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Fabrication and magnetic property of monocrystalline cobalt nanowire array by direct current electrodeposition

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Abstract

Ordered monocrystalline cobalt nanowire array has successfully been synthesized in a porous alumina template by direct current electrodeposition. The as-obtained cobalt nanowires with diameters of 35 nm, 45 nm, 60 nm, and length of 18 μm have been observed by transmission electron microscopy (TEM). A highly preferential orientation of the cobalt nanowires has been obtained by X-ray diffraction (XRD), and the orientation grows better as the hole diameter gradually reduces. M–H hysteresis loops determined by a vibrating sample magnetometer (VSM) indicate that the nanowire arrays obtained possess an obvious magnetic anisotropy.

Keywords: Porous alumina template; Direct current electrodeposition; Nanowire array; Monocrystalline cobalt; Magnetic materials; Nanomaterials

1. Introduction

In recent years, there has been an increasing interest in the investigation of one-dimensional nanowire arrays because of their potential applications in optical [1], electrical [2], and magnetic [3,4] devices. Porous alumina membrane as a template to fabricate the array has received a great deal of attention because of its self-organised, cylindrical, and uniform holes, of which the size can be controlled, ranging from 5 nm to 200 nm, by changing anodizing conditions and subsequent procedure. A serial of methods has also been applied to produce the array, such as electroless plating [5], sol–gel [6], and chemical vapour deposition [7]. But electrodeposition is one of the simplest and most inexpensive, easily controlled methods.

So far, many nanowire arrays of Fe, Co, Ni, and their alloys have been synthesized by electrodeposition. These magnetic arrays have distinctive magnetic property, displaying promising use in applications such as patterned recording media, nanosensors, and nanodevices. However, most of the works on electrodepositing magnetic nanowire arrays have been focused on the preparation and characterization of polycrystalline and amorphous materials, such as Fe, Co, Ni, FeCo [8], NiP, and CoP [9]. It is great interesting for us to investigate the preparation and magnetic properties of monocrystalline nanowire array in the way by which the crystalline state influences magnetic properties, such as magnetization reversal.

In this work, we report on the direct current (DC) electrodeposition of monocrystalline cobalt nanowire array in the highly ordered porous alumina template. DC electrodeposition is an important type of electrodeposition using the alumina membrane as a template, which in fact is divided into two types: DC and altering current (AC). It is a challenge for us to conduct DC electrodeposition because of the insulating and fragile properties of porous alumina template. We succeeded in doing it and the structure and magnetic property of the as-obtained array have been characterized by scanning electron microscopy, transmission electron microscopy (TEM), X-ray diffractometer, and vibrating sample magnetometer.

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2. Experimental

2.1. Preparation of highly ordered porous alumina template

An aluminium sheet (purity 99.999%, thickness 0.3 mm) was used in this work. A two-step anodic oxidation technique, which had been described in Ref. [10], was applied to prepare the porous alumina template. The anodization was carried out in 0.3 M oxalic acid solution at 40 V and 0–5 °C. The duration of the first step and the second step anodization were 8 h and 12 h, respectively. After anodization, the remaining aluminum substrate was removed in a saturated $HgCl_2$ solution. The bottom part of the anodic oxide film, called the barrier layer, was removed in 5 wt.% H_3PO_4 at 30 °C. Moreover, to obtain different hole diameters, various etching durations were used in this work. A thin Au layer was evaporated on one face of the continuous holes film, serving as the cathode during direct current electrodeposition.

2.2. DC electrodeposition of cobalt

An Ag/AgCl reference electrode was combined into a three-electrode system experimental facility, in which a graphite electrode served as a counterelectrode, to conduct DC electrodeposition. The electrolytic solution of DC electrodeposition had the following composition: $CoSO_4 \cdot 7H_2O$ 120 g/L and H_3BO_3 45 g/L. The pH value of electrolyte was maintained at 2.0–3.0.

