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Influence of Cu Layer Thickness on Morphology and Magnetic Properties of Co/Cu Nanowires

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We studied changes of morphology and magnetic properties of Co/Cu multilayered nanowires, electrodeposited in polycarbonate membranes, as a function of Cu layer thickness. The morphology and structure of wire assemblies with an average diameter of 200 nm and length of 10 μm , investigated by X-ray diffraction and scanning electron microscopy techniques, revealed polycrystalline structure of Cu and Co layers with smooth lateral surface of nanowires. Overdeposited nanowires created caps which showed flower-like dendrites with shape changing as a function of Cu thickness and electrodeposition parameters. Chemical composition of Co and Cu nanowires analysed by energy dispersive spectroscopy and proton induced X-ray emission showed Cu nanowires free from Co atoms while in Co nanowires, Cu contamination with concentration below 10% was observed. The oxidation traces observed in single-component Cu nanowires did not appear in multilayered nanowires. Magnetic measurements indicated easy axis of magnetization in membrane plane for nanowires with Cu thickness smaller than 20 nm, whereas for larger Cu thicknesses isotropic orientation of magnetization was observed. The presence of Cu atoms in single-component Co nanowires resulted in the appearance of magnetic anisotropy with easy axis along nanowire axis and the increase of coercivity value.

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1. Introduction

The studies of low-dimensional layered magnetic structures are one of the hottest topics in solid-state physics, due to fundamental interests and numerous developments and technological applications. A special attention in recent investigations is focused on one-dimensional magnetic nanostructures such as nanowires. The control of geometrical parameters of nanowires and their structure determined by process parameters, allows one to tune the magnetic properties [1, 2], offering a variety of applications from high density magnetic recording media to high quality sensors and microwave devices [3]. The magnetic multilayered nanowires composed of alternatively aligned magnetic and non-magnetic layers represent an important family of materials attractive for GMR sensor applications [4, 5].

Metallic nanowires can be produced using template-assisted electrodeposition into porous alumina [6, 7] or ion-track etched polycarbonate membranes [4, 8, 9]. This is simple and cost-effective method which enables the production of nanowires in high volume and on large area. Such nanowires exhibit a high aspect ratio, which make them good candidate for magnetoresistance measurements in current perpendicular to plane geometry [10, 11].

In this paper, we studied morphology and magnetic

properties of multilayered Co/Cu nanowires with different Cu spacer thickness.

2. Materials and methods

The multilayered nanowires composed of alternating Co and Cu layers were electrodeposited in porous polycarbonate membranes (Sterlitech Corporation) with an average pore diameter of 200 nm and length of 10 μm . Prior to nanowires growth, a gold layer was sputtered onto one side of template to serve as working electrode in three-electrode electrochemical cell. A platinum sheet and Ag/AgCl double junction electrode were used as the counter and reference electrodes, respectively. The deposition solution containing 120 g/l $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, 1.76 g/l $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 45 g/l H_3BO_3 was kept at room temperature during electrodeposition process. The Cu and Co layer were subsequently deposited by applying alternating cathodic potential of -0.54 V or -1.0 V vs. Ag/AgCl. Moreover, as reference samples, we electrodeposited Co and Cu nanowires separately, from electrolytes containing only Co^{2+} or Cu^{2+} ions, respectively, or both ions to obtain Co or Cu nanowires with concentration identical as a layer composition in multilayered nanowires. The electrodeposition process was controlled using potentiostat (AUTOLAB PGSTAT302N). Layer thicknesses were determined by quartz balance with nominal crystal frequency of 6 MHz and *in situ* charge measurements. The structural properties of nanowires kept in the templates were analysed by X-ray diffraction (XRD) performed using Philips X'Pert MRD Pro diffractometer with Cu K_α radiation operated at 40 kV and

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30 mA in $\theta-2\theta$ geometry. The magnetic properties of as-prepared nanowires were measured using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS) by applying an external field up to 7 T in plane and out of plane of the membrane. The diamagnetic signal, related to the sample holder and the polycarbonate membrane, was subtracted from the hysteresis loops. The morphology and chemical composition of Co nanowires, were investigated by scanning electron microscope (SEM) (FEI Nova NanoSEM 450) equipped with energy dispersive spectrometer (EDS) after dissolving polycarbonate membranes using dichloromethane. The chemical analysis was complemented by proton induced X-ray emission (PIXE) measurements. In PIXE method 2 MeV proton microbeam of linear, electrostatic Van de Graaff accelerator (IFJ PAN, Cracow) was used. The beam diameter was equal to 20 μm . Spectra were collected by semiconductor Si(Li) detector with 190 eV of FWHM for Mn K_α line and analysed using GUPIX program [12].

