

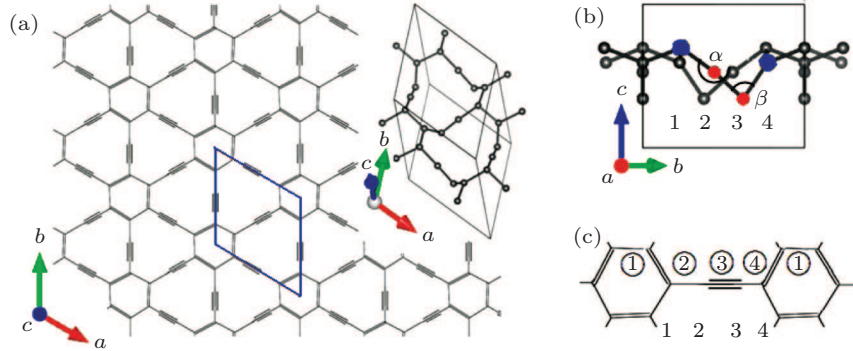


each  $a$ , the atom positions and bond lengths are optimized. As an initial condition, Si atoms on the hexagonal rings are set the same as a two-dimensional honeycomb network structure of silicene, while Si atoms on the disilynic linkage are set the same as the planar sheet structure of graphyne. All bond lengths are set equal, ranging from 2.10 Å of a triple bond to 2.35 Å of a single bond. Because of the height along the  $z$  axis,

we need to reduce the minimum lattice length to  $1.8 \times 5$  Å. The bond length reads

$$D_{\text{bond}} = \sqrt{d_x^2 + d_y^2 + d_z^2}, \quad (1)$$

where  $d_x$ ,  $d_y$ , and  $d_z$  are the partial bond length along the  $x$ ,  $y$ , and  $z$  axis, respectively, and  $D_{\text{bond}}$  falls into the range from the triple bond length to the single bond length.



**Fig. 1.** (color online) (a) Geometric structure of silicyne. The parallelogram (blue solid line) represents a unit cell. The three-dimensional structure of a unit cell is shown on the upper right corner. (b) Three-dimensional structure of a unit cell. The atoms  $\text{Si}_1$  and  $\text{Si}_4$  on hexagonal ring are drawn as blue circles;  $\text{Si}_2$  and  $\text{Si}_3$  on the acetylenic linkage are drawn as red circles. The  $\text{Si}_1$ - $\text{Si}_2$ - $\text{Si}_3$  angle is  $\alpha$  and  $\text{Si}_2$ - $\text{Si}_3$ - $\text{Si}_4$  angle is  $\beta$ . (c) Assignment for bonds. Bonds are numbered with ①, ②, ③, and ④, respectively.

## 4. Results and discussion

In this section, we will present our numerical results and discussion of the optimized geometry and electronic band structures.

