FABRICATION OF GDC-BASED MICRO SOFC WITH MICROHEATERS

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Abstract: This paper mainly describes the fabrication technology of micro solid oxide fuel cell (SOFC) using Gd-doped CeO_2 (GDC) solid oxide electrolyte. A GDC membrane is made extremely thin (~300 nm thick) for low temperature operation, and a microheater is formed on a suspended membrane for local heating. To fabricate the self-supported GDC membrane, the stress of GDC films deposited by pulse laser deposition (PLD) was reduced by controlling partial O_2 pressure during deposition. Using the designed fabrication process, the structure of the micro SOFC was successfully fabricated. The ionic conductivity of the self-supported GDC membrane is is higher than that of the bulk YSZ below 400 °C, suggesting the possibility of low temperature operation. The area specific resistivity of the self-supported GDC reaches 0.15 Ωcm^2.

Key words: micro SOFC, Gd-doped ceria (GDC), thin solid oxide electrolyte, pulsed laser deposition

1. INTRODUCTION

Recently, increasing demand for the longer operation time of portable devices makes fuel cells attractive for portable energy sources. Several types of fuel cells have been widely studied, e.g. direct methanol fuel cell (DMFC) [1], polymer electrolyte membrane fuel cell (PEFC) with fuel reformer [2], PEFC with hydrogen storage [3, 4] and solid oxide fuel cell (SOFC) [5–7].

At the present, the power density of micro DMFC and PEFC is still low. Therefore, a large cell is needed to supply power required by applications, and a volume available for a fuel cartridge becomes small in the limited volume of portable devices. Consequently, the operation time by a single refueling is limited, and in addition, the large cell will raise the cost of fuel cell systems. SOFC has a higher power density in comparison with DMFC [7], and has potential to replace DMFC and PEFC for portable uses, if problems deriving from its high operation temperature (e.g. 800~1000 °C) are solved.

In this study, the following two new technologies were introduced into micro SOFC for self-sustained operation without external heating. First, a thin Gd-doped CeO_2 (GDC) solid oxide electrolyte is applied for low temperature operation. Actually, the maximum power density of the micro SOFC with a 70 nm thick YSZ electrolyte was reported to be 861 mW/cm^2 at 450 °C [7]. If the electrolyte membrane is made of GDC, which has higher ionic conductivity in medium temperature (~600 °C), further reduction of operation temperature is possible.

Second, a local heating structure is fabricated on the GDC membrane. The GDC membrane is self-supported for excellent thermal isolation and low thermal capacity. In addition, a microheater is embedded in it, and is used for quick startup until the fuel cell reaches thermally self-sustained state.

In this paper, we describe the fabrication technology of the micro SOFC and the evaluation of ionic conductivity of a self-supported GDC membrane.

2. STRUCTURE

Figure 1 shows the structure of a micro SOFC fabricated in this study. The self-supported GDC membrane is approximately 300 nm thick, and has corrugation to relax the intrinsic and thermal stress [8]. A Pt/Ta microheater is embedded in a SiO_2 insulation layer, which is surrounding and supporting the GDC membrane. The anode and cathode electrode are sputter-deposited porous Pt.

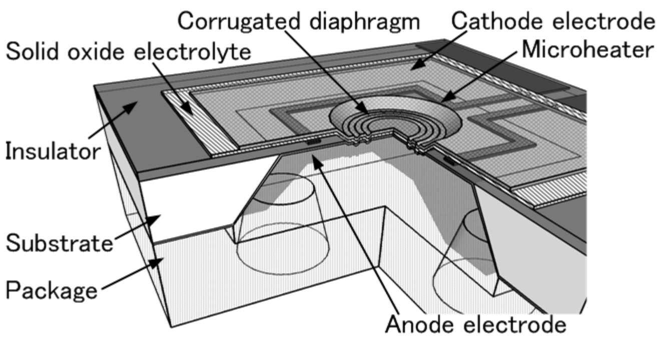

Fig. 1: Schematic of micro SOFC with microheater.

