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Development of an electroless post-processing technique for depositing gold as electrode material on CMOS devices

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Abstract

The limited electrode density and thus, the limited spatial resolution of substrate-integrated microelectrodes arrays (MEAs) used in in-vitro electrophysiology are currently considered as the main constraints of this technique. By taking advantage of the commercially available complementary metal oxide semiconductor (CMOS) standard technology, high density miroelectrode arrays on large active areas could be realized. However, the aluminum alloy used in CMOS as the metallic layer shows poor electrochemical stability in physiological media as well as a poor biocompatibility. A post-processing technique is therefore necessary for depositing a suitable electrode material. The methodology developed in this work relies on a gold electroless deposition technique using commercially available gold cyanide plating solutions. The main advantage of the electroless process is that it needs neither a photolithographic step nor the application of a reduction potential. The electroless process was developed in two stages, to begin with on aluminum–MEAs test structures and then the optimized process was transposed to the CMOS devices. The gold layers were characterized by ESEM, cyclic voltammetry and XPS.

Keywords: High-density microelectrode arrays; Electrophysiology; Gold electroless; CMOS

1. Introduction

With the commercial availability of microelectrode arrays (MEAs), the extracellular recordings of the electrical activity of in-vitro electrogenic cells, e.g. neurones or cardiomyocytes, are now largely accepted as an interesting methodology complementary to the standard patch-clamp technique [1–4]. The arrays comprise typically 30–120 microelectrodes (Pt, Au, IrO_x, ITO, and TiN) embedded in an insulation layer (Si_3N_4, EPON SU-8, polyamide) and are fabricated mainly by thin-film technology. The cells are plated and cultured directly on the active area allowing the non-invasive, long-term (up to several months) monitoring and stimulation of the network electrophysiological activity.

In order to further enhance the functional features of the MEAs, the current research efforts are directed towards the increase of the spatial resolution and the improvement of the recorded signal quality, with the ultimate goal of providing to electrophysiologists a high-resolution device for studying the complex network dynamics [5–7]. To enhance the spatial resolution, the electrode density on a large active area should be strongly increased. However, the limiting factors of the current thin-film technology are the manageable number of electrodes, contact pad connections and the increasing complexity of the external amplification circuit. Improvement of the signal quality (signal-to-noise ratio) can be achieved by modifying the electrode material and of its roughness as well as by placing the recording electronic circuit as closely as possible to the electrode [8,9].

The use of the complementary metal oxide semiconductor (CMOS) technology might be beneficial for both aspects mentioned above: it would allow to integrate a local amplification just behind the electrodes as well as to significantly increase the electrode density. The main drawback of the standard CMOS technology is that it uses aluminum alloys as the metallic layer. Since these alloys present limited stability in physiological solutions and, even more importantly, poor biocompatibility, they are not suitable as electrodes' material. Thus, prior to investigating a possible use of CMOS technology for the fabrication of high-density MEAs, the electrode material has to be adapted to the foreseen application.

As mentioned above, gold has proven to be a suitable electrode material for MEAs. Different technologies, such as

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evaporation/sputtering followed by lift-off or wet etch patterning, electrodeposition and electroless deposition might be used as a post-processing step of the CMOS devices. Among them, the autocatalytic electroless deposition of gold appears to be the most convenient. It needs neither a photolithographic process nor the application of a reduction potential. Electroless deposition of gold has been investigated fundamentally [10–12] and applied to different substrates such as Ni, Pd, Pt, Rh, Au or Cu [13]. On aluminum, gold electroless deposition is largely described in the literature for solder bumping and wire bonding where it is usually plated following a deposition of Zn and/or Ni [14–17]. Gold modification of aluminum microelectrodes by Ni/Au plating has been reported by Krasopoulos for the case of an array of integrated microelectrodes [18].

In an attempt to simplify the plating process and to avoid inter-layers between aluminum and gold, we have investigated the direct gold electroless deposition on aluminum microelectrodes and silicon–aluminum alloy microelectrodes resultant from a CMOS process. A systematic investigation of various plating parameters was performed to begin with on aluminum test microelectrodes. The optimized process was then transposed to the CMOS device, consisting of 64 × 64 (4096) microelectrodes. The gold layers were characterized using environmental scanning electron microscopy (ESEM), cyclic voltammetry and analyzed by X-ray spectroscopy (XPS).

