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Three-dimensional pentagonal silicon: Stability and properties

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ABSTRACT

Motivated by the compatibility with the well-developed Si-based semiconductor technology, research on new Si allotropes is of importance. Here, we study a new three-dimensional (3D) silicon (named as pentagonal-Si), which is entirely composed of pentagons with all atoms in sp^3-hybridized states. State-of-the-art theoretical calculations confirm that the new silicon phase is dynamically, thermally and mechanically stable. The calculations of electronic band structure with HSE06 functional show that pentagonal-Si is a semiconductor with an indirect band gap of 2.05 eV that is much larger than that of diamond-Si, leading to distinguished optical absorption. Moreover, pentagonal-Si has a lower mass density (2.09 g/cm^3) compared with diamond-Si (2.34 g/cm^3), and exhibits a higher carrier mobility ($\sim 3 \times 10^3$ cm^2/V·s) at ambient temperature, adding new feature for optoelectronic applications.

1. Introduction

Carbon is one of the most versatile elements in the periodic table, and it can adopt sp, sp^2 and sp^3-hybridized states to form diverse structures such as fullerenes [1], graphene [2], penta-graphene [3,4] and diamond, and all of them show excellent physical properties. Recently, motivated by the unique geometry and novel properties of 2D penta-graphene and other 2D pentagonal structures [3–7], a 3D carbon allotrope, called chiral *pentagon only* diamond-like structures (CHIPODS), was proposed by Zhu et al. [8]. This 3D pentagonal carbon allotrope has extraordinary electronic and mechanical properties [9], which sparks an interest in finding 3D pentagon materials for other elements.

Silicon, next to carbon in the periodic table, is the second most abundant element in the earth's crust that is widely used in optoelectronic devices. Due to their broad applications, searching for new silicon allotropes has been of great interests over the past few decades, and many unconventional structures have been experimentally synthesized or theoretically investigated such as Si_{96}, Si_{24}, Si_{10}, c/24-Si, silicene [10–18]. Although both carbon and silicon belong to the same group in the periodic table, they can behave differently due to the larger atomic radius of Si with a larger energy level difference between 3*s* and 3*p*, it is much more difficult for silicon to form double or triple bonds. As a result, silicon prefers to adopt sp^3-hybridized states, displaying less varieties in geometry as compared to those of carbon. For example, silicon is unable to form structures like fullerene cages [19] or penta-graphene [20]. However, sometimes, silicon does behave like carbon. For instance, the two-dimensional (2D) structure of silicon called silicene can be regarded as the analogue of graphene, because of their similar honeycomb like geometry and Dirac cone like electronic properties. In addition, the structures of diamond-C and diamond-Si are also quite similar. Then, here comes a question: Can we find a 3D silicon structure that is entirely composed of pentagons just like CHIPODS we mentioned above? Currently, there is no study reported to address this question. In fact, for 3D silicon structures, the motif of pentagon is rather rare, because the disadvantageous bonding angles of pentagon will easily destroy the stability of the whole structure [21]. If this particular structure can be constructed and proved to be stable, it will be very inspiring for the theoretical study on new silicon allotropes.

In this paper, we propose a new 3D silicon allotrope, which is entirely made up of pentagonal silicon rings, named as pentagonal-Si. The dynamic, thermal and mechanical stability has been confirmed by using first-principles calculation. Our results show that as compared to the conventional diamond-Si, pentagonal-Si exhibits the following distinguished features: a larger indirect band gap of 2.05 eV, different optical absorption, lower mass density (2.09 g/cm^3), and higher carrier mobility ($\sim 3 \times 10^3$ cm/V·s) at ambient temperature.

2. Methods

All of the calculations that we performed are based on density functional theory (DFT) as implemented in the Vienna *ab initio*

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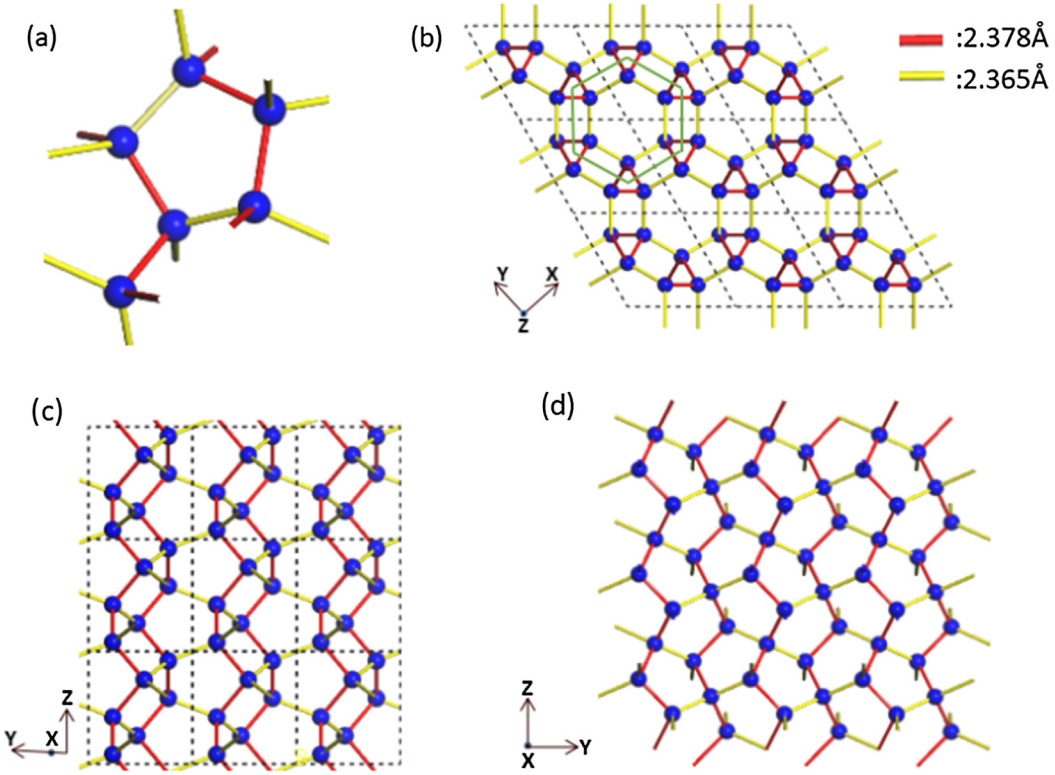

