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Fabrication and electrochemical characterization of ruthenium nanoelectrodes

Abstract: The Fraunhofer IMS has recently developed a technique for producing nanoelectrodes that are generated by atomic layer deposition (ALD) in a via deep reactive ion etching (DRIE) structured sacrificial layer. This method enables the fabrication of CMOS- and biocompatible nanoelectrodes with suitable ALD-materials. Improvements of the established fabrication processes and the electrochemical characterization of such electrodes are presented. In the frame of the Fraunhofer-Max-Planck-cooperation project *ZellMOS* different types of nanoelectrodes are studied. Their diameter is in the range of 200 nm and thereby sufficiently small to be taken up by living cells. In addition, the electrodes are mechanically enforced by an oxide layer at the nanoelectrodes' bottom.

Keywords: nanoelectrodes, intracellular recording, electrochemical characterization, atomic layer deposition, deep reactive ion etching

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1 Introduction

Multi electrode arrays (MEAs) are a basic instrument for research in the field of biological cell systems, like brain or cardiac tissue. They are suitable to measure electrical signals of cells and hence can detect influences of drugs and toxins on cell systems [1]. The integration of MEAs in a complementary metal oxide semiconductor integrated circuit (CMOS IC) enables complex, programmable measurements and stimulation of cells on a small chip [2]. Extracellular electrodes allow the recording and stimulation of cells on a subcellular, cellular and on a network level [3][4][5]. If the electrodes are sufficiently small - i.e. if their diameter is in the order of 200 nm – they can penetrate the cell membrane and hence measure intracellular signals [6][7]. This results in an improved electrical coupling and enables the detection of sub-threshold events [6][7]. By the integration of penetrating electrodes on a CMOS IC, the advantages of the sensitive intracellular contacts and the programmable recording and stimulation are combined. Partly insulated silicon nanoelectrodes with platinum on top placed on a CMOS IC were already implemented [8].

Here we present a technique for producing CMOS- and biocompatible nanoelectrodes with the advantage to use different electrode materials, deposited by atomic layer deposition (ALD). The nanoelectrodes were electrochemically characterized by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). In order to customize the electrodes for an intracellular contact, they are tapered post-lithographically by a double hard mask technique, mechanically strengthened by an additional oxide layer at their bottom and implemented on flat electrodes in a low density.

2 Ruthenium nano-lawn

2.1 Fabrication process

The Fraunhofer IMS developed a technique for the CMOS-compatible fabrication of free-standing three-dimensional nanoelectrodes which is schematized in **Figure 1** [9][10][11]. Ti/TiN base electrodes with different diameters are covered by a sacrificial amorphous silicon (a-Si) layer. This layer is used as a template and structured via deep reactive ion etching (DRIE) with alternating fluxes of C_4F_8 and SF_6 for passivation and etching respectively. Thus, a structure width of about 400 nm and an aspect ratio of about 1:7.5 can be achieved [11]. The template is subsequently filled via ALD of ruthenium as an electrode material. The covering ALD layer is etched by inductively coupled plasma (ICP). Afterwards, on chip level, the sacrificial a-Si is removed by an isotropic etch process with XeF_2 or SF_6.

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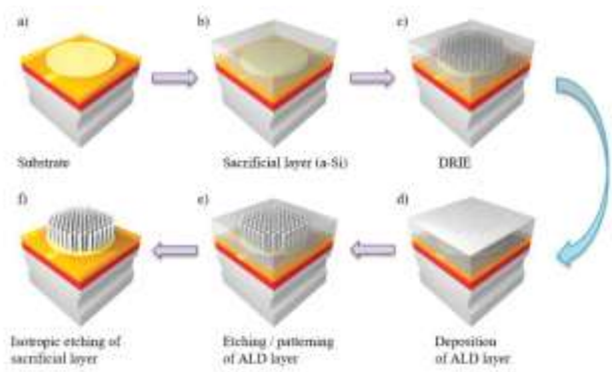

Figure 1: Process flow for the fabrication of ruthenium nanoelectrodes arranged in a nano-lawn [10].

