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Strain effects on the modulation of band gap and optical properties of direct band gap silicon

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ABSTRACT

Based on the first-principles calculations, the strain effects on the optical properties of direct band gap silicon crystal D135-Si were systemically investigated. The stress-strain relations and phonon spectra show that the realistic peak tensile strengths in three principle symmetry crystallographic directions [100], [010] and [001] are 4.5, 9.7 and 12.1 GPa, respectively. By imposing the pressure and strain on structure, we studied the direct-indirect band gap transitions and obtained the ranges of the direct band gap, namely 0–4 GPa on pressure, −0.07–0, −0.04–0.08, and −0.01–0.03 on strain along *a*-, *b*- and *c*-direction, respectively. The imaginary part of the dielectric function was calculated to analyze the optical absorption property, which shows the strong adsorption coefficients in the visible range of the sunlight. The effect of pressure on the optical absorption property of structure is the smallest, and the strain effects are gradually enhanced along *c*-, *b*- and *a*-direction, respectively.

1. Introduction

As a traditional photovoltaic material, bulk silicon is usually applied to the first-generation solar cells to act as the absorber layer, and the spin-dependent properties make silicon promising in the spin-based quantum-information processing and spintronics. However, the indirect band gap makes the optical transitions at the threshold energy must need the assistance of momentum-conserving phonons [1,2], and makes the standard optical methods of spin injection and detection difficult [3]. In the hope of solving the limitation, many efforts have been made [4–10]. Ng et al. [4] introduced the dislocation loops by implanting boron into silicon as a dopant to form a local strain field, modifying the band structure and providing spatial confinement of the charge carriers. This means the room-temperature electroluminescence in a silicon light-emitting diode (LED) is achieved. Green et al. [5] reported that they utilized the reciprocity between light absorption and emission by maximizing absorption at relevant sub-bandgap wavelengths while reducing the scope for parasitic non-radiative recombination within the diode, to get a large increase of power conversion efficiency in the silicon LED. Compared to the common oxide thin films [11,12], the thin-film crystalline silicon, which is utilized into the solar cells, is more difficult. Pillai et al. utilized the surface plasmons to increase the spectral response and studied the effect of varying the particle size on that enhancement. [13] Moreover, searching for new silicon structures which has a direct band gap is also an alternative approach [14–22]. As we know that the traditional silicon need the sufficient thickness to ensure the light absorption in solar cells, failing to the thin-film silicon solar cell applications. Benefit from the successful Si-based microelectronics industry, searching novel Si phases which have the direct band gap is promising for the large-scale implementation of thin-film solar cells. Recently, Kim et al. [17] provided a unique two-step high-pressure precursor synthesis methodology of *Cmcm*-Si_{24}, which possesses a quasidirect band gap near 1.3 eV with an excellent optical property. Oh et al. [19] discovered the super-stable $Si(111)_n/Si(SC)$ superlattice structures with dipole-allowed direct band gaps, providing ideal conditions for the investigation of a direct-indirect band gap transition, and discussed the thermal stability and the possible synthesis through wafer bonding.

Recently, Lee et al. [20,23] uncovered various direct and quasi-direct band gap silicon crystal structures by using conformational space annealing, and calculated the optical absorption spectrums. Compared to the spectrums of solar, diamond Si, amorphous Si and polycrystalline Si, D135-Si shows a significant overlap with solar spectrum and a great improvement over other Si structures in the absorption spectrum,

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indicating an excellent photovoltaic efficiency. And shown in Ref [23], the D135-Si has a lower energy than the existing β-Sn phase [24,25] and *bct*5 phase [26], indicating a possible synthesis method. D135-Si is suitable for thin-film solar cell applications in view of its direct band gap characteristic and strong absorption ability, if it can be synthesized in future experiments successfully. More optical property studies such as the external effect to the material have not been discussed to give suggestions for experiments based on the promising material. In this paper, we studied the tensile stress-strain relations and ensure the dynamical stability in theoretical calculations. We explored the direct-indirect band gap transitions by imposing the pressure and strain on the lattice constants. On the condition that the material possesses a direct band gap, we thus investigated the pressure and strain effects on the optical absorption properties.

2. Computational methods

All of the calculations are performed based on the first-principles calculations. The exchange and correlation functional is the generalized gradient approximation (GGA) parameterized by Perdew, Burke and Ernzerrof (PBE) [27] in the Cambridge Serial Total Energy Package (CASTEP) code [28], and the density functional theory (DFT) [29,30] is within the Vanderbilt ultrasoft pseudopotentials [31]. The Broyden-Fletcher-Goldfarb-Shanno (BFGS) [32] minimization scheme is used in geometry optimization, and the total energy convergence tests are within 1 meV/atom. The energy cutoff is taken as 400 eV, and the *k*-points mesh is $4 \times 9 \times 8$ in the Brillouin zone. The self-consistent convergence of the total energy is 5.0×10^{-6} eV/atom, the maximum ionic Hellmann-Feynman force is 0.01 eV/Å. The maximum stress is 0.02 GPa and the maximum ionic displacement is 5.0×10^{-4} Å. For the final accurate calculations of bandgaps and optical properties, we adopt the Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional [33].

