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Transformation of Sn nanowires to oxide nanotubes by a localized corrosion process

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ABSTRACT

Amorphous SnO nanotubes were synthesized from Sn nanowires (NWs) electrodeposited into anodic aluminum oxide templates by a localized corrosion process in an aqueous solution composed of chromic, phosphoric, and hydrochloric acids. Initially, phosphoric acid dissolves the template, while chromic acid generates a SnO passivation layer on the NW surface. As a volume expansion occurs during the surface oxidation, some cracks occur at the top surface of the passivation layer. In addition, Cl ions from the hydrochloric acid assist the cracking. Subsequently, Sn atoms in the core of the NW dissolve into the acidic solution while the oxide layer at the shell remains to form nanotubes. Finally, Sn NWs with a length of 10 μm and diameter of 30 nm are completely transformed to amorphous SnO nanotubes with a wall thickness of 10 nm. After heat-treatment, the amorphous nanotubes were crystallized into polycrystalline SnO phase with a rough surface morphology.

1. Introduction

Nanostructures of wide band-gap semiconductors such as ZnO, SnO_2, In_2O_3, TiO_2, and CdO, have attracted much attention in many research fields due to their potential applications. Although most metal oxides with a wide band gap are known to be n-type semiconductors, SnO is a p-type semiconductor due to naturally formed vacancies at Sn lattice sites [1–3]. Therefore, tin oxides, which are n-type and p-type semiconductors in the respective phases of SnO_2 and SnO, are more versatile in device applications, e.g., semiconductor devices composed of metal oxide p-n junctions [4], sensors [5], electrodes for Li-ion batteries [6], and supercapacitors [7].

Recently, one-dimensional tin oxide nanostructures including nanowires, nanotubes, nanobelts, and nanoribbons, have been produced by various fabrication methods [8–12]. Better alignment and more uniform size distribution of nanostructures are required for device applications because such characteristics can reduce the uncertainty in properties resulting from a distribution of size and aligned orientation. The anodic aluminum oxide (AAO) template-assisted electrochemical deposition method is one of the promising approaches for synthesizing one-dimensional structures with a highly ordering and uniform size distribution. Thus, this method is frequently utilized for the purpose of investigating the size-dependent physical properties because the AAO's pore diameters are easily controlled by a pore widening process [13].

In this study, we synthesized a Sn oxide nanotube (ONT) array of a high aspect ratio and uniform diameter using the electrodeposition of Sn NWs and subsequent localized corrosion of the NWs.

2. Experimental

AAO templates were made out of Al foil (99.99%, Alfa Aesar) by a two-step anodization process at 274 K [13]. The as-prepared AAO template had pores of approximately 15 nm in radius and approximately 10 μm in thickness. The barrier layer of AAO was thinned by the voltage reduction process [14] in order to electrodeposit Sn NWs within the templates. The electrolyte (pH 1.8) for the Sn deposition was composed of 18.8 g/l $SnSO_4$ (Junsei Chemical, EP grade) and 25 g/l H_3BO_3 (Junsei Chemical, GR grade). Electrochemical deposition was carried out using a two-electrode system with a Pt counter electrode using a sine wave voltage of $V_{max} = 0$ V and $V_{min} = -10$ V at 298 K. The growth rate of Sn NWs was 2.2 μm/min. More experimental details can be found in the previous report [13].

To transform the metal Sn NWs into Sn ONTs, we carried out a localized corrosion process in the etching solution that was composed of 0.33 M chromium (VI) oxide (Junsei Chemical, GR grade), 0.44 M phosphoric acid (Junsei Chemical, EP grade), 0.03 M hydrochloric acid (Sigma-Aldrich, ACS reagent) and balanced deionized water. The samples of Sn NWs in the AAO template were immersed into the etching solution at 363 K for 4 h. The Sn NWs were gradually converted into amorphous Sn ONTs. Subsequently, the Sn ONTs were heat-treated at 873 K for 2 h in a vacuum of 5×10^{-4} Torr. The heating ramp rate was 10 K/min. The microstructures were analyzed by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800) and transmission electron microscopy (TEM, Tecnai G² F30S-TWIN). The elemental

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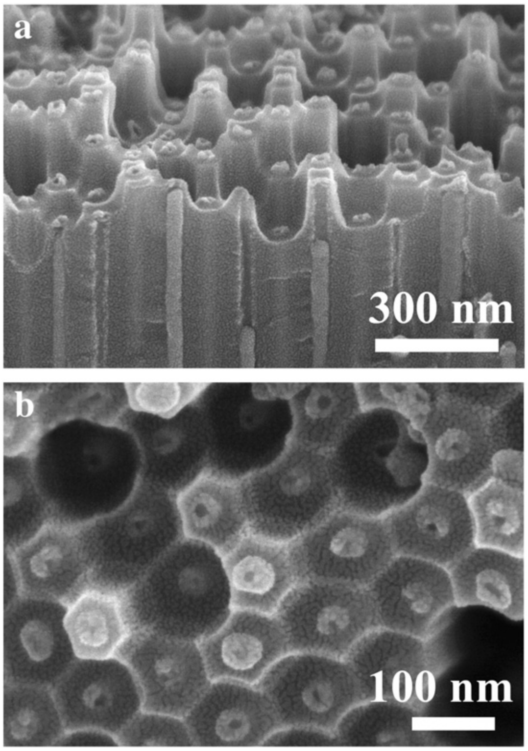

Fig. 1. (a) Tilted and (b) top-view SEM images of Sn NWs within the AAO template after etching the Sn NWs-free AAO template.

analysis was conducted by an energy dispersive X-ray spectrometer (EDS, Bruker Quantax 200).

