

Electroless Post-Processing Deposition For Water Quality Microsensor

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Abstract — The electroless deposition as a post-processing step in a microsensor fabrication is described in this paper. The main application of the sensor is the detection of heavy metals in the water, mainly mercury. The sensor consists in an array of up to 8 gold microelectrodes ($10\ \mu\text{m} \times 10\ \mu\text{m}$), a silver/silver chloride reference and a large gold electrode used as auxiliary. To provide fully compatibility with integrated circuits technology, the sensor lines and interconnection was made by doped polysilicon. The required gold was obtained by electroless post-processing where several deposition conditions were analyzed. Preliminary results, using wedge bonding, indicated the need of palladium activation film following nickel depositions prior the gold to enhance the adhesion.

Index Terms— Chemical microsensor, Electroless deposition, Heavy metals detection, Water quality.

I. INTRODUCTION

There is an increasing demand for in situ analysis of heavy metal contaminants in drinking, industrial and natural water, due to their high toxicity. Electroanalytical methods using microelectrodes are very suitable for quantification of heavy metals [1], due to their low detection limits and the possibility of construction of portable and low cost instrumentation. Our main focus is the detection of mercury in rivers and tap water.

The traditional method of collecting water and its analysis in a laboratory became time consuming with lack of reliability, making an on-line monitoring not only advantageous but also required in some cases.

A multi-electrode sensor for electro-chemical detection of heavy metal in water was implemented and reported in previous work [2]. To provide compatibility with silicon technology, we introduced a modification in the previous work using doped polysilicon as material for lines, contact pads and electrode areas, which were modified by electroless deposition to obtain the required gold surface. The general purpose electrochemical sensors were fabricated using silicon technology and displays suitable characteristics for doing static or dynamic analysis, multipoint and multi-species measurements.

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I - ELECTROANALYTICAL DETECTION [1,3]

Among several electroanalytical methods, differential pulse anodic stripping voltammetry (DPASV) and square-wave anodic stripping voltammetry (SWASV) are candidates for this application due to their inherent characteristics of pre-concentration, achieving part-per-billion sensitivity. Gold is a chosen material for the detection electrode due its sharp and high stripping peaks.

Several methods are proposed in order to obtain the ionic phase of the mercury to be electrochemically detected, such as: mixing the sample with potassium permanganate or using UV radiation, both suitable for in flow analysis. The electrochemical detection starts with a process called “pre-concentration”, where the electrode is held at a cathodic potential (reduction) so that metal ions from the solution are reduced at the electrode surface, concentrating on it, as indicated in Figure 1(a) As long is the concentration time as higher is the reduced material, making this a compromising step.

Next, the potential is scanned in the anodic direction to reoxidize the metal concentrated on the electrode, process called stripping. This cause a current peak at specific reduction potential of the ion and it is proportional to the concentration of the ions in the solution, Figure 1(a). Increasing the specific ion concentration causes an intensification of the reduction peak, as shown in Figure 1(b). Finally a calibration curve (current x concentration) can be obtained from the peak current or from the area under the reduction curve, Figure 1(c).

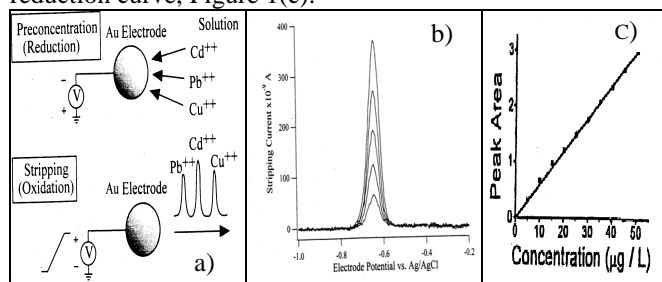


Figure 1. Electrochemical detection of heavy ions: a) pre-concentration and stripping steps, b) oxidation curve for increasing concentration and c) calibration curve.

II - MICROSENSOR FABRICATION

The array consists of up to 8 gold detection microelectrodes ($10\ \mu\text{m} \times 10\ \mu\text{m}$), one silver/silver chloride reference electrode ($\sim 70 \times 10^{-3}\ \text{mm}^2$) and a gold auxiliary electrode ($1\ \text{mm}^2$). This sensor is a new version of one previously reported [2]. On this new approach, figure 2, we kept the same design, but the fabrication steps were changed to provide fully integrated circuits compatibility. Phosphorus doped polysilicon ($R_s=20\ \Omega/\text{sq}$) was used as conducting lines and gold was obtained by nickel electroless deposition as described in the next section. For the reference electrode, electrodeposition of silver followed by the silver chloride formation was performed. Silicon dioxide was used to insulate the electrodes from the silicon substrate and silicon

nitride was used as passivation material. Typical dimensions of the sensor are: a length of 10 mm and a width of 3 mm.

