

MINIATURE FUEL CELL WITH CONDUCTIVE SILICON ELECTRODES

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ABSTRACT

We report on a direct methanol fuel cell (DMFC) with conductive silicon electrodes. In our design, the electrodes are made of silicon instead of carbon. We fabricated a porous structure at the bottom of the channels using the DRIE process. Pt catalyst was electrodeposited onto the surface of the electrodes. A Nafion 115 membrane was sandwiched between two 280- μm -thick electrodes with a micro porous structure 30 μm thick. Open circuit voltage of 150 mV was observed with 1M methanol feed. Maximum power density of 0.016 mW/cm^2 was achieved. Since the electrode and the channels are fabricated in a single wafer, it is possible to decrease the total thickness of the fuel cell by a using thinner wafer.

Keywords: DMFC, porous structure, miniature fuel cell

INTRODUCTION

Direct methanol fuel cells (DMFCs) with a micro solid-polymer-electrolyte are promising power sources for portable devices^[1-2]. Not only high performance but also thinness is required for batteries in portable devices.

The structure of a DMFC was the same as that of a polymer electrolyte fuel cell (PEFC) operating on H_2/O_2 except for the composition of catalyst. Micro fuel cells (including both DMFC and PEFC) based on MEMS fabrication has been reported. Kelley *et al.* reported that micro fuel cells achieved comparable cell performance of large size fuel cells^[3]. Yu *et al.* suggested that the cell performance was improved by using a Cu/Au composite layer as the current collector because of low cell resistance^[4].

To achieve thinner fuel cells, one solution is to connect some cells in series in a single plane. Lee *et al.* proposed “flip-flop” configuration and evaluated the cell performance^[5]. In their design, two and four cells were interconnected in series to make a planer array of cells. The output voltage was achieved as the sum of individual cells, while the arrayed cells are as thick as a single cell.

Another solution is to decrease the thickness of electrodes. Fuel cells usually use carbon electrodes which constitute MEA (membrane electrode assembly). Electrodes of fuel cells need high conductivity and porous structure to obtain large area of the catalyst. Highly doped semiconductors and “porous silicon” were used to achieve high conductivity and large area

respectively. The “porous silicon” was obtained by anodic etching in HF solution. Hayase *et al.* fabricated electrodes of the fuel cell using 250- μm -thick n^+ wafer and reported on the power generation^[6].

We propose another electrode structure fabricated with the DRIE (Deep Reactive Ion Etching) process. To improve the fuel cell performance, the porous structure should be optimized. Pores with a desired diameter, however, are difficult to make by anodic etching. To solve this problem, we used the DRIE process to fabricate micro porous structures, which allowed us to control the pore diameter precisely.

STRUCTURE OF THE FUEL CELL

Fig. 1 is a schematic of the fuel cell of our design. One electrode is a p^+ silicon substrate. Channels were fabricated from one side. Pores were made from the other side to penetrate the bottom of the channels. The DRIE process was used to fabricate the pores. We call the bottom of channels with the pores “micro porous structure”. Pt catalyst was electrodeposited onto the surface of the pore walls and the channel walls. A proton exchange membrane (PEM) was sandwiched between two electrodes which work as an anode and a cathode.

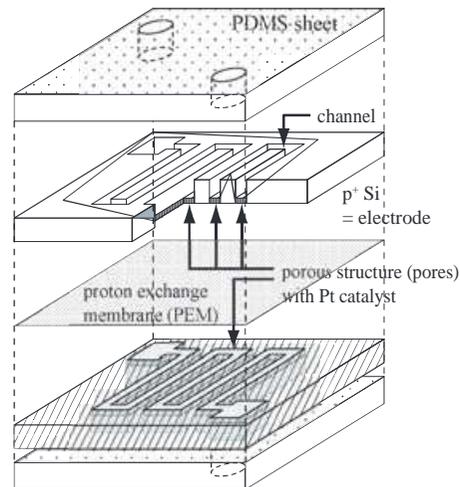


Fig. 1. Schematic of the fuel cell with conductive silicon electrodes.

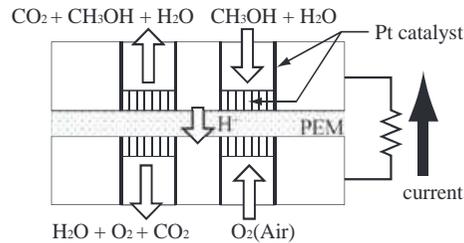
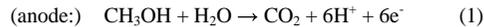


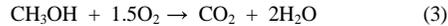
Fig. 2. Schematic diagram of the DMFC.

