第27卷 第3期 半 导 体 学 报 Vol.27 No.3
2006年3月 CHINESE JOURNAL OF SEMICONDUCTORS Mar.,2006

An Air-Breathing Micro Direct Methanol Fuel Cell with 3D KOH-Etched Cathode Structure*

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Abstract: A micro direct methanol fuel cell (μDMFC) using MEMS technology is reported. The prototype features a unique 3D air-breathing cathode structure fabricated using KOH etching and double-side lithography. The optimization of the MEMS fabrication process is analyzed. The experimental results show the prototype generates a maximum power density of 2.52mW/cm^2 at room temperature. This performance is better than the published results of other silicon-based passive μDMFCs. Moreover, it is comparable with that of our previous active μDMFCs which require an external pump, certificating the feasibility of this new configuration.

Key words: μDMFC; air breathing; bulk etching; MEMS; micro power source
EEACC: 2575F; 8410G
CLC number: TM911.48 **Document code:** A **Article ID:** 0253-4177(2006)03-0478-04

1 Introduction

Recently, MEMS has been actively applied in portable electronics and wireless communication systems, such as digital cameras, cell phones, and sensor networks.

For these applications, a stand-alone micro power source (MPS) is essential to the operation of the micro system. Of the various candidates, the micro direct methanol fuel cell (μDMFC) has lately drawn increasing attention from worldwide scientists and researchers[1~6]. Due to its outstanding advantages such as high energy density, environmental friendliness, low temperature operation, lack of moving parts, and easy storage[7,8], the μDMFC has been regarded as one of the most promising micro power sources to be commercialized soon in the future.

Many researchers, including us, have investigated active μDMFCs[2~4], in which methanol and oxygen pumps are used to supply the reactants. However, since the most promising applications of μDMFCs are intended for portable electronics and stand-alone micro systems, independence of the power supply is necessary. Therefore, external pumps or other ancillary devices should be simplified or eliminated to reduce the volume and parasitic power loss, as long as no great performance degradation occurs. In the μDMFC presented in this paper, an air-breathing cathode plate (i.e. oxygen is taken directly from the atmosphere) was used to replace the cathode pump. Due to high precision, good repeatability, cheap batch-production, and potential integration with other MEMS devices, MEMS technology has been used to fabricate the μDMFCs on the silicon substrate. The prototype features a unique 3D KOH-etched air-breathing structure and an optimized MEMS fabrication process.

2 Design

A schematic of the air-breathing μDMFC is shown in Fig. 1, which consists of two silicon plates with a membrane electrode assembly (MEA, shown as two carbon papers and a PEM in the figure) between them. A serpentine flow-field was used on the anode for high flow velocity, uniform fuel distribution, and easy removal of CO_2[9]. The design of the cathode, however, is relatively complex. To design a proper air-breathing cathode structure, air permeability, contact area with the MEA, and intensity of silicon structure must be considered. Normally the first two factors contradict each other since they share a common micro-

* Project supported by the National Natural Science Foundation of China (No. 90207023)
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Received 30 September 2005, revised manuscript received 20 December 2005

channel area, and they are limited by the third factor. The larger the opening on the cathode plate, the more easily the ambient air can access the MEA through the cathode, and produced water can evaporate into the air. However, this also means less current-collecting contact area with the MEA, worse distribution of external pressure, and higher risk of the fracture. A similar dilemma occurs if the window openings are too small. Therefore, the essential goal of the air-breathing cathode design should be to solve these conflicts as completely as possible.

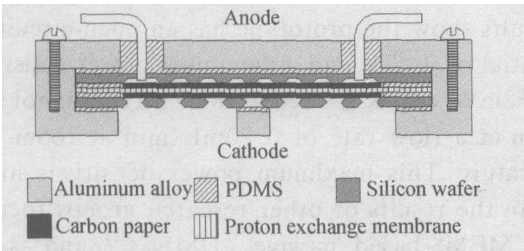

Fig. 1　Schematic of the air-breathing μDMFC

We propose a new method to address these issues. This method has been implemented by first using double-sided lithography to transfer different but interrelated patterns (designed according to certain considerations) onto each side of the cathode plate, and then using KOH timed etching to etch through the wafer. Thus a unique 3D KOH-etched cathode structure is formed. Two types of cathode plates were fabricated with this method, as shown in Figs. 2 and 3. Sample C1 features large openings to the air on one side and a large contact area with the MEA on the other side. C2 was designed in a different way, which features an extremely high opening ratio but a robust structure. Note that a pattern transition may occur from the structure of C1 to that of C2, so other variations of air-breathing plates may be obtained using this method.

