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"Template Synthesis of Bismuth Telluride Nanowires"

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11. Abstract: We report the fabrication of thermoelectric bismuth telluride nanowires using the template synthesis method. A simple electrodeposition procedure was used to produce the nanowires within the pores of an alumina filtration membrane. The resulting bismuth telluride/alumina composite membranes constitute an array of thermoelectric nanowires surrounded by a thermally and electrically insulating matrix. The individual bismuth telluride nanowires can be isolated by removal of the template membrane. These nanowires were characterized and found to be composed of stoichiometric bismuth telluride.

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Template Synthesis of Bismuth Telluride Nanowires

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Abstract

We report the fabrication of thermoelectric bismuth telluride nanowires using the template synthesis method. A simple electrodeposition procedure was used to produce the nanowires within the pores of an alumina filtration membrane. The resulting bismuth telluride/alumina composite membranes constitute an array of thermoelectric nanowires surrounded by a thermally and electrically insulating matrix. The individual bismuth telluride nanowires can be isolated by removal of the template membrane. These nanowires were characterized and found to be composed of stoichiometric bismuth telluride.

Introduction

The template method has proven to be a versatile approach for preparing nanomaterials.[1-3] Nanotubes and nanowires composed of metals, semiconductors, insulators, polymers, conducting polymers, and various composites of these materials have been prepared.[1-4] It would also be of interest to prepare nanowires composed of metal alloys or solid solutions. These materials often have useful mechanical, thermal, and electrical properties. For example, some alloys exhibit the ability to convert heat to electrical energy (or vice versa) and are termed thermoelectric materials. Bismuth, tellurium, and/or selenium alloys are commonly used in commercially-available Peltier cooling devices, and among these, bismuth telluride (Bi_2Te_3) has proved very useful for devices operating at room temperature.[5,6]

Optimal characteristics of thermoelectric materials include a high electrical conductivity and a low thermal conductivity. In bulk materials each of these properties is fixed and thermal conduction, which is often high, acts to reduce the thermoelectric efficiency of the material. Nanostructured materials and composites offer the potential advantage that the overall material properties may be tailored according to size and/or composite structures. Very recently it was suggested that such a new generation of "complex" materials may exhibit enhanced thermoelectric properties.[7]

The electrodeposition of bismuth telluride was recently reported to yield the near stoichiometric crystalline material at room temperature.[8] We have used this method, in conjuction with template synthesis techniques to prepare nanowires of bismuth telluride

within the pores of an alumina template membrane. This report focuses on the fabrication process and on initial characterization of these new thermoelectric nanostructures.

Experimental

Materials

$Bi(NO_3)_3 \cdot 5H_2O$ (99.997%) and tellurium powder (99.997%) were purchased from Aldrich and used as received. Nitric acid (Mallinckrodt AR grade) and sodium hydroxide (Sigma reagent grade) were used as received. House distilled water was further purified through a Milli-Q (Millipore) filtration system. Anopore alumina membranes (200 nm pore diameter, Anodisc 25) were purchased from Whatman and used as received.

Deposition Solution

The deposition solution was prepared according to the published procedure.[8] Tellurium powder (150 mg) was dissolved in 1.0 M nitric acid (100 mL) at 80° C under vigorous stirring in a fume hood. Initially, all the tellurium dissolved, but after cooling and aging at room temperature, tellurium dioxide (TeO_2) precipitated from solution in the form of a white solid.[8] The solution concentration of tellurium in the form of $HTeO_2^+$ was calculated to be 25 mM based on the amount of TeO_2 which was recovered. $Bi(NO_3)_3 \cdot 5H_2O$ was then added to a final concentration of 33 mM. This $Bi^{3+}/HTeO_2^+$ solution was then stored under ambient laboratory conditions until use.

Electrochemistry

Electrochemistry was carried out using an EG&G PAR model 273 potentiostat/galvanostat. Cyclic voltammetry was carried out on the deposition solution using a Teflon®-capped three-electrode cell under nitrogen purge. The working electrode was a polished gold disk (7.1×10^{-3} cm^2) and the counter electrode was a platinum flag (1.2

cm^2). The reference electrode was a Ag/AgCl (3.0 M NaCl) electrode (0.175 V vs. NHE), and all potentials are reported with reference to this.

Electrodeposition of Nanostructures

Thermal evaporation was used to coat a ca. 100 nm-thick gold film onto one surface of the alumina membrane. This gold film was used as the working electrode in the deposition cell shown in Figure 1. After assembly of the cell, the $Bi^{3+}/HTeO_2^+$ solution was added and purged with nitrogen. Bismuth telluride was then deposited galvanostatically within the pores of the membrane using a current density of 3.5 mA/cm^2.[8] Charge was passed until the upper surface of the membrane became dark gray. Typically this occurred after the passage of 8.0 C/cm^2.

