Superparamagnetic behavior in cobalt iron oxide nanotube arrays by atomic layer deposition

Yuen Tung Chong,1 Man Yan Eric Yau,2 Yang Yang,3 Margit Zacharias,3 Detlef Görlitz,1 Kornelius Nielsch,1 and Julien Bachmann1,a)
1Institute of Applied Physics, University of Hamburg, 20355 Hamburg, Germany
2Max Planck Institute of Microstructure Physics, 06120 Halle, Germany
3IMTEK, Albert-Ludwigs-University Freiburg, Georges-Koehler-Allee 103, 79110 Freiburg, Germany

(Received 25 May 2011; accepted 24 July 2011; published online 31 August 2011)

Cobalt iron oxide nanotube arrays with various wall thicknesses were prepared by atomic layer deposition in porous anodic alumina template. Nanotubes uniform in thickness and homogeneous in composition can be obtained with aspect ratios on the order of 50. These nanotubes have a polycrystalline spinel structure. Both the mean grain size and the grain size distribution increase with the tube wall thickness. Correspondingly, their magnetic properties (remanence and coercive field) also have a strong dependence on the thickness for measurements carried out at 300 K. This dependence is attributed to the superparamagnetic behavior of the grains that constitute the nanotube. © 2011 American Institute of Physics. [doi:10.1063/1.3627369]

INTRODUCTION

Data storage in magnetic media relies on the presence of an energy barrier to magnetization reversal and thereby on some form of anisotropy. Typically, the magnetocrystalline anisotropy of hard magnetic materials has been used, but because the magnetocrystalline anisotropy energy depends on the grain size, it may no longer be sufficient to prevent random magnetization reversal in very small magnets at room temperature. Shape anisotropy in elongated nanomagnets has been proposed as an alternative barrier to prevent the rotation of magnetization for data storage applications.1 Anisotropy effects could also be utilized to enhance the magnetomechanical response of magnetic suspensions and broaden their application spectrum.2,3 Fundamental investigation of the shape anisotropy effects can be performed ideally with materials having zero magnetocrystalline anisotropy—typically, such studies have been performed on model systems based on permalloy nanowires.4,5

Magnetic nanotubes could also serve as anisotropic objects.6 However, they have not been studied as extensively as wires so far due to limitations in the preparative methods. More crucially, previous investigations in this area have been based on materials (in particular Fe3O4) with a low but significant magnetocrystalline anisotropy.7,8 We interpreted the shape-dependent magnetic properties of our tubes as resulting from shape anisotropy effects, but there remains some ambiguity as to the extent to which the results are affected by magnetocrystalline anisotropy, as well.9 In the present paper, we investigate magnetic nanotubes of a material (cobalt iron oxide) known for its large magnetocrystalline anisotropy; here, shape anisotropy will not have any direct relevance. We observe that despite this, the magnetic properties of such tubes do depend on their geometric parameters (i.e., tube wall thickness) and we elucidate the origin of this effect.

A full study of geometric effects on the magnetic properties of nanotube arrays depends on the ability to prepare series of samples with a systematic variation of geometric parameters. For this purpose, a unique strategy has been established that combines atomic layer deposition (ALD) with an appropriate porous template.8 The wall thickness of the nanotubes is precisely controlled by the number of ALD cycles, whereas their diameter and length are fixed by the pores of the porous anodic alumina membrane. In this work, we focus on a material known for its considerable magnetocrystalline anisotropy, cobalt iron oxide. We use an ALD process that yields this spinel in its polycrystalline form without subsequent annealing.10

EXPERIMENTAL DETAILS

Preparation

Self-ordered anodic aluminum oxide membranes were synthesized under 195 V with two-step anodization using 1 wt. % H3PO4 at 1 °C, forming nanopores with a diameter of ~150 nm, interpore distance of ~500 nm, and lengths set to values between 5 and 60 μm. They were used as template for the subsequent growth of nanotube arrays. The cobalt iron oxide ALD reaction reported previously10 was carried out to form spinel nanotubes inside the pores, with long exposure and purge times of 25 and 35 s, respectively. The thickness of the nanotubes was varied by the number of ALD supercycles. The Al layer was removed before carrying out any magnetic measurements to avoid the paramagnetic contribution from Al. This was carried out by first covering the as-prepared sample with photore sist and etching the Al underneath the anodic membrane with an aqueous 0.16 M CuCl2/2.5 M HCl solution, after which the photore sist was removed with acetone. To prepare samples for transmission electron microscopy (TEM) investigation, the arrays obtained after removing the photore sist were further etched in ~10 wt. % NaOH solution to remove the alumina matrix. The solutions containing suspended cobalt iron oxide nanotubes were then diluted with deionized water to neutral pH value. After that, the suspension was dropped on a Cu TEM grid with a carbon film.

