Enhancement of Thermoelectric Performance by using nano-structures

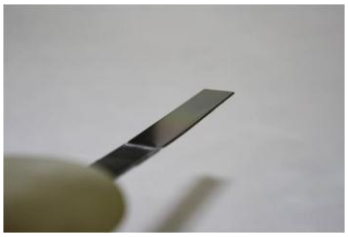
Koji Miyazaki
Department of Mechanical and Control Engineering
Kyushu Institute of Technology
Sensui-cho 1-1, Tobata-ku, Kitakyushu 804-8550 Japan

Abstract

Thermoelectricity is the direct conversion of thermal energy to electrical energy. The performance of thermoelectric materials is characterized by the dimensionless figure-of-merit, ZT, which is defined as $ZT=S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, and κ is the thermal conductivity. Here, we made a porous thin film of $Bi_{0.4}Te_3Sb_{1.6}$ with extremely low thermal conductivity. The measured enhanced figure of merit of 1.8 at room temperature The reduction in thermal conductivity was rationalized using a model for the full distribution of the phonon mean free path in the film.

The heat conduction of nano-structured materials is currently receiving the greatest attention in the thermoelectric energy conversion. Semiconductor nanowires[1], semiconductors with embedded nanostructures[2], and semiconductor superlattices[3,4] are under intense investigation for the promise of enabling practical systems with significantly higher efficiencies for the conversion of heat to electrical power. In this study, we fabricated $Bi_{0.4}Te_{3.0}Sb_{1.6}$ nano-porous thin films on anodized porous alumina[5] by a flash deposition method[6], and measured their thermoelectric properties. The in-plane electrical conductivity and Seebeck coefficient are measured, and the cross-plane thermal conductivity was measured by a pico-second thermoreflectance method[7], at room temperature. Furthermore, we calculated phonon MFPs and a normalized cumulative thermal conductivity by using the kinetic theory ($\kappa_L=Cv_gL/3$), where C is the specific heat used Debye model, v_g is group velocity, L is the phonon MFP used impurity scattering and umlkapp scattering. The reduction in therml conductivity was rationalized using the model of the full distribution of the phonon mean free

(a)



(b)

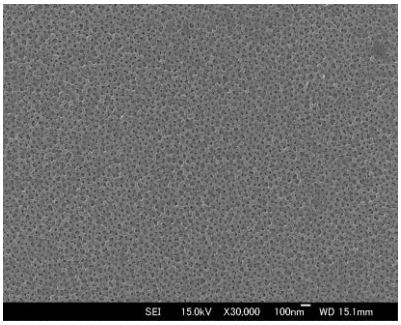


Fig.1 Porous thin film of $Bi_{0.4}Te_{3.0}Sb_{1.6}$ (a) $Bi_{0.4}Te_{3.0}Sb_{1.6}$ thin film on porous alumina substrate (b) SEM image

Table 1 Thermoelectric properties of $Bi_{0.4}Te_{3.0}Sb_{1.6}$

	Porous thin film	Thin Film[6]	Bulk
Seebeck Coefficient, μV	198	252	200
Electrical Conductivity, S/cm	398	550	800
Thermal Conductivity, W/(m·K)	0.25	1.0	2.3
ZT at 300K	1.8	1.0	0.6

path.

We made a porous thin film o f bismuth antimony telluride ($Bi_{0.4}Te_3Sb_{1.6}$) on porous alumina substrate as shown in Fig.1. The thickness of the $Bi_{0.4}Te_3Sb_{1.6}$ film was 100 nm while that of the porous alumina was 1 μm. The average diameter of the holes was 20 nm, and the average pitch of the hexagonally arranged holes was 50 nm. The packing density was 78%.

The thermoelectric properties of the porous $Bi_{0.4}Te_3Sb_{1.6}$ thin film were measured at room temperature, and are compared with parameters for typical $Bi_{0.4}Te_3Sb_{1.6}$ thin films in Table 1. The in-plane electrical conductivity σ of the porous film was measured at room temperature by a four-point probe method with the accuracy of ±3%. The measured value is proportional to the packing density of the material, which can be explained by the conventional model related to the diffusive transport of electrons. The mean free path of electrons is roughly calculated to be 30nm. The in-plane Seebeck coefficient S was also measured at room temperature with accuracy of ±5%. One end of the thin film is connected to a heat sink and the other end to a heater. The Seebeck coefficient is determined as the ratio of the potential difference (ΔV) along the films to the temperature difference (ΔT). The thermal conductivity of the sample was 0.25 W/(m·K), which was measured by the picosecond thermoreflectance method with a fitting error of 0.05W/(m·K) assuming the specific heat of bulk $Bi_{0.4}Te_3Sb_{1.6}$.[7] Although the cross-plane thermal conductivity of the film was determined in the present study, the in-plane thermal conductivity is considered to be in the same order as that of the cross-plane. Cross-plain and in-plain thermal conductivities of nanostructured materials are usually both reduced by strong phonon scattering.[8,9] The measured thermal conductivity is in the same order as the theoretical minimum value because long-range phonon transport is suppressed by the porous structure.

