Fabrication and Magnetic Properties of Amorphous $Co_{1-x}P_x$ Alloy Nanowire Arrays

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Abstract: Amorphous $Co_{1-x}P_x$ alloy nanowire arrays with different sizes and 6.8 wt% ≤ x ≤ 9.9 wt% were fabricated in an anodic aluminum oxide film by electrodeposition. Transmission electron microscopy, selected area electron diffraction, X-ray fluorescence spectrometer, inductively coupled plasma-atomic emission spectrometer, X-ray diffraction spectrometer and vibrating sample magnetometer are employed to study the morphology, chemical composition, structure and magnetic properties of the nanowire arrays, respectively. The results show that the $Co_{1-x}P_x$ alloy nanowire arrays with x≥6.8 wt% are amorphous. Due to the shape anisotropy effect, the coercivity of nanowire arrays is large for the applied field along the nanowires axis, and nanowire arrays have obvious magnetic anisotropy. The amorphous Co-P alloy nanowire arrays are good candidates for ultra-high-density magnetic recording media.

Keywords: Nanowire arrays, chemical synthesis, magnetic properties.

INTRODUCTION

In the field of amorphous materials, great attention has been paid to basic research and new possible application due to their unique magnetic, chemical and electrical properties [1-3]. For example, the ferromagnetic amorphous alloys based on binary transition metal-metalloid (such as Fe-P, Co-P and Ni-P) can be used for electronic components, transformers and memory devices because they possess low coercivity, high magnetic permeability and other valuable technological properties [4,5]. In general, the amorphous alloys can be prepared by rapid quenching, sputtering, ion implantation and electrodeposition. Amorphous Co-P alloys have magnetic and electrical properties that are very attractive for technological applications. One of the major advantages of Co-P alloys is that they can be easily prepared by electrodeposition methods in the amorphous state and on different shaped substrates with controlled composition and magnetic properties. Amorphous Co-P alloys with desired phosphorous content, for example, are produced by a proper selection of electrolyte composition and current density [6, 7].

The study of preparation and properties of nanowire arrays, especially focused on polycrystalline magnetic nanowire arrays such as Co, Ni, Fe, and their alloys, have become the subject of intensive research due to their potential applications in ultra-high density magnetic storage devices and novel physical properties which are different from those of their bulk counterparts [8-10]. In such materials, the magnetic behavior is governed by the shape anisotropy, the magnetocrystalline anisotropy and the dipolar interaction between wires. So it is a main trouble that coexistence of the magnetocrystalline anisotropy, the dipolar interaction and the shape anisotropy in metallic alloys or metals magnetic nanowire arrays, which is difficult to distinguish their influence on the magnetization and reversal magnetization process of the nanowire arrays. For amorphous magnetic nanowire arrays, due to the lack of the magnetocrystalline anisotropy, magnetic behavior is mainly decided by the shape anisotropy and the dipolar interaction between wires, so it is an advantage to investigate the magnetization and reversal magnetization process of the nanowire arrays for fundamental science and application research. It is therefore significant to investigate the magnetic behavior of nanowire arrays made from amorphous magnetic materials. Here we successfully fabricated the binary amorphous $Co_{1-x}P_x$ alloy nanowire arrays in an anodic alumina oxide (AAO) film by electrodeposition. It is well known that, due to the shape anisotropy effect, the coercivity of the nanowire arrays may be large for the applied field along the nanowires axis, so the amorphous Co-P alloy nanowire arrays are good candidates for commercial ultra-high-density magnetic recording media. In this work, conditions and processes that yield continuous and high ordered nanowire arrays are described and their magnetic properties are discussed.

