Applied Surface Science 257 (2011) 8974–8980

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Synthesis and magnetic properties of ordered barium ferrite nanowire arrays in AAO template

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ARTICLE INFO

Article history:
Received 22 March 2011
Received in revised form 15 May 2011
Accepted 17 May 2011
Available online 26 May 2011

Keywords:
Sol–gel
$BaFe_{12}O_{19}$
Nanowire arrays
AAO template
Magnetic properties

ABSTRACT

$BaFe_{12}O_{19}$ nanowire arrays having single magnetic domain size (≤460 nm) in anodic aluminum oxide (AAO) templates were prepared by sol–gel and self-propagating high-temperature synthesis techniques. The diameter of the nanowire arrays is approximately 70 nm and the length is about 2–4 μm. The specimens were characterized using X-ray diffraction, vibrating sample magnetometer, field emission scan electron microscope, atomic force microscopy and microwave vector network analyzer. The magnetic properties of $BaFe_{12}O_{19}$ nanowire arrays embedded in AAO templates were measured by VSM with a field up to 1274 KA/m at room temperature. The results indicate that the nanowire arrays exhibit large saturation magnetization and high coercivity in the range of 6000 Oe and an obvious magnetic anisotropy with the easy magnetizing axis along the length of the nanowire arrays, probably due to the shape anisotropy and magneto-crystalline anisotropy. Finally the microwave absorption properties of the nanowires were discussed.

1. Introduction

With the development of information industry, the research about the preparation and characterization of nanowire arrays, especially magnetic metal oxide nanowire arrays, has received considerable scientific and commercial attention because of their potential applications in magnetic recording [1]. Also, the synthesis and analysis of low-dimensional nanostructure magnetic materials attract much more attention for their unique physical properties and their potential applications in nanoscale devices, such as nanowires, nanorods and nanotubes [1–7]. For example, $CoFe_2O_4$ nanowire arrays were fabricated by electrodeposition of Fe^{2+} and Co^{2+} into anodic aluminum oxide (AAO) templates and further oxidization which provide a facile technology to fabricate oxide nanowires with uniaxial magnetic anisotropy [7]. $Ni_{0.23}Cu_{0.11}Zn_{0.66}Fe_2O_4$ nanowire arrays were fabricated by a simple ethanol-nitrate method using AAO templates [2]. Cu–ferrite nanorods (NRs) array and nanowires (NWs) on Cu substrate were prepared by an aqueous solution method, which exhibit a clear uniaxial anisotropy with the easy axis along rods [3]. Self-organized and ordered $CoFe_2O_4$ nanotube arrays were prepared in porous anodic aluminum oxide template using an improved sol–gel approach [4]. Highly ordered $ZnFe_2O_4$ nanotube arrays were successfully prepared using porous AAO template from sol–gel solution. The $ZnFe_2O_4$ nanotubes were orderly arranged in parallel and each nanotube is composed of many agglutinating nanoparticles [5].

Several synthesis routes have been exploited to prepare the special morphologies of magnetic nanowires, such as template synthesis [8–10], electroless synthesis [11], organic gel-thermal reduction method [12], electro spun [13,14], and sol–gel method [4,5]. In some cases, the crystal growth is limited along some directions, and in the other cases, the growth of crystals is preferential in definite directions. Templates are reported to play a key role in the growth of nanowires. Different kinds of templates such as anodic porous alumina, polymer and nanochannel glass templates have been widely investigated. Compared with other templates, the size of the holes of the template can be readily controlled by properly adjusting the conditions of anodization. Normally anodized aluminum in appropriate acid solution forms an anodic porous-alumina membrane template [1–5].

Barium ferrite is an attractive material for high density magnetic data storage material. Its magnetic properties arise from interactions between metallic icon occupying particular positions and the oxygen ions in its hexagonal crystalline structure. It exhibits a high coercivity due to the relatively high magnetocrystalline anisotropy field and the nanometer size much smaller than the critical single magnetic domain size about 460 nm which is beneficial to form the single magnetic domain structure [15]. The high-aspect ratio nanowire arrays of the $BaFe_{12}O_{19}$ have been prepared by means of anodic alumina membrane (AAM) template method, however, the magnetic and other properties of the nanowire have not been investigated [16]. In this work, oriented channels in the mesoporous regime (pore-diameter approximately 60 nm) are investigated for

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doi:10.1016/j.apsusc.2011.05.075

an efficient filling with a ferromagnetic material. Here we have combined the concepts of sol–gel synthesis and template preparation of nanomaterials to yield a new general route for preparing $BaFe_{12}O_{19}$ nanoarrays, which was accomplished by conducting sol–gel and self-propagating high-temperature synthesis (SHS) techniques [17–20] within the pores of various nanoporous membranes. Monodispersed nanoarrays of $BaFe_{12}O_{19}$ nanowires were obtained and the magnetic and the electromagnetic properties of the nanowires were discussed.

2. Experimental

2.1. Membrane preparation

High-purity aluminum sheets (99.99%, 40 mm × 12 mm) were employed in our experiment. Prior to anodization in oxalic acid (20–30 V, 273 K, another Al sheet as a counter electrode, 5 h), the metal surfaces were degreased in ethanol by ultrasonic cleaner, etched in alkaline solution (0.3 mol/L) for 3–5 min, rinsed with distilled water, annealed at 773 K for 5 h, and then electropolished for 10 min in a mixture of perchloride acid and ethylene glycol (1:4, volume ratio) to achieve a smooth surface. It was necessary to immerse the samples in concentrated acid or alkaline solution for several minutes to remove the oxide layer formed during the electropolishing process. The resultant clean aluminum samples were firstly anodized in 0.3 mol/L oxalic acid solution at constant potential according to the above conditions for 5–8 h. The membrane was rinsed with distilled water and immersed in the mixture solution of 0.6 M H_3PO_4 and 0.18 M H_2CrO_4 for about 1 h at 323 K in order to dissolve the barrier-type part on the bottom of the nano-holes. Then the membrane was secondly anodized at the same conditions as used in the first step for 6 h. Afterwards, NaOH solution of 20 wt.% was dripped on the backside of the foils to dissolve the alumina lamina, and then the foils were dipped into the supersaturated perchloric acid solution of $CuCl_2$ to remove aluminum matrix quickly. In order to remove the barrier layer on the backside of the AAO templates and enlarge the holes, the above treated foils were dipped into the phosphoric acid solution of 5 wt.% at 323 K for 30 min. AAO templates were characterized by field emission scan electron microscope (FESEM) and Molecular Imaging, model PicoPlus atomic force microscopy (AFM).

