Materials Science in Semiconductor Processing 87 (2018) 126–133

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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

Ultrasonic-assisted hot pressing of Bi_2Te_3-based thermoelectric materials

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ARTICLE INFO

Keywords:
Bi_2Te_3
Ultrasonic-assisted hot pressing
Dynamic recrystallization
Thermoelectric property

ABSTRACT

In this study, *n*-type Bi_2Te_3-based bulk materials were prepared using the ultrasonic-assisted hot pressing. The effects of ultrasonic vibration on the mechanical and thermoelectric properties of the prepared samples were investigated. Field-emission scanning electron microscope (FESEM) tests revealed that the ultrasonic vibration refined the grain size to the submicron level. The grain size became smaller as the ultrasonic vibration duration is extended. The results showed that the sample with an ultrasonic vibration duration of 20 min (namely, Ultra 20) has a hardness of 64 HV0.3 and a flexural strength of 22.4 MPa, which represents an 82.9% and 50.2% improvement, respectively, over the untreated hot-pressed sample (namely, Ultra 0). As the ultrasonic vibration duration increased, the absolute value of the Seebeck coefficient was found to increase, whereas the electrical conductivity and the thermal conductivity decreased. The maximum dimensionless figure of merit (ZT_{max}) was 0.78 at 480 K for the Ultra 20 sample, which was 10.9% and 16.4% higher than the Ultra 10 and Ultra 0 samples, respectively. The results proved that both the mechanical properties and the thermoelectric properties of the $Bi_2Te_{2.7}Se_{0.3}$ bulk materials are improved by ultrasonic vibration.

1. Introduction

Bismuth telluride (Bi_2Te_3) and its alloys have been used as the predominant thermoelectric materials for applications near room temperature [1]. Continuous efforts have been made by the scholars around the world [2] to increase the figure of merit (*ZT*) value of the Bi_2Te_3-based bulk materials. On the other hand, the mechanical properties of the Bi_2Te_3-based bulk materials are also critical for the long-term reliability of the thermoelectric module. Simultaneously increasing both the thermoelectric and the mechanical properties of the Bi_2Te_3-based bulk materials will greatly promote the actual application of the materials.

There are numerous processes to fabricate the Bi_2Te_3-based bulk materials, which significantly affected their thermoelectric and mechanical properties [3,4]. Wang et al. [5] applied hot-deforming of powders to fabricate $Bi_2Te_{2.7}Se_{0.3}$ alloys with high thermoelectric performance, resulting in a flexural strength of 10 MPa. Zheng et al. [6] investigated the mechanical properties of p-type $Bi_{0.5}Sb_{1.5}Te_3$ commercial zone-melting (ZM) ingots, and the results showed that the flexural strength perpendicular to the ZM direction was 9.6 MPa. Shin et al. [7] fabricated $Bi_{0.5}Sb_{1.5}Te_3$ bulk materials with a flexural strength of 50.1 MPa by the hot-pressing of powders, with a maximum dimensionless figure of merit of 0.87 at room temperature. Ivanova et al. [8] combined hot-pressing with annealing in $Bi_{0.5}Sb_{1.5}Te_3$ solid solutions to remove imperfections in the structure. The compressive strength of the obtained material was 67 MPa while the annealing process tends to induce grain growth. Williams et al. [9] fabricated p-type $Bi_{0.5}Sb_{1.5}Te_3$ thermoelectric materials by spark plasma sintering using powder dispersed with nano-B_4C. The Vickers hardness was 80 HV0.3 in the direction perpendicular to solidification, while it dropped to 57 HV0.3 in the direction parallel to solidification.

