Electronic band transformation from indirect gap to direct gap in Si–H compound*

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The electronic band structures of periodic models for Si–H compounds are investigated by the density functional theory. Our results show that the Si–H compound changes from indirect-gap semiconductor to direct-gap semiconductor with the increase of H content. The density of states, the partial density of states and the atomic charge population are examined in detail to explore the origin of this phenomenon. It is found that the Si–Si bonds are affected by H atoms, which results in the electronic band transformation from indirect gap to direct gap. This is confirmed by the nearest neighbour semi-empirical tight-binding (TB) theory.

Keywords: Si–H compounds, band structure, density functional theory, tight-binding calculation
PACC: 7125R, 7115M, 7115F, 7155F

1. Introduction

Although silicon is a conventional semiconductor material, it has received much attention since an important discovery of superconductivity below critical temperature in heavy B-doped cubic silicon was achieved by using gas immersion laser doping recently.[1] Meanwhile silicon nanostructures also have attracted much attention in nanoscience and nanotechnology[2−5] because of the well-established Si technology and the integration on Si circuits.

Various types of silicon photonic devices have been investigated because silicon has merits in cost and process ability,[6−9] but the usage of the bulk silicon is limited due to its indirect and small band gap feature. Because of the quantum confinement effect, Si nanocrystals and nanowires are expected to have a wide band gap and due to zone folding to the Γ-point they can exhibit a direct band gap characteristic. In addition, the direct band gap characteristic can also be obtained in Si nanowires by means of the lattice strain.[10]

However, is it possible for silicon bulk material to exhibit a direct band gap? Hydrogen plays a crucial role in surface etching, passivation and growth. The interaction of hydrogen with semiconductor surfaces is of great technological importance and fundamental scientific significance. Normally, adsorption of H leads to a saturation of dangling bonds on semiconductor surfaces and an elimination of surface states from the band gap, making the surface semiconducting and chemically inert.[11,12] Yet, recent experiments [13−15] provided clear evidence for such a surprising hydrogen-induced metallization of a particular silicon carbide surface.

In the rest of this paper we present calculation results from the density functional theory (DFT) according to the periodic model of Si–H compound with different contents of H atoms in Section 2. Then we discuss the density of states (DOS) and atomic charge population in Section 3. The results are also supported by the band structure calculated based on tight-binding theory in Section 4. Finally, the conclusion is given in Section 5.

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2. Calculational method

The calculations are carried out in the framework of the DFT in the local density approximation (LDA). Geometry optimization and electronic structures are studied by using the CASTEP code [16] in the generalized gradient approximation (GGA) of PW91 form.[17] The ion–electron interaction is modeled by ultrasoft pseudopotentials in the Vanderbilt form.[18] The plane-wave cutoff energy is taken as 290 eV and the sampling with 2×2×2 for 64-atom super cell Monkhorst–Pack k-point[19] is used. In the self-consistent calculation, the total energy convergence value of each atom in the system is fixed at 2.0×10^{-6} eV, the force of each atom is under 0.05 eV/Å, the tolerance displacement is under 0.002 Å (1 Å=0.1 nm), and stress is under 0.1 GPa.

The optimized lattice constant for silicon is 5.410 Å. The positions of the atoms in all models are optimized in the condition of fixed lattice parameters.

3. Results

3.1. Direct gap resulting in $Si_{60}H_{16}$ compound alloy

A $Si_{60}H_{16}$ supercell structure is reconstructed from 64-atom defect-free crystal Si supercell (shown in Fig. 1(a)), in which four Si atoms are taken out, and the Si atoms around the four Si vacancies are saturated by sixteen H atoms.

After the geometry optimization, the distance of Si–H bond length is 1.462 Å. The smallest distance between Si–Si atoms adjacent to the vacancies is 2.3064 Å, and other Si–Si bond lengths are in a range from 2.318 to 2.3355 Å, which are less than 2.364 Å in defect-free Si crystal. The band structure of the above supercell is shown in Fig. 1(b). The valence band edge of the Si–H compound is set to be zero.