In this design, the micro porous structure and the channels can be fabricated on a single wafer. It is easy to make a fuel cell thinner because the thickness of the electrode depends only on that of the wafer. Furthermore, it is easy to obtain pores with a desired diameter. This design is also compatible with recent techniques for MEMS pumps and valves.

The basic scheme of the DMFC is shown in Fig. 2. The half reactions in the anode and the cathode are described as follow:



which can be combined as the overall reaction:



In this research, we used Pt catalyst because of the good adhesion to the silicon electrode.

FABRICATION

The fabrication process is shown in Fig. 3. We used (1 0 0) oriented 280- μm -thick p^+ silicon wafers and their resistivity were 0.01-0.02 Ωcm . First, positive photoresist was spin-coated on one side as an etching mask. After patterning, pores were fabricated by the DRIE process. Etching time was determined by the etching rate of designed pores. Then channels and feed ports were fabricated on the other side of the wafer by the DRIE process. The channel was 250 μm deep, i.e. the pore was 30 μm deep. An Au layer about 100 nm thick was deposited on the wafer. This Au layer works as a current collector.

The wafer was cleaned in a piranha solution ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2 = 3:1$) for 1 hour and in a 1% HF solution for 1 min to remove silicon dioxide from the surface. Pt catalyst layer was formed by electrodeposition^[6,7] onto the wall surface of the pores and the channels. Electrodeposition solution was 20 mM $\text{H}_2\text{PtCl}_6 + 0.5$ mM $(\text{CH}_3\text{COO})_2\text{Pb} \cdot 3\text{H}_2\text{O}$ ^[7]. The counter electrode was a carbon rod. The electrodeposition was carried out at 30 mA/cm². The catalyst mass loading was controlled by measuring charge passing between the wafer and the counter electrode. The actual mass loading of Pt was 2.5 mg/cm². A PDMS sheet with a rectangular window was used as a mask of the electrodeposition. The effective area of the electrode was 6.95 x 9.20 mm². After Pt electrodeposition, the wafer was immersed into H_2SO_4 solution and a positive and a negative voltage were applied for 30 seconds, respectively, to remove Cl^- ion.

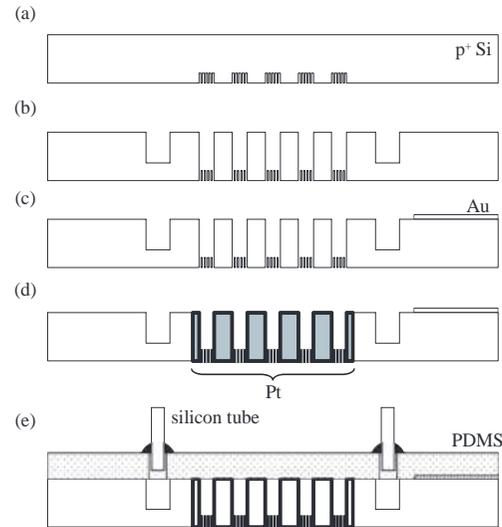


Fig. 3. Process Flow.

(a) Si etching by the DRIE process (pores). (b) Si etching by the DRIE process (channels and feed ports). (c) 100- μm -thick Au layer was deposited. (d) Electrodeposition with Pt onto the effective area. (e) A PDMS sheet was attached to the wafer and silicon tubes were bonded to the feed ports by epoxy adhesive.

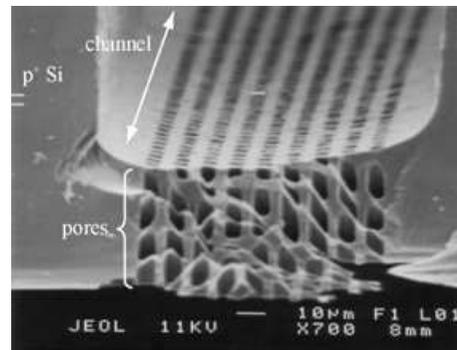


Fig. 4. SEM image of a diced cross section of the pore structure fabricated by the DRIE process.

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Fig. 4 is an SEM (Scanning Electron Micrograph) image of a diced cross section of the micro porous structure (before the electrodeposition). Each pore is about 7 μm in diameter and about 30 μm in depth. Each pore is vertical to the wafer surface.

A PDMS sheet was attached to the channel side of the wafer for sealing. This PDMS sheet had two

windows which were positioned at the feed ports on the silicon electrodes. Silicon tubes were bonded to the windows of the PDMS sheet by epoxy adhesive. We used Dupont™ Nafion® 115 as a proton exchange membrane. The membrane was pretreated by the process shown in Table 1. After the pretreatment, Nafion 115 membrane was sandwiched by two wafers fabricated as the electrodes.

Table 1. Pretreatment procedure of Nafion membrane.