Since the bismuth telluride crystals are easily cleaved perpendicular to the direction of the *c*-axis (basal plane) [10], the mechanical properties parallel to the crystal-growth direction were worse than those perpendicular to the crystal-growth direction for most of the studies mentioned above. Considering that ultrasonic vibration is able to refine grains and make the materials more isotropic [11–13], the mechanical properties of the materials can be improved by the ultrasonic vibration. Furthermore, finer grains contribute to a lower thermal conductivity [14,15], which potentially improve the thermoelectric properties of the materials. Appling ultrasonic vibration in hot pressing of Bi_2Te_3-based thermoelectric materials potentially improve both the mechanical and

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https://doi.org/10.1016/j.mssp.2018.07.019
Received 12 December 2017; Received in revised form 6 June 2018; Accepted 10 July 2018

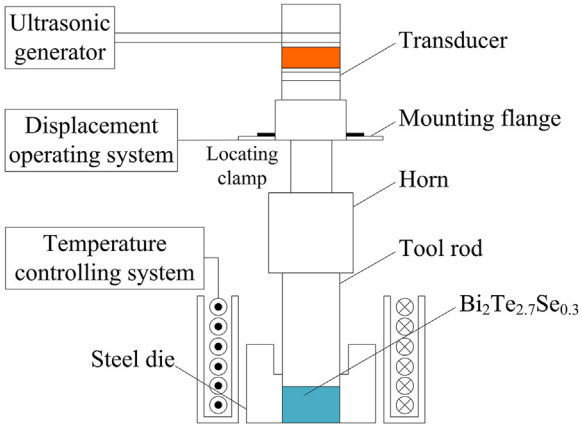

Fig. 1. Schematic diagram of the experimental setup for ultrasonic-assisted hot pressing.

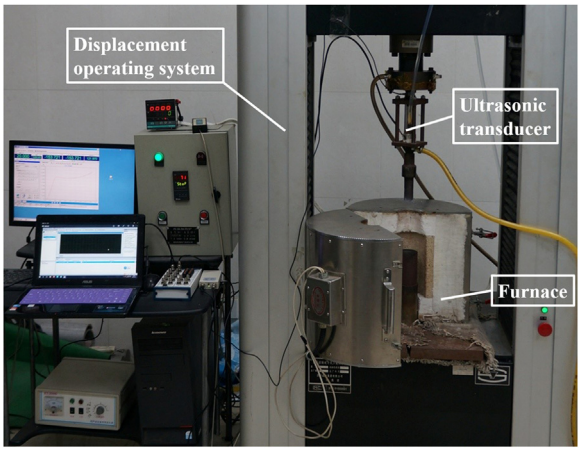

Fig. 2. Experimental setup for ultrasonic-assisted hot pressing.

the thermoelectric properties. To the authors' best knowledge, there is still no studies focusing on the ultrasonic-assisted hot pressing of bulk thermoelectric materials.

In this study, ultrasonic-assisted hot pressing was used to fabricate Bi_2Te_3-based alloys. The effects of ultrasonic vibration on the microstructures of the Bi_2Te_3-based alloys were investigated, along with its influence on the thermoelectric and the mechanical properties.

2. Experimental setup and procedures

An experimental setup was developed to apply the ultrasonic vibrations in the hot pressing process. The experimental setup consisted of an ultrasonic transducer, a horn, a tool rod, a heating furnace, and a die, as shown in Fig. 1. The transducer is made up of cylindrical piezoelectric elements, and its frequency and voltage can be adjusted continuously by the ultrasonic generator. The shape and the length of the horn are designed to have a longitudinal resonance frequency of 20 kHz. The displacement and the load are controlled by the displacement operating system (WDW-100E, Time Group Inc.). The furnace temperature is controlled by the temperature controlling system (GH-1, Yangzhou Guihao Inc.).

The *n*-type $Bi_2Te_{3-x}Se_x$ has proved to have excellent thermoelectric properties near room temperature. According to the previous reports [16], doping with Se element by x = 0.15–0.3 in $Bi_2Te_{3-x}Se_x$ system is able to obtain appropriate carrier concentrations to balance the electrical conductivity and the Seebeck coefficient, and thus optimize the power factor. Therefore, in this study, the *n*-type $Bi_2Te_{2.7}Se_{0.3}$ was selected and purchased from Leshan KaiYada Photoelectric Technology Co., Ltd. The as-received *n*-type $Bi_2Te_{2.7}Se_{0.3}$ ingots were made by the zone melting process, which is as follows. The constituent elements of Bi, Te, and Se with a purity of 99.9% were weighted in the stoichiometric proportions of $Bi_2Te_{2.7}Se_{0.3}$. The powder mixtures of elements were charged into a carbon-coated quartz tube that was sealed under 10^{-5} Torr. Bi, Te, and Se in the quartz tube were melted at 650 °C for 2 h using a rocking furnace to ensure composition homogeneity, and quenched to room temperature. The crystals were grown by the zone melting method using the temperature gradient of 25 °C/mm and growth rate of 8 mm/h.