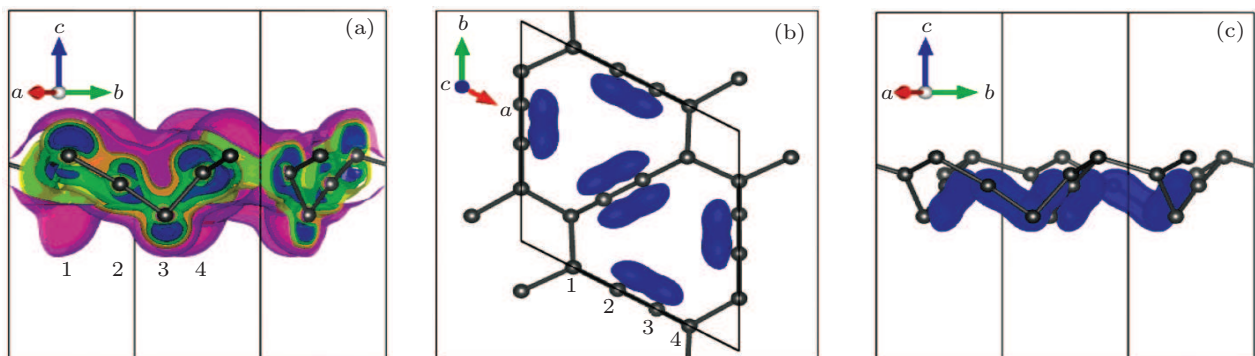
### 4.1. Optimized geometry

The optimized lattice constant of the hexagonal primitive cell is found to be 9.5 Å and the bond lengths are 2.34, 2.30, 2.17, and 2.32 Å for the bonds ①–④ shown in Fig. 1(c). The bond length ① is slightly longer than ② and ④. The type of bond ① is  $\text{Si}(\text{sp}^3)$ - $\text{Si}(\text{sp}^3)$ , as is the same in silicene (2.28 Å), and the bond ④ is a typical single bond  $\text{Si}(\text{sp}^3)$ - $\text{Si}(\text{sp}^3)$  (2.35 Å). The type of the bond ② is very different from bond ④, which can be considered as  $\text{Si}(\text{sp}^3)$ - $\text{Si}(\text{sp}^2)$ . The type of bond ③ is considered to be  $\text{Si}(\text{sp}^2) \equiv \text{Si}(\text{sp}^3)$  triple bond, and the bond length value is also consistent with the results of trans-bent disilyne of  $\text{H-Si} \equiv \text{Si-H}$  (2.10 Å). The difference in the bond length is probably due to the asymmetric

structure ( $\alpha = 174.0^\circ \neq \beta = 89.7^\circ$ , bond ②  $\neq$  bond ④) and the conjugated atoms mentioned above.

The bond length ③ is about 3% larger than 2.10 Å and is closer to the typical double bond ( $\text{Si}=\text{Si}$ ) length, which is 2.16 Å,<sup>[25]</sup> while the bond lengths ② and ④ are 2% and 1% smaller than the typical single bond length. Thus, with the bond length alone, we cannot determine whether silicon atoms form  $-\text{Si} \equiv \text{Si}-$  or  $=\text{Si}=\text{Si}=-$  bond, so we need to take the charge densities into account.

We project each band on Si atoms and obtain corresponding partial charge densities of silicyne, as shown in Fig. 2, for determining the bond type. There are both  $\text{sp}^3$  and  $\text{sp}^2$  hybridized Si atoms in silicyne. In Fig. 2, we project the band structure on atom  $\text{Si}_1$  and  $\text{Si}_4$  at the hexagonal ring with  $\text{sp}^3$  hybridization, and atom  $\text{Si}_2$  with  $\text{sp}^2$  hybridization and  $\text{Si}_3$  with  $\text{sp}^3$  hybridize at the acetylenic linkage. The bond ② between  $\text{Si-sp}^3$  and  $\text{Si-sp}^2$  atom is a single  $\sigma$  bond contributed by  $s$  and  $p_x + p_y + p_z$  orbitals of  $\text{Si-sp}^3$ , as well



**Fig. 2.** (color online) (a) The partial charge densities. (b), (c) Partial charge densities of the valence band maximum from different angles. The  $\pi$  bond is indicated by dark blue shadow.



## 5. Conclusions

The lattice parameter of silicyne is 9.5 Å and the silicon chain between hexagons is not composed of cumulative linkages (=Si=Si=), but composed of disilynic linkages (–Si≡Si–) instead. The effects of asymmetric structure and conjugated multiple bonds are very important for silicyne. The binding energy of silicyne is about 87% of that of silicene. Consequently, silicyne is expected to be stable when it is synthesized. The band structure of silicyne is calculated by both GGA-PBE and HSE06. The gap value produced by HSE06 is 0.73 eV, which is nearly triple that by GGA-PBE. Both band structures show similar features.

Moreover, due to the much higher surface reactivity compared with graphyne, adsorption of suitable guest atoms on silicyne can lead to a more stable semiconductor. Thus, surface modifications should be very important to adjust the intrinsic properties of silicyne and for designing promising nano-electronic devices.

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