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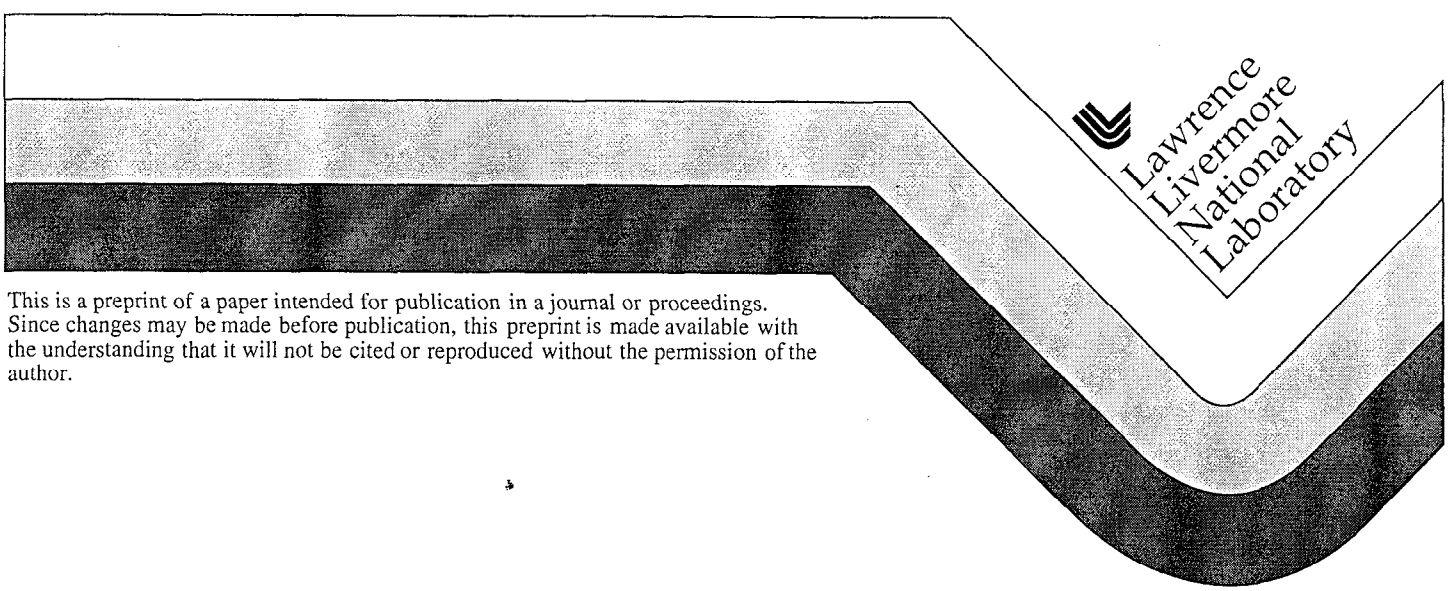

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A NOVEL THIN FILM SOLID OXIDE FUEL CELL FOR MICROSCALE ENERGY CONVERSION

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ABSTRACT

A novel approach for the fabrication and assembly of a solid oxide fuel cell system is described which enables effective scaling of the fuel delivery, manifold, and fuel cell stack components for applications in miniature and microscale energy conversion. Electrode materials for solid oxide fuel cells are developed using sputter deposition techniques. A thin film anode is formed by co-deposition of nickel and yttria-stabilized zirconia (YSZ). This approach provides a mixed conducting interfacial layer between the nickel electrode and electrolyte layer. Similarly, a thin film cathode is formed by co-deposition of silver and yttria-stabilized zirconia. Additionally, sputter deposition of yttria-stabilized zirconia thin film electrolyte anables high quality, continuous films to be formed having thicknesses on the order of 1-2 μm. This will effectively lower the temperature of operation for the fuel cell stack significantly below the traditional ranges at which solid oxide electrolyte systems are operated (600°-1000°C), thereby rendering this fuel cell system suitable for miniaturization. Scaling towards miniaturization is accomplished by utilizing novel micromachining approaches which allow manifold channels and fuel delivery system to be formed within the substrate which the thin film fuel cell stack is fabricated on, thereby circumventing the need for bulky manifold components which are not directly scalable.