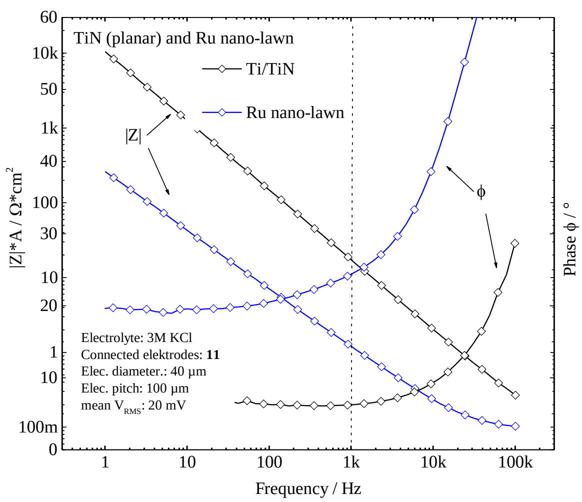

Figure 2: Electrochemical impedance spectroscopy data of ruthenium nano-lawn [10].

2.2 Electrochemical characterization

EIS and CV were applied to the nanoelectrodes, which were arranged in a nano-lawn and compared to planar Ti/TiN electrodes [11][10][11]. 11 clusters à 16 electrodes were connected to the same potential. Electrodes with a diameter of 40 µm and a pitch of 100 µm were measured in 3M KCl solution. EIS data taken with an applied root mean square voltage of 20 mV, a Pt counter electrode and an Ag/AgCl reference electrode are shown in **Figure 2**. The overall impedance decreases vastly when nanoelectrodes are deposited on top of the base electrodes (see **Figure 2**). At 1 kHz the impedance is reduced up to 93% [10]. This is probably induced by the enlarged surface area.

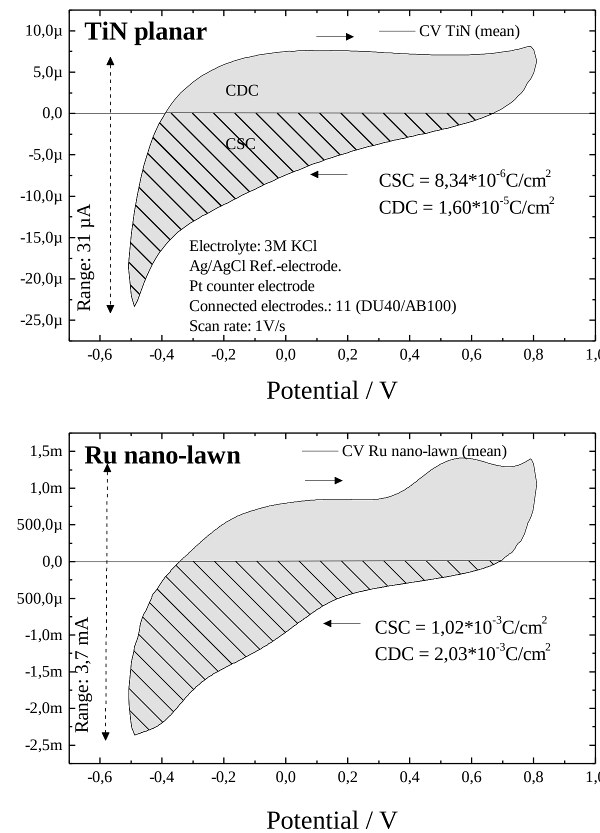

Figure 3: Cyclic voltammetry data of flat TiN electrodes and ruthenium nano-lawn implemented on top [10].

CV measurements were taken with a voltage sweep rate of 1 V/s. The voltage was varied between -0.5 V and 0.8 V. The charge delivery capacitance (CDC) and the charge storage capacitance (CSC) could be identified in the cyclovoltammograms [10]. Like shown in **Figure 3**, the CDC and CSC are increased by more than two orders of magnitude due to the nano-modification of the base electrodes [10]. By reasons of the nanoelectrodes' good performance, i.e. low impedance and a high CDC, applications in different fields like sensor technologies, biomedical research or implants are feasible.

