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Towards smooth and pure iron nanowires grown by electrodeposition in self-organized alumina membranes

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Abstract

Due to their high aspect ratio, magnetic nanowires are interesting for various applications. Fe nanowires are of particular interest due to their high magnetization, which suggests high shape anisotropy is possible. Here, we show how the electrodeposition process can be adapted to the constraints of a high aspect ratio template in order to approach an ideal behaviour of smooth and pure Fe nanowires. An adjustment of the Fe^{2+} concentration and the addition of H_3BO_3 result in smooth and continuous nanowires; saturation polarization is achieved, together with an anisotropy field of up to 70% compared to pure Fe. Mössbauer spectroscopy reveals a negligible amount of impurities. Together with magnetic measurements we show that shape anisotropy aligns the preferential magnetization axis along the wire axis.

Keywords: Electrodeposition; AAO template; Iron nanowires; Mössbauer spectroscopy

1. Introduction

The broad application potential for magnetic nanowires ranges from high-density magnetic recording [1], nanoelectrodes to sensors [2,3]. Most of these concepts utilize the high aspect ratio of these nanowires. For magnetic nanowires this should result in high shape anisotropy, favoring an alignment of magnetization along the wire axis. For a single nanowire, the shape anisotropy field $\mu_0 H_{A\mathrm{shape}} = J_S \Delta N$ is expected to depend only on two parameters: (1) its shape and therefore demagnetizing factor ΔN; and (2) spontaneous polarization J_S of the magnetic material used. From this, the selection of optimum geometry and material appears to be straightforward: (1) Utilize templates which reach a very high aspect ratio of length l to diameter d in order to approach the maximum value of $\Delta N = 0.5$. Self-organized alumina nanopore arrays fulfill these requirements especially well, since their pores reach lengths up to several tens of micrometers and diameters down to a few tens of nanometers [4]. (2) Use the material with the highest J_S. From this point of view, Fe–Co ($J_S = 2.4$ T) [5,6] is the best choice, closely followed by pure Fe ($J_S = 2.2$ T) [1,7].

Here we examine how to approach this ideal magnetic nanowire. To fill alumina templates with magnetic material, electrodeposition is selected, since this method allows templates with a very high aspect ratio to be filled. In addition, this method is relatively easily scalable and cost-efficient. In order to avoid the additional complications of alloy electrodeposition, required for Fe–Co, we selected elemental Fe. We examine which deposition conditions, such as potential and electrolyte composition, are required to come close to bulk polarization. Since all models assume the ideal shape of a smooth, continuous nanowire, we analyze in detail the influence of deposition conditions on wire

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morphology. Finally, the consequences on the anisotropic magnetic properties are analyzed by using magnetization measurements and Mössbauer spectroscopy.

Only a few publications have reported the morphology of Fe nanowires [1,8]. In most cases, alumina templates with a remaining Al backside are used, which require deposition under AC conditions [9,10]. Constant potential conditions [11,12] facilitate an understanding of the underlying electrochemical process, but require the use of freestanding alumina membranes.

For the discussion of the magnetic properties it is helpful to briefly summarize the key additional parameters. Magnetocrystalline anisotropy of low-symmetry materials, such as hexagonal Co [13,14] and $L1_0$ ordered CoPt [15,16] and FePt [17,18], can reach or even exceed shape anisotropy by one order of magnitude. Since to date, however, no well-defined crystallographic alignment of the easy axis with respect to the wire axis had been obtained, a clear separation of both effects is difficult. The use of Fe, which exhibits low cubic magnetocrystalline anisotropy, allows this aspect to be neglected here. Magnetoelastic anisotropy, originating from external stress on the ferromagnetic material, may also affect the direction of favored magnetization. By using an array of Ni nanowires we could show that this effect can compete with shape anisotropy [19,20]. Since we could trace this effect back to the different expansion coefficients of Ni and the Al substrate at the backside of the template [19], for the present experiments we removed the Al by etching. Magnetostatic dipole or multipole interactions between the nanowires can also strongly influence the magnetic properties [21,22]. This effect, favoring an antiparallel magnetization direction of neighboring wires, is expected to be most dominant for wires consisting of a high J_S material such as Fe, creating strong stray fields, which will be discussed in detail in a subsequent publication.

