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# Ni–Pt Multilayered Nanowire Arrays with Enhanced Coercivity and High Remanence Ratio

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Highly ordered Ni–Pt multilayered nanowire arrays have been fabricated using a porous anodic aluminum oxide (AAO) template by pulse electrodeposition. The cylindrical Ni nanoparticles with different lengths and diameters in these arrays were characterized by transmission electron microscope (TEM) and alternating-gradient magnetometer (AGM) measurements. Magnetization measurements revealed that an array of such nanowires with 20-nm diameters has an enhanced coercivity (ca. 1169 Oe) and a high remanence ratio (ca. 0.96).

Nanostructured materials have attracted considerable attention because of their novel optical, electrical, catalytic, and magnetic properties and their potential applications in nanoelectronic devices, nanosensors, catalysts, and information storage systems.[1−4] For example, ordered ferromagnetic nanoparticle arrays within a single magnetic domain size show a remarkably enhanced coercivity and a high remanence ratio, which makes them prospective materials for magnetic recording media. Recently, it has been demonstrated that, among many techniques including hard template synthesis and soft template synthesis, the combination of porous anodic aluminum oxide (AAO) template with electrodeposition is an effective and powerful method for obtaining highly ordered nanostructured magnetic composites.[5−7] In particular, pulse electrodeposition combined with a template synthesis strategy is a simple method for obtaining multilayered nanowires by controlling electrochemical parameters.[8] By this method, we have fabricated high-density magnetic nanoparticle arrays of Ni−Cu in which the Ni nanoparticles are in a single magnetic domain.[9] However, improving the coercivity and remanence ratio for use in magnetic recording media remains a challenge.

Ni−Pt multilayered magnetic films have been extensively studied because of their unusual magnetic and magneto-optic properties.[10] Most of these studies have been focused on Ni−Pt multilayered films mainly prepared by magnetron sputtering and electron-beam evaporation, which require harsh conditions such as high temperature, high vacuum, and expensive equipment. On the other hand, it is of great scientific significance to study the magnetic behaviors of single-magnetic-domain nanoparticles with varying sizes. However, owing to the methods used, the magnetic nanoparticles prepared by most techniques are usually not uniform, easily aggregate, or are covered by surfactants, which makes studies of their magnetic behaviors difficult and renders their use as magnetic recording media inconvenient. Herein, we report the successful fabrication of ordered Ni−Pt multilayered nanowire arrays using porous AAO templates by pulse electrodeposition. The magnetic properties of the cylindrical Ni nanoparticles with different lengths and diameters in the resulting Ni−Pt multilayered nanowires were investigated.

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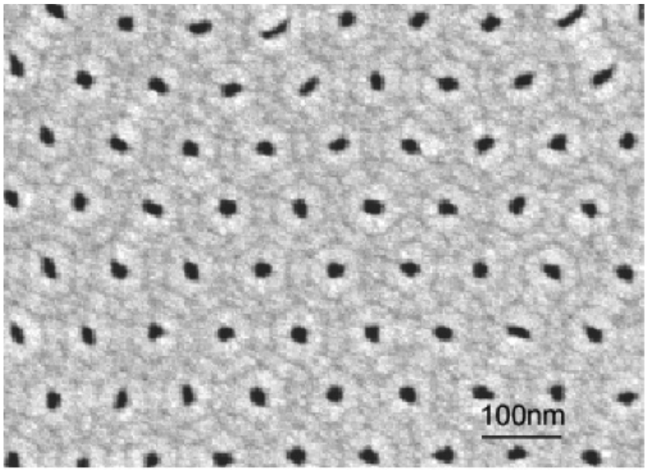

**Figure 1.** Top-view SEM images of AAO template with an average diameter of 20 nm.

AAO templates with the diameters of 20 and 50 nm were prepared by the procedure reported previously.[9,11] The cyclic voltammetry and pulse electrodeposition were carried out in a three-electrode electrochemical system. Ni−Pt multilayered nanowires were fabricated from a single sulfate bath, containing nickel sulfate (2 M), chloroplatinic acid (2 mM), and boric acid (0.5 M), using potentiostatic control and a pulse deposition technique. The field-dependent magnetization hysteresis was measured for Ni−Pt multilayered nanowire arrays embedded in the AAO templates at room temperature with an alternating-gradient magnetometer (AGM, 2900-4C). The external field was applied parallel (||) and perpendicular (⊥) to the axes of the nanowires.

By immersing the as-grown 20-nm AAO template into a solution of 5% phosphoric acid, we can obtain nanochannels with different diameters while keeping the interpore distance constant. Figure 1 shows a typical scanning electron microscope (SEM) image of the AAO template with an average diameter of 20 nm. AAO templates with 30- and 50-nm diameters are shown in Figure S1 of the Supporting Information. All of these images show an almost-perfect close-packed array of columnar hexagonal cells, each containing a central pore normal to the surface. The interpore distances for all AAO templates are ca. 100 nm. The density of AAO template is about $1.2 \times 10^{10}$ pores/cm$^2$.

