# The effect of optical radiation of different wavelengths on the transport characteristics of thin SiN membranes with integrated single nanopores

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Studying of solid-state nanopores is of great interest in view of creating biosensors that can be used for the label-free analysis of biological molecules. The paper presents a study of influence of optical radiation of different wavelengths in a wide spectral range on the transport properties of solid-state SiN membranes with integrated nanopores. It has been shown that photo-induced changes in the pore surface states have a greater effect on the ion transport than heating of the system.

**Keywords:** nanopores, solid-state nanopores, microfluidics, ion transport, SiN membranes, biosensor.

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Solid-state nanopores are of great interest for label-free detection of DNA/RNA and proteins, and also for single-molecule studies [1]. When a potential difference (10 to 500 mV) is applied to a nanopore located in a thin membrane that separates two electrolyte volumes, ionic current arises (the current magnitudes being pA–nA). When the analyte passes through the pore, the ionic current gets blocked. Variation in the ionic current not only indicates the presence of the analyte, but, depending on the signal shape and amplitude, provides valuable information on its properties, such as shape, size, length and charge [2]. Thus, variations in the signal allow electrical detection of molecules.

Currently, most studies are devoted to nanopores of two types: biological nanopores based on pore-forming proteins [3] and solid-state nanopores based on such materials as silicon nitride or graphene [4]. Compared to protein nanopores, the solid-state pores possess a high mechanical, thermal and chemical stability, and, in addition, creation of different-size pores becomes possible [5].

Solid-state nanopores may be used in analyzing the size of molecules, studying biomolecular interactions at the single-molecule level, and creating biosensors and DNA/RNA sequencing devices [6].

A technique combining nanopore sensors with optical detection methods is quite promising [7], since the nanopore exposure to light can result in modulation of the nanopore surface charge density, which makes possible optical control of the ion flow through the pore. Combining optical and electrical approaches enables also local light-induced heating leading to variations in conductivity, due to which the signal magnitude and detection accuracy increase [8].

As shown in literature, irradiation with monochromatic light is typically used to make effect on the ion transport through nanopores [9,10]. This method requires a complicated experimental design allowing for precise beam focusing on the nanopore and adjustment of the laser power. At the same time, studies of the dependence of the spectral radiation effect upon the ion transport are insufficiently presented in up-to-date publications, although this approach allows achieving a remarkable and stable increase in the nanopore conductivity.

In this work, we have investigated the effect of different-wavelength optical radiation of a wide spectral range on the transport characteristics of thin SiN-membranes with integrated single nanopores.

The samples were prepared using the technique for creating nanopores in a freely suspended semiconductor membrane [11]. At the initial stage, the semiconductor membrane was formed in a silicon substrate. First, a $SiO_2$ layer 100 nm thick was deposited by thermal oxidation on a double-sided polished Si (100) wafer. Next, a layer of $Si_xN_y$ 40 nm thick was grown on the $SiO_2$ surface by low-pressure chemical vapor deposition (LPCVD). After that, mask patterns were formed by photolithography on one side of the $Si_xN_y$ layer, which was necessary for further anisotropic etching of the silicon substrate. The photoresist used for this purpose was AZ3027 deposited by the spin-coating method and exposed according to the guidelines [12]. As a result, a mask with exposed square-shaped areas was obtained on the $Si_xN_y$ surface. To remove from $Si_xN_y$ the „exposed" windows, plasma-chemical etching was used. The working gas was $CF_4$. The next stage was liquid anisotropic etching of the silicon wafer performed in 20% KOH at 85°C. The etching time was 4 h. The etching mask was $Si_xN_y$. The result was a freely suspended $Si_xN_y$ membrane 40 nm thick. Then, single nanopores $\sim 5$ nm in diameter were formed

