

Microscopic containers for sample archiving in environmental and biomedical sensors

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Abstract—This report describes our work on microfabricated containers that store small amounts of environmental samples for analysis. The containers are based on “strain architecture,” a fabrication technique which causes planar microstructures to fold out of plane from the substrate. These structures remain connected to electrodes for thermal actuation, electrochemical sample collection, and gas generation through electrolysis. Results are shown for collection of dissolved metals by electroplating using small voltages and currents that are compatible with the power resources of wireless sensor networks. Such containers will be useful for rapid in-situ analysis of concentrated samples, for maintaining a sample archive that can corroborate the results of an in-situ biochemical sensor, or for time-stamped collection of samples for offsite analysis using equipment that is unavailable in the field such as mass spectrometry or electron-beam based analysis methods.

Keywords—calibration, distributed measurement systems, environmental sensors, wireless sensor networks

I. INTRODUCTION

Storage of small amounts of an environmental or biomedical sample is important in numerous sensor applications for increasing sensitivity, reliability and accuracy.

Preconcentration: Autonomous chemical sensors, sometimes called “lab on a chip” systems, usually have a sample preconcentration system at the beginning of the analysis stream. This approach increases the instrument’s sensitivity by collecting and storing a dilute analyte over a long period of time. The preconcentrated sample is periodically released into the sensor for in-situ measurement of chemical concentration in the environment, for instance in a capillary electrophoresis system for measuring biological analytes [1].

Corroboration: Because an autonomous sensor may go without maintenance for weeks or months, sensor drift is a common problem. Having a stored, time-stamped archive of the sample that can later be correlated with the in-situ measurement will help quantify the amount of drift. Collection of such an archive during a routine maintenance visit, followed by laboratory analysis of the archive and comparison with sensor readings, will indicate whether the sensor needs to be brought in for more extensive maintenance.

Sample Return: Some types of analysis are too expensive or bulky to perform in the field—especially techniques using isotopes or other costly reagents, heavy magnets (mass spectroscopy), X-rays, or vacuum (electron- or ion-beam techniques). In those cases, the autonomous sensor simply collects an array of samples labeled with the time and date, and the sample array is retrieved for analysis back at the laboratory.

In all of these applications, a container is needed for sample storage. Such “containers” range from familiar plastic vials such as those used in stream sediment samplers, to microscopic polymer sponges that adsorb chemicals in bioanalysis chips. This report describes a microfabricated container with a high surface area and with electrical contacts for electrolytic collection of dissolved metals out of the surrounding liquid environment. These cage-like containers can be thermally actuated to open for sample analysis, and gas bubbles can be generated and trapped within the container to protect the fresh metal deposits from contamination. We demonstrate electroplating into the microcontainers from test solutions of nickel and a 25-element standard solution, and discuss chemical analyses of the resulting deposits using X-ray fluorescence (XRF), atomic absorption spectroscopy (AA), and energy dispersive X-ray spectroscopy (EDX).

II. STRAIN ARCHITECTURE FABRICATION

The microcontainers are formed on a silicon substrate by depositing a metal/oxide bimorph with a strain mismatch. When released from the substrate using a highly selective silicon etch process, the bimorph structures curl up, forming an out-of-plane structure with a well-defined radius of curvature [2]. Fabrication steps are illustrated in Fig. 1.

The microcage’s diameter is important in defining the structure’s surface area and sample capacity. By adjusting the thicknesses of the materials in the bilayer, their Young’s moduli, and the strain mismatch, it is possible to adjust the microcage’s radius of curvature from sub-10 nm to mm as described in Eq. [1]:

$$\frac{1}{\rho} = \frac{6\varepsilon(1+m)^2}{d[3(1+m)^2 + (1+mn)\{m^2 + (mn)^{-1}\}]} \quad [1]$$

