ENHANCEMENT OF PERPENDICULAR ANISOTROPY OF Co/Cu MULTILAYER NANOWIRES BY PHASE DOPING

P. Y. Chen
Institute of Electro-optical Science and Technology
National Taiwan Normal University
Taipei 116, Taiwan

S. F. Hu and C. Y. Huang
Department of Physics
National Taiwan Normal University
Taipei 116, Taiwan

R. S. Liu
Department of Chemistry
National Taiwan University
Taipei 106, Taiwan

Abstract—A multisegment structure of Co/Cu nanowires with tunable perpendicular anisotropy, associated with phase transformation, was fabricated. The mixed crystal structure, formed by doping nano grains of the hcp phase into the fcc phase in the cobalt structure, markedly improves the perpendicular anisotropy. Cobalt nano grains with the hcp phase with a preferred orientation, which were transformed from (100) to (002), by doping fcc nano grain with high preferred (111) orientation and additionally the effective magnetocrystalline energy density of mixed structure was increased, the perpendicular magnetic anisotropy can be enhanced and tunable. The magnetoresistance ratios along the parallel and perpendicular axes of nanowires are 23.4% and 7.2% respectively. This novel approach promises to be of strong interest for subsequent fabrication of phase-locked arrays of spin transfer nano-oscillators with increased output power for microwave applications.

Corresponding author: S. F. Hu (sFhu.hu@gmail.com).
1. INTRODUCTION

The fabrication and characterization of a one-dimensional magnetic nanoscale structure have received increasing interest owing to its application in ultra-high-density magnetic recording media [1, 2] and electronic devices [3, 4]. The magnetic characteristics of a nanoscale ferromagnetic material depend on its size, shape and crystallinity. Nanowires with a high aspect ratio not only have the advantage of a greater surface-to-volume ratio than both bulk material and thin films, but also exhibit favorable dipolar magnetic properties. Synthesis using electrochemical templates is a versatile method for producing single component and multisegment nanowires or nanorods [3, 4]. Ferromagnetic nanowires of materials such as Fe, Co and Ni [5–8], and multilayer nanowires such as NiFe/Cu, Ni/Cu, Co/Cu and CoPt/Pt [9–11], have been fabricated using this method. Ferromagnetic nanowires typically exhibit very high coercivity and remanence along the magnetic easy axis, parallel to the wire axis, owing to the inherent shape anisotropy and reduced dimensions [12]. Co- or Fe-based multilayer films prepared by the alternating deposition of a transition metal (Co or Fe) and a nonmagnetic element (Pd, Ag, Pt, Au, etc.) have reportedly exhibit strong perpendicular magnetic anisotropy when the thickness of the transition metal Co or Fe was less than a few monolayers [13–15]. In the past year, the ferromagnetic multilayer nanowires was interesting in studying effects related to spin transfer torque from a spin-polarized current in a nanosize structure and it was also shown that the high density spin-polarized current passed through to multilayer nanowires can be induced the torque [16, 17]. The magnetic anisotropy of Co/Cu multilayer nanowires can be controlled by changing in magnetocrystalline anisotropy [18], the easy magnetization direction perpendicular to the nanowires axis due to the separation of cobalt layers [19], the magnetization reversal appeared to be a combination of rotation and spin flipping, which was dependent on the copper thickness [20] and the spin-flip diffusion length was measured to be about 21 nm for Co/Cu system [21]. This work describes the fabrication of Co/Cu magnetic multilayer nanowires by the electrodeposition in porous alumina templates and a novel method for enhancing perpendicular anisotropy by doping nano grains with the hcp phase into the fcc phases, Co segments in multilayer nanowires, shown the evidence of enhancement in magnetocrystalline anisotropy due to the crystal orientation transformation and demonstrate the magnetic perpendicular anisotropy can be controlled by the methods of phase doping and shape variation.
2. EXPERIMENTAL

Anodic aluminum oxide (AAO) is herein as the template because AAO has a structure of isolated, non-connected, and parallel pores with tunable pore diameters. The AAO templates that are used in the experiments herein were prepared by anodic oxidation of Al foil (99%, 0.25 mm-thick). The Al foil was initially electropolished in a mixed sulfuric acid/phosphoric acid solution and then anodized in 0.3 M oxalic acid at 10°C for 16 hours to form a nano-sized channel template. The voltage of anodization was maintained at 30 V to keep a constant pore diameter and a constant interpore distance in the AAO template. The template was dipped in saturated HgCl₂ solution to remove the remaining aluminum, and then dipped in 5 wt% H₃PO₄ to dissolve the barrier layer.