3 Ruthenium nanoelectrodes for Intracellular measurements

In order to contact the cytosome directly and thereby undertake more sensitive electrical measurements, penetrating electrodes are needed. The as described nanoelectrodes have to be slightly modified. The nano-lawns are replaced by maximal 9 electrodes on top of a base electrode. For the improvement of the mechanical stability,

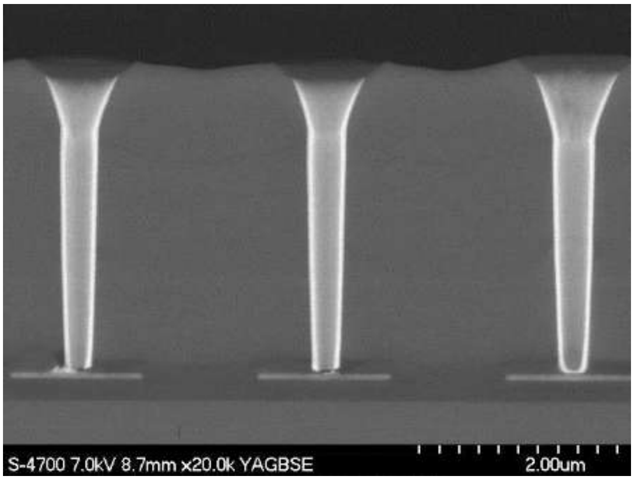

Figure 4: Scanning electron microscope image of nanoelectrodes embedded in a sacrificial layer. The electrodes are mechanically stabilized by an oxide layer at their bottom.

the nanoelectrodes' bottoms are embedded in an undoped silicon glass (USG) stabilization layer of about 150 nm thickness. It appears as a dark layer in the scanning electron microscope (SEM) image shown in **Figure 4**.

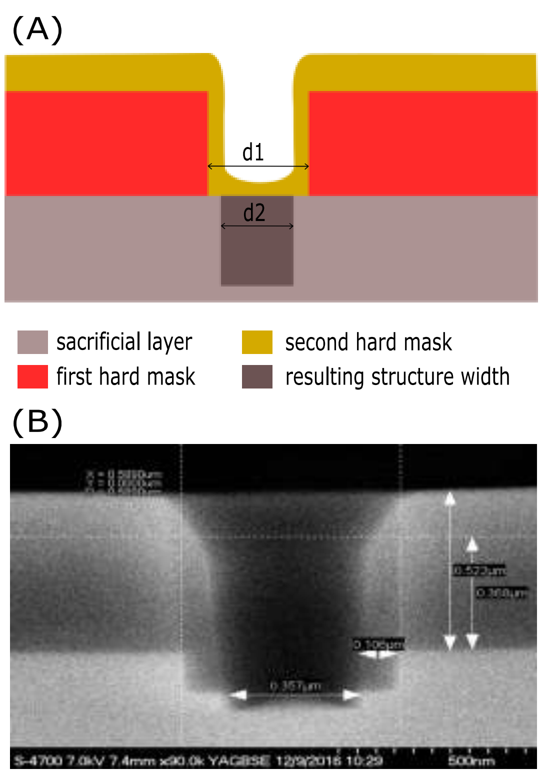

Figure 5: (A) Scheme of the use of a double hard mask for narrowing the structure width. **(B)** Scanning electron microscope image of the opened TEOS oxide hard mask.

It was shown by researchers from the Max Planck Institute IS that electrodes with a diameter smaller than about 200 nm are incorporated by living cells [7]. Hence, the electrodes' diameter needs to be reduced. This could be achieved using an advanced photo technique like deep ultra violet or electron beam lithography. In this work a double hard mask technique to narrow the structures post-lithographically is used instead. The hard mask is patterned by standard i-line lithography. Tetraethyl orthosilicate (TEOS) oxide is deposited on top of a structured USG hard mask. The resulting structure width is hence reduced like schematized in **Figure 5 (a)**. Using reactive ion etching (RIE) with C_4F_8 and Ar plasma results in a narrowing of the structures by about 210 nm.

4 Summary and outlook

CMOS- and biocompatible nanoelectrodes were produced via DRIE and ALD in a sacrificial layer. In comparison to flat electrodes, the electrode-nano-lawn-system shows greatly reduced impedance as well as much higher CDC. Approaches for customize the nanoelectrodes for intracellular contacts were presented. The nanoelectrodes are mechanically stabilized by an oxide layer at their bottom. The diameter of the nanoelectrodes is reduced by about 210 nm via a double hard mask technique. Henceforth, the nanoelectrodes need to interface living cells and the usability as an intermediate between CMOS ICs and living systems needs to be proven. The CMOS-integration of the nanoelectrodes on a read out circuit is ongoing.

Author's Statement

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