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Diameter and composition modulated bismuth telluride nanowires by galvanic displacement reaction of segmented NiFe nanowires

Hoyoung Suh[a,1], Hyunsung Jung[b,1], Carlos M. Hangarter[b], Hosik Park[b], Youngin Lee[c], Yongho Choa[c], Nosang V. Myung[b,*], Kimin Hong[a,*]

[a] Department of Physics, Chungnam National University, Daejeon 301-150, Republic of Korea
[b] Department of Chemical and Environmental Engineering and Center for Nanoscale Science and Engineering, University of California-Riverside, CA 92521, United States
[c] Department of Bionanotechnology, Hanyang University, Ansan 426-791, Republic of Korea

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ABSTRACT

Dumbbell-like BiTe nanowires with segmentally tailored composition and dimension were synthesized by galvanic displacement reaction of multi-segmented NiFe nanowires with Ni-rich and Fe-rich segments. The composition and dimension of each segment were determined by the tuned sacrificial segments to control the galvanic displacement reaction rate. The composition and dimension of each segment were determined by the tuned sacrificial segments to control the galvanic displacement reaction rate. For examples, the bismuth content in Bi_xTe_{1-x} adjusted from 32 to 60 at.% by controlling the Fe content in NiFe sacrificial nanowires. The ability to tune the dimension of segments was demonstrated by the diameter variation from 99 to 551 nm with the segment length from 97 nm to 1 μm.

1. Introduction

Nanostructured metals, semimetals, and semiconductors have been extensively studied for use in various electronic, photonic, catalytic, and magnetic applications because of its ability to "tune" the properties by engineering the dimensions and composition. In many cases, these materials were synthesized by physical/vacuum processes or wet chemical reactions, which have limited control to modulate composition within a single construct. Additional control over nanowire features such as shape or geometric features is consequently a significant hurdle for one-dimensional (1-D) nanostructures, often requiring complex processing for just a single radial modulation. Although template directed electrodeposition with anodized aluminum oxide templates permits axial modulation, coordinating shape and dimension control of these scaffolds with compositional variation would be difficult for most materials due to concentration changes along the pore length and consequently has yet to be demonstrated with significant periodicity [1–7].

Recently, we demonstrated the ability to synthesize complex nanostructures (i.e., nanopeapods) by coupling template-directed electroplating with galvanic displacement reaction (GDR), in which a single galvanic reaction occurs in the presence of noble metal constituents, demonstrating potential for extended periodicity in nanowires [8]. In addition to industrial relevance for coating metallic layers without aids of external power source, GDR has been studied to create hollow nanostructures and to alter the surface of materials, particularly in catalysis [9,10]. Furthermore, GDR is a versatile method to synthesize various functional materials including metals (e.g., Au, Ag, Pb and Pt) and few semiconductors (e.g., Te and BiTe) at near room temperatures [11–27].

Herein, we demonstrate a facile synthesis of bismuth telluride nanowire containing compositional and structural modulation utilizing galvanic displacement reaction. High precision periodicity is readily achieved with control of segment length, dictated by electrodeposition, and diameter, determined by two different sacrificial materials. Corrosion engineering, by compositional change in the sacrificial materials, was used to control reaction rates and driving force to generate distinct diameters and compositions, which may be a general route to create advanced semiconducting nanostructures.

Bi_2Te_3 was examined in this study for its unique electron transport properties and high thermoelectric figure-of-merit at near room temperature. Various processes have been employed to synthesize Bi_2Te_3 for the purposes of structure analysis [28,29], thermal conductivity measurements [30], and thermoelectric power measurement [31–33]. In addition, a micro- and

* Corresponding authors. Tel.: +1 951 827 7710; fax: +1 951 827 5696.
E-mail addresses: myung@engr.ucr.edu (N.V. Myung), kmhong@cnu.ac.kr (K. Hong).
[1] Both authors contributed equally to this work.

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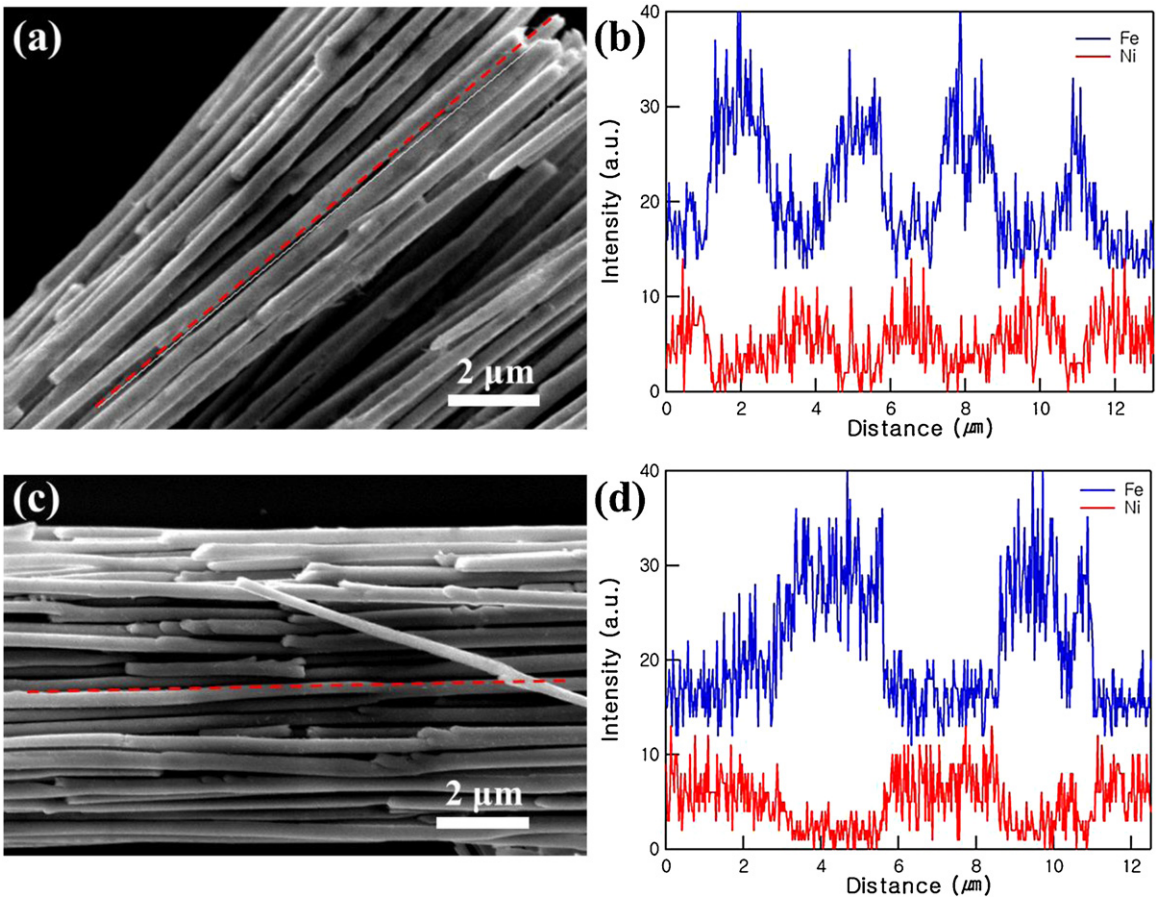

