Catalyst Layer Formation onto Meso Pore Porous Silicon Layer for Miniature Fuel Cells

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Abstract
In order to prevent collapse of catalyst layer formed onto a porous Si layer, a novel method was developed. A miniaturized fuel cell using monolithically fabricated Si electrodes has been proposed and power generation was verified though the output was poor. Pore diameter and porosity of the porous Si layer which works as a diffusion layer and a catalyst support layer was enlarged for easy penetration of electrolyte and fuel, but the porous layer was collapsed when the catalyst metals were deposited onto the porous layer. It is assumed that the porous layer shrinks because platinum, whose atomic size is smaller than the size of Si, replaces Si at equal stoichiometric ratio in a plating bath using Pt4+ ion. Pt2+ ion was mixed into the plating bath and the collapse of the porous layer was prevented.

Keywords: miniature fuel cell, meso pore, porous silicon, electrodeposition, MEMS

1 INTRODUCTION
The micro fabrication technology of Si is an important tool to reduce the fuel cell structure to micrometer sizes and have been employed by several research groups1−12. Miniaturized fuel cells using various degrees of micro fabrication techniques have been reported. However, most of the miniaturized fuel cells use carbon supported catalyst layer and that is not suitable for Si batch process. In order to adapt the construction process to more Si processing steps, several approaches, in which catalyst metals are deposited on porous layers by PVD, has been reported. Generally, it is difficult to deposit materials inside porous layer by PVD and the performance of the catalyst is poor10. Therefore, different approach to form catalyst layer should be developed. Recently, Neah Power Systems9 announced new miniature fuel cells with Si-based electrodes, but detailed information is not available. D’Arrigo et. al. proposed a novel Si-based electrode fabrication technique11, though the power generation is not reported yet. In this technique, Pt and Ru were electrodeposited into the porous layer and the catalyst layer was formed. Resistivity of porous Si is high and it has been supposed difficult to use porous Si layer as catalyst support layer. But porous Si has large surface area which is comparable with that of activated carbon13,14. The porous Si is quite attractive if it works as catalyst support layer. Our approach is close to the one by D’Arrigo and we have proposed more simple structure of the electrode. Power generation was verified by our preliminary prototype cell, but the performance was quite poor12. In order to improve the performance, we are now trying to enlarge pore diameter and porosity of porous Si layer so that polymer electrolyte and fuel can penetrate easily into the catalyst layer.

2 CELL DESIGN AND PROBLEMS
2.1 Monolithically fabricated Si electrodes
Fig.1 shows the structure of our miniaturized fuel cell. Si substrate is expected to work as current collector, the lowest resistivity Si wafer among commercially available products was chosen and its resistivity was 0.001Ωcm. Fuel channels are fabricated by anisotropic etching of crystal Si. The Si chip is anodized in HF solution and a porous layer is formed from PEM side through the bottom of the fuel channels. A catalyst metal is deposited into the porous layer by wet plating.
Two Si electrodes are hot-pressed onto either side of a Nafion 112 membrane. The miniature cells are 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.

2.2 Problems of the Si electrodes

Though the power generation of 1.5mW/cm$^2$ with hydrogen feed was observed, the output was far inferior to large fuel cells with carbon-support based catalyst layers. Fig.2 shows the EDS analysis of the electrode cross-section. Strong EDS signal of the catalyst metals was obtained inside the porous Si layer until 10µm depth. But there is little signal of F which indicates PEM in the porous layer. Several factors of the poor performance can be considered, we put emphasis on following points.

* **Lack of polymer electrolyte**: It is assumed that large amount of catalyst could not contribute for the reaction due to the lack of polymer electrolyte inside the catalyst layer.

* **Poor diffusibility**: The porosity and pore diameter is too small to deliver fuel to the catalyst layer.

* **High resistivity of porous Si**: Although the electrical resistivity of the Si substrate is low, resistivity of the porous layer is high and IR loss might be large.

In order to improve the above points, enlargement of pore diameter and porosity of the porous Si layer is attempted. By the enlargement, easier penetration of plating solution of catalyst deposition, polymer electrolyte and fuel into the porous Si layer can be expected.

### 3 ENLARGEMENT OF PORE DIAMETER

#### 3.1 Method

Morphology of the porous Si depends on the doping density and type of the Si substrate, HF concentration of anodization bath and anodization current density. Although the doping density is critical, low resistivity is needed because Si substrate is expected to work as a current collector. Therefore, we did not vary the doping density and Si wafer of 0.001Ωcm$^2$ (As doped) is used in this study. Current density and HF concentration in the anodization is varied and the enlargement of the pore diameter and porosity is attempted.

#### 3.2 Experimental and results

Anodization is performed in the vessel made of fluorocarbon polymers as shown in Fig.3. Ohmic contact is formed on the backside of the Si chip by depositing copper or gold. Anodization current is applied through the contact pins and is controlled by a potentiostat. The composition of the basal anodization electrolyte is a mixture of HF(46wt%The HF concentration is varied by diluting this basal electrolyte with pure water. The porous Si layer of our preliminary prototype was formed with the basal electrolyte applying 100mA/cm$^2$. The porosity of the porous layer is estimated at 55% by the weight change. Pore diameter was not clearly observed and was presumed to be about 30nm according to some literatures. Example results obtained by varying anodization parameters are shown in Fig.4 and Table 1. Excess current density causes electropolishing and no porous layer is obtained. Critical current density of each HF solution was checked and the example results were obtained at about 10% smaller current density to the critical value of electropolishing. It was confirmed that larger pore is obtained with lower HF concentration and larger current density. Anodization time was determined to obtain 10µm thick porous layer. The case of condition C, the porous Si layer sometimes broke during drying and condition B was mainly investigated. The porosity of the condition B is estimated at 90% by the weight change.

