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# Influence of the synthesis parameters on the crystallization and magnetic properties of cobalt nanowires

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**Abstract**

Cobalt wires have been synthesized by electrodeposition in porous polycarbonate membranes with a pore diameter of $\approx 200$ nm and a thickness of $\approx 6$ μm. The influence of the citrate concentration, and different substrates (Ag, Cu), sputtered on the bottom of membranes, on the nanocrystalline structure and magnetic properties of the wires are discussed. Crystallization of the wires as a function of the synthesis bath conditions was measured by X-ray diffraction and the magnetic properties at room temperature were measured using vibrating-sample magnetometry. Differences, on deposition rate and crystalline domains size, have been observed, as well as the coercive forces and the hysteresis squareness change in the hysteresis loops of the wires depending on the citrate concentration in the electrochemical bath. 

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## 1. Introduction

The electrodeposition of Co nanowires from aqueous solutions has received a great deal of attention in the last few years in comparison with metals such as Cu, Ni, Si, Au or Ga [1–3]. However, attempts have been made to electrodeposit Co nanowires from different baths [1–7]. The advantages of these baths are their low cost, simplicity and, the fact that they do not contaminate the environment. Besides, the magnetic properties of Co nanowires are of special interest in electronic applications and particularly in the computer industry [8].

In this work we report the effects of citrate concentration on the structure and magnetic properties of electrodeposited Co nanowires in solutions of $CoSO_4 \cdot 7H_2O$ and $H_3BO_3$. It can be seen that the citrate concentration affects the crystallization and magnetic properties.

## 2. Synthesis of the samples

A single-compartment electrochemical cell made of Pyrex glass was used throughout this work. Previous to the electrodeposition of the wires, a layer of Cu or Ag was sputtered on one side of track-etched polycarbonate membranes with a pore diameter of $D_p \approx 200$ nm and a thickness of $L \approx 6$ μm [9–11] to act as the substrate and working electrode during the electrodeposition. An

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(Ag/AgCl) electrode was employed as reference and the auxiliary electrode was platinum (Pt). Electrodeposition was performed using a potentiostat (Potentiostat Autolab PGSTAT20) in quiescent conditions at $T \approx 25°C$. The work was carried out at constant potentials in the range (0.75–0.95 V) and the composition of the electrolyte is displayed in Table 1. To study the magnetic properties as a function of the length of the nanowires, the electrodeposition process was stopped before the wires emerge from the surface of the membrane as indicated by an increase of the current (see Fig. 1). Fig. 1(a) shows the three regions of wires growth [12]. Region I corresponds to the deposition of the electrodeposits into the pores until they are filled up to the top surface of the membrane. Beyond this, growth can continue in

Table 1
Bath composition

| $H_3BO_3$ | $CoSO_4 \cdot 7H_2O$ | $(NH_4)_2HC_6H_5O_7$ |
|---|---|---|
| 40 g/l | 40 g/l | 0–40 g/l |
| Sigma | Sigma | Aldrich |
| 99.5% | 99% | 99.9% |

