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Tailoring of the *c*-axis orientation and magnetic anisotropy in electrodeposited Co nanowires

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Abstract

The magnetic properties of arrays of electrodeposited Co nanowires have been studied by ferromagnetic resonance as a function of the electrolytic bath acidity and the plating current intensity. It is observed that by adjusting the pH or the plating current it is possible to find appropriate electrolyte-deposition conditions which lead to the deposition of Co nanowires with a *c*-axis orientation either parallel or perpendicular to the wires. At relatively high plating currents, systems containing a dominant fraction of grains having the *c*-axis oriented perpendicular to the wires are favoured. Such wires show a significant decrease of the effective anisotropy due to the competition between the magnetocrystalline and the shape anisotropy that can be as low as 4.3 kOe. In contrast, at low plating currents the *c*-axis is aligned parallel to the wires and an effective anisotropy field, that can be as high as 12 kOe, is observed.

1. Introduction

Arrays of magnetic nanowires electrodeposited in nanoporous templates have attracted a lot of attention and research efforts in recent years. Their simple geometry and high aspect ratios make them a model system for the study of magnetic phenomena in arrays of uniaxial nanomagnets and are, potentially, a promising system for perpendicular magnetic recording media as well as for microwave absorption devices.

Despite significant improvements reported in the control of the structural quality, the dispersion of the diameter and length of the wires and their distribution, most of these advancements do not involve the use of cobalt. Indeed, numerous reports have shown that

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electrodeposition of Co nanowires leads to a polycrystalline structure in which any given wire has a few hcp grains, each of which has a random *c*-axis oriented, within a few degrees, normal to the wire axis [1–7]. These structural characteristics have a strong influence on the magnetic properties which differ significantly from those observed in Ni and Fe wires [1–3, 5, 7]. These differences are attributed to the lowering of the effective anisotropy which results from the competition between the shape anisotropy and an average magnetocrystalline anisotropy (MCA), which due to the lack of order among different hcp grains is lower than the known value of the MCA field in bulk Co ($K_{MC} = 4.5 \times 10^6 \text{ erg cm}^{-3}$, $H_{MC} = 2K_{MC}/M_S = 6.4 \text{ kOe}$) [1, 5]. This particular property of Co has important consequences, since, as pointed out by several authors [1, 2], as long as the crystalline orientation cannot be controlled, cobalt is not a suitable candidate for perpendicular storage media, underlining the importance of modifying and eventually controlling the microstructure and magnetic properties of the electrodeposited Co nanowires.

This structural feature of Co is a general property; indeed, the presence of this pseudo texture is observed regardless of the kind of template (anodized alumina [1–4] or polycarbonate [5–7]), the Co concentration in the electrolyte [1–7], addition of additives to the electrolyte [7], galvanostatic or potentiostatic deposition modes, or AC [1, 3] or DC [4–7] deposition in alumina templates. Moreover, anomalous results have been reported concerning the structural and magnetic properties of Co nanowires as a function of the diameter. Below a certain value of the wire diameter, in the 30–40 nm range, several groups have observed substantial changes in the magnetic properties. These changes have been attributed either to an apparent rotation of the *c*-axis from perpendicular to parallel to the wires [5] or to the presence of a FCC Co phase which is enhanced at small diameters [8]. In both cases, an increase of the uniaxial anisotropy is observed.

Numerous studies on the electrochemical deposition of cobalt films have shown that the electrolytic bath acidity, or pH, can lead to drastic changes in the structure of the electrodeposited Co [9–13]. In particular, Croll [13] showed that by changing the pH, Co films can exhibit either an in-plane or perpendicular anisotropy depending on the pH of the electrolyte. In this sense, a preliminary study in Co nanowires has shown that when the pH is lowered to a value of 2.0, the perpendicular hcp Co phase can be eliminated, resulting in arrays of nanowires whose magnetic properties correspond to those given only by the shape anisotropy and the interwire dipolar coupling [14]. In this contribution we show that by adjusting the pH or the plating current it is possible to find appropriate electrolyte-deposition conditions which lead to the deposition of Co wire with a *c*-axis orientation parallel to the wires, resulting in uniaxial anisotropy fields as high as 12 kOe.

