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12% Yield and 370-mV OCV of 0.36 mm^2 Solid-State CMOS-Compatible Glucose Fuel Cell by Using Repeated Separator Coating

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Abstract

Development of 0.36-mm^2 (0.6-mm □) solid-state CMOS-compatible glucose fuel cell, which delivers 10%-yield and the world's highest open circuit voltage (OCV) of 370 mV, has been presented. By introducing the repeated separator coating, the electrical shortage between the anode and cathode can be avoided, resulting in higher yield when compared to that with the conventional single coating. The higher yield allows improvement of peak OCV. The measurement results show a 370-mV OCV and 12% yield with a 30 mM glucose solution.

1. Introduction

Bio fuel cells is one of the most preferable power sources for biomedical IoT due to its inherent stability[1-3]. In addition to its stability, bio fuel cells can be used not only power sources but also sensing transducer by exploiting its selectivity[4]. In spite of these advantages, their application is not yet broadened because of its low output power and yield.

The previous work presented the world's smallest 0.36 mm^2 (0.6 mm □) CMOS-compatible solid-stage glucose fuel cell that generates 228 mV OCV [3]. However, its OCV is insufficient for practical application since the optimum supply voltage for CMOS LSI design is almost same as transistor's threshold voltage [5]. Besides, yield for driving 180-mV CMOS processor [6] of the previous work is only 1.5%.

For addressing this issue, this work presents a 0.36 mm^2 solid-stage glucose fuel cell that generates 370-mV OCV, which is highest record as glucose fuel cells whose size is smaller and equal to 1 mm^2. As well as OCV improvement, yield (180-mV threshold) is improved from 1.5% to 12% which corresponds to 8 times. Since yield degradation can be caused by electrical shortage between the anode and cathode in the latter cathode forming, the conventional single separator layer (Nafion) coating is assumed to be one of the bottlenecks. For addressing this bottleneck, we have newly introduced the repeated coating and verified its effectiveness for the first time.

2. Wafer-scale development of glucose fuel cells

Figure 1 shows the structure and operational principle of the developed fuel cell. The fabrication of wafer-scale glucose fuel cell is based on previous works [1,3]. The conceptual image of development process is shown in Fig. 2. The summary of developing process is as follows:

1) We used a 6-inch silicon wafer of 625 μm thickness with 1 μm thermal oxide. Each fuel cell is developed in 0.36 mm^2 (0.6 mm × 0.6 mm).
2) Ti/Pt deposition for the electrode.
3) Al deposition on the Pt in the anode area. We form Pt/Al alloy in the anode by annealing. After annealing, we etch Al from the alloy. And we formed porous Pt layer in the anode area.
4) A Nafion membrane is formed as a cation exchange layer. To make Nafion layer thick, we repeated spin-coating twice. Formed thickness was 100 nm.
5) A carbon nanotube (CNT)-based cathode is developed by coating of CNT/Nafion solution.

In above process, the difference from [3] is regarding to process 4). The spin-coating process of Nafion layer was repeated twice to make thick layer because Nafion layer forming is difficult especially in small size [1,3]. In process 5), the solution degrade the separator (Nafion) layer and may penetrate into the anode, which results in electrical shortage and malfunction.

3. Prototype and measurement setup

Figure 3 shows the developed prototype and measurement setup. The developed wafer was cut into each 0.36-mm^2 device by stealth dicing. We used a DC multi-contact probe, a tester (U1252A, Agilent Technologies) and a SMU (GS610, Yokogawa) for electrical performance measurement. Phosphate buffered saline (PBS)-based glucose solution was dropped on the anode and cathode area of the fuel cell with a micropipette. D(+)-Glucose (Wako) and PBS 10X (Irvine Scientific) was used for body fluid simulated solution. We used 30-mM glucose solution to prevent the fuel cells from lack of glucose in all the measurement in this work.

4. Measurement results

Figure 4 shows the polarization curve of the cell which has highest OCV in the measured samples. The polarization curve is based on data from the SMU. We controlled current and measured voltage in the measurement. Some of the measured current has multiple data because the output voltage changes slightly during measurement. We consider that this output fluctuation is caused by unequal fuel diffusion. The OCV is 370 mV. The peak power is 108 pW when the current is 1.0 nA and it corresponds to 0.27 μW/cm^2 and 2.5 μA/cm^2. The voltage drop rapidly in low current is considered to be caused mainly by activation losses. The linear voltage drop in the middle range is considered to be caused by ohmic polarization. The drop in high current area is considered to be a diffusion polarization caused by diffusion control. These polarizations are common phenomena in fuel cells.

Figure 5 shows the performance variation of measured 49 samples and comparison with prior work [3]. It shows the yield of this work is superior than that of [3]. Ratio of samples with less-than-2.5mV OCV of decreases from 58% to 43%. Sample ratio that have 100 mV or higher OCV is

22%, which is about 4.9 times. That of 150 mV is 14%, corresponds to 9.4 times. That of 200 mV is 10%, 13 times. All comparison is to that of the previous work [3].

