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Preparation of Au/TiO_2/Ti memristive elements via anodic oxidation

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In the present paper we report utilization of porous and barrier type of titania films formed by anodic oxidation as an active layer of the memristive element in the Au–TiO_2–Ti structure. The comparison of semiconductor properties of porous and barrier type of anodic titania was performed via the Mott–Schottky technique. The obtained memristive elements show the bipolar type of switching governed by Schottky barrier screening. For barrier type film the switching potential is equal to -1.5 V and the ratio of resistance in OFF and ON stage (R_{off}/R_{on}) is equal to 34. For porous type films, the switching potential is equal to -0.6 V and $R_{off}/R_{on} = 131$. Moreover, we observed the dependence of R_{off}/R_{on} on the voltage sweeping rate, which can be explained by the limitation in diffusion of oxygen vacancies through the oxide layer.

Keywords: memristor, anodic titania, anodic oxidation, memristive element, Schottky barrier, oxygen vacancies diffusion.

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1. Introduction

Memristive phenomena is one of the most promising way to form non-volatile and magneto-independent information storage devices. A memristor is a circuit element which can be switched between a high resistance state (HRS) and a low resistance state (LRS) by applying a switching potential. A memristor possesses the layered structure in which a semiconductor layer is sandwiched between two metal contacts. Different types of non-stoichiometric oxide semiconductors are often used as an active layer of a memristor. In thin semiconductor films, unipolar mechanism of switching is realized by the formation of ionic, vacancy and metal filaments [1–3]. In thick films, a bipolar resistive switching mechanism is realized due to increasing of defect concentration (for example, oxygen vacancies) near one of the electrode under an applied electric field, which leads to the screening of the Schottky barrier at the metal-oxide interface. The formation of the Schottky barrier occurs in the case of the formation of the space charge region – semiconductor's ionized donors or acceptors. Typically, memristive elements are assembled as the prototypes of memory storage devices using cross-bar architecture [4, 5]. This means that the active layer of a memristor should be formed via techniques which are compatible with the techniques typically used for the manufacturing of semiconductors and electronic devices, such as photolithography, magnetron sputtering, reactive-ion etching, and so on. Anodic oxidation of valve metals appears to be one of promising method for the formation of the memristor active layer due to its compatibility with the photolithography [6] and magnetron sputtering [7] and possibility to control the thickness and the stoichiometry of a formed film [8–10].

Anodic titania is an n-type semiconductor with a chemical composition of TiO_{2-x}, where high mobility oxygen vacancies exist [11, 12]. By anodization of titanium in non-dissolving electrolytes (such as aqueous solution of $Na_2B_4O_7$, ammonium tartrate, etc.) nonporous dense film with thickness of up to one micron can be formed [13, 14]. Anodization in fluorine-containing electrolyte leads to the formation of a self-organized porous film, which consists of vertically oriented nanotubes. Nanotube geometry depends on an applied voltage, current mode and electrolyte composition [15–17]. Because of its unique porous structure, anodic titania is widely used in photocatalysis and photochromic systems [18, 19], biomedical applications [20], gas sensors [21, 22] and pigment preparation [23]. At the same time, the study of memristive properties was performed only in the few articles [24–26]. However, anodic oxidation technique allows to form amorphous highly non-stoichiometric titania, which can be considered as a promising active layer for memristive elements. That's why in the present work we compare two types of anodic titania: a porous film formed in fluorine-containing electrolyte and a non-porous film formed in boron-containing electrolyte. The microstructure and semiconductor properties of titania films are characterized. Finally, the resistive switching behavior of Au/TiO_2/Ti memristive device is studied.

2. Experimental

2.1. Sample preparation

Titanium foil (0.25 mm thick, 99.9 % purity) was used as a starting material for the preparation of memristive structures. Before anodization, initial titanium foil was chemically polished in the mixture of 80 vol. % of H_2O_2 and 20 vol. % of saturated HF. After chemical polishing, the sample was repeatedly washed with deionized water and dried at ambient temperature in air.

