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Strain and grain size effects on thermal transport in highly-oriented nanocrystalline bismuth antimony telluride thin films

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ABSTRACT

We investigated the effects of strain and grain size on the thermal transport of highly-oriented nanocrystalline bismuth antimony telluride thin films using both experimental studies and modeling. The fabricated thin films had preferred crystal orientation along the *c*-axis, average grain sizes of $30 < d < 100$ nm, and strain of $-0.8\% < \varepsilon < -1.4\%$ in the *c*-axis direction, whereas the strain in the *a*–*b*-axis direction was constant at 1.7%. The thermal conductivities were measured to be $0.32 < \kappa < 0.52$ W/m/K using a 3ω method at room temperature. To gain insight into the thermal transport in the strained nanocrystalline thin films, we estimated the lattice thermal conductivities from the measured thermal conductivities. We then calculated the lattice thermal conductivity using a simplified phonon transport model that accounts for the strain effect based on the Christoffel equation and uses Lennard–Jones potentials, and the grain size effect based on the full distribution of mean free paths. The theoretical calculations were in good agreement with our experimental results, and we conclude that the decrease of the lattice thermal conductivity of nanocrystalline thin films can be mainly attributed to the nano-size effect rather than the strain effect.

1. Introduction

The development of nanotechnology makes a significant contribution to improving material performance. In particular, the properties of thermoelectric materials have been considerably improved by developments in nanotechnology [1]. Thermoelectric materials can directly produce electrical power from thermal energy, and vice versa. The thermoelectric performance is characterized using the dimensionless figure of merit (ZT), which is defined as $ZT = \sigma S^2 T/(\kappa_e + \kappa_{ph})$, where σ is the electrical conductivity, S is the Seebeck coefficient, T is the absolute temperature, and κ_e and κ_{ph} are the electronic and lattice thermal conductivities, respectively. To improve thermoelectric performance, the thermoelectric power factor σS^2 should be maximized and the lattice thermal conductivity should be minimized.

Nanostructured materials, such as superlattices, nanocomposites, and nanocrystalline materials, have shown to be able to decrease the lattice thermal conductivity. Recently, Bi_2Te_3/Sb_2Te_3 superlattice thin films made using metal organic chemical vapor deposition have exhibited a ZT value of 2.4 at room temperature, which represents a significant improvement in thermoelectric performance compared with state-of-the-art bulk alloys near room temperature [2]. This improvement in ZT is mainly because of the lower lattice thermal conductivity caused by phonon scattering at the superlattice interfaces. In addition, superlattices are highly strained, which may play a significant role in thermal transport [3].

Strained materials are widely studied in thermoelectrics [4–6], and the strain effects are known to enhance the thermoelectric performance [7,8]. The strains affect the electrical properties, as well as the thermal transport properties. The electrical properties, such as the Seebeck coefficient, may correlate with an electronic topological transition that happens when a band extremum crosses the Fermi level [7,9,10]. Thermal transport has been investigated using numerical simulations, which show that the thermal conductivity increases with increasing compressive strain and decreases with increasing tensile strain [3,11]. Moreover, the nanostructures of strained thermoelectric materials have recently been investigated [12], and their thermal conductivity was calculated using equilibrium molecular dynamics simulations [13]. We have also studied the lattice thermal conductivity of bismuth antimony telluride thin films using a simplified phonon transport model [14], which is based on the full distribution of mean free paths (MFPs) [15,16]. In this model, we used the Debye model to obtain the phonon group

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Nomenclature

a	a–b-axis direction
a_{std}	standard a–b-axis direction
A_1	fitting parameter (s^3) [32]
B_1	fitting parameters (s/K) [33]
B_2	fitting parameters (K) [33]
c	c-axis direction
c_{std}	standard c-axis direction
c_{ijkl}	elastic modulus (Pa)
C	specific heat per unit frequency ($J/m^3/K$)
D_{ave}	average grain size (m)
l	cutoff MFP (m)
Ln	Lorenz number ($W\,\Omega/K^2$)
L	phonon MFP (m)
L_{eff}	effective phonon MFP (m)
N_j	primitive per unit cells (m^{-3})
r	distance between any pair of atoms (m)
S	Seebeck coefficient (V/K)
T	absolute temperature (K)
U_k	directions cosines of the particle motion (J)
v	sound velocity (m/s)
v_{ave}	average sound velocity (m/s)
v_g	group velocity (m/s)
v_L	longitudinal sound velocities (m/s)
v_T	transverse sound velocities (m/s)
Z	figure of merit (1/K)
$Z(\vec{c})$	principal axis

