Short communication

Realization of porous silicon based miniature fuel cells

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Abstract

In this paper, we demonstrate a new way of making low-cost miniature fuel cells for portable applications based on proton conducting porous silicon membranes. Our solution consists in the chemical grafting of silane molecules containing ionizable groups on the pores walls to mimic the structure of ionomer, such as Nafion®, usually used to ensure the proton conductivity of PEM fuel cells. We obtain an inorganic, dimensionally stable, proton conducting membrane with many optimizable parameters such as the pore size, the pore structure of the membrane and the nature of the grafted molecules. Moreover, the use of a silicon substrate offers advantages of serial and parallel integration, the possibility of encapsulation by wafer bonding and gas feed and electrical contacts can be included into the membrane etching process thanks to simple KOH wet etching processes and metal sputtering. A power density of $17\,\mathrm{mW\,cm^{-2}}$ was obtained.
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1. Introduction

If miniature fuel cells will soon be challenging with current batteries for the supply of portable applications such as cellular phones or PDA and nomadic electronic, recent papers [1–4] have shown the growing interest turned to the development of silicon based miniature fuel cells for chip-scale power. Most of these fuel cells have used Nafion® as the proton exchange membrane, yet it does not seem to be the right solution. Indeed, Nafion® membranes are inadequate to standard microfabrication techniques: they cannot be easily patterned with standard photolithography and their volumetric variations due to hydration are a real problem for the assembly with silicon substrates.

Many alternate ways have been proposed to avoid these problems, one of the solutions being to use organic–inorganic hybrid membranes. Literature reports original research axes like hybrid silica/Nafion® membranes [5,6] or a porous silica membrane filled with sulfonated polyelectrolyte [7] yet not suitable to obtain easily integrated miniature cells.

The revival of activity since 1990 concerning the study of porous silicon (PS), revival partly aroused by Canham [8] and Lehmann and Gosele [9] works on PS photoluminescence phenomenas, allowed a better knowledge about the properties of PS and the discovery of new applications for this material. In the case of fuel cells, the use of PS as a gas diffusion layer [10] or as a support for catalyst [11,12] has been demonstrated. Recent papers [13,14] have shown the relevance of using PS as the membrane of the fuel cell.

Our approach consists in a new way of making miniature fuel cells using a silicon substrate with PS membranes on which appropriate molecules for proton conduction are grafted. This solution allows to avoid the use of expensive ionomers and to take advantage of silicon for mass production, easy etching process, possibility of integration and metallization of electrical contact within the process.

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2. Experimental

2.1. Silicon membrane

The first stage is the realization of the silicon membranes using classical photolithography and wet chemical etching in KOH of phosphorus-doped 0.012–0.014 Ω cm n$^+$-type(1 0 0) oriented silicon wafers. Such substrate doping was chosen as a function of the desired PS morphology. Masking is obtained with a sputtered Cr–Au layer (Cr layer of 15 nm thick and Au layer of 800 nm thick). A previous thermal oxidation of the silicon wafer ensures the electrical insulation of the membrane. More details on the process can be found in ref. [13]. Membranes thickness is fixed to 50 μm by adjusting processing time and temperature. Collective processing allows to obtain simultaneously 69 membranes on a 4 in. wafer with active areas of 7 mm^2 on a 4 in. wafer (Fig. 1).

2.2. Porous silicon

Silicon membranes are made porous by anodization in a double-tank cell [15] conceived by AMMT GmbH. It consists of two half-cells in which Pt electrodes are immersed and the silicon wafer separates and isolates the two half-cells.

The electrolyte used is an ethanoic–HF solution (50% of pure ethanol and 50% of a 48% HF solution). Anodization is carried out in the dark at constant current, with a current density from 18 to 36 mA cm^{-2} to obtain pores from 6 to 10 nm diameter and a porosity of about 50% [16].

