Superhydrophobic surfaces' influence on streaming current based energy harvester

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Abstract. The purpose of this paper is to report the design, fabrication and characterization of silicon-based microfluidic channels with superhydrophobic walls for energy harvesting. We present the fabrication step of silicon based streaming current energy harvester and the nanostructuration of the microchannel walls. We characterize the superhydrophobic properties of the surface in a closed system. Our preliminary results on the electrical characterization of the device show a 43% increase of power harvested with our superhydrophobic surface compared to a planar hydrophobic surface.

1. Introduction
Energy harvesting via streaming current has been investigated since the early 2000 with the growing field of microfluidics. Passing a fluid through a microchannel creates a net ionic current, which can be collected by an external electrical system. As predicted by physics, efficiency improvement has been reached by reducing the size of the microchannel, with efficiencies of 1.3% reached for micron-sized channels [1] and 3-5% for nanoslit [2]. In 2007, Pennathur et al.[3] have projected that 35% energy conversion efficiency could be obtained by using superhydrophobicity inside channels. Despite experiments showing liquid slip at the solid/liquid interface and the resulting decrease in pressure [3], [4], to the authors' knowledge, no experimental work has shown this promising predicated improvement in energy harvesting efficiency.

2. Design and fabrication
The first streaming current harvesting device built contains a "trench"-like microchannel. The accesses, reservoirs and channels are etched in a single process of deep-reactive ion etching (DRIE) on a silicon wafer (diameter 3", thickness 360 µm), and sealed by anodic bonding a 1 mm pyrex cover. The resulting microchannel is 1 mm long, 127 µm deep and 22 µm wide. In order to produce the superhydrophobic surface on vertical walls we adapted a version of the MACE process used to engineer silicon nanowires on orthogonal surfaces [5]. The structured surface is then made superhydrophobic by coating with a hydrophobic material (PFTS) in vapor phase. Water on a flat surface with these coated nanowires has a contact angle of 168° (6° hysteresis) and a stable Cassie-Baxter state.
Our process generates a 2 µm-long nanowire structuration on both the bottom and the sides of the channel (Figure 1). Nanowire covering ranges from 5 to 100% of the surface (C). We used devices with more than 90% of the wall surface covered with nanowire structuration (3 out of 10 devices produced). However we could not verify the presence of the Cassie state in this geometry, which prompted the development of a second device.

The second device developed has a thin-slit microchannel and a pyrex cover allowing for optical observation of the surface. It decreases the percentage of structured surface of the microchannels to 50% but enables real-time optical monitoring of the wetting state of the surface independently from pressure measurements.

The microfabrication process is shown on Figure 2. Three DRIE steps (A1) are needed to etch (a) the reservoirs (100µm), (b) the channels and (c) the microfluidic accesses through the silicon. Each device contains five microchannels 10 µm deep, 1 mm wide and 5 mm long between reservoirs 100 µm deep. After etching the microchannels are structured (A2) by the same MACE process as previously used and coated with PFTS. The 100 nm thick gold microelectrodes are deposited on the pyrex wafer by sputtering and chemical etching (B), and silicon and pyrex are assembled by anodic bonding (C). The completed system is visible on Figure 3.
3. Results
The electrical characterization of the hydrophilic silicon version of the first device is given at Figure 4.

![Figure 4: Electrical characterization of the hydrophilic trench-like structure.](image)

| Electrical Characterization          |
|-------------------------------------|
| Streaming Potential                 | 18 V                                      |
| Streaming Current                   | 5 nA                                      |
| Efficiency                          | 0.3%                                      |
| Optimal Load                        | 4 GΩ                                      |
| Power Density                       | 1.6 µW.cm⁻²                               |

No noticeable improvement could be observed in this device by using superhydrophobic surfaces. The high pressures needed to move the liquid in the channel may induce the impalement of the liquid on the nanotexturation. However, it is impossible to confirm this hypothesis.

The wetting state of the superhydrophobic surface of the second device has been monitored with an optical camera (Figure 5) showing either Cassie-Baxter (5.A) or Wenzel (5.B) states. The superhydrophobic surface can sustain overpressures superior to 170 kPa. After impalement, the superhydrophobic behaviour can be regenerated several times by drying.

![Figure 5: Optical picture from the glass side of the second device with 10 channels either in (A) a Cassie Baxter state (no wetting of the silicon nanowires) or (B) a Wenzel state (impalement of the liquid on the silicon-nanowires).](image)

We did not observe noticeable pressure drop reduction in this device between the Cassie-Baxter state and the fully wetted Wenzel state. Two hypothesis can be formulated. First, since only 50% of the
channel is covered by silicon nanowires (the remaining being the glass substrate), we have a strong heterogeneity in the slip conditions. It has been shown that for confined systems, the flow is strongly controlled by this heterogeneity [6]. Second, even if the optical characterization shows a Cassie Baxter state, we do not have any information about the degree of impalement of the liquid on the nanostructures and thus on the hysteresis (i.e. adhesion force). Additional characterization are mandatory.

Figure 6 (A) gives the variation of the streaming current as a function of pressure for the second device. At high pressures, streaming currents up to tens of nano-amperes and streaming potentials up to 3.5 V have been measured in the device. Preliminary results on the comparative power output of flat hydrophobic surfaces and superhydrophobic surfaces are reported on Figure 6 (B). One can observe an increase of up to 40% of the output power for superhydrophobic surfaces, depending on the load resistance of the external electrical circuit. Power measurement were made at a pressure of 20 kPa.

4. Conclusion
Our preliminary results add experimental evidence that using superhydrophobic nanostructured surfaces in microchannels can increase the efficiency of energy generation through streaming current harvesting.

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