Development of a miniature silicon wafer fuel cell using L-ascorbic acid as fuel[*]

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Abstract: In the current studies a miniature silicon wafer fuel cell (FC) using L-ascorbic acid as fuel was developed. The cell employs L-ascorbic acid and air as reactants and a thin polymer electrolyte as a separator. Inductively coupled plasma (ICP) silicon etching was employed to fabricate high aspect-ratio columns on the silicon substrate to increase the surface area. A thin platinum layer deposited directly on the silicon surface by the sputtering was used as the catalyst layer for L-ascorbic acid electro-oxidation. Cyclic voltammetry shows that the oxidation of L-ascorbic acid on the sputtered platinum layer is irreversible and that the onset potentials for the oxidation of L-ascorbic acid are from 0.27 V to 0.35 V versus an Ag/AgCl reference electrode. It is found that at the room temperature, with 1 mol/L L-ascorbic acid/PBS (phosphate buffered solution) solution pumped to the anode at 1 ml/min flow rate and air spontaneously diffusing to the cathode as the oxidant, the maximum output power density of the cell was 1.95 mW/cm² at a current density of 10 mA/cm².

Key words: L-ascorbic acid, Fuel cell (FC), Silicon wafer

INTRODUCTION

With the development of labs on a chip technology, micro power sources become highly demanded. Fuel cells (FCs) are electrochemical devices that convert the chemical energy of a reaction directly into electricity. A miniaturized FC power source can be realized through an approach that combines thin film materials with MEMS (micro-electro-mechanical system) technology (Kelley *et al.*, 2002; Yen *et al.*, 2003). One common approach for FC implementation is to fabricate distributing channels and feedholes on silicon substrates, followed by a deposition of a thick metal film to serve as current collectors. Then a conventional membrane electrodes assembly (MEA) is sandwiched in between two silicon substrates to

form an FC (Yu *et al.*, 2003a; 2003b; Lu *et al.*, 2004; Chan *et al.*, 2005). This kind of structure requires thick metal film to cover the steps of fuel channels to reduce electronic resistance. An alternative is to sputter catalyst directly on silicon substrate and then assemble the catalyzed anode and cathode with the proton conducting membrane (Seo and Cho, 1997; 1998). The drawback of this approach is the small active catalyst surface area.

Most of these reported miniaturized FCs use hydrogen, methanol, or ethanol as fuels. For labs on chip applications, especially for these in vivo applications, an FC which can use biomaterials as fuels could be very interesting. Mano *et al.*(2004) reported a miniature membraneless biofuel cell that uses glucose as fuels. The cell can operate at +0.60 V under physiological conditions. In this cell, glucose oxidase is required to catalyze the oxidation of glucose. Besides glucose, Fujiwara *et al.*(2003) proposed to using L-ascorbic acid as fuel. They adopted the conven-

tional polymer electrolyte membrane (PEM) FC structures and preparation methods. High loading ($3{\sim}5$ mg/cm^2) precious metal black (nano particles with very high active surface area) was used as the catalyst and carbon cloth as the gas diffusion layer. These methods and materials are not compatible to silicon micro fabrication technology that is powerful in miniaturization.

In the present studies, we designed a miniaturized FC in which the anode and cathode catalyst layers are formed by directly sputtering platinum on the inductively coupled plasma (ICP-etched) high aspect-ratio columns on silicon substrate. Furthermore, we investigated the electrochemical oxidation of L-ascorbic acid on the above catalyst layers and demonstrated a miniaturized FC using L-ascorbic acid as fuel. Such kind of device has promising applications in the fields such as in vivo telemetry sensing system.

EXPERIMENTAL PROCEDURES

Device fabrication

A cross-sectional schematic of the miniaturized FC is illustrated in Fig.1. It is a typical sandwiched electrode/membrane/electrode structure. The major electrode components (catalyst, current collectors, feedholes, flow field) were integrated on silicon substrate. Silicon surface was textured by dry etching to increase the surface area for catalyst. The low resistivity bulk silicon provides good electrical connection between catalyst layer and metal current collector, which minimizes the negative effect of surface roughness on electrical conductance. The glass substrate was bonded to the silicon substrate to seal the fuel reservoir, increase the mechanical strength and provide output metal pad. The major fabrication processes for silicon substrate, glass substrate and the bonding pairs are exemplified in Fig.2. For silicon
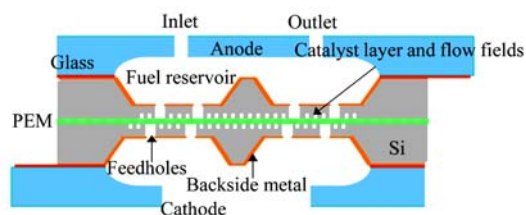