Electrodeposition in a single solution of both Co²⁺ and Cu²⁺ ions was performed to synthesize Co/Cu nanowires. First, a 5000 Å-thick silver film was thermally evaporated onto one side of AAO to serve as the back electrode. The electrodeposition was carried out using a three-electrode method. The counter electrode was Pt wire and the Ag/AgCl electrode was the reference electrode. The deposition solution contained 2 M CoSO₄, 0.02 M CuSO₄ and 0.6 M H₃BO₃ and the concentration ratio of Co²⁺/Cu²⁺ was 200/1 to prevent the formation of the copper impurities in cobalt segments during the electrodeposition process. To form a multilayer nanowires structure, the reduction voltage was set to −1 V for Co²⁺ ions and −0.16 V for Cu²⁺ ions. The duration of each pulse can be adjusted to tune the thickness of each layer. After the nanowires were formed, the silver electrode was removed using 1 M HNO₃ and then the AAO was dissolved in 1 M NaOH to obtain Co/Cu nanowires. The morphology of AAO templates was characterized by field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6700F). The Co/Cu multilayer nanowires that were embedded in AAO were observed by transmission electron microscopy (TEM, Hitachi H-7100), X-ray powder diffraction (XRD, BL-01C2 NSRRC, Taiwan) was performed to obtain the morphology and crystallographic structures. The deposition rates of cobalt and copper were measured using a electrochemical quartz crystal microbalance (EQCM, D3100 Digital Instrument) and the magnetic hysteresis loops were carried out using a commercial vibrating sample magnetometer (VSM) with fields of up to 8 T at room temperature. Measurements were made on a silica micro-slide perpendicular and parallel to the magnetic field. The magnetoresistance measurements were performed made using a four-point probe station in magnetic fields from 8 T to −8 T at room temperature.
Figure 1. Typical top-view SEM image of AAO templates prepared by two-step anodization.

3. RESULTS AND DISCUSSION

The morphologies of the formed structures of nanoporous AAO membranes were characterized by FE-SEM. Figure 1 presents a plan-view SEM image of nanoporous AAO templates, which contain uniform pores (50 nm in diameter). The pore interval length of AAO is 20 nm, the pore density is $12.1 \times 10^{10}$ cm$^{-2}$, and the aspect ratio (height/diameter) of the pores is maintained at around 700. In a previous investigation [22] self-organized pore growth results in the formation of a densely packed hexagonal pore structure for particular sets of parameters. The diameter and the interval of the pores depend on the applied voltage and electrolytes. Any repulsive interaction between the pores explains the self-organized arrangement of neighboring pores in hexagonal arrays. The pores of the front surface of the AAO template are also etched during the process of barrier layer-removal, tending to form a spherical array structure. Because of this, the magnetic anisotropy effect in spherical shape of the Co/Cu multilayer nanowires can be neglected.

Figure 2(a) presents a typical deposition current and the corresponding EQCM responses of the cobalt and copper layer. Two deposition potentials ($-0.16$ V and $-1$ V versus Ag/AgCl) were applied to deposit Co/Cu multilayer nanowires. The deposition rates of cobalt and copper, calculated from mass versus time data, for a unit area and the average length of the individual thickness of the nanowires, was also confirmed by the TEM image in Figure 2(b). The Sauerbrey equation [23] yielded the thickness of the multilayer structure: $\Delta m = -\Delta f/C_f$, where $\Delta m$ is the change of mass per unit area in g cm$^{-2}$; $\Delta f$ is the shift in the resonance frequency in Hz; $C_f$ is the sensitivity factor of the crystal in Hz ng$^{-1}$cm$^2$ and the deposition rates of cobalt and copper are 1.6 nm/s and 0.1 nm/sec,
Figure 2. (a) Current response and corresponding thickness of cobalt and copper metal during electrodeposition of Co/Cu multilayer nanowires. and (b) Transmission electron microscopic image of 50 nm diameter nanowire with 40 nm-thick Co layers and 20 nm-thick layers.

