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Individual thermoelectric properties of electrodeposited bismuth telluride nanowires in polycarbonate membranes

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ABSTRACT

In this study, we examined individual bismuth telluride nanowires (NWs) electrodeposited in polycarbonate membranes (PCM) used as sacrificial templates. It has been demonstrated that the composition of Bi_2Te_3 is controlled by the electrodeposition conditions, e.g. the applied potential. High-resolution transmission electron microscopy (HRTEM) shows that the average grain size of NWs increases with increasing Te content. Our results also reveal that the electrodeposited bismuth telluride NWs are n-type, and their electrical conductivity increases with increasing Te content. These NWs also demonstrated a maximum power factor of 195.8 mW/m·K^2 for the Te-rich NW (d = 162 nm) at 300 K.

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1. INTRODUCTION

Thermoelectricity is the phenomenon which results from the conversion of heat into electrical energy (Seebeck effect) or vice versa (Peltier effect). These materials offer a number of advantages, including high durability, no emission of toxic gases, and high reliability. They are suitable for a wide range of applications at various temperature regimes, such as power generation, refrigeration, sensing, and solid-state cooling [1]. On the other hand, the widespread use of thermoelectric (TE) materials has been restricted by their relatively low energy-conversion efficiency. Many efforts to improve their efficiency have focused entirely on improving the thermoelectric figure of merit, ZT, defined as $ZT = S^2\sigma T/(\kappa_l + \kappa_e)$, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, and κ_l and κ_e are the lattice and the electronic thermal conductivities respectively.

Among TE materials, bismuth telluride (Bi_2Te_3) and related alloys have proven to be among the most promising thermoelectric materials at room temperature ($ZT \approx 1.0$). These alloys are particularly attractive because they can be fabricated as n- or p-type TE materials by slightly varying their composition [2,3].

Generating nanostructures with low dimensionality is necessary for raising the electronic density of states closer to the Fermi level, increasing surface phonon scattering, and modifying phonon dispersion so as to improve values of ZT and make Bi_2Te_3 more efficient as regards TE properties [4–6]. Previously, significant improvements of ZT values were reported for nanostructured bulk alloys [7], nanoinclusions [8], nanocomposites [9], and thin-film superlattices [10,11]. Moreover, many different growth techniques have been explored to produce Bi_2Te_3 materials, including vapor-phase techniques [12–13], on-film formation of nanowires (OFF–ON) [14–16], and electrochemical deposition [17–21].

For Bi_2Te_3 nanowires (NWs) grown by electrodeposition, a high density of NWs along with a small diameter is required for producing miniaturized TE devices. High-density Bi_2Te_3 NWs are predominantly synthesized by a number of template-assisted methods using track-etched membranes [20–22], diblock copolymers [23,24], or anodized aluminum oxide (AAO) templates [25,26]. Of these, AAO templates have found particularly widespread usage owing to the simplicity and flexibility of their fabrication methods. AAO templates have thus been used in electrodeposition not only to obtain dense arrays of parallel NWs, but also to yield high deposition rates. However, the high thermal conductivity of alumina matrices has been known to induce thermal leakages in the alumina template [27,28]. A key challenge is to synthesize the NWs in a template-assisted membrane with lower thermal conductivities. Such a polymer membrane provides suitable electrical, thermal, chemical, and mechanical properties in the electrodeposition method.

In this paper, we report on thermoelectric properties of potentiostatically deposited Bi_2Te_3 NWs in polymer membranes (polycarbonate). The pore diameter can be controlled by chemical etching whereas the Bi:Te ratio of the Bi_2Te_3 NW can be tuned during the electrodeposition by applying different potentials. The thermoelectric properties of non-stoichiometric n-type Bi_2Te_3 (Bi_xTe_{1-x}) NWs showed that the NW electrical conductivity increases when Te is in excess in the deposit, and leads to an increase of the power factor at elevated temperatures.

2. EXPERIMENTAL

2.1. Template preparation

Polycarbonate membranes (PCMs) were used as templates to synthesize Bi_2Te_3 NWs. Polycarbonate foils (PCF, $\sim$30 μm) were first irradiated using accelerated gold ions (energy $\sim$2 GeV, fluence = 10^8 ions/cm^2) at the heavy ion accelerator UNILAC at the GSI Helmholtz Centre (Darmstadt, Germany). The resulting ion tracks were then sensitized by a 1 h UV exposure before being selectively dissolved and enlarged to make pores in a 6 N caustic soda solution (NaOH, Carlo Erba Reagents, 97%) at 50 °C. The resultant membranes contained pores of approximately 30, 60, and 120 nm in diameter, which were produced at a rate of 30 nm/min [29]. Following the etching process, a layer of platinum ($\sim$160 nm thick) was deposited by sputter deposition (Polaron SC7620) on one side of the PCFs to serve as a working electrode.

