

Research Article

Growth and Magnetic Properties of Polycrystalline Self-Assembled Bifurcated Co Nanowires

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We use anodization of aluminum foil with variable applied anodization voltage to create an alumina template with bifurcated porous structures. The template is then used to electrodeposit Co, fabricating unique bifurcated Co nanowires. In order to better understand the crystal structure of our new material, we then report magnetic properties of these self-assembled bifurcated Co nanowires. Magnetic measurements of the bifurcated wires are studied as functions of branch/stem ratios, wire length, and temperature. The results are compared with those of straight Co nanowires of similar dimensions and thin film Co samples to find that a different crystal lattice structure prevails in the stems than in the branches of the wires.

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1. INTRODUCTION

The fabrication of magnetic nanowires and investigation of their magnetic properties have been the focus of much research [1–4]. Particularly, the combined process of anodization of aluminum foil to produce nanoporous alumina templates and electrodeposition of magnetic nanowires inside such templates has attracted significant attention for its high yield, low cost, and rapid throughput of ordered nanowires arrays [1–5]. Interest lies in understanding the crystalline geometry and temperature-dependent properties due to the possible applications in magnetic recording devices and interesting fundamental physical phenomena [1, 6–9]. However, because these wires are grown using self-assembled techniques, their crystal structure can be somewhat questionable [10, 11]. As-deposited ferromagnetic wires tend to exhibit multiple magnetic domains due to graininess. And, as the wires get smaller in diameter, single domain particles are extant, manifesting in superparamagnetic effects. Moreover, magnetocrystalline anisotropies, due to interactions between different crystal structures in the wire, can greatly affect the measured magnetic behavior.

In this work, we show that we have created a new type of nanostructure, bifurcated Co nanowires, using porous alumina templates and electrodeposition. We prepared these nanowires in a unique bifurcated geometry, where the wires

consist of a single stem bifurcating into two branches with smaller diameters which subsequently join together to form a single stem at the other end. We report our results on the crystal structure as probed by the magnetic properties of the Co nanowires. We have investigated the effects of wire length, sectional proportions, and temperature dependence. The results are compared with straight (unbranched) nanowires and also thin film specimens.

2. FABRICATION

In order to fabricate the alumina templates, a 99.997% pure Al foil of 0.125 mm thickness is first degreased in ethanol and then loaded into an electrolytic cell. The Al foil acts as the anode, and at a distance of 11 cm, a Pt mesh acts as the cathode. The cell is filled with a solution of 15% sulfuric acid (v/v) and held under potentiostatic (i.e., controlled voltage) conditions. The mechanics of anodic porous alumina is adequately discussed in [12, 13] and will not be repeated here. For the straight nanowires, we first prepared a nanoporous alumina template consisting of an array of vertically arranged cylindrical pores. For this, a constant voltage of 10 V is applied across the electrodes. Under these conditions, nanoporous alumina forms at the surface with pore diameters of around 10 nm. Subsequently, Co nanowires are prepared inside the pores by means of

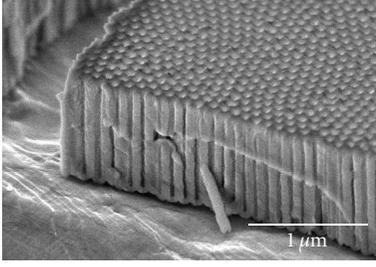


FIGURE 1: SEM image of straight alumina template. Anodization conditions yield 40 nm pore diameters and approximately 1 μm pore lengths.

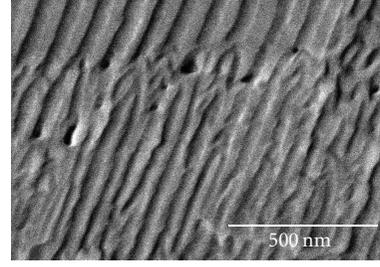


FIGURE 2: SEM image of bifurcated alumina template. Anodization conditions yield 40 nm branch diameters and 20 nm stem diameters. Note the region of bifurcation where the larger pores form Y-shaped junctions.

electrodeposition. Electrodeposition is carried out under AC conditions at 20 V and 250 Hz with a cobalt solution containing 10 g cobalt heptahydrate and 2.5 g of boric acid dissolved in 250 mL of water and with a Pt mesh acting as a counter electrode. In order to prepare the bifurcated nanowires, we started with a template consisting of the desired branched pore structure. For the magnetic studies reported here, during the anodization process, the applied voltage was initially set at 10 V and then reduced to 7.1 V and subsequently set back at 10 V. This results in 10 nm diameter stems at the two wire ends with 7 nm diameter branches in the midsection. However, more generally, the selection of bifurcation voltages is based on a simple relation between the stem voltage V_S and the branch voltage V_B given by

$$V_B = \frac{V_S}{\sqrt{n}}, \quad (1)$$

where n is the desired number of branches [14]. Thus, for two branches, the anodizing voltage for the branches turns out to be 7.1 V when the anodizing voltage for the stem is 10 V. Anodization time for each step was adjusted depending on the desired lengths of the individual wire sections.

