



Title	First-principles calculation of electronic density of states and Seebeck coefficient in transition-metal-doped Si-Ge alloys
Author(s)	Yamada, Ryo; Masago, Akira; Fukushima, Tetsuya; Shinya, Hikari; Nguyen, Tien Quang; Sato, Kazunori
Citation	Solid state communications, 323, 114115 https://doi.org/10.1016/j.ssc.2020.114115
Issue Date	2021-01
Doc URL	http://hdl.handle.net/2115/86964
Rights	©2021. This manuscript version is made available under the CC-BY-NC-ND 4.0 license http://creativecommons.org/licenses/by-nc-nd/4.0/
Rights(URL)	http://creativecommons.org/licenses/by-nc-nd/4.0/
Type	article (author version)
File Information	doped-Si-Ge_RYamada_2020.pdf



[Instructions for use](#)

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

Ryo Yamada^{1*}, Akira Masago², Tetsuya Fukushima³, Hikari Shinya^{2,4}, Tien Quang Nguyen⁵, and Kazunori Sato^{1,2**}

¹*Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan*

²*Center for Spintronics Research Network (CSRN), Osaka University, Toyonaka, Osaka 560-8531, Japan*

³*Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan*

⁴*Research Institute of Electrical Communication, Tohoku University, Sendai, Miyagi 980-8577, Japan*

⁵*Institute for NanoScience Design, Osaka University, Toyonaka, Osaka 560-8531, Japan*

* ryamada@eng.hokudai.ac.jp; Present address: Division of Materials Science and Engineering, Faculty of Engineering, Hokkaido University, Sapporo, Hokkaido 060-8628, Japan

** ksato@mat.eng.osaka-u.ac.jp

Abstract

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 was qualitatively reproduced from the computed electronic density of states, where a hybrid functional, HSE06, was 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 dopant that produces a large Seebeck coefficient in Si–Ge alloy systems was explored. It was found that the Mn-doped system produces a large Seebeck coefficient comparable with the Fe-doped system.

Keywords: first-principles calculation, Si–Ge alloys, Seebeck coefficient

1. Introduction

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 [1]. The dimensionless figure of merit, ZT , of Si–Ge alloys, however, is quite small; $ZT < 1$ for both p - and n -type thermoelectric materials [2].

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 have been some attempts to modify their

electronic band structure by doping transition metals [1,3,4], and it has been reported that a quite high ZT value, $ZT > 1.88$ (at $T = 873$ K), was obtained in the nanostructured $\text{Si}_{0.55}\text{Ge}_{0.35}\text{P}_{0.10}\text{Fe}_{0.01}$ sample, as well as a large Seebeck coefficient, $|S| > 517 \mu\text{V/K}$ (at $T = 673$ K) [1]. 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, $ZT \propto S^2$. 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- and Ni-doped systems [3,4], their ZT values and Seebeck coefficients were not as high as that of the Fe-doped system.

Although an occurrence of the $3d$ impurity states has been confirmed in an Fe-doped Si system using an electronic band structure calculation [1], 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. In addition, by substituting Fe with other transition metals (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.

2. Theory

2.1. Electronic density of states

Si–Ge alloy forms a single solid solution over the whole composition range [5]. To describe this material, a special quasi-random structure (SQS) is employed to mimic its true disordered configuration using a small number of particles [6,7] as is done in Ref. [8,9]. In this work, a 64-atom SQS with a diamond structure ($2 \times 2 \times 2$) is searched using *mcsqs* code from the Alloy Theoretic Automated Toolkit [10]. Two alloy compositions are considered here: $\text{Si}_{0.500}\text{Ge}_{0.484}\text{TM}_{0.016}$ and $\text{Si}_{0.500}\text{Ge}_{0.484}\text{TM}_{0.016}$.

