Lashkov, Andrey V.; Fedorov, Fedor S.; Vasilkov, Mikhail Yu; Kochetkov, Alexey V.; Belyaev, Ilia V.; Plugin, Ilia A.; Varezhnikov, Alexey S.; Filipenko, Anastasia N.; Romanov, Stepan A.; Nasibulin, Albert G.; Korotcenkov, Ghenadii; Sysoev, Victor V.

The Ti wire functionalized with inherent TiO2 nanotubes by anodization as one-electrode gas sensor

Published in:
Sensors and Actuators, B: Chemical

DOI:
10.1016/j.snb.2019.127615

Published: 01/03/2020

Document Version
Other version

Please cite the original version:
Lashkov, A. V., Fedorov, F. S., Vasilkov, M. Y., Kochetkov, A. V., Belyaev, I. V., Plugin, I. A., Varezhnikov, A. S., Filipenko, A. N., Romanov, S. A., Nasibulin, A. G., Korotcenkov, G., & Sysoev, V. V. (2020). The Ti wire functionalized with inherent TiO_2 nanotubes by anodization as one-electrode gas sensor: A proof-of-concept study. *Sensors and Actuators, B: Chemical*, *306*, [127615]. https://doi.org/10.1016/j.snb.2019.127615

Supplemental file
to

The Ti wire functionalized with inherent TiO_2 nanotubes by anodization as one-electrode gas sensor: a proof-of-concept study

by

Andrey V. Lashkov[1], Fedor S. Fedorov[2*], Mikhail Yu. Vasilkov[1,3],
Alexey V. Kochetkov[1], Ilia V. Belyaev[1], Ilia A. Plugin[1], Alexey S. Varezhnikov[1],
Anastasia N. Filipenko[1], Stepan A. Romanov[2], Albert G. Nasibulin[2,4],
Ghenadii Korotcenkov[5], and Victor V. Sysoev[1*]

[1]Yuri Gagarin State Technical University of Saratov, 77 Polytechnicheskaya str., 410054 Saratov, Russia
[2]Skolkovo Institute of Science and Technology, 3 Nobel str., Moscow, Russia
[3]Saratov Branch of Kotelnikov Institute of Radioengineering and Electronics of RAS, 38 Zelenaya str., 410019 Saratov, Russia
[4]Aalto University, P.O. Box 16100, 00076 Aalto, Finland
[5]Moldova State University, Mateevici 60, MD-2009 Chisinau, Moldova

1. The experimental setup

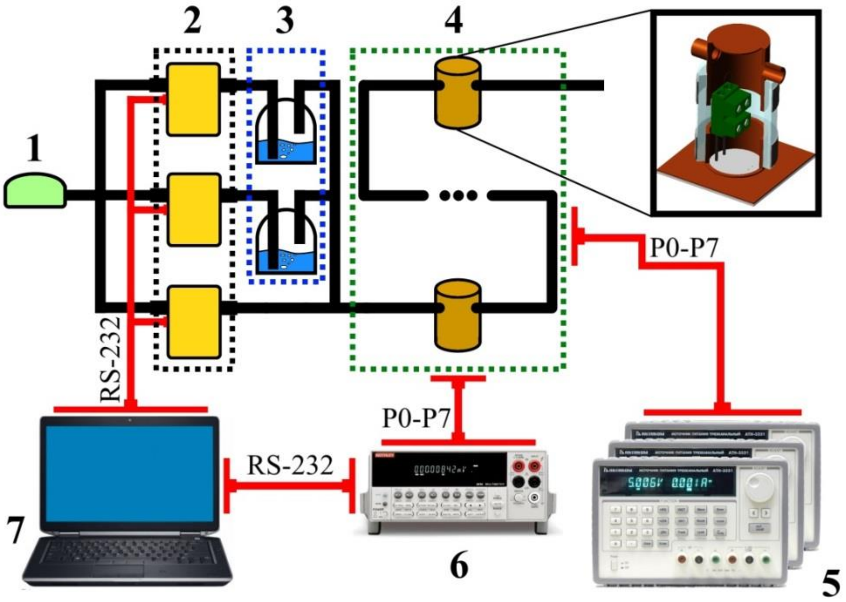

Fig. S1. The setup to measure gas-sensing characteristics of Ti-TIO2 NT wire, the positions are, 1 the air compressor, 2 the mass-flow controller, 3 the babbler, 4 the gas chamber with the one-electrode sensor mounted, 5 the number of dc sources, 6 the multichannel multimeter, 7 the PC to manage the setup with home-made software; the insert shows the gas chamber with the mounted wire.

