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Materials Today: Proceedings 7 (2019) 860–865

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NanoFIS 2017

A simple way to control the filling degree of the SiO_2/Si template pores with nickel

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Abstract

The paper demonstrates a simple way to control the filling degree of the pores of a silicon oxide template on silicon substrate with nickel. SiO_2/Si template was formed using the swift heavy ion tracks technology, which includes irradiation with high energy ions and chemical transformation of the obtained latent tracks into the pores. The preparation of SiO_2(Ni)/Si nanostructures with different filling degree of pores in SiO_2 with nickel was performed using the electrodeposition method by changing the duration of the process. A study and analysis of the morphology of SiO_2(Ni)/Si nanostructures using scanning electron and atomic force microscopy was carried out to determine the nature of pore filling by metal.

Selection and/or peer-review under responsibility of NanoFIS 2017 - Functional Integrated nano Systems.

Keywords: Ion-track technology; SiO_2/Si template; template synthesis; electrodeposition; nickel nanostructures

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Selection and/or peer-review under responsibility of NanoFIS 2017 - Functional Integrated nano Systems.

1. Introduction

The use of template synthesis, including ion-track technology for porous matrix (template) formation [1–6] and electrochemical deposition for pore filling, makes it possible to realize nanostructures for wide range of practical applications [7–13]. For example, SiO_2 templates with separately standing pores with shape of truncated cones [14] can be promising to production of micro- and nanodevices based on multilayered films (ferro-/diamagnetic metal – giant magnetoresistance sensors of magnetic field, metal/dielectric – capacitor and etc.) [15–18], metal microdisks (for destruction of cancer cell membranes due to magnetomechanical action) [19–21], and also during formation of substrates based on copper and silver nanostructures, which enhance the Raman signal during detection of various substances with low concentrations [22,23]. The presence of open pores makes it possible, after their filling, to obtain nanoscale metal-semiconductor and semiconductor-semiconductor contacts, it makes possible to create diodes and transistors [16,24]. The ability to control pore filling degree allows realizing nanostructures with predetermined morphology. The resulting systems are promising as substrates for creation of extended two-dimensional structures consisting of correlated micro- and nanoobjects. The structures, which are realized on basis of matrix, during filling with materials with different conductive characteristics, are interesting due to presence of such properties as giant tunneling magnetoresistance, anomalous Hall effect, anomalously high Kerr effect, high coefficient of microwave radiation absorption, and a number of other unconventional physical phenomena [15,22,25–27]. Considering that in literature insufficient attention is given to possibility to control filling degree of SiO_2/Si templates pores with metal, in this work simple way to control pore filling degree is demonstrated on example of nickel by varying of electrochemical deposition time, and thorough study of formed nanosystems is carried out by using of scanning electron and atomic force microscopy.

2. Methods

To create SiO_2(Ni)/Si structures it were used porous templates of silicon oxide on silicon (electronic type of conductivity, doping with phosphorus with donor impurity concentration $N_D = 9 \times 10^{14}$ cm^{-3}, resistance 4.5 $\Omega*cm^{-1}$) obtained by using of swift heavy ion tracks technology (irradiation with $^{197}Au^{26+}$ ions with energies of 350 MeV and fluence of 5×10^8 cm^{-2}). Template pores have shape of truncated cones with base diameters of ~ 300 nm on SiO_2 surface and ~ 200 nm on the boundary with Si, height corresponding to dielectric layer thickness (~ 350 nm), and with average distances between them to ~500 nm.

The formation of SiO_2(Ni)/Si nanostructures with various degrees of pore filling with nickel was made from boric acid electrolyte (0.5 mol/l H_3BO_3) and nickel sulfate containing solution (0.5 mol/l $NiSO_4$), which was used as cations source. The selected concentration of $NiSO_4$ promoted maximum process speed [28]. The electrodeposition potential value was minus 1 V, it ensured the current efficiency of metal of about 93%. The control of degree of pores filling with metal was carried out by variation of process time. The error in potentials measuring during deposition was not more than 1 mV, and the current was not more than 25 nA.

The structural and morphological features of SiO_2(Ni)/Si samples were measured by scanning electron microscopy (SEM) with using microscope LEO-1455VP manufactured by Carl Zeiss (Germany) under normal electron beam orientation to surface. A study of statistics of metal clusters deepenings distribution over SiO_2 surface and the study of its morphology was carried out by atomic force microscopy (AFM). For this, a microscope "NT-206" manufactured by company "Microtestmachinery" (Belarus) with silicon nitride (Si_3N_4) cantilever with rounding radius of 10 nm was used, so that a resolution of about 10 nm was achieved in the sample plane and of about 1 nm perpendicular to it. Determination of degree of metallic phase localization in dielectric pores and its outgrowth to SiO_2 surface was carried out by X-ray spectral microanalysis with using of energy dispersive SiLi detector by Röntec company.