The previous deposition of the Au layer allows the localization of the porosity on silicon membranes during anodization. Indeed, a simple LPCVD Si$_3$N$_4$ layer generally used as the masking layer for localized PS (see for example, [17]) would not allow long time anodization as precious metals (Au, Pt, Ag) do. The silicon oxide layer under the Cr–Au layer avoids any parasitic formation of PS with the possible internal current generated between silicon substrate and the metallic layer [18].
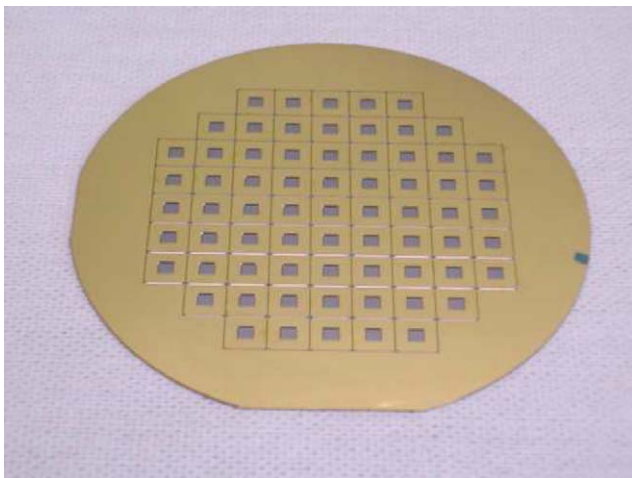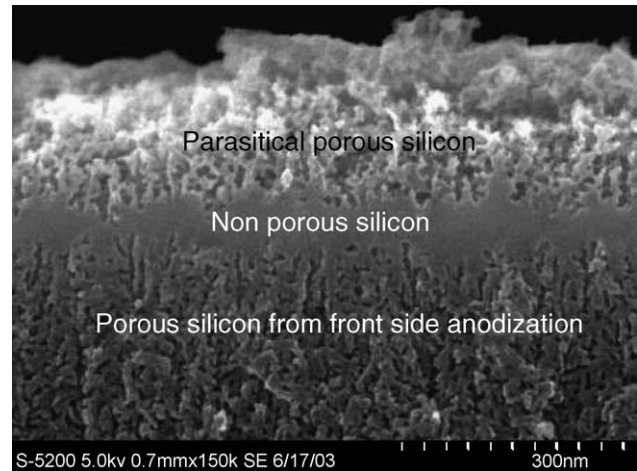

Fig. 2. FESEM cross-section view of the rear side of a membrane after anodization. Only a few pores are opened and the PS layer at the surface of the rear side is made by a parasitical anodization due to a contact between gold and silicon.

Once anodization is achieved, membranes are rinsed into an oxydizing bath neutralizing HF solution then into several deionized water baths and finally isopropyl alcohol for reducing stress into pores. Membranes are finally dried at ambient air. PS membranes with a silica surface layer are obtained. The characterization of these porous membranes is made by FESEM imaging (Fig. 2).

As proved by conductivity measurements (see ref. [13]) and FESEM imaging (Fig. 3), only a few channels are totally opened with this anodization process. Indeed, when first channels open on the rear side of the membranes, the current goes through these opened pores and anodization no longer continues on the other pores. This can be explained by the inhomogeneity of the wafer thickness and by the parasitical anodization reaction between the metal layer and the silicon. Even though the silicon is isolated by the silicon oxide layer,
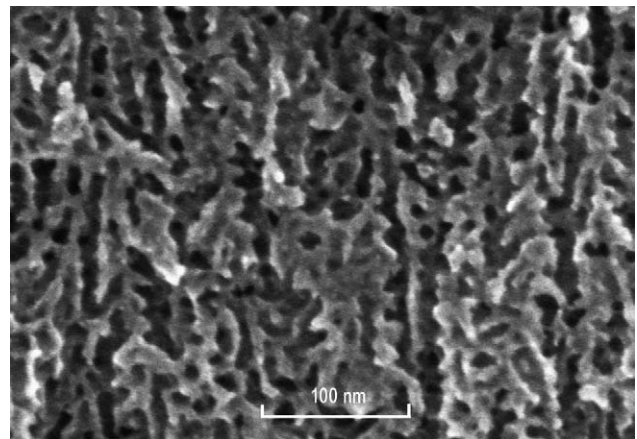

Fig. 1. Four inch wafer with 69 membranes of 7 mm^2 with a thickness of 50 μm.