Electronic structure calculations are performed using the projector augmented-wave [11] method as implemented in the Vienna *Ab Initio* Simulation Package (VASP). For exchange-correlation interaction, a HSE06 hybrid functional [12,13] is used. The plane-wave cut-off energy is set to 350eV and the Brillouin zone is sampled using $2 \times 2 \times 2$ and $6 \times 6 \times 6$ k -points for structure relaxation and density of states calculations, respectively. The k -grid has been chosen carefully to ensure that the total energy and band gap calculations are converged within 2 meV per atom and 5 meV, respectively. All SQSs are fully relaxed until atomic force components are smaller than 0.01 eV/Å. 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 in a cubic lattice: the equilibrium volume of $\text{Si}_{0.500}\text{Ge}_{0.500}$ (or $\text{Si}_{32}\text{Ge}_{32}$), $V = 5.5480^3 \text{ \AA}^3$, and $\text{Si}_{0.781}\text{Ge}_{0.219}$ (or $\text{Si}_{50}\text{Ge}_{14}$), $V = 5.4757^3 \text{ \AA}^3$, are used for those of $\text{Si}_{0.500}\text{Ge}_{0.484}\text{TM}_{0.016}$ and $\text{Si}_{0.781}\text{Ge}_{0.203}\text{TM}_{0.016}$, respectively.

Note that a Seebeck coefficient is quite sensitive to the magnitude of a band gap. Because an experimentally reported band gap has been relatively well-reproduced using the HSE06 functional [14] compared with generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof

(PBE) [15], the use of the HSE06 functional is important to reliably evaluate the Seebeck coefficient in the doped Si–Ge alloys. It is also notable that there are multiple possible atomic configurations which satisfy the criteria used in the determination of SQSs, but here we will investigate just one atomic configuration as a first attempt.

2.2. Seebeck coefficient

The Seebeck coefficient, S , is given from the linear response theory as [16]

$$S(T) = -\frac{1}{|e|T} \frac{\int_{-\infty}^{\infty} \sigma(\epsilon - \mu)(\epsilon - \mu) \left(\frac{\partial f_{\text{FD}}(\epsilon, T)}{\partial \epsilon} \right) d\epsilon}{\int_{-\infty}^{\infty} \sigma(\epsilon - \mu) \left(\frac{\partial f_{\text{FD}}(\epsilon, T)}{\partial \epsilon} \right) d\epsilon}, \quad (1)$$

where e is the unit charge of electron, μ is the chemical potential, ϵ is the energy, $f_{\text{FD}}(\epsilon, T)$ is the Fermi-Dirac distribution, and $\sigma(\epsilon - \mu)$ is the spectral conductivity. From the Bloch–Boltzmann theory, the spectral conductivity for an isotropic material is written as

$$\sigma(\epsilon - \mu) = \frac{e^2}{3} D(\epsilon) v^2(\epsilon) \tau(\epsilon, T), \quad (2)$$

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

For a nanostructured bulk sample, an electron mean-free path, $l (= v\tau)$, may be approximated to a nanograin size, a (i.e., $v\tau \approx a$) (a so-called small-grain-size limit [17,18]). Then, the Seebeck coefficient, Eq. (1), becomes

$$S(T) \approx -\frac{1}{|e|T} \frac{\int_{-\infty}^{\infty} D(\epsilon) v(\epsilon) (\epsilon - \mu) \left(\frac{\partial f_{\text{FD}}(\epsilon, T)}{\partial \epsilon} \right) d\epsilon}{\int_{-\infty}^{\infty} D(\epsilon) v(\epsilon) \left(\frac{\partial f_{\text{FD}}(\epsilon, T)}{\partial \epsilon} \right) d\epsilon}. \quad (3)$$

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

$$S(T) \approx -\frac{1}{|e|T} \frac{\int_{-\infty}^{\infty} D(\epsilon) (\epsilon - \mu) \left(\frac{\partial f_{\text{FD}}(\epsilon, T)}{\partial \epsilon} \right) d\epsilon}{\int_{-\infty}^{\infty} D(\epsilon) \left(\frac{\partial f_{\text{FD}}(\epsilon, T)}{\partial \epsilon} \right) d\epsilon}. \quad (4)$$

From Eq. (4), the Seebeck coefficient for a nanostructured bulk sample can be roughly estimated from an electronic density of states. Note that the chemical potential, μ , depends on temperature through the relation: $n = \int_0^{\infty} D(\epsilon) f_{\text{FD}}(\epsilon, T) d\epsilon$, where n is the number of electrons in a system.

