A New Silicon Phase with Direct Band Gap and Novel Optoelectronic Properties

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Due to the compatibility with the well-developed Si-based semiconductor industry, there is considerable interest in developing silicon structures with direct energy band gaps for effective sunlight harvesting. In this paper, using silicon triangles as the building block, we propose a new silicon allotrope with a direct band gap of 0.61 eV, which is dynamically, thermally and mechanically stable. Symmetry group analysis further suggests that dipole transition at the direct band gap is allowed. In addition, this new allotrope displays large carrier mobility (~10⁴ cm²/V·s) at room temperature and a low mass density (1.71 g/cm³), making it a promising material for optoelectronic applications.

Due to limited supply of fossil fuels and its adverse effect on the environment, one of the greatest challenges in this century is to find clean and sustainable energy sources. Of all the renewable energy sources available, solar energy provides the best solution¹, but development of efficient photovoltaic materials to convert solar energy into electricity is essential. Silicon, because of its high stability and abundance, has been widely used as a photovoltaic material for solar cell devices. However, crystalline silicon does not absorb sunlight as efficiently as some other materials do. Its indirect band gap of 1.1 eV² significantly limits the efficiency of solar cells as electron transition needs the assistance of phonons to change the momentum, thus, requiring a long optical pathway (thick film) for effective light absorption²,³. On the other hand, its direct band gap of 3.4 eV is too large⁴ and only allows high energy photons to be absorbed. Metastable silicon allotropes, such as R8, T12-Si, and lonsdaleite structures also exhibit indirect band gaps⁵–⁷ and the hotly-pursued silicene and BC8 phases show semimetal feature⁵,⁸. None of these materials are suitable for solar absorption. These limitations have led to a constant search for new silicon structures with small direct band gaps and desired optical properties.

Botti et al. studied several low-energy silicon allotropes with quasi-direct and dipole-allowed band gaps from 0.8 to 1.5 eV⁹. Similarly, Xiang et al. proposed a cubic Si₃₆ phase with a quasi-direct band gap of 1.55 eV, while the dipole transition at direct band gap is allowed². Although these structures exhibit better optical absorption than diamond silicon, their performance is not comparable with that of a direct band gap phase. Recently, using particle swarm optimization (PSO) algorithm, Wang et al. proposed six silicon structures. Among them, the of16-, tp16-, mC12-, and t16-Si show direct band gaps ranging from 0.81 to 1.25 eV¹⁰. Subsequently, using density functional theory (DFT) with generalized gradient approximation (GGA) for exchange-correlation potential at the PBE level, Lee et al. presented a series of direct band gap silicon crystals with band gaps ranging from 0.29 to 0.77 eV¹¹. Even through these silicon structures can absorb sunlight at lower energies than other silicon allotropes and exhibit significantly enhanced optical absorption, there is a large room to enhance the conversion efficiency because photons with energy below the band gap cannot be absorbed¹². This requires a small gap absorber to...
capture the low-energy photons. Note that photons in the visible and infrared spectra contain over 90% of solar energy.

In this paper we propose a three dimensional (3D) silicon structure built of Si triangles, h-Si$_6$, whose dynamical, thermal and mechanical stability is confirmed by state-of-art theoretical calculations. Our results show that the h-Si$_6$ phase has a direct band gap of 0.61 eV with good optical properties. The small effective mass and the large carrier mobility make h-Si$_6$ a promising candidate for electronic device as well as solar absorber. The conversion efficiency of h-Si$_6$ can be further enhanced by stacking it with other silicon allotropes having different band gaps$^{13}$. We show that such an array can break the Shockley-Queisser limit$^{14}$.

