Electrodeposited hard-magnetic $Fe_{50}Pd_{50}$ nanowires from an ammonium-citrate-based bath

Darja Pečko [a,*], Kristina Žužek Rožman [a], Nina Kostevšek [a], M. Shahid Arshad [a], Boštjan Markoli [b], Zoran Samardžija [a], Spomenka Kobe [a]

[a] Department for Nanostructured Materials, Jožef Stefan Institute, Ljubljana, Slovenia
[b] Department for Materials and Metallurgy, Faculty of Natural Science and Engineering, University of Ljubljana, Slovenia

ABSTRACT

Fe–Pd nanowires were synthesised in anodic alumina templates by applying both potentiostatic and pulsed electrodeposition regimes. When using potentiostatic deposition, only fragmented nanowires were obtained; however, the use of pulse deposition was shown to be effective for producing solid nanowires. In order to achieve this, different *on*-times for the deposition and *off*-times between the pulses in an electrolyte with a constant concentration of Fe(III) and Pd(II) ions at pH 9 were employed. Homogeneous nanowires with the composition $Fe_{55\pm5}Pd_{45\pm5}$, lengths of 2.5 μm and diameters of 200 nm were synthesised under the following pulsed conditions $E_{on} = -1.4$ V, $t_{on} = 2$ s and $E_{off} = -0.1$ V, $t_{off} = 10$ s for 5000 cycles. The as-deposited nanowires had a *fcc* crystal structure and were magnetically soft ($H_C \approx 5$ kA/m) with the easy axis of magnetization perpendicular to the long axes of the nanowires, mainly due to the dipolar coupling within the template. In order to promote the ordering into the $L1_0$ phase, annealing in the temperature range 400–700 °C for 1–9 h in Ar + 7% H_2 was performed. The highest coercivity of 122 kA/m was achieved by annealing at 600 °C for 5 h.

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1. Introduction

One-dimensional nanostructures, such as nanowires, nanorods and nanotubes, have been the topic of many investigations due to their small size and unique and tuneable properties, all of which make them appropriate for a very broad range of applications, such as electronic (in nano/micro-electro-mechanical systems), thermoelectric devices and for sensing in biology and chemistry [1–3]. There have been many methods used for the synthesis of one-dimensional nanostructures, such as: chemical vapour deposition [4,5], vapour–liquid–solid (VLS) growth [6], lithographically patterned nanowire electrodeposition [7], reductive sulphidization [8], hydrothermal reduction [9], sol–gel [10] and template-assisted electrodeposition. Template-assisted electrodeposition is, in comparison to the other methods, highly selective, since it relies on electron transfer, which is the fastest along the highest conductivity path. Therefore, it offers the possibility to deposit different nanostructures with a high technological potential. When using

nanoporous membranes it is possible to deposit and tailor the nanostructure's properties with high aspect ratios that are densely and continuously packed and possess a high crystallinity [11]. The most commonly used membranes are polycarbonate (PC) and anodized alumina oxides (AAO). The AAO-based template has been considered as an ideal template as it possesses many desirable characteristics, including tuneable pore dimensions, good mechanical strength, thermal stability and ordered nanopores with a high density (10^9–10^{11} cm^2) [11,12]. Successful depositions of metal nanowires, such as Ni, Pd, Cu, [2,13–15] and different alloys, Co–Zn, Co–Cu, Cd–Se, Co–Pt, Fe–Pt [16–19] and Fe–Pd [3,20–23], have been performed in AAO templates. Nanostructures with an ordered $L1_0$ phase have attracted a lot of attention in the past few years due to their large magnetocrystalline anisotropy along the *c*-axis of their tetragonal crystal structure, which makes them appropriate for high-density magnetic recording media [24–26]. So far, many studies and investigations have been made on the Co–Pt and Fe–Pt systems because they have higher magnetocrystalline anisotropies (6.6 and 4.9 MJ/m^3) [25]. In comparison to Co–Pt and Fe–Pt, Fe–Pd (1.8 MJ/m^3) [23] possesses a lower a magnetocrystalline anisotropy; however, the Fe–Pd alloy exhibits a lower disorder–order transition temperature, and the low cost of Pd in comparison with Pt makes this material interesting for

* Corresponding author. Address: Department for Nanostructured Materials, Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia. Tel.: +386 1 4773 945; fax: +386 1 4773 221.

