First-principles calculation of electronic density of states and Seebeck coefficient in transition-metal-doped Si–Ge alloys

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High ZT value and large Seebeck coefficient have been reported in the nanostructured Fe-doped Si–Ge alloys. In this work, the large Seebeck coefficient in Fe-doped Si–Ge systems is qualitatively reproduced from the computed electronic density of states, where a hybrid functional, HSE06, is used for an exchange-correlation functional, as well as a special quasi-random structure (SQS) for a disordered atomic configuration. Furthermore, by replacing Fe with other transition metals, such as Mn, Co, Ni, Cu, Zn, and Au, a better dopant that produces a larger Seebeck coefficient in Si–Ge alloy systems is explored.

A vast amount of available energy has been wasted as heats, and it is expected that thermoelectric materials are employed to extract electricity from wasted-heats. Si–Ge alloys are known as one of the cheapest nontoxic thermoelectric materials utilized at high temperatures. The dimensionless figure of merit, ZT, of Si–Ge alloys, however, is quite small; ZT < 1 for both p- and n-type thermoelectric materials [1].

The small ZT values in Si–Ge alloys have been somewhat improved with the use of a nanostructuring approach, where a phonon conductivity is reduced by making a grain size small. To further increase the ZT values of Si–Ge alloys, there are some attempts to modify their electronic band structure by doping transition metals [2–4], and it has been reported that a quite high ZT value, ZT > 1.88 (at T = 873 K), was obtained in the nanostructured Si0.55Ge0.45Fe0.10 sample, as well as a large Seebeck coefficient, |S| > 517 μV/K (at T = 673 K) [2]. It is believed that the large Seebeck coefficient originated from a strong peak at the edge of the conduction band in the electronic density of states generated by the Fe-doping (a so-called 3d impurity state), and this large Seebeck coefficient increased the ZT value through the relation, ZT ∝ S². Although high ZT values as well as large Seebeck coefficients have also been observed in other transition-metal-doped Si–Ge alloys, such as Au- [3] and Ni-doped systems [4], their ZT values and Seebeck coefficients were not as high as those of the Fe-doped system.

Although an occurrence of the 3d impurity states have been confirmed in an Fe-doped Si system using an electronic band structure calculation [2], that in Fe-doped Si–Ge system has not been confirmed yet either from an experimental or theoretical approach. In this work, therefore, the electronic density of states in Fe-doped Si–Ge alloys is calculated using an electronic band structure calculation, and the reported large Seebeck coefficient is reproduced from the computed electronic density of states of states. In addition, by substituting Fe with other transition metal (TM=Mn, Co, Ni, Cu, Zn, or Au), a better dopant for Si–Ge alloys that produces a larger Seebeck coefficient than that of Fe-doped systems is sought.

Si–Ge alloy forms a single solid solution over the whole composition range [5], and it has been reported that the nanostructured Si0.55Ge0.45Fe0.10 sample sintered at 873 K and 400 GPa was also composed of a single solid solution [2]. To describe a disordered configuration in a solid solution, a special quasi-random structure (SQS) [6, 7] is employed here, which is the best periodic supercell to mimic the true disordered configuration using a small number of particles.

A SQS, which contains 64 atoms with a diamond structure (2 × 2 × 2), is searched using mcsqs code available in the Alloy Theoretic Automated Toolkit (ATAT) [8]. The following criterion is used to determine the SQS: pair correlation functions of SQS become nearly identical to those of the random alloy up to the third-nearest neighbors. The following alloy compositions are considered here; Si0.50Ge0.484Fe0.016 (or Si32Ge31Fe1) and Si0.781Ge0.219Fe0.016 (or Si30Ge13Fe1) for Fe-doped systems, and Si0.50Ge0.484TM0.016 (or Si32Ge31TM1) for TM-doped ones, where TM=Mn, Co, Ni, Cu, Zn, and Au from either 3d or 5d transition metals.

