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Supplementary Information

Anomalous enhancement of thermoelectric power factor by themal management with resonant level effect

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Thermal management in composite materials.

In general, in composite materials, temperature gradient is developed mostly across low thermal conductivity parts (namely, high thermal resistance (R) parts), as written in Ref. S1. In our composite materials, material A with high Seebeck coefficient (S) has much lower κ (higher R) than that of material B with high electrical conductivity (σ). As a result, temperature difference (ΔT) is mostly applied to material A, not material B, as shown by the equivalent thermal circuit in Fig. S1. As a result, high S of material A mainly contributes as effective S of entire composites, and effective σ of entire material is increased by introduction of material B with high σ, leading to high thermoelectric power factor (thermal management). In our composite materials, resonant level effect happens in material A (SiGe with Au) leading to high S of material A. This $S^2\sigma$ enhancement method is "thermal management with resonant level effect".

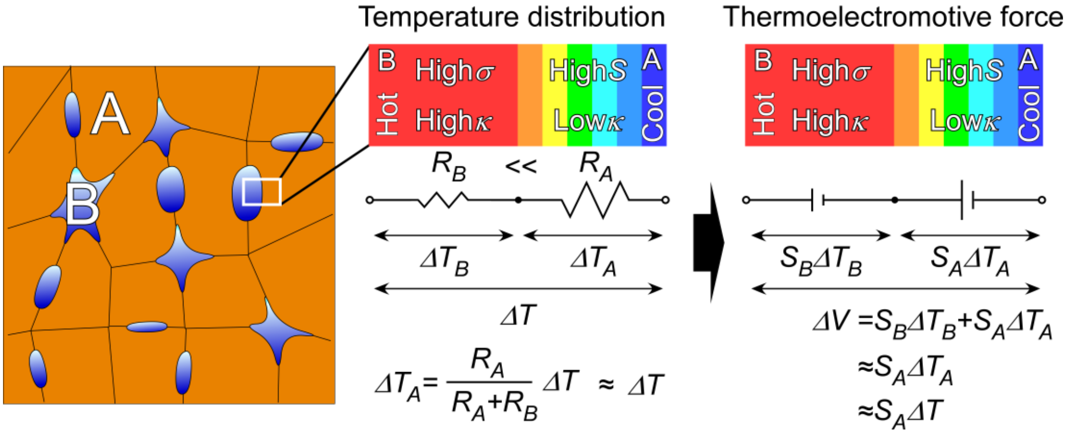

Fig. S1. The schematic illustration of thermal management of composite material.

Density of states calculation of SiGe crystals with different distributions of Ge atoms.

Ge atoms are randomly distributed in lattice sites of SiGe crystals. We calculated density of states (DOS) of SiGe with different distributions of Ge atoms by preparing the 4x4x4 unit cell of the diamond structure where Si atoms randomly substitute with Ge atoms. Fig. S2 shows typical DOS calculation results of SiGe with different distribution of Ge atoms. It was found that the changing spatial distribution and the number of the Ge atoms does not affect the DOS significantly.