2. Experimental setup

Arrays of cobalt nanowires have been fabricated by standard three-probe electrodeposition into the pores of polycarbonate membranes characterized by a constant pore diameter and a given porosity, *P* (or surface fraction). Prior to the electrodeposition, a Cr(20 nm)/Au(600 nm) electrode is evaporated on one surface of the membrane. Cobalt wires have been grown at room temperature from a $239.48 \text{ g l}^{-1} \text{ CoSO}_4 \cdot 7\text{H}_2\text{O} + 30 \text{ g l}^{-1} \text{ H}_3\text{BO}_3$ electrolyte at a constant potential of $V = -0.95 \text{ V}$, or under galvanostatic conditions. The as-prepared solution has typical pH values in the range of 3.7–4.0, which has been gradually lowered down to 2.0 by the addition of diluted H_2SO_4 or increased up to 6.6 by the addition of diluted NaOH. Ferromagnetic resonance (FMR) measurements have been carried out using a microstrip transmission line fabricated by evaporation of a Cr(20 nm)/Au(800 nm) layer on the free surface of the membrane through a 500 μm wide metallic mask, see [15] for further details.

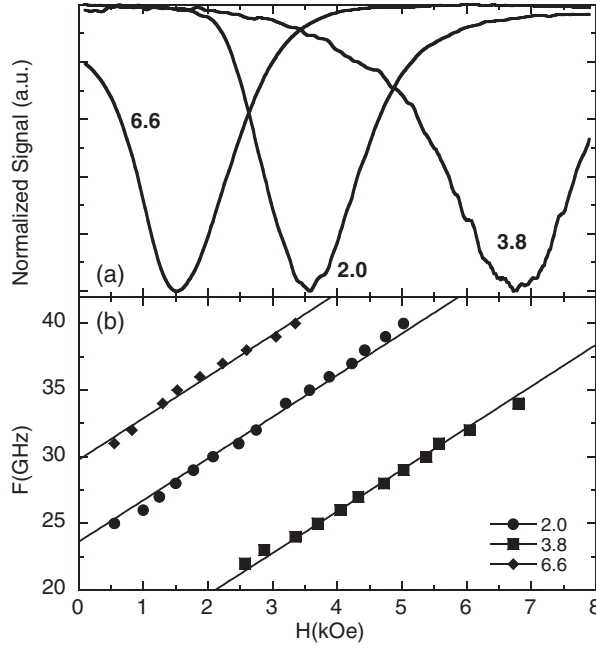


Figure 1. FMR measurements of three arrays of Co nanowires prepared from solutions having their pH set to 2.0, 3.8 and 6.6; the wire diameter is 29 nm and the porosity is 3.0%. (a) FMR spectra measured at 34 GHz, and (b) the corresponding dispersion relations.

The microwave transmission coefficient measurements were performed at room temperature by sweeping the magnetic field applied parallel to the wires at different constant excitation frequencies. Ferromagnetic resonance allows direct and precise quantification of the effective anisotropy field and, moreover, the lineshape of the FMR peaks allows us to identify and follow the presence of different structural phases in a manner analogous to spectra obtained by nuclear magnetic resonance [4, 6, 16].

3. Results and discussion

Figure 1 presents the FMR absorption spectra recorded at a constant frequency of 34 GHz in samples prepared from solutions having their pH set to 2.0, 3.8 and 6.6; the wires have a diameter of 29 nm and a porosity, P , of 3%. These results show a clear change in the position of the resonance peak as a function of the pH. The lowest resonance field is measured in the pH = 6.6 sample, while the highest resonance field is observed in the pH = 3.8 sample. The difference between the highest and lowest resonance fields is close to 5.5 kOe. At a given frequency, the position of the resonance field is given by the effective field, H_{EF} , which in a system that has no magnetocrystalline or magnetoelastic anisotropy contributions is given only by the shape anisotropy, $2\pi M_S$, and the dipolar interwire coupling, which in a mean field approximation can be written as $6\pi M_S P$ [15]. If the Co hcp c -axis introduces an additional average MCA, H_K , it can be taken into account by including an additional term in the uniaxial anisotropy coefficient. From classical FMR theory, the resonance condition when the magnetic field is applied parallel to the wires is [15]:

$$H_R = \frac{f}{\gamma} - [2\pi M_S(1 - 3P) \pm H_K]. \quad (1)$$

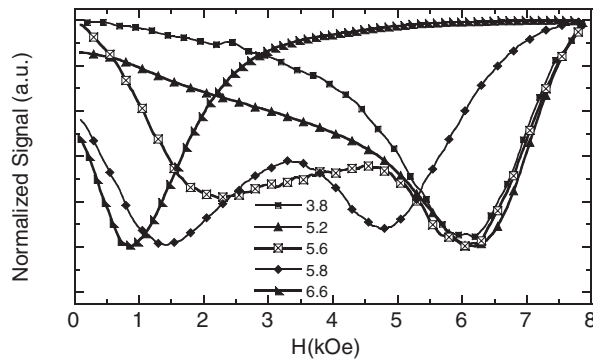


Figure 2. FMR measurements at 32 GHz in a series of arrays of Co nanowires having a diameter of 29 nm and porosity of 3.0% prepared from solutions having their pH set to 3.8, 5.2, 5.6, 5.8 and 6.6.