Methods to synthesize anodes for thin film solid-oxide fuel cells (TFSOFCs) from the electrolyte and a conductive material are developed using photolithographic patterning and physical vapor deposition. The anode layer must enable combination of the reactive gases, be conductive to pass the electric current, and provide mechanical support to the electrolyte and cathode layers. The microstructure and morphology desired for the anode layer should facilitate generation of maximum current density from the fuel cell. For these purposes, the parameters of the deposition process and post-deposition patterning are developed to optimize a continuous porosity in the anode layer. The fuel cell microstructure is examined using scanning electron microscopy and the power ouput generated is characterized through current-voltage measurement. Results demonstrating the generation of electrical current in the temperature range of 200-400°C for a thin film solid oxide fuel cell stack fabricated on a silicon wafer will be presented.

INTRODUCTION

A solid-oxide fuel cell (SOFC) device consists of manifolded stacks of cells which combine a fuel and oxidant at elevated temperatures to generate electric current. The basis of each fuel cell is an anode and cathode separated by an electrolyte layer. SOFCs provide an efficient and enviromentally clean method of energy conversion. SOFCs are routinely made using bulk ceramic powder processing.[1] A traditional synthesis approach uses a cermet electrode on which an electrolyte is layered, for example, by tape casting. The unit cell is completed by lamination to the counterpart electrode. SOFCs are traditionally operated at temperatures exceeding 900°C.

[1] N. Minh, J. American Ceramic Society 76, 563 (1993).

The common approach to incorporate thin film technologies in SOFCs is based on coating the cermet electrodes with an electrolyte layer. To decrease the thickness below that obtainable using tape calendaring, thin ceramic films can be deposited by a variety of techniques including variations of sol-gel and colloidal deposition.[2] In addition, thin electrolyte layers can be dc magnetron sputtered from metal alloy targets to optimize ion conductivity and rf magnetron sputtered from oxide targets to form continuous coatings on porous substrates.[3-5]

A thin electrolyte reduces the path for oxygen ion diffusion. A decrease in the electrolyte thickness from ~100 μm to <10 μm can potentially lower the fuel cell operating temperature by several hundred degrees centigrade.[6] 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. This process always leads to polarization losses at the electrode-electrolyte interface(s). To address this problem, interfacial layers can be added at both the anode and cathode sides of the electrolyte to reduce interfacial reaction resistances.[7,8] For example, yttria-stabilized Bi_2O_3 is added at the cathode-side and yttria-doped CeO_2 is added at the anode-side of the yttria-stabilized zirconia (YSZ) electrolyte layer.

Thin film processing can be used to produce alternative cermet electrodes.[9,10] Anodes for a YSZ electrolyte can be synthesized as thin wafers. For example, the anode wafers can be sintered compacts of Ni-coated zirconia powder. Metal coating the zirconia powder uniformally distributes the conducting element of the electrode. Sufficient electrical conduction is provided while reducing the metal content to <10 volume percent ensuring a near match in coefficient of thermal expansion to the electrolyte. In comparison, bulk cermet processing involves sintering a powder composite that often contains >30 volume percent metal. The high metal content is needed to yield sufficient conductivity a elevated temperature but often leads to a delamination failure when subjected to routine thermal-cycling.

Chemical and physical vapor deposition methods are shown to be advantageous to produce either the electrolyte layer or the electrodes. A clear advantage exists to explore additional methods to form the anode-electrolyte-cathode trilayer through an integrated synthesis process. In addition to the use of vacuum deposition to form electrolyte thin films, we investigate the use of sputter deposition to form both electrodes as thin films and to provide a composition graded electrode-electrolyte interface for improved kinetics. We will examine electrode materials for a SOFC based on a YSZ electrolyte that is compatible with low temperature (< 700°C) operation. Specifically, nickel (Ni)-YSZ is selected for the anode and silver (Ag)-YSZ for the cathode. Furthermore, this SOFC stack is fabricated on a silicon wafer having micromachined cavities to form free standing membranes. The specific fuel cell structure described has advantages over alternative fuel cell designs for the purpose of scaling and miniaturization.

EXPERIMENTALS

The use of thin film deposition enables the fuel cell unit to be synthesized in a continuous process. A sequential deposition starting with the anode and concluding with the cathode bridges the difficulties of joining electrolyte-coated electrodes (e.g. anodes) to counterpart electrodes (e.g. cathodes). The electrodes are formed as metal and ceramic composites by the co-sputter deposition of targets operated in the dc and rf modes, respectively. The ceramic material chosen for the electrode matrix is the same as that used for the vapor deposition of the electrolyte layer. Synthesis of a dense, thin electrolyte layer is established by the rf-sputter deposition of a $(Y_2O_3)_{5.6}(ZrO_2)_{94.4}$ target.[5] 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.