3. FABRICATION

Figure 2 illustrates the fabrication process of the micro SOFC. First, a Si substrate is isotropically wet-etched using a SiO_2 mask to form corrugated patterns. The SiO_2 mask is formed by thermal oxidation and patterned with buffered HF. Once all SiO_2 etched away, low-stress SiO_2 is newly deposited by TEOS (tetraethyl orthosilicate) plasma CVD on both sides. On the topside, the Pt/Ta microheater and Au wirings are formed. Low-stress SiO_2 is again deposited on the topside for electrical insulation, and then patterned to open a GDC membrane window. At the same time, low-stress SiO_2 on the backside is patterned into a mask for Si anisotropic wet etching.

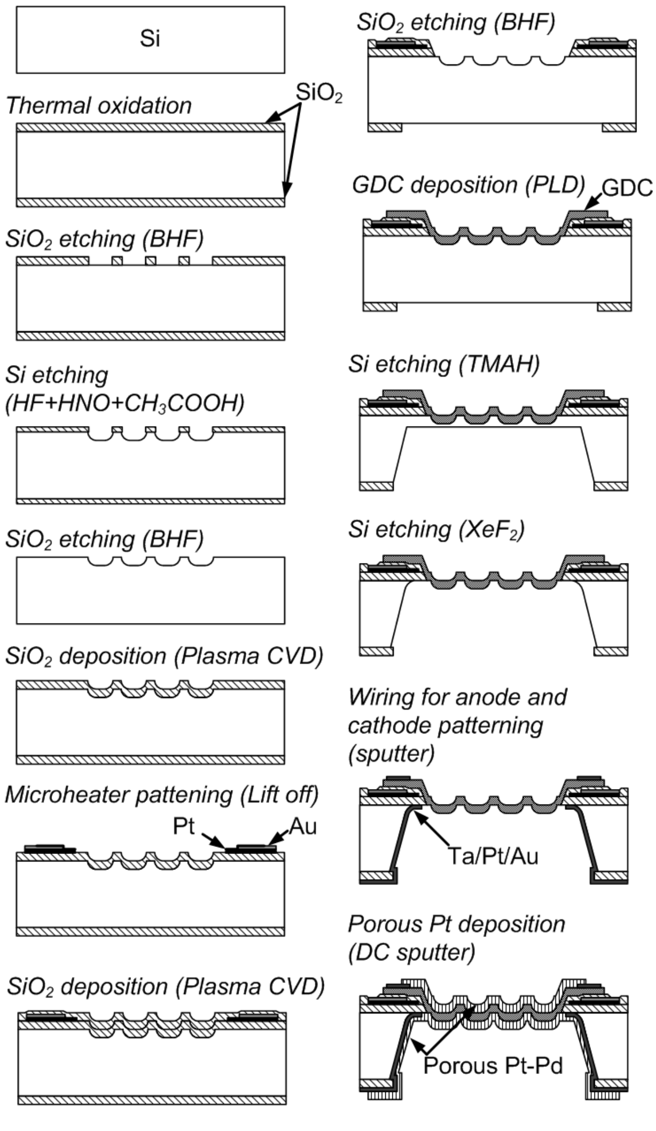

Fig. 2: Fabrication Process of the micro SOFC.

Low-stressed GDC is deposited by pulse laser deposition (PLD) with a stencil mask (as described later). For backside Si etching, the topside is masked with a passivation film (ProTEK B3, Nissan Chemical Industries, Ltd.) for TMAH and KOH. The Si substrate is etched from the bottom side by TMAH as a thickness of ca. 10 μm remains unetched. This is for preventing the GDC membrane from being broken by fluidic force in wet etching, surface tension force in drying or the residual stress of the passivation film. After that, Ta/Pt/Au wirings for the anode and cathode are deposited by sputtering with a stencil mask.

Finally, porous Pt-Pd (8 : 2) is deposited by dc sputtering. The sputtering conditions are an Ar pressure of 0.1 Torr, a target-sample distance of 30 mm, a discharge current of 0.7 mA/cm^2 and a deposition time of 10 min. Figure 3 shows the scanning electron micrograph (SEM) of the fabricated micro SOFC. Figure 4 shows the SEM of the porous Pt-Pd on the GDC corrugated diaphragm.