It is noteworthy that Eq. (4) is obviously a first approximation, because in general the group velocity, v , highly depends on energy and this dependence cannot be neglected for a reliable estimation of Seebeck coefficients. In a solid solution, such as Si–Ge alloys, however, it is not easy to calculate the group velocity, $v \left(= \frac{1}{\hbar} \frac{\partial E}{\partial k} \right)$, because the dispersion relation (or E – k curve) is blurred due to the disorder nature of alloy system. For a SQS, on the other hand, it would be possible to calculate the energy dependence of group velocity because a clear dispersion relation can be obtained, however, it is not a “real” electronic structure of disordered configuration. In this work, therefore, the energy dependence of group velocity was just ignored. We focus only on the density of states, which is well defined for the disordered systems, and employ Eq. (4) to “qualitatively” evaluate the Seebeck coefficients.

3. Results and Discussions

3.1. Fe-doped Si–Ge systems

The calculated electronic density of states in the $\text{Si}_{0.500}\text{Ge}_{0.484}\text{Fe}_{0.016}$ alloy is shown in Fig. 1, where their site-projected density of states of Si, Ge, and Fe are also presented. Here, the Fermi level is shifted so that it is located at the bottom of conduction band. From this result, one can see that there are two strong peaks mainly originating from the Fe-doping at the edge of the conduction band. The same strong peaks were observed in the $\text{Si}_{0.781}\text{Ge}_{0.203}\text{Fe}_{0.016}$ alloy as well (see supplemental material). A similar impurity state has been reported in the $\text{Si}_{0.993}\text{Fe}_{0.007}$ (or $\text{Si}_{143}\text{Fe}_1$) alloy system [1], where its electronic density of states was calculated using density functional theory with the GGA/PBE functional.

The Seebeck coefficient calculated from Eq. (4) using the total density of states shown in Fig. 1 is presented in Fig. 2, where various amounts of carrier (or electron) concentration, n , are considered: n is in a range from 1.0×10^{18} to $1.0 \times 10^{20} \text{ cm}^{-3}$. It can be seen that the Seebeck coefficient gets smaller as n is increased for the both alloy compositions (see supplemental material for the result in the $\text{Si}_{0.781}\text{Ge}_{0.203}\text{Fe}_{0.016}$ alloy). The experimental data for the nanostructured $\text{Si}_{0.55}\text{Ge}_{0.35}\text{P}_{0.10}\text{Fe}_{0.01}$ sample are also shown in Fig. 2. One can see that the calculated Seebeck coefficients are close to the experimental data [1] when $n = 1.0 \times 10^{18} - 5.0 \times 10^{18} \text{ cm}^{-3}$. This amount of electron concentration is much smaller than the experimentally measured value, $1.24 \times 10^{19} \text{ cm}^{-3}$ [1]. There are some possible reasons for this discrepancy, such as that we ignored the energy dependence of group velocity in this work. Another possible reason would be that we assumed that the doped Fe occupies a substitutional site. However, in fact, it is uncertain whether it is located at a substitutional or interstitial site. To make clear its preferred site from density functional theory, their formation energy needs to be calculated and compared, but this is beyond the scope of this paper and is left for future work.

3.2. Other TM-doped Si–Ge systems

Next, electronic density of states and Seebeck coefficient in other transition-metal-doped systems are presented. The calculated electronic density of states in the $\text{Si}_{0.500}\text{Ge}_{0.484}\text{TM}_{0.016}$ alloy systems is shown in Fig. 3. Similar to Fig. 1, the Fermi level is shifted so that it is located either at the top of valence band or the bottom of conduction band. From Fig. 3, the impurity state

originating from the TM-doping can be seen at the bottom of the conduction band in the Mn-doped system, whereas those in other TM-doped systems are at the top of the valence band. (Although there is no band gap in the Co-doped system, we still use the terms, valence and conduction bands, to make discussion easy). In this work, the transition metals are doped into SiGe SQS supercell at substitutional sites. Due to this, some bonds between Si, Ge atoms are broken and/or there is bond/anti-bond formation between the transition metal and host atoms. In addition, the local structure around the transition metal is re-constructed. As we can see in Fig. 3, the partial DOSs of Si and Ge slightly changed, especially in the energy range where appears the partial DOS of transition metal. The change of partial DOSs of Si and Ge are self-consistently calculated and included in the calculations of Seebeck coefficients.

