A.K. Fedotov[1],
I.L. Baranov[2],
M.V. Malashchonak[3],
E.A. Streltsov[3],
I.A. Svito[1],
A.V. Mazanik[1*]

[1]Physical Faculty,
Belarusian State University,
Nezalezhnastsi Av. 4,
Minsk 220030, Belarus;
mazanikalexander@gmail.com;

[2]Belarusian State University of Informatics and Radioelectronics,
P. Brovka 6,
Minsk 220013, Belarus;

[3]Chemical Faculty,
Belarusian State University,
Nezalezhnastsi Av. 4,
Minsk 220030, Belarus;

Magnetoresistive properties of Ni/TiO2/Ti and Ni/SiO2/Si structures: comparative analysis

Keywords: Ni/TiO_2/Ti, Ni/SiO_2/Si, magnetoresistance

1. Introduction

Development of new types of heterostructures based on nanostructured ferromagnetic metals and semiconductors is of a great fundamental and practical importance because it enables one to hope for the expansion of the operating temperature and frequency ranges of spintronic devices [1]. These structures can be used in 2D matrices for visualization of magnetic field distribution, in information recording and storage devices, highly sensitive magnetic sensors, etc.

For creation of such structures a template-based approach can be used [2]. Porous silicon and aluminum oxides, as well as titanium dioxide nanotubes can be used as templates. Silicon oxide based templates can be produced using different methods (lithography, ion-track methods, electrochemically, etc.). Templates based on aluminum and titanium oxides with vertical pores are created most often by anodization of corresponding metals.

Titanium dioxide belongs to wide band gap oxide semiconductors (band gap energy E_g=3.1 eV). It is under investigation for more than 40 years as a photocatalyst, sensitive element of gas sensors, photoanode in the dye- and quantum dot sensitized solar cells, material for self-cleaning coatings and biomedical applications [3,4]. At the same time, magnetic and spintronic properties of TiO_2 based structures have been studied to a much lesser extent.

Anodic nanotubes of titanium dioxide (TiO_2 NTs) are investigated relatively recently (last 15 years, [5,6]). Anodization of metallic titanium in aqueous and non-aqueous solutions containing fluoride ions with concentration 0.05–0.5 M under DC voltage in the range from 1 to 150 V enables one to obtain TiO_2 NT arrays with controllable inner and outer diameter, wall thickness, height, density of location on the surface, etc. [7]. For anodic TiO_2 NTs the hexagonal ordered structure inherent to the anodic aluminum oxide films is expressed to a much lesser extent. Other distinctions between TiO_2 and Al_2O_3 are related to TiO_2 semiconductor properties and pronounced dielectric properties of Al_2O_3. In particular, this difference manifests itself in possibility of DC cathodic deposition of metals on TiO_2 NTs, as well as under UV illumination.

To date, magnetic and magnetotransport properties of the nanoheterostructures obtained by electrochemical deposition of metals on TiO_2 NTs have not been studied. Therefore, a comparison of the properties of “ferromagnetic metal/semiconductor” structures obtained using both SiO_2/Si and TiO_2/Ti templates is of a great scientific interest.

2. Experimental

For preparation of Ni/SiO_2/Si structures, 1 μm thick SiO_2 layer was thermally grown on the (100) surface of 4.5 Ω·cm phosphorous doped Cz Si wafer. Using standard photolithography procedures, a set of windows was formed in the oxide layer (Fig. 1). Electrochemical deposition of Ni was carried out through these windows from 0.5 M $NiSO_4$ + 0.5 M H_3BO_3 aqueous solution according to the method described in [8]. Ti-Ni contacts (1x5 mm^2) were evaporated onto Ni filled windows and then copper wires were connected to them using ultrasonic soldering. Rear ohmic contact was formed by Ti-Ni evaporation with a preliminary donor doping.