Interestingly, it can be obviously seen from Fig.1(b) that the minimum energy point of the conduction bands moves from the location near X-point to Γ-point, while the top of the valence bands still locates at Γ-point, which yields a direct band gap and the calculated band gap is 0.74 eV.

For Si crystal the bottom of the conduction bands is located near the X-point and the top of the valence bands is located at Γ-point, with an indirect band gap of 1.17 eV. The band gap calculated by the DFT is only 0.68 eV, which is obviously lower This difference is attributed to the well-known drawback of DFT. However the transformation trends of the band structure predicted by DFT are reliable.

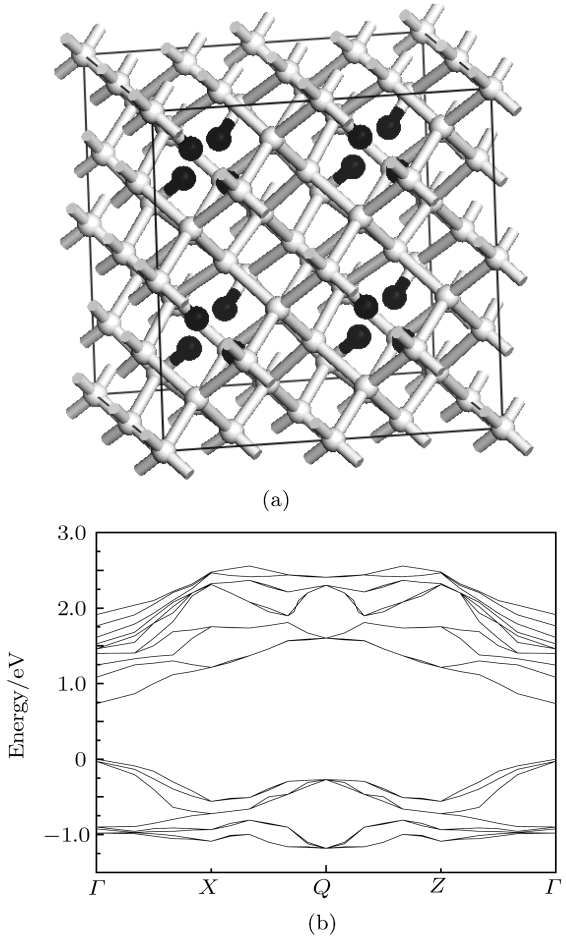


Fig. 1. (a) Optimized structure of $Si_{60}H_{16}$ supercell, where white balls represent Si atoms and black balls represent H atoms, and (b) electronic band structure of the $Si_{60}H_{16}$ supercell as shown in (a).

3.2. Effect of H content on electronic band structure of Si–H compound

To study the influence of H content on electronic band structure of Si–H compounds, the other two different supercells of $Si_{63}H_4$ and $Si_{62}H_8$ are considered. In a way similar to that for the $Si_{60}H_{16}$, the two supcells are also reconstructed from Si_{64} supecell by removing out one and two Si atoms and passivating Si atoms with four and eight H atoms, respectively.

The calculated band structure characteristics of different Si–H compounds are listed in Table 1. The electronic band structure indicates that the energy level of the lowest conduction band near (0.85 0 0) $2\pi/a$ is uplifted and the uplift increases with the increase of the H content. But the energy level at Γ-point decreases. This will eventually result in a di-

rect band gap. The calculations demonstrate that the band gaps in Si–H compounds can be tuned by the H content.

