Enhanced Seebeck Coefficients of Thermoelectric Bi$_2$Te$_3$ Nanowires as a Result of an Optimized Annealing Process

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Supporting Information

ABSTRACT: Although an annealing approach for bulk or thick Bi–Te material had been done for the enhancement of thermoelectric efficiency, this is the first time to report an annealing process for a Bi–Te nanostructure with a high aspect ratio. As is well-known, the Seebeck coefficient, one of the thermoelectric efficiency factors, is strongly influenced by the chemical composition of the material. However, tellurium element tends to be easily evaporated in the high-temperature range (more than 400 °C) due to its low melting point and high evaporation pressure. Furthermore, it is more serious in such a nanostructure with a high aspect ratio. In this article, we suggested the way to prevent the evaporation of tellurium element in the high annealing temperature range (300–623 °C) and investigated why the Seebeck coefficients for annealed Bi–Te nanowires were enhanced. Seebeck coefficients for Bi–Te nanowires were improved 3 times higher than those for the as-prepared ones at the optimized annealing process due to increased crystal defect concentrations, especially for edge dislocations. Consequently, this annealing process can be applied for nanostructured TE devices for the enhancement of thermopower (S).

INTRODUCTION

A lot of efforts have been pursued in order to enhance the dimensionless thermoelectric efficiency (figure of merit, ZT) by various aspects of approaches. Recent research trends can be summarized as follows: (i) looking for advanced new families of thermoelectric materials and (ii) linking to nanoscale phenomena embedded in bulk samples as well as nanoscale samples themselves.1,2 The former approach is mainly focused on the significant reduction of thermal conductivity. The Kanatzidis group reported n-type thermoelectric AgPb$_m$Sb$_{3m}$Te$_{2m}$ (LAST, ZT ∼ 2 at 800 K)3 and p-type thermoelectric Ag(Pb$_{1−y}$Sn$_y$)$_2$SbTe$_{2m}$ (LASTT, ZT ∼ 1.4 at 630 K)4 due to their reduction of thermal conductivity. The latter one is first focused on the reduction of lattice thermal conductivity owing to the introduction of plenty of nanostructured interfaces, leading to increased phonon boundary scatterings5 and, second, focused on the enhancement of the power factor owing to the quantum confinement effect and the modification of electronic band structures, leading to improved thermopower (Seebeck coefficient) without a significant reduction of electrical conductivity.6 Thermopower (S) is generally dependent on the electronic band structure of the material near the Fermi energy level, which is a function of the concentration of charge carriers and imperfections (or defect concentrations), as well as the chemical composition of materials.7 Bulk Bi–Sb–Te alloy with embedded nanostructures exhibits ZT ∼ 1.4 at 373 K,6 and the Venkatasubramanian group9 reported superlattice structured Bi$_2$Te$_3$/Sb$_2$Te$_3$ film with ZT ∼ 2.4 due to a reduction of lattice thermal conductivity. In the perspective view of the modification of

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electronic band structures for low-dimensional thermoelectric materials, such as nanowires and nanotubes, the annealing process would be a very efficient method for tuning the crystallinity of nanostructures.

Herein, since the number of reports have been very few so far about the annealing effect on low-dimensional thermoelectric materials (almost no results reported about the annealing effect on thermoelectric nanostructures) as well as the demonstration of Seebeck coefficient results, we report on the investigation of crystal defects of Bi–Te nanowires from the annealing process at optimized annealing conditions, leading to the corresponding Seebeck coefficient enhancement as a function of annealing temperature.

**EXPERIMENTAL SECTION**

**Annealing Process for Bi–Te Nanowires.** Bi–Te nanowires were fabricated by pulsed electrodeposition in an anodic aluminum oxide (AAO) membrane with a diameter of 50 nm. Detailed procedures were described in our previous works. It is well known that Te compound is easily evaporated at certain annealing temperatures in bulk and thin film structures due to its high vapor pressure. Therefore, nanowire samples were put in a completely sealed ceramic container by alumina paste (alumina paste used is resistant up to 500 °C) in order to prevent the evaporation of Te element from the nanowires. Additionally, pure Te powder was put together in this container. All of the preparation process was performed in a glovebox. As-prepared nanowires in an alumina matrix were annealed from 150 to 400 °C for 4 h in quartz chamber with a nitrogen (N₂) atmosphere. The annealing temperature was increased at every 50 °C.

