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Template-based fabrication of nanowire-nanotube hybrid arrays

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Abstract

The fabrication and structure characterization of ordered nanowire–nanotube hybrid arrays embedded in porous anodic aluminum oxide (AAO) membranes are reported. Arrays of TiO_2 nanotubes were first deposited into the pores of AAO membranes by a sol–gel technique. Co nanowires were then electrochemically deposited into the TiO_2 nanotubes to form the nanowire–nanotube hybrid arrays. Scanning electron microscopy and transmission electron microscopy measurements showed a high nanowire filling factor and a clean interface between the Co nanowire and the TiO_2 nanotube. Application of these hybrids to the fabrication of ordered nanowire arrays with highly controllable geometric parameters is discussed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Porous anodic aluminum oxide (AAO) membranes have been widely used for fabricating highly ordered nanowire arrays [1, 2]. Nanowires are usually directly deposited into the pores of the membranes by electrochemical deposition [1, 2]or pressure injection [3]. This is a simple, convenient, and low cost approach for fabricating large high density ordered nanowire arrays. These nanowire arrays are of great interest from both a technological and a fundamental point of view. For example, high density magnetic nanowire arrays are potential candidates for new magnetic recording media. Such magnetic nanowire arrays have also found important applications in fundamental research. Due to their large aspect ratio, magnetic nanowires can provide local magnetic fields of thousands of oersteds on nanometer-to-submicron scales [4]. Recently, Lyuksyutov et al proposed a hybrid system in which an array of magnetic nanowires is covered by a superconductor film [5, 6]. This magnetic nanowire array provides a flux bundle array perpendicular to the superconducting film. Vortices may be nucleated and/or tightly pinned by magnetic nanowires due to magnetic interactions which are strongly dependent on the diameter and the center-to-center spacing of the magnetic nanowires.

In these applications, the independent control of geometric parameters, such as the diameter and the center-to-center

spacing of the nanowires, is of critical importance. For nanowire arrays fabricated by conventional electrochemical deposition into the AAO membranes, these geometric parameters are set by the pore diameter and the pore spacing of the AAO membranes. It is virtually impossible to independently tune these two parameters during the growth of AAO membranes, since they are coupled to each other and are both nearly proportional to the applied anodization voltage. Although some other techniques, such as two-step anodization [7] and the pre-anodization molding process [8], can significantly improve the pore ordering, they cannot break the coupling between pore diameter and spacing. To independently tune these two parameters, one may first fabricate AAO membranes with a desired pore spacing using a proper anodization voltage. Then, the pore diameter may be enlarged by isotropic chemical wet etching. However, this approach has a very limited tuning range, since it is not possible to fabricate membranes with a smaller pore diameter and larger pore spacing. To our knowledge, no effective way of reducing the pore diameter without reducing the pore spacing has been reported. In this work, we demonstrate a simple and efficient way of reducing the pore diameter and independently tuning the geometric parameters of nanowire arrays by depositing first an array of insulating oxide nanotubes and then magnetic nanowires into the AAO pores.



Figure 1. Schematic diagram displaying the fabrication of a nanowire–nanotube hybrid array. (a) The vacant AAO membrane with a honeycomb pore array. (b) TiO_2 was coated into the pores as well as the membrane surfaces. (c) An Au electrode was deposited on one surface and Co was then electroplated into the TiO_2 nanotubes from the other surface. (d) The surfaces of the structure shown in (c) were polished.

2. Experimental details

Figure 1 shows a schematic diagram of this new method. First, the porous AAO membrane is fabricated from an Al sheet, where the desired pore spacing is determined by the anodization voltage (figure 1(a)). An insulating or semiconducting layer is then deposited on the entire surfaces of the membrane, including the inner surfaces of the pores, by an isotropic sol-gel deposition technique. It has been reported recently that metal oxide films, such as titania [9], silica [10], vanadia [11] and tin oxide [12] films, can be coated on various substrates of complex shapes by the solgel technique. The sol-gel coating inside the AAO pores thus forms a nanotube array of the coating material (figure 1(b)). By controlling the thickness of the sol-gel coating, the effective pore diameter is reduced in a controlled fashion. Magnetic nanowires of a reduced diameter can be electrochemically deposited into the reduced pores to form an array of magnetic nanowires (figure 1(c)) after the deposition of an Au cathode layer on the other surface. Surfaces of the samples are then mechanically polished for structure analysis and device fabrication (figure 1(d)).

In this study, commercial AAO membranes purchased from Whatman Co., with a nominal pore diameter of \sim 200 nm and a pore spacing of ~ 300 nm, were used. For the solgel deposition of TiO₂ nanotubes, the precursor solution was prepared by dissolving pure TiF₄ powder in de-ionized water and stirring for 1 h at room temperature. The concentration of the solution was 0.76 g $l^{-1}.\,$ The AAO membranes were immersed in the solution for 30 min with the temperature maintained at 60 °C. Following the TiO₂ deposition, the sample was baked at 225 °C in the atmosphere for 2 h. Co nanowires were then electrochemically deposited into the TiO₂ nanotubes. For this deposition, a thick Au layer (~300 nm) was first deposited on one surface of the TiO2 coated AAO membrane to serve as the cathode for electrochemical deposition. This Au layer fully blocked all the pores on that surface. The electrolyte was a solution of 1 M CoCl₂ with



Figure 2. (a) SEM image of TiO_2 nanotubes. (b) Cross-sectional TEM image of TiO_2 nanotubes in AAO membrane. Inset: schematic diagram of sample ion milling.