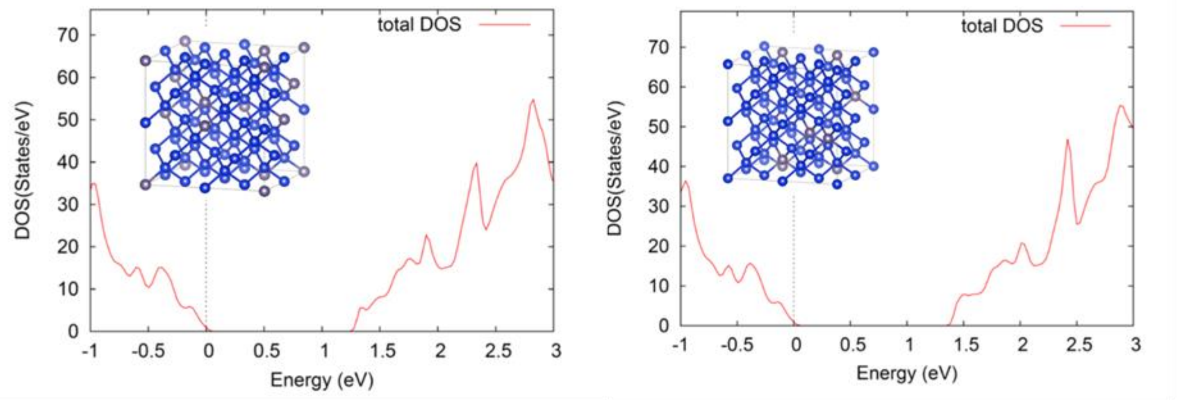

Fig. S2 DOS of SiGe crystals with different distributions of Ge atoms. Insets show the corresponding supercells of the SiGe crystals. Blue (Gray) circle represents the Si (Ge) atom.

Density of states calculation of SiGeAu.

The two nearest neighbor Au atoms form resonant level near conduction band bottom in SiGe as shown in the main text. Now, to confirm that it is not absolutely necessary that the two Au atoms locate at the nearest neighbor sites for forming the resonant level, we calculated the DOS by using a model of two Au atoms positioned a little apart as shown in Fig. S3(a). The Au atom locates at the center of the supercell and another Au atom locates at the next nearest neighbor site in SiGe. The calculated DOS in Fig. S3(b) indicates that the resonant revel is formed in SiGe by the two Au atoms which are not positioned at the nearest neighbor sites. It should be noted that resonant energy level formed by these Au atoms was found even in the lattice site far from Au atoms, as shown by the arrows in Fig. S3(b). This indicates that the hybridization between Au atom state and SiGe state spatially spreads to some extent. Therefore, the situation of dilute Au impurities, which form resonant energy level, is statistically possible.

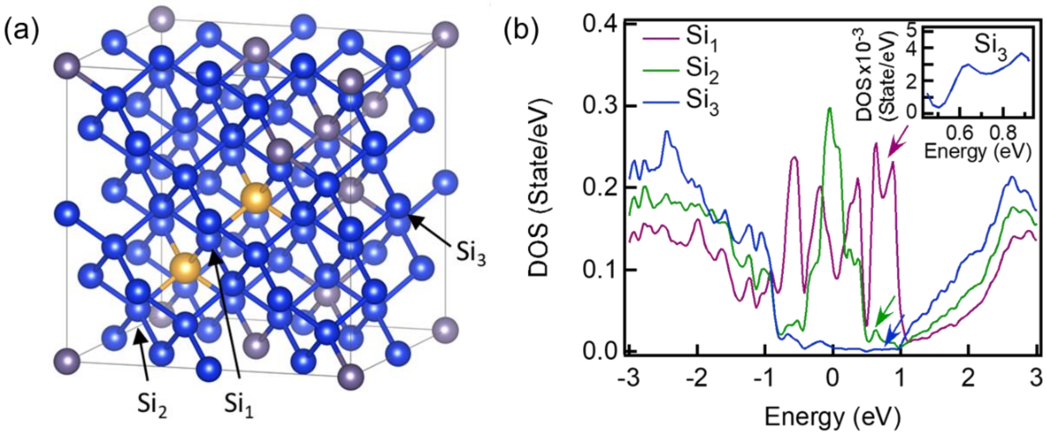

Fig. S3 DOS calculation by using a model of two separate substitutional Au atoms. (a) Supercell of the SiGeAu. (b) DOS at the various positions of Si atoms. As shown in (a), Si_1 locates between Au atoms, Si_2 is the neighbor of the Au atom and Si_3 is far from the Au atom. In (a), blue, gray and gold circles represent the Si, Ge and Au atoms, respectively. In (b), the inset shows enlarged DOS of Si_3 in the region indicated by the blue arrow. This state is not observed in SiGe without Au atoms.

Structural characterization of SiGe parts by HRTEM.