For preparation of the porous anodic titania film, the synthetic approach early described in [27, 28] has been used. The anodization of the titanium foil was carried out in a two-electrode cell in solution containing 10 g/L NH_4F and 10 vol. % of H_2O in ethylene glycol at a constant voltage of 60 V. The thickness of the obtained film was controlled by passing the required charge through the cell. Preparation of the barrier type anodic titania films was carried out in a galvanostatic regime with a current density of 0.2 A/cm^2 with a voltage limit of 60 V in 0.16 M solution of $Na_2B_4O_7$. After anodization, all samples were repeatedly washed with ethanol and water and dried under an air stream.

The top metal contact was sputtered on the anodic titania surface by magnetron sputtering on a Quorum Technologies Q150T ES setup.

2.2. Sample characterization

Microstructure of the obtained samples was characterized by scanning electron microscopy (Leo Supra 50VP). Mott-Schottky analysis was performed for the determination of a conductivity type and a charge current density using electrochemical impedance spectroscopy [29–32] with a Solartron SI 1287 potentiostat. Experiments were conducted in 0.5 M H_2SO_4 and a DC potential range from -0.5 to 0.8 VSCE with a potential step of 50 mV at the constant frequencies of 10 Hz, 50 Hz, and 100 Hz for an amplitude of 5 mV. The dependence of a semiconductor layer capacitance *vs.* DC potential was used for the determination of a conductivity type and for the calculation of charge carrier concentration. The capacitance of the semiconductor layer was calculated according to following equation:

$$C = \frac{-1}{2\pi S f Z_{im}},$$

where S – sample area, f – frequency, Z_{im} – the imaginary component of the impedance.

Solid-state current-voltage (I–V) and current-time (I–t) (memristive behavior) dependencies were obtained on an Autolab PGSTAT302N potentiostat.

3. Results and discussions

3.1. Microstructure

The microstructure of the obtained films was characterized via scanning electron microscopy (Fig. 1). According to SEM data, the surface of the sample obtained in $Na_2B_4O_7$ electrolyte was dense and nonporous (Fig. 1a). We were unable to determine the thickness of the formed film by microscopy, that's why we used Fabri–Perot interferometric analysis for the film thickness determination. The barrier film thickness determined from optical spectra is equal to 250 nm. At the same time, anodization in fluorine-containing electrolyte led to the formation of a highly-organized porous layer with a pore diameter of 80 ± 10 nm. The thickness of the porous film was equal to 500 nm and the required thickness was obtained by passing the charge density of 0.88 Q/cm^2. The correlation coefficient between the thickness of the obtained film and the passed charge density determined in the set of experiments was equal to 0.4 μm/(Qcm^2).

Both oxidation conditions led to the preparation of uniform amorphous films without cracks on the surface of titanium. Moreover, the preparation technique provided the presence of bottom contact between metallic titanium and titanium dioxide film.

3.2. Mott–Schottky analysis

The Mott–Schottky behavior both for the barrier and porous type of anodic titania is in accordance with expected behavior of n-type semiconductor: increasing of the anodic bias above the flat band potential leads to decreasing of the semiconductor layer capacitance. This can be explained due to the repulsion of electrons from generated electron-hole pairs to the bulk of semiconductors, which leads to the formation of the positively charged space charge region at the surface of the semiconductor. It should be noted that for the barrier type of anodic titania, the Mott–Schottky curve contains only one linear region (Fig. 2a), at the same time, the curve for porous anodic titania contains two linear regions with different slope (Fig. 2b). The presence of two regions can be explained by the presence of multiple donor stages in the band gap formed by absorbed F^- or $[TiF_6]^{2-}$ ions [33–35].

