Effect of pH on Crystallographic Orientation and Magnetic Behavior of Arrays of Continuous Electrodeposited Co Nanowires

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We investigate the dependence of the magnetic properties of continuous Co wire arrays on the electrolyte pH. The microstructure of the magnetic electrodeposited Co nanowires was characterized by X-ray diffraction. Hcp Co wires were obtained when electrodeposition was performed under pH ≈ 4. Data is presented, which contrasts the crystallographic orientation and magnetic properties of wires electrodeposited at low and at high electrolyte pH values. Plating from a single $CoSO_4$ bath, a transition in preferred orientation is observed to occur in the region of pH ≈ 4, from orientation of the hexagonal c-axis predominantly perpendicular to the axis of the wires below a pH of 4, to c-axis orientation predominantly parallel to the axis of wires for pH > 4. Co wires structure changes from being fcc at low pH, Hcp with the c-axis out of the plane of polycarbonate membranes below pH ≈ 4, and Hcp with the c-axis in the plane of polycarbonate membranes at higher pH values. Torque measurements of arrays of Co wires confirm that when the pH of the solution is increased, the easy direction of magnetization changes from perpendicular to parallel to the axis of the wire. Our results show that appreciable changes in the effective anisotropy constant could be induced depending on the pH value of the solution.

1. Introduction

When ferromagnetic materials are deposited into the pores of a nanoporous matrix to create nanowires, the real density of the nanowires is the same as that of the nanopores. If the easy magnetization axis is along the nanowires, then this kind of nanowire array can be used as an ultra high density perpendicular storage medium [1]. Cobalt wires can crystallize in either the cubic or the hexagonal phase, but the latter is the most commonly observed and stable phase at room temperature [2]. The orientation of the hexagonal axis with respect to the axis of the wires is important when considering Co nanowire arrays for parallel or perpendicular recording media because there is strong magnetocrystalline anisotropy along the hexagonal axis comparable to the magnetostatic energy of a nanowire [3]. Preferred crystallographic orientation in electrodeposited wires and films from $CoSO_4$ solutions with high or low pH values has been reported previously [2, 4, 5]. Preferred orientation and the appearance of the cubic phase have also been outlined for more complex plating conditions [4, 5].

The characterization and the control of the microstructure of electrodeposited nanowires are necessary for a detailed understanding of their magnetic properties [2d, 6]. The samples used for this study were continuous Co nanowires of length L ≤ 7 μm, prepared using a single electrochemical route in track-etched polycarbonate membranes.

It is the purpose of this paper to study the influence of pH (values between pH ≈ 1.65 and pH ≈ 5.80) of $CoSO_4$ electrolytes on the magnetic behavior of continuous electrodeposited Co nanowires.

2. Sample preparation and structural characterization

The polycarbonate membranes used in this study have a thickness of L ≈ 7 μm and pore diameters of D_p ≈ 200 nm, and an average separation of d ≈ 480 nm between pores. All membranes were coated with a thin film of silver on the side that was not exposed to the electrolyte in order to serve as a cathode (working electrode) for the electrolytic bath. A series of arrays of continuous Co nanowires were synthesized by electrodeposition at room temperature from baths consisting of aqueous solutions of 40 g/*l* cobalt sulfate ($CoSO_4{\cdot}7H_2O$) and 40 g/*l* boric acid (H_3BO_3) having a range of pH values inside the pores of commercial track-etched polycarbonate membranes [7]. The pH values were adjusted by adding appropriate sulfuric acid (H_2SO_4) or sodium hydroxide (NaOH) solution. Co nanowires were deposited at the constant deposition potential of – 0.85 V against a Ag/AgCl reference electrode and at room temperature during the equal deposition times. A platinum wire was used as the

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counter electrode in a three-electrode electrochemical cell.

