Fabrication and magnetic properties of $\text{Co}_x\text{Pd}_{1-x}$ composite nanowire


Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China

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Abstract

A series of $\text{Co}_x\text{Pd}_{1-x}$ ($x = 0.37–0.85$) nanowire arrays have been successfully deposited in a single $\text{Co}^{2+}/\text{Pd}^{2+} = 20:1$ solution by applying the various depositing potentials. We found that the nanowires are the composites of CoPd alloy with some Co and Pd clusters, but the overall structure of the composite wires followed the binary phase relation of Pd–Co. The existence of Pd content makes the nanowires structured in FCC phase, except for $\text{Co}_{0.85}\text{Pd}_{0.15}$ sample in which some HCP Co phase coexists with the dominating FCC phase. Between Co-rich and Pd-rich nanowires, we found that the optimized composition for $\text{Co}_x\text{Pd}_{1-x}$ nanowire is around $\text{Co}_{0.73}\text{Pd}_{0.27}$ in which the coercivity ($H_c$) and squareness ($M_r/M_s$) have their maximum values consistently.

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1. Introduction

One-dimensional nanostructures are of great interest because of their potential applications in many fields, such as high-density perpendicular magnetic recording media and nanosensors [1–3]. Electrodepositing the magnetic metal wires with nanoscale into the porous anodic aluminum oxide (AAO) templates have been utilized previously by many groups to prepare the one-dimensional nanostructure [1–3]. Recently, ferromagnetic–nonmagnetic alloy systems have attracted much interest [4–11]. For example, Blythe et al. [4] have fabricated CoCu alloy in polymer membranes, Fedosyuk et al. [5] reported granular Ag/Co in porous AAO, and Co–Cu, Fe–Ag and Co–Ag nanowire arrays embedded in the AAO template have been reported by Wang et al. [6–8]. Also Ji et al. [9] have fabricated $\text{Co}_x\text{Pb}_{1-x}$ nanowire arrays in AAO template. In the numerous related
publications, only Ding et al. [10] have reported CoPd nanowire with 50 nm diameter and a composition of Co:Pd = 3:7 fabricated by AC deposit, which showed a coercivity of 1000 Oe and a squareness of 74%. In this work, we report a series of Co$_x$Pd$_{1-x}$ nanowires (55 nm diameter) fabricated by DC electrodeposition. Magnetic measurements show the highest coercivity of 1130 Oe and the best squareness of 94% corresponding to an optimum composition of Co$_{0.73}$Pd$_{0.27}$ at 300 K.

2. Experimental

Porous AAO templates with pore length about 40 μm and uniformity diameter about 55 nm were prepared by a two-step anodizing process on aluminum foils (with a high purity of 99.999%) in 0.3 M oxalic acid solution [6,12]. Then about 300 nm Cu layer was sputter deposited on one side of the AAO template to serve as the working electrode.

Deposition was carried out as follows: First, an aqueous bath containing rich Co$^{2+}$ solution of 0.12 M CoCl$_2$ + 0.006 M PdCl$_2$ (Co$^{2+}$:Pd$^{2+}$ = 20:1) with pH = 3 which was adjusted by adding an appropriate quantity of dilute HCl. Then, electrodeposition of Co$_x$Pd$_{1-x}$ nanowires was carried out at different depositing potentials, −1.2 V to −0.7 V relative to the saturated calomel reference electrode (SCE) to obtain the required $x$ values in Co$_x$Pd$_{1-x}$ nanowires, using a three-electrode system with a graphite rod which works as counter electrode.

Chemical compositions of the nanowires were determined by energy-dispersed X-ray spectrometry (EDXS) in scanning electron microscopy (SEM) [6–8]. The structures of the wires are characterized by X-ray diffraction (XRD) with Cu Kα radiation. SEM and transmission electron microscope (TEM) were used to observe their morphology and structure. Magnetic measurements of the nanowire arrays embedded in the AAO template were performed by superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS-5s) at 5 and 300 K, respectively.

3. Results and discussion

A series of Co$_x$Pd$_{1-x}$ nanowire arrays with $x$ = 0.37, 0.49, 0.64, 0.73 and 0.85 were obtained by electrodeposition. The composition of the nanowires was controlled by applying different deposit potentials. Table 1 shows the depositing potential dependence of the Co composition. The Co composition decreased with the decrease of the depositing potential in an almost linear form. It should be pointed out that the nanowires with a relatively low Co/Pd (such as Co$_{0.37}$Pd$_{0.63}$) ratio were also deposited from the same rich Co$^{2+}$ solution. This implies that Pd has a much higher deposition rate than Co at a lower potential even in rich Co$^{2+}$ solution. Similar results have also been reported by Su et al. [11].

