Ordered Ni−Cu Nanowire Array with Enhanced Coercivity

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Received September 6, 2002. Revised Manuscript Received November 27, 2002

A highly ordered composite Ni−Cu nanowire array has been fabricated within the pores of an anodic aluminum oxide (AAO) template by pulsed electrodeposition, and it has been characterized by transmission electron microscopy (TEM), selected-area electron diffraction (SAED), magnetic force microscopy (MFM), and superconducting quantum-interference device (SQUID) measurements. It was found that all the Ni segments are single magnetic domain and aligned to the same direction after magnetizing under an external field (perpendicular or parallel to the axes of the nanowires). Magnetization measurements on the array revealed a remarkably enhanced coercivity and a similar high-saturation magnetization compared to that of bulk nickel. Owing to its high bit density (up to 70 Gbits/in^2), the structure may be suitable for ultrahigh-density magnetic recording media.

Introduction

In the past several years, magnetic nanoparticles have been of considerable interest because of both fundamental physics involved and technical applications in diverse areas such as the magnetic storage media, ferrofluids, and catalysts.[1−3] Ferromagnetic nanoparticles are in the size of a single magnetic domain, in which the magnetic spins are aligned to produce a magnetic moment in one direction. The particle size for single-domain formation in the ferromagnetic elements Fe, Co, and Ni is typically several tens of nanometers. For applications using high-density magnetic recording materials high coercivity (representing the resistance to demagnetization) and high magnetization are essential. It was reported that a typical feature found in ferromagnetic nanoparticles with crystallite in size close to the single magnetic domain was the remarkably enhanced coercivities compared to that of the bulk materials (e.g., Fe powder with a crystallite size of 13 nm showed a coercivity of 900 Oe in comparison with 10 Oe for bulk Fe).[4] Owing to their nanoscale sizes and high coercivities, a high-density and low-noise magnetic recording medium might be designed based on the ferromagnetic particles. One strategy is through ordered magnetic nanoparticle arrays (OMA), where one information bit corresponds to one single-domain particle

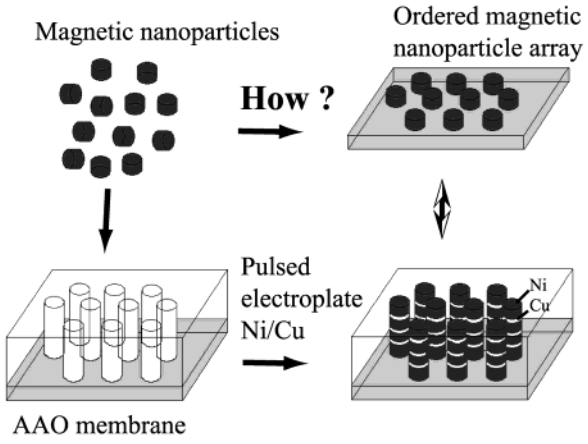

Figure 1. Schematic illustration for fabricating a composite Ni−Cu nanowire array — a substitute for ordered magnetic nanoparticle arrays.

(Figure 1). To achieve this goal, many methods, including nanoimprint lithography[5] and self-assembly,[6] have been developed for fabrication of OMA. However, these methods often need harsh conditions and expensive equipment, and are only applicable for some special materials. Therefore, it is still a challenge to develop a versatile and cost-effective approach to preparing high-density OMA.

Recently, the template synthesis method, pioneered by C. R. Martin,[7] provides a versatile approach and has had considerable success in the preparation of arrays of metals, polymers, semiconductors, and multilayered nanostructures (nanowires and nanotubules).[8] One key

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10.1021/cm0208962 CCC: $25.00
Published on Web 01/07/2003

idea in the method is synthesizing a desired material within the pores of a porous membrane. If some ordered systems are adopted as templates in the synthesis process, the ordered structure of nanomaterials can be obtained. In fact, many arrays of magnetic nanowires including Fe, Co, Ni, and their alloys have been prepared based on this method.[9] However, the remarkably enhanced coercivities as found in their nanoparticles are often missing with the single magnetic domain structure losing. One approach to overcome this limit is through an array of composite nanowires which have the feature of magnetic nanoparticles with the size of a single magnetic domain alternated with nonmagnetic nanoparticles (Figure 1). This structure may be used as a substitute for OMA with a number of interesting and useful features. First, it is applicable for almost all magnetic materials. Second, template materials with highly ordered monodisperse pores are available, and thus highly ordered monodisperse nanostructures can be obtained. Finally, the stability of the nanoparticles can be enhanced as they are encapsulated in the pores of template. In fact, similar semiconductor nanowires with modulated structures have been successfully fabricated recently.[10] A diversity of possible applications may be found for the novel structures, including engineered one-dimensional waveguides, thermoelectrics, nanobarcodes, and injection lasers.[10] Here, we report the preparation of an array of composite Ni−Cu nanowires using a pulsed electroplate technique. The magnetic property of the product is also described.

