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Oriented cobalt nanowires prepared by electrodeposition in a porous membrane

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Abstract

Porous alumina membranes with a uniform pore size of 100 nm have been used to prepare arrays of oriented cobalt nanowires by electrodeposition in an applied magnetic field. The hexagonal *c*-axis lies in the plane of the membrane, perpendicular to the nanowire axis, for material deposited in 0 T or 1.5 T, but in 5 T the *c*-axis lies at about 70° to the axes of the wires. The degree of field-induced crystallographic orientation is insufficient to overcome the macroscopic demagnetizing field in samples with a large volume fraction of cobalt. The effective demagnetizing factors perpendicular and parallel to the plane of the membrane are $N_{\text{eff}}^{\perp} = 0.7$ and $N_{\text{eff}}^{\parallel} = 0.15$, respectively. Pole figures of the vector magnetization measured in a small rotating field of fixed amplitude in a permanent-magnet vector vibrating sample magnetometer are used to deduce torque and hence the effective magnetocrystalline anisotropy.

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Keywords: Shape anistropy; Magnetic nanowires; Electrodeposition; Nanoporous alumina membrane; Cobalt

A promising method to obtain nanowires with large shape anisotropy is based on membrane technology [1]. Magnetic metals such as Fe [2], Co [3–6] and Ni [7] have been embedded into the nanoscale pores of membranes by electrodeposition. The use of a nanoporous membrane improves coercivity and squareness of the hysteresis loop, compared to that of thin film or bulk material. Shape anisotropy can dominate when magnetocrystalline anisotropy of the material is weak. This is the case for iron or nickel nanowires in well-separated pores, which give square hysteresis loops with coercivity as high as 30% of that expected for a coherent rotation reversal mechanism, $\mu_0 M_s/2$ [8]. Magnetisation reversal proceeds via nucleation and domain-wall propagation process in the smallest wires, and by curling in wires with greater diameters. In the case of cobalt however, little hysterisis is found because the hexagonal *c*-axis, which is the magnetocrystalline anisotropy axis tends to lie in the plane perpendicular to the axis of the electrodeposited nanowires.

Here, we report the effect of applying a strong magnetic field during electrodeposition of Co nanowires on the magnetic properties and structural texture of the deposits.

A conventional three-electrode electrochemical cell was used to fabricate the Co nanowires. A platinum layer of thickness ~100 nm was sputtered on one side of 100 nm pore diameter 'Anodisc 47' alumina membrane obtained from Whatman and used as a working electrode to fabricate an array of cobalt nanowires. Platinum wire and Ag/AgCl were used as the counter and reference electrode, respectively. Co was electrodeposited at room

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temperature from an aqueous electrolyte containing 0.9 M $CoSO_4$ $7H_2O$, 0.11 M NaCl and 0.8 M H_3BO_3. Boric acid was used to adjust the pH of the bath to 3.5. Deposition was carried out at room temperature for a few hours to grow 20–25 μm long nanowires with no stirring during the deposition. The volume fraction of ferromagnetic material in the filled membrane is about 70%. During the deposition a 1.5 T field was applied parallel or perpendicular to the membrane using an electromagnet or else a superconducting magnet with a 105 mm room-temperature bore was employed to apply a 5 T field perpendicular to the membrane. When necessary for characterization of the electrodeposit, the membrane was dissolved in 1.5 M NaOH solution at room temperature for 15 min.

The magnetic properties at room temperature have been determined using an automated vector vibrating sample magnetometer (VVSM) with a 2 T permanent-magnet variable flux source. Pole figures of the vector magnetization measured in a rotating field of fixed amplitude ranging from 20 mT to 2 T are used to deduce the effective demagnetising factor and the hence the magnetocrystalline anisotropy constant K_1.

Fig. 1 shows cobalt nanowires which were electrodeposited at –1.0 V relative to the Ag/AgCl reference electrode. The SEM cross section view of the wires is obtained after dissolving the membrane.

Fig. 2 shows the X-ray diffraction pattern of the Co nanowires electrodeposited at −1.0 V without field (a); 1.5 T parallel (b); 1.5 T perpendicular (c) and 5 T parallel (d) to the nanowires during growth. As can be seen in Fig. 2a the main peak is from (1 1 0) planes of the HCP cobalt structure; Figs. 2b and c show an intense (1 0 0) peak. In all the cases the cobalt *c*-axis lies in the plane of the membrane. On the other hand, when a 5 T field is applied during deposition, the texture is quite different. The (0 0 2) peak in Fig 2d show that the *c*-axis is no longer perpendicular to the axis of the wire.

