Hydrogen Fuel Cells and Monitoring Bioconversion Processes

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Introduction

The hypothesis of our GCEP supported research assumes that advanced fabrication methods enable the creation of unique measurement devices, which may lead to new scientific insights regarding electro chemical reactions inside biological cells. The combination of reactive ion etching with focused ion beam milling and material deposition allows for the generation of a new class of electrochemical probes. Such probes are capable of mapping biochemical reactions inside cell membranes. Together with Professors Swartz and Spormann we will apply this technology, once matured, towards investigating reduction-oxidation potentials inside of hydrogen producing biological cells.

Electrochemical Probes with Nanometer Dimensions

A pencil-shaped electrochemical transducer system for characterization of reduction oxidation potential in live biological cells with nanometer dimensions is being developed. High aspect ratio silicon tip structures are fabricated, combining isotropic and anisotropic deep reactive etch processes. In this way, aspect ratios of greater than 20, with tip radii of smaller than 50 nm can be achieved. Subsequently, a three-layer system consisting of (1) isolation layer: silicon nitride, (2) metal layer: platinum or gold, (3) isolation layer: silicon nitride is deposited on the silicon tips. Planarization of this structure in combination with an etch-back process enables precise exposure of the buried metal layer, producing an electrode with a diameter about 100 nm or less at the tip.

Electrochemical and impedance spectroscopic characterization show the functionality of the probe. Due to the high aspect ratio topography, the probe is well suited for Scanning Electrochemical Microscope (SECM) methodologies. The fabrication process has been developed on four-inch wafers and consists of two fabrication sequences.

In the first stage, High Aspect Ratio Silicon (HARS) tips are shaped combining isotropic etching with anisotropic Deep-RIE-silicon etching. This process is based on the 'direct fabricated tip' technique introduced for AFM probes [5]. A 1 μm oxide layer is grown on a 500 μm thick (100) oriented wafer using wet oxidation. Next, oxide patterns (caps) for silicon tip-shaping are formed. Using an isotropic SF_6 based reactive ion etch, the top of the tip structure becomes shaped while retaining the silicon oxide cap. A Deep-RIE process is used to etch the shaft, exploiting the remaining silicon oxide caps as an etch mask. Using this process, an aspect ratio greater than 20 is achievable. Subsequently, wafers are thermally oxidized (temperatures lower than 1050 °C) [6, 7]. Finally, the grown oxide is removed using a Buffered Oxide Etch (BOE) to release the oxide caps, and form sharpened HARS tips. Repetitive oxidizing and BOE etching can lead to further sharpening of the tip [7, 8]. We routinely run two sharpening cycles and achieve tip radii smaller than 50 nm.

During the second part, electrode tips are fabricated by patterning metal nano-electrodes on top of the silicon tips and subsequently connected to the bonding structures as depicted in Fig. 1. The process begins with a Low Pressure Chemical Vapor Deposition (LPCVD) of a silicon layer with thickness of 200 nm. This layer serves as isolation between the metal layer and silicon substrate. Platinum is used as electrochemically active material. Platinum sputtering is being used to achieve good wall coverage and adhesion. Patterning of the metal layer is done with a lift-

off technique. Next, a Plasma Enhanced Chemical Vapor Deposition (PECVD) silicon nitride layer (deposition temperature at 350°C) is deposited onto the structured metal. Thick-photo-resist (Shipley SPR 220) is spun on in two steps in order to planarize the wafer surface. A RIE etching process is used to simultaneously etch back the resist and the silicon nitride layer on top of the platinum. The chemistry of the etch-back process is based on SF_6 and Freon 14 (CF_3Br). The etch rate of the photo resist is 60 nm/min, and the PEVCD for the silicon nitride is 80 nm/min. Platinum does not get etched by these etchants and is used as etch stop layer. In this way, exposure of the platinum on top of the tip in the sub micron range is achieved. Finally, the bonding pads are opened, exposing the metal contacts.

A detailed view of the top of the pencil probe is depicted in Fig. 2. It shows the platinum tip with a 100 nm-thick silicon nitride passivation layer. The tip radius is approximately 200 nm and significantly increased compared to the radius of the pure HARS tips as shown in Fig.2b.