The test gas mixtures which were delivered to the sensor-equipped chambers contained the analyte concentration to be calculated in ppms according to

$$W_g = \frac{P_g F_g}{P_g F_g + (P_a - P_g) F_g + P_a F_a} \cdot 10^6,$$

where P_g is analyte‘s saturation vapor at environment pressure P_a of about 0.1 MPa, F_g and F_a are the analyte vapor and background air rates.

2. The NT growth over Ti wires

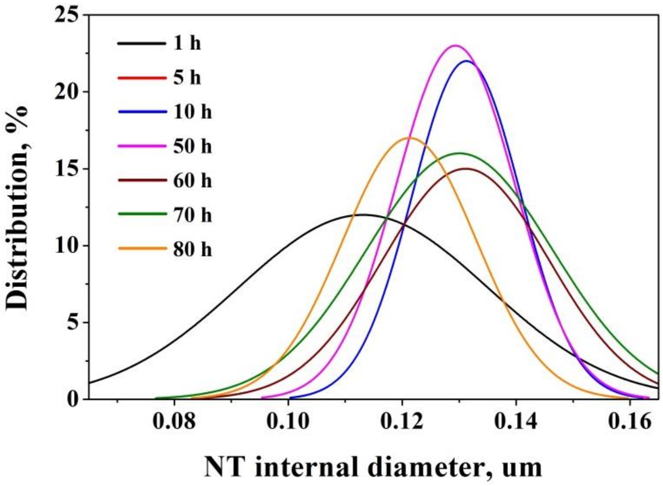

Fig. S2. The internal NT diameter distribution in dependence on the Ti-TiO_2 NT wire anodization time.

3. The temperature visualization of the Ti-TiO_2 NT wire with IR camera

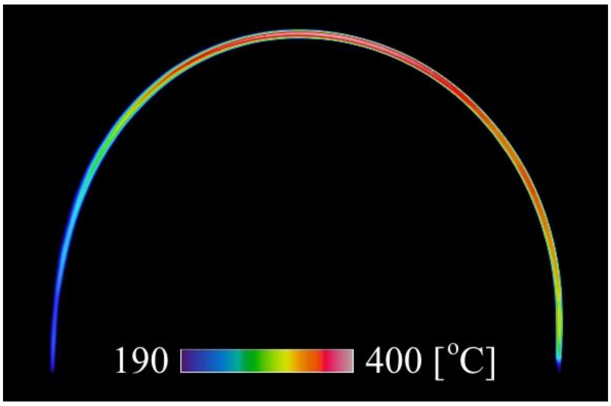

Fig. S3. The IR image of Ti-TiO_2 NT wire anodized for 60 h under applying a dc current equal to 520 mA. The emission coefficient of the IR camera is equal to 0.6.

4. The calculation of heat dissipation in Ti-TiO_2 NT wire with Comsol Multiphysics@

We performed modelling of the resistive heating process in the Ti-TiO_2 NT wire under dc impact using Comsol Multiphysics @5.3a software. We have utilized finite elements method implemented into the software package. The main advantage of the COMSOL@ comparing to other available packages is a mutliphysical approach which allows one to solve coupled effects like a resistive heating. The model included electromagnetic and heat conductivity equations presented in Electric Currents interface and a Heat Transfer in Solids interface, respectively. The coupling of the heat/resistivity processes in the software is implemented by introduction of the electromagnetic power dissipation into the heat conductivity equations and taking into account a dependence of the electromagnetic material properties on the temperature in the electromagnetic equations.

The modeling was performed for Ti-TiO_2 NT wire of 60 h anodization with total diameters of 135 μm in the middle part. The wire geometry has been modelled with 40 mm Ti wire covered in the 20 mm middle with TiO_2 layer. In general, the model included a boundary condition for thermal and electrical parts. The input electrical power was introduced into the wire tips with the help of Electric potential boundary condition in Electric Currents interface, which allowed us applying a potential on the wire. In order to match the experimental conditions we made a voltages sweep from 0 V to the 3.0 V for 60 h anodized Ti-TiO_2 NT wire. The Heat Transfer in Solids interface included boundary conditions of natural convection (Heat flux settings), radiation (Diffuse Surface settings) and heat conduction (Temperature settings). One should notice that the temperature observed in the wire middle did not depend on the heat conduction which was checked by applying insulation boundary conditions instead of Temperature boundary. As for a radiation, the TiO_2 part of the wire has much higher energy dissipation when compared to Ti one because of greater emissivity coefficient that resulted in higher radiation heat flux from the TiO_2 when compared to one going from Ti (Figure S4).

