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Fabrication and magnetic properties of Fe nanostructures in anodic alumina membrane

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Several Fe nanostructures with different lengths, diameters, and separations of the constituting magnetic components have been synthesized using anodized alumina membranes (AAMs) to understand the influence of these parameters on their magnetic properties. Fe nanostructures with high crystallinity and (110) orientation were synthesized by electrodeposition at room temperature in regular AAMs and mild-hard AAM (Mi-Ha AAM). Fe nanostructures with different aspect ratios (1:1, 1:10, and 1:75) in the form of nanodots, nanorods, or nanowires were synthesized in regular AAMs with the 100 nm interpore distance. Mi-Ha AAMs with two different pore sizes (70 and 120 nm) and 250 nm interpore distances were used to investigate the effect of the interactions and of the diameter of the wires on their magnetic behavior. Nearly linear magnetization characteristics with small coercivity, observed for Fe nanowires, suggest the magnetization rotation to be the predominant magnetization process for the field applied transverse to the wires. The anisotropy of the arrays was governed by the shape anisotropy of the magnetic objects with different aspect ratios. Reduced interactions between the nanowires grown in Mi-Ha AAMs resulted in enhancement of the average anisotropy. It is believed that due to difference in spin configuration, the increased diameter of the nanowires led to reduction in the coercivity in the case of the field applied along the wires.
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I. INTRODUCTION

One-dimensional materials have been synthesized by electron-beam lithography,[1] self-organization-based method,[2] or template-assisted electrodeposition.[3] The template-assisted electrodeposition is a simple technique, compared with other methods, to achieve highly ordered nanostructure arrays. A commonly used template is the anodic alumina membrane (AAM), which is a self-ordered nanoporous template synthesized by anodization of Al foil.[4–8] Masuda *et al.*[6] significantly enhanced the long-range ordering of assembled cylindrical pores in the AAM by applying a simple two-step anodization method. Cylindrical pore diameter and interpore distance could facilely be controlled by either pore-widening process or by increasing applied potential, respectively.[7,8] Therefore, the AAMs with controlled porosity and long-range pore ordering were used as unique templates for the fabrication of novel one-dimensional nanostructures.[9]

Previously, we synthesized and characterized Co and Ni nanostructures with various aspect ratios in AAMs.[10,11] Magnetic properties of Co and Ni nanostructures in AAMs depend on the shape anisotropy associated with the aspect ratio of nanostructures. Additionally, they are significantly influenced by strong magnetostatic interactions among nanowires, because the nanowires synthesized in AAM are separated by relatively thin walls, typically of the order of tens or hundreds of nanometers. In order to investigate the effect of the magnetostatic interactions among the nanowires,[12] several Fe nanowire arrays have been fabricated using AAMs with different interpore distances.

II. EXPERIMENTAL

The mild-hard AAM (Mi-Ha AAM) (Ref. 8) was synthesized by three-step anodization, which is a process involving mild and hard anodizing in 0.3 M $H_2C_2O_4$. For electrodeposition, both Al substrate and barrier layer were removed by electrochemical process in a 1:1 mixture solution of $HClO_4$ and CH_3CH_2OH at 100 V (10 °C). To completely remove a barrier layer, the templates were immersed in 5 wt % H_3PO_4 for several minutes. One side of AAM was coated with Ag to act as a conducting electrode. Electrodeposition was carried in the Fe electrolyte containing 240 g/L $FeSO_4 \cdot 7H_2O$, 45 g/L H_3BO_4, and 1 g/L of ascorbic acid with the current of −0.9 mA for several minutes using a Princeton Applied Research VMP2 instrument.

III. RESULTS AND DISCUSSION

A series of Fe nanostructures was synthesized in a regular AAM by electrodeposition. FESEM images in Fig. 1

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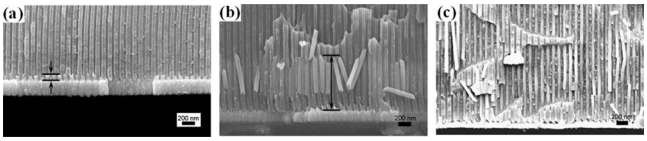

FIG. 1. FESEM images of cross section of Fe nanostructures in regular AAM: (a) nanodots, (b) nanorods, and (c) nanowires.

show the morphology of Fe nanostructures with various aspect ratios and a fixed diameter. The diameter of all nanostructures was around 60 nm and the length varied from (a) 60 nm for the nanodots, (b) 600 nm for the nanorods, and (c) 4.5 μm for the nanowires. The interparticle (interdot, -rod, or -wire) distance was about 100 nm. All of the pore channels were uniformly filled with Fe nanostructures.

