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Solid Oxide Fuel Cell with Corrugated Thin Film Electrolyte

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ABSTRACT

A low temperature micro solid oxide fuel cell with corrugated electrolyte membrane was developed and tested. To increase the electrochemically active surface area, yttria-stabilized zirconia membranes with thickness of 70 nm were deposited onto prepatterned silicon substrates. Fuel cell performance of the corrugated electrolyte membranes released from silicon substrate showed an increase of power density relative to membranes with planar electrolytes. Maximum power densities of the corrugated fuel cells of 677 mW/cm^2 and 861 mW/cm^2 were obtained at 400 and 450 °C, respectively.

Solid oxide fuel cells (SOFCs) have attracted attention because of their potential of achieving efficient energy conversion. SOFCs utilize a range of ceramic electrolyte materials, with yttria stabilized zirconia (YSZ) as the most common choice. Traditional SOFCs operate at relatively high temperatures (800−1000 °C) because of the low oxide ion conductivity and high activation energy for YSZ. Reducing the operating temperature is important to broaden the field of possible applications. However, reduction in temperature is accompanied by a decrease in ionic conductivity and power density.

This paper presents a method for fabricating a thin film SOFC featuring a three-dimensional corrugated catalyst/electrolyte membrane. The resulting increase in the electrochemically active area increased the power output relative to an equivalent cell with a flat membrane.

Expectedly, reducing membrane thickness can significantly reduce ohmic losses. A variety of thin film deposition techniques employed for this purpose has demonstrated the feasibility of synthesizing YSZ films with thicknesses ranging from 500 nm to 2 μm. Methods include pulsed laser deposition (PLD),[1] chemical vapor deposition (CVD),[2–4] spin coating,[5] and physical vapor deposition (PVD).[6] Free-standing YSZ membranes with minimum thickness of 500 nm were tested at 600 °C and delivered 145 mW/cm^2 peak power density.[7,8] To further decrease the thickness of membrane films operating at even lower temperatures, Huang et al. demonstrated reducing membrane thickness to 50 nm of YSZ deposited on silicon substrate by RF sputtering, thereby achieving power densities of 131 mW/cm^2 at 350 °C.[9] Recently, our laboratory also demonstrated the practical utility of atomic layer deposition (ALD) for fabricating thin film electrolytes.[10] In particular, it was successfully shown that ALD processing enables realization of pinhole free, surface conformable electrolyte membranes. Comparatively, high power densities we observed at these relatively low temperatures originate not only from reduced ohmic resistance but also from the high exchange current densities at the Pt catalyst/YSZ interface.

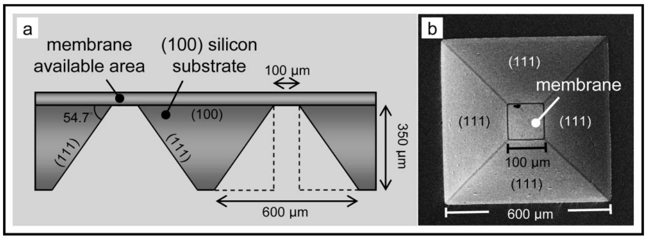

Figure 1. (a) Illustration of poor surface area utilization due to crystallographic constraints on KOH etching of (100) silicon substrate. (b) Membrane view from bottom. Four (111) planes confine the size of membrane. Percentage of surface utilization for 100 μm square membrane is only (100 μm)^2/(600 μm)^2 = 2.8%.

Despite such high power densities reported by Huang[9] and Shim,[10] the absolute power output of these cells was too low for practical use because of the small electrochemically active area. The largest stable free-standing membrane was about 100 μm by 100 μm, and the corresponding maximum power at 350 °C was only 27 μW. Such inefficient utilization of the membrane surface area, caused by the constraints imposed by wet etching of (100) silicon wafers, is illustrated in Figure 1.