A typical image of straight and branched pore templates is shown in Figures 1 and 2. A 3/4 top-down view of a straight pore template (anodized at 40 V) obtained using SEM is shown in Figure 1 while Figure 2 shows a bifurcated template made by anodizing under 40 V/28 V/40 V conditions. Figure 3 shows a schematic and an SEM micrograph of a typical bifurcated nanowire prepared in a bifurcated template. We used larger samples for visualization than we did for the magnetic measurements due to the extreme difficulty in viewing the smaller size wires with SEM. However, here we are only interested in the magnetic properties of the smaller nanowires, which, due to their small size, provide a perfect platform for studying the effect of low magnetic domain materials, as discussed below. For comparison of magnetic properties of the wire samples with thin films, we prepared Co films deposited on commercial Al foil by thermal evaporation of Co (99.5% pure from Alfa Aesar). Using this method, we created a polycrystalline film whose thickness was approximately 2 μm which is comparable to the total length of straight and bifurcated nanowires.

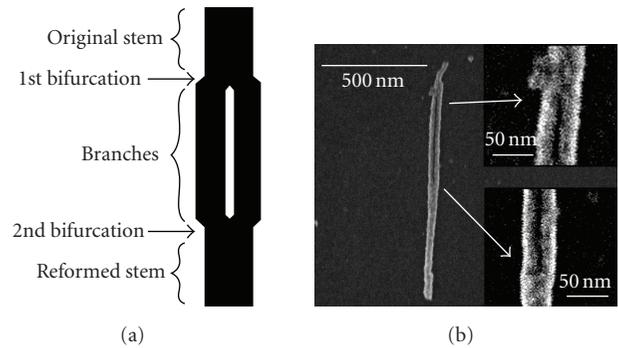


FIGURE 3: (a) Schematic representation of a bifurcated nanowire with taxonomy (b) micrograph of a Co bifurcated nanowire with insets on the regions of bifurcation and convergence.

Magnetic measurements were subsequently taken with a Princeton Measurements Corporation AGM, for room temperature measurements (~ 300 K) and a Quantum Designs Corporation SQUID for variable temperature measurements (4–350 K).

3. RESULTS AND DISCUSSION

First, we discuss our results on the magnetization versus field curves for the nanowires in both perpendicular and parallel orientations of the nanowires. For clarity, we define the perpendicular alignment to be one in which the field is applied perpendicular to the surface of the template, or parallel to the cylindrical axis of the nanowires. The parallel alignment is defined as one in which the field is applied parallel to the surface of the film or perpendicular to the cylindrical axis of the nanowires.

Typical hysteresis loops are shown in Figure 4 for a typical bifurcated and straight Co nanowire-array sample with similar total wire length. In the case of the straight nanowires, the coercivity in the perpendicular direction is around 1000 Oe. In the parallel direction, the coercivity is negligible and is only around 151 Oe. This behavior is typical of magnetic nanowires where the magnetic properties are largely determined by shape anisotropy effects when compared to magnetocrystalline anisotropy. Also because