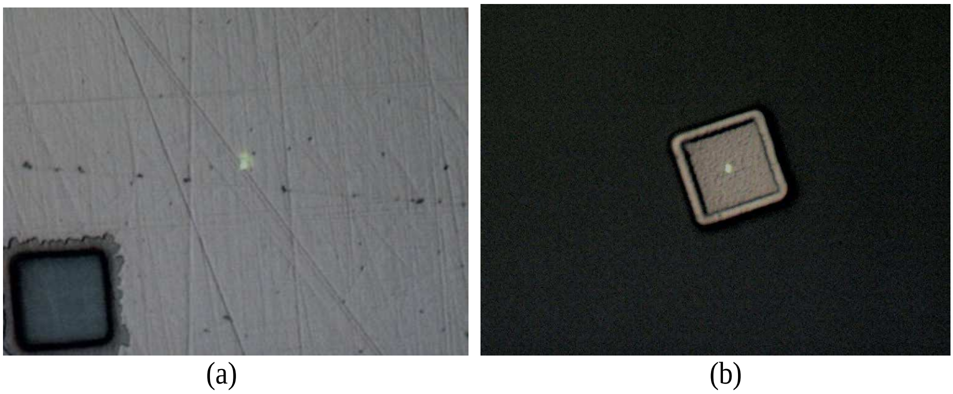

Fig. 1. Optical photographs of 10x10 μm2 window in SiO2 before (a) and after (b) Ni electrodeposition

Synthesis of the titanium dioxide nanotube array (Fig. 2) was carried out according to the procedure used in [9]. Metallic titanium plate was anodized in a two-electrode electrochemical cell with graphite counter electrode in aqueous electrolyte containing 1 mol/l $(NH_4)_2SO_4$, 0.1 mol/l NH_4F and 0.2 mol/l $H_2C_2O_4$ with pH 2.8 (corrected with NaOH) under the electrode potential bias of 25 V for 20 h at room temperature. The rate of potential bias sweep from 0 V to 25 V at the initial stage was 250 mV/s. After anodization, the electrodes were immediately immersed into 1.2 mol/l $(NH_4)_2SO_4$ solution for 24 hours, then rinsed with distilled water, air dried and finally heat treated at 450 °C for 1 hour in air.

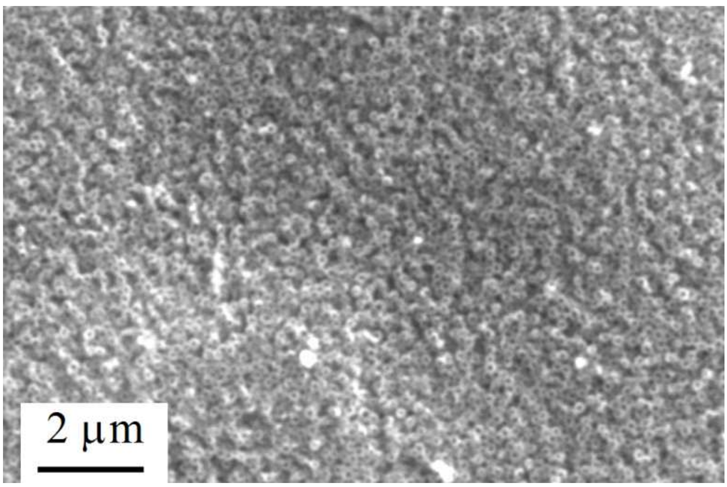

Fig. 2. SEM image of TiO_2 nanotube array formed on Ti substrate

For electrical measurements on Ni/TiO_2/Ti structures, a front contact with diameter of 2 mm was formed with a silver paste, whereas a rear contact (to Ti substrate) was created using In ultrasonic soldering.

Measurements of electrical properties were carried out using the two-probe method in the 2 – 300 K temperature range and in magnetic fields up to 8 T with a closed-cycle measuring system produced by Cryogenic Ltd. (London). The direction of both current flow through an electrodeposited nickel and magnetic field was normal to the sample plane.

3. Results and Discussion

3.1. Ni/TiO2/Ti structures

Experiments have shown that current-voltage characteristics of the Ni/TiO_2/Ti structures are linear in the whole studied temperature range (Fig. 3a), and their electrical conductivity changes less than by 2 % passing through a minimum when the temperature is increasing (Fig. 3b).

