Supporting Information

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Giant Enhancement of Seebeck Coefficient by Deformation of Silicene Buckled Structure in Calcium-Intercalated Layered Silicene Film

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S1. Structural and compositional measurements of epitaxial CaSi₂ thin films

Figure S1a, b and c are the bright-field scanning transmission electron microscopy (STEM) image and the corresponding energy dispersive X-ray spectroscopy (EDS) mapping images of Ca and Si, respectively. To analyze the distribution of Ca, we obtained the average EDS profiles of Ca and Si with the uncertainty of ~5% (Figure S1d). It was observed that Ca atoms were homogeneously distributed in CaSi₂ film. In addition, the CaSi₂ thin film had the atomically sharp interface between film and substrate. Figure S1e shows the EDS spectrum of the dashed region in Figure S1a. The Ca/Si ratio was obtained to be 0.47 from the integrated intensity peaks of Si Ka and Ca Ka peaks in Figure S1e, when corrected for the background. The Ca/Si ratio (0.47) is slightly lower than the stoichiometric ratio of 0.50.
Figure S1. STEM and EDS results of CaSi$_2$ thin film. a-c) the bright-field STEM image (a) and EDS mapping images of Si (b) and Ca (c) in epitaxial CaSi$_2$ thin film. d) Average EDS profile of Si and Ca. e) EDS spectrum.
Next, to confirm “Si-rich” CaSi$_2$ thin films, we measured Si 2p core-level photoemission spectrum in the CaSi$_2$ film taken with a 130 eV photon energy after the surface oxidation layer of the film was removed by Ar sputtering. Figure S2 shows the Si 2p core-level photoemission spectrum in CaSi$_2$ film as a function of a relative energy to Si 2p binding energy of Si substrate. It was reported that the binding energy of the Si 2p was sifted depending on the composition in Ca-Si compounds due to the difference of the electronegativity between Ca and Si.$^{[1]}$ In a previous report, the Si 2p binding energies in Ca$_2$Si, CaSi and CaSi$_2$ positioned at -1.63, -0.77 and -0.28 eV, respectively.$^{[1]}$ Therefore, in Si-rich Ca-Si compounds, it is predicted that the binding energy is shifted to a higher value. In this study, the Si 2p binding energy in the present epitaxial film exhibited a higher value than that of Ca-Si compound with the Ca-Si ratio of 0.5 (CaSi$_2$),$^{[1]}$ indicating that our epitaxial CaSi$_2$ film is Si-rich CaSi$_2$ (Figure S2).

![Figure S2](image)

**Figure S2.** The Si 2p core-level photoemission spectrum of CaSi$_2$ thin films as a function of a relative energy to that of Si substrate. The dotted, broken, and dashed lines denote the binding energy of Si 2p, reported CaSi$_2$, CaSi and Ca$_2$Si.$^{[1]}$
S2. Atomic position analysis

Figure S3a and b show the experimental STEM images of Si substrate region of the different samples (CaSi$_2$ films on Si), which were viewed from the [\(\overline{1}0\)]$_{\text{Si}}$ azimuth. These images were almost the same as the simulated images of Si substrate regions with crystal thickness along the [\(\overline{1}0\)]$_{\text{Si}}$ azimuth, $t_{\text{TEM}}$, of 90 and 30 nm, which simulated images are shown in the dashed rectangles in Figure S3a and b, respectively. Then, the $t_{\text{TEM}}$ was determined by comparing Si-Si height $\Delta z$ (defined in Figure S3a) of the simulated and experimental STEM images of Si substrate regions. Figure S3c shows the $\Delta z$ difference between the simulated and the experimental images shown in Figure S3a and b. The $\Delta z$ differences are minimized to be 0.68 and 0.10 % at $t_{\text{TEM}}$s of 90 and 30 nm in two different samples. These small $\Delta z$ differences indicate that simulation successfully reproduces experimental STEM image within $\sim$1 %. The simulated image is also consistent with crystal structure model, indicating that blight contrast positions in the simulated image and ADF-STEM image reflects atomic positions. Therefore, we used the minimum value (90 and 30 nm) as an actual $t_{\text{TEM}}$ value for ADF-STEM simulation of CaSi$_2$ regions in each sample.
Figure S3. The STEM images of Si substrate regions. a, b) The experimental STEM images of Si substrate regions with different $t_{\text{TEM}}$s. The dashed rectangle areas exhibit the simulated STEM image of Si viewed from the [1\bar{1}0]$_{\text{Si}}$ azimuth. c) The $t_{\text{TEM}}$ dependence of $\Delta z$ difference between the simulated and the experimental STEM images. The arrows denote $t_{\text{TEM}}$s with minimum $\Delta z$ difference, which were adopted as actual $t_{\text{TEM}}$s.