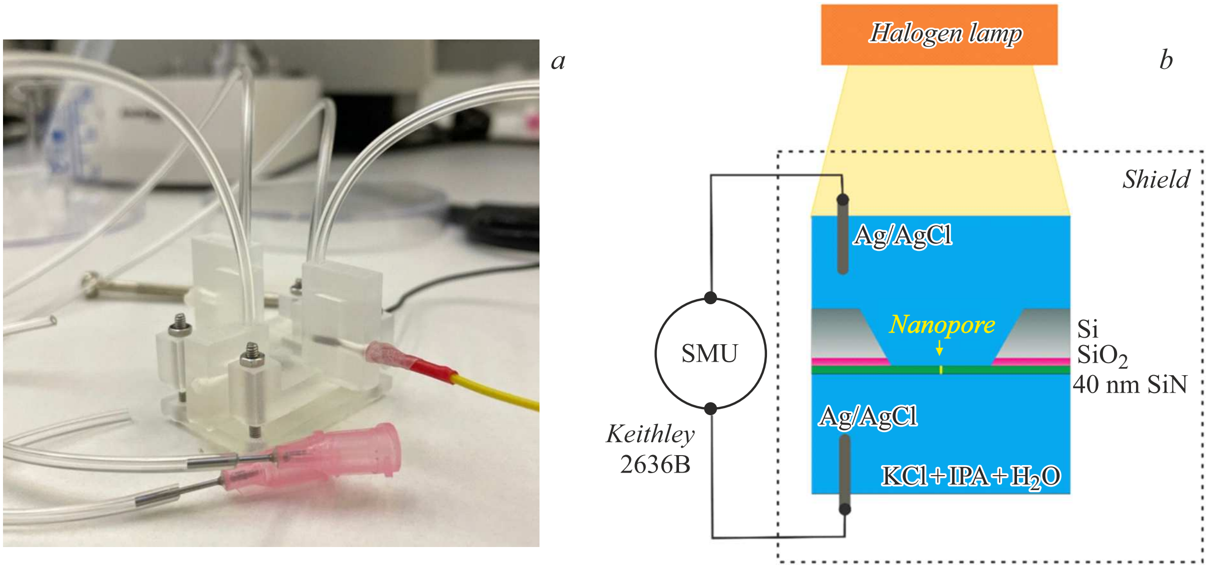


**Figure 1.** *a* — *a* — measuring cell with optical access; *b* — layout of the experimental setup.

by the focused electron beam of a transmission electron microscope.

With the aid of the measuring cell with optical access fabricated from transparent photopolymer by using a Form-Labs 3D printer (Fig. 1, *a*), the effect of different-wavelength optical radiation on the transport properties of nanopores was studied. The cell consisted of two electrolyte volumes separated by the $Si_xN_y$ membrane with a single nanopore (Fig. 1, *b*). The cell reservoirs were filled with 1 M solution of KCl electrolyte mixed with isopropanol (IPA) in the 1:1 ratio in order to increase the wettability. The nanopore ionic conductivity was studied by measuring the ionic current in the potentiostatic mode (0.3 V) with a Keithley 2636B source-meter. In the measurements, Ag/AgCl electrodes were used, whose working surfaces were renewed by chlorinating the silver wires in the 1 M KCl solution. In the process of measurements, the assembled cell with the installed-inside membrane with the pore was irradiated with a halogen lamp of an Olympus U-LH100L-3 microscope in a wide spectral range (the wavelength ranged from 400 to 1000 nm) and with the use of optical filters designed for transmission in the UV and IR ranges, and also in the visible spectrum part.

In the case when the sample was exposed to the wide-spectral-range radiation, a significant (by 24%) increase in current was observed; thereby, the pore conductivity got increased (Fig. 2, *a*). It is important to note that the current does not decrease with time to the initial values but remains at a persistently high level. This effect may be explained by an increase in temperature, which promotes enhancement of the ion transport.

To understand whether the conductivity depends on heating or is photo-induced, experiments with optical filters installed between the cell and lamp were carried out.