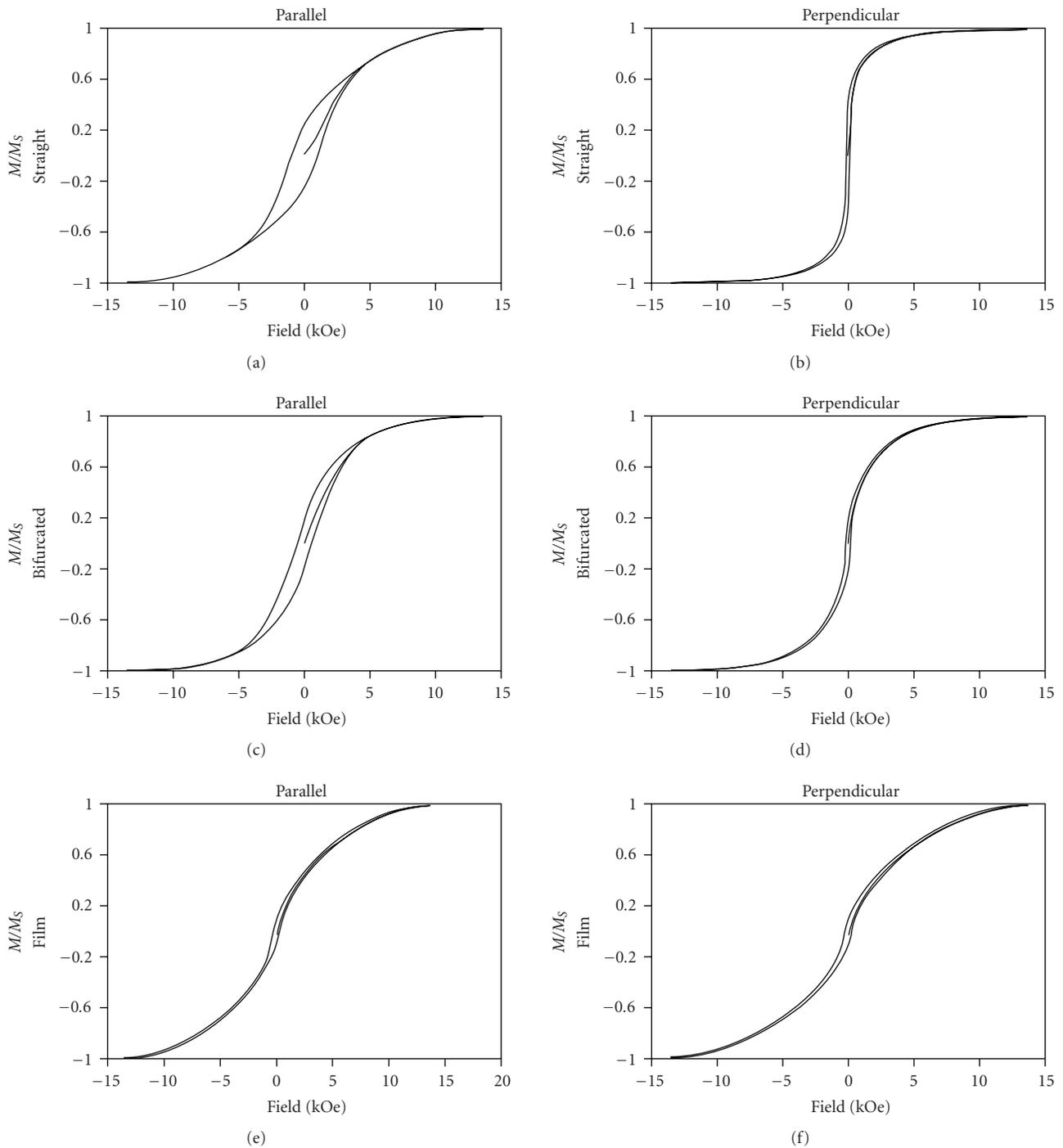


FIGURE 4: Hysteresis curves for perpendicular and parallel orientations of straight, bifurcated, and thin-film samples.

of the very large aspect ratio of the nanowires (>100), shape anisotropy effects clearly dominate magnetocrystalline anisotropy effects. For the bifurcated nanowires, the coercivity in the perpendicular orientation is only about 500 Oe (much lower than that for the straight nanowires). This reduced coercivity may be related to the reduced aspect ratio of the nanowires. The bifurcated nanowires can be thought of as consisting of four segments (two at the

midsection and one each at the two ends) with reduced aspect ratio (~ 30). Here, the magnetic properties are a result of competing shape anisotropy and magnetocrystalline anisotropy. In consistence with this explanation, it may be noted that the coercivity in the parallel direction is reasonable, ~ 150 Oe, as in the case of the straight wires. For comparison, Figure 4 also shows the magnetization versus field curves for polycrystalline thin film samples. Here, the

