

## Preparation of a New Proton Conducting Silicon Membrane for Miniature Fuel Cells

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**Abstract:** The membranes based on silicon substrate filled with Nafion<sup>®</sup> have been fabricated as a proton exchange membrane for miniature fuel cells. This fabrication utilizes the micromachining procedures including photo-lithography, plasma-enhanced chemical vapor deposition (PECVD), and dry and wet etching processes. The device size of the silicon membrane filled with Nafion<sup>®</sup> was 1 cm × 1 cm. The pores were smaller than 500 nm. The cross-sectional shape of the silicon membrane was an inverse pyramid structure to improve its mechanical strength and to enhance its surface treatment process. This technique combines the advantages of Nafion<sup>®</sup> with a good proton conductivity and silicon membrane, such as easy serial and parallel integration, respectively.

**Keywords:** Proton Conducting Silicon Membrane, PEM, Nafion, Miniature Fuel Cells.

### 1. INTRODUCTION

The Polymer electrolyte membrane (PEM) fuel cell is considered to be one of the most promising clean and efficient alternative energy technologies of the 21<sup>st</sup> century when it is used with sustainable hydrogen source. With increased interest in developing light and portable electronic systems, technological research was driven towards the use of integrated and small regeneration power sources. In recent years, PEM based miniature fuel cells have been adopted in portable electronic products, such as laptops, cellular phones, PDAs, etc. Silicon is an ideal material for constructing future micro fuel cell, because the silicon based micro fuel cells can be mass produced at a low cost *via* existing MEMS technology. This advantage has attracted several studies on the fabrication of the silicon based micro fuel cells [1-10]. In its early development, the anode and cathode structures (e.g. current collectors, flow fields, fuel reservoir, etc.) were micro-fabricated using silicon wafer followed by stacking them with Nafion<sup>®</sup> membranes. However, Nafion<sup>®</sup> is polymer and, unlike silicon, is not compatible with conventional MEMS technology. To mitigate this problem, there have been attempts to replace this polymer membrane with

acid functionalized inorganic membrane. A pioneer work by Pichonat et al. demonstrated that the use of porous silicon filled with Nafion<sup>®</sup> can replace a bulk Nafion<sup>®</sup> membrane as a proton exchange membrane in fuel cells [11].

In general, the porous silicon membrane is fabricated by anodizing a silicon wafer in a hydrofluoric solution. This fabrication process produces long narrow channels with a typical diameter of 30 nm. These channels need to be functionalized with acid groups in order to conduct protons. However, due to the long channels with very small diameter of porous membrane, it is almost impossible to wet the entire channel surfaces with these acid-functional-group solutions. For example, if the silicon porous membrane is functionalized with Nafion<sup>®</sup> by filling the channels with Nafion<sup>®</sup> solutions, only the top and bottom portions of each channel would be filled with Nafion<sup>®</sup> due to high surface tension. In addition, Nafion<sup>®</sup> filled inside the channels will swell to crack the walls when the porous silicon membrane is hydrated.

Therefore, we report here a different way of preparing porous silicon membrane using a KOH anisotropic etching process. This new process provides a porous membrane with the V-shaped (or inverse pyramid shaped) channels, which is advantageous for avoiding aforementioned surface tension and swelling problems.

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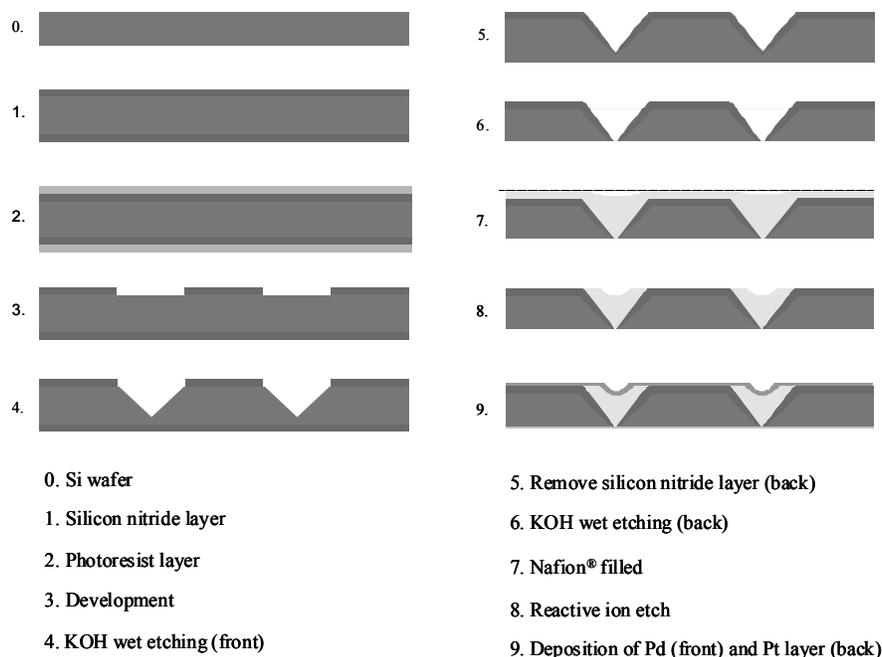