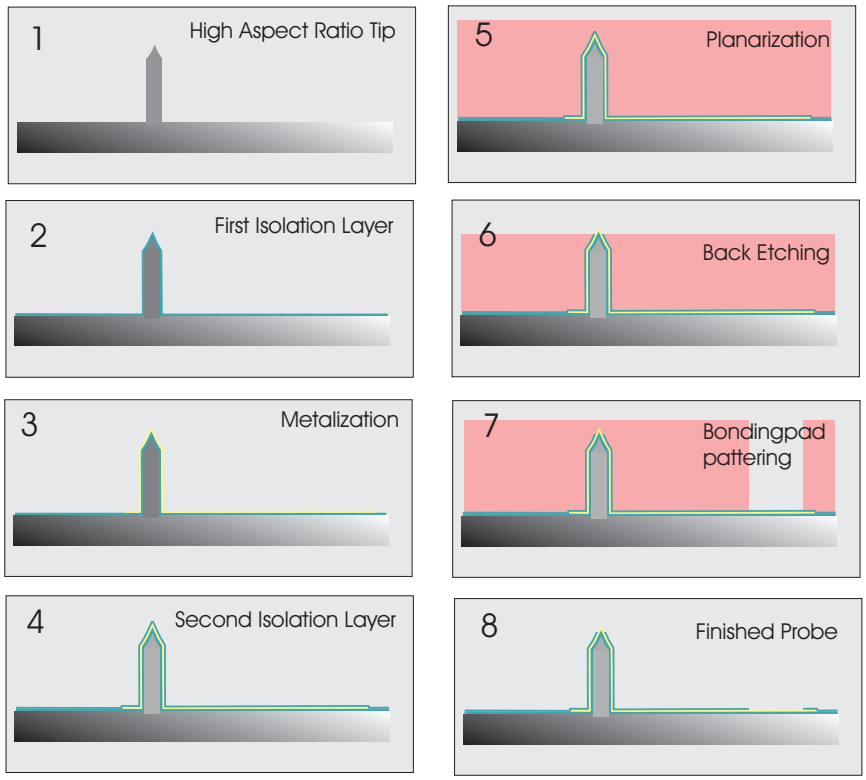

Figure 1. Fabrication of the pencil probes: (1) Starting with HARS tips, (2) Deposition of LPCVD Silicon nitride as an Isolation layer, (3) Deposition and pattering of a metal layer, (4) Deposition of the PECVD Silicon nitride as an passivation layer, (5) Planarization using thick photo resist, (6) Etch-back of resist and silicon nitride layer to expose the buried metal layer, (7&8) patterning and etching of the bonding pads.

Using magnetron sputtering techniques for platinum deposition, a homogenous metal layer is formed. Due to this layer, a sufficient wall coverage of the HARS tip structures can be observed. This conformal metallization establishes a reliable electrical connection between the electrode on top of both the tip and the bonding structure.

Cyclic voltammetry is applied to investigate electrochemical behavior of the tip probes. The cyclic voltammograms of tip probe electrodes in phosphate buffer has been investigated. All

important electrochemical surface reactions such as oxidation and reduction of platinum, hydrogen adsorption/desorption and hydrolysis reaction of a platinum electrode can be identified

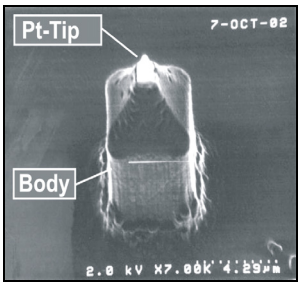

Figure 2.
a) SEM picture of the pencil probe (height: 13µm, width: 4µm, electrode area: 0.7µm^2),

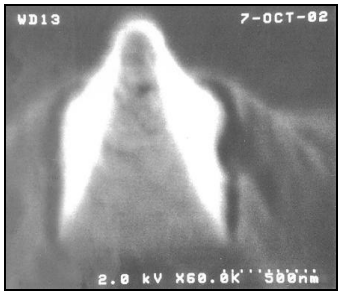

Figure 2.
b) Detailed view of the platinum tip of pencil probes with a tip radius of 100 nm.