Fig. 3. FESEM cross-section view of a n$^+$-type silicon membrane made porous by anodization carried out at 36 mA cm^{-2} in the dark in an ethanoic–HF bath. Channels have an average diameter of 10 nm.

it seems that the least contact between silicon and gold can lead to this non-controlled porous layer at the surface of the rear side of the membrane. The phenomena may also occur on the front side but the classical anodization is preponderant.

To solve this problem, we add a short reactive ion etching (RIE) process using SF_6 and O_2 gases for silicon etching on the rear side of the membranes in order to make sure that all the pores are opened [13]. This additional process allows us to etch around 2 μm thick in 3 min which are necessary to open the whole rear side porosity. The characterization of opened pores is carried out by conductivity measurements in a 3% hydrochloric acid electrolyte solution.

To ensure the protonic conductivity, previous solution consisting in filling pores with a Nafion® solution has been fully described and successfully demonstrated in ref. [13].

The new solution, described here, does not need Nafion® nor any ionomeric solution to fill the pores. It consists in taking advantage of the great specific surface of PS by grafting the pores internal surface with silane molecules bearing acid functions. In doing so, we hope to mimic the supposed structure of Nafion® membranes and obtain significant proton conductivity. The *N*-[(3-trimethoxysilyl)propyl]-ethylenediamine triacetic acid in the form of trisodium salt, commercially available from United Chemical Technologies Inc. (UCT), was chosen to our first investigations.

$$NaOOCCH_2 \diagdown \qquad\qquad CH_2COONa$$
$$N-CH_2-CH_2-N$$
$$NaOOCCH_2 \diagup \qquad\qquad CH_2CH_2CH_2Si(OMe)_3$$
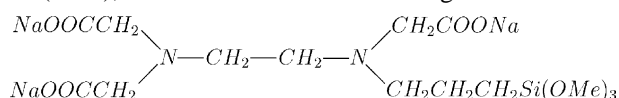
This molecule bears three carboxylic acid functions suitable for protonic conduction.

As the surface of PS is covered with a silica layer a classical process of silanization can be directly used.

The first step consists in creating silanol functions (Si–OH) at the surface of PS. It may be realized by immersing membranes into "Piranha" solution, consisting in a mixture of a 80% solution of pure sulfuric acid with 20% of a 33% aqueous solution of hydrogen peroxide, for 10 min.

The second step is to immerse these hydrophilic porous membranes into a 1% acid silane solution in ethanol for 1 h.

The third step is the activation of the protonic conduction by replacing the –Na endings of silane molecules by –H endings. This is realized by immersing the membranes in a 20% solution of sulfuric acid for 12 h followed by a careful rinsing in deionized water.

We control the efficiency of the process by measuring the conductivity of the membrane in a home-made cell. This allows us to optimize the grafting process.

2.3. Electrodes

We use E-tek electrodes composed of a carbon conducting cloth filled with platinum (20% Pt on Vulcan XC-72) used as H_2/O_2 catalyst. They are fixed to the membrane in the same way as previously done in the case of the PS membranes filled with Nafion® [13].

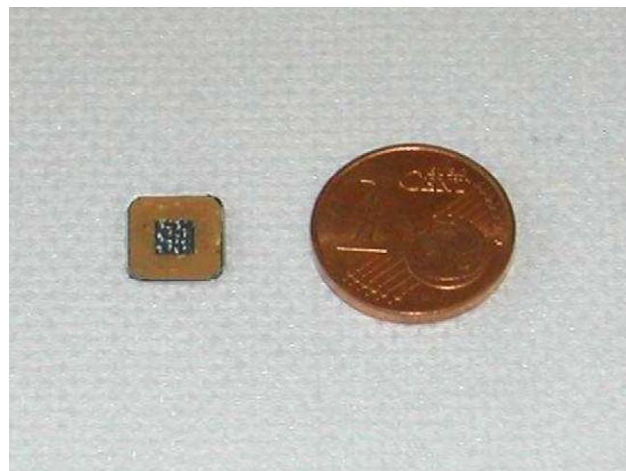

Fig. 4. Membrane electrodes assembly, scale comparison with a 1 cent (0.01 €) coin.