Fig. 1a shows the typical top view of Co$_{0.73}$Pd$_{0.27}$ nanowire array on which part of the AAO template was dissolved before the SEM observation. One can see that, due to the partly free state, the nanowires distributing in a quite uniform area with a diameter of 15–20 μm were conglomerated together. This indicates a very strong dipolar–dipolar interaction among the wires. Fig. 1b shows the cross-sectional view of Co$_{0.73}$Pd$_{0.27}$ nanowires. It shows that the wires have a uniform diameter and fill the nanochannels uniformly and continuously.

Fig. 2 shows a representative TEM image of the isolated Co$_{0.73}$Pd$_{0.27}$ nanowire. It can be seen that the Co$_{0.73}$Pd$_{0.27}$ nanowire has a uniform diameter of 55 nm, with some cluster defects appearing on the surface. Therefore, it is easy to understand that the deposited Co$_{0.73}$Pd$_{0.27}$ nanowire is polycrystalline, as shown by the selected-area electron diffraction (SAED) pattern (inset in Fig. 2). We will see below that the Co$_x$Pd$_{1-x}$ nanowires actually are the composite of CoPd alloys and some Co and Pd clusters.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(d)</th>
<th>(e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposition potential (V)</td>
<td>−1.2</td>
<td>−1.0</td>
<td>−0.9</td>
<td>−0.8</td>
<td>−0.7</td>
</tr>
<tr>
<td>Co composition (x)</td>
<td>0.85</td>
<td>0.73</td>
<td>0.64</td>
<td>0.49</td>
<td>0.37</td>
</tr>
</tbody>
</table>
Fig. 3 shows the XRD of Co$_x$Pd$_{1-x}$ nanowire arrays embedded in AAO templates. Figs. 3a–e denote the compositions of Co$_{0.85}$Pd$_{0.15}$, Co$_{0.73}$Pd$_{0.27}$, Co$_{0.64}$Pd$_{0.36}$, Co$_{0.49}$Pd$_{0.51}$ and Co$_{0.37}$Pd$_{0.63}$, respectively. For all samples, Pd (1 1 1) peak can be clearly observed. One may see that the Pd (1 1 1) peaks were widening apparently, which implies the existence of CoPd alloy (because CoPd alloy (1 1 1) peak is very close to Pd (1 1 1) peak). And FCC Co (1 1 1) peaks can also be seen in most of the selected samples except Co$_{0.37}$Pd$_{0.63}$. The appearance of Co (1 1 1) and Pd (1 1 1) peaks implies that the crystallization of Co$_x$Pd$_{1-x}$ was not perfect, which indicates that the nanowires are composed of CoPd alloy with some Co and Pd clusters [10]. For Co$_{0.85}$Pd$_{0.15}$, XRD shows the coexistence of two structured Co with peaks of face centered cubic (FCC) Co (1 1 1), hexagon close packed (HCP) Co (1 0 1) and (1 1 0), respectively. With the increase of Pd content, Co in Co$_x$Pd$_{1-x}$ nanowire changed from HCP Co phase to FCC Co phase and finally disappeared at Co$_{0.37}$Pd$_{0.63}$, and the peak of Pd (2 2 0) appeared and enhanced at the same time. This HCP to FCC structure change may be due to the effect of Pd; similar result has
been reported by Ding et al. in Co$_{0.7}$Pd$_{0.3}$ nanowires [10].

Based on the Co–Pd phase diagram, Co–Pd has complete solubility and forms FCC phase at all compositions. But in the present work, HCP Co phase still appeared in the highest Co composition sample, i.e. Co$_{0.85}$Pd$_{0.15}$. On further increase of the Pd content, the composite nanowires formed FCC phase, including FCC Co, Pd and CoPd alloys. In our earlier work, pure Co and Pd metal nanowires were also electrodeposited, where XRD of pure Co nanowire arrays consist of single HCP phase with a strong (1 0 0) preferred orientation along the wire [13]. Pure Pd metal nanowire electrodeposited formed FCC phase with a (1 1 1) preferred orientation. So it is reasonable to conclude that the form of FCC phase in most of the Co$_x$Pd$_{1-x}$ nanowires may be due to the effect of Pd content.

