Concepts for micro-thrusters based on solid state ion conductors

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Abstract: We present two concepts for electric micropropulsion thrusters based on the ion conductor yttria stabilized zirconia (YSZ). One of the concepts is based on microfabricated YSZ membranes where oxygen from the gas phase out of a reservoir is incorporated in the form of ions at the YSZ surface and conducted through the membrane to the opposite surface where it is extracted as O⁻ and accelerated into vacuum. The other approach is based on an oxygen-rich thick YSZ film where the excess oxygen is extracted from the layer and accelerated into vacuum. First results of the realization of such devices are shown and the corresponding measurement set-ups for the characterization are discussed.

I. Introduction

As small thrusters with thrusts below 1 μ N gain more and more importance, new concepts are needed as conventional thruster concepts reach the technological limits of miniaturization. One such concept is the extraction of negative oxygen ions from the well-known ion conductor yttria stabilized zirconia (YSZ) and their acceleration by an electric field. YSZ is the material of choice due to its high ion conductivity and ease of production. It is widely used as electrolyte in solid state fuel cells or as an oxygen sensor material (lambda probe). In 1997 the group of Sadakata [1] demonstrated the extraction of oxygen ions from an YSZ sintered pellet and determined the type of extracted ions by mass spectrometry. Oxygen ion extraction from sintered YSZ material requires temperatures of about 1000 K and electrical field strengths between 300 and 1500 V/cm [1–5]. However, it is anticipated that the temperature and the field required for extraction can be considerably reduced using thin films of a suitable surface morphology. Such YSZ thin films can be prepared by rf-sputtering on silicon wafers or on fused silica substrates with an integrated heater mesh. Thus, the power consumption to achieve temperatures for effective ion conduction can be kept below 5 Watts.

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We are focusing on two thruster designs based on YSZ thick layers and YSZ membranes. The two designs differ in the type of oxygen supply. In the layer design the oxygen is provided by the excess oxygen within the thick YSZ layer whereas in the membrane design gaseous oxygen is provided from a reservoir in contact with the backside of the membrane.

The YSZ layer design consists of an YSZ layer sputtered onto a gold mesh which is used as a resistive heater. Photolithography followed by gold evaporation on a fused silica substrate is used for preparing the heater. The lateral dimension of this design is around 1.6×1.2 cm² with an active extraction area of 1 cm². Calculations based on values for bulk YSZ (ion current density: $2 \mu A/cm^2$) give a thrust of 36 nN at an extraction voltage of 2 kV for an active area of 1 cm². A thruster with an active area of 100 cm² should thus produce a thrust of 3.6 μ N. For the extraction of oxygen ions from the layer an external extraction grid is needed. We developed a setup for testing which allows one to easily mount the devices opposite to an extraction grid made of copper.

For the YSZ membrane thruster design we deposited YSZ layers on silicon wafers which were then etched from the backside at several positions to prepare free standing membranes. The typical size of a membrane is about $50 \times 50 \ \mu\text{m}^2$. To achieve a significant thrust they can be arranged in an array where many of them are operated in parallel. The heater in the test setup for the YSZ membranes is a metal halide lamp. While the fabrication of the YSZ layers for both designs is well established, the preparation of the membranes poses a severe challenge as they tend to break due to the strain in the deposited layer when the membrane reaches a critical lateral dimension. Even if they are not broken the bigger membranes (size about $80 \times 80 \ \mu\text{m}^2$) show deformation patterns visible under an optical microscope. This challenge can be overcome in square shaped membranes with lateral dimensions below $50 \times 50 \ \mu\text{m}^2$.

Another critical point is the measurement set-up for both types of samples because the measurement of such low thrusts and extraction currents is rather challenging.

We present the fabrication of the two different designs, the results from theoretical simulations of the electric field distribution of the extraction set-up and simulations of the strain distribution in the membranes.

