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Structural and magnetic properties of $(FePt)_{1-x}Cu_x$ nanowires

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ABSTRACT

Highly ordered $(FePt)_{1-x}Cu_x$ nanowire arrays have been fabricated successfully by double-pulse electro-deposition into the pores of a porous anodic aluminum oxide template. We have found that the addition of Cu to FePt nanowires is an effective approach for reducing the ordering temperature of FePt. The coercivity of the $(FePt)_{88}Cu_{12}$ nanowire arrays is around 2 kOe after annealing at 300 °C for 1 h, whereas that of FePt nanowire arrays shows several hundred Oe. X-ray diffraction characterization showed that only one set of $L1_0$ diffraction peaks appeared and no elemental Cu diffraction peaks were visible. This result, along with a varying *c/a-lattice* parameter ratio, suggests that Cu substitutes Fe or Pt in the ternary FePtCu alloy nanowires.

1. Introduction

Nanopatterned magnetic recording media offer a number of advantages over conventional continuous magnetic recording media, including the ability to provide a much higher recording density [1–6]. Various forms of nanopattern formation have been tried in order to reach the 10 nm resolution required for $>1\ Tb/in^{-2}$ recording density. Face-centered-tetragonal (fct)-structured FePt clusters have large magnetocrystalline anisotropy, high magnetization, and chemical stability. They are promising as building blocks for the fabrication of future high-density recording media and nanocomposite permanent magnets [7–11]. In recent years, it has been found that CoPt and FePt alloy nanowire arrays with perpendicular magnetic anisotropy and adequate coercivity can be easily prepared by electro-deposition [12,13]. However, the transition temperature from the chemically disordered face-centered-cubic (fcc) phase to the ordered fct phase in these nanowire arrays is as high as 700 °C. In this article, we present a simple and economical way of fabricating highly ordered $(FePt)_{1-x}Cu_x$ nanowire arrays. We found that the addition of Cu to FePt nanowires is an effective approach for reducing the ordering temperature of FePt nanowire arrays. The morphologies and magnetic properties of the samples at different annealing temperatures have been characterized.

2. Experimental procedures

The nanoporous anodic alumina oxide (AAO) membranes were prepared by using a modified two-step anodizing process reported elsewhere [14]. Briefly summarized, high-purity Al foils were anodized in 0.3 M oxalic acid solution at 8–10 °C at a bias of 40 V for 8 h. After removing the resultant aluminum oxide film formed by the first anodization one side of the Al plate was coated with manicure. A second anodization was performed for 6 h under the same conditions as the first one. The as-prepared template was dipped into 5% phosphoric acid for 1 h to eliminate the obstacle film, and then an AuCu film of 1 μm thick was sputtered onto one side of the template to act as a conductive contact. Like FePt alloy, in the vicinity of equiatomic ratio, the AuCu alloy also displays a structural disorder–order transformation along with a slight lattice distortion from fcc to fct, but the ordering temperature of AuCu alloy is much lower than that of FePt alloy [15]. Besides, the equiatomic AuCu alloy has lattice constants close to those of equiatomic FePt alloy with either fcc or fct structure.

FePt nanowire arrays were electrodeposited at room temperature from an aqueous electrolyte consisting of 0.012 mol/L H_2PtCl_6, 0.1 mol/L NaCl, 0.02 mol/L $FeCl_2$, and 0.02 mol/L ammonium tartrate. The solution pH was adjusted to around 7.0 by adding NaOH. In this bath, Fe ions are stabilized as a complex of Fe tartrate. A specific amount of $CuCl_2$ were added as the Cu source to prepare the $(FePt)_{1-x}Cu_x$ nanowires. The counter electrode was a Pt mesh and the reference electrode was Ag/AgCl. The composition of the samples was analyzed with energy dispersive X-ray spectroscopy (EDS). Magnetic properties were measured by a Quantum Design superconducting quantum interference device (SQUID). The crystal

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structures were characterized by X-ray diffractometer (XRD). The morphology of nanowire arrays was characterized by field emission scanning electron microscopy (FESEM).

3. Results and discussion

Fig. 1 shows FESEM image of the porous alumina template used in this work. It can be seen that the template exhibits a two-dimensional array with a hexagonal pattern. Also, there the particles are found on the AAO surface. They are the residual aluminum. The pore diameter and interpore distance are about 40 and 100 nm, respectively. To observe the morphology of FePt nanowire arrays by FESEM, after electro-deposition the sample was eroded by an aqueous solution of 2 wt% NaOH in order to remove the upper part or the whole anodic alumina membrane. Fig. 2 shows a planform where the alumina matrix of the AAO template has been dissolved away and large quantities of FePt nanowires remain. From Fig. 2, we can find that the nanowires are very uniform with a diameter of about 40 nm, which basically equals the pore diameter of the porous alumina template used in the experiment. Fig. 2 also shows several clusters of nanowires. The nanowires are uncovered from the anodic alumina template, but they are incompletely freestanding and stick together which result in clusters of nanowires.

