

MICRO FUEL CELL WITH LITHOGRAPHICALLY DEFINED FLOWFIELD CHANNELS AND RANDOM PATTERNS FOR GAS DIFFUSION LAYER

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Abstract: We present a silicon microfabricated hydrogen micro fuel cell (MFC) with a proton-exchange membrane (PEM). The device has an integrated gas diffusion layer (GDL) using silicon nanograss (also known as black silicon), and the highly doped silicon wafer itself acts as a current conductor. The device is extremely straightforward to fabricate, requiring only three photolithographic steps. In addition to good manufacturability, further savings are obtained by replacing platinum with chromium on the electrodes. However, an unexpected behavior is experienced in its electro-chemical properties that lead to very fast degradation and a negative resistance region in the U/I plot.

Keywords: silicon, MEMS, nanograss, gas diffusion layer, micro fuel cell, negative resistance.

INTRODUCTION

Micro fuel cells (MFC) have the potential to replace traditional batteries in mobile applications, owing to their high energy density. Furthermore, miniaturization of power sources is essential for autonomous MEMS applications. In order to enable massive employment of MFCs, their cost should be brought down. In this work, we show that silicon MEMS fabrication technology enables us to integrate flow channels, electrodes, GDL and current conductors into a single structure. We also discuss usage of non-noble metal chromium as a replacement for platinum in the MEMS part of the device, further simplifying the goal of low cost. The focus of development of our device is the elimination of physically separate layers and minimization of fabrication steps, as well as maximization of areal power density.

EXPERIMENTAL

Fabrication

The electrodes are microfabricated from a highly-doped ($\rho = 0.01 \Omega \text{ cm}$) silicon wafers. The gas channels are created with anisotropic deep reactive ion etching (DRIE) of silicon. Integrated gas diffusion layer is formed by etching silicon to form nanograss. This step is undertaken in RIE under high oxygen partial pressure in O_2/SF_6 plasma. The MFC itself is constructed by sandwiching a Nafion® membrane between two identical silicon electrodes, as illustrated in Fig. 1.

The fabrication steps are (Fig. 2) as follows: The

wafer is thermally oxidized (oxide thickness 300 nm), photolithography is done and the oxide etched in buffered hydrofluoric acid (BHF) (2b).

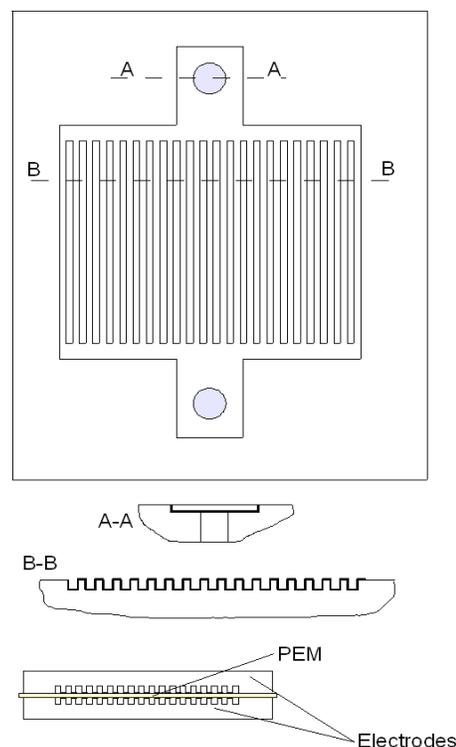


Figure 1. Construction of the micro fuel cell.

This will define the area that will later on be transformed into GDL. Thin photoresist (AZ® 1505) is spun at 4000 RPM – resulting in a thickness of 0.5 μm – and patterned to form the mask for the flowfield (2c), followed by a silicon DRIE etch step performed in a cryogenic ICP RIE (Oxford Instruments

