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Citation: Appl. Phys. Lett. **86**, 072508 (2005); doi: 10.1063/1.1866636
View online: http://dx.doi.org/10.1063/1.1866636
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v86/i7
Published by the American Institute of Physics.

Electrochemical control and selection of the structural and magnetic properties of cobalt nanowires

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(Received 21 June 2004; accepted 13 January 2005; published online 10 February 2005)

In this letter we present a convenient way of controlling the direction of the uniaxial magnetocrystalline anisotropy in arrays of electrodeposited hcp Co nanowires. Combining electron microscopy and ferromagnetic resonance measurements, it is shown that using an appropriate *p*H of the electrolytic solution, the hcp *c* axis can be oriented parallel or perpendicular to the wires axes simply by changing the deposition current density or deposition rate. This reorientation of the *c* axis leads to a drastic change in overall magnetic anisotropy as the crystal anisotropy either competes for perpendicular oriented *c* axis or adds to the shape anisotropy for parallel oriented *c* axis. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1866636]

Among the different magnetic nanowires produced until now, cobalt has been the focus of much attention motivated by its large crystal anisotropy when growth occurs in the hcp structure. Indeed, numerous reports have shown that electrodeposition of Co nanowires leads to a "polycrystalline" structure in which hexagonal close packing (hcp) is the usual structure for most grains. Under usual deposition conditions, these grains exhibit preferred orientation of the hexagonal axis within a few degrees normal to the wire axis and are randomly distributed.[1,2] In this case, the large magnetocrystalline anisotropy competes directly with shape anisotropy which tends to align the magnetization along the wire axis, giving rise to a lowering of the effective anisotropy. Furthermore, the coexistence of varying amounts of the two hcp and fcc cobalt phases was found by several groups.[3–5] These observations constitute a major drawback in the use of Co nanowire arrays in applications such as perpendicular recording media, where an alignment of the *c* axis along the wire axis is desired. This underlines the importance of controlling the microstructure and in particular the magnetic easy axis of the electrodeposited nanowires.

Though a thorough understanding of the mechanism participating in the formation of Co films by electrodeposition is still lacking, the phase selection as related to deposition conditions or substrate influence has been studied in detail.[6–8] From these studies, the electrolytic bath acidity, or *p*H, is known to be the most important parameter in determining the structure of electrodeposited cobalt. Other relevant parameters of the operative conditions in cobalt electrocrystallization, though minor ones compared to the *p*H, are the current density and temperature of deposition.[9]

In a previous study our group has shown the role of the *p*H for the control of the orientation of the hcp *c* axis in arrays of Co nanowires. In particular a reorientation of the hcp *c* axis along the wires axes could be obtained for *p*H above 6.0.[10] In contrast to this previous study, we show here that besides the *p*H, the deposition rate, or current density, strongly affects the growth process of the cobalt nanowires. In particular, it leads to a significant shift of the critical *p*H range where the reorientation of the *c* axis from a perpendicular to a longitudinal direction occurs. As a consequence, for a limited *p*H range (5–6), it is possible to selectively obtain high quality Co nanowires with either a parallel or a perpendicular orientation of the *c* axis only by changing the deposition current. This makes it possible to control in a very simple way the overall magnetic anisotropy.

Arrays of Co nanowires are grown by electrodeposition into the cylindrical pores of lab-made track-etched polycarbonate membranes using a standard three-probe technique. The diameter of the pores is 30 nm with membrane porosity, *P*, of 3.5% (5×10^9 pores per cm^2). Prior to deposition a Cr (20 nm)/Au (300 nm) layer is evaporated on one face of the membrane to serve as a cathode. The electrolyte is 250 g/l $CoSO_4$, $7H_2O$ and 30 g/l H_3BO_3, the *p*H of the as-prepared solution is 4.0 and adjusted with diluted NaOH. Galvanostatic room temperature deposition is done with current densities set from 5 to 50 mA/cm^2, over a constant membrane surface of 1.2 cm^2. Structural characterization has been done by transmission electron microscopy (TEM) after dissolving the polycarbonate membrane and spreading of the wires onto a grid.