Fig. 3 shows the coercivity (H_c) values of the $(FePt)_{1-x}Cu_x$ nanowire arrays annealed at 400 °C for 1 h in vacuum as a function of Cu content. As seen in this figure, H_c has a strong dependence on Cu content. The H_c is proportional to the composition of Cu at low copper concentration. However, as the copper concentration rises higher than 12%, the H_c drops rapidly. It indicates that when the Cu composition is too high, the structure is no longer similar to that of FePt phase. Therefore, it is found that the most effective Cu content for reducing the ordering temperature is around 12 at%.

Fig. 4 shows the relationships among H_c and the annealing temperature (T_a) of the FePt and $(FePt)_{88}Cu_{12}$ samples. It was found that the H_c of both FePt and $(FePt)_{88}Cu_{12}$ nanowires show several hundred Oe, but after annealing for 1 h, samples exhibit a hard magnetic property. The H_c of both FePt and $(FePt)_{88}Cu_{12}$ increase with increase in the annealing temperature up to 600 °C. One can notice that H_c of FePt nanowire arrays gently rises as T_a moves upward from 300 to 400 °C, but it climbs up promptly

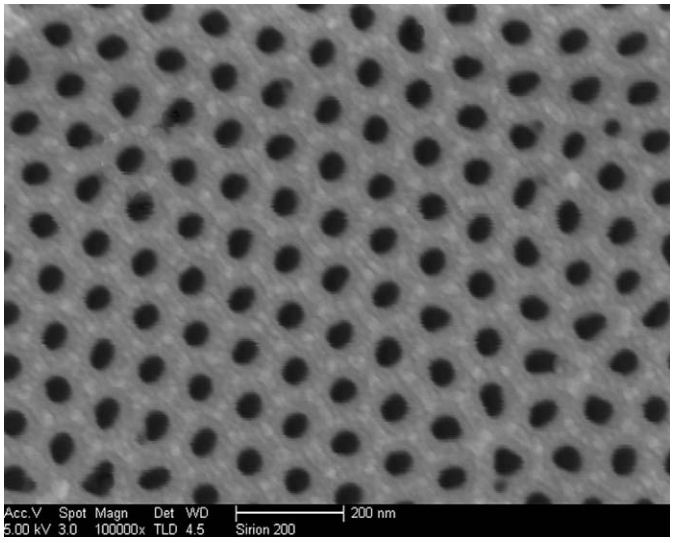

Fig. 1. FESEM image of anodic alumina membranes.

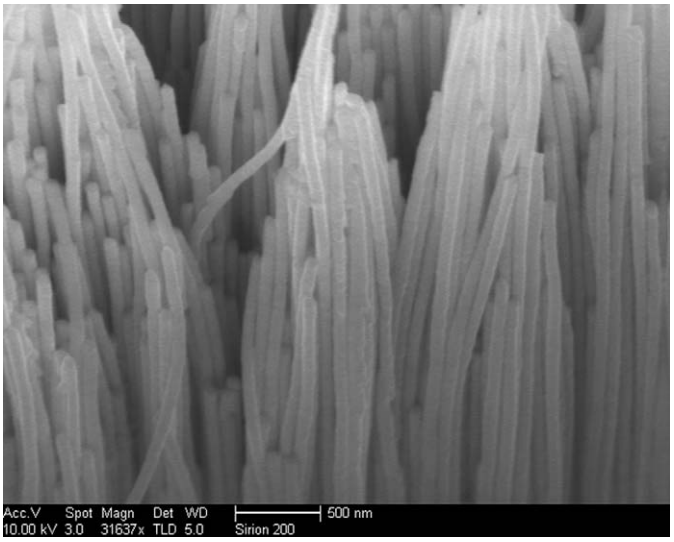

Fig. 2. FESEM image FePt nanowire arrays.

