SILICON-BASED PROTON EXCHANGE MEMBRANE FOR MICRO DIRECT METHANOL FUEL CELLS

X. H. Wang[1], W. J. Wang[1], Q. Zhang[1], X. P. Qiu[2], X. Guo[2], and L. T. Liu[1]
[1]Institute of Microelectronics, Tsinghua University, Beijing 100084, China
[2]Chemistry Department, Tsinghua University, Beijing 100084, China

Abstract: This paper presents our research on silicon-based proton exchange membranes for silicon-based micro fuel cell applications. The porous silicon membranes with a thickness of 20-40 μm were fabricated. And the porous silicon-based proton exchange membranes were formed by using the combination of the porous silicon membranes and Nafion® solution. The proton conductivities of the porous silicon-based PEMs are 0.01~0.07s/cm comparable to Nafion® (0.05~0.08s/cm). It makes possible to realize a kind of simple structure, silicon-based micro fuel cell, which can be integrated with other MEMS devices.

Key Words: Micro Fuel cell, Porous Silicon, Proton Exchange Membrane, Nafion®

1. INTRODUCTION

As a leading candidate power source for portable electronic devices, micro direct methanol fuel cell (DMFC) has drawn increasing attention recently due to its high energy density, low pollution and room temperature operation [1-5]. Most of these fuel cells have used polymer, such as Nafion®, as a proton exchange membrane (PEM). However, Nafion® is not readily compatible with standard microfabrication techniques used in making micro fuel cells. It also cannot be easily patterned using photolithography, and bonding it to the silicon is often problematic for the assembly with silicon substrates. Additionally, the contacting is not tight enough for getting better performance when a fuel cell with sandwich structure is assembled by Polydimethylsiloxane (PDMS) [3].

Therefore, a silicon-based PEM is very important for miniaturization of fuel cells and their integration with other MEMS devices. In order to solve these problems, some approaches have been tried. Scott Gold et al. used sulfuric acid loaded nanoporous silicon as a PEM material for micro fuel cell applications [6]. T. Pichonat et al. demonstrate a way of making low-cost miniature fuel cells based on proton conducting porous silicon membranes [7].

We present a simpler process to make a silicon-based PEM for the motivation of a simple structure micro DMFC in this paper. Fig. 1 shows a kind of potential silicon-based micro DMFC we proposed. There are channels flowing methanol fuel on the top of the plate that is anode. In the middle, the porous silicon membrane combining Nafion® solution is used as PEM. The other side of the plate is the cathode breathing the oxygen by itself from the surrounding air. A catalyst metal deposited on the both-side surface of the porous silicon membrane serves as the catalyst electrodes and the current collecting layers.

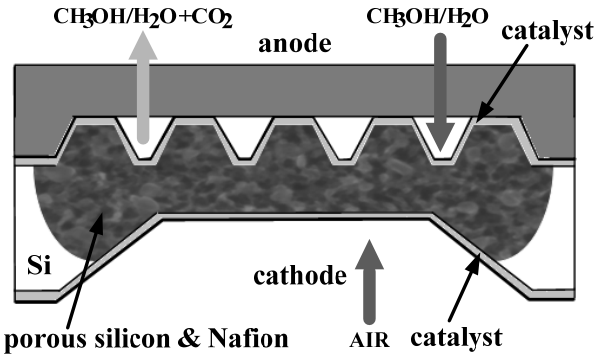


Fig. 1: Schematic of the micro DMFC we proposed, whose flow channels and PEM are formed on one silicon wafer.

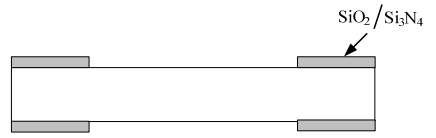
2. EXPERIMENTAL

2.1 Porous Silicon Membrane

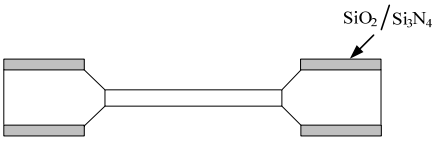
In order to get a suitable porous silicon membrane with a thickness of 20-40 μm for the micro DMFC we proposed, a corresponding

silicon membrane is fabricated by using wet chemical etching in KOH first.

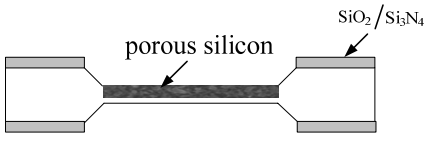
The fabrication process of the porous silicon membranes presented in Fig. 2 is described below. (a) Thermal oxide and LPCVD Si_3N_4 were deposited on both sides of a 400μm thick 3-inch double-polished, N^+-type silicon wafer as the mask layers. And double-side lithography was introduced to pattern on both sides. (b) Double-side wet etching in KOH was used to obtain a silicon membrane with a thickness of 20-40 μm and halve KOH etching time. It also can avoid the failure of anodization due to the pin holes in nitride layer comparing to one-side etching. Additionally, both the anode and the cathode can be formed simultaneously by etching the both sides of the wafer for the micro DMFC we designed. (c) The porous silicon was formed by anodization with HF-ethanol solution in a Teflon tank, as shown in Fig. 3, at a certain current density. (d) The silicon membrane can not be anodized completely, which means the pores of porous silicon are not permeable. Therefore, reactive ion etching (RIE) was used to etch the rear side of the porous silicon to get the permeable