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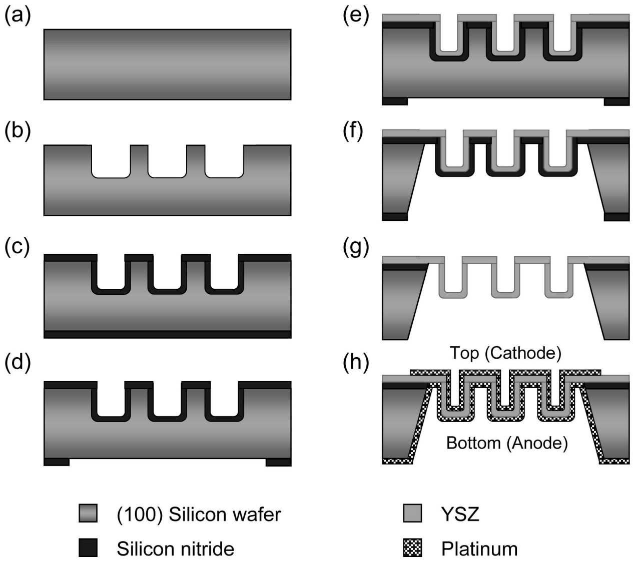

Figure 2. Process flow diagram for fabrication of the corrugated thin film SOFC. The (100) silicon substrate is etched by DRIE to generate the template for pattern transfer (a,b). A 100 nm thick silicon nitride layer is deposited with LPCVD on both sides of wafer (c). The backside of silicon nitride is patterned with openings (d), followed by ALD deposition of YSZ onto template (e). Silicon template is etched in KOH (f) and silicon nitride etch stop is removed by plasma etching (g). The free-standing corrugated electrolyte is deposited with porous platinum on top (cathode) and bottom (anode) sides acting as both electrode and catalyst.

In the present study, an advanced method is introduced to increase effective surface area density by creating corrugated YSZ electrolyte films. The corrugated electrolyte is generated by a pattern transfer technique. YSZ electrolyte is first deposited onto a template that is prepatterned with the desired shape and geometry. The deposited YSZ replicates the shape of the patterned silicon "mold". A portion of the silicon substrate is subsequently removed, releasing a free-standing YSZ membrane. The challenge of the present method rests with achieving film conformality and thickness uniformity, and avoiding pinholes in the electrolyte film, which inevitably would result in voltage losses. ALD deposition is capable of producing pinhole free films.[10] However, observations indicate that pinhole free membranes can be consistently fabricated only if the underlying template avoids sharp corners and if the surface roughness is less than the membrane thickness.

Membrane fabrication is carried out employing a sequence of MEMS processing steps shown in Figure 2. A four inch, 350 μm thick, (100) n-type silicon wafer is used to generate the template. One side of the silicon surface is patterned by standard photolithography and deep reactive ion etching (DRIE) to create cup-shaped trenches with smooth cup side wall surface. The trench depth ranges from 10 to 40 μm. A 100 nm thick low stress silicon nitride is deposited on both sides of the wafer with low pressure chemical vapor deposition (LPCVD). On the opposite side to the etched trenches, the silicon nitride layer is patterned to generate square openings for subsequent silicon etching. Next, ALD technique is applied to deposit the ultrathin YSZ electrolyte. The ALD YSZ layer coats the prepatterned surface geometry and forms a corrugated film. The film composition is produced by depositing 7 zirconia ALD cycles and 1 yttria cycle as one unit, for a total of 125 units. The thickness is approximately 70 nm.[10] To release the YSZ membrane, the silicon substrate is immersed into 30 wt % KOH solution for 5 h at 85 °C until the etching stops at the silicon nitride