**Investigation on Crystalline Structures of Nanowires.** The crystalline structure of nanowires was investigated by X-ray diffraction (XRD), high-resolution transmission electron microscopy (HR-TEM, Phillips, Technai, F20, Gwangju center KBSI at 200 kV), and selected area electron diffraction (SAED) patterns. The composition of the nanowires was investigated by energy-dispersive X-ray spectroscopy (EDX) attached to a TEM system.

**Seebeck Coefficient Measurement for Bi–Te Nanowires in Alumina Matrix.** As-prepared and annealed ones were placed on a sample holder, which contained wood metal. Wood metal is made up of bismuth, lead, tin, and cadmium with a melting point of 70 °C. The probe tip with a diameter of several tens of micrometers directly contacted on the nanowire samples within the alumina matrix while a stable temperature gradient between the probe tip and the samples was applied for 5 K. Spatial resolution of the Seebeck coefficient was characterized by a potential Seebeck microprobe (PSM) (Panco, Germany) with at least more than 30 points. The average Seebeck coefficient was calculated based on the deduced values from more than 30 points.

**RESULTS AND DISCUSSION**

Figure 1 shows the elemental analysis of the nanowire by the line scan of EDX attached to the TEM system as a function of annealing temperature. In particular, independent of the annealing temperature, the atomic percentage of Bi and Te for individual nanowires exhibited stably 40% and 60%.

![Figure 1](image-url)
respectively, as shown in Figure 1a,b. Additionally, EDX elemental mapping images for the nanowires annealed at 250 and 350 °C revealed the uniform distribution of Bi and Te throughout the nanowire, as shown in Figure 1c. On the basis of the above results, Bi–Te nanowires exhibit a thermodynamically stable Bi$_2$Te$_3$ phase, indicating that Te element is not evaporated during the annealing process. However, the chemical composition of the nanowires annealed above 400 °C led to the imbalance of the stoichiometric composition (Bi$_4$Te$_6$). More details are described in the Supporting Information (Figure S1 and Table S1).

The Seebeck coefficient for Bi–Te nanowires was measured by PSM, and the results are shown in Figure 2. Seebeck coefficients show a negative value, indicating an n-type thermoelectric material. It is obviously demonstrated that the Seebeck coefficient increases linearly and is significantly increased at the annealing temperature of 350 °C. The Seebeck coefficient (average: $-119.68$ (μV/K)) for the nanowires annealed at 350 °C became 3 times higher than that (average: $-38.99$ (μV/K))) for as-prepared nanowires. It is expected that the influence of the Seebeck coefficient by annealing is positively attributed to the combination of enhanced crystal quality and increased defect concentrations. In addition, Yamashita et al. reported that annealing had a favorable effect on the improvement in ZT of n-type bismuth telluride bulk compounds, but an adverse effect on the p-type ones. On the other hand, the Seebeck coefficient measured for the nanowires annealed at 400 °C was decreased to $-69.25$ (μV/K). However, the data measured are not trustable, which will be explained in the next figure.

From the abundance distribution of the Seebeck coefficient measured, as shown in Figure 3, it was revealed that the Seebeck coefficient values for as-prepared nanowires and the nanowires annealed up to 350 °C mostly belonged to the very narrow regime, which exhibited a high homogeneity, but the Seebeck coefficient for the nanowires annealed at 400 °C belonged to the very broad regime, which showed much inhomogeneity. It is in good agreement with the previous report that the homogeneity was reduced despite the enhancement of the Seebeck coefficient with the increase of annealing temperature. Therefore, the Seebeck coefficient value for the sample annealed at 400 °C is not reasonable due to inhomogeneous variations.