Figure 2 shows a cyclic voltammogram obtained during eletrodeposition of Ni and Pt. The scan rate for cyclic voltammetry was 50 mV s$^{-1}$. The reduction of $Ni^{2+}$ to Ni begins at ca. −0.33 V and reaches the pronounced peak current at ca. −0.46 V. Because the concentration of chloroplatinic acid is very low, Pt deposition is evidenced by the appearance of a weak reduction peak at ca. −0.26 V. The majority of the deposit was Ni when a proper depostion potential was chosen because the concentration of $Ni^{2+}$ was 1000 times higher than that of $PtCl_6^{2-}$. The deposition potential was alternately switched between a potential of −0.28 V to deposit Pt and a potential of −1.3 V to deposit Ni. Five samples, samples A−E, of Ni−Pt multilayered nanowire arrays were fabricated to study the magnetic properties of Ni nanoparticles with different lengths and different diameters. The pulse times for the deposition of Ni for samples A−C with diameters of 50 nm were 10, 20, and 30 s, respectively, and the pulse time to for the deposition of Pt for all samples was 80s. Sample D and E were fabricated under the same conditions as used for sample A.

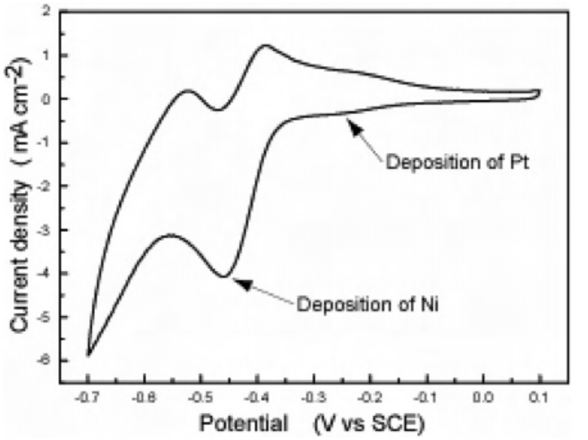

**Figure 2.** Cyclic voltammogram from a single plating bath containing nickel sulfate (2 M), chloroplatinic acid (2 mM), and boric acid (0.5 M), at room temperature, Scan rate = 50 mV s$^{-1}$.

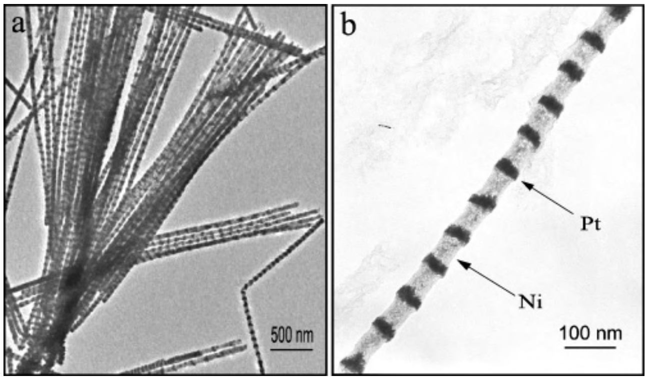

**Figure 3.** (a) Low- and (b) high-magnification TEM images of Ni−Pt multilayered nanowires liberated from AAO template with an average diameter of 50 nm.

Figure 3a and 3b shows typical low- and high-magnification TEM images of sample A liberated from the AAO template. A bundle of Ni−Pt multilayered nanowires with an average diameter of about 50 nm can be seen in Figure 3a. In Figure 3b, the areas shown by dark contrast and bright contrast correspond to cylindrical Pt and Ni nanoparticles, respectively. The feature of cylindrical Ni nanoparticles alternating with Pt segments can be clearly observed in the bamboo-like nanowire images. The average diameter of the nanowires was measured to be ca. 50 nm, consistent with the pore size of the AAO template used. The detailed features of cylindrical Ni nanoparticles with different diameters and lengths of samples A−E are listed in Table 1. In all of the samples, the length of the Pt segments is 18 nm. All samples show bamboo-like features.