The crystal structure and the morphology of the Co wires were investigated by X-ray diffraction and scanning electron microscopy, respectively. Fig. 1 shows X-ray diffraction patterns of continuous hcp Co nanowires, which demonstrates a predominance of the hexagonal close packed (hcp) phase of cobalt stable at room temperature and a slight amount of face-centred cubic (fcc) Co.

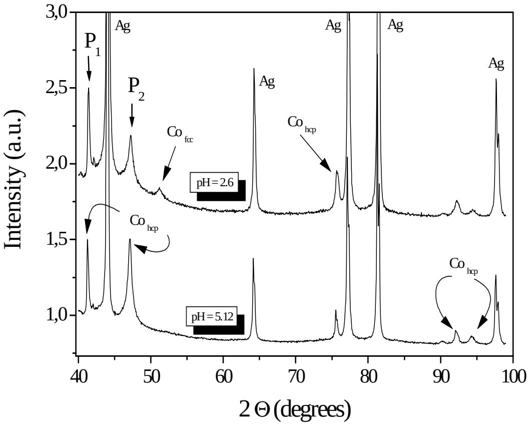

FIG.1: X-ray diffraction patterns of continuous hcp Co nanowires.

The above figure shows two different patterns for Co nanowires produced with electrolytes pH of 2.6 (top) and 5.12 (bottom). At $2\Theta = 41.5\pm0.1$ and $2\Theta = 47.3\pm0.1$ degrees are peaks P1 and P2, respectively. Also seen in the pattern of Fig. 1 are polycrystalline fcc (200), (220), (311), (222) peaks from the sputtered Ag electrode. In Fig. 2, it can be seen that the peak intensity ratio Co $(10\bar{1}1)$ / Co $(10\bar{1}0)$ of the same pattern increases with increasing value of solution pH indicating the existence of a strong $(10\bar{1}1)$ texture at high pH (> 4). At low pH (< 2), the face-centred cubic (fcc) phase is the mostly expected microstructure of Co wires.

Fig. 3 shows the dependence of the relative peak intensities Co $(10\bar{1}1)$ / Co $(10\bar{1}0)$ on the electrolyte pH. Comparing the relative peak intensities of our samples with that of polycarbonate membranes coated with a thin film of silver, one can observe that the intensity ratio of the Co $(10\bar{1}1)$ / $(10\bar{1}0)$ peak increases as the solution pH increases up to pH ≈ 4, it then decreases as the pH value increases up to 5.80. This is shown in Fig. 3.

The hexagonal c-axis lies preferentially perpendicular to the wires [2c, 8]. This change in cobalt peak intensity ratio may be understood as the corresponding change in the crystallographic orientation of Co wires. The hcp $(10\bar{1}0)$ texture is typical for these wire diameters [4c, 9] as opposed to shorter diameters (near 35 nm), which have hcp structures with the crystalline c-axis parallel to the wire axis [4]. In any case, the final texture of the wires obviously depends on the plating procedure. In fact, Paulus *et al.* [9d] found that the direction of the hexagonal c-axis is nearly independent of the wire diameter and that the change of the easy axis is

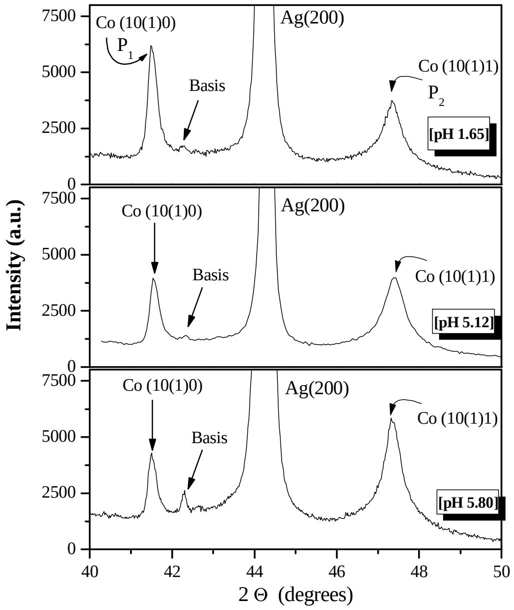

FIG.2: X-ray diffraction patterns from membranes containing typical three Co nanowires samples prepared at various electrolyte pH values.