Table I is performance comparison with prior works about wafer-scale-developed glucose fuel cells. This work achieved the highest OCV within 1 mm^2 devices. In terms of power density, this work inferior than other works. Despite of lower output power, higher OCV is preferable from the viewpoint of circuit design [5].

5. Discussion

The developed fuel cell outperformed in terms of OCV but underperformed in terms of power density compared with previous works fabricating 1 mm^2 or smaller devices. Compared with conventional sub-mm^2 glucose fuel cell, sample ratio with sufficient OCV increased. We consider that the repeated Nafion separator coating is an effective way to improve the yield. However, we have to apply another method for further yield enhancement because sample ratio with OCV of less than 2.5 mV is still about 40%.

6. Conclusions

This work demonstrated repeated separator coating is effective to form thick ion exchange layer in sub-mm^2-sized fuel cell. Developed fuel cell showed performance yield improvement by a factor of 8. The verified highest OCV was 370 mV, which is higher than energy-minimum point of CMOS LSIs.

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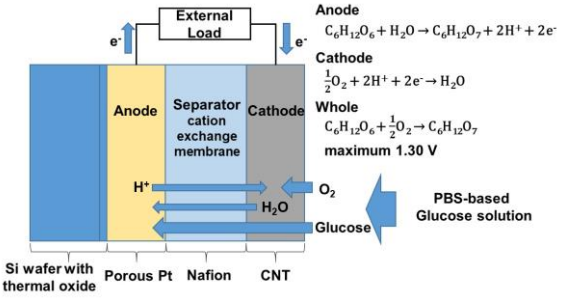

Fig. 1. Conceptual image of structure and work principle of developed fuel cell.

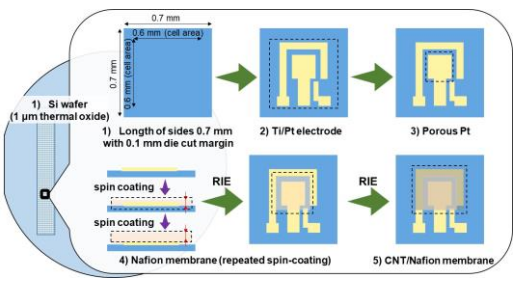

Fig. 2. Conceptual image of the development procedure.

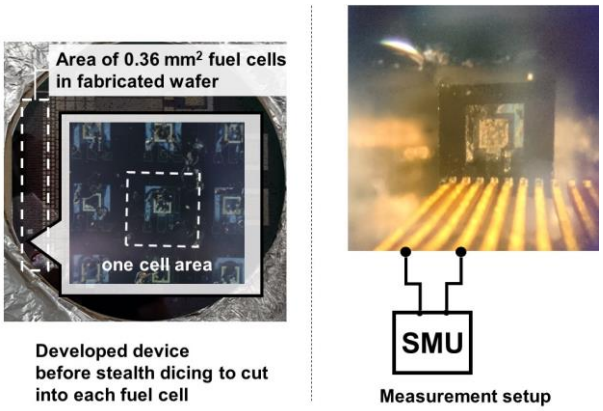

Fig. 3. Photograph of the developed prototype and measurement setup.

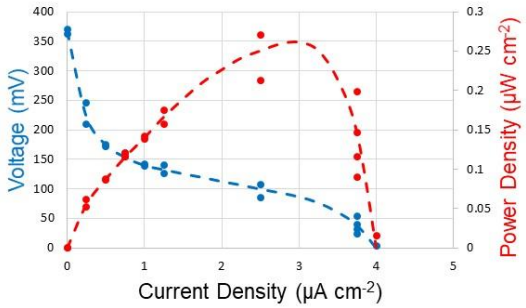

Fig. 4. Output voltage and power density dependence on output current density.

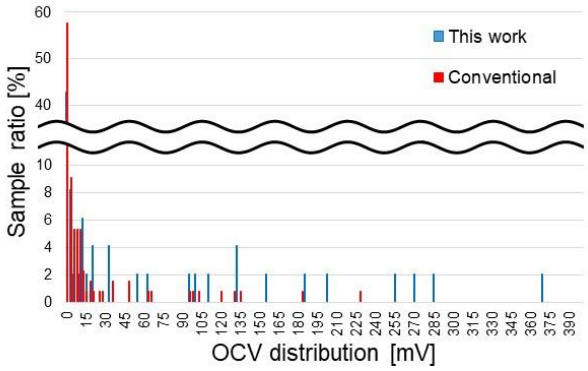

Fig. 5. Performance variations comparison with conventional fabricating process.

Table I Performance comparison with previous works.

	Ref. 1		Ref. 2	Ref. 3	This work
Anode area (mm^2)	2	1	25	0.04	0.04
Device area (mm^2)	-	-	-	0.36	0.36
Open circuit voltage (mV)	192	-	550	228	370
Peak power density (μW/cm^2)	over 180	3.4	2.3	1.32	0.27