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Field effect transistor based on protons as charge carriers

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Abstract

We demonstrated a field effect transistor based on the modulation of the proton flow in confined water-containing nanochannels. The device resembles an MOSFET transistor with the difference that the charge carriers here are ions (i.e. protons) instead of electrons. The effective cross-section of the conductive channels in the transistor is defined by the intensity of the electrical double layer and by the potential applied to the transistor gate.

1. Introduction

The accurate mechanism of proton transport in water remains unclear, despite decades of extensive research. Proton ions are very specific: they exist in electrolytes only in the form of hydronium ions, associated with clusters of water molecules. Owing to the specific "hopping mechanism" of transport [1] protons have abnormally high mobility compared to similar cations like Li^+, Na^+ or K^+. A better knowledge of proton transport would have a profound importance for the understanding of biological processes, but also for various man-made devices, such as sensors, batteries and particularly fuel cells [2]. Furthermore, it has been reported that the proton transport in uninterrupted 1-D water chains (water nanowires) is ensured through fast transport of charge defects rather than through the transport of protons themselves [3].

Two methodologies are available for the experimental investigation of proton transport in narrow channels: the examination of proton transport enabled by macromolecules within well defined nanochannels filled with water or through artificial nanochannel devices allowing the variation of high impact parameters in a controlled manner. For the first method it is necessary to synthesize different organic compounds which contain nanochannels with fixed parameters (i.e. diameter, surface states, etc.). The second approach implies the fabrication of an artificial nanochannel device with its control parameters varied by an external electric field. Such structures could also potentially serve as the basis for a number of novel devices, including nanofluidic transistors and sensors, as well as various digital nanofluidic elements [4].

2. Theoretical consideration of ions transport in confined nanochannels

Ion/proton transport through nanochannels differs from that in bulk, due to the high surface to volume ratio of nanochannels. The electric fields from surface charges alter the ion conductance by orders of magnitude [5-6]. When the cross section of a channel is reduced to a value near to the Debye screening length, the distribution of ions/protons across the channel can not be regarded as homogenous. In the case of electrostatically bonded Pyrex glass and oxidized silicon, which are the materials used in our device, negatively charged ions (i.e. SiO^-_2) are in the contact with the fluid/SiO_2 interface. Therefore, the equivalent number of the positive ions in the fluid is electrostatically attracted by the negatively charged glass walls [7].

The spatial distribution of charges across the nanochannel depends on the fluid properties (e.g. pH value, type and concentration of ions in the fluid), but also on the applied external electric field. The field variation therefore causes *modulation of the transport properties of protons/ions within the channel*. The total channel conductance G in nanochannel can be described as [10]

$$G = \frac{w}{L}F^2 c_b \int_{-h/2}^{h/2} \left(\mu_+ e^{-F\psi/RT} + \mu_- e^{F\psi/RT}\right) dy + \frac{w(\varepsilon_0 \varepsilon_r)^2}{L\eta} \int_{-h/2}^{h/2} \left(\frac{d\psi}{dy}\right)^2 dy \tag{1}$$

where w, h and L are the channel width, height and length, F is the Faraday number, c_b is the bulk ion concentration, ψ is the electrostatic potential, μ_+/μ_- is the mobility of positive/negative ions, R is the Reynolds number, T is the temperature, $\varepsilon_0\varepsilon_r$ is the permittivity and η denotes the fluid velocity.

In order to realize unipolar ionic environment it is necessary to work with a medium offering sufficiently low ionic strength (i.e. water). In this paper, we present the modulation of the proton conductivity in nanochannels in a fast and reversible manner with applied voltages as low as 1 V. Recently, Sparreboom *et al.* reported on their active modulation in a two to four-fold range [8].

3. Design and fabrication

In our experiments nanochannels and water reservoirs are made in Pyrex wafers (Boroslikatglass MDF, Planoptik, Germany). We have defined the position and the size of nanochannels using standard photolithography, as illustrated in Fig. 1a. Nanochannels were plasma etched 4 µm wide and 155 nm deep. We made various test structures with different nanochannels lengths (i.e. 10 µm, 60 µm and 460 µm) as well as with different numbers of channels per chip (i.e. 1, 5, or 10) in order to have a large variety of test samples for characterization.

After processing of the nanochannels, the electrolyte reservoirs were wet etched to a depth of about 18,4 µm in highly concentrated HF solution (40%) by using a Cr/Au masking layer (50 nm/400 nm). Reservoirs were made large enough to hold sufficient quantities of fluid during characterization. In this way, the impact of fluid evaporation on measurement results was significantly reduced. Additionally, larger dimensions of the reservoirs enabled good electrical contact to the electrolyte. The same hard mask based on the Cr/Au bi-layer used for the etching of the glass substrate in HF was also used to pattern via a lift-off process the Ta/Pt (10 nm/200 nm) electrodes on the bottom of the reservoirs, as shown in Fig. 1e.

The transistor gate was made of dry oxidized silicon. The starting material was a silicon wafer coated with 250 nm thermal SiO_2 and 70 nm of LPCVD Si_3N_4 (see Fig. 1a). The standard processing was used for the deep wet etching of Si in 40% KOH (see Fig. 1b). Next, the hard mask was completely removed on both wafer sides. The wafers were once again cleaned in plasma following again a dry oxidation process for the gate isolation (100 nm SiO_2). The glass wafer was subsequently cleaned, cut into chips (10×10 mm^2) and anodically bonded to the silicon gate (see Fig. 1f). Finally, the bottom Pt electrodes in the fluid reservoirs were electrically connected with copper wires using silver paste as fixture.

