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FORC-investigation of magnetic properties of Ni nanowire arrays synthesized using Al_2O_3 templates with different order of pores

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Abstract: This paper focuses on the investigation of magnetic properties of Ni nanowire arrays synthesized using Al_2O_3 porous templates with different durations of first anodization. It has been shown that the diameter of the pores in the template is increasing with an increase in the first anodization time up to 2 hours, and the interpore distance becomes more uniform. Using porous templates with short times of anodization results in synthesis of branched Ni nanowires, while templates with longer times allow to achieve cylindrical nanostructures. Magnetic properties of Ni nanowires arrays were studied using the FORC method, which allowed to investigate the distribution of interaction fields and coercive forces in the arrays. It was found that two magnetic phases with different coercive forces and interaction field are observed in the samples with a short duration of first anodization.

Keywords: anodization, aluminum oxide matrices, nanowires, electrochemical deposition, FORC-method

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Материалы конференции
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Исследование FORC-методом магнитных свойств массивов Ni нанопроволок, синтезированных с использованием шаблонов Al_2O_3 с разным порядком пор

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Аннотация. Данная работа посвящена исследованию магнитных свойств массивов нанопроволок Ni, синтезированных с использованием пористых мембран Al_2O_3 с разной продолжительностью первого анодирования. Показано, что с увеличением времени первого анодирования до 2 часов медианный диаметр пор на верхней поверхности мембраны увеличивается, а расстояние между порами становится более равномерным.

Использование пористых шаблонов с малым временем анодирования приводит к получению разветвленных нанопроволок Ni, а шаблоны с большим временем позволяют получить цилиндрические наноструктуры. Магнитные свойства массивов нанопроволок Ni изучались с использованием FORC метода, который позволил исследовать распределение полей взаимодействия и коэрцитивных сил в массивах. Он показал, что в образцах с малым временем первого анодирования присутствуют две магнитные фазы с разными коэрцитивными силами и полем взаимодействия.

Ключевые слова: анодирование, пористые оксидные матрицы, нанопроволоки, электрохимическое осаждение, FORC-метод

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Introduction

Many recent studies have focused on the magnetic properties of one-dimensional ferromagnetic nanostructures because of their nontrivial magnetic behavior due to strong uniaxial shape anisotropy [1]. Their potential applications range widely, from biomedicine to nanoelectronics, notably including sources of secondary irradiation in radiotherapy, agents for targeted drug delivery, agents for destroying cancer by hyperthermia and mechanical destruction of tumors, elements of magnetic memory and nanoelectronics, various biosensors and sensors of magnetic fields [2].

Many methods for synthesizing various one-dimensional nanostructures are discussed in the literature [3–5]. Method of electrodeposition into porous alumina matrices, in which the deposited nanostructures replicate the shape of pores in the membrane, is one of the most common and widely used method due to a number of notable advantages. They include, in particular, the possibility to precisely and easily control the geometrical parameters of arrays of synthesized one-dimensional nanostructures by controlling the conditions during two-step anodization of porous Al_2O_3 matrices. This method can be used to obtain arrays of hexagonal ordered high-uniform one-dimensional nanostructures with different diameters, distance between neighbors and the thickness of wall between them [6]. Changing certain parameters can allow to modify the geometry even further, synthesizing one-dimensional nanowires with a shape different than a cylinder.

The goal of this work is to study the effect of the first anodization time on the structure of porous Al_2O_3 matrices and, consequently, on the magnetic properties of Ni nanowire arrays synthesized inside them using the FORC method [7], which allows to estimate the distribution of interaction fields and coercive forces in the investigated samples.

Materials and Methods

To produce porous matrices of aluminum oxide, we used 2×2 cm Al plates with a thickness of 1.7 mm, annealed at 500 °C for 5 hours under vacuum conditions. To obtain a smooth surface, the samples were mechanically polished with abrasive paper and subjected to chemical polishing in HNO_3 (50%) + HF (40%) at T = 100 °C for 60 s. After chemical treatment, samples were electropolished in 1:4 $HClO_4$ + C_2H_5OH solution with the current density of 500 mA/cm, resulting in a mirror-like surface. The non-working side of the plates was coated

