The pH Rule for Fabricating Composite CoCu Nanowire Arrays

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(Received October 23, 2006; CL-061245; E-mail: ghwu@aphy.iphy.ac.cn)

A series of $\text{Co}_{1-x}\text{Cu}_x$ ($x = 0.05\text{--}0.70$) composite nanowire arrays have been electrodeposited in alumina templates. An apparent pH value rule for nanowire phase and composition has been found. Based on it, composite nanowires can be obtained and the composition becomes more controllable. In the composite nanowires, the cubic and hexagonal structures coexisted. The specific magnetic properties, coercivity and squareness of the composite arrays are enhanced by three times, apparently preceding to those in single phase nanowires.

In the investigation of magnetic nanowire arrays,^{1,2} more and more ferromagnetic–nonmagnetic alloy systems, including CoCu, have been reported for exhibiting special magnetic characters.^{3–6} For CoCu nanowires, most studies mainly focus on Co/Cu multilayer,^{3,4} or the face-centered cubic (fcc) single phase,^{3,5} and very few literature has been found on the fabrication and characterization of composite CoCu nanowires. The magnetic properties of the composite Co-based nanowire should be much better than the single phase nanowires, because more boundaries and grain surfaces can improve the effective anisotropy and enhance the magnetic coercivity.

In this paper, a series of CoCu electrodeposition experiments have been carried out under the different pH values and potentials. We found that the structure and the composition dependences exhibit a strong pH value rule: 1) the nanowires with wider composition range can be prepared by using a moderate pH value of 3.3; 2) using this pH value, the nanowires are of composition with hexagonal close packed (hcp) and fcc structures. Due to containing rich phase boundaries, the magnetic properties of the nanowire arrays apparently precede to those in single phase samples.

Nanoporous anodized alumina oxide (AAO) templates with diameter of 50 nm were prepared by a two-step anodization process. The CoCu nanowires were electrodeposited into the pores by DC electrolysis in an electrolyte consisting of 0.08 M CoSO_4 , 0.008 M CuSO_4 ($\text{Co}^{2+}:\text{Cu}^{2+} = 10:1$), and 0.5 M H_3BO_3 . The pH 3.1, 3.3, and 3.5 are adjusted by adding NaOH solution. The electrodeposition of $\text{Co}_{1-x}\text{Cu}_x$ nanowires was carried out at different depositing potentials (-1.0 to -1.4 V) at given pH values. The chemical compositions of the nanowires were determined by energy-dispersed X-ray spectrometry (EDXS), the microstructure and magnetic properties were detected by transmission electron microscopy (TEM), X-ray diffraction (XRD) and vibrating sample magnetometer (VSM).

A series of $\text{Co}_{1-x}\text{Cu}_x$ nanowire arrays have been obtained by electrodeposition in the AAO templates. The nanowires are all straight and parallel to each other with uniform diameter of 50 nm and total length of about 15–20 μm .

Table 1 shows the $\text{Co}_{1-x}\text{Cu}_x$ composition and structure dependence of pH values and depositing potentials. The Cu content

Table 1. The composition (Co:Cu) and structure of deposited CoCu nanowires at different pH values and depositing potentials

Potential/V	pH		
	3.1	3.3	3.5
–1.0	71:29 (hcp)	38:62 (fcc&hcp)	30:70 (fcc)
–1.1	77:23 (hcp)	49:51 (fcc&hcp)	42:58 (fcc)
–1.2	84:16 (hcp)	60:40 (fcc&hcp)	46:54 (fcc)
–1.3	90:10 (hcp)	75:25 (fcc&hcp)	53:47 (fcc)
–1.4	95:5 (hcp)	87:13 (fcc&hcp)	65:35 (fcc)

is in a large composition range of $x = 0.05\text{--}0.70$ and monotonously increases with the increase of the depositing potential. The fact that Cu rich samples (for example, $\text{Co}_{0.30}\text{Cu}_{0.70}$) still can be deposited in these rich Co^{2+} solutions implies that the depositing rate of Cu is much higher than that of Co. This result was also reported in previous works.^{3,5}

Comparing to the potential, however, the Cu depositing rate is more sensitive to the pH values. At pH 3.1, the copper concentration ranged in 5–29% which is a Co-rich composition, and at pH 3.5, it ranges in 35–70% turning to Cu-rich side. Therefore, a moderate pH value, pH 3.3 provides a good condition for covering a wide range of Cu content of 13–62%, as shown in Table 1, and thus the Cu concentration becomes more controllable.