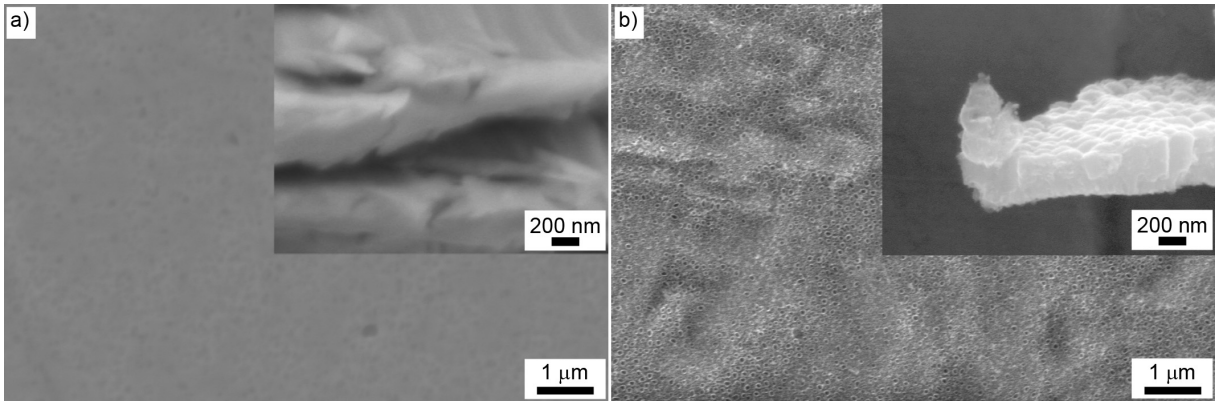

FIG. 1. The microstructure of anodic titania films formed in boron-containing (a) and fluorine-containing (b) electrolyte. The cross-section of the titania films are shown on the insets

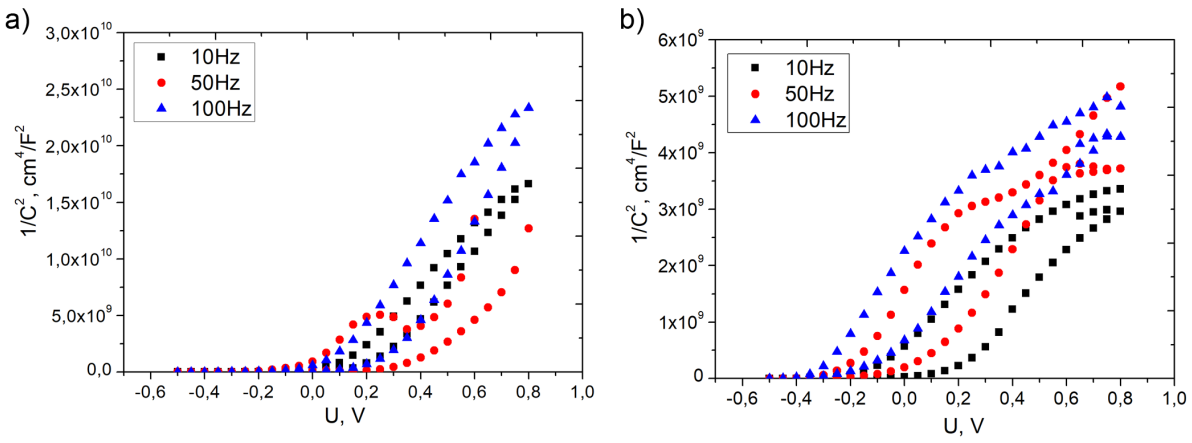

FIG. 2. Mott–Schottky analysis of the barrier (a) and porous (b) type anodic titania films at the DC potential in the range of -0.5 to $0.8V_{SCE}$ and frequencies of 10, 50 and 100 Hz

From the slope of Mott–Schottky curve, the charge carrier density was calculated according to the following equation:

$$\frac{1}{C^2} = \frac{2}{N_d q \varepsilon \varepsilon_0} \cdot \left(U - E_{fb} - \frac{kT}{q} \right),$$

where C – the capacitance of semiconductor layer, N_d – charge carrier density, ε – semiconductor dielectric constant, E_{fb} – flat band potential.