a)Author to whom correspondence should be addressed. Electronic mail: julien.bachmann@physik.uni-hamburg.de.
Characterization

Scanning electron microscope (SEM) images were taken with a JEOL 6340 SEM, and the elemental compositions of the nanotubes were determined using energy-dispersive x-ray spectroscopy (EDX) on the SEM at 15 kV. TEM images were obtained on a Jeol JEM 1010 operating at 100 kV. The selected-area electron diffraction (SAED) patterns were obtained from isolated nanotubes and the dark-field images were taken at the (311) plane. The magnetic moments of samples of approximately 2 mm² were recorded at both 5 K and 300 K by a Quantum Design superconducting quantum interference device (SQUID) magnetometer MPMS-XL or MPMS-2 in which a magnetic field $H$ of up to 5 T or 1 T, respectively, was applied parallel or perpendicular to the long axis of the nanotube array. The field-cooled (FC) and zero-field-cooled (ZFC) measurements were carried out after heating the sample to 350 K and cooling it with and without an applied field, respectively. The magnetic moments were then measured as a function of temperature from 5 K to 350 K.

RESULTS AND DISCUSSION

Microstructure and morphology

The feasibility of applying the cobalt iron oxide ALD procedure to pores of high aspect ratio was explored with pore lengths of ~60 μm (aspect ratio > 300). Figure 1 shows a SEM image of free-standing cobalt iron oxide nanotubes obtained after removing the anodic alumina template in NaOH. They are continuous and have the same length as the template. EDX measurements were carried out in three different regions along the nanotubes (top, middle, and bottom) to obtain the composition and thickness homogeneity along the nanotubes. The atomic ratios between Fe and Co in the three regions are 1.3, 1.2, and 1.1, respectively, indicating a slight change in stoichiometry along these very elongated pores. The change in the total intensity from both Fe and Co emission is more significant between top and bottom (Fe+Co: top 31 at. %, middle 22 at.%, and bottom 11 at.%). Thus, the segment of homogeneous tube wall thickness is definitely shorter than 30 μm. This observation can be explained by the limited diffusion of the precursors deep into the pores. As the molar masses of ferrocene (186 g/mol) and cobaltocene (189 g/mol) are very close, their diffusion coefficients are similar as well. Therefore, the diffusion limitation of both precursors is comparable and their atomic ratio remains essentially constant along the tube length.

Due to the thickness variation observed in tubes of very high aspect ratio, the cobalt iron oxide nanotubes prepared for magnetic investigation are chosen to be much shorter, 5 μm in length. Figure 2 shows the TEM image of an isolated nanotube free of
any discontinuity and with thickness homogeneity better than \( \sim 10\% \) along its whole length. The enlarged section of the nanotube displayed in the inset shows that it is composed of grains. Those grains are randomly oriented as indicated by the ring pattern obtained from the corresponding SAED, which can be indexed to the spinel phase. Dark-field images obtained from the (311) plane were used to identify the grain size of nanotubes with various thicknesses. Figure 3 shows dark-field images taken from nanotubes of \( \sim 6, 9, 12, 15, \) and \( 21 \) nm wall thicknesses. The bright spots originate from the grains that satisfy Bragg’s diffraction condition and give rise to the (311) diffraction ring in the SAED. A large grain size distribution is observed for each investigated nanotube. The grain size distribution widens with the increasing tube wall thickness \( (d_w) \) (Table I). Moreover, the mean grain size also increases with the thickness of the nanotube. Thus, the distribution of grain sizes and the mean values have a strong dependence on the thickness of the ALD prepared nanotubes.

