*Physics of the Solid State, 2023, Vol. 65, No. 12*

# Study of photoinduced processes in single solid-state nanopores with integrated plasmonic structures

© *N.V. Vaulin*[1,2], *P.K. Afonicheva*[2], *D.V. Lebedev*[1,2,3], *A.S. Bukatin*[1,2], *I.S. Mukhin*[1], *A.A. Evstrapov*[2]

[1] Alferov Federal State Budgetary Institution of Higher Education
and Science Saint Petersburg National Research Academic University of the Russian Academy of Sciences,
St. Petersburg, Russia
[2] Institute of Analytical Instrument Making, Russian Academy of Sciences,
St. Petersburg, Russia
[3] St. Petersburg State University,
St. Petersburg, Russia

E-mail: nikitavaylin@mail.ru

*Received May 19, 2023*
*Revised July 26, 2023*
*Accepted October 30, 2023*

The transport properties of solid-state nanopores with integrated plasmonic bow-tie antennas are studied. Plasmonic antennas were formed on „freely suspended“SiN membranes 20 nm thick. Nanopores with a diameter of $\sim 5$ nm were formed in the regions between the arms of the plasmonic bow-tie antennas. Irradiation of the nanopore region with a laser with a wavelength of 632 nm leads to an increase in the level of ion current and an increase in the conductivity of the pore by 10%. Irradiation of a membrane of similar thickness without a nanopore does not lead to a sustained increase in the current level. The increase in nanopore conductivity may be associated with a change in the configuration of double electrical layers on the pore walls, as well as with local heating of the pore region caused by the presence of plasmonic structures.

**Keywords:** SiN membrane, plasmonic antennas, microfluidics, ion transport, optical lithography.

DOI: 10.61011/PSS.2023.12.57679.5216k

## 1. Introduction

Membranes with integrated nanoscale pores are the basis of promising methods for detecting [1], analyzing [2] and manipulating [3] small concentrations of substances. Nanopore technologies have become widespread in devices aimed at analyzing biological compounds and DNA sequencing [4]. The operating principle of nanopore devices is the transport of molecules of the substance under study through the internal volume of the pore. At the same time, the ionic current flowing through the pore is measured. During the passage process (translocation), molecules of substance partially close the internal volume of the pore. This leads to a change in the configuration of double electrical layers (DEL) on the pore walls and prevents the flow of ions through the structure. Thus, the translocation process causes abrupt change in the level of the ion current (blockade current). The magnitude of the current change depends on the ratio of the sizes of the molecule under study and the pore, as well as on the electrochemical properties of their surfaces.

Today, two types of nanopores are most common: biological pores, which are membranes with integrated transmembrane proteins; solid-state pores formed by lithography in thin semiconductor or dielectric membranes. Factors limiting the efficiency of solid-state nanopores are the low signal-to-noise ratio of the measured current, as well as the high velocity of molecule translocation. One of the ways to solve these problems is the formation of plasmonic structures (antennas) in the nanopore region [5,6]. When plasmonic antennas are irradiated with monochromatic light at a resonant frequency, the electromagnetic field is localized in the antennas region due to its the near-field component [7]. Due to radiation-excited plasmon resonance, antennas can be used for effective local heating of the surrounding space (solution), increasing the solution conductivity and increasing the detection accuracy [8].

The goal of this paper was to study the effect of optical radiation on ion transport in solid-state nanopore with integrated Au plasmonic antennas.