The as-received *n*-type $Bi_2Te_{2.7}Se_{0.3}$ ingot was loaded into a high-speed vibratory ball mill (SFM-3, Hefei Ke Jing Materials Technology Co., LTD, China), and was pulverized for 2 h into fine powder at a speed of 1200 rpm without the protection of inert atmosphere. The ball-to-powder weight was 20:1. Before hot pressing, the powders were cold compacted under 60 MPa without evacuation to densify the powders at room temperature. The cold compacting was conducted in a steel die with an internal diameter of 12.7 mm. The cold-compacted powders were then hot-pressed at 823 K under a uniaxial pressure of 60 MPa for 20 min. Ultrasonic vibration generated by the ultrasonic transducer with a frequency of 20 kHz and amplitude of 26 μm was applied from the beginning of the hot pressing process to influence the material microstructures, as shown in Fig. 2. To study the effect of ultrasonic vibration duration on the materials, the samples were applied with vibration durations of 0, 10, and 20 min, respectively. After hot-pressing with various ultrasonic vibration durations, the samples were furnace cooled to room temperature. The as-achieved $Bi_2Te_{2.7}Se_{0.3}$ bulk samples were then named Ultra 0, Ultra 10, and Ultra 20, respectively.

The phase identification of the samples were performed by X-ray diffraction (XRD, PANalytical X'pert PRO with a Cu K_α radiation, wavelength = 1.54 Å). The chemical composition measurements of the *n*-type $Bi_2Te_{2.7}Se_{0.3}$ bulk sample after consolidation were performed by energy-dispersive X-ray spectroscopy (EDS, Hitachi S-3700N, Hitachi, Japan). The flexural strength of the bulk material was tested using a three-point flexural method as shown in Fig. 3. The flexural test was conducted on a three-axis linear stage (Newport 460 P, Irvine, CA, USA) and the three-point flexural test was carried out using a rectangular bar with the dimension of 11 mm × 3 mm × 2 mm. The flexural strength (σ_f) was calculated using the equation $\sigma_f = 3PL/2bh^2$, where P is the measured peak load at failure, L is the span length, and b and h are the width and thickness of the sample, respectively. The span length for three-point flexural test was 6 mm. The load was measured using a force sensor (Interface 3A120, USA) with a resolution of 0.01 N. At least 5 samples were used for the flexural strength test for Ultra 0, Ultra 10, and Ultra 20, respectively. The Vickers hardness tests were performed with a Vickers microhardness tester (MH-5, Everone, China). A load of 2.94 N (0.3 kgf) was applied for 10 s using a square-base diamond pyramid. Five indentations were performed on each sample and the average of five samples was used to evaluate the Vickers hardness value for Ultra 0, Ultra 10, and Ultra 20 samples, respectively. The morphologies of the bulk samples were analyzed by field-emission scanning electron microscopy (FESEM, FEI Sirion100, USA). Disk samples (Φ12.7 mm × 2 mm) were prepared for measurement of the thermal conductivity κ. Rectangular samples (3 mm × 2 mm × 10 mm) were prepared for measurement of the electrical conductivity σ and the Seebeck coefficient α. The specific heat C_p was measured using a Netzsch DSC 404C (Netzsch, Selb, Germany), and the thermal diffusivity λ was measured using a Netzsch LFA 457 (Netzsch, Selb, Germany). The sample density ρ was measured by the Archimedes method. The thermal conductivity κ was then calculated using the formula: $\kappa = \lambda\rho C_p$. The electrical conductivity σ and the Seebeck coefficient α were simultaneously measured when a temperature difference was applied between two ends of the sample, using a commercial Linseis® LSR-3 system (Linseis, Germany). The Hall coefficient R_H of the sample was measured at 298 K on a Quantum Design PPMS-9T instrument using a four-probe configuration, with the magnetic field sweeping