Fabrication and growth mechanism of metal (Zn, Sn) nanotube arrays and metal (Cu, Ag) nanotube/nanowire junction arrays

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Received 1 August 2007; accepted 24 September 2007

Available online 29 September 2007

Abstract

We report the successful synthesis of metal (Zn, Sn) nanotube arrays and metal (Cu, Ag) nanotube/nanowire junction arrays electrochemically deposited through nanoporous anodic alumina membranes. The metal (Zn, Sn) nanotube arrays were achieved by preferentially plating at circular step edges of the Au nanorings with hydrogen gas generation, critical to the evolution of tube formation. Quite interestingly, if there is no hydrogen gas generation, the metal (Cu, Ag) nanotube/nanowire junction arrays were obtained. This approach is very simple, molecular anchor free, and is generally capable of growing other metal nanotube arrays and nanotube/nanowire junction arrays.

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Keywords: Nanotubes; Nanowires; Anodic alumina membranes; Electrodeposition

1. Introduction

Tubular nanostructures have stimulated extensive research efforts in recent years because of their technological importance in advanced electronic devices [1] and prospective application in sensors [2] and biological separation and transport [3]. To date, various methods including reductive sulfidization [4], atomic layer deposition [5], hydrothermal pyrolysis [6], and template-based growth [7] have been developed for the fabrication of such tubular nanostructures. Among them, template-based synthesis using anodic alumina membranes (AAM) or track-etched polymeric membranes has attracted intensive attention, because it provides several distinct advantages over other approaches. It offers a convenient way for producing structurally uniform nanostructures periodically aligned in template matrices. A wide range of materials including metals [8], semiconductors [9], and polymers [10] have been prepared in the form of nanotubes (NTs). However,

only a few reports on the synthesis of metal NTs have been published, which deal with the chemical reduction of metallic complexes and chemical vapor infiltration within a porous alumina template. Metal NTs, such as Au [11], Pd [12], and Ni [13] NTs, have been synthesized via a template-assisted synthesis method with chemical modification of inner surface of the pores of the template prior to deposition. However, this technique might yield impurities [14]. To the best of our knowledge, the systematic preparation and detailed growth mechanism of metal NT arrays and NT/nanowire (NW) junction arrays by an electrodeposition method have never been reported. This has aroused our interesting in probing the growth mechanism of metal NT arrays and NT/NW junction arrays. In this paper, we report the systematic preparation of well-aligned metal (Zn, Sn) NT arrays and metal (Cu, Ag) NT/NW junction arrays. Meanwhile, possible growth mechanism was discussed.

2. Experimental

The anodic alumina membranes were formed by a two-step anodic anodization process, as described previously [15]. After the second anodization, the pore size of AAM was widened to about 100 nm by etching treatment in H_3PO_4 solution. In order

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Fig. 1. Energy dispersive spectra of as-prepared metal NT arrays and NT/NW junction arrays: (a) Zn; (b) Sn; (c) Cu; (d) Ag.

to fabricate the metal (Zn, Sn) NT arrays and metal (Cu, Ag) NT/NW junction arrays, a layer of Au thin film was deposited as a working electrode on the bottom surface of the AAM. The electrochemical deposition solutions contained: (1) ZnSO_4 (80 g L^{-1}) and H_3BO_3 (20 g L^{-1}); (2) SnSO_4 (25 g L^{-1}) and gelatin (20 g L^{-1}); (3) CuSO_4 (150 g L^{-1}) and H_3BO_3 (25 g L^{-1}); (4) AgNO_3 (25 g L^{-1}) and H_3BO_3 (45 g L^{-1}). These solutions were confined to the bare side of the membrane to synthesize metal (Zn, Sn) NT arrays and metal (Cu, Ag) NT/NW junction arrays, respectively. All the electrodepositions were carried out at a constant current density of 5 mA cm^{-2} , with pure Pt wire as the anode at room temperature for 1 h. The morphology and the size of the products were determined by field emission SEM (FE-SEM, JSM-6500F) equipped with EDX spectrometer. X-ray diffraction (XRD) patterns were obtained on a PANalytical X'Pert Pro diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at 45 kV and 40 mA.

3. Results and discussion

Metal NT arrays and NT/NW junction arrays were obtained within the pores of an alumina membrane using template-based electrochemical deposition technology at room temperature. The EDX spectroscopies of the as-grown samples shown in Fig. 1a–d confirmed that these products were composed of Zn, Sn, Cu and Ag, respectively. The Al and O peaks originate from the remaining AAM and the Au peak originates from the Au substrates, as shown in Fig. 1a–d.

Typical XRD patterns of the as-synthesized samples are shown in Fig. 2. The XRD patterns clearly show that the four samples reveal common polycrystalline structures. The reflection peaks can be indexed to the hexagonal close packed (hcp) zinc structure, the

Fig. 2. X-ray diffraction patterns of as-prepared metal NT arrays and NT/NW junction arrays: (a) Zn; (b) Sn; (c) Cu; (d) Ag.

