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Field effect transistor based on ions as charge carriers

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ABSTRACT

We demonstrated a field effect transistor based on modulation of the flow of positive changed ions (dominantly protons) in confined water-containing nanochannels. The device resembles a semiconductor MOSFET transistor with the difference that the charge carriers here are ions (i.e. protons and others) instead of electrons as in the case of semiconductor devices. The transconductance of the nanofluidic transistor is a complex function of the gate potential, ion concentration, charges at the solid/fluid interface, temperature and more. Preliminary experimental results from fabricated devices are in a reasonably good agreement with the theoretical predictions.

1. Introduction

We are surrounded and routinely supported by millions of transistors, a fact we take for granted. Various communication devices, vehicles, computers, even common home appliances often incorporate complex systems that sense external stimuli, process the signal and output the results in the form of air pressure variations (we perceive it as sound), photon flux (picture), or can act autonomously. In the heart of such systems is the transistor, the device able to modulate the flow of electrons or holes in semiconductor via simple electrokinetic phenomena. However, we are much less aware of the fact that the outputs of these artificial systems are further processed in our brain, again with the help of billions of transistor-like structures, but different from their semiconductor counterparts. Better known in biophysics as “gated ion channels”, these structures closely resemble the basic functions of the semiconductor transistors. However, the biological transistors are more complex, efficient and their size is nanoscopic. While the artificial, semiconductor transistor deals exclusively with electrons and holes, the “biological transistor” processes various ions differing in sizes, mobilities and charges. Furthermore, the biological transistors are highly selective, for example they may be conductive solely to N^+ ions but not to the related H^+ or K^+ ions [1].

From the practical point of view, the knowledge of the transport of hydrogen ions in nanochannels, especially the externally controlled transport, has a profound importance for the understanding of the vital biological processes, but also for various man-made devices, such as sensors, batteries and particularly fuel cells [2]. Protons are very specific ions which generally exist in electrolytes only in the form of hydronium ions (H_3O^+) associated with clusters of water molecules. The accurate mechanism of proton transport in water remains not fully understood, despite decades of research. Owing to the specific “hopping mechanism” of transport, the protons exhibit abnormally high mobility compared to the related cations like Li^+, Na^+ or K^+ [3]. Furthermore, it has been reported that the proton transport in uninterrupted 1D water chains (water nanowires) is ensured through fast transport of charge defects rather than through the transport of protons themselves [4].

Two methodologies are available for the experimental investigation of proton transport in narrow channels: the examination of proton transport through macromolecules containing a well defined nanochannel filled with water or through an artificial nanochannel that enables us to study this process by controlled modification of the principal nanochannel parameters. 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 device with integrated nanochannels, fluid reservoirs and a control structure (the gate). In this case, the effective cross section of a nanochannel or nanochannels array can be varied solely by variation of an external electric field.

Actually, the last proposed structure is basically the field effect transistor, and to our best knowledge this concept was first proposed by Gajar [5], and later physically realized by same authors [6]. The first nanofluidic transistors required the gate voltage in the range of 50–100 V; however, those structures confirmed the

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feasibility of concept. In this paper we present our results in realization of a nanofluidic transistor which works satisfactorily at a source–drain potential of $V_{sd} < 1$ V, but also requires the gate voltage less than 1 V. The nanofluidic transistor presented here was manufactured using the standard MEMS and planar techniques, since this approach enables low-cost production and in addition a satisfactorily accurate control of the geometrical and the electrical parameters of the device. Besides the main task of this device, the study of proton transport in confined 1D water wires, the presented structures could also potentially serve as a basis for numerous novel devices, including other types of nanofluidic transistors, nanofluidic sensors, as well as for prospective digital nanofluidic elements [7].

2. Theoretical consideration on ion transport in confined nanochannels

Proton/ion transport through nanochannels differs from the transport in bulk. This can be explained by the high surface-to-volume ratio of nanochannels, where surface charges can alter the conductance by orders of magnitude [6,8]. In a silicate glass, formation of a surface leads to Si–O- and Si-bonds that are unsatisfied. These bonds react rapidly with atmospheric water to form SiOH groups. Therefore the surface of an oxide glass is normally negatively charged hydroxyl groups [15]. Negative charges accumulate in the glass channels at the interface with the fluid. On the other side, in the fluid, the same amount of the positive ions is being electrostatically attracted by the negatively charged glass walls in order to maintain electroneutrality (Fig. 1a).

