Electronic Supplementary Material (ESI) for Lab on a Chip

Fabrication of integrated porous glass for microfluidic applications

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ELECTRONIC SUPPLEMENTARY INFORMATION

1 Anodization setup

Porous silicon was formed by electrochemical etching of the p++ Si wafer in a single-cell Teflon reservoir. The front (polished) side of the wafer was sealed with a leak-tight O-ring and exposed to aqueous hydrogen fluoride (HF) solution, while the backside was in direct contact with a 3 mm thick copper electrode (anode), which covered the backside completely. The counter electrode (cathode) was immersed in the electrolyte solution in order to complete the circuit (Figure 1). The cathode was a platinum (Pt) coated perforated Si wafer. A regularly distributed hole grid was created in a double side polished p++ Si wafer by means of powder blasting. After dicing into a proper size (a polygon to fit in the Teflon container), 300 nm thick Pt layer was sputtered on the electrode, and a 400 μm diameter Pt wire was knitted through the holes. The electrode was placed in the electrolyte and the Pt wire was connected to the hook-shaped probe of the power supply. In order to maintain a uniform anodization process (as the rate of formation of the porous layer is proportional to the distance between the electrode and the surface to be anodized), the electrode was positioned on a Teflon separator ring, which was placed on the wafer to be anodized: the electrode was kept in horizontal position parallel to the wafer surface with a 5 mm separation (Figure 1). A Keithley (Model 2410) high voltage source meter was used for applying a potential to the anode while the cathode was grounded.

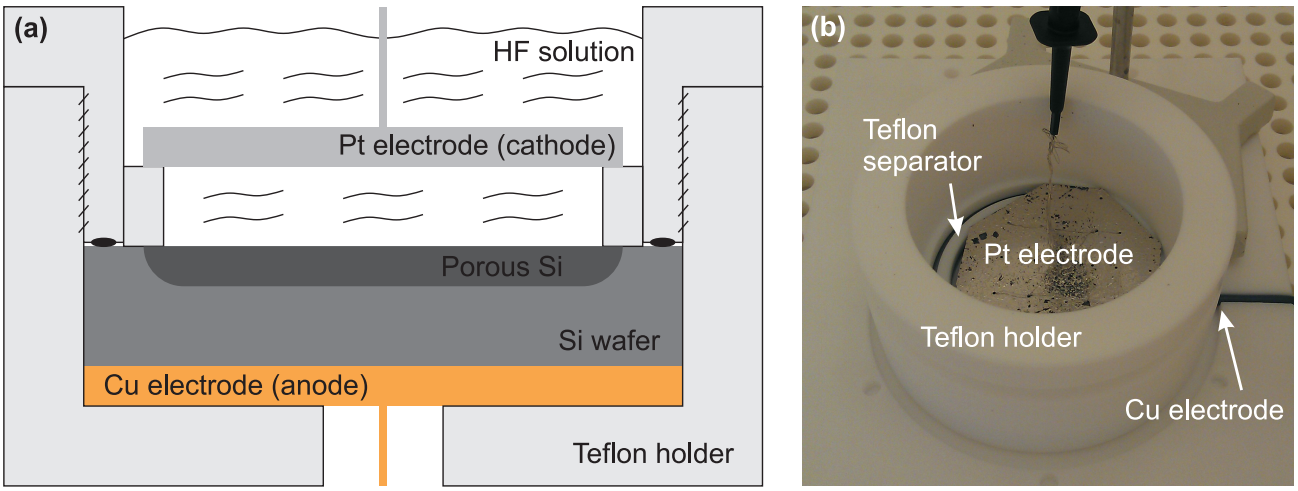

Fig. ESI 1 Schematic representation **(a)**, and a picture **(b)** of the anodization chamber.

2 Using masking layer for selectively anodize the targeted areas

Masking is needed to selective anodization of 3-D structures. Fig. ESI-2 illustrates how a porous bridge is formed between two separate microchannels without masking, causing the exchange of materials during the experiments.