2. Experimental

Hexagonally ordered anodic alumina arrays are obtained by the well-established two-step anodization process [23]. Details of the preparation are described in a previous paper [19], though here the remaining aluminum and the barrier layer were removed by chemical etching using $CuCl_2$ and H_3PO_4. The alumina template exhibits a typical pore diameter D_p of 70 nm; the pore length varies between 15 and 20 μm. As a next step, Au was sputter-deposited on one side of the membrane to serve as an electrical contact and as a working electrode for electrodeposition. The mechanical stability of the membranes was enhanced by electrodepositing a Cu layer a few microns thick onto the Au backside.

Fe deposition was performed in an aqueous solution of $FeSO_4{\cdot}7H_2O$ using different concentrations (0.1, 0.5 and 1 M) and 0.525 M Na_2SO_4. Furthermore, the electrolyte was varied by the addition of 0.4 M H_3BO_3. The pH was adjusted to 3.0 by adding diluted H_2SO_4 or NaOH. The counterelectrode was a Pt foil. A saturated calomel electrode (SCE, 241 mV_{SHE}) was used as reference electrode and all electrode potential in this work are referred to the potential of the SCE. Depositions were carried out in a potentiostatic mode using an EG&G Potentiostat/Galvanostat Model 263 A.

To investigate the correlation between morphology, length and magnetic properties, the applied constant potential was varied between $E_{SCE} = -0.9$ V and $E_{SCE} = -1.4$ V at a constant deposition time of $t_{dep} = 5$ - min. When changing the Fe^{2+} concentration and/or adding boric acid H_3BO_3 the deposition was carried out at $E_{SCE} = -1.1$ V for 10 min.

High-resolution scanning electron microscopy (SEM, Leo 1530 Gemini/Zeiss) was used to examine the morphology of the nanowires at cross-sectional areas of the membrane obtained by breaking. For transmission electron microscopy (TEM), the samples were mechanically polished with a modified tripod to thicknesses of some 10 μm and subsequently subjected to Ar ion milling at small angles and low engergy by means of a Leica RES101 system. The nanowires were investigated using a FEI Tecnai T20 microscope operating at 200 kV. The crystal structure was analyzed by X-ray diffraction (XRD, Phillips X'Pert PW 3400, Co K_α radiation). Magnetization curves were measured using a vibrating sample magnetometer (VSM insert for Quantum Design PPMS) in fields up to 3 T applied parallel and perpendicular to the wire axis.

Mössbauer spectra (MS) were acquired at room temperature with a $^{57}Co/Rh$ source having an activity of about 185 MBq and a constant acceleration drive. The γ-rays were applied along the wire axis [24,25] in transmission geometry [26]. All Mössbauer spectra were taken at room temperature. The spectra were stored in a multichannel scaler with 1024 channels and fitted by a least-squares routine. Velocity calibration was performed with a 12.5 μm Fe foil at room temperature, and all isomer shifts are given relative to the center of this calibration.

3. Results and discussion

3.1. Influence of deposition potential

Since during electrodeposition the applied potential determines which specimen can be deposited, this is the first parameter to be examined. Both length and morphology of the nanowires are strongly influenced by the applied potential, as visible in cross-sectional SEM images (Fig. 1). At −0.9 V, Fe deposition is possible and wires of 425 nm length are achieved. With increasing negative potential the wire length increases and a maximum length of 2700 nm is obtained at −1.1 V. Applying even more negative potentials between −1.2 V and −1.4 V results again in shorter wires of approximately 250 nm. In addition, the morphology of the nanowires depends on the deposition potential. The shorter wires fabricated at −0.9 V and −0.975 V show a very smooth surface (Fig. 1a, b). The lon-