To obtain a large Seebeck coefficient, it is important to have not only a sharp peak at the end of either valence or conduction band, but also a large band gap (as can be seen in the Fe-doped system, Fig. 1). Because our primary focus in this work is to investigate an effect of transition-metal-doping on electronic density of states as well as Seebeck coefficient, only Seebeck coefficients at either conduction band or valence band side (which corresponds to electron or hole doping) are shown here, depending on the position of the impurity: an electron doping for the Mn-doped system, and a hole doping for Co-, Ni-, Cu-, Zn-, and Au-doped systems. Because the band gap in the Mn-doped system is larger than that in the Fe-doped one (see Fig. 1) and there are large impurity states, it is expected that the Mn-doped system has a large Seebeck coefficient. For the other TM-doped systems, on the other hand, their band gap is smaller than that in the Fe-doped system, and cannot be expected to have a large Seebeck coefficient.

The calculated Seebeck coefficients in the TM-doped systems are shown in Fig. 4 for various carrier concentrations. From Fig. 4, the magnitude of the Seebeck coefficients of the Co-, Ni-, Cu-, Zn-, and Au-doped systems are smaller than that of the Fe-doped system (see Fig. 2), but that in the Mn-doped system is as large as that of the Fe-doped system, as expected from their calculated electronic density of states.

From Figs. 3 and 4, it is clear that as the atomic number for the 3d transition metals is increased (from Mn to Zn), the position of 3d impurity states is shifted to the lower energy side, which affects the magnitude of the Seebeck coefficients. For the Mn- and Fe-doped systems, 3d-bands are located at the bottom of the conduction band resulting in the large Seebeck coefficients. For the Co- and Ni-doped systems, on the other hand, 3d-bands have appeared in the middle of the energy gap of Si-Ge alloy, which leads small Seebeck coefficients. For the Cu- and Zn-doped systems, the positions of 3d-bands are further shifted to a low energy side, and band gaps are somewhat increased compared with those of Co- and Ni-doped systems, which produce a relatively large Seebeck coefficient.

The experimentally measured Seebeck coefficients in the nanostructured $\text{Si}_{0.62}\text{Ge}_{0.31}\text{Au}_{0.04}\text{B}_{0.03}$ sample for $n = 4.19 \times 10^{19} \text{ cm}^{-3}$ [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 for the all hole concentrations considered here. 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. Because a 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.

Note that only one SQS for each impurity type is considered in this work. We confirmed that impurity peak positions in the electronic density of states do not change significantly, but their magnitudes vary a little among various SQSs. In addition, it has been suggested that 64-atomic site supercells are sufficient for the convergence of structural parameters and energy in Si-Ge alloy systems [9]. For transition metal doped systems with small doping concentration investigated in this work, the same trend should be expected.

4. Conclusion

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 $\text{Si}_{0.55}\text{Ge}_{0.35}\text{P}_{0.10}\text{Fe}_{0.01}$ sample were quantitatively reproduced from the computed electronic density of states. Using the same methodology, the electronic density of state and Seebeck coefficient in other TM-doped Si-Ge systems were calculated. It was found that Mn-doping produces strong impurity states at the bottom of conduction band, and the Seebeck coefficient becomes as large as that of the Fe-doped system. Thus, Mn may be considered as a promising dopant for the Si-Ge systems as well as Fe from the perspective of the Seebeck coefficient.

Acknowledgements

This work was supported by Japan Science and Technology Agency (JST) Core Research for Evolutional Science and Technology (CREST), Grant Number: JPMJCR18I2.

