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Vadim Bayev
Julia Fedotova
Aleksei Maximenko
NC PHEP Belarusian State University
Belarus, Minsk
Eugenij Streltsov
Mikolai Malashchonak
Igor Azarko
Alexander Fedotov
Ivan Svito
Belarusian State University, Minsk, Belarus,

Aleksy Patryn
Politechnika Koszalińska
Koszalin, Poland
Pavel Apel
Serguey Tyutyunnikov
Joint Institute for Nuclear Research,
Dubna, Russia
Momir Milosavljević
Vinča Institute of Nuclear Sciences,
Beograd, Serbia

Electric and magnetic properties of nickel and nickel-plladium nanowires deposited in anodic aluminum oxide template

Keywords: template-assisted electrodeposition, magnetic anisotropy, magnetoresistance, porous alumina templates

Introduction

New technological approaches to fabrication of template-based ordered nanoarrays of nanorods or nanowires is of great importance not only because of the fundamental new physics involved in such highly correlated systems, but also because of a diversity of applications. In the first place, nanoarray based structures are the object of particular interest for creation of nanoelectronic devices because modern electronic components are approaching the size limit of standard photo-lithography techniques. While self-assembled template-assisted nanostructures have the potential to circumvent such limitations and thus could be used as alternative future electronic components. Therefore they can be used in such applications as high density storage media, functional nanomaterials exhibiting quantum size effects, highly sensitive sensors to magnetic fields and temperature, nanoelectronic devices and functional bio-chemical sensors and membranes [1, 2].

Investigations of structure, electric and magnetic properties of such systems favor the development of nanosized semiconductor-metal junctions on different substrates like Si and GaAs with perpendicular magnetic anisotropy relatively to substrate and GMR/TMR effects that provides an opportunity to create perspective magnetically sensitive namostructures for magnetoelectric devices of a new type. The important advantages of the proposed heterostructures are their compatibility with Si or GaAs planar technology, low production costs as well as reliable reproducible technology processing.

This paper is related to our recent achievements in template-assisted electrochemical deposition of nickel and nickel-palladium nanowires (nanorods) inside porous anodized alumina templates on Al and GaAs substrates.

1. Experimental

In this paper we used two types of anodized aluminum oxide (AAO) templates which were prepared by the double-anodization method [3]. For manufacturing of the first type of alumina template we used high purity (99.99 %) Al plates annealed at temperature 550 °C in the air for 5 h and chemically polished in mixture of mineral (H_3PO_4, HNO_3) and acetic (CH_3COOH) acids. For the preparation of the second type of alumina template we used total anodized Al film deposited on GaAs substrate. Regimes of anodization for both types of templates were very similar.

First stage of anodization was carried out in 0.3 M oxalic acid at 10 °C and applied voltage 40 V during 20 h with the following immersing in phosphoric (H_3PO_4, 6 %) and chromic (CrO_3, 1.8 %) acids mixture at 80 °C for 30 min. Second stage of anodization (to create ordered pores) was performed for 1 h at temperature 10 °C and 40 V. The formed pores were widened in 0.3 M oxalic acid solution at 35 °C during 2.5 h. Nanowire arrays of pure Ni or Ni(1-x)Pd(x) metal composition nanorods were synthesized via ac electrochemical deposition from nickel chloride ($NiCl_2$) and potassium tetrachloropallidate (K_2PdCl_4) in dimethyl sulfoxide (DMSO) solution into AAO/Al or AAO/GaAs templates with frequency of electric current of 50 Hz and voltage of 12±1 V for 20 min.

Microstructural characterization was performed using a field-emission scanning electron microscope (SEM) LEO1455VP **(**Carl Zeiss) with four-compartment reflected electron detector. More detailed structure investigation was performed by transmission electron microscope (TEM) Philips CM200 with accelerating potential 200 keV. Elemental composition of Ni(1-*x*)Pd(*x*) nanowires was analyzed by energy-dispersive X-ray spectroscopy (EDX) with Ronteg analyzer.