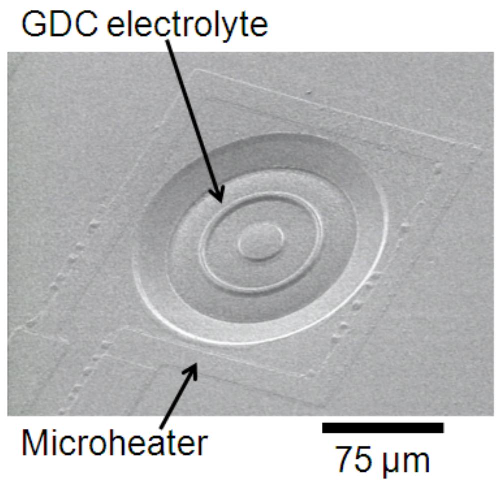

Fig. 3: SEM of the micro SOFC.

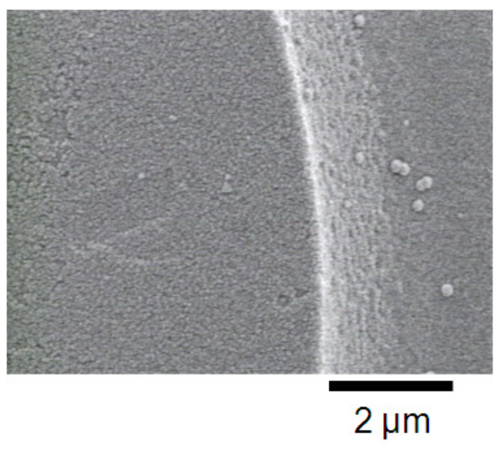

Fig. 4: SEM of porous Pt-Pd on the GDC corrugated diaphragm.

4. STRESS CONTROL OF GDC MEMBRANE

The stress control of a GDC film is important for forming a very thin self-supported GDC membrane. The residual stress of GDC is caused by the difference of thermal expansion coefficients (TEC) between GDC and Si, and chemical strain. Because a TEC of Si and GDC are approximately 3 ppm/K and 10 ppm/K, respectively [9], the thermal stress of GDC membrane on a Si substrate is tensile.

The chemical strain is depended on the concentration of oxygen defects. The oxygen defects electrically repel each other and expand the grid interval of GDC, resulting in compressive stress [10]. Because the oxygen defects decrease with increase in partial O_2 pressure during deposition, the chemical strain reduces at high partial oxygen pressure. Figure 5 shows the relationship between the partial O_2 pressure and the residual stress of 300 nm thick GDC membrane deposited at 500 °C. The residual stress is – 160 MPa (compressive) at 100 mTorr partial oxygen pressure.

5. MESUREMENT OF IONICS CONDUCTIVITY

Figure 6 shows a setup for the measurement of the ionic conductivity of the self-supported GDC membrane. The ionic conductivity is measured by using an impedance analyzer (1255B, Solatron). The substrate with the self-supported GDC membranes is heated at 300~500 °C using an external heater. The flow ratio of Ar and O_2 are 80 sccm and 20 sccm, respectively.

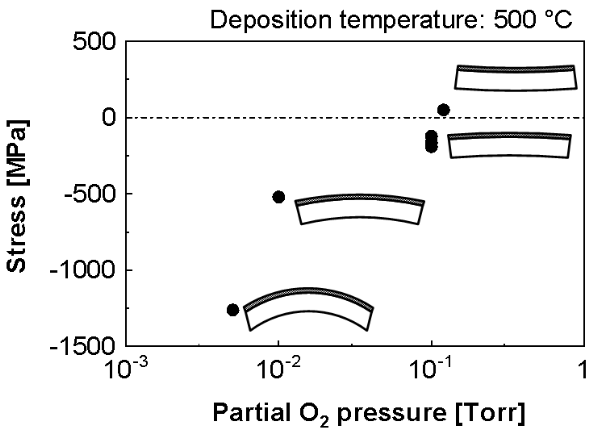

Fig. 5: Relationship between partial O_2 pressure and the residual stress (The deposition temperature is 500 ℃).