In the case of irradiation in the UV (240–400 nm) and IR (800–2900 nm) ranges, no variations in the ion current were detected. However, the radiation of just these wavelengths was expected to make the greatest contribution to the conductivity variation due to heating. When a UV filter (240–400 nm) was used, no variations in the ion current were detected since the measuring cell was made from photocurable plastic absorbing the UV radiation. In addition, by using the IR filter (800–2900 nm) we have marked out a spectrum beginning from 800 nm (and above), since in this spectral range silicon nitride possesses a certain absorption and heating with subsequent increase in current is expected. The absence of the expected effect was presumably due to the lack of the system heating and presence of the photo-induced effect.

To cut off the halogen lamp IR and UV ranges, filters transmitting in the visible spectrum part (350–750 nm) were applied. This led to an 8% increase in the stable current level (Fig. 2, *b*). Filters provide the light flux attenuation; therefore, the increase in current was lower in the case of using the filters than in the case of irradiation in a wide spectral range.

In addition, the effect of radiation on the temperature inside the cell was studied using a thermocouple connected to a multimeter. The thermocouple was mounted in place of the Ag/AgCl electrode in the lower volume of the cell. Within 15 min of illuminating the cell with a halogen lamp, the temperature increased from 24.4 to 28.3°C. This temperature increase evidences that irradiation with light in a wide spectral range does not induce significant heating of the system.

Thus, the detected increase in current upon the visible-spectrum irradiation, as well as the observed slight heating of the system, allowed us to conclude that the photo-induced

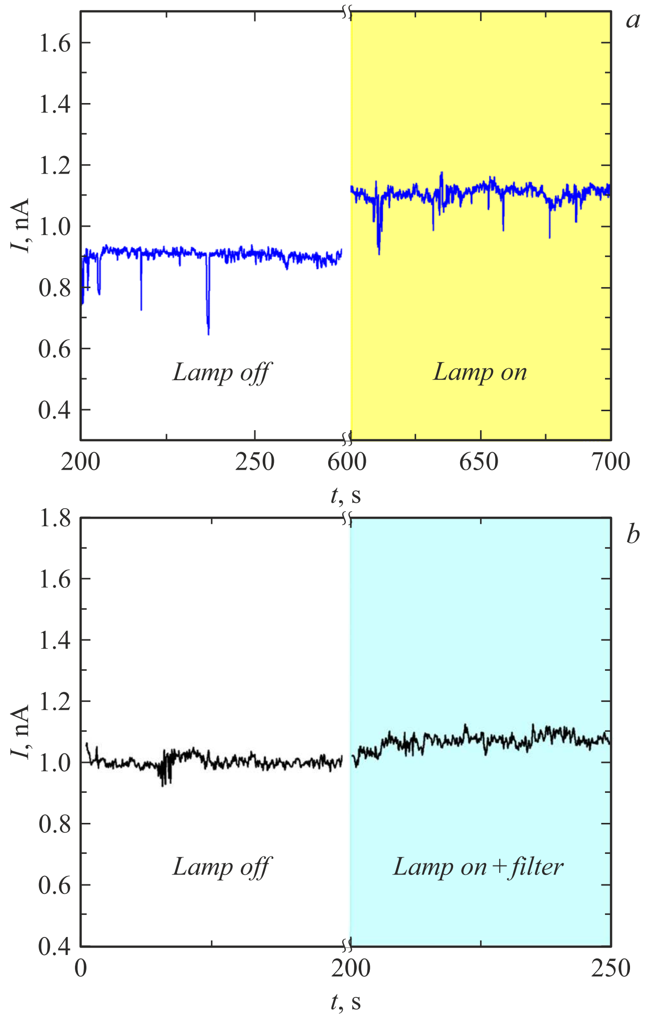


**Figure 2.** Time dependences of current in the case of the sample irradiation in a wide spectral range (*a*) and visible spectral range (350–750 nm) (*b*).

variations in the pore surface states has a greater effect on the transport than heating.

The results obtained can find wide application in creating new-generation biosensors. Controlling the transport characteristics by using the external impact, namely optical radiation, enables increasing the efficiency of nanopore biosensors in the label-free analysis.

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## Conflict of interests

The authors declare that they have no conflict of interests.

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