Effect of Pore Morphology on the Catalyst Metal Deposition into the Porous Si Layer

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Miniaturized Direct Methanol Fuel Cells are highly expected as portable power sources. Several studies using MEMS technology for the miniaturization of fuel cells have been reported. In these studies, usually only separators of the fuel cell are produced by MEMS technology and conventional MEA (Membrane Electrode Assembly) are used in the electrode section. In the conventional MEA, catalyst is supported by carbon powder and treating powder is not suitable for the Si batch process. Besides, conventional MEA needs to be tighten and the separators need mechanical strength. Therefore, there is a limit in the miniaturization of the fuel cell using conventional MEA structure. In order to adapt the fabrication process to the silicon batch process, we proposed a novel simple cell structure as shown in Figs.1-2 and power generation was verified by a prototype of the fuel cell [1]. In our design, fuel channels are formed on the silicon wafer by using photolithographic patterning and subsequent wet etching. Porous Si layer is formed by anodization in a HF solution from the PEM (Polymer Electrolyte Membrane)side of the Si wafer through the bottom of the fuel channels. Catalyst metals are deposited into the porous Si layer by wet plating and catalyst layer was formed. Then two Si electrodes were hot-pressed onto either side of a PEM and the prototype was made. Although the power generation was achieved with hydrogen-air or methanol-air feeds, performance of the prototype cell was far poorer than that of conventional fuel cells. In order to realize higher performance of the cell, significant improvements in the catalyst layer are needed. There are few studies about using porous Si as a catalyst support layer and it is supposed that pore morphology, such as pore size and dissolution valence of the anodized porous Si layer, affects the performance of the catalyst layer. In this study, morphology of the porous Si layer is modified and behavior of the catalyst deposition on the porous Si layer is investigated.

EXPERIMENT

Porous layer: It is known that the morphology of the anodized porous Si changes with some parameters, such as doping density of substrates, applied current density and composition of anodization bath. There is little flexibility on doping densities of the substrate because low resistivity of the substrate is required and highly doped n-type Si wafer of 0.001Ω cm resistivity was used as a specimen substrate. Therefore, current density and composition of anodization bath were modified in the anodization of the Si chips. Anodization time was determined to obtain 20µm thick porous Si layer.

Catalyst layer: Catalyst metals were deposited into porous Si by wet plating. Following composition was

used as the plating bath, which is same as that used in our previous study.

 $\begin{array}{l} 1.0 \text{ M } \text{H}_2 \dot{\text{SO}}_4 + 10 \text{ mM } \text{H}_2 \text{PtCl}_6 + 5 \text{mM } \text{K}_2 \text{RuCl}_6 \\ + 50 \text{mM } \text{HF}. \end{array}$

Deposition was performed for 15 minutes applying 1Hz pulse current of 5mA/cm² for 0.2 s following 0mA/cm² for 0.8 s. Then the catalyst layer was observed by SEM.

RESULT

Various conditions of anodization were tested and it was found that the pore size and dissolution valence of the porous Si can be controlled in some extent. Fig.3 shows an example of the porous Si layer after catalyst deposition. Both layers had optically black surface. In Fig.3(a), it is observed that surface of the porous Si seems to be filled with the catalyst deposit because the vacant space is small, while larger vacant space is observed in Fig.3(b).Smaller grain size is observed in Fig.3(b) compared with Fig.3(a) and higher performance of the catalyst layer is expected. However, porous layer was sometimes damaged during the plating process. In our future work, fuel cell will be constructed with the new catalyst layer formation sand the effect of the porous Si morphology to the catalyst performance will be discussed.

REFERENCES

[1] M.Hayase, T.Kawase and T.Hatsuzawa, *Electrochem.* and Solid-State Lett., **7**,8 (2004)



Fig1. Cell design with monolithically fabricated Si electrode.



Fig.2 The prototype of the fuel cell.



Fig.3 Catalyst deposition on the porous Si layer. (a) anodization with 200mA/cm^2 , <u>Base bath HF(46%) :EtOH =1:1(vol)</u> (b) 70mA/cm^2 , Base bath:H₂O=1:1(wt).