Applied Surface Science xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

The influence of interfacial defect-region on the thermoelectric properties of nanodiamond-dispersed $Bi_2Te_{2.7}Se_{0.3}$ matrix composites

Tae Sik Min[a,b], Kyung Tae Kim[a,*], Injoon Son[b]

[a] Korea Institute of Materials Science, 797 Changwon-daero, Seongsan-gu, Changwon, Gyeongnam 51508, Republic of Korea
[b] Dept. of Metallurgical Engineering, Kyungpook National University, 80 Daehakro, Buk-gu, Daegu, 41566, Republic of Korea

ARTICLE INFO

Article history:
Received 20 August 2016
Accepted 7 November 2016
Available online xxx

Keywords:
Nanodiamond
$Bi_2Te_{2.7}Se_{0.3}$
Interface
Thermoelectric properties

ABSTRACT

Nanodiamond-dispersed $Bi_2Te_{2.7}Se_{0.3}$ (ND/BTSe) matrix composites were fabricated by a high energy ball milling followed by spark plasma sintering process. The fabricated ND/BTSe composites show that ND powders with 5 nm in size are dispersed in the BTSe matrix grain rather than agglomerated at the grain boundary. It was found that atomically disordered-lattice structure present nearby the newly formed ND/BTSe interfaces. This interfacial region artificially formed by addition of ND powders plays a role as atomic-scaled defects increasing electron concentration. Electric conductivities of all the ND/BTSe composites show significantly increased values compared to that of pure BTSe in the temperature range from 298 K to 473 K. However, total thermal conductivity of the composites exhibit higher values than the BTSe due to superior electric conductivity even though active lattice phonon scattering at the interfaces affect lowering thermal conductivity. The maximum ZT, 0.97 was obtained from 0.5vol%ND/BTSe composite at 473 K and enhancement in ZT values was clearly revealed above 348 K. Therefore, these results elucidate that addition of ND powders into n-type BTSe matrix is promising method to improve thermoelectric performances.

1. Introduction

Thermoelectric materials are interest for applications in power generation from waste heat using the Seebeck effect, in addition to being valuable for refrigeration by means of the Peltier effect [1–4]. The energy conversion efficiency of a thermoelectric device is dependent on the dimensionless figure of merit of the constitute materials expressed as $ZT = \alpha^2\sigma/(\kappa_e + \kappa_l)$, where α is Seebeck coefficient, σ is the electrical conductivity, κ_e is the electronic thermal conductivity, κ_l is lattice thermal conductivity and T is the absolute temperature. Hence, thermoelectric materials necessarily require a suitable combination of high power factor ($\alpha^2\sigma$) and low thermal conductivity (κ) in order to achieve high ZT value. Because all of factors have trade-off relation, many researchers have suffered difficulty to control reducing thermal conductivity (κ) and increasing power factor ($\alpha^2\sigma$) at the same time.

It is known that bismuth telluride (Bi_2Te_3) based alloys have high capability to control thermal and electrical transport properties by anisotropic crystal structure [5–7]. However, since the ZT of bismuth telluride is still low than expected, many works have been made to further grow the thermoelectric properties of Bi_2Te_3 materials focused on p-type, until now. However, relatively the reports about n-type Bi_2Te_3 based alloys have been rarely investigated except several researches [8–10]. In viewpoint of materials engineering, it has mostly been considered that the feasible method to enhance ZT values of Bi_2Te_3 based alloy is to reduce the total κ by inducing nanostructured grain [11,12] or effectively incorporating nanoparticles into the matrix [13,14]. That is the reason why active phonon scattering at the intrinsic grain boundary or extrinsic interfaces has been expected without a critical decrease on the electrical properties [15,16].

Among many dispersion agents such as alumina, graphene, carbon nanotube and etc. [17,18], nanodiamonds (NDs) with 5 nm in average diameter are expected to provide large interfacial area when they are homogeneously dispersed in the matrix. It is also expected that artificial implanting of ND powders into the BTSe matrix make strained-fields that result in formation of defect region to cause scattering of phonons with various wavelengths.