3. Results and discussions

The morphological features were studied on SiO_2/Si samples with pores filled with nickel by 50%, 75%, 100%, 200%. The control of pores filling degree with nickel was made by varying of electrochemical deposition time.

Study of surface of SiO_2/Si structure with pores partially filled with nickel, by approximately 50% (Fig. 1) and 75% (Fig. 2), prove corresponding degree of pore filling with metal. The SEM images obtained with large pore magnification (Fig. 1a) indicates cluster structure of nickel deposit. The histogram of metal deposition depths distribution (Fig. 1c), obtained on the basis of surface scanning data by AFM method (Fig. 1b), shows that the most probable metal deposition depth is ~ 150 nm, it corresponds to half pore filling. The small peak width on histogram indicates that most pores are filled to the same extent.

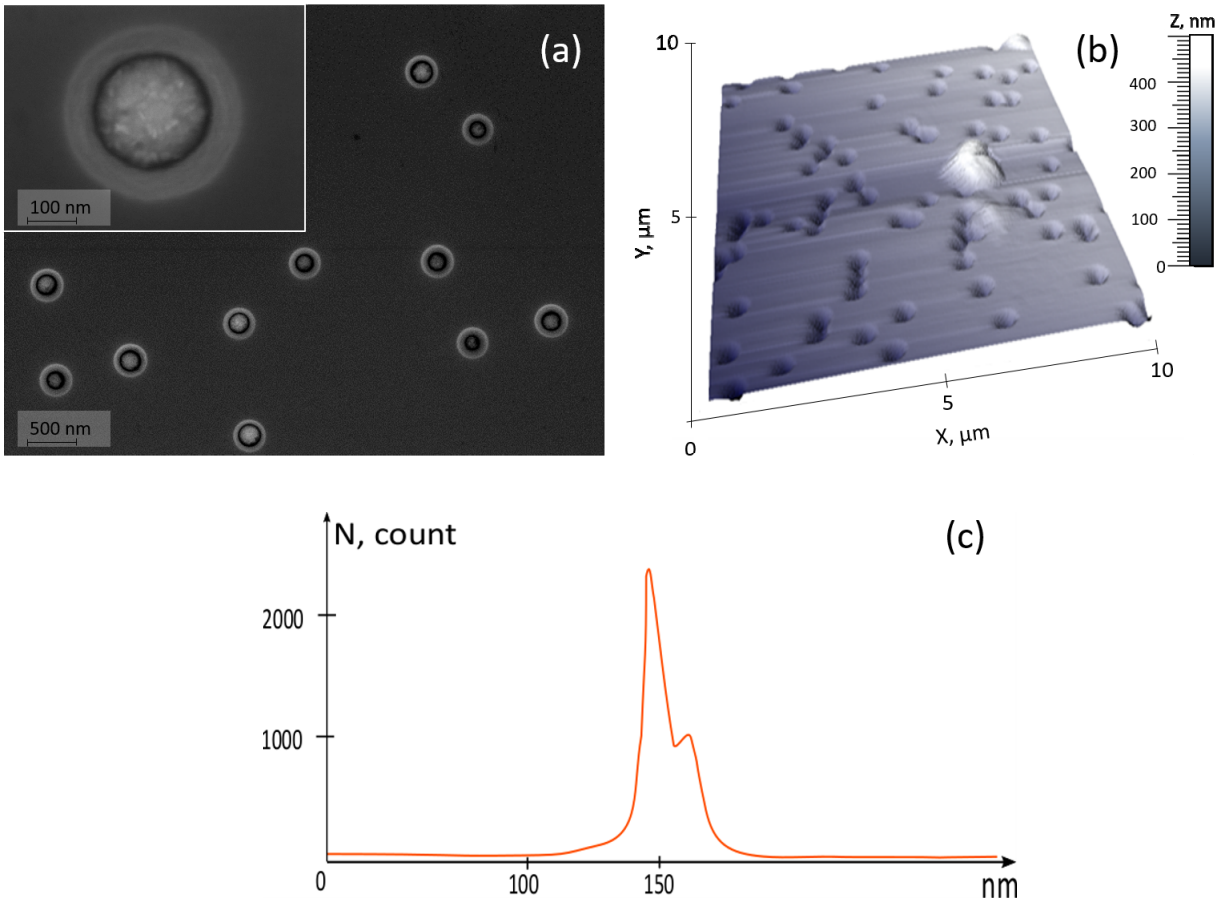

Fig. 1. SiO_2(Ni)/Si structure with partially (50%) filled pores: (a) SEM surface image; (b) AFM image of surface morphology; (c) histogram of distribution of Ni deposition depths relative to SiO_2 surface according to AFM data.