The structures of all nanowire arrays have been examined by XRD, as also listed in Table 1. It can be seen that, for relatively low pH of 3.1, the samples formed as hcp structure. For high pH of 3.5, the arrays were dominated by fcc CoCu alloy.

Based on the fact that the single hcp or fcc structures are supported by using pH 3.1 and 3.5, respectively, one may believe that the composite phase with fcc and hcp can be obtained by using a moderate condition of pH value. At pH 3.3 is taken, a composite phase, hcp plus fcc structures have been obtained in overall Co:Cu range from 87:13 to 38:62 as shown in Table 1. It should be noted that the composite nanowires have a wide composition range even covered those of single phase samples. Therefore, we may conclude that the results in Table 1 indicate an apparent pH value rule: contrasting to the usage for lower or higher pH values to producing Co- or Cu-rich composition and single phase, the optimized pH value of 3.3 supports the nanowires depositing in a composite phase and additionally, in a wider composition range. This result can be attributed to that the pH value strongly affects the depositing rate of Cu^{2+} , which further dominates the overall composition and the structure of the nanowires. This effect has also been observed in the works on pure Co nanowires.²

Figure 1 shows the detail XRD results of $\text{Co}_{1-x}\text{Cu}_x$ nanowire arrays prepared under pH 3.3 condition. For all samples, hcp Co(100) peak can be clearly observed, which indicates the hcp Co always exists in nanowires. For Co-rich sample of $\text{Co}_{87}\text{Cu}_{13}$, only (100) peak of hcp Co can be observed. This

Figure 1. XRD of the nanowire arrays deposited at the same pH 3.3 and different depositing potentials.

Figure 2. Coercivity (a) and squareness (b) of the as-deposited $\text{Co}_{1-x}\text{Cu}_x$ nanowire arrays deposited at different pH values and potentials.

means that the nanowires are preferentially oriented in this direction with a textured state. The reason for no sign of elementary Cu was found in this sample by XRD is due to the Cu stating in too small grains to be detectable.⁵ Increasing the depositing potential, the Cu content increases and more peaks which represent other phase gradually appear. The peaks located at 50.55 and 74.19° belong to the pure Cu and the others stand for CoCu alloy based on their locations and the apparent wideness.⁷ Indexing the XRD, we have the lattice parameters for those phases: $a = 2.509 \text{ \AA}$, $c = 4.096 \text{ \AA}$ (hcp Co), $a = 3.571 \text{ \AA}$ (CoCu fcc alloy) and $a = 3.600 \text{ \AA}$ (fcc Cu). Thus, it can be confirmed that three phases, hcp Co, fcc CoCu and elemental fcc Cu coexist in these nanowires. The portion of CoCu and Cu increases with the increase of the overall content of Cu.

In the previous works,^{3,5} excepting for optimized pH value, many other modified depositing conditions were used to prepared CoCu nanowires in the different structures. But the acquired structures are always single phase: either hcp or fcc. No composite phase like we found in this work has been observed. This strongly suggests that the pH value condition is

a very important condition to affect the structure of nanowires.

Magnetizations of the array samples have been measured to reveal the composite effect to magnetic properties. Figure 2 shows the comparison of the magnetic properties between the single phase samples and the composite ones. These two kinds of sample cover the same Co–Cu composition ranges and have the same diameter/length, but the composite samples show the apparently improved results: the peak values of the coercivity $H_c = 1400 \text{ Oe}$ and the squareness $M_r/M_s = 91\%$, about three times higher than those of single phase samples. This should be attributed to the existence of the composite phase, hcp plus fcc structures with much more phase boundaries which enhance the domain pinning in the nanowires and increase the demagnetization field.

Composite CoCu nanowires have been successfully electro-deposited by using an optimized pH value. We found that, comparing to the depositing potential, the pH value has much stronger influence on dominating the composition and structures than the other depositing conditions. An apparent pH rule has been concluded. Based on it, the composite nanowires with the structure of hcp and fcc phase and a quite large composition range can be obtained. Their magnetic properties apparently precede to those in the single phase samples.

This work was supported by the CNNSF Grant No. 50471056, and the CNNSF Grant No. 50472034.

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