Demonstration of Performance Improvement in Nanostructured Si-Ge Thermoelectric Materials Utilizing Novel Co-doping Technique

Masahiro ADACHI*, Kotaro HIROSE, Yoshiyuki YAMAMOTO, and Tsunehiro TAKEUCHI

Thermoelectric generation that directly converts waste heat into useful electric power has attracted considerable attention as one of the most efficient techniques leading to a low carbon, sustainable society. For automobile exhaust heat power generation, the figure of merit (*ZT*) of thermoelectric materials, which parameterizes the efficiency of energy conversion, needs to be more than 4, but at present it is considered to be extremely difficult to reach. We are conducting research and development to overcome this issue by modulating the electronic structure of materials, that is, with precise control of nanostructures. By controlling nanostructures, we have succeeded in lowering the thermal conductivity of conventional Si-Ge thermoelectric materials to 1/7 and improved their materials figure of merit. In this study, in order to improve the performance even further, we propose a unique technique called a co-doping method (modulating electronic structures with doped Au and controlling the Fermi level with doped B). With this method, we have achieved $ZT = 1.38$, which is the best result for the same materials of the same type.

Keywords: thermoelectric material, nanostructure, co-doping, linear response theory

1. Introduction

To build a sustainable society, it is necessary to reduce fossil fuel consumption and carbon dioxide emissions. Thermoelectric materials convert temperature differences (thermal energy) to power (electric energy) using waste heat. They attract attention as technologies used to improve the efficiency of energy use. Thermoelectric conversion efficiency is an increasing function of the dimensionless materials figure of merit*1 *ZT*. Therefore, strong demand exists for improved *ZT* to achieve high efficiency. At present, *ZT* remains between 1 and 2 (conversion efficiency is approximately 10% when $ZT = 1$), while it is necessary to achieve $ZT \geq 4$ for automobiles to recover waste heat as power for improved fuel efficiency.[1] Accordingly, when developing a thermoelectric material, the issue is to control *ZT*. *ZT* comprises the following physical quantities, as expressed below.

$$ZT = S^2\sigma T/\kappa = S^2\sigma T/(\kappa_{ele} + \kappa_{lat}) \quad \cdots\cdots (1)$$

where, S is the Seebeck coefficient,*2 σ is the electrical conductivity, T is the absolute temperature, κ is the thermal conductivity, κ_{ele} is the electron thermal conductivity, and κ_{lat} is the lattice thermal conductivity.[2] Among properties that need to be controlled, we worked on the lattice thermal conductivity. We made it possible to reduce it to 1.1 W/mK (from the previous 8 W/mK) by fabricating nanostructures*3 measuring approximately 5 nm in an amorphous material.[3],[4] The other controllable factors are the Seebeck coefficient, electrical conductivity, and electron thermal conductivity. These are known to be determined by electronic structures such as the density of states near the Fermi level. (It is necessary to control the Fermi level to ensure the electronic structure $< \pm 3k_BT$, where k_B is Boltzmann's constant.)[5],[6] Accordingly, if it becomes possible to form a characteristic artificial electronic structure near the Fermi level, an effective means will be created for improved thermoelectric characteristics.

Techniques for controlling electronic structures have been proposed that modulate the density of states by means of nanostructures, such as quantum wells, quantum wires, and quantum dots.[7]–[10] However, no significant improvement in *ZT* has been reported.[10]–[16] Reasons include that the position of the Fermi level is not controlled with respect to the formed electronic structure and that the number of states*4 that contributes to electronic transport is inherently small. (For example, a 1 nm quantum dot accommodates only two electrons, i.e. 0.05 electron/atom. This number of states is too small, by an order of magnitude, to contribute to electronic transport.)

To overcome this challenge, we noted transition metals with d-orbitals to form a new level that has a sufficient number of states. Transition metals with d-orbitals when used as a dopant at a few percent are expected to form a new level with a number of states of a few electrons per atom. Meanwhile, because the solid solubility of a doped element is low to single crystals, we noted amorphous materials with the aim of increasing the solid solubility. Incidentally, in general, thermoelectric materials with a non-uniform density of states (band gap) show good characteristics. Therefore, an amorphous silicon-germanium (Si-Ge) material was selected as the base material due to its characteristics to generate a band gap despite its amorphous nature.