Fig. 3. (a) SEM image of the highly ordered Zn nanotube arrays. (b) SEM image of the highly ordered Sn nanotube arrays.

body-centered tetragonal (bct) β -tin structure, the face-centered cubic (fcc) copper structure, and the face-centered cubic (fcc) silver structure. There is no metal oxide phase observed from the XRD patterns. The diffraction peaks at 44.7° , 65.1° and 78.2° are attributed to the background signals of the Al tape used for fixing our samples in XRD

measurements and the signal at 41.5° is originated from residual alumina after the removal of alumina membrane. This structural characterization further suggests that our controlled conditions are suitable for NT arrays and NT/NW junction arrays deposition with pure metal phase at room temperature.

Fig. 3a–b shows the SEM images of metal (Zn, Sn) NT arrays on the Au substrates, respectively. The SEM images reveal that the as-grown samples are clearly composed of well-aligned NTs. The length of the NTs is about several micrometers. It can be seen that the NTs have open ends on top and are arranged in parallel and well-ordered way. The outer diameter of the NTs is in the range of 90–110 nm, which corresponds to the pore diameter of the AAM. The inner diameter of the nanotubes is in the range of 40–60 nm. The compactness of the nanotubes is quite high, about $1 \times 10^9 \text{ cm}^{-2}$, corresponding to the pore density of the AAM.

Fig. 4a–b shows the SEM images of metal (Cu, Ag) NT/NW junction arrays on the Au substrates, respectively. The SEM images reveal that the as-grown samples are clearly composed of well-aligned NT/NW junction arrays. The length of the NT/NW junction arrays is about several micrometers. The diameters and the compactness of the NT/NW junction arrays are similar to those of the NT arrays described above, which were pre-determined by the characteristic of the AAM. In addition, it can be clearly seen that the NT/NW junction arrays have close caps on top and open roots at bottom and are arranged in parallel, as shown in Fig. 4a. The bottom of the metal (Cu, Ag) NT/NW junction arrays shown in Fig. 4c–d once again confirmed that the roots at the bottom of metal (Cu, Ag) NT/NW junction arrays were open. Besides, it is shown that an ordered Au nanoring arrays were obtained by using the bottom surface of the AAM as a mold [16]. The two dashed circles are the metal nucleations which were preferentially electroplated at circular step edges of Au nanorings [17].

An understanding of growth mechanism plays an important role in controlling and designing nanostructures. The growth procedure of metal nanostructures is schematically shown in Fig. 5. To interpret this

Fig. 4. (a) SEM image of the Cu NT/NW junction arrays with closed caps and open roots. (b) SEM image of the Ag NT/NW junction arrays with closed caps. (c) High-magnification SEM image of the bottom of the Cu NT/NW junction arrays. (d) High-magnification SEM image of the bottom of the Ag NT/NW junction arrays.

Fig. 5. Schematic of the growth mechanism of metal (Zn, Sn) NTs and metal (Cu, Ag) NT/NW junctions via the template-based electrochemical deposition method.

growth mechanism of metal (Zn, Sn) NT arrays and metal (Cu, Ag) NT/NW junction arrays, we propose the hypothesis that circular step edges of the Au nanorings serves as preferential sites for the deposition of metal ions (Fig. 5b). It can be attributed to the fact that circular step edges have the ability to catalyze electron transfer to metal ions in solution [18]. However, it cannot explain why the tubes do not deposit radial to create wires. It was suspected that the hydrogen gas evolution plays a significant role in the formation of the nanotubes (Fig. 5c) [19]. During the electrochemical deposition of metal (Zn, Sn) NT arrays within AAM, hydrogen gas evolution ordinarily accompanies metal (Zn, Sn) electrochemical deposition because the reductive potential of hydrogen gas is higher than metal (Zn, Sn). Hence, hydrogen gas continuously evaporates from the cathode through the central region of nanopores, the metal elements are therefore preferentially attached to the pore wall. Subsequently, metal (Zn, Sn) NT arrays were formed (Fig. 5d). When there is no hydrogen gas generation, as in the electrochemical deposition of metal (Cu, Ag) NT/NW junction arrays (Fig. 5e), hydrogen gas evolution does not accompany metal (Cu, Ag) electrochemical deposition. This occurs because reductive potential of the metal (Cu, Ag) is higher than hydrogen gas. Thus, the metal (Cu, Ag) NT will ultimately close up to form solid NW at the final segment, and metal (Cu, Ag) NT/NW junction arrays were formed (Fig. 5f).

4. Conclusion

In summary, we have demonstrated that the process based on template-based electrodeposition synthesis is an efficient method for the fabrication of highly ordered metal NT arrays and NT/NW junction arrays. Notably, this method does not require chemical modification of the inner surface of the template pores, which might decrease the possibility of introducing impurities. This simple method should be able to serve as a general approach for the growth of other metal NT arrays and NT/NW junction arrays. This general synthesis method could make metal NT arrays and NT/NW junction arrays a material platform for systematic studies of unique physical properties, as well as novel applications.

Acknowledgment

This work was supported by the Education of Ministry and National Science Council of the Republic of China.

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