In Figs. 2 a) and b), the Pyrex wafer with nanochannels and the assembled nanofluidic transistor are presented.
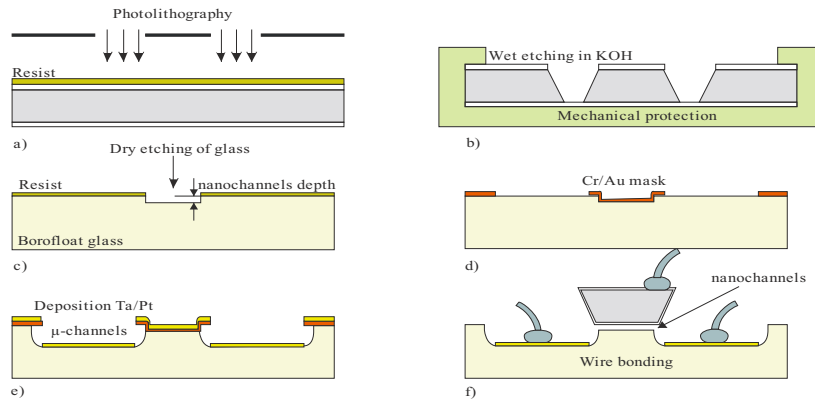
Fig. 1. Processing of the proton conductive structures: (a) deposition of masking layer SiO_2/Si_3N_4, photolithography to define the opening for etching in KOH, dry etching of SiO_2/Si_3N_4, removing of the resist and wafer cleaning (b) back protection of wafer and etching in KOH, removal of the mask, cleaning and thin dry oxidation of Si wafer, (c) spinning of resist, photolithography for defining nanochannels, plasma etching, (d) deposition of Cr/Au masking layer, resist deposition, photolithography and wet etching of Cr/Au layer, (e) wet etching of deep microchannels in highly concentrated HF, deposition of Ta/Pt layer, wet etching of the mask Cr/Au, (f) anodic bonding of glass with silicon chips and wire bonding.

Fig. 2. (a) Optical micrograph the nanochannel array etched in a Pyrex substrate; (b) Photo of an assembled device, chip dimensions 1 x 1 cm. The transistor gate (top) is electrostatically bonded to the Pyrex substrate covering the nanochannels array. Contact pads are denoted by *S* for the source, *G* for the gate and *D* for the drain, respectively.

4. Device characterization and measurements

The performances of the assembled devices were tested using bi-distilled water as the proton-containing medium. Pure water is an almost perfect isolator; however, pure water practically does not exist. Water molecules turn by auto-ionization into hydronium ion (H_3O^+) and an associated hydroxide ion (OH^-) at a rate of $K_w = 1.0 \times 10^{-14}$ mol/l at 25^oC [9]. This ion concentration contributes to the maximal resistivity of water of 18 MΩ·cm. Furthermore, marginal amounts of contaminants from the atmosphere (mainly carbon dioxide and salt particles) in concentrations less than few ppb further reduce the resistivity of water to ~ 1 MΩ·cm [7]. While generally the water purity is questionable, it was considered in our experiments that the main charge transport proceeded via proton ions [1, 2]. It is also assumed that the SiO_2^- charges in the surfaces of the nanochannels were partially neutralized by highly mobile K^+ ions during the electrostatic bonding of the gate structure.

For a first pre-evaluation the ohmic resistance of a single channel was measured. The resistivity of a single channel was R ≈ 4 GΩ, as shown in Fig. 3a). Next measurement cycles were dedicated to the characterization of the device operated in a typical MOS transistor configuration. The source-drain voltage was swept in a range of ±1 V with constant gate voltage for 7 cycles. In each cycle, the gate voltage was increased in steps of 250 mV, from –1 to

+1 V (see Fig. 3b). Based on the measured U/I curves, the tranconductance of the nanofluidic transistor was calculated as $g_m = 5 \times 10^{-7}$ S for small signal demonstrating the basic functionality of the nanofluidic device as transistor.
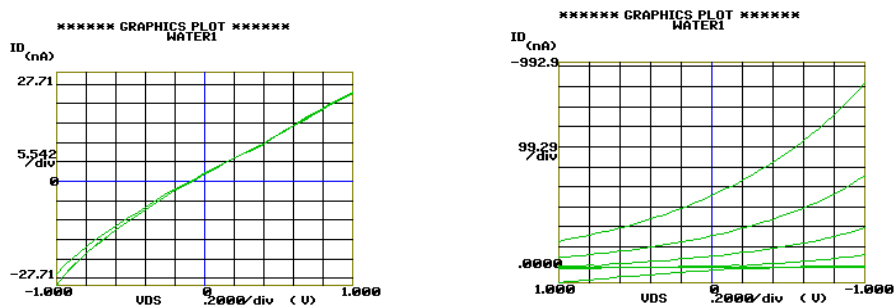

Fig. 3. (a) U/I characteristics of a single-channel device connected as resistor, the gate is floating. The device has a near-linear response showing no significant electrochemical reactions between electrodes (Pt) and electrolyte (water). (b): U/I characteristics of device connected as MOS transistor. Source-gate voltage was swept in the range of ± 1 V and the gate voltage was in the range of -1 V to + 1 V with increments of 250 mV. Device parameters: array of 5 nanochannels (length: 460 µm, depth: 15 nm, width: 4 µm) connected in parallel.

5. Conclusion

The results of our experiments confirm the confinement of the effective cross-section of nanochannels via external electrical field, causing a modulation of the proton flow in the nanochannel. The novel device works at a low gate voltage of < 1 V and has a higher transconductance (i.e. by a factor of 10) than those reported in previous publications, due to thin gate isolation used in our device. Further experiments are currently underway.

Acknowledgements

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