

3.2. Gold Microband Electrochemical Characterization:
Electrochemical investigations were undertaken employing a potentiostat with a Faraday cage to apply an appropriate potential sweep range in a three-electrode set-up utilizing a microband array working electrode versus Ag wire reference with gold counter electrode.

Preliminary voltammetric experiments were conducted in 0.1 M sulphuric acid to confirm that microband electrodes were fully functional and additionally to clean the metal electrode surface. A typical cyclic voltammogram (CV) recorded in 0.1 M H₂SO₄ for the gold microband electrode is shown in figure 2. Characteristic gold oxide formation and reduction peaks are clearly visible, at 1.02 V and 0.55 V, respectively. A stable reduction peak current at microband array was achieved within a few successive cycles confirming that the electrodes were extremely clean. The low values of current measured (~80 nA) strongly suggests that only the microbands were exposed to the electrolyte and that the passivation layer was functioning. This figure is in agreement with data in literature. [2, 6]
3.3. **CV of Copper:**

CV was used to determine the potentials of the monolayer formation (i.e. underpotential deposition) and bulk deposition, as well as their stripping (oxidation) potential. Figure 3 illustrates the peaks corresponding to the formation and oxidation of the copper monolayer, respectively at -0.16 V and 0.12 V, within a voltage range of -0.4 V to 1.5 V. Peaks denoting bulk deposition (-0.45 V) and bulk oxidation (-0.09 V) were found to appear when CVs were conducted at more negative potential ranges. The electrochemical deposition of copper monolayer onto the gold microband surface was thus performed by applying -0.16 V for various preconcentration times at the working electrode. Linear Stripping Voltammetry (LSV) was carried out immediately after in 0.1 M sulphuric acid solution.

3.4. **Cu²⁺ UPD-ASV Optimization:**

Electrochemical UPD was performed on microband arrays for pre-concentration times of 5, 10, 15, 20 and 30s in a variety of CuSO₄ solutions ranging from 10 nM to 750 nM. LSV was performed immediately after each deposition step, at potentials ranging from -0.25 V to 0.55 V, at a scan rate of 5V.s⁻¹. Figure 4a, shows an increase in measured electrochemical stripping current with increasing
deposition times associated with increased amounts of deposited copper on the microband electrode surface.

Figure 4: (a) UPD-SV of 10 nM Cu\(^{2+}\) in 0.1M H\(_2\)SO\(_4\) at a gold microband array electrode. Scan Rate: 5 V.s\(^{-1}\). Deposition times: 5, 10, 15, 20 and 30s. (b) Evaluation of the dependence of electrochemical signal vs. deposition time of 10 nM Cu\(^{2+}\) in 0.1M H\(_2\)SO\(_4\).

To further explore this, the relationship between the increasing signals with respect to the deposition time was analyzed. Figure 4b shows a linear dependence of the copper stripping peak height versus deposition time. This trend was observed for all concentrations of Cu\(^{2+}\) examined. The amount of deposited copper on the microband electrode surface was quantified using equation (1):

\[
\Gamma = \frac{Q}{(nFA)}
\]

where \(\Gamma\) is the surface coverage (mol/cm\(^2\)), Q is the integrated charge of the stripping voltammetric peaks (C), n is the number of electrons exchanged, F is Faraday constant (A/mol) and A is the geometric surface area of the electrode (cm\(^2\)). Estimated surface coverage values recorded in 10 nM Cu\(_2\)SO\(_4\) at microband electrodes, ranged from 2.29 x 10\(^{-10}\) mol/cm\(^2\) (5 s) to 2.38 x 10\(^{-10}\) mol/cm\(^2\) (30 s) of deposition. To avoid saturation of the electrodes a deposition time of 20 s was selected as a suitable interval for deposition for further measurements.
3.5. **Calibration of Cu\textsuperscript{2+} UPD-ASV**: Measurement of the sensitivity of the gold microband arrays to UPD-ASV Cu\textsuperscript{2+} was investigated across a range of nanomolar concentrations at the optimized deposition time of 20s. Stripping peak current was observed to increase with respect to concentration, see figure 5a. Analysis of the relationship between the increasing electrochemical signal and copper concentration was found to be linear across the concentration range 10 - 750 nM, see figure 5b. From this linear range the sensitivity of the microband electrode arrays was estimated to be 2.8 µA/cm\textsuperscript{2}/M

![Figure 5: (a) UPD-SV of a series of Cu\textsuperscript{2+} solutions and sample in 0.1M H\textsubscript{2}SO\textsubscript{4} at a gold microband array electrode. Scan rate: 5 V.s\textsuperscript{-1}. Deposition time: 20s. (b) Evaluation of the dependence of electrochemical signal vs. concentration for a deposition time of 20s.](image)

To investigate application of gold microband arrays for copper detection, determination of copper was undertaken for potable water samples. A domestic sample containing unknown copper concentration was diluted with 0.1 M H\textsubscript{2}SO\textsubscript{4} to bring it within the linear range of method. A dilution of 1:100 turned out to be the most suitable sample preparation and UPD-ASV was carried out under conditions described above, the resulting LSV is shown in figure 5a (red line). From the calibration plot obtained for known concentrations of CuSO\textsubscript{4}, the concentration of copper in the real sample was found to be 1.25 mg/L (ppm), which is lower than the current EU standard of 2 mg/L (ppm) in drinking water (EU Directive 98/83). This work clearly shows the potential of the UPD-ASV technique for the rapid and quantitative detection and measurement of copper ions in real sample matrices.
4. Conclusions:
Gold microband electrode arrays with highly reproducible dimensions were fabricated using photolithography metal deposition and lift-off methods. Cyclic voltammetry in 0.1 M sulphuric acid was employed to confirm the functionality of the microbands as electrochemical devices. Under potential deposition coupled with anodic stripping voltammetry was applied to the microband electrodes as a method of trace metal analysis of copper in 0.1 M H2SO4. The optimized under-potential was assessed to be -0.16 V vs Ag wire and linear sweep voltammetry was used to record the stripping electrochemical response at fast scan rates (5 V.s\(^{-1}\)). The optimum deposition time at microband electrodes was evaluated to be 20 s, applying this deposition interval to measurements in increasing concentrations of Cu\(_2\)SO\(_4\) generated a linear calibration curve across a range of nanomolar concentrations. Detection of copper at concentrations as low as 10 nM was easily achievable. Increasing sensitivity could be simply achieved by increasing deposition time. A sensitivity of 2.8 \(\mu\)A/cm\(^2\)/M was estimated for a deposition time of 20s. To assess potential real sample applications for these microband electrodes, determination of copper concentration present in tap water was measured using UPD-ASV. From the resulting peak current the concentration of the unknown sample was estimated to be 1.25 mg/L of Cu\(^{2+}\). Future work is now focusing on detection of a variety of other metals including lead, cadmium, selenium and chrome ions in complex matrices.

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