Silicane nanoribbons: electronic structure and electric field modulation

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Abstract
We present electronic band structure, Gibbs free energy of formation, and electric field modulation calculations for silicane nanoribbons (NRs), i.e., completely hydrogenated or fluorinated silicene NRs, using density functional theory. We find that although the completely hydrogenated silicene (H-silicane) sheet in the chair-like configuration is an indirect-band-gap semiconductor, a direct band gap can be achieved in the zigzag H-silicane NRs by using Brillouin-zone folding. Compared to H-silicane NRs, the band gaps of completely fluorinated silicene (F-silicane) NRs reduce at least by half. For all silicane NRs considered here, the Gibbs free energy of formation is negative but shows different trends by changing the ribbon width for H-silicane NRs and F-silicane NRs. Furthermore, by analyzing the effect of transverse electric fields on the electronic properties of silicane NRs, we show that an external electric field can make the electrons and holes states spatially separated and even render silicane NRs self-doped. The tunable electronic properties of silicane NRs make them suitable for nanotechnology application.

Keywords: silicane nanoribbon, electronic structure, electric field
1. Introduction

Silicene, a two-dimensional (2D) monolayer of silicon (Si) atoms in the honeycomb lattice, has recently aroused tremendous attention in the scientific community, owing to its graphene-like electronic properties [1], such as the presence of a Dirac cone in the vicinity of \( K \) points, and its compatibility with current Si-based electronics. Synthesis of silicene on the different substrates, such as Ag(110), Ag(111), and ZrB\(_2\)(0001), has been reported by some groups [2–6]. Being different from the flat geometry of graphene, silicene has a stable, low-buckled honeycomb structure, as a result of which a perpendicular electric field can induce a tunable band gap in silicene by breaking the inversion symmetry [7, 8]. Adsorption of a foreign chemical species, such as hydrogen (H), fluorine (F), or chlorine (Cl), is also a promising approach to tailor the electronic properties of silicene [9–13]. Houssa \( et \ al \) [10] demonstrated using density functional theory (DFT) calculations that completely hydrogenated silicene, also called silicane, has a wide band gap. Quhe \( et \ al \) [13] predicted that single-side adsorption of alkali atoms can open a band gap in silicene, and the band gap size is controllable by changing the adsorption coverage, with a maximum band gap up to 0.50 eV. Furthermore, the dimensionality of materials plays a crucial role in modulating their electronic properties. One-dimensional (1D) silicene nanoribbons (NRs) possess distinct electronic and magnetic properties depending on their chirality, width, and edge structure. Ding \( et \ al \) [14] found that the band gap of edge hydrogenated armchair silicene NRs oscillates with the width in a period of three. Fang \( et \ al \) [15] studied the effect of edge hydrogenation and doping on the properties of zigzag silicene NRs, showing that the dihydrogenated edges can effectively stabilize the antiferromagnetic semiconducting ground state of zigzag silicene NRs and nitrogen (or phosphorus) doped monohydrogenated zigzag silicene NR is a magnetic semiconductor. Though the chemical functionalization is considered one of the important methods to tune the properties of silicene, few theoretical works have systematically examined the properties of surface-functionalized silicene NRs.

In this work, we present a DFT study on the electronic band structure and relative stability of completely hydrogenated and fluorinated silicene NRs. Moreover, we investigate the effect of transverse electric fields on the electronic properties of NRs, showing that an external electric field can make the electrons and holes states localized at the different sides of an NR and even render the NR self-doped.

2. Method

Our calculations were performed using DFT with the norm-conserving pseudopotential method as implemented in the Siesta [16, 17] code. The Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) [18] was used for the exchange-correlation functional. Double-zeta plus polarization numerical atomic orbitals were used for all atoms. A cutoff of 250 Ry for the grid integration was employed to guarantee a good description of the charge density. One primitive unit cell was used in all calculations. A vacuum region larger than 10 Å was used to avoid interaction between the neighboring images of NRs. Brillouin-zone (BZ) integration was performed on a \((30 \times 1 \times 1)\) and \((1 \times 18 \times 1)\) Monkhorst–Pack \( K \) POINTS [19] meshes for the atomic relaxation of zigzag NRs and armchair NRs, respectively. All geometries were relaxed.
until the maximum atomic force was smaller than 0.03 eV Å$^{-1}$. The uniform transverse electric field was modeled by a sawtooth-like potential.