Fig.1 Schematic cross-sectional view of the micro fuel cell

substrate, the starting material was a 475 μm thick, double-side polished, <100> oriented, *n*-type silicon wafer with a resistivity lower than 0.05 Ω·cm. First, a thermal oxide was grown and patterned by reactive ion etch (RIE) to provide masks for etching columns at later step (Fig.2a). Next, feedholes were inscribed by ICP etching (Fig.2b) and photoresist was removed. A second ICP etching was followed to create small columns at catalyst surface (Fig.2c), using oxide masks patterned in Fig.2a. Then, a 150 nm low temperature oxide (LTO) layer and a 140 nm nitride layer were deposited to provide protecting mask for tetra-methyl ammonium hydroxide (TMAH) etching. A 220 μm deep fuel reservoir was etched by a 25% (v/v) TMAH solution at 85 °C (Fig.2d). A wafer holder was used to protect the front side silicon surface during reservoir etching. A 15 nm TiW adhesion layer and a 200 nm Au layer were sputtered and patterned by the lift-off process, serving as integrated micro current collectors (Fig.2e). The silicon wafer was ready for bonding after this step.

The starting material of glass substrate was Corning 7740. First, chambers, inlets and outlets were created by wet etching in 49% (v/v) HF solution (Fig.2f), using composite film of photoresist and gold as the etching masks. Subsequently a 15 nm TiW adhesion layer and a 200 nm gold layer were sputtered and lifted-off on the chamber side to provide electrical connection to external load (Fig.2g).

The silicon substrate and the glass substrate were bonded together (Fig.2h) by anodic bonding at 320 °C. The applied voltage was 400 V and the applied pressure was $1.8{\times}10^5$ Pa. Then, the bonded pairs were sputtered with 15 nm TiW and 200 nm Pt (Fig.2i). The active area of the electrodes was 11 mm$\times$13 mm. Finally, the fabricated electrodes were bonded with a polymer electrolyte film (DuPont's Nafion$^\circledR$117) at 135 °C and the fabrication of an integrated micro FC unit was completed.

Electrochemical characterization

In this work, electrochemical oxidation of L-ascorbic acid on the platinum film formed by directly sputtering on the ICP-etched high-aspect-ratio columns was investigated. Electrochemical measurements were performed with a CHI 660 electro-chemical workstation from CHI Instruments Inc., USA. All process control and data collecting were
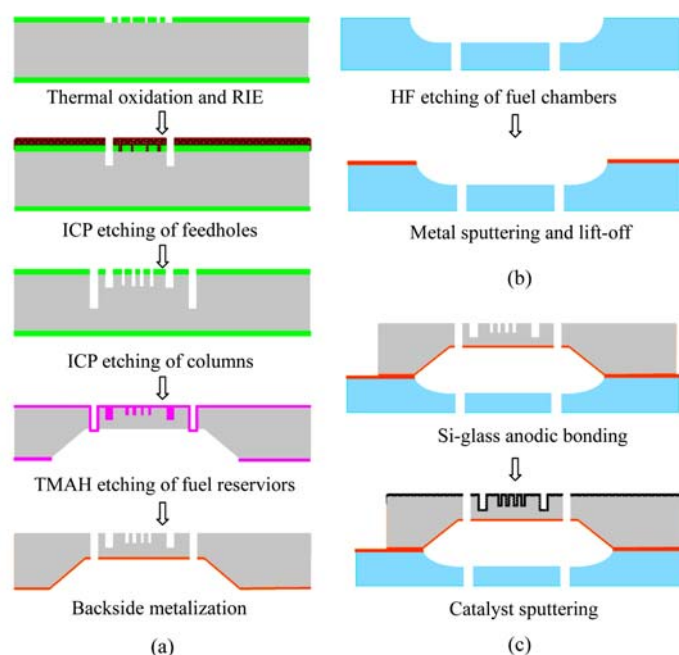
Fig.2 Major fabrication steps (a) for silicon substrate, (b) for glass substrate and (c) for bonding process

carried out using a personal computer via a RS 232 series port communicating to the CHI electrochemical analytic station.

The electrochemical cell consists of three electrodes. The working electrode was the platinum layer formed by sputtering on silicon substrate (the part "TMAH etching of fuel reservoirs" shown as Fig.2a). For electrical connection, a copper wire was soldered on the gold layer on the backside of the silicon wafer and protected by an epoxy resin layer. Platinum electrode and silver/silver chloride electrode from CHI Instruments Inc., USA were used as the counter and reference electrodes, respectively. The electrolyte used is phosphate buffered solution (PBS) with different concentrations of L-ascorbic acid. PBS was prepared by dissolving 45 g NaCl, 11.8 g KH_2PO_4 and 53 g K_2HPO_4 in 10 L deionized (DI) water (pH=7.3). The measurements were performed at 25 °C room temperature. Ascorbic acid was purchased from Fluka, Basel, Switzerland.