Table 1. Band structure characteristics and total energies of different Si–H compounds.

structure	Si_{64}	$Si_{63}H_4$	$Si_{62}H_8$	$Si_{60}H_{16}$
gap	indirect	indirect	direct	direct
band gap/eV	0.73	0.78	0.80	0.74

3.3. DOS of Si and H atoms

Figure 2 shows the DOSs of the different Si atoms. We refer to the Si which is the nearest to the H atom as the first nearest neighbour. The farther atoms are called the second nearest neighbour and the rest of atoms are named analogically. Compared with the DOS shown in Fig. 2(a), the DOS of the first nearest neighbour Si in $Si_{63}H_4$ supercell has an obvious difference from that in Si_{64} supercell. The difference in the DOS of Si atoms between in $Si_{63}H_4$ supercell and in Si_{64} supercell decreases as the distance between Si and H atoms increases. The difference can be ignored for the third nearest neighbour. The comparison of the DOS of Si atoms between in $Si_{60}H_{16}$ (shown in Fig. 2(b)) and in $Si_{63}H_4$ supercells indicates that not only distance but also the content of H atom will influence the DOS of Si atoms and the influence will become more obvious as the H content increases. In fact, the Si orbital is first changed from set $\{|s\rangle, |p_x\rangle, |p_y\rangle, |p_z\rangle\}$ orbital to the set of sp^3 hybridized orbital and then Si and H atoms form the Si–H bonds.[20] The induced effects of Si–H bonding result in the difference in the DOS of Si atoms.

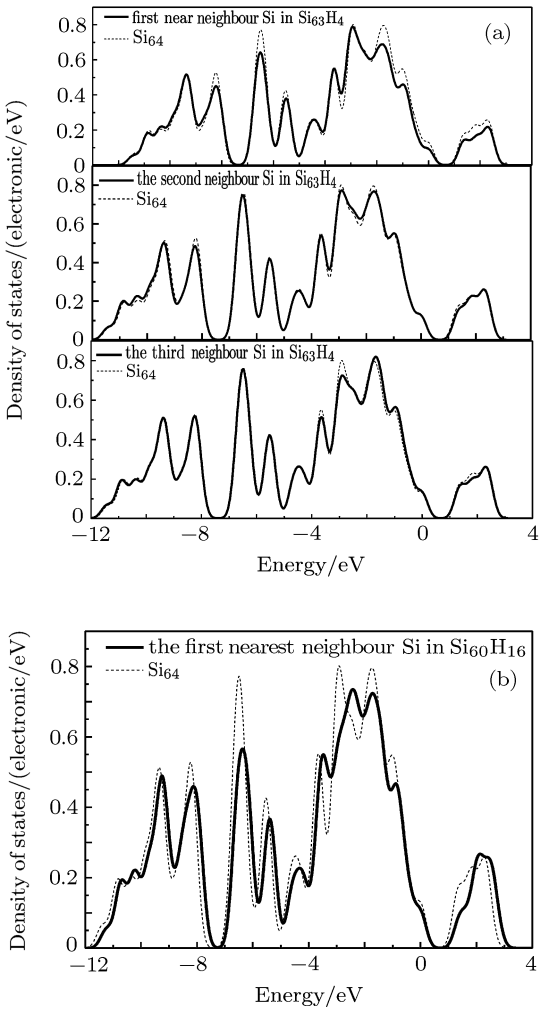


Fig. 2. (a) DOS of the three nearest neighbour Si atoms in $Si_{63}H_4$ supercell compared with the DOS of Si atom in Si_{64} supercell, and (b) the DOS of the first nearest neighbour Si atom in $Si_{60}H_{16}$ supercell compared with the DOS of Si atom in Si_{64} supercell.