Figs. 4a and b show the Co composition dependence of coercivity ($H_c$) and squareness ($M_r/M_s$) of the as-deposited Co$_x$Pd$_{1-x}$ nanowire arrays measured at 5 and 300 K, respectively. It can be clearly seen that all the selected samples have a parallel to the wire easy magnetization. When the magnetic field was applied parallel to the wire, $H_c$ increases with the increase of Co content and reaches its maximum at $x = 0.73$ and then decreases. Similarly, $M_r/M_s$ of Co$_x$Pd$_{1-x}$ increases with increase of Co composition and also shows a peak value at $x = 0.73$, as shown in Fig. 4b. When turning to the magnetic field applied perpendicular to the wire, one can see that, $H_c$ and $M_r/M_s$ show little changes with change of Co content.

To see the magnetization properties clearly, the hysteresis loops of Co$_{0.73}$Pd$_{0.27}$ and Co$_{0.37}$Pd$_{0.63}$ measured at 5 and 300 K with field applied parallel and perpendicular, respectively, to the wire axis are shown in Fig. 5. One can see that Co$_{0.73}$Pd$_{0.27}$, which has the highest $H_c$ and the best $M_r/M_s$ among all nanowire arrays, shows an $H_c$ of 1230 Oe and $M_r/M_s$ of 84% at 5 K with applied field parallel to the wire axis. And $H_c$ and $M_r/M_s$ decrease to 440 Oe and 11% with the applied field perpendicular to the wire, showing a dominating field parallel to the wire easy magnetization. At 300 K, Co$_{0.73}$Pd$_{0.27}$ has an $H_c$ of 1130 Oe and $M_r/M_s$ of 94%, showing a largely improved squareness, whereas for Co$_{0.37}$Pd$_{0.63}$, we observe a much lower $H_c$ of 850 Oe and $M_r/M_s$ of 60% at 5 K, and an $H_c$ of 800 Oe and $M_r/M_s$ of 65% at 300 K. It shows clearly that both of the two samples have parallel to the wire easy anisotropy dominates at 5 and 300 K.

Combining XRD with magnetic property it can be seen that too rich Co, for example Co$_{0.85}$Pd$_{0.15}$ in this work, caused the formation of HCP Co phase. And this HCP phase decreased the squareness by enhancing the competition of the crystallographic anisotropy against the shape anisotropy. Then for Co$_{0.73}$Pd$_{0.27}$, the HCP Co phase disappears, and the left highly symmetrical FCC Co phase decreases the competition between the crystallographic and shape anisotropies, thus improving the squareness of the arrays compared with Co$_{0.85}$Pd$_{0.15}$. And further increase of the nonferromagnetic Pd damaged the magnetic properties, such as $H_c$ and $M_r/M_s$ both at 5 and 300 K, as shown in Fig. 4. This is the reason why the
coercivity and squareness reach the maximum at component Co$_{0.73}$Pd$_{0.27}$ congruously. Therefore, we found that the optimized composition for Co$_x$Pd$_{1-x}$ nanowire array is around Co$_{0.73}$Pd$_{0.27}$.

4. Conclusions

We have successfully deposited a series of Co$_x$Pd$_{1-x}$ nanowire arrays and controlled the composition by selecting the various depositing potentials in a Co$^{2+}$ rich solution with mixed Pd$^{2+}$. XRD shows that the nanowires are the composite of CoPd alloy with Co and Pd clusters. The existence of Pd content made the nanowires preferred to form FCC phase, except for the highest Co case in which the Co$_{0.85}$Pd$_{0.15}$ sample shows some HCP Co phase coexisting with FCC Co phase. The existence of HCP Co phase enhances the competition of the crystallographic anisotropy against the shape anisotropy and decreases the squareness. With Pd increase, only FCC Co phase exists, and the highly symmetrical FCC Co decreases the competition between the crystallographic anisotropy and shape anisotropy, thus improving the squareness. Between Co-rich and Pd-rich nanowires, we found that the $H_c$ and $M_r/M_s$ have their maximum value at the composition Co$_{0.73}$Pd$_{0.27}$ consistently and conclude it as an optimized composition.

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References