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Synthesis and microwave magnetic properties of magnetite nanowire arrays in polycarbonate templates

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ABSTRACT

Magnetic nanowire arrays have potential applications in magnetic memory, microwave magnetic devices and many other fields. Spinel ferrite nanowire arrays exhibit a higher resistivity compared with metal counterparts; they also possess a strong shape anisotropy, such that they have high feasibility in microwave magnetic devices. Herein crystalline Fe_3O_4 nanowire arrays were synthesized in polycarbonate porous membranes with pore sizes of 100 nm in diameter by one-step electrochemical deposition without heating. The phase structures, morphologies and magnetic properties were studied by XRD analysis, SEM and TEM observations and microwave magnetic measurements. The results showed that the as-prepared nanowires, characterized by polycrystalline phase structures, were uniform in size, with about 200 nm in diameter and 6–10 μm in length. Microwave magnetic properties of the arrays were characterized from microwave absorption parameters of the flip-chip on a microstrip line using a vector network analyzer (VNA). The ferromagnetic resonance (FMR) frequencies of ferrite arrays reached up to 25 GHz under a magnetic field of 9 kG, and more importantly it could be tuned in a wide frequency range by an external magnetic field. The results indicated that the Fe_3O_4 nanowire arrays are promising absorbing microwave materials for flexible high-performance microwave devices.

1. Introduction

Microwave ferrite plays an important role ranging from very high frequency (VHF, 30 ~ 300 MHz) to millimeter-wave (30 ~ 300 GHz) systems for a long period because of its outstanding electromagnetism performance [1]. To fit the miniaturization and high frequency of devices, recently, two ways are come up with to improve the operating frequencies of ferrites. One is utilizing the magneto-crystalline anisotropy of hexagonal ferrites [2,3]. Monocrystal or high quality textured hexagonal ferrite thick films can possess a ferromagnetic resonance (FMR) frequency of 40 ~ 60 GHz, which suggests hexagonal ferrite has much higher magneto-crystalline anisotropy compared with widely used spinels and garnets. However, hexagonal ferrites have complicated structures and are difficult to prepare. The other is utilizing shape anisotropy of materials, such as 1D materials, particularly nanowire arrays. As nanowire arrays have a strong perpendicular magnetic anisotropy and low eddy current loss, spinels, garnets and even magnetic metals can be used in high frequency gyromagnetic device. Meanwhile, either single-layered or multi-layered nanowire arrays can be achieved to better fulfil the demand of miniaturization and multi-function of modern microwave components, which has gained much attention during the past few decades [4].

To date, a variety of magnetic alloy nanowire arrays have been synthesized by electrolyte deposition in porous membranes [5–7]. It especially profits from the progress of anodic aluminum oxide (AAO), which can be used as ideal template to assemble nanowire arrays for its highly ordered hexagonal nanopore arrays. However, AAO is fragile and can not endure hyperthermia over 600 °C. In addition, it will be dissolved in alkaline solutions immediately. These problems greatly limit its use in electrical deposition method, and actually the magnetic nanowire arrays deposited in AAO are only metal nanowires (like Co, Ni). Although the eddy current in nanowire is greatly deceased because of the narrow diameter, it can not be eliminated in metal for its high conductivity. Therefore, the undesired loss of metal is certainly larger than that of ferrite [8]. To deposit ferrite nanowires in AAO, an ordinary method is to form iron alloy nanowire arrays in AAO firstly, and then to oxidize them to ferrite by heating them in air. As mentioned above, AAO is weak in heating, which would bring some problems in such preparing method [9]. Another way is using physical method to infill ferrite precursors or ferrite particles into the pores of AAO [10,11]. In this process, the problem of heating still exits and the nanowires could not be closely stacked. By comparison, using one-step electrical deposition method to produce ferrite nanowire could avoid

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such deficiencies mentioned above, especially without heating process. Meanwhile, polycarbonate is a kind of typical porous membranes and quite stable in acid and alkali, hence, it would be beneficial for the synthesis of metallic oxide under alkaline solutions. Moreover, the products can maintain the flexibility of polycarbonate, and have potential applications in wearable electronic devices. FMR is one type of the magnetic resonance that usually occurs at high field value in ferromagnetic materials. The FMR technique can provide information on the magnetization, magnetic anisotropy, dynamic exchange/dipolar energies and relaxation times, as well as the damping in the magnetization dynamics [12]. For microwave ferrites, the optimum working frequency is always closely related to their FMR frequency.

The present work is mainly aimed at preparing Fe_3O_4 nanowire arrays by one-step electrical deposition using polycarbonate porous membranes as the template. The microstructure and microwave properties of Fe_3O_4 nanowire arrays were investigated meticulously. The relationship between depositing condition and the morphology of nanowires was discussed. Also, the grains composing the nanowire were discussed in detail. More importantly, the microwave properties of the arrays were measured covering wide range of frequencies.

2. Materials and method

In this work, Fe_3O_4 nanowire arrays were produced by one-step cathodic electrodeposition from an alkaline solution, which contained 0.09 M $Fe_2(SO_4)_3$, 0.1 M triethanolamine (TEA), and 2 M NaOH (Sinopharm Chemical Reagent Co. ,Ltd, AR) [13,14]. The deposition potentials were −1.05 ~ −0.95 V vs Ag/AgCl (3.5 M KCl) and the deposition temperature was 65 °C. Cyclopore track etched polycarbonate membranes with diameter of 0.1 μm and thickness of 6 ~ 10 μm (Whatman, England) were used as the porous membranes. Silver was deposited as back electrode by magnetron sputtering. In order to produce high length-diameter ratio and high quality nanowires, different depositing conditions were conducted during experiments.