EXPERIMENT

An ordered AAO template was fabricated using a superpurity Al sheet (99.99%). The first step is the pretreatment process of Al sheet. An aluminium sheet was degreased ultrasonically in absolute ethyl alcohol for approximately15 min, etched in 1.0 M NaOH at room temperature for 15 min to remove the native oxide and washed thoroughly with distilled water, then electropolished in a mixed solution of $HClO_4$:CH_3CH_2OH = 1:4 for 2 min and immediately rinsed

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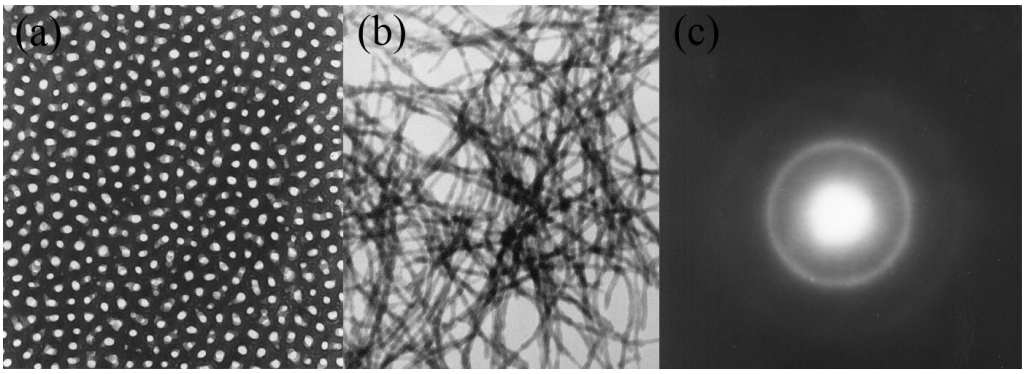

Fig. (1). The representative images: (**a**) SEM image of AAO films; (**b**) TEM image and (**c**) SAED of the $Co_{1-x}P_x$ alloy nanowires with x=6.8 wt%.

with distilled water. The second step is the oxidization process, the AAO films were fabricated by two-step anodizing process [11]. In brief, the pretreated Al sheet was anodized in different acid solution for 30 mins at different concentration, oxidization voltage and temperature for the first oxidization. Then the oxide film was dissolved in a mixed solution of 0.2 M H_2CrO_4 and 0.4 M H_3PO_4 for 15 min at 60°C. Finally, the dissolved aluminum membrane was anodized for 2 h in the same acid solution and in the same condition with the first oxidization again.

Electrodeposition of the Co-P alloy nanowire arrays was performed by using a standard double electrode bath. The AAO film is used as the anodic electrode, and the graphite is used as the cathodal electrode. The bath contained $CoSO_4 \cdot 7H_2O$ (120 g/l), H_3BO_4 (45 g/l), $Na_3C_6H_5O_7 \cdot 2H_2O$ (20 g/l), $NaH_2PO_2 \cdot H_2O$ (y g/l) (where y was controlled as 5, 10, 20, and 30, respectively). Here boric acid (H_3BO_4) was added as a buffering agent, while sodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) was added as a stabilizer of cobalt ions. The pH of solution was adjusted to 4 with sulfuric acid. The deposition voltage and frequency are 10 V_{AC} and 200 Hz, respectively.

The image of AAO film is obtained by using a scanning electron micrograph (SEM, JSM-5600). The nanowire arrays were separated from AAO film by dissolving the aluminum oxide film in a mixed solution of 0.2 M H_2CrO_4 and 0.4 M H_3PO_4 for transmission electron microscopy investigation. The image of Co-P nanowires is obtained using a transmission electron microscopy (TEM, JEOL 2000). X-ray fluorescence spectrometer (Magix, PW, 2403 XRF), inductively coupled plasma-atomic emission spectrometer (IRIS, ER/S), selected area electron diffraction (SAED) and X-ray diffraction (XRD, X ' Pert PRO PHILIPS, with Cu Kα radiation) are employed to study the chemical composition and the structure of the nanowire arrays. The magnetic properties of nanowire arrays are characterized by using a vibrating sample magnetometer (VSM, Lakeshore 7304) with the applied field parallel and perpendicular to nanowires axis.

RESULTS AND DISCUSSION

Fig. (**1**) shows the representative images. The SEM image of the AAO film is shown in Fig. (**1a**). It was found that the nanopores are uniform and highly ordered with diameters of about 10 nm. The TEM image of the $Co_{1-x}P_x$ nanowires with x=6.8 wt% is shown in Fig. (**1b**). The average diameter is about 10 nm. The diameter of nanowires is in agreement with the diameter of nanaopores of AAO film. Fig. (**1c**) shows the SAED patterns that reveal an amorphous structure of the nanowires with x=6.8 wt%.