Solution (80 °C)	Time [hour]
H ₂ O ₂ :H ₂ O=1:9 (by volume)	1
H ₂ O	2
H ₂ SO ₄ :H ₂ O=1:9 (by volume)	1
H ₂ O	2

The photograph of our fuel cell assembly is shown in Fig. 5. Whole structure was packaged within two acrylic boards.

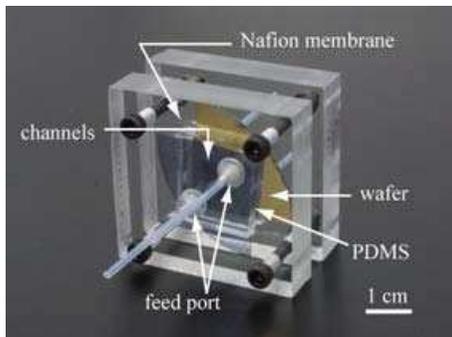


Fig. 5. The photograph of the fuel cell assembly.

RESULTS AND DISCUSSION

To examine device properties, we measured open circuit voltages. This experiment was done at room temperature. Methanol solution (1M) was fed to the anode side port by a pump and the cathode side port was open to ambient air (generated H₂O was pulled off by a pump). Fig. 6 is the response of the open circuit voltage of the fuel cell. After the voltage increased temporarily in response to a methanol supply, it decreased to a certain stable point. The experimental result shows that our cell performs as a fuel cell.

The polarization curve of the fuel cell is shown in Fig. 7. Each value in Fig. 7 was measured after the open circuit voltage became stable in Fig. 6. The operating conditions of the fuel cell were the same as those of Fig. 6. The open circuit voltage was 150 mV and the maximum current density was 0.57 mA/cm². Fig. 8 shows the power density curve. The peak level was about 0.016 mW/cm².

280-μm-thick electrodes with 30-μm-thick micro-

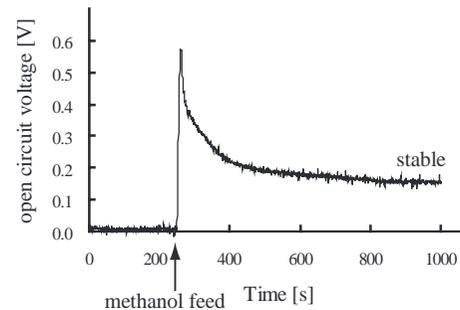


Fig. 6. The response of the open circuit voltage.

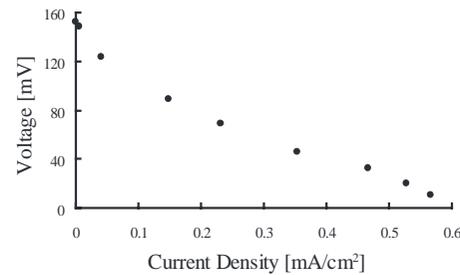


Fig. 7. Polarization curve.

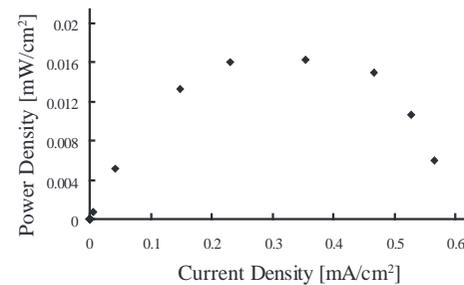


Fig. 8. Power density curve.

porous structure were used in all the experiments. The thickness of the electrode was determined by the wafer. Since a micro porous structure plays a role of an electrode of a fuel cell, thinner structure can be achieved by thinner silicon wafers.

Pt-Ru catalyst is usually used as a catalyst for DMFCs. It will be possible to improve the cell performance by electrodepositing Pt-Ru as a catalyst^[7]. The micro porous structure will be optimized easily by changing the pore side mask pattern.

CONCLUSION

In this paper, a design of electrodes for DMFCs has been proposed and prototypes were fabricated. The electrodes were p⁺ silicon substrate which had a micro porous structure fabricated by the DRIE process. The fuel cell with 280- μm -thick p⁺ silicon electrodes has supplied the maximum power density of 0.016 mW/cm² at room temperature by using 1M methanol solution.

This design allows us to decrease the thickness of fuel cells and to modify the porous structure of electrodes. The cell performance will be improved by depositing Pt-Ru as a catalyst.

ACKNOWLEDGEMENT

This research was supported by the Program for Promotion of Basic Research Activities for Innovative Biosciences (PROBRAIN). The photolithography masks were fabricated with the EB equipment of VDEC (VLSI Design and Education Center) - The University of Tokyo. Alcatel ICP plasma etching system A601E (DRIE) was used to etch the silicon structures.

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