When the dimensions of the channels reduce significantly to reach the Debye screening length (λ_D), the distribution of ion/protons across the channel depth assumes its characteristic exponential shape (Fig. 1b). The value of the λ_D is determined by formula [9,10]:

$$\lambda_D = \sqrt{\frac{\varepsilon_0 \varepsilon_r RT}{2F^2 z^2 c_b}} \qquad (1)$$

where $\varepsilon_{0,}$ ε_r are the dielectric permittivities of vacuum and the fluid, R is the gas constant, T is the temperature, F is the Faraday number, z_i is the valence number and c_b is the bulk concentration of ions in water.

In our experiments, we used double-distilled water with low impurity concentrations. It was assumed that the protons in water were mainly induced by dissolving CO_2 from the air and the concentration of protons resulting from the equilibration with air was estimated to be $c_b \sim 10^{-3}$ mol/m^3 [11]. According to Eq. (1), the calculated value of λ_D was 97 nm for the case of pure water with dissolved CO_2. Under real working conditions, in the presence of a small amount of impurities, it was assumed that λ_D had a slightly smaller value than calculated for pure water.

According to [9,10], the total channel conductance G in a nanochannel is described by

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

where w, h and L are the nanochannel width, height and length, ψ is the electrostatic potential, μ_+/μ_- are the mobilities of positive/negative ions, respectively and η denotes the fluid velocity. The first term is the conductance contributed by electrophoresis and the last term is contributed by electroosmosis. The contribution of electroosmosis in nanochannels is usually significantly smaller than that of electrophoresis and can be neglected. Since the fluidic flow in such small channels is comparably low and a negligible, most of the current is contributed by the migration of ions. The electrostatic potential ψ as a function of the position across the channel can be obtained from Poisson–Boltzmann equation [9]. Under this condition Eq. (2) can be approximated as:

$$G = q(\mu_+ + \mu_-) n_b \frac{wh}{L} + 2\mu_+ \sigma_s \frac{w}{L} \qquad (3)$$

where the q is the electron charge and μ_+/μ_- are the mobilities of proton/$HCO_3{}^-$ ions, respectively. It is assumed here that $n_b = n_{H+} = n_{HCO3}{}^-$ is the number of ions/protons in water, equal to $N_A \cdot c_b$ (where N_A is the Avogadro constant). Here it is considered that the electroneutrality is preserved in the nanochannel [10]. The first term is dominant for high ion concentrations, while the second term dominates for low ion concentrations, which was the case in our experiment. Dimensions of our channel were $w = 4$ μm, $h = 155$ nm and $L = 460$ μm. σ_S stands for the surface charge density.

The value of the surface charge density (σ_S) on the contact surface glass/liquid is dependant on the properties of the fluid (the pH value, the type of ions and the concentration of ions in the fluid) and is defined as the charge density contained in the Stern layer and the diffusive double layer. The typical values reported in the literature for σ_S, are in the range from 2.5×10^{-2} C/m to 6×10^{-2} C/m [10].

In the case when the impurity concentration is very low (e.g. double-distilled water), the first term in Eq. (3) is significantly smaller (four orders of magnitude) than the second term and can thus be neglected. Taking the value for $\sigma_S = 4 \times 10^{-2}$ C/m and mobility of protons $\mu_+ = 36 \times 10^{-8}$ m^2/sV [12], we obtained the conductivity of a single nanochannel $G = 2.5 \times 10^{-10}$ S (resistance $R \sim 4$ GΩ). The measured values for the resistivities were in the range 800 MΩ to 1 GΩ per channel, so that the values are in good agreement with theoretical prediction.

The value of σ_S can be tuned externally by the electric potential applied to the gate electrode. This results in the modulation of protons/ions flow, i.e. the modulation of the channel electrical current. In this paper, we present the modulation of the protons/ions conductivity in nanochannels in a fast and reversible manner with gate potential as low as 1 V.

3. Design and device fabrication

The nanochannels and water reservoirs were manufactured in Pyrex wafers (Borosilikatglass MDF, Planoptik, Germany). The position and the size of nanochannels were defined using the standard photolithography, as illustrated in Fig. 2a. The nanochannels were plasma etched 4 μm wide and 155 nm deep. We made various test structures with different nanochannel lengths (10 μm, 60 μm and 460 μm). In addition, number of channels per chip was varied (1, 5, or 10) in order to have a larger variety of different test samples for the subsequent characterization measurements.

After fabrication of nanochannels, 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). The reservoirs were made large enough to hold sufficient quantities of fluid during characterization. In this way, impact of fluid evaporation on measurement results was significantly reduced. Additionally, larger dimensions of reservoirs enabled good electrical contact with 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 in a lift-off process to pattern the Ta/Pt (10 nm/200 nm) electrodes on the bottom of the reservoirs, as shown in Fig. 2e. The processed glass wafer was subsequently cleaned and cut into the chips 10 mm × 10 mm size. A finished Pyrex chip with 10 nanochannels, but without Ti/Pt electrodes is shown in Fig. 3a.