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Materials Research Bulletin 41 (2006) 1045–1051
Materials Research Bulletin
www.elsevier.com/locate/matresbu

Template synthesis of $LaMnO_{3+\delta}$ ordered nanowire arrays by converse diffusion or convection

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Received 19 May 2005; received in revised form 23 November 2005; accepted 30 November 2005
Available online 20 December 2005

Abstract

A method, whereby metal ions and precipitation reagents were transported in the nanochannels of anodic alumina membrane (AAM) templates by converse diffusion or convection and reacted in situ to form into one-dimensional nanostructure of the precursor, was developed. A high-aspect ratio nanowire array of the $LaMnO_{3+\delta}$ was prepared by this method. Electron microscope images showed that the $LaMnO_{3+\delta}$ nanowire array was abundant, uniformly distributed and well-ordered in large area. The individual nanowires are about 60 nm in diameter and their length corresponds to the thickness of the applied AAM template. The analysis of X-ray diffractions demonstrated that the $LaMnO_{3+\delta}$ nanowires are pseudocubic with typical perovskite lattice parameter.

Keywords: A. Oxides; B. Chemical synthesis; C. Electron microscopy; C. X-ray diffraction

1. Introduction

$LaMnO_3$ belongs to a class of the perovskite oxides that attract the scientific interest by more than 50 years due to novel physical and chemical properties. More recently, the interest to the manganite perovskite materials has increased considerably after revealing its colossal magnetoresistance properties [1,2]. Great effort has been made for both their potential application of the efficient technological devices and the theoretical and experimental understanding of the magnetism and the electronic structure [3–5]. In addition, manganite perovskite oxides are characterized by great stability at high temperature, high mobility of oxygen, and stabilization of unusual cation oxidation states in the structure. Both latter properties lead to oxygen non-stoichiometry that makes them suitable for the catalytic oxidation, including hydrogenation and hydrogenolysis of hydrocarbons, CO oxidation, ammonia oxidation, and catalytic combustion [6–8]. Manganite perovskite-type oxides also prove to be promising materials for application as electrode materials in solid oxide fuel cells, exhaust gas sensors in automobiles, membranes for separation processes and as catalysts [9–11]. Recently, a lot of attention has been paid to the method of fabricating these materials, as the properties depend very much on the synthesis. The compounds of the $LaMnO_3$ family prepared by traditional solid-phase reaction exhibit usually small specific areas. In order to overcome it the new methods such as gel–sol and coprecipitation were used to obtain nanoparticles of the perovskite oxides [12,13]. In this paper, a new method was developed to fabricate the $LaMnO_{3+\delta}$ nanowire array by the anodic alumina membrane (AAM) templates.

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0025-5408/$ – see front matter
doi:10.1016/j.materresbull.2005.11.018

One-dimensional (1D) nanostructures (nanowires or quantum wires) are ideal systems for investigating the dependence of electrical transport and mechanical properties on size and dimensionality. They are expected to play an important role as both interconnects and functional components in the fabrication of nanoscale electronic and optoelectronic devices. Many unique and fascinating properties have already been proposed or demonstrated for this class of materials, such as superior mechanic toughness [14], higher luminescence efficiency [15], enhancement of thermoelectric figure of merit [16], and lowered lasing threshold [17]. Although there is no general guideline that could be consulted for the design of any kind of desired novel nanowires (or nanorods), there are some major synthetic methods that are often successfully employed for nanowire formation [18,19]: gas-phase reaction methods, solvothermal routes, template-directed as well as liquid–crystal assisted syntheses, various solution-based techniques, and sonochemically driven reactions are widely used. A wealth of templates including step edges present on the surfaces of a solid substrate [20], channels within a porous material [21], mesoscale structures self-assembled from organic surfactants [22] or block copolymers [23], biological macromolecules such as DNA strains or rod-shaped viruses [24], and existing microstructures synthesized using other approaches [25] have been proven to be versatile for preparing ordered nanostructures. Among these templates, the anodic alumina porous membranes (AAM) have received considerable attention in synthetic nanostructure materials due to its several unique structure properties, such as controllable pore diameter, extremely narrow size distribution for pore diameters and their intervals, and ideally cylindrical shape of pores [26,27], besides they also exhibit good chemical and thermal stability, making them a suitable material for a variety of deposition method and conditions. Thus, they have been extensively used to fabricate nanometer-size fibrils, rods, wires, and tubules of different solid materials by a variety of synthetic strategies. Some metal and alloy nanowire arrays were synthesized by electrochemical deposition with AAM templates [28]. Several researches used sol–gel method to produce inorganic oxide nanowires inside pores of template [29]. Although it is relatively advantageous in fabrication of the nanoparticles, this method will encounter serious difficulty in preparing nanowires with high-aspect ratio because it is hard to pour the viscous sol in the nanochannels with a small pore diameter. So it is necessary to make an effort to obtain more effective route that the precursor generates in situ and forms into the nanostructure in the nanochannels of the anodic alumina membrane. In this paper, we report a new technique to synthesize the long, straight, and uniform $LaMnO_{3+\delta}$ nanowires. In this technique, the mixed solution containing La^{3+} and Mn^{3+} and precipitation reagents were transported in the nanochannels of AAM templates by converse convection or diffusion and reacted in situ to form into one-dimensional nanostructure of the precursor. Subsequently, they were changed into $LaMnO_{3+\delta}$ nanowires at high temperature.

2. Experimental

2.1. Preparation of anodic alumina membrane

The AAM templates were produced from pieces of high-purity aluminum foil (30 mm × 12 mm, 99.99%) via two-step anodization processes. Before anodization, the aluminum sheets were degreased, etched in alkaline solution, carefully rinsed, dried, and then annealed under nitrogen ambient at 673 K to remove mechanical stresses and recrystallize. To obtain the smooth surface the aluminum sheets were electropolished in a mixed solution of $HClO_4$:CH_3CH_2OH = 1:4. In the first step of the anodization process, aluminum foils were anodized at constant voltages of 40 V in 0.3 M $H_2C_2O_4$ aqueous solution at 273–278 K for 24 h, then the alumina layer obtained was removed in a mixture of phosphoric acid (6 wt%) and chromic acid (1.5 wt%) at 333 K for 3 h, afterwards, the foils were re-anodized at the same conditions as these used in the first step for 48 or 72 h. Next, the whole sample was immersed in saturated Hg_2Cl_2 solution to separate anodic oxide film from aluminum substrate. A subsequent etching treatment was carried out in a 6 wt% phosphoric acid solution at 310 K for 1 h to remove the barrier layer on the bottom side of the AAM, resulting in the freestanding template.

2.2. Preparation of $LaMnO_{3+\delta}$ nanowires

In the course of experiment, the prepared template was used as membrane to separate a vessel into the two parts. One of compartments was filled with the stoichiometric mixture solution composed of lanthanum nitrate and manganese nitrate, and the other was filled with 0.2 M ammonia carbonate solution. The metal ions and carbonate ions migrated conversely in the nanochannels of AAM templates and reacted in situ to form into one-dimensional