3. Results and discussion

Following the convention of graphene and graphane [20], the hydrogenated and fluorinated silicene are named as H-silicane and F-silicane, respectively. Here, we consider only the chair-like configurations of H-silicane and F-silicane, as shown in figure 1 (a), the stabilities of which have been verified recently [9–11]. The optimized lattice constants are $a = 3.87$ Å, 3.88 Å, and 3.93 Å for silicene, H-silicane, and F-silicane sheets, respectively. Our calculations show that H-silicane sheet has an indirect gap of 2.282 eV with the valence band maximum (VBM) at the $\Gamma$ point and the conduction band minimum (CBM) at the M point, while the F-silicane sheet has a direct gap of 0.887 eV with both the VBM and CBM at the $\Gamma$ point, which are in good agreement with the previous calculations [9–11]. We then construct the 1D zigzag and armchair silicane NRs by cutting the 2D chair-like silicane sheets. The zigzag H-silicane NR with $n$ zigzag chains is named as H-$n$ZSNR, while the armchair H-silicane NR with $n$ dimer lines is named as H-$n$ASNR. The same definitions are used for the F-silicane NRs. The edge Si atoms are all saturated with H or F atoms to avoid the effects of dangling bonds. Li et al [21] have shown that the bare edges of zigzag silicane NRs can induce magnetic moments, whereas the passivated edges have no magnetism. We define the width of a silicane NR as the distance between the Si atoms at two edges, as shown in figures 1 (b) and (c). The width of ZSNRs and ASNRs is dependent on the parameter $n$ and given by

$$W_Z = \frac{\sqrt{3}}{6} (3n - 2)a$$  (1)
\[ \Delta W_n = \frac{1}{2} (n - 1) a \]

with the silicane lattice constant \( a \).

3.1. Electronic structures of silicane NRs

We now study the electronic band structures of zigzag and armchair silicane NRs. Figures 2(a)–(c) show the band structures of H-4ZSNR, H-10ZSNR, and H-17ASNR with widths of 11.20 Å, 31.36 Å, and 31.04 Å, respectively. Interestingly, for H-4ZSNR and H-10ZSNR, the VBM and CBM are all located at the \( \Gamma \) point, which is different from the indirect band gap of the H-silicane sheet. The VBM has a main contribution from the Si 3\( p \) states, while the CBM consists mainly of the Si 3\( s \) and 3\( p \) states (see figures 2 (d) and (e)). For H-17ASNR, however, it has an indirect band gap with the VBM at the \( \Gamma \) point and the CBM at the Y point. All the H-ZSNRs studied here exhibit direct band gaps, whereas the H-ASNRs have indirect band gaps. The calculated band gaps for H-4ZSNR, H-10ZSNR, and H-17ASNR are 2.526 eV, 2.348 eV, and 2.410 eV, respectively, which are slightly larger than that of the H-silicane sheet due to the quantum confinement effect. On the other hand, our results show that all the F-silicane NRs are direct-band-gap semiconductors. Figures 3 (a) and (d) show the band structures of F-10ZSNR and F-17ZSNR with widths of 31.77 Å and 31.44 Å, respectively. The calculated band gaps for F-10ZSNR and F-17ZSNR are 0.979 eV and 1.025 eV, respectively, which are about half of that of H-10ZSNR, indicating that fluorination is an effective avenue to tune the band gap of silicene NRs.