Room temperature magnetisation loops and low-temperature (2 – 300 K) magnetoresistance R(T,B) were measured on cryogenic high field universal measuring system (CFHF Cryogenic Ltd) using special vibrating sample magnetometric (VSM) unit and magnetoresistance unit. Magnetic resonance spectrometry at room temperatures were performed with continuous wave X-band EPR spectrometer Varian E112.

The sample temperature at R(T,B) measurements was controlled with accuracy 0.001 K by special GaAs Lakeshore transistor thermometers and stabilized at constant value with accuracy 0.005 K when I-V measurements and sweeping of magnetic field using Lakeshore Temperature Controller Model 331. Keathley 345 voltmeter was used for measurement of operating current and voltage. Vector B was directed normally to nanostructure plane (along Ni nanorods) during electric measurements.

2. Results and discussion

2.1. Al/AAO/Ni-Pd nanostructures

Typical surface and cross section SEM micrographs of Al/AAO template with Ni(1-*x*)Pd(*x*) nanowire arrays are shown in fig. 1.

Cross sectional analyses of filled templates reveals a dispersion of wire length value from 1 to 5 μm. According to TEM (fig. 2*a*) nanowires consist of metal nanoparticles with 5 nm in diameter though extended structure of metal nanowires remains after the bleeding of AAO matrix with 0.1 M NaOH solution (fig. 2*b*). It should be noted that the minimal wire length was observed for sample Al/AAO/Ni(78)Pd(22). The pore diameter was determined to be $d = 70$ nm and pore center-to-center distance – $r = 120$ nm. Thus assuming the fact that wires conform to pore shape and are relatively uniform along their length the packing factor P for nanowire arrays was defined as $P = (\pi / 2\sqrt{3})(d/r)^2 = 0.3$.

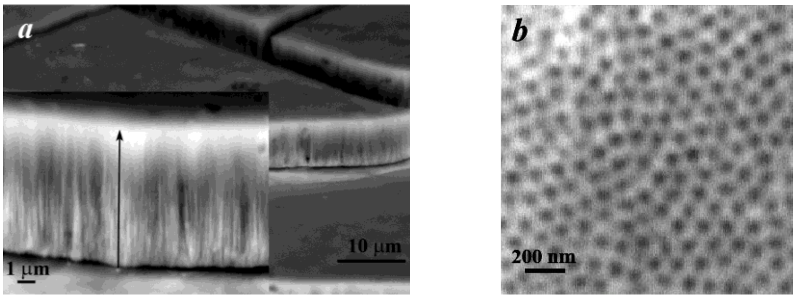

Fig. 1. Cross section (*a*) and surface (*b*) SEM images of Al/AAO template filled with Ni(50)Pd(50) metal composition

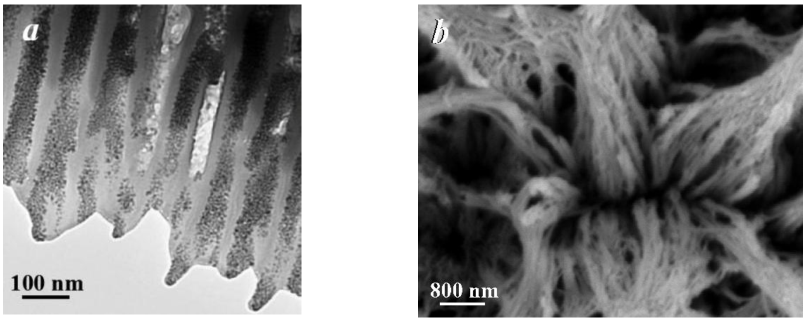

Fig. 2. Cross section TEM image (*a*), SEM image (*b*) of metal nanowires on aluminum substrate after the bleeding of AAO matrix of Al/AAO

In order to reveal palladium influence on magnetic anisotropy of Ni(1-*x*)Pd(*x*) nanowires magnetization data *M*(*H*) (fig. 3) and magnetic resonance spectra (fig. 4) were obtained in perpendicular and parallel orientations of Al/AAO templates towards the induction vector of applied magnetic field. Determined magnetic parameters are presented in tabl. 1. The values of saturation magnetization M_S are normalized on the mass of whole template by the reason of difficult metal content determination in samples.