#### Table 1. Anodization parameters.

<table>
<thead>
<tr>
<th>Current density mA/cm$^2$</th>
<th>Composition of HF solution</th>
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<tbody>
<tr>
<td>A</td>
<td>Basal solution</td>
</tr>
<tr>
<td>B</td>
<td>Basal solution : Water = 1:1 (weight)</td>
</tr>
<tr>
<td>C</td>
<td>Basal solution : Water = 1:3 (weight)</td>
</tr>
</tbody>
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| Basal solution: HF(46wt%) : Ethanol = 1:1 (volume) |

![Figure 3. Vessel for anodization and plating](image)

![Figure 4. Larger porosity obtained with new anodization condition](image)
trodeposition. To eliminate the Si dioxide, dilute HF was added to the plating bath and the deposition of catalyst metals was prompted.

Fig.5 shows an example of the catalyst deposit on the enlarged porosity porous Si (condition B) using 1.0 M H$_2$SO$_4$ + 10 mM H$_2$PtCl$_6$ + 5 mM K$_2$RuCl$_5$ + 50 mM HF plating bath at 283K. Deposition was performed for 30 minutes applying 1Hz pulse current of 5mA/cm$^2$ for 0.2 s following 0mA/cm$^2$ for 0.8 s. Bright area shows high catalyst metal signals in the EDS analysis, so it is found that significant catalyst deposition occurred. A lot of space inside the porous layer can be seen and high catalyst performance can be expected. The porous Si layer was formed about 20µm thick, however, the catalyst deposited porous layer has only 10µm thick in Fig.5. It was found that large part of the porous Si peeled off from the substrate.

Stirring of the plating bath is performed by pumping siringe as shown in Fig.3. and the stirring might break the porous layer. But during the plating, bubbles form on the porous layer surface and moderate stirring is indispensable. The collapse of the porous layer could not be avoided by weakening the stirring.

By changing the anodization current, porosity was varied in some extent. But when the significant catalyst metal deposition observed, the porous layer collapsed and the improved catalyst layer with the higher porosity porous Si was not obtained.

5 PREVENTION OF POROUS LAYER COLLAPSE

5.1 Shrinkage of the porous layer

Under careful observation, it was found that the porous layer collapsed mainly during drying. With SEM observation, the collapse is supposed to occur due to the shrink of porous layer. In the plating bath, the deposition of catalyst metals proceeds without applying electric current by the addition of dilute HF. Si reduces metal ions and metal deposit forms on the porous Si surface, while Si itself forms Si oxide. The Si oxide is removed by HF added in the plating bath. Therefore, following reaction can be assumed by ignoring Ru reaction.

\[
\text{Pt}^{4+} + \text{Si} + 2\text{H}_2\text{O} \rightarrow \text{Pt} + \text{SiO}_2 + 4\text{H}^+ \quad (1)
\]

\[
\text{SiO}_2 + 6\text{HF} \rightarrow 2\text{H}^+ + \text{SiF}_6^{2-} + 2\text{H}_2\text{O} \quad (2)
\]

In this reaction, it is considered that Pt replaces Si at equal stoichiometric ratio in a plating bath using Pt$^{4+}$ ion. It is supposed that the volume of the porous layer decreases because atomic size of Pt is smaller than the one of Si. This decrease of volume may cause the porous layer shrinkage as shown in Fig.7.

5.2 Shrink prevention by Pt$^{2+}$

It is known that platinum has the oxidation states of +2 and +4. It can be expected that the volume of the porous layer is increased when complex ion of +2 oxidation state is used instead of +4 oxidation state. Then prevention of the shrinkage was attempted by K$_2$PtCl$_4$ plating bath. Fig.6 shows the deposit by immersing the porous Si into the plating bath of 1.0 M H$_2$SO$_4$ + 10 mM K$_2$PtCl$_4$ + 10 mM HF for 15 min at 283K. No obvious collapse was found, though the penetration of the Pt deposit inside the porous layer is poor. It is assumed that the opening of the porous layer surface was closed by the increase of the volume. Then the mixture of the conven-
Figure 8. Pt deposition with Pt$^{2+}$ and Pt$^{4+}$ mixed plating bath

The +4 oxidation state and +2 oxidation state plating bath was tested. Fig. 7 shows the result by immersing the plating bath of 1.0 M H$_2$SO$_4$ + 5 mM K$_2$PtCl$_4$ + 5 mM H$_2$PtCl$_6$ + 2.5 mM + 5 mM K$_2$RuCl$_5$ + 10 mM HF for 30 min at 283K. No obvious collapse of the porous layer can be observed and the deposit can be observed deeply inside the porous layer.

Conclusion

In order to improve the catalyst performance of the monolithically fabricated Si electrodes for miniature fuel cells, enlargement of pore diameter and porosity of the porous Si layer was attempted. It was found that the porous layer collapses when the catalyst metals are heavily deposited on the porous Si layer. In the HF added plating bath, it is supposed that Pt replaces Si. Based on the replace model, it is speculated that the porous layer shrinkage due to the volume decrease of the porous layer causes the porous layer collapse. Prevention of porous shrinkage was attempted using Pt$^{2+}$ plating bath and the inhibition of porous layer collapse was verified.

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References