ATOM PHYSICS AND PHYSICS OF CLUSTERS AND NANOSTRUCTURES

Conference materials
UDC 539.232; 542.06; 546–1; 544.654.2
DOI: https://doi.org/10.18721/JPM.173.226

The method of obtaining Ni and Co nanowires in porous anodic alumina matrices

E.A. Grushevsky✉, N.G. Savinsky, O.S. Trushin

[1]Valiev Institute of Physics and Technology of RAS, Yaroslavl Branch, Yaroslavl, Russia

✉ yaregor@mail.ru

Abstract. This paper focuses on the investigation of producing Ni and Co nanowire arrays synthesized using Al_2O_3 porous template. Porous alumina samples were obtained by double electrochemical anodizing of the prepared foil in 0.5 M oxalic acid, at a voltage of 60 V and a temperature of 25 °C. The pore diameter distribution maximums are about 85 nm. Nanowires were electrodeposited in a 3-electrode electrochemical cell into prepared matrices in a potentiostatic and galvanostatic mode. Studies of the surface of porous membranes and the geometry of nanowires were carried out using scanning electron microscope.

Keywords: anodization, aluminum oxide matrices, nanowires, electrochemical deposition

Funding: The work was carried out within the framework of the State program no. FFNN-2022-0018 of the Ministry of Science and Higher Education of Russia on the equipment of the center for the collective use of scientific equipment "Diagnostics of micro- and nanostructures".

Citation: Grushevsky E.A., Savinsky N.G., Trushin O.S. The method of obtaining Ni and Co nanowires in porous anodic alumina matrices, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 17 (3.2) (2024) 135–138. DOI: https://doi.org/10.18721/JPM.173.226

Материалы конференции
УДК 539.232; 542.06; 546–1; 544.654.2
DOI: https://doi.org/10.18721/JPM.173.226

Метод получения Ni и Co нанопроволок в матрицах пористого анодного оксида алюминия

Е.А. Грушевский✉, Н.Г. Савинский, О.С. Трушин

Ярославский филиал Физико-Технологического института РАН им. К.А. Валиева, г. Ярославль, Россия

✉ yaregor@mail.ru

Аннотация. Данная статья посвящена исследованию создания массивов нанопроволок Ni и Co, синтезированных с использованием пористого шаблона Al_2O_3. Образцы пористого оксида алюминия были получены методом двойного электрохимического анодирования подготовленной фольги в 0.5 М щавелевой кислоте, при напряжении 60 В и температуре 25 °C. Максимумы распределения пор по диаметру составляют около 85 нм. Нанопроволоки электроосаждались в 3-электродной электрохимической ячейке на подготовленные матрицы в потенциостатическом и гальваностатическом режимах. Исследования поверхности пористых мембран и геометрии нанопроволок проводились с помощью сканирующего электронного микроскопа.

Ключевые слова: анодирование, матрицы оксида алюминия, нанопроволоки, электрохимическое осаждение

Финансирование: Государственное задание ФТИАН им. К.А. Валиева РАН Минобрнауки РФ по теме № FFNN-2022-0018.

Ссылка при цитировании: Грушевский Е.А., Савинский Н.Г., Трушин О.С. Метод получения Ni и Co нанопроволок в матрицах пористого анодного оксида алюминия // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2024. Т. 17. № 3.2. С. 135–138. DOI: https://doi.org/10.18721/JPM.173.226

Introduction

One of the best and most extensive methods for ensuring repeatability and high quality of the resulting nanostructures is the use of porous anodic aluminium oxide (PAAO) templates [1–3], in particular arrays for the growth of controlled, self-organizing, as well as highly ordered structures, including nanorods, nanowires, nanotubes, nanocomposite materials with strict adherence to product dimensions at a packing density of 10^9–10^{11} units/cm^2. Much attention has been drawn to the study of magnetic nanomaterials and nanostructures with strong shape anisotropy, promising for use in nanosensors, spintronic devices and high-density magnetic recording. It is known that one of the most common method obtaining such nanowires (NW) is a template synthesis – filling required material in narrow channels in porous matrices. The unique properties of porous anodic aluminum oxide (PAAO) membranes make this material potentially the best template for electrochemical deposition of Ni nanowires [4–5].