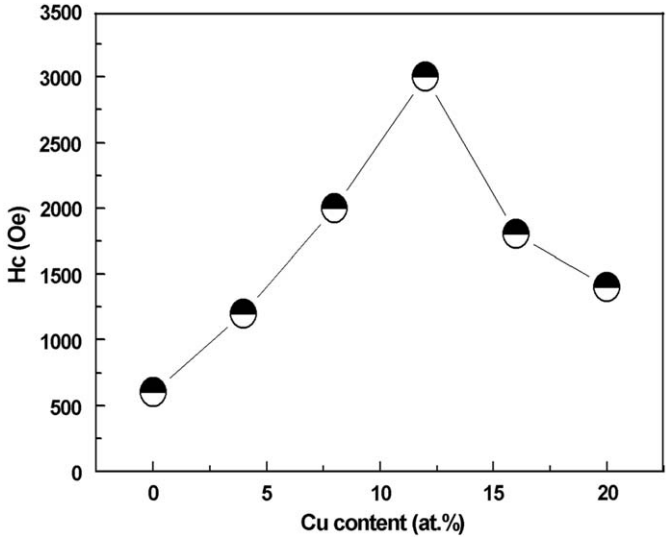

Fig. 3. The coercivity as a function of Cu composition.

when T_a is higher than 400 °C. This result indicates that the FePt nanowires transform from the soft magnetic phase to the hard magnetic phase as$T_a \geq 400$ °C. On the other hand, H_c of $(FePt)_{88}Cu_{12}$ annealed at 300 °C is already over 2 kOe. This means that the ordering of the $(FePt)_{88}Cu_{12}$ nanowire arrays starts from 300 °C or less temperature, and that the ordering temperature of the $(FePt)_{88}Cu_{12}$ nanowire arrays is lower than that of the FePt nanowire. The dependence of H_c on the annealing temperature can be understood from the XRD experiment. Fig. 5 shows X-ray diffraction data of $(FePt)_{88}Cu_{12}$ samples with various annealing temperatures for 1 h in vacuum. At low annealing temperatures of 200 °C, the (1 1 1) fundamental peak of fcc disordered structure have been observed. When annealed at 300 °C, fct (0 0 1) and fct (2 0 0) superlattice reflections appear indicating that the transformation from fcc to ordered phase starts at 300 °C. For the higher annealing temperature of T_a=400 °C, the intensities of superlattice reflections increase, and the diffraction peak of (2 0 0) plane splits into two peaks corresponding to the fct (2 0 0) and fct (0 0 2) planes. This

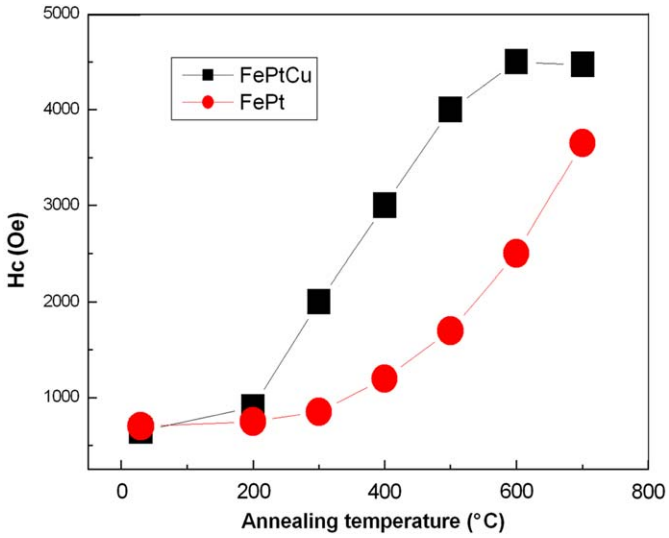

Fig. 4. The coercivity as functions of annealing temperatures for the FePt and $(FePt)_{88}Cu_{12}$ nanowire arrays.

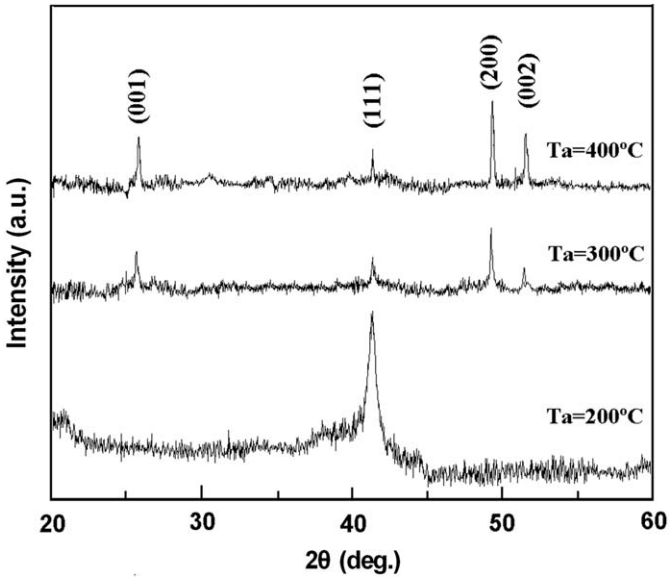

Fig. 5. XRD patterns for $(FePt)_{88}Cu_{12}$ nanowires at various annealing temperatures.

indicates that cubic fcc phase is transformed to a tetragonal fct order phase.

