

Design, Fabrication, and Testing of Hg/Au Microelectrodes for Voltammetric Sensing of Trace Metals for Environmental Monitoring

Andrew Raebig

Electrical Engineering and Chemistry, Butler University

NNIN REU Site: Lurie Nanofabrication Facility, University of Michigan, Ann Arbor, MI

NNIN REU Principal Investigators: Dr. Hélène Craigg, Electrical and Computer Engineering, University of Michigan;

Dr. Becky Peterson, Electrical and Computer Engineering, University of Michigan

NNIN REU Mentor: Dr. Hélène Craigg, Electrical and Computer Engineering, University of Michigan

Contact: araebig@butler.edu, helenec@umich.edu, blpeters@umich.edu

Abstract:

In electroanalytical chemistry, electrodes are used in voltammetry to detect trace amounts of an analyte in an aqueous system. Microelectrode arrays can be made using nanofabrication techniques. A series of mercury/gold (Hg/Au) microelectrode arrays was designed as a working electrode in a voltammetric system for trace metal sensing; these arrays test the influence of electrode diameter, array size, and electrode spacing on signal detection. After device fabrication, all electrode arrays were taken to the Georgia Institute of Technology for mercuric electroplating and testing by our geochemistry collaborator.

Introduction:

Microelectrode (ME) arrays have come into highly increased use since their first invention in the 1970s due to several unique characteristics. They are very advantageous compared to individual microelectrodes, exhibiting increased sensitivity and high spatial resolution. Their small size and workable area allow them to be used for measurement without overly disturbing the system. Since they are often made from noble or heavy metals, they can be used to detect a virtually unlimited range of compounds and elements. In this study, ME arrays with varying characteristics were created on a gold (Au) film covered with silicon nitride (Si_3N_4) and electroplated with mercury (Hg) similar to the procedure done by Belmont, et al. [1]. The electrode array characteristics were varied both individually and collectively to determine their impact on performance.

Mask Development. For the lithographic process, two masks were designed using AutoCAD. The first mask was used to pattern the Au pads. The second mask was used to pattern the electrode arrays on the top Si_3N_4 layer. Multiple arrays were created to encompass variations of electrode diameter (5-30 μm), electrode spacing [2] (25-900 μm), and array size (30-1800 electrodes). Figure 1 shows an AutoCAD drawing of a device.

Electrode Fabrication. Figure 2 displays a cross-sectional sketch of the finished device. On standard 100 mm Si wafers, a 200 nm layer of Si_3N_4 was deposited via low pressure chemical vapor deposition (LPCVD). Then a 200 nm

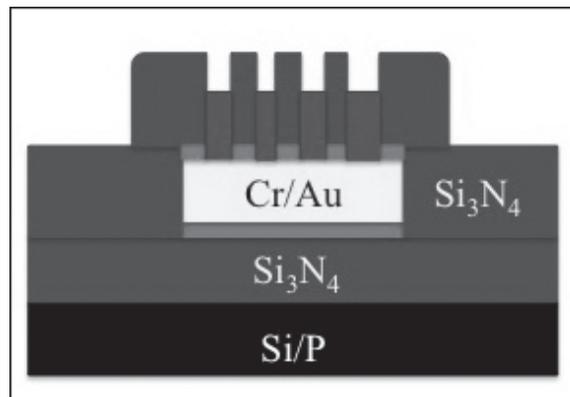
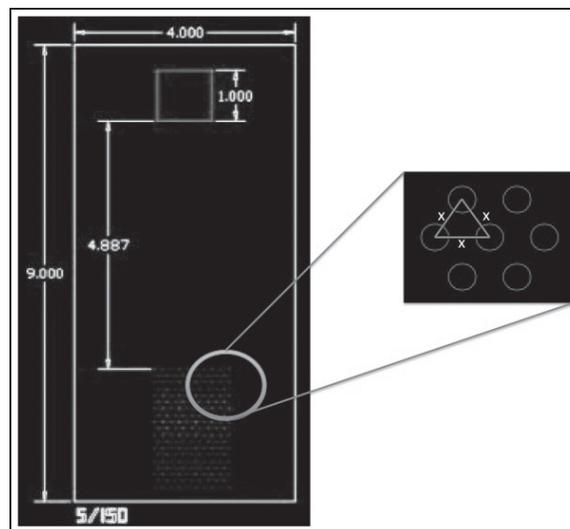


Figure 1, top: Mask layout of a basic array. The yellow lines indicate the Au mask; the red lines the Si_3N_4 mask.

Figure 2, bottom: Cross-section sketch of the finished device.