E-mail address: darja.pecko@ijs.si (D. Pečko).

potential applications in perpendicular magnetic recording media [25,27]. In this paper we have synthesised near-equiatomic $Fe_{55\pm5}Pd_{45\pm5}$ nanowires using the template-assisted electrodeposition method. The main challenge in the electrodeposition of alloys is to co-deposit two metals with a large difference in their standard reduction potential, as in the case of Fe^{2+} and Pd^{2+} ($\Delta E \approx 1.4$ V). This can be achieved by using a complexing agent, which forms a complex with the metal and shifts the reduction potentials of the metals closer together, thus making the co-deposition possible. In our case, the main problem lies in finding an appropriate complexing agent that would shift the reduction potential of palladium ($E^0_{Pd^{2+}/Pd} = 0.95$ V) towards the less-noble iron ($E^0_{Fe^{2+}/Fe} = -0.447$ V), while keeping the electrolyte chemically stable and preventing the precipitation of heavy, soluble hydroxides of both metals. Until now there have been successful depositions performed from baths based on sulphosalicylic acid [20,25,28], ammonium tartrate [29] and ammonium citrate [24,30,31]. Here, ammonium citrate was used to complex the iron ($\log K(Fe(II)Cit) = 15.5$ and $\log K(Fe(III)\text{-}Cit) = 25.0$ [32]) and the ammonia to complex the palladium ($\log \beta_4[Pd(NH_3)_4]^{2+} = 29.6$) [33]. Furthermore, for the deposition of nanowires an Fe(III)-based electrolyte was chosen, because of the higher stability of Fe(III)–citrate complexes in comparison with Fe(II)–citrates [31] and to avoid the partial oxidation of Fe(II)–Fe(III) by dissolved oxygen at the anode during deposition that could lead to an unknown concentration of various species in the solution [34]. Equiatomic Fe–Pd nanotubes have been successfully deposited and characterized in our previous study [35]; however, the nanotube ordering was lost upon annealing due to the thermally unstable PC template, which made any discussion about the magnetic properties measured parallel and perpendicular to the long tube/wire axis impossible. In this study we synthesised near-equiatomic 200-nm-thick $Fe_{55\pm5}Pd_{45\pm5}$ nanowires using the template-assisted electrodeposition method in thermally stable AAO templates. The present study analyses and proposes the requirements (such as the electrolyte concentration, the deposition potential and, subsequently, the pulse-plating conditions) for the successful deposition of morphologically consistent and compositionally homogenous nanowires. Furthermore, equiatomic $Fe_{55\pm5}Pd_{45\pm5}$ nanowires with a cubic *fcc* crystal structure were transformed into the tetragonal *fct* or L1$_0$ ordered structure after annealing at 600 °C, with a coercivity of $H_C = 122$ kA/m. These good magnetic properties, low ordering temperature and the short annealing times make $Fe_{55\pm5}Pd_{45\pm5}$ nanowires interesting for many applications in nano(micro)-electro-mechanical systems or as a potential material for perpendicular recording.

2. Experimental

The depositions of the Fe–Pd nanowires and the cyclic voltammetry measurements were carried out using a Gamry, Reference 600 potentiostat/galvanostat equipped with PHE200 software. A stable electrolyte was prepared from the 300-mM FeCl$_3$ (Sigma Aldrich, 99.9%), 3-mM PdCl$_2$ (Sigma Aldrich, 99%), 0.4-M (NH$_4$)$_2$C$_6$H$_6$O$_7$ (Sigma Aldrich, 99%) and 0.5-M NH$_3$(aq) (Merck, 25%) for the pH adjustment to 9. The excess of ammonia and ammonium citrate ensured that all the Pd(II) and Fe(III) in the electrolyte were present in the complex form: Pd was converted in the [Pd(NH$_3$)$_4$]$^{2+}$ complex [36] and Fe in the Fe(III)–citrate complex. The abbreviation Fe(III)Cit will be used throughout the paper for the Fe(III)–citrate complexes. The Fe–Pd nanowires were electrochemically deposited in the commercially available AAO membranes (Whatman, Anapore, pore diameter 200 nm). The conductivity of the membranes was achieved by first sputtering the back side of the membrane with 20 nm of Pt, which was followed by electrochemically deposited Au at −0.7 V for 20 min (the back side of the pores was completely covered, to promote deposition from the top only). The AAO template was then glued with Cu-tape on the Al-foil sheet and used as a cathode. A circular platinum mesh was used as a counter electrode. The nanowires were deposited in the potential regime from −1.4 V to −1.6 V, measured versus a Ag/AgCl/3 M KCl//(SSCE) at room temperature in the potentiostatic and pulse-plating modes, where the pulse-plating conditions t_{on} (2–120 s) and t_{off} (10–240 s) were varied. The cyclic voltammetry (CV) measurements were recorded on the flat substrate (SiO$_2$/Cr/Au) and on the AAO template (with the same conductive layer (Pt/Au) as used for the deposition of the nanowires) with a scanning rate of 50 mV/s. The as-deposited nanowires were subsequently annealed in a reducing atmosphere (Ar + 7% H$_2$) from 400 to 700 °C for 1–9 h. The Fe–Pd nanowires were characterized using a field-emission-gun scanning electron microscope (FEG-SEM) JEOL JSM-7600F equipped with an Oxford Instruments INCA system for energy-dispersive X-ray spectroscopy (EDXS) with a 20-mm^2 silicon drift detector (SDD). The chemical composition of the Fe–Pd nanowires was determined by quantitative EDXS analyses, which were carried out with an SEM accelerating voltage of 6.5 kV and with a 100-s spectrum-acquisition time. The SDD efficiency/response was calibrated for the 6.5-kV experimental set-up using pure silicon as a standard. The EDS spectra were quantified using the XPP matrix-correction procedure and a stored-standards database for the Fe Lα and Pd Lα spectral lines. A SEM accelerating voltage of 6.5 kV was sufficient to detect Fe and Pd and also to perform a quantitative analysis of the Fe–Pd alloy using the Fe Lα spectral line with an energy of 0.704 keV and the Pd Lα spectral line with an energy of 2.838 keV (with LIII edge at 3.187 keV). Consequently the overvoltage ratio was kept at ⩾2 for both elements (Fe, Pd), which is appropriate for the EDXS analysis. The crystal structures of the as-deposited and annealed Fe–Pd nanowires inside the alumina templates were investigated by XRD using a diffractometer (D4 Endeavor, Bruker AXS, Karlsruhe, Germany) with Bragg–Brentano geometry, a Cu Kα radiation source and a Sol-X energy-dispersive detector. The magnetic measurements were performed using a vibrating-sample magnetometer (VSM LakeShore 7003) with magnetic fields in the range ±1200 kA/m.

