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Synthesize of barium ferrite nanowire array by self-fabricated porous silicon template

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ABSTRACT

In this work, we synthesize barium ferrite ($BaFe_{12}O_{19}$) nanowire array in porous silicon template. The porous silicon templates are prepared via gold-assisted chemical etching method. The gold (Au) nanoparticles with mean diameter of 30 nm and distance of 100 nm were ordered on the surface of Si substrate through the Polystyrene (510000)-block-poly (2-vinylpyridine) (31000) (PS_{510000}-b-$P2VP_{31000}$) diblock copolymer. Porous silicon templates with mean diameter of 500 nm and distance between the pores of 500 nm were fabricated by two etching steps. $BaFe_{12}O_{19}$ nanowires with mean diameter of 200 nm were synthesized into a porous silicon template by a sol–gel method. Magnetic hysteresis loops show an isotropic feature of the $BaFe_{12}O_{19}$ nanowires array. The coercivity (H_c) and squareness ratio (M_r/M_s) of nanowire arrays are 2560 Oe and 0.6, respectively.

1. Introduction

In recent years, one–dimensional magnetic structures, especially magnetic nanowire arrays, have attracted much attention because of their unique potential applications in millimeter wave devices [1–4]. M-type barium hexagonal ferrite ($BaFe_{12}O_{19}$) has been widely used in millimeter wave devices for its high magnetocrystalline anisotropy field, high coercivity and high saturation magnetization [5–10]. Lately, it was reported that $BaFe_{12}O_{19}$ nanowires can be fabricated by sol–gel in template of porous anodic aluminum oxide (AAO) [11,12]. However, the AAO templates are very fragile and easy to break into pieces [13]. Therefore, AAO templates are required to be handled with much caution, which makes them extremely difficult to be assembled into sturdy devices. Currently, there is a trend to incorporate many functions in silicon substrates, such as systems on chips. Therefore, it is very important to be capable of fabricating $BaFe_{12}O_{19}$ nanowire array in silicon, which will be compatible with semiconductor industry in the future for the integrated nanosystems. Porous silicon (Si) which was consisted of nanometer to micrometer sized pores has attracted lots of attentions due to its potential applications in optoelectronics, chemical and biochemical sensing devices [14–19]. In this paper, we report the fabrication of $BaFe_{12}O_{19}$ nanowire array on porous Si template which no one else has done before.

Recently, porous Si has been widely prepared by the method of metal-assisted chemical etching for its simplified and low-cost fabricating process [20,21]. In this method, the Si substrate is firstly covered by a layer of metal particles used as catalysts. Then the metal-modified Si substrate is immersed in an aqueous solution containing HF and an oxidant (such as H_2O_2) without electrical bias. Here, we firstly fabricate the Au nanoparticles array by using the PS_{510000}-b-$P2VP_{31000}$. Subsequently, the porous Si is prepared by Au-assisted chemical etching in the aqueous solution containing HF and H_2O_2. Lastly, the $BaFe_{12}O_{19}$ nanowire is fabricated by using sol–gel method in the porous Si template. The fabrication processes of the $BaFe_{12}O_{19}$ nanowire and their characteristics are studied.

2. Experimental

2.1. Preparation of porous Si template

Si wafers were washed by the ordinary method consisting of successive immersion in acetone for 10 min, ethyl alcohol for 10 min and 5% HF for 5 min, which removed the organic contaminants and a thin silicon dioxide layer. Subsequently, the experiments were carried out in three steps, which were

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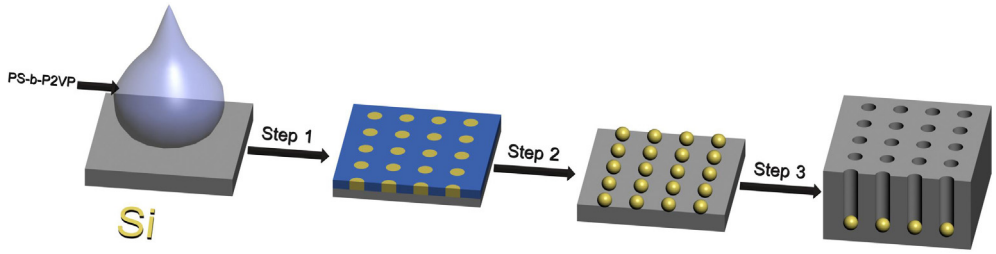

Fig. 1. Schematic procedures of preparation of porous silicon template.

schematically shown in Fig. 1. Firstly, PS-b-P2VP thin films were formed by spin coating at room temperature on the Si substrates, typically at 5000 rpm and 10 min. The coated Si substrate was then immersed in $HAuCl_4$ solution (5 mg/ml) with methanol solvent for 2 min to load $HAuCl_4$ solution in the P2VP cores. The $HAuCl_4$-loaded film was immersed into sodium citrate solution (0.03 M) of mixed water and methanol (H_2O/methanol = 2:1, volume ratio) at 60 °C for 15 min to reduce $HAuCl_4$ precursors into Au nanoparticles in the P2VP cores. Secondly, the thin film with Au nanoparticles was burnt by the alcohol lamp for 25 min to remove the organic copolymer. Thirdly, after the fabrication of Au nanoparticles array, the wafers were etched in aqueous solution contained HF and H_2O_2 for two steps (conditions of step 1: $HF/H_2O_2/H_2O$ = 1/1/2 (volume ratio), room temperature for 30 min; conditions of step 2: $HF/H_2O_2/H_2O$ = 1/5/10 (volume ratio), 60 °C for 1 h).