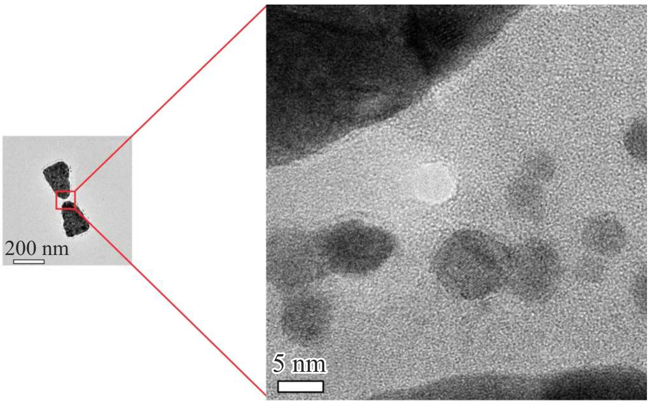

**Figure 1.** TEM image of plasmonic butterfly antenna, between the halves of which a single nanopore (bright spot) with a diameter of $\sim 5$ nm is formed.

## 2. Materials and methods

The paper examines samples consisting of 20 nm thick SiN membrane with a plasmonic Au „butterfly“ antenna, between the halves of which a single nanopore with diameter of $\sim 5$ nm is formed. The first stage of membrane creation is the formation of $SiO_2$ layer 100 nm thick on Si substrate by thermal oxidation. Next, on the surface $SiO_2$ a SiN layer is grown by method of low-pressure chemical vapour deposition (LPCVD). After this, the Si and $SiO_2$ layers are removed using selective chemical and plasma-chemical etching methods, leaving a „freely suspended“ SiN membrane. A plasmonic Au butterfly-antenna is formed on the membrane using electron-beam lithography, which is 2 equilateral triangles (side $\sim 200$ nm), with their vertices directed towards each other. Figure 1 shows an image of plasmonic antenna obtained using transmission electron microscope (TEM). The selected dimensions of the antennas ensure the excitation of plasmon resonance by laser radiation with a wavelength $\lambda = 632$ nm. The next step is to create a single nanopore with diameter of $\sim 5$ nm in the area between the antenna vertices (see Figure 1). Nanopores are formed by etching with a focused electron beam using TEM: an electron beam (200 kV) is focused into spot of size 2–3 nm on the membrane, and then held for 20 s until pore appears. This method makes it possible to achieve reproducible formation of nanopores. The dark spots near the plasmonic antennas are gold particles remaining on the membrane surface after the antennas were formed. We believe that, due to their small sizes, these particles do not have a significant effect on the interaction of radiation with plasmonic antennas. We do not exclude the presence of small pores (much smaller than the size of the pores formed in the region of plasmonic antennas) in the continuous membranes used. The equipment used makes it possible to record currents from pores with a diameter of 0.5 nm. However, the electrical resistance of such small pores is so large that the leakage currents through them will be less than the leakage currents through the silicon wafer. Besides, studies of the membrane surface using transmission and scanning electron microscopes did not reveal the presence of such pores. Therefore, we consider the presence of small pores in membranes to be unlikely, and their possible influence on electrical measurements is insignificant. Figure 2 shows the dark-field scattering spectra of the resulting plasmonic butterfly-antennas in the presence and absence of the pore. The spectra show a wide resonance band in the visible part of the optical radiation, which is typical for gold structures of this size. According to the spectra, the presence of nanopore has little effect on the dark-field scattering spectrum of the plasmonic antenna. Therefore, a laser with $\lambda = 632$ nm is suitable for exciting plasmon resonance in antenna with integrated nanopore.

To study the effect of radiation on the characteristics of the studing structures we create a experimental flow cell with an optical window using 3D printing methods. The measuring cell consists of photopolymer cis- and trans-volumes separated from each other by the sample under study. The cell also contains connectors for installation the measuring Ag/AgCl electrodes (according to a two-electrode scheme) and capillaries for injection and discharge of the electrolyte solution. During the experiment, the cell is filled with electrolyte of a given concentration. The experimental setup scheme is described in detail in the papers [6,9].

