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Journal of the European Ceramic Society 32 (2012) 3229–3238

www.elsevier.com/locate/jeurceramsoc

Processing of Foturan® glass ceramic substrates for micro-solid oxide fuel cells

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Received 4 October 2011; received in revised form 23 March 2012; accepted 1 April 2012
Available online 12 May 2012

Abstract

The microfabrication of Foturan® glass ceramic as a potential substrate material for micro-solid oxide fuel cells (micro-SOFC) was investigated. Foturan® was etched in 10% aqueous hydrofluoric (HF) acid solution at 25 °C with a linear rate of 22 ± 1.7 µm/min to create structures with an aspect ratio of 1:1 in 500 µm-thick Foturan® substrates for micro-SOFCs. The concentration of the HF etchant was found to influence the etching rate, whereas the UV-exposure time creating nuclei in the glass for subsequent crystallization of the amorphous Foturan® material had no significant influence on the etching rates. The surface roughness of the crystallized Foturan® was determined by the crystallite size in the order of 10–15 µm. Free-standing micro-SOFC membranes consisting of a thin film Pt cathode, an yttria-stabilized-zirconia electrolyte and a Pt anode were released by HF etching of the Foturan® substrate. An open-circuit voltage of 0.57 V and a maximum power density of 209 mW/cm^2 at 550 °C were achieved.

Keywords: Foturan®; Photostructurable glass ceramic; HF etching; Micro-solid oxide fuel cell; Micro device

1. Introduction

The demand for micro-electro-mechanical-systems (MEMS) and micro-electro-ceramic-systems (MECS) with short response times and high functionality has increased in the last years. Microfabricated planar micro-solid oxide fuel cell (micro-SOFC) systems are considered as promising battery replacements due to their high energy density and specific energy.[1–3] The heart of these micro-SOFC systems consists of a less than 1 µm thin free-standing ionic-conducting ceramic membrane that is integrated on a microstructurable substrate.[2,4–16] Up till now, the integration of micro-SOFC membranes in portable electronics is still under investigation. Recently, the proof-of-concept for such micro-SOFC membranes based on thin film technologies and microfabrication was demonstrated by several research groups.[2,4–16]

Possible substrates for micro-SOFC membranes are silicon or glass ceramic such as Foturan®. The former approach is adopted from typical silicon processing and was used to support free-standing micro-SOFC membranes.[4,13–16] The latter approach is based on direct structuring of Foturan® which is a photosensitive Li_2O–Al_2O_3–SiO_2 glass ceramic.[2,12]

Foturan® glass can be structured for a variety of purposes. This material combines the properties of glass and the opportunity to achieve very fine structures with tight tolerances and high aspect ratios (hole depth/hole width) by chemical etching. The Foturan® surface is masked and exposed to UV light in order to initiate seeds in the glass for the later crystallization by thermal treatment. During the subsequent annealing in the temperature range of 500–600 °C, the nuclei in the UV-exposed areas initiate crystallization of the glass. The crystalline regions, when etched with a 10% aqueous HF acid solution at room temperature, have an etching rate up to 20 times higher than that of the vitreous regions.[17–19] The advantage of a glass-ceramic substrate for the fabrication of a support for micro-SOFC membranes is its thermal expansion coefficient of $\alpha = 10.6 \times 10^{-6}\,K^{-1}$ (at 20 °C)[20] which is very close to that of the oxygen ionic-conducting ceramic thin films such as yttria stabilized zirconia with $\alpha = 10.8 \times 10^{-6}\,K^{-1}$ (between 20 °C and 800 °C).[21] The electrical resistivity of crystallized Foturan®

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0955-2219/$ – see front matter
http://dx.doi.org/10.1016/j.jeurceramsoc.2012.04.006

is $5.6 \times 10^{16}\,\Omega\,cm^{-2}$ [22] and, thus, Foturan® is electrically insulating.

The literature reports about the fabrication of holes, pits, cavities or channels with Foturan® substrates for applications such as micro fluidics, mechanics, optical and micro-total analysis systems (micro-TAS) applications.[23,24] The fabrication of free-standing membranes on Foturan® substrates was reported for the first time by Muecke et al. for the application of a micro-SOFC membrane.[12]

For the fabrication of free-standing membranes deposited on Foturan®, the exact etching times have to be known in order to avoid contact of the membrane with the etchant. A possible attack of adjacent layers during HF etching of Foturan® at 25 °C is discussed with respect to microstructural changes and the impact on the electrical conductivity in Refs. 25,26. It was found that the microstructures of gadolinia-doped-ceria thin films were attacked by HF, whereby the less crystalline films are more seriously affected. The electrical conductivity of the thin films becomes smaller due to contact with HF, but does not break down.[25,26] Kossoy et al. reported that yttria-stabilized-zirconia thin films are resistive toward HF attack.[27]