The electronic density of states of the SQSs is calculated using the projector augmented-wave (PAW) method [9] as implemented in the Vienna Ab Initio Simulation Package (VASP). Since it was confirmed that magnetic moments disappear during the electronic self-consistent-loop for all the transition-metal-doped systems, a non-spin-polarization calculation is conducted in this work. As an exchange-correlation functional, a hybrid functional introduced by Heyd, Scuseria, and Ernzerhof (HSE) [10] is employed, setting the range-separation parameter to 0.207 Å⁻¹ (known as HSE06...
The total energy of the supercell is minimized in terms of the volume, and their atomic positions are optimized until all force components are smaller than 0.01 eV/Å. The plane wave cut-off energy is set to 350 eV, and the integration over the Brillouin zone is done, using Gaussian smearing of 0.05 eV with \(2 \times 2 \times 2\) and \(6 \times 6 \times 6\) \(k\)-points for the structure relaxation and density of states calculations, respectively. Note that the equilibrium volume of the non-doped system is used for those of the doped systems, assuming that the volume change by doping is negligible; i.e., the equilibrium volume of \(\text{Si}_{0.50}\text{Ge}_{0.50}\) (or \(\text{Si}_{32}\text{Ge}_{32}\)) and \(\text{Si}_{0.78}\text{Ge}_{0.21}\) (or \(\text{Si}_{50}\text{Ge}_{14}\)) are used for those of \(\text{Si}_{0.50}\text{Ge}_{0.48}\text{Fe}_{0.016}\) (\(\text{Si}_{0.50}\text{Ge}_{0.48}\text{TM}_{0.016}\)) and \(\text{Si}_{0.78}\text{Ge}_{0.203}\text{Fe}_{0.016}\) systems, respectively.

It is noteworthy that because a Seebeck coefficient is quite sensitive to the magnitude of a band gap, the use of a hybrid functional (HSE06) is important to evaluate the Seebeck coefficient in the doped Si–Ge alloys reliably. The band gap in the Si–Ge systems, as well as lattice constant, calculated using the HSE06 and generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) [12] are compared in supplementary data. It is shown that HSE06 can reliably estimate both the band gap and lattice constant of the Si–Ge system compared to the GGA/PBE functional (see figures in supplementary data).

The Seebeck coefficient, \(S\), is defined as a constant of proportionality between the electric field, \(\mathbf{E}\), and temperature gradient, \(\Delta T\); i.e., \(\mathbf{E} = S\Delta T\). The Seebeck coefficient is given from the linear response theory as [13]

\[
S(T) = -\frac{1}{|e|T} \int_{-\infty}^{\infty} \frac{\sigma(\epsilon, T)(\epsilon - \mu)}{\sigma(\epsilon, T)} \left( \frac{\partial f_D(\epsilon, T)}{\partial \epsilon} \right) d\epsilon,
\]

where \(\epsilon\) is the unit charge of electron, \(\mu\) is the chemical potential, \(\epsilon\) is the energy, \(f_D(\epsilon, T)\) is the Fermi-Dirac distribution, and \(\sigma(\epsilon, T)\) is the spectral conductivity. From the Bloch-Boltzmann theory, the spectral conductivity for an isotropic material is written as

\[
\sigma(\epsilon, T) = \frac{e^2}{3} D(\epsilon) \nu^2(\epsilon) \tau(\epsilon, T),
\]

where \(D(\epsilon)\) is the electronic density of states, \(\nu(\epsilon)\) is the group velocity, and \(\tau(\epsilon, T)\) is the relaxation time.

For a nanostructured bulk sample, an electron mean-free path, \(l (= \nu \tau)\), can be approximated to a nanograin size, \(a\) (i.e., \(\nu \tau \approx a\)) (a so-called small-grain-size limit [14, 15]). Then, the Seebeck coefficient, Eq. (1), becomes

\[
S(T) \approx -\frac{1}{|e|T} \int_{-\infty}^{\infty} \frac{D(\epsilon)\nu(\epsilon)(\epsilon - \mu)}{D(\epsilon)\nu(\epsilon)} \left( \frac{\partial f_D(\epsilon, T)}{\partial \epsilon} \right) d\epsilon.
\]

Furthermore, by assuming that the group velocity, \(\nu(\epsilon)\), is not sensitive to energy (i.e., \(\nu(\epsilon) \approx \nu\)), Eq. (3) can be simplified to

\[
S(T) \approx -\frac{1}{|e|T} \int_{-\infty}^{\infty} D(\epsilon)(\epsilon - \mu) \left( \frac{\partial f_D(\epsilon, T)}{\partial \epsilon} \right) d\epsilon.
\]
FIG. 1. Calculated electronic density of states in the (a) Si$_{0.500}$Ge$_{0.484}$Fe$_{0.016}$ and (b) Si$_{0.781}$Ge$_{0.203}$Fe$_{0.016}$ alloys. The black solid line is the total density of states, and the red dash, blue dotted, and green dash-dotted lines indicate the partial density of states of Si, Ge, and Fe, respectively.

