

Fabrication of micro channel reactor for catalyst supporting within macroporous structure

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Abstract

Micro channel reactor composed of macroporous silicon was fabricated using an organic-based electrolyte and showed a high dimensional structure. For micro fuel reformer, ruthenium catalyst was supported into the fabricated macroporous silicon structure and packaged for fuel delivery/output port.

Keywords: macroporous silicon, microchannel reactor, catalyst support, micro fuel reformer

1. INTRODUCTION

Recently, micro channel structure for micro fluidic system applications has been widely researched that high reaction control and fast reaction in the micro channel structure are possible over macro channel structure. Micro channel is a very key component in the micro fluidics system that has required a large surface-to-volume ratio, high aspect ratio and high structure freedom. In the fabrications of the micro channels, there have been used many fabrication techniques such as silicon etching technologies, non-silicon etching technologies [1-3]. But, these methods have difficulties in the fabrication of micro channel for above requirements of the micro reaction applications. Anodic aluminium oxide structure has been usually used in the micro channels fabrication for the porous alumina-based catalyst supporting [4]. However, the porous aluminium structure grows only along a vertical direction to aluminium substrate.

Macroporous structure has widely gained many interests in the applications of photonics, micro total analysis system,

and micro chemical reactor system [5-6]. These applications have required the specific structure with a high aspect ratio, large surface area and high variety in orientation. For the needs like as above requirements, the macroporous silicon with three-dimensional structure seems to be very good a substitute of porous aluminium structures because macroporous silicon structure has the high aspect ratio over a hundred, large surface area [7]. However, a micro channel structure work with p-type macroporous silicon has been insufficient for the practical uses. Our research has obtained the porous structure with a high surface area in the bottom and wall of a silicon substrate simultaneously. In this research letters, we mention a fabrication of the p-silicon macroporous structure with an organic-based electrolyte for the ruthenium catalyst supporting within micro channels.

2. EXPERIMENTAL and RESULTS

The macroporous silicon growth includes organic-based electrolyte and LabVIEW control system for

three-dimensional structure formation. Used electrolyte was an organic of dimethylformamide(DMF), widely the known for growth of macroporous formation in the p-type silicon wafer [8], mixed with solutions of HF 4% + H₂O 4%. P-type silicon wafer of (100) orientation with resistivity of 8-12Ωcm was used. To etch electrochemically, samples were prepared with micro channels having the 500 μm width and 150 μm depth in p-type silicon wafer using the standard photolithography and deep reactive ion etching. Silicon oxide as a masking material was used during electrochemical etching. For an ohmic contact of silicon wafer, a gold/chromium layer was evaporated on the backside of a silicon wafer. Current density of 6.2mA cm⁻² was applied for 30minute to the p-type silicon wafer for the electrochemical etching.

P-type silicon with a resistivity of 5-12 Ω cm was electrochemically etched under current density of 18.5mAcm⁻² and 6.2mAcm⁻² for 30minute. Fig. 1(a), (b) show the obtained macroporous silicon structure. We concluded that this electrochemical etching of Fig. 1(a) was over by a concentrated current density from an anodic electrode.

We obtained the macroporous silicon in the wall and bottom of the micro silicon channels fabricated by deep reactive ion etching under conditions of the low current density of 6.2mAcm⁻² for 30 minute. Fig. 1(b) shows the three-dimensional macroporous silicon micro channels grown in the bottom and wall of a silicon substrate simultaneously into silicon micro channels fabricated by deep reactive ion etching. We can observe the macroporous silicon that was grown along to the vertical direction very well. The grown macroporous silicon structures had a pore size below 1 μm. This macroporous channels had a high aspect ratio and a large surface area enough for the micro channels reaction device applications. Moreover, the grown macroporous channels structures had the three-dimensional structure with high structure freedom. Electrochemically

grown macroporous silicon had the porous depth of 18.5 μm at bottom and 12 μm under the conditions of current density of 6.2mA cm⁻² for 30minute at sidewall. The grown macroporous silicon etched electrochemically by dimethylformamide(DMF) organic-based electrolyte grew along the (100) orientation plane in the p-type silicon wafer as shown in Fig. 1(b).

Well- known catalyst for a borohydride fuel reforming, a ruthenium-catalyst was supported within a macroporous silicon wafer using the dip coating method. A RuCl₃-3H₂O solution was mixed with an HCl, and then the mixtures were treated ultrasonically for 2 hours. The fabricated macroporous silicon wafers as shown in Fig. 1 were dipped in the ruthenium-catalyst mixtures. The ruthenium- catalysts supported into a macroporous silicon were dried and heated at 100 °C for 30minute in the air condition. SEM micrographs of ruthenium-catalyst supported into a macroporous silicon wafer are shown in Fig. 2(a), (b) respectively. Fig. 3 shows the energy dispersive spectroscopy(EDS, Oxford Instruments) result of ruthenium-catalyst supported within silicon macroporous micro channels shown in Fig. 2(a), (b). From this result, we conformed some peaks that show 1.74keV(Si_{Kα}) of macroporous silicon channels and 2.56keV(Ru_{Lα1}) of ruthenium catalyst supported into the macroporous silicon channels. Fabricated macroporous silicon structure was bonded with a cover silicon wafer for an inlet/outlet of the reactants as shown in figure 4.

