Preparation and structure dependent thermoelectric properties of nanostructured bulk bismuth telluride with graphene

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A B S T R A C T

Nanostructured graphene/Bi_2Te_3 composites were fabricated with either Bi_2Te_3 powder or nanowires (NWs) and various graphene contents, and their thermoelectric properties were investigated. The Bi_2Te_3 powder was produced from Bi_2Te_3 beads with a conventional ball milling process, whereas the Bi_2Te_3 NWs were fabricated with a solution-phase synthetic route. The composites with a graphene content of 0.5 wt.% exhibited enhanced power factors, presumably because of an improvement in the Seebeck coefficients of the samples, which overwhelmed the reduction in electrical conductivity. In addition, the introduction of graphene reduced the lattice thermal conductivity of the composites because it caused the formation of many boundaries in the Bi_2Te_3 matrix. The maximum thermoelectric figure of merit (ZT) of 0.4 was achieved at 300 K with the 1 wt.%-graphene/Bi_2Te_3-NW composite; it was larger than that of the pristine Bi_2Te_3 NWs and graphene/Bi_2Te_3-powder composites.

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1. Introduction

Thermoelectric power generation has attracted increasing attention in recent years because of its potential to provide clean and efficient energy via the direct conversion of thermal energy to electrical energy and vice versa. Previous studies have focused mainly on bulk inorganic thermoelectric materials, which have been utilized commercially for the past 50 years. Of the various thermoelectric materials, Bi_2Te_3 is the most efficient near room-temperature n-type thermoelectric material because of its high Seebeck coefficient and low thermal conductivity [1,2].

The thermoelectric performance of a material is evaluated with the figure of merit, $ZT = (S^2 \cdot \sigma \cdot T)/\kappa$, where S is the Seebeck coefficient, σ is electrical conductivity, κ is thermal conductivity, and T is absolute temperature. Theoretically, to obtain a high ZT value, thermoelectric material must have high electrical conductivity, a high Seebeck coefficient, and low thermal conductivity. Hence, a number of studies about thermoelectric materials have focused predominantly on the requirements of either a greatly reduced thermal conductivity or dramatically increased power factor ($S^2 \cdot \sigma$).

Low thermal conductivity can be achieved by nanostructuring a thermoelectric material, thereby increasing the lattice scattering of phonons. The introduction of nanostructures to bulk thermoelectric materials generates many boundaries that act more effectively than electrons in scattering phonons [3–7]. In principle, two approaches can be applied to fabricate nanostructured materials: bottom-up or top-down techniques. The bottom-up method uses atoms to create building blocks that are subsequently assembled into nanoscale clusters. In contrast, the top-down strategy starts with a bulk solid, and nanostructures are produced via structural decomposition. Yang et al. [8] obtained a significantly reduced thermal conductivity by fabricating Bi_2Te_3 nanoflakes that were prepared using a bottom-up approach. Xu et al. [9] prepared nanostructured BiSbTe alloy samples via the hot deformation of ingots (a top-down approach), which exhibited substantially decreased thermal conductivity. However, in addition to low thermal conductivity, material must have a large power factor to achieve a high thermoelectric performance.

Thus, many researchers have investigated methods to enhance the thermoelectric power factor of inorganic materials by introducing carbon-based conductive fillers, such as carbon nanotubes (CNTs) and graphene. Their addition to a thermoelectric material can improve the electrical conductivity or Seebeck coefficient of the material, thereby leading to an enhanced power factor. Lai et al. [10] embedded MWCNTs into rutile TiO_2, which resulted in an enhanced power factor. Bhardwaj et al. [11] introduced graphene nanosheets into MgSbBi-based system to produce ~130% increased thermoelectric power factor. More recently, Li et al. [12] reported that

graphene nanosheet/$(Bi_2Te_3)_{0.2}(Sb_2Te_3)_{0.8}$ composites exhibited high power factor than the sample without graphene. Of all carbon-based materials, graphene is the best filler material for achieving a high electrical conductivity because of its sp^2-hybridized carbon atoms and outstanding charge-carrier mobility [13]. However, very few studies have investigated the thermoelectric properties of nanostructured Bi_2Te_3 matrices doped with well-dispersed graphene fillers and their thermoelectric applications. Graphene-based layered thermoelectric composites with a small amount of Bi_2Te_3-NW content were discussed in our previous papers [14,15]. However, these composites exhibited low thermoelectric performance in spite of low thermal conductivity and high electrical conductivity. Hence, we tried to fabricate the nanostructured Bi_2Te_3-based materials with the addition of a small amount of graphene for obtaining higher Seebeck coefficients and lower thermal conductivity than the graphene-based composites. We expected that the added graphene would greatly improve the performance of those thermoelectric composites.

In this work, a strategy, for enhancing the thermoelectric properties of two different Bi_2Te_3 matrices via the incorporation of graphene particles, was studied. The nanostructured Bi_2Te_3 matrices were prepared according to different manufacturing processes, and a Bi_2Te_3 powder was produced by ball milling of Bi_2Te_3 beads (a top-down approach), whereas Bi_2Te_3 nanowires (NWs) were fabricated from Te templates with a solution-phase synthetic process (a bottom-up approach). The two graphene/Bi_2Te_3 composites were prepared with various graphene contents using a wet chemical synthetic route and a subsequent sintering process. We expected the randomly dispersed graphene sheets in the Bi_2Te_3 matrices to affect the intrinsic conduction of the composites, which could improve the thermoelectric properties of the composites. The effects of the graphene content on the thermoelectric properties—such as σ, S, κ, the power factor, and ZT—of the graphene/Bi_2Te_3 composites were also investigated.

