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# Synthesis and magnetic properties of multilayer Ni/Cu and NiFe/Cu nanowires

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**Abstract.** Highly ordered composite nanowires with multilayer Ni/Cu and NiFe/Cu have been fabricated by pulsed electrodeposition into nanoporous alumina membrane. The diameter of wires can be easily varied by pore size of alumina, ranging from 30 to 100 nm. The applied potential and the duration of each potential square pulse determine the thickness of the metal layers. The nanowires have been characterized by transmission electron microscopy (TEM), magnetic force microscopy (MFM), and vibrating sample magnetometer (VSM) measurements. The MFM images indicate that every ferromagnetic layer separated by Cu layer was present as single isolated domain-like magnet. This technique has potential use in the measurement and application of magnetic nanodevices.

**Keywords.** Nanowires; Ni/Cu; NiFe/Cu; anodic aluminum oxide.

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## 1. Introduction

Magnetic nanomaterials fabricated by various methods [1], have attracted a great deal of attention for fundamental interest and technological applications such as magnetic storage media, sensors and magnetic random access memory (MRAM). In these nanomaterials, each ferromagnetic region is a single domain in which the magnetic spins are aligned in one direction. Thus every ferromagnetic region represents a single domain magnet, which exhibits unique magnetic properties for further applications, such as high squareness and high coercivity [2]. Among these nanomaterials, nanowires are of intense interest. Many methods for the fabrication of nanowires have been developed [3,4]. Among these methods, template synthesis was regarded as quite useful because it is extremely general with regard to the types of materials that can be prepared. Many ferromagnetic nanowires of Fe, Co, Ni and their alloys are fabricated by this method. The shape and size of nanowires synthesized by the template method can be confined within the pores of the template [5]. However, these nanowires often lose their high coercivity due to demagnetization by neighboring magnetic domains. In order to overcome this drawback, the non-magnetic layer (NM) is inserted between each ferromagnetic layer (FM), to form FM/NM/FM... periodic structure. The magnetic properties of these multilayer nanowires can be varied according to the thickness of FM and NM layers [6]. In this work we report the synthesis of an array of Ni/Cu and NiFe/Cu composite nanowires. The relationship between magnetic properties and layer thickness are discussed. The potential use of magnetic multilayer nanowires is also described.

## 2. Experimental details

In template-based synthesis, there are a variety of materials such as templates. Here anodic aluminum oxide (AAO) is chosen as template because AAO has an isolating, non-connecting, and parallel pore structure with tunable pore diameters. The AAO membranes used in our experiments were prepared via anodic oxidation of Al foil (99%, 0.25 mm thick). Al foil was first electropolished in sulfuric acid/phosphoric acid mixed solution ($H_2SO_4 : H_3PO_4 : H_2O = 4:4:2$ in wt%) at room temperature for 10 min. After electropolishing, the Al foil was anodized in 0.3 M oxalic acid at 10°C for 5–16 h to form AAO (dc current). The pore size of anodized AAO is tunable and proportional to voltage of anodization. The membrane was dipped into saturated $HgCl_2$ solution to remove the remaining Al, and then dipped in 5 wt% $H_3PO_4$ for 3–4 h to dissolve the barrier layer. After the anodization and cleaning process the AAO membranes are ready for deposition. In this paper we will discuss the effect of magnetic or non-magnetic layer thickness on magnetic properties of nanowires. The condition of AAO templates was kept unchanged, including pore diameters and the distance between wires.

In the synthesis of nanowires via template method, the pulsed electrochemical deposition in one bath containing $Ni^{2+}$ ($Ni^{2+}$ and $Fe^{2+}$) and $Cu^{2+}$ ion was used. First silver of 5000 Å thickness was thermally evaporated onto one side of AAO to serve as back electrode. The electrochemical deposition was performed via a 3-electrode method. Pt wire is chosen to be the counter electrode and the Ag/AgCl electrode is the reference electrode.

In order to achieve proper deposition efficiency, the reduction voltage was set at −1 V for Ni and −0.16 V for Cu in the case of Ni/Cu nanowires. The sulfates of Ni and Cu are chosen as the sources of metal ions, and the buffer solution is 0.6 M $H_3BO_3$. The concentration ratio of $NiSO_4/CuSO_4$ is set at 100 to decrease the rate of Cu reduction during deposition of Ni. The concentration of $NiSO_4$ and $CuSO_4$ are 2 M and 0.02 M, respectively.

