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ScienceDirect
Trans. Nonferrous Met. Soc. China 22(2012) s95−s99
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Controllable synthesis of $Zn_{0.95}Co_{0.05}O$ nanowires and nanotubes by electrophoretic deposition method

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Received 9 July 2012; accepted 17 August 2012

Abstract: $Zn_{0.95}Co_{0.05}O$ nanotubes, as well as nanowires, were controllably synthesized by electrophoretic deposition method using anodic aluminum oxide (AAO) as template, and the mechanism of electrophoretic deposition was discussed. Careful characterization indicates that the prepared nanotubes and nanowires are of poly-crystal wurtzite structure and composed with 8−15 nm nano-crystals. The doped Co^{2+} occupied the Zn^{2+} sites in the ZnO lattice. Magnetic investigation indicates that the obtained nanotubes and nanowires are of room-temperature ferromagnetic. The magnetism of the nanotubes is much higher than that of the nanowires for the surface-preferential Co distribution.

Key words: $Zn_{1-x}Co_xO$; nanowires; nanotubes; electrophoretic deposition; AAO template; room-temperature ferromagnetism

1 Introduction

Diluted magnetic semiconductors (DMSs) have attracted great interests for their potential applications in semiconductor spintronics devices. Transition-metal doped ZnO has been predicted to be one of the most promising candidate DMSs for achieving room-temperature Curie temperature and thus, it has been receiving great attentions in recent years [1]. Current studies mainly focus on $Zn_{1-x}Co_xO$ nanoparticles, thin films, and bulk materials [2−7]. In contrast, the studies on one-dimensional (1D) $Zn_{1-x}Co_xO$ DMSs are still at a nascent stage despite very limited previous efforts, mostly focusing on $Zn_{1-x}Co_xO$ nanowires [8,9]. However, the integration of DMS materials into modern electronics requires very low dimensions in order to make real use of the advantage offered by spins, where dimensionality and size are known to play a significant role in determining various properties of the systems. Therefore, synthesis and study of 1D $Zn_{1-x}Co_xO$ DMSs nanomaterials are of great importance. Since the tubular form is generally available in layered materials such as carbon nanotubes, it seems more difficult to obtain the tubular nano-structure for the unlayered ZnO materials [10]. In this work, uniform morphology, highly ordered $Zn_{0.95}Co_{0.05}O$ nanotube and nanowire arrays were fabricated via electrophoretic deposition method with the aids of AAO template. Their structure and magnetic property were carefully investigated and the mechanism of electrophoretic deposition was discussed.

2 Experimental

2.1 Reagent and apparatus

The AAO template used in this work was purchased from Whatman Co., England, with pore diameter of 200 nm. All the reagents used in this experiment were of analytical grade, purchased from Shanghai Sinopharm Chemical Reagent Co. Ltd.

2.2 Experiment and characterizations

The $Zn_{0.95}Co_{0.05}O$ nanotubes were synthesized by an electrophoretic deposition method. Certain molar ratio of $Zn(OAc)_2{\cdot}2H_2O$ and $Co(OAc)_2{\cdot}4H_2O$ were dissolved in 200 mL of dimethyl sulfoxide. Then 50 mL of 0.5 mol/L $NH_4(CH_3)_4OH{\cdot}4H_2O$ dissolved in ethanol were added dropwise to the previous solution. The colloid was stirred

Foundation item: Project (21001003) supported by the National Natural Science Foundation of China; Project (1208085ME84) supported by Natural Science Foundation of Anhui Province of China; Project (LZUMMM2012001) supported by Open Project of Key Laboratory for Magnetism and Magnetic Materials of Ministry of Education, Lanzhou University, China
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under 333 K for 2 h. Electrophoretic deposition was performed in a bi-electrodes system under constant voltage mode. An AAO template membrane, with a surface sputter-coated with gold, acted as working electrode (negative electrode) and a reeled Pt thread acted as counter electrode. The electrodes were set parallel to each other and 3.6 cm apart. For $Zn_{0.95}Co_{0.05}O$ nanowire electrophoretic deposition, a direct potential of 4.5 V was applied on the electrodes and sustained for 45 min. While for the nanotube electrophoretic deposition, the deposition potential and time were 5.5 V and 2 h, respectively. At the end of electrophoretic deposition, excess sol was blotted off the membrane with filter paper. Then the prepared samples were annealed at 550 °C for 6 h in air atmosphere. Careful wet chemical etching with 1 mol/L NaOH was required to remove the alumina membrane before structural and magnetic characterization.