3. Results and discussions

The crystal structure of D135-Si, of which space group is *Cc* (No. 9) with a monoclinic symmetry, is shown in Fig. 1(a). It has 24 silicon atoms per unit cell, including six inequivalent atoms. The ideal strength is an upper bound for material strength when a perfect crystal becomes mechanically unstable [34]. In Fig. 1(b), we calculated the ideal strength to study the mechanical behavior of D135-Si. Along the three principle symmetry crystallographic directions [100], [010] and [001], the stress-strain relations under tensile strains are shown. The peak tensile strengths along the three directions are 5.9, 16.9 and 17.4 GPa, respectively. The weakest stress response is in the [100] direction, while the strongest stress response is in the [001] direction. All the calculated ideal strengths of D135-Si are smaller than the weakest stress response of Diamond-Si [35] of 22 GPa in the [111] direction. It can be found that D135-Si will first cleave in the (100) plane under tensile loading. The strain of peak tensile strength in the [100], [010] and [001] directions are 0.14, 0.21 and 0.18, respectively. Moreover, the stress-strain relation shows that the material has an obvious mechanical anisotropy. To ensure the dynamical stability of structures under pressure and strain, we calculated the phonon spectra of the structures under pressure and strains. The structure from 0 to 4 GPa is dynamically stable (see Fig. 2(a) and (b)). The solid symbol represents dynamical stability shown in Fig. 1(b), and the phonon spectra are plotted in Fig. 2(c)–(e). We found that the strains of dynamically stable structures only reach to 0.08, 0.1 and 0.1 along [100], [010] and [001] directions, respectively. There will be imaginary frequency at Γ point when the strain keeps up increasing. As a result, the realistic peak tensile strengths along the three directions are 4.5, 9.7 and 12.1 GPa, respectively.

In engineering applications, the device is always sensitive to the external conditions, and thus study on the effect of pressure or strain on materials is significant. It is known that the indirect band adsorption requires the assistance of phonon moments, so for the thin-film solar cell applications, we should ensure the material holds the direct band gap. In this paper, we imposed the pressure and strain on the D135-Si and calculated the electronic band structures to investigate the direct-indirect band gap transitions. It is known that the band gap usually is underestimated by common first-principles DFT methods for semiconductors. To obtain the gap value more accurately, in the band calculations, we used the HSE06 hybrid functional, which preserve a good calculation accuracy for band gap in solids. As seen in Table 1, the pressure range, which is satisfied to the demands of direct band gap, is from 0 to 4 GPa, and the strain ranges are from -0.07 to 0, -0.04 to 0.08, and -0.01 to 0.03 along *a*-, *b*-, and *c*-direction, respectively. These are in ranges of the strain of realistic peak tensile strengths in the [100], [010] and [001] directions, respectively.

From Table 1, one can see that, when the strain is imposed along *a*-direction, the optimized length of lattice constant *b* is decreasing with that of *a*, while that of *c* changes slightly. This indicates the required strain along *a*-direction mainly results in an opposite change of *b*. When the strain is along *b*- and *c*-direction, respectively, the lengths of the other two lattice constants are both decreasing. The angle β is increasing with both strain and pressure. The volume per atom *V* is increasing with strain and decreasing with pressure, whereas the variation tendency of density *g* is opposite to that of *V*.

The electronic band structure at 0 GPa are shown in Fig. 3(a), and the dash line represents the Fermi level (E_F). As seen, D135-Si at 0 GPa is semiconductive with a direct band gap of $E_{d0} = 1.185$ eV, which is in accordance with the previous result by quasiparticle G_0W_0 calculation of 1.05 eV [20]. We use an arrow line to link the valence band maximum (VBM) and conduction band minimum (CBM). Similar to the structure at 0 GPa, all of the other direct band gap structures under

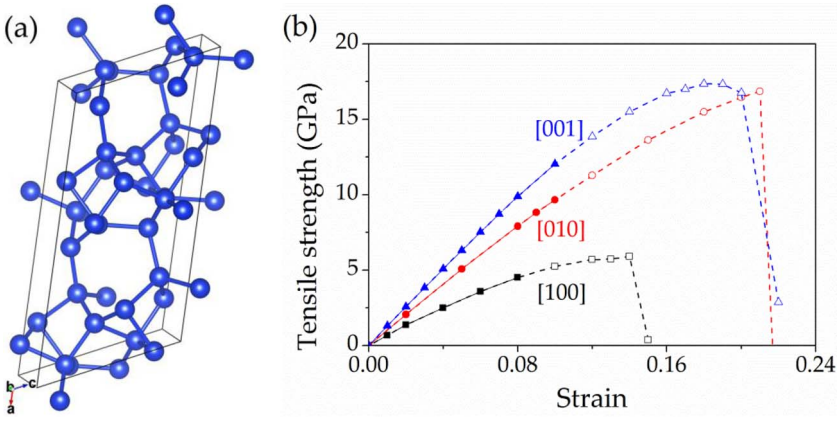

Fig. 1. Crystal structure (a) and tensile strength of D135-Si as a function of tensile strain (b). The solid symbol represents dynamical stability, whereas hollow symbol instability.