3. Results and discussion

Fig. 1(a) shows a cross-sectional SEM image of the Sn NWs in the AAO template after the etching process for 1 h. The Sn NWs were surrounded by the remaining AAO template while the Sn-empty AAO template has been etched away. The etching solution was not able to infiltrate the gap between the Sn NWs and the AAO walls. The surface of the Sn NWs that was exposed to the etching solution was oxidized by the chromic acid to form a Sn oxide passivation layer. In the top-view SEM image of Fig.1(b), small openings can be observed at the top surfaces of the NWs. The openings were the broken part of the oxide passivation layer and were the result of the localized corrosion, as discussed below.

Fig. 2 shows the typical SEM images of Sn ONTs after the etching process for 4 h. The uniform Sn ONT array was formed over the entire surface of the Al substrate, as shown in Fig. 2(a). In the magnified SEM image shown in Fig. 2(b), it can be seen that every ONT has an opening at its top surface. Fig. 2(c) shows a perspective SEM image of vertically-aligned Sn ONTs on the Al substrate after bending. The Sn ONTs agglomerated due to surface tension during the rinsing and drying processes. Fig. 2(d) shows the EDS elemental mapping results for the magnified area of the specimen shown in Fig.2(a). These results indicate that the Sn ONTs were composed of elemental Sn and O. And, elemental P and Cr were also observed in the regime of Sn ONTs. The Cr might come from the chromic acid in the etching solution due to insufficient

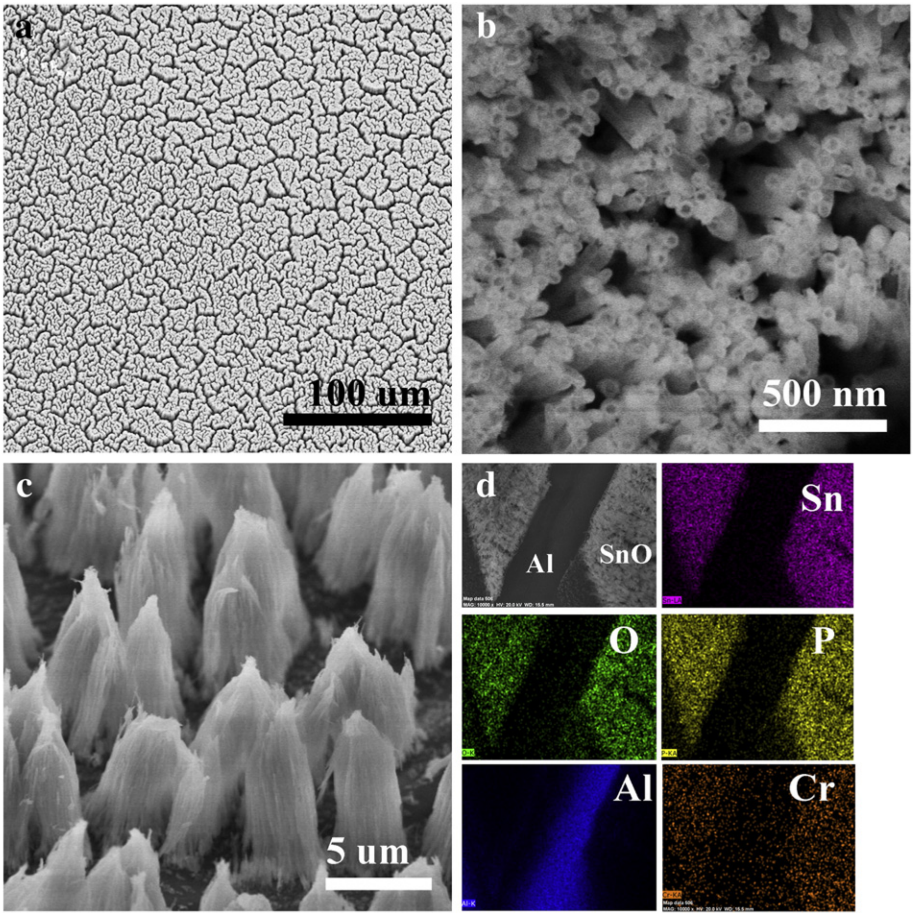

Fig. 2. SEM images and EDS area mapping results of Sn ONTs after etching process for 4 h. (a) top-view of the Sn ONTs on Al substrate, (b) a magnified top-view of the image shown in (a), (c) Sn ONT bundles vertically aligned on the Al foil, and (d) EDS mapping results of Sn, O, P, Al, and Cr elements for the enlarged image of the top-view area shown in (a).