FIG. 2. Calculated Seebeck coefficients in the Si$_{0.500}$Ge$_{0.484}$Fe$_{0.016}$ (solid line) and Si$_{0.781}$Ge$_{0.203}$Fe$_{0.016}$ (broken line) alloy systems. The experimental data measured in the nanostructured Si$_{0.62}$Ge$_{0.31}$Au$_{0.04}$B$_{0.03}$ sample [3] are also shown in Fig. 4. Compared to the experimental data, the calculated Seebeck coefficients in the Au-doped system are significantly underestimated at high temperatures. The main reason of this discrepancy would be the existence of a secondary phase in the measured sample [3]. In addition, the difference in the alloy compositions between the calculation and experiments is also considered to be the cause of the discrepancy. Since band gap of Si is larger than that of Ge, it is expected that band gap is increased by increasing the fraction of Si in the calculated Au-doped system, which will result in the increase of Seebeck coefficient at high temperatures.

The calculated Seebeck coefficient in the TM-doped systems are shown in Fig. 4, where the result of the Fe-doped system (the same result shown in Fig. 2) is presented as well. Depending on the value of the Fermi energy, $\mu_0$, the TM-doped systems show either $p$- or $n$-type thermoelectric characteristics. Here, the $\mu_0$ is set to either the end of valence or conduction band depending on the position of the impurity states. From Fig. 4, the magnitude of the Seebeck coefficients of the Co-, Ni-, Cu-, Zn-, and Au-doped systems are smaller than that of Fe-doped system, but the Mn-doped system shows larger Seebeck coefficient than that of the Fe-doped system at high temperatures (400 $\sim$ 1000 K), as expected from their calculated electronic density of states.

The experimentally measured Seebeck coefficients in the nanostructured Si$_{0.62}$Ge$_{0.31}$Au$_{0.04}$B$_{0.03}$ sample [3] are also shown in Fig. 4. Compared to the experimental data, the calculated Seebeck coefficients in the Au-doped system are significantly underestimated at high temperatures. The main reason of this discrepancy would be the existence of a secondary phase in the measured sample [3]. In addition, the difference in the alloy compositions between the calculation and experiments is also considered to be the cause of the discrepancy. Since band gap of Si is larger than that of Ge, it is expected that band gap is increased by increasing the fraction of Si in the calculated Au-doped system, which will result in the increase of Seebeck coefficient at high temperatures.
FIG. 4. Calculated Seebeck coefficients in the Si$_{0.50}$Ge$_{0.48}$TM$_{0.016}$ alloys (TM=Mn, Fe, Co, Ni, Cu, Zn, and Au). The Fermi energies used in the calculations, $\mu_0$, are provided in the legend (the unit is eV). The experimental data measured in the nanostructured Si$_{0.62}$Ge$_{0.31}$Au$_{0.04}$B$_{0.03}$ sample for the heating/cooling condition are shown together as open/filled orange squares [3].

From the calculated Seebeck coefficients, it is expected that the Mn-doping is better than the Fe-doping for the Si–Ge alloy system. However, the ZT value depends not only on the Seebeck coefficient but also on the electrical resistivity, $\rho$, as $ZT = S^2T/\rho\kappa$, where $\kappa$ is the thermal conductivity. In general, the electrical resistivity is increased with the band gap. Thus, the electrical resistivity (as well as the thermal conductivity) needs to be evaluated to conclude whether the Mn-doped system is better thermolectric materials than the Fe-doped system or not.

Note that it is assumed that the doped transition metals occupy substitutional sites, but it is uncertain whether they are located at substitutional or interstitial sites. To make clear their preferred sites from density functional theory, their formation energies need to be calculated and compared. However, this is beyond the scope of this paper and is left for future work.