The calculated value of the charge carrier density for the barrier layer type anodic titania is $6.7 \cdot 10^{19}$ cm^{-3}. For the porous type anodic titania, the calculation of the charge current density was performed from the first linear region (from -0.1 to 0.4 V). The calculated value – $3.0 \cdot 10^{20}$ cm^{-3} is 3 – 4 times higher in comparison with the value obtained for barrier type. This can be explained by the presence of additional donor stages formed by the absorbed anions.

3.3. Memrisitve behavior of formed structures

For the preparation of Schottky barrier-type memristor we should choose the top electrode with the work function higher than the work function of titania. It can be gold or platinum electrodes. At the same time, the bottom contact formed on the TiO_2/Ti interface during anodization is non-rectifying contact because the work function of Ti (4.3 eV) is lower than that of TiO_2 (4.9 eV) [36, 37]. We measured the I–V curves for two different systems Cr/TiO_2/Ti where both contacts were non-rectifying (Cr work function is 4.5 eV) and Au/TiO_2/Ti where the top contact was rectifying. The Cr/TiO_2/Ti system exhibits ohmic behavior, whereas the I–V curve for Au/TiO_2/Ti has a typically rectifying characteristic (Fig. 3).

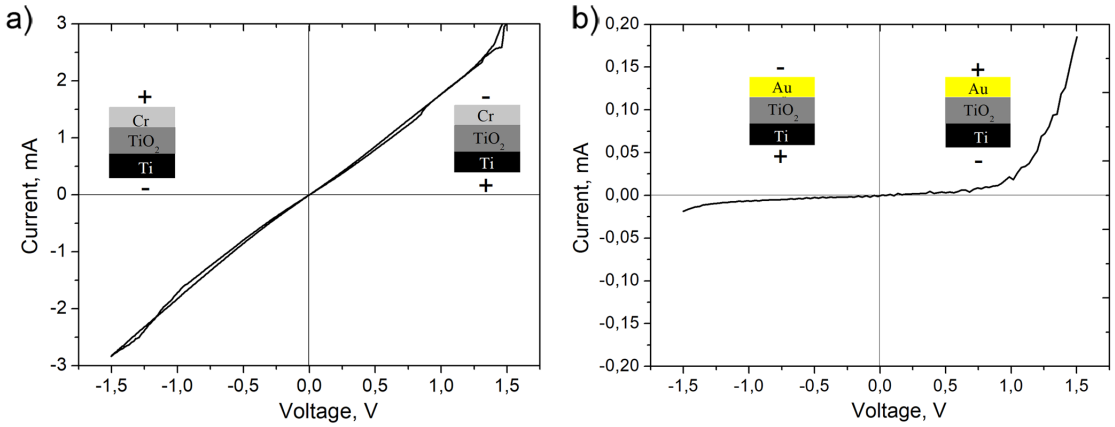

FIG. 3. I–V Curves for Cr/TiO_2/Ti structure where both contacts are non-rectifying (a), and Au/TiO_2/Ti where the top contact is rectifying (b)

The resistive switching behavior of Au/TiO_2/Ti structures both with the porous (Fig. 3a) and barrier (Fig. 3b) type of anodic titania was studied using cyclic voltammetry. The I–V curve characteristic for both type of memristors shows bipolar resistive switching behavior. Bipolar resistive switching behavior and the formation of a symmetric ohmic contact in the case of Cr/TiO_2/Ti structure and a Schottky junction in the case of Au/TiO_2/Ti allow us to conclude that the Schottky barrier screening is the main mechanism of switching between resistance stages. The Schottky barrier screening occurs due to diffusion of oxygen vacancies to the Au/TiO_2 interface under negative applied bias. The formation of oxygen vacancies in the titania structure can be described by the following quasi-chemical equation:

$$O_O^{\cdot\cdot} \longleftrightarrow V_O^{\cdot\cdot} + 2e^- + \frac{1}{2}O_2,$$

where $O_O^{\cdot\cdot}$ is the oxygen on the TiO_2 lattice, and $V_O^{\cdot\cdot}$ is a positively charged oxygen vacancy. This reaction also explains the n-type conductivity of TiO_2. Moreover, the mobility of oxygen vacancies in TiO_2 is quite high [38], so we expect that the diffusion of oxygen vacancies to the Au/TiO_2 interface leads to the screening of Schottky barrier.

