MICROMACHINED PLATFORMS ON SILICON FOR MICRO-SOFC

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Abstract: This communication reports on the design, fabrication and testing of special high temperature Si/SiN based micro-hotplates as micromachined platforms for micro-SOFCs. Different designs and materials have been evaluated to realise micro-heating platforms compatible with spray pyrolysed anode, cathode and electrolytes materials. The potential of these micromachined platforms for further integration of micro-SOFCs has been demonstrated with the characterisation of the properties of thin $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF) cathode films deposited on them. As a conclusion of these investigations, a complete process flow for the integration of all the active layers with heater current collectors and gas access through the membrane is proposed.

Key words: micro-SOFC, micromachined fuel cell, micro-hotplate, LSCF

1. INTRODUCTION

Miniaturised Solid Oxide Fuel Cells (SOFCs) are of high interest to power portable devices such as mobile phones, computers and also in the future more complex smart systems based on microsystem technologies. The work on the miniaturization of fuel cells is mainly concentrated on PEM and methanol fuel cells [1]. The facts that they work at a lower operating temperature and that they can be fabricated using processes with a lower thermal budget have led to the first commercial products of miniaturized fuel cells [2]. Efforts dedicated to that topic for SOFCs mainly involve a hybrid approach for the realization of miniaturized SOFCs that can still not be qualified of microscopic. However, complete miniaturization of the SOFC system could be of interest with the integration of gas channels, current collectors, low-power heating elements for start up operation of the fuel cell and electrical connections between different micro-SOFCs built on a same platform.

Up to now, some groups have addressed some of the issues related to the realization of miniaturized SOFCs. Work has started in USA with the use of multi stack micromachined parts to fabricate micro-SOFCs [3-5]. One research group has addressed the design issues of miniaturized micromachined SOFCs based on suspended membranes, work presented in a previous edition of the PowerMEMS conference [6]. Efforts have also been dedicated to the realization of SOFCs with thinner active layers to decrease significantly the operating temperature of the fuel cell, with very interesting results from the group of Prof. Prinz at Stanford University, USA [7]. In their case, they use silicon micromachining to suspend the very thin active layers (anode, cathode and electrolyte) to obtain some interesting power densities at a operating temperature of 400°C. A strong research program is also on going at ETHZ, Switzerland, with the development of thin films active layers deposited by spray pyrolysis and their integration on micromachined glass substrates for the realization of micro-SOFC [8]. Another interesting option is the realization of single chamber SOFC which can simplify the integration of the complete system with the drawback of smaller power density generated [9].

Compared to these on going developments, we propose to combine technologies established for Microsystems with electronic and ionic conducting oxides made by thin film deposition techniques to enable the miniaturization of SOFCs on a single micromachined platform with current collectors and heaters integrated. By using spray pyrolysis, active layers can be processed (deposition and annealing) and operated at lower temperature compared to traditional materials (such as YSZ) which makes possible their integration on micromachined platforms. These platforms can be realized using different types of materials with their related advantages /

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*Currently at Oerlikon NE, Neuchâtel, Switzerland disavantages depending of the active materials to integrate: photo structurable glass, anodic alumina, and micromachined silicon and silicon carbide are some of the candidates.

In this communication, we report on the design, fabrication and testing of special high temperature Si/SiN based micro-hotplates as micromachined platforms for micro-SOFCs [10]. Different designs and materials have been evaluated to realise micro-heating platforms compatible with spray pyrolysed anode, cathode and electrolytes materials. The potential of these micromachined platforms for further integration of micro-SOFCs has been demonstrated with the characterisation of the properties of thin $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF) cathode films deposited on them. As a conclusion of these investigations, a complete process flow for the integration of all the active layers with heater current collectors and gas access through the membrane is proposed.

2. EXPERIMENTAL

2.1 Compatibility of standard micro-hotplates on silicon with SOFCs active layers

Firstly, standard micro-hotplates developed at IMT-Neuchâtel and industrially produced [11], were used to evaluate their compatibility with the spray pyrolysis process used to deposit the SOFC materials. They consist of a platinum heating element embedded in a free standing Si_3N_4 film of 1 µm thickness spanning over an area of 1 mm^2. These hotplates can operate at temperatures up to 900°C with a thermal time constant less than 100 ms. Platinum electrodes were implemented on top of the hotplates to allow the electrical characterisation of the SOFCs materials, as shown in Fig. 1.

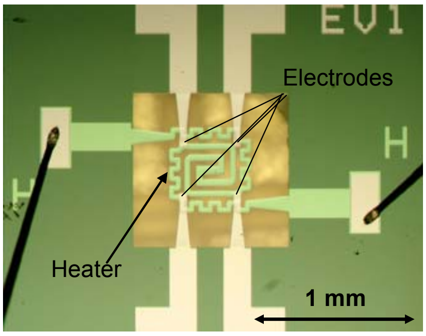

Fig.1: Picture of the micro-heating platforms before the spray pyrolysis of LSCF thin films.