**Results and Discussion**

It has been demonstrated that the electronic structure of silicon crystals can be modified by varying the distribution of dihedral-angles while keeping the covalent bonds between the silicon atoms intact$^{11}$. Similarly, the improvement of silicon's optical transition and solar absorption has been shown to be closely related to its triangular motifs$^5$. Thus, we conceived an idea of building a new 3D silicon structure with a direct band gap by combining these two factors. To accomplish this we changed the arrangement of silicon atoms in a unit cell by using the triangular motifs as building block. We constructed several possible structures before we reached the one with a pair of up-down equilateral triangles in a unit cell, as shown in Fig. 1. For convenience of discussion, we term this structure as h-Si$_6$, since the newly designed phase has a hexagonal primitive cell (space group $P6_3/mmc$, No. 194) containing six silicon atoms. The optimized lattice parameters are $a = b = 6.94$ Å, and $c = 3.90$ Å. This structure features 4-fold coordination with two bonds of 2.37 Å in the triangular building block and the other two of 2.33 Å between the silicon atoms in the neighboring triangles. The bond lengths are very close to that of diamond silicon (2.35 Å), showing a similar bonding character. Because there are three different bond angles among the silicon atoms (60°, 113.8°, and 118.2°), the silicon atoms show a characteristic of imperfect $sp^3$ hybridization.

To confirm the dynamical stability, phonon dispersion of h-Si$_6$ was calculated by using the finite displacement method. The results are plotted in Fig. 2(a). We see that all the vibrational frequencies are positive in the first Brillouin zone, which clearly demonstrates that h-Si$_6$ is dynamically stable and the structure belongs to a local minimum in the potential energy surface. We note that the highest frequency reaches 16.9 THz, which is slightly higher than that in diamond silicon (15.5 THz). We also checked its dynamical, thermal and mechanical stability is confirmed by state-of-art theoretical calculations. Our results show that the h-Si$_6$ phase has a direct band gap of 0.61 eV with good optical properties. The small effective mass and the large carrier mobility make h-Si$_6$ a promising candidate for electronic device as well as solar absorber. The conversion efficiency of h-Si$_6$ can be further enhanced by stacking it with other silicon allotropes having different band gaps$^{13}$. We show that such an array can break the Shockley-Queisser limit$^{14}$.

Figure 1. Optimized crystal structure of h-Si$_6$. (a) Perspective view, (b) view from the [0001] direction, and (c) view from the [01T0] direction.
To study the mechanical strength of the h-Si₆ phase, we have calculated its elastic response under external strain. In the linear elastic range, the elastic constant tensor forms a symmetric $6 \times 6$ matrix with 21 independent components. For a stable hexagonal structure, there only exist five independent elastic constants $C_{11}$, $C_{33}$, $C_{44}$, $C_{12}$, and $C_{13}$, and they have to obey the condition $C_{33} > C_{44} > C_{11} > |C_{12}|$, $(C_{11} + 2C_{12})C_{33} > 2C_{13}^2$.

Using the strain-stress relationship, we calculated the elastic constants of h-Si₆. For comparison, similar calculations for the diamond silicon and cubic Si₂₀ phase were also performed. All results are given in Table 1. Because the calculated elastic constants of this structure satisfy the above conditions, we conclude that that the h-Si₆ structure is mechanically stable. The bulk and shear moduli were calculated using the Voigt-Reuss-Hill approximation. The corresponding values for h-Si₆ are 57.6 GPa and 32.8 GPa, respectively. Note that h-Si₆ has a much smaller bulk and shear moduli than those of diamond silicon and cubic Si₂₀ phase (see Table 1). In addition, it is also smaller than those of direct band gap hP12-Si and tP16-Si phases which are considered as the most porous structures in their proposed allotropes. To further compare the porosity with other 3D silicon structures, the mass density of h-Si₆ was calculated. Besides being much lower than that of diamond silicon (2.34 g/cm³), h-Si₆ has an even smaller density (1.71 g/cm³) than most previously reported bulk silicon allotropes. This would help to reduce the material weight in practical applications.

For measuring optical absorption performance of the photovoltaic material, we have calculated the electronic structure of the h-Si₆ phase because the conversion efficiency is closely related to the band

Table 1. Elastic constants and bulk and shear moduli of h-Si₆, diamond silicon, and the cubic Si₂₀ structure (GPa).

| Structure | h-Si₆ | Diamond silicon | Cubic Si₂₀ |
|-----------|-------|-----------------|------------|
| $C_{11}$  | 83.0  | 160.7           | 147.3      |
| $C_{33}$  | 156.9 |                 |            |
| $C_{44}$  | 24.1  | 78.0            | 34.1       |
| $C_{12}$  | 34.3  | 63.9            | 46.3       |
| $C_{13}$  | 36.8  |                 |            |
| $B$       | 57.6  | 96.2            | 80.0       |
| $G$       | 32.8  | 64.5            | 40.2       |