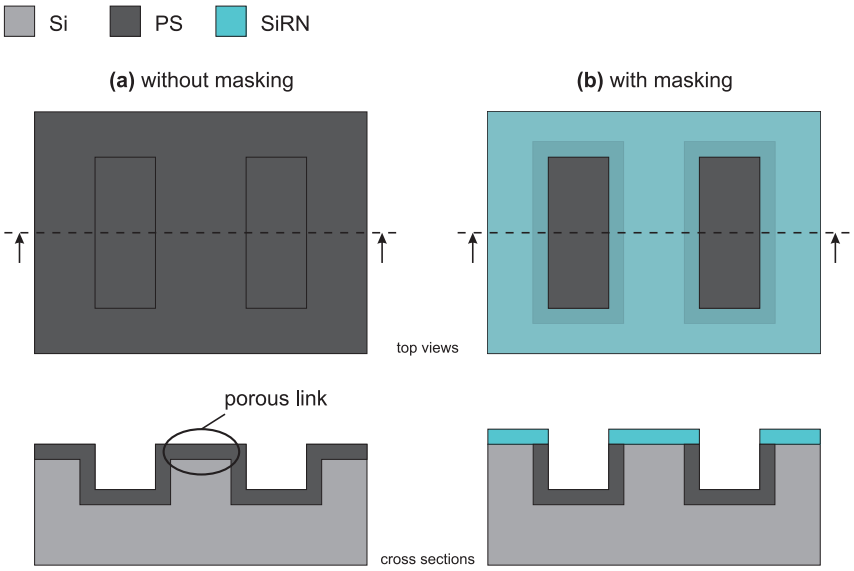

Fig. ESI 2 PS layer formation on 3-D structures with **(a)** and without **(b)** masking.

3 Fully porous pillars and PS formation rate differences between parallel/perpendicular faces

Unlike the other anodization experiments reported in the paper, the masking SiRN layer was removed prior to anodization and a constant current was applied instead of a constant potential. The reason was to enable the possibility of comparing the measured pore size and porosity values with the data in literature and to confirm the validity of the measurement method. In 2008, our group reported a detailed study on anodization of non-processed p++ Si wafers without masking (100% loading) with constant current application (Tiggelaar 2008). Etching the channels increased the total exposed surface area only by 2%, which allowed a direct comparison with BET measurement data in that paper. For the same anodization conditions, the measured pore size and the porosity were 5.4 nm and 55%, respectively as determined from BET adsorption experiments. Image processing measurements over HR-SEM images showed a good agreement with BET-adsorption/desorption. Therefore it was decided to use HR-SEM analyses for determining the pore size and the porosity as a quick and easy method for further experiments. The error margin of the measurements with this method was 10%.

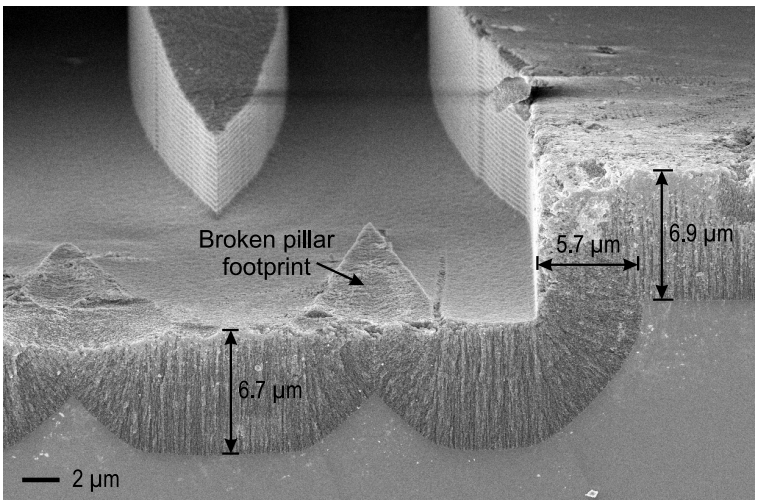

Fig. ESI 3 HR-SEM image of the anodization results for 5% loading design without masking (100% loading case). Fully porous pillars were obtained after 15 min. at 200 mA in 5% HF. Mean pore size and the porosity are 5.2 nm and 53%, respectively.

4 Successful anodic bonding of Borofloat glass onto channels with pillars with layers of integrated PG

Figure 4 shows a SEM picture of a cleaved cross-section of a bonded microchannel with 1 μm PG thickness and a 400 nm thick silica layer underneath.

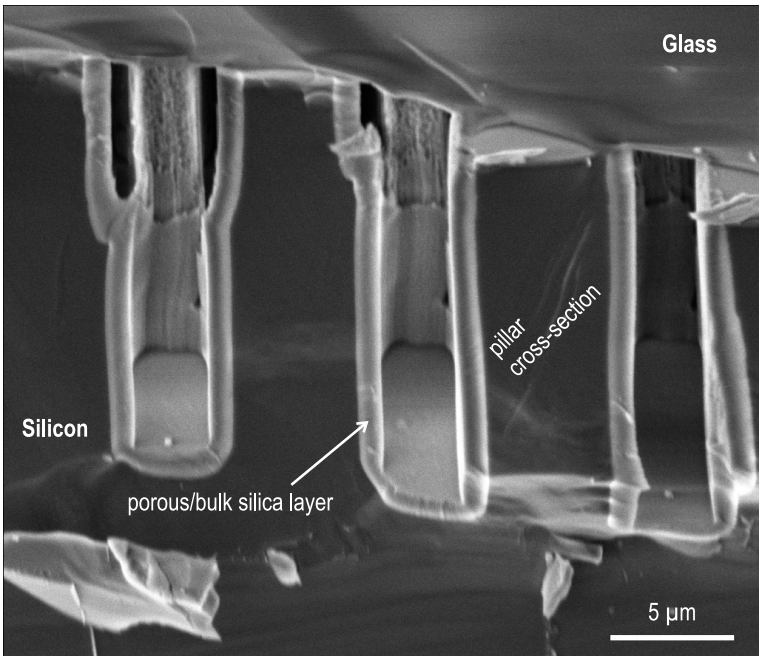

Fig. ESI 4 SEM image of a cleaved microchip. The PG layer thickness is 1 μm and the silica isolation layer thickness is 400 nm. The pillar thickness and height are 6 and 10 μm, respectively.