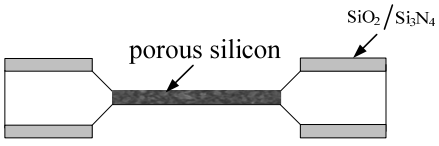
(a) Deposition of SiO_2/Si_3N_4 and patterning



(b) KOH etching



(c) Porous silicon formation



(d) RIE etching the rear side of the porous silicon

Fig. 2: Fabrication process of the porous silicon membranes.

membranes. The porous silicon chips were made finally.

Photos of the silicon membrane and the porous silicon membranes were taken by a scanning electron microscope (SEM). Fig. 4 shows the silicon membrane fabricated using wet etching.

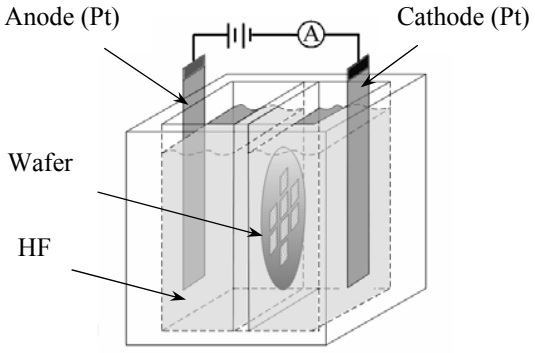


Fig. 3: Schematic of the anodization with HF - ethanol solution.

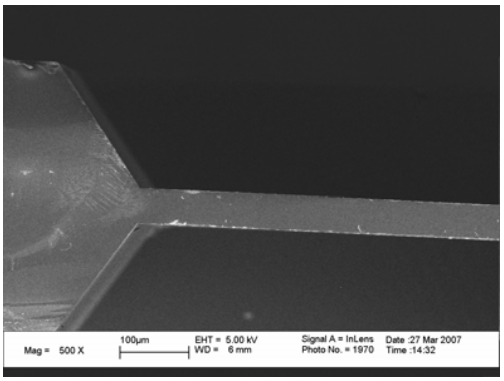


Fig.4: Cross section view of the silicon membrane.

2.2 Porous Silicon-based PEM

The last process is covering the pores of the porous membranes with Nafion® solution. The porous silicon chips cleaned were immersed into Nafion® solution for 1-2 hours. The chips were turned over 2-3 times to ensure the pores filling Nafion® fully. Then the chips, called porous silicon-based PEMs were taken out from the solution and absorbed excess water.

Proton conductivities of the porous silicon-based PEMs were measured on a measurement setup as shown in Fig. 5, with a Solartron 1255B frequency response analyzer coupled with a Solartron 1287 electrochemical interface in

frequency range of 0.1Hz to 1MHz at 25°C. The membranes were sandwiched between two stainless steel electrodes. An AC perturbation of 10mV was applied in the experiments. The conductivity was calculated according to the electrode area of the cell and the thickness of the membrane.

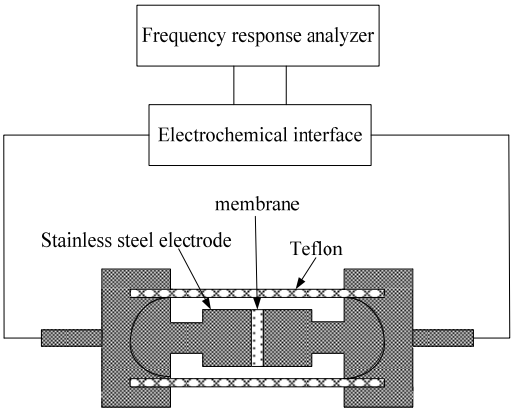


Fig. 5: Schematic of the measurement setup.

3. RESULTS AND DISCUSSION

In this paper, N^+-type silicon wafers were studied for porous silicon with HF concentration of 24.5% ~ 36.75% (49%HF: ethanol=1:1~3:1), at the current density of 10~55 mA/cm^2. The experiments show that the pore dimension of porous silicon increases with the increase of the HF concentration and the current density, while the porosity increases with the decrease of the HF concentration and the increase of current density. Suitable porous silicon membranes were carried out at the current density of 30 mA / cm^2, the HF concentration of 24.5%. Fig. 6 shows a permeable porous silicon membrane formed finally, whose front surface is shown in (a), rear surface made via RIE technique is shown in (b), and the cross section view is show in (c).

The Nyquist Z plots of impedance data are obtained by the measurement setup. For the porous silicon–based PEM, the shape of the plot is semi-circle. According to the semi-circle Nyquist Z plot measured, the membrane can be represented in terms of an equivalent circuit that comprises a combination of the body resistance of membrane (R_M), charge transfer resistance (Rct), and the double layer capacity (C_D), as shown in Fig. 7.

