Thin film, solid-oxide fuel cells (TFSOFCs) are developed using photolithographic patterning and physical vapor deposition. In this study, both electrode layers of nickel (Ni) and silver (Ag) as well as the solid-oxide electrolyte layer of yttria-stabilized zirconia (YSZ) are synthesized on the micrometer scale for thickness. The anode layer enables combination of the reactive gases, is conductive to pass the electric current, and provides mechanical support to the electrolyte and cathode layers. The morphology desired for both the anode and cathode layers facilitates generation of maximum current density from the fuel cell. For these purposes, the parameters of the deposition process and post-deposition patterning are optimized for continuous porosity across both electrode layers. The electrodes are characterized using scanning electron microscopy and the power output generated through current-voltage measurement. We find that a TFSOFC based on Ni-YSZ-Ag can be operated with dilute fuel mixtures at temperatures below 300 °C.

INTRODUCTION

Miniature fuel cells have recently experienced renewed interest for applications in portable power generation. Simply put, fuel cells store energy as a fuel rather than as an integrated part of the system which is the case for batteries. Therefore, fuel cells can potentially exhibit significantly higher energy densities. Present applications in portable power include the full range of consumer electronics, as cell phones, laptop computers, video camcorders, and radios. New applications in portable power span the range of power consumption from micro, as in long duration sensors and remote communication devices, to macro as in light-weight packages for use in the field. We propose that solid-oxide fuel cells based on thin film technology can address the need for power generation from the micro to macro range.

A solid-oxide fuel cell (SOFC) device is comprised of cell stacks that combine a fuel and oxidant at elevated temperatures to generate electric current. Each fuel cell is based on an anode and cathode separated by an electrolyte layer. SOFCs are usually made using bulk ceramic powder processing and synthesis approaches as layering an electrode on an electrolyte on a cermet electrode substrate.(1) Traditionally, SOFCs are operated at temperatures in excess of 900°C. A reduction in the operating temperature can be achieved by decreasing the diffusion path of the oxygen ions in the solid-state, i.e. reducing the electrolyte layer thickness. To decrease the electrolyte layer thickness below that obtainable using techniques as tape calendaring, thin ceramic films can be fabricated by a variety of methods including sol-gel and colloidal deposition.(2) Additionally, even thinner electrolyte layers can be formed by physical vapor deposition from metal alloy targets to optimize ion conductivity and by rf magnetron sputtered from oxide targets to form continuous coatings on porous substrates.(3-5)
A decrease in the electrolyte thickness from 0.10 mm to less than 10 μm for a fuel cell based on yttria-stabilized zirconia (YSZ) lowers the operating temperature by several hundred degrees centigrade.(6,7) Although a thin electrolyte layer can be deposited onto an electrode, a bonding procedure is still required to attach the counterpart electrode and form the unit cell of the anode-electrolyte-cathode trilayer. To address the problem of resulting polarization losses at the electrode-electrolyte interface(s), composition graded and compound layers can be added at both the anode and cathode sides of the electrolyte to reduce interfacial reaction resistances. For example, simultaneous deposition of the electrode and electrolyte species can be applied to produce a graded interfacial transition at both anode and cathode sides.(7) Alternatively, yttria-stabilized Bi₂O₃ can be added at the cathode-side and yttria-doped CeO₂ added at the anode-side of the yttria-stabilized zirconia (YSZ) electrolyte layer.(8,9)

There are certainly advantages for using chemical and physical vapor deposition methods to produce either the electrolyte layer or the electrodes. A clear advantage exists to explore an additional synthesis method to form the anode-electrolyte-cathode trilayer as through an integrated-circuit process. In addition to the use of sputter deposition to form electrolyte thin films, we investigate use of vapor deposition combined with standard lithographic patterning and several etching processes to form both a “porous” base anode and top cathode for improved gas flow, eased reaction kinetics, and structural support. Specifically, we examine the use of nickel (Ni) for the anode, YSZ for the electrolyte, and silver (Ag) for the cathode to form a thin film, solid-oxide fuel cell (TFSOFC).