3. Results and discussion

Figure 1 shows electrical charge measured as a function of time, during subsequent Co and Cu layer deposition into polycarbonate membrane for Cu spacer thickness of 5 nm. The Cu deposition starts at positive charge because of Co dissolution due to significant difference in discharge potentials of Cu^{2+} and Co^{2+} [13]. Optimal values of applied potential were adjusted during cyclic voltammetry measurements. It was observed using PIXE and EDS that Cu nanowires deposited at potential $U = -0.54$ V from electrolyte containing Co and Cu ions, are free from Co. Relatively high value of Cu potential reduces anodic dissolution of Co [13] and results in less rough interfaces and small intermixing between Co and Cu layers [14]. In the case of Co nanowires, low Cu concentration in electrolyte and fast Co deposition resulted in small amount of Cu in Co with maximum concentration of Cu below 10%, which is smaller value than reported in other works [15]. This value can be reduced even to 1%–2% for very fast (over -1.2 V) Co deposition, impossible to apply in multilayered nanowire because of short deposition time.

Chemical composition of Co/Cu nanowires analyzed by PIXE and EDS studies did not show good correlation with assumed layer thickness because of multilayered structure of nanowires embedded in polycarbonate membrane and very rough surface covered by nanowire caps, which both disturb the detection. However, studies performed on nanowires embedded in templates demonstrated larger fraction of copper as compared to measurements performed on nanowire matrix after membrane dissolving. This effect was observed, because during dissolving process, nanowires caps were removed and measured signal came only from nanowires. It follows that Cu concentration in nanowires was smaller than in caps. It can be explain by low Cu concentration in electrolyte

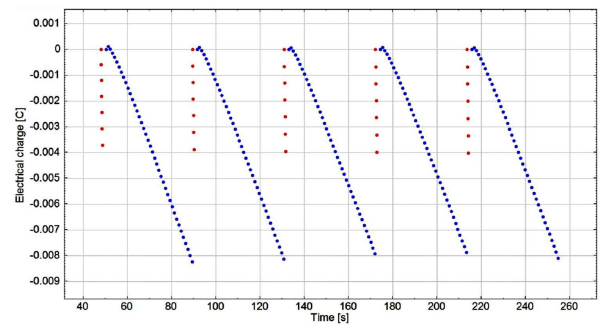


Fig. 1. Electrical charge measured versus time, during subsequent Co (red points) and Cu (blue points) layer deposition with spacer thickness of 5 nm.

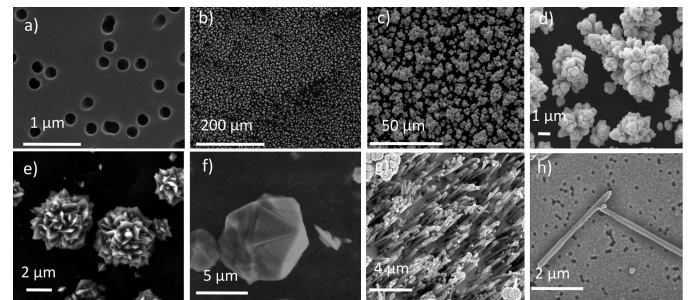


Fig. 2. SEM pictures of: polycarbonate membrane (a), Co/Cu filled templates with flower-like overdeposition (b, c, d, e), Co overdeposition (f), Co/Cu nanowires assembly (g), and single Co/Cu nanowires (h).

and, related to this, diffusion control of deposition process which is responsible for difficulties in Cu ion movement along nanochannels.

SEM pictures of polycarbonate membranes show (Fig. 2a) irregularly arranged nanopores with round shape and diameter of 200 nm. The multilayer deposition process was carried out up to the moment when nanowire caps created contact layer on the top of membrane. This overdeposited top Co/Cu layer, shown in Fig. 2b,c, is not continuous and has flower-like form. The shape and dendrite form of the caps depend on Cu concentration and on electrodeposition parameters, such as electrolyte temperature and cathodic current, which both determine the deposition rate. High deposition rate resulted in more developed dendritic structure of nanowire caps (Fig. 2d), while decrease of Cu concentration caused the spike-like form with sharp edges (Fig. 2e). The overdeposited Co nanowires show facets with threefold symmetry which can indicate (111) orientation of fcc Co surface (Fig. 2f).