Experimental Section

The AAO templates used in our experiment, with pore sizes of about 50 nm, were grown by potentiostatically anodizing aluminum plates (0.2-mm thick, 99.999%) in an aqueous solution of 5% oxalic acid under 40 V at 3 °C. After the anodization, the remaining aluminum was etched by a 20% HCl/0.1 M $CuCl_2$ mixed solution. Then the barrier layer was dissolved using 5% H_3PO_4. Finally, a silver film was deposited by vacuum evaporation onto a surface of the template membrane to provide a conductive contact. The order of the pore array, the pore density, and the channel shape of AAO templates were characterized by a JEOL JSM-6700F SEM.

Composite Ni−Cu nanowires were made from a single sulfate bath, containing nickel sulfate (2 M), copper sulfate (0.02 M) and boric acid (0.5 M), using potentiostatic control and a pulsed deposition technique. The plating potential was alternately pulsed between a constant potential V_{Cu} of −0.3 V (vs SCE) for 30 s to deposit Cu only and a potential V_{Ni} of −1.4 V (vs SCE) for 10 s to get a majority of Ni. After liberating the Ni−Cu nanowires from their AAO matrix by dissolving the AAO template in 2 M NaOH at 25 °C for 90 min, being ultrasonically dispersed in water, and dropping on TEM grids, we obtained their TEM images on a JEM-200CX operated at 160 kV.

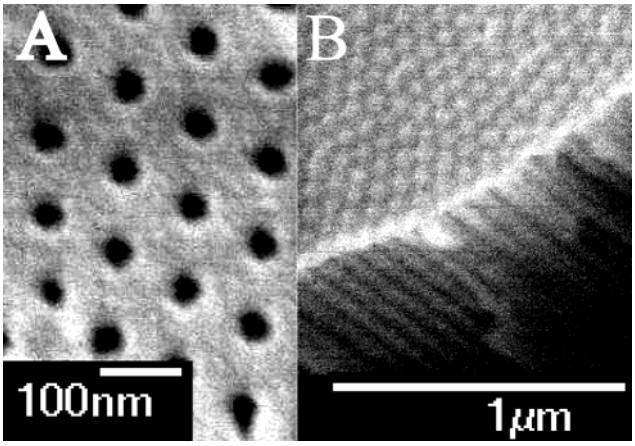

Figure 2. SEM images of (A) the surface view of AAO template and (B) the oblique cross-section view near the barrier layer of AAO template.

The magnetic domains of the composite Ni−Cu nanowires were imaged by magnetic force microscopy (MFM). A Nanoscope IIIa Dimension 3000 scanning probe microscope (Digital Instruments Inc.) was employed. The cantilever was a Nano-Probe magnetically coated tip with 225-μm length with a resonant frequency of approximately 70 kHz. The tip was magnetized along the tip direction, which was perpendicular to the mica surface upon which the samples were lyingn. The topographical and magnetic images were obtained simultaneously using tapping and lift modes, respectively. Prior to imaging, the nanowires were saturated by means of an external field (perpendicular or parallel to the axes of the nanowires) and observed in their remanent state.

The magnetization of Ni−Cu nanowire array with the AAO membrane support was measured by using a Quantum Design MPMS-5 superconducting quantum-interference device (SQUID) at room temperature (300 K).

Results and Discussion

Nanoscale templates play an important role in fabricating nanowire arrays. To date, the porous anodic aluminum oxide membrane with its ordered honeycomb structure has been extensively used as a template.[11] Typical SEM images of the AAO template used are shown in Figure 2. Hexagonal close-packed arrays of parallel cylindrical pores normal to the surface can be clearly seen. The average diameter of the pore was about 50 nm and the pore density was 1.2×10^{10} pores/cm^2. This indicates that a similar ordered array of Ni−Cu nanowires can be prepared by using the AAO membrane as template. If one information bit corresponds to one nanowire, the corresponded recording density is up to 70 Gbits/in^2. This storage density is much higher than that of current commercial hard disks (3.7 Gbits/in^2, IBM Deskstar 25GP), and also beyond the projected thermal limit of 40 Gbits/in^2 in continuous magnetic films.[12]

