Nano Energy 31 (2017) 168–173

Contents lists available at ScienceDirect

Nano Energy

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

Ultra-long vertically aligned lead titanate nanowire arrays for energy harvesting in extreme environments

Alireza Nafari[a], Christopher C. Bowland[b], Henry A. Sodano[a,c,*]

[a] Department of Aerospace Engineering, University of Michigan, Ann Arbor, MI 48109, United States
[b] Department of Material Science Engineering, University of Florida, Gainesville, FL 32611, United States
[c] Department of Material Science Engineering, University of Michigan, Ann Arbor, MI 48109, United States

ARTICLE INFO

Keywords:
Extreme environments
Energy harvesting
Lead titanate
Nanowires
Energy densities

ABSTRACT

Recent research has shown that nanowire arrays can be fabricated into power harvesting devices that convert ambient vibrations to electrical power. These devices, however, are limited to low temperature environments due to material constraints. To solve this problem, this paper offers a route to obtain a nanowire energy harvester that is capable of operating at extreme temperatures. This is achieved by developing a method to synthesize vertically aligned arrays of ultra-long lead titanate nanowires and fabricating them into an energy harvester. Performing power characterization measurements of the device in a temperature-controlled environment illustrates useful power generation at temperatures up to 375 °C. This work offers a new method for the fabrication of extreme temperature device thereby offering a significant advancement in the field of energy harvesting by demonstrating energy production in extreme environments where previous systems would fail.

1. Introduction

The increasing demand for self-powered devices has led to the development of energy harvesting systems that seek to convert sources of abundant ambient energy in the form of structural vibrations, acoustic waves or impact energy to electrical power. Nano/micro electromechanical systems (NEMS/MEMS) have attracted attention in the past few decades as a mechanism to harvest this lost energy. The one dimensional form of piezoelectric materials, such as nanowires [1–6], nanofibers [7–9], and nanotubes [10–13] show particular promise, since the high aspect ratio nature of these materials provides compliance even at small dimensions. Therefore, unlike the bulk form, one dimensional nanostructures have lower natural frequencies and can produce higher piezoelectric response to small, low intensity mechanical disturbances which often exist in the range of 0-1 kHz [14].

Among the different types of piezoelectric nanowires (NWs), vertically aligned semiconducting ZnO NWs have received the most attention in the literature [1,2,4,8,15]. This is mostly due to its biocompatibility, ability to exhibit diverse configurations and intrinsic piezoelectric properties. However, compared to ferroelectric ceramics such as lead zirconate titanate (PZT) [9,16], lead titanate ($PbTiO_3$) [10] and barium titanate ($BaTiO_3$) [17], ZnO has a lower piezoelectric coupling coefficient, which in turn restricts its piezoelectric performance [18]. On the other hand, ferroelectric materials exhibit a Curie temperature (T_c) at which point the material undergoes a phase change and produces a centrosymmetric cubic unit cell [19]. Upon heating above the Curie temperature, the ceramic settles into the low energy state with zero net polarization thus losing its piezoelectricity and ability to generate useful electrical energy. With the increasing demand for sensors to monitor the conditions in extreme environments, such as those found in turbine engines, oil and gas exploration, hypersonic aircraft rockets [20,21], etc., the development of energy harvesting devices that exhibit both a high coupling coefficient and high temperature stability is a necessity. However, to the best of the authors' knowledge, no demonstration of nanoscale piezoelectric based energy harvesters have been developed for use in extreme temperatures. Among the many ferroelectric materials, $PbTiO_3$ is chosen for this research due to its high piezoelectricity at extreme temperatures (T_c=490 °C) [22,23] For the first time in this paper, ultra-long vertically aligned $PbTiO_3$ NW arrays are used as the core material for an extreme temperature vibrational energy harvester.