The memristor with barrier type of oxide film switches to LRS at the negative polarity $U < -1.3$ V and reverse switching to HRS at the positive polarity $U > 1.4$ V (in following discussion the polarity is equal to polarity of the top gold electrode). For the porous type of anodic alumina, switching to LRS occurs at a negative polarity at the voltages in range from -0.6 to -0.8 V (depending on the voltage sweeping range) and reverse switching to HRS occurs at the positive polarity $0.6 \div 0.8$ V.

Average slope values of the I–V curves were used for the calculation of the specific resistivities (ρ) for high and low resistance stages (Fig. 4). For the barrier type of anodic titania the calculated specific resistivities are 285 ± 5 Ω·m (LRS) and 6700 ± 100 Ω·m (HRS), which corresponds to $R_{off}/R_{on} = 23.5$. For the porous anodic titania the corresponding values of the specific resistance are equal to 20 ± 5 Ω·m LRS) and 250 ± 5 Ω·m (HRS), and $R_{off}/R_{on} = 12.5$. It should be noted that for the porous type of anodic alumina the resistivity ratio between on and off stages depends on the voltage sweeping rate. Measured off/on resistance ratios were equal to 131, 12.5 and 10.8 for sweeping rates 1, 10 and 50 mV/s, respectively. This dependence can be explained by the limitation in the diffusion of oxygen vacancies throughout the oxide layer: decreasing the voltage-sweeping rate leads to an increase in the duration of a potential influence. This leads to an increase in the quantity of the oxygen vacancies diffused to the Au/TiO_2 interface and to an increase in the degree of the Schottky barrier screening.

The difference between the resistivities in high resistance stage for the porous and barrier type of anodic titania films can possibly be explained by the different stoichiometry of the formed oxide film. It is well known that the conductivity of titania strongly depends on oxygen stoichiometry [39]. Oxidation in the ethylene-glycol electrolyte, containing F^- ions leads to the formation of a non-stoichiometric oxide with intermediate oxidation states [12], whereas oxidation in non-dissolving electrolytes leads to the formation of titania films with chemical composition closer to a stoichiometric TiO_2 [40]. Moreover, the concentration of charge carriers for the barrier and porous types of anodic titania measured using the Mott–Schottky technique also proves that the porous film should have higher conductivity.

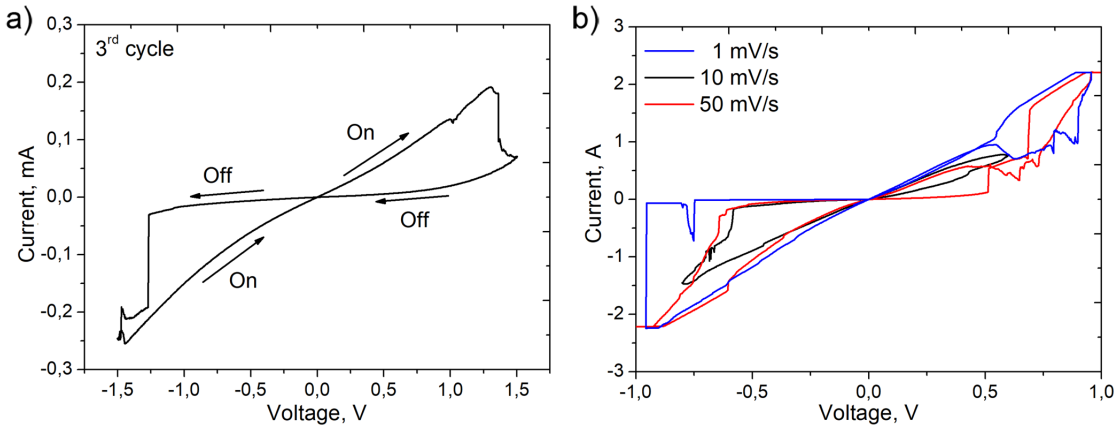

FIG. 4. I–V Curves for Au/TiO$_2$/Ti structure with barrier (a) and porous (b) active layer