2. Materials and methods

2.1. Aluminum MEAs test structures

A previously described design, comprising 32 microelectrodes of 10 μm diameter and four pseudo-references was used for the aluminum-test MEAs structures [4]. The arrays were fabricated on 4 inch and 525 μm thick silicon wafers insulated with a 2000 Å-thick layer of silicon nitride deposited by low-pressure chemical vapor deposition (LPCVD). A 250 Å-thick layer of tantalum (adhesion layer) and 1 μm thick aluminum layer were deposited by evaporation and patterned by a lift-off process. The top insulation layer of 2000 Å-thick LPCVD silicon nitride was opened by SF_6/O_2 plasma etching. A schematic cross-section of the electrode is shown in Fig. 1. For electrochemical characterization, the individual devices were mounted on a printed circuit board (PCB), wire-bonded and encapsulated with epoxy resin.

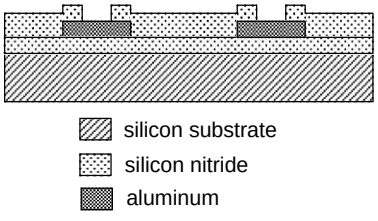

Fig. 1. Schematic cross-section of the test Al–MEAs.

2.2. CMOS high density MEAs

These devices are based on active pixel sensor technology (APS) and were designed in collaboration with the Image Sensing Section of the Centre Suisse d'Electronique et Microtechnique SA (CSEM SA, Zurich, Switzerland) [19]. The array consists of 64 × 64 (4096) pixels on an active area of 2.56 × 2.56 mm^2. Each pixel has a dimension of 40 × 40 μm^2 integrating a microelectrode of 20 × 20 μm^2 and underneath a local pre-amplifier. Each electrode can be individually addressed with the on-chip addressing logic integrated on the sides. These devices have been fabricated using ALCATEL 0.5 μm standard CMOS technology.

2.3. Electroless gold deposition

The electroless gold deposition was performed in two steps using commercially available plating solutions. First, the aluminum electrodes were treated with the Atomex solution (Engelhard-Clal, Bienne, Switzerland), allowing to deposit gold by galvanic displacement. Then, the process was continued autocatalytically in the Catagold 2A solution (Engelhard-Clal, Bienne, Switzerland).

The Atomex solution was prepared as indicated by the manufacturer, by dilution in deionised water to obtain a gold concentration of 3–4 g/l. The pH of this solution is between 7 and 8. The manufacturer specifies typical deposition temperatures between 45 and 75 °C and, on a copper substrate, a deposition rate of 0.055 μm/5 min.

The Catagold 2A solution is a highly alkaline gold cyanide solution with a pH of 13.7. The solution is provided ready for plating, and contains 3.75 g/l of $KAu(CN)_2$. The typical deposition temperature specified by the manufacturer is 75 °C with a deposition rate of ∼2 μm/h.

2.4. Characterization of the gold layers

Gold deposits were characterized by environmental scanning electron microscopy (Philips XL 30 ESEM-FEG), cyclic voltammetry (CV) and X-ray spectroscopy (XPS). CVs were performed using a standard three-electrode set-up (Pt counter electrode and Ag/AgCl reference electrode, Metrohm) in a deaerated 1 M H_2SO_4 solution.

The XPS analysis was performed on a Kratos Axis Ultra spectrometer. Due to the small size of the electrodes, the X-ray spot of 50 μm in diameter was focused on the contact pads. The spectra were collected over a binding energy range between 0 and 1100 eV with a pass energy of 80 eV and an acquisition time of 480 s.