Fig. 1. SEM images and elemental EDS line scan of segmented NiFe nanowires with tailored composition and length: (a, b) segmented NiFe nanowires with Ni-rich $Ni_{75}Fe_{25}$ segment in length of 1.5 ± 0.07 μm and Fe-rich $Ni_{36}Fe_{64}$ segment in length of 1.4 ± 0.04 μm, and (c, d) Ni-rich $Ni_{77}Fe_{23}$ segment in length of 2.5 ± 0.12 μm and Fe-rich $Ni_{33}Fe_{67}$ segment in length of 3.1 ± 0.16 μm.

nanostructured Bi_2Te_3 composite prepared by hot pressing of microstructured BiTe powders with galvanically displaced BiTe nanopowders has demonstrated the highest figure of merit, suggesting GDR is a promising route for synthesis of such materials [8–27].

2. Experimental

The plating electrolyte to fabricate compositionally modulated NiFe wires consisted of 0.9 M $FeCl_2$, 0.6 M $NiCl_2$, 1.0 M $CaCl_2$, and 0.03 M L-ascorbic acid in deionized water. Commercially available anodized alumina with nominal pore size of 200 nm (Whatman Inc.) and polycarbonate membrane (Whatman Inc.) with the nominal pore size of 50 and 100 nm were utilized as templates to synthesize nanowires with different diameter. Alternating Ni-rich and Fe-rich segments were grown by applying two plating current densities alternately in the bath; 5 mA cm^{-2} (2.5 mA cm^{-2}) for Ni-rich segment and 20 mA cm^{-2} (40 mA cm^{-2}) for Fe-rich segment. Length of each segment was controlled by the plating time. The operating temperate and agitation were fixed at 40 °C and 200 rpm, respectively. Nanowires were suspended by dissolving the templates. The solution for dissolution of AAO was 1.0 M NaOH for 2 h and that for polycarbonate was 99.5% 1-methyl-2-pyrrolidinone for 1 h. Composition of the segments was analyzed with TEM-EDX. Diameter of the segmented NiFe wires was 298 ± 13 nm.

GDR electrolyte consisted of 0.02 M Bi^{3+} and 0.01 M $HTeO_2^+$ in 1.0 M HNO_3. The mutli-segmented NiFe nanowires were immersed into the electrolyte solution at room temperature, where the reaction time was controlled to be 4, 6, 8, and 10 min. To determine the open circuit potential during GDR, Ni-rich and Fe-rich thin films were electrodeposited on 100 nm thick Pt-coated 300 nm thick silicon oxide/silicon substrate and immersed into the electrolyte. Three electrode configurations were utilized to measure OCP where Pt wire and SCE (saturated calomel electrode) were utilized as the counter and reference electrodes, respectively. Biologic multipotentiostat (VMP2, Princeton Applied Research) was used to measure the OCP.

Morphology, crystallinity and composition of the synthesized nanowires were investigated by SEM (XLG-30FEG, Philips), TEM (JEM-2100F, JEOL) with high resolution-TEM and SAED analyses, and energy dispersive spectroscopy (EDS) which was conducted with TEM at the acceleration voltage of 200 kV (Inca x-stream, OXFORD) and SEM at the acceleration voltage of 20 kV (Phoenix). XRD patterns of thin films were analyzed by X-ray diffractometer (D8 Advanced Diffractometer, Bruker).

3. Results and discussion

The synthesis process initiated with template directed electrodeposition of multi-segmented nanowires with alternating Ni-rich and Fe-rich sections. Sacrificial NiFe wires were prepared by electroplating into porous AAO (nominal diameter of 200 nm) and polycarbonate (nominal diameter of 50 nm) membranes. Different membranes were utilized to investigate this effect on the formation of nanostructures. Alternating Ni-rich and Fe-rich segments were achieved by changing the applied current density, where Ni-rich and Fe-rich segments were electrodeposited at 5 and 20 mA cm^{-2}, respectively [6,7]. The composition and length of each segment in