The band gap versus the width of silicane NRs is shown in figure 4. For silicene NRs, the band gap decreases as the NR width increases, and the armchair NRs have a slightly larger band...
gap than the zigzag NRs. We ascribe the emergence of a direct band gaps in H-ZSNRs to the BZ folding, i.e., the $M$ point in the 2D BZ of the H-silicane sheet is folded to the $\Gamma$ point in the 1D BZ of the H-ZSNRs, resulting in the CBM located at the $\Gamma$ point. To quantify the change of the energy of conduction band bottom states of H-ZSNRs, we define $\Delta E$ as the energy difference between the energy of the conduction band bottom at the X point and the energy of

**Figure 3.** Band structures and isosurfaces (0.05 e Å$^{-3}$) of the VBM and CBM wavefunctions for F-10ZSNR [(a)–(c)] and F-17ASNR [(d)–(f)], respectively. The Fermi energy is set to zero.

**Figure 4.** Variation of the band gap of zigzag ($4 \leq n \leq 16$) and armchair ($8 \leq n \leq 20$) silicane NRs as a function of NR width. The energy gap levels of H-silicane and F-silicane sheets are denoted by black and blue dashed lines, respectively. The inset shows the value of $\Delta E$ varying with the width of H-ZSNRs.
the CBM at the $\Gamma$ point (see figure 2 (a)). As shown in the inset of figure 4, $\Delta E$ also decreases with increasing NR width; $\Delta E$ is 0.433 eV for H-4ZSNR and changes to 0.047 eV for H-16ZSNR, showing an obvious size effect.

3.2. Relative stability of silicane NRs

Next, we study the relative stability of silicane NRs. As these NRs have different chemical compositions, the cohesive energy per atom does not offer an appropriate criterion to compare their relative stability. Therefore, we adopt the approach in references [22, 23] and define a zero-temperature molar (per atom) Gibbs free energy of formation $\delta G$ for a silicane NR as

$$\delta G = E_c - x_i \mu_i - (1 - x_i) \mu_{\text{Si}}$$

where $E_c$ is the cohesive energy per atom of a silicane NR, $x_i$ is the molar fraction of atom $i$ ($i = \text{H or F}$) in the NR. We choose $\mu_i$ as the binding energy per atom of $i_2$ molecule and $\mu_{\text{Si}}$ as the cohesive energy per atom of silicene sheet. Using $E_c = (E_{\text{tot}} - n_i E_{i_2 - \text{atom}} - n_{\text{Si}} E_{\text{Si-atom}})/(n_i + n_{\text{Si}})$, $\mu_j = (E_j - 2E_{i_2 - \text{atom}})/2$, and $\mu_{\text{Si}} = E_{\text{silicene}} - E_{\text{Si-atom}}$, we obtain another formula for the $\delta G$ of a silicane NR as follows

$$\delta G = \left( E_{\text{tot}} - n_i E_{i_2}/2 - n_{\text{Si}} E_{\text{silicene}} \right)/(n_i + n_{\text{Si}})$$

where $E_{\text{tot}}$ is the total energy of a silicane NR, $E_{i_2}$ is the total energy of an $i_2$ molecule, and $E_{\text{silicene}}$ is the energy per atom of silicene sheet. The number of Si (i) atoms in a silicane NR is $n_{\text{Si}} (n_i)$.

Figures 5 (a) and (b) show the $\delta G$ versus the width of H-silicane NRs and F-silicane NRs, respectively. The Gibbs free energy of formation decreases monotonically with increasing NR width for H-silicane NRs but increases monotonically as the NR width increases for F-silicane NRs, which implies that wider NRs are energetically favorable for H-silicane NRs, but narrower NRs are more likely to form for F-silicane NRs. We note that the calculated Si–H bond energy (BE) in H-silicane, Si–Si BE in silicene, and Si–F BE in F-silicane are $-3.021$ eV, $-4.581$ eV,

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**Figure 5.** The Gibbs free energy of formation $\delta G$ versus the width of H-silicane NRs (a) and F-silicane NRs (b). The inset shows the result of $\delta G$ versus $n_{\text{Si}}/n_{\text{H}}$ or $n_{\text{Si}}/n_{\text{F}}$.
and $-5.887 \text{ eV}$, respectively. The different strengths of Si–H and Si–F bonds at the edges of NRs result in the different trends of $\delta G$ versus width for H-silicane NRs and F-silicane NRs. Interestingly, the Gibbs free energy of formation for silicane NRs has a novel linear relationship with the ratio of Si atoms to H or F atoms, as shown in the inset of Figure 5. Using the linear fitting $\delta G = A + Bx (x = n_{Si}/n_i)$, we obtain $A = -0.11098$ and $B = -0.26645$ for H-ZSNRs, but $A = -3.3198$ and $B = 1.0688$ for F-ZSNRs.