To determine the stability of low resistance stage of the formed memristors, we measured the chronoamperometric curves of binary on-off operations (Fig. 5). The measurement was performed by applying SET potential -0.8 V for 30 s, then – READ potential -0.2 V for 30 s followed by applying RESET potential of 0.6 V for 30 s and READ potential. Applying a SET potential led to switching the memristor to LRS, and applying a RESET potential leads to switching the memristor to HRS. The values of resistance in HRS and LRS were quite stable during the 110 cycles. At the same time, applying a potential lower than SET potential (-0.4 V) didn't lead to resistance switching – the sample stay in high resistance stage (Fig. 5b).

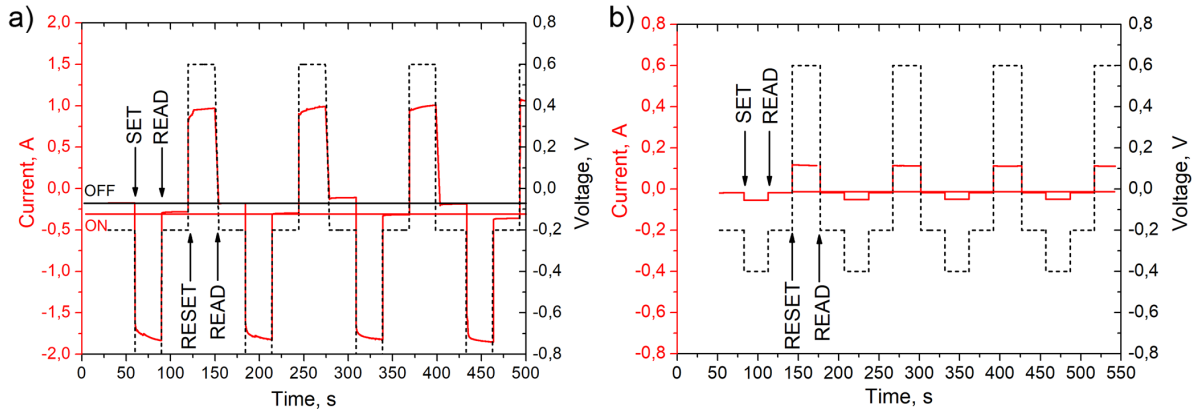

FIG. 5. I–t curves obtained by applying -0.8 V (a) and -0.4 V (b) SET potential, -0.2 V read potential and 0.6 V RESET potential with duration of 30 s

4. Conclusions

In the present work, anodic titania films of porous and barrier type were formed by anodic oxidation in fluorine-containing and boron-containing electrolytes respectively. Comparison of the semiconductor properties of the formed films was performed via the Mott-Schottky technique. It was shown that both type of films exhibit the n-type conductivity, whereas the charge carrier density in the case of the porous titania film was higher than that of the barrier type film. This can be explained by the presence of local donor impurity levels, which were formed by fluorine-ion impurities absorbed during anodization.

The obtained memristive elements show the bipolar type of switching governed by Schottky barrier screening. For the barrier type film, the switching potential is equal to -1.5 V and the ratio of resistivity in high and low resistance stage is 34. For the porous type film, the resistance strongly depends on the voltage sweeping rate, and the highest value of R_{off}/R_{on} is equal to 131, switching potential is equal to -0.6 V. This dependence can be explained by the limitation in diffusion of oxygen vacancies throughout the oxide layer. At the same time, memristive element based on barrier type film ofanodic titania exhibits higher switching stability (more than

1000 cycles), has the structure with lower defect concentration and is more suitable for the application as a cell in memory storage devices.