The effective field can then be determined by fitting the experimental dispersion relation to equation (1). Figure 1(b), shows the full dispersion relation measured on the three samples discussed in figure 1(a). As expected, the dispersion relation is linear and the continuous lines correspond to the fit of the experimental data to equation (1). From these fits, the effective fields are found to be 5.0, 7.8 and 10.4 kOe for the pH = 3.8, 2.0 and 6.6 samples, respectively. The importance of these results lies in the fact that the effective field corresponds to the total, or effective, anisotropy field of the system [15].

If there is no MCA contribution, the effective field for an array of Co wires ($M_S = 1400 \text{ emu cm}^{-3}$, and $\gamma = 3.05 \text{ GHz kOe}^{-1}$) having a porosity of 3.0% is, after equation (1), 8.0 kOe (corresponding to a resonance field of 3.53 kOe at 34 GHz, see figure 1(a)). These results correspond to those measured in the sample grown from the solution having a pH equal to 2.0. That is, the Co nanowires obtained from this solution correspond to a system which has no significant contribution from the MCA in agreement with previous findings [14]. On the other hand, the samples obtained from the as-prepared electrolyte, pH = 3.8, have a lower effective field (5.0 kOe), which is consistent with a lowering of the effective anisotropy due to the perpendicular orientation of the Co c -axis, as expected from the as-prepared electrolyte. The most outstanding result is that obtained in the pH = 6.6 sample, in which the effective field (10.4 kOe) exceeds the value expected for a system with no MCA. Indeed, if this contribution is not present ($H_K = 0$), then it follows from equation (1) that the value of the effective field has an upper bound at $H_{EF} = 2\pi M_S = 8.8 \text{ kOe}$, which corresponds to the case of an isolated ($P = 0$) infinite cylinder. This result implies that there is an additional contribution to the effective field, which favours an easy axis parallel to the wires. By analogy to the case in which the grains have their c -axis oriented perpendicular to the wires, the increase of the effective field in the pH = 6.6 sample is attributed to the rotation of the c -axis, which is no longer perpendicular to the wires, but rather aligned towards the axis of the wires.

To further corroborate this effect, the FMR properties have been measured by varying the pH between 3.8 and 6.6. Figure 2, shows the FMR spectra recorded at 32 GHz with the magnetic field applied parallel to the wires in a series of samples (wire diameter 29 nm and $P = 3.0\%$) deposited from solutions having their pH set to 3.8, 5.2, 5.6, 5.8 and 6.6. The results show that as the pH increases from the value of the as-prepared electrolyte (pH = 3.8), a secondary absorption peak appears on the low field side and whose intensity increases by further increasing the pH. The co-existence of two absorption peaks in the spectra indicate the presence of two different structural phases. These phases can be identified by considering

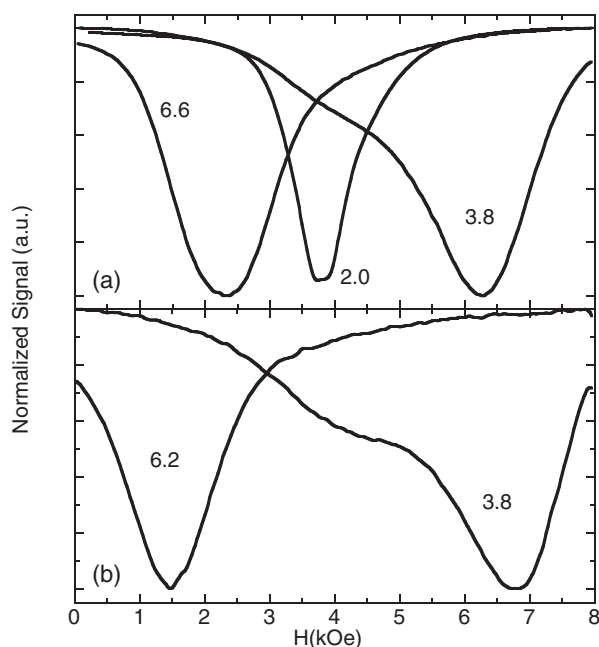


Figure 3. FMR spectra measured with the magnetic field applied parallel to the wires: (a) at 36 GHz in three arrays of Co nanowires with diameter of 70 nm and $P = 2.3\%$ grown from pH = 2.0, 3.8 and 6.6 electrolytes, and (b) at 35 GHz in 50 nm, $P = 3.15\%$ grown from pH = 3.8 and 6.2 electrolytes.