with a photoresist to prevent oxide formation, while the working side was left open for contact with an acidic solution. Anodizing was carried out using an Agilent 6030A power supply in 0.3 M solution of oxalic acid ($C_2H_2O_4$) cooled down to 2–3 °C in a soft potentiostatic mode at 40 V. The duration of the first anodization was selected as t = 0, 15 and 120 minutes for different samples, after which the oxide layer was removed with the solution of H_2CrO_4 (1.8%) + H_3PO_4 (6%) at T = 60 °C and magnetic stirring for 15–20 minutes. Second anodization for all samples was carried out for 18 hours. After preparation of porous membranes, a 1 μm thick layer of Cu was deposited by thermal sputtering on the working side to be used as a conductive layer during subsequent electrodeposition and impart additional strength to fragile porous membranes. After Cu deposition, non-oxidized Al was dissolved in 0.08 M CuCl2 + 8% HCl at room temperature until only porous Al_2O_3 membrane left. After that the barrier layer at the bottom of the pores was subjected to dissolution in 1 M H_3PO_4 for 60 minutes to form through pores. Nanowires were electrodeposited using Watts solution containing $NiSO_4$, $NiCl_2$, and H_3BO_3 into prepared matrices in a potentiostatic mode at −1 V for 10 minutes using a Keithley 2460 power supply.

Studies of the surface of porous membranes and the geometry of nanowires were carried out using ThermoScientific $SCIOS_2$ scanning electron microscope (SEM). To study Ni nanowire geometry, they were etched from the oxide matrix using H_2CrO_4 (1.8%) + H_3PO_4 (6%) at T = 60 °C and deposited on a copper plate. The study of the distribution of pore diameters, interpore distances and Fast Fourier Transform (FFT) analysis of SEM pictures were carried out using the Fiji software. Investigation of the magnetic properties of Ni nanowires arrays and FORC-method were performed using LakeShore 7400 vibrating sample magnetometer (VSM) at room temperature.

Results and Discussion

Results of SEM investigation of porous matrices surfaces for all samples are presented in Figure 1. The sample with t = 0 min (Fig. 1, *a*) showed comparably uniform distribution of the pore diameters (D) in the range of 20–50 nm, with the median D = 33 nm (Fig. 1, *g*). FFT image (Fig. 1, *d*) displayed a blurred circle, which corresponds to a somewhat uniform distribution of interpore distances in the matrix. Increasing the time of first anodization t to 15 min results in a drastically changed surface of the porous template (Fig. 1, *b*). Pores with diameters from 25 nm to 125 nm (median D = 50 nm) (Fig. 1, *g*) were placed with no order, resulting in completely vague FFT picture (Fig. 1, *e*). The sample synthesized with t = 120 min (Fig. 1, *c*) revealed that D has increased to 45 nm, with the distribution of diameters 30–60 nm. The FFT image appeared as a thin, non-blurred circle, because of identical interpore distances and close-range order of pores in the membrane. It should be noted that no sample exhibited a long-range order, which would result in non-blurred peaks in hexagonal shape on the FFT picture. Analysis of the SEM pictures of the surface of porous templates demonstrated that the average distance between the pores r_{ip} is about 120 nm for the sample with t = 0 min, r_{ip} = 20–200 nm for the sample with t = 15 min and r_{ip} = 70 nm for the sample with t = 120 min.

