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A Micro-Machined Safety Valve for Power Applications with Optimized Low Leakage

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Abstract

A novel micro safety valve for portable hydrogen fuel cells has been designed, fabricated and characterized. This device is intended to prevent over-pressure in the hydrogen side of the fuel cell. A careful study of its sealing properties has been conducted. The leakage rate depending on the size of the sealing surface and on the material of the gasket (fluorocarbon and parylene films) have been investigated using hydrogen gas. The experimental results show that small sealing surfaces lead to small leakage rates and that the parylene films are easily damaged, leading to important leakage rates. Moreover, it is shown that the fluidic resistivity of the device is reduced by reducing the width of the valve nozzle.

Keywords: fuel cell, micro valve, hydrogen, leakage rate, gasket

I. INTRODUCTION

Fuel cells are now seen as a promising solution to provide miniature energy sources for portable electronic appliances due to their high energy, low pollution and short recharge time [1]. In such systems, it is needed to well control the hydrogen pressure in order to achieve high efficiency and protect the membrane electrode assembly (MEA) from fracture. A passive micro safety valve has thus been designed, fabricated and characterized. This device passively releases excess hydrogen when the pressure is higher than a set value. Moreover, a careful study on the nozzle/seat contact surface has been conducted which results in low leakage rates. Previous studies on low leakage micro-valves have already been reported in the past [2]. However, they concern active micro-valves in which a high force can be applied between the nozzle and the seat. In passive micro-valves, the force acting between the nozzle and the seat is limited, especially at pressures close to the opening pressure. Two gasket materials have been investigated: fluorocarbon and parylene which are soft enough to deform in the presence of dusts and can be deposited in conformal coatings. They have been used in the past for various applications [3] [4]. Moreover, as the properties of leaks are highly dependent on the nature of the gas and cannot be deduced from one gas to another, this study is conducted using hydrogen gas [5]. We believe this study gives general guidelines useful for other passive leak-tight micro gas regulators for fuel cells [6].

II. DESIGN

The working principle of this device is similar to macroscopic direct-acting safety valves with modulating lift [7] and to the regulators used in pressure cookers invented by Denis Papin in 1679. A scheme of the device is shown in Fig. 1. The total dimensions of the device are $8 \times 8 \times 1$ mm^3. It consists of three silicon wafers which are around 300 μm thick each. The first wafer includes a circular input channel (100 μm in radius) and a circular valve seat (500 μm in radius and 6 μm in height). The second wafer includes a nozzle and a flexible membrane. The nozzle is 400 μm wide and its inner channel is 100 μm in radius. The membrane radius is 1 mm and its thickness is 25 μm. Depending on the samples, two rings have been included on the nozzle (Fig. 2). The width of the ring can be varied from 30 μm to 500 nm. The height

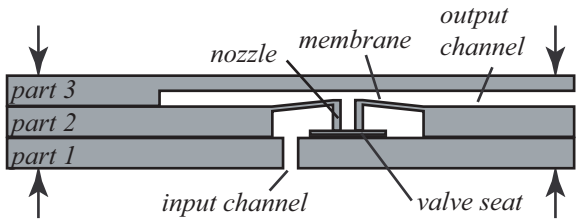

FIG. 1: A scheme of the cross-section of the micro safety valve after assembly. The arrows represent the packaging pressure.

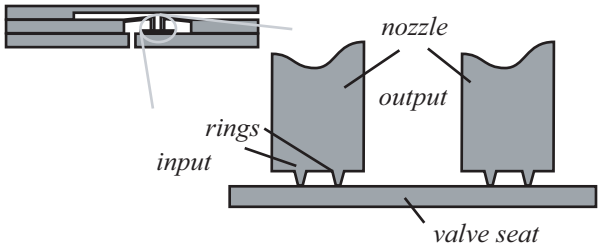

FIG. 2: Zoom on the nozzle showing the sealing rings.

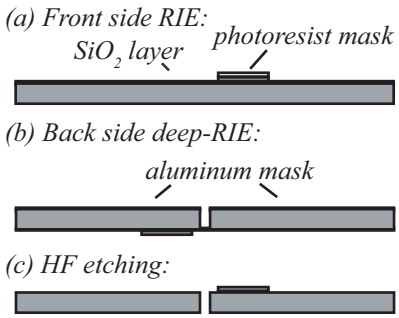

FIG. 3: A scheme of the cross-section showing the fabrication process of the first part.

of the rings can also be varied and is generally around a few μm. The third wafer is used to redirect the gas flow. It includes a gap which is 50 μm high. The output channel is 1 mm wide. The first wafer is coated on the valve seat side with a fluorocarbon film or a parylene film. The thickness of the film can be varied by changing the deposition conditions. The dimensions of the device are chosen such that the required alignment between the three wafers during the assembly is 300 μm or less. Moreover, the membrane and valve seat dimensions are chosen such that the set pressure is 100 kPa G (G: gage) according to the thin plate theory [6].