On top of this SiN membrane a 500 nm thick LSCF thin film was deposited by spray pyrolysis using a shadow mask and annealed at 600°C (Fig. 2). The microstructure of the LSCF was characterized and the electrical conductivity of LSCF was measured on the micro-hotplate as a function of temperature.

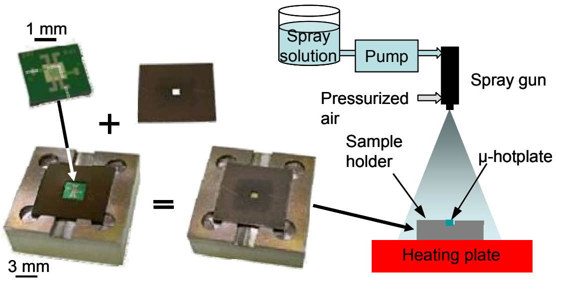

Fig. 2: Deposition set-up for SOFCs materials on micro-heating platforms.

2.2 Optimised micro-machined platforms on silicon for micro-SOFCs

As reported in [10], when operating the standard micro-hotplate coated with LSCF at 600°C, the membrane buckles up due to the thermal stress generated by the local elevation of temperature and the different temperature coefficients of expansion (TCE) of the materials involved (see Table 1).

Table 1: Thermal Coefficients of Expansion.

	TCE [10^{-6} K^{-1}]
Si_3N_4 / Si	**1.6 / 2.6**
Pt	**8.8**
Al_2O_3	**8.7**
CGO / Ni-CGO	**10.5 / 11**
LSCF	**14-19**

In order to increase the reliability of the micromachined heating platforms, the use of CVD (at 900°C) Al_2O_3 films as membrane, with a thermal expansion coefficient close to the solid oxide materials used in SOFCs (Table 1), and a circular membrane (ϕ= 0.5 and 1.0 mm) with a corrugated design (as suggested in [6], see Fig. 3) released using DRIE of silicon, were evaluated.

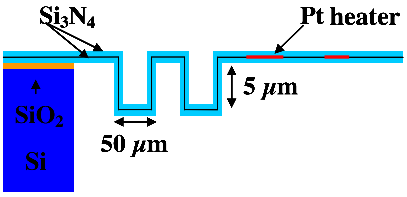

Fig. 3: Design of the micromachined platform with a circular corrugated Si_3N_4 membrane.

3. RESULTS AND DISCUSSION

The conductivity of LSCF thin films deposited onto standard micro hotplates (Fig. 4) was in the same order of magnitude as the conductivity of the reference samples indicating proper functioning of the LSCF thin films at an operating temperature of 600°C (Fig. 5).

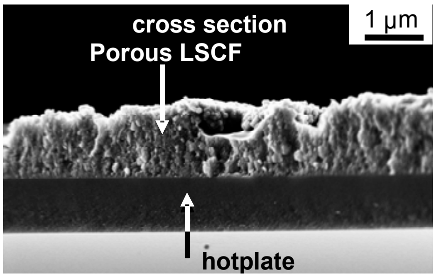

Fig. 4: SEM cross-section of a LSCF film deposited on a thin suspended silicon nitride membrane.

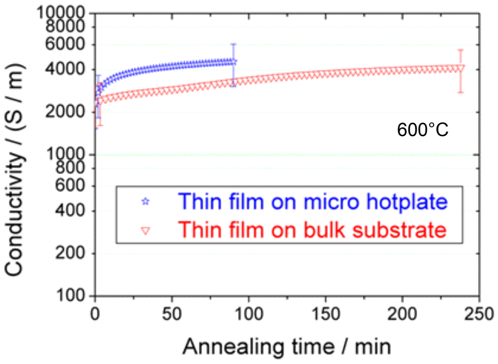

Fig. 5: Electrical conductivities of LSCF deposited on a hotplate and on bulk substrate.

Interesting results were obtained with a selective deposition of the LSCF films on the alumina membrane (Fig. 6) caused by the parameters used for the spray pyrolysis of the films [8]. However, the integration of the platinum heater was incompatible with the deposition at high temperature of a CVD Al_2O_3 film used as a passivation layer on top.

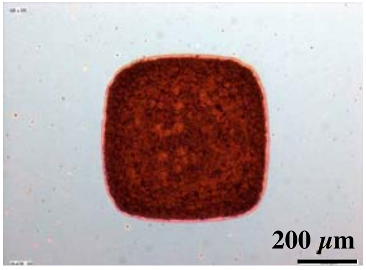

Fig. 6: LSCF deposited locally on the Al_2O_3 membrane without shadow mask.