Figure 2. Structural stability of h-Si₆. (a) Phonon dispersions and (b) energy fluctuation of h-Si₆ with respect to time in MD simulations at 500 K.
The calculated band structure of h-Si$_6$ throughout the hexagonal Brillouin zone is shown in Fig. 3. At the GGA/PBE level of density functional theory, the h-Si$_6$ phase is predicted to be a direct band gap semiconductor with a small band gap of 0.14 eV, as both the valence band maximum (VBM) and conduction band minimum (CBM) are located at the $\Gamma$ point. This value of 0.14 eV is less than half of the minimum band gap (0.29 eV) of previously reported direct band gap silicon crystals. Because conventional DFT calculations are known to significantly underestimate band gap, we repeated the above calculations using the HSE06 functional. Although the band structure using the HSE06 functional is similar to that obtained at the PBE level, the band gap is increased to 0.61 eV. This value is much smaller than that of all the predicted direct band gap silicon allotropes at the HSE06 level. In addition, we note that the highest occupied state at the $\Gamma$ point is doubly degenerate; this is because h-Si$_6$ has hexagonal symmetry in the dihedral point group.

In a solar cell, when photoelectrons are produced, recombination of electrons and holes is not desired because this process decreases the solar conversion efficiency. Thus, large carrier mobility is needed. Therefore, we investigated the charge transport properties of the h-Si$_6$ phase using the deformation potential approximation. The carrier mobility of a 3D solid can be written as

$$\mu_{3D} = \frac{e}{3m^*E_k^{2/3}}$$

where $E_k$ denotes the deformation potential, which is obtained by varying the lattice constant along the transport direction and studying the change of band energy under the lattice compression and strain. The effective mass $m^*$ can be calculated by a quadratic polynomial fitting of the conduction and valence bands. Additional remarks on the effective mass are given in Table 2. For an intuitive description, we rebuilt the band structure of h-Si$_6$ along several directions in wave vector space. The elastic modulus $C_{33}$ along different directions refers to the elastic constants given in Table 1; $C_{11}$ represents the value along the $x(y)$ directions while the $C_{33}$ stands for the modulus in the $z$-direction. For an intuitive description, we rebuilt an orthorhombic crystal lattice along the three vertical directions $\hat{a}$, $\hat{b}$, and $\hat{c}$ for h-Si$_6$, as plotted in Supplementary Information Figure S1. The effective masses, deformation potential, and carrier mobility of electrons and holes along the three basis vector directions are listed in a table (Table 2).

We begin our discussion by first looking at the carrier effective mass. Due to the intrinsic hexagonal structure, $m_e = m_h$ showing an isotropic character in the $x$-$y$ plane. For electrons, the effective mass along the $z$ direction ($m_z^e = 0.14 m_0$) is smaller by an order of magnitude than that in the $x(y)$ direction ($m_{x(y)}^e = 1.45 m_0$). This can be understood from the fact that the first conduction band has more significant dispersions along the $\Gamma - A$ direction than that in the $\Gamma - M(K)$ direction as shown in Fig. 3. For holes, we note that there are two valence bands near the $\Gamma$ point, making the VBM a doubly degenerate state. So, there exist two kinds of holes, termed as light and heavy holes, respectively. Along the $x(y)$ direction, the effective mass of heavy holes is $-0.19 m_0$, which is nearly twice that of the light holes ($-0.10 m_0$). Along the $z$ direction, these two bands merge together, leading to an equivalent effective mass.

**Table 2.** Effective mass (in $m_0$), deformation potential (in eV), and carrier mobility (in $10^3$ cm$^2$/V·s) along the three stretching directions for electrons and holes of h-Si$_6$ at 300 K.
The result is the potential for the light holes, which makes them less prone to acoustic phonon scattering than the electrons. This notable difference is due to the relatively small deformation potential for the light holes, which makes them less prone to acoustic phonon scattering than the electrons. Our calculations show that the mobility for h-Si6 can reach as high as $10^4 \text{ cm}^2/\text{V} \cdot \text{s}$ at room temperature, making it ideal for application as a photovoltaic material for solar energy conversion.