The shape of hysteresis loops shown on fig. 3 and values of coercivity (tabl. 1) indicate a magnetic anisotropy of “easy axis” type along growth direction of metal nanowires for samples Al/AOA/Ni and Al/AOA/Ni(78)Pd(22). Ratio $H_{C\perp}$ (the applied magnetic field is out of template plane) to $H_{C||}$ (the applied magnetic field is in template plane) for nickel nanowires was determined as 4.5. For Ni(78)Pd(22) the ratio $H_{C\perp}/H_{C||}$ upraises to 8 times while further increase of palladium content reduces this amount to 1.1. Observed perpendicular magnetic anisotropy is caused by stretched form anisotropy of nanowires.

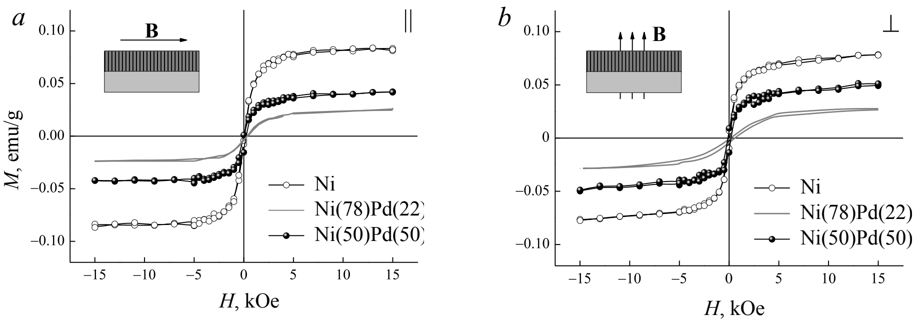

Fig. 3. Magnetization loops of anodized alumina templates filled with Ni(1-*x*)Pd(*x*) metal composition in perpendicular (*a*) and parallel (*b*) orientations of template towards the induction *B* vector of applied magnetic field

The increase of coercivity can be explained by a formation of multi quasi-layered structure Ni/Pd during the ac electrochemical deposition that reduces cluster size of nickel and as a consequence enlarges coercivity [4, 5]. Further increment of palladium content in Ni(1-*x*)Pd(*x*) nanowires reduces the magnetic exchange interaction between nickel clusters and suppresses magnetic anisotropy as a result of form anisotropy. This explanation also clarify the rise of $H_{C||}$ with the increment of palladium content in Ni(1-*x*)Pd(*x*) nanowires.

Table 1. Magnetic parameters of Al/AAO templates filled with Ni(1-*x*)Pd(*x*) metal compositions

Sample	H_C, Oe		M_S, emu/g		*g*-factor	B_a, mT	$N_\perp$	$N_{\|\|}$
	⊥	||	⊥	||				
Al/AOA/ Ni	20	90	0.084	0.078	2.21	– 28.4	0	0.50
Al/AOA/ Ni(78)Pd(22)	30	240	0.026	0.027	2.21	– 7.3	0.14	0.43
Al/AOA/ Ni(50)Pd(50)	160	180	0.047	0.051	2.10	+ 24.8	0.26	0.37

Obtained magnetic resonance spectra of samples (fig. 4) denote a ferromagnetic character of resonance microwave absorption and distinctly reveals magnetic anisotropy of “easy axis” type along growth direction of metal nanowires for samples Al/AOA/Ni and Al/AOA/Ni(78)Pd(22) and of “easy plane” for Al/AOA/Ni(50)Pd(50).

