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Preparation and properties of novel magnetic composite nanostructures: Arrays of nanowires in porous membranes

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Abstract

In the present work, we introduce our latest achievements in the development of novel highly ordered composite magnetic nanostructures employing anodized nanoporous membranes as precursor templates where long-range hexagonal symmetry is induced by self-assembling during anodization process. Subsequent processing as electroplating, sputtering or pressing are employed to prepare arrays of metallic, semiconductor or polymeric nanowires embedded in oxide or metallic membranes. Particular attention is paid to recent results on controlling the magnetic anisotropy in arrays of metallic nanowires, particularly Co, and nanohole arrays in Ni membranes.

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1. Introduction: arrays of magnetic nanowires in porous membranes

The study of highly ordered densely packed arrays of nanowires in porous membranes is receiving increasing attraction owing to their application in various devices. Although first manifested interest has been related to information storage by perpendicular magnetic recording employing arrays of magnetic nanowires, more realistic applications are related to functionalization of those arrays and of the porous membranes for their use in sensor devices [1–4]: biomedical (i.e., a number of organics-related detection), environmental and energy safety (i.e., optimized filtering membranes), optomagnetic improved sensing devices (i.e., surface plasmon resonance sensors), etc. In addition, new opportunities are being opened to prepare novel composite nanostructured materials exibiting long-range ordering of hexagonal symmetry that confer them optimized properties [5].

The objective of the present work has been to update most recent results obtained in our laboratories on that topic. We pay particular attention to the design and preparation of novel composite nanostructures consisting of arrays of nanowires, nanotubes and nanoholes embedded in various matrices. The nature of both wires and membranes extend from oxide to polymeric and metallic. Different replica/antireplica processes are introduced to finally prepare such variety of nanostructures. Subsequently, their characterization is performed from structural and particularly magnetic points of view. The magnetic response of such nanostructures can be controlled by suitable processing, having in mind their final utility in various sensor devices.

2. Preparation of templates by anodization

One of the most typical templates to prepare ordered arrays of nano-objects is that of anodized porous alumina

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membranes. Anodization of pure aluminium is known to give rise to ordered arrays of nanopores with hexagonal symmetry [6]. A two-step anodization process is usually employed where an ordered template grows in a self-assembled way, so arranging with hexagonal symmetry during a long first anodization (see Fig. 1b). The size of long-range ordering (typically of around few μm^2) as well as the pore diameter and the hexagonal lattice parameter are controlled by anodization parameters. In a second anodization process, length of the pores is controlled, and their diameter is further tailored by subsequent treatment in acid solutions. Typically, pore diameter can be tailored between 15 and 200 nm, length between 300 and 10,000 nm, and interpore distance are around 65, 100 and 500 nm. All experimental details can be found in various reports [7,8].

Alternative polycarbonate or mica templates have been also considered to prepare arrays of nanowires (see Ref. [9]). As has been recently reported, self-aligned nanotubes can be also grown by similar anodization process of Ti disks [10]. In this case, nanotubes are nevertheless randomly disordered, with diameter and wall thickness range 60–100 and 20–40 nm, respectively, and are controlled by anodization parameters and electrolytical bath.

Spatial ordering of the arrays of nanopores and nanotubes is currently performed by high-resolution scanning electron microscopy (HRSEM), atomic force microscopy and fast Fourier transform. As an example, Fig. 2 shows HRSEM images of anodized Al_2O_3 and TiO_2 membranes where ordering of nanopores in alumina membrane is to be compared with disordered nanotubes in titania.

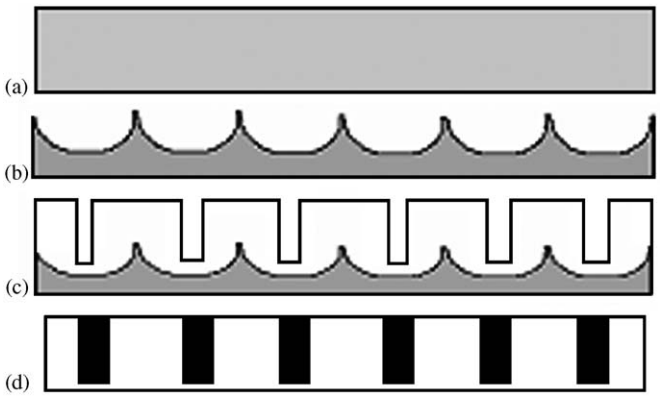

Fig. 1. Starting from a pure Al disk (a), self-assembled ordered template is formed during long first anodization (b), highly ordered nanopores grow during second anodization (c). Filling nanopores with metallic elements is achieved typically by electroplating (d).