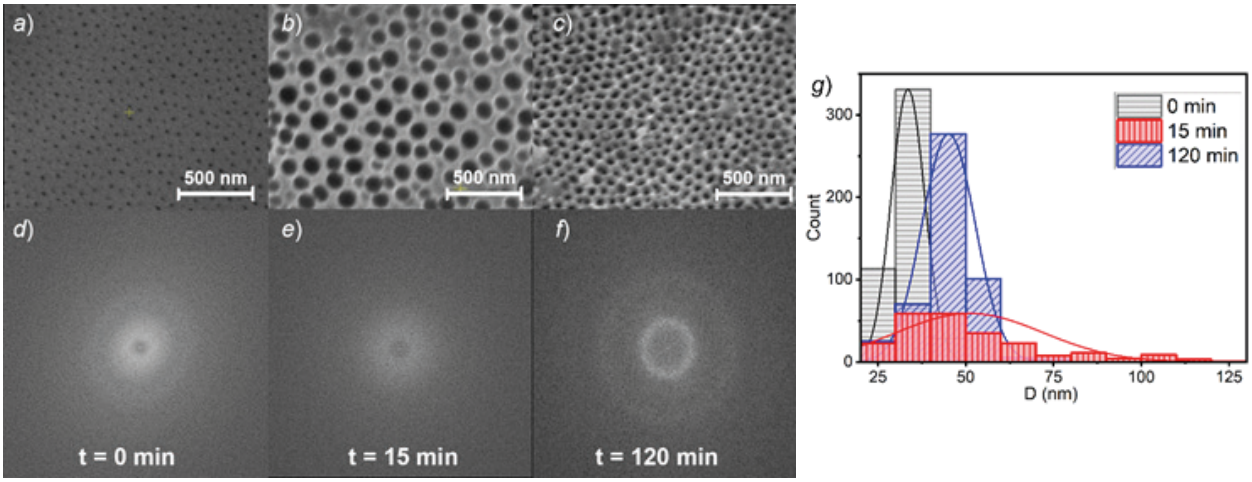

Fig. 1. SEM-images of porous membrane surface, obtained for 0 (*a*), 15 (*b*) and 120 min (*c*) of first anodization; images corresponding to the FFT analysis (*d* – *f*); histogram of distribution of pore diameters for all samples (*g*)

SEM-investigation of Ni nanowires, etched out of porous membrane, revealed that the nanowires appeared branched in samples with $t = 0$ min and $t = 15$ min, due to the branched structure of the pores. The sample with $t = 120$ min showed a cylindrical shape of the nanowires, with no branches. Such geometry of the pores originates in pore creation and merging in the process of oxide growth. Their D followed the diameter of the pores in the template, and the length amounted to 4, 2.5 and 3 μm for 0, 15 and 120 min of the first anodization accordingly.

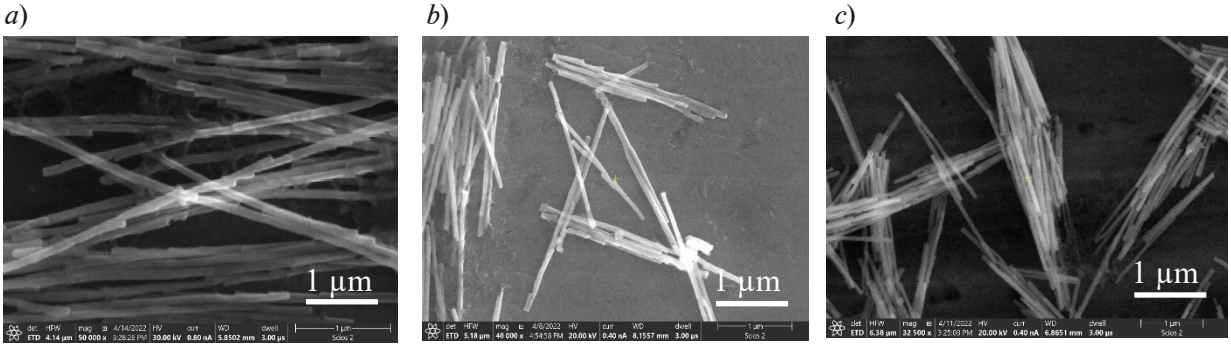

Fig. 2. SEM-images Ni nanowires etched out of porous template with time of first anodization 0 (*a*), 15 (*b*) and 120 (*c*) min on top of the Cu substrate

Magnetic measurements in the direction of external magnetic field H along the long axis of nanowires are presented in Fig. 3 and summarized in Table 1. Measured from the hysteresis loops, the coercive force H_c^{loop} is increasing from $H_c^{loop} = 690$ Oe to $H_c^{loop} = 914$ Oe with first anodization time changing from 0 to 15 min. The sample with $t = 120$ min showed slightly lower coercivity $H_c^{loop} = 914$ Oe than the sample with no first anodization. Such behavior of H_c can be related to the changing D of nanowires, since H_c is very sensitive to that parameter in the single-domain range of diameters (40 − 150 nm). Moreover, nanowires synthesized with the first anodization time below 15 nm are of branched structure (Fig. 2, *a*, *b*), which also can be the reason for increasing Hc, with branches acting as pinning centers.

