Electronic Supplementary Information

A Penta-Silicene Nanoribbon-based 3D Silicon Allotrope with High Carrier Mobility and Thermoelectric Performance

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Text S1 Assembling process for cco-Si₄₈

We assemble the planar penta-silicene nanoribbons (PSNRs) along the *x* direction in an AA stacking pattern, where each periodic cell contains two layers of PSNR, as shown in Fig. S1(a). The Si-Si bond lengths in the PSNRs are set to \sim 2.35 Å, which is taken from that of diamond silicon. The interlayer distance is set to be 3.4 Å, which is taken from that of graphite.

We then align the AA-stacked PSNR piles in an AB stacking pattern along the z direction, where each periodic cell contains two PSNR units, as shown in Fig. S2(b). In this step, each two-fold coordinated Si atom in the PSNRs is aligned to one of its equivalents in the neighboring units with an interatomic distance of 2.35 Å.

After setting up the initial configuration we perform geometry optimization and find that the PSNRs deforms from the planar configuration, where each of the three-fold coordinated atoms shifts along the *x* axis to one side or the other and connects with its equivalence from the neighboring PSNR, naturally forming the cco-Si₄₈ configuration.



Fig. S1 Assembling process from PSNRs to bulk cco-Si₄₈.



Fig. S2 Geometry of cco-Si48 at the end of the AIMD simulation at (a) 500 K and (b) 800 K.

Text S2 Linear optical properties of cco-Si₄₈

The photon-energy-dependent complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i \cdot \varepsilon_2(\omega)$ is calculated based on its electronic structure at the PBE level by considering the direct interband transitions.¹ Here $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real and imaginary part, respectively. The underestimated band gap at this level is compensated by a scissors correction of 0.58 eV. The linear optical properties are deduced from $\varepsilon(\omega)$,² including the absorption coefficient

$$\alpha(\omega) = \sqrt{2}\omega \left[\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega) \right]^{\frac{1}{2}}, \quad (\text{Eq. S1})$$

the refraction index

$$n(\omega) = \frac{\sqrt{2}}{2} \left[\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} + \varepsilon_1(\omega) \right]^{\frac{1}{2}}, \quad (\text{Eq. S2})$$

and the reflectivity

$$R(\omega) = \left| \frac{\varepsilon^{\frac{1}{2}}(\omega) - 1}{\varepsilon^{\frac{1}{2}}(\omega) - 1} \right|.$$
 (Eq. S3)

As shown in Fig. S3(a), the absorption coefficient of cco-Si₄₈ possesses weak anisotropy as the values along the *x*-axis are larger than those along the other two directions. Due to its direct band gap of 1.46 eV, cco-Si₄₈ possesses small optical absorption in the infrared region (0~1.4 eV). The absorption coefficients along the three axial directions increase rapidly with the photon energy in the visible (1.4~3.1 eV) and near-ultraviolet (3.1~4.0 eV) regions to over 10⁶ cm⁻¹. Especially, they exceed the absorption coefficient of diamond silicon^{3.4} at ~2 eV. Combined with the fact that materials with a band gap of ~1.5 eV tend to possess predominant power conversion efficiencies,^{5.6} cco-Si₄₈ can be promising for application in solar cells. The refraction rate and reflectivity of cco-Si₄₈ are also anisotropic, as shown in Fig. S3(b) and (c), and they both increase monotonically with photon energy within the visible region.



Fig. S3 (a) Absorption coefficient, (b) refraction index, and (c) reflectivity of cco-Si₄₈.



Fig. S4 Electronic band structure of $cco-Si_{48}$ obtained by the QE and VASP.



Fig. S5 (a) Carrier mobility μ , (b) electric conductivity σ , and (c) electronic thermal conductivity κ_e of diamond silicon.



Fig. S6 $\kappa_e/\sigma T$ value of cco-Si₄₈ with carrier concentration.



Fig. S7 Grüneisen parameter of $cco-Si_{48}$ and diamond silicon.



Fig. S8 (a) Seebeck coefficient, and (b) ZT of diamond silicon.

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