2.3. Instrument

The surface of the porous alumina template was observed by scanning electron microscopy (SEM; Hitachi 8010). TEM (Hitachi 800) was employed to survey the cobalt nanowires liberating from the alumina film. The microstructure and property of cobalt nanowire arrays were characterized by X-ray diffraction (XRD; D/Max-RB diffractometer with Cu Kα radiation) and vibrating sample magnetometer (VSM; LDJ9600), respectively.

3. Results and discussion

The SEM image of the porous alumina film prepared by the two-step anodization is shown in Fig. 1. The holes are regularly arrayed throughout the film. So, the array fabricated by using it as a template should be regular. The cobalt nanowires with removal of the film, determined by means of TEM and as shown in Fig. 2a and b, indicate that cobalt has been electrodeposited in the nanoholes of the film. Because of the loss of the bearing film, the nanowires exhibit various figures, such as breakdown or other irregular shapes. The diameter of the nanowires, shown in Fig. 2, is about 45 nm and the length is 18 μm (i.e., the aspect ratio (length to diameter) is over 300).

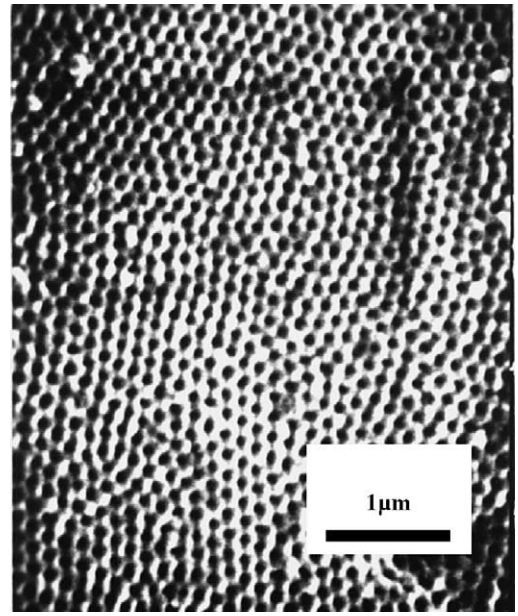

Fig. 1. SEM image of the porous alumina film prepared by two-step anodic oxidation.

Monocrystalline cobalt nanowires detected by the electron diffraction pattern in the inset of Fig. 2b have been obtained in this work. In contrast to the result obtained, the nanowires electrodeposited by AC were polycrystalline [11]. It may be attributed to the different mechanisms of electrodeposition between DC and AC. However, some other studies similar to our experimental procedure indicated that not monocrystalline, but polycrystalline, nanowires have been gained by DC electrodeposition, For example, Ni and Co nanowires were synthesized by Whitney et al using the polycarbonate membrane as a template [12], and the cobalt nanostructure was prepared by Bao et al. in alumina template [13]. The difference may be due to the applied parameters of DC electrodeposition, such as current density, pH value, composition of electrolyte, etc.

No diffraction peak of cobalt oxide is shown in XRD patterns (see Fig. 3) of the cobalt nanowires/porous alumina samples, so cobalt with high purity has been obtained by DC electrodeposition. At the same time, no diffraction of amorphous alumina is visible in Fig. 3 because of the sharp diffraction peaks of cobalt nanowires. (100), (002), and (110) diffraction peaks corresponding to the hcp cobalt structure are shown in the XRD pattern of the cobalt nanowires/porous alumina array when the nanohole diameter of the porous alumina template is 60 nm. It is concluded that the nanowires have a preferential orientation [002] by comparing it with the diffraction of the bulk cobalt, wherein the sharpest peak (101) is invisible in the diffraction pattern of the array, and the weak peak (100) shows a little stronger. As the nanohole diameter of the alumina template changes from 65 nm to 45 nm, a more ideally preferential orientation [002] is shown because the peak (100) in the diffraction pattern of the array of 45 nm nanohole diameter is obviously weaker than that of 60 nm