This paper reports on our achievements using amorphous Si-Ge: in order to form a new level, amorphous Si-Ge was doped with gold (Au), a transition metal with d-orbitals, moreover, to control the Fermi level, doped with boron (B). This co-doping technique demonstrated improved material properties and achieved the world's highest[17]–[24] materials figure of merit $ZT = 1.38$ compared with the same materials of the same type.

2. Fabrication Method

A molecular-beam epitaxy system was used to make a film, on a sapphire substrate at room temperature, of alternating layers of approximately 1 nm Si, approximately 1 nm Ge, 0.1 nm Au, and approximately 1 nm Ge, for a total film thickness of 220 nm.

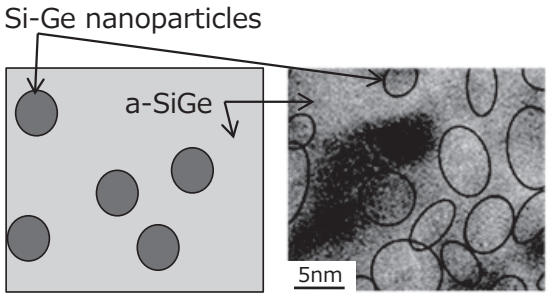

Fig. 1. Image of nanostructured Si-Ge thermoelectric material

Additionally, B was supplied during the film formation process and controlled to 3 atomic (at) %. The fabricated thin-film specimens were subjected to heat treatment at 300°C for 15 min or at 500°C for 15 min to disperse Si-Ge nanoparticles (single crystals a few nanometers in dimension) into amorphous (a-)Si-Ge, as illustrated in Fig. 1. Doped Au and B were dispersed in the amorphous material and the nanoparticles.

The Seebeck coefficient was estimated through measurement of the thermos-electromotive force generated when a thermal gradient of a few Kelvins was applied at both ends of the specimen. The electric conductivity was measured by the four-terminal method. The thermal conductivity was measured by the thermo-reflectance method (pico-TR). The materials figure of merit *ZT* was estimated based on the measured Seebeck coefficient, electric conductivity, and thermal conductivity.

3. Calculation of Electronic Structures

First, suitable transition metals were explored through first-principle calculations. The calculation was made using Si as the base material for the sake of simplification. (Si and Ge make up a complete solid solution and form a diamond structure throughout the composition range, exhibiting very high affinity. Meanwhile, mixed Si-Ge crystals take an enormous number of atomic position configurations, requiring a very long calculation time before getting an overview of the results. Therefore, we determined that the use of Si as the base material for the calculation would be appropriate for an overview.) The calculation used the full-potential linearized augmented plane-wave in generalized gradient approximation (FLAPW-GGA) method implemented in Wien2K. This paper refrains from showing the calculation results for all transition metal elements since space does not permit. Based on the linear response theory,[5] we determined that Au would be promising as a dopant element with the potential to improve the materials figure of merit.

Next, we conducted first-principle calculations of plural proportions of Au to ascertain the position of the level formed by Au and its density of states and to understand likely suitable proportions of Au (Fig. 2). Figure 2 reveals sharp formation, within the band gap, of a level derived from Au at an approximate proportion of Au of 1 at%. At higher proportions of gold, a broad level was formed because of 4d-orbital overlaps. According to the linear response theory, to improve the materials figure of merit, it is necessary to form a sharp level with a high number of states near the Fermi level. The calculations revealed that doping of Au at a few percent was sufficient for improving materials performance.

