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Production of Y–Ba–Cu–O Nanowires and Nanotubes by Electrochemical Method

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In this work, the technological aspects of great importance $YBa_2Cu_3O_{7-x}$ superconducting materials were produced in the form of nanotube by electrochemical method. The electrochemical deposition conditions for the Y–Ba–Cu deposition in nanoporous Al_2O_3 were investigated. The heat treatment was applied to Y–Ba–Cu/Al_2O_3 nanopatterns, to form superconductive phase. The resulting nanostructures were found to be in length 4–5 μm, 177–210 nm in diameter. The produced nanostructures at -4 V and more positive potentials were Y–Ba–Cu nanowires, while the nanostructures deposited at the more negative potentials were of nanotube form.

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1. Introduction

In the last few years, the synthesis of nanoscale materials and the followed strategies in the designing of the equipment necessary for the characterization of nanomaterials have led to a big explosion in field of nanoscience and technology. Low-dimensional nanomaterials such as nanowires and nanotubes have been attractive nanostructured materials for electronic, optoelectronic, and sensor applications because of their unique properties [1–3]. Many methods (MBE, CVD, etc.) combined with conventional lithographic, have been used for the production of low-dimensional nanostructures. One of the high-temperature superconductor $YBa_2Cu_3O_{7-x}$ (YBCO) has been fabricated as a bulk material, or as thin or thick films by employing several different techniques such as conventional solid state reaction, chemical vapor deposition, sol–gel techniques and pulsed laser deposition [4]. As a kind of important functional materials, superconductors in nanoscale have attracted great attention [5]. The synthesis of YBCO nanowires/nanotubes has been challenging subject. In this work, for the first time Y–Ba–Cu–O nanowires/nanotubes were fabricated by electrodeposition in nanoporous Al_2O_3 for various values of the deposition potential.

2. Experimental

A three-electrode cell was used for the electrochemical experiments. The volume of the electrochemical bath was approximately 80 ml. An Ag/AgCl electrode (BAS, 3 M NaCl, and -35 mV versus SCE at 25 °C) was used as the reference electrode. A platinum electrode approximately 5 times larger than the cathode was used as an auxiliary electrode. Anodic alumina oxide (AAO) membranes, with specified pore diameters of 200 nm and pore length of 60 μm, were used as a cathode with an exposed area of approximately 1 cm^2 for the nanowire and nanotube synthesis. These membranes were supplied by the Whatman Company.

Before the electrodeposition, one side of the AAO templates was coated with Au with a thickness of 20 nm and also adhesive copper foil stuck on for electrical contact [6]. The bath contained a mixed solution 15 mM $Y(NO_3)_3 \cdot 4H_2O$, 20 mM $Ba(NO_3)_2$, 15 mM $Cu(NO_3)_2 \cdot 2.5H_2O$, 4 mM EDTA and 40 mM $NaNO_3$. All solutions were prepared by dissolving reagent-grade chemicals in DMF. In order to minimize the crystal water of the compounds and the solvent, the metallic Ba particles have been put into solution for 2 days. Due to oxidization of reduced metallic barium, precipitates were formed at the bottom of the solution. Then the solution was filtered and prepared for the electrodeposition process. The electrodeposition was carried out at 25 °C in stirred solution and at a constant potential of $-3 \div -5$ V versus Ag/AgCl for 180 min to produce nanostructures. The electrodeposition of Y–Ba–Cu were performed by means of an electrochemical analyzer system, Iviumstat potentiostat/galvanostat. Produced Y–Ba–Cu/Al_2O_3 nanoarrays were annealed in air at 200 °C for 30 min and then at 950 °C for 2 h with the temperature ramped from room temperature to 200 °C and then 950 °C at a rate 1 °C/min. They were then annealed at 540 °C for 12 h and cooled down to room temperature at a rate 1 °C/min, while maintaining oxygen gas flow during these steps.

The morphology of nanowire/nanotube arrays was investigated by scanning electron microscopy (SEM; LEO-EVO-40) and transmission electron microscopy (TEM; FEI Tecnai G2 F30). Conductivity measurements were performed with four-probe techniques. Diffraction studies were carried out by using Philips X'Pert diffractometer equipped with Cu K_α radiation.