The micro-morphology of the nanowire arrays was analyzed by SEM (ZEISS Merlin Compact, Germany) and TEM (FEI Tecnai G2 20, America). The phase structure of the ferrite was recognized by an X-Ray Diffractometer (D8 Advance A25, Bruker, Germany) through θ-2θ scanning. Microwave properties of the arrays were characterized by measuring complex two-port scattering (S)-parameters (S_{21}) using a vector network analyzer (E8361C, Agilent, America) [15]. The range of frequency was 0.04 ~ 40 GHz, and external magnetic field was 0 ~ 9000 G.

3. Results and discussion

Micro-morphology is incontrovertibly one of the most important issues for nanowire arrays. Fig. 1 shows the SEM micrographs of the nanowire arrays. Fig. 1a is the front surface of nanowire arrays deposited for 1800 s in the porous membrane of diameter of 0.1 μm. However, the porous and the protrusive nanowires are both having diameters of 200 ~ 300 nm, which is much larger than the porous diameter before depositing. This is maybe because the hot alkaline solution will slightly damage the polycarbonate porous. About one-third of nanowires have grown out of the surface, and a few are aligned with the surface while other porous seem empty. When depositing time increases, the grains of protrusive ferrite nanowires will grow rapidly and cover the whole surface to form a film. In order to confirm the filling rate of the porous, the back surface after removing silver electrode is shown in Fig. 1b. Almost all porous are filled in view, and the diameter of nanowires is about 150 ~ 200 nm, which is narrower than front side. It is because the production of ferrite will isolate solution and stop dissolving the template. Therefore, preparing high length-diameter ratio and ordered nanowires requires appropriate depositing time and a depositing rate as fast as possible. To avoid the appearance of iron, the mostly used depositing condition in this work is − 1.0 V vs Ag/AgCl and depositing for 1800 s. Fig. 1c is the nanowire arrays after dissolving the polycarbonate template, while Fig. 1d is the enlarged detail of occasionally lying nanowires in Fig. 1c. Similar to Fig. 1a and b, the growth of nanowires is uneven and the arrays are arranged densely. The diameters of the nanowires lie in a range of 200 ~ 300 nm. However, as the lying nanowires agglomerate tightly, it seems difficult to obtain the diameters accurately.

To further characterize the microstructures of nanowires, particularly the orientations, TEM observations were conducted on the ferrite arrays. Fig. 2 shows the TEM micrographs of the Fe_3O_4 nanowires. Fig. 2a is the high-resolution image of the nanowire. As spinel ferrite has an FCC structure, the diffraction pattern at the lower right corner suggests the zone axis of this region is [110]. Presuming the normal direction is [110], the lattice orientations in plane are as the right triangle showed in Fig. 2a. The inter-planar spacing of different direction can be obtained by measuring the distance between bright points. As a result, the calculated lattice parameter is 0.8580 nm. On the other hand, the more macroscopical intact grains of nanowires is shown in Fig. 2b. The diameter of the particle is about 150 ~ 200 nm and the length is about 0.5 ~ 1 μm, which is consistent with the result of SEM observations (Fig. 1b). The orientation of nanowires is obtained from the high-resolution image of grains by indexing the lattice direction. However, the orientation is random among different grains within the same nanowire species. In fact, the XRD analysis also suggests the nanowires have a polycrystalline structure like Fe_3O_4 powders.

Though the crystal anisotropy is extraordinarily weak for the nanowire arrays, the high shape anisotropy, which can also improve the anisotropic field of the materials, is expected to influence the magnetic properties of the magnetite. The FMR is represented by the mobile absorption peak of S_{21} with different magnetic field, since the condition of FMR is showed blew:

$$\omega = \gamma\left(\mathrm{H} - 4\pi\mathrm{M_s} + \frac{2\mathrm{K_1} + 4\mathrm{K_2}}{\mathrm{M_s}}\right) = \gamma(\mathrm{H} - 4\pi\mathrm{M_s} + \mathrm{H_{anis}}) \tag{1}$$

where H is the applied field, M_s is the magnetization, γ is the gyromagnetic ratio, and K_1 and K_2 are anisotropy constants. Fig. 3 showed the response of S_{21} of as-prepared ferrite arrays. The absorption peak at 20 ~ 25 GHz shifts to higher frequencies when the external magnetic field increases, suggesting it indicates the FMR frequency. With a magnetic field of 9 kOe, the FMR frequency can reach 25 GHz, while the general Fe_3O_4 films can only reach 15.5 GHz in our previous work [16]. Even at a zero field, the frequency extrapolated can reach about 12 GHz, which is much higher than generic spinel ferrites. It reveals that the nanowire arrays may have potential application in passive devices at high microwave frequency.

4. Conclusions

Vertical-layout magnetite nanowire arrays were fabricated in polycarbonate porous membranes by one-step electrochemical deposition. Almost all the porous were filled with ferrite nanowires. The diameter of the nanowires is about 150 ~ 200 nm, and the total length is the same as the thickness of template (6 ~ 10 μm). From high-resolution image of the nanowire, the lattice parameter of the ferrite is 0.8580 nm, which is typical for spinel. The size of the grains is about 0.5 ~ 1 μm. And the orientation is random for different sections of the nanowire. The high shape anisotropy greatly improves the FMR frequency of the nanowire arrays, which can reach 25 GHz with an external magnetic field of 9 kOe, and 12 GHz in zero field. With the merits of easy-process, flexibility and high microwave performance, these magnetite nanowire arrays may have potential application in wearable high frequency microwave devices.