Acknowledgements

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References

[1] Kyung M.K., Tae H.P. Dual Conical Conducting Filament Model in Resistance Switching TiO_2 Thin Films. *Scientific Reports*, 2015, **5**, P. 7844.
[2] Zhang F., Li X.M., Gao X.D. The unification of filament and interfacial resistive switching mechanisms for titanium dioxide based memory devices. *Journal of applied physics*, 2011, **109**, 104504.
[3] Ssenyange S., Yan H. Redox-driven conductance switching via filament formation and dissolution in carbon/molecule/TiO_2/Ag molecular electronic junctions. *Langmuir*, 2006, **22** (25), P. 10689–10696.
[4] Pickett M.D. The Materials Science of Titanium Dioxide Memristors. Electronic Thesis and Dissertations UC Berkeley, 2010, URL: http://digitalassets.lib.berkeley.edu/etd/ucb/text/Pickett_berkeley_0028E_11006.pdf
[5] Yang J.J., Pickett M.D., Li X. Memristive switching mechanism for metal/oxide/metal nanodevices. *Nature Nanotechnology*, 2008, **3**, P. 429–433.
[6] Albu S.P. et al. TiO_2 nanotube layers: Flexible and electrically active flow-through membranes. *Electrochemistry Communications*, 2010, **12**, P. 1352–1355.
[7] Prusakova V., Collini C., Nardi M. The development of solgel derived TiO_2 thin films and corresponding memristor architectures. *RSC Adv.*, 2017, **7**, P. 1654–1663.
[8] Diamanti M.V., Pisoni R., Cologni A. Anodic oxidation as a means to produce memristive films. *J. Appl. Biomater. Funct. Mater.*, 2016, **14** (3), P. 290–295.
[9] Abunahla H., Mohammad B. *Memristor Technology: Synthesis and Modeling for Sensing and Security Applications*. Springer International Publishing, 2018, 106 p.
[10] Diamanti M.V., Spreafico F.C., Pedeferri M.P. Production of anodic TiO_2 nanofilms and their characterization. *Physics Procedia*, 2013, **40**, P. 30–37.
[11] Pham Hieu H., Wang Lin-Wang. Oxygen vacancy and hole conduction in amorphous TiO_2. *Phys. Chem. Chem. Phys.*, 2015, **17**, P. 541–550.
[12] Petukhov D.I., et al. Formation mechanism and packing options in tubular anodic titania films. *Microporous and Mesoporous Materials*, 2008, **114**, P. 440–447.
[13] Zixue S., Wuzong Z. *Porous Anodic Metal Oxides*, University of St. Andrews, 2010.
[14] Wei W. Advanced Electrochemical Approaches for the Self-organized Formation of One-Dimensional Oxide Nanoarchitectures: From Transition Metals to Superlattices. Universiry of Erlangen–Nürnberg, 2012, URL: https://opus4.kobv.de/opus4-fau/files/2334/wei_thesis.pdf.
[15] Chen X., Mao S.S. Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications. *Chem. Rev.*, 2007, **107**, P. 2891–2959.
[16] Keller F., Hunter M.S., Robinson D.L. Structural Features of Oxide Coatings on Aluminum. *J. Electrochem. Soc.*, 1953, **100** (9), P. 411–419.
[17] OSullivan J.P., Wood G.C. The morphology and mechanism of formation of porous anodic films on aluminium. *Proc. R. Soc. Lond. A*, 1970, **317** (1531), P. 511–543.
[18] Nakata K., Fujishima A. TiO_2 photocatalysis: Design and applications. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, 2012, **13**, P. 169–189.
[19] Diop D.K., Simonot L. Magnetron Sputtering Deposition of Ag/TiO_2 Nanocomposite Thin Films for Repeatable and Multicolor Photochromic Applications on Flexible Substrate. *Adv. Mater. Interfaces*, 2015, **2**, 1500134.
[20] Roy P., Berger S., Schmuki P. TiO_2 Nanotubes: Synthesis and Applications. *Angew. Chem. Int. Ed.*, 2011, **50**, P. 2904–2939.
[21] Kim I.D., Rothschild A., Lee B.H., Kim D.Y. Ultrasensitive chemiresistors based on electrospun TiO_2 nanofibers. *Nano Lett.*, 2006, **6** (9), P. 2009–2013.
[22] Seo M.-H., Yuasa M., et al. Detection of organic gases using TiO_2 nanotube-based gas sensors. *Procedia Chem.*, 2009, **1**, P. 192–195.
[23] Middlemas S., et al. A new method for production titanium dioxide pigment. *Hydrometallurgy*, 2013, **131-132**, P. 107–113.
[24] Yoo J.E., Lee K. Highly ordered TiO_2 nanotube-stumps with memristive response. *Electrochemistry Communications*, 2013, **34**, P. 177–180.
[25] Vokhmintsev A.S., Weinstein I.A. Memristive Effect in a Nanotubular Layer of Anodized Titanium Dioxide. *Bulletin of the Russian Academy of Sciences. Physics*, 2014, **78** (9), P. 932–935
[26] Miller K., Nalwa K.S. Memristive Behavior in Thin Anodic Titania. *IEEE Electron device letters*, 2010, **31** (7), P. 737–739.
[27] Smith Y.R., Ray R.S. Self-Ordered Titanium Dioxide Nanotube Arrays: Anodic Synthesis and Their Photo/Electro- Catalytic Applications. *Materials*, 2013, **6** (7), P. 2892–2957.
[28] Ghafar A., Chong C. Fabrication of complete titania nanoporous structures via electrochemical anodization of Ti. *Nanoscale Research Letters*, 2011, **6**, P. 332–338.
[29] Baram N., Yair E.-E. Electrochemical Impedance Spectroscopy of Porous TiO_2 for Photocatalytic Applications. *J. Phys. Chem. C*, 2010, **114**, P. 9781–9790.
[30] Jeong D.S., Schroeder H., Waser R. Impedance spectroscopy of TiO_2 thin films showing resistive switching. *Applied Physics Letters*, 2006, **89**, 082909.

