

# Thin Fuel Cell with Monolithically Fabricated Si Electrodes

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## Abstract

A novel fabrication technique of miniature fuel cell electrodes from Si wafers was developed. The fuel channels, porous layer and catalyst layer were monolithically formed on a Si chip. The fuel channels were fabricated by photolithographic patterning and subsequent wet etching on the Si. The porous layer was formed by anodization of Si from PEM (Proton Exchange Membrane) side through the bottom of the fuel channels. Pt and Ru were deposited inside the porous layer by wet plating. The two electrodes were hot-pressed with a PEM sheet. Open circuit voltage of 870 mV and maximum power density of 1.5mW/cm<sup>2</sup> were observed by hydrogen feed.

*Keywords: miniature fuel cell, porous silicon, electrodeposition, MEMS*

## 1 INTRODUCTION

The increasing interest for portable electronic systems drives the research toward integrated regenerating power sources with small dimensions and the miniaturized fuel cells are quite attractive. Several companies are about to put small fuel cells on the market. In order to reduce the fuel cell structure much more, the micro fabrication technology of Si is an important tool and have been employed by several research groups [1-11]. Those miniaturized fuel cells using various degrees of microfabrication techniques have been reported. Prinz et.al. [1] created flowfields on Si substrate and formed hydrogen feed fuel cell array on a Si wafer. Kelley et.al. [4] created catalyst layer supporter on a Si chip and demonstrated that the miniaturized direct methanol fuel cell (DMFC) has almost same performance of state-of-the-art larger fuel cells. However, those miniaturized fuel cells uses conventional catalyst layers, in which Pt/Ru on activated carbon is splayed on the gold sputter deposited silicon electrodes or conventional membrane electrode assembly (MEA) is used, and treating powders such as activated carbon is not suitable for silicon batch fabrication process.

In order to adapt the construction process to more Si processing steps, various approaches have been tried. In those studies, catalyst metals were deposited by physical vapor deposition (PVD) on porous layer formed by photolithographic patterning or anodization of Si [5-8]. Generally, it is difficult to deposit materials inside porous layer by PVD and the catalyst deposits only on the surface of porous layer and the performance of the catalyst will be poor. Therefore, different approach to form catalyst layer should be developed. Recently, Neah Power Systems announced new miniature fuel cells with Si-based electrodes[9], but detailed information is not available. D'Ariggo et. al. [10] proposed a novel Si-based electrode fabrication technique, though the power generation is not reported yet. In this technique, the fuel channels were formed inside the Si substrate by depositing epitaxial Si layer after wet etching of Si substrate, then the deposited

epitaxial Si layer was anodized and the porous Si layer was obtained. Pt and Ru were electrodeposited into the porous layer and the catalyst layer was formed. Generally, resistivity of porous Si is high and it has been supposed difficult to use porous Si layer as catalyst support layer. However, the porous Si has large surface area up to 1700m<sup>2</sup>/cm<sup>3</sup> [12] which is comparable with that of activated carbon and the porous Si is quite attractive if it works as catalyst support layer, because fabrication of porous Si is easy and suits for the batch Si process. Our approach is close to the one by D'Arrigo and we propose more simple structure of the electrode and simple fabrication method.

Fig.1 shows the structure of our miniaturized fuel cell. Fuel channels, fuel diffusion layer and the catalyst support layer are formed on the Si wafer without addition of any substances. Porous Si layer is formed from the polymer electrolyte membrane (PEM) side through the bottom of the fuel channels and quite simple cell structure will be realized. Highly doped low resistivity Si is used and the Si wafer itself is expected to work as current collector. Thickness of the Si wafer is 100μm and the total thickness of the cell will be 250μm. In this paper, we describes the fabrication procedure of this fuel cell and preliminary experimental results of power generation.

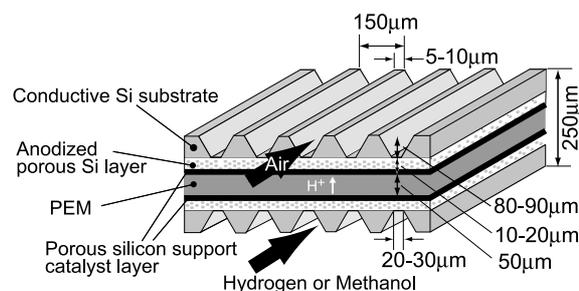


Figure 1. Schematic view of the thin fuel cell

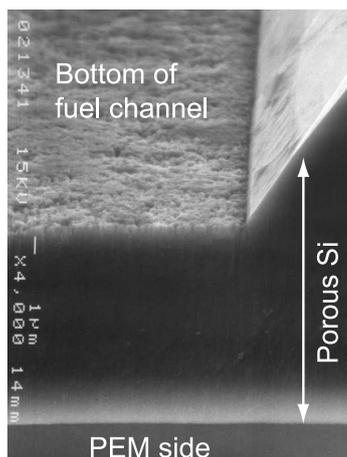


Figure 2. Porous Si through layer.