The ratio of remnant magnetization M_r to saturation magnetization M_s was determined from hysteresis loops (Fig. 3, *a*) as 0.85 for all samples. A ratio so close to 1 corresponds to that in the absence of H, the majority of the nanowires in the array are keeping their magnetization in the way, predetermined by the previously applied H. This behavior can originate from two possible factors: a single-domain micromagnetic state of nanowires and relatively weak interaction fields between them. A single-domain state is common for nanowires with D below 100 nm [8] and resulting in a square hysteresis loop with ratio $M_r/M_s = 1$ for an individual nanowire in the array. On the other hand, strong magnetostatic interaction fields Hu in the array, induced by nanowires with a high value of M_s, often result in the M_r/M_s value tending to zero, changing the critical fields and shifting the hysteresis loop of the single nanowire, due to self-demagnetizing effect. Thus, in our case, it is safe to assume that interwire interactions in investigated samples are limited due to the low M_s of Ni and do not induce any serious changes to magnetic behavior of the array.

To prove this assumption and investigate the H_c distribution in the samples, FORC-method analysis was employed. A set of 70 first-order reversal curves was measured on VSM in the range of the fields from −2000 Oe to +2000 Oe. Using second order derivative of magnetization M

Table 1

Magnetic and structural properties of Ni nanowire arrays

Sample	Time of 1st anodization, min	D, nm	H_c^{loop}, Oe	min H_c^{FORC}, Oe	max H_c^{FORC}, Oe	H_u, Oe
1	0	33	690	594	1013	600
2	15	50	914	712	1382	1200
3	120	45	675	670	1272	980

on starting field of each curve H_r and applied field H, a density of states ρ was achieved from experimental loops, as presented in Fig. 3, $b - d$. The overall similarity of the shape of FORC-diagrams suggests that they have similar magnetization switching processes. Nevertheless, H_c^{FORC} distribution varies differently for samples with different first anodization times. A wide distribution of H_c^{FORC} from 712 Oe to 1382 Oe for the sample with t = 15 min points to their geometrical irregularity, originating from non-uniform pores in the matrix. The range of H_c^{FORC} distribution is comparably lower in the samples with t = 0 and 120 min: H_c^{FORC} = 594–1013 Oe for t = 0 min and H_c^{FORC} = 670–1272 Oe for t = 120 min, due to their comparably more even distribution of D. The FORC-diagram of the sample with t = 0 min is characterized, in contrast to other samples, by an additional ρ distribution peak with a smaller H_c^{FORC} = 280 Oe. This peak could stand for a low-coercive phase, possibly located close to the work surface of the Al_2O_3 template, which has a smaller D of nanowires and thus smaller coercive forces. The interaction fields H_u in the sample with t = 0 min is twice as smaller as in the sample with t = 15 min (H_u = 600 Oe and H_u = 1200 Oe, respectively), possibly due to large distances between nanowires in the first sample and much more closely packed nanowires in the second sample. The sample with t = 120 min is characterized with an average H_u = 980 Oe because of the small distance between the nanowires in the array.