As shown in a previous report,[10] the average, or dominant orientation, of the *c* axis induces significant changes in the total effective anisotropy of the system. Therefore, the effects of the deposition current on the electrocrystallization characteristics have been determined by measuring the uniaxial crystal anisotropy field H_U in arrays of nanowires as a function of both the deposition current and the *p*H of the electrolyte. For this purpose, ferromagnetic resonance (FMR) measurements were carried out using a microstrip transmission line.[10]

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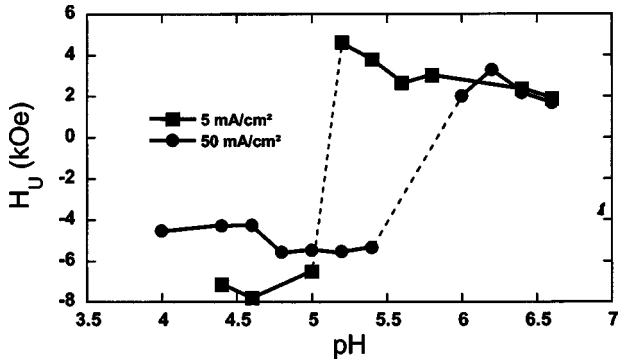

FIG. 1. The value of magnetocrystalline anisotropy field as a function of the *p*H for 30 nm Co nanowires electrodeposited at current densities of 5 and 50 mA/cm^2.

At a given constant frequency f, the ferromagnetic resonance conditions when the magnetic field is swept parallel to the wires are:
(i) c axis and, hence, magnetocrystalline easy axis parallel to the wire axis ($H_U > 0$):

$$\frac{f}{\gamma} = H_R + 2\pi M_S(1-3P) + H_U, \tag{1}$$

(ii) c axis and, hence, magnetocrystalline easy axis perpendicular to the wire axis ($H_U < 0$):

$$\left(\frac{f}{\gamma}\right)^2 = [H_R + 2\pi M_S(1-3P) + H_U] \times [H_R + 2\pi M_S(1-3P)]. \tag{2}$$

In Eqs. (1) and (2), $\gamma(\mathrm{Co}) = 3.05$ GHz/kOe, H_R is the resonance field, $2\pi M_S \sim 8.8$ kOe is the shape anisotropy field [$M_S(\mathrm{Co}) \sim 1370$ emu/cm^3] and $6\pi M_S P$ is the dipolar coupling field between the wires (~ 900 Oe for $P = 3.5\%$).[10] Therefore, FMR studies provide a direct quantification of the anisotropy crystal field.

Measurements were performed at room temperature by sweeping down the magnetic field applied parallel to the wires from 10 kOe to zero, at different constant excitation frequencies up to 50 GHz, see Ref. 10 for further details. The crystal anisotropy field is obtained by fitting expressions (1) and (2) once the resonance field has been determined at different frequencies.[11]

Figure 1 shows the variation of the crystal anisotropy field as a function of the *p*H for samples deposited using a high current density of 50 mA cm^{-2} (circles) and a low current density of 5 mA cm^{-2} (squares).

For both deposition currents, the overall dependence of the crystal anisotropy field is similar. In particular, H_U is negative at low *p*H and positive at high *p*H, which is consistent with a dominant fraction of grains having (a) the c axis perpendicular ($H_U < 0$) and, (b) the c axis parallel ($H_U > 0$) to the wires axes. However, the change in sign for H_U takes place around different *p*H values depending on the deposition current density. At higher deposition currents, the crystal anisotropy fields are in the range of -4.0 to -5.5 kOe for *p*H values between 4.0 and 5.5. Above this *p*H value, H_U rapidly increases and reaches values around +2 to +3 kOe for a *p*H above 6.0. For low deposition currents, the increase in H_U, takes place at considerable lower *p*H values, around 5.0, and the transition is also more abrupt

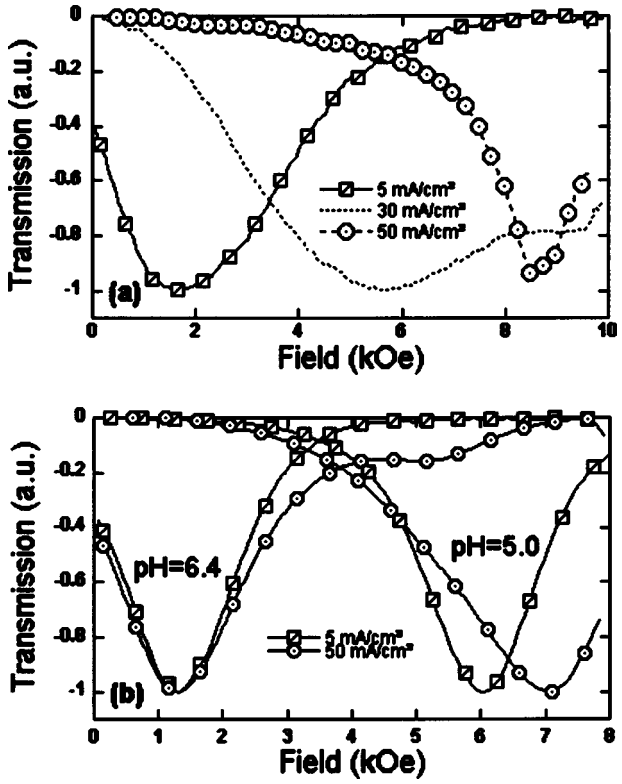

FIG. 2. FMR spectra with a magnetic field applied parallel to the wires for 30 nm Co nanowires grown (a) at *p*H 5.2 and current densities of 5, 30, and 50 mA/cm^2 recorded at 43 GHz and, (b) at *p*H 5.0 and 6.4 with current densities of 5 and 50 mA/cm^2 recorded at 35 GHz.

than at high currents. At *p*H 5.2, H_U reaches a maximum value of +4.6 kOe, and then decreases slowly as the *p*H increases until it reaches a value of 2 kOe at a *p*H of 6.6.

