Applied Surface Science 287 (2013) 252–256

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Template-assisted electrodeposition of indium–antimony nanowires – Comparison of electrochemical methods

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ARTICLE INFO

Article history:
Received 20 August 2013
Accepted 22 September 2013
Available online 29 September 2013

Keywords:
Anodic aluminum oxide (AAO)
Electrodeposition
Pulse electrodeposition
Indium antimonide (InSb)
Nanowire arrays

ABSTRACT

Indium antimonide (InSb) is a III–V compound semiconductor that in a form of nanowires can possess improved thermoelectrical and optical properties compared to the corresponding bulk crystal. Here, we applied three electrodeposition techniques for a fast and inexpensive template-assisted fabrication of InSb nanowires from a sodium citrate-citric acid solution at room temperature. The home-made anodic aluminum oxide (AAO) templates with the pore diameter of 100 nm were used. InSb nanowires were synthesized by potentiostatic, galvanostatic and periodic pulse reverse techniques. The morphology, composition and crystallinity of as-obtained and annealed nanowires were investigated and compared with the literature data. It was found that the potentiostatic and pulse reverse methods gave crystalline nanowires. On the other hand, the constant current density deposition results in a partially amorphous nanowire material.

1. Introduction

Indium antimonide (InSb) is a semiconductive material well known for its narrow band gap (0.163 eV at 300 K), thermal conductivity (16.0 $W m^{-1} K^{-1}$), as well as very high electron mobility (7.7×10^4 $cm^2 V^{-1} s^{-1}$) and electron saturation velocity (5×10^7 $cm s^{-1}$). Due to its unique electronic and optoelectronic properties, InSb can be widely applied as, e.g. infrared detectors [1], magnetic field sensors [2], gas sensors [3] and components in low-power high speed electronic devices [4,5]. There are a few theoretical papers on electric transport properties and applications of InSb for thermoelectric generators [6–8].

The synthesis of one-dimensional materials for utilization in energy generators, sensing and energy conversion is a rapidly growing branch of science. It is a well-known fact that nanostructures exhibit unique physical and chemical properties compared to traditional bulk materials. Therefore, it is not surprising that one-dimensional (1D) materials are within the scope of research interest, and are used as powerful thermoelectric materials in heating/cooling systems. Simulations, theoretical calculations and laboratory tests have performed over the past few years suggest that there is a relationship between the size of nanostructures (nanodots, nanowires, nanotubes, and superlattices) and efficiency of thermoelectric materials [9–12]. The synthesized high-performance thermoelectric 1D materials should possess a high degree of arrangement and regularity, as well as should be characterized by anisotropy of properties. Thus, if a relatively inexpensive and not overly complicated method for the preparation of thermoelectric nanowires were to be developed, they could have a broad spectrum of applications.

There are limited number of methods used for fabrication of InSb nanowires and typical examples include pulse laser deposition (PLD) [13], chemical vapor deposition (CVD) [14], metal organic chemical vapor deposition (MOCVD) [15,16], chemical beam epitaxy (CBE) [17,18], and vapor–liquid–solid (VLS) growth method [19]. However, the major disadvantage with these methods is a fundamental difficulty in achieving a repeatable stoichiometric growth of InSb nanowires due to a narrow range of processing temperatures, differences in vapor pressure of In and Sb, and formation of the thin In_2O_3 layer on the surface of nanowires [20,21]. For these reasons, developing methods for synthesis of InSb nanowires with controlled stoichiometry and crystallinity are desirable. As one of the promising alternative strategy to overcome these problems and fabricate high crystalline InSb nanowires, the electrochemical deposition inside nanoporous anodic aluminum oxide (AAO) templates has been considered [22–26]. Since nanoporous AAO templates are characterized by well-defined parameters such as: pore diameter, distance between the pores, pore density and porosity [27,28], the AAO-template-assisted method offers a versatile and cost effective approach to synthesis of nanowires with well-controlled morphology and chemical composition.

Although electrochemical deposition is widely used for metallic materials deposition, the method is rather occasionally employed for deposition of III–V compound semiconductors, especially from

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0169-4332/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2013.09.135

aqueous solutions. During electrodeposition of semiconductors some challenging task have to be overcome, e.g. higher resistivity of semiconducting deposit and its sensitivity to crystal lattice defects. These problems are complicated by the fact that resistivity of the deposit can constantly change during electrodeposition. So far, InSb nanowires were electrodeposited from a single bath containing oxidized precursors of both elements using a single potential technique [22,25,26,29] and an unipolar pulse technique with a sequence of on-off cathodic pulses in a two-electrode cell [23,24].

In this paper, InSb nanowires were synthesized from a sodium citrate-citric acid solution inside home-made nanoporous alumina templates using three different electrochemical techniques, namely potentiostatic, galvanostatic and periodic pulse reverse methods. To the best of our knowledge, no report is available on pulse reversed electrodeposition of InSb nanowires in porous templates. The detailed morphology of InSb nanowires depending on process conditions was investigated by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD).

2. Experimental

$InCl_3 \cdot 3H_2O$, $SbCl_3 \cdot 3H_2O$, tartaric acid, oxalic acid from Alfa Aesar were of analytical grade and used as received. A high-purity aluminum foil (99.999%, Goodfellow) was used for porous AAO templates preparation.