The results of the measurement of the arrays of magnetic objects with different aspects ratios (and consequently different shape anisotropy values) are summarized in Fig. 2. For nearly spherical nanoparticles with the demagnetizing factor $N=1/3$ no significant difference in coercivity or the shape of the hysteresis loop is expected for different directions of the applied field. Indeed, both curves in Fig. 2(a) have the same coercivity of 70 Oe and similar shapes. Stoner–Wohlfarth (SW) model[13] for elongated single domain particle predicts marked difference between the curves measured with the field at different angles. In particular, magnetization vector rotation due to field applied along the hard magnetization direction (i.e., transverse to the long axis) gives rise to nonhysteretic and linear magnetization characteristic. Computer simulations,[14] based on Gibbs' free energy and Gilbert equation, clearly show that the magnetization reversal is predominantly due to magnetization vector rotations within magnetic domains when the field is applied transverse to the wires. The tilt and the saturation field of the hysteresis loops for the hard magnetization direction increase with increasing aspect ratio of the nanostructures, due to large shape According to SW model, coherent reversal of magnetization should occur at anisotropy field H_A, corresponding to the saturation field H_S when the field is applied along the wires. The coercivities of the hysteresis loops of the rods and wires are substantially smaller for the transverse magnetization direction than for the parallel one, and this tendency becomes stronger for the objects with larger aspect ratio. The measured values of H_C were 185 Oe at 0° compared with 130 at 90° for nanorods and 400 Oe at 0° compared with 90 Oe at 90° in the case of

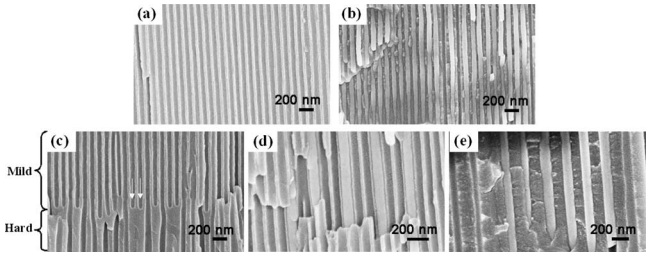

FIG. 3. FESEM images of cross section of AAM and Fe nanowires: (a) regular AAM, (b) Fe nanowires in regular AAM (70 nm in diameter and 100 nm interwire distance), (c) Mi-Ha AAM, (d) Fe nanowires synthesized in the mild side of image (c) (70 nm in diameter and 250 nm interwire distance), and (e) Fe nanowires synthesized in the hard side of image (c) (120 nm in diameter and 250 nm interwire distance). Scale bar is 200 nm.

long nanowires. Although increased squareness and coercivity were observed for the field applied along the wires, it is clear that the shapes of the hysteresis loops presented in Figs. 2(b) and 2(c) cannot be explained through coherent magnetization rotation. Indeed, computer simulations by Ross *et al.*[15] and Nielsch *et al.*[16] show that the magnetization process in the nanostructures is evidently different from the abrupt coherent magnetization reversal predicted by SW model. For the nanostructures with small aspect ratio, the magnetization occurs through incoherent magnetization reversal,[15] whereas in nanowires domain walls nucleate at the ends of the wires and propagate along the wires.[16]

A Mi-Ha AAM with large interpore distance of 250 nm was synthesized in order to check the effect of magnetostatic interactions among the nanowires, compared with regular membranes with about 100 nm interpore separations. Also, Mi-Ha AAM provided an opportunity to grow nanowires with two different sizes. The pores with 70 nm in diameter were on the top surface of the membrane, whereas those with 120 nm in diameter were made at the bottom surface of the membrane. Fe nanowires with different diameters were deposited starting from either the mild side or hard side of Mi-Ha AAM. FESEM images in Fig. 3 show (a) normal AAM with 100 interpore distances and (c) Mi-Ha AAM with 250 nm interpore distances. Figure 3(c) demonstrates both the mild and hard sides of Mi-Ha AAM and white arrows indicate closed pore channels at the boundary of the mild and hard anodized sides. Selectively opened channels in mild side of Mi-Ha AAM can be available to connect with the Ag conducting metal at the bottom and be filled with Fe nano-