The working principle of the device is as follows. The membrane takes into account the pressure difference between the input and output channels. When the input pressure P_0 and the output pressure P_1 are the same, the nozzle is pushed against the valve seat and the valve is closed. When the pressure in the input channel is high enough to overcome the initial deformation of the membrane, the nozzle lifts up and the valve opens.

III. FABRICATION

The fabrication of the device is as follows. The three parts are fabricated separately using standard MEMS fabrication techniques. The fabrication of the first wafer starts with an SOI wafer with a 5 μm thick device layer and a 1 μm thick buried oxide layer. The front side and the back side are patterned by deep-RIE to form the valve seat and the input channel respectively (Fig. 3-a and b). The buried oxide layer is then etched by an HF solution (Fig. 3-c). The side etching is 100 μm in order to lift-off any remaining dusts. The process of the second part starts with an oxidized SOI wafer with a device thickness of 25 μm (Fig. 4-a). The SiO_2 layer on the front side and the device layer are patterned in order to form the upper part of the nozzle (Fig. 4-b). The back side SiO_2 layer is then patterned by a vertical etching (CHF_3 plasma in RIE) to serve as a mask for the sealing rings (Fig. 4-c). The membrane and the nozzle are then patterned by deep-RIE on the backside (Fig. 4-d). Using the previously patterned

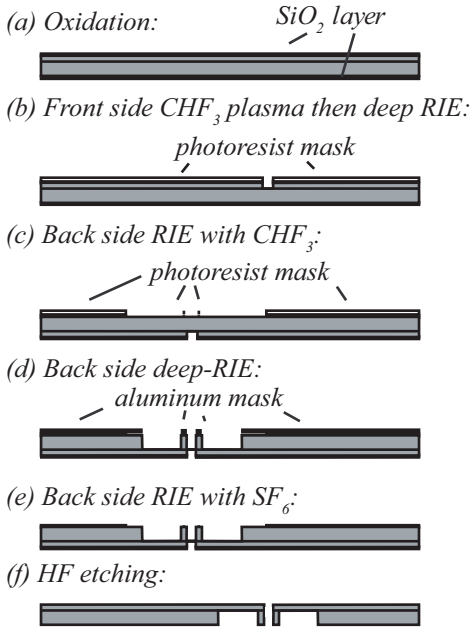

FIG. 4: A scheme of the cross-section showing the fabrication process of the second part.

SiO_2 mask, the rings are formed by an SF_6 plasma in RIE (Fig. 4-e). As this etching is isotropic, rings with width smaller than the initial mask can be obtained. Finally, the remaining SiO_2 layers are removed using a HF solution (Fig. 4-f). The process of the third wafer starts with a 300 μm thick silicon wafer. This wafer is etched using deep-RIE in order to form the output channel and each part is separated by dicing saw. At this point, all the parts are separated from one another. Three optical micrographs showing the three parts are presented in Fig. 5. A close view of the nozzle and the two sealing rings is show in Fig. 6. In the insert, a close view on a sealing ring which width is less than 500 nm can be seen.

Prior to assembly, the individual parts are cleaned by SPM cleaning. The front side (containing the valve seat) of the first part are coated with either a fluorocarbon film or a parylene film. The fluorocarbon film is deposited by CHF_3 plasma in RIE (SAMCO RIE-10 NR). The conditions are the following: a plasma power of 50 W, a CHF_3 flow rate of 100 sccm and a process pressure of 5 Pa. The deposition time is depending on the desired thickness. The parylene is deposited by chemical vapor deposition (CVD). The roughness of the deposited films have been characterized by an AFM (Atomic Force Microscope) with a scan area of 1×1 μm^2. Measuring a step of the films by AFM or a profilometer (DEKTAK) gives the thickness. The deposition rate of the fluorocarbon film is constant with the deposition duration and is about 14 nm/min. The roughness is not depending on the deposition duration but on the sample lot. The average roughness is between 0.2 and 1 nm. The maximum height difference is between 1 and 6