**EXPERIMENTAL**

The use of thin film deposition, patterning and etching processes provide a direct path to synthesis of a stackable or singular fuel cell on a chip. The deposition sequence starts with the anode followed by the electrolyte and concludes with the cathode. The thin-film fuel cell must eventually have exposed free-standing region(s) suitable for manifolded gas transport from both the fuel and oxidant supplies. A schematic of the TFSOFC design with these features is shown in Figure 1. The side view shows the layer sequence to the fuel cell. An etchable substrate and removable membrane layer provide the platform for the free-standing anode-electrolyte-cathode trilayer. A top view shows the circuit tabs that access electronic integration from the anode and cathode.
The procedure for preparing the substrate platform is reviewed in brief. A thin layer of silicon nitride is grown on a substrate wafer using a low pressure chemical vapor deposition process. The 0.22 μm thick film is formed at 800°C using 112 cm³ m⁻¹ flow of dichlorosilane and 30 cm³ m⁻¹ flow of NH₃ at 33 Pa. The backside of the substrate wafer is patterned by standard photolithographic techniques and etched to reveal windowed regions of silicon nitride (SiN) with areas that range from 0.14 to 16 mm² in size. An example is seen in Figure 2 for 2 mm x 2 mm SiN windows. The substrate is etched at a rate of 1 μm mm⁻¹ using 44% KOH at 85°C. A reactive ion etch rate of 0.42 μm mm⁻¹ is achieved during nitride removal using 500 W of power with a 2.7 Pa pressure at a 40 cm³ m⁻¹ flow of CHF₃ and a 80 cm³ m⁻¹ flow of CF₄.

The sequence of deposition process steps to synthesize the fuel cell trilayer is reviewed as follows. The sputter deposition chamber is evacuated to a base pressure of 5.3 x 10⁻⁶ Pa. The substrate wafer is positioned 10 cm from the array planar magnetron sources. A 10 Pa sputter gas pressure of Ar at a constant flow of 30 cm³ m⁻¹ is used to operate the magnetron sources. The deposition begins by sputtering Ni at 4.2 W cm⁻² power to yield a 9.3 nm m⁻¹ rate for a layer thickness of 0.5 μm. After deposition of the Ni anode film, pores are formed in the layer to enhance gas flow to the electrolyte and effectively control an increase in the area of the catalyst-electrolyte interface. Pores are fabricated using photolithographic techniques to define an array of cylindrical vias in a photoresist mask. The present pattern creates 3 to 5 μm diameter vias having 3 μm spacings. After developing the photoresist to form the template, the pattern is then etched into the Ni layer. The etching procedure utilizes H₂O: HNO₃ (20:1) at 45 °C. This results in a nominal etch rate of 1000 Å m⁻¹. Figure 3 illustrates a scanning electron micrograph of the resulting anode structure prior to deposition of electrolyte and cathode layers. The continuous anode matrix provides the path for sufficient electrical conductivity while the array of pores formed in the anode enables the diffusion of reaction product species to sustain the generation of electrical current. Further increase in pore density can be readily achieved using advanced lithographic and etch techniques.

Synthesis of a dense, thin electrolyte layer is accomplished by rf-sputter deposition of a (Y₂O₃)₅.₆(ZrO₂)₉₄.₄ target. A defect-free electrolyte layer of cubic YSZ is confirmed through transmission electron microscopy (TEM) using plan-view bright-field imaging and selected-area electron diffraction. Thus, the deposition process for the TFSOFC continues as the YSZ target is sputtered at 38.2 W cm⁻² power to yield a 10.6 nm m⁻¹ rate. Ni and YSZ are co-deposited to form a anode-electrolyte interface that is 25
Figure 3. A top view of the 0.5μm thick Ni anode layer as imaged using scanning electron microscopy at higher magnification.

nm thick. The YSZ target is then sputtered alone to yield an electrolyte layer that is 2.5 μm thick. The Ag target is sputtered at 4.2 Wcm⁻² power to yield a 33.3 nm/min⁻¹ rate. YSZ and Ag are co-deposited to form the electrolyte-cathode interface that is 25 nm thick. Lastly, a porous Ag cathode is deposited to a layer thickness of 0.85 μm and/or as applied via a Ag contact mesh to complete the fuel cell, unit trilayer.