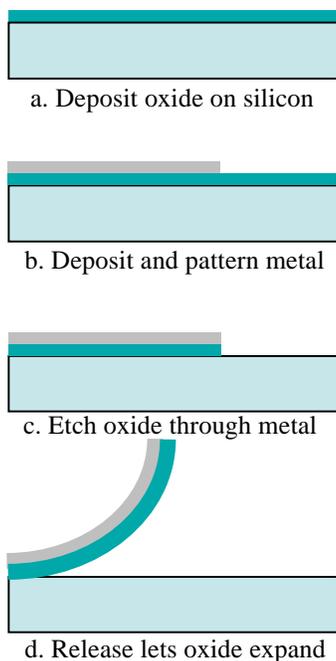


Fig. 1: Fabrication sequence.

thick silicon dioxide layer. Because most metals have 10x to 20x larger coefficients of thermal expansion than the oxide, the curled-up devices open and flatten towards the substrate during external heating or when heated by running an electrical current (Joule heating) through the platinum. Fig. 2 shows sequential top-view electron micrographs of a device opening by Joule heating.



Fig. 2: Top view of a spherical microcage opening as temperature increases from 25C (left) to approximately 160C (right) by driving a current through the entire structure from contact pads to the right of each frame. Sphere diameter is 250 microns (leftmost image).

III. COLLECTION OF DISSOLVED METALS BY ELECTROPLATING

For electroplating experiments, microcages were arrayed within a 50 microliter sample well for exposing the cages to liquids, and with traces leading to an array of contact pads for a computer-controlled fixture to apply a sequence of plating voltages to the array (Fig. 3). These cages were designed for actuation by external heating rather than Joule heating. Fig. 4 shows a scanning electron micrograph of a released electrode array with a relatively large radius of curvature (approximately 500 microns). This released three-dimensional structure is expected to improve collection efficiency by interacting with a larger volume of fluid than a planar non-released structure would. Planar structures were also produced for comparison.

where ρ is the radius of curvature, d is the combined thickness of the two layers (d_1+d_2), ϵ is the strain or fractional difference in the relaxed length of the two layers, n is the ratio of the Young's modulus of the layers (Y_1/Y_2), and m is the ratio of their thickness, (d_1/d_2).

The layer width, thickness and materials are important in determining the device's thermal and current-carrying properties as well as the overall diameter. In this application, approximately 200 nm of platinum was used as the metal layer for its stability during electroplating. A 20 nm layer of titanium aided adhesion of platinum to the 400 nm



Fig. 3: Chips with sample wells and electrical contacts for collecting metal samples by electroplating. Sample well volume is 50 microliters.

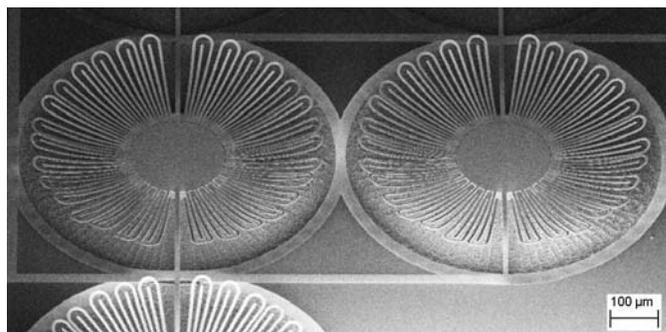


Fig. 4: Electron micrograph of open cage structures for electroplating. The central disk and rays are held at ground while the outer surrounding electrode is held at a positive voltage. Metal ions plate onto the inner electrode. Similar structures were left unreleased for comparison.

During experiments a direct-current (DC) power supply or a LabView computer-controlled analog voltage board was used to apply 1 to 5 volts to the outer electrodes of an array of 6 plating structures, while the inner electrodes were held at ground. There were four independent arrays of electrodes on each chip. For long experiments, to prevent evaporation, electrodes were immersed in beakers of solution, while for shorter experiments the sample well was used.