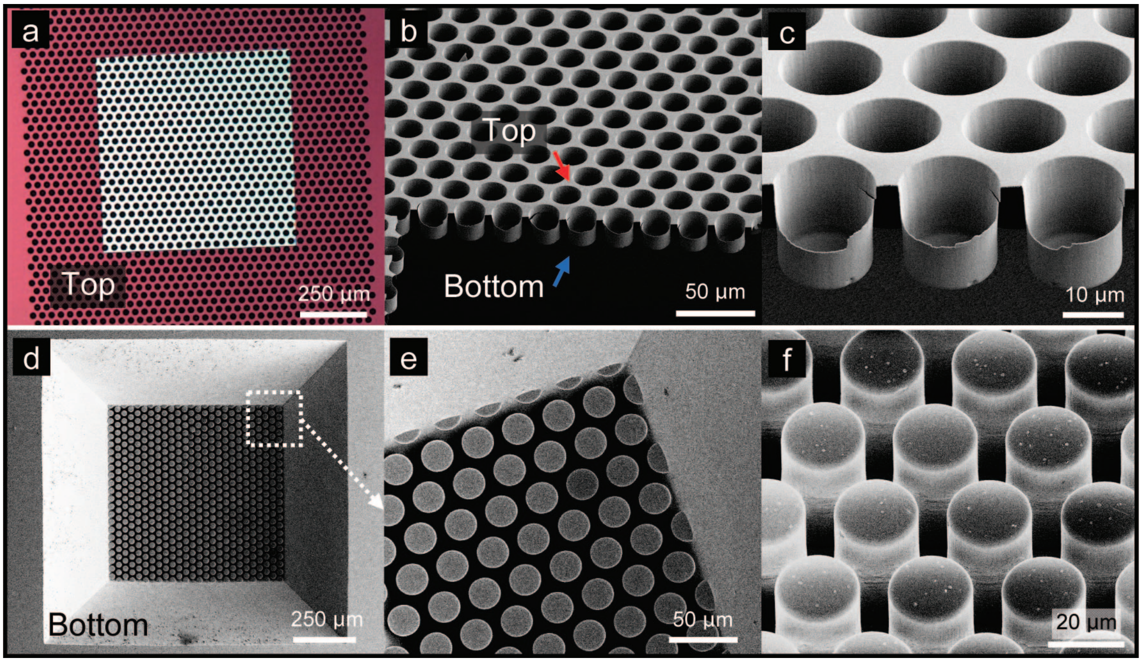

Figure 3. Images of corrugated YSZ membrane, view from top (a−c) and bottom (d−f). (a) Optical microscopy image of free-standing corrugated YSZ membrane. The white square in the middle is the free-standing YSZ membrane released after KOH etching. The black dots represent cup-shaped trenches. (b,c) Cross section of cups in corrugated membrane. (d) Bottom view of membrane after silicon removal. (e) Bottom corner view of membrane, (f) perspective after tilting 40°.

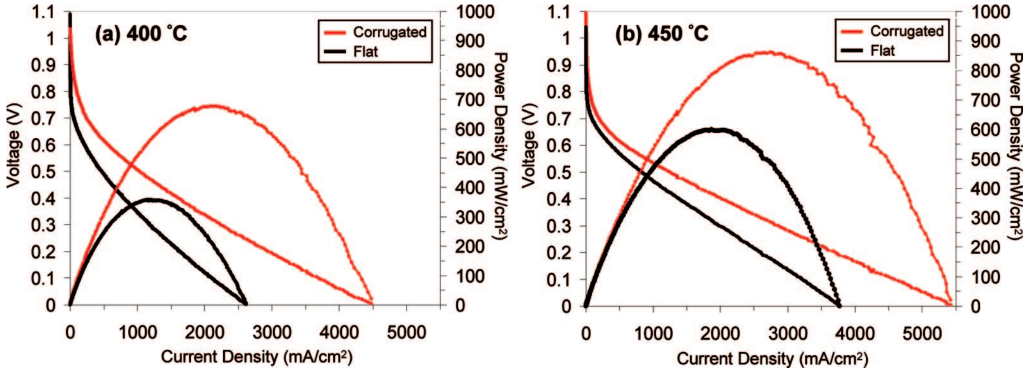

Figure 4. Fuel cell performance of corrugated (red line) and flat (black line) YSZ electrolyte at (a) 400 °C and (b) 450 °C. The membrane size is 0.0036 cm^2 (600 μm × 600 μm). The size of the cups embedded is 15 μm in diameter and 20 μm in depth. Maximum power densities of corrugated YSZ are slightly less than two times that of flat ones.

layer. During etching, a custom-made wafer holder is used to protect YSZ from KOH solution. The YSZ membrane release is completed by removing the silicon nitride layer underneath with plasma etching. At last, the fuel cell structure is finished by DC magnetron sputtering of 120 nm thick porous Pt electrode/catalyst on both sides of the free-standing YSZ membrane. The deposition is carried out at a partial pressure of 10 Pa Argon, and 100 W of power at room temperature. The resulting pore size is of the order of 100 nm. We estimate volume fraction of resulting porosity between 30∼40%.[9]

The corrugated YSZ electrolyte structure fabricated in this manner is shown in Figure 3, with a−c showing plan view of the membrane from the top and d−f showing plan view of the membrane from the bottom. In Figure 3a, the white square in the optical microscopy image represents the free-standing YSZ membrane with cup-shaped corrugation. The purple part next to the membrane represents the YSZ film lying on the template that is not released by the etching. The aerial dimensions of the YSZ membranes range from 600 μm to 2 mm, significantly larger than the 100 μm × 100 μm flat membranes reported earlier.[9,10] The square-shaped YSZ membranes are stable and free-standing, with a thickness of 70 nm. Thus, the corrugated membrane design allows surface utilization to increase by 30% to 64% based on projected area. No buckling of the membrane from intrinsic stress is observed. Figure 3b,c shows the SEM images of the cross-sectional view of the corrugated membrane. The depth of the cups shown here is 20 μm and the diameter is 15 μm. Figure 3d shows the SEM image of the bottom of the membrane. The zoom-in image and a tilted view of the cups are shown in e and f, respectively. In comparing with a flat membrane, the added surface area originates from the sidewall of the cups. Depending on the dimensions of cups, the active surface may be increased two to five times of the projected area occupied by the free-standing membrane alone.