The SEM study of SiO_2(Ni)/Si structure surface, shown in Fig. 2a, indicates higher degree of pores filling with metal than in Fig. 1. The AFM scanning of surface (Fig. 2b) and corresponding histogram of deposited metal depth distribution (Fig. 2c) indicates that most probable depth of metal deposition is ~ 70 nm, it corresponds to filling pore by about 3/4. The peak width indicates that most pores are filled to the same extent. Fig. 2d gives an isometric image of structure surface, which gives an absolute understanding of surface nature and of pores filling degree. In addition, this image confirms that maximum Ni deposition depth relative to SiO2 surface is ~ 70 nm. Scanning the surface of sample with half-filled tracks along selected line (Fig. 2e) indicates that surface of metal in pores is relatively flat with fairly homogeneous and dense pore filling with metal.

The study of SiO_2(Ni)/Si nanostructures with pores filled with metal by 100% (Fig. 3) showed that nickel deposit fully evenly fills the pores, without forming any outgroths or deepenings on surface. The AFM-scanning of surface showed that change in surface relief does not exceed 40 nm. Carrying out qualitative analysis of elemental composition of samples under study by mapping of surface and samples chips during X-ray spectral microanalysis

made it possible to establish that nickel is localized exclusively in the pores of SiO_2/Si matrices, without nucleation on SiO_2 surface.

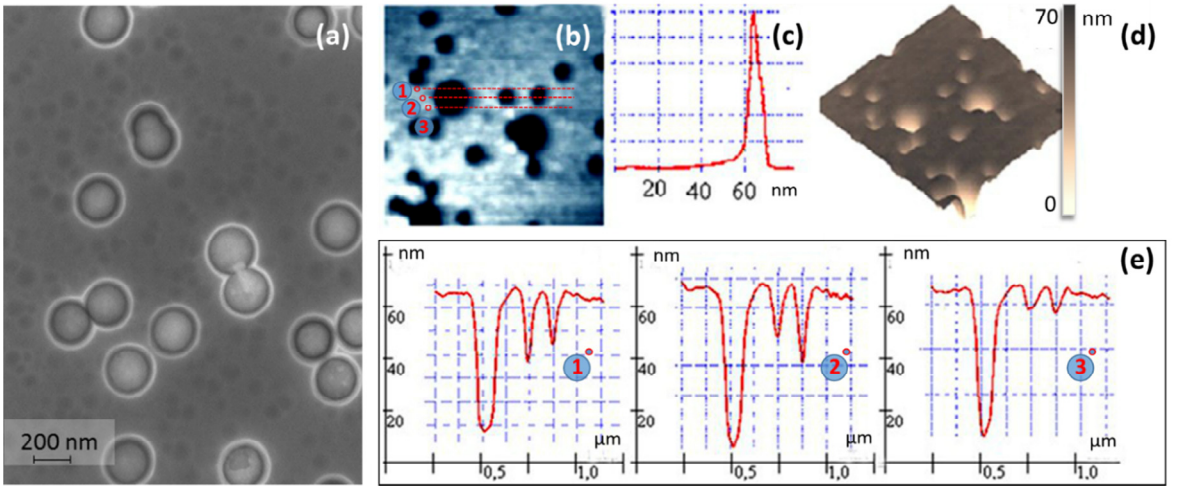

Fig. 2. (a) SEM image of SiO_2(Ni)/Si surface with partially (75%) filled tracks; scanning of structure surface with partially filled tracks measuring 1.5*1.5 µm: (b) surface topology; (c) histogram of Ni deposition depths distribution relative to SiO_2 surface; (d) isometric AFM image of surface profile; (e) scanning surface along line: 1, 2, 3 – relief profiles corresponding to secants.