Figure 3. Sputter deposited Pt and Ru.

## 2 FABRICATION PROCESS

### 2.1 Fuel channels

Si electrodes were prepared using a usual micro fabrication techniques.  $\langle 100 \rangle$  oriented  $100\mu\text{m}$  thick double-side mirror polished Si wafer which has thermal oxide films of  $500\text{nm}$  thickness on both sides was used. For the substrate, n-type Si was used because of the slow wet etching rate of p-type Si. Because Si substrate is expected to work as current collector, the lowest resistivity Si wafer among commercially available products was chosen and its resistivity was  $0.001\Omega\text{cm}$ . Using a photolithographic patterning and subsequent wet etching, fuel channels of  $80\text{-}90\mu\text{m}$  depth were formed.

### 2.2 Porous Si layer

It is widely known that Si becomes porous by anodization in a concentrated HF solution and this technique was used for the formation of porous layer on the electrodes. Morphology of the porous Si largely depends on the current density of anodization and the dope ratio of the Si wafer. To find a proper conditions, the anodization of the highly doped Si wafer was performed with several current densities. The composition of HF solution was  $\text{HF}(46\%) : \text{Ethanol} = 1:1$  (volume). Porous Si layer was obtained stably around  $100\text{mA}/\text{cm}^2$  and  $100\text{mA}/\text{cm}^2$  was chosen for the anodization process.

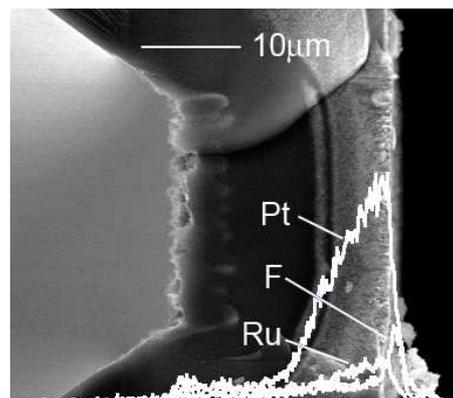


Figure 4. Sputter deposited Pt and Ru.

After the fuel channel formation, about  $100\text{nm}$  thick Cu layer was sputtered for stable conductivity and the contact pins were used for the current supply to the Si wafer from a potentiostat. The Cu layer was removed after the catalyst deposition by immersing the chip in  $40\text{wt}\%$   $\text{FeCl}_2$  solution at  $313\text{K}$  for  $3\text{-}5$  min. The anodization was performed from the PEM side of the Si wafer until the porous layer reached at the bottoms of the fuel channels. Excess anodization damages the porous layer especially around the bottoms of the fuel channels and strict time control of the anodization was required. The depth of the trench varies up to a few micro meters even though close attention was paid in the etching process. Therefore, the time of anodization was determined empirically by observing the results with same lot of trench formed chips and typical time for the anodization was  $5\text{-}6$  min.

Fig.2 shows an example of the porous layer which was formed from the PEM side of the Si wafer through the bottom of the fuel channel. It is found that uniform porous layer was obtained by the anodization. Though clear images of the pore morphology could not be obtained, similar feature reported by Lehman [12-13], in which there are main straight pores of  $10\text{-}100$  nm diameter with many branches, was supposed to be formed from the PEM side to the bottom of the fuel channel by our vague SEM observations.

### 2.3 Catalyst layer

To deposit catalyst metals on the porous layer, sputtering was employed at first. However, the sputtering can deposit catalyst metals only on the surface of the porous layer as shown in Fig.3 and the performance of the catalyst layer is supposed to be poor. Kelley and D'Arrigo employed electrodeposition and we tried to deposit catalyst metals into porous Si layer using a same composition plating bath [4,8] of  $1.0\text{ M H}_2\text{SO}_4 + 16\text{ mM H}_2\text{PtCl}_6 + 8\text{ mM K}_2\text{RuCl}_5$ . However, energy dispersive X-ray spectroscopy analysis (EDS, JEOL JED-2200) showed that catalyst metals deposited mainly on the surface and little deposition could be observed. Various conditions were tested and deposited metal often formed films on the porous surface and peeled off from the porous Si layer.