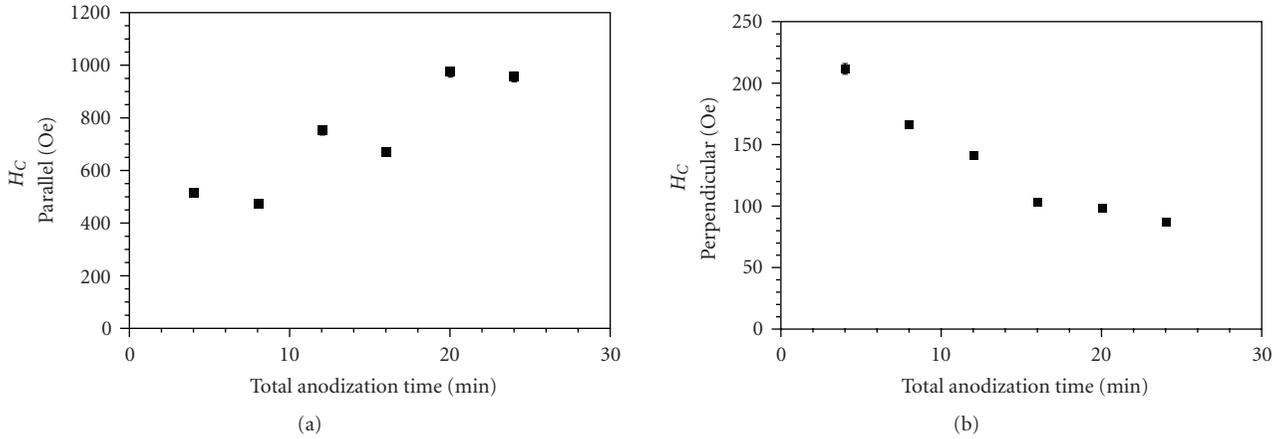


FIGURE 5: Coercivity as a function of anodization time for 1:2:1 bifurcated nanowires.

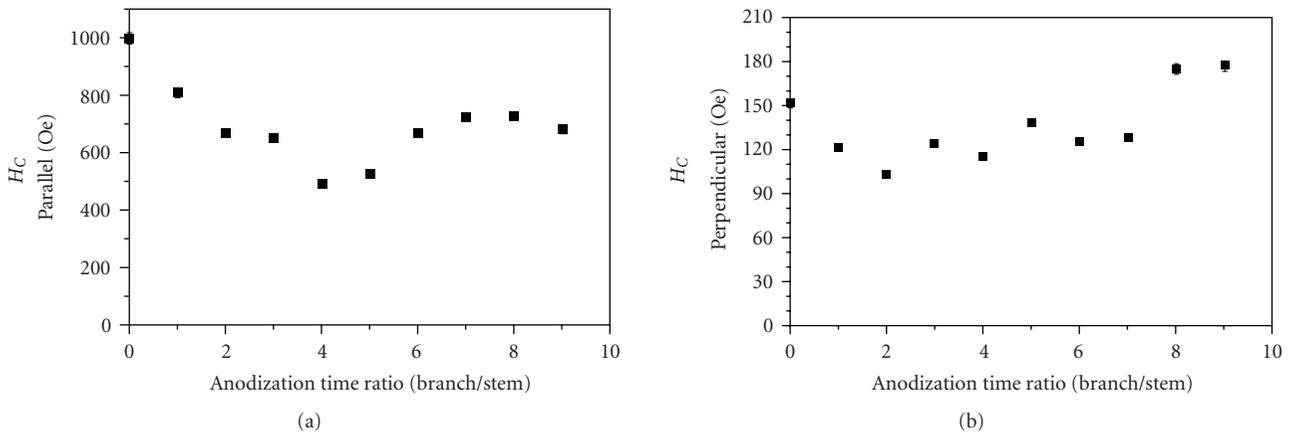


FIGURE 6: The anodization ratio is calculated as anodization time for the branch/anodization time for the stem.

coercivity in both the perpendicular and parallel direction is about 250 Oe. In thin films, the magnetization behavior is mostly dominated by magnetocrystalline anisotropy and multidomain effects. By comparing the thin films to the bifurcated and straight nanowires, it is evident that the magnetocrystalline anisotropy effects are only implicated in the reduced coercivities of thin films and larger diameter nanowires. In straight nanowires, clearly shaped anisotropy dominates. In the bifurcated wires, there appears to be a mixture of shape anisotropy and multidomain effects caused by the presence of ample defects and separate grains in the branched region of the wires (discussed below).

We have studied the dependence of coercivity as a function of total length of the nanowires and also as a function of branch/stem length ratios of the nanowires. For this, we first prepared the bifurcated templates with specific ratios of branch/stem and also specific total length of the pores. The obtained templates were then completely filled with Co. The anodization times took place in ratio of 1:2:1. For example, one sample was anodized for 2 minutes at 10 V, 4 minutes at 7.1 V, and 2 minutes at 10 V at 10/7.1/10 V (a total of 8 minutes). Each sample underwent electrodeposition until signs of overfilling were present. We

will not discuss the process of electrodeposition here, as it is adequately discussed elsewhere in the literature [15]. However, electrodeposition was halted before significant portions of the template were made to contain wires linked at the top.