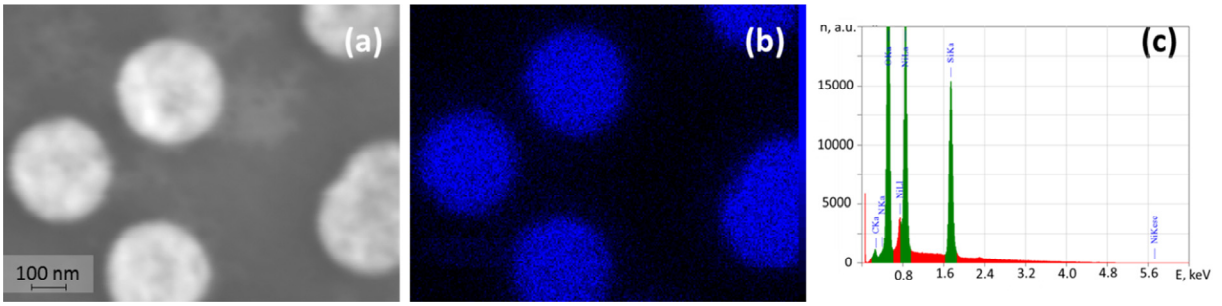

Fig. 3. (a) SEM image and (b) mapping with X-ray spectral microanalysis of surface of SiO_2(Ni)/Si samples with full pore filling; (c) EDS spectrum of studied samples.

During pores filling with nickel by 200%, electrochemical deposition, as well as in previous cases, occurs evenly with filling of all SiO_2/Si matrix pores (Fig. 4a). The data from studies of SiO_2(Ni) surface profiles obtained by AFM method show that when silicon oxide reaches Ni surface, local outgrowths with height up to 300 nm appear (Fig. 4b).

The results of SEM and AFM studies of SiO_2(Ni)/Si structure with different pore densities surface are systematized in Table 1. Thus, studies of morphology of SiO_2(Ni)/Si structures surface by SEM method showed that Ni electrochemical deposition leads to selective nanopores filling, i.e. metal does not form continuous film on SiO_2 surface, but nickel clusters growth occurs directly in pores. The results of AFM studies indicate that, depending on nickel, electrochemical deposition mode, channels of ion tracks are filled, either with formation of hemispherical outgrowths over SiO_2 surface, or at certain depth without reaching of SiO_2 surface. In addition, analysis of SEM and AFM results makes it possible to estimate average distance between pores filled with metal and spreading density of nickel nanostructures over surface of Si/SiO_2 matrix, which in general is 5-20% different from predetermined irradiation fluence.

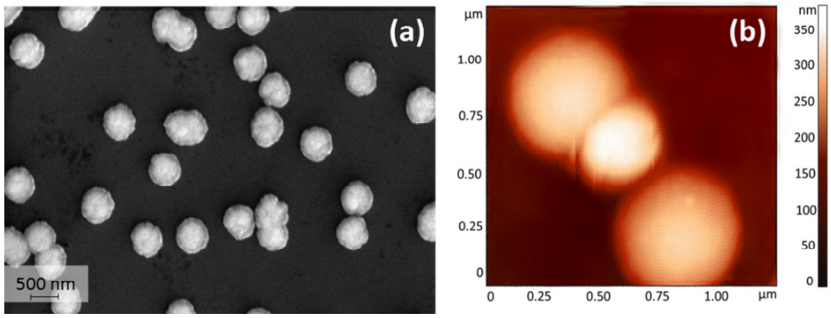

Fig. 4. SEM image of SiO_2(Ni)/Si with fully filled pores: (a) SEM image of surface; (b) image of surface profile scanning by atomic force microscopy.

Table 1. Results of Si/SiO_2(Ni) structures studies by SEM and AFM methods.

№	Pore filling degree, %	Density, cm^{-2} (by AFM and SEM data)	Height of Ni deepenings, nm	Diameter of Ni deepenings, nm
1	50	$4{,}5 \times 10^8$	– 130-170	220-270
2	75	$4{,}7 \times 10^8$	– 60-80	250-290
3	100	$4{,}7 \times 10^8$	0-20	270-320
4	200	$4{,}8 \times 10^8$	230-320	450-620

4.Conclusions

By using of electrochemical deposition SiO_2(Ni)/Si nanostructures with different degrees of silica pores filling with nickel (50%, 75%, 100%, 200%) are formed. Studies of morphology of nickel deposit surface by atomic force and scanning electron microscopy confirmed high selectivity of electrochemical metal deposition into the pores, without formation of metal nuclei on SiO_2 surface. It is shown that selection of process time makes it possible to fill pores with nickel both at certain depth, not reaching SiO_2 surface, and with formation of hemispherical outgrowths above SiO_2 surface, i.e. due to simple variation of deposition time, it is possible to set required filling degree. The simplicity of electrochemical synthesis, jointly with flexibility of ion-track technology for formation of porous patterns, makes it possible to create wide range of nanostructures with a predetermined density and degree of pores filling with metal for a large number of practical applications.

Acknowledgements

The authors acknowledge the support of the work in frames of H2020 - MSCA - RISE2017 - 778308 - SPINMULTIFILM Project and the Scientific-technical program ‘Technology-SG’ [project number 3.1.5.1].

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