Magnetic Field Assisting DC Electrodeposition: General Methods for High-Performance Ni Nanowire Array Fabrication

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One-dimensional magnetic nanowires are generally thought to show fine axial magnetism for their special high aspect ratio of the shape. However, the magnetic nanowire arrays fabricated by DC electrodeposition in template pores always show a low squareness in parallel to the nanowire direction. We developed two general and simple methods to improve the squareness of the as-fabricated Ni nanowire arrays parallel to the nanowire direction. The nanowires are found to be polycrystalline. The magnetism of the nanowire is also analyzed based on the microstructure.

1. Introduction

Magnetic nanowire arrays electrodeposited in anodic aluminum oxide template have attracted interest for their potential applications in magnetic devices, as well as for the scientific research of one dimension nanomagnets.[1−3] As a magnetic device, high squareness ($S_{//wire}$) and coercivity ($H_{c//wire}$) along the wire's axial direction are always needed. To date, most of the high $S_{//wire}$ and $H_{c//wire}$ magnetic nanowire arrays are fabricated by AC electrodeposition.[4−6] In the microelectronic industry DC electrodeposition is widely utilized; however, the $S_{//wire}$ and $H_{c//wire}$ of the nanowire arrays fabricated by DC electrodeposition are quite low, even though the nanowires were made to be alloy or multilayer.[7,8]

In DC electrodeposition, control of the nanowire's growth is easier but control of the magnetic property is harder, while precise control of the nanowires' growth is difficult in AC electrodeposition.[9] Therefore finding a way to improve the $S_{//wire}$ and $H_{c//wire}$ by DC electrodeposition is important not only to technological applications but also to magnetism research. In this paper, we report novel methods to fabricate nanowire arrays of high $S_{//wire}$ and $H_{c//wire}$ by DC electrodeposition.

2. Experimental Methods

The anodic aluminum oxide template used in experiments is made by a two-step anodic oxidation process.[10] After oxidation, the template with regularly distributed pores could be made. The remnant aluminum layer and barrier layer are removed by acidic $CuCl_2$ solution and 5% H_3PO_4, respectively. A thin Ag layer is sputtered on one side of the template as an electrode.

Two DC electrodeposition pools used in our experiments are shown in Figure 1. In Figure 1a, a magnetic stirrer is put in the pool. In Figure 1b, an external magnetic field generator is outside the pool, which can supply a field up to as high as 0.8 T. The highly pure Ni plate is anodic and the Cu plate is cathode in both pools. The thorough-pore template with sputtered Ag electrode is stuck on the Cu plate.

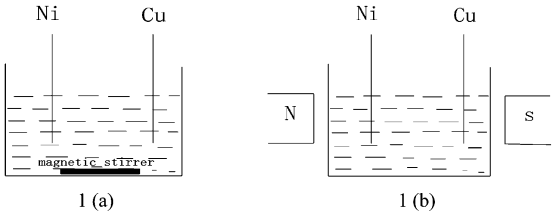

Figure 1. Schematics of the electrodeposition pools. A magnetic stirrer in the pool (a) and an external magnetic field generator outside the pool (b).

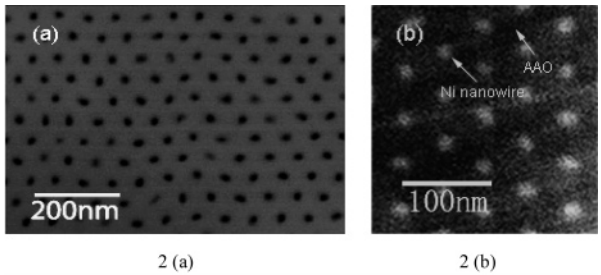

Figure 2. SEM top view of the AAO template (a) and Ni-in-AAO (b).

During the deposition experiments, the stirrer is kept at a speed of 60 r/min in one pool; the magnetic field generator supplies 3000 Oe of magnetic field parallel to the counter electrode direction in the other pool. The deposition current is kept at a constant 1A/dm^2 in both pools. Nanowires with different lengths can be fabricated by controlling the deposition time. After DC electrodeposition, the template is dissolved by 10 wt % of NaOH to separate the Ni nanowires. The Ni nanowires are then dispersed on the Cu grid coated with a carbon film for TEM observation. The magnetism of the array is measured by vibration sample magnetometer (VSM) and alternated gradient magnetometer (AGM).

3. Results and Discussion

Figure 2 is the SEM (JSM 6301F) top view of the template (a) and the template filled with Ni nanowires (b). In Figure 2a, we can see highly ordered pore arrays have been fabricated.