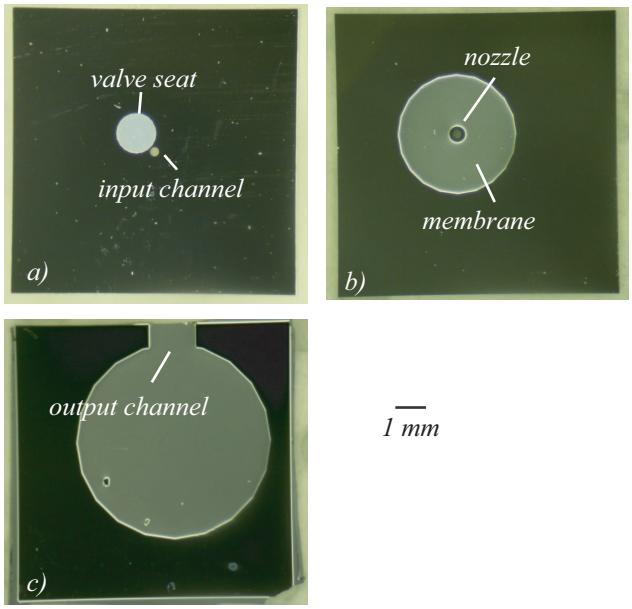

FIG. 5: An optical micrograph of the three parts of the safety valve. a: Part 1; b: Part 2; c: Part 3.

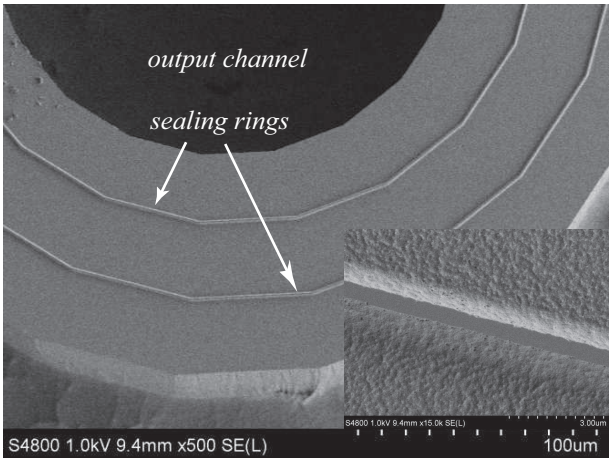

FIG. 6: An SEM micrograph showing a close view of the nozzle with the two sealing rings. Insert: an SEM micrograph showing a sealing ring on the nozzle. The width of the ring is less than 500 nm.

nm. The deposition of the parylene film is proportional to the mass of parylene in the CVD. Around 115 nm is deposited for 0.1 g. The average roughness is 0.17 nm. The maximum height difference is 11.3 nm.

The three parts can be directly assembled using the force of the external packaging, no bonding being required. For convenience during our experiments, as only one packaging chamber is used, the three parts are contacted into a press and definitively assembled using epoxy glue on the side of the device.

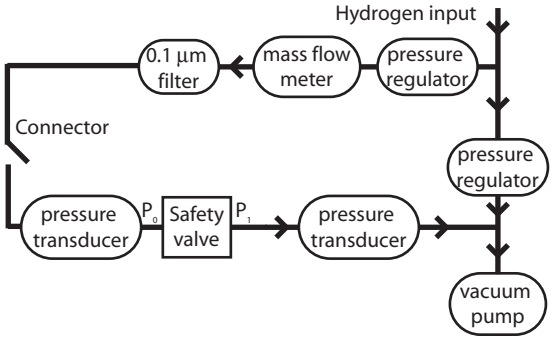

FIG. 7: Layout of the experimental set-up.

IV. EXPERIMENTAL CHARACTERIZATIONS

The samples have been tested in order to measure the flow rate as a function of the pressure difference and the leakage rate. The method used to measure the leakage is the V ΔP calibration method and is one of the methods for leakage rate calibration recommended by the Calibrated Leak Subcommittee of the American Vacuum Society [5]. The set-up used for this calibration is depicted in Fig. 7. The safety valve is packaged into a chamber made of SUS and sealed by Viton sheets. The chamber is connected to Swagelok pipes. The input and output pressures are regulated with two STEC UR-7340 pressure regulators. The input pressure is measured with a Nagano Keishi pressure transducer. The flow rate is measured with a STEC SEF 400 flow meter. Before the device, the flow is filtered by a Fujikin 0.1 μm particle filter. The output pressure is measured by a Sensotec STJE pressure transducer.

