## Ionic Current Rectification and Switching in Heterogeneous Oxide Nanofluidic Channels

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Nanofluidic device exhibiting ion current rectifying behavior is of great interest because it provides a basis to control the ion flow in the channel. Ionic current rectification can be generated in a nanofluidic channel that contains asymmetric distribution of cation-anion concentration ratios. Such an asymmetric distribution can be readily established in nanofluidic diodes. One of the key challenges to producing nanofluidic diodes is to create different surface charges along a nanochannel.

In this work, we investigated ion transport behavior in sub-20 nm nanofluidic channels consisting of heterogeneous oxide materials. By utilizing distinct isoelectric points of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> surfaces and lithography to define the charge distribution, nanofluidic channels containing positively and negatively charged surfaces are created to form an abrupt junction. This method provides much more robust surface charges than previous approaches by surface chemical treatment [1,2]. The fabrication method used to make heterogeneous nanochannel is similar to that reported in our previous work on SiO<sub>2</sub> nanochannels, which is based on a sub-20 nm thick sacrificial layer approach to precisely define the height of the nanochannel [3]. To produce heterogeneous nanochannels, two additional Al<sub>2</sub>O<sub>3</sub> thin films were patterned by photolithography to sandwich half of the sacrificial layer in order to form a sub-20 nm thick nanochannel comprising of two sections made of different oxide surfaces. A high selectivity XeF<sub>2</sub> plasma etch was used to remove the sacrificial amorphous Si layer and open the nanochannels (Fig. 1).

The fabricated nanofluidic diodes exhibit high rectification of ion current and achieve record-high rectification factors of over 300. The current-voltage characteristics of the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> nanofluidic diode was measured at varied bath concentrations ranging from 10  $\mu$ M to 1 M. A voltage bias V<sub>d</sub> was applied to the bath that connects to SiO<sub>2</sub> nanochannel while the Al<sub>2</sub>O<sub>3</sub> side was grounded (Fig. 1b). The experimental I-V curves are presented in Figure 2(a)-(f) (red empty circles). It is shown that the I-V characteristics display strong rectification effect at every concentration except at 1 M. Figure 2(g) summarizes the channel conductances obtained at varied bath concentrations and the associated rectifying factors (shaded bars). We found that the current-voltage property of the device follows our theoretical model quantitatively except that at low ion concentrations, which can be attributed to access resistance and breakdown effect. In addition, we also demonstrated ionic switching in a three-terminal heterogeneous nanofluidic triode in which the ionic current can be electrically regulated.

[3] L. J. Cheng and L. J. Guo, Nano Letters, 7, 3165 (2007)

<sup>[1]</sup> R. Karnik, C. H. Duan, K. Castelino, H. Daiguji and A. Majumdar, Nano Letters, 7, 547 (2007)

<sup>[2]</sup> I. Vlassiouk and Z. S. Siwy, Nano Letters, 7, 552 (2007)



Figure 1. (a) Microscope image and (b) schematic of a 20-nm thick heterogeneous nanochannel consisting of two different oxide surfaces, which forms a nanofluidic diode.



Figure 2. Ion current vs. Voltage characteristics of a nanofluidic diode (equivalent channel width =  $2.5 \ \mu m \times 10$ ) measured at different bath concentrations: (a) 0.01 mM, (b) 0.1 mM, (c) 1 mM, (d) 10 mM, (e) 100 mM and (f) 1 M. The red symbols are experimental data and the black dashed curves are calculated result based on a simplified 1D transport model. (g) Log-log plot of the experimental forward-conductances (blue squares), reverse-conductances (red circles) and the rectifying factors (shaded bars) at different bath concentrations.