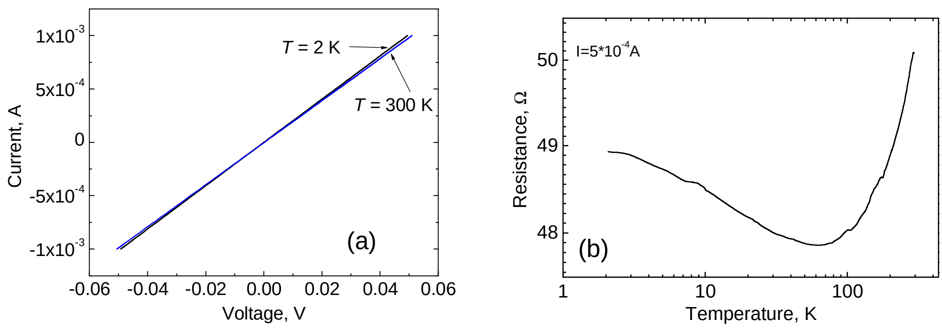

Fig. 3. Current-voltage characteristics at different temperatures (a) and temperature dependence of resistance (b) for Ni/TiO2/Ti structures

The observed behavior of resistivity corresponds qualitatively to the case of highly defective metal. Resistance decrease in the low temperature range is probably related to electron weak localization phenomena, whereas resistance growth at higher temperatures is determined by increase of electron scattering on phonons. A slight (less than 2%) variation of resistance with temperature points to the fact that scattering on defects remains the dominant mechanism of electron scattering in the whole studied temperature range.

The Ni/TiO_2/Ti structures demonstrate a positive magnetoresistance which reaches a few tenths of percent at 2 K and decreases monotonically with increase in the temperature (Fig. 4).

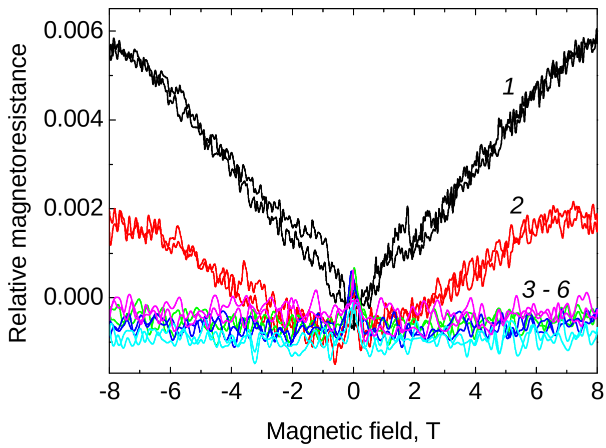

Fig. 4. Magnetoresistance of $Ti/TiO_2/Ni$ structure at 2 K (1), 5 K (2), 25 K, 50 K, 150 K, and 300 K (3 – 6)

3.2. Ni/SiO2/Si structures

Current-voltage characteristics of the $Ni/SiO_2/Si$ structures measured at different temperatures in both presence and absence of magnetic field are given in Fig. 5. An asymmetrical shape of I-V curves points to good rectifying properties of the Schottky barrier formed between Ni and Si substrate.

In the whole studied temperature range the formed $Ni/SiO_2/Si$ structures demonstrate a positive magnetoresistance, which increases monotonically when the temperature is decreasing (Fig. 6).

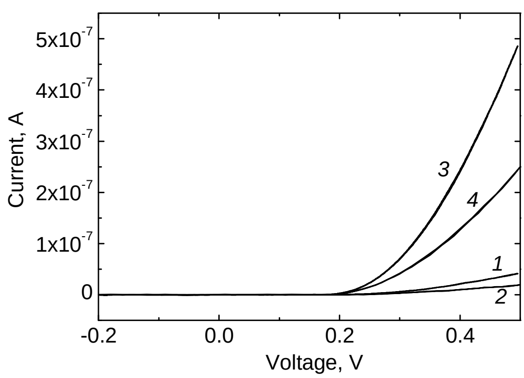

Fig. 5. Current-voltage characteristics of Ni/SiO2/Si structures at 20 K (1,2) and 25 K (3,4) without (1,3) and with magnetic field B = 8 T (2,4)

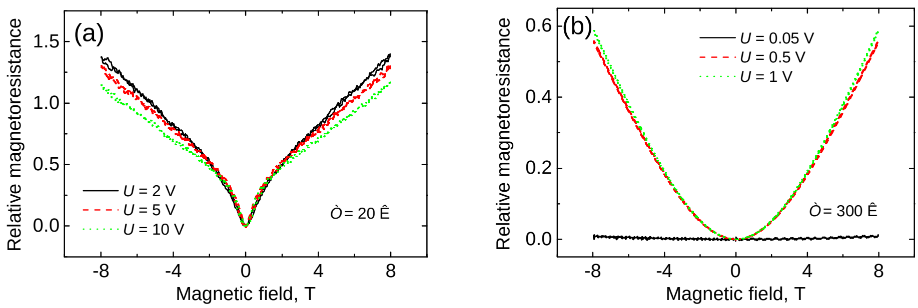

Fig. 6. Magnetoresistance of $Ni/SiO_2/Si$ structure at 20 K (a) and 300 K (b) and different bias voltages *U*

As is seen from Figures 4 and 6, magnetoresistance of the $Ni/SiO_2/Si$ structures is much higher in comparison with $Ni/TiO_2/Ti$ ones indicating that the main contribution to the observed magnetoresistive properties is given by the silicon substrate. The square-low dependence of magnetoresistance on magnetic field may point to its Lorentz nature.