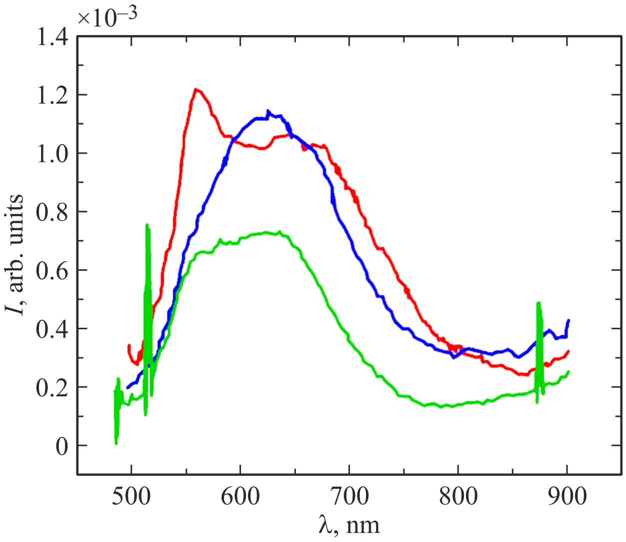

**Figure 2.** Scattering spectra of Au plasmonic butterfly-antennas. Blue and green curves — spectrum of antennas without nanopores, red curve — spectrum of the antenna with integrated nanopore.

## 3. Experiment

Experimental studies of photoinduced processes in nanopores involve measuring the current flowing through a sample in a measuring cell filled with 1 M KCl + IPA (1 : 1) solution at given potential difference (potentiostatic mode). During current measurements the samples were irradiated with laser radiation ($\lambda = 632$ nm) with power of 10 mW. To determine the effect of radiation on the SiN membrane and nanopore separately, both membranes with integrated nanopores and membranes without pores were studied. When nanopore samples are irradiated with laser radiation, their conductivity increases by 10% (see Figure 3, *a*). We consider the conductivity of the pore as the conductivity of the electrolyte solution inside nanopore internal volume. At the same time, membranes without nanopores do not demonstrate changes in the steady-state current level (leakage current through the membrane) upon irradiation (see Figure 3, *b*).

According to the results obtained, it can be assumed that there are several effects that occur when the samples under study are irradiated with light. Firstly, this is local heating of the solution in the nanopore region. Local heating can occur due to the excitation of plasmon resonance in the