In conclusion, the electronic density of states and Seebeck coefficient in the TM-doped Si–Ge systems (TM=Mn, Fe, Co, Ni, Cu, Zn, and Au) were investigated from the first-principles calculations with a hybrid functional (HSE06) using disordered configurations prepared based on the SQS. The impurity states in the Fe-doped Si–Ge systems were successfully produced, and the reported large Seebeck coefficients in the nanostructured Si$_{0.55}$Ge$_{0.35}$P$_{0.10}$Fe$_{0.01}$ sample were quantitatively reproduced from the computed electronic density of states. Using the same methodology, the electronic density of state and Seebeck coefficient of other TM-doped Si–Ge systems (TM=Mn, Co, Ni, Cu, Zn, and Au) were calculated. It was found that Mn-doping produces strong impurity states at the bottom of conduction band, and the Seebeck coefficient is larger than that of the Fe-doped system at high temperatures. Thus, Mn is considered to be a better dopant for the Si–Ge systems from the perspective of the Seebeck coefficient.

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[1] D. M. Rowe, CRC handbook of thermoelectrics (CRC press, 1995).
[2] K. Delime-Codrin, M. Omprakash, S. Ghodke, R. Sobota, M. Adachi, M. Kiyama, T. Matsuura, Y. Yamamoto, M. Matsunami, and T. Takeuchi, Applied Physics Express 12, 045507 (2019).
[3] M. Omprakash, K. Delime-Codrin, S. Ghodke, S. Singh, S. Nishino, M. Adachi, Y. Yamamoto, M. Matsunami, S. Harish, M. Shimomura, and T. Takeuchi, Japanese Journal of Applied Physics 58, 125501 (2019).
[4] T. Takeuchi, private communication.
[5] R. W. Olesinski and G. J. Abbashian, Journal of Phase Equilibria 5, 180 (1984).
[6] A. Zunger, S.-H. Wei, L. G. Ferreira, and J. E. Bernard, Physical Review Letters 65, 353 (1990).
[7] S.-H. Wei, L. G. Ferreira, J. E. Bernard, and A. Zunger, Physical Review B 42, 9622 (1990).
[8] A. Van de Walle, P. Tiwary, M. De Jong, D. L. Olmsted, M. Asta, A. Dick, D. Shin, Y. Wang, L.-Q. Chen, and Z.-K. Liu, Calphad 42, 13 (2013).
[9] G. Kresse and J. Furthmüller, Computational Materials Science 6, 15 (1996).
[10] J. Heyd, G. E. Scuseria, and M. Ernzerhof, The Journal of chemical physics 118, 8207 (2003).
[11] A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, and G. E. Scuseria, The Journal of chemical physics 125, 224106 (2006).
[12] J. P. Perdew, K. Burke, and M. Ernzerhof, Physical review letters 77, 3865 (1996).
[13] N. F. Mott and H. Jones, The Theory of the Properties of Metals and Alloys, Oxford (1936).
[14] C. Bera, M. Soulier, C. Nuvone, G. Roux, J. Simon, S. Volf, and N. Mingo, Journal of Applied Physics 108, 124306 (2010).
[15] Q. Hao, D. Xu, N. Lu, and H. Zhao, Physical Review B 93, 205206 (2016).
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SUPPLEMENTARY DATA

The lattice constant and band gap in the Si–Ge alloys are calculated using a hybrid functional (HSE06) or GGA/PBE functional, and their results are compared in this supplementary data. The calculated equilibrium lattice constant and energy band gap are, respectively, shown in Figs. 1 and 2, where the same calculation conditions described in the main article are employed. From the calculated results, it can be seen that HSE06 can predict both the lattice constant and band gap in the Si–Ge alloys much more reliably than the GGA/PBE functional.

FIG. 1. Calculated equilibrium lattice constant in the Si(1−x)–Ge x alloys using HSE06 (red line) or GGA/PBE functional (black line). The experimental data are shown together as open circles [1].

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[1] J. P. Dismukes, L. Ekstrom, and R. J. Paff, The Journal of Physical Chemistry 68, 3021 (1964).
[2] C. Kittel and H. Kroemer, Thermal physics (2nd edition), Vol. 9690 (Wiley New York, 1980).
FIG. 2. Estimated band gap in the Si$_{(1-x)}$Ge$_x$ alloys using HSE06 (red line) or GGA/PBE functional (black line). The experimental data in pure Si and Ge are shown together as open circles [2].