Greek symbols

α	numerical constant
ε_{LJ}	strength of the potential energy (J)
$\phi(r)$	Lennard–Jones potential (J)
κ	thermal conductivity (W/m/K)
κ_e	electrical thermal conductivity (W/m/K)
κ_{ph}	lattice thermal conductivity (W/m/K)
$\kappa^*(l)$	normalized cumulative thermal conductivity function (%)
ρ	density (kg/m^3)
σ	electrical conductivity (S/m)
σ_{LJ}	characteristic diameter of the molecules (m)
ω	frequency (rad/s)
ω_0	Debye cut off frequency (rad/s)

Subscripts

impurity	impurity scattering
umklapp	umklapp scattering
boundary	boundary scattering

velocities. The averaged phonon group velocity by Debye model can be declared the straight-line approximation. It is important to understand the full distribution of mean free paths that contribute to heat transfer in a bulk material. Therefore, there is greater potential for thermal conductivity reduction in a given nanostructure [17]. The next step is to investigate the combined effect of the nanoscale grain size and the strain on the thermal transport.

In this study, we calculated the lattice thermal conductivity based on the phonon transport model of the full distribution of MFPs to investigate the effect of grain size and the fluctuation of the group velocity to investigate the effect of strain. The specific heat was assumed to be constant. The strained nanocrystalline bismuth antimony telluride thin films with preferred orientation were made using a flash evaporation method followed by annealing in hydrogen ambient. The magnitude of the strain in the thin films was analyzed by X-ray diffraction (XRD), and then the transport properties were estimated at room temperature. In particular, the thermal conductivity of the thin films was measured using a 3ω method. Finally, we compared the lattice thermal conductivity derived from the model with the experimental results.

2. Experimental

Bismuth antimony telluride thin films were fabricated on glass substrates (size: 50 mm × 50 mm, 1.1 mm thick) using a flash evaporation method. The detailed experimental setup has been described elsewhere [18,19]. Briefly, the starting material for the flash evaporation was spherical-shaped bismuth antimony telluride powder ($Bi_{0.4}Sb_{1.6}Te_{3.0}$) with an average powder size of 200 μm prepared by a centrifugal atomization method [20]. Inside the flash evaporation chamber, the distance between the tungsten boat and the substrate was 200 mm. After the chamber was evacuated to 1.4×10^{-3} Pa, a current of 80 A was applied to the tungsten boat until the substrate temperature reached 200 °C. By gradually tilting the powder vessel, the powders were fed onto the tungsten boat, which evaporated the powder on the glass substrate. The thickness of the thin films was approximately 190 nm with an accuracy of ±10 nm. Next, hydrogen annealing was performed. The samples were placed in an electric furnace that was evacuated to 1.0 Pa and purged five times with high-purity (99.999%) argon gas. The furnace was then filled with hydrogen gas at atmospheric pressure, with the hydrogen gas flow rate maintained at 0.3 standard liter per minute throughout the annealing process. The annealing conditions were at temperatures ranging from 200 to 350 °C for 30 min. The temperature was steadily increased at 5 K/min to the required temperature. After annealing, the samples were allowed to cool naturally to room temperature. Finally, the adhesion of the samples was checked by a tape delamination test to confirm that the thin films had good contact with the substrate.

The crystal structures of the thin films, including the crystal orientation, average grain size, and lattice parameters, were analyzed by XRD (XRD apparatus: PHILIPS X'Pert, X-ray source: Cu–Kα). The surface and cross-plane morphologies were investigated using scanning electron microscopy (SEM) (SEM apparatus: Hitachi S4500, operation voltage: 15 kV). The atomic composition was estimated by energy dispersive X-ray spectroscopy (EDX) (EDX apparatus: Horiba EMAX-5770W, operation voltage: 15 kV) with an accuracy of ±3%.

The in-plane electrical conductivity of the thin films was measured at room temperature by a four-point probe method with an accuracy of ±3%. The in-plane Seebeck coefficient was also measured at room temperature with an accuracy of ±5%. To determine the Seebeck coefficient, one end of the thin film was connected to a heat sink and the other end to a heater. The Seebeck coefficient was calculated as the ratio of the potential difference along the film to the temperature difference. The cross-plane thermal conductivity was determined at room temperature by the 3ω method with an accuracy of ±10% [21]. Details of the thermal conductivity measurement and the sample fabrication process for the 3ω method have been described in previous publications [22–24]. In brief, a SiO_2 film (700 nm thick) was deposited on the bismuth antimony telluride thin film at a low deposition rate (0.12 nm/s) by a sputtering method. A thin aluminum wire was deposited on the sample by electron beam evaporation through shadow masks. The thin aluminum wire was 20 μm wide and the length of the heater part was