As suggested by these results (Fig. 1), the effect of the current is to shift the *p*H value at which the structural and magnetic changes take place. Specifically, the lowering of the deposition current shifts this transition to lower *p*H values.

Another remarkable and important property derived from Fig. 1 is that, in a limited *p*H range, both structural phases (c axis parallel and perpendicular to the wires) can be obtained from the same electrolyte simply by changing the deposition current. This is illustrated in Fig. 2(a) which shows the resonance spectra measured in two Co nanowire arrays deposited from a *p*H 5.2 electrolyte using high and low currents (indicated in the figure). As can be observed, by changing the current density from 50 down to 5 mA cm^{-2}, the resonance field can change as much as 8 kOe, which is consistent with a dominant fraction of hcp Co grains having their c axis perpendicular (high current) and parallel (low current) to the wires axes. Figure 2(a) also shows an absorption curve measured on a sample grown at an intermediate deposition current (30 mA cm^{-2}). In this case, a much broader peak appears as a clear signature of the inhomogeneous crystallographic structure of the so-prepared Co nanowires. In these same lines, and in agreement with the results in Fig. 1, below and above a *p*H of 5.0 and 6.0, respectively, the orientation of the c axis is independent of the deposition current. This is shown in Fig. 2(b) for high *p*H (6.4), and low *p*H (5.0). To be noted is that for the *p*H 5.0 samples, the resonance fields for the two deposition currents

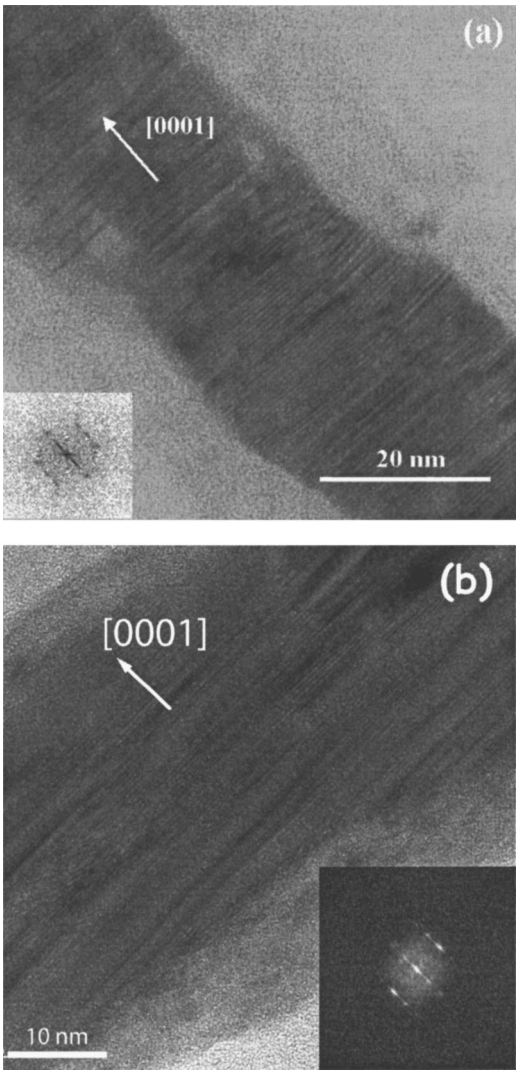

FIG. 3. TEM bright field images and corresponding diffraction patterns of two 30 nm Co nanowires electrodeposited at pH=5.2 and current densities of (a) 5 and (b) 50 mA/cm^2.

differ, but these values are consistent with a c axis oriented perpendicular to the wire axis.

The dependence of the hcp c-axis orientation on the deposition current is corroborated by TEM investigations as shown in Figs. 3(a) and 3(b) for Co wires deposited at a pH of 5.2. In the case of low current density [Fig. 3(a)], the TEM bright field and diffraction images clearly show an orientation of the c axis oriented parallel to the wire axis ($+/-5°$). Similarly, in the case of high current density [Fig. 3(b)], the TEM bright field and diffraction images clearly show an orientation of the c axis oriented perpendicular to the wire axis ($+/-5°$). Although only short sections are shown in the images, no grain boundaries were observed along longer sections of the ten wires that have been examined in detail.