Figure S4a and S5a show low-magnification annular dark field (ADF) STEM images with different crystal thickness ($t_{\text{TEM}}=90$ and 30 nm, respectively). Figure S4b and S5b are the represented enlarged images in Figure S4a and S5a, respectively. Figure S4c and S5c exhibit line profiles with $z$ direction in the areas 1-4, in which the Ca atomic positions at both edge positions
are corresponding to those of simulation. To determine atomic positions, we obtained the line profiles of atomic rows along z direction within smaller width $\Delta x$ than one atom size, as shown in Figure S4b and S5b. The line profiles of atomic rows in the areas 1-4 are displayed in Figure S4c and S5c, where line profiles of 7 equivalent atomic rows are shown as 7 purple lines in each area. The atomic positions were determined by Gaussian fitting of peaks in each line profile, and average atomic positions are denoted by the solid line marks in Figure S4c and S5c. Next, from the atomic positions, we obtained the deformation ratio of silicene buckling height ($\Delta z_1$ and $\Delta z_2$) that is defined as the difference between simulated and experimental STEM images (Table S1). As a result, averaged deformation ratio of $\Delta z_1$ from all $\Delta z_1$ data is found to be about 17.7%. On the other hand, averaged deformation ratio of $\Delta z_2$ is extremely small (-0.56%). As a result, $\Delta z_1$ is mainly elongated and $\Delta z_2$ is not so changed in epitaxial CaSi$_2$ thin films on Si compared with those of the most stable 6R-CaSi$_2$, leading to manipulation electronic structure.
**Figure S4.** Analysis of atomic positions. a, b) the low and high-magnification ADF-STEM images, respectively. The dashed rectangles in (b) show atomic rows. c) the line profiles for z direction of atomic rows shown in (b) (purple lines) and the line profiles in simulated image with $t_{\text{TEM}}=90$ nm (black lines). The descriptions of the areas 1-4 are corresponding to those in (a).
Figure S5. Analysis of atomic positions. a, b) the low and high-magnification ADF-STEM images, respectively. The dashed rectangles in (b) show atomic rows. c) the line profiles for z direction of atomic rows shown in (b) (purple lines) and the line profiles in simulated image with $t_{TEM}=30$ nm (black lines). The descriptions of the areas 1-4 are corresponding to those in (a).
Table S1. Deformation ratios of silicene buckling height between experiment and simulation.

|                  | Deformation ratio of buckling height (%) | Sample with $t_{\text{TEM}}$ of 90nm | Sample with $t_{\text{TEM}}$ of 30nm |
|------------------|------------------------------------------|--------------------------------------|--------------------------------------|
| Si               | $\Delta z$                                | 0.68                                 | 0.10                                 |
| Area 1           | $\Delta z_1$                              | 28.1                                 | 2.31                                 |
|                  | $\Delta z_2$                              | -6.24                                | -1.78                                |
| Area 2           | $\Delta z_1$                              | 32.5                                 | 10.4                                 |
|                  | $\Delta z_2$                              | -0.51                                | -2.24                                |
| Area 3           | $\Delta z_1$                              | 22.3                                 | 10.7                                 |
|                  | $\Delta z_2$                              | 0.74                                 | -2.52                                |
| Area 4           | $\Delta z_1$                              | 27.2                                 | 8.00                                 |
|                  | $\Delta z_2$                              | 8.54                                 | -8.33                                |
| Average          | $\Delta z_1$                              | 17.7                                 |                                      |
|                  | $\Delta z_2$                              | -0.56                                |                                      |
S3. Electronic structure of CaSi$_2$ with deformed buckled structure