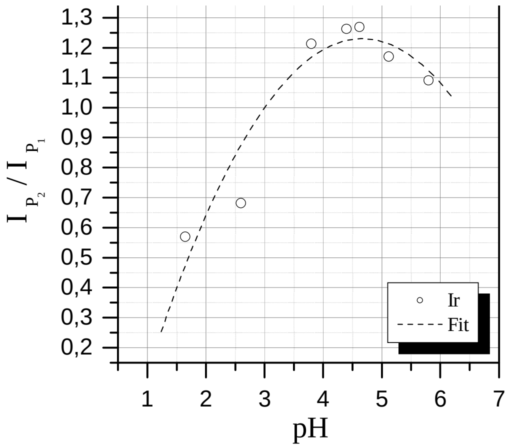

FIG.3: Dependence of the relative peak intensities Co $(10\bar{1}1)$ / Co $(10\bar{1}0)$ on the electrolyte pH.

due to an increasing amount of fcc-Co in smaller pores, whereas Fert *et al*. [4c] argue that this is due to a reorientation of the hexagonal c-axis. The preferred crystallographic orientation of the Co wires seems to be very sensitive to the growth conditions [10].

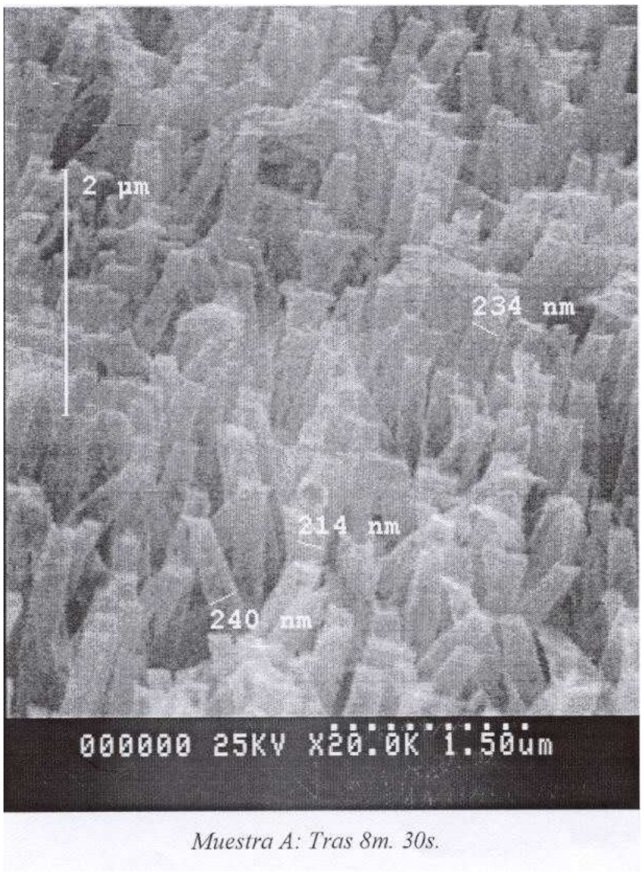

FIG.4: SEM micrograph image of Co wires of 200 nm diameter after removal of a part of polycarbonate membrane.

Fig. 4 shows a SEM image of Co wires of 200 nm diameter after removal of a part of polycarbonate membrane. The wires are cylindrical.

3. Results and discussion

3.1 Influence of pH on H_c, SQ and $M_{H=11\ kOe}$

We used a vibrating sample magnetometer (VSM) and a torque magnetometer at a maximum applied magnetic field of 11 kOe at room temperature and recorded the magnetization and torque curves in order to determine magnetic properties, such as M_H, H_c, SQ and K_{eff}.