The values of g-factor and induction of effective anisotropy magnetic field B_a were determined from following system of equations for magnetic resonance conditions given by the Landau – Lifshitz dynamical equation of motion for magnetization in perpendicular and parallel orientations of template plane towards induction of applied magnetic field:

$$\begin{aligned} h\nu &= g\mu_B(B_\perp - B_{an}), \\ (h\nu)^2 &= g\mu_B B_\parallel (B_\parallel + B_{an}), \end{aligned} \qquad (1)$$

where h – Plank constant, ν – microwave frequency, μ_B – Bohr magneton, $B_\parallel$ and $B_\perp$ – induction values of resonance field in case of parallel and perpendicular sample orientation. Positive value of B_a corresponds to “easy plane” magnetic anisotropy type of the whole template filled with metal composition while negative value of B_a – to “easy axis” magnetic anisotropy type. The change of anisotropy type explains the behavior of coercivity in parallel and perpendicular directions of applied magnetic field observed by VSM.

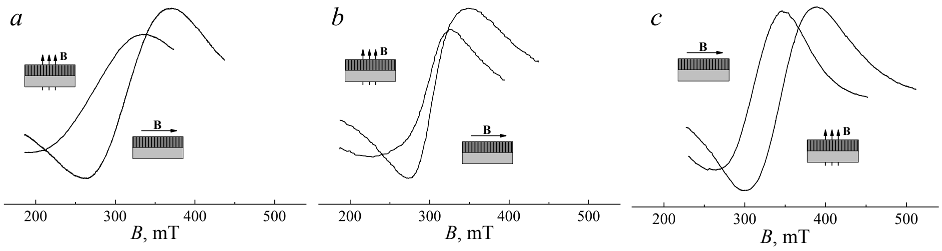

Fig. 4. First derivative of magnetic resonance absorption of anodized alumina templates filled with Ni (*a*), Ni(78)Pd(22) (*b*) and Ni(50)Pd(50) (*c*) metal compositions in perpendicular and parallel orientations of nanowires towards the induction vector of applied magnetic field

Calculated values of g-factor are in perfect agreement with those of nickel for samples Al/AOA/Ni and Al/AOA/Ni(78)Pd(22) [6]. On the other hand for Ni(50)Pd(50) nanowires g-factor appears to be lower (g = 2.10) that may be caused by small (less than 10 nm) thickness of nickel quasi-layers in Ni/Pd multi quasi-layered nanostructure [7].

The induction of effective magnetic anisotropy field B_a in assumption of homogeneously nanowire magnetization and the uniform length of nanowires can be represented as:

$$B_{an} = P'\mu_0 M - (1-P')(N_\parallel - N_\perp)\mu_0 M \qquad (2)$$

where (1-x) – nickel content, μ_0 – vacuum permeability, M – magnetization of Ni(1-x)Pd(x) nanowires, P' – volume nickel fraction determining as $V_{Ni}P/(V_{Ni}+V_{Pd})$, $N_\parallel$ and $N_\perp$ – demagnetizing factor of individual nanowire in parallel and perpendicular direction towards template plane. The first term of B_a corresponds to “easy plane” type of magnetic anisotropy due to magnetic interaction between nanowires, while the second one – to “easy axes” type due to magnetic anisotropy of nanowires provided by its form. Thus positive meaning of

The values of demagnetizing factors were obtained using equation for B_a. As one can see from tabl. 1 the increase of palladium content in samples reduces the perpendicular magnetic anisotropy provided by the form anisotropy of Ni(1-x)Pd(x) nanowires in Al/AAO templates. It confirms assumption made previously of multi quasi-layered structure Ni/Pd formation during the ac electrochemical deposition that causes a cluster size decrease of nickel and reduction of form factor role in anisotropy origin.