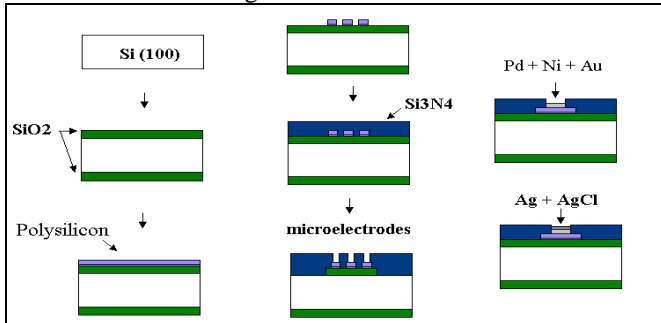


Figure 2. Microelectrode array fabrication sequence.

III- ELECTROLESS POST-PROCESSING [4]

In order to obtain the required gold electrode, we performed several electroless schemes as described in table 1 and 2.

We started using a classical electroless reaction that occurs on catalytic surfaces, in the presence of hipofosfite ions that acts as reductor agents which occurs only in alkaline environment. The solution composition was: 15 g/l NiCl₂, 10 g/l Na₂H₂PO₂, 30 g/l NH₄Cl₂, 35 g/l (NH₄)₂C₆H₆O₇, 10 ml/l NH₄OH, 85 °C, pH = 7.8 and deposition rate of 1000Å/min

The second solution adopted, takes advantage of the palladium catalytic centers to promote the nickel deposition. This nickel solution is acid and has the following composition: 15 g/l NiCl₂, 10 g/l CH₃COHNa, 50 g/l NH₄Cl₂, 30 g/l NaH₂PO₂, 1 ml/l HCl, 65 °C, pH = 3.4 and deposition rate also of 1000Å/min.

After gold deposition over all exposed electrodes and contacts, we electrodeposited silver (-200mV) in the reference electrode area using a solution of 0.1 M AgNO₃ + 10% vol.NH₄OH followed by its oxidation (+200mV) in chloride solution of 3M NaCl, as described in previous work [5].

Table 1. Electroless deposition schemes

• Deposition scheme 1:
a) cleaning : 5min. acetone : 5min. alcohol : 5 min. DI water, 10 min. 2 H ₂ SO ₄ : 1 H ₂ O ₂ and 5 min. 1 HF : 20 H ₂ O ₂
b) nickel alkaline electroless solution
c) gold electroless solution
• Deposition scheme 2:
a) cleaning : 10 min. 2 H ₂ SO ₄ : 1 H ₂ O ₂ and 5 min. 1 HF : 20 H ₂ O ₂
b) electroless palladium solution (1HF:80H ₂ O:0,2 g/l PdCl ₂ , T=RT, t=1 min.) + 10 min. hot plate (200°C)
c) nickel acid electroless solution
d) gold electroless solution (Degussa B512), T=95 °C, rate=150 Å/min.

Table 2. Electroless deposition in several samples and adhesion results. T_{Ni}:T_{Au} means time in the nickel and gold solution, respectively.

Sample	Scheme	T _{Ni} : T _{Au} (min)	Wire Bonding (adhesion)
A	1	10 : 60	Poor
B	1	20 : 10	Poor
C	1	30 : 20	Poor
D	1	10 : 10	Poor
E	2	10 : 10	Low
F	2	10 : 10	Good
G	2	20 : 20	Low
H	2	30 : 30	Low

III- RESULTS AND DISCUSSION

From table 2 one can observe that using deposition scheme 1 (samples A-D) resulted in a poor adhesion, regardless depositions times of nickel and gold solutions. In fact, the obtained gold film wiped off after the nitrogen drying step. An improvement came using scheme 2 with palladium intermediate film. In this case the gold films resisted after nitrogen blow and attempt to edge bonding gold wires (25µm) resulted in adhesion, although low. Sample F presented the best results and several reproducible connection were performed, as shown in figure 3. The conflicting results from samples E and F (same conditions) pointed a possible aging factor of the solution, since sample F utilized fresh nickel solution.

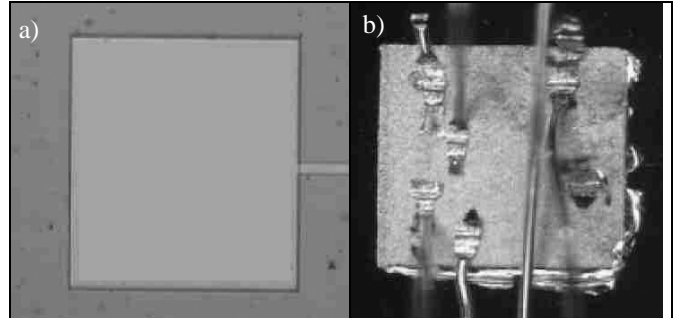


Figure 3. Sample F : a) polysilicon contact and b) after depositions and gold wire edge bonding.

IV - CONCLUSIONS

We presented several schemes for electroless deposition as a post-processing step in a microsensor for detection of heavy metals in the water. The sensor consists in an array of up to 8 gold microelectrodes (10 µm x 10 µm), a silver/silver chloride reference and a large gold electrode used as auxiliary. Fully compatibility with integrated circuits technology was provided using phosphorous doped polysilicon as base material for lines, electrodes and contacts. The required gold was obtained by electroless post-processing. Preliminary results, indicated the need of palladium activation film following nickel depositions prior the gold to enhance the adhesion.

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