[31] Harrington S.P., Devine T.M. Analysis of Electrodes Displaying Frequency Dispersion in Mott-Schottky Tests. *Journal of The Electrochemical Society*, 2008, **155** (8), P. 381–386.
[32] Ling Y., Ren F., Feng J. Reverse bias voltage dependent hydrogen sensing properties on Au–TiO_2 nanotubes Schottky barrier diodes. *International journal of hydrogen energy*, 2016, **41**, P. 7691–7698.
[33] Regonini D., Bowen C.R., Jaroenworaluck A., Stevens R. A Review of Growth Mechanism, Structure and Crystallinity of Anodized TiO_2 Nanotubes. *Materials Science and Engineering R*, 2013, **74**, P. 377–406.
[34] Macak J.M., Tsuchiya H., Schmuki P. High-Aspect-Ratio TiO_2 Nanotubes by Anodization of Titanium. *Angew. Chem. Int. Ed.*, 2005, **44**, P. 2100–2102.
[35] Czoska A.M., Livraghi S. The Nature of Defects in Fluorine-Doped TiO_2. *J. Phys. Chem. C*, 2008, **112** (24), P. 8951–8956.
[36] Lide D.R. *CRC Handbook of Chemistry and Physics*, 89 edition, CRC Press, Boston, 2008, P. 12–114.
[37] Smith G.X R., Crook R., Wadhawan J.D. Measuring the work function of TiO_2 nanotubes using illuminated electrostatic force microscopy. *Journal of Physics: Conference Series*, 2013, **471**, 012045.
[38] Miller K.J. Fabrication and modeling of thin-film anodic titania memristors, 2010, URL: http://lib.dr.iastate.edu/cgi/viewcontent.cgi?article=2430&context=etd.
[39] Yang L. *Resistive switching in TiO_2 thin films*. Forschungszentrum Jülich, Jülich, 2011.
[40] Gils S.V., Mast P., Stijns E., Terryn H. Colour properties of barrier anodic oxide films on aluminium and titanium studied with total reflectance and spectroscopic ellipsometry. *Surf Coat Technol.*, 2004, **185** (2-3), P. 303–310.