In Fig. (**2**), the XRF analysis of the nanowire arrays shows that Co and P were the main elemental components. Quantitative analysis indicates that P content is 6.8 wt% by using inductively coupled plasma-atomic emission spectrometer. Oxygen and aluminum are also observed in the XRF analysis, which may come from surface adsorption of the oxygen or the AAO film.

Fig. (**3**) illustrates the XRD patterns of different diameters Co-P alloy nanowire arrays with P content about 6.8 wt%, which also reveal that nanowire arrays are amorphous structure that is in agreement with the result of SAED. At the same time, the measurements of the Co-P alloy nanowire arrays, with P content about 7.6, 8.7 and 9.9 wt%, respectively, show the same results by using XRD. The possible reactions in the fabrication of the Co-P nanowire arrays are as follows:

$$Co^{2+} + 2e \Leftrightarrow Co \quad (1)$$

$$H_2PO_2^- + e \Leftrightarrow P + 2OH^- \quad (2)$$

During electrodeposition process of the transition metals, there is always a simultaneous hydrogen evolution reaction. For acidic solution, it can be described by the following reaction:

$$2H^+ + 2e \Leftrightarrow H_2 \quad (3)$$

Fig. (**4**) shows the hysteresis loops of the $Co_{1-x}P_x$ alloy nanowire arrays with x=8.7 wt% and with diameter about 40 nm, measured at ambient temperature, where $H_{//}$ and $H_{\perp}$ indicate that the applied field is parallel and perpendicular to the nanowires axis, respectively. The deposition time is 1, 2, 4, 6 min, the length of nanaowires is about 1 μm, 2 μm, 3 μm, 4 μm and their aspect ratios are about 25, 50, 75 and 112, respectively. It can be seen that the squareness ratio for the $H_{\perp}$ is smaller than that for the $H_{//}$, which results from the effect of demagnetization field ($-NM_s$). For an infinite cylinder, the demagnetizing factors N are 0 and 1/2 for applied field being parallel and perpendicular to the nanowires axis, respectively. The saturation field (H_s) for the $H_{//}$ ($H_s \approx 5000$ Oe) is smaller than that for the $H_{\perp}$ ($H_s \approx 9000$ Oe), which in-