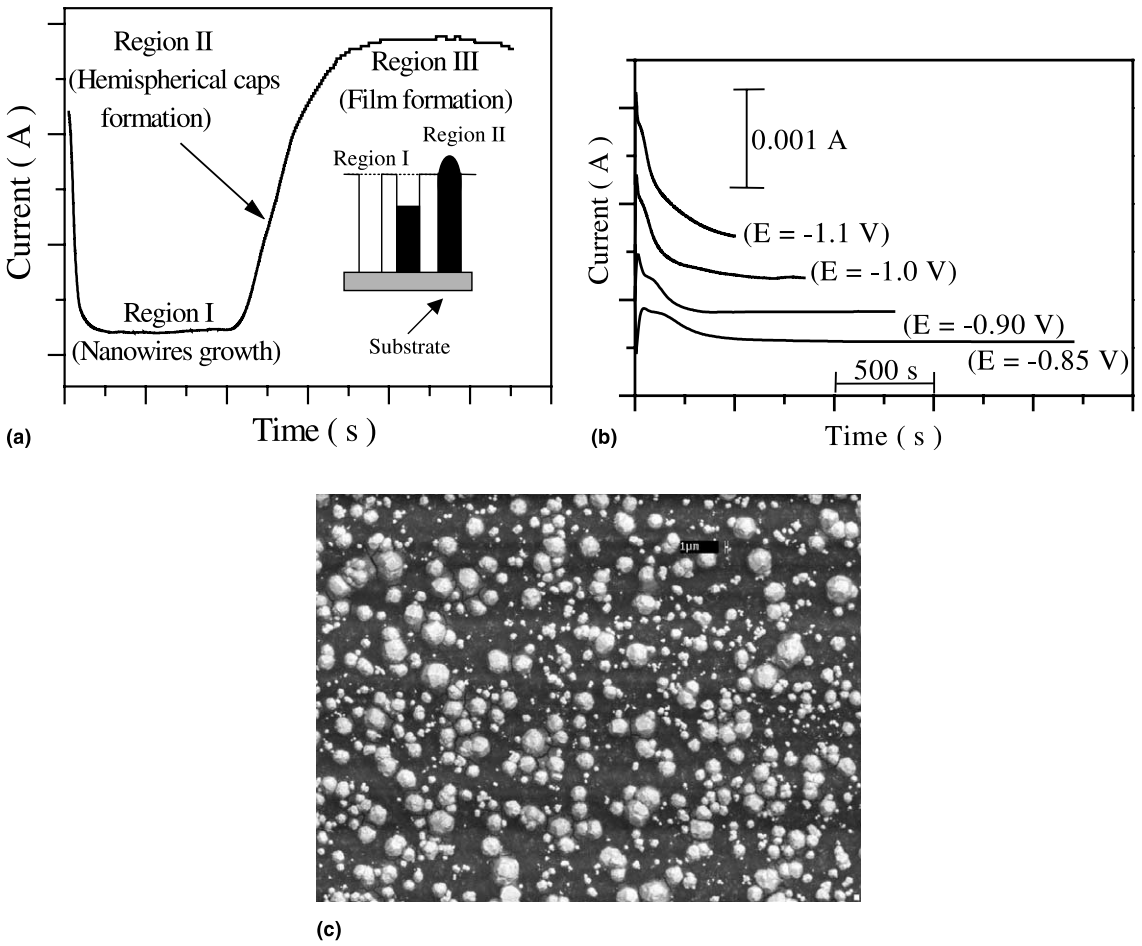


Fig. 1. (a) Current–time $I(t)$ curve for electrodeposition of Co in a polycarbonate membrane with 200 nm diameter pores. (Inset the schematic displays two different stages of the growth process: in Region I, Co wires grow into the pores; in Region II, the pores are completely filled and upon them hemispherical caps are formed). The Region III corresponds to the film formation. (b) Current $I(t)$ as a function of the synthesis-time curve for distinct reduction potentials. (c) SEM image of the top surface of polycarbonate membrane with hemispherical caps formed.

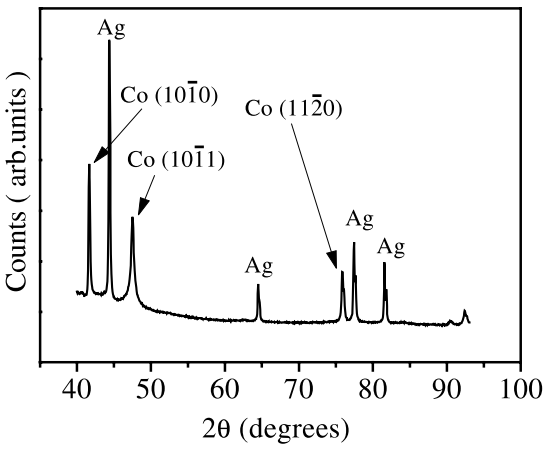


Fig. 2. X-ray diffraction patterns of Co hcp with a $\langle 10\bar{1}0\rangle$ texture in polycarbonate membranes with pore diameters of 200 nm.

the three dimensions: hemispherical caps are formed over the ends of the wires (see Fig. 1(a) Region II and Fig. 1(c)). The third region corresponds to the formation of a metallic layer on the top surface of the membrane. Fig. 1(b) shows the curves of electric current as a function of the deposition time at distinct reduction potentials for nanowires of equal length, therefore the final time of each curve corresponds to the end of the Region I. It can be seen that, at larger potentials, it is difficult to determine the end of the synthesis, because no constant currents are observed before the current increases. For this reason, it is preferable to use smaller deposition potentials in order to decrease the deposition process rate.

Structures, determined by means of X-ray diffraction, as shown in Fig. 2, indicate that Co is stabilized in the hcp structure and that its easy $c$-axis is perpendicular to the axis of the wire.

## 3. Results

Room temperature magnetic properties of the array Co wires were measured using a vibrating sample magnetometer (DMS model 1660).