Characterization

The bismuth telluride nanowires obtained were imaged via both scanning and transmission electron microscopy (SEM and TEM, respectively). In order to obtain such images, the nanowires must be freed from the template membrane. This was accomplished as follows: The gold surface layers and any electrodeposited material were removed by careful polishing using 600 grit silicon carbide polishing paper (Buehler). The alumina membrane containing the nanowires was then removed by dissolution in 5.0 M sodium hydroxide for 2 hours. For SEM sample preparation, the dissolution step was carried out after cementing an intact membrane to a sample stub using epoxy (Torr Seal, Varian). TEM and x-ray diffraction samples were prepared by filtering a suspension of isolated nanowires onto a carbon-coated copper TEM grid or an alumina membrane respectively. SEM and energy dispersive spectroscopy (EDS) were carried out on a Phillips model 505 SEM equipped with a Kevex Super 8000 analyzer. TEM was performed using a JEOL

JEM 2000EX II TEM. Accelerating voltages were 20.0 kV for SEM (spot size 50 nm) and 100 kV (camera length 80 cm) for TEM. X-ray powder diffraction spectra were obtained on a Phillips Cu K-α x-ray source diffractometer.

Results

Cyclic Voltammetry

The cyclic voltammogram (CV) of the $Bi^{3+}/HTeO_2^+$ solution is shown in Figure 2. Our results are in good agreement with the findings of Lecuire et al. when Bi^{3+} is at a higher concentration than $HTeO_2^+$.[8] Upon reduction, there is a sharp cathodic wave centered at 21 mV, after which the electrode appears dark gray owing to the deposition of bismuth telluride. On the anodic scan, first a broad wave is observed at 295 mV and then a sharp stripping peak is seen at 518 mV which is attributed to the anodic stripping of Bi_2Te_3. The first broad anodic wave was also observed by Lecuire et al. and was found to disappear if the cathodic scan was limited to potential values below the peak reduction potential. This wave was also not observed in solutions where Bi^{3+} concentrations were lower than $HTeO_2^+$.[8] However, we used a higher Bi^{3+} concentration because Lecuire et al. found that this resulted in material closest to stoichiometric Bi_2Te_3 even at low current densities.[8] Furthermore, we have found no evidence to suggest that any material other than bismuth telluride is being deposited even when this second anodic signal is observed.

Nanostructures

We found that electrodeposition carried out in an anopore alumina membrane (see Figure 1) resulted in the formation of nanowire arrays of bismuth telluride. The SEM micrographs in Figure 3 clearly show these nanowires. Figure 3a shows isolated clusters of nanowires and 3b shows the edge of a structure resulting from the incomplete removal

of a surface layer. Clusters are obtained because after removal of the template membrane the individual nanowires aggregate. This is observed for nearly all of the nanostructures we have studied.[9] In both cases the template membrane was completely removed and EDS spectra revealed peaks corresponding only to the presence of bismuth and tellurium.

TEM was also used to image the nanowires (Figure 4), and wire diameters were measured from these micrographs. The average wire diameter from five samples was 280±30 nm. In most cases, the length of the wires corresponded to the membrane thickness (ca. 60 μm) suggesting that the wires are mechanically stable under the sample preparation conditions.

Further characterization by x-ray powder diffraction (Figure 5) confirmed that our nanostructures were composed of stoichiometric bismuth telluride. The sharp diffraction peaks indicate the material to be highly crystalline, and comparison with the standard diffraction spectrum of Bi_2Te_3 (PDF entry No. 08-0027) resulted in a nearly exact match.

Conclusions

Using the technique of template synthesis we have shown that nanowires of bismuth telluride can be made using a simple electrodeposition process. Clearly the thermoelectric properties of these nanowires must now be investigated. Ultimately this line of research may lead to the production of smaller, more efficient Peltier devices and thermoelectric power generators.

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Figure Captions.

Figure 1. Electrochemical cell for the galvanostatic deposition of bismuth telluride.

Figure 2. Cyclic voltammetry of the $Bi^{3+}/HTeO_2^+$ deposition solution.

Figure 3. Scanning electron micrographs of isolated bismuth telluride nanowires (a) and the edge of a sample with an intact surface layer (b).

Figure 4. Transmission electron micrograph of isolated bismuth telluride nanowires.

Figure 5. X-ray powder diffraction of isolated bismuth telluride nanowires with reference Bi_2Te_3 spectrum (below).