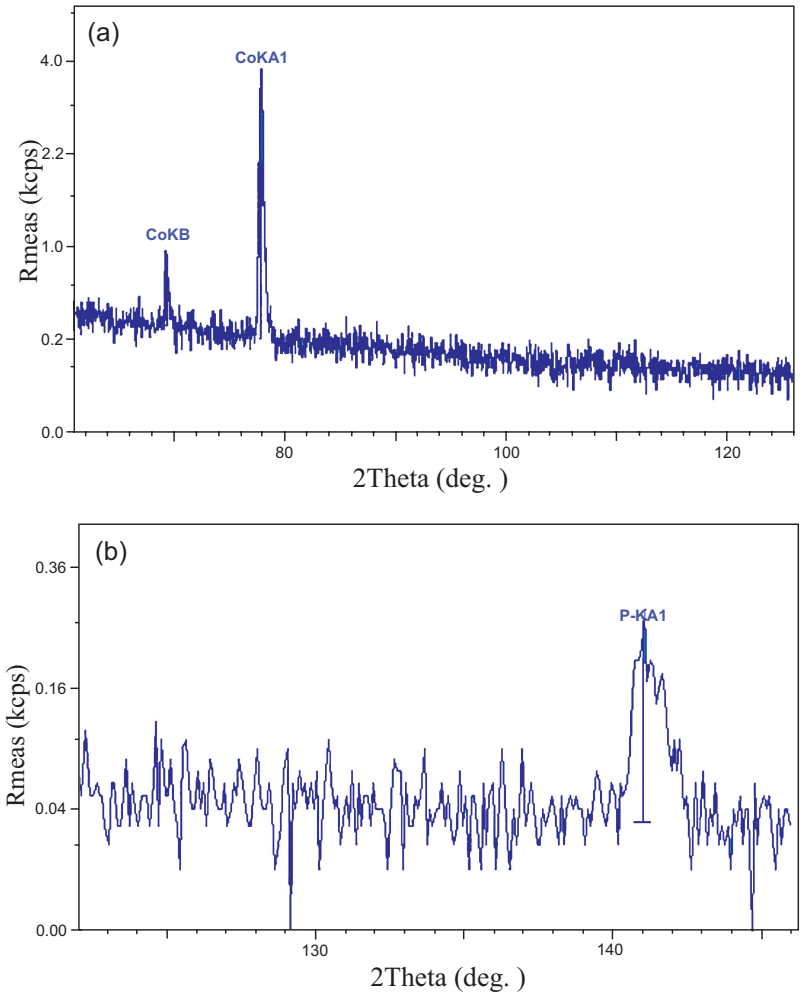

Fig. (2). XRF analysis of the $Co_{1-x}P_x$ alloy nanowires with x=6.8 wt%.

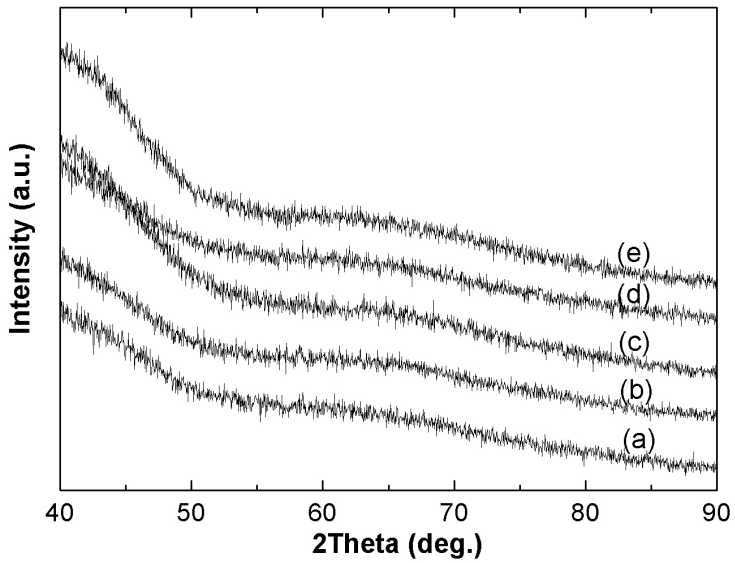

Fig. (3). X-ray diffraction patterns of the $Co_{1-x}P_x$ alloy nanowires with x=6.8 wt% for different diameter: (**a**) 10 nm; (**b**) 40 nm; (**c**) 80 nm; (**d**) 100 nm; (**e**) 130 nm.

dicates that the nanowire arrays have obvious magnetic anisotropy along the wire axis. From Fig. (**4**), the coercivities (H_c) for the $H_{//}$ are about 1390 Oe at different deposition time, which indicates that the easy magnetization direction is along the nanowires axis. It can be explained from the main contribution of shape anisotropy, and magneto-crystalline anisotropy is unlikely to occur in amorphous structure of Co-P alloy nanowire arrays. The fact may be also that the nanaowires could be partially crystallized for the observed higher values of coercivity, but it was not observed the partially crystallization by the measurements of XRD and TEM [6]. It can be also noticed that the squareness ratio for the $H_{//}$ in the Fig. (**4a**) is smaller than that of other loops (the Fig. **4** (**b**), (**c**), (**d**)) because its aspect ratio is small (≈25).

Fig. (**5**) shows the hysteresis loops of the $Co_{1-x}P_x$ alloy nanowire arrays for different diameters, with x=7.6 wt% and with deposition time about 5 min. The length of nanowire arrays is about 4 μm and their aspect ratios are about 400, 100, 50 40 and 30, respectively. The H_c change is shown in Table **1**. It can be seen that both $H_{c//}$ and $H_{c\perp}$ decrease with increasing diameter. It is the fact that the dipolar interaction between wires becomes strong to make the squareness ratio for the $H_{//}$ be small when the diameter increases. So the magnetic behavior is decided by the shape anisotropy and the dipolar interaction between wires for amorphous Co-P alloy nanowire arrays.