2.2. AAO/Ni/GaAs nanostructures

The samples of AAO/Ni/GaAs nanostructures were prepared on substrates containing semi-insulating (100) GaAs plates of n-type covered with 2 μm low-ohmic epitaxial Si-doped GaAs layer with electron concentration $1\cdot10^{18}$ cm^{-3} at 300 K. The samples with dimensions 10×2 mm, cut from nanostructures, were supplied by 2 electric probes prepared on front of the sample (1 and 2 in Insert in Fig. 5) using

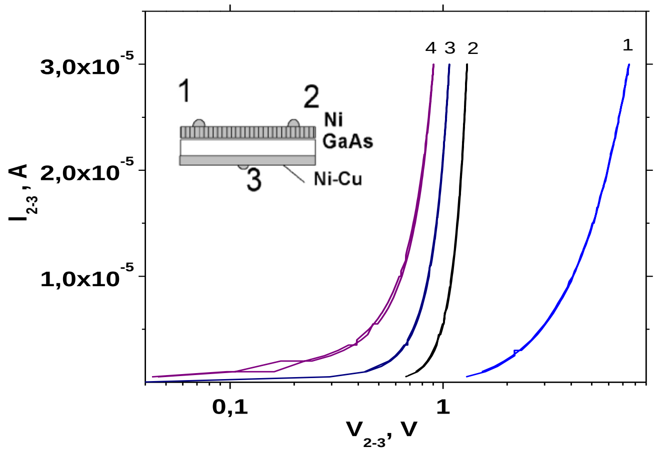

Fig. 5. Transversal I-Vs of AOA/Ni/GaAs nanostructured sample at different temperatures: 1 – 77 K, 2 – 150 K, 3– 250 K, 4 - 293 K. Insert: schematic view of electric probes in the sample.

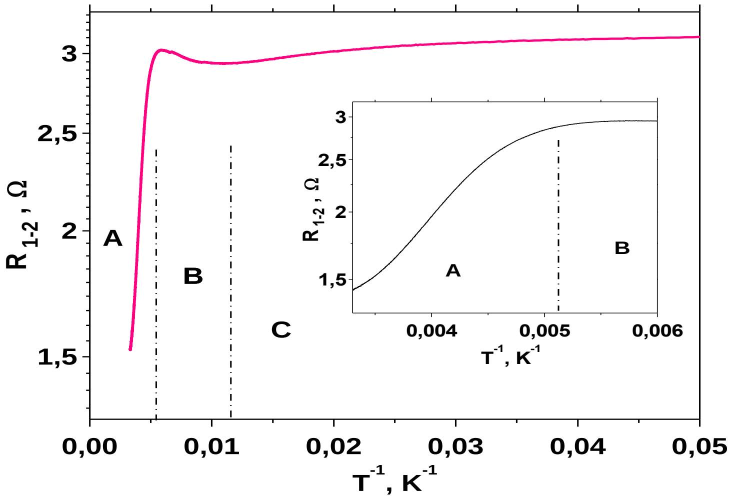

Fig. 6. Temperature dependences of resistance $R(T)$ in B = 0 for AAO/Ni/GaAs nanostructure measured between 1 and 2 probes at operating current I = 10 mA. The induction B vector of applied magnetic field is normal to the template plane. Insert: High-temperature part of R(T) curve.

ultrasound In soldering and one backside Cu-Ni electrode thermally deposited on GaAs substrate (3 in Insert in Fig. 5). Quality of these probes checked by linearity of longitudinal (measured between contacts 1 and 2 in Insert) and transversal (between 2 and 3 probes) I-V characteristics at room temperatures. As was shown, the longitudinal I-Vs were linear at the whole temperature range 2 – 300 K whereas the transversal I-Vs became non-linear below 70 K (see, Fig. 6). The mentioned means that for longitudinal geometry of electric measurements the AAO/Ni/GaAs nanostructure, shown in Insert in Fig. 6, does not lead itself as a double Schottky barrier neither at high temperatures (due to strong doping of epitaxial GaAs layer) nor at low temperatures (probably due to high-doped epitaxial GaAs layer). Non-linearity of I-Vs at T < 70 K is probably connected with the influence of semi-insulating GaAs substrate.