Materials and Methods

To produce porous matrices of aluminum oxide, we used 2×2 cm Al (99, 9% purity) plates with a 1 mm thickness. To obtain a smooth surface, the samples were electropolished, resulting in a mirror-like surface. Anodizing was carried out using 0.5 M oxalic acid with the temperature about 25 °C in a potentiostatic mode at 60 V. The duration of the first anodization was τ = 60 minutes, after which the oxide layer was removed in CrO_3 (1.8%) + H_3PO_4 (6%) at T = 80 °C for 10 minutes. Second anodization for all samples was carried out for 1 hour. Then the voltage was lowered to 5 V at a speed of 60 mV/s to thin the barrier layer out. In this work, aluminum was not removed, and the barrier layer was destroyed when the polarity was reversed at the beginning of the deposition process. [3] Ni nanowires were electrodeposited in a 3-electrode electrochemical cell using $NiSO_4 \cdot 7H_2O + NiCl_2 \cdot 6H_2O + H_3BO_3 + H_2O$ solution into prepared matrices in a galvanostatic mode at a current density of 75 mA/cm^2 for 10 minutes. Co nanowires were electrodeposited in a 3-electrode electrochemical cell using $CoSO_4 \cdot 7H_2O + CoCl_2 \cdot 6H_2O + H_3BO_3 + H_2O$ solution into prepared matrices in a potentiostatic mode at a voltage of 850 mV for 10 minutes.

Results and Discussion

Fig. 1, *a* shows an SEM image of the PAAO template before deposition. The SEM image of PAAO was further analyzed using ImageJ software, and pore diameter (D_p) = 85 ± 2.2 nm, pore distance (D_c) = 116 ± 5 nm and pore length (L_p) = 50 ± 1.5 microns were determined.

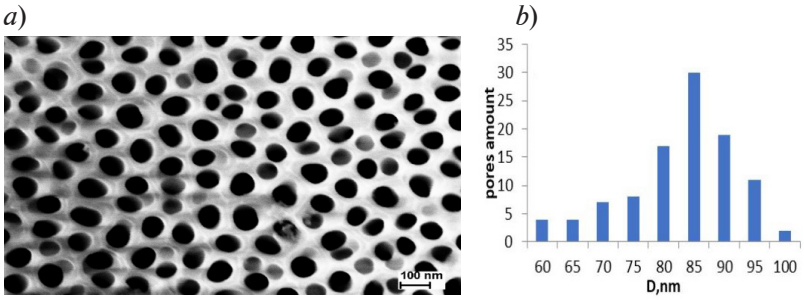

Fig. 1. SEM image of the PAAO template before deposition (*a*) with pores distribution (*b*)

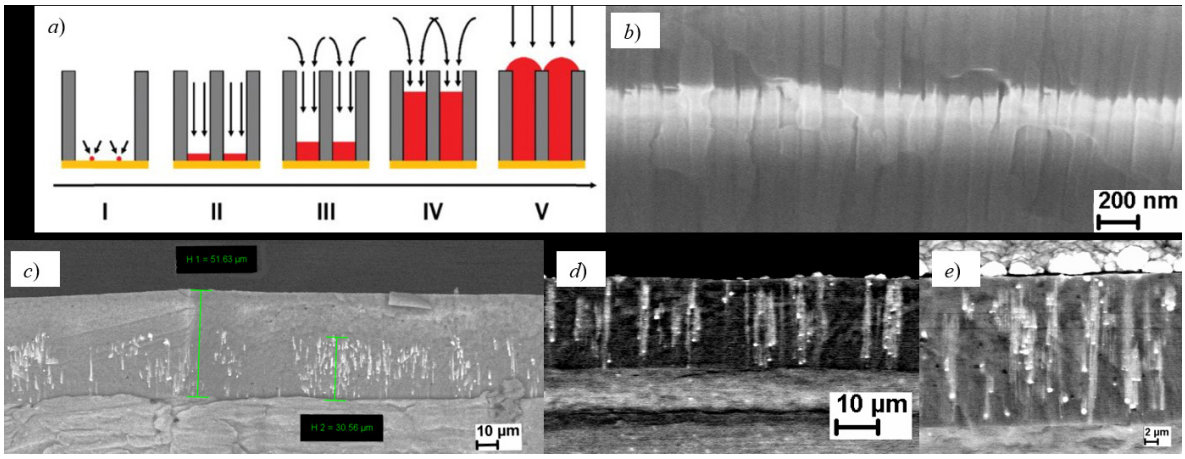

Fig. 2. Scheme of deposition process (*a*) [6], empty pores (*b*), SEM image of Ni nanowires on stage II-III (*c*), SEM image of Ni nanowires on stage IV (*d*), SEM image of Ni nanowires on stage V (*e*)