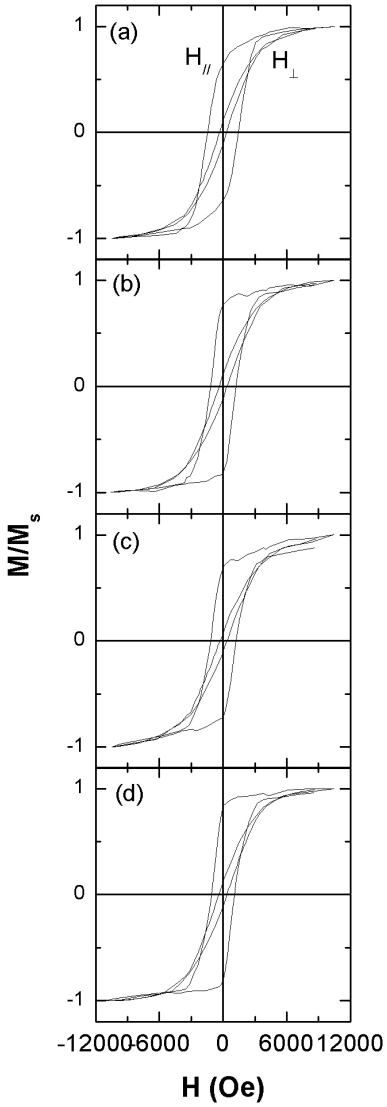

Fig. (4). Hysteresis loops of the $Co_{1-x}P_x$ alloy nanowires with x=8.7 wt% for different deposition time at ambient temperature: (**a**) 1 min; (**b**) 2 min; (**c**) 4 min; (**d**) 6 min. $H_{//}$ and $H_{\perp}$ represent that the applied field H are parallel and perpendicular to the wires axis.

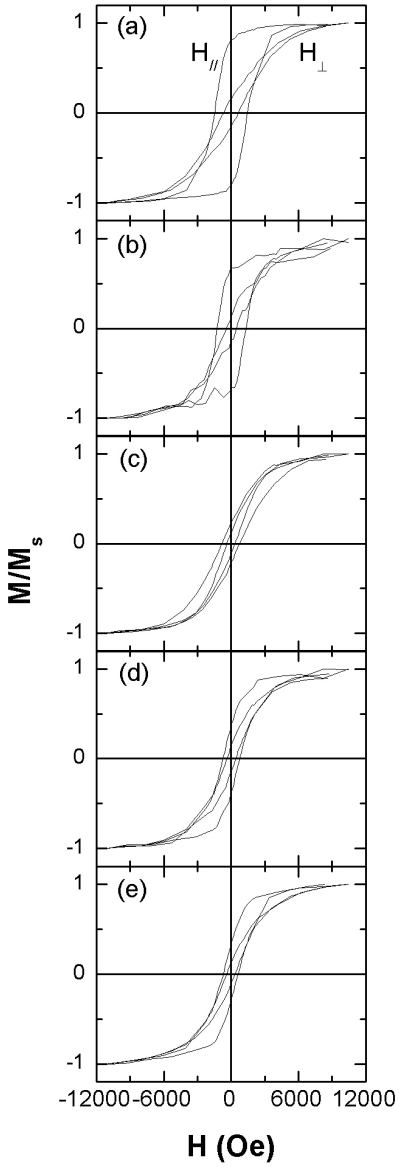

Fig. (5). Hysteresis loops of the $Co_{1-x}P_x$ alloy nanowires with x=7.6 wt% for different diameter at ambient temperature: (**a**) 10 nm; (**b**) 40 nm; (**c**) 80 nm; (**d**) 100 nm; (**e**) 130 nm. $H_{//}$ and $H_{\perp}$ represent that the applied field H are parallel and perpendicular to the wires axis.