To synthesize a thin film fuel cell with an exposed free-standing region suitable for subsequent testing, a brief review of the substrate platform preparation is necessary. A thin layer of silicon nitride is grown using a low pressure chemical vapor deposition process. The 0.22 μm thick film is formed at 800°C using a 112 cm^3m^{-1} flow of dichlorosilane and a 30 cm^3m^{-1} flow of NH_3 at 33 Pa. The backside of the substrate wafer is patterned by standard photolithographic techniques and etched to reveal windowed regions of silicon nitride with areas having 4 mm^2 in size. The substrate is etched at a

[2] S. deSouza, S. Visco and L. DeJonghe, Solid State Ionics **98**, 57 (1997).

[3] E. Thiele, L. Wang, T. Mason and S. Barnett, J. Vac. Sci. Technol. A 9, 3054 (1991).

[4] A. Jankowski and J. Hayes, Surface and Coatings Technology **76-77**, 126 (1995).

[5] A. Jankowski and J. Hayes, J. Vac. Sci. Technol. A **13**, 658 (1995).

[6] S. Barnett, Energy **15**, 1 (1990).

[7] L. Wang and S. Barnett, J. Electrochemical Society **139**, 2567 (1992); ibid., **139**, L89 (1992).

[8] L. Wang and S. Barnett, Solid State Ionics **61**, 273 (1993).

[9] A. Jankowski, Internat. J. Environmentally Conscious Design & Manufacturing 5, 39 (1996).

[10] A. Jankowski, in Ionic and Mixed Conducting Ceramics III, edited by T. Ramanarayanan (The Electrochemical Society Proceeding Series PV-24, Pennington, NJ, 1997) in press.

rate of 1 μmm^{-1} using 44% KOH at 85°C. The result is a free standing silicon nitride window suitable for deposition of the fuel cell stack materials.

The sequence of deposition process steps to synthesize the fuel cell unit is reviewed as follows. The sputter deposition chamber is evacuated to a base pressure of 5.3 x 10^{-6} Pa. The substrate is positioned 10 cm from an array of three planar magnetron sources. The deposition begins by sputtering Ni at 4.2W/cm^2 power to yield a 9.3nm/min rate for a layer thickness of 0.5 μm.

The deposition process continues as the YSZ target is sputtered at 38.2 W/cm^2 power to yield a 10.6 nm/min rate. Ni and YSZ are co-deposited to form a anode-electrolyte interface that is 25 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 W/cm^2 power to yield a 33.3 nm/min 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 structure.

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. A reactive ion etch rate of 0.42 μm/min is achieved during nitride removal using 500 W of power with a 2.7 Pa pressure at a 40 cm^3/min flow of CHF_3 and a 80 cm^3/min flow of CF_4. This results in a final free standing fuel cell membrane structure as schematically shown in Figure 1.

The current vs. cell potential is measured as the TFSOFC is incrementally voltage loaded using a galvanostat. An Ar-20%O_2 mixture is supplied as the oxidant to the cathode and a humidified Ar-4%H_2 mixture is supplied as the fuel to the anode. A continuous flow of both gases at 0.6 cm^3/min with a backflow pressure of 0.0025 atm (equivalent to 0.036 psi as achieved using 1" of H_2O) is maintained during testing. The fuel cell, as furnace mounted in a manifolded test fixture, is heated at a 3°C/min rate. A thermocouple is placed in contact with the fuel cell manifold.

RESULTS

A thin-film solid-oxide fuel cell (TFSOFC) consisting of a Ni anode, a YSZ-electrolyte, and a Ag cathode is formed through the continuous deposition process described. Scanning electron microscopy

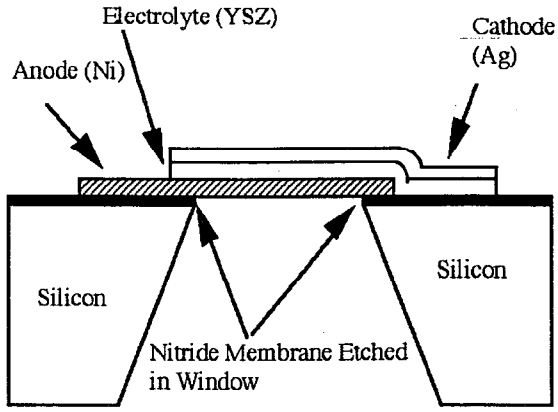

Fig. 1. Schematic diagram of thin film solid oxide fuel cell on micromachined silicon substrate.

indicates that the electrolyte and electrode layers appear continuous both in-plane and through the growth direction. As mentioned, interfacial layer additions or a composition-graded electrolyte-electrode interface can be added to improve the fuel cell performance by enhancing catalytic activity.