For synthesis of NiFe/Cu nanowires Ni, Fe and Cu sulfate bath with 0.1 M $H_3BO_3$ as buffer solution was used. The concentration of $NiSO_4$, $FeSO_4$ and $CuSO_4$ are 0.6 M, 0.08 M and 0.006 M, respectively. To obtain nanowires about 2000 nm long only 10–20 pulses for each segment were used. Plating voltage for Cu is 0.3 V and for NiFe alloy it is 1.3 V, that is higher than for Ni/Cu nanowires to diminish Cu incorporation in NiFe segment instead of Fe.

The time of each pulse can be changed to tune the thickness of each layer. After the nanowires were formed, the silver electrode was removed by 6 M $HNO_3$, and then the AAO was dissolved by 6 M NaOH to achieve Ni/Cu nanowires.

These nanowires were analyzed using TEM (H-7100, Hitachi) and X-ray diffraction (BL17A, NSRRC, Taiwan) to obtain the morphology and composition. VSM (EV5 VSM, ADE Technologies) and MFM (D3100, Digital Instrument) were used to characterize the magnetic properties of these nanowires.

## 3. Discussion

The bamboo-like structure of Ni/Cu nanowires is shown in figure 1. From the TEM micrograph the thickness of Ni layer and Cu layer are 400 nm and 50 nm, respectively. The existence of this structure confirms that the Ni/Cu multilayer nanowires were successfully synthesized. The diameter of nanowires is 40 nm, slightly larger than the nanowires inside the AAO ($\sim$35 nm). This is because the surface of nanowires was slightly oxidized by NaOH during the process.

From the X-ray diffraction pattern of AAO deposited with Ni/Cu, we can easily find the diffraction peaks of Ni and Cu. By using the Scherrer equation to calculate the grain size of Ni and Cu, the grain sizes were found to be 36 nm and 34 nm, respectively. These values are close to the diameter of nanowires.

Figure 2 shows the lift-mode MFM phase-shift graphs of Ni/Cu nanowires. The deposition time of Ni and Cu are 20 s ($\sim$300 nm) and 30 s ($\sim$200 nm), respectively, with a wire diameter around 300 nm. In the phase-shift graph the difference of the brightness represents the difference of the magnetic moment. Shown on the bottom right of figure 2 is the presentation of how the magnetic tips of MFM detects the

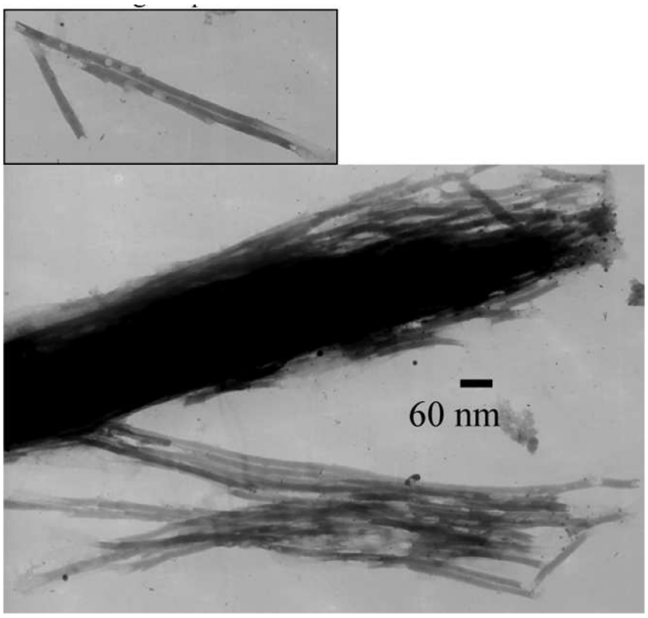


**Figure 1.** TEM micrograph of a bundle of Ni/Cu nanowires with a diameter of 40 nm. The inset shows the bamboo-like structure.