Figure 4 shows high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) patterns of as-prepared nanowires and the nanowires annealed at different temperatures. The crystal quality of as-prepared individual nanowires and the individual nanowires annealed up to 350 °C shows a very good single-crystalline structure without any significant change. It will be confirmed by XRD data for the nanowires within the alumina matrix annealed at different temperatures, as shown in the Supporting Information (Figure S2). Therefore, the influence on the enhancement of the Seebeck coefficient caused by improved crystal quality is insufficient. On the other hand, there are significant differences in the crystal defects, as shown in the HRTEM of Figure 4. As usual in the HRTEM (straight lattice planes) of the as-prepared nanowire, a lot of dislocations (unusual lattice arrangements) were observed in the HRTEM of the nanowire annealed at 350 °C. In particular, considering the magnified HRTEM of the nanowire annealed at 350 °C, it would be concluded that edge dislocations were formed during the annealing process due to stress and strains associated with this temperature. Edge dislocations are a kind of crystallographic defect where an extra half-plane of atoms is introduced midway through the crystal, distorting nearby planes of atoms, like the magnified HRTEM. On the basis of the above results, it is good evidence that the enhancement of the Seebeck
The coefficient is influenced by the increased defect concentrations (edge dislocations with the increase of annealing temperature). As the annealing temperature approached 400 °C, partial diffusion of Te compound was observed in the nanowire. Figure 5a shows HRTEM of the individual nanowire annealed at 400 °C. Dislocations were not observed any more, indicating the straight lattice arrangement like the nanowire annealed lower than 350 °C. However, the unusual feature, as indicated by the arrow, was interestingly observed in another area of the same nanowire, as shown in Figure 5c. To the best of our knowledge, based on that the melting point of Te element is 440 °C, the Te compound in the nanowire itself or added in the container was possibly diffused in the nanowire at this annealing temperature, leading to the coexistence of the Bi₂Te₃ phase and a relatively Te-rich Bi–Te phase due to incongruent melting of the Te element. More details are described in the binary Bi–Te phase diagram (Supporting Information, Figure S3). According to the SAED, as shown in Figure 5b, it is revealed that the nanowire basically possessed a single-crystalline structure with the Bi₂Te₃ phase as a major one. However, several weak (bright) spots, which are indicated by an arrow, were additionally observed. It indicated that another Bi–Te phase as a minor one coexisted with the Bi₂Te₃ phase. Unfortunately, it is not exactly understood what the Te-rich Bi–Te phase is. Furthermore, comparing with the FFT of Figure 5c-1, which is investigated by the area except for the indication of an arrow (Figure 5c), several faint spots were also observed, as shown in the FFT of Figure 5c-2, which is investigated by the indication of an arrow (Figure 5c). It is also supporting that Bi₂Te₃ and Te-rich Bi–Te phases coexisted in the nanowire annealed at 400 °C. Consequently, the coexistence of two kinds of phases from the diffusion of Te element, leading to the unbalanced chemical composition of Bi–Te nanowires, is potentially influencing on the reduction of the Seebeck coefficient. Additionally, up to an annealing temperature of 350 °C, the nanowires should be chemically stable due to the reduction of the Gibbs free energy provided from the thermal energy during the annealing process. However, when they are annealed at more than 350 °C, the nanowires are chemically unstable due to more Te evaporation factor than chemical stability. It could be concluded that 350 °C is the most appropriate annealing temperature in the perspective view of enhancement of thermopower (S).

**CONCLUSIONS**

Thermoelectric bismuth telluride nanowires fabricated by pulsed electrodeposition in an anodic aluminum oxide membrane were annealed at different temperatures in order to enhance the Seebeck coefficient. To prevent the evaporation of Te element due to high vapor pressure, the container for annealing was completely sealed with the addition of pure Te.
powder. Consequently, the annealing process for nanostructures at optimized conditions (350 °C) resulted in the enhancement of the Seebeck coefficient for Bi–Te nanowires due to increased crystal defect (edge dislocations) concentrations, maintaining chemical stability, and the single-crystalline structure. However, with further increasing the annealing temperature, the homogeneity of the Seebeck coefficient distribution became worse and the Seebeck coefficient also was decreased due to the diffusion of Te element with the high aspect ratio of nanowire structures, leading to an unbalanced chemical composition of nanowires and the coexistence of Bi₂Te₃ (major one) and a relatively Te-rich Bi–Te phase (minor one).

It will be expected that the annealing process at optimized conditions can be favorably applied to the future thermoelectric nanostructured devices with high thermoelectric efficiency.

■ ASSOCIATED CONTENT

* Supporting Information

SEM and EDX for overgrown film, XRD, and phase diagram for nanowires are shown for a better understanding of the low-dimensional Bi₂Te₃ structure and phase change as a function of annealing temperature. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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