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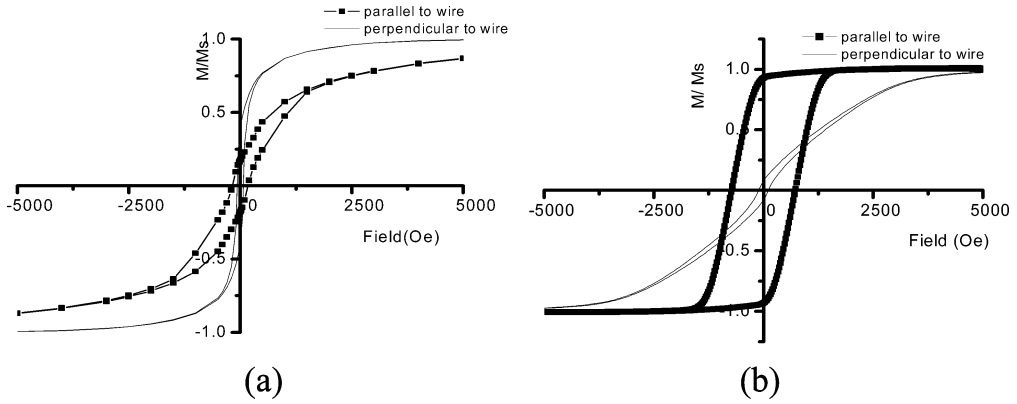

Figure 3. Magnetic hysteresis of Ni nanowire arrays fabricated by DC electrodeposition: (a) without and (b) with a magnetic stirrer in deposition.

TABLE 1: Magnetism Parameters of the Ni Nanowire Arrays

	with magnetic stirrer		without magnetic stirrer	
	parallel to wire	perpendicular to wire	parallel to wire	perpendicular to wire
H_c (Oe)	733.9	108.7	175.2	72.501
$S = M_r/M_s$	0.93	0.07	0.19	0 0.38
H_s (Oe)	2500	5000	10000	4000

The diameter of the pores is about 20 nm, and the distance between pore centers is nearly 60 nm. In Figure 2b, it can be seen that Ni nanowire filling causes almost no change to the template.

3.1. Ni Nanowire Array Fabricated by DC Electrodeposition with a Magnetic Stirrer in the Pool. The magnetic hystereses of the Ni nanowire arrays fabricated without and with magnetic stirrer are shown in Figure 3, parts a and b, respectively. The deposition time is 30 min and TEM shows the nanowires are nearly 2.3 μm in length. The remnant magnetization is higher perpendicular to the nanowire than parallel to the nanowire direction. So the magnetization's easy axis is not along the nanowire. Calculations have suggested that if each nanowire in the array is a single domain, shape anisotropy energy will dominate the magnetism of the nanowires and high-squareness hysteresis parallel to the nanowire direction will be obtained for long nanowires.[11] Our experimental results give no hints that shape anisotropy energy dominates the magnetism of the nanowires. Furthermore, it can be inferred that the nanowires in the array are multidomain.

To study the essence of the Ni nanowire array, a magnetic stirrer is used in the deposition, and the resultant hysteresis of the array is shown in Figure 3b. It can be seen that parallel to the nanowire direction the array has a higher squareness. The measured magnetic parameters are listed in Table 1, where H_s is the saturation field, H_c is the coercivity, and S is the squareness. Apparently with magnetic stirrer in deposition, the magnetism of the array along the nanowire axial direction has been improved greatly.

The effects of the nanowires' length on the magnetic properties have been studied in the array fabricated with a magnetic stirrer. In Figure 4a,b, the coercivity H_c and squareness S parallel to the nanowire direction are plotted versus the nanowires' length l_{nw}. It can be seen that both the H_c and S increase with l_{nw}. The increasing rate is higher when l_{nw} is below 600 nm, and much lower when l_{nw} is between 600 nm and 1.2 μm. While l_{nw} is longer than 1.2 μm, another fast increase could be observed in both H_c and S. This indicates that the nanowires with length ranging from 600 to 1200 nm are in a transition zone. Perpendicular to nanowire direction, the coercivity of the array fluctuates with shorter length nanowires. The squareness of the array decreases steadily as the length of the nanowires decreases, except that there is also a very slow decreasing zone between 600 and 1200 nm, which also justifies the existence of the transition zone. When the nanowires are shorter than 200 nm, the squareness parallel to the nanowire direction is lower than that perpendicular to the nanowire direction.

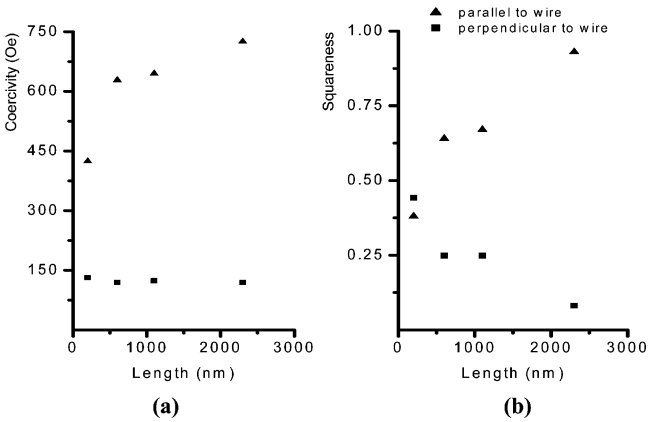

Figure 4. The effects of the length of the nanowire on the arrays' coercivity and squareness. The nanowire array is fabricated with a magnetic stirrer in deposition.