A 1 μl drop of Nafion®-117 solution provides, after evaporation of the solvents, a proton conducting link between the electrodes and the membrane. This amount of Nafion® solution used as glue is too small to fill the pores of and generate proton conductivity in the membrane.

As the membrane borders are covered with a Cr–Au layer to collect current, we just have to make sure that the electrodes and the membrane plated borders are in contact (Fig. 4).

This process allows direct comparison of the results obtained with the two techniques.

3. Results and discussion

All results presented here have been measured with single membrane electrodes assemblies. Measurements are carried out at room temperature. H_2 feeding is provided by a 20% NaOH solution electrolysis and O_2 directly by ambient air. In order to bring the gas to the membrane, we use a home-made test cell in which the membrane electrodes assembly is mounted. Moreover, it allows us to take electrical contacts on each side of the membrane and to evacuate gas exhausts.

The test cell is electrically connected to an ammeter and a voltmeter. Measurements with a Nafion®-filled PS membrane previously reported in ref. [13] have been added to the *I–V* characteristic of the grafted PS membrane for comparison.

We obtain a current density of about 120 mA cm^{-2} in minimal charge and 470 mV for open circuit tension (Fig. 5). These performances are preserved for several hours as long as the assembly is supplied with H_2.

If the performances achieved with both solutions are comparable in terms of power density (17 mW cm^{-2} for the grafted membrane and 18 mW cm^{-2} for the Nafion®-filled membrane) and current density (20 and 101 mA cm^{-2}, respectively), the open circuit tension of the grafted membrane is really lower than the one of the Nafion®-filled
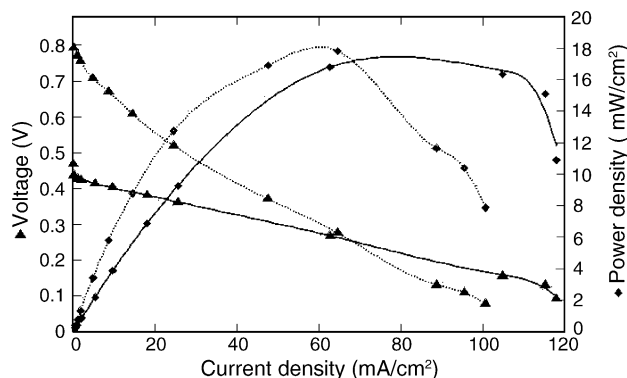
Fig. 5. *I–V* characteristic of a grafted PS membrane (plain curves) compared with a mesoporous silicon membrane filled with Nafion® (dotted curves). Both voltage (triangle-shape points) and power density (lozenge-shape points) are represented.

membrane. This can be explained by the cross-over of gas through the grafted porous membrane.

In that solution, the pores of diameter 10 nm are not filled with polymer and substantial gas diffusion through the membrane induces partial reverse voltage.

This cross-over should be reduced, in future experiments, by decreasing the pore diameter to a value closer to the assumed pore size in Nafion® structure (about 3–4 nm diameter).

A comparison of the slopes of both *I–V* curves in the linear regime shows clearly a lower slope with the grafted membrane indicating a better conductivity than obtained with Nafion® filling.

4. Conclusion

We have demonstrated a new way of making miniaturized fuel cells using a porous silicon membrane and a silane grafted on pores walls. This technique allows to use the great specific surface of the PS and to avoid the problems due to the use of ionomeric membranes. Its main advantage is the total compatibility with silicon micromachining which allows cell integration. First tests are encouraging and allow hope for even better performances in the future. At present time, the present performances are enough to power, by way of parallel and serial coupling of elementary cells, nomadic electronics as long as an hydrogen source is available.

The limitations of this fuel cell are presently the supply in H$_2$ and the assembly with the electrodes which are ways we are investigating.

Acknowledgements

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