$R(T)$ dependence in Fig. 6, measured in regime of constant I, have shown that in the studied samples impurity conductance by GaAs epitaxial layer dominates in the temperature range 200-300 K (curve in region A). When lowering of temperature, in part B, we probably observe a “depletion” of impurities where $R(T)$ depends only on mobility of electrons in doped GaAs layer. Below 200 K (region C) continuous decreasing of slope of lg$R(1/T)$ curve in Arrhenius scale is observed that can be attributed to variable range hopping (VRH) of electrons by impurities [8].

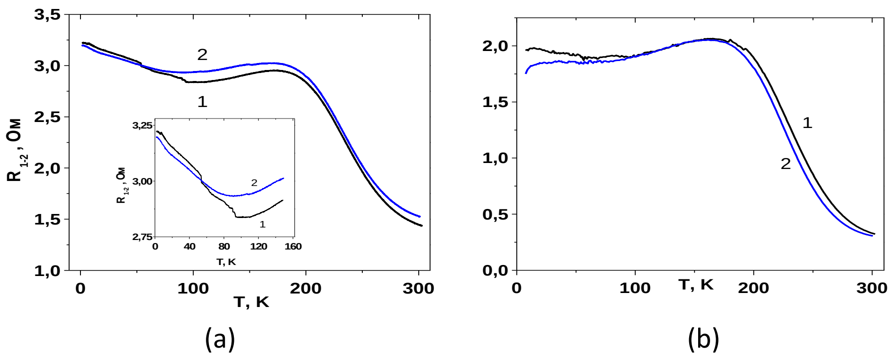

Fig. 7. Temperature dependences of resistance $R(T)$ in $B = 0$ (curve 1) and $B = 8$ T (curve 2) for AAO/Ni/GaAs nanostructure measured between 1 and 2 (a) and 2 and 3 (b) probes at operating current $I = 10$ mA. The induction B vector of applied magnetic field is normal to the template plane. Insert: Low-temperature part of curves in (a)

As follows from Fig. 7, application of magnetic field B = 8 T normally to the substrate plane results in change of $R(T)$ progress, i.e. magnetoresistive effect. Comparison of curves 1 and 2 in these figures shows that the value and sign of $MR = MR(B) = [R(\mathrm{B}) - R(0)]/R(0)]$ was dependent on temperature and measurement geometry. As is seen, in both longitudinal ($MR_{1\text{-}2}$) and transversal ($MR_{2\text{-}3}$) geometry of measurements (Figs. 7a and 7b) the sign of is changed from positive (PMR effect) to negative (NMR effect) when lowering the temperature below 70 K. The presence of NMR confirms the above mentioned assumption concerning VRH conductance by localized states (impurities) in highly doped epitaxial GaAs layer at T < 70 K and it can be considered as tunneling (TMR) effect [9]. Note that the value of TMR effect increases with temperature lowering and approaches maximal values at 2 K (up to 25 % for $MR_{2\text{-}3}$ and 1 % for $MR_{1\text{-}2}$). Reasons of more high values of MR_{23}, measured in transversal regime, as compared with $MR_{1\text{-}2}$, requires an additional detailed study. However, it is not excluded that the mechanism of impurity avalanche in GaAs substrate is convenient in this case as was observed for similar template-based SiO_2/Ni/Si nanostructures with Ni nanorods embedded into porous SiO_2 matrix (see, our paper [10]).

The highest $MR_{1\text{-}2}$ values for longitudinal geometry (up to 5%) are observed at transition of $R(T)$ in Fig. 6 to the region of impurity “depletion” (region B in Fig. 7) when concentration of electrons ceases to change when cooling. The observed behavior of PMR effect in regions B and A, including its decrease with increasing temperature, probably indicates its Lorence-like nature.