Figure 1. Fabrication process steps to construct the proton conducting silicon membrane

Based on this new approach, we expect to achieve a higher performance of future micro fuel cells.

## 2. EXPERIMENTAL

In this study, the (100) oriented and p-typed (1-10  $\Omega\text{cm}$ ) silicon wafer with  $525 \pm 25 \mu\text{m}$ -thickness were micro-fabricated using the wet etching processes. As shown in Fig.1, The first step was to deposit silicon nitride film on both sides of wafer to act as an etch mask for the subsequent silicon wet etching processes. Next, using photo-lithographic patterning and subsequent plasma-based etching, windows were opened in the silicon nitride film on the front of the wafer. Then, the exposed surface of silicon was etched with 33% KOH solution at  $80^\circ\text{C}$ . After the V-shaped grooves were created, the silicon nitride on both sides of the wafer was removed by exposing it to phosphoric acid at about  $175^\circ\text{C}$ . Then, the silicon nitride film was deposited on the front-side of the wafer again. The back-side of the wafer was etched with 33% KOH solution at  $80^\circ\text{C}$  to create the open channel. These inverse pyramid structures were filled with 5% Nafion® 1100EW solution by using a spin coater. This spin coating process is routinely used in the existing silicon micro-fabrication processes. We used the reactive ion etching to remove the excess Nafion® that was present on the membrane's surface. Then, the palladium and platinum layers were deposited on the front and back side of membrane, respectively. The dimension of silicon membrane is  $1 \text{ cm} \times 1 \text{ cm}$  with thickness of  $250 \mu\text{m}$ . Within the  $1 \text{ cm} \times 1 \text{ cm}$  membrane area, we processed a total of 100 V-shaped channels in  $10 \times 10$  arrays. On single 4 in. wafer, twenty four of  $1 \text{ cm} \times 1 \text{ cm}$  membranes are fabricated. The diameter of the pores is controlled by the etching time.

In order to test the feasibility of using our novel membrane for the micro fuel cell applications, a voltage-current (V-I) characteri-

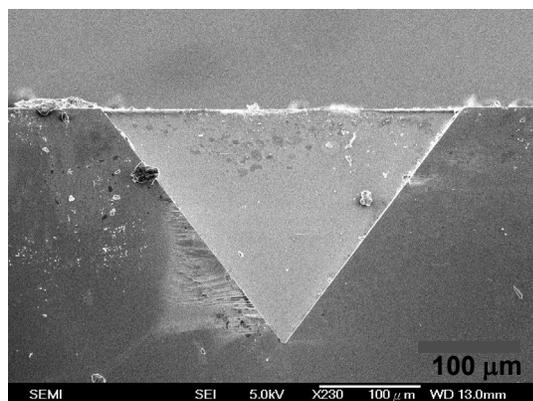
zation was performed. Formic acid was chosen as a model fuel due to its simple chemistry and well-known application in PEM fuel cells [12]. To properly collect the current from the catalyst layers, a gold paste was used to construct mesh type current collectors on the top of catalyst's layers. A more robust and efficient current collector prepared by an e-beam evaporation technique is under development as part of our future work.