Figure 5 shows the coercivity as a function of total anodization time. We see that in the perpendicular alignment, the coercivities tend to increase with time and in the parallel alignment, the coercivities tend to decrease with time. The reduced coercivity for the wires with shorter anodization time is attributed to presence of defects and possibly uncoupled superparamagnetic components in the wires. Thermal fluctuations can reduce the energy barrier for magnetization reversal which in turn reduces the coercivity. Interestingly, in Figure 6, the perpendicular coercivity is found to decrease with increased branch/stem ratio. This is consistent with the previous explanation. Presence of superparamagnetic components is expected to be comparatively higher in the branched sections of the nanowires due to the reduced diameter. This can lead to reduced coercivity for the wires with largest branch lengths.

Finally, we have also studied the temperature dependence of the net magnetization of the nanowires. For each

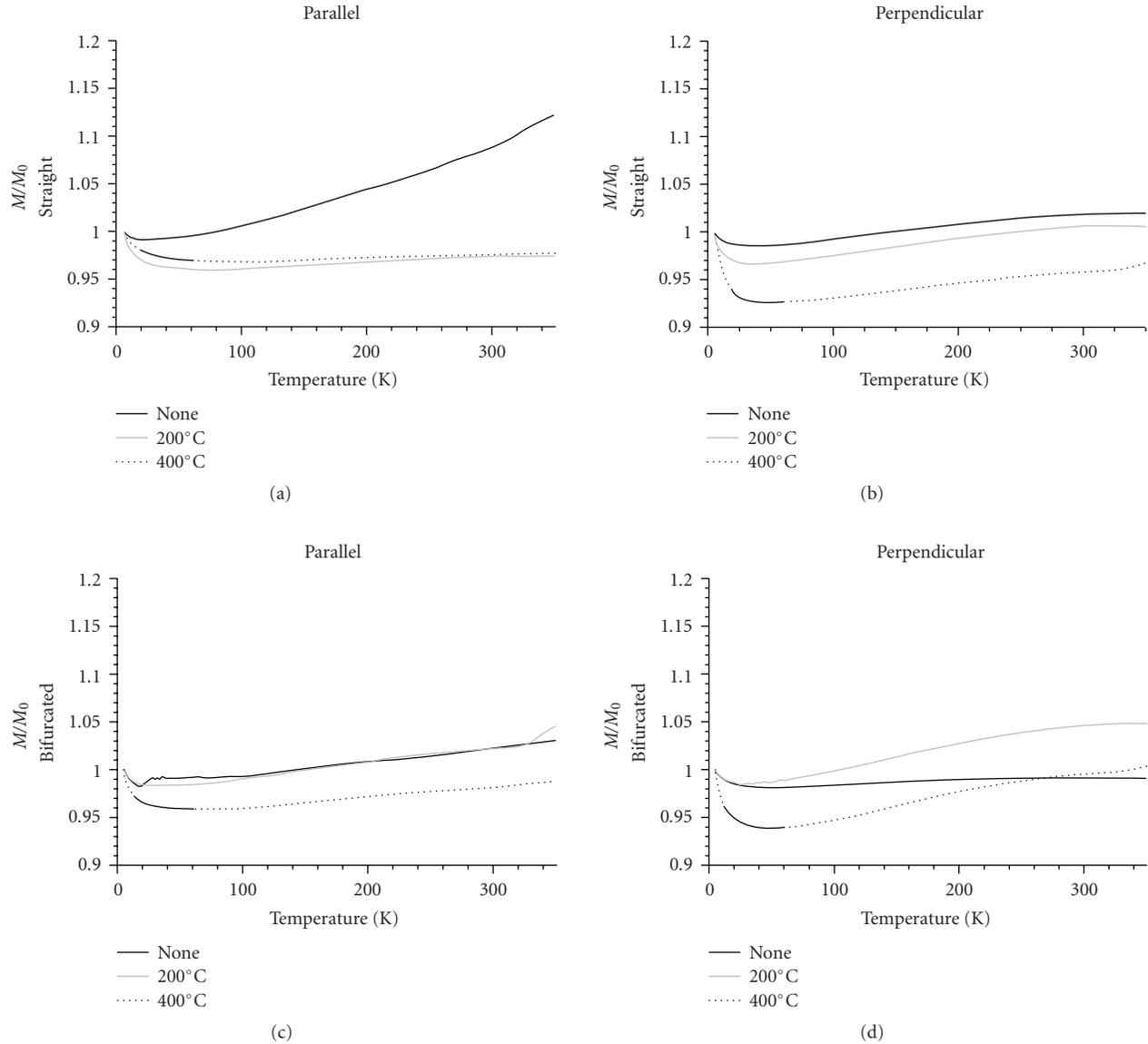


FIGURE 7: Zero field cooled magnetization versus temperature for straight and bifurcated nanowires in parallel and perpendicular alignments. Samples were annealed at 200°C and 400°C for comparison. Applied field was 5 kOe.

type of nanowire and alignment, samples were made as-deposited as well under two different annealing conditions 200°C and 400°C in air for 3 hours. Figure 7 shows the magnetization versus temperature plots for straight and bifurcated nanowires in both alignments (perpendicular and parallel) to applied field of 5000 Oe and zero-field cooled (ZFC). Field-cooled (FC) measurements were also taken (not shown here), however were found not to deviate significantly from the ZFC data. Interestingly, we observed no evidence of superparamagnetism when comparing the ZFC and FC plots, which is typically revealed in a maximum corresponding to the blocking temperature. Such a peak is expected due to the previous explanation of lowered coercivities being caused by increased superparamagnetic interactions. However, we expect the ferromagnetism of the wires to dominate, which could mask the appearance of a

blocking peaking. Moreover, the observed slight upturn the ZFC plots near low temperature can be partially attributed to superparamagnetic domains becoming ferromagnetic, thus contributing to the overall ferromagnetic moment.

Also, the magnetization versus temperature dependence does not demonstrate the expected Bloch law behavior. In general, the magnetic moment of alumina (as measured in blank alumina templates) is several orders of magnitude lower than that of the ferromagnetic wires; however, it does seem to contribute slightly to a paramagnetic upturn at lower temperatures. Moreover, this non-Bloch behavior could be due to magnetoelastic effects, as described by Kumar et al. in [16]. Expansion and contraction of the aluminum (upon which the template sits) due to the temperature change could be altering the orientation of the wires in the field. The expansion and contraction of aluminum under temperature