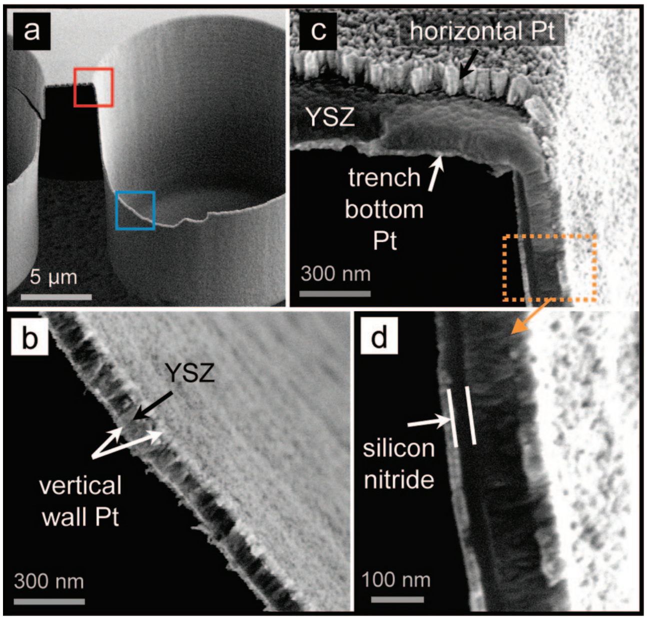

Figure 5. (a−c) SEM images illustrating thickness variation of sputtered platinum layers at different sections of the membrane. (a) The blue frame and red frame are shown in b and c, respectively. (d) The enlarged image of the vertical part in c shows incomplete removal of silicon nitride on the vertical wall.

Fuel cell performance of the corrugated membrane is tested in a fixture similar to that described earlier.[9,10] The fuel was pure hydrogen stream supplied to the anode, while the cathode was exposed to ambient air as oxidant. The OCV at 400 and 450 °C, was in a range between 1.03 and 1.09 V. Comparative performance measurements between flat and corrugated membrane geometries with the same projected area were made at 400 and 450 °C. As expected, substantial increase of power due to addition of surface area is observed. This is shown in Figure 4. The size of both flat and corrugated membrane measured in this result is 0.0036 cm^2 of projected area (600 μm × 600 μm), and the depth of cups in the corrugated membrane is 20 μm. At 400 °C, the maximum power density of the corrugated membrane is 677 mW/cm^2, which is 1.9 times that of the flat membrane (358 mW/cm^2); at 450 °C, the corrugated membrane generates 861 mW/cm^2, which is 1.5 times that of the flat membrane (597 mW/cm^2). Total power output is 2.44 mW and 3.10 mW at 400 and 450 °C, respectively. The electrochemically active surface area is approximately five times that of the projected area. Accordingly, a 5-fold increase of power density is expected. However, the observed increase of power density from the flat to the corrugated membrane is slightly less than a factor of 2. At least two possible causes may be responsible for a reduction in the active surface area and lower than expected cell performance: First is the nonuniformity in the thickness of the sputtered electrode/catalyst layer due to shadowing effects and limited access inside the trenches. Figure 5b,c compares and shows thickness variations between the platinum catalyst layer on planar, horizontal sections versus those on vertical walls and deep trenches. Such variations may cause deviations in electrical conduction and electrochemical behavior relative to planar membrane sections. Furthermore, incomplete removal of silicon nitride may also block portions of the electrochemically active area and render it inactive. Indeed, Figure 5d depicts such a residue of silicon nitride, close to trench corner.

Despite inherent difficulties, observed power densities normalized by projected area are, nevertheless, believed to be the highest achieved in the literature to date. Continuing work on improving conformal coverage of the platinum electrode/catalyst on corrugated YSZ and fully utilizing all available surface area for the charge transfer reaction is expected to achieve even higher performance in the future.

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