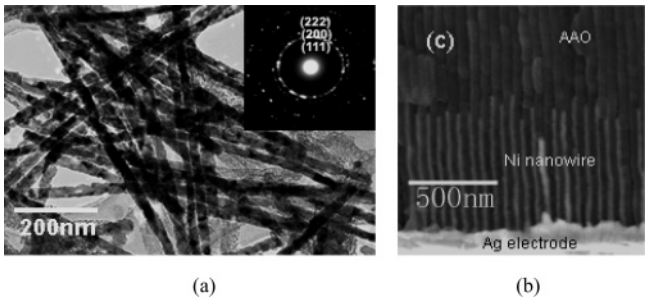

Figure 5. (a) The morphology and the SEAD of Ni nanowires fabricated with external magnetic field and (b) a cross-section view of the Ni-in-template.

3.2. Ni Nanowire Arrays Fabricated by DC Electrodeposition with an External Magnetic Field. In Figure 4, we can see that when the nanowire is shorter than 1 μm, the squareness parallel to the nanowire direction is lower than 0.75. To improve the magnetic properties further, an external magnetic field was introduced, as shown in Figure 1b. The magnetic field is 3000 Oe and is applied parallel to the counter electrode direction. The deposition time is 5 min. Figure 5a is the morphology and diffraction pattern of Ni nanowires. The nanowires are of almost equal diameter (nearly 20 nm) and the surface is smooth. From

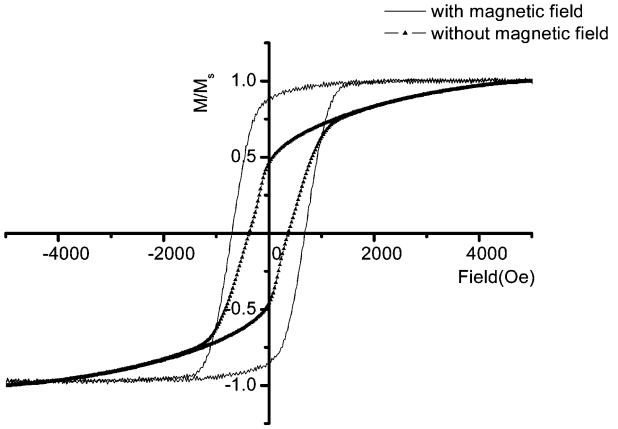

Figure 6. The M−H loop of Ni nanowire arrays fabricated with and without external magnetic field measured parallel to the nanowire direction.

TABLE 2: Comparison of the Magnetism of the Ni Nanowire Arrays with and without External Magnetic Field in Growth

external magnetic field	structure	H_c (Oe)	squareness	H_s (Oe)
with	polycrystalline	378	0.46	10000
without	polycrystalline	690	0.88	2000

the diffraction pattern, the nanowires could be identified as pure Ni nanowires. Figure 5b is the SEM cross-section view of the Ni-in-template. It shows that the neighboring nanowires keep fine spaces. The Ni nanowires in the template are not absolutely equal in length. The average length is 700 nm.

The magnetism of the nanowire arrays is studied by AGM (alternated gradient magnetometer). Figure 6 is the M−H loop of the Ni nanowire array along the wire axial direction. In an array without magnetic field applied during the growth of nanowires, the coercivity parallel to the nanowire direction is 378 Oe and the squareness of the array is 0.46 if M_s is taken as the magnetization at 5000 Oe. In fact we find the array is hard to saturate until 1 T. So the real squareness is much lower than 0.46. In an array with a 3000 Oe magnetic field applied during the growth of nanowires, the coercivity and squareness was improved sharply, reaching 690 Oe and 0.88, respectively. The hysteresis also shows that 2000 Oe is the array's saturation field (H_s). These measured parameters are listed in Table 2.

From the results shown in Figure 6 and Table 2, the magnetic field applied during the growth of nanowires improved the nanowire array's magnetic performance greatly. But what causes the revolution is still unclear.

3.3 Discussion. The nanowires have a 20 nm diameter in this work. The scale of 20 nm is important for nickel because the single domain critical diameter of Ni is regarded to be 20−25 nm.[6] The length of the nanowire is far longer than the critical diameter so that the nanowire might not be in a single domain. Our results in Figures 3 and 6 show that the magnetism of the nanowires depends on the fabrication condition. The magnetic stirrer and magnetic field can improve magnetism of the Ni nanowire arrays parallel to the nanowire direction.

With magnetic field applied during DC deposition, the nanowire arrays show fine axial magnetism. What really causes the revolution? Ni is a metal where magnetic crystalline anisotropy is very small. The nanowire has a polycrystalline structure. The assisted magnetic field applied during deposition might make the magnetic phases smoother in the nanowire.[12] As a result, the axial magnetism of the nanowire array is improved significantly.

4. Conclusions

In this article, magnetic field assistances were applied in DC deposition to improve the axial magnetism of the Ni nanowire's array. It is found that a nanowire array shows different magnetism by changing the fabrication condition and the length of the nanowires. The squareness of 2.3 μm long Ni nanowire arrays is higher than 0.9 with magnetic stirrer during deposition; and the squareness of 700 nm long Ni nanowires is 0.88 with 3000 Oe magnetic field applied during deposition.

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