In our results, we show that a change in the pH value of the electrochemical solution causes change in the crystallographic orientation of the Co wires (Figs. 2 and 3) and thus a corresponding change of magnetic properties.

Table 1 summarises the dependence of $M_{H=11kOe}$, H_C and SQ on the electrolyte pH for electrodeposited wires on a silver substrate. Fig. 5 shows the variation of the maximum magnetization, coercive field and hysteresis loop squareness with the electrolyte pH for Co wires electrodeposited at room temperature and the same deposition potential of – 0.85 V. From Fig. 5, it may be seen that as the electrolyte pH increases from 1.65 to 5.80, the

Table 1: Dependence of $M_{H=11kOe}$, H_C and SQ on the electrolyte pH for electrodeposited wires on a silver substrate.

pH	Voltage (V)	$M_{H=11\ kOe(Oe)}$ (emu)	$H_{C\perp\,|\,//}$ (Oe)	$SQ_{\perp\,|\,//}$
1.65	-0.85	5.15 E-3	250 / 211	0.12 / 0.13
2.60	-0.85	4.95E-3	272 / 215	0.13 / 0.15
3.81	-0.85	4.48 E-3	314 / 234	0.14 / 0.20
4.40	-0.85	4.41 E-3	298 / 227	0.14 / 0.21
4.62	-0.85	4.47 E-3	323 / 211	0.18 / 0.20
5.12	-0.85	34.00E-3	295 / 250	0.10 / 0.11
5.80	-0.85	4.00 E-3	338 / 255	0.16 / 0.23
7.80	-0.85	6.70 E-4	465 / 551	0.20 / 0.55

maximum magnetization decreases, and both the coercive field and squareness of the Co wires increase and then reach a transition point at pH ≈ 4. From these results, one can observe that pH adversely affects the maximum magnetization and Co wires exhibit enhanced magnetic coercitive field H_c and squareness SQ in comparison to bulk Co.

At pH of 7.80, the $CoSO_4$ solution was not stable and we saw the Co-hydroxide precipitation. That is the reason why we worked with samples prepared below the pH value of 6.

3.2 Influence of pH on the effective anisotropy constant k_{eff}

Magnetic torque measurements were carried out at room temperature using a Digital Measurement Systems model 1660 Torque Magnetometer, as a function of the electrolyte pH.

Fig. 6 shows the torque curves measured at room temperature on arrays of Co nanowires of 200 nm diameters with fixed length and varying electrolyte pH, and fits to the experimental data according to equation (2). As can be seen from the above figure, the shape and the periodicity of the torque curves prove the existence of a uniaxial magnetic anisotropy with an easy axis of magnetization parallel to the plane of the membrane. The torque experiments data were performed with the external magnetic applied field (H_{max} = 11 kOe) perpendicular to the sample plane.

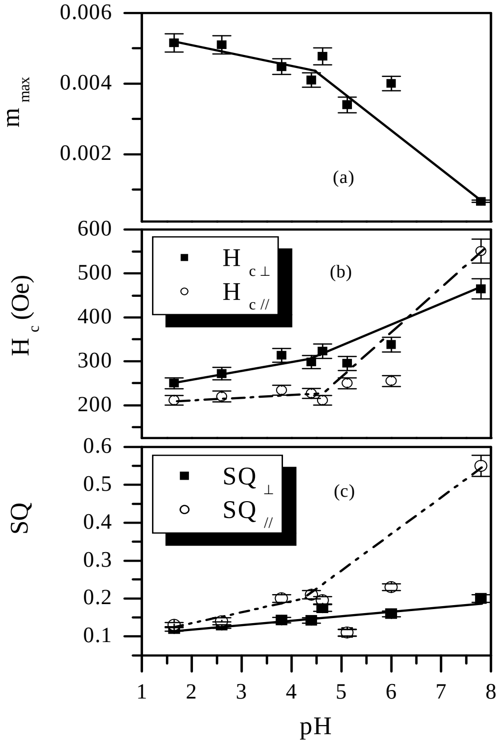

FIG.5: Variations of: (a) the maximum magnetization, (b) the coercive field and (c) the hysteresis loop's squareness with the electrolyte pH for Co wires electrodeposited at room temperature and at the same deposition potential of – 0.85.