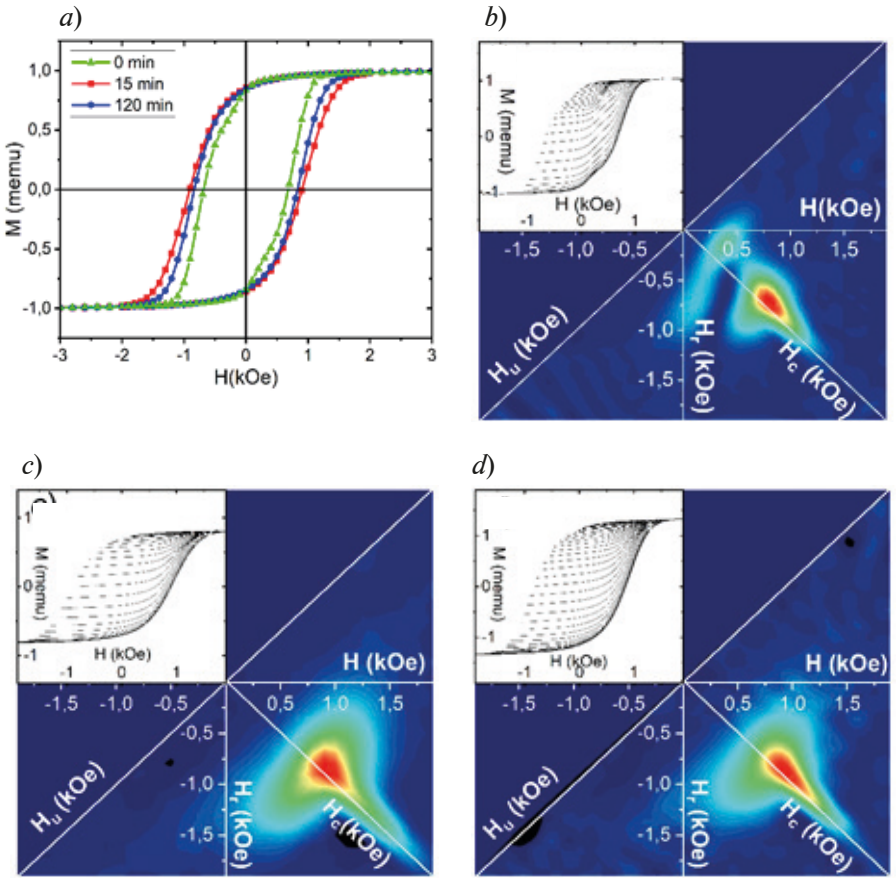

Fig. 3. Hysteresis loops measured in the direction of the external field H along the long axis of nanowires for all samples (*a*). FORC-diagrams in the same orientation of H for samples with t = 0 (*b*), 15 (*c*) and 120 (*d*) min of first anodization.

Conclusion

As a result of the study, magnetic properties of Ni nanowires depending on the time of first anodization of Al_2O_3 membranes were studied. Ni nanowires were obtained by electrochemical deposition into porous matrices, synthesized with the time of first anodization varied from 0 to 120 min. SEM investigation of morphology of the porous templates revealed a heavy dependence of the pore diameters, interpore distance and pore order in the membrane on the time of first

anodization. A morphological study of Ni nanowires showed that samples with $t < 15$ min were characterized by branched structure. A study of magnetic properties demonstrated a possible single-domain micromagnetic structure of the Ni nanowires and low interaction fields in the array. FORC-studies indicated strong dependence of coercive forces on the geometrical parameters of Ni nanowires in the array. It has been shown that the sample with $t = 15$ min possesses a wide distribution of coercive forces due to ununiform diameters of nanowires in the array, while other samples have a more uniform distribution of coercive forces and thus geometrical parameters of the samples. Magnetostatic interactions are also heavily dependent on the distance between pores and show the highest fields for the sample synthesized with a porous matrix anodized for 15 min.

REFERENCES

1. **Samardak A.S., Ognev A.V., Samardak A.Yu., Stebliy E.V., Modin E.B., Chebotkevich L.A., Komogortsev S.V., Stancu A., Panahi-Danaei E., Fardi-Ilkhichy A., Nasirpouri F.,** Variation of magnetic anisotropy and temperature-dependent FORC probing of compositionally tuned Co-Ni alloy nanowires, Journal of Alloys and Compounds. 732 (2018) 683–693.

2. **Moreno J. A., Bran C., Vazquez M., Kosel J.,** Cylindrical Magnetic Nanowires Applications, IEEE Transactions on Magnetics. 57 (4) (2021) 1–17

3. **Nam D. Y., Samardak A. Yu., Jeon Y. S., Kim S. H., Davydenko A. V., Ognev A. V., Samardak A. S., Kim Y. K.,** Magnetization reversal of ferromagnetic nanosprings affected by helical shape. Nanoscale 10 (2018) 20405–20413

4. **Scott J. A., Totonjian D., Martin A. A., Tran T. T., Fang J. H., Toth M., McDonagh A. M., Aharonovich I., Lobo C. J.,** Versatile method for template-free synthesis of single crystalline metal and metal alloy nanowires. Nanoscale 8 (5) (2016) 2804–2810.

5. **Lau Y. M., Chee P. C., Thong J. T. L., Ng V.,** Properties and applications of cobalt-based Material produced by electron-beam-induced deposition. Journal of Vacuum Science & Technology a-Vacuum Surfaces and Films. 20 (4) (2002) 1295–1302.

6. **Ebihara K., Masaichi N.,** Structure and Density of Anodic Oxide Films Formed on Aluminum in Oxalic Acid Solutions. Journal of the Metal Finishing Society of Japan. 34 (11) (1983) 548–553

7. **Mayergoyz I. D.,** Hysteresis Models from the Mathematical and Control-Theory Points of View. Journal of Applied Physics. 57 (8) (1985) 3803–3805.

8. **Ivanov, Y., Chuvilin, A., Vivas, L., Kosel J., Chubykalo-Fesenko O., Vazquez M.,** Single crystalline cylindrical nanowires-toward dense 3D arrays of magnetic vortices. Scientific Reports 6 (2016) 23844.

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