II. Design and fabrication of the YSZ thrusters

The concept of the membrane thruster is shown in Figure 1a. It consists of a thin YSZ layer which is deposited onto a silicon wafer. This wafer is etched from the backside to obtain a free standing YSZ membrane. As it is shown in Figure 1a, this membrane is supplied with molecular oxygen through the channel in the silicon wafer. To achieve the splitting of the molecular oxygen at the surface and incorporation of oxygen ions into the YSZ a platinum coating is needed to establish a three phase boundary (Figure 1b) between the molecular oxygen, the YSZ and the oxygen ions in the YSZ. The oxygen is split on the surface of the platinum electrode and can then occupy an oxygen vacancy in the crystal (black squares in the Figure 1b). This process can be written in the *Kröger-Vink* notation as: $V_0^{\bullet} + 1/2O_2(g) \rightarrow 2h^{\bullet} + O_0^{\times}$. V_0^{\bullet} denotes a vacancy on an oxygen site with a formal charge of +2, h[•] is a defect electron (hole) with a charge of +1 and O_0^{\times} is an oxygen atom on an oxygen site without a formal charge.

By applying a potential difference (φ) the O⁻ ions are transported to the opposite surface by a vacancy hopping mechanism [6]. If an external voltage is applied to the membrane by an extraction grid (which is insulated from the membrane), it is possible to extract O⁻ ions from the YSZ. The red continuous line in Figure 1b shows the potential gradient in this case.

The heater structure used for the YSZ layer thruster is shown in Figure 1c. Onto the bar structure of the gold heater the YSZ is deposited covering an area of 1×1 cm². The edges of the gold heater structure of 1.6×1.2 cm² are



Figure 1. (a) Concept of the membrane thruster, (b) scheme of the oxygen transport through the YSZ layer and (c) heater structure (yellow) for the YSZ layer thruster (YSZ in blue).

The 33rd International Electric Propulsion Conference, The George Washington University, USA October 6 – 10, 2013 not covered by YSZ and serve as contact areas. The extraction principle is based on an external grid and thus is similar to that of the membrane thruster.

A. Fabrication of the YSZ layers

The YSZ layers are deposited by reactive rf-sputtering from a ZrO₂ target of 99.9% purity stabilized by 9.5 mol% Y_2O_3 . To obtain a columnar growth of the YSZ the substrate heater was set to 500 °C and a mass flow of 50 sccm argon was used with an applied sputter power of 160 W to deposit the membrane layers. Additional 5 sccm of oxygen are used for preparation of the YSZ layers used in the design where the YSZ is used as oxygen reservoir. Thermally oxidized 100 µm thick both side polished (100) silicon 4" wafers and fused silica glass are used as substrates for the deposition of YSZ for preparing membranes and thick oxygen-rich layers, respectively. Figure 2 shows a scanning electron microscopic image of a typical YSZ layer. One can see the columnar growth and the surface of the YSZ in the upper part of the image.



Figure 2. Scanning electron microscopic image of a tilted YSZ layer on a silicon wafer.

B. Fabrication of the membranes

Before the YSZ is deposited onto the wafer, the wafer is thermally oxidized at 1100 °C for 2 h under atmospheric conditions to get a 200 nm thick oxide layer on both sides. Afterwards one surface of the wafer is patterned by electron beam lithography using PMMA as resist. The other surface is coated with PMMA but not structured. The wafer is etched in buffered hydrofluoric acid to selectively remove the SiO₂ layer in order to transfer the desired structure into the SiO₂. In the next step the PMMA is removed and the YSZ is deposited on the unpatterned side as described above. After deposition the channel is defined in the silicon wafer by anisotropic wetchemical etching in KOH with a concentration of 20 wt% at a temperature of 50 °C in a water bath. The pattern transferred into the SiO₂ determines the shape of the channel etched into the silicon and thus also that of the membrane.

C. Influence of the mask pattern on the shape of the membranes

The pattern defined by electron beam lithography on the backside of the silicon wafer is used to control wetchemical etching of the silicon wafer and therefore the shape of the membrane. We used five different cross-shaped patterns each in ten different lateral dimensions to investigate the etching behavior and the resulting shapes of the membranes. We found that after at least 6.5 h in all cases one obtains a square shape of the membrane [7]. This is due to the anisotropic etching of the silicon, the <100> direction is etched a hundred times faster than the <111> direction. The angle between the directions is 54.7° . Because of this fact the etching yields a pyramidal shape of the walls each time and the membrane is always smaller than the etched square on the backside of the wafer.