The morphology and shape of Co/Cu nanowires were observed after dissolution of polycarbonate membrane. Array of nanowires attached to gold contact layer, seen in Fig. 2g, indicates a high degree of nanopore filling. SEM images of single nanowires (Fig. 2h) revealed their continuous structure with smooth lateral surfaces and constant diameter.

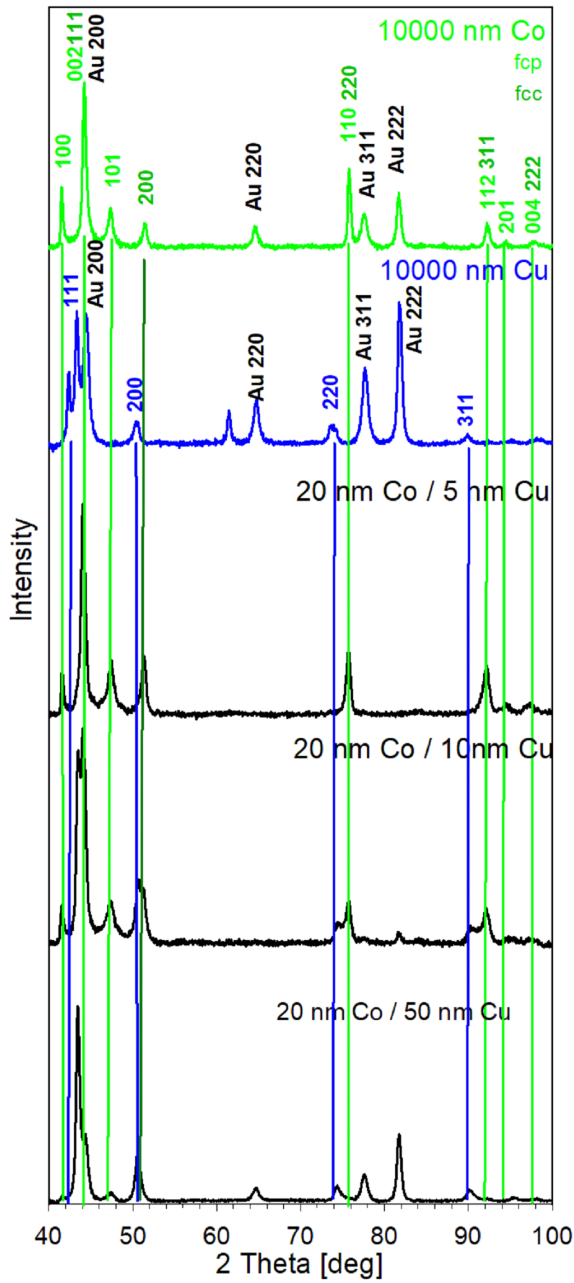


Fig. 3. XRD spectra measured for Co and Cu nanowires as well as for Co/Cu multilayered nanowires.

The structure of nanowires was analyzed using X-ray diffraction technique. In Fig. 3 X-ray diffraction pattern of Co, Cu, and Co/Cu multilayered nanowires with different Cu layer thickness are shown. Beside peaks attributed to Co and Cu, peaks related to Au contact layer are also seen. Diffractogram of Co nanowires shows peaks indicating both fcc and hcp Co structure, while for Cu nanowires, aside from peaks characteristic for fcc Cu, we observe also peaks at $2\theta = 42^\circ$ and 61° being the evidence of Cu oxide (Cu_2O) appearance. The Co/Cu nanowire diffraction pattern for the smallest Cu spacer thickness

(5 nm) exhibits only peaks corresponding to Co layers without trace of Cu peaks. However, EDS measurements confirm presence of Cu with amount much larger than Cu concentration in Co layers. With increase of Cu layer thickness the diffraction peaks coming from Cu appear and are more intensive than Co peaks. Copper oxides are not observed in multilayered nanowires due to protection role of last Co layer (20 nm). Thus, multilayered Co/Cu nanowires with pore diameter of 200 nm show polycrystalline structure of Co and Cu without oxidation traces.