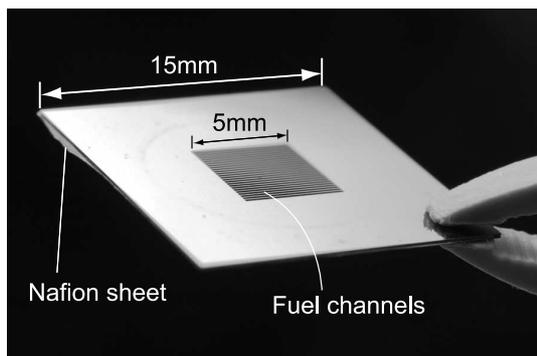


Figure 5. Prototype of the thin fuel cell.

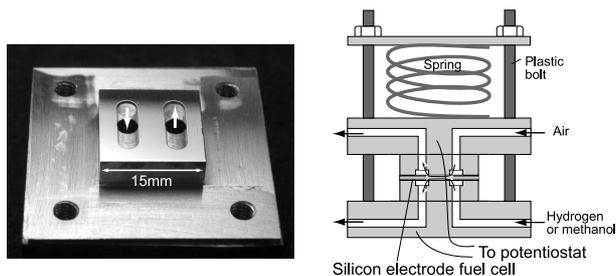


Figure 6. Casing for the power generation test.

Our EDS analysis showed high oxygen signal in porous Si layer after electrodeposition. Si is a moderate reducing agent and it reduces catalyst metal ions and simultaneously forms silicon dioxide on bare Si, that is supposed to inhibit further electrodeposition [14]. To eliminate the silicon dioxide, dilute HF was added to the plating bath and the deposition of catalyst metals was prompted. It is noticed that the addition of HF removes silicon dioxide and prompts the reduction of catalyst metal ions by increased bare Si surface [15-17]. It was also observed that Pt and Ru deposition occurred without applying electric current when the dilute HF was added into the plating bath. Therefore, electroless deposition occurs simultaneously with electrodeposition and the amount of deposited catalyst metals is unable to be estimated from the applied charge. Example of the catalyst deposited porous Si layer using 1.0 M  $H_2SO_4$  + 10 mM  $H_2PtCl_6$  + 5 mM  $K_2RuCl_5$  + 50 mM HF plating bath at 293K is shown in Fig.4. Deposition was performed for 5 minutes applying 1Hz pulse current of  $5mA/cm^2$  for 0.2 s following  $0mA/cm^2$  for 0.8 s.

## 2.4 Cell assembly

Two Si electrodes were hot-pressed onto either side of a Nafion 112 membrane. The miniature cells were assembled by placing a piece of Nafion 112 sheet with Nafion 5% solution as an adhesive between a catalyzed Si electrodes aligning edges of the chips. The assembly was hot-pressed at approximately 0.05 MPa and 443K for 30 minutes and was then cooled to room temperature. Fig.5 shows the assembled cell. The cell was set into an aluminum casing as shown in Fig.6, which feeds the fuel to the fuel channel and collects current from the cell.

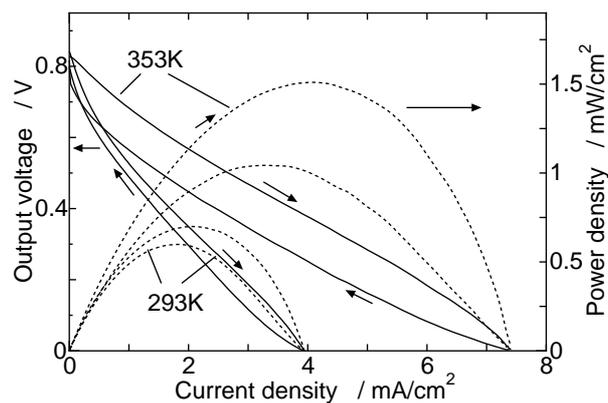


Figure 7. Current-voltage characteristics of the cell.

## 3 POWER GENERATION TEST

### 3.1 Experimental

The fuel cell testing was performed in a temperature controllable chamber. Fuel and air supply lines were connected to the aluminum casing. As shown in Fig.6, fuels were fed from the inlet hollow into the edge of the fuel channels and passes through the channels on Si electrodes to the outlet hollow. Clamping pressure was adjusted by the spring. To humidify the PEM, hydrogen gas was passed through the water contained tank heated at 353K and was then cooled to the testing temperature in the feed line. No humidifying was performed to the air feed. Current vs. voltage was measured by a potentiostat (Hokuto Denko, HABF501) with scanning the cell potential at 5 mV/s.