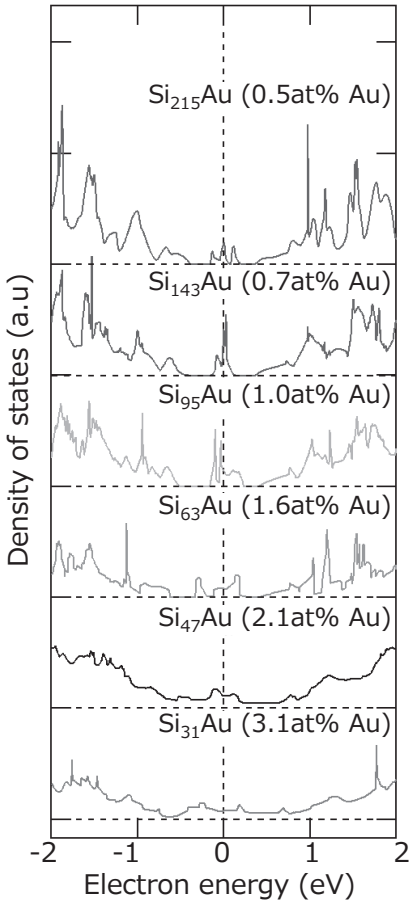

Fig. 2. Density of states of Si:Au calculated by first-principle calculations

4. Improving Materials Figure of Merit by Co-doping Technique

The next step was to dope the specimen with B in addition to Au, with the aim of controlling the Fermi level. Figure 3 shows the dependence of the materials figure of merit *ZT* on the proportion of Au, using the doping level of B as a parameter. The doping levels of B shown on the graph are 0 at% and 3 at%. The materials figure of merit *ZT*

was calculated on the assumption that the thermal conductivity would be constant even at elevated temperatures. (This assumption is more or less valid because the electric conductivity of the specimen decreasing with temperature makes the contribution of the electron thermal conductivity negligible.) Both curves representing two doping levels of B exhibit finite maximum values with respect to the proportion of Au. The materials figure of merit *ZT* was 0.9 for doping levels of 3 at% for B and 0 at% for Au, which is almost equal to the maximum value of p-Si-Ge reported.[18] By contrast, co-doping of Au and B, with the doping level of Au being a few atomic percent notably allowed several specimen to exhibit $ZT > 1$ with good reproducibility. The result is clearly owing to the effect of co-doping with Au and B. We demonstrate that the performance of the thermoelectric material remarkably improved because B controlled the Fermi level to be near the new level attributed to Au.

The highest materials figure of merit, $ZT = 1.38$, appeared at 1,100 K. The Seebeck coefficient, electric conductivity, and thermal conductivity were 170 μV/K, 4,780 S/m, and 1.09 W/mK, respectively. This materials figure of merit is the world's highest when compared with the same materials of the same type, proving the effectiveness of the novel co-doping technique advocated here.

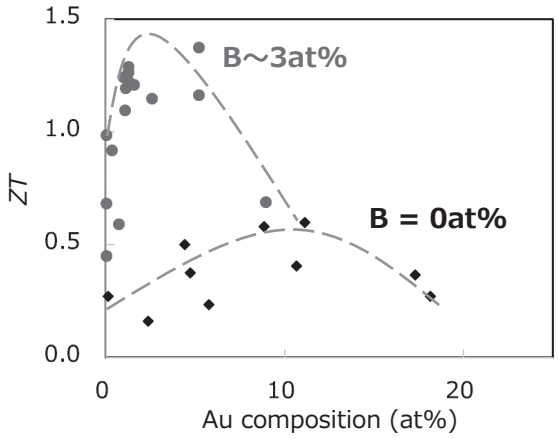

Fig. 3. Dependence of materials figure of merit *ZT* (maximum value) on composition of Au

Finally, the new level formed by Au will be explained. Figure 4 presents the optical absorption characteristics of thin Si-Ge films using doping level of Au as a parameter. The graph reveals that in the proximity of 1 eV, the absorption signal increased with increasing doping level of Au. This suggests that, as predicted through first-principle calculations, dopant Au formed an impurity level in the band gap. Thermoelectric performance can vary and improve when a new level is formed by Au near the Fermi level, in line with our proposal based on the linear response theory. As a future, we plan to measure the new level with an ultra-high-resolution photoelectron spectrometer to clarify detailed electronic structures.