Plasmalab® System 100) in SF₆/O₂ (etch parameters: ICP 2kW, CCP 3W, SF₆ flow 100 sccm, O₂ flow 15 sccm, pressure 10 mTorr, temperature -110°C). Etching under these conditions for 5 minutes results in 30 μm deep channels. On the backside of the wafer a 200 nm aluminum layer is deposited by sputtering (Plasmalab® System 400) and patterned with commercial H₃PO₄-based wet etchant. Aluminum serves not only as electrical contact pad but also as an etch mask for fluidic inlet DRIE etching. Inlet etch process is identical to flowfield etching but because the etchable area is smaller, the rate is higher, 7 μm/min vs. 5 μm/min. Finally, silicon nanograss (black silicon) is formed on the top side by plasma etching in passivating conditions (ICP 1kW, CCP 2W, SF₆ flow 40 sccm, O₂ flow 18 sccm, p=10mTorr, T=-120°C, t= 10 min). A SEM micrograph of silicon nanograss is shown in Fig. 3. Finally a thin layer (30 nm) of chromium or platinum is sputtered over nanograss (2f). This metal layer should increase durability and conductivity of the black silicon GDL.

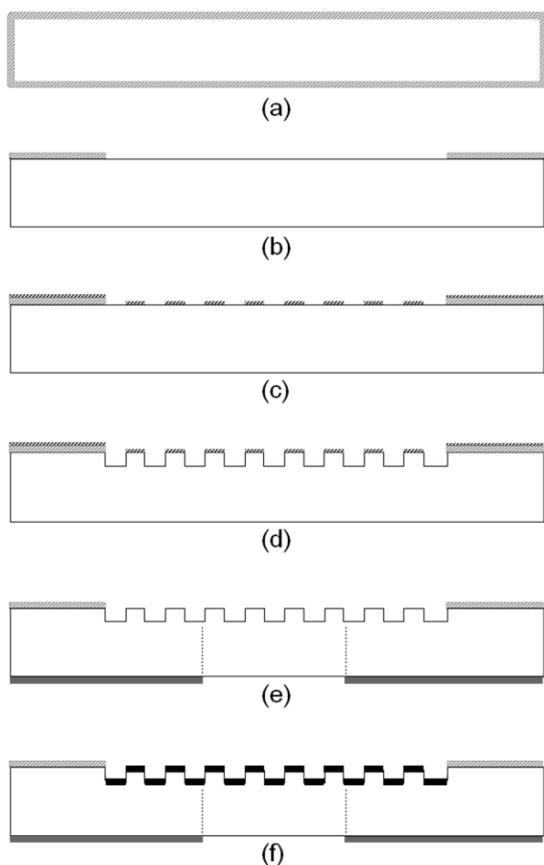


Figure 2. Microfabrication steps of one electrode. See text for details.

The electrodes are diced and a Nafion® membrane coated with carbon supported platinum

catalyst is sandwiched between two.

The catalyst is coated on the membrane with the thin-film method of Wilson et al. [6]. The catalyst ink is produced by mixing carbon supported platinum catalyst (60% platinum) with a Nafion® solution. Sonication is used to homogenize the mixture. The painting is done by an air-brush producing a thin and smooth catalyst layer on the membrane. The mass of platinum is 0.5 mg/cm² on both sides of the membrane and the catalyst layer contains 40 mass% of platinum, 30 m-% of carbon and 30 m-% of Nafion. After painting, the membrane is hot-pressed at 140 °C for 2 minutes (50 kN) to finalize the catalyst layer structure.

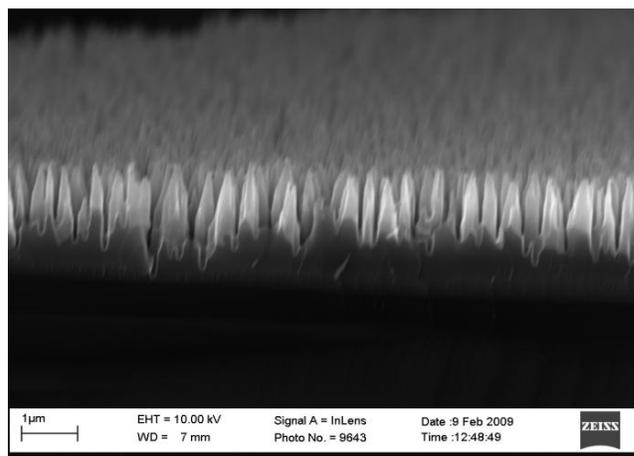


Figure 3: SEM micrograph of black silicon GDL: the typical diameter of silicon nanopillars is 200 nm.