The 6R-CaSi$_2$ with perfect crystal structure has two silicene layers with different buckling height ($\Delta z_1=0.823$ Å and $\Delta z_2=0.965$ Å). We calculated the electronic structure of 6R-CaSi$_2$ with the same buckling height ($\Delta z_1=\Delta z_2=0.965$ Å) named as SD-6R-CaSi$_2$, where $\Delta z_1$ was deformed from 0.823 Å to 0.965 Å (Figure S6a). Figure S6b shows electronic band structures of 6R-CaSi$_2$ with perfect crystal structure (original) and SD-6R-CaSi$_2$. We found two remarkable facts shown in Figure S6: (1) convergence of conduction bands and bands with electron pockets near $E-E_F=0$ and (2) decrease of contribution of valence bands near $E-E_F=0$. The bands with electron pockets at M and L points were shifted upward by deforming the buckled structure, resulting in the convergence of bands near $E-E_F=0$, namely high valley degeneracy near $E-E_F=0$ leading to $|S|$ increase. Furthermore, the deformation of the buckled structure moved the valence bands at $\Gamma$ point away from $E-E_F=0$. This results in the decrease of hole contribution to electrical conduction, namely the suppression of bipolar conduction, leading to $|S|$ increase. Thus, the present calculations revealed that the deformation of the buckled structure increases $|S|$ value through the variation of electronic structure.
Figure S6. Crystal and electronic structure in the case of SD-6R-CaSi$_2$. a, b) Crystal structure (a) and calculated energy dispersion relation (b) of 6R-CaSi$_2$ with $\Delta z_1=\Delta z_2=0.965$ Å. In (b), “original” denotes electronic structure of 6R-CaSi$_2$ with perfect crystal structure. c) The schematic of the manipulation of band structure by deformation of the buckled structure.

Figure S7a and b show the crystal structure and the electronic structure in 6R-CaSi$_2$ with $\Delta z_1=0.965$ Å and $\Delta z_2=1.131$ Å, respectively, which is named as LD-6R-CaSi$_2$. As is the case with SD-6R-CaSi$_2$, we also found two remarkable facts in LD-6R-CaSi$_2$, as shown in Figure S7c: (1) convergence of conduction bands and bands with electron pockets near $E-E_F=0$ and (2) decrease of contribution of valence bands near $E-E_F=0$. In the case of SD-6R-CaSi$_2$, the bands with electron pockets at M and L points were mainly moved. On the other hand, in LD-6R-CaSi$_2$, the conduction
bands at K and H points were also shifted downward by deforming the buckled structure, resulting in the higher convergence of bands near $E-E_F=0$. In addition, the deformation of the buckled structure moved the valence bands at $\Gamma$ and A points away from $E-E_F=0$. This results in the decrease of hole contribution to electrical conduction. Thus, the present calculations revealed that the deformation of the buckled structure brings high valley degeneracy and suppresses the bipolar conduction, resulting in the increase of $|S|$.

**Figure S7.** Crystal and electronic structure in the case of LD-6R-CaSi$_2$. a, b) Crystal structure (a) and calculated energy dispersion relation (b) of 6R-CaSi$_2$ with $\Delta z_1=0.965$ Å and $\Delta z_2=1.131$ Å. In (b), “original” denotes electronic structure of 6R-CaSi$_2$ with perfect crystal structure. c) The schematic of the manipulation of band structure by deformation of the buckled structure.
S4. Contribution of Si substrate to electrical properties

The discussion of electrical properties requires the information of Ca atom distribution in the sample because the amount of Ca atom is related to that of carrier. Therefore, the depth ($d$) profile of Ca atoms was measured by X-ray photoelectron spectroscopy (XPS) using an Al K$\alpha$ X-ray source (1486.6 eV) and Ar sputtering. Figure S8a shows the XPS spectra in the binding energy range of 0-500 eV. We obtained an integrated intensity ratio of Ca 2p/Si 2p, $I_{\text{Ca}}/I_{\text{Si}}$ (Figure S8b). In the $d$ range of ~10-15 nm, $I_{\text{Ca}}/I_{\text{Si}}$ increased with increasing $d$, whereas $I_{\text{Ca}}/I_{\text{Si}}$ decreased with increasing $d$ in the $d$ range of ~30-40 nm. It is considered that these slopes of $I_{\text{Ca}}/I_{\text{Si}}$ at amorphous-Si/CaSi$_2$ and CaSi$_2$/Si substrate interfaces come from knock-on effect by Ar sputtering. From TEM result in Figure 3A that the CaSi$_2$ thin film has about 30 nm thickness, it was found that film edges are at $d$=~10 and ~40 nm (the arrows in Figure S8b).