As pointed out in previous works involving electroplated Co films, these structural changes can be attributed to the influence of absorbed hydrolysis products at the cathode as well as to evolution of hydrogen, which are known to depend on the pH and the plating current.[9,12] For bulk hcp Co, the magnetocrystalline anisotropy has an upper bound of 7.8 kOe[13] ($K=5.3\times10^6$ erg/cm^3 and $H_U=2K/M_S$). It is noted that for perpendicularly oriented c axis, the maximum crystal anisotropy field found in this study ($\sim$7.8 kOe) corresponds closely to the earlier mentioned upper bound. Such large values are consistent with the very good structural quality demonstrated by our TEM studies. In contrast, values for H_U are well below the maximum expected value when the c axis is parallel to the wires. Furthermore, a gradual decrease of H_U with increasing pH clearly appears. This behavior can be associated to the influence on crystalline growth by adsorbed hydrolysis products (such as Co hydroxides) at the cathode when the pH is sufficiently high. Another possible reason for the reduction of H_U are stacking faults, which might increase in number in the high pH samples.[14] However, further structural characterization is required to provide a better understanding on the relation between the growth, crystalline structure and the value of the magnetocrystalline anisotropy field.

In conclusion, the crucial role of the deposition current on the preferential orientation of the hcp c axis in Co nanowires with respect to the wire axis has been shown. In particular, both structural phases, hcp Co with the c axis parallel and the c axis perpendicular to the wires, can be obtained from a single electrolyte by changing the deposition current in a limited pH range (5.0–5.5) by one order of magnitude. This reorientation of the c axis leads to changes in sign of the crystalline anisotropy field. This allows not only to chose the desired orientation of the c axis, but also to simply grow wires in which both phases are alternated, providing a simple and convenient way to control the magnetic properties of electrodeposited cobalt nanowire arrays to a large extent.

The authors would like to thank R. Legras and E. Ferain for providing the polycarbonate membrane samples used in this study, Th. Fournier for fabrication of Si/SiN membranes used in the TEM experiments, and Dr. L. Vila for his valuable help in the experiment. This work was supported in part by the European Program Contract No.: HPRN CT1999 00150 as well as by the Belgian Science Policy through the Interuniversity Attraction Pole Program PAI (5/1/1). One of the authors (A.E.) thanks CONACyT for financial support through Grant No. J-40426.

[1] J. L. Maurice, D. Imhoff, P. Etienne, O. Durand, S. Dubois, L. Piraux, J.-M. George, P. Galtier, and A. Fert, J. Magn. Magn. Mater. **184**, 1 (1998).
[2] R. M. Metzger, V. V. Konovalov, M. Sun, T. Xu, G. Zangari, B. Xu, M. Benakli, and W. D. Doyle, IEEE Trans. Magn. **36**, 30 (2000).
[3] V. Scarani, B. Doudin, and J.-P. Ansermet, J. Magn. Magn. Mater. **205**, 241 (1999).
[4] G. J. Strijkers, J. H. J. Dalderop, M. A. A. Broeksteed, H. J. M. Swagten, and W. J. M. de Jonge, J. Appl. Phys. **86**, 5141 (1999).
[5] M. Kröll, W. J. Blau, D. Grandjean, R. E. Benfield, F. Luis, P. M. Paulus, and L. J. de Jongh, J. Magn. Magn. Mater. **249**, 241 (2002).
[6] S. Nakahara and S. Mahajan, J. Electrochem. Soc. **127**, 283 (1980).
[7] T. A. Tochitskii, A. V. Boltushkin, and V. G. Shadrov, Russ. J. Electrochem. **31**, 178 (1995).
[8] I. M. Croll, IEEE Trans. Magn. **23**, 59 (1987).
[9] T. Chen and P. Cavallotti, Appl. Phys. Lett. **41**, 205 (1982).
[10] M. Darques, A. Encinas, L. Vila, and L. Piraux, J. Phys. D **37**, 1411 (2004).
[11] In a first fit, H_u was obtained using Eq. (1). When H_u turned out to be negative, the fit was repeated using Eq. (2).
[12] T. Cohen-Hyams, W. D. Kaplan, and J. Yahalom, Electrochem. Solid-State Lett. **5**, C75 (2002).
[13] E. Du Tremolet de Lacheisserie, in *Magnétisme*, edited by J. Bornarel (Presses Universitaires de Grenoble, Grenoble, 1999), p. 168.
[14] B. Bian, W. Yang, D. Laughlin, and D. Lambeth, IEEE Trans. Magn. **37**, 1456 (2001).