Measurement setup

The device was characterized by clamping the electrode-membrane assembly (MEA) between two blocks of aluminum, provided with the necessary apertures for gas tubing and sockets for electrical contacts (Fig. 4).

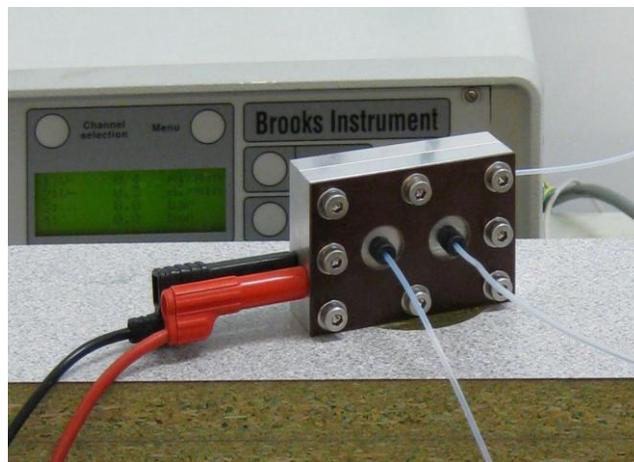


Figure 4. Jig with MFC in the measurement setup.

The reactants were pure, humidified oxygen and hydrogen, flowing at a rate of 50 ml/min and a temperature of 22 °C. The load on the MFC is swept from open-circuit (OCV) to 0.1 V with an Autolab® PGSTAT100 potentiostat, at a speed of 1 mV/s. The MFCs have an active area of 1.5x1.5 cm².

RESULTS AND DISCUSSION

The fabrication of the MFCs presented here is a further simplified version of the process presented in [1]. There were two designs for the flow field channels: straight and serpentine, which effectively triples the path traveled by the gases (the feature is clearly visible on Fig. 7). The two types of MFCs have not exhibited discernible differences in performance, leading to the conclusion that gas diffusion through the GDL is overwhelming and rendering the serpentine insignificant. A liquid fuel may change the situation.

The results of the measurements are presented on figures 5. and 6.

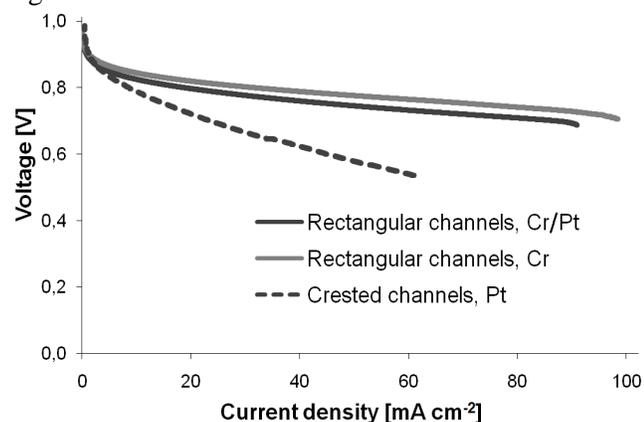


Figure 5. Current density of MFC, compared with the one from [1].

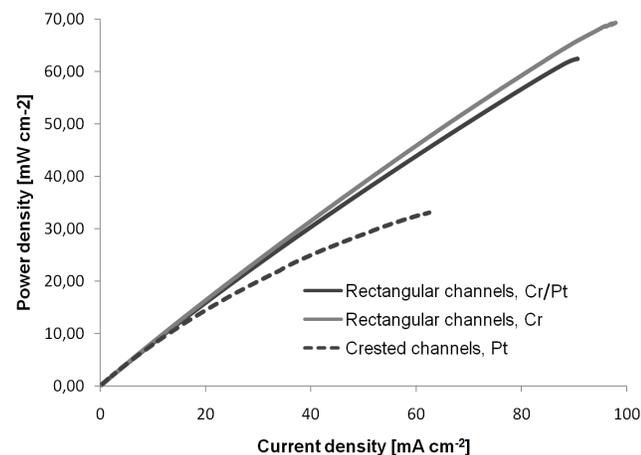


Figure 6. Power density of MFC, compared with the one from [1].