The experiment shows that the larger membranes with sizes of $75 \times 75 \ \mu\text{m}^2$ and above tend to break due to a large stress building up whereas the smaller membranes are stable. Examples for this behavior are given in Figure 3. The smallest membrane with a size of $25 \times 25 \ \mu\text{m}^2$ (Figure 3a) shows no stress-induced deformation, the membrane with a size of $70 \times 70 \ \mu\text{m}^2$ (Figure 3b) exhibits a cross-like deformation. In the lower left corner (Figure 3c), the membrane with the size of $125 \times 125 \ \mu\text{m}^2$ shows a curved cross-like stress deformation and the membrane shown in Figure 3d with a size of $395 \times 395 \ \mu\text{m}^2$ is broken due to high stress. To obtain a better understanding up to which size the membranes are stable we fabricated a large number of membranes with different edge lengths. The analysis of the stress-induced deformation, whereas membranes with edge lengths between 75 and 150 \ \mu\text{m} possess a well-defined cross-like deformation pattern where the cross is formed between the four corners of the square-shaped membrane. Above an edge length of 150 \ \mu\text{m} some of the membranes tend to break, however, up to 250 \ \mu\text{m} most membranes are stable and show the curved cross-like deformation patterns.



Figure 3. Optical microscope images of different square-shaped membranes: no deformation at $25 \,\mu\text{m}$ edge length (a), cross shaped deformation at 70 μm edge length (b), curved cross-shaped deformation at 125 μm edge length (c) and a crack formation broken in the membrane at 395 μm edge length (d). [7]

D. Simulation of strain in the membranes

We have demonstrated that the strain distribution occurring in the membrane varies with its size. We performed finite-element simulations using the commercial software package *COMSOL* to investigate this behavior. The modeling is based on the assumption of that the YSZ-layer is crystalline and of cubic crystal symmetry, thus, the elasticity tensor possesses three independent non-zero tensor elements c_{12} , c_{11} and c_{44} . A typical result of the finite element calculations is shown in Figure 4. The strain pattern calculated for a membrane with an edge length of 100 µm possesses a cross-like distribution similar to the deformation patterns observed in the experiment. Extending the modeling of the strain distribution in the membranes taking into account additional thermal effects we will be able to fully access the stability of such membranes. This will allow us to identify the sizes which are suitable for the incorporation in thruster structures.



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E. YSZ-Layer thruster

Compared to the thruster design based on YSZ membranes the fabrication of thruster structures based on thick YSZ layers on a heater grid is somewhat easier. The resistive gold heater grid is prepared on the substrate by photolithography followed by an evaporation step. During the sputtering process a mask made of an aluminum plate with a square-shaped hole with a size of 1×1 cm² is used to cover the substrate such that the gold heater structure is located in the center of the square hole. This procedure ensures that the YSZ layer deposited in the rf-sputtering process covers the heater area only. Figure 5 shows a photograph of a substrate after fabrication of the gold heater structure and deposition of the YSZ. The gold bars are clearly visible and the deposited YSZ causes the slight blue color impression. Whereas the preparation of the layers is quite simple, the measurement of the ion extraction poses a severe challenge. For measuring the ion extraction we developed a setup and modeled its electrical properties. Figure 6a shows a scheme of the measurement setup. The wide contact areas on the edges of the gold heater structure of the YSZ layer sample are pressed onto two copper electrodes (heater electrodes) of the sample holder. The heater electrodes of the sample holder are separated by an insulator plate of 3 mm thickness from the copper extraction grid. The extraction voltage is applied between the heater contacts



Figure 5. Gold heater grid with YSZ layer on top which has a slight blue color.

and the extraction grid. Modeling the electric field distribution in the space between sample surface and extraction grid for an extraction voltage of 1000 V (Figure 6b) yields a rather homogeneous field distribution with the electric field vector perpendicular to the sample surface. The magnitude of the electric field at the surface of the YSZ is around 2000 V/cm and thus comparable to the values used by Sadakata and the other groups to extract O⁻ from YSZ. First experiments showed that the heater works well. For the measurement of the extracted ion current we are currently developing a measurement bridge which will enable us to measure currents in the picoampere range.



Figure 6. (a) Scheme of the measurement setup and (b) simulation of the electric field with a voltage of 1000 V applied to the extraction grid.

III. Summary and Outlook

We proposed two novel concepts for micropropulsion thrusters based on the solid-state ion conductor YSZ and showed first steps of their realization. In the case of YSZ, O⁻ ions will be extracted. For neutralization it can be anticipated to combine these YSZ devices with counterparts based on a positive ion conductor such as AgI to form a thruster system.

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