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Figure 1

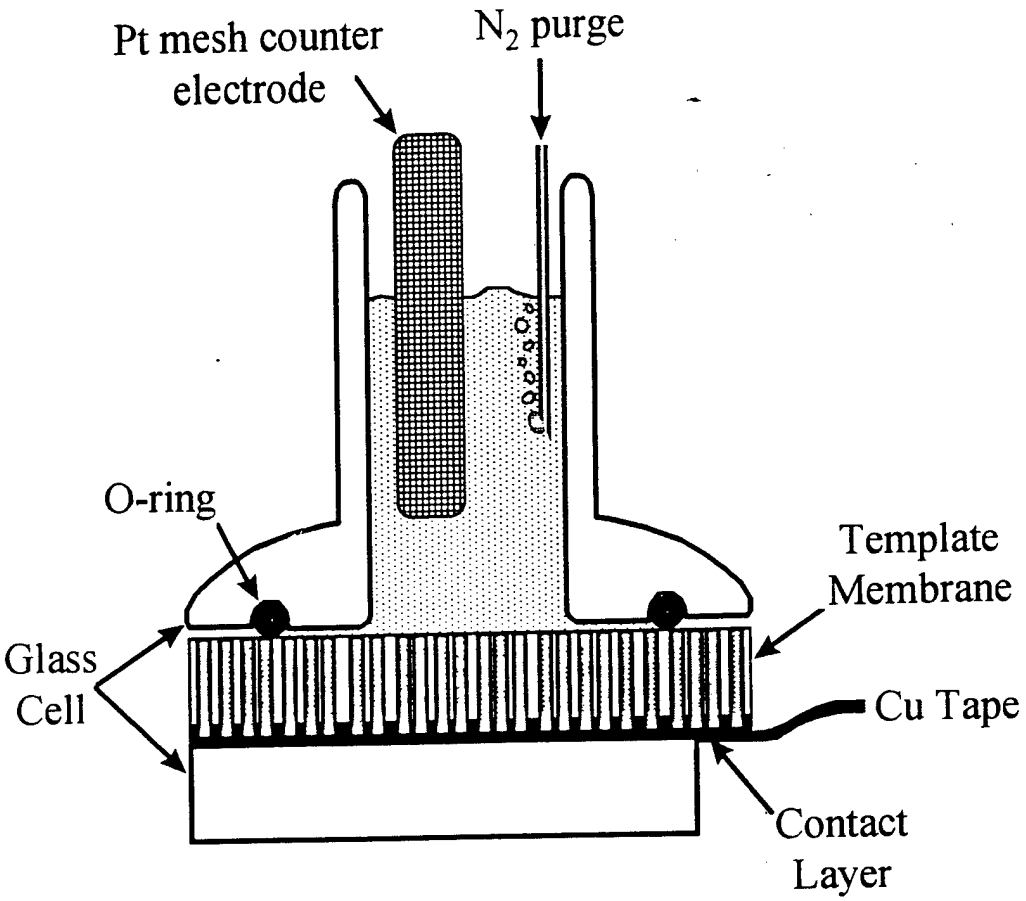

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Figure 2.

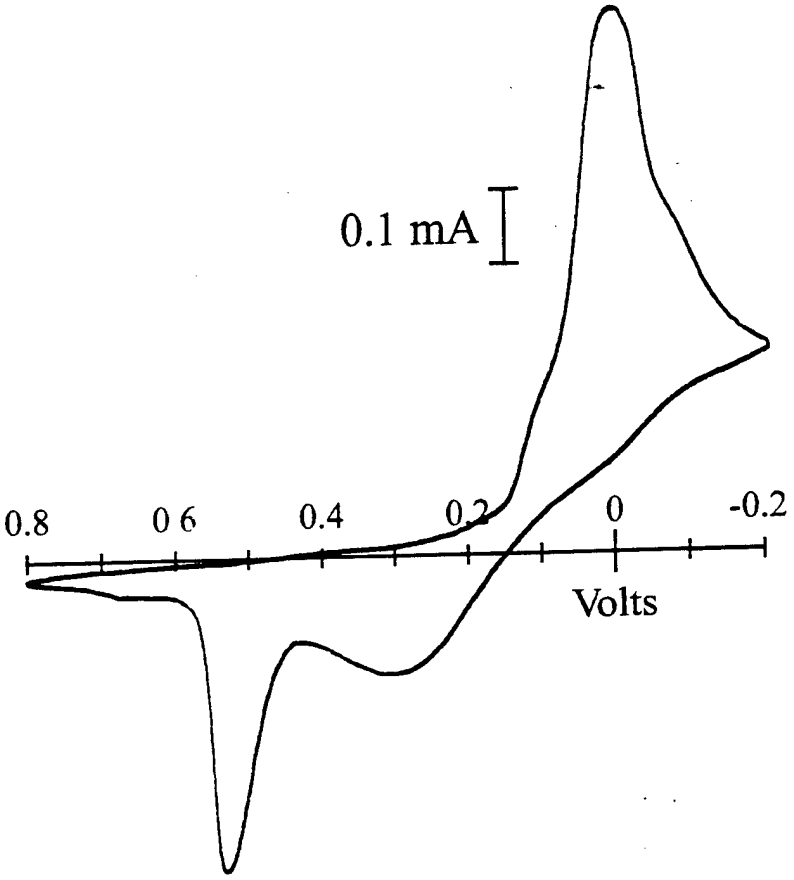

Figure 3.