3. CONCLUSION

In conclusion, for micro chemical engineering applications with micro channel structure, macroporous silicon structure was formed by an organic-based electrolyte, dimethylformamide. Macroporous micro channel structure was grown at sidewall and bottom of the silicon channel simultaneously under the conditions of current density of

6.2mA cm⁻² for 30minute at sidewall. The obtained macroporous silicon had high aspect ratio and large surface area. Macroporous silicon showed the porous structure grown along (100) plane in the sidewall and bottom of micro channels of silicon wafer simultaneously. We supported the ruthenium catalysts into the grown macroporous structure. Future work includes the characterization of micro fuel reformer with the catalyst-supported macroporous devices.

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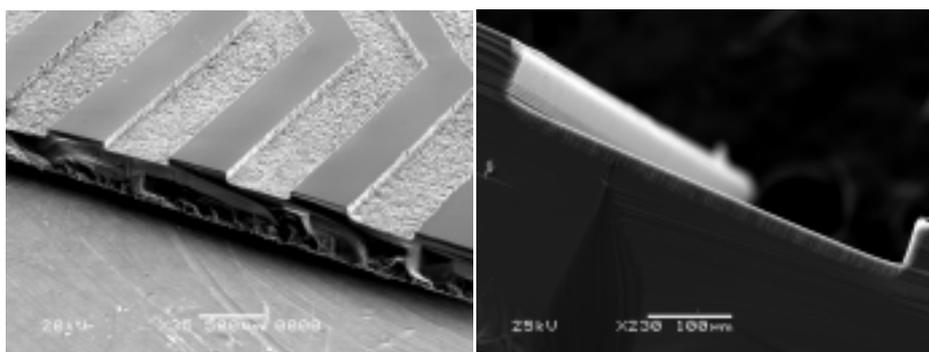


Figure 1. SEM figures of the macroporous silicon structure grown under current density of 18.5mAcm⁻² (a) and 6.2mA cm⁻² (b), electrolyte of dimethylformamide(DMF) 92% + HF 4% + H₂O 4% for 30 minute in the 8-12Ωcm (100) p-type silicon wafer.

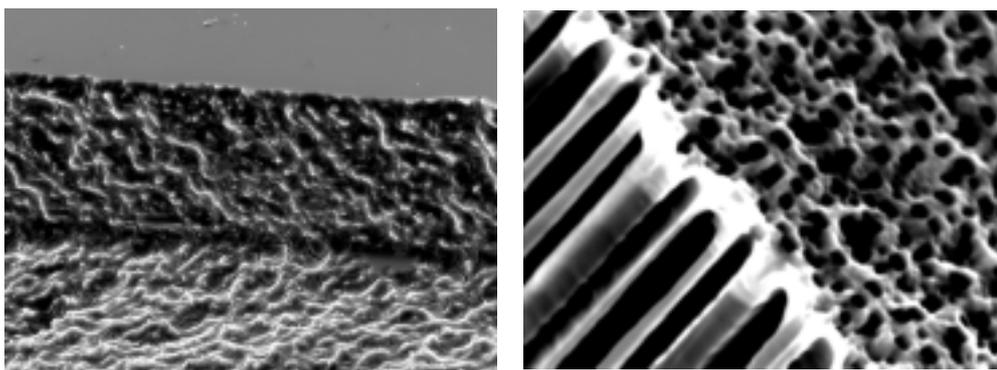


Figure 2. SEM figures of ruthenium catalyst supported into the fabricated macroporous silicon structure: (a) is that of Fig. 1(a) and (b) is that of Fig. 1(b).

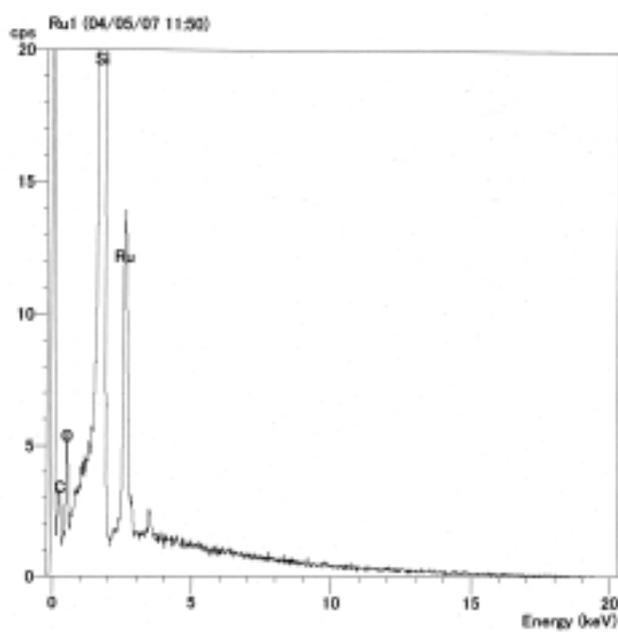


Figure 3. Energy Dispersive Spectroscopy(EDS) result of ruthenium catalyst supported within silicon macroporous structure.



Figure 4. Macroporous micro channel reactor with a ruthenium catalyst supported into a macroporous silicon structure.