## 3. RESULTS AND DISCUSSION

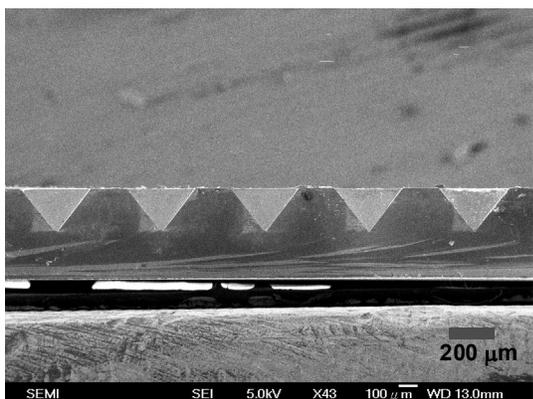
The inverse pyramid structures are made on silicon wafer after the wet etching process is performed on the front-side of the silicon wafer (step 4 in Fig. 1). Results are shown in Fig. 2. Fig. 2a is the SEM cross-section imaging of a V-shaped groove on silicon wafer. To produce the nano-size pore the tip of V-shaped groove must be sharp. Fig. 2b shows the array of the V-shaped grooves arranged in order on the same sample.

In order to open the tip of the inverse pyramid (or V-shaped groove) and to form the V-shaped channels, the wet etching process is performed on the back-side of the wafer (step 6 in Fig. 1). Fig. 3a and 3b are images of the SEM cross-section and top view of a V-shaped channel, respectively. The depth of the V-shaped channel is around  $250 \mu\text{m}$  and the angle between its base and lateral edge is  $53.92^\circ$ . This angle is very close to its theoretical value of  $54.74^\circ$  for (100) oriented silicon wafer. To reduce the fuel cross-over through the membrane for the fuel cell application, the tip-opening diameter of all pores on the membrane was made to be smaller than  $500 \text{ nm}$  (see Fig. 3b).

Fig. 4 is a SEM cross-section image showing the V-shaped channels filled with Nafion® prior to the reactive ion etching process for removing the excessive Nafion® from the membrane surface (step 7 in Fig. 1). It is extremely difficult to cut the Nafion® filled mem-



(a)



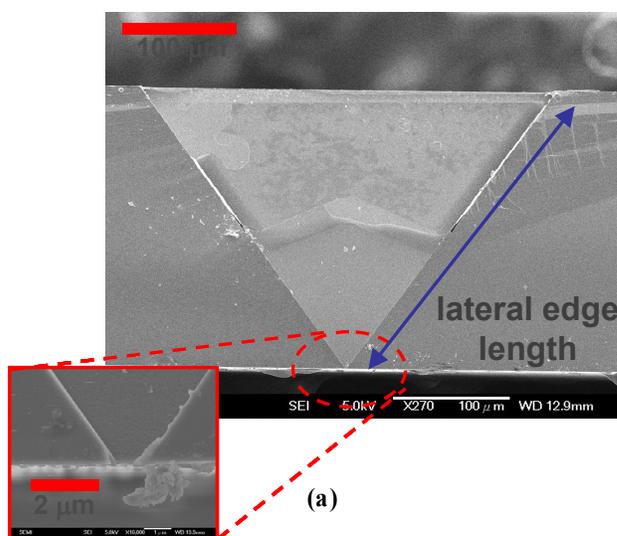
(b)

Figure 2. (a) A SEM cross-section image of a V-shaped groove after the anisotropic etching. (b) A SEM cross-section image of a sequence of V-shaped grooves on the single wafer. 33% of KOH at 80 °C is used for the anisotropic etching process.

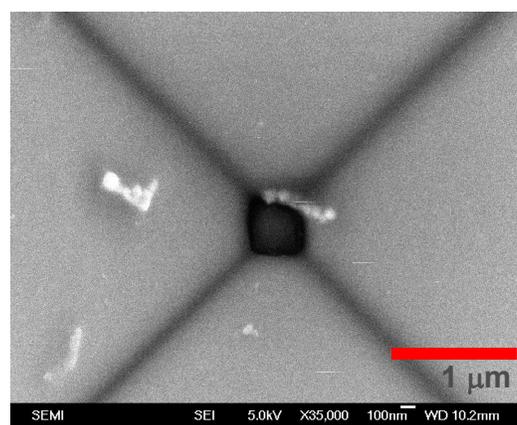
brane at the center of its V-shaped channel. During the cutting process, the Nafion<sup>®</sup> is peeled off and pushed out from the channel. As results, in Fig. 4, we were not able to cut the cross section of the channel at the center of its tip. Therefore, even though we have fabricated perfect V-shaped channels in the membrane (see Fig. 3), the channels in Fig. 4 seem like they are not all the way through the backside of membrane. However, we still can see the V-shaped Nafion<sup>®</sup> that is pushed out from and resting on the silicon membrane surface. The lateral edge length of V-shaped Nafion<sup>®</sup> is about 305 μm. When Fig. 3a and Fig. 4 are compared, we can notice that the lateral edge length of V-shaped Nafion<sup>®</sup> from Fig. 4 is almost same as that of the V-shaped channel in Fig. 3a. For this reason, we believe that the Nafion<sup>®</sup> was able to diffuse down to the tip of the channel during the spin coating process.