Fig. 6 shows XRD patterns of $(FePt)_{1-x}Cu_x$ nanowire arrays with (a) x=0 at%, (b) x=6 at%, and (c) x=12 at% annealed at 300 °C for 1 h. For the sample with x=0 at%, only fcc FePt (1 1 1) peak is observed. As the Cu content increased to 6 at%, the superlattice (0 0 1) peak and the fundamental (2 0 0) peak of $L1_0$-FePt are observed and the intensity of fcc FePt (1 1 1) peak decreased, which suggests that the value of c decreases. The behavior of structure transition from fcc disordered phase to the fct ordered structure was revealed in the intensities of (0 0 1) and (2 0 0) peaks of the XRD. Thus the increase of I (0 0 1)/I (1 1 1) ratio reflected an enhancement of (0 0 1) orientation with an increase of the Cu content, at least up to 12 at%. This indicates that the crystal structure transfers from fcc to fct, i.e. the $L1_0$-FePt phase. In the XRD patterns no elemental Cu diffraction peaks are visible, which indicates that Cu substitutes for Fe or Pt in the $L1_0$-FePt lattice to form alloy with FePt.

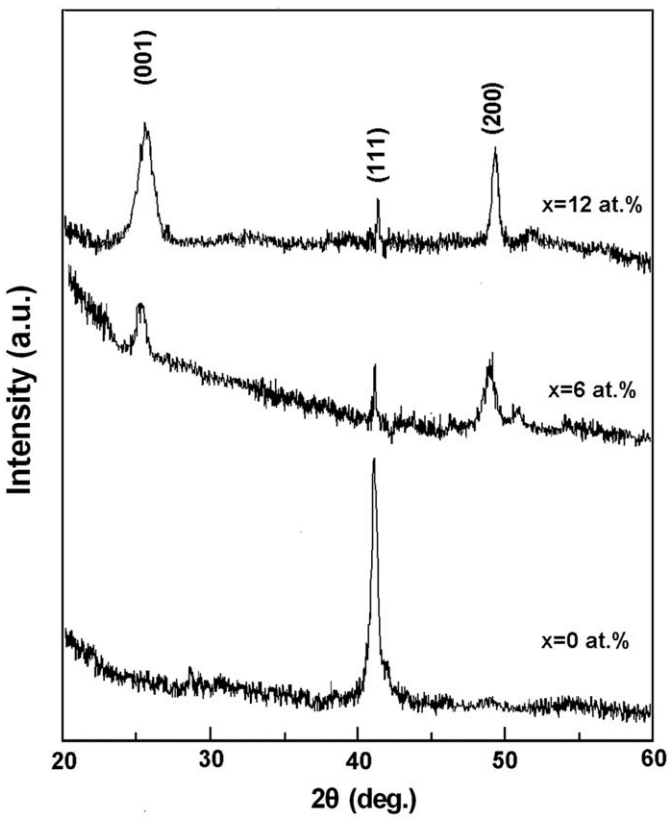

Fig. 6. XRD patterns of $(FePt)_{1-x}Cu_x$ nanowire arrays with (a) x=0 at%, (b) x=6 at%, and (c) x=12 at% annealed at 300 °C for 1 h vacuum.

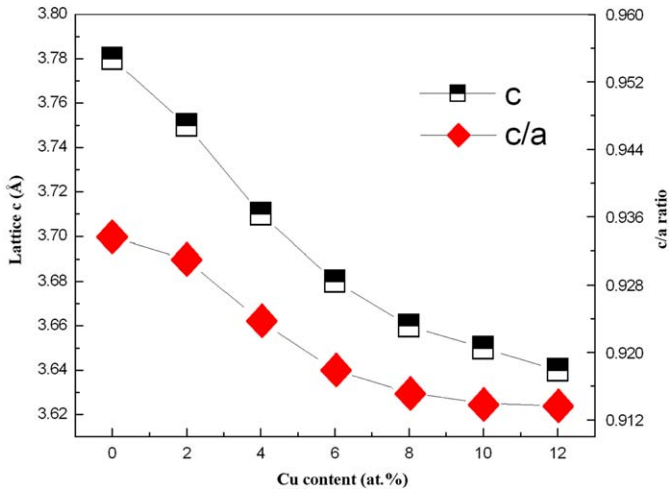

Fig. 7. a-lattice parameter and c/a ratio of FePt nanowires with Cu additive. All samples were annealed at 300 °C for 1 h in vacuum.

