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Texture-induced reduction in electrical resistivity of p-type $(Bi,Sb)_2Te_3$ by a hot extrusion

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ABSTRACT

The electrical resistance of a thermoelectric module is an important parameter as well as the thermoelectric figure-of-merit for the application of both waste energy harvesters and solid-state cooling devices. High resistance causes energy dissipation through Joule heating, leading to the degradation of the device's generating or cooling performance. Therefore, it is highly desirable to reduce the electric resistivity of the thermoelectric materials. Here, we report a hot extrusion technique to fabricate p-type bismuth antimony tellurides that has low electrical resistivity. Extrusion is a promising tool to fabricate a fiber-like texture of the microstructure, where the 001 normal vector of grains is pointing perpendicular to the extrusion direction. Such a textured microstructure can enhance the mobility of electrical carriers along the extrusion direction due to the anisotropic nature of electrical transport in bismuth telluride-based alloys. Beyond bismuth telluride-based thermoelectric materials, we believe that our result will offer a simple tool to manipulate physical properties of any two-dimensional, layered materials by controlling microstructure.

1. Introduction

The performance of the thermoelectric materials is evaluated by the thermoelectric figure-of-merit (Z), $Z = \alpha^2/\rho\kappa$, where α, ρ, and κ are the Seebeck coefficient, electrical resistivity, and thermal conductivity, respectively [1–6]. Although the figure-of-merit represents the overall thermoelectric property, the electrical resistivity is often important for the performance of the practical devices. Especially for the solid-state cooling devices, the resistance of the thermoelectric module should be as low as possible since the resistance causes Joule-heating during operation, degrading the coefficient of performance (COP) of cooling [7–14]. Therefore, it is necessary to reduce the electric resistance of the thermoelectric materials while maintaining the other terms.

There are two ways to reduce electrical resistivity: either by increasing carrier density or by increasing carrier mobility. It should be noted that the Seebeck coefficient is a strong function of the carrier density rather than of the mobility. Consequently, it may not be an ideal approach to increase the carrier density as it significantly affects the Seebeck coefficient. On the other hand, increasing only the carrier mobility can reduce the electrical resistivity while minimally affecting other terms.

Carrier mobility is closely related to a material's microstructure. Bismuth telluride-based, layered materials exhibit a strong anisotropy along different crystallographic directions. They have strong covalent bonding along the a- and b-axis, and weak van der Waals bonding along the c-axis. Given the electrical carrier density, carriers can move much faster along the a- and b-axis than the c-axis [15–17]. Therefore, a texturing technique, in which the orientation of grains are controlled in a particular direction, is necessary to reduce the electrical resistivity [18,19]. There have been several reports on the texturization of the microstructure of bismuth telluride-based thermoelectric materials, using re-pressing, equal

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channel angular pressing (ECAP), and extrusion. In the re-press process, the pressed ingot is *re-pressed* within a mould that has a larger diameter than the ingot size [20]. As the ingot expands laterally to fit into the mould, the grains are aligned in such a way that the 001 normal vector is parallel to the pressing direction. Both ECAP and extrusion utilize a shear stress resulting from deformation. In ECAP, the ingot is pushed through a mould with a 90° elbow shape [21], while in extrusion this is done through a narrowed channel [22–24]. In both the ECAP and extrusion processes, the 001 normal direction is perpendicular to the pressing direction.

In this work, we use a hot extrusion process to fabricate p-type bismuth antimony tellurides with a low electrical resistivity as shown in the schematic illustration of Fig. 1. We analyzed the microstructure of the extrudates by scanning electron microscopy (SEM) and x-ray diffraction (XRD). In order to evaluate the anisotropy of electrical transport, Hall measurement was performed parallel and perpendicular to the extrusion direction. We confirm that there is a significant difference in the hole mobility along the parallel and perpendicular directions and that the Seebeck coefficient remains almost unchanged. This leads to an enhancement of thermoelectric properties of the extrudates over spark plasma sintered (SPS) samples which have randomly-oriented grains without any texture.

2. Experimental procedure

P-type $(Bi_xSb_{2-x})Te_3$ samples were prepared using Bi (99.999%), Sb (99.999%), and Te (99.999%) granules as starting materials. The p-type alloy composition corresponds to $x = 0.3$, 0.4, 0.5. These materials were weighed with a nominal composition of $(Bi_xSb_{2-x})Te_3$, loaded into quartz ampoules, and sealed under vacuum (10^{-6} Torr). Before sealing, the quartz ampoules were cleaned with Acetone and ethanol using an ultrasonic washing machine. The elements in the quartz ampoule were melted and mixed at 1023 K in a rocking furnace. After 4 h, the quartz ampoules were water-quenched. The cylindrical ingots were then crushed into a fine powder using steel balls. The ball-to-material weight ratio was 5:1. Mechanical alloying was performed by rotating the vial at approximately 1200 rpm for 6 h using a SPEX mixer and mill. The mechanically alloyed powders were then loaded into a steel mould with an inner diameter of 20 mm and compacted. The compacted billet was annealed at 723 K in an evacuated quartz tube at ~10^{-6} Torr. It was then hot-extruded at a temperature of 673 K under an extrusion ratio of 10:1. Finally, the extruded samples were annealed at 673 K in an evacuated quartz tube at ~10^{-6} Torr.