The output from a TFSOFC is measured as tested to temperatures in excess of 300 °C. An open circuit voltage (OCV) approaching 0.8 V is achieved at only 316 °C (shown in Figure 2). In fact, output from this cell is seen at temperatures as low as 214°C. The maximum current output of 0.42 mA for this cell at 316°C corresponds to a current density of >11 $mAcm^{-2}$ as based on the estimated test area. The maximum power of 0.15 mW (corresponding to an estimated power density of 3.8 $mWcm^{-2}$) is found at a current of 0.3 mA, as illustrated in the cell power vs. current plot in Figure 3. The OCV is less than the optimal value of 1.1 V but is consistent with an intrinsically low impedance 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 SOFCs composed of a Ni-YSZ anode, a $La_{.85}Sr_{.15}MnO_3$-YSZ cathode, and deposited electrolyte layers of YSZ (or YSZ with yttria-doped ceria) generated power at temperatures of 500 °C or more.[11,12] The low temperature of operation for the present TFSOFC is conducive with scaling and miniaturization.

[11] T. Tsai, E. Perry and S. Barnett, J. Electrochemical Society **144**, L130 (1997).

[12] A. Atkinson, in Proceedings of the Second European Solid-Oxide Fuel Cell Forum, edited by B. Thorstensen (The Electrochemical Society, Pennington, NJ, 1996) p. 707.

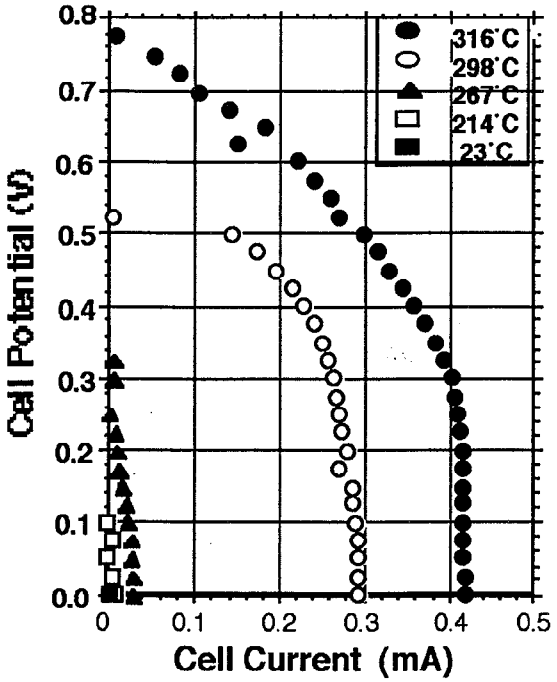

Fig. 2. Current vs voltage output from the thin film solid oxide fuel cell.

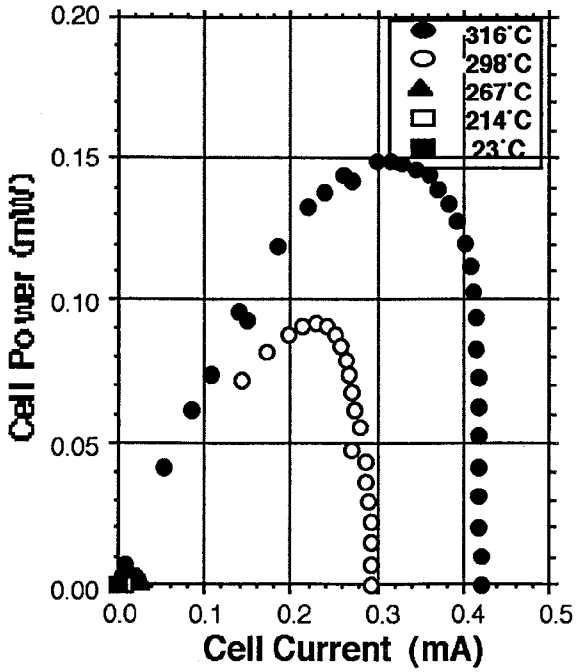

Fig. 3. Resulting output power vs. current from the thin film solid oxide fuel cell at various temperatures.

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 fuel cell on a silicon chip. The TFSOFC can potentially yield greater specific power than found in any other available fuel cell configuration. Substrates were patterned and processed to reveal well-defined windowed regions. The current-voltage and power output from the fuel cell is measured using a dilute hydrogen fuel and oxygen gas mixtures. The TFSOFC deposited on the porous Ni anode yields power output at low (<300°C) operating temperatures unlike all other SOFCs based on a YSZ electrolyte.

ACKNOWLEDGMENTS

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