Dietrich et al. reported an etching rate of 10 μm/min for Foturan® structures larger than 500 μm in 10% HF. The minimal achieved feature size was holes with a diameter of 25 μm and a hole depth of 75–200 μm. Smaller feature sizes were not possible due to the size of the Foturan® crystals of about 10 μm which are formed during crystallization of the Foturan®. The authors point out that the minimum achievable hole diameter depends on the thickness of the substrate or the depth of the required structure.[18] Hülsenberg and Bruntsch reported on the tolerance of the size of holes etched into Foturan® wafers with different thicknesses.[28] They reported smallest achievable holes of 120 μm in diameter etched into plates with a thickness between 500 μm and 1 mm.[28] An etching depth of 0.4 mm after 8 min was observed with the use of an ultrasonic etching bath. For the same time without ultrasonication, the etching depth was only 0.15 mm.[29] Brokmann reported an etching rate for a feature size of 100 μm in diameter and a substrate thickness of 700 μm in an ultrasonic etching bath with 10% HF. The etching rate of 28 μm/min was determined for etching times between 1 and 4 min.[30] During the first minutes of wet etching of a 1 mm thick Foturan® substrate in 5% HF, Stillman et al.[31] found an average etching rate of 18.7 ± 2.2 μm/min for pit widths of 10–1280 μm for the first 3 min of etching. In a second experiment under the same conditions, a few plates with different outline widths could be released after 30 min, and all plates were released after 60 min. The authors expected the plates to be released after 27 min calculated from the maximum etching rate. The reason for the variation in the etching rates was due to a chemically inhomogeneous base material as well as the variation in the laser power from pulse to pulse in their experiments.[31]

In summary, Foturan® glass ceramic is a substrate material for the fabrication of holes or cavities with etching rates from 10 to 28 μm/min depending on the use of ultrasonication of the etchant concentration and the substrate exposure time.[18,28,31,32]

On the other hand, it was also reported that both, silicon and Foturan® are promising substrate candidates for fabricating power-delivering free-standing micro-SOFC membranes.[12,16] However, it is still unclear whether silicon or Foturan® glass ceramic is the best substrate material choice for this application, since both substrate materials have advantages and disadvantages with respect to SOFC application. Foturan needs high temperature annealing processes, which might damage thin films, it requires HF etching and it is known to be not fully homogeneous. Silicon, on the other side is electrically not insulating, it is not transparent and has a very different thermal expansion coefficient compared to the functional thin films used in the micro-SOFC membrane.

In this work, we thus studied in detail the processing of Foturan® glass ceramic with the aim of fabricating power delivering free-standing micro-SOFC membranes. Foturan® wafers are characterized and the influence of the wafer thickness, aspect ratio, UV-exposure time and etchant concentration on the etching characteristics is investigated. The fabrication of free-standing membranes on Foturan® substrates is critically discussed.

2. Experimental

All experiments were carried out on 4-in. Foturan® wafers with thickness of 250 μm and 500 μm provided by Mikroglas, Chemtech, Mainz, Germany.

2.1. Etching of the Foturan® substrate

The double-side polished, amorphous Foturan® substrates were covered by a 30 nm thick Cr adhesion layer and a 100 nm thick platinum layer with circular holes of 200 μm in diameter by sputtering. The Cr/Pt film is a hard mask acting as a protective layer during UV exposure. Both layers were deposited with a custom-made RF sputtering tool with 100 W, 3×10^{-3} mbar base pressure, 80 mm working distance through a 0.3 mm thick stainless steel mask and a working pressure of 2×10^{-3} mbar Ar. After deposition of the Cr/Pt layer, the wafer was irradiated using UV light (Electronic Visions Group AL 6-2, 312 nm, 500 W) for 1 h and 2 h, respectively at a distance of 5 cm. The Foturan® wafer was then cut with a dicing saw (Disco DAD 321, Tokyo, Japan) into 2.5 cm × 2.5 cm chips. For crystallization, the irradiated Foturan® chips were sandwiched between two alumina plates in order to avoid warping during annealing in air (Nabertherm controller P320, Lilienthal, Germany). Annealing was performed at a heating and cooling rate of 1 °C/min up to 500 °C and 600 °C with a dwell time at the highest temperatures of 2 h for complete crystallization of the UV-exposed Foturan®. The wafer piece was then covered by a HF protective photo resist coating (FSC-H, Rohm and Haas, Coventry, UK) on the Cr/Pt side in order to prevent double side etching. For this, the chip was first pre-baked on a hotplate at 120 °C for 30 min in order to remove adsorbed species and then the HF protective coating was brushed over the whole chip surface, followed by a post bake at 100 °C for 45 min on the hotplate.

For wet etching, the Foturan® chips were mounted horizontally in a custom made etch bath. In order to determine the wet