30 g l^{-1} H₃BO₃. The deposition voltage was between 2.5 and 3 V. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to characterize the structure of TiO₂ nanotubes and Co nanowire/TiO₂ nanotube hybrids at each stage of the fabrication. Both SEM and TEM are equipped with energy dispersive spectroscopy (EDS) which was used to determine the composition of the materials.

3. Results and discussion

3.1. Microstructure of TiO₂ nanotube arrays

Figure 2 shows the SEM and TEM images of the TiO_2 nanotubes before the deposition of Co nanowires. Figure 2(a)is a SEM image of the extracted TiO₂ nanotubes. For SEM imaging, the sample surfaces were polished to remove the surface coating of TiO₂. The AAO membrane was then dissolved with a 0.5 M NaOH solution to extract free TiO₂ nanotubes. The tubular structures of the nanotubes are clearly visible. The length of the nanotubes was found to be equal to the thickness of the AAO membrane, which was $\sim 60 \ \mu m$. To investigate the cross-section of the TiO₂ nanotubes, the TiO₂ coated membrane was first mechanically polished and then further thinned down by ion milling with two Ar⁺ ion beams tilted at an angle of 5° , as shown in the inset of figure 2(b). Figure 2(b) shows a TEM cross-section image of an array of TiO₂ nanotubes (the dark rings) embedded in the remaining AAO matrix. The filling of TiO₂ nanotubes in the AAO pores is perfect. The variation in the nanotube diameter and shape is due to the irregular pore structure in typical commercial AAO membranes. The coating of the TiO₂ layer is uniform with a thickness of 50 nm for 30 min of sol-gel deposition. The composition of the TiO₂ nanotubes was confirmed by EDS mapping and Raman spectroscopy.

3.2. Microstructures of TiO₂-Co hybrid arrays

Figures 3 and 4 show the results of SEM and TEM microstructure characterizations of the Co nanowire/TiO₂ nanotube hybrids. The pores of the membrane remain open after the TiO₂ coating. This is the key for electroplating Co nanowires into the TiO₂ nanotubes. To investigate the filling factor, we took SEM images of the polished surface of the Co/TiO₂ hybrids embedded in the AAO membrane (figure 3(a)). The Co/TiO₂ hybrids are clearly visible. The



Figure 3. (a) SEM image of the Co nanowire– TiO_2 nanotube hybrid array in an AAO membrane. Inset: EDS spectrum showing Al, Ti and Co peaks. (b) Cross-sectional TEM image of Co nanowire– TiO_2 nanotube hybrids in the AAO membrane. Inset: EDS mappings of Al, O, Ti and Co.

filling factor of Co going into the TiO₂ nanotubes is nearly 100%. The EDS spectrum taken for the imaging area clearly shows the peaks corresponding to chemical compositions of Al, Ti and Co (figure 3(a) inset). The TEM image in figure 3(b) shows the detailed cross-section structures of the Co/TiO₂ hybrids embedded in the AAO. The hybrids are composed of Co cores surrounded by TiO₂ nanotubes, which are embedded in the Al₂O₃ matrix. To investigate the composition distribution of the hybrid structure, EDS mappings on Al, O, Ti and Co were carried out. EDS signals of the selected elements were collected in separate images as the electron beam is scanned over one of the Co/TiO₂ hybrids. The EDS mappings of Al, O, Ti and Co (figure 3(b) inset) demonstrate a structure consistent with the TEM image in figure 3(b).

Figure 4 shows a high resolution TEM image on the boundary between a Co nanowire and a TiO₂ nanotube in a cross-section of the hybrid sample. The darker region on the left is a portion of the Co nanowire, while the brighter region on the right is a portion of the TiO_2 nanotube surrounding the Co nanowire. The electron diffraction pattern (figure 4 inset) for the Co region indicates a single-crystal structure. The diffraction pattern matched the hexagonal close-packed structure (hcp) of bulk Co crystals at room temperature. The incident electron beam was along the [001]_{hcp} direction. Two diffraction spots, (100) and (010), were indicated in the diffraction pattern. Most of the Co nanowires in these samples are polycrystalline, however, with crystal size comparable to the nanowire diameter. The TiO₂ nanotubes are composed of nanometer-sized TiO_2 crystals, as pointed out by the white arrows. The subsequent growth of Co nanowires does not influence the microstructure of TiO₂. Neither does the presence of TiO₂ nanotubes change the microscopic structure of Co nanowires.

4. Conclusion

In conclusion, an effective method for independently adjusting the geometric parameters of the nanowire arrays fabricated in AAO membranes has been demonstrated. In this approach, an array of oxide nanotubes is deposited inside the pores of an AAO membrane by a sol–gel technique, to effectively reduce the pore diameter. This process can also be extended to other



Figure 4. High resolution TEM image of the interface between Co and TiO₂. Inset: electron diffraction pattern of the Co nanowire.

porous templates such as track etched polymer membranes. The nanowire and AAO pore diameter can be continuously tuned over a large range, from a few nanometers to hundreds of nanometers, with overall sample sizes on the centimeter scale. This method may also be applied for fabricating nanowire/nanotube hybrids or nanocables [13, 14] of various material compositions. Therefore, it is a promising technique for fabricating complex nanowire array systems for a variety of applications.

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