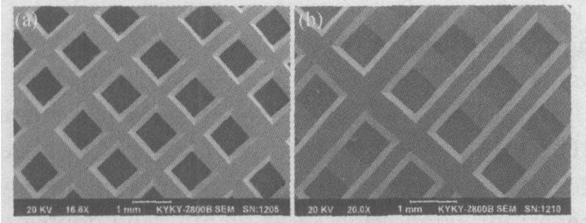

Fig. 2　SEM photos of C1, one type of the air-breathing cathode plate　(a) Front side (in contact with the MEA) of C1; (b) Back side (facing the ambient) of C1

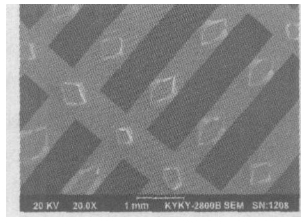

Fig. 3　SEM photo of C2, another type of the air-breathing cathode plate (front side only)

3　Fabrication

The MEMS fabrication process of the silicon plates, shown in Fig. 4, was modified and optimized on the basis of the previous process[3]. The detailed steps are as follows: (a) Thermal oxide and LPCVD Si_3N_4 were deposited as mask layers on both sides of a 400μm double-polished 〈100〉 silicon wafer; (b) Double-sided lithography was used to form the patterns of microchannel and feeding holes (for the anode) or patterns contacting the MEA (for the cathode) on the front side of the silicon wafer (top side of the wafer in Fig. 4), at the same time form aligned feeding holes (for the anode) or the patterns exposed to the air (for the cathode) on the backside; (c) KOH timed etching was used to anisotropically etch the wafer until the feeding holes were etched through; (d) Finally 0.8μm Ti/Cu and 0.2μm Au were sputtered onto the front side of the silicon wafer to form the current collecting layers.

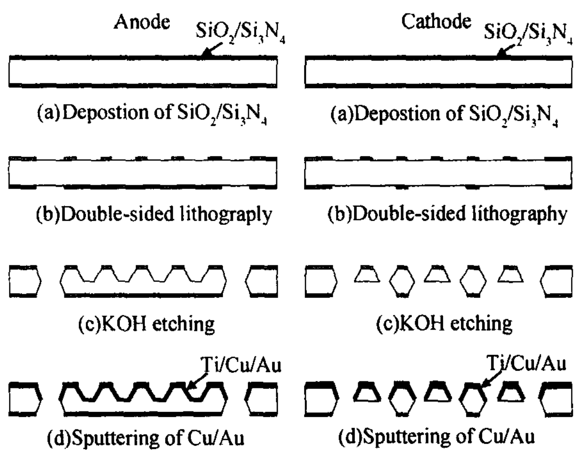

Fig. 4　Fabrication process of the anode and cathode plates

Low-cost wet etching, rather than an expensive process such as DRIE, was used to make the plates. The anode and cathode plates were fabricated on the same wafer with the same process, but they are quite different in construction. Note that although the depth of the microchannel fabricated in this paper was 200μm, half of the thickness of the silicon wafer, other depths can be easily obtained by modifying the beginning times used to etch each side of the plates. The air-breathing structure was realized by using double-sided lithography rather than the previous two single-side lithography steps. Two other reasons also led to this replacement. One reason is that in the previous second single-side lithography, the spin-coated photoresist tended to pile up around the cavity formed by the first KOH etching. The thick photoresist was difficult to develop fully, leading to blockage of the connection between the microchannel and feeding holes. The other reason is that the double-sided lithography has reduced the etching time by almost half by etching the wafer from both sides simultaneously rather than from one side to the other as in the previous process. The MEA used in the experiments consisted of two sheets of carbon paper (20wt. % FEP wet-proofed TGP-H-060) coated with the catalyst (anode: E-TEK, Pt-Ru/C (60 %), 13.4mg/cm^2; cathode: Pt/C (60 %) and Pt black, 29.2mg/cm^2) and the proton exchange membrane (PEM), Nafion 117 in the core. PDMS membranes and an external aluminum holder were employed to assemble the μDMFC, as Figure 5 shows. PDMS membranes were used to seal the gaps between the components, while the aluminum holder held all the components together compactly. The current is conducted outside by mechanically clamping the parts of the plates extruding from the holder. Table 1 lists the important dimensions of the fabricated μDMFC.