RESULTS AND DISCUSSIONS

For conventional FCs, precious nano metal powders (e.g., Pt black or Pt/C) are used as high performance catalyst. The nano powders provide very high active surface area with small loading. However, they are not fully compatible with silicon micro fabrication process. In our approach, catalyst layer is directly sputtered on silicon substrate with high aspect-ratio microcolumns that are formed by ICP dry silicon etching on the silicon wafer surface. The height of these columns is 100 μm and the diameter is 30 μm, as shown in Fig.3. These columns can greatly increase the surface area. Fig.4 is the cyclic voltammogram of the platinum layer sputtered on the silicon surface with ICP-etched microcolumns (curve b) and a CHI platinum electrode (curve a) in PBS solution, respectively. The applied potential range is 0~0.7 V versus an Ag/AgCl reference electrodes and the scan rate is 50 mV/s. For the CHI platinum electrode, it mainly behaves as a double-layer capacitor in this potential range. For the sputtered platinum layer, when the applied potential is higher than 0.5 V, the current starts to increase. Actually the properties of the sputtered thin platinum film are quite complicated. Generally the current increase in the high potential range can be ascribed to the surface condition of the platinum layer. Nevertheless, the double-layer capacitance charging/discharging current of the sputtered platinum layer is almost four times larger than that of a normal CHI platinum electrode with the same surface area, which indicates a larger active surface area.
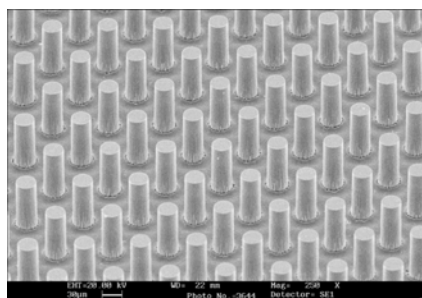
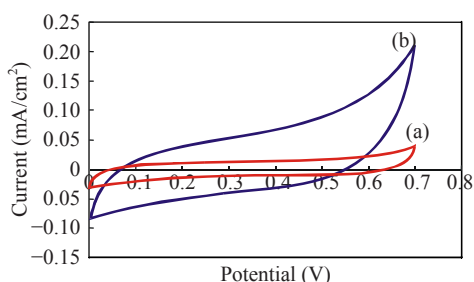**Fig.3 SEM graph of microcolumns formed by ICP dry etching on the silicon substrate**

Fig.4 Cyclic voltammogram in phosphate buffer solution. The working electrode: (a) a CHI platinum electrode; (b) the platinum layer sputtered on the silicon surface with ICP-etched microcolumns. The reference electrode: Ag/AgCl; the scanning rate: 50 mV/s

L-ascorbic acid, better known as Vitamin C, plays an essential role in biological metabolism and the mechanism of electro-oxidation of ascorbic acid has been examined by many researchers. Normally it is believed that the electro-oxidation of L-ascorbic acid to dehydroascorbic acid is a process involving two electrons (Ruiz *et al.*, 1977), which is shown in Fig.5.
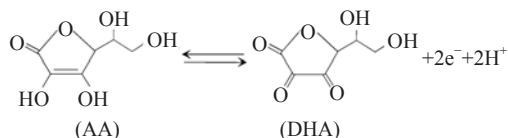

Fig.5 Electro-oxidation mechanism of L-ascorbic acid (AA) to dehydroascorbic (DHA)

Fig.6 is the cyclic voltammogram of the sputtered platinum layer in the PBS solutions with different concentrations of L-ascorbic acid with scanning rate of 50 mV/s. It is shown that the electro-oxidation of L-ascorbic acid is irreversible and that the onset potentials for the oxidation of L-ascorbic acid are from 0.27 V to 0.35 V versus