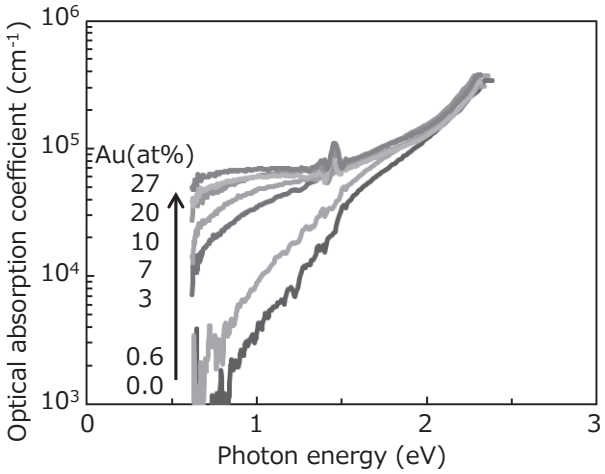

Fig. 4. Optical absorption coefficient characteristics of Si-Ge:Au

5. Conclusion

This paper proposed a novel co-doping technique based on the linear response theory with the aim of achieving high materials performance. More specifically, our proposal is to form a new level by doping Au and control the Fermi level by doping B. Our findings are as follows.

Co-doping of Au and B into Si-Ge demonstrated the world's highest materials figure of merit $ZT = 1.38$ (at 1,100 K) compared with the same materials of the same type. It is highly likely that this materials figure of merit is attributable to the formation of a new level by Au and control of the Fermi level by B.

We propose the present co-doping technique as a method with the potential of remarkably improving the performance of thermoelectric materials. Theoretically, this technique is applicable to other thermoelectric materials as well. Our future plan is to additionally improve the performance of thermoelectric materials by following the theory and adjusting electronic structures, and to apply our materials to waste heat power generation.

6. Acknowledgments

This study was partially conducted under a project commissioned by the New Energy and Industrial Technology Development Organization (NEDO). We acknowledge Professor Okamoto of the National Defense Academy of Japan for his valuable suggestions and support in this R&D work.

Technical Terms

∗1 Dimensionless figure of merit, *ZT*: A dimensionless quantity used to represent the thermoelectric conversion performance (efficiency) of a material. Thermoelectric conversion efficiency ζ is given by the following equation:

$$\zeta = \frac{T_h - T_l}{T_h} \frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+T_l/T_h}$$

where, T_h and T_l are the higher and lower temperatures, respectively, and T is $(T_h + T_l)/2$. This equation shows that thermoelectric efficiency ζ increases monotonically as ZT increases. This means that increasing ZT is essential to the development of a thermoelectric material.

∗2 Seebeck coefficient: An intrinsic physical quantity of a material, which represents its voltage generation characteristic under a temperature difference. Assuming a temperature difference of ΔT generates a voltage of ΔV between the hot and cool points of the material, its Seebeck coefficient is then calculated as $-\Delta V/\Delta T$.

∗3 Nanostructure: A structure composed of crystals a few nanometers in size. The presence of crystal structures inhibits heat propagation and therefore is expected to control the thermal conductivity to low levels.

∗4 Number of states: A number that expresses how many electrons can be accommodated at a level where electrons can exist; the number of accommodated electrons; integration of the density of states with respect to energy. The higher the number of states, the greater the influence on the electron transport.