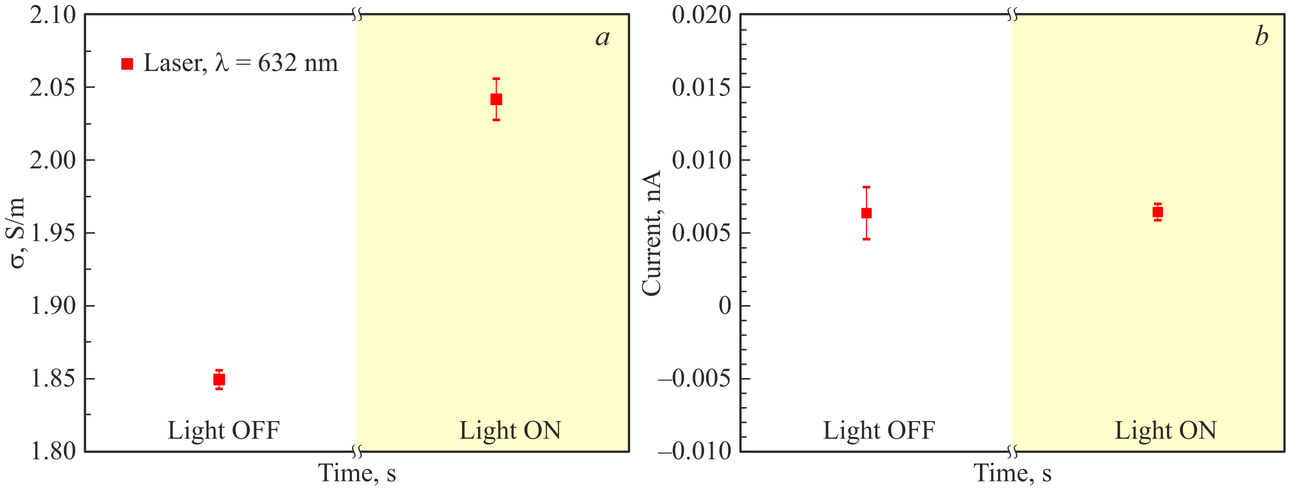

**Figure 3.** *a*) Conductivity of 20 nm thick SiN membrane with plasmonic butterfly-antenna and nanopore with diameter of 5 nm vs. irradiation with laser power of 10 mW ($\lambda = 632$ nm); *b*) leakage current of SiN membrane 20 nm thick, without nanopore vs. irradiation.

butterfly-antenna, which increases the solution conductivity in the region around the antenna and nanopore by reducing the viscosity of the electrolyte solution. We believe that the interaction of radiation with the solution is negligible and cannot lead to uniform heating of the entire volume of the electrolyte. Also, the increase in conductivity may be associated with the generation of photoelectrons on the walls of the nanopore, which leads to change in the DEL configuration.

## 4. Conclusion

The effect of radiation on the transport characteristics of SiN membranes with integrated plasmonic Au butterfly-antennas and nanopores was studied. According to the results obtained, irradiation with laser radiation leads to a steady increase in the current and conductivity of the nanopore sample by 10%. A stable change in current level is not observed on membranes without nanopores. The effect of pore conductivity increasing upon irradiation may be associated with change in the DEL configuration on the pore surface, as well as with local heating caused by the presence of plasmonic structures.

### Funding

The study was supported by a grant provided by the Russian Science Foundation (Project No. 20-74-10117). The authors thank the Ministry of Science and Higher Education of the Russian Federation (state order project number No. 0791-2023-0007).

### Conflict of interest

The authors declare that they have no conflict of interest.

## References

[1] J.D. Spitzberg, A. Zrehen, X.F. van Kooten, A. Meller. Adv. Mater. **31**, *23*, 1900422 (2019). https://doi.org/10.1002/adma.201900422

[2] R. Wang, T. Gilboa, J. Song, D. Huttner, M.W. Grinstaff, A. Meller. ACS Nano **12**, *11*, 11648 (2018). https://doi.org/10.1021/acsnano.8b07055

[3] D. Garoli, H. Yamazaki, N. Maccaferri, M. Wanunu. Nano Lett. **19**, *11*, 7553 (2019). https://doi.org/10.1021/acs.nanolett.9b02759

[4] I.M. Derrington, T.Z. Butler, M.D. Collins, E. Manrao, M. Pavlenok, M. Niederweis, J.H. Gundlach. Proc. Nat. Acad. Sci. **107**, *37*, 16060 (2010). https://doi.org/10.1073/pnas.1001831107

[5] X. Shi, D. Verschueren, S. Pud, C. Dekker. Small **14**, *18*, 1703307 (2018). https://doi.org/10.1002/smll.201703307

[6] W. Lu, R. Hu, X. Tong, D. Yu, Q. Zhao. Small Structures **1**, *1*, 2000003 (2020). https://doi.org/10.1002/sstr.202000003

[7] W. Li, J. Zhou, N. Maccaferri, R. Krahne, K. Wang, D. Garoli. Anal. Chem. **94**, *2*, 503 (2022). https://doi.org/10.1021/acs.analchem.1c04459

[8] F. Nicoli, D. Verschueren, M. Klein, C. Dekker, M.P. Jonsson. Nano Lett. **14**, *12*, 6917 (2014). https://doi.org/10.1021/nl503034j

[9] N.V. Vaulin, P.K. Afonicheva, D.V. Lebedev, A.S. Bukatin, I.S. Mukhin. Peter the Great St. Petersburg Polytechnic University J. Phys. Math. **16**, *1.1*, 385 (2023). https://doi.org/10.18721/JPM.161.165

*Translated by I.Mazurov*