respectively. Figure 2(b) presents a TEM bright field image of part of a 50 nm diameter [Co(50 nm)/Cu(20 nm)]ₙ multilayer nanowire in which the Co segments have an aspect ratio of 1. The measured diameter of the nanowires closely approximates the pore diameter. To prevent inaccuracies in the average length of the nanowires (by breaking), the nanowires that were used to measure the deposition rate were not grown longer than 1 μm. Based on these results, multilayer nanowires with controlled compositions and lengths were fabricated by manipulating the applied-potential waveforms and pulse durations.

Figure 3 presents the XRD profile of a specimen with a length of 1 μm and diameter of 50 nm Co/Cu multilayer nanowires. All of the observed peaks fit the fcc phase (PDF #015-0806) and hcp face (PDF #089-4308) of standard cobalt material. At room temperature, the only stable phase in bulk (or bulklike) Co is hcp, while in a nanostructure or very thin film of Co, an fcc phase can also appear [24]. According to the analysis herein, the fcc and hcp phases dominate the cobalt layer and the fcc phase dominates the copper layer. The result is similar to that concerning the hcp phase in cobalt nanowires, published by Li et al. [25], whose preferred orientation is (100). However, a significant transformation of the preferred orientation from (101) to (002) was observed, probably by the the cobalt hcp phase with (002)
Figure 3. X-ray diffraction patterns of 50 nm-diameter Co/Cu multilayer nanowires with crystalline structure in Co segment with mixed hcp and fcc phases and Cu segment with fcc phase.

Table 1. The value of coercivity, saturation magnetization, residual magnetization, and squareness of hysteresis loops for diameters of 50 nm Co(fcc)/Cu(fcc) and Co(fcc+hcp)/Cu(fcc) nanowires.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hc (Oe)</th>
<th>Mr</th>
<th>Ms</th>
<th>Mr/Ms</th>
</tr>
</thead>
<tbody>
<tr>
<td>H ( \perp ) Co(fcc)/Cu</td>
<td>324</td>
<td>6.25\times10^{-4}</td>
<td>3.13\times10^{-3}</td>
<td>0.20</td>
</tr>
<tr>
<td>H ( \parallel ) Co(fcc)/Cu</td>
<td>551</td>
<td>5.61\times10^{-4}</td>
<td>2.97\times10^{-3}</td>
<td>0.19</td>
</tr>
<tr>
<td>H ( \perp ) Co(fcc, hcp)/Cu</td>
<td>304</td>
<td>1.71\times10^{-4}</td>
<td>1.59\times10^{-3}</td>
<td>0.11</td>
</tr>
<tr>
<td>H ( \parallel ) Co(fcc, hcp)/Cu</td>
<td>694</td>
<td>6.88\times10^{-4}</td>
<td>2.21\times10^{-3}</td>
<td>0.31</td>
</tr>
</tbody>
</table>

preferred orientation was induced to form by the cobalt and copper fcc phases. Rietveld refinement was applied using the general structure analysis system (GSAS) program to determine the ratio of the fcc to hcp phases in the crystal structure and the results reveal that the ratio of the fcc to hcp phases is almost 1:1. The grain sizes, as determined from the full width at half-maximum of the fcc-Co (111) and hcp-Co (101) peaks, all exceed approximately 30 nm.