References

- [1] 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).
- [2] D. M. Rowe, *CRC handbook of thermoelectrics* (CRC press, 1995).
- [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 (2019).
- [5] R. W. Olesinski and G. J. Abbaschian, *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] P. Venezuela, G. M. Dalpian, A. J. R. da Silva, and A. Fazzio, *Physical Review B* 64, 193202 (2001).
- [9] A. Chroneos, H. Bracht, C. Jiang, B. P. Uberuaga, and R. W. Grimes, *Physical Review B* 78, 195201 (2008).
- [10] 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).
- [11] G. Kresse and J. Furthmüller, *Computational Materials Science* 6, 15 (1996).
- [12] J. Heyd, G. E. Scuseria, and M. Ernzerhof, *The Journal of chemical physics* 118, 8207 (2003).
- [13] A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, and G. E. Scuseria, *The Journal of chemical physics* 125, 224106 (2006).
- [14] L. Schimka, J. Harl, and G. Kresse, *The Journal of Chemical Physics* 134, 024116 (2011).
- [15] J. P. Perdew, K. Burke, and M. Ernzerhof, *Physical Review Letters* 77, 3865 (1996).
- [16] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys*, Oxford (1936).
- [17] C. Bera, M. Soulier, C. Navone, G. Roux, J. Simon, S. Volz, and N. Mingo, *Journal of Applied Physics* 108, 124306 (2010).
- [18] Q. Hao, D. Xu, N. Lu, and H. Zhao, *Physical Review B* 93, 205206 (2016).

Figures

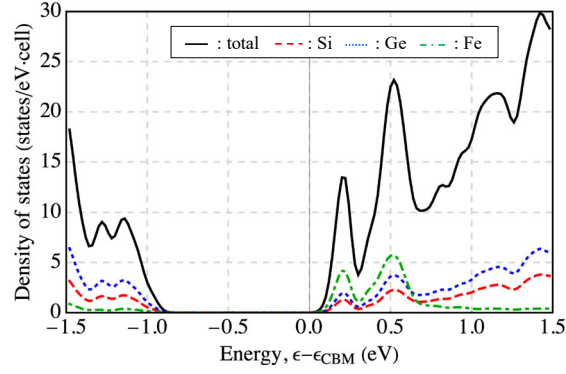


Fig. 1. (Color) Calculated electronic density of states of the $\text{Si}_{0.500}\text{Ge}_{0.484}\text{Fe}_{0.016}$ alloy. The black solid line is the total density of states, and the red dash, blue dotted, and green dash-dotted lines indicate the site-projected density of states of Si, Ge, and Fe, respectively.

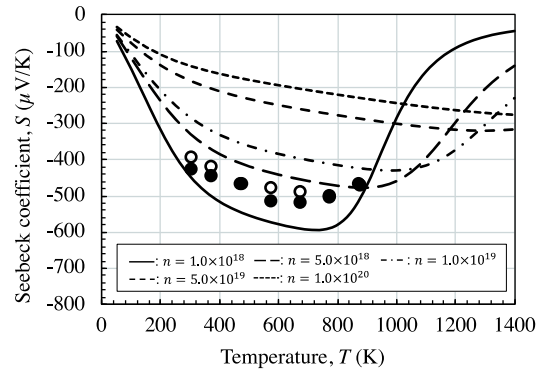


Fig. 2. Calculated Seebeck coefficients in the $\text{Si}_{0.500}\text{Ge}_{0.484}\text{Fe}_{0.016}$ alloy system for various electron concentrations. The experimental data measured in the nanostructured $\text{Si}_{0.55}\text{Ge}_{0.35}\text{P}_{0.10}\text{Fe}_{0.01}$ sample for the heating/cooling condition are also provided as open/filled circles [1].

