Study of ion transport in single solid state nanopores formed by optical and ion lithography

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Abstract. This work studies the transport properties of solid-state nanopores. Nanopores with a diameter of 35−40 nm formed in a thin "free-standing" silicon nitride membrane of 300 nm thick. An experimental setup has been developed to study the transport characteristics of single nanopores. Based on the results of electrical measurements, the pore conductivity was calculated for concentrations of KCl electrolyte in the range of $10^{-4}-1$M. An increase of nanopore conductivity was observed with an increase of the electrolyte concentration above 10^{-2} M. This dependence can be explained by the electrical double layer overlapping that leads to appearance of a charged region inside the nanopore.

Keywords: nanopores, solid state nanopores, microfluidic, ion transport, optical lithography, ion lithography

Ионный транспорт в единичных твердотельных нанопорах, сформированных методами оптической и ионной литографии

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Аннотация. Данная работа посвящена изучению транспортных свойств твердотельных нанопор. Нанопоры диаметром 35–40 нм были сформированы в тонкой «свободностоящей» мембране из нитрида кремния толщиной 300 нм. Была разработана экспериментальная установка для изучения транспортных характеристик одиночных нанопор.

На основании результатов электрических измерений была рассчитана проводимость нанопор для концентраций электролита KCl в диапазоне 10^{-4}–1 М. Увеличение проводимости нанопор наблюдается при увеличении концентрации электролита выше 10^{-2} М. Эта зависимость может быть объяснена перекрытием двойного электрического слоя, что приводит к появлению заряженной области внутри нанопор.

Ключевые слова: нанопоры, твердотельные нанопоры, микрофлюидика, ионный транспорт, оптическая литография, ионная литография

Introduction

Nowadays, the development of microfluidic technologies makes it possible to manipulate small volumes (μl, nl, pl, fl) of liquids. The use of nanostructures in microfluidics, such as nanosized channels and pores, opens up opportunities for selective transport and separation of substances [1], energy conversion [2], and detection of particles in solutions [3]. The last one is especially useful for biology and medicine, because it allows studying small concentrations of biological molecules, proteins and DNA. Thus, microfluidic technologies are promising for such devices as lab-on-a-chip, molecular sensors [4] and DNA sequencers [5].

The principle of detection and analysis of small concentrations of dissolved substances (typically biological molecules) is to pass them through nanopores. When a molecule passes through the nanopore, a change in current can be observed. Therefore, the measurement of the current change allows one to detect and analyze the molecules dissolved in the solution. For better detection, the inner diameter of the nanopore should be as small as possible. There are two main types of nanopores: biological and solid-state. Biological nanopores are composed of transmembrane proteins embedded in lipid membranes. Their main advantages are small pore diameter (2nm for α-hemolysin [6] and 1,2nm for MspA [7]), size reproducibility, and low translocation velocity. Their disadvantages include sensitivity to pH, physical influences, temperature, and electrolyte concentration. Solid-state nanopores are thin membranes, such as a monolayer of graphene [8] or a thin film of SiNx [9], in which pores of the required diameter are created using lithography methods. Such nanopores are distinguished by the ease of fabrication, resistance to external conditions and longevity. Solid-state nanopores also have great potential for surface modification [10], which is promising for the study of selective transport.

Since the walls of nanopores are electrically charged, as the molecules under study are, characteristics such as pore conductivity, surface charge, and wall geometry affect the transport through the nanopore. Accordingly, the purpose of this work is to study ion transport of solid-state nanopores.

Experiment

For this work, we employed SiNx as the nanopore material because the formation of pores in thin semiconductor films is a well-established process [11]. First, a Si substrate with a thin 300 nm layer of SiN was formed. Then, using optical lithography, the Si substrate was partially etched, leaving a "free-standing" SiNx membrane with dimensions of 80×80 μm. After that, pores with a diameter of 35–40 nm were created in the SiNx membrane by ion beam milling (see scanning electron microscopy (SEM) image in Fig. 1).