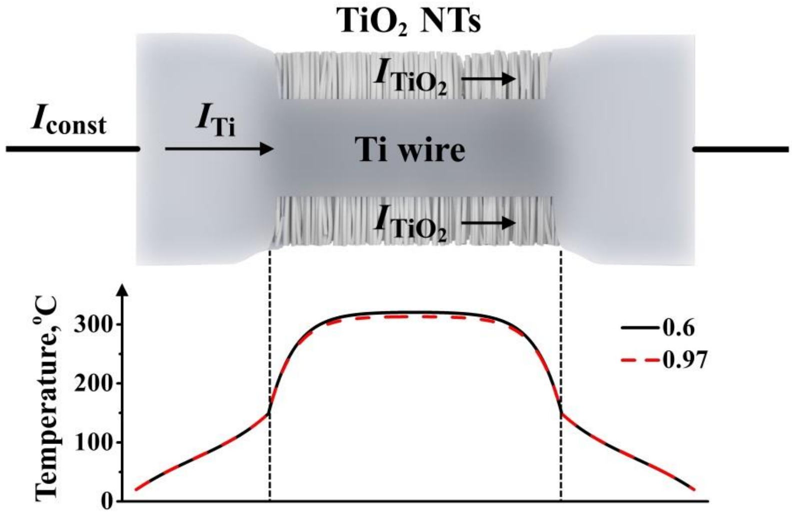

Fig. S4. The distribution of temperature in the Ti-TiO2 NT wire of 60 h anodization calculated with Comsol Multiphysics@.

The typical emissivity coefficient provided for the TiO2 lies in the range of 0.4-0.6 which drastically increases in porous oxide[1]. However, in the structure under study the effect of radiation is still much smaller than that of convection. We plotted the power dissipation due to conduction, convection and radiation in Figure S5b.

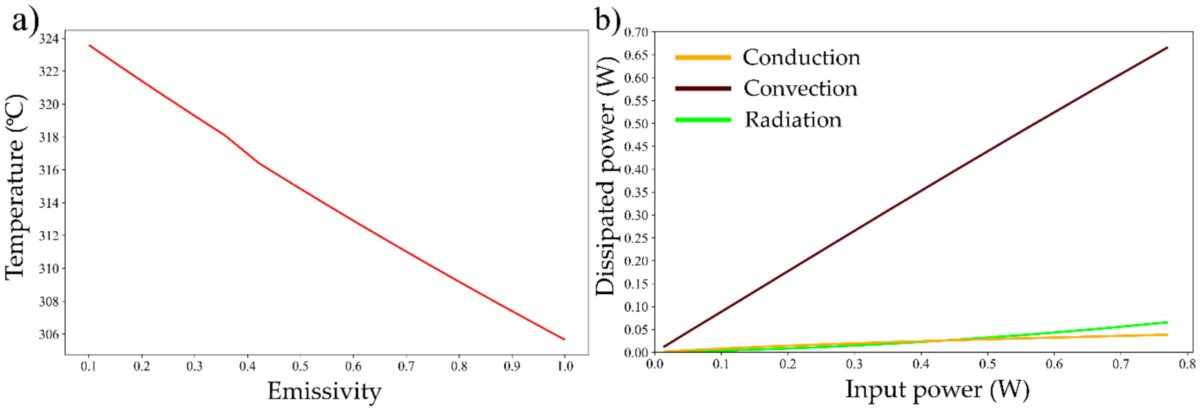

Fig. S5. a) The dependence of temperature in the middle of Ti-TiO2 NT wire, 60 h of anodization, under input power of 0.62 W when varying the emissivity from 0.1 to 1.0; b) the dependence of dissipated power on the input electrical power under effects of convection, radiation and conduction in the n the middle of Ti-TiO2 NT wire, 60 h of anodization, with emissivity value of 0.97.