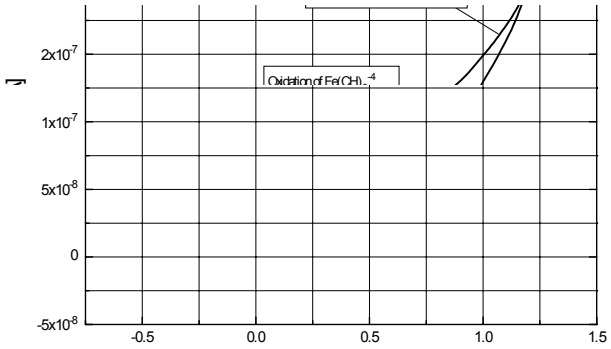

Figure 3.
Cyclic Voltammogram of Tip probe in 0.1 M Phosphate buffer electrolyte with 5mM $K_4Fe(CN)^6$ as Redox-substance and in Phosphate buffer only is plotted. The potential is related to a 0.1 M KCl Ag/AgCl-Reference electrode, Potential sweep rate was 50 mV/s.

A Ferricyanide/Ferrocyanide-system is used to study the response to a reversible redox-system. In Fig. 3 voltammograms taken in a phosphate buffer with 5mM and 0mM concentration of potassium ferrocyanide are shown. Tip probes with an electrode area of 0.7 µm^2 are used. The oxidation peak of ferrocyanide to ferricyanide appears in the potential regime above 200mV. At these potentials, a high faradic current compared to the voltammogram in phosphate electrolyte is generated. Determining and translating this behavior numerically using Electrochemical Impedance Spectroscopy (EIS) leads to a faradic impedance of the pencil probe transducer system at a DC working potential of 500 mV of 3 x 10^6 Ohm for 5mM $Fe(CN)_6^{4+}$ and 2 x 10^8 Ohm for phosphate buffer only.

Multi-Layer Connection for High Density Electrochemical Probe Array

Multi-layer technology for electrical high-density connections between the two opposing sides of a wafer has been developed. This technology will be used to connect probes of an array to a signal processing CMOS circuit on the back-side of the wafer. Openings in a double-side polished wafer are created by applying a deep reactive ion etching technique. Hole structures with a diameter of 20 µm are formed through a 350-µm thick wafer. A multi-layer system of up to eight layers consisting of alternating conducting layers (N-type doped poly-silicon) and isolating layers (silicon-oxide) were grown until the vias were filled.

The applied low-pressure chemical vapor deposition techniques guarantee a sufficient homogenous coating outside and inside of the entire structure to a minimum layer thickness of one µm. The connection quality has been examined combining impedance spectroscopy and Focused Ion Beam technology. Depending on the geometry and the doping profile of the poly-silicon layers, a connection resistance of less than 80 Ohms can be achieved with sufficient DC isolation. In this way, the multi-connection of up to four-isolated signal lines per opening, which is shown in Fig. 4 was manufactured. This corresponds to a local connection density higher than 30.000/cm^2.

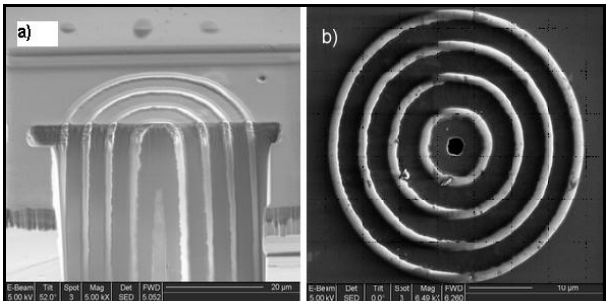

Figure 4: A 40µm-diameter ETWI consisting of four 2µm-thick poly-silicon layers and four 1µm-thick thermal silicon-oxide layers (a) SEM image of the cross section (b) SEM image of the top view (poly-silicon and silicon appears as dark, silicon-oxide appears as bright).

References

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