Hysteresis loops of samples A−E embedded in the AAO template were recorded at room temperature on an AGM with the magnetic field applied parallel (||) and perpendicular (⊥) to the axes of the nanowires. Figure 4 shows the typical

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**Table 1.** Magnetic Properties and Morphologic Features of Ni−Pt Multilayered Nanowire Arrays (Samples A−E)

| sample | diameter (nm) | length of Ni segments (nm) | $H_c^{\parallel}$ (Oe) | $M_r/M_s$ (∥) | $H_c^{\perp}$ (Oe) | $M_r/M_s$ (⊥) |
|---|---|---|---|---|---|---|
| A | 50 | 50 | 596 | 0.57 | 88 | 0.08 |
| B | 50 | 100 | 682 | 0.51 | 56 | 0.03 |
| C | 50 | 150 | 828 | 0.50 | 59 | 0.03 |
| D | 30 | 50 | 1146 | 0.90 | 96 | 0.09 |
| E | 20 | 50 | 1169 | 0.96 | 134 | 0.06 |

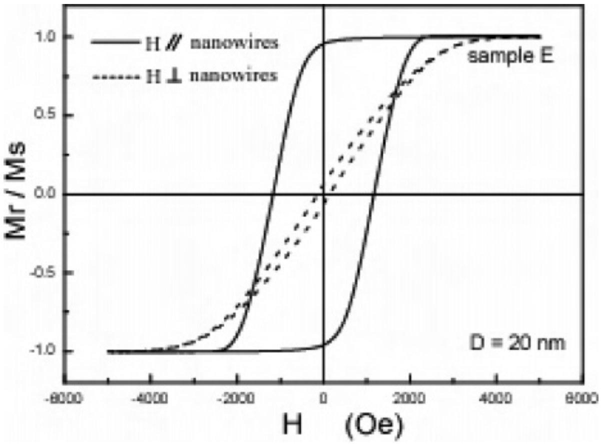

**Figure 4.** Magnetization hysteresis loops of sample E embedded in AAO template with the magnetic field applied parallel (∥) and perpendicular (⊥) to the axes of the nanowires at room temperature.

hysteresis loops of sample E, and the hysteresis loops of samples A−D can be found in Figure S2 of the Supporting Information. From these loops, the coercivities ($H_c$) and ratios of the remanence ($M_r$) to the saturation magnetization ($M_s$) were extracted, as reported in Table 1. In the present study, all coercivity and remanence ratio values were calculated by the AGM. From Table 1, it is clear that the magnetic properties of the samples vary with the diameters and lengths of the cylindrical Ni nanoparticles. On the other hand, the data in Table 1 show differences in coercivity when the external fields are applied in different directions. The coercivity in the parallel direction is much higher than that in the vertical direction, indicating that the nanowires exhibit strong uniaxial magnetic anisotropy, with the easy axis parallel to nanowires.

As the length of the cylindrical Ni nanoparticles increases, the coercivity field of samples A−C increases, and the remanence ratio decreases. The results indicate that it is difficult to obtain high coercivity and high remanence ratio by varying the length of Ni nanoparticles with average diameter of 50 nm. Samples A, D, and E were designed to investigate the magnetic properties of the nanowires when their diameters were decreased while the length of the Ni nanoparticles was kept constant. With the diameter reduced, the shape anisotropy is increased, resulting in an enhancement of the switching field of the multilayered nanowires. Furthermore, the interactions between the neighboring nanowires are reduced because the diameters of the nanowires decrease while the interpore distance remains constant. The gradually enhanced coercivity and remanence ratio can be seen from sample A, to D, to E.

A nearly square hysteresis curve was obtained for sample E under a field applied parallel to the long axis of the wires, as can be seen in Figure 4. The coercivity was 1169 Oe, showing a remarkably enhanced value in comparison with those of bulk Ni (ca. 0.7 Oe),[13] Ni nanowire arrays (ca. 290 Oe),[14] and Ni−Cu multilayered nanowires (ca. 490 Oe).[9] The remanence ratio of sample E is as high as 0.96. It has been reported that Ni nanowires with diameters smaller than 55 nm are expected to exist as single-domain wires.[6,12] Our earlier results for Ni−Cu multilayered nanowires suggest that Ni nanoparticles with lengths of 55 nm have a single magnetic domain.[9] In the present study, the diameters of the nanowires are less than 55 nm. Furthermore, the lengths of the cylindrical Ni nanoparticles in samples A, D, and E are less than 55 nm. Therefore, the observed enhanced coercivity and high remanence ratio can be attributed to single magnetic domain of cylindrical Ni nanoparticles.

In summary, we have fabricated highly ordered Ni−Pt multilayered nanowire arrays by a simple pulse electrodeposition technique. TEM results indicated that the cylindrical Ni nanoparticles in the multilayer nanowires were uniform, highly stable, and alternating with Pt segments. Magnetization measurements revealed that the arrays exhibit uniaxial magnetic anisotropy with the easy axis parallel to the nanowires. An array of such nanowires with 20-nm diameters has an enhanced coercivity and a high remanence ratio. From the technological point of view, the Ni−Pt multilayered nanowire arrays have prospective applications in chemical sensors, nanodevices, nanoelectrode ensembles, and particularly in ultra-high-density magnetic recording media.

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**Supporting Information Available:** Detailed experimental procedure, SEM images of AAO templates, and hysteresis loops of samples A−D. This material is available free of charge via the Internet at http://pubs.acs.org.

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