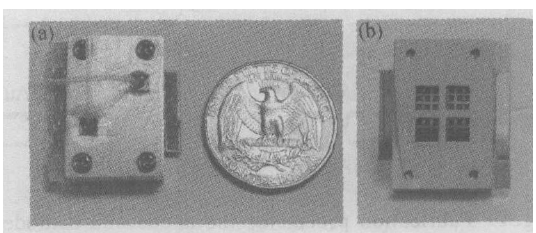

Fig. 5 Fabricated μDMFC (a) Anode side; (b) Cathode side A US quarter is shown for scaling reference.

Table 1 Important dimensions of the μDMFC

Total size *	25.4mm ×17mm ×6.2mm
Plate area	20mm ×15.2mm
Microchannel area	9.2mm ×9.2mm
Channel/rib width	400μm (anode)
Channel depth	200μm (anode)

* The volume of the holder is included.

4 Results and discussion

The experimental data were obtained with a constant current method using an electrochemical interface, a Solartron SI1287. The experimental results show the prototype has an open-circuit potential of 0.47V and a maximum power density of 2.52mW/cm^2 when fed with 0.5M methanol solution at a flow rate of 0.20mL/min at room temperature. This maximum power density is higher than the results of other research groups focusing on MEMS-based passive μDMFCs[5] and is also close to that of our previous active μDMFC[3,4], demonstrating the feasibility of this structure. Figure 6 presents a comparison of the two types of cathode structure. C1 has better performance, possibly due to the moderate trade-off between opening area and contact area.

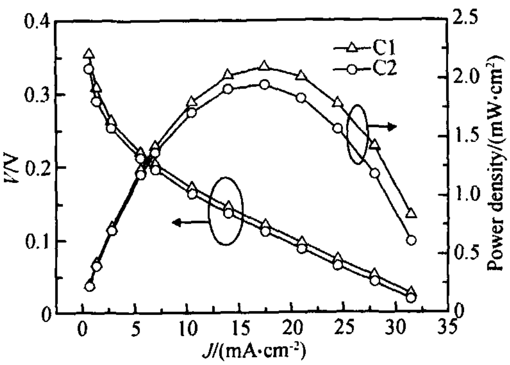

Fig. 6 Performance of the two types of air-breathing cathode designs 2M methanol, 0.20mL/min, room temperature (25 ℃)

5 Conclusion

An MEMS-based μDMFC featuring a unique 3D KOH-etched air-breathing structure has been developed. Two types of air-breathing plates have been fabricated using KOH etching and double-sided lithography. The optimized MEMS fabrication process takes less time and yields better quality than our previous process did. The experimental results show the prototype generated a maximum power density of 2.52mW/cm^2 when fed with 0.5M methanol solution at room temperature. This performance is better than the published results of other MEMS-based passive μDMFCs, and is comparable to our previous active μDMFCs, demonstrating the practicability of this new configuration. Our team aims further to implement the MEMS-based μDMFC system for practical applications.

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基于 MEMS 技术的自呼吸式微型直接甲醇燃料电池 *

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摘要: 报道了一种利用 MEMS 技术制作的微型直接甲醇燃料电池. 其特点在于, 利用 KOH 体硅腐蚀和双面光刻工艺制作了一种独特的三维自吸氧阴极结构. 分析了 MEMS 制作工艺的改进. 实验结果表明, 该电池室温下产生了 2.52mW/cm^2 的最大功率. 此性能好于国外报道的同类基于 MEMS 技术制作的被动式微型直接甲醇燃料电池, 并同本课题组之前报道的需使用外部泵的主动式微型直接甲醇燃料电池性能相当, 证明了文中提出的新结构的可行性.

关键词: 微型直接甲醇燃料电池; 自呼吸; 体硅腐蚀; 微机电系统; 微型能源

EEACC: 2575F; 8410G

中图分类号: TM911.48　　**文献标识码**: A　　**文章编号**: 0253-4177(2006)03-0478-04

* 国家自然科学基金资助项目(批准号: 90207023)

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2005-09-30 收到, 2005-12-20 定稿