Figure 3A and B are the typical TEM images obtained in composite Ni−Cu nanowires. The feature of Ni segments alternated with Cu layers is clearly seen in the images. The physical basis of the electron contrast in the TEM images is the crystallization and the difference in atomic weights, which results in the

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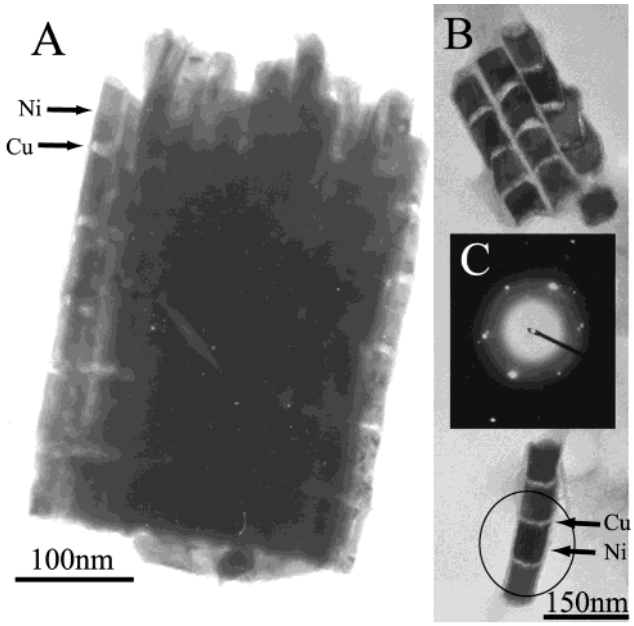

Figure 3. TEM images of (A) a bundle of, and (B) dispersed, composite Ni−Cu nanowires. (C) Selected-area electron diffraction pattern from the area indicated by circle in B.

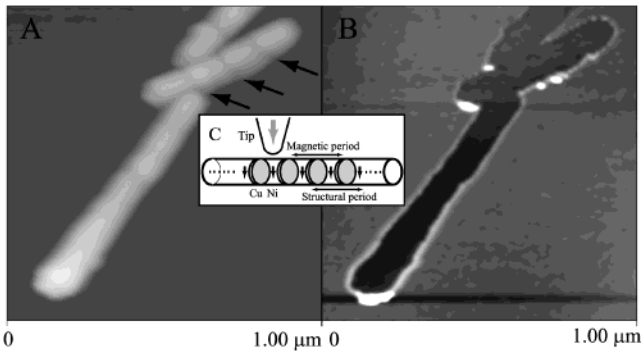

Figure 4. Topographic (A) and MFM (B) images of Ni−Cu nanowires after magnetizing under a field perpindicular to the axes of the nanowires. (C) Schematic relative orientations of the tip and multistripe nanowire magnetizations.

electron-dispersing ability of Ni segments being stronger than that of Cu segments, and hence the darker sections correspond to Ni and the brighter sections correspond to Cu. From Figure 3A, a bundle of bamboo-like nanowires with six uniform Ni segments (∼55 nm long) and five Cu segments (∼8 nm long) can be clearly seen. In a well-dispersed TEM image (Figure 3B), the average diameter of the nanowires is measured to be ∼50 nm, which corresponds to the pore size of the template used. The selected-area electron diffraction (SAED) pattern taken from the region indicated by a circle is shown in Figure 3C. The SAED pattern is consistent with cubic Ni crystal. Indexing this pattern demonstrates that the axes of the nanowires are along the ⟨111⟩ direction. The SAED result demonstrates that the Ni segments are single crystal with a preferred ⟨111⟩ orientation.

We used MFM to study the magnetic domains of the composite Ni−Cu nanowires. Figure 4 show the typical topographic (A) and MFM (B) images of Ni−Cu nanowires after magnetizing under a field perpendicular to the axes of the nanowires. The feature of bamboo-like also can be observed in Figure 4A as indicated by

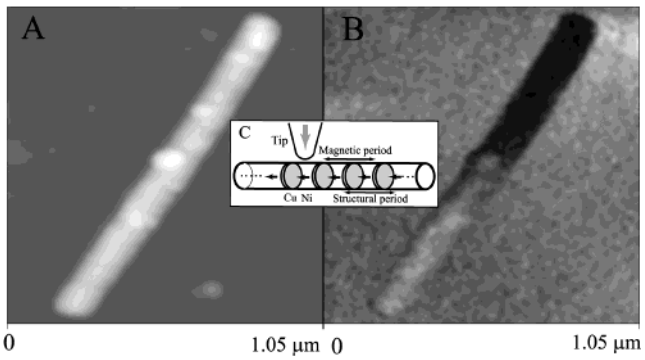

Figure 5. Topographic (A) and MFM (B) images of Ni−Cu nanowires after magnetizing under an axial field. (C) Schematic relative orientations of the tip and multistripe nanowire magnetizations.