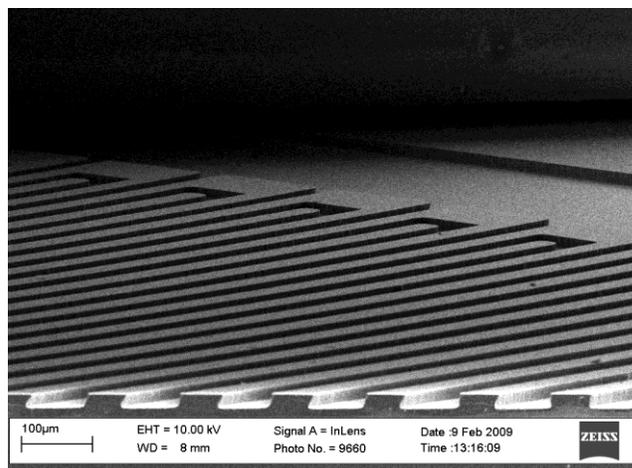


Figure 7. SEM micrograph of the flow channels. The black area is the silicon nanograss (black silicon).

To enhance current collection, microfabricated fuel cells are often coated with a relatively thick layer of gold for current collection ([2-4]). Since our device uses thin, highly-doped silicon wafers, such layer was deemed unnecessary. The previous generation device [1] had a 40 nm layer of platinum on the black silicon GDL, for improved reaction kinetics. In contrast, the new device uses either Cr/Pt (15 nm chromium adhesion layer/25 nm platinum) or only ~30 nm chromium. Surprisingly, the fuel cells which had only chromium on the GDL, performed better than the ones with platinum. While the reason for such behavior is not clear at this point, it indicates that cheaper materials may be used in MFCs. It should be borne in mind that platinum is not completely eliminated: the Nafion membrane is still coated by platinum nanoparticles.

The new device displayed peculiar performance degradation during a single voltage sweep (Fig. 8).

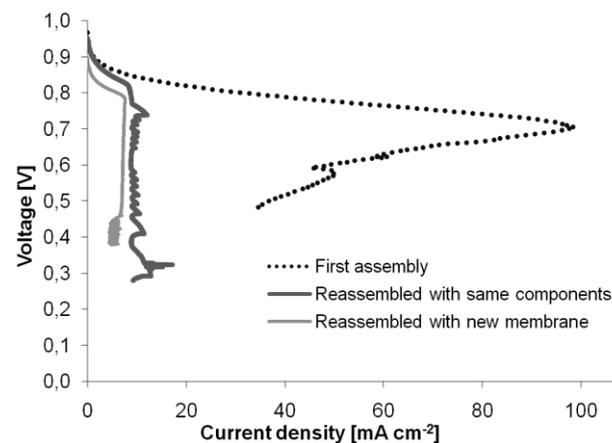


Figure 8. Performance degradation after a single measurement.

As can be seen from the plot, after a certain point, increasing the load (decreasing the voltage) will cause the output current to decrease, instead of increasing it. In power supplies, this behavior is commonly called “foldback”. After one measurement, the fuel cell would maintain its degraded performance, and drying the flowfield and membrane brings no benefit. In fact, disassembling the MEA, drying and reassembling it, did not help, either. Since replacing the membrane with a new one brought no improvement, it is concluded that the change did not occur there. SEM imaging of the electrode surface has, thus far, not revealed anything. A number of experiments have been devised to study this phenomenon in detail.

CONCLUSIONS

The MFCs we fabricated and characterized show promising high power density characteristics comparable to similar devices found in literature [2-5]. Ours is very simple to fabricate and the elimination of noble metal current carrying metallization will bring major cost benefits. Elimination of a separate GDL further simplifies the design. The simplicity of the design allows for easy miniaturization and integration with other MEMS components, and the small vertical dimensions make these fuel cells prime candidates for stacks in portable devices. The rapid degradation mandates further research to understand the phenomena at the interfaces involved.

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