3. Results and discussion

Aluminum is not a standard substrate for the gold electroless deposition. Indeed, the manufacturer specifies that the deposition in the Catagold 2A solution can only be per-

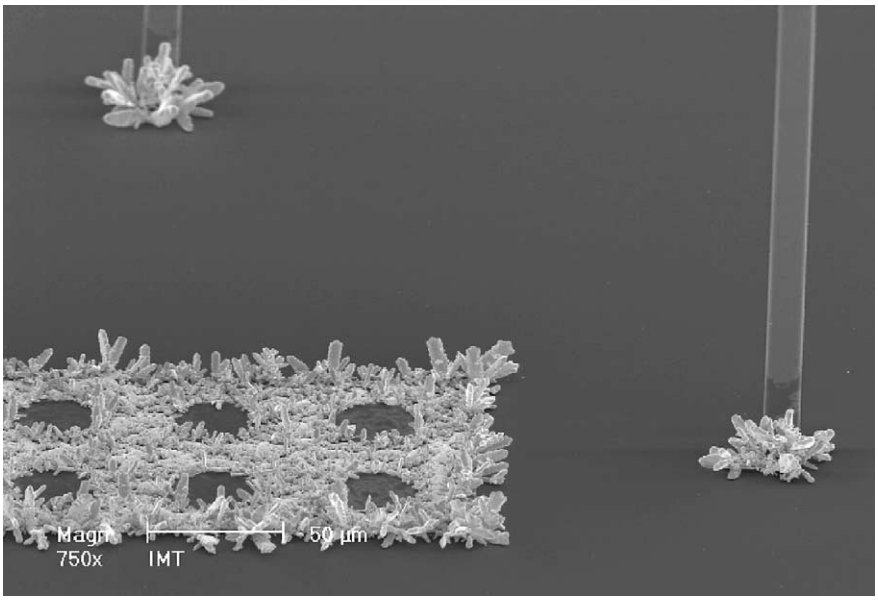

Fig. 2. ESEM picture of the deposited Au on two Al–MEA (5 min in Atomex solution and 5 min in Catagold, $T = 57\,^{\circ}\mathrm{C}$). Bottom-left, a part of the integrated pseudo-reference Al structure.

formed on gold or copper substrates. The other normally used substrates, i.e. nickel, zinc or iron alloys, need to be pre-coated with gold. The use of the Atomex solution for Au deposition by galvanic displacement is therefore required for Al substrates. This step allows a gold seed layer to be formed, creating initiation points for the subsequent growth of the gold electroless layer. Following a series of initial tests, a deposition time of 5 min at 25 °C in the Atomex solution was found to be sufficient to activate the subsequent Catagold 2A deposition process. These conditions were thus used in all experiments described below.

The first electroless depositions on aluminum–MEAs were performed following the conditions specified by the solution manufacturer i.e. temperature of 75 °C in the as received Catagold 2A solution. This results in a deposition rate of 2 μm/h. After 1 h, the resulting microelectrodes did not show a visible gold deposit and the silicon nitride insulating layer around the microelectrodes was severely damaged. Surprisingly, however the aluminum did not show the effect of a vigorous etching as would be expected to occur in a high alkaline solution. The absence of gold deposits on the microelectrodes could be due to a too fast deposition rate and lack of adhesion of the resulting thick layers which lift-off of the microelectrodes.

This hypothesis was confirmed upon reducing the deposition time in Catagold 2A. The ESEM picture in Fig. 2 shows the deposition on a pseudo-reference electrode and on two microelectrodes for a deposition time of 5 min in Catagold 2A solution at 60 °C. A close up view of a single microelectrode is shown in Fig. 3a. The resulting dendritic deposition has a maximal height of about 20 μm, which corresponds to an estimated deposition rate of 4 μm/min. This means a deposition rate of about 120 times faster than that specified by the solution provider.

The deposition rate of a gold electroless process can be reduced by decreasing the deposition temperature and/or the gold concentration. A systematic investigation of the influence of these two parameters on the morphology of the gold layers was performed. The deposition shown in Fig. 3b was obtained for a deposition time of 1 min in the non-diluted Catagold 2A solution at 25 °C. However, even if the lateral outgrowth is reduced the resulting microelectrode is still about two times larger than the original one. When the deposition temperature in the Catagold 2A solution was further reduced to −9 °C, a completely different morphology was obtained for a deposition time of 1 min (Fig. 3c). However, as in the previous experiment, the modification of the deposition temperature was not sufficient for limiting the lateral outgrowth.