In this study, we investigated the structures of P-doped SiGeAu samples by high resolution transmission electron microscopy (HRTEM) microscopically. The schematic illustration of P-doped SiGeAu is shown in Fig. S4(a). The region near the interface between SiGe/Au is displayed in Fig. S4(b). The upper black and lower white regions represent Au and SiGe parts, respectively. In the enlarged image of SiGe parts (Fig. S4(c)) corresponding to the rectangular region in Fig. S4(b), nanograins (dashed circles) were observed in the polycrystalline SiGe parts relatively close to Au parts. From the above results, we confirmed the structures of P-doped SiGeAu samples including SiGe nanograins in the polycrystalline SiGe parts, as shown in the illustration in Fig. S4(a).

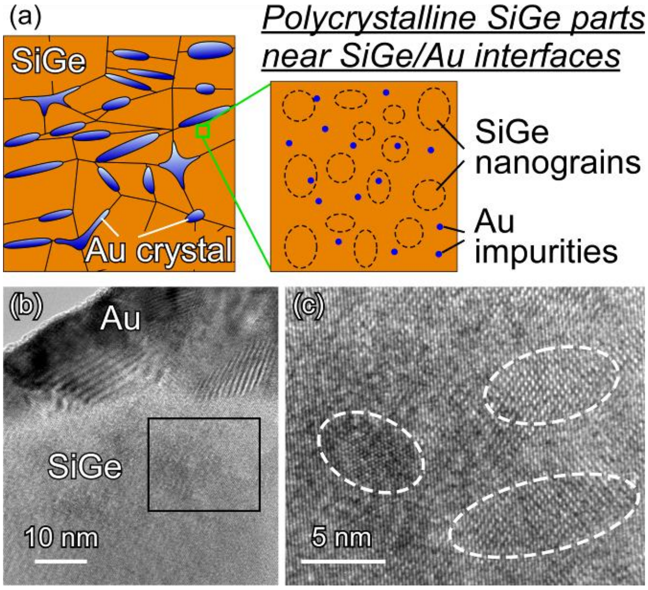

Fig. S4. (a) The schematic illustration of the structure in SiGeAu samples. (b) The HRTEM image near the interface between SiGe/Au in P-doped SiGeAu sample. (c) The enlarged image corresponding to the rectangular region in the polycrystalline SiGe parts of (c). In (c), dashed circles represent SiGe nanograins.

The mass density and relative mass density of P-doped SiGeAu and SiGe samples.

The mass density of each sample was estimated from each sample's geometry and mass. We showed the mass density and the relative mass density of P-doped SiGeAu and SiGe samples in Tables S1 and S2, respectively. The relative mass density is defined as the measured mass density divided by theoretical mass density. We found that all of the P-doped and undoped SiGeAu samples, and P-doped SiGe samples exhibited as high mass densities as theoretical ones. From the above results, the thermoelectric performance in this study was not affected by the difference of the mass density.

Table S1. Mass density and relative mass density of P-doped and undoped SiGeAu samples (Au: 2 at.%).

P amount [at.%]	0	0.1	0.2	0.3	0.5
Mass density [g cm^{-3}]	3.2	3.54	3.39	3.28	3.48
Relative mass density	~0.97	~1	~1	~1	~1

Table S2. Mass density and relative mass density of P-doped SiGe samples.

P amount [at.%]	0.3	0.5	1
Mass density [g cm^{-3}]	2.86	2.99	2.96
Relative mass density	~0.95	~1	~0.98

Confirmation of bipolar conduction.

When P dopant amount was very low in SiGeAu sample (<0.05 at.%) or SiGeAu sample was not doped, p-type conduction was observed due to the acceptor-like defects. Hall carrier concentration of ~2×10^{20} cm^{-3} in such p-type SiGeAu sample with low P amount was larger than that of undoped p-type SiGeAu sample (2×10^{19} cm^{-3}) even though P dopants in SiGe work as donors. This result denies carrier compensation between P donor and defect-related acceptor, and revealing bipolar conduction as follows.