* Corresponding author.
E-mail addresses: anafari@umich.edu (A. Nafari), cbowland@ufl.edu (C.C. Bowland), hsodano@umich.edu (H.A. Sodano).

http://dx.doi.org/10.1016/j.nanoen.2016.11.015
Received 28 August 2016; Received in revised form 19 October 2016; Accepted 9 November 2016
Available online 12 November 2016

2. Experimental methods

2.1. Synthesis of hydrogen titanate nanowire arrays as precursor

A new synthesis method is developed to obtain NWs with a length of 40 μm and an aspect ratio (AR) of 75 by utilizing an inexpensive two-step hydrothermal reaction. Through optimization of the synthesis parameters, the length and AR of the NWs are engineered to obtain high deformability and compliance in order to increase the piezoelectric voltage. The synthesis method for obtaining ultra-long $PbTiO_3$ NWs consists of two separate hydrothermal reactions. In the first step, ultra-long arrays of $Na_2Ti_3O_7$ NWs were grown on a titanium foil substrate (MTI Corporation, 99.9%, 100 μm thick). The substrates were cut in 1 cm^2 square sections and sonicated for 30 min in deionized (DI) water, acetone and 2-propanol solution with a 1:1:1 volume ratio, followed by a DI water rinse. Then the cleaned substrates were oxidized at 750 °C (15 °C/min) for 8 h in a furnace and cooled down slowly to room temperature at a rate of 50 °C/hour. Next, two oxidized titanium foil substrates were immersed in a Teflon lined autoclave reactor (Parr Instrument Co.) filled with 30 ml (Fill Factor: 67%) of 12 M sodium hydroxide aqueous solution (97% Alfa Aesar). The reactor was then maintained at 210 °C in a convection oven for 8.5 h and cooled down in ambient air. The resultant substrates containing high aspect ratio vertically aligned $Na_2Ti_3O_7$ NWs were then washed gently with DI water.

Then, the resulting NWs were washed and soaked in a 0.2 M hydrochloric acid (Fisher, 30%). As a result, Na^+ ions were substituted with H^+ ions in the NWs crystal structure yielding hydrogen titanate ($H_2Ti_3O_7$) NWs [5]. To avoid NW tip wicking, reaction parameters were controlled so that the NW arrays were sufficiently rigid [24]. This hydrothermal reaction and ion exchange resulted in ultra-long, vertically aligned arrays of $H_2Ti_3O_7$ NWs, which then act as the precursor for the next hydrothermal reaction.

2.2. Synthesis of lead titanate nanowire arrays

In the second hydrothermal reaction, the H_2TiO_3 precursor substrate was immersed in a Teflon lined autoclave containing 20 ml CO_2 free DI water (Fill Factor: 44%), 0.662 g lead nitrate (Acros Organics, 99%) and 0.16 g potassium hydroxide (Alfa Aesar, flake, 85%). The solution was saturated with nitrogen and kept at 200 °C for 4 h. During this reaction, Pb^{+2} ions replaced H^+ ions in the crystal structure while retaining the NWs' morphology. The resultant ultra-long $PbTiO_3$ NW arrays were then washed in a dilute 0.2 M HCl solution to remove any unwanted byproducts, such as lead oxide (PbO) and other salts. Finally, the samples were covered with PbO powder (MP Biomedicals, LLC) and heat treated at 600 °C in a furnace. This heat treatment is essential for two reasons. First, it anneals the NWs creating a more thorough perovskite structure. Second, the high temperatures remove any hydroxyl groups resulting from the hydrothermal reaction that increase the NW conductivity thus screening the generated piezoelectric charges [16].

It should be noted that the concentration of reactants, reaction time, and temperature are the main contributors to the resultant NW morphology and degree of $PbTiO_3$ conversion. Usually, an increase in these parameters will result in a more complete conversion but degrades the NW morphology. However, decreasing these parameters preserves the morphology of the precursor but results in incomplete conversion. Therefore, there is a trade-off between conversion efficiency and morphology preservation to consider when optimizing the conversion parameters.