The scanning electron microscopy (SEM) image and back-scattered electron image (BEI) were obtained by a JSM−5600LV SEM equipped with energy dispersive spectrometer (EDS). The transmission electronic microscopy (TEM) and high resolution transmission electronic microscopy (HRTEM) images were obtained by a JEM−2100F TEM operated at 200 kV. The structure of the nanowires were characterized by a Rigaku D/Max−2200 X-ray diffraction (XRD) with Cu K_α (15.4 nm) line. The Raman spectra were obtained with JY−T64000 micro-Raman spectrometer in the backscattering geometry excited by Ar^+ laser 532 nm line. The UV-vis absorption spectra (UV-vis) were measured on a Cintra-10e spectrophotometer in diffuse reflectance mode and the magnetic properties were characterized by a vibrating sample magnetometer (VSM, LakerShore 7410) at 300 K.

3 Results and discussion

The prepared nanotubes and nanowires have unique morphology and orderly distribution, as shown in the SEM images (Fig. 1(a) and (b)). They are tens of microns in length, corresponding to the thickness of the AAO template. The EDS spectrum (Fig. 1(c)) suggests that the nanotubes are only composed of Zn, Co, and O elements. The presence of the Au peak is due to the sputt-coated Au layer on the sample for SEM observation. The EDS surface scan results (not shown) indicate the homogenous distribution of Zn and Co element in the nanotubes. The atomic ratio of Zn to Co is measured as 92:5, very close to the nominal Co doping

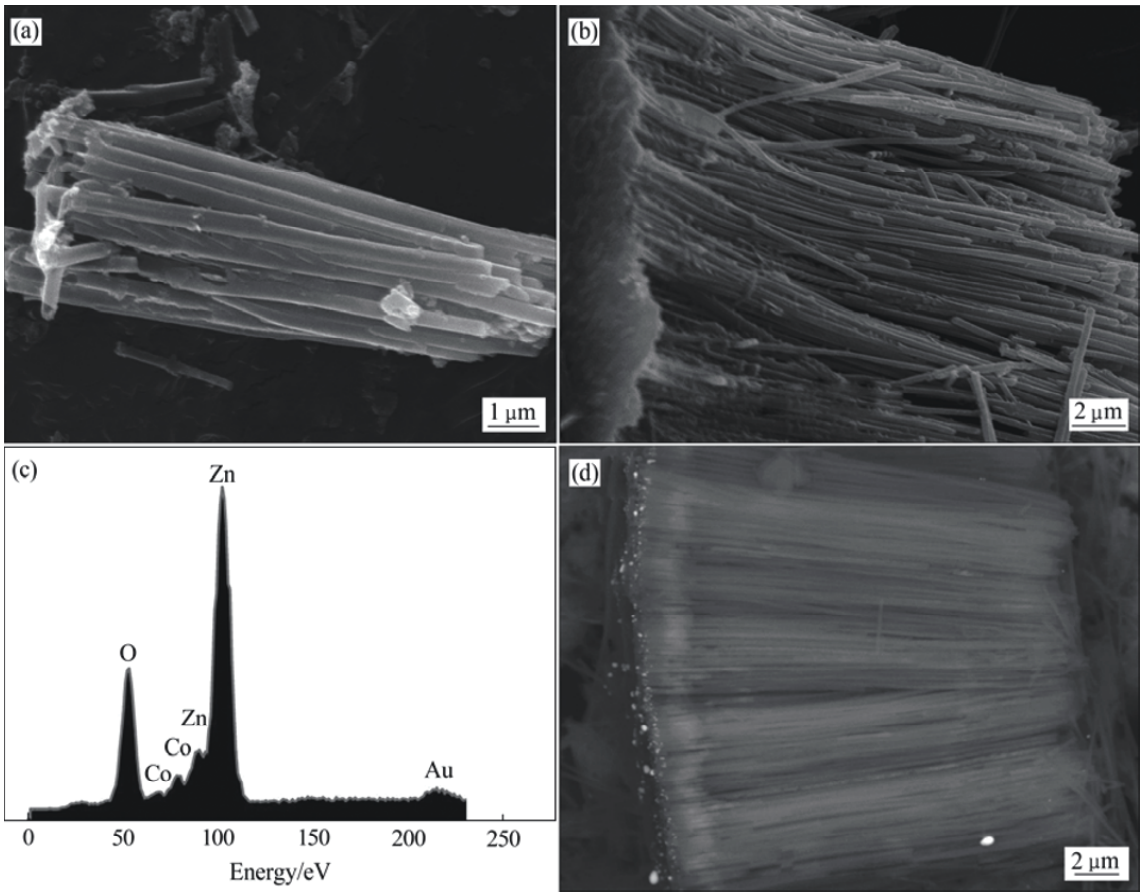

Fig. 1 SEM images ((a), (b)) of $Zn_{0.95}Co_{0.05}O$ nanotubes and nanowires and EDS spectrum (c) and BEI image (d) of $Zn_{0.95}Co_{0.05}O$ nanotubes arrays