The imaginary part of dielectric function of h-Si6 is calculated at the HSE06 level. For comparison, calculations were also carried out for diamond silicon and other metastable silicon phases studied previously. The results are displayed in Fig. 4. According to the spectral range, we divided the spectrum into three parts, namely the infrared, visible, and ultraviolet regions, respectively. As mentioned above, due to the large direct band gap, diamond silicon can absorb photons mostly in the ultraviolet range. However, this part only occupies a small percentage of the sunlight, implying that plenty of energy is wasted. In addition, other metastable silicon allotropes can only absorb the photons with energy larger than about 1.5 eV, which is also not enough to make the best use of solar energy. For h-Si6, the absorption of low-energy photons starts from about 0.6 eV, which is very close to its direct band gap at the $\Gamma$ point. Moreover, h-Si6 exhibits higher optical absorption than all the other silicon allotropes when the photon energy is below 2.2 eV. It also exhibits better optical absorption than diamond Si, hPi2-Si, oC12-Si, t116-Si, and mC12-Si from 2.2 to 3.4 eV. This implies that h-Si6 can be an ideal candidate for photovoltaic material. It was demonstrated that the maximum photovoltaic conversion efficiency that can be achieved is 33.7% when the band gap is 1.34 eV for a single-gap photovoltaic device. However, being tied to transition mechanism, the solar energy below this gap could not be really utilized, which inhibits the ability to further enhance the efficiency of solar cells. To overcome this limitation, a tandem solar cell system was proposed by stacking several homojunction cells together to form arrays, and it was found that a three- or four-stacked cell can bring the highest efficiency up to more than 60%, which requires a 0.5 ~ 0.6 eV band gap absorber to capture the low-energy photons. The sketch of a tandem solar cell along with a detailed mathematical treatment for estimating the efficiency are given in the Supplementary Information. Thus, h-Si6 exactly satisfies the requirement, leading to potential application in photovoltaic layer, which would significantly increase the utilization of the sunlight.
allowed. Interestingly, the wave functions of both the VBM and CBM are around the equilateral triangle units. Thus, it can be concluded that the optical transition is closely related to the silicon triangles, which is consistent with the similar mechanism observed in previous cubic Si_{20} structure.

Summary
To effectively harvest the sunlight in the whole wavelength range, it is a good strategy to use arrays consisting of Si structures with different direct band gaps. However, in this array the structure with a direct band gap of about 0.6 eV has been missing. In this study, we found this missing structure, the h-Si_{6} phase, by using silicon triangles as the building block. Using state-of-art theoretical calculations, we confirmed its thermal, dynamical, and mechanical stability. We further calculated its electronic band structure, optical properties and wave functions of the VBM and CBM. We also performed symmetry group analysis. We show that this new structure not only exhibits a good light absorption, but also exhibits high intrinsic mobility and low mass density. We hope that these features of the new Si allotrope will motivate experimental effort to synthesize the h-Si_{6} phase.

Methods
Our studies are based on density functional theory (DFT) and the projector augmented wave (PAW) method as implemented in the Vienna ab initio Simulation Package (VASP). Plane waves with kinetic energy cutoff of 500 eV were used to expand the valence electron wave functions. The electronic exchange-correlation interaction was treated using Perdew-Burke-Ernzerhof functional (PBE) within generalized gradient approximation (GGA). To ensure an accurate determination of electronic and optical properties, calculations were repeated using the hybrid Heyd-Scuseria-Ernzerhof functional (HSE06). Full geometry optimizations were carried out by using the convergence thresholds of 10^{-3} eV and 10^{-3} eV/Å for total energy and force component, respectively. The Brillouin zone was represented with 9 × 9 × 16 Monkhorst-Pack special k-point mesh. Thermal stability was studied using ab initio MD simulations with temperature controlled by Nosé heat bath scheme. To study the dynamic stability, phonon calculations were performed using finite displacement method as implemented in the phonopy program.

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Author Contributions
Q.W. designed the project; Y.G. performed the calculations; Y.G., Q.W., Y.K. and P.J. analyzed the results and wrote the manuscript.

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