Scanning electron microscopy (SEM, TESCAN VEGA3 LM) micrographs of the $Na_2Ti_3O_7$ and $PbTiO_3$ NWs are illustrated in Fig. 1a-d. As shown in the figure, the average length of the NWs is about 40 μm and the aspect ratio is about 75. From this figure, it is evident that the diameter of the $PbTiO_3$ NWs increased after substitution of Na^+ with H^+ and then Pb^{+2}. This is because Pb^{+2} ions have a larger atomic radii than Na^+ ions, and this conversion increases the size of the unit cell which results in swelling of the NWs. By reducing the reaction time in the first hydrothermal reaction, shorter NWs were synthesized (see Supplementary information, Fig. S1). It is shown that the reduction in NWs length result in reduction of the performance of energy harvesting device. Hence, it should be noted that the length of the NWs plays an important role in the performance of the fabricated device.

The Chemical composition of the $PbTiO_3$ NWs were analyzed using energy dispersive spectroscopy (EDS). EDS results are depicted in Fig. 1e which demonstrate that the NWs are composed of Pb, Ti, and O. Note that C peak is due to the carbon tape used for holding the sample. To confirm the conversion from $Na_2Ti_3O_7$ to $PbTiO_3$, the crystallographic structure of these NWs is analyzed using X-ray diffraction. As shown in Fig. 1f, the diffraction pattern of the NWs match completely with perovskite $PbTiO_3$ (Joint Committee on Powder Diffraction Standards, Card No. 06-0452). In this figure, the red ovals represent the $PbTiO_3$ peaks and green squares represent the excessive PbO residue in the material. Further characterization was performed to analyze the phase transition behavior of the $PbTiO_3$ NW arrays near Curie temperature. The tetragonal phase in $PbTiO_3$ transfers to cubic phase around Curie temperature. This phase transition is associated with a change in specific heat constant of the material which can be measured using differential scanning calorimeter (DSC) [5,25]. The heat flow measurement (see Supplementary information Fig. S2) using DSC showed that the as-synthesized $PbTiO_3$ NWs exhibit tetragonal to cubic phase transition at 474 °C which is less than the known value for $PbTiO_3$ (T_c=490 °C) [22,23]. This reduction in Curie temperature is expected to be due to the presence of small PbO residue [26].

3. Results and discussion

3.1. Energy harvester fabrication

Upon successfully synthesizing the $PbTiO_3$ NW array, a resonating beam-based energy harvesting device is fabricated, and its application in harvesting vibrational energy at extreme temperatures above 300 °C is demonstrated through the characterization of open circuit voltage and power measurements. The resonating beam-based energy harvester allows for a lower resonance frequency of the device, which is suited for ambient vibration energy harvesting [18]. To fabricate the energy harvester device, a small piece of $PbTiO_3$ NW arrays was removed from the oxidized titanium foil substrate by washing with dilute HCl acid and soaking in ethanol [14]. The oxidation layer under the NW array provided a support structure that allows the NW array to stay intact during removal from the foil substrate. It is then transferred and bonded to a rectangular shim stock stainless steel beam (5 by 25 mm) using conductive silver paint (SPI Supplies). To increase the adhesion to the beam and conductivity of the silver paint, it was cured at 80 °C in a vacuum oven for 2 h. The beam served as both the bottom electrode contacting the NWs and as a spring to transfer mechanical energy from the base acceleration to the NWs by an impact mechanism [18]. The beam can be effectively considered a frequency conversion device to allow tuning of the beams frequency to match that of the vibration in the harvester's environment, since an impact will excite the nanowires independent of their natural frequency. Furthermore, a thin layer of gold was sputtered (PELCO SC-7 Auto Sputter Coater) on a square piece of borosilicate glass (5 by 5 mm) and attached to the base of the device to serve as the top electrode for the NWs. Therefore, the NW arrays were sandwiched between the stainless steel beam and the gold sputtered glass as electrodes 1 and 2, respectively. As shown in Fig. 2a, both electrodes were assembled on a piece of borosilicate glass for handling and installing of the device on a permanent magnet shaker. Lastly, the output voltage wires were attached to the electrodes using silver paint and silver epoxy.

After device fabrication, the NW arrays were poled by applying an