Direct and quasi-direct band gap silicon allotropes with remarkable stability

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In our present work, five previously proposed sp3 carbon crystals were suggested as silicon allotropes and their stabilities, electronic and optical properties were investigated by first-principles method. We find that these allotropes with direct or quasi-direct band gaps in range of 1.2-1.6 eV are very suitable for applications in thin-film solar cells. They display strong adsorption coefficients in the visible range of the sunlight in comparison with diamond silicon. These five silicon allotropes are confirmed possessing positive dynamical stability and remarkable thermodynamical stability close to that of diamond silicon. Especially, the direct band gap M585-silicon possessing energy higher than diamond silicon only 25 meV per atom is expected to be experimentally produced for thin-film solar cells.

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Silicon is becoming the fundamental element in our daily life. Almost all the semiconductor components in high technology of today are silicon-based. As the second most abundant element in earth crust, silicon possesses many advantages not only for applications in the semiconductor industry. It is also the leading material foundation in the important field of photovoltaic energy production. Due to its abundance and ability to translate the solar energy, as well as the reducing non-renewable traditional energy, silicon is believed as the future of human. Theoretically, silicon can form many allotropes due to its ability of sp3 hybridization like carbon. But, unfortunately, it is always locked in oxide or lie in its diamond like ground state.

Although the band gap of diamond silicon of about 1.12 eV lies in the optimal adsorption range of the sunlight, its indirect characteristic seriously affects its adsorption efficiency. Thus, many efforts have been paid on searching for viable silicon allotropes with direct or quasi-direct band gaps overlapping the sunlight in visible range, for the purpose of improving the translating efficiency of the solar energy. For example, Botti et al. have proposed some low-energy silicon allotropes with quasi-direct band gaps in the range of 0.8-1.5 eV and possessing strong adsorption coefficients for thin-film solar cell applications. Also, an approach named as Inverse Band Structure Design Approach (IBSDA) based on the particle swarming optimization algorithm (PSO) was developed by Xiang et al. for the purpose of searching for materials with expected electronic properties and a quasi-direct band gap silicon allotrope Sf10-T was predicted. Based on the IBSDA as implemented in PSO, Wang et al. have also found six low energy direct and quasi-direct silicon allotropes. Very recent, Lee et al. suggested another approach to search for direct band gap silicon allotropes and they successfully discovered many direct and quasi-direct band gap allotropes. Especially, a recent experimental progress shows that a cage-like silicon allotrope Si24 with a quasi-direct band gap of about 1.3 eV can be synthesized by Na-assistanted two step approach. The crystal structure is confirmed as the same as that of the previously suggested CAS-Si24. The authors also show that Si324 possesses strong adsorption coefficient higher than diamond silicon by first-principles calculation. All these theoretical successful examples make us in confident in using computational-alchemy in the engineering of materials.

In this paper, we predict five low energy silicon allotropes (M585-silicon, S-silicon, Z-CACB-silicon, H-silicon and Z-ACA-silicon as shown in Fig. 1) based on the crystal structures of our previously proposed sp3 carbon phases and find that they are direct or quasi-direct band gap semiconductors with strong adsorption coefficients for thin-film solar cell application. Such a transplanting idea of crystal structures have made a lot of successes in crystal prediction, such as zeolite nets to carbon allotropes and carbon crystals to silicon allotropes like Bet-C4 silicon, M4 silicon, M10 silicon and Cco-Si8. Our calculating results show that these five silicon allotropes possess positive dynamical stability and remarkable thermodynamical stability comparable to that of diamond silicon. Especially, the direct band gap M585-silicon possessing energy higher than diamond silicon only 25 meV per atom is expected to be experimentally produced for thin-film solar cells.

In our present work, we perform the structure optimizations and total energy calculations using the density functional theory within local density approximation (LDA) as implemented in Vienna ab initio simulation package (VASP). The interactions between nucleus and the 3s23p2 valence electrons of silicon are described by the
TABLE I: Total energies, energy band gaps and fundamental structural information including space group, lattice constants and mass densities of diamond silicon, M585-silicon, S-silicon, Z-CACB-silicon, H-silicon and Z-ACA-silicon.

| Items               | Diamond silicon | M585-silicon | S-silicon | Z-CACB-silicon | H-silicon | Z-ACA-silicon |
|---------------------|-----------------|--------------|-----------|----------------|-----------|---------------|
| Space group         | FD-3M (No.227)  | P21/M (No.11)| CMCM (No.63) | IMMA (No.74)   | PBAM (No.55) | PMMN (No.59) |
| Lattice a           | 5.407 Å         | 14.64 Å      | 3.825 Å   | 3.833 Å        | 11.832 Å  | 3.807 Å       |
| Lattice b           | 5.407 Å         | 3.814 Å      | 17.141 Å  | 7.289 Å        | 7.234 Å   | 7.055 Å       |
| Lattice c           | 5.407 Å         | 6.772 Å      | 7.399 Å   | 17.41 Å        | 3.812 Å   | 12.002 Å      |
| Mass density        | 2.361 Mg/cm³    | 2.311 Mg/cm³| 2.307 Mg/cm³ | 2.302 Mg/cm³  | 2.284 Mg/cm³ | 2.315 Mg/cm³ |
| Relative energy     | 0 meV/atom      | 25 meV/atom  | 42 meV/atom | 70 meV/atom    | 61 meV/atom | 78 meV/atom   |
| Band gap            | 1.11 eV         | 1.51 eV      | 1.41 eV   | 1.33 eV        | 1.52 eV   | 1.29 eV       |
| Direct band gap     | 3.32 eV         | 1.51 eV      | 1.53 eV   | 1.38 eV        | 1.63 eV   | 1.43 eV       |