References

(1) http://www.nedo.go.jp/activities/ZZJP_100097.html
(2) A. F. Ioffe, Semiconductor Thermoelements and Thermoelectric Cooling (Infosearch Limited, London, 1957), pp. 1–35
(3) M. Adachi, S. Fujii, M. Kikyama, Y. Yamamoto, and T. Takeuchi, SEI Tech. Rev. No.84 April (2017) 151
(4) S. Nishino, S. Ekino, M. Inukai, M. Omprakash, M. Adachi, M. Kiyama, Y. Yamamoto, and T. Takeuchi, J. Elec. Mat. 47 (2018) 3267
(5) T. Takeuchi, Mater. Trans. 50 (2009) 2359
(6) N. F. Mott and H. Jones, The Theory of the Properties of Metals and Alloys (Clarendon Press, Oxford, 1960), pp. 308–314
(7) L. D. Hicks, and M. S. Dresselhaus, Phys. Rev. B 47 (1993) 12727
(8) L. D. Hicks, and M. S. Dresselhaus, Phys. Rev. B 47 (1993) 16631
(9) L. D. Hicks, Dr thesis (1996)
(10) M. S. Dresselhaus, G. Chen, M. Y. Tang, R. Yang, H. Lee, D. Wang, Z. Ren, J. P. Fleurial, and P. Gogna, Adv. Mater. 19 (2007) 1043
(11) S. Yamasaka, K. Watanabe, S. Sakane, S. Takeuchi, A. Sakai, K. Sawano, and Y. Nakamura, Scientific Reports 6 (2016) 22838
(12) X. Hu, P. Jood, M. Ohta, M. Kunii, K. Nagase, H. Nishiate, M. G. Kanatzidis, A. Yamamoto, Ene. & Env. Sci.9 (2016) 517
(13) N. T. Hung, E. H. Hasdeo, A. R. T. Nugraha, M. S. Dresselhaus, and R. Saito, Phys. Rev. Lett. 117 (2016) 036602-1
(14) G. Chen, M. S. Dresselhaus, G. Dresselhaus, J. P. Fleurial, and T. Caillat, Int. Mat. Rev. 48 (2003) 45
(15) M. S. Dresselhaus, M. Y. Lin, B. S. Cronin, O. Rabin, M. R. Black, G. Dresselhaus, T. Koga, Semicond. Semimet. 71 (2001) 1
(16) C. Chang, C. Qin, A. Makino, A. Inoue, J. Alloy. Comp. 533 (2012) 67
(17) G. Joshi, H. Lee, Y. Lan, X. Wang, G. Zhu, D. Wang, R. W. Gould, D. C. Cuff, M. Y. Tang, M. S. Dresselhaus, G. Chen, and Z. Ren, Nano Lett. 8 (2008) 4670
(18) G. Joshi, H. Lee, Y. Lan, X. Wang, G. Zhu, D. Wang, R.W. Gould, D. C. Cuff, M. Y. Tang, M. S. Dresselhaus, G. Chen, and Zhifeng Ren, Nano Letters 8 (2008) 4670
(19) M. Zebarjadi, G. Joshi, G. Zhu, B. Yu, A. Minnich, Y. Lan, X. Wang, M. S. Dresselhaus, Z. Ren, and G. Chen, Nano letters 11 (2011) 2225
(20) T. Koga, S. B. Cronin, M. S. Dresselhaus, J. L. Liu, and K. L. Wang, Appl. Phys. Lett., 77 (2000) 1490
(21) T. Koga, Dr. theisis, Havard Uni. (2000)
(22) A. Samarelli, L. Ferre Llin, S. Cecchi, J. Frigerio, T. Etzelstorfer, E. Müller, Y. Zhang, J. R. Watling, D. Chrastina, G. Isella, J. Stangl, J. P. Hague, J. M. R. Weaver, P. Dobson, and D. J. Paul1, J.App.Phys. 113 (2013) 233704
(23) L. Ferre Llin, A. Samarelli, S. Cecchi, T. Etzelstorfer, E. Müller Gubler, D. Chrastina, G. Isella, J. Stangl, J. M. R. Weaver, P. S. Dobson, and D. J. Paul, App. Phys. Lett. 103 (2013) 143507
(24) F. Schaffler: "in Properties of Advanced Semiconductor Materials GaN, AlN, InN, BN, SiC, SiGe., (Eds. Levinshtein M.E., Rumyantsev S.L., Shur M.S., John Wiley & Sons, Inc., New York, 2001), p. 149

Contributors

The lead author is indicated by an asterisk (∗).

M. ADACHI*
• Doctor of Engineering
Group Manager, Transmission Devices Laboratory

K. HIROSE
• Transmission Devices Laboratory

Y. YAMAMOTO
• Department Manager, Transmission Devices Laboratory

T. TAKEUCHI
• Doctor of Engineering
Professor, Toyota Technological Institute