3. Results and discussion

Figure 1a displays the current-vs.-time curves recorded during electrodeposition of Y–Ba–Cu–O nanostructures for various deposition potential. It has been shown that depending on the rate of nucleation, the growth mechanisms are of two types, instantaneous nucleation and progressive nucleation [7]. In order to study the electrochemical nucleation and growth mechanisms of Y–Ba–Cu–O electrodeposition onto AAO, the current–time transients

are further analyzed by plotting the $(I/I_{\max})^2$ versus $(t/t_{\max})$ for the instantaneous and progressive growth. A theoretical plot for the Scharifker and Hills model [7] and the experimental plots of Y–Ba–Cu–O alloy deposition are shown in Fig. 1b. It can be observed that at less negative potentials (from −4 V) the nucleation is progressive, while at more negative potentials (−5 V) the nucleation is instantaneous.

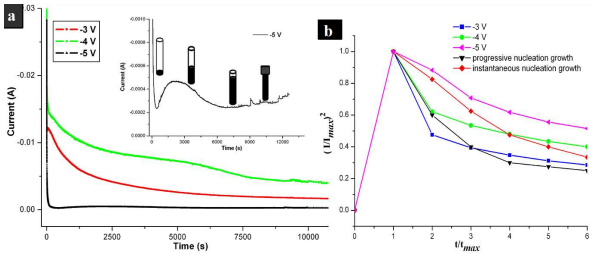

Fig. 1. (a) Current density versus time transients for Y–Ba–Cu deposition at various constant deposition potentials for 180 min versus Ag/AgCl. Inset shows low current region for −5 V. (b) Dimensionless plot analysis of the current density versus time transients of (a). ♦ and ▼ lines correspond to the calculated curves of the growth laws for 3D instantaneous and progressive nucleation, respectively, under diffusion control.

The general morphologies of the electrodeposited Y–Ba–Cu–O nanowires/nanotubes obtained inside the pores of the AAO were studied by SEM and TEM. SEM images of nanostructures at various deposition potentials are shown in Fig. 2a–c, after 10 min partial dissolution time of the membrane in 2 M NaOH. The nanowires/nanotubes deposited inside the nanopores of the AAO template are parallel, aligned regularly and densely distributed. SEM images show nanowires obtained at −3 V and −4 V, but nanotubes at −5 V. The average diameter of the nanowires/nanotubes corresponded closely to a pore diameter of 177–210 nm. The length of the nanowires/nanotubes was approximately 4–5 μm. This result was supported by TEM images of Y–Ba–Cu–O nanotube (Fig. 2d). For the TEM images, the sample obtained at electrodeposited −5 V was kept in NaOH until the AAO template had entirely dissolved to see individual Y–Ba–Cu–O nanotube images (Fig. 2d–f), then the liberated nanotubes were suspended in hexane.

Figure 3a shows XRD pattern of the Y–Ba–Cu–O nanotubes embedded in the AAO template. As shown in Fig. 3a, diffraction lines of orthorhombic $YBa_2Cu_3O_{7-x}$ and Al_2O_3 are obtained for nanotube arrays within the AAO. The peaks observed at 2θ = 22.58°, 32.44°, 38.05°, 39.66°, 46.02°, 46.30° can be indexed as (003), (013), (014), (113), (020), (006), respectively, reflections of $YBa_2Cu_3O_{7-x}$ orthorhombic phase. X-ray diffraction peaks (220), (311), (400) and (440) of the γ-Al_2O_3 also appeared, with a significant intensity. This could be Al_2O_3 diffusion to Y–Ba–Cu–O nanotubes. Zhao et al. [8] claimed that if Al_2O_3 used as a substrate for YBCO thin film, Al_2O_3 diffusion may occur during