3.4. Atomic charge population of Si–H compound

The atomic charge population can describe the transfer of charges between different atomic orbitals.[21] Figures 3(a) and 3(b) show the atomic

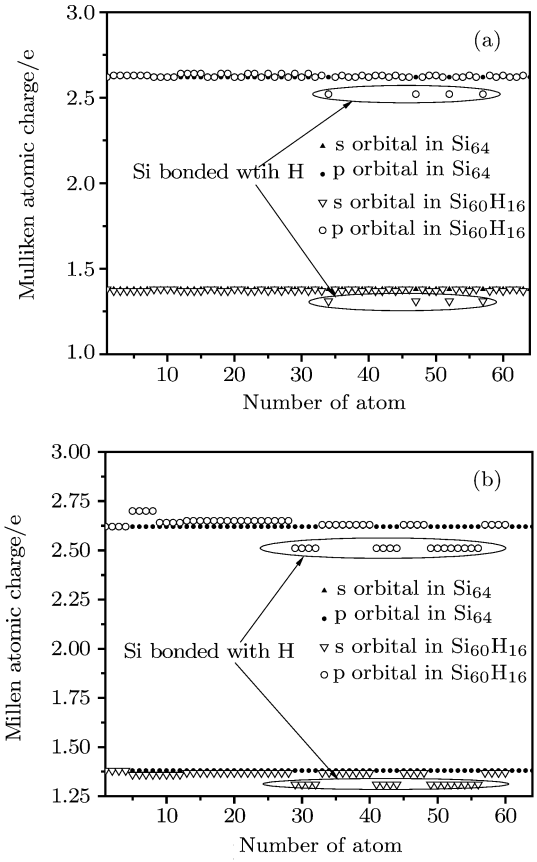


Fig. 3. (a) Atomic charge population in $Si_{63}H_4$ supercell and (b) atomic charge population in $Si_{60}H_{16}$ supercell.

charge populations in the $Si_{63}H_4$ and $Si_{60}H_{16}$ supercells, respectively.

As shown in Fig. 3(a), the points in the ellipse denote Si atoms which are bonded with H atoms, and the charges on Si 3s orbital and Si 3p orbital decrease. For the other Si atoms that are not bonded with H atoms, the charges on Si 3s orbital decrease, but the charges on the Si 3p orbital increase. This indicates that the charges on the Si 3s orbital transfer to H 1s orbital, and the charges on the Si 3p orbital that are bonded with H atoms transfer to the other atoms that are not bonded with H atoms. Comparing Fig. 3(a) with Fig. 3(b), the transfer is increased obviously with the increase of H content in the compound.

4. Discussion of results from density functional theory results

The above results show that the Si–H bonding can influence the DOS of Si atoms. In the Si–H supercell the bondings between H 1s orbital and Si 3s, Si 3p orbitals are the possible reason for the change in DOS of Si. The atom population (shown in Fig.3) indicates that the Si–H bonding causes the charge transfer on Si orbital, which leads the charges on Si 3s to decrease and those of Si 3p to increase. Thus, we suppose that this change of charges will cause the neighbour Si orbital to hybridize with H 1s, so such an obital is referred to as equivalent hybrid orbital. This hybrid effect is equal to the weakening of the interaction between Si 3s and Si 3s, along with the strengthening of the interaction between Si 3p and Si 3p. We refer to this effect as equivalent hybrid interaction. The effect is strengthened with the reduction of distance between Si and H atoms. Moreover, the higher the content of H atom in a supercell is, the more obvious the impact will become. The equivalent hybrid impact changes band structures and may produce a direct band gap.

5. Energy band calculation based on TB method

We try to use the nearest neighbour semi-empirical tight-binding theory of energy bands (TB) method to discussion the effect of equivalent hybrid interaction. The TB theory has improved the pioneering work of Slater and Kostor.[22−25] It has been used in Si–H systems[26,27] and nanowire calculation.[28] According to the discussion in Section 4, we need to change the Slater parameters of TB theory as follows:

(i) cutting down the amount of $\left\langle s|\hat{H}|s\right\rangle$,

(ii) enhancing the value of $\left\langle p|\hat{H}|p\right\rangle$,

(iii) treating the Si vacancies as defects in bulk Si.