The ferromagnetism of multilayer nanowires is well modulated by changing the aspect ratio of the length of the cobalt segments to the wire diameter. Figure 4 presents M-H curves for the Co/Cu multilayer nanowires whose ferromagnetic Co segments have aspect ratios of 2.0 (rod-shaped), 1.0 (intermediate), and 0.1 (disk-shaped), and various crystal structure, fcc and fcc and hcp mixed. The value of coercivity \( H_c \), saturation magnetization \( M_s \), residual magnetization \( M_r \), and squareness \( M_r/M_s \) of hysteresis loops were shown in Tables 1 and 2. The external magnetic field was applied parallel (\( \parallel \)) and perpendicular.
Figure 4. Magnetic hysteresis loops of electrodeposited Co/Cu multilayer nanowires embedded in AAO templates at 300 K for various directions of applied field relative to wire axis. Crystalline structures of Co segment with single fcc phase and fcc and hcp mixed phase. (a) Applied field parallel to wire axis, (b) applied field perpendicular to wire axis in multilayer nanowires. Aspect ratios of multilayer nanowires with Co/Cu ratios of 0.1, 1 and 2 with (c) applied field parallel to wire axis, (d) applied field perpendicular to wire axis.

Table 2. The value of coercivity, saturation magnetization, residual magnetization, and squareness of hysteresis loops for diameters of 50 nm Co(5, 50, 100 nm)/Cu(4 nm) nanowires.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hc(Oe)</th>
<th>Mr</th>
<th>Ms</th>
<th>Mr/Ms</th>
</tr>
</thead>
<tbody>
<tr>
<td>H ⇓Co(a. r.=0.1)/Cu</td>
<td>368</td>
<td>3.21×10⁻³</td>
<td>1.62×10⁻²</td>
<td>0.20</td>
</tr>
<tr>
<td>H //Co(a. r.=0.1)/Cu</td>
<td>489</td>
<td>2.49×10⁻³</td>
<td>9.54×10⁻³</td>
<td>0.26</td>
</tr>
<tr>
<td>H ⇓Co(a. r.=1.0)/Cu</td>
<td>232</td>
<td>5.20×10⁻⁴</td>
<td>3.55×10⁻³</td>
<td>0.15</td>
</tr>
<tr>
<td>H //Co(a. r.=1.0)/Cu</td>
<td>572</td>
<td>1.23×10⁻³</td>
<td>3.24×10⁻³</td>
<td>0.38</td>
</tr>
<tr>
<td>H ⇓Co(a. r.=2.0)/Cu</td>
<td>109</td>
<td>5.65×10⁻⁵</td>
<td>4.14×10⁻⁴</td>
<td>0.14</td>
</tr>
<tr>
<td>H //Co(a. r.=2.0)/Cu</td>
<td>621</td>
<td>2.43×10⁻⁴</td>
<td>5.68×10⁻⁴</td>
<td>0.43</td>
</tr>
</tbody>
</table>
(⊥) to the axes of the nanowires. Figs. 4(a) and (b) present the magnetization curves in an applied parallel and perpendicular field for multilayer nanowires with diameters of 50 nm [Co(fcc)/Cu(fcc)] and [Co(fcc+hcp)/Cu(fcc)]. The coercivity of nanowires with fcc phase or fcc and hcp mixed phase in cobalt segment in an applied parallel field were both higher than perpendicular field and the gain ratios of coercivity and the squareness of fcc and hcp mixed phase were higher than fcc phase. The magnetocrystalline anisotropy energy density in hcp phase\(^{19}\) \(K_1 = 5 \times 10^6\) erg cm\(^{-3}\) was higher than fcc phase\(^{19}\) \(K_1 = 6.3 \times 10^5\) erg cm\(^{-3}\) of cobalt and the gain ratios of coercivity and squareness in mixed phase were raised significantly than single fcc phase, result from the effective magnetocrystalline anisotropy energy density increasing by doping a hcp phase into a fcc phase in the cobalt segment. Figure 4(c) presents the magnetization curves in an applied parallel field for multilayer nanowires with diameters of 50 nm [Co(5, 50, 100 nm)/Cu(4 nm)]. The coercivity reveals the change in shape of the Co segments from disk-shaped to rod-shaped and the change in the easy axis from perpendicular to parallel to the wire axis (from 489 Oe to 621 Oe). Figure 4(d) presents the magnetization curves when a perpendicular field is applied to multilayer nanowires with a diameter of 50 nm [Co(5, 50, 100 nm)/Cu(4 nm)]. Similarly, the easy axis of the multilayer nanowires tends to become parallel to the wire axis, as revealed by the decline in coercivity (from 368 Oe to 109 Oe) as the aspect ratio of the Co segments increases. The results reveal that the magnetic easy axis tends rapidly to become parallel to the axis of nanowires as the aspect ratio increases and the enhancement in magnetic perpendicular anisotropy can be achieved by doping a hcp phase into fcc phase in the cobalt segment.