5 Full conversion of PS into PG: evidence based on dissolvation of PG

As a simple method to evidence PG, dissolvation experiments were performed. The sample shown in Fig. 5(a) was dipped into 1% HF solution for 5 minutes in order to dissolve the PG layer. Fig. ESI-5 represents the SEM picture of the remaining structures after removal of the PG/silica layer. The HF etching process resulted in conical structures in case of fully anodized/oxidized circular pillars with a "rough" bottom. The conical shape of the remaining solid Si core underneath the fully porous pillars was defined by the pore direction perpendicular to the exposed silicon surface, and this direction itself was defined by the electric field lines during the anodization. The etching solution was checked after etching for any released traces of non-oxidized Si skeleton, but nothing was observed. This demonstrated that PS was fully converted into PG, since 1% HF solution did not etch PS.

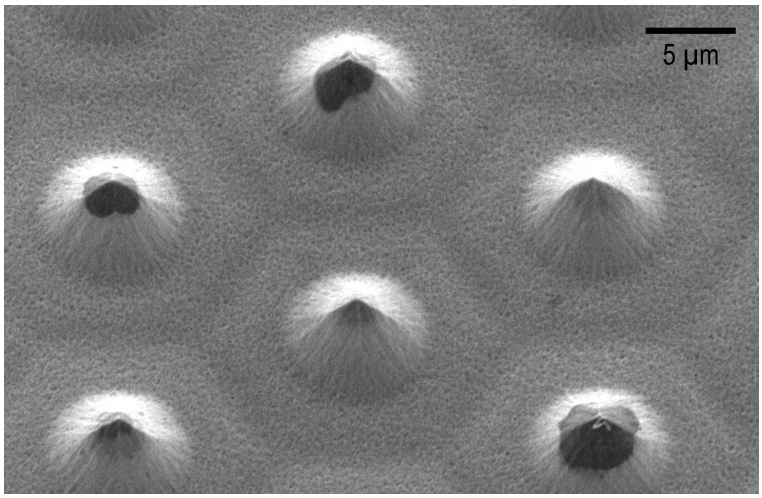

Fig. ESI 5 SEM picture of the leftover conical structures after dissolvation of the PG/silica layer of the fully porous circular pillars in 1% HF.

6 Merging of pores into canals at sharp edges

Fig. ESI-6 shows the bright field microscope image (top view) of a pillar after anodization and subsequent removal of the masking SiRN layer. Pore formation starts on the surface and penetrates through the structure with a growth direction that coincides with the electric field lines. At the corners/sharp edges of the structures, Nanocanals are formed due to combined pore formation. Please note the color change due to the differences in pore size and porosity. This is a typical optical property of PS, whilst it becomes optically transparent after conversion into porous glass.

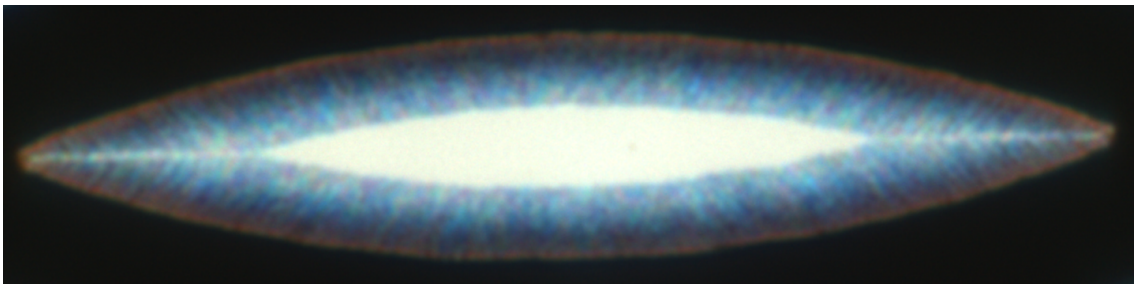

Fig. ESI 6 Microscope image (top view) of custom shaped pillar after anodization. SiRN layer was removed. The bright region in the middle is the non-porous solid Si core, which highly reflects the light. Straight nanochannels, which are open at the tip of the structures, are created due to combined pore formation.