We construct the tight-binding Hamiltonian in a basis of quasi-atomic functions[18]

$$|\phi_{mfk}\rangle = N^{-1/2}\sum_{i,f}\exp\left(\mathrm{i}\,\boldsymbol{k}\boldsymbol{R}_i + i\boldsymbol{k}\boldsymbol{v}_m\right)|mf\boldsymbol{R}_i\rangle, \quad (1)$$

where quantum number m runs over s, p_x, p_y, p_z, s^* and d orbitals; N wavevectors for k lie in the first Brillouin zone; site index f is either a (for anion) or c (for cation); R_i is the anion positions δ is the Kronecker We have $v_\mathrm{b} = \delta_{\mathrm{b,c}}(aL/2)(1,1,1)$. The quasiatomic functions are of Löwdin orbital.

Equivalent hybrid orbital can be expressed as

$$\phi_j = \alpha\phi_\mathrm{s}^\mathrm{H} + \beta\phi_j^\mathrm{Si}, \quad (2)$$

where j is the s or p atomic orbital. Thus, the Slater parameters can be expressed as

$$\begin{aligned}
&\langle\phi_\mathrm{s}|\hat{H}|\phi_\mathrm{s}\rangle = \alpha^2 V_\mathrm{Hs} + 2\alpha\beta V_\mathrm{Hss} + \beta^2 V_{ss},\\
&\langle\phi_\mathrm{s}|\hat{H}|\phi_\mathrm{p}\rangle = \alpha^2 V_\mathrm{Hs} + \alpha\beta\left(V_\mathrm{Hsp} + V_\mathrm{Hss}\right) + \beta^2 V_{\mathrm{sp}\sigma},\\
&\langle\phi_\mathrm{p}|\hat{H}|\phi_\mathrm{p}\rangle = \alpha^2 V_\mathrm{Hs} + 2\alpha\beta V_\mathrm{Hsp} + \beta^2 V_{\mathrm{pp}\sigma}, \quad (3)\\
&\varepsilon_j = \alpha^2\varepsilon_\mathrm{s}^\mathrm{H} + \beta^2\varepsilon_j^\mathrm{Si}, \quad (4)
\end{aligned}$$

where V_Hss and V_Hsp are the equivalent interactions between H 1s and Si 3s states, and between H 1s and Si 3p states, respectively; V_Hs is the equivalent interaction between H 1s on the anion site and H 1s on the cation site; $\varepsilon_\mathrm{s}^\mathrm{H}$ is the H orbital parameter. The rest of parameters are listed in Table 2.[20]

Table 2. Energy band parameters for Si.[20]

eV	$\varepsilon_\mathrm{S}^\mathrm{A}$	$\varepsilon_\mathrm{P}^\mathrm{B}$	$\varepsilon_\mathrm{d}^\mathrm{B}$	$\varepsilon_{\mathrm{s}*}^\mathrm{B}$	$V_{\mathrm{ss}\sigma}$	$V_{\mathrm{s}*\mathrm{s}*\sigma}$	$V_{\mathrm{ss}*\sigma}$	$V_{\mathrm{sp}\sigma}$	$V_{\mathrm{s}*\mathrm{p}\sigma}$
Si	–2.1517	4.2293	13.7895	19.1165	–1.9593	–4.2414	–1.6933	3.0256	3.1557
	$V_{\mathrm{sd}\sigma}$	$V_{\mathrm{s}*\mathrm{d}\sigma}$	$V_{\mathrm{pp}\sigma}$	$V_{\mathrm{pp}\pi}$	$V_{\mathrm{pd}\sigma}$	$V_{\mathrm{pd}\pi}$	$V_{\mathrm{dd}\sigma}$	$V_{\mathrm{dd}\pi}$	$V_{\mathrm{dd}\delta}$
	–2.2849	–0.8099	4.1036	–1.5180	–1.3555	2.3848	–1.6814	2.5888	–1.8140