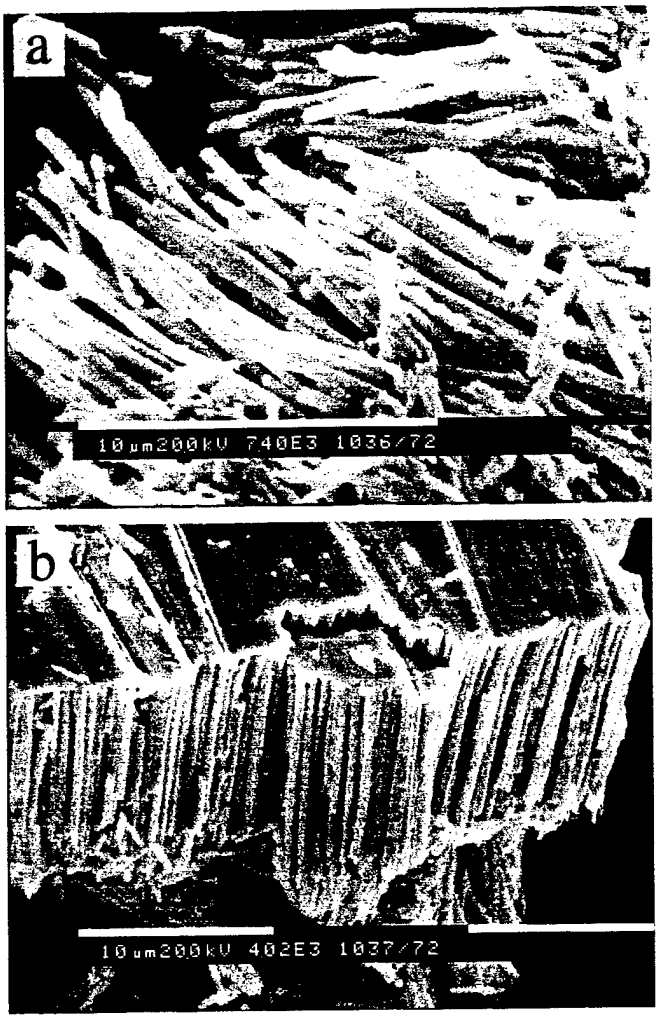

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Figure 4.

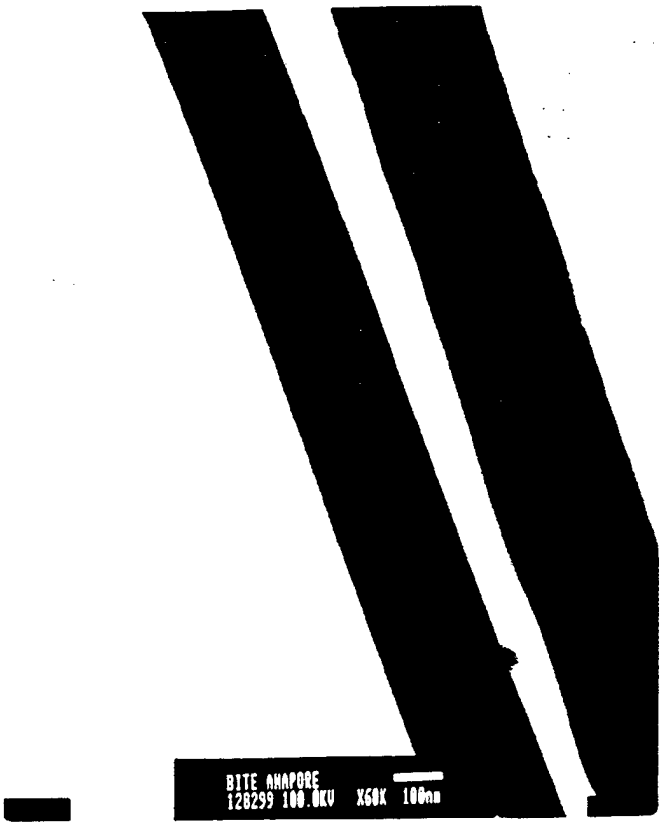

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Figure 5.