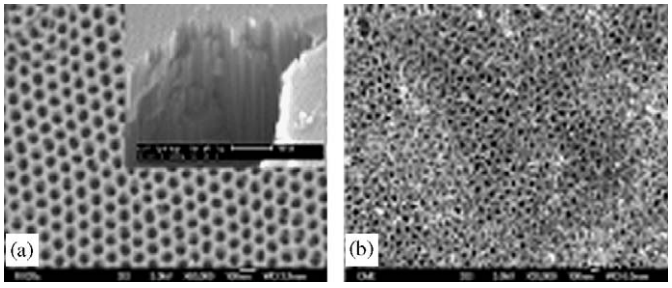

Fig. 2. HRSEM images of anodized Al_2O_3 (pore diameter 55 nm and interpore distance 105 nm) (a) and TiO_2 (65 nm nanotube diameter and 25 nm wall thickness) membranes (b).

3. Preparation of arrays of nanowires with controlled magnetic response

The filling of nanopores and nanotubes with metallic elements and alloys is usually performed by electroplating. In this way, arrays of magnetic metallic nanowires out of Fe, Ni, Co and their alloys are being currently achieved [11–13]. Factors such as the long-range ordering of the array, the homogeneity of nanowires and the filling factor of the porous membrane play an important role in the final magnetic behaviour of the arrays [13]. Consequently, the quality of the array must be controlled and improved by respective polishing and etching processes of the top and bottom surfaces of the membrane. Control of composition and checking of the nanopore/nanotube filling is performed by different techniques as energy dispersive X-ray spectrometry, Rutherford back-scattering and RF-glow discharge optical emission spectroscopy [14,15].

The final ferromagnetic behaviour of these nanowire arrays is determined by their effective magnetic anisotropy, which actually represents a balance between shape, magnetocrystalline and magnetoelastic anisotropy contributions [7,16]. In addition, magnetostatic interactions among nanowires can play also an important role as has been experimentally and theoretically shown [13].

Nanowire arrays is a typical case where shape anisotropy is very important. Shape anisotropy contribution giving rise to axial easy axis is dominant in the case of $Fe_xNi_{(1-x)}$ ($0 \leqslant x \leqslant 1$) arrays of nanowires with a large length-to-diameter ratio. An example is given in Fig. 3 where axial anisotropy (parallel to wire's axis) can be deduced from the comparison between longitudinal and in-plane hysteresis loops (see Fig. 3a) in array of Ni nanowires 1500 nm long and 23 nm in diameter with 65 nm hexagonal lattice parameter. In fact, as shape anisotropy is modified, i.e, reduced, with increasing nanowires' diameter, the easy magnetization direction rotates towards an in-plane direction as can be deduced from the significant reduction of the

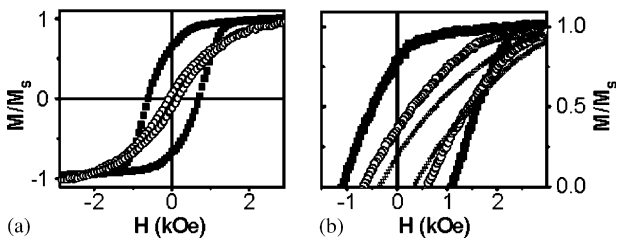

Fig. 3. Axial (■) and in-plane (○) hysteresis loops of Ni nanowires array (a), and axial loops of $Ni_{88}Fe_{12}$ nanowire arrays (b) with different wire diameter (■, 35 nm, ○, 43 nm and +, 52 nm).