The lateral outgrowth is better controlled by decreasing the concentration of the gold complex. Following a series of tests using different dilution factors, the 1:20 (1 part of Catagold 2A solution in 20 parts of deionised water) was found to yield, for a 15 min deposition time at 25 °C, well controlled and reproducible gold layers (Fig. 3d). This process allows a homogeneous deposition on the 32 microelectrodes of the array, without any damage of the silicon nitride passivation layer to be performed. Moreover, the resulting gold microelectrodes seem particularly well adapted for the electrophysiological application due to the rather compact and rough layer as well as to the small lateral outgrowth. Additionally, the deposition is fast at room temperature and at low gold cyanide concentration.

The gold layers deposited in the diluted Catagold 2A solution were evaluated by cyclic voltammetry and analyzed by XPS. Comparing the CVs of a gold wire, Fig. 4a, and of the deposited gold layer Fig. 4b, identical oxidation–reduction behavior is observed. This is a first indication of the good

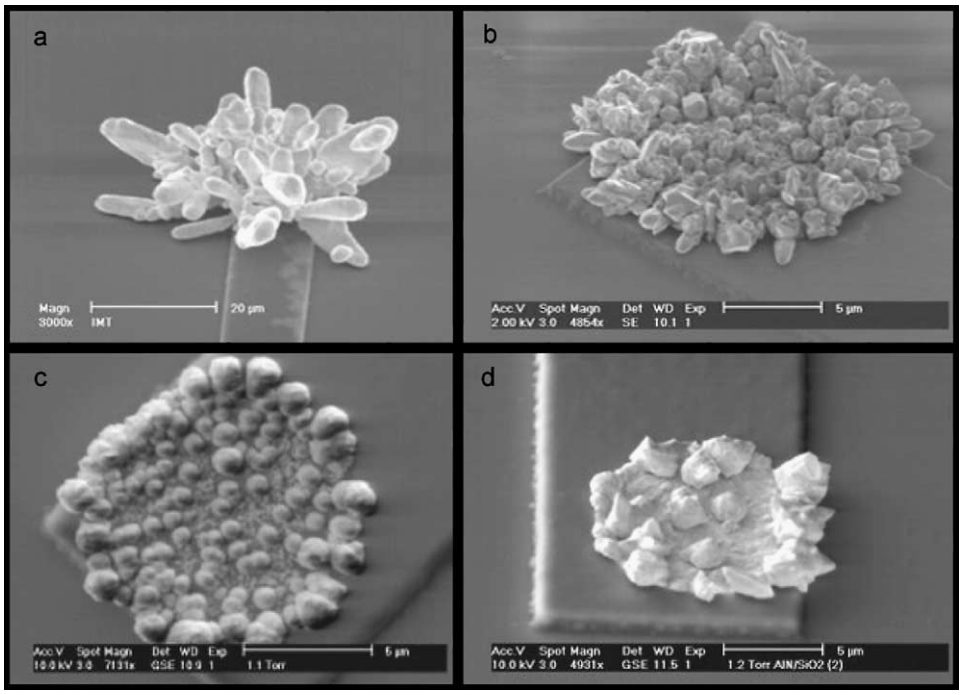

Fig. 3. ESEM images of different Au electroless depositions on Al microelectrodes: (a) 5 min in Atomex followed by 5 min in Catagold, $T = 60\,^{\circ}$C, (b) 5 min in Atomex followed by 1 min in Catagold, $T = 25\,^{\circ}$C, (c) 5 min in Atomex, $T = 25\,^{\circ}$C followed by 1 min in Catagold, $T = -9\,^{\circ}$C, and (d) 5 min in Atomex followed by 1 min in 1:20 Catagold: DI water, $T = 25\,^{\circ}$C.