the initial (for pH = 3.8) and final (for pH = 6.6) position of the corresponding resonance fields which, in the light of the results of figure 1, correspond to Co grains having their c -axis perpendicular (pH = 3.8) and parallel (pH = 6.6) to the wires. The progressive transition observed in figure 2 indicates that the structure changes gradually with the pH and that the c -axis does not rotate abruptly from perpendicular to parallel to the wires at a certain pH value, but rather these changes take place by the increase or decrease of the total fraction of a given type of Co grain.

So far it has been shown that by varying the pH it is possible to change in a gradual fashion the structural and magnetic properties of Co nanowires. However, the results presented in figures 1 and 2 concern only wires having a diameter of 29 nm. In order to verify the generality of these results, similar experiments have been performed in wires of larger diameter. Figure 3 presents the FMR spectra recorded with the magnetic field applied parallel to the wires in samples having a wire diameter of (figure 3(a)) 70 nm and porosity of 2.3% for Co nanowires grown from pH = 2.0, 3.8 and 6.6 electrolytes and measured at 36 GHz, and (figure 3(b)) at 35 GHz in 50 nm, $P = 3.15\%$, Co wires deposited from pH = 3.8 and 6.2 electrolytes. A clear difference is observed in the measured resonance fields as the pH passes from 3.8 to ≥ 6.0 . The shift of the resonance fields are ~ 4 and 5.5 kOe for the 70 and 50 nm samples, respectively. In the case of the 70 nm Co wires, figure 3(a), it is observed that with respect to the pH = 2.0 sample, which corresponds to the case in which no MCA contribution is present, an increase close to 2 kOe is observed for the pH = 6.6 sample. The shift observed between the pH = 3.8 and ≥ 6.0 corresponds to the difference of the effective anisotropy field which indicates the rotation of the c -axis from perpendicular to parallel to the wire axis. This proves that up to wire diameters of 70 nm the preferential orientation of the c -axis can be controlled by adjusting the pH of the electrolyte.

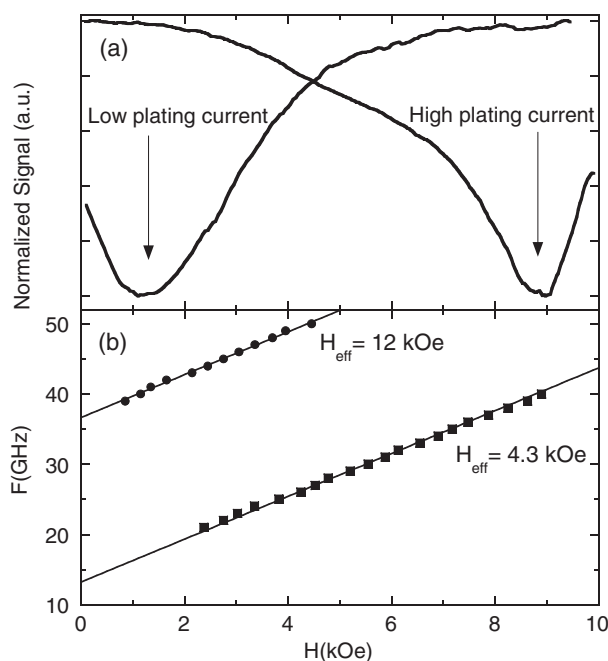


Figure 4. (a) FMR spectra measured at 40 GHz with the magnetic field applied parallel to the wires in two Co samples with wire diameter of 29 nm and 3% porosity, plated in the potentiostatic ($V = -0.95 \text{ V}$, $i = 90 \text{ mA cm}^{-2}$) and galvanostatic ($i = 5 \text{ mA cm}^{-2}$, $V = -0.76 \text{ V}$) mode from the same electrolyte having a pH = 5.2, and (b) the corresponding dispersion relations.