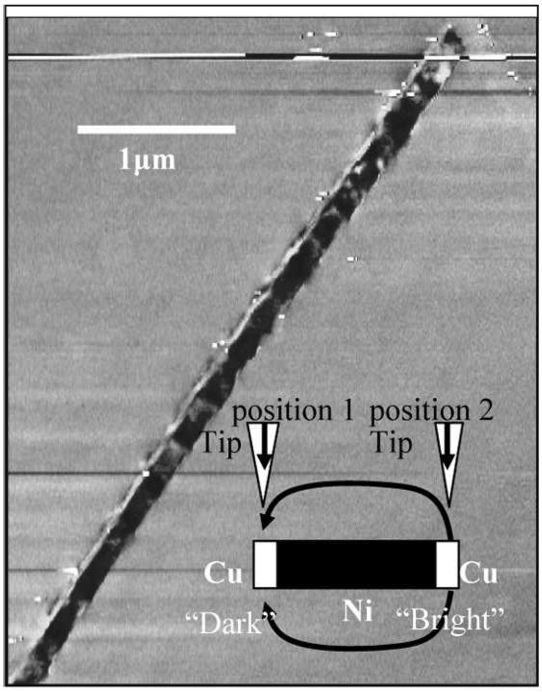


**Figure 2.** Lift-mode MFM graphs of Ni/Cu nanowires. The deposition time of Ni and Cu are 20 s (∼200 nm) and 30 s (∼50 nm), respectively.

magnetic signal. The black arrows represent the direction of magnetic field. When the tip moves to position 1, the magnetic field produced by Ni segment within Ni/Cu nanowires is parallel to the direction of magnetization of the tip. The phase-shift image shows a 'dark' region. When the tip moves to position 2, the magnetic field is antiparallel and shows a 'bright' region. The period length of bright to dark is the size of magnetic domain. However, the synthesized Ni/Cu wires are polycrystalline. The appearance of a single isolated domain-like structure in our MFM image may indicate that the magnetic moments in the small single crystals of polycrystallines are nearly arranged in the same direction. High resolution MFM may be needed to prove this assumption. Furthermore, the direction of magnetic moment is parallel to the nanowires. This result is consistent with what Guo *et al* [7] found. However they did not see the bamboo-like structure in the MFM graphs. This might be due to the difference of thickness of Cu. From Guo's experiment, the thickness of Cu was only 8 nm, but in our case was 50 nm. The difference causes the magnetic moment of each Ni layer in Guo's research merged, but was totally separated in our case.

Figure 3 show the hysteresis loops of 35 nm (diameter) Ni/Cu wires with different deposition time of Cu and constant deposition time (20 s) of Ni (∼200 nm). The coercivity and squareness (remanent magnetization/saturated magnetization; $M_{\mathrm{r}}/M_{\mathrm{s}}$) result are shown in table 1. From table 1, the highest coercivity value among all samples is 895 Oe, higher than what Whitney *et al* [8] reported and

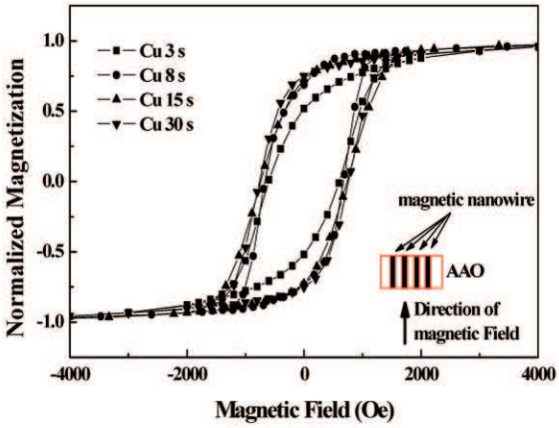


**Figure 3.** Hysteresis loops of 35 nm Ni/Cu wires with different deposition time of Cu and constant deposition time (20 s) of Ni (∼200 nm). The applied field is perpendicular to the membrane.