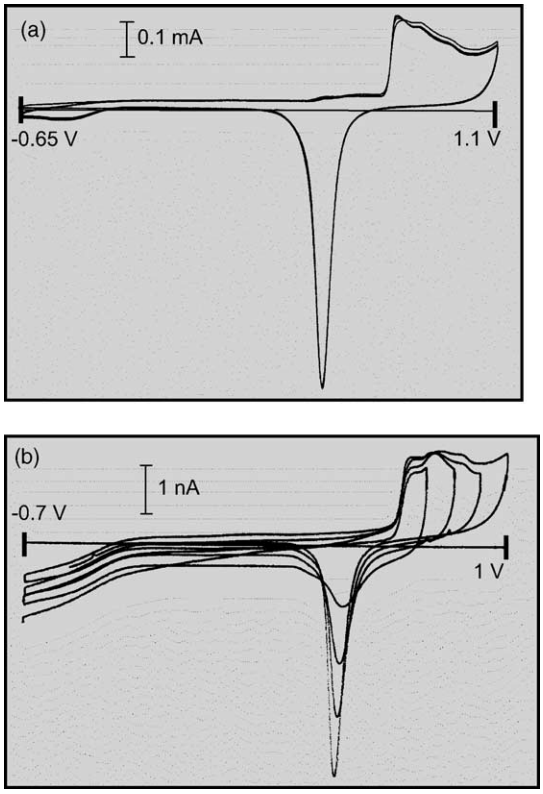

Fig. 4. Cyclic voltammograms in a deaerated 1 M H_2SO_4 solution of (a) a gold wire, (b) electroless Au on Al microelectrode (anodic potential sequentially increased). Commercial Ag/AgCl reference electrode, Pt counter electrode, scan rate 100 mV/s.

quality and purity of the electroless gold layers. Moreover, the electrical interface between aluminum and gold does not introduce resistive or capacitive components, which confirms the good contact between the two layers. The XPS spectrum, shown in Fig. 5, shows a clear evidence of gold, in particular in form 4f. It should be mentioned that due to the difficulties in focusing the X-ray spot on the microelectrodes of 10 µm diameter, the XPS analysis was performed on the larger (100 µm × 100 µm) bonding pads. However, while the deposition on the microelectrodes results in compact layers, the contact pads show slightly less dense deposits. Therefore a small contribution from the underneath Al can be seen on the spectrum.

The optimized deposition protocol (1:20 dilution, deposition time 15 min at 25 °C) was then transposed to the CMOS device. It should be noted that, in this case, the metallic layer is not pure aluminum, but a silicon–aluminum alloy.

Due to the packaged chip geometry, instead of immersing the device into the Atomex and Catagold 2A solutions, gold was deposited using only a drop of the solutions on the active area of the chip. At first, the active area was treated for 5 min with a drop of the Atomex solution at 25 °C. Then, after rinsing in deionised water and drying, a drop of 1:20 diluted Catagold 2A solution was used to deposit the gold (15 min at 25 °C). Fig. 6a shows an optical image of four pixels before and Fig. 6b after the electroless process. The deposition was homogeneous on the whole active area and well localized on the aluminum microelectrodes. It is interesting to note that the chips were not cleaned before the deposition and that no treatment was used for removing the native aluminum

