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Synthesis and optimization of the magnetic properties of aligned strontium ferrite nanowires

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ABSTRACT

High aspect ratio strontium hexaferrite nanowires were fabricated by dip coating in alumina template. Fe/Sr ratio was changed from 10 to 12 in precursor, and the samples were annealed at a range of temperatures 500–900 °C in order to optimize the magnetic properties of strontium ferrite in the form of nanowires. Field emission scanning electron microscope (FESEM) proved the formation of nanowires in the templates, while TEM images revealed a high degree of crystallinity. The ferrites were further characterized by X-ray diffraction (XRD) and energy dispersive X-ray spectrometer (EDS). Magnetic properties of the specimens were studied by a SQUID at 10–300 K. The results showed that the coercivity of packed density nanowires in the template was much less than that of the nanopowders. On the other hand, the coercivity of nanowires at ambient temperature was less than low temperature coercivity.

1. Introduction

The small size and the unique properties of nanowires make them an attractive choice to miniaturize conventional devices in many application areas such as electronics, thermoelectric, optics, chemical and biological sensors [1,2]. A lot of inquiries have been undertaken to fabricate such nanowires by electron beam lithography, vapor liquid solid, wet chemical and template based methods [3–5]. Recent progress on magnetism has made the magnetic nanowires a particularly interesting class of materials for both scientific and technological applications. Moreover, magnetic nanowires have received considerable attention due to their potential in high-density magnetic data storage devices, as well as magneto-electronic and microwave applications. For most applications, it is desirable to have high aspect ratio nanowires uniformly produced in high spatial order. The self-organized porous aluminum oxide (PAO) template displays most of the desirable template properties, such as high pore density, uniform pore distribution and controlled diameter and length of the pores (easily determined by anodizing conditions). Nanowire arrays such as Fe, Co, Ni and their alloys have been fabricated based on a PAO template and their magnetic properties have been investigated too [6–8]. To form nanowires, the pores must be filled with a metal or another material by electrodeposition, electroless or other coating methods. Sol–Gel based synthesis process is the most common approach employed in the preparation of complex oxide nanowires of no electrical conductivity in template [9].

Barium and strontium ferrite are a considerable class of hexaferrites with simpler chemical formula that can be used for high-frequency devices [10]. The separation of the nanowires from the templates is another important issue in the fabrication of wires as the building blocks.

Strontium ferrite ($SrFe_{12}O_{19}$), has various advantages such as relatively high saturation magnetization, high coercivity, considerably high uniaxial magnetic crystalline anisotropy, chemical stability and corrosion resistance. It has been found that this ferrite can be used in electronic components, magnetic memories, biotechnological and magnetic substrates for magnetic catalysts, making it an attractive option in synthesis and research. $SrFe_{12}O_{19}$ is a very structure-sensitive material whose properties greatly depend on the preparation process and the synthesized particle size and shape.

Although ferrite nanostructures have been widely investigated [11], magnetic properties of one dimensional ferrite nanowires have been less explored. In the present study, high aspect ratio strontium ferrite nanowires were fabricated by employing a template assisted technique and filling the pores by dip coating in a solution. Fe/Sr ratio was changed from 10 to 12 in precursor while different annealing temperatures ranging from 500 to 900 °C were used to optimize the phase formation of strontium nanowires. The magnetic properties of nanowires were compared with those

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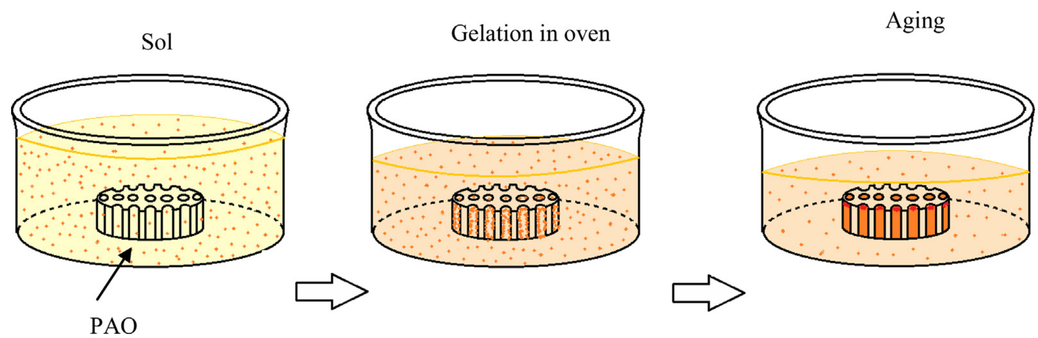

Fig. 1. Schematic picture of wires construction in the dip coating method.

ferrite nanopowders synthesized by the same method, at ambient and low temperatures.