Electrodes were exposed to a standard test solution containing 25 metal elements at a concentration of 10 μ g/mL in 2% HNO_3 with trace amounts of HF. The elements were Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Ag, Tl, Th, U, V, and Zn. The central electrode was typically held at 3V for 1 hour or longer while the outer electrode was grounded. Solid deposits formed on the inner electrodes at currents of 1 mA or less. Figure 5 shows SEM micrographs of the deposits on released and non-released (planar) electrodes after 1 hour in the multi-element solution under these conditions. With the relatively concentrated standard solution, deposits grew to the extent that the metals touched the outer electrode, but much slower growth is expected in environmental samples containing trace minerals. Plating occurred on all parts of the grounded electrodes, whether released from the surface or planar. Interestingly, the planar electrode showed dendritic deposits that are characteristic of mass transport-limited electroplating [3], while the deposits on the released electrodes were more granular, possibly indicating greater access to diffusing metal

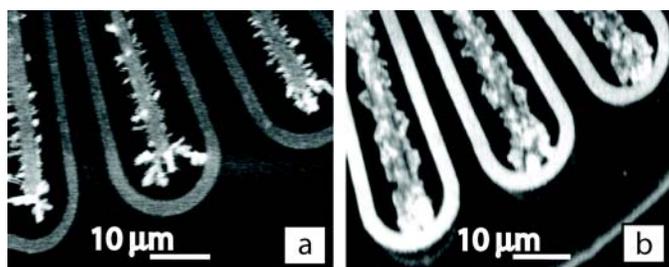


Fig. 5: (a) 25-element test solution plated onto planar electrodes after 1 hour, and (b) onto released three-dimensional electrodes after one hour. The inner electrode was grounded while outer electrode was held at $\sim 3V$.

ions for the three-dimensional structure. In other experiments, electrode arrays were exposed to single-element solutions (Ni, Zn), and the effects of plating time and voltage were studied. The LabView program also enabled scheduling of plating on each of the four electrode banks for cross-contamination studies. Metal was observed to plate on electrodes that were “off” if the electrode potentials were left floating; it is important that all unused electrode pairs are held at the same positive voltage applied to the outer plating electrodes.

In these aqueous solutions, plating voltages in excess of approximately 1 V were observed to generate gas bubbles through electrolysis. Gas bubbles typically floated up to the surface of the test solution, enabling plating to continue on the electrodes. However, the bubbles were observed to stay on electrodes until they became large enough that buoyant forces and surface tension caused them to move. Cages that had a smaller radius of curvature or that were otherwise designed to capture bubbles *under* the metal filaments were able to retain larger bubbles.

IV. CHEMICAL ANALYSIS OF COLLECTED SAMPLES

Analysis techniques applicable to the microcages include electron-beam probe based methods such as energy dispersive X-ray analysis (EDX) and Auger electron spectroscopy, and X-ray probe based methods including X-ray fluorescence (XRF) and X-ray diffraction. These methods are capable of probing a small area without destroying the sample. Other methods based on analytical chemistry are more destructive to the sample. Atomic absorption spectroscopy (AA) was conducted nondestructively by plating the sample with a nickel solution of known volume and concentration, then measuring how much nickel remained in solution after plating. However, for an unknown environmental sample, the AA sample would be generated instead by dissolving the deposited metal into solution and vaporizing the solution into the instrument. Thermal desorption methods are also possible when the electrodes are designed for Joule heating. The released filaments can be brought to high temperatures using small currents (40-100 mA) since they have very small thermal mass and excellent thermal isolation from the substrate. Such methods typically destroy the device by creating an open circuit, but are attractive for desorbing small amounts of material into a mass spectrometer for identifying elements and even isotopes. Of these methods, EDX, XRF, and AA were used to characterize the deposited materials. Figure 6 shows

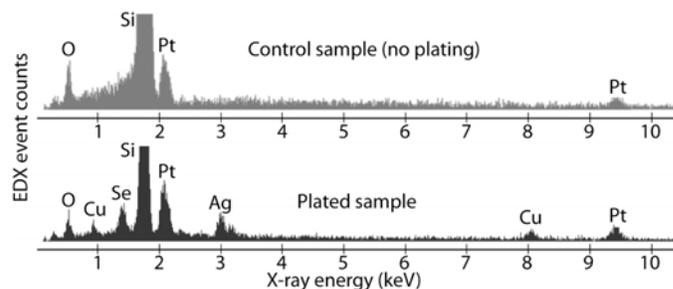


Fig. 6: Top (light gray) EDX spectrum from control sample; bottom (dark gray) EDX spectrum from 1-hour plated sample shows new peaks from elements in the 25-component standard solution.