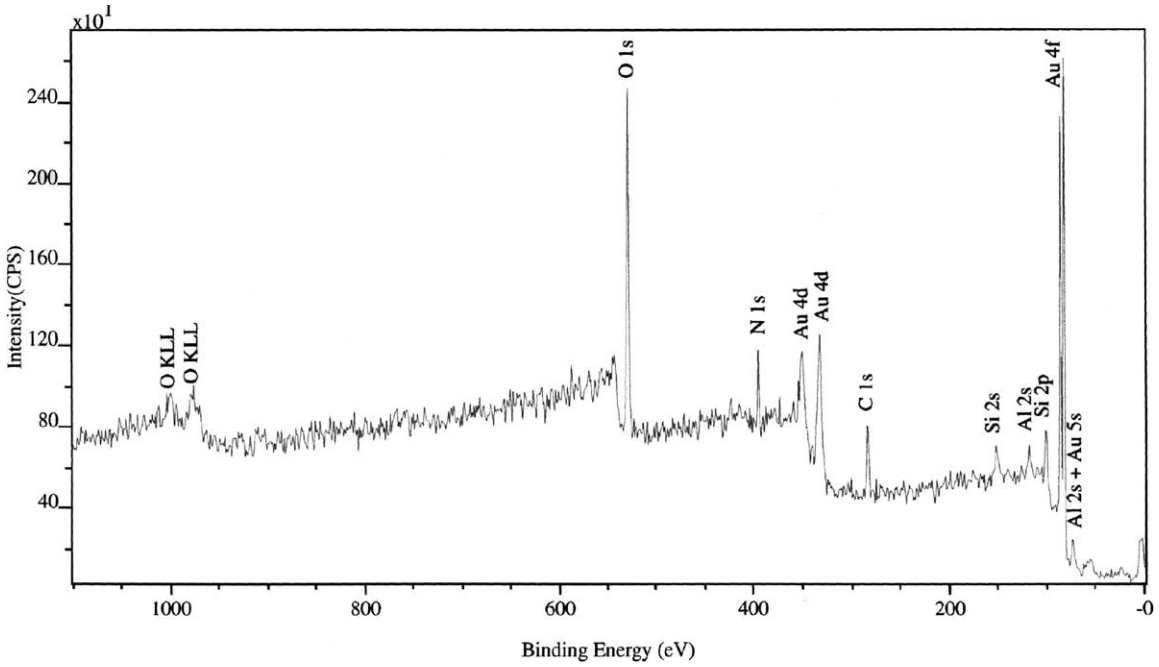

Fig. 5. XPS survey spectra of the electroless Au on an Al contact pad.

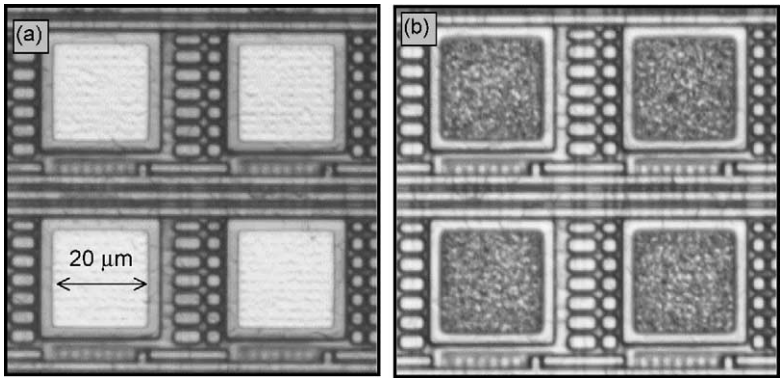

Fig. 6. Optical image of the CMOS device showing four electrodes before (a) and after (b) the electroless deposition.

oxide layer. Unfortunately, an electrochemical evaluation of the deposited gold on the CMOS chip could not be realised since it was not possible to directly contact the electrodes and perform cyclic voltammetry measurements. However, the electrical characterization in a phosphate-saline buffer solution showed excellent results, good electrical contacts between the aluminum alloy and the gold and no damage of the integrated circuit.

4. Conclusions

Although aluminum has never been used so far without a prior modification as a substrate material for gold electroless deposition we could demonstrate that it is possible to deposit gold on aluminum microelectrodes using a commercially available gold cyanide solution.

Gold depositions were performed in two steps: by galvanic displacement in the Atomex solution and then by electroless deposition in the Catagold 2A solution. The treatment by galvanic displacement, producing a gold seed layer, is necessary for activating the following electroless deposition process.

Different morphologies of gold can be obtained by modifying the electroless deposition conditions, i.e. temperature and solution concentration. For our application, the best deposits with respect to the morphology, control of the lateral outgrowth and homogeneity were obtained in a 1:20 diluted Catagold 2A solution at a deposition temperature of 25 °C. This process was then successfully applied to a CMOS chip, where the metallic layer is not pure aluminum but a silicon–aluminum alloy.

The good quality of the gold layers as well as the rapidity and convenience of the electroless process make this

post-processing technique particularly attractive for the development of high density microelectrode arrays based on CMOS technology. The deposition can be performed from a drop of solution on the packaged chip. This aspect is rather convenient and interesting, as it would allow the gold depositions shortly before the electrophysiological experiments, ensuring thus clean and reproducible electrode surfaces. Furthermore, the preliminary electrical characterization of the gold-modified CMOS devices in a phosphate-saline buffer solution confirmed the good functionality of the integrated pre-amplifier circuit. This, together with positive biocompatibility evaluation results, suggest that the CMOS technology can be a possible approach towards realizing high-density microelectrode arrays for in-vitro electrophysiology.

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