Fig. 3 displays the coercive force, $H_c$, and the hysteresis squareness, $SQ$, as a function of the reduced magnetic moment $m_{max}/m_0$ for synthesized wires at different potentials. In our results,

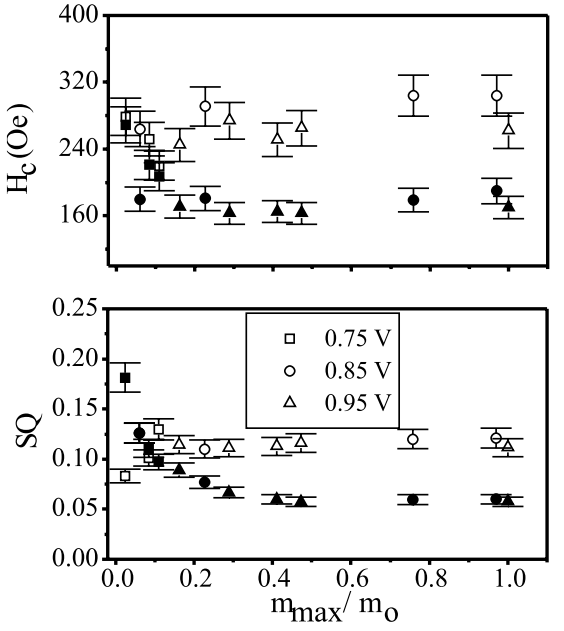


Fig. 3. Coercitive force, $H_c$, and squareness, $SQ$, as a function of reduced magnetic moment $m/m_0$, with the applied field perpendicular (○) and parallel (●) to the nanowires axes.

$SQ = m_r/m_{max}$ , where $m_r$ is the remanent magnetic moment and $m_{max}$ is the maximum magnetic moment reached at the maximum applied field, $H_{max} = 11$ kOe, for each sample. Moreover, as $m_0$ is the maximum of the magnetic moment for the longest wires, the reduced magnetic moment $m_{max}/m_0$ is proportional to the length of deposited Co wires.

## 4. Discussion

From these results, we conclude that the values of $H_c$ and $SQ$ obtained are quasi-independent of deposition potentials. Both quantities decrease as the lengths of wires increase, with the applied magnetic field parallel to the wires' axes.

To determine the influence of citrate on the crystallization of these systems, we have been performing experiments in which, citrate concentration was changed as indicated in Table 1. Other authors [6,7] report experimental evidences that the citrate has a tendency to be adsorbed by the surface of the working electrode (case of Cu) and

may form a complex with Co in many forms, so modifying the crystalline grain size. Fig. 4 shows the voltammetric cycles that correspond to the citrate variation in the reaction medium. A displacement of voltammetric curves towards more negative potentials and a reduction in the intensity of peak, corresponding to reduction in the electroactive species, $Co^{2+}$, when citrate concentration increases were observed (Fig. 4). These variations are due to the change in the sphere of coordination of the $Co^{2+}$ ions, which form a complex with citrate molecules [6,7]. As citrate is added in the synthesis process, a change in the width of the X-ray diffraction of the crystals can be seen (Fig. 5). This change, in the widths of the peak for Co situated at $2\theta \approx 41.6°$ and 46.6°, implies a decrease in crystalline size [6,7]. Fig. 6 shows the magnetic properties, $m_{max}/m_0$, $H_c$, and $SQ$ of the wires with respect to citrate concentration (wires synthesized at 0.85 V with citrate in the electrochemical medium). Fig. 6(a) shows a decrease in the maximum magnetic moment which may be interpreted, from the electrochemical point of view, as a decrease in the intensity of current (in the case of a fixed deposition potential) when the citrate concentration increases. For this reason the deposition process rate decreases and we obtain the shortest wires at the same deposition time. Meanwhile, Figs. 6(b) and (c) show an increase in both $H_c$ and $SQ$ as the citrate concentration increases. This increase in $H_c$

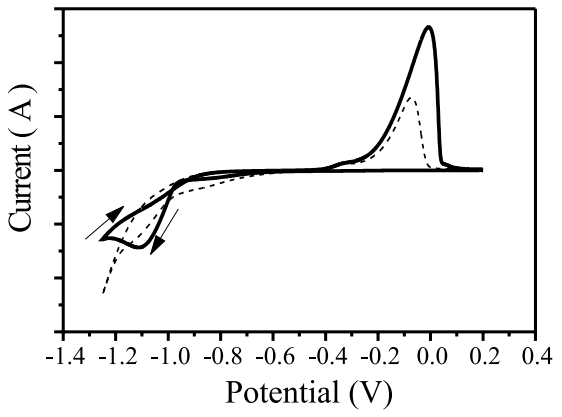


Fig. 4. Voltammetric cycles obtained from electrolytes containing variable citrate concentration in the electrochemical medium. Dash line (- - - - 0.25 g/50 ml) and solid line ( – - 2.00/50 ml). The arrows indicate the cycling direction of the voltage.