As shown in Fig. 1 is the optimized crystal structures of M585-silicon, S-silicon, Z-CACB-silicon, H-silicon and Z-ACA-silicon. Their relative energy, energy band gaps, as well as fundamental structural information including space groups, lattice constants, mass densities are summarized in Table I, those of diamond silicon are also listed for comparison. We can see that the mass density of M585-silicon, S-silicon, Z-CACB-silicon, H-silicon and Z-ACA-silicon are 2.311 Mg/cm³, 2.307 Mg/cm³, 2.302 Mg/cm³, 2.284 Mg/cm³ and 2.315 Mg/cm³, respectively. These results indicate that M585-silicon, S-silicon, Z-CACB-silicon, H-silicon and Z-ACA-silicon are dense close to diamond silicon, which is good consistent with their sp³ configurations.

From the total energies as listed in Table I and shown in Fig. 2, we find that all these five silicon allotropes are metastable with energies higher than that of diamond silicon in 80 meV per atom. That is to say, they are thermodynamically favorable than most of the previously proposed silicon allotropes, such as the quasi-direct band gap Si20,24,25 as well as the direct band gap D135 and Q135L as well as the direct band gap D135 and Q135L. In Fig. 2, we also show the total energy per atom as a function of volume per atom for these new silicon allotropes (Results about other phase with energies higher than diamond silicon up to 80 meV per are not shown in it for the considering of simplification). From the quadratic E-V relation near the equilibrium V₀, we can see that all of them are thermodynamically stable protected by obvious energy barriers in their individual local state. From Table I and Fig. 2, we can easily know that the most stable one among these five silicon allotropes is M585-silicon, followed by S-silicon and H-silicon. Its energy is just 25 meV per atom higher than that of diamond silicon, which indicates that it possesses the very high probability to be synthesized in experiment.

To further confirm the dynamical stabilities of these five new silicon allotropes, we then investigated their vibrational properties through simulation their phonon band structures and density of state. Their phonon band structures are shown in Fig. 3. According to our results, there is no any imaginary frequency appearing in these phonon vibrational spectra and no any imaginary models appearing it their phonon density of state. Such vibrational properties indicate that these five new silicon allotropes are dynamically stable.

As mentioned before, direct or quasi-direct band gap characteristics are expected for sunlight adsorption, which can avoiding the requirement of thick absorber layer (for indirect band gap semiconductors such as diamond silicon) to provide necessary phonon moment. Thus, we firstly care about the electronic band structures of these five promising silicon...
allotropes. Considering that traditional DFT-method always underestimate the band gap of semiconductor in comparison of the experiment results, we employ the HSE06 method in our present work to investigate the electronic properties of M585-silicon, S-silicon, Z-CACB-silicon, H-silicon and Z-ACA-silicon. The calculated band structures are shown in Fig. 4 and corresponding band gaps are summarized in Table I. From the band structures we can see that the most stable M585-silicon is a typical direct band gap semiconductor with a gap of 1.51 eV. S-silicon, Z-CACB-silicon, H-silicon and Z-ACA-silicon behave as quasi-direct band gap semiconductors with band gaps of 1.41 eV, 1.29 eV, 1.33 eV and 1.52 eV, respectively. Their corresponding direct band gaps are 1.53 eV, 1.38 eV, 1.63 eV and 1.43 eV, respectively. These results indicate that they are suitable for applications in thin-film solar cells as absorbers.

We then turn our interesting on the absorption abilities of these five promising silicon allotropes. Absorption spectra of these allotropes are also calculated based on HSE06 method. The results are shown in Fig. 5 in comparison with that of the diamond silicon and the air mass 1.5 solar spectral irradiance. We can see that all of these five silicon allotropes possess strong absorption coefficients better than that of diamond silicon in the energy range between 1.5 and 3.2 eV. It is well known that indirect band gap diamond silicon needs necessary phonon moments to assist its indirect band adsorption. Thus it is always prepared with thickness about 100 µm to ensure the adsorption of solar energy below...
its direct optical gaps. Our discoveries suggest that these five new silicon allotropes are suitable for thin-film solar cell applications in views of their direct or quasi-direct band gap characteristics and strong adsorption abilities, if they can be successfully synthesized in future experiment.

Usually, silicon is always locked in oxide or lies in its ground state of diamond silicon. There is no any graphite-like silicon allotrope that can provides abundant pathways to the ground state of diamond silicon. There is no any graphite-like silicon allotrope that can be successfully synthesized in future experiment.

In summary, five previously proposed sp carbon crystals were theoretically suggested as silicon allotropes for the first time and their stabilities, electronic and optical properties were investigated by first-principles method. We find that these allotropes with direct or quasi-direct band gaps in range of 1.2-1.6 eV are very suitable for applications in thin-film solar cells. They display strong adsorption coefficients in the visible range of the sunlight in comparison with diamond silicon and remarkable thermodynamical stability superior to most of the previously proposed direct or quasi-direct band gap silicon allotropes such as Si72-T, Q135, D135 and nC12-Si. Especially, the direct band gap MS45-silicon possessing energy only 25 meV per atom higher than that of diamond silicon and about 80 meV lower than that of the recently synthesized Si128 is expected to be experimentally produced for thin-film solar cells.

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