As pointed out by other authors [9, 11, 12] these structural changes can be attributed to the hydrolysis of Co ions and their adsorption on the cathode, favoured by the evolution of hydrogen during deposition, which is known to depend on the pH. Moreover, as shown by Chen and Cavallotti [11] the effects induced by the co-deposition of hydrogen during plating can also be modulated by performing deposition of Co films in the galvanostatic mode. Indeed, by plating at a constant current, there is a potential difference established between the cathode and the working electrode. Since the evolution of hydrogen depends on this potential, by working at low plating currents it is possible to establish low deposition potentials which will limit the amount of deposited hydrogen. On this basis, Chen and Cavallotti [11] have reported the growth of Co films with the *c*-axis either parallel or perpendicular to the film plane. In order to explore these mechanisms, we have studied the effects of growth at a constant plating current (galvanostatic mode) in the FMR properties of Co nanowires. Figure 4 compares the recorded FMR spectra measured at 40 GHz with the magnetic field applied parallel to the wires in two Co samples with wire diameter of 29 nm and 3% porosity. Both samples have been plated from an electrolyte having a pH = 5.2, one of them was grown at a constant potential of -0.95 V (corresponding to a mean plating current of 90 mA cm^{-2}) which is known to lead to a dominant fraction of Co having the *c*-axis oriented perpendicular to the wires (see figure 2), while the other sample has been grown at a constant plating current of 5 mA cm^{-2} .

As seen in figure 4(a), at the same frequency there is a huge difference between the corresponding resonance fields. In particular, the peak measured in the sample grown at low constant plating current is consistent with a predominant *c*-axis aligned parallel to the wires. From the dispersion relation for each of the samples, in figure 4(b), the effective anisotropy fields are 4.3 and 12 kOe for the samples grown at high and low plating current, respectively.

This leads to a change of 7.7 kOe in the anisotropy field, which is consistent with a change in the preferential orientation of the c -axis. Moreover, the MCA contribution for the c -axis oriented parallel to the wires can be determined from the shift of the effective field with respect to the pH = 2.0 sample grown in the same template, for which we find an effective field of 7.8 kOe, leading to an MCA contribution of 4.2 kOe. Furthermore, these results show that Co wires can be grown at low constant plating current with the c -axis parallel to the wires from solutions having a pH which would typically lead to a preferential c -axis perpendicular to the wires when grown in the potentiostatic mode (or at high plating currents).

Finally, if the c -axis is indeed parallel to the wires, then from equation (1) and taking $P = 3.0\%$, and the bulk value for the Co MCA, $H_K = 6.4$ kOe, an anisotropy field of 14.2 kOe would be expected. The results obtained thus far, show values that are somewhat lower than this value, the highest effective field obtained so far is 12 kOe due to a MCA contribution of 4.2 kOe. Two possible reasons that could explain such discrepancies are, first, that the c -axis is not fully aligned with the wire axis but rather aligned at some finite angle close to the wire axis. Secondly, the addition of NaOH needed to increase the electrolyte pH could also result in the co-deposition of non-magnetic species. Studies are currently in progress with the purpose of giving some insight into these possible mechanisms. However, it is worth noting that the results shown in figure 4 are important since they show that the c -axis parallel to the wires can be obtained at lower pH values by plating at lower currents. That is, in solutions with lower NaOH concentrations that will eventually limit the amount of non-magnetic species that might be co-deposited.

4. Conclusions

In conclusion, the FMR results presented show that by controlling the electrochemical solution and the deposition parameters it is possible to grow in a controlled manner Co nanowires with a c -axis preferentially oriented parallel or perpendicular to the wires. For a parallel orientation, the Co nanowires are characterized by a greatly enhanced anisotropy field which results from the superposition of the shape and magnetocrystalline anisotropies. This corresponds to an effective anisotropy field as high as 12 kOe, and an increase of 7.7 kOe with respect to the effective anisotropy field in wires with a c -axis oriented perpendicular to the wires. It also means that the plating current and pH of the sulfate bath rather than the wire diameter are the relevant parameters to determine the orientation of the c -axis in such electrodeposited Co nanowires. In particular, the rotation of the c -axis from perpendicular to parallel to the wire axis for diameters smaller than 40 nm, previously reported in [5], is not observed in our FMR results. The possibility of controlling the effective anisotropy field in Co nanowires opens interesting options for the control and engineering of the magnetic properties of these arrays of nanowires and their applications in perpendicular recording media, microwave absorption devices and giant magnetoresistive sensors.

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