The porous alumina templates were prepared by a two-step anodization of aluminum in 0.3 M $H_2C_2O_4$ at 60 V and 20 °C, as described previously [27,30–32]. Briefly, Al specimens were degreased in ethanol and electrochemically polished in a stirred mixture of $HClO_4$ and C_2H_5OH (1:4, v/v) under the constant current density of 0.5 A cm^{-2} for 1 min at 0 °C. The first anodizing step was performed at the constant cell voltage of 60 V for 1 h. The resulting porous alumina layer was removed by chemical etching in a mixture of 6 wt.% H_3PO_4 and 1.8 wt.% $H_2Cr_2O_4$ at 45 °C for 24 h. Subsequently, the second anodization was performed at 60 V for 2 h. All anodizations were carried out in a 0.5 dm^3 electrochemical cell cooled by a circulating system (Thermo Fisher, Haake DC10-K15) with vigorous stirring. The working surface area of samples was 0.5 cm^2. A Pb plate was used as a cathode, and the distance between both electrodes was about 3 cm. After anodization, nanoporous films were separated from the remaining aluminum substrate by immersion in a saturated $HgCl_2$ solution. Then, a chemical etching of alumina barrier layer was performed in a 5 wt.% H_3PO_4 solution at 45 °C for 35 min. The average pore diameter of prepared AAO membranes was 100 nm.

The electrodeposition of indium and antimony was performed in nanopores of the home-made AAO templates using a Reference 3000 potentiostat/galvanostat (Gamry Instruments). Prior to electrodeposition, an Au layer was deposited on one side of the AAO membrane to make the surface electrically conductive. All electrodepositions were performed at room temperature in a conventional three-electrode cell (50 cm^3 volume) with a platinum counter electrode and a saturated calomel electrode (SCE) coupled to a fine Luggin capillary as a reference electrode. The potentiostatic (at the constant potential of −1.5 V vs. SCE) and galvanostatic (at current densities ranging between 10 and 220 mA cm^{-2}) depositions of In and Sb were carried out for 40 min in an aqueous solution containing 0.15 M citric acid, 0.06 M sodium citrate, indium and antimony cations at a ratio of 4:1. The potentiostatic pulse reverse electrodeposition of binary nanowires was carried out for 120 min from a citric bath (0.2 M citric acid, 0.15 M sodium citrate) containing 0.06 M In^{3+} and 0.045 M Sb^{3+}. For the periodic pulse reverse electrodeposition a sequence of cathodic pulse of −2.1 V vs. SCE (0.5 s) and anodic pulse of 0 V vs. SCE (1 s) was applied.

In order to examine the influence of annealing on the crystallinity of InSb nanowires, the annealing process was carried out under argon atmosphere at the temperature of 300 °C for 2 h. For SEM analysis, the AAO templates with deposited nanowires were immersed in a 1 M NaOH solution for 30 min and washed with distilled water to remove the dissolved AAO template.

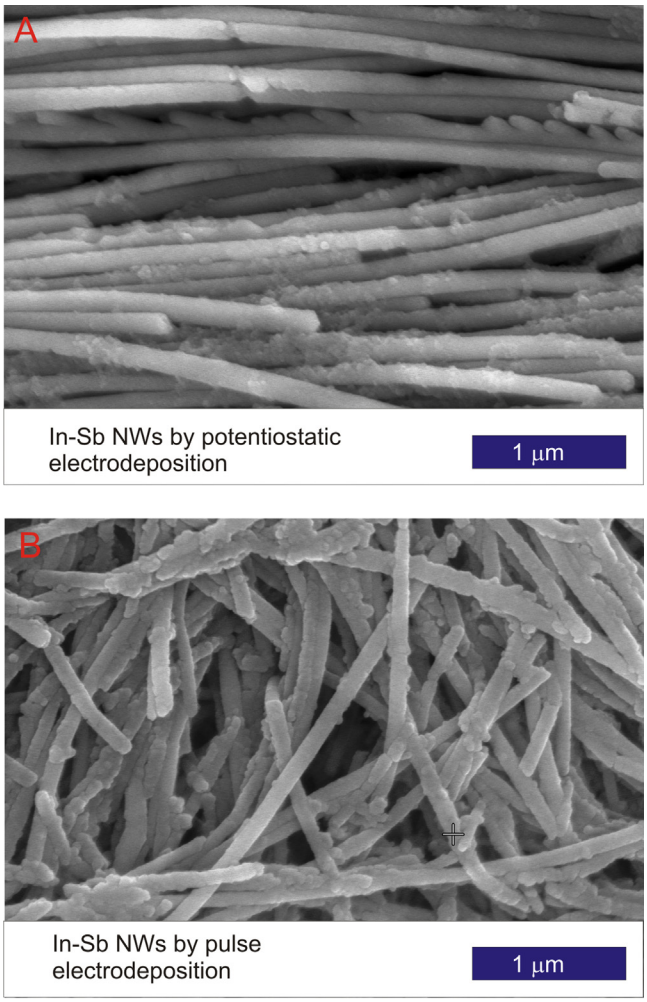

Fig. 1. SEM images of binary InSb nanowires (NWs) obtained by (A) potentiostatic electrodeposition at −1.5 V vs. SCE and (B) periodic pulse reverse electrodeposition together with (C) EDS spectrum of In–Sb.