As one can see, the convective energy dominates over other two mechanisms of heat dissipation. Therefore, the change the emissivity from 0.6 to 1.0 leads to rather minor variation of operating temperature of 6 °C (Fig. S5a). The natural convection was approximated in Heat flux settings with the model of a long cylinder[2] which is built in COMSOL@. However, the approximation did not take into account the pore structure of the titanium oxide layer and overstate the resulted temperature of the wire[3]. To define the correct heat transfer coefficient, we optimized it by fitting the experimental dependence of R(T) on the input power. In other words, knowing the R(T) dependence and geometry of the wire we can find the values of the temperature from the resistance of the wire. The Figure S6 displays the agreement between model calculations and experimental data for the Ti-TiO_2 NT wire, 60 h of anodization.

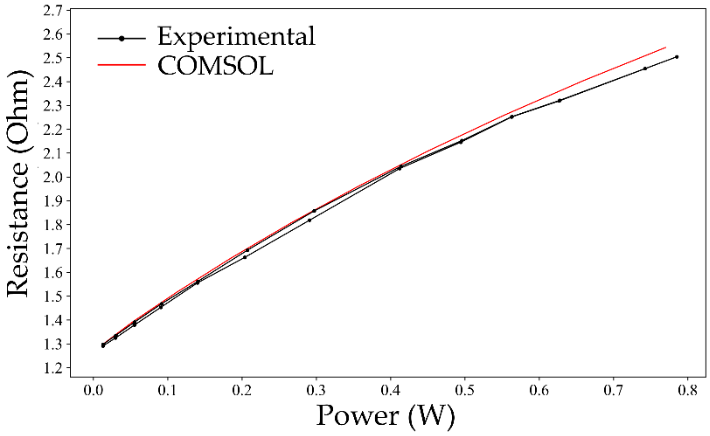

Fig. S6. The dependence of resistance of the Ti-TiO_2 NT wire, 60 h of anodization, on the input electrical power; red and black lines corresponds to the numerical model values and experimental values, respectively.

5. Gas response stability of Ti-TiO_2 NT wire-based one-electrode sensor

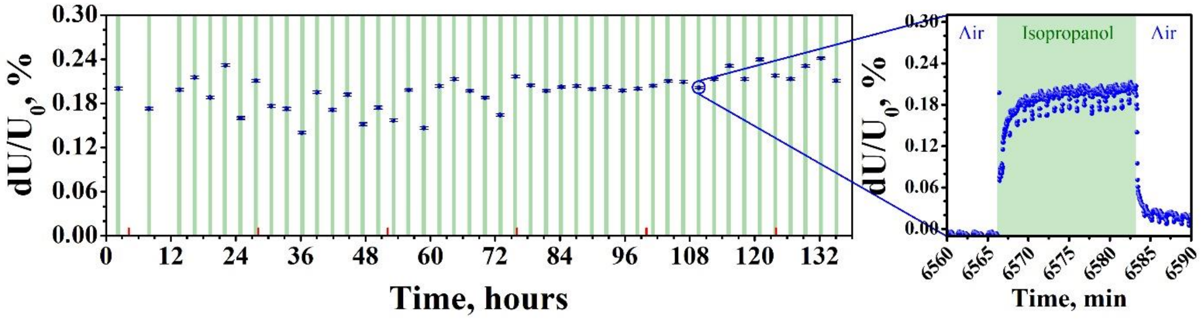

Fig. S7. The response stability of exemplary Ti-TiO_2 NT wire-based one-electrode sensor made of wire prepared at 60 h of anodization *versus* multiple pulsed, of 20 min duration, exposures to isopropanol vapors, 0.5 %, in mixture with background dry air under flow mode, 1000 sccm. The feed power is about 0.4 W. The observed response fluctuations appear due to variations of ambient lab temperature.

References:

(1) Z. Yao, B. Hu, Q. Shen, A. Niu, Z. Jiang, P. Su, P. Ju, Preparation of black high absorbance and high emissivity thermal control coating on Ti alloy by plasma electrolytic oxidation, Surf. Coatings Technol. 253 (2014) 166. https://doi.org/10.1016/j.surfcoat.2014.05.032.

(2) F. P. Incropera, D. P. DeWitt, T. L. Bergman, A. S. Lavine, Fundamentals of Heat and Mass Transfer, 6th Ed., John Wiley & Sons, 2007, 1024 p.

(3) D. A. Nield, A. Bejan, Convection in Porous Media, Springer, 2017, 664 p.