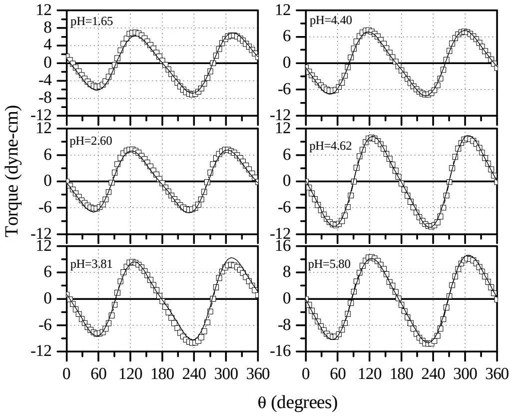

FIG.6: Torque curves measured on arrays of Co nanowires.

To simplify the analysis of torque measurements, we have assumed that the magnetization and the applied field are nearly collinear in all cases, and the fourth order anisotropy constant is negligible. In this case the angle dependent part of the uniaxial anisotropy energy is given by [11]:

$$E_A = k_{eff}\,\sin^2(\theta) \qquad (\mathrm{erg/cm^3}) \qquad (1)$$

where θ is the angle between the magnetization and the normal to the plane of the membrane, and k_{eff} is the effective anisotropy constant . Then, the torque is expressed by:

$$\Gamma = -k_{eff}\,\sin(2\theta) \qquad (\text{dyne-cm}) \qquad (2)$$

Equation (2) was fitted (solid lines on Fig. 6) to the experimental data (open squares) to determine the effective anisotropy constant. Fig. 7 shows the dependence of the effective anisotropy constant k_{eff} on the electrolyte pH. From this figure, it is clear that the electrolyte pH can cause significant changes to the effective magnetic anisotropy constant of electrodeposited Co wires, which reaches a maximum at pH ≈ 4. Comparing the X-ray diffraction data and the data obtained from magnetic measurements, this change in k_{eff} as a function of pH can be understood as due to the change in the crystallographic orientation of the Co wires. Fert *et al.* [4c] have observed a similar change in the crystallographic orientation of Co wires. Croll [4a] had observed the effect of electrolyte pH on crystallographic orientation for Co films and Schwarzacher *et al.* [12] had also observed a similar behavior on the measured GMR for Co films (*actually Co-Ni-Cu/Cu multilayers).* Valizadeh *et al.* [2c], Cheng *et al.* [2b] and Darko *et al.* [13] have similarly found that the obtained electrodeposited Co film depends on the pH of the electrolyte.

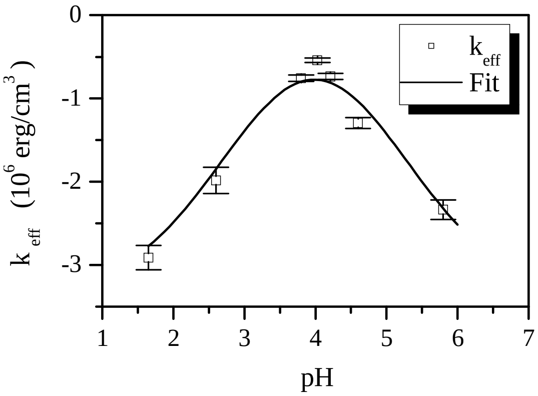

FIG.7: Dependence of the effective anisotropy constant k_{eff} on the electrolyte pH. The solid line is a guide for the eye.