**Table 1.** The coercivity and squareness of Ni/Cu nanowires observed in figure 3.

| Deposition time of Cu (s) | Applied field | Coercivity $H_c$ (Oe) | Squareness $M_r/M_s$ |
|---|---|---|---|
| 3 (∼5 nm) | Parallel to nanowires | 607 | 0.52 |
| 8 (∼12 nm) | Parallel to nanowires | 775 | 0.69 |
| 15 (∼25 nm) | Parallel to nanowires | 855 | 0.74 |
| 30 (∼50 nm) | Parallel to nanowires | 860 | 0.75 |

pristine Ni nanowires with the same diameter. The squareness is as high as 0.75, and the nanowires can remain well-magnetized when applied field is removed. Combining the results of coercivity/squareness and the previous observation of MFM, it implies that each Ni segment inside the nanowires is a single isolated domain-like and separated by Cu segment. Comparing all samples in figure 3, it is found that the coercivity increases with the deposition time and saturates in samples when Cu deposition time is more than 15 s (roughly 25 nm thick, estimated from the TEM micrograph). It was seen that the demagnetization interaction weakened as thickness of Cu layer increased. When the Cu layer thickness is larger than 25 nm, the neighboring Ni layers were totally isolated and the demagnetization interaction decreased to the lowest value.

Figures 4a and 4b display the hysteresis loops of short (10–20 segments) 45 nm diameter NiFe/Cu wires with different deposition time of Cu (30, 40 and 50 s) and constant deposition time of NiFe alloy (10 s) in magnetic field applied perpendicular and parallel to the AAO membrane, respectively.

The atomic ratio of Ni, Fe and Cu in ferromagnetic segment (NiFe) was about 80 : 10 : 10 according to EDS. The magnetic characteristics – coercivity and squareness are given in table 2. It is obvious that nanowire arrays have easy magnetization

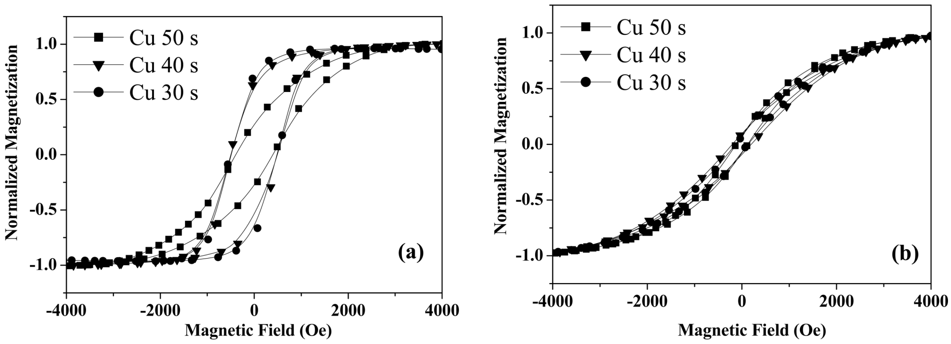


**Figure 4.** Hysteresis loops of 45 nm NiFe/Cu wires with different deposition time of Cu and constant deposition time (10 s) of NiFe alloy. (**a**) The applied field is perpendicular to the membrane (parallel to the wires). (**b**) The applied field is parallel to the membrane (perpendicular to the wires).

**Table 2.** The coercivity and squareness of NiFe/Cu nanowires observed in figure 4.

| Deposition time of Cu (s) | Applied field | Coercivity $H_c$ (Oe) | Squareness $M_r/M_s$ |
|---|---|---|---|
| 30 | Parallel to nanowires | 577 | 0.60 |
| | Perpendicular to nanowires | 115 | 0.08 |
| 40 | Parallel to nanowires | 502 | 0.64 |
| | Perpendicular to nanowires | 197 | 0.1 |
| 50 | Parallel to nanowires | 332 | 0.31 |
| | Perpendicular to nanowires | 124 | 0.09 |

direction parallel to the wires (perpendicular to the membrane). Moreover, the coercivity and squareness of the magnetic field perpendicular to the wires of NiFe/Cu decrease by increasing the deposition time of Cu from 30 to 50 s.

## 4. Conclusions

We have successfully synthesized 35 nm Ni/Cu and 45 nm diameter NiFe/Cu composite nanowires. Both have easy magnetization direction parallel to the wire. Each Ni layer represents a single separated domain with the same direction as the magnetic moment. This caused the unique high coercivity and squareness, which are beneficial for future application of magnetic storage. This phenomenon might be useful for the assembly of future nanodevices.

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