### Magnetic properties

Typically, shape anisotropy in elongated magnetic objects is evidenced by comparing the magnetization measurements taken in a magnetic field applied parallel and perpendicular to the long axis of the system. Figure 4 shows the magnetization isotherms recorded on a cobalt iron oxide nanotube array with wall thickness of \( \sim 21 \) nm at 5 K and at 300 K in both configurations. At each temperature, there is only a minor difference between both field orientations in the remanence \( (M_r) \) and almost no difference is observed in the coercive field \( (H_c) \) values of the magnetization isotherms. The resemblance of the two magnetization isotherms indicates that shape anisotropy is insignificant in cobalt iron oxide nanotubes at 5 K as well as 300 K. This is consistent with the high magnetocrystalline anisotropy of cobalt iron oxide \( (\text{on the order of } 10^6 \text{ ergs/cm}^3) \),\(^{12}\) which overwhelms the effect of shape anisotropy. The difference in coercive fields

![FIG. 3. TEM dark field images taken from the (311) plane of nanotubes with various thicknesses: (a) 6 nm; (b) 9 nm; (c) 12 nm; (d) 15 nm; and (e) 21 nm. The images evidence that the grain size distribution and its mean value increase with the wall thickness of the nanotube.](image)

![FIG. 4. (Color online) Magnetization isotherms of a sample with \( d_w = 21 \text{ nm} \) obtained with magnetic field parallel and perpendicular to the sample at 300 K and at 5 K. At each temperature, the measurements carried out in both configurations have minor difference in remanence and no differences in their coercivity, suggesting that shape anisotropy is negligible.](image)

#### Table I. Grain size distribution and its mean value for nanotubes with various wall thicknesses. Both the distribution and mean grain size increase with wall thickness. The distributions were obtained by processing the corresponding TEM images with Image J.

<table>
<thead>
<tr>
<th>( d_w/\text{nm} )</th>
<th>Grain size range/( \text{nm}^2 )</th>
<th>Mean grain size/( \text{nm}^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.5–298</td>
<td>16.6</td>
</tr>
<tr>
<td>9</td>
<td>0.5–362</td>
<td>24.1</td>
</tr>
<tr>
<td>12</td>
<td>1–405</td>
<td>28.2</td>
</tr>
<tr>
<td>15</td>
<td>1–426</td>
<td>34.8</td>
</tr>
<tr>
<td>21</td>
<td>1–554</td>
<td>42.8</td>
</tr>
</tbody>
</table>
observed between both temperatures hints at a superparamagnetic behaviour.

To investigate this aspect more systematically, Figure 5 shows both the coercive field and the relative remanence of the nanotube arrays with various thicknesses measured at 5 K and 300 K. The first observation is the very large difference observed in both $H_c$ and $M_r$ for all values of $d_w$ between the two temperatures. The significant increase in magneto-crystalline anisotropy of cobalt iron oxide at low temperature certainly contributes to this difference. A transition between the ferromagnetic and superparamagnetic states between 5 K and 300 K could also have an influence. The second aspect obvious from Figure 5, however, is the systematic increase of coercivity and remanence with the wall thickness $d_w$ at 300 K. A priori, this shape-dependent effect seems to be in contradiction with the insignificance of shape anisotropy claimed previously. However, it can be explained by invoking superparamagnetism.

To investigate the effect of thermal energy on the magnetic properties of our nanotube arrays, FC and ZFC measurements were carried out. Figure 6(a) shows the FC and ZFC curves of a 6 nm thick sample measured in various applied fields. The curves exhibit the typical features of a superparamagnetic system: (1) a large divergence between the FC and ZFC curves at low temperature; (2) a maximum in the ZFC curve, defined as the blocking temperature $T_b$ of the system, above which the magnetic moments fluctuate thermally; and (3) merged FC and ZFC curves at high temperature with an inverse relationship between magnetization and temperature. Given that the nanotubes are $\sim$5 µm long, a length much larger than the size of typical superparamagnetic particles ($<15$ nm), and the effect of shape anisotropy is negligible in the nanotube array, the superparamagnetic behaviour must originate from the grains that constitute the nanotube. These grains are oriented in different directions, with a mean size compatible with superparamagnetic properties. The fact that FC and ZFC curves merge somewhat beyond $T_b$ (maximum of the ZFC curve) and the presence of broad ZFC peaks indicate that the grain size distribution is large. This is consistent with the TEM observations. The applied magnetic field significantly affects the blocking temperature value as shown in Figure 6(b). In our system, $T_b$ experiences a small increase at low field (by 10–50 mT) and then shows the usual linear decrease at large field (100–500 mT). This dependence of $T_b$ on $H$ has been reported before in iron oxide, rubidium oxide, and iron platinum nanoparticle systems. It can be explained by the distribution of particle sizes (energy barrier) and the slow decrease of ZFC magnetization at higher applied field.