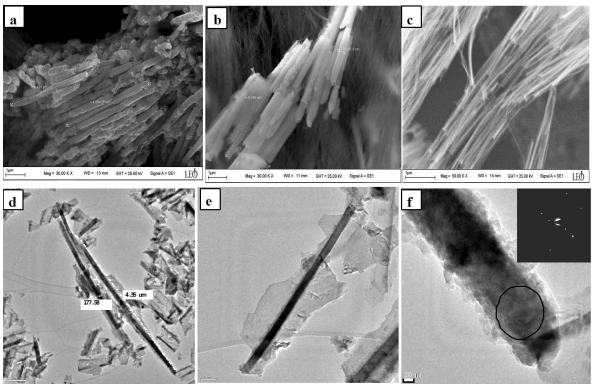

Fig. 2. SEM images of Y–Ba–Cu nanostructures at various deposition potentials after etching in 2 M NaOH for 10 min: (a) −3 V, (b) −4 V, (c) −5 V, (d–f) HRTEM images of freestanding Y–Ba–Cu nanotubes at electrodeposited −5 V.

the annealing process, this could greatly deteriorate the superconducting properties of the thin film. Figure 2f shows the high resolution TEM (HRTEM) micrograph of a nanotube. It can be clearly seen that the nanotube has a two-layer structure with great contrast between the end and middle parts of nanotube.

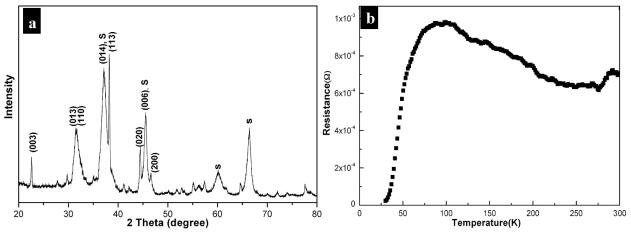

Fig. 3. (a) XRD spectrum of Y–Ba–Cu–O nanotubes arrays within AAO. (b) Temperature dependence for the four-point resistance of Y–Ba–Cu–O nanotubes arrays within AAO.

The resistance–temperature (R–T) measurement was carried out in a four-point probe configuration and the superconducting transition is shown in Fig. 3b. The onset of the broad transition drop in resistance occurs at ≈ 87 K and resistance reaches the zero at ≈ 30 K. Escudero et al. [9] reported that the Y–Ba–Al–Cu–O system shows a broad transition starting at 90 K and reaching the zero-resistance at 22.5 K. The similar behavior was observed in our sample.

4. Conclusion

Y–Ba–Cu–O nanowires/nanotubes were produced using template-based electrodeposition. The nucleation is progressive and produced sample is in nanowire form for potential values between −3 V and −4 V, while for higher negative potentials (−5 V) the nucleation is instantaneous and produced sample is of nanotube form.

Acknowledgments

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References

[1] L. Piraux, J.M. George, J.F. Despres, *Appl. Phys. Lett.* **65**, 2484 (1994).

[2] Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim, H. Yan, *Adv. Mater.* **15**, 353 (2003).

[3] F.E. Atalay, H. Kaya, S. Atalay, S. Tari, *J. Alloys Comp.* **469**, 458 (2009).

[4] J.T. Dawley, P.G. Clem, M.P. Siegal, D.R. Tallant, D.L. Overmyer, *J. Mater. Res.* **17**, 1900 (2002).

[5] G. Zhang, X. Lu, T. Zhang, J. Qu, W. Wang, X. Li, S. Yu, *Nanotechnology* **17**, 4252 (2006).

[6] F.E. Atalay, H. Kaya, V. Yagmur, S. Tari, S. Atalay, D. Avsar, *Appl. Surf. Sci.* **256**, 2414 (2010).

[7] P.M. Shirage, D.D. Shivagan, R.S. Kalubarme, V. Ganesan, S.H. Pawar, *Supercond. Sci. Technol.* **21**, 065009 (2008).

[8] X. Zhao, L. Li, C. Lei, Y. Tian, *Sci. China* **45A**, 1183 (2002).

[9] R. Escudero, L.E. Rendon-Diazmiron, T. Akachi, J. Heiras, C. Vazquez, L. Banos, F. Estrada, G. Gonzales, *Jpn. J. Appl. Phys.* **26**, L1019 (1987).