The reactive ion etching process was able to remove the most of excessive Nafion<sup>®</sup> that are present on the membrane surface. After this reactive ion etching process, the filled Nafion<sup>®</sup> in the channel was not level with the silicon surface of the membrane frame as shown in step 8 of Fig. 1. Instead, it formed a puddle in its center.

In order to check the swelling condition, the reactive ion etched



(a)



(b)

Figure 3. SEM images of (a) a side view and (b) a top view of micro inverse pyramid channel with an opening pore size of 400 nm x 400 nm. 33% KOH solution at 80°C is used to form this micro opening at the tip of the pyramid.

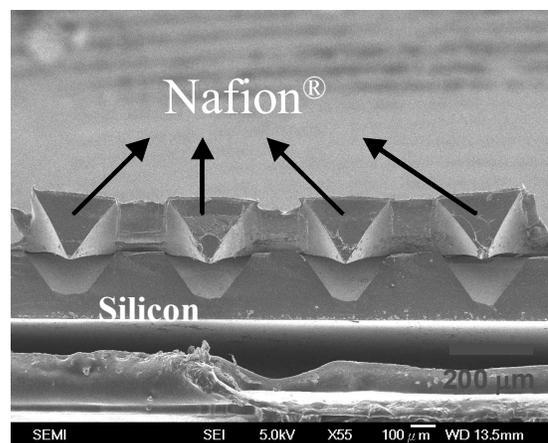


Figure 4. A SEM cross-section image of a Nafion<sup>®</sup> filled inverse pyramid structure silicon membrane.

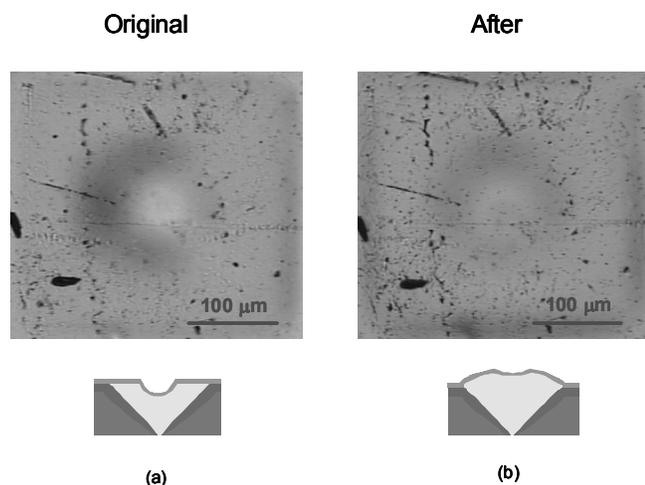


Figure 5. Optical microscope images (a) before and (b) after immersing the Nafion<sup>®</sup> filled membrane with a thin catalysts layer into DI water for three days. The schematic cross-section diagrams are also shown right below their corresponding SEM images.

membrane was immersed into DI water. Fig. 5a and b are the optical microscope images of the membrane before and after immersing it into the DI water for three days, respectively. Even though the swelling occurred, the palladium layer is still undamaged. As it was mentioned earlier, the filled Nafion<sup>®</sup> in the channel was not level with the silicon surface of the membrane frame. Therefore, the surface of Pd thin film was not flat; instead it was concave down at the center of the channel as shown in Fig. 5a. In Fig. 5a, the optical image is brighter at the center because its bottom is open and the Nafion<sup>®</sup> is transparent as the light passes through.

While this membrane hydrated in the DI water for three days, the filled Nafion<sup>®</sup> swelled in the V-shaped channel. A decrease in the contrast at the center of image in Fig. 5b can be observed when compared to that of Fig. 5a. This indicates that the height difference in the channel decreases due to the swelling of the filled Nafion<sup>®</sup>. In other words, as the Nafion<sup>®</sup> swelled, it expanded and the depth of the puddle decreased as shown in Fig. 5b.

During the Nafion<sup>®</sup> swelling, the Pd catalyst layer did not rupture because its thickness is only 75 nm (estimated from atomic force microscope) and this thin Pd layer was flexible enough to sustain the pressure inflicted by the expanding Nafion<sup>®</sup>. Similar to the Pd layer, the Pt catalyst layer was very thin (30 nm) and it did not rupture during the hydration process (Figure not shown).