Summary

Presented results indicate a possibility of forming magnetic ordered nanostructured arrays with perpendicular magnetic anisotropy relatively to substrate in AAO templates using ac electrochemical deposition of magnetic (Ni) / non-magnetic (Pd) metal composition. According to TEM metal nanowires consist of nanoparticles of 5 nm in diameter. Structure of metal nanowires becomes extended even after the bleeding of AAO matrix.

Analysis of the observed PMR and NMR effects in arrays of Ni nanorods in Al_2O_3/Ni templates display their strong difference for longitudinal and transversal (Schottky barrier regime) configurations of measurements and also on temperature range. Negative sign of MR is observed for both geometries of measurements at T < 50 K and can be attributed to TMR effect due to VRH carrier transport, i.e. tunneling of electrons by the localized centers (impurities). PMR effect observed at T > 100 K we explain by Lorence-like mechanism.

Results of magnetometry and magnetic resonance spectroscopy reveal magnetic anisotropy of “easy axis” type along wire axis for individual Ni(1-x)Pd(x) nanowire with palladium content up to $x = 50$. However magnetic interaction between nanowires results in the formation of magnetic anisotropy of “easy plane” type for the whole array of nanowires with Ni(50)Pd(50) composition.

As our experiments show, the used template-assisted electrodeposition technique of coercivity and magnetoresistivity increment can be successfully used in fabrication of magnetically sensitive nickel and nickel-palladium nanowires (nanorods) arrays inside porous anodized alumina templates on Al and GaAs substrates which are convenient for manufacturing of magnetoelectric devices of a new type.

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Abstract

Structure, electric and magnetic properties of ordered Ni and Ni-Pd nanostructures synthesized by means of electrochemical deposition in porous anodic aluminum oxide templates were investigated. Templates were filled with nickel and nickel-palladium compositions using the alternative current. Matrix parameters (pores diameter and depth) determine the sizes and morphology of the formed metal nanowires. Negative sign of magnetoresistance was observed at $T < 50$ K and attributed to TMR effect due to variable range hopping carrier transport mechanism. Positive magnitoresistance was observed at $T > 100$ K and explained by Lorence-like mechanism. The presence of magnetic perpendicular anisotropy towards template plane in synthesized nanostructures was revealed. Demagnetizing factors of individual nanowire in parallel and perpendicular direction towards template plane were determined by magnetic resonance spectroscopy. Revealed increase of coercivity in nanowires containing palladium was explained by the formation of quasi- multilayered structure of Ni/Pd nanowires during the ac electrochemical deposition.

Streszczenie

Struktura, właściwości elektryczne i magnetyczne uporządkowanych Ni Ni-Pd nanostruktur syntezowanych metodą elektrochemicznego nanoszenia w porowatej matryce z utlenionego aluminiowego anodu. Matryca została wypełniona Ni lub Ni-Pd mieszanką z wykorzystaniem prądu zmiennego. Parametry matrycy (średnica i głębokość pór) wpływały na rozmiary i morfologię tworzących się metalicznych nanodrutów.

Ujemna magnetorezystancja była obserwowana w temperaturze T<50K i mogła być opisana w ramkach mechanizmu skokowej przewodności. Pozytywna magnetorezystancja została obserwowana dla T>100K i odpowiada mechanizmowi typu Lorence. Obecność magnetycznej prostopadłej anizotropii w stosunku do płaszczyzny matrycy była zanotowana. Demagnezujący czynnik pojedynczych nanodrutów w kierunkach równoległych i prostopadłych do płaszczyzny matrycy był wyznaczony z badań metodą magnetycznej

spektroskopii rezonansowej. Zaobserwowany wzrost komercyjności w nanodrutach zawierających palladium może być związany z formowaniem kwasi-wielowarstwowej struktury w Ni/Pd nanodrutach w trakcie elektrochemicznego osadzenia.