2.2. Preparation of $BaFe_{12}O_{19}$ nanowire arrays

Metal nitrates were used as the cationic sources, and citric acid and ethylene glycol as the monomers for forming the polymeric matrix. $Ba(NO_3)_2$, $Fe(NO_3)_3{\cdot}9H_2O$ and citric acid were dissolved in distilled water according to the molar ratio 1:12:26. A clear solution was then produced, and it was stirred in a water bath at 70 °C to induce esterification. Thus the sol was obtained. Two drops of the gel were dropped on one side of the alumina template membrane for the desired amount of time, and the excess sol on the membrane surface was wiped off with a laboratory tissue, followed by drying under vacuum at 150 °C for 1 h. After that, 3 drops of 3 M NaOH were dropped on the other side of the sample to partially dissolve the membrane, and then the whole sheet was put into saturated $CuCl_2$ solution to separate the template membrane from the Al substrate. The membrane surface was carefully wiped again to remove salts crystallized on the surface and heated at 773 K for 2 h and 1073 K for 2 h in open air, resulting in formation of arrays of $BaFe_{12}O_{19}$ nanowires in the inside of the pores of the AAO template.

2.3. Characterization of $BaFe_{12}O_{19}$ nanowire arrays

The structure and morphology properties of $BaFe_{12}O_{19}$ nanowire arrays were characterized by several techniques. X-ray diffraction (XRD) data of the template membrane were collected by a Rigaku D/MAX2400 diffractometer with CuKα-radiation. In addition, the quantitative compositional analysis of the nanowire was performed by energy dispersive spectrometer (AMRAY 1000B EDS).

FESEM was used to observe the morphology and degree of agglomeration of the nanowires. Before FESEM observation, the alumina template membrane was dissolved in 3 M NaOH and diluted with distilled water for three times. And then, the samples were sputter-coated with gold before the FESEM measurement in order to increase their conductivity.

Magnetic properties of the nanowire arrays were measured at room temperature using a permanent-magnet vibrating-sample magnetometer with a field up to 1274 KA/m (VSM, Lake Shore7307). The external field was applied parallel and perpendicular to the membrane to analyze their magnetic of anisotropic effect.

Rectangular blocks used for microwave absorption analysis were made by mixing $BaFe_{12}O_{19}$ nanowire arrays with paraffin according to a certain proportion about 1:1, and the size of the blocks was 34.48 mm × 15.42 mm × 2 mm, 22.86 mm × 10.16 mm × 2 mm and 16.76 mm × 7.88 mm × 2 mm, respectively, for the frequency range of 5–8 GHz, 8–12 GHz and 12–18 GHz. The S parameters (scattering parameters) were measured and used to calculate the complex permittivity ($\varepsilon = \varepsilon' - j\varepsilon''$) and permeability ($\mu = \mu' - j\mu''$) of the composites. The measurements were performed according to the transmission/reflection method using a network analyzer (Agilent technologies E8362B: 10 MHz–20 GHz), adapted with a wave-guide method in the frequency range of 5–8 GHz, 8–12 GHz and 12–18 GHz, respectively [21].

3. Results and discussion

3.1. Structure and surface morphology of AAO membrane

Fig. 1(a) shows the FESEM image of a typical porous alumina film used as a template for fabrication of $BaFe_{12}O_{19}$ nanowire arrays by two-step anodization. This figure shows that the surface of the resulting film is composed of pores with narrow or nearly closed entrance. Some pretreatment was made before anodization including degreasing, annealing, alkali cleaning and electrochemistry polishing, afterwards two-step anodization was operated and aluminum matrix was removed quickly, finally porous anode aluminum oxide templates were obtained.

Fig. 1(b) shows a FESEM image of top surface after surface pore were enlarged by chemical etching treatment in 5 wt.% phosphoric acid and 1.8 wt.% chromic acid. As shown in this figure, the measured pore diameter size is enlarged from 30 to 50 nm of the untreated pore size to about 70 nm, and the density of the pores is 5×10^{10} cm^{-2}. Thus, to control accurately concentration, temperature and etching time is essential for preparing the anodic alumina templates with uniform pore channels. The optimal experimental conditions were gained as follows. The etching alkaline solution concentration is 0.3 mol/L, the etching time is 3–5 min, the annealing temperature is at 773 K for 5 h, and then electropolished for 10 min in a mixture of perchloride acid and ethylene glycol (1:4, volume ratio). The aluminum samples were firstly anodized in 0.3 mol/L oxalic acid solution at constant potential as above for 5–8 h. The membrane was rinsed with distilled water and then immersed in the mixture solution of 0.6 M H_3PO_4 and 0.18 M H_2CrO_4 for about 1 h at 323 K. Then the membrane was secondly anodized at the same conditions as used in the first step for 6 h. Afterwards, the above treated foils were dipped into the phosphoric acid solution of 5 wt.% at 323 K for 30 min. Fig. 2 indi-