change, are much greater than that of alumina. Thus, the expansion and contraction would cause a slight curling of the sample in the field, which would alter the orientation of the wires in the applied field. This could be the cause of the slight decrease in magnetic moment as the temperature decreases (see Figure 7).

Annealing may help to reduce the graininess of the deposited Co, forming structures that are more crystalline. For the straight nanowires, the magnetization of the as-deposited sample is seen to be significantly larger at higher temperatures. This is not the case for the bifurcated nanowires. This may be attributed to multiphased nature of Co. Bulk Co is typically known to exist in hcp form at room temperature while the fcc phase is known to exist only at very high temperatures. However, in nanoscale forms of Co, particularly when prepared by means of electrodeposition, Co has been reported to exist in both forms hcp and fcc. It has been observed by Kröll et al. in [17, 18], through XPS and EXAFS studies, that in small Co nanoparticles, there is a decrease in hcp-Co in favor of fcc-Co. Hcp-Co is known to exhibit strong magnetocrystalline anisotropy in contrast with fcc-Co. This in turn reduces magnetocrystalline anisotropy in smaller Co nanowires—another indication of the strong shape anisotropy in our nanowire samples outweighing the effects of magnetocrystalline anisotropy. Interestingly annealing the sample appears to reduce the magnetization of the nanowires, which may be indicative of a phase-stabilization process achieved through the annealing process. Also for the annealed samples, the magnetization versus temperature exhibits a more typical Bloch law kind of behavior. This is also true for the bifurcated nanowires (both as-deposited and annealed samples) where the behavior is of the Bloch-law type. The smaller diameters of the midsection of the wires possibly ensure a more single-phased fcc-type Co in such small dimension wires.

4. CONCLUSIONS

In conclusion, we fabricated an interesting new geometry of nanowire using bifurcated anodic porous alumina templates. The pores were filled with Co using electrodeposition, and the magnetostatic properties were investigated in order to better understand the crystal structure of the wires. The magnetic properties indicate strong shape anisotropy effects which outweigh magnetocrystalline anisotropy. Also, magnetoelastic effects are visible in temperature dependent samples. Our results may also indicate the presence of Co in fcc-form rather than the usually observed hcp-form for bulk Co.

ACKNOWLEDGMENT

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