Ag/AgCl reference electrode. These values are quite close to the theoretical potential of L-ascorbic acid oxidation (0.471 V versus standard hydrogen electrode (SHE)), which suggests that the overpotential of electro-oxidation of L-ascorbic acid on the sputtered platinum layer is relatively small. Fig.6 also shows that when the applied potential reaches 0.5 V, the passing through currents become somehow saturated. At this potential, the current is proportional to the concentrations of L-ascorbic acid. In Fig.4, it is mentioned that when the applied potential is higher than 0.5 V, there are some background faradaic current passing through the sputtered platinum layer even in pure PBS solution. It is shown clearly in Fig.6 that these background currents are much smaller compared to the oxidation current of L-ascorbic acid.
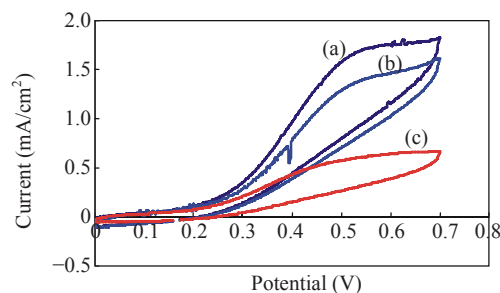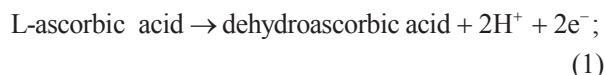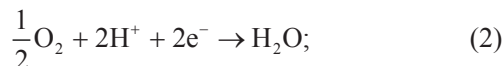

Fig.6 Cyclic voltammogram of the sputtered platinum layer in the PBS solutions with different concentrations of L-ascorbic acid. The reference electrode: Ag/AgCl; the scanning rate: 50 mV/s. Concentrations of L-ascorbic acid are (a) 1 mol/L; (b) 0.7 mol/L and (c) 0.2 mol/L

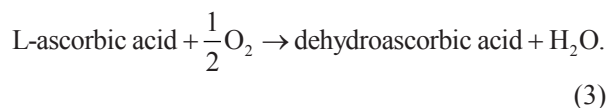For FCs using L-ascorbic acid as fuel, the expected electrode reactions are as follows:

At the anode,

$$\text{L-ascorbic acid} \rightarrow \text{dehydroascorbic acid} + 2H^+ + 2e^-; \quad (1)$$

at the cathode,

$$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O; \quad (2)$$

and the overall reaction is:

$$\text{L-ascorbic acid} + \frac{1}{2}O_2 \rightarrow \text{dehydroascorbic acid} + H_2O. \quad (3)$$

The standard redox potentials for Eqs.(1) and (2) are 0.471 V and 1.229 V, respectively. Therefore, the theoretical voltage of the FC is 0.758 V. The characterization of FC performance was carried out at the room temperature. During the measurement, 1 mol/L L-ascorbic acid PBS solution was pumped through to the anode at 1 ml/min flow rate, and air was spontaneously diffused to the cathode as the oxidant. Fig.7 is the cell polarization (curve a) and current density vs power density (curve b) of the μFC (micro fuel cell) using L-ascorbic acid as fuel. It is shown that the open-circuit potential of the cell is around 550 mV. With the increase of the output current density, the cell voltage drops rapidly and when the current density is 20 mA/cm^2, the output voltage is 70 mV. Curve b in Fig.7 shows that the maximum output power density of the cell is 1.95 mW/cm^2 at a current density of 10 mA/cm^2. This value is smaller compared to that reported by Fujiwara *et al.*(2003). However, the platinum loading of both our cathode and anode is only 0.43 mg/cm^2, which is one order of magnitude lower than Fujiwara *et al.*(2003)'s device. The surface texturing is not fully optimized in our present approach. The performance is expected to be improved with much denser and smaller posts that can be easily fabricated by the mature dry etching and patterning technology from integrated circuit (IC) industry.
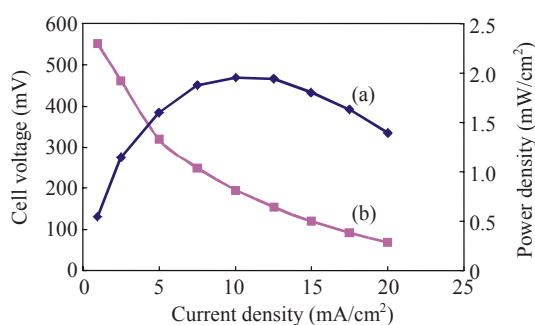

Fig.7 Performance of L-ascorbic acid fuel cell. (a) Cell polarization curve; (b) Current density vs power density curve

CONCLUSION

In this work a miniature silicon wafer FC using L-ascorbic acid as fuel was developed. In this cell, the catalyst layer was deposited directly on the silicon surface by sputtering. The inductively-coupled plasma silicon etching was employed to fabricate high aspect-ratio columns on the silicon surface, which greatly increases the surface area of catalyst layer. Cyclic voltammetry of the sputtered platinum layer shows high electrochemical activity of L-ascorbic acid. At the room temperature, when 1 mol/L L-ascorbic acid PBS solution was pumped through to the anode at 1 ml/min flow rate, and air was spontaneously diffused to the cathode as the oxidant, the maximum output power density of the cell is 1.95 mW/cm^2 at a current density of 10 mA/cm^2.

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