In addition, $V_{\rm Hss} = -1.95$ eV, $V_{\rm Hsp} = -1$ eV. The values of α and β are calculated as follows:

$$\alpha = -\sqrt{\frac{P_{\rm H}}{4}}, \quad \beta = \sqrt{1 - \frac{P_{\rm H}}{4}} \quad \text{or}$$
$$\alpha = \sqrt{\frac{P_{\rm H}}{4}}, \quad \beta = -\sqrt{1 - \frac{P_{\rm H}}{4}}, \qquad (5)$$

where $P_{\rm H}$ is the H content in Si–H alloy. It is worth noting that α is so small that it can be ignored in formulas (3) and (4).

The band structure of Si–H compound calculated by TB theory is shown in Fig. 4(a). The solid line represents the band structure of c-Si. The bottom of the conduction band is near X point. It has an indirect band structure. The dash dot line corresponds to Si–H compound with an H atom content of 11%. The band gap almost turns into a direct gap because the energy level at the conduct band bottom rises and the energy level at Γ point decreases. It is worth noting that the band gap value caused by the uplifting of the conduct band bottom also increases.

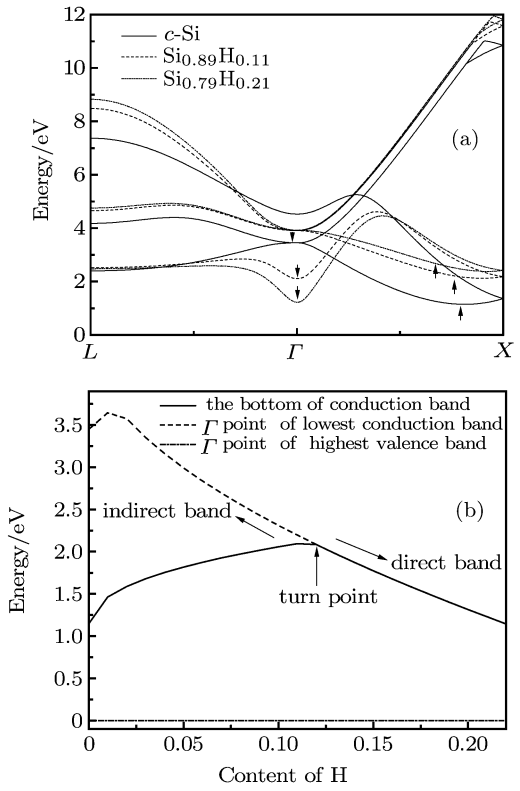


Fig. 4. (a) Band structure of Si–H system calculated by TB, and (b) energies at the bottom of conduction band, Γ point of the lowest conduction band and Γ point of the highest valence band of Si–H compounds with different H contents, calculated by TB theory.

The energies at the bottom of conduction band, Γ point of the lowest conduction band, Γ point of the highest valence band and the bottom of conduction band with different H contents are calculated by the TB theory, and the results are shown in Fig. 4(b). From Fig. 4(b) it can be seen that the compound begins to change from an indirect to a direct gap structure at a critical content value of H atoms 12%. For Si–H compound, with the increase of H atom content, the band gap increases at the beginning and decreases after the turning point. This result is in agreement with that from DFT calculation, which has been discussed above.

6. Conclusion

The electronic band structures of Si–H compounds are investigated by DFT calculations. Our results show that the Si–H compound changes from an indirect-gap semiconductor to a direct-gap semiconductor with the increase of H content. It is found that the H atoms play a critical role in changing the band structure. They cannot only eliminate the defect states in the band gap, but also influence the Si–Si bonds. Thus, the interaction between Si 3s and Si 3s are weakened, whereas the interaction between Si 3p and Si 3p are strengthened. This result is confirmed by the TB theory, showing that the direct-gap in the Si–H compound is caused by the equivalent hybrid effect. Our findings indicate that the Si–H compounds could be a novel material for photonic devices.

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