2.2. Preparation of $BaFe_{12}O_{19}$ nanowires

Metal nitrates were used as the cationic sources, and polyethylene glycol (PEG 20000) as the monomers for forming the polymeric matrix. Citric acid and PEG were dissolved in 50 ml deionized water by stirring at 80 °C to make the first solution. $Ba(NO_3)_2$ and $Fe(NO_3)_3{\cdot}9H_2O$ were dissolved in 50 ml deionized water according to the molar ratio 1:12, and then mixed with the first solution; The result of solution was stirred at 80 °C for 3 h to induce esterification and form a sol. The molar proportion of all nitrates to citric acid was 1:1. The weight proportion of $BaFe_{12}O_{19}$ to Poly (ethylene glycol) 20000 was 1:2. After the porous Si template was oxidated under the 800 °C at air atmosphere for 1 h, it was immersed in sol with the aid of ultra sound. Excess sol on the template surface was carefully wiped off and then heated at 800 °C for 3 h in open air.

2.3. Characterizations of porous Si and $BaFe_{12}O_{19}$ nanowire

The morphologies of Au nanoparticles, $BaFe_{12}O_{19}$ nanowire, surface and cross section of porous Si template were investigated by a scanning electron microscope (SEM). The composition of $BaFe_{12}O_{19}$ nanowire was checked by an energy dispersive spectrometer (EDS). The phase of nanowires was examined by X-ray diffraction (Cu $K\alpha$ radiation). The static magnetic properties were investigated by a vibrating sample magnetometer (VSM).

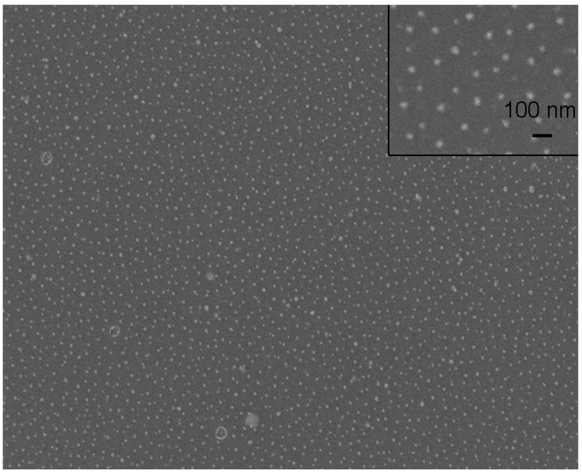

Fig. 2. Plane view SEM image of Au nanoparticles array on the surface of Si substrate.

3. Results and discussion

Fig. 2 displays the SEM image of Au nanoparticles array on Si surface. As shown, the Au nanoparticles are higher degree of order. The enlarged image of the area enclosed by a rectangle in Fig. 2 showed that the mean diameter of Au nanoparticles is about 30 nm and the distance between the Au nanoparticles is about 100 nm. The size of Au nanoparticles and distance between the Au nanoparticles can be controlled by the molecular weight of the block copolymers and the interactions between the polymer blocks and the blocks with the solvent [22].

After the array of Au nanoparticles has been obtained, the silicon template with the surface modified by Au was immersed in an aqueous solution containing HF and H_2O_2 for two steps. Firstly, it was etched in solution ($HF/H_2O_2/H_2O$ = 25/25/50, volume ratio) at room temperature for 30 min. The function is mainly reduced

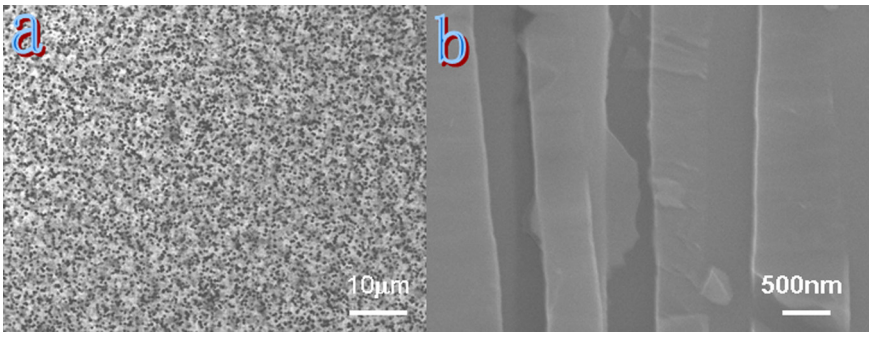

Fig. 3. SEM images of porous Si template prepared by two etching steps: (a) top view; (b) cross section view.