Table 1. Coercivity Change of the $Co_{1-x}P_x$ Alloy Nanowires with x=7.6 wt% and with Deposition Time About 5 min for Different Diameter. $H_{c//}$ and $H_{c\perp}$ Represent the Coercivity of the Applied Field *H* are Parallel and Perpendicular to the Wires Axis

Coercivity (H_c)	*d*=10 nm	*d*=50 nm	*d*=80 nm	*d*=100 nm	*d*=130 nm
$H_{c//}$ (Oe)	1452	1320	920	846	756
$H_{c\perp}$ (Oe)	584	420	419	350	302

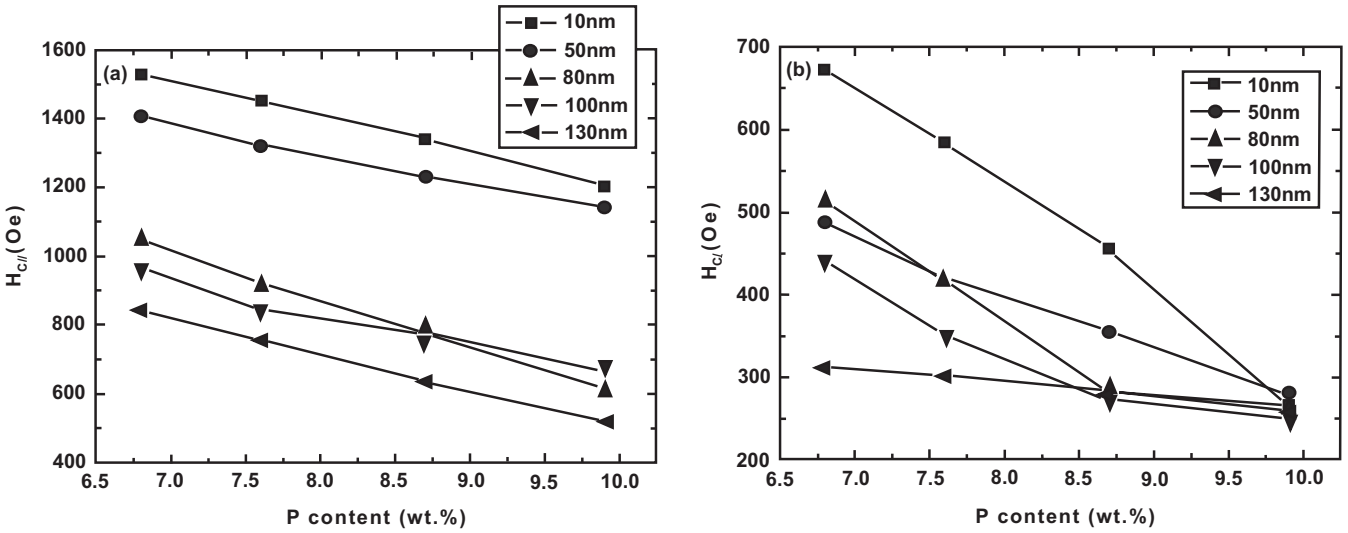

Fig. (6). The dependence of the nanowire arrays coercivity on P content for different diameter: (**a**) $H_{c//}$; (**b**) $H_{c\perp}$. $H_{c//}$ and $H_{c\perp}$ represent the coercivity of the applied field *H* are parallel and perpendicular to the wires axis.

Fig. (**6**) shows the dependence of the nanowire arrays $H_{c//}$ and $H_{c\perp}$ on P content for different diameters. Both $H_{c//}$ and $H_{c\perp}$ decrease with increasing P content because of the decrease of magnetic atom Co content [6]. From Fig. (**6a**), it can be also seen the $H_{c//}$ decreases with increasing diameter for same P content, this is because the shape anisotropy plays an important role in Co-P amorphous nanowire arrays.

CONCLUSION

In conclusion, amorphous Co-P alloy nanowire arrays were assembled into the AAO film by electrodeposition. The possible reaction mechanisms were presented. The nanowire arrays have obvious perpendicular magnetic anisotropy. Due to the shape anisotropy effect, the coercivity of nanowire arrays is large for the applied field along the nanowires axis. The magnetic behavior of the nanaowire arrays is decided by the shape anisotropy and the dipolar interaction between wires. The magnetic anisotropy indicates that Co-P alloy nanowires arrays hold a new possible application in ultra-high-density magnetic recording media.

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