To investigate whether the film thickness (~10 nm<$d$<~40 nm) corresponds to the thickness of electrical conduction path experimentally, we measured the electrical sheet resistance ($R(d)$) by van der Pauw method as a function of $d$ where $d$ is increased by Ar ion milling, as shown in Figure S8b. The $R(d)$ inside the film (10 nm<$d$<30 nm) exhibited low value of ~10 $\Omega$/□. At $d$ ~40 nm, the $R(d)$ drastically increased by a factor of ~$10^3$ compared with that inside the film (10 nm<$d$<30 nm). This indicates that at $d$ ~40 nm, conducting parts were removed by Ar ion milling, resulting in the high sheet resistance which comes from undoped Si substrate with high resistivity (>~1000 $\Omega$cm). Because the position at $d$=~40 nm corresponds to the edge of film, CaSi$_2$ film thickness is found to be consistent with the thickness of electrical conduction path. From these results, we consider the contribution of Si substrate to electrical properties using the parallel conduction model described as

$$R_{\text{CaSi}_2} = R_{\text{meas.}} \left(1 - \frac{R_{\text{meas.}}}{R_{\text{sub.}}}\right)^{-1} \quad \text{(S1)},$$
\[ S_{\text{CaSi}_2} = S_{\text{meas}} \left( 1 + \frac{R_{\text{CaSi}_2}}{R_{\text{sub}}} \right) - S_{\text{sub}} \frac{R_{\text{CaSi}_2}}{R_{\text{sub}}} \]  \hspace{1cm} (S2),

where \( R_{\text{meas}} \) (\( S_{\text{meas}} \)) is the measured electrical sheet resistance (Seebeck coefficient), and \( R_{\text{CaSi}_2} \) (\( S_{\text{CaSi}_2} \)) and \( R_{\text{sub}} \) (\( S_{\text{sub}} \)) are the electrical sheet resistances (Seebeck coefficients) of CaSi\(_2\) thin film and Si substrate, respectively.\(^{[2]}\) In the present CaSi\(_2\) film, \( R(d) \) in the \( d \) range of ~10-30 nm was \(~10 \, \Omega/\square\), while \( R(40 \, \text{nm}) \) was over \( 10^4 \, \Omega/\square\). Considering the present situation: \( R_{\text{meas}} = R(d) \) in the \( d \) range of ~10-30 nm and \( R_{\text{sub}} = R(40 \, \text{nm}) \), \( R_{\text{meas}}/R_{\text{sub}} \) becomes negligibly small, resulting in \( R_{\text{CaSi}_2} \sim R_{\text{meas}} \) in Equation (S1). This indicates that the contribution of Si substrate to electrical conduction is negligible in the present CaSi\(_2\) film. We also consider the contribution of Si substrate to Seebeck coefficient using Equation (S2). \( R_{\text{CaSi}_2}/R_{\text{sub}} \) is very small \((\sim 10^{-3})\) as mentioned above.

The present CaSi\(_2\) film exhibited \( S_{\text{meas}} \) of ~\( 40 \, \mu\text{VK}^{-1} \). The Si substrate we used in this study had \( S_{\text{sub}} \) of ~\( 1200 \, \mu\text{VK}^{-1} \). From these results, \( S_{\text{sub}} R_{\text{CaSi}_2}/R_{\text{sub}} \) was acquired to be ~\( 1.2 \, \mu\text{VK}^{-1} \). This value is less than 5 % of \( S_{\text{meas}} \). Therefore, the contribution of Si substrate to Seebeck coefficient is considered to be negligible. This discussion concluded that the contribution of Si substrate to electrical properties is negligible in the present CaSi\(_2\) film/Si.
REFERENCES AND NOTES

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