EDX data from a sample that was not plated, and from a sample that had visible deposits after plating for one hour. New peaks for selenium, copper, and silver appear in the plated sample, while silicon, platinum, and oxygen peaks are present in both due to the composition of the devices. Similar results were seen for EDX spectra from both planar and released devices. The XRF and AA techniques, however, were not sensitive enough to reliably detect the elements plated from the 25-metal standard under the same conditions. Better results were seen with these techniques when nickel was plated from a single-element concentrated solution (1 g/mL). In that case, a distinct nickel peak appeared in both XRF and EDX spectra, and the atomic absorption (AA) measurement was able to quantify that 0.935 mg of nickel had plated onto one of the sample arrays. This mass corresponds to an approximately 8 micron thick layer of nickel over the 4-mm diameter electrode array. The electrode arrays did have deposits in this thickness range and sometimes much greater, unevenly distributed over the device. However, the mass measurement was near the limit of accuracy for the AA instrument.

V. CONCLUSIONS AND FUTURE WORK

Trace elements were plated on the electrode arrays in quantities detectable by EDX. For XRF, larger quantities were needed, meaning much longer sample collection times for a given solution. Furthermore, the XRF had a 5mm spot size requiring masking for analysis of deposits on individual electrodes, but electron beam based analysis could focus on a single plated device. While the AA instrument produces a more quantitative result than either EDX or XRF, the AA could only analyze one element at a time, and its sensitivity was near the edge of viability for these samples. Experiments with the 25-element standard solution demonstrated that Cu, Se, and Ag plated and were detected readily under the conditions used here while other elements were not, so that careful calibration is needed to correlate results with original solution concentration. To quantify EDX results on unknown samples, one should plate standard solutions on reference electrodes for the same time and duration as the environmental samples for side-by-side EDX analysis, and temperature and pH should be logged alongside sample collection because these parameters influence plating efficiency. A similar reference sample could be used for mass spectroscopy based analysis techniques.

Plating occurred on both planar and released devices, with no obvious difference in element abundance seen in the chemical analysis methods. The real utility of the three-dimensional electrodes is likely to be in thermal actuation during sample analysis, stirring during sample collection, and in control of gas bubbles generated by electrolysis.

Thermal opening of an individual microcage electrode will expose only the metals on that part of the sample to analysis techniques that use a broad beam, such as XRF. This will enable sequential analysis of a closely packed array of samples collected at different times. Higher temperatures achieved by Joule heating in vacuum will enable opening followed by scheduled desorption of one sample at a time into a mass spectrometer.

During sample collection, thermal actuation by Joule heating will be more difficult than during analysis. Submerged thermal actuators suffer from heat loss to the surrounding liquid, and metal sample collectors would have conflicting needs for exposed metal plating surfaces and for insulated current-carrying heater wires. However, two other effects occur at the three-dimensional electrodes that will aid sample collection and retention: stirring without moving parts by electro-osmosis at metal electrode surfaces, and trapping of electrolysis-generated gas bubbles.

The electro-osmotic effect is well known to generate local pumping in dilute electrolytes at the surface of three-dimensional electrodes having similar widths and voltages to the ones discussed here, at DC and AC [4] voltages. Stirring in the vicinity of the electrodes is known to dramatically increase plating efficiency [5] by bringing fresh solution near the electrode, resulting in faster sample collection in a given environment. This effect can be investigated with fluorescent tracer particles that indicate whether vortices are induced around the electrodes. Meanwhile, bubbles have been observed to interact with the microcages, staying trapped beneath filaments until they grow large enough to push the filaments aside. We are investigating the effect of hydrophobic coatings and hydrostatic pressure on bubble stability, and are developing methods to generate, control, and detect the bubbles with electrical signals. In aquatic environmental sampling projects, these microscale (<1mm) bubbles will provide an inert seal for the microcontainers, keeping electrodes clean until ready for use in autonomous chemical sensor networks [6] and preventing archived samples from interacting further with the surroundings.

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