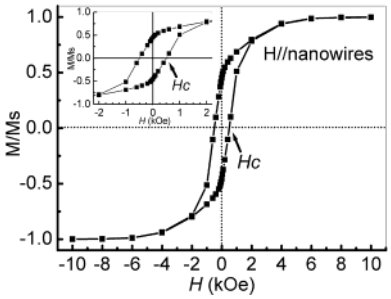

Figure 6. Hysteresis loop for a hexagonal array of Ni (55 nm) [Cu (8 nm)/Ni (55 nm)]$_{21}$ nanowires (50 nm diam.) at 300 K under a field applied parallel to the long axis of the wires. Inset is the enlargement at low field.

arrows. In the MFM image in Figure 4B, the nanowires appear in the feature of a dark belt with bright edges with uniform contrast along the wire's axis. As we know, if the magnetic interaction between tip and the stray field emanating from the sample was attractive, the MFM image will show reduced contrast, whereas in the case of repelling interaction, bright contrast appears. Thus, it is assumed that the magnetization directions within the Ni segments of the nanowires in Figure 4 are parallel and in the same direction as that of the tip (Figure 4C).[13]

Typical topographic (Figure 5A) and corresponding MFM (Figure 5B) images of Ni−Cu nanowires after magnetizing under an axial field were also obtained. The strong black or white end-contrast gradually changes along the nanowire and may thus be associated with monopolar type charge sources. Because the end-contrasts are opposite, this nanowire is globally behaving as a dipole, namely the axial magnetization components of the whole nanowire have the same orientation (Figure 5C).

As each of the segments of Ni is a single magnetic domain and aligned to the same direction after magnetizing under an axial field, a remarkably enhanced coercivity comparable to that of Ni nanoparticles of the composite Ni−Cu nanowire array should be supposed. Figure 6 shows hysteresis curves at room temperature (300 K) for a hexagonal array of Ni (55 nm)[Cu (8 nm)/Ni (55 nm)]$_{21}$ wires with 50-nm diameter under a field applied parallel to the long axis of the wires. The

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coercivity is ca. 490 Oe, which is much enhanced compared to that of bulk Ni (ca. 0.7 Oe) and that of Ni nanowire array (ca. 290 Oe).[14] At this temperature, we have determined a high saturation magnetization (Ms) of 54.4 emu/g_{Ni},[15] close to that found for bulk nickel (55.15 emu/g_{Ni}). The curve is highly sheared indicating strong interwire interaction.[16] Further evidence supporting this is the fact that the array of Ni−Cu nanowires has a very low remanent magnetization, less than 45% of Ms. Such strong interwire interaction is expected because the Ni−Cu nanowires in the array are very close to each other.

In summary, by using an AAO membrane as the template, a highly ordered composite Ni−Cu nanowire array was prepared by pulsed electrodeposition. The Ni segments alternated with nonmagnetic Cu layers are single crystals with a preferred ⟨111⟩ orientation. MFM observation reveals that all the Ni segments are single magnetic domain and aligned to the same direction after magnetizing under an external field (perpendicular or parallel to the axes of the nanowires). Magnetization measurement on the array of ordered Ni−Cu nanowires demonstrates a remarkably enhanced coercivity and a similar high saturation magnetization compared to that of bulk nickel. From a technological point of view, this new type of magnetic nanostructure is more suitable for the application in ultrahigh-density magnetic recording than OMA. The template-directed assembly strategy is a simple, effective, and versatile approach for the fabrication of ordered nanowire arrays of bi- or multicomponents, as well as magnetic−nonmagnetic nanowires, in a wide range of metals, alloys, and semiconductors. The novel structures of nanowires have potential applications in catalysts, chemical sensors, nanoelectrodes, and nanodevices.

Acknowledgment. We thank the National Natural Science Foundation and the Foundation of the Chinese Academy of Sciences for financial support. Support from the National Key Project on Basic Research (grant G2000077501) is also acknowledged.

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