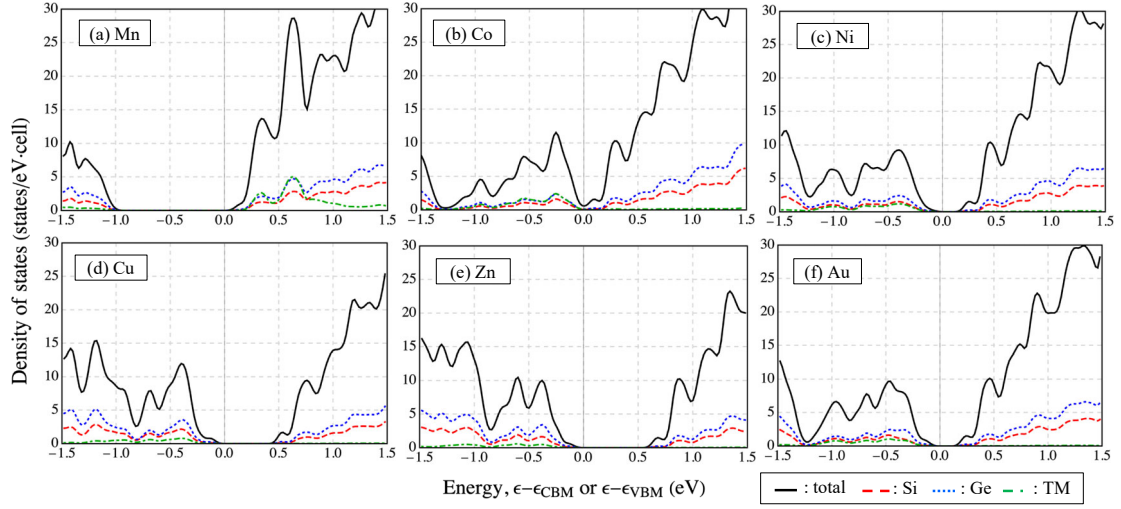


Fig. 3. (Color) Calculated electronic density of states of the $\text{Si}_{0.500}\text{Ge}_{0.484}\text{TM}_{0.016}$ alloy systems, where (a) Mn-, (b) Co-, (c) Ni-, (d) Cu-, (e) Zn-, and (f) Au-doped systems. The black solid lines are the total density of states, and the red dash, blue dotted, and green dash-dotted lines indicate the site-projected density of states of Si, Ge, and TM, respectively.

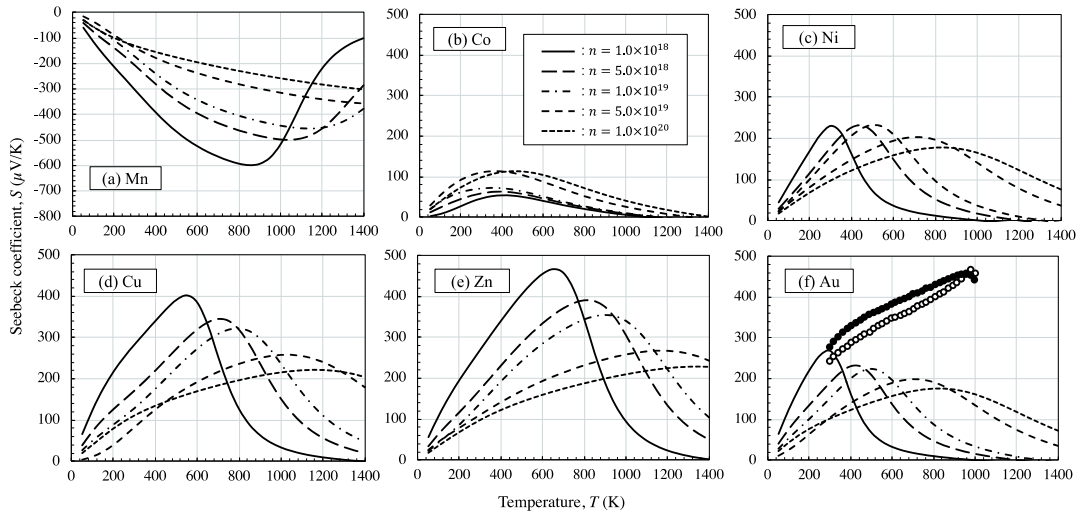


Fig. 4. Calculated Seebeck coefficients in the $\text{Si}_{0.500}\text{Ge}_{0.484}\text{TM}_{0.016}$ alloy systems for various carrier concentrations, n , where (a) Mn-, (b) Co-, (c) Ni-, (d) Cu-, (e) Zn-, and (f) Au-doped systems. The experimental data measured in the nanostructured $\text{Si}_{0.62}\text{Ge}_{0.31}\text{Au}_{0.04}\text{B}_{0.03}$ sample for the heating/cooling condition are shown together as open/filled orange squares [3].