The measurement of power requires that the active area of the thin film cell be free-standing. After the sputter deposition process is completed, the thin nitride windows are removed by reactive-ion etching to expose the active fuel cell anode over a well-defined area. The fuel cell is mounted in a manifolded test fixture (shown in Figure 4), loaded into a furnace and heated to >300 °C at a 3 °C/min⁻¹ rate. A thermocouple is attached to the fuel cell manifold assembly. The current versus cell potential of the TFSOFC is measured using a galvanostat. The current output is recorded as voltage is loaded in 25 mV increments. An Ar-20%O₂ mixture is supplied as the oxidant to the cathode and a humidified Ar-4%H₂ mixture is supplied as the fuel to the anode. A continuous flow of both gases at 0.6 cm³/min⁻¹ with a backflow pressure of 0.0025 atm (equivalent to 0.036 psi as achieved using 1” of H₂O) is maintained during testing. These specific nominal gas flows may not maximize cell performance over this temperature range.

RESULTS

The output from a TFSOFC is measured as tested to temperatures in excess of 300 °C. An open circuit voltage (OCV) of 0.8 V is achieved at 316 °C (shown in Figure 5). In fact, power output from this fuel cell is seen at temperatures as low as 214 °C. The maximum current output of 0.42 mA for TFSOFC at 316 °C corresponds to a current density of >11 mA/cm² as based on an estimate of the sample test area. The maximum power of 0.15 mW (corresponding to an estimated power density of 3.8 mW/cm²) is found at a current of 0.3 mA. The OCV is less than the optimal value of 1.1 V but is consistent with a low impedance often found for very thin electrolyte layers. The non-linear behavior in current vs. cell potential seen at higher currents may indicate that the cell is receiving an insufficient flow of the reactant gases. No attempt to optimize gas flow or composition is made in these preliminary tests.

In comparison, testing of a similar Ni-YSZ-Ag trilayer as deposited with continuous, i.e. “non-porous”, Ni anode and Ag cathode layers (7,11) did not yield any measurable
current output at the present, low operating temperatures. Prior test results with the “non-porous” electrodes indicated a 39 mW cm\(^{-2}\) power output at 400 °C. Similarly, SOFCs composed of a Ni-YSZ anode, a La\(_{0.85}\)Sr\(_{1.5}\)MnO\(_3\)-YSZ cathode, and deposited electrolyte layers of YSZ (or YSZ with yttria-doped ceria) generated power only at temperatures of 500 °C or more.\(^{(12)}\) The low temperature of operation for the present TFSOFC is indeed remarkable.

**SUMMARY**

Thin film deposition in combination with photolithographic patterning and etching technologies provide a means to synthesize thin-film solid-oxide fuel cells (TFSOFCs) on a thin wafer platform, i.e. a miniature fuel cell on a silicon chip. The TFSOFC can potentially yield greater specific power than found in any other available fuel cell configuration and is an ideal candidate for power generation from the micro to macro range. The TFSOFC substrates were patterned and processed to reveal well-defined windowed regions. The “porous” anode layer provides a base electrode that eases gas flow, gas reaction, and provides a stable conducting support structure. The current-voltage and power output from the fuel cell is measured using a dilute hydrogen fuel and oxygen gas mixtures. The TFSOFC deposited with porous electrodes yields power output at low (<300 °C) operating temperatures unlike all other fuel cells based on a YSZ electrolyte layer.

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Figure 5. The measured current (mA) versus potential (V) and power (mW) output of the TPSOFC.

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