2. Experimental details

2.1. Synthesis of nanowires

In order to achieve the desired ordered nanoporous template, a double-anodization process was employed. Specimens made from pure aluminum foil were cleaned ultrasonically in acetone bath for 5 min. The samples were degreased using 10% sodium hydroxide at 70 °C for 5 min, rinsed and immersed for 1 min in nitric acid at room temperature. Annealing treatment was performed at 400 °C for 4 h in an electrical tube furnace under nitrogen atmosphere to increase the grain size and regularity of PAO pores. By achieving a smooth surface, the samples were electropolished for 10 min in a mixture of perchloric acid and ethanol (1:5 volume ratio). The anodizing process was carried out in an electrolyte containing 0.3 M oxalic acid ($H_2C_2O_4$) using a constant voltage of 40 V at 4 °C for 12 h. The obtained alumina layer was removed by immersing the samples in a mixture of 6 wt% phosphoric acid and 1.8 wt% chromic acid ($H_2Cr_2O_7$) at 60 °C for 1 h. The second anodizing was carried out under the same conditions employed in the first step, for 15 h. An additional pore widening step in the phosphoric acid solution was applied; for this purpose, the alumina was immersed in phosphoric acid solution of 5 wt% for 20 min.

Thickness of the porous oxide film was determined by FESEM through the examination of the cross sections. In order to separate the template from aluminum substrate, 0.2 M $CuCl_2$ solution was used for a sufficient time to ensure the removal of all aluminum.

To synthesize $SrFe_{12}O_{19}$ nanowires, an appropriate amount of Fe $(NO_3)_3.9H_2O$ was dissolved in deionized water and then, $Sr(NO_3)$ was added. After completely dissolving the salts, citric acid was added to the solution; solutions with different molar ratios of Fe/Sr were prepared (10, 11, 12) while the ratio of cations to acid was set at 1:1. Ammonium hydroxide was used to adjust the pH value of 7 in the solution in order to prevent dissolving the template. The solution was subsequently evaporated at 80 °C until the desired viscosity of a sol was obtained. In the dip coating technique employed to form the nanowires, the template was dipped into the sol at 80 °C for 2 h. After the precipitation of nanowires into the pores, the sample was dried at 120 °C. Fig. 1 shows a schematic picture of wires construction in the dip coating method. By controlling such synthesis parameters as temperature and viscosity of solution, the formation of wires was started from the walls of nanopores, hence making it possible to produce tubes or wires [9]. In order to synthesize powders, a similar solution was used and it was followed by the evaporation of the sol at 80 °C to form a gel; then, heating was continued until the gel was dried.

After the construction of nanostructures, calcination was carried out in the air atmosphere furnace to form crystalline ferrite nanopowders and nanowires. The powders were calcinated at 900 °C for 1 h while nanowires calcination conditions were selected as 1 °C/min heating rate to avoid the bending of the samples and 1 h annealing at various temperatures in the range of 500–900 °C, in the steps of 50 °C.

2.2. Characterization of samples

After the preparation of the samples, their morphologies were studied by an LEO 1530 field emission scanning electron microscope. EDS was employed to determine the chemical composition of the nanowires. Before the examination of the nanowires, 1 M NaOH was used to remove the template partially or completely. Since the template surface had no electrical conductance, a 10–15 nm gold layer was provided. The structure of the nanowires was analyzed by transmission electron microscope (TEM). Samples with varied Fe/Sr ratios in the precursor were annealed under different temperatures and further studied using XRD and diffraction patterns recorded in a 2θ range of 20–90 degrees. The magnetic measurements of powders were carried out in a vibrating sample magnetometer (VSM) at room temperature and 10 K. The hysteresis loops of the nanowires were recorded by a SQUID, parallel and perpendicular to the wire axis for samples in the temperature range of 10–300 K, from which magnetization and coercivity of wires were studied.

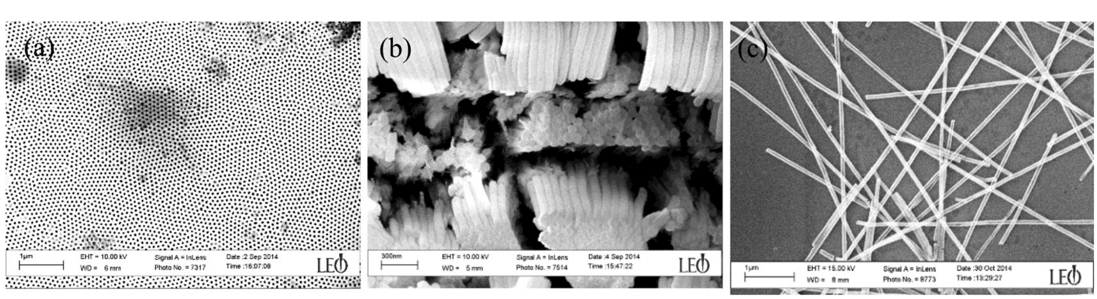

Fig. 2. (a) FESEM micrographs of the surface of template, (b) same templates upon pore filling and subsequent etching and (c) released ferrite nanowires.