Based on the above investigation, this work proposes a model of the enhancement of perpendicular anisotropy by doping the hcp phase into the fcc phase structure of cobalt nano grains, as shown in Figure 5. The shape anisotropy energy density of the pure phase of the fcc [25] \(\pi M_s^2 = 6 \times 10^6\) erg cm\(^{-3}\) and hcp\(^{19}\) \(\pi M_s^2 = 6 \times 10^6\) erg cm\(^{-3}\) crystal were almost equal and can be neglected to calculate the enhancement in magnetic perpendicular anisotropy in the cobalt segment of multilayer nanowires. The magnetocrystalline anisotropy energy density can be increased by doping hcp phase with higher energy density into fcc phase and the preferred orientation of hcp phase was transformed from (101) to (002) which induced by fcc cobalt nano grains and copper layers, result in enhancement of the magnetic perpendicular anisotropy. This model helps to elucidate the magnetic dipole interaction between the shape and magnetocrystalline anisotropy on the nanoscale structures.
Figure 5. Mechanism of transition of perpendicular magnetic anisotropy: local structure, magnetic domain and net effective anisotropy.

Figure 6. Magnetoresistive hysteresis curve of 1µm-long Co(40 nm)/Cu(4 nm) multilayer nanowires electrodeposited into AAO templates.

Figure 6 presents the magnetoresistive hysteresis loop of 1 µm Co(40 nm)/Cu(4 nm) multilayer nanowires electrodeposited into AAO templates and 35 µm-length copper nanowire was electrodeposited as the connector between the top electrode and the multilayer nanowires and the top electrode, Au pad, was evaporated on the AAO template before electrodeposition. The measurement conditions were a source current of 1 µA, a temperature of 298 K and magnet fields from 8 kOe to −8 kOe. The 1 µm-length multilayer Co(40 nm)/Cu(4 nm) nanowires were obtained an magnetoresistance ratio (MR ratio) of 0.65% when the magnetic field is parallel to the nanowires and 0.2% when the magnetic field is perpendicular to the nanowires. The resistance
of nanowires are including the 1 µm Co(40 nm)/Cu(4 nm) multilayer nanowires and 35 µm-length copper nanowire, without considering the contribution of the copper resistance, the MR ratio which was calculate to multiply the ratio \([36 \mu m \text{-length}(\text{Co/Cu} + \text{Cu})/1m \text{-length}(\text{Co/Cu})]\) is 23.4% when the magnetic field is parallel to the nanowires and 7.2% when the magnetic field is perpendicular to the nanowires.

4. CONCLUSION

This work systematically investigated the fabrication of Co/Cu multilayer nanowires by anodization and electrodeposition. The magnetism can be modulated by controlling the aspect ratio and the crystalline structure of the Co segments in the multilayer nanowires. Doping nano grains with the hcp phase into the fcc phase of the cobalt segment of multilayer nanowires can efficiently increase the magnetic perpendicular anisotropy and this method also overcome the obstacle to the processing of multilayer nano-scale structures. The magnetic/non-magnetic multilayer nanowires have potential applications as key components in the next generation nanoscale perpendicular magneto-electronic devices, including perpendicular magneto-resistive random access memory devices.

ACKNOWLEDGMENT

The authors would like to thank the National Science Council of the Republic of China, Taiwan (Contract Nos. NSC 97-2112-M-003-007-MY3 and NSC 97-2113-M-002-012-MY3) and the Ministry of Economic Affairs of the Republic of China, Taiwan (Contract Nos. MOEA98-EC-17-A-01-S1-026 and MOEA98-EC-17-A-08-S1-006) for financially supporting this research.

REFERENCES