Thus, we synthesize the ND-dispersed $Bi_2Te_{2.7}Se_{0.3}$ matrix composites based on mechanical alloying process. In order to confirm the effect of ND addition, pristine $Bi_2Te_{2.7}Se_{0.3}$ powders are fabricated by the same process without ND powders. Compared with ND-free bulk $Bi_2Te_{2.7}Se_{0.3}$, the microstructures and thermoelectric properties of the ND/BTSe composites are investigated, respec-

* Corresponding author.
E-mail address: ktkim@kims.re.kr (K.T. Kim).

http://dx.doi.org/10.1016/j.apsusc.2016.11.054
0169-4332/

tively, and the role of ND on the carrier and phonon transport in n-type BTSe materials is analyzed in this study.

2. Experimental procedure

2.1. Material and methods

Bi, Te and Se powders (Materion Co. Ltd, USA) with purity about 99.999% were utilized as raw materials. Detonation-synthesized NDs (purchased from AG, Switzerland, purity over 99.5%, specific gravity of 3.5g/cm^3, mean diameter of 5 nm) were used in this study. Bi, Te and Se powders were alloyed to the stoichiometric compositions of $Bi_2Te_{2.7}Se_{0.3}$, by ball milling process. The ND powders were homogeneously mixed with BTSe powders by using a mechanical alloying (MA) process (Fritsch Monomill, pulverisette) for 2hr at 450 rpm. The mechanically alloyed ND/BTSe composite powders were then consolidated by Spark Plasma Sintering (SPS, Sumitomo Dr. Sinterlab) process. Approximately 12 g of each composite powder was compacted into a carbon mold with diameter of 22.5 mm and sintered under vacuum at 350 °C for 10 min under uniaxial pressure of 60 MPa.

2.2. Characterization techniques

Microstructures and crystal structures were characterized by transmission electron microscopy (TEM) analysis (a JEOL 2100F, 200 kV). An HAADF-STEM (High-Angle Annual Dark-Field, JEOL JEM-2100F) technique was utilized in order to distinguish 5nm-sized ND powders from the matrix phase. And the phase and composition of the powders and bulks were confirmed by X-ray diffractometer (XRD, D/MAX–25 V/PO). The electrical resistivity and Seebeck coefficient were measured in an Ar atmosphere between 298 K and 473 K using a ZEM-3(ULVAC-RIKO) instrument system. Carrier concentrations of all samples were characterized using a HMS-8400 (LAKESHORE) instrument at 298 K. The thermal diffusivity (D) was measured at 298 – 473 K by using the laser flash method in a commercial LFA-447(NETZSCH) instrument. The heat capacity (C_p) was measured at 298 to 473 K by Perkin Elmer Differential Scanning Calorimeter (DSC). The total thermal conductivity was calculated using the formula $\kappa = D^*C_p{}^*\rho$, where ρ is the material density.

3. Results and discussion

3.1. Microstructures

Fig. 1(a) shows a TEM image of the ND/BTSe composite with the 0.5vol.% ND powders. The TEM image representatively shows that grain size of BTSe is about a few hundreds of *nm* and there are no agglomeration of ND powders. Fig. 1(b) shows the XRD patterns of all the composites with different NDs contents compared to pure BTSe matrix. The main diffraction peaks for all composites match well with the JCPDS data card No.50-0954 showing clear compositions of $Bi_2Te_{2.7}Se_{0.3}$, which means the dispersion of NDs does not affect the crystal structure of BTSe matrix.