Figure 7 shows the relationship between temperature and the ionic conductivity of the self-supported GDC membrane together with those of bulk GDC and bulk YSZ [11, 12]. The measured ionic conductivity of the self-supported GDC membrane is lower than those of the bulk GDC, but is higher than that of the bulk YSZ below 400 °C. The micro SOFC using the self-supported GDC membrane is expected to operate at low temperature. The area specific resistivity of the self-supported GDC reaches 0.15 Ωcm^2, which is known as a general target value to achieve high power density.

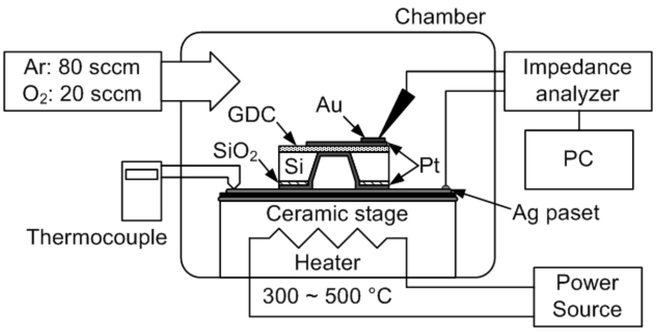

Fig. 6: Setup to measure the ionic conductivity of the self-supported GDC membrane.

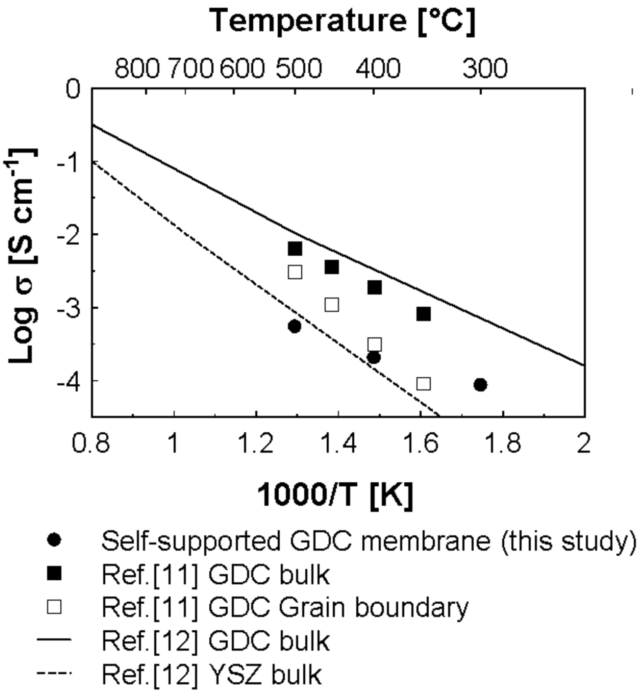

Fig. 7: Relationship between the temperature and ionic conductivity of the self-supported GDC membrane.

6. CONCLUSION

This paper mainly described the fabrication technology of a micro solid oxide fuel cell (SOFC) using Gd-doped CeO_2 (GDC) solid oxide electrolyte. A GDC membrane is made extremely thin (~300 nm thick) for low temperature operation, and a microheater is formed on a suspended membrane for local heating. To fabricate a self-supported GDC membrane, the stress of GDC films deposited by pulse laser deposition (PLD) was reduced by controlling partial O_2 pressure during deposition.

The structure of the micro SOFC was successfully fabricated, and evaluated in terms of the ionic conductivity of the self-supported GDC membrane. The measured ionic conductivity is higher than that of the bulk YSZ below 400 °C, suggesting the possibility of low temperature operation. The area specific resistivity of the self-supported GDC reaches 0.15 Ωcm^2, which is known as a general target value to achieve high power density.

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