Silicon nitride membranes with corrugations have revealed to be of interest with minimized membrane deformation when operating at 600°C. Picture of a hotplate with a corrugated membrane is shown in Fig. 7. Some residual stress can be noticed which is probably due to the photolithographic masks that were fabricated on transparencies. Some simulation work is also needed to optimize the design of the heater in relation with the temperature distribution on the active area and on the thermal stress generated.

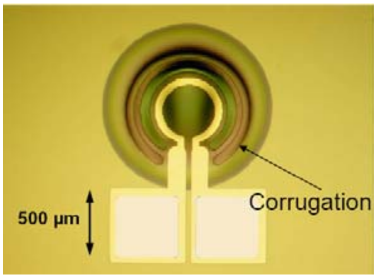

Fig. 7: Micromachined hotplate with corrugated Si_3N_4 membrane and platinum heater integrated.

Following these experiments, propositions are made for the complete integration of micro-SOFCs on micromachined heating platforms with corrugated membrane, gas access in the membrane, current collectors and integration of the complete SOFCs stack of materials on top. The cross-section view and the layout are presented in Figure 8.

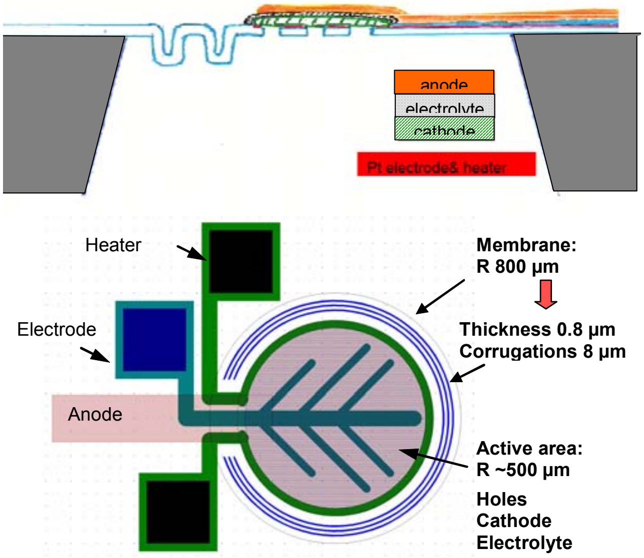

Fig. 8: Proposition of a design for a micro-heating platforms for the complete integration of micro-SOFCs: Artistic view of the cross-section and mask layout.

As shown in Fig.7, corrugations and small holes, about 1 μm in diameter, are made in the 1.0 μm-thick membrane. Corrugations allow releasing the stress in the membrane and holes will serve as an access for the gas to reach the cathode. A circular platinum heater is integrated on the membrane in between the area covered by the small holes in the membrane for the gas access and the corrugations. A passivation of silicon nitride covers the heater with the current collector made of platinum sitting on top, patterned around the small holes in the membrane. Finally, the whole design is completed by stacking the LSCF cathode, the CGO electrolyte, and the Ni-CGO anode and a patterned thin-film platinum current collector for the anode.

The processing is the following: deep reactive ion etching of silicon (DIRE) is performed with a depth of few μms to define the corrugations on the top side of the silicon wafer. Then a thermal silicon oxide film is grown (0.5 μm-thick) on the silicon wafer to act as a etch stop when releasing the membranes using DRIE. This is followed by the deposition of a 0.5 μm-thick LPCVD low-stress silicon nitride film to form the membrane. Pt/Ta heater is patterned by lift-off using a thick AZ4562 photoresist to cover the steps of few μms formed by the corrugations. An another 0.5 μm-thick LPCVD low-stress silicon nitride is deposited to complete the membrane and passivate the heater. On top of which the platinum current collector is patterned by lift-off with holes of few μms. In these areas on the membrane without platinum, reactive ion etching is performed to etch holes in the silicon nitride membrane for the gas access. The micromachined platform with heater and current collector is now ready for the integration of the active layers to form the fuel cell. The whole process is completed by stacking the cathode, electrolyte and anode by spray pyrolysis through a shadow mask with optimized sequences for their annealing [8].

4. CONCLUSION

Micromachined hotplates on silicon with integrated low-power heaters and current collectors have been evaluated as micromachined platforms for micro-SOFC with the successful integration of an SOFC thin film cathode material.

Optimisation of the design and processing of the micromachined platforms on silicon has been performed with the addition of the corrugation to the silicon nitride membrane, of a circular heater at the edge of the corrugation, of a current collector for the cathode and of very small holes in the membrane for gas access.

Further work to integrate also the electrolyte and anode and fabrication of gas channels is needed to fabricate an entire micro SOFC based on a micromachined platform, providing a low-power integrated heating system for start up operation of the fuel cell.

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