2. Experimental methods

2.1. Materials

The following were purchased from Sigma Aldrich (St. Louis, USA): graphite nanopowder (mean particle size < 20 μm), sulfuric acid (H_2SO_4, 95% purity), potassium permanganate ($KMnO_4$), and bismuth(III) telluride (Bi_2Te_3) beads. Phosphoric acid (H_3PO_4, 85%), hydrochloric acid (HCl, 35–37%) and hydrogen peroxide (H_2O_2, 34.5%) were purchased from Samchun Pure Chemical Co. (Pyeongtaek, Korea). The following were purchased from Daejung Chemicals & Metals Co., Ltd. (Seoul, Korea): bismuth(III) nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$, 98%), tellurium(IV) oxide (TeO_2, 99%), potassium hydroxide (KOH, 93%), polyvinylpyrrolidone (PVP, $(C_6H_9NO)_n$, molecular weight $\approx$ 40,000 g/mol), tetrahydrofuran anhydrous (THF, $(CH_2)_4O$, 99.5%), ethylene glycol (EG, $C_2H_4(OH)_2$, 99%), ethanol (C_2H_5OH, 94%), and hydrazine monohydrate ($N_2H_2 \cdot H_2O$, 80%). All materials were used without further purification. The Bi_2Te_3 powder was prepared from the Bi_2Te_3 beads with a conventional ball milling process using zirconia balls in an inert atmosphere to avoid oxidizing the surface of the particles. Then, the ball-milled powder was rinsed with a dilute solution of HCl to remove any oxidized layers on the surface.

2.2. Synthesis of the Bi_2Te_3 NWs

The Bi_2Te_3 NWs were synthesized, based on the procedures previously described [14], with a few variations. Specifically, 2.3 g of PVP, 1.1 g of TeO_2, and 2.1 g of KOH were added to a round-bottom flask; this action was followed by the addition of 70 mL of EG. This solution was heated to 393 K under stirring; then, 2.3 mL of $N_2H_2 \cdot H_2O$ was injected into the mixture to synthesize the Te NWs. A Bi precursor solution was prepared by dissolving 2.3 g of $Bi(NO_3)_3 \cdot 5H_2O$ and 0.45 g PVP in 15 mL of EG. After a reaction time of 40 min, the Bi precursor solution and 2.3 mL of $N_2H_2 \cdot H_2O$ were injected into the as-prepared Te-NW solution to synthesize the Bi_2Te_3 NWs. The resulting Bi_2Te_3 NWs were obtained after washing and centrifuging this mixture.

2.3. Preparation of graphene oxide (GO)

GO nanosheets were synthesized with a modified Hummers' method, as described in previously reported works [14,16]. The prepared GO sheets were several micrometers across and 4–5 nm thick.

2.4. Fabrication of the graphene/Bi_2Te_3 composites

Initially, 0.5 g of the Bi_2Te_3 powder were suspended in 500 mL of deionized (DI) water containing 0, 0.5, 1, 3, 5, or 10 wt.% of GO (0, 0.9, 1.9, 5.6, 9.3, or 18.6 vol.%, respectively); then, ultrasonification of the mixture was performed for 1 h. The dispersion was subsequently reduced by the addition of a sufficient amount of $N_2H_2 \cdot H_2O$. Under stirring, this mixture was heated at 368 K for 2 h. The resulting product was filtered and washed with DI water, and dried at 333 K for 24 h. The final product was ground into a fine powder, loaded into a Fe mold, and pressed at 623 K under 50 MPa for 10 min to produce the graphene/Bi_2Te_3-powder composites. The same procedure was employed to prepare composites with the Bi_2Te_3 NWs. Thus, two different graphene/Bi_2Te_3 composites were fabricated via a wet-chemical synthetic route and subsequent sintering process.

2.5. Characterization

The morphology and microstructure of the materials were determined with field-emission scanning electron microscopy (FE-SEM, SIGMA, Carl Zeiss) and field-emission transmission electron microscopy (FE-TEM, JEM-2100F, JEOL), respectively. Elemental mappings of the samples were analyzed by energy-dispersive X-ray spectroscopy (EDS, NORAN System 7, Thermo Scientific). X-ray diffraction (XRD, New D8 Advance, Bruker AXS) was performed at 40 mA, 40 kV, and a scan rate of 1°/s, with 2θ ranging from 5 to 70°; Cu Kα radiation (λ = 0.154056 nm) was used to characterize the crystal structure of the materials. A four-point probe method with disk-shaped compressed pellets was used to measure the σ values of the composites. A homemade device containing a pair of thermocouples and voltmeters was used to measure S. The charge-carrier concentration (n) was determined by conducting Hall effect measurements, using a Van der Pauw four-point probe configuration (HMS-3000, Ecopia) at 300 K. The carrier mobility (μ) was calculated using the measured σ and n values. The κ values of the composites were estimated with the relationship $\kappa = \alpha \cdot \rho \cdot C_P$, where α is thermal diffusivity, ρ is bulk density, and C_P is the specific heat of the material. An LFA 447 NanoFlash (NETZSCH) was used to measure α, whereas C_P was measured with differential scanning calorimetry (DSC, DSC 131 Evo, Setaram Instrumentation). The thermal transition behavior of the composites was described by DSC measurements for samples that were heated from 253 to 393 K at a rate of 10 K/min under a N_2 atmosphere.

3. Results and discussion

Fig. 1 shows a schematic diagram of the fabrication processes used to prepare the graphene/Bi_2Te_3 composites. The ball-milled