### 3.2 Result

Fig.7 shows the fuel cell polarization curves taken at two different temperatures with hydrogen gas feed. About  $20\text{ cm}^3/\text{min}$  of hydrogen gas and air were fed to the cell at ambient pressure. Varying the flow rate of the fuel gases did not affect the performance at this testing very much. Rather larger flow rate of the fuel gases reduced the current density. This may indicate that larger gas flow dried the PEM or the porous Si layer and the resistivity of the PEM or the porous Si layer increased. The silicon electrode is brittle and large clamping pressure was not applied. The pressure was varied from 0.1-0.3MPa and no obvious change was observed. This may suggest that no large clamping pressure is necessary because the electrodes are monolithic and no improvement of the conductivity between a catalyst layer and a separator by high pressure is expected. As expected, cell performance improved at higher temperature. If the resistivity of the porous Si layer or Si substrate dominated the performance, polarization curve would show linear line. The obtained polarization curves drew gentle curves and this may suggest that the cell performance was dominated by the catalyst performance. Methanol solution feed was also examined.  $1\text{ cm}^3/\text{min}$  of 1 M methanol solution was fed. The open circuit voltage of 320mV was obtained 3 min after the fuel feed start and polar-

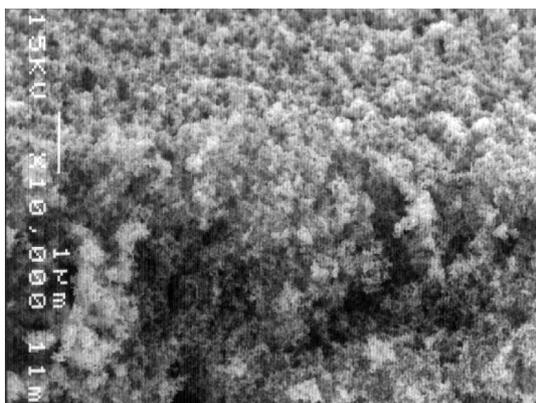


Figure 8. Catalyst deposition on the large pore porous Si layer.

ization was measured. Though  $0.5\text{mA}/\text{cm}^2$  was observed, the performance deteriorated significantly and the cell became inactive, maybe due to the poor performance of the catalyst and the methanol cross over.

### Discussion

The obtained result showed relatively high performance compared with recent miniature fuel cells proposing new catalyst layer structures [5-11]. However, it was far inferior to large fuel cells with carbon-support based catalyst layers. Fig.4 shows the EDS intensity of Pt, Ru and F integrated along y direction. Strong EDS signal of the catalyst metals was obtained inside the porous Si layer until  $10\mu\text{m}$  depth. Slight nonuniformity due to the fuel channel was observed, but it can be said that good catalyst deposition was obtained by the plating for this preliminary experiments. It was found that the addition of dilute HF enhanced the catalyst metals deposition inside the porous layer and this method was used for the formation of catalyst layer. But there is little signal of F which indicates PEM in the porous layer. It is assumed that large amount of catalyst could not contribute for the reaction, due to the lack of polymer electrolyte. In order to improve the performance, we are now trying to enlarge pore size of porous Si layer so that polymer electrolyte solution can penetrate. Fig.8 shows the new catalyst layer formed on the larger pore size porous Si layer. It is interesting that characteristic straight pore of porous Si layer disappeared after electrodeposition of catalyst metal. This morphology might indicate that catalyst metal replaced Si by electrodeposition in HF contained bath. EDS analysis showed that little Si signal in this area and further study will be needed to verify this speculation.

### Conclusion

The  $250\mu\text{m}$  thick miniature fuel cell design was proposed and a prototype was produced. The Si electrodes had etched fuel channels and a porous Si layer which was formed by anodization from the PEM side through the bottom of the fuel channels. Catalyst metals were deposited inside the porous Si layer by the new wet plating process, in which the deposition of catalyst metals was enhanced by addition of dilute HF into

the plating bath. Power generation of the miniature fuel cell was verified and relatively high performance was shown compared with the recent miniature fuel cells proposing catalyst layer structures without conventional carbon-support catalyst layer. It was verified that the porous Si layer can work as a catalyst support layer and further study will be performed and interesting catalyst deposition behavior was observed with high porosity Si layer.

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