Fig. 1. (a) Unit cell of pentagonal-Si. (b) The top view and (c), (d) side views of a 3 * 3 * 3 supercell.

Simulation Package (VASP) [22] with the projector augmented wave (PAW) method [23]. And the kinetic energy cutoff of 380 eV is chosen to expand the valence electron wave functions. Perdew-Burke-Ernzerhof functional (PBE) within generalized gradient approximation (GGA) [24] is used for electronic exchange and correlation interaction. Full geometry optimizations are carried out by using the convergence of 10^{-6} eV and 10^{-3} eV/Å for energy and force, respectively. The first Brillouin zone is sampled by 11 × 11 × 10 Monkhorst-Pack k-point mesh [25]. To ensure the accuracy of electronic and optical properties, the calculations based on the hybrid Heyd-Scuseria-Ernzerhof functional (HSE06) [26,27] are repeated. In addition, the phonon spectra of pentagonal-Si is obtained by using finite displacement method that implemented in the phonopy package [28,29]. And *ab initio* molecular dynamics (AIMD) simulations is also used to examine the thermal stability.

3. Results and discussion

The unit cell of pentagonal-Si contains six silicon atoms, and all of them adopt sp^3-hybridized states, which is shown in Fig. 1(a). The optimized lattice parameters of this hexagonal primitive cell are a = b = 5.476 Å, and c = 5.122 Å. For each pentagon, there are two kinds of bond lengths (2.378 Å and 2.365 Å) and three kinds of bond angles (107.6°, 105.0°, and 105.9°). And the corresponding values of diamond-Si in which all silicon atoms adopt canonical sp^3 hybridization are 2.368 Å and 109.5°, respectively. These very similar results imply the good stability of pentagonal-Si. Fig. 1(b) and (c) show the top view and the side view of a 3 * 3 * 3 supercell of pentagonal-Si. It can be seen that pentagonal-Si owns a periodically spiral structure along the z-axis, and it fills the xy-plane with a hexagonal basic unit cell (green[1] lines in Fig. 1(b)). As a result, we can see that pentagonal-Si is assembly of spiral nanowires. From Fig. 1(d) which is another side view of the supercell, we can see the full pentagon features of pentagonal-Si more clearly.

To confirm the stability of pentagonal-Si, we first calculate the cohesive energy and then make a comparison with other silicon allotropes [12,13,15,30]. And the results are shown in Fig. 2 below. One can see that pentagonal-Si phase is only 0.053 eV/atom higher in cohesive energy than that of diamond-Si which is considered the most stable 3D silicon allotrope. Meanwhile, pentagonal-Si is energetically more favorable compared with many other reported 3D silicon allotropes. This indicates the excellent thermodynamic stability of pentagonal-Si.

Next, to estimate the dynamic stability of the pentagonal-Si, we calculate the phonon dispersion at ambient pressure as shown in Fig. 3(a). It can be seen that no imaginary frequencies are observed throughout the whole Brillouin zone, which conforms that pentagonal-Si is dynamically stable.

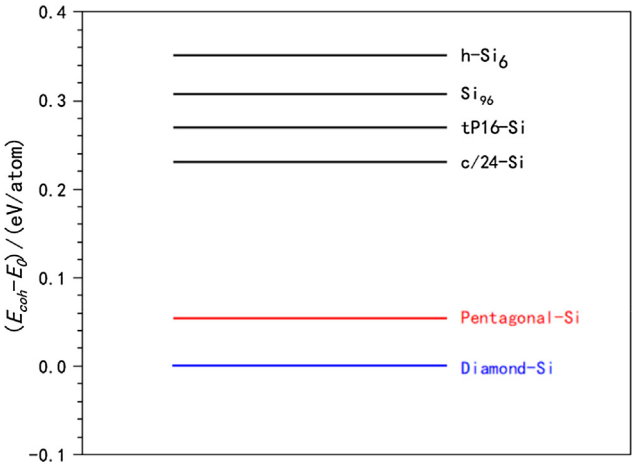

Fig. 2. Comparison of relative stability of pentagonal-Si with other known Si allotropes.

[1] For interpretation of color in Fig. 1, the reader is referred to the web version of this article.