Fig. 1(c) shows an enlarged TEM image to find out dispersed-ND powders in BTSe matrix. It was observed that many dark-colored spots with 5–20 nm in size are homogenously embedded within the grain but also partly on the grain boundary of the matrix phase as indicated by black arrows. As shown in Fig. 1(d), the EDS results on the AB line of Fig. 1(c) reveal that black-colored dots are corresponded to carbon-rich region defined as ND phase. A high-resolution STEM image of one ND powder is displayed in Fig. 1(e). The reduced FFT as inset figure of Fig. 1(e) confirmed that planar space, 3.25Å in the lattice indicates (015) plane of BTSe matrix. Fig. 1(e) also displays a STEM image of interfacial region having a planar space, 2.72 Å at the lattice. The lattice structure of the interfacial region does not match with the lattice of $Bi_2Te_{2.7}Se_{0.3}$ but also appears to be surrounded on the ND powder. In addition, Fig. 1(f) enlarged on the ND/BTSe interface more clearly reveals that there is atomically-disordered lattice at the interface which is different from the ordered lattice of the BTSe matrix. The reduced FFT image also confirmed that interfacial region has different crystal structure with BTSe matrix region. It is speculated that these interfacial region is formed by addition of ND from mechanical alloying (MA) process and there may be composed of atomistic defects such as Te or Se vacancy changing crystal structure. For sure, it should be noted that our speculation is based on the increase in carrier concentration obtained from ND/BTSe composites.

3.2. Thermoelectric properties

Fig. 2 shows the electric conductivity (σ), Seebeck coefficient (α), and power factor ($\alpha^2\sigma$) and thermal conductivity of all ND/BTSe composites measured at temperature ranging from 298 K to 473 K. Fig. 2(a) shows the temperature dependence of σ for ND/BTSe composites. Electrical conductivities of all the ND/BTSe composites show significantly increased values compared to that of pure BTSe matrix. Fig. 2(b) shows the variation of α for BTSe composites expressed as a function of temperature. The values of α for all composites express negative as n-type semiconductor and decrease compared to pure BTSe. The results display that the absolute α values for BTSe sample decreases with increasing temperature in the range of 400–478 K. And α value of the ND/BTSe samples are found to somewhat increase with temperature in the range of 300 – 478 K. Fig. 2(c) shows comparison of power factors of the composites with pristine BTSe. The 0.5vol% ND/BTSe composite apparently shows the highest values in the whole temperature range, which is attributed to the modulation of improved σ and appropriately decreased α.

Fig. 2(d) shows total thermal conductivity of the composites compared to BTSe as a function of temperature. The results elucidate that addition of ND powders increase in total thermal conductivity originated from the high electrical conductivity. The total thermal conductivity (κ) is known as the sum of the lattice thermal conductivity (κ_l) by phonons and the electronic thermal conductivity (κ_e) by carriers. Both conductivities can be estimated by the wiedemann Franz law ($K_e = L\sigma T$), where the Lorenz number is assumed to be a constant ($L = 2.0 \times 10^{-8}\ W\Omega K^{-2}$) for the evaluation [19,20]. Fig. 2(d) also shows the calculated lattice thermal conductivities of the composites. Lattice thermal conductivity of 0.5vol%ND/BTSe composites shows lowest value about $0.2 \sim 0.4\ Wm^{-1}K^{-1}$. It is analyzed that the reduction in lattice thermal conductivity originates from phonon scattering at the large density of extrinsic interfacial region creating between the BTSe matrix and NDs. In particular, the reduction in k_l when NDs are embedded within grains is similar to that reported for other thermoelectric materials like L. D. Zhao etc. [21].

3.3. Roles of interfacial defect region

Fig. 3(a) shows variation of carrier concentration and mobility with increasing contents of ND. The carrier concentration significantly increases up to $1.4 \times 10^{20}\ cm^{-3}$ at 0.5 vol%ND/BTSe composite while electron mobility abruptly decreases from 110 to $43\ cm^2\ V^{-1}\ s^{-1}$. Addition of NDs in BTSe matrix results in an increase in carrier concentration and subsequent increase in electrical conductivity as shown in Fig. 2(a). The significantly increased carrier concentration is probably related to the lattice defects generated from the severe deformation during the high energy ball

Please cite this article in press as: T.S. Min, et al., The influence of interfacial defect-region on the thermoelectric properties of nanodiamond-dispersed $Bi_2Te_{2.7}Se_{0.3}$ matrix composites, Appl. Surf. Sci. (2016), http://dx.doi.org/10.1016/j.apsusc.2016.11.054