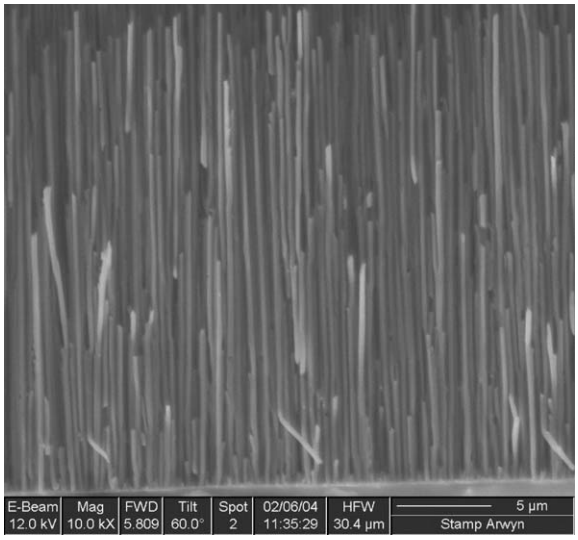

Fig. 1. Cross section of the electrodeposited cobalt wires after the removal of the 100 nm nanoporous alumina membrane.

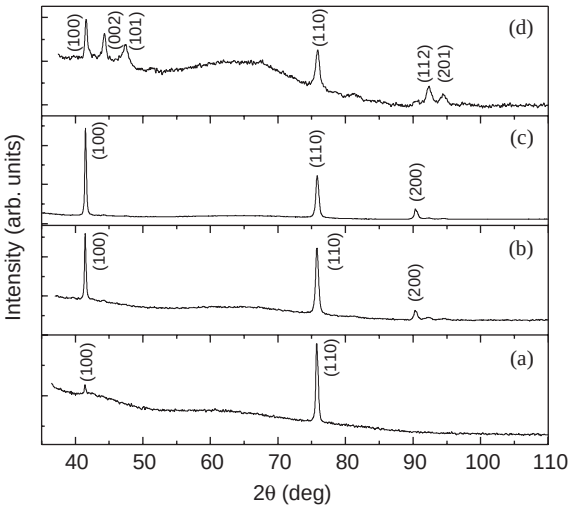

Fig. 2. X-ray diffraction of the cobalt nanowires electrodeposited at growth potential −1.0 V without field (a), 1.5 T parallel (b), 1.5 T perpendicular (c) and 5 T parallel (d) to nanowire during growth.

The texture in Fig. 1 shows that the cobalt (1 1 0) axis tends to lie along the wire in zero field, but in 1.5 T, the (1 0 0) peak becomes prominent. The second order (2 0 0) peak also appears in Figs. 2b and c. In both cases the magnetically easy *c*-axis is in the plane of the membrane, tending to reinforce the in-plane shape anisotropy. The 5 T X-ray diffraction pattern indicates that the *c*-axis has moved out of the plane of the membrane which does not seem to agree with the magnetization measurement (Fig. 3).

The slope of the magnetisation curve when the field is applied along the wire is steeper for the sample deposited in 0 T in comparison with the one deposited at 5 T, which contradicts the expected development of an easy axis along the wires (as the easy axis for α-Co is normally collinear with the *c*-axis). The reason for this inconsistency is unclear, but may be related to a similar phenomenon observed in anisometric cobalt nanoclusters (around 100 nm in size), which exhibit on easy axis of magnetisation [10].

The coercivity is small but it has increased both along and perpendicular to the wire. We find an increase from 2.5 mT (0 T) to 16 mT (5 T) along the wire when field is applied during deposition. These changes in coercivity are associated with the appearance of (0 0 2) reflection.

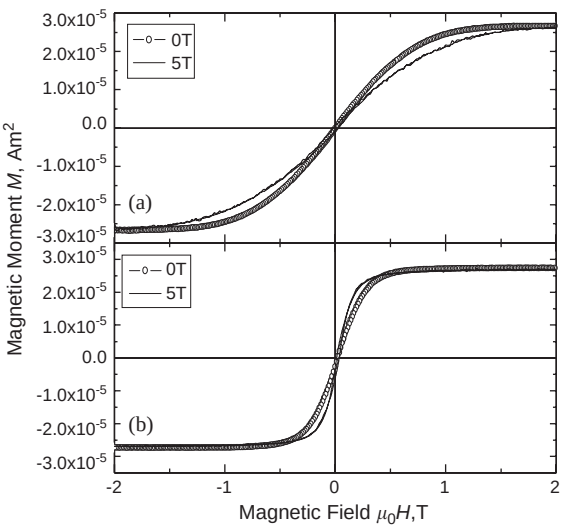

Fig. 3. Magnetization loops at room temperature for 100 nm cobalt nanowires with magnetic field applied parallel (a) and perpendicular (b) to the wire axis during measurements. The magnetic field 0 and 5 T stand for the field applied parallel to the wires during the deposition.