To perform the V-I characterization of our Nafion<sup>®</sup> filled silicon membrane with the catalyst layers, we dropped enough amount of 5M formic acid solution on the Pd catalyst layer to completely cover it with the solution. The Pt catalyst layer is open to the ambient air and used as an air breathing cathode. Fig. 6a and 6b show its V-I plot and power density curve respectively at the room temperature operation. With 5M formic acid, our cell shows an open cell potential of 0.45 V and the maximum power density of 5 mW/cm<sup>2</sup>. Because our catalyst layers do not contain any electrolytes and there can be a gap between the catalyst layers and Nafion<sup>®</sup> functionalized silicon membrane, our prototype fuel cell would possess a high resistance to a proton flow. The lack of elec-

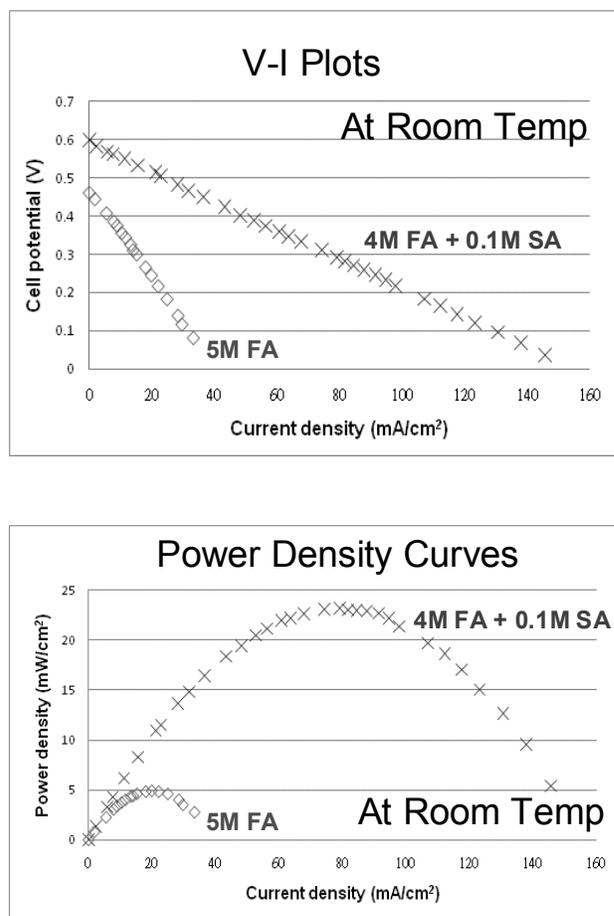


Figure 6. (a) V-I characteristic plots and (b) power density curves of miniature fuel cell using our Nafion<sup>®</sup> filled porous silicon membrane at the room temperature operation. The Pd and Pt catalyst layers are used as the anode and cathode electrodes respectively. Both 5M formic acid (FA) and mixture of 5M FA and 0.1M sulfuric acid (SA) are used as a model fuel for the performance tests.

trolyte within the catalyst layer significantly limits the available number of active triple-phase boundary. This high resistance for the proton flow leads to a high over-potential of our cell. To improve the ion conductivity of our cell and to increase its power outputs, we also have mixed a sulfuric acid into 5M formic acid. As shown in Fig. 6a and 6b, the addition of sulfuric acid into 5M formic acid improves both the open cell potential and the maximum power density outputs up to 0.6 V and 23 mW/cm<sup>2</sup> respectively.

#### 4. CONCLUSIONS

In this study, we successfully fabricated a silicon based porous membrane with the V-shaped nano-size channels for portable fuel cell applications. One of its advantages is the total compatibility with silicon microfabrication process, which will allow us to reduce the cell size furthermore and mass produce it at a low cost in the future. By controlling the aspect ratio of our V-shaped channel and reducing its tip diameter down to the order of 10 nm, we hope to manage the fuel crossover problem for future micro fuel cells.

Additionally, we will optimize the design of our current collectors as well as their fabrication process for our future works. Our present prototype fuel cell produces a maximum power density of 5 mW/cm<sup>2</sup> without sulfuric acid and 23 mW/cm<sup>2</sup> with sulfuric acid in 5M formic acid fuel at the room temperature operation. We speculate that this positive performance enhancement with the addition of sulfuric acid is originated from the lack of electrolyte presence within the catalyst layers.

## 5. ACKNOWLEDGEMENTS

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