The procedure to measure the leakage rate is as follows. First, the system is flown with hydrogen for a few minutes in order to remove any air. The output pressure is set to the atmospheric one. The input pressure is set to the opening pressure. The upper flow pressure transducer and the valve chamber are then disconnected from the upper part of the circuit. At the same time, a chronometer is started while the upstream pressure is monitored. When the upstream pressure has decreased by 5 kPa, the chronometer is stopped. Knowing the volume V of the chamber and using the ideal gas law, it is possible to calculate the leakage rate by:

$$Q = \frac{dN}{dt} = \frac{V}{RT}\frac{dP}{dt}, \qquad (1)$$

where T is the temperature (K), V the volume of the chamber (m^3), $\frac{dP}{dt}$ the pressure decay (Pa s^{-1}) and R the gas constant (8.31 J mol^{-1} K^{-1}). The leakage rate unit is mol s^{-1}. The volume of the chamber used is 3.1 cm^3. The leakage rate of the system itself is measured using a plain silicon wafer instead of the safety valve in the chamber and is 2.2×10^{-10} mol s^{-1} at 298 K for an input pressure of 102 kPa G.

Sample number	Sample 1	Sample 2	Sample 3
Nozzle ring quantity × width (μm)	1 × 100	1 × 100	2 × 3
Valve seat	polished silicon	rough silicon	polished silicon
Opening pressure (kPa G)	110	186	93
Upstream pressure (kPa G)	100	100	90
Leakage rate (mol s^{-1})	1.3×10^{-7}	9.7×10^{-9}	3.0×10^{-9}

TABLE I: Measured leakage rates for three samples.

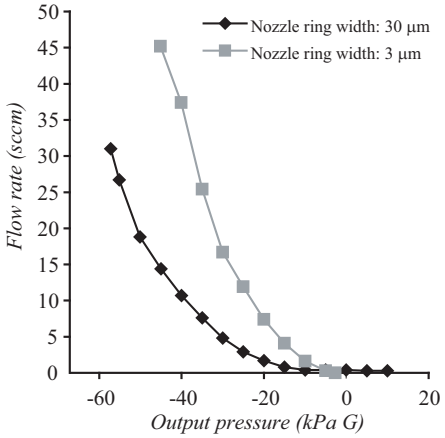

FIG. 8: Flow rate of hydrogen for two micro safety valves as a function of the output pressure. The input pressure is 90 kPa G.

Table I shows the measured leakage rate for three samples. The valve seat is coated by a 80 nm thick fluorocarbon film. The leakage rate is measured with an upstream pressure close to the opening pressure. Comparing samples 1 and 3, it is clear that thinner sealing rings lead to an improved sealing (in this case reduced by 100). In sample 2, there is no sealing ring, however the valve seat has been made rough using an SF_6 plasma etching in RIE. In this case, the sealing is also improved compared to sample 1. Two samples coated with a 1 μm thick parylene film show mixed results. One sample with 4 μm wide sealing rings has a leakage rate of 7.4×10^{-7} mol s^{-1} while another sample with 21 μm wide sealing rings has a leakage rate of 4.6×10^{-9} mol s^{-1}. Microscopic observations of a third sample shows that the parylene film is easily damaged by the sealing rings. Finally, Fig. 8 shows the flow rate through two devices as a function of the input pressure. The fluidic resistivity of the valve is therefore reduced by smaller sealing rings.

V. CONCLUSIONS

A novel micro safety valve has been designed, fabricated and characterized. This device is intended to protect the hydrogen side of the MEA from over-pressure and passively release the excess of gas. A careful study has been conducted in order to measure and reduce the leakage rate from the device. Fluorocarbon and parylene films has been investigated as gaskets and sealing rings have been added. It is found that the fluorocarbon films lead to good sealing while parylene films are easily damaged. Moreover, the sealing rings also improve the sealing of the device and reduce the flow resistivity of the valve.

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[1] M. Winter and R.J. Brodd. What are batteries, fuels cells, and supercapacitors? *Chem. Rev.*, 104:4245–69, 2004.
[2] E.-H. Yang, C. Lee, J. Mueller, and T. George. Leak-tight piezoelectric microvalve for high pressure gas propulsion. *J. Microelectromech. Syst.*, 13:799–807, 2004.
[3] H.V. Jansen, J.G.E. Gardeniers, J. Elders, H.A.C. Tilmans, and M. Elwenspoek. Applications of fluorocarbon polymers in micromechanics and micromachining. *Sensors and Actuators A*, 41-42:136–140, 1994.
[4] Y.-C. Tai C.-M. Ho X. Yang, J.M. Yang. Micromachined membrane particle filters. *Sensors and Actuators A*, 73:184–191, 1999.
[5] C.D. Ehrlich and J.A. Basford. Recommended practices for the calibration and use of leaks. *J. Vac. Sci. Technol. A*, 10(1):1–17, 1992.
[6] A. Debray, T. Nakakubo, K. Ueda, S. Mogi, M. Shibata, and H. Fujita. A passive micro gas regulator for hydrogen flow control. *J. Micromech. Microeng.*, 15:S202–S209, 2005.
[7] P.L. Skoussen. *Valve Handbook*. McGraw-Hill, New York, 1998.