The experimental setup (Fig. 2) for studying the transport characteristics consists of 2 tanks with KCl electrolyte, connected by a membrane with a nanopore using elastic gaskets. The tanks have several openings for the inlet and outlet of electrolyte and for the installation of electrodes. AgCl wires were used as electrodes. The assembled setup with a nanopore and electrodes were placed in a Faraday cage to minimize the effect of electrical noise on measurement results. Electrical measurements were made using a Keithley 2636b SourceMeter. Before each measurements, nanopores and containers were treated in oxygen plasma to impart hydrophilic properties to the surfaces.
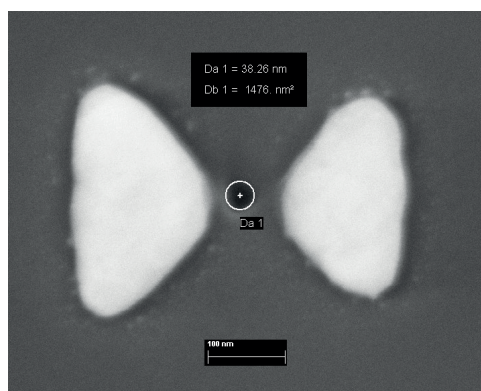
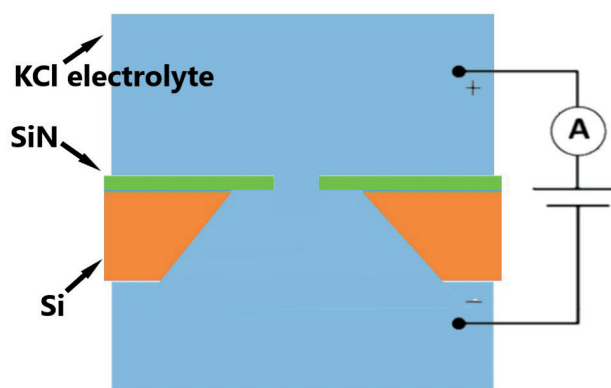Fig. 1. SEM image of a SiNx nanopore with diameter of 38 nm

Fig. 2. Scheme of the experimental setup

Results and discussion

Nanopore transport measurements were carried out in an aqueous solution of KCl at concentrations from 10^{-4} to 1M. To determine the ionic conductivity of the pore, the current-voltage characteristics of the system were measured in the potentiostatic two-electrode mode. The applied voltage was varied from -0.3 to 0.3V. The current was measured for 8 minutes at a given voltage. Further, according to the obtained data, the values of nanopore conductivity were obtained for the broad range of electrolyte concentrations (Fig. 3).

According to the results, in the concentrations range of 10^{-4}–10^{-2} M, the conductivity practically does not change and remains at the level of $4.5 \cdot 10^{-11}$ S. At a concentration of 10^{-2}—1M, the conductivity increases with concentration, and at 1M, the conductivity is $1.5 \cdot 10^{-10}$ S. This behavior can be explained by the overlap of electrical double layers (EDL). EDL of opposite walls can overlap the transport channel, creating a continuous charged region in the nanopore, thereby affecting its transport properties.

Conclusion

Fig. 3. Dependence of nanopore conductivity on KCl electrolyte concentration

In this work, solid-state SiNx nanopores were fabricated. Nanopores with a diameter of 35—40 nm were formed in a "free-standing" membrane of 300 nm thick by focused ion beam milling. Then, the values of the current passing through the nanopore were measured for a KCl solution at concentrations of 10^{-4}–1M. According to the measurement results, with an increase in the concentration of KCl above 10^{-2} M, the conductivity of the nanopore increases and reaches the valye of $1.5 \cdot 10^{-10}$ S at a concentration of 1M. Such dependence can be explained by the mutual the electrical double layer overlapping of opposite pore walls. Thus, the overlap of the electric double layer creates a continuous charged region in the nanopore, which affects the transport properties of the nanopore.
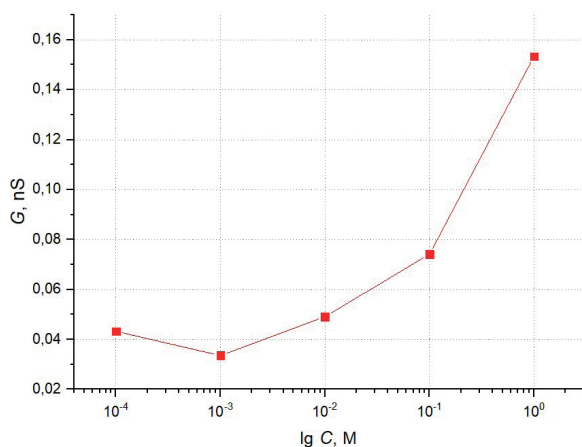
Acknowledgments

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