From the positions of the (0 0 1), (2 0 0), and (1 1 1) XRD peaks, the average values for a- and c-lattice parameters were calculated for $(FePt)_{1-x}Cu_x$ nanowires. Fig. 7 shows c-lattice parameters and the c/a ratio for FePt nanowires with Cu additive. All samples were annealed at 300 °C for 1 h. For the bulk $L1_0$ FePt, a- and c-lattice parameters were reported as 3.852 and 3.713 Å, respectively [16]. The origin of high Ku is deeply related to the c/a, especially for fct FePt alloy. When the value of c/a becomes small, FePt alloy is transformed from a disordered face-centered-cubic phase to an ordered face-centered tetragonal phase, the latter one has a CuAu I-type structure with high magnetocrystalline anisotropy energy

($Ku = 7 \times 10^7$ erg/cm^3) [17]. As shown in Fig. 7, for the sample without adding Cu, the c-lattice parameter is close to a. By adding Cu atoms, the c-lattice parameter and the c/a ratio decrease as the composition of Cu increases. When the Cu content was increased to 12 at%, the c-lattice parameter decreased to 3.589 Å. This result implies that the Cu is in a substitutional position instead of interstitial one during the ordering arrangement.

4. Conclusion

To summarize, highly ordered $(FePt)_{1-x}Cu_x$ composite nanowire arrays were prepared by pulsed electro-deposition in the porous of AAO membrane. The effects of Cu alloying on lattice parameters and magnetic properties were investigated. We have found that the approach proposed in this paper is effective for reducing the ordering temperature of FePt composite nanowires. XRD data provided evidence of Cu alloying with FePt by substituting Fe or Pt in the $L1_0$ lattice to form ternary $(FePt)_{1-x}Cu_x$. FePt nanowires for magnetism recording, after being separated from the holes of AAO film, can be changed into a layer of magnetic film of oxide. This kind of materials presents more and more widely significant applications in the high density and plumb magnetism recording mediums.

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References

[1] C.Y. You, Y.K. Takahashi, K. Hono, J. Appl. Phys. 100 (2006) 056105.
[2] Y.J. Tang, J.F. AuBuchon, L.H. Chen, S. Jin, J.W. Kim, Y.H. Kim, C.S. Yoon, J. Appl. Phys. 99 (2006) 08G909.
[3] H.J. Liu, S.L. Lim, C.K. Ong, Mater. Lett. 62 (2008) 2006.
[4] B.D. Terris, T. Thomson, J. Phys. D 38 (2005) R199.
[5] H. Masuda, K. Fukuda, Science 268 (1995) 1466.
[6] K. Fukutani, K. Tanji, T. Motoi, T. Den, Adv. Mater. 16 (2004) 1456.
[7] D. Hinzke, U. Nowak, R.W. Chantrell, Appl. Phys. Lett. 90 (2007) 082507.
[8] J.M. Vargas, R.D. Zysler, L.M. Socolovsky, M. Knobel, D. Zanchet, J. Appl. Phys. 101 (2007) 023903.
[9] S.H. Sun, C.B. Murray, D. Weller, L. Folks, A. Moser, Science 287 (2000) 1989.
[10] Y. Sui, L. Yue, R. Skomski, X.Z. Li, J. Zhou, D.J. Sellmyer, J. Appl. Phys. 93 (2003) 7571.
[11] Y.C. Sui, J. Zhou, X.Z. Li, R. Skomski, D.J. Sellmyer, J. Appl. Phys. 95 (2004) 6741.
[12] H. Zeng, J. Li, J.P. Liu, Z.L. Wang, S.S. Sun, Nature (London) 420 (2002) 395.
[13] D.J. Sellmyer, Nature (London) 420 (2002) 374.
[14] H. Masuda, M. Satoh, Jpn. J. Appl. Phys. Part 1 35 (1996) L126.
[15] T. Claeson, J.B. Boyce, Phys. Rev. B 29 (1984) 1551.
[16] T. Maeda, T. Kai, A. Kikitsu, T. Nagase, J. Akiyama, Appl. Phys. Lett. 80 (2002) 2147.
[17] D Weller, A. Moser, IEEE Trans. Magn. 35 (1999) 4423.