Fig. 2 shows a diagram of filling nanopores with metals during the electrodeposition process. This process can be divided into 5 conventional stages, the first of which is the formation of a seed at the bottom of the pore. Then metal begins to precipitate predominantly on this seed. The process continues until the pore is completely filled and ends with the release of metal to the surface in the form of a "cap". With further deposition, the metal is preferentially deposited on this cap, forming a continuous film and slowing down the deposition process in adjacent pores. This happens because the transport of the substance goes to the development of the emerging cap. The cap grows faster because planar diffusion towards the cap surface becomes greater than hemispherical diffusion in the pore. As a result, the diffusion current density decreases, while the total current increases due to the increase in surface area. The influence of the conditions of nanowire growth at the pore mouth and subsequent growth into a continuous horizontal layer has a very strong effect on the magnetic properties of nanowires. It is well known [7], that the magnetization vector of magnetic films lies in the plane of the magnetic film, but in nanowires shape anisotropy appears and the magnetization vector is directed perpendicular to the surface. Thus, in nickel agglomerations "caps" forming a film on the upper surface of PAAO, the magnetization vector is directed horizontally to the surface, which makes a significant contribution to the magnetization of the entire sample. Obviously, to direct the easy magnetization axis along the nickel nanowire, it is necessary to eliminate the growth of a horizontal nickel film on the surface of PAAO. There are two possible ways to form metal nanowires in a porous substrate: galvanic and potentiostatic. At the same time, the potentiostatic method is more applicable for growing multicomponent/segmented structures, and the galvanostatic method for monocomponent structures. Fig. 3 shows SEM images of nickel (Fig. 3, *a*) and cobalt (Fig. 3, *b*) nanowires obtained by galvanic and potentiostatic methods, respectively.

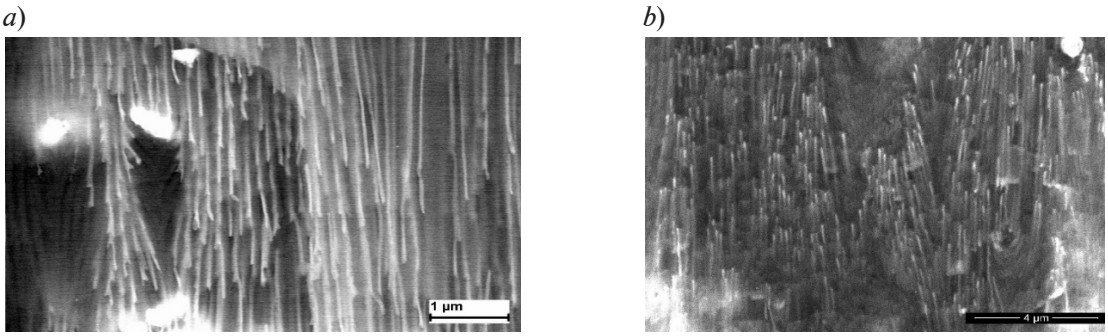

Fig. 3. SEM image of the PAAO template with nanowires of Ni (*a*) and Co (*b*)

The process of electrodeposition of nanowires must be carried out in such a way as to ensure uniform filling of all pores with metal. It is necessary to find the end point of the electrodeposition process, i.e., stop or sharply slow down the process of further metal deposition after the nanowire formed in the pore reaches the surface of the membrane.

Conclusions

Porous templates were obtained by double electrochemical anodizing in 0.5 M oxalic acid at a temperature of 25 °C in a potentiostatic mode at 60 V. A technological scheme for obtaining Ni and Co nanowires with 250 aspect ratio in porous anodic alumina matrices has been developed and were investigated by scanning electron microscopy.

Acknowledgments

The work was carried out within the framework of the State program № FFNN-2022-0018 of the Ministry of Science and Higher Education of Russia on the equipment of the center for the collective use of scientific equipment "Diagnostics of micro- and nanostructures".

REFERENCES

1. **Masuda H., Yamada H., Satoh M.,** Highly-ordered nanochannel-array architecture in anodic alumina, Appl. Phys. Lett. 71 (1997) 2770.

2. **Muratova E.N.,** Artificially and naturally ordered micro- and nanoscale capillary membranes based on anodic aluminum oxide: Ph.D. Thesis, St. Petersburg: ETU "LETI"/. (2014) 232.

3. **Vorobeva A.I., Utkina E.A., Komar O.M.,** Homogeneous deposition of nickel in the pore of ordered thin aluminum oxide, Russian Microelectronics. 42 (2013) 79–88.

4. **Safeer A., Ahmad N., Khan S., et al.,** Magnetization behavior of electrochemically synthesized Co2MnSn full Heusler alloy nanowire arrays, J. Appl. Phys. 125 (2019) 034302.

5. **Varvaro G., Casoli F.,** Ultrahigh–density magnetic recording storage materials and media designs, Stanford: Pan Stanford Publishing (2016) 509.

6. **Jaugstetter M., Blanc N., Kratz M., Tschulik K.,** Electrochemistry under confinement Chem. Soc. Rev. 51 (2022) 2491.

7. **Grushevski E.A., Savinski N.G., Trushin O.S., Shendrikova L.A.,** Magnetic Properties of Ni Nanowires in Porous Anodic Alumina Matrix Russian, Russian Microelectronics. 52 (2023) 67–70.

THE AUTHORS

GRUSHEVSKY Egor A.
yaregor@mail.ru

TRUSHIN Oleg S.
otrushin@gmail.com

SAVINSKY Nikolay G.
savinski1@yandex.ru
ORCID: 0000-0003-1913-0924

Received 30.07.2024. Approved after reviewing 12.08.2024. Accepted 13.08.2024.