The proton conductivity of the porous silicon PEM is calculated using the equation

$$\sigma = d/R_M S \quad (1)$$

where σ is the conductivity, d is the thickness of the membrane, R_M is the body resistance of the membrane, and S is the contact area between the membrane and the stainless steel electrodes (0.785cm^2).

Table 1 lists the detailed parameters of 5 porous silicon-based PEM samples and their calculated proton conductivities.

Fig.8 is the Nyquist Z plot of the simple 1 measured. We can see the resistance value of the membrane, approximate 4.8Ω, from the plot

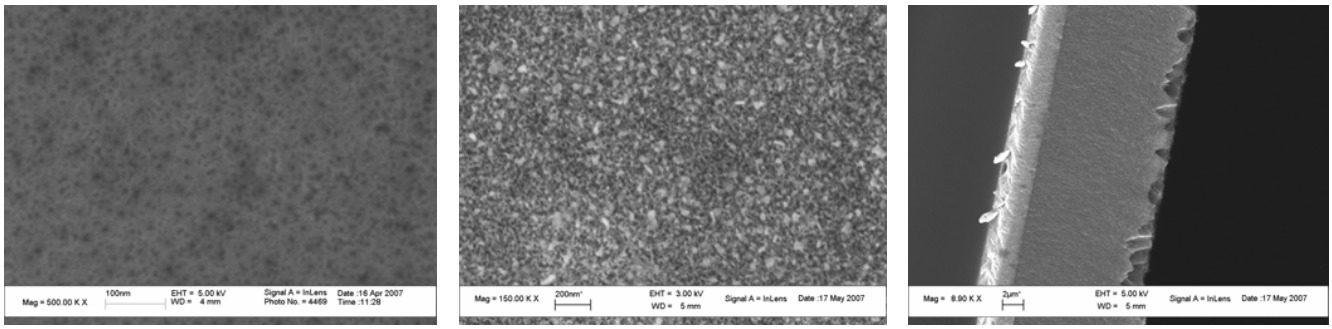


Fig. 6: SEM photos of a permeable porous silicon membrane formed at the current density of 30mA/cm^2, the HF concentration of 24.5%: (a) the front surface of the membrane, (b) the rear surface of the membrane, and (c) the cross section view of the membrane.

directly according to the intersection of the semi-circle curve and Z_{Re} axis at the highest frequency. Therefore the proton conductivity can be calculated by the equation (1) and the value is 0.05s/cm.

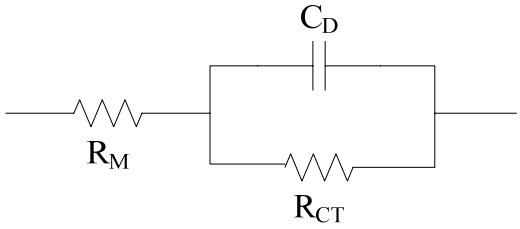


Fig. 7: The equivalent circuit of the porous silicon membrane.

number	1	2	3	4	5
d (μm)	20	20	25	40	30
$\boldsymbol{R_M}$ (Ω)	4.8	21	4.8	8.3	12.4
σ (s/cm)	0.05	0.01	0.07	0.06	0.03

Table 1: The parameters of 5 porous silicon-based PEMs and their calculated proton conductivities.

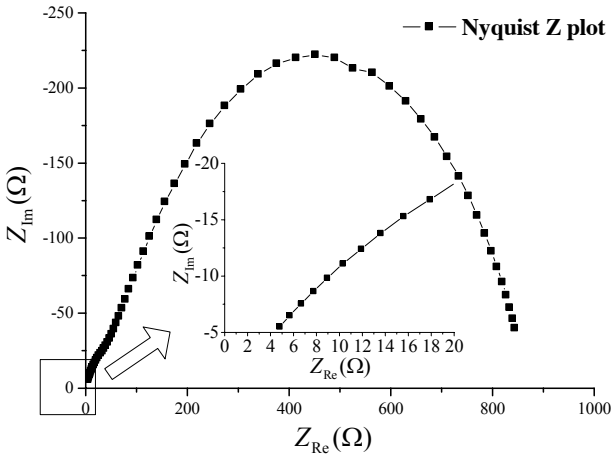


Fig. 8: Nyquist Z plot of impedance of a porous silicon-based membrane, sample 1.

4. CONCLUSION

Our research on the silicon-based membrane as PEM to make micro fuel cell is presented. The porous silicon membranes with a thickness of 20-40 μm were fabricated. And the porous silicon-based PEMs were formed by using the combination of porous silicon membranes and Nafion® solution. Some samples were tested and a group of impedance data was obtained. The results show that the proton conductivities of the porous silicon-based PEMs are 0.01~0.07s/cm comparable to Nafion® (0.05~0.08s/cm). It makes possible to realize the total compatibility with MEMS technology which allows cell to integrate with other MEMS devices.

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