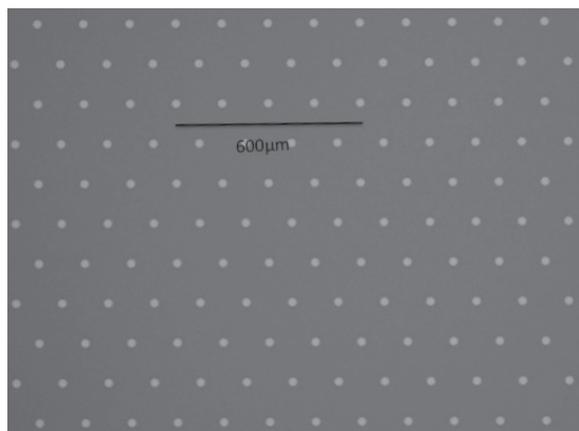


Figure 3, above: Zoom of electrode array.

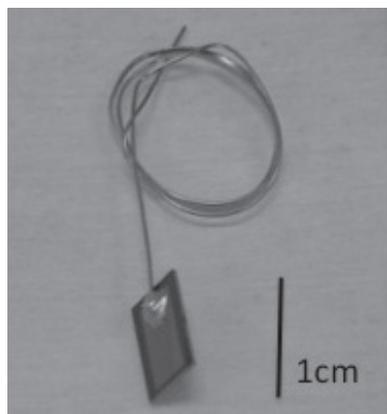


Figure 4, left: Diced and bonded electrode.

layer of Au was evaporated; a 5 nm layer of chromium (Cr) was evaporated above and below as an adhesion layer and protection layer, respectively. Pre-spun wafers were exposed for 6 s under the light-field Au pattern mask. Once development was complete, each wafer was wet-etched to pattern Au and Cr. Photoresist was stripped in a hot acetone bath, quenched in isopropanol, and rinsed in deionized water before a 10-minute O_2 plasma etch.

A 200 nm layer of Si_3N_4 was then deposited using plasma-evaporated CVD (PECVD). Compared to LPCVD-deposited films, PECVD films have many inherent flaws; the most prolific of which is the presence of pinholes. Pinhole testing was done by submerging wafers in buffered hydrofluoric acid (HF) for short periods of time (~ 5 s). The electrode arrays were patterned using photolithography and reactive-ion etching (RIE) for an average of 6 min. Following photoresist strip, a final Cr etch was done to reveal the Au electrodes. The finished array is shown in Figure 3.

Each wafer was diced to separate the devices. On each device, a solid copper wire was bonded to the Au contact pad using silver colloidal conductive epoxy. The completed working electrode is shown in Figure 4.

Results and Discussion:

This study had three primary goals: mask development for the photolithographic production of microelectrode arrays;

design and characterization of a microfabrication process; and fabrication and testing of the physical electrodes themselves. Creation of a mask that tested many different scenarios of microelectrodes required detailed planning. All controllable characteristics of the device were manipulated in as many ways as possible in order to narrow the search for an optimal device. In order to create these electrodes, the microfabrication process had to be characterized. In order to optimize Si_3N_4 layer thickness and quality, vapor deposition parameters had to be adjusted. The RIE etch rate also required careful characterization and timing in order to avoid over-etching.

After the devices were fitted with wires, each one was electrically tested for shorts or poor connections. Using electrochemical apparatus provided by the Georgia Institute of Technology, each electrode was placed in mercuric solution and plated at -0.1 V for ~ 30 s. The plated electrodes were subjected to a cyclic voltammetry test to measure the stability of the Hg/Au amalgam, and then tested overnight in 0.5 M NaCl (seawater) doped with 10 mM manganese to determine long-term stability.

Conclusions:

In this study, it was determined that usable microelectrode arrays of differing dimensions could be created through microfabrication in order to design a voltammetric working electrode. The voltammetry profiles, while successful, indicated that more optimization of electroplating was required. Several modifications to this process can be made in future studies: fabrication with different mercury-compatible metals, deposition of conductors and insulators via different methods, and adjustment of electrode specifications.

Acknowledgements:

I would like to thank the National Nanotechnology Infrastructure Network Research Experience for Undergraduates Program for the opportunity to conduct this project; the Lurie Nanofabrication Facility (LNF) for providing the instrumentation; my PI, Dr. H el ene Craig; Dr. Becky Peterson for her assistance in mask design and electrical testing; Dr. Katharine Beach for her suggestions regarding fabrication; the Georgia Institute of Technology for their assistance plating and testing the devices; and all the LNF staff for providing aid whenever needed.

References:

- [1] Belmont, C., Tercier, M.L., Buffle, J., Fiaccabrino, G.C., Koudelka-Hep, M. "Mercury-plated iridium-based microelectrode arrays for trace metals detection by voltammetry: optimum conditions and reliability." *Anal. Chim. Acta*, 329, 203 (1996).
- [2] Wang, J., Lu, J., Tian, B., Yarnitzky, C. "Screen-printed ultramicroelectrodes arrays for on-site stripping measurements of trace metals." *J. Electroanal. Chem.*, 361, 77 (1993).