A model using a full distribution was employed to describe the phonon mean free path in the porous thin film.[10] The lattice thermal conductivity is expressed as

$$\kappa_L = \frac{1}{3}\int C v_g L d\omega, \qquad (1)$$

where ω is the angular frequency, C is the specific heat per unit frequency by using Debye model, v_g is the group velocity by using a sinusoidal model, and L is the effective phonon MFP which can be divided into terms of impurity/alloy scattering and umklapp scattering:

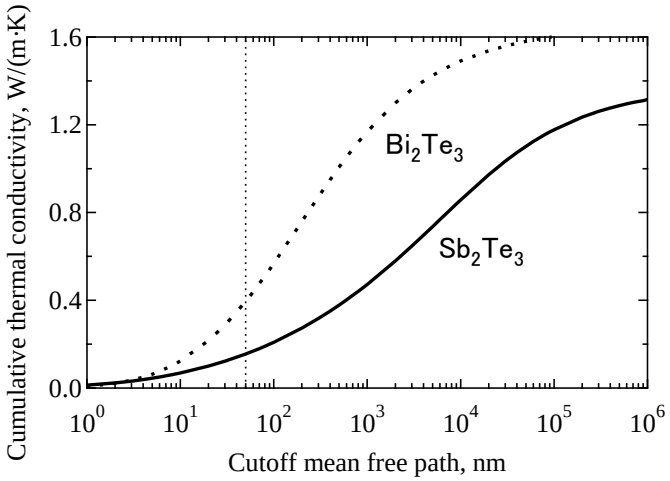


Fig.2 Cumulative thermal conductivity of Bi_2Te_3 and Sb_2Te_3

$$L^{-1}(\omega,T) = L_{impurity}{}^{-1}(\omega) + L_{umklapp}{}^{-1}(\omega,T)\cdot \qquad (2)$$

Impurity scattering is calculated using impurity scattering $L_{impurity}{}^{-1}=A_1\omega^4/v_s$, where v_s is the sound velocity, A_1 is a fitting parameter which may also be estimated from other properties. For umklapp scattering, we use $L_{umklapp}{}^{-1}=B_1\omega^2 T\exp(-B_2/T)/v_s$, where B_1 and B_2 are fitting parameters. We find fitting parameters of Bi_2Te_3 are A_1= 1.3 x 10^{-42} s^3, B_1=1.1 x 10^{-18} s/K, and B_2= 120 K and of Sb_2Te_3 A_1= 1.2 x 10^{-41} s^3, B_1=4.4 x 10^{-19} s/K, and B_2= 120 K. The distribution function κ_L for the thermal conductivity per unit mean free path was calculated. The cumulative thermal conductivity $\kappa(l)$ calculated by phonons with a mean free path between 0 and l:

$$\kappa(l) = \int_0^l \kappa_L dL \qquad (3)$$

where l is the cutoff mean free path, was plotted. The cumulative thermal conductivities of Bi_2Te_3 and Sb_2Te_3 as a function of the mean free path are depicted in Fig.2. When the cutoff mean free path is greater than 100 μm, the cumulative thermal conductivities of Bi_2Te_3 and Sb_2Te_3 reach approximately that of a single crystal. The cumulative thermal conductivity is reduced as the cutoff mean free path decreases. The experimental result 0.25 W/(m·K) thermal conductivity is fairly similar to the calculated value 0.155 W/(m·K) for the model at a cutoff mean free path of 50 nm. Here, the cutoff mean free path was assumed according to the average pore spacing. The significant reduction of the thermal conductivity is caused by significant scattering of long-range phonons by the pores in the thin film.

In conclusions, nano-porous thin film is proposed as the nano-structure to enhance the performance of thermoelectricity. By making nano-porous structure with the size between electron and phonon mean free path (MFP), it is possible to decrease phonon transport more than electron transport.

Acknowledgement

This work was supported by the New Energy and Industrial Technology Development Organization (NEDO). The authors wish to thank Dr. Saburo Tanaka for discussion of mean free path calculations, Prof. Chihaya Adachi and Dr. Shuzo Hirata for making nano-porous alumina, and Dr. Kazuko Ishikawa for thermal conductivity measurements.

1) A.I. Hochbaum, R. Chen, R.D. Delgado, W. Liang, E.C. Garnett, M. Najarian, A. Majumdar, and P. Yang: Nature **451** ,163(2008).
2) K.F. Hsu, S. Loo, W. Chen, J. S. Dyck, C. Uher, T. Hogan, E.K.Polychroniadis, and M.G. Kanatzidis: Science **303**, 818 (2004).
3) R.Venkatasubramanian, E. Siivola, T. Colpitts, and B. O'Quinn: Nature **413**, 597 (2001).
4) T.C. Harman, P.J. Taylor, M.P.Walsh, and B.E. LaForge: Science **297** , 2229 (2002).
5) H. Masuda, and M. Satoh: Jpn. J. Appl. Phys **35**, L126 (1996).
6) M. Takashiri, S. Tanaka, M. Takiishi, M. Kihara, K. Miyazaki, and H. Tsukamoto: J. Alloys Compd. **462**, 351(2008).
7) N Taketoshi, T Baba, and A. Ono, Rev. Sci. Instrum. 76, 094903 (2005).
8) W. K. Liebmann, and E. A. Miller, J. Appl. Phys. 34, 2653 (1963).
9) G. Chen, C. L. Tien, X. Wu, and J. S. Smith, J. Heat Trans. 116, 325 (1994).
10) C. Dames, and G. Chen, J. Appl. Phys. 95, 682 (2004).