Let's consider the electrical transport based on the bipolar conduction. In the case of Hall effect measurement with weak magnetic field in materials having bipolar carriers, measured Hall coefficient R_{meas} is shown as follows:

$$R_{meas} = \frac{\sigma_e{}^2 R_e + \sigma_h{}^2 R_h}{\left(\sigma_e + \sigma_h\right)^2} \quad \text{(S1),}$$

where R_{e} and R_{h}, are electron and hole contributions of Hall coefficients, and σ_{e} and σ_{h} are electron and hole contributions of electrical conductivity. Equation (S2) is obtained from equation (S1), as follows:

$$R_h - R_{meas} = \frac{\left(\sigma_e{}^2 + 2\sigma_e\sigma_h\right)R_h - \sigma_e{}^2 R_e}{\left(\sigma_e + \sigma_h\right)^2} \quad \text{(S2).}$$

Because R_{e} and R_{h} are negative and positive, respectively, equation (S2) is positive, leading to the inequation (S3):

$$R_{meas} < R_h \quad \text{(S3).}$$

When $R_{\mathrm{meas}} > 0$, measured carrier concentration p_{meas} ($=1/qR_{\mathrm{meas}}$) is larger than hole concentration p_{h} ($=1/qR_{\mathrm{h}}$), where q is elementary charge. Namely, materials with bipolar conduction exhibit $p_{\mathrm{meas}} > p_{\mathrm{h}}$.

In this study, we can assume that P-doped SiGeAu sample is corresponding to the one formed by doping P atoms into the p-type undoped SiGeAu sample. Then, the carrier concentration of the p-type undoped SiGeAu sample is corresponding to p_{h}. If P dopants introduced into the p-type undoped SiGeAu sample compensate defect-related acceptors (carrier compensation), namely decreasing hole concentration, the inequation $p_{\mathrm{meas}} < p_{\mathrm{h}}$ has to be obtained. On the other hand, in the case of bipolar conduction, not carrier compensation, the inequation $p_{\mathrm{meas}} > p_{\mathrm{h}}$ is obtained as shown by the above discussion. In the present case, p_{meas} of $\sim 2\times10^{20}$ cm^{-3} in P-doped SiGeAu sample with low P amount was larger than that of undoped SiGeAu sample ($p_{\mathrm{h}} \sim 2\times10^{19}$ cm^{-3}), namely $p_{\mathrm{meas}} > p_{\mathrm{h}}$. This reveals that the present P-doped SiGeAu samples have bipolar conduction, not carrier compensation.

Seebeck coefficient of SiGeAu samples as a function of carrier concentration.

We evaluated the carrier concentration (n_{Hall}) of SiGeAu samples by Hall measurement, as shown in Fig. S5. In Fig. S5, there seems to be a hump of *S* indicated by the dashed curve, compared with single crystalline $Si_{1-x}Ge_x$ (x=15, 30, 30, 40, 80) [S2]. This unique tendency is one of the evidence that SiGeAu samples have resonant level, leading to high *S*.

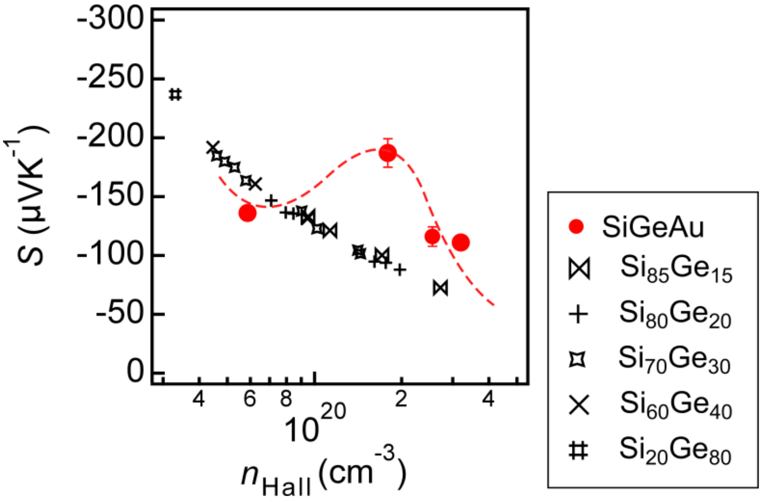

Fig. S5 *S* of SiGeAu samples as a function of n_{Hall}. The dashed line is eye guide.

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[S2] J. P. Dismukes, L. Ekstrom, E. F. Steigmeier, I. Kudman, and D. S. Beers, *J. Appl. Phys.* 1964, **35**, 2899-2907.