2.2. Electrochemical deposition

First Tellurium (Prolabo, 99.7%) was oxidized to $HTeO_2^+$ in 7 M HNO_3 (Carlo Erba Reagents, 65%) before adding $Bi(NO_3)_3$, $10H_2O$ (Fluka, >98%), deionized water (15MΩ) and then dimethyl sulfoxide (DMSO, Fisher Scientific, >99.9%). The quantities were adjusted to obtain the following concentrations in the electrolyte: 10 mM $HTeO_2^+$, 15 mM Bi^{3+}, 1 M HNO_3 and 50 v/v % DMSO. Before each experiment, dissolved oxygen was removed from the solutions by degassing with an argon flux for 20 min. Bi_2Te_3 was grown using a potentiostat (Autolab PGSTAT302) between −75 to −100 mV at room temperature (RT) with a three-electrode (Pt on PCM, Pt disc, and sat. Ag/AgCl reference) configuration. A more detailed description of this setup can be found elsewhere [20].

2.3. Device fabrication

Bi_2Te_3 NWs were first released from the template by dissolving the PCM in Dimethylformamid (DMF). The NWS, thereby suspended in DMF, were then collected by drop casting onto a thermally oxidized Si (500 nm SiO_2) substrate presenting alignment marks. All electrodes and micro-heaters were patterned using electron-beam (e-beam) lithography (VEGA 3 LM, Tescan Korea). The contact regions on the NWs were then etched by Ar plasma to remove their native oxide layers. For electrodes, chromium/gold (5-nm/250-nm thickness) films were deposited *in situ* via ultra-high vacuum (UHV) direct current (DC) magnetron sputtering at a base pressure of 4×10^{-8} Torr to prevent oxidation. A lift-off process was then used to remove the resist and release the nanowire device.

2.4. Characterization

After removal of the PCM templates, the microstructures and nanostructures of the Bi_2Te_3 NWs were characterized by transmission electron microscopy (TEM, Philips CM200) with energy-dispersive X-rays (EDX, X Max Oxford). Both the NW arrays and the fabricated devices were observed using scanning electron microscopy (SEM, ZEOL 7001 F). Thermoelectric property measurements were performed in a helium cryostat system in the temperature range 100–300 K. Measurements of Seebeck coefficients were conducted via two thermometers, with $S = \Delta V/\Delta T$, where ΔT is the temperature gradient across the NW, and ΔV is the Seebeck voltage generated by ΔT. ΔT was obtained by measuring the resistance of each thermometer with a lock-in amplifier (SR850, USA) whereas the voltage difference between the two thermometers was measured by a nanovoltmeter. The conductivity of the NWs was obtained using 4-probe measurement technique to remove contact resistance.

3. RESULTS AND DISCUSSION

Fig. 1 shows a typical current transient curve recorded during the potentiostatic deposition of Bi_2Te_3 NWs along with schematic views of the different steps during the PCM filling. After an initial nucleation (regime 1), the deposition current stabilizes to a steady-state value (regime 2). Nucleation occurs during the first stage, where current is controlled by charge transfer. The second stage corresponds to the growth process governed by diffusion mass transport [20]. Once the pores are filled (regime 3), the cathodic current increases sharply with the increase of the active surface area due to the NW outgrowths on the template surface. NWs were synthesized at both −75 mV and −100 mV in porous templates of various pore sizes based on our previous work [20].

Fig. 2 presents TEM images of Bi_2Te_3 NWs deposited at −75 mV and −100 mV in PCM templates. The diameter for both types of non-stoichiometric Bi_2Te_3 (Bi_xTe_{1-x}) NWs was $\sim$60 nm. An enrichment of bismuth was observed with increasing cathodic potential. These observations are in agreement with previous results on electroplated films and can be explained by a larger overpotential which is favorable to the co-deposition of Bi^0 [20]. Selected area electron diffraction (SAED) patterns (insets in Fig. 2) are consistent with a polycrystalline state, which exhibit a preferential growth perpendicular to the (015) plane. These patterns display individual spots with small circular-arc shapes, which correspond to a weak disorientation around the zone axis of the analyzed grains.

To further observe the microstructure across the NWs, high-resolution TEM (HRTEM) was conducted, as shown in Fig. 3. The micrographs of both $Bi_{0.392}Te_{0.608}$ and $Bi_{0.442}Te_{0.558}$ NWs show a clear difference in grain sizes (average size of $\sim$9.94 nm and

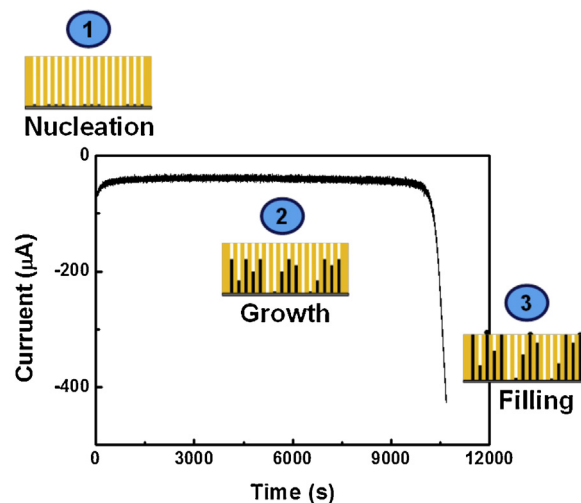**Fig. 1.** A schematic of typical chronoamperometric response for Bi_xTe_{1-x} electrodeposition at −100 mV/sat. Ag/AgCl inside ion track etched polycarbonate membrane.