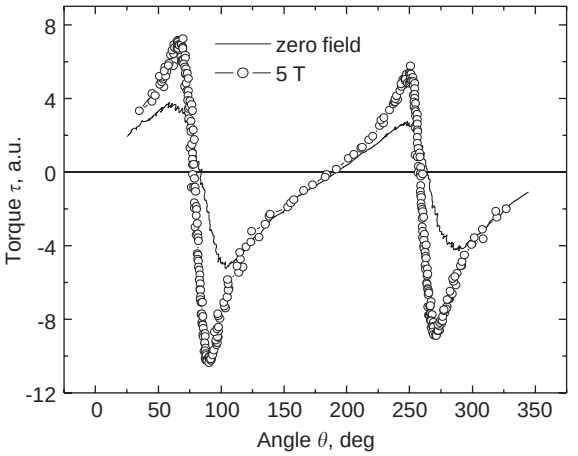

Fig. 4. Torque curves measured with a 0.1 T applied field at room temperature for a 100 nm array of cobalt nanowires. Note that the 0 and 5 T field was applied during the growth of nanowires.

The effective demagnetizing factor N_{eff} of the filled membrane is given by expression [9]

$$N_{\text{eff}} = N + f(N' - N), \tag{1}$$

where N is the demagnetizing factor of the individual wire, N' is the overall demagnetizing factor for the membrane and f is the fill factor (0.7). Hence, when the field is perpendicular to the membrane we find $N_{\text{eff}}^{\perp} = 0.7$, and in the parallel direction $N_{\text{eff}}^{\parallel} = 0.15$. Therefore, despite the structure in nanowires, shape anisotropy forces and easy direction of magnetization to lie in the plane of the membrane. The fill factor must be less than $\frac{2}{3}$ for the shape anisotropy to favour an easy direction perpendicular to the plane of the membrane.

The torque pattern measured as the field is rotated in a plane containing the wire is deduced from the VVSM experiment, as the two components of the magnetisation are simultaneously recorded the torque may be estimated from $\tau = \mu_0 \vec{M} \times \vec{H}$ [11]. Data in Fig. 4 shows a primary signal with period 2π due to the in-plane demagnetizing factor. In addition, there is a large harmonic with period π which reflects the uniaxial magnetocrystalline anisotropy constant K_1 and a smaller signal with period $\pi/2$ due to K_2. The misalignment angle ($\sim 70^\circ$) was estimated from the zeros of the torque curves.

From the maximal value of the magnetisation perpendicular to the applied field and a geometrical estimate of the volume occupied by the nanowires (from the SEM images), we estimated the primary anisotropy constant using $K_1 = \mu_0 H M_{\perp\max}$ to be 50 kJ/m^3 and 200 kJ/m^3 for the samples deposited in 0 and 5 T, respectively.

In conclusion, we have demonstrated that the magnetic anisotropy axis and crystallographic texture can be controlled to some extent by applying an external field during electrodeposition of cobalt in a nanoporous alumina membrane. Shape anisotropy favours the membrane plane for a fill factor $f > 2/3$, and the natural texture is with the c-axis of the nanowires in the plane of the membrane. While it is possible to induce some c-axis texture by depositing nanowires in 5 T magnetic field, this was insufficient to overcome the shape anisotropy of the membrane.

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References

[1] A. Fert, L. Piraux, J. Magn. Magn. Mater. 200 (1999) 338.
[2] Y. Peng, H.L. Zhang, S.L. Pan, H.L. Li, J. Appl. Phys. 87 (2000) 7405.
[3] L. Piraux, S. Dubois, Phys. Rev. B 56 (1997) 14066.
[4] H. Zeng, M. Zheng, R. Skomski, D.J. Sellmyer, J. Appl. Phys. 87 (2000) 4718.
[5] R.M. Metzger, V.V. Konovalov, M. Sun, T. Xu, G. Zangari, B. Xu, M. Benakli, W.D. Doyle, IEEE Trans. Magn. 36 (2000) 30.
[6] S. Valizadeh, J.M. George, P. Leisner, L. Hultman, Electrochim. Acta 47 (2001) 865.

[7] K. Nielsch, R.B. Wehrspohn, J. Barthel, J. Kirschner, U. Gosele, S.F. Fischer, H. Kronmuller, Appl. Phys. Lett. 79 (2001) 1360.
[8] P.M. Paulus, F. Luis, M. Kroll, G. Schmid, L.J. de Jongh, J. Magn. Magn. Mater. 224 (2001) 180.
[9] R. Skomski, J.M.D. Coey, Permanent Magnet, IOP, Bristol, 1999.
[10] C.P. Gibson, K.J. Putzer, Science 267 (1995) 1338.
[11] K. Ounadjela, R. Ferre, L. Louail, J.M. George, J.L. Maurice, L. Piraux, S. Dudois, J. Appl. Phys. 81 (1997) 5456.