3. Results and discussion

3.1. Characterization of the electrochemical process

Prior to the electrodeposition, cyclic voltammetry measurements of single-metal-ion electrolytes containing 300-mM Fe(III)-Cit, 3 mM [Pd(NH$_4$)$_2$]$^{2+}$ and an electrolyte containing both metals were performed in order to find the optimum potentials for a successful deposition of the alloy. Before the CV measurements the solution was de-aerated by bubbling with N$_2$ gas for 15 min in order to avoid any oxygen-reduction peaks.

The blue curve in Fig. 1a represents the CV of the 3-mM [Pd(NH$_3$)$_4$]$^{2+}$ solution at pH 9 recorded on the AAO template, where an increase of the cathodic current C_{1Pd} at potential −0.3 V is observed, and is attributed to the reduction of the [Pd(NH$_3$)$_4$]$^{2+}$ + 2e$^-$ → Pd^0. The reduction of Pd is, up to a potential of −0.4 V, activation controlled and is followed by a diffusion-controlled deposition for potentials more negative than −0.4 V. An exponential increase in the cathodic current C_{1H} at potentials more negative than −1.0 V is observed and is attributed to the decomposition of H$_2$O, according to the reaction 2H$_2$O + 2e$^-$ → H$_2$ + 2OH$^-$ and consequently to hydrogen evolution reaction (HER). The red curve in Fig. 1a represents the solution containing 300-mM Fe(III)Cit at pH 9 recorded on the AAO template, where one cathodic peak C_{1Fe} ($E = -0.7$ V, $j_C = -0.9$ mA) is observed and is attributed to the reduction of Fe(III)Cit to Fe(II)Cit$^-$, which is continued with the reduction of Fe(II)Cit to elemental Fe together with HER, at potentials more negative then −1.0 V, C_{2Fe+H}. The red curve in Fig. 1b represents the CV of the complete electrolyte, containing both metals, 300 mM Fe(III)Cit and 3 mM [Pd(NH$_3$)$_4$]$^{2+}$ recorded on the AAO template. The cathodic peak C_{1Fe+Pd} indicates a reduction consisting of two process, i.e., [Pd(NH$_3$)$_4$]$^{2+}$ to Pd^0 and at the same time the Fe(III)Cit ions are reduced to Fe(II)Cit$^-$, which is then further reduced to elemental Fe, together with HER, (C_{2Fe+H}), at a potential more negative than −0.9 V.

The blue curve in Fig. 1b represents the CV of the complete Fe–Pd electrolyte recorded on the flat substrate. The main idea of recording on a flat substrate was to help us with the determination of the reduction peaks, which are usually not well defined on a porous substrate [1]. One cathodic peak C_{1Fe+Pd} is observed and a current increase C_{2Fe+H}. In a comparison of both CV curves, recorded on the AAO template and the flat substrate, there are two major differences. The first noticeable difference is the current decrease in the CV of the AAO template, which may be due to the lower electrochemically available surface area of the AAO in comparison with the flat substrate [13,37]. The other noticeable difference is the