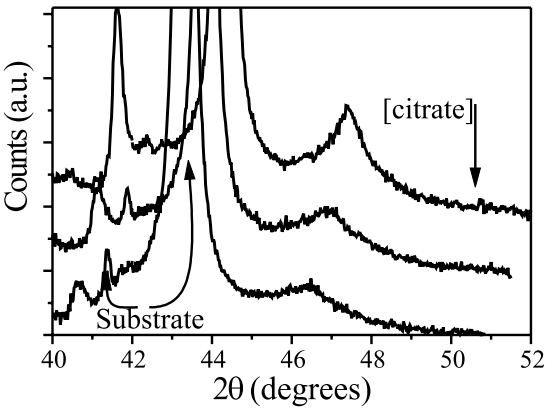


Fig. 5. X-ray diffraction patterns of Co wires deposits prepared from electrolytes with variable citrate concentration (g/50 ml).

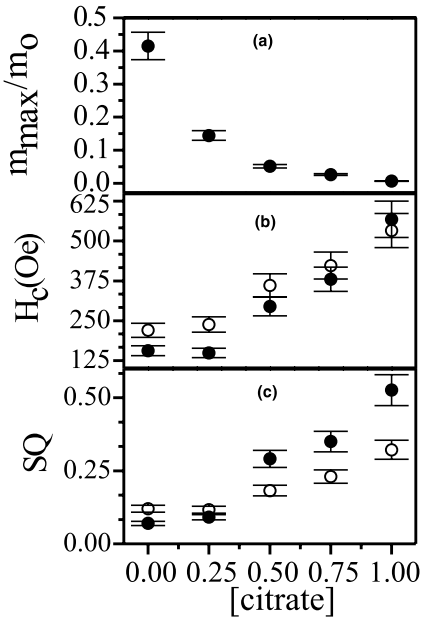


Fig. 6. (a) Reduced magnetic moment $m_{max}/m_0$, (b) coercitive force $H_c$ and (c) squareness $SQ$ as function of citrate concentration, with the applied field perpendicular (○) and parallel (●) to the nanowires axes.

and $SQ$ may be understood as a decrease in both the size of crystalline domains and the total length of nanowires, which act as arrays of magnetic dipoles. The $H_c$ and $SQ$ of these arrays of magnetic dipoles correspond to the competition between magnetocrystalline, shape, and interaction energy between nanowires [12,13]. In Fig. 7, the changes

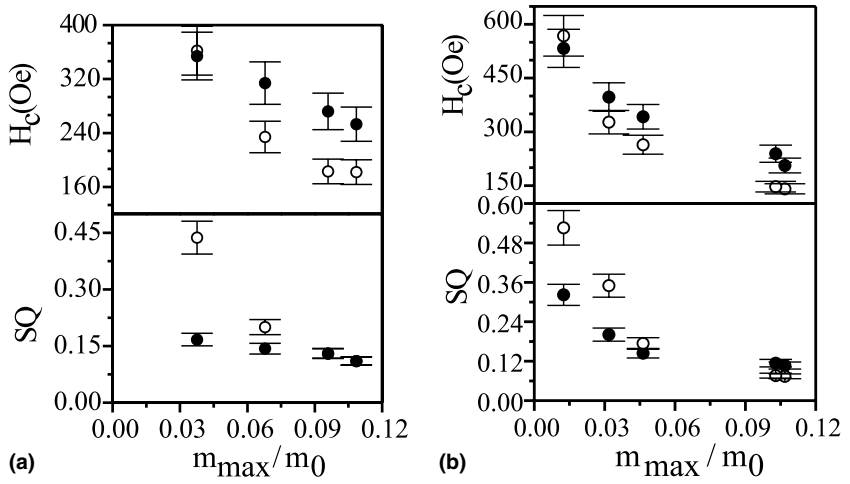


Fig. 7. Coercitive force, $H_c$, and squareness, $SQ$, for (a) Ag and (b) Cu used as substrate, with respect to the reduced magnetic moment, with the applied field perpendicular (○) and parallel (•) to the nanowires axes.

in $H_c$ and $SQ$ with respect to $m_{max}/m_0$ (with citrate in electrochemical bath synthesis) are shown. Similar dependence to that observed in Fig. 3 is seen, but in this case, $SQ \approx 0.5$ are obtained regardless of whether Ag (Fig. 7(a)) or Cu (Fig. 7(b)) is used as the substrate, whilst when citrate is not present in the synthesis medium, $SQ \approx 0.2$ (Fig. 3). That is to say, we have doubled the parameter $SQ$. However, the relation of $H_c$ in both directions perpendicular and parallel, is almost constant, although these $H_c$ increase when the size of the wires decreases.

## 5. Conclusion

Based on the results obtained, we conclude that citrate produces two effects: it slows the synthesis process rate down and it diminishes the size of the crystalline domains and tends to cause the formation of non-crystalline systems: But the same distribution of the existing crystalline domains is maintained all along a wire.

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