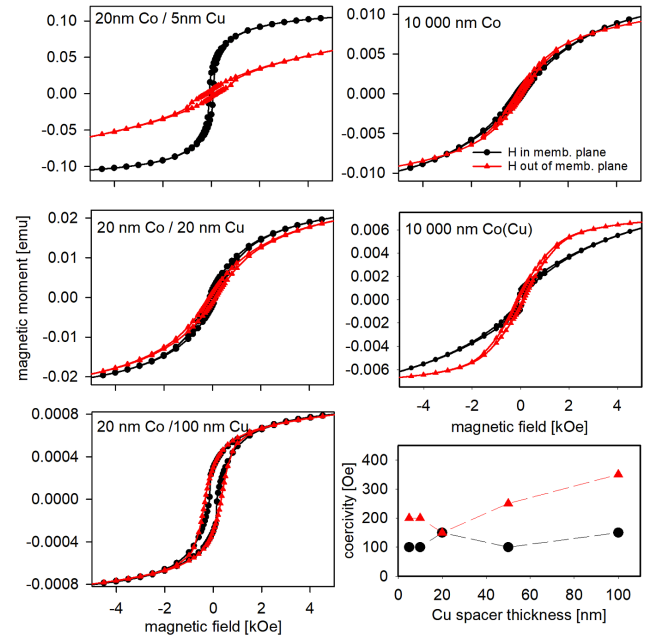


Fig. 4. Magnetic hysteresis loops measured for Co/Cu multilayered nanowires as a function of Cu layer thickness with Cu thicknesses changing from 5 nm to 100 nm, and for Co and Co contaminated by Cu ions nanowires. The coercivity values as a function Cu layer are also shown.

Magnetic hysteresis loops with magnetic field applied in plane and perpendicularly to the membrane plane, measured for Co/Cu multilayered nanowires and single-component and contaminated by Cu atoms — Co nanowires — are presented in Fig. 4. Analysis of multilayered nanowires with Cu spacer thickness smaller than thickness of Co layer indicates in plane easy axis of magnetic anisotropy with coercivity equal to approximately 100 Oe (Fig. 4). These samples reached saturation of magnetization at fields about 10 kOe and 25 kOe for in and out of plane geometry, respectively. The magnetization for the sample with the same thicknesses of Co and Cu layers has isotropic orientation with coercive field of 150 Oe. For larger Cu layer thicknesses, the isotropic distribution of magnetization was preserved, accompanied by an increase of coercive field. Single-component Co nanowires were also characterized by isotropic magnetic arrangement without differences in coercivity measured

in both directions. Surprisingly, magnetic anisotropy with easy axis along nanowires axis was observed for Co nanowires contaminated by Cu atoms. Additionally, coercivity measured for out of membrane plane geometry, increased as compared to pure Co nanowires to 150 Oe. Such influence of Cu atoms was reported in [3] and was also seen in, synthesized by us, Fe nanowires doped by Cu atoms (paper in preparation). All analyzed nanowires possessed caps, which strongly influenced magnetic behavior, favoring in plane orientation of magnetic easy axis, when continuous layer is reached [1]. In our case, caps separated from one another should rather give contribution to isotropic magnetic arrangement. The presence of cap layer can be also responsible for smaller in plane coercivity values of magnetically isotropic nanowires. Small anisotropy with in plane easy axis was also observed by authors of [10] in multilayered nanowires with Co layer thickness in the range of 10–55 nm separated by 250–350 nm thick Cu layers. With increasing Cu spacer thickness dipolar interaction between subsequent Co layers is minimized and Co films can be described as nearly non interacting nanodisks, which should be magnetically ordered in layer (membrane) plane because of shape anisotropy. Such arrangement of magnetic easy axis is desirable orientation for magnetoresistance measurement [11, 14]. We observed it only for thin Cu layers, where the thicknesses are still too thick to give rise to antiferromagnetic coupling [16, 17]. Isotropic magnetic arrangement observed for multilayered nanowires with large Cu thickness is likely caused by discontinuity of Co layer [14] due to Cu penetration.

4. Conclusions

We deposited template-assisted single-component Co and Cu nanowires, Co nanowires with small amount of Cu atoms and multilayered Co/Cu nanowires with diameter of 200 nm. The Cu layers were free from Co atoms, while Co layers contained small amount (less than 10%) of Cu atoms. The flower-like cap layer changed shape depending on Cu concentration and electrodeposition parameters. Multilayered nanowires are continuous with smooth lateral surface independent of Cu layer thickness. The Co/Cu nanowires revealed polycrystalline structure without oxidation traces observed for single-component Cu nanowires. Magnetic measurements indicated in membrane plane anisotropy for multilayered nanowires with Cu thickness smaller than 20 nm. Introduction of Cu impurities into single-component Co nanowires resulted in appearance of magnetic anisotropy with easy axis along nanowires axis and increased coercivity value.

Acknowledgments

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