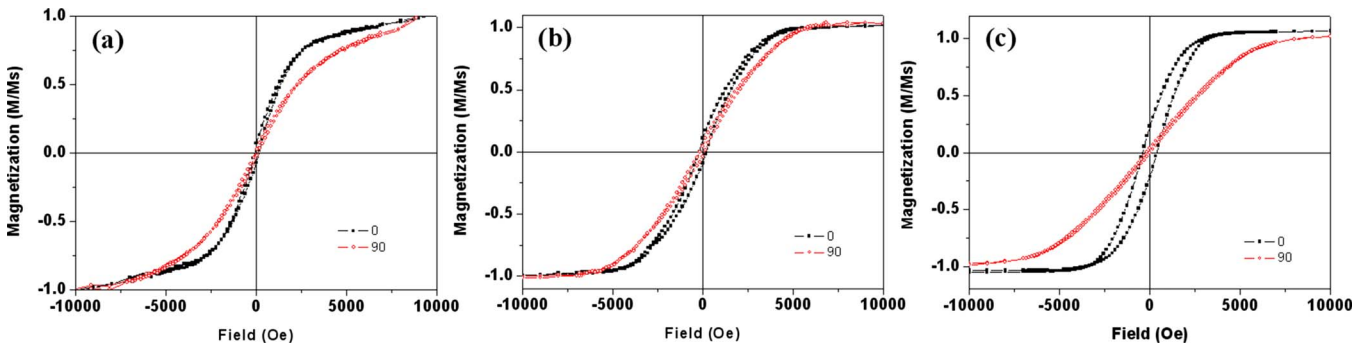

FIG. 2. (Color online) Hysteresis loops of Fe nanostructures in AAM: (a) nanodots, (b) nanorods, and (c) nanowires.

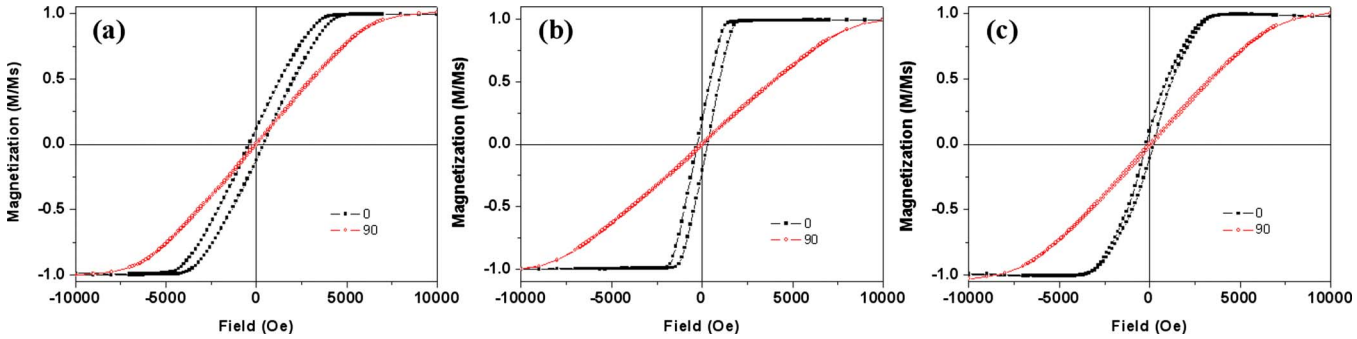

FIG. 4. (Color online) Hysteresis loops of Fe nanowires synthesized in (a) regular AAM, (b) mild side of Mi-Ha AAM, (c) and hard side of Mi-Ha AAM.

wires, as shown in Fig. 3(d). When we synthesized Fe nanowires in a regular AAM [Fig. 3(b)], the Fe nanowires grew in all the pore channels. Figure 3(e) image shows the Fe nanowires synthesized in hard side of Mi-Ha AAM.

The magnetic characteristics of these arrays of nanowires are summarized in Fig. 4. The magnetic hysteresis loops measured with the magnetic field applied parallel ($\theta=0°$) to the wires and perpendicular ($\theta=90°$) to their axes are displayed for Fe nanowires synthesized in regular AAM in Fig. 4(a), for the mild side of Mi-Ha AAM [Fig. 4(b)], and the hard side of Mi-Ha AAM [Fig. 4(c)]. A comparison between the curves in Figs. 4(a) and 4(b) provides information about the magnetostatic interactions among neighboring nanowires. Smaller slope and larger saturation field for the Ha-Mi AAM result from weaker interaction which promote shape anisotropy of individual wires. Strong interactions can eventually lead to complete suppression of the shape anisotropy of the wires and result in in-plane anistropy. Weaker interactions increased squareness of the hysteresis loops for the field applied along the wire axis [Fig. 4(b)]. Distribution of the strength of interactions, as recently analyzed by Serantes *et al.*,[17] may be the reason of more gradual approach of the regular array to saturation.

A comparison between magnetization characteristics in Figs. 4(b) and 4(c) demonstrates the effect of the diameter of the wires on their magnetic properties. However, significant difference in the shape and coercivity of the hysteresis loops was found for the direction of the field along the wires. This result is consistent with recent results by Carignan *et al.*[18] who also measured reduced coercivity and squareness for Ni nanowires with larger diameters.

IV. CONCLUSIONS

In summary, we are able to control not only the diameter and the length of nanowires, but also the interwire distance using regular AAMs and Mi-Ha AAMs. The aspect ratio of nanowires was controlled by changing the length while keeping the diameter constant. The evolution of the hysteresis loops with the aspect ratio was consistent with the effect of shape anisotropy of the magnetic objects forming the arrays. A comparison between structures grown in regular AAMs and Mi-Ha AAM allowed examining magnetic interactions between nanowires. It was found that the increasing interactions (decreasing interpore distance) result in suppression of average magnetic anisotropy of the nanowires. Larger diameter of the nanowires gave rise to reduced coercivity associated with domain wall motion.

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