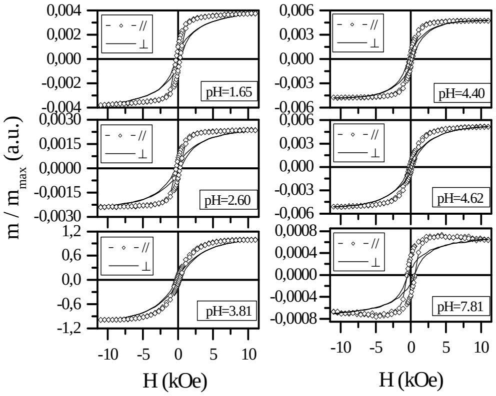

FIG.8: Normalized hysteresis loops at room temperature of arrays of Co nanowires of 200 nm diameter deposited at different electrolyte pH, and recorded with the field applied parallel (–◊–) and perpendicular (—) to the wire axis.

Finally, we would like to note that the presence of asymmetrical sine curves in torque measurements are most likely a result of an assumption that co-linearity between the direction of magnetization and the maximum applied field of H_{max} = 11kOe is not exactly correct. Fig. 8 shows a comparison, at room temperature, of the normalized hysteresis loops of arrays of 200 nm diameter Co nanowires deposited at different electrolyte pH, recorded with the field applied parallel (–◊–) and perpendicular (—) to the wire axis. Details of the magnetic properties of Co wires are described elsewhere [10, 11, and 14]. Clearly, they present different structural and magnetic behavior as a consequence of changes in electrolyte pH values that will allow the possibility of predetermining the preferential orientation of c-axis of wires. Fig. 8 essentially reflects results given in Table 1. One can see that from pH value of 1.65 to 4.62, the c-axis of wires changes from perpendicular to parallel to the plane of polycarbonate membranes. At pH value of 7.80, our solution was not yet stable and we saw the precipitation of Co-hydroxide.

In general, the pH value can influence the electrodeposition process by changing the coordination of metal ions in solution and at electrodes, and by changing the rate of hydrogen evolution at the cathode. But, we think that the pH value could have an influence on the growing mechanism of Co nanowires due to the hydrogen evolution at higher pH value. This could hinder the deposition of Co material.

4. Conclusion

In conclusion, continuous Co nanowires with diameters of 200 nm have been successfully synthesized by electrodeposition into commercial track-etched polycarbonate membranes with thicknesses of $L \approx 7\ \mu m$. X-ray diffraction measurements showed the hexagonal close-packed structure for all samples with only a small amount of the cubic phase (see Fig. 1). We think that this presence of fcc Co may be due to the use of an fcc substrate (Ag). Wires, electrodeposited from Co sulphate baths at pH values below 4, exhibit strongly preferred orientation of the hexagonal axis in the plane of the polycarbonate membranes. Whereas, wires obtained from solutions with pH values above 4 are characterized by weak $(10\bar{1}0)$ peaks and strong peaks corresponding to the $(10\bar{1}1)$. This implies that the electrolyte pH induces a strong modification of crystal anisotropy of Co wires. The overall uni-axial anisotropy was always negative (see Fig. 7) at room temperature (25ºC), which implies a preference for a transversal orientation of the magnetization, i.e. perpendicular to wire's axis. The change in preferred crystallographic orientation occurs at approximately pH ~ 4 (see Fig. 7). The preferred crystallographic orientation is most pronounced just below and just above the transition point (pH ≈ 4). Thus, the pH value controls the crystallographic orientation of Co wires and their magnetic behavior.

From torque magnetic measurements, we found that the effective anisotropy constant increases with the increase of the electrolyte pH value. This result suggests that at pH ≈ 4, the Co wires change their crystallographic orientation. The Co wires growth conditions, which we have demonstrated by ours studies, is a key factor to an understanding of their magnetic behaviour [14]. Finally, the magnetic measurements confirmed that there is an enhancement of coercitive field and squareness in Co nanowires.

Note added: Recently, it came to our notice a study that deals with the effect of electrolytic bath acidity on magnetic properties of electrodeposited Co nanowires arrays and their correlation with the crystalline properties [15].

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