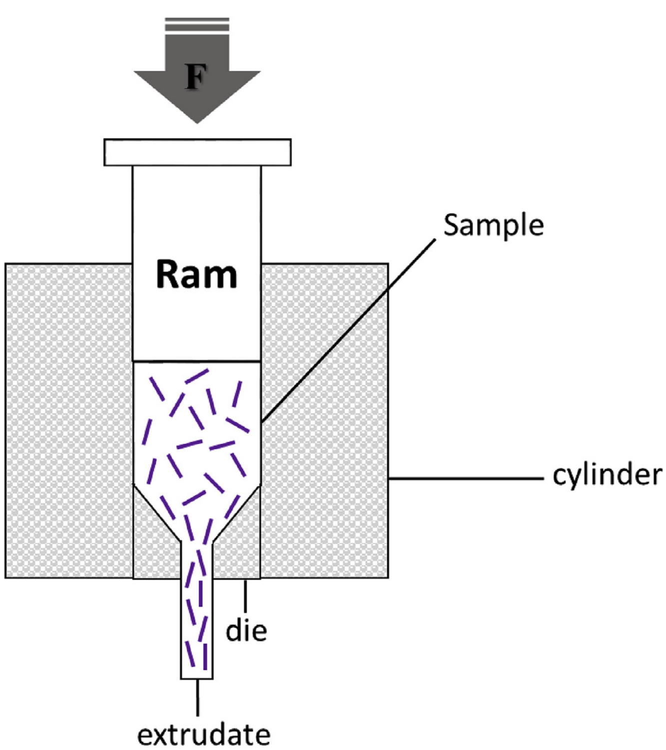

Fig. 1. Schematic illustration of hot-extrusion.

In order to investigate the phase and microstructure of the $(Bi_xSb_{2-x})Te_3$, XRD patterns of the extruded samples were obtained using an X-ray diffractometer (D8 Discover; Bruker AXS Korea, Korea) using Cu $K\alpha$ radiation. Microstructural analysis was carried out using a scanning electron microscope (SEM) (Hitachi S-4300; Hitachi High-Tech Korea, Korea). The Seebeck coefficient was measured using a method based on the slope of the voltage versus temperature difference curve, using commercial equipment (TEP600; Seepel, Korea). The electrical resistivity was measured by the four-point probe method with specimen dimensions of $0.7065 \times 1 \times 15\ mm^3$. The Harman method was conducted to measure the figure-of-merit (Z), and the thermal conductivity was calculated by $\kappa = \alpha^2/\rho Z$ [25–28]. The carrier density and mobility were measured by Hall measurement (PPMS Dynacool 14 T, Quantum Design, USA), with an applied magnetic field of 5 T and an electrical current of 10 mA.

3. Results and discussion

The microstructure of the extrudates was analyzed by SEM and XRD. Fig. 2a and b are the SEM images of the fractured surfaces of the extrudate parallel and perpendicular to the extrusion direction, respectively. As the bismuth antimony telluride is a 2-dimensional layered material with a rhombohedral crystal structure, the grains usually have the shape of hexagonal plates. A large portion of the surface parallel to the extrusion directions showed the flat side of grains (Fig. 2a). On the other hand, there was no flat area on the surface perpendicular to the extrusion direction, and only the sides of the hexagonal plates could be seen without any particular preference along the radial direction (Fig. 2b). Based on these distinct surface morphologies, it can be deduced that the extrudate has a fibrous structure, where the 001 normal vector is perpendicular to the extrusion direction. Such a textured microstructure was also confirmed by the XRD technique. For the simple evaluation without any misleading information on the texture [29], we perform x-ray diffraction (XRD) technique with a two-dimensional area detector. Fig. 2c and d shows XRD patterns of the two different orientations of the extrudate. Note that the ($00\underline{15}$) diffraction peak is observed along the chi angle with the full width at half maximum (FWHM) of ~22° while other non-($00l$) peaks show a ring pattern in the measurement geometry shown in the inset of Fig. 2c. When the sample was rotated by 90° along the azimuthal direction, all peaks showed a ring pattern. These results reveal that the extrudate has a <*110*> fiber texture.

In order to evaluate the anisotropic physical properties of the extrudates, we characterized the carrier density and mobility along the two different directions, parallel and perpendicular to the extrusion directions, by Hall measurement. The measurement schematics are shown in the inset of Fig. 3. The carrier density was almost the same in both directions. However, the hole mobility shows a dramatic difference. The mobility along the extrusion direction was ~290 cm^2/V-s while that along the perpendicular direction was only ~180 cm^2/V-s. This indicates that holes can transport along the extrusion direction 50% faster than along the perpendicular direction. As the Seebeck coefficient is strongly