The superparamagnetic behaviour of nanotubes having 9 and 12 nm wall thickness was investigated with small applied fields in order that $T_b$ reflects the actual energy barrier for magnetization reversal in the nanotubes as closely as possible. Their FC and ZFC curves (Figure 7(a)) are similar to those obtained from the 6 nm sample. However, the peaks of the ZFC curves obtained at a small applied field (10 mT) are beyond 350 K, which is the maximum

---

**FIG. 5.** (Color online) Graph showing relative remanence and coercive field of cobalt iron oxide nanotube arrays with various tube wall thicknesses obtained at 5 K and at 300 K. Both, remanence and coercive field, remain almost constant with wall thickness at 5 K, whereas both values increase with wall thickness at 300 K.

**FIG. 6.** (Color online) (a) Field-cooled and zero-field-cooled curves of the 6-nm sample obtained under various magnetic fields. The shape of the curves shows that the nanotubes have a superparamagnetic behaviour with blocking temperature well below 300 K. (b) Graph showing the dependence of the blocking temperature (maxima of ZFC curve) on the applied field for the same sample. The blocking temperature first increases at small applied fields and then decreases linearly at larger fields.
temperature that the SQUID magnetometer can achieve. Thus, their intrinsic blocking temperature is obviously higher than 350 K. Given this experimental constraint, a large magnetic field (500 mT) was applied to obtain the dependence of the blocking temperature on the thickness of the nanotubes.

Figure 7(b) shows that the blocking temperature increases with wall thickness. Therefore, their intrinsic blocking temperature is obviously higher than 350 K. Given this experimental constraint, a large magnetic field (500 mT) was applied to obtain the dependence of the blocking temperature on the thickness of the nanotubes. The curves obtained at 10 mT indicate that the blocking temperatures (maxima of ZFC curve) of the 9- and 12-nm samples are higher than 350 K. The curves obtained at 500 mT show that the blocking temperature increases with wall thickness.

CONCLUSIONS

Our study on the magnetic properties of polycrystalline cobalt iron oxide nanotube arrays shows that in a material exhibiting large magnetocrystalline anisotropy, shape anisotropy plays no significant role at low temperature. The characteristic values remanence and coercivity do not depend on the tube wall thickness at 5 K. At room temperature, however, both remanence and coercive field strongly depend on the wall thickness of the tubes. We demonstrated that this is not due to shape anisotropy itself but is instead a result of the superparamagnetic effect. As the wall thickness increases, so does the mean crystallite size, the blocking temperature also increases monotonically. Thus, not all shape-dependent effects can directly be interpreted as originating from shape anisotropy in elongated magnetic nanostructures, unless very soft magnetic materials are used. However, this aspect has not been taken into account explicitly in most studies so far.

The observations reported in the present paper are also relevant to applications of magnetic nanomaterials in liquid medium. Indeed, so-called ferrofluids based on suspended superparamagnetic nanoparticles are commercially used for their magnetomechanical properties and potential biomedical applications of magnetic suspensions include drug delivery and magnetic hyperthermia. In this realm, a superparamagnetic behaviour at the working temperature is of paramount importance, since it prevents the agglomeration of the solid particles in the absence of an applied magnetic field. The tubular geometry could be advantageous for drug loading but usually results in a ferromagnetic response at room temperature. Our results show a way of tuning the superparamagnetic blocking temperature in this geometry based on structural parameters alone.

ACKNOWLEDGMENTS

Financial support was provided by the Ernst Cassirer Stiftung via the Cluster of Excellence “Nanospintronics.” Y.T.C. acknowledges the DAAD for a predoctoral fellowship. M.Z. and K.N. acknowledge funding by the DFG (ZA 191/23-1 and NI 61611-1).