Resume

$Ni/TiO_2/Ti$ and $Ni/SiO_2/Si$ structures have been prepared using electrochemical deposition of Ni on TiO_2 nanotubes and windows in SiO_2 layer, respectively. Magnetoresistance of these structures was measured depending on the temperature and magnetic field. The performed experiments have shown that the maximal value of magnetoresistance is achieved in the case of $Ni/SiO_2/Si$ structures and reaches about 60 % at room temperature in magnetic field 8 T.

Acknowledgments

The work was financially supported by the Research Program “Nanomaterials and Nanotechnologies” of the Republic of Belarus (contract No 2.4.08).

Bibliography

1. Y. Imry, in: *Nanostructures and Mesoscopic Systems*, edited by W. P. Kirk and M. A. Reed, (Academic, New York), p. 11. 1992.
2. *Template-based synthesis of nanorod or nanowire arrays*. In: Springer Handbook of nanotechnology. Bharat Brushan (ed.). Springer, pp. 161–178. 2007.
3. A. Fujishima, K. Honda. *Electrochemical photolysis of water at a semiconductor electrode* Nature 238, pp. 37–38. 1972.

4. Y. Wang, Y. He, Q. Lai, M. Fan. *Review of the progress in preparing nano TiO_2: An important environmental engineering material* Journal of Environmental Sciences 26, pp. 2139–2177. 2014.
5. Q. Zhou, Z. Fang, J. Li, M. Wang. *Applications of TiO_2 nanotube arrays in environmental and energy fields: A review* Microporous and Mesoporous Materials 202, pp. 22–35. 2015.
6. X. Zhou, N.T. Nguyen, S. Özkan, P. Schmuki. *Anodic TiO_2 nanotube layers: Why does self-organized growth occur – A mini review* Electrochemistry Communications 46, pp. 157–162. 2014.
7. Q. Cai, M. Paulose, O.K. Varghese, C.A. Grimes. *The effect of electrolyte composition on the fabrication of self-organized titanium oxide nanotube arrays by anodic oxidation* Journal of Materials Research 20, pp. 230–236. 2005.
8. S.Yu. Turishchev, E.V. Parinova, F. Kronast, R. Ovsyannikov, N. V. Malashchenok, E. A. Streltsov, D. K. Ivanov, A. K. Fedotov. *Photoemission electron microscopy of arrays of submicron nickel rods in a silicon dioxide matrix* Physics of the Solid State 56 (9), pp. 1916–1921. 2014.
9. M.V. Malashchonak, A.V. Mazanik, O.V. Korolik, E.A. Streltsov, A.I. Kulak. *Influence of Wide Band-Gap Oxide Substrate on Photoelectrochemical Properties and Structural Disorder of CdS Nanoparticles Grown by Successive Ionic Layer Adsorption and Reaction (SILAR) Method* Beilstein Journal of Nanotechnology (in print).

Abstract

Magnetoresistive properties of $Ni/TiO_2/Ti$ and $Ni/SiO_2/Si$ structures obtained using template-based approach have been examined in the temperature range from 2 to 300 K. It was established that the main contribution into observed magnetoresistance is given by the silicon substrate, whereas influence of Ni is negligible small.

Streszczenie

Właściwości magnetyczne struktur $Ni/TiO_2/Ti$ oraz $Ni/SiO_2/Si$ otrzymanych z zastosowaniem tzw. „podejścia szabłonowego” zostały zbadane w zakresie temperatur od 2 do 300 K. Ustalono, że główny wkład do obserwowanej magnetorezystancji jest rezultatem wpływu podłoża krzemowego , podczas gdy wpływ Ni jest znikome mały.

Słowa kluczowe: Struktury $Ni/TiO_2/Ti$ oraz $Ni/SiO_2/Si$, magnetorezystancja