### 3.3. Electric field modulation

Taking F-10ZSNR and F-17ASNR as examples, we investigate the effect of transverse electric fields on the electronic properties of silicane NRs. It is found that an external electric field affects the electronic band structure of silicane NRs significantly. Figures 6 (a) and (d) show the band structures of F-10ZSNR under a 0.1 V Å$^{-1}$ electric field and F-17ASNR under a 0.15 V Å$^{-1}$ electric field, respectively. The band gap of F-10ZSNR becomes 0.057 eV under 0.1 V Å$^{-1}$ and that of F-17ASNR becomes 0.020 eV under a 0.15 V Å$^{-1}$. Compared to the pristine band structure (see figures 3 (a) and (d)), the sub-band states within the valence bands and conductance bands redistribute due to the perturbation of the electric field. If no electric field is applied, the VBM and CBM states spread uniformly across the ribbon (see figures 3(b)–(c) and (e)–(f), respectively). Upon imposing an electric field, the VBM state moves along the direction of the electric field and is finally localized in the low potential region, whereas the CBM state shifts along the opposite direction and is finally localized on the high potential region (see figures 6(b)–(c) and (e)–(f), respectively).

To further understand the electronic property of silicane NRs under an external electric field, we plot the partial density of states (PDOS) of Si atoms at the high, medium, and low potential regions of F-10ZSNR under 0.1 V Å$^{-1}$ and 0.2 V Å$^{-1}$, as shown in figure 7.
electric field makes the energy of the electronic states at the low potential region increase, and the energy of the electronic states at the high potential region decrease, so that the VBM on one side of the ribbon is leveled to the CBM on the opposite side when a threshold electric field is reached (see figures 7(a)–(c)). Moreover, the band gap of the ribbon on the two sides remains unchanged, leading to the possibility of the generation of electrons and holes via tunneling [24] across the ribbon, which could induce novel optical and electric properties. When we increase the electric field to 0.2 V Å\(^{-1}\), the VBM at the low potential region stays above the Fermi energy, and the CBM at the high potential region below the Fermi energy (see figures 7(d)–(f)), indicating that the electric field renders the NR self-doped; \(p\)-type on one side and \(n\)-type on the opposite side.

Finally, we analyze the dependence of electric field modulation on the width of silicane NRs. Figure 8 plots the band gap of silicane NRs as a function of electric field. The band gap of all silicane NRs decreases as the strength of the electric field increases and reaches almost zero at the threshold electric field. The wider the NR is, the smaller the threshold electric field. For NRs of similar width, the threshold electric field for F-ZSNR is about half of that for H-ZSNR and the armchair NRs have a larger threshold electric field than the zigzag NRs. Although the

\[ \text{PDOS (number of states/eV)} \]

\[ \text{0.1 V/Å} \]

\[ \text{0.2 V/Å} \]
band gap underestimation by the PBE functional makes the threshold electric field smaller than the actual value, the qualitative trend is usually right.

4. Conclusion

On the basis of density functional theory calculations, we have studied the electronic band structure and relative stability of silicane nanoribbons. The zigzag H-silicane NRs exhibit a direct band gap, differing from the indirect band gap of H-silicane sheet, whereas the armchair H-silicane NRs are still indirect-band-gap semiconductors. The band gaps of F-silicane NRs become about half of those of H-silicane NRs. For all silicane NRs considered here, the Gibbs free energy of formation is negative and decreases monotonically with the ribbon width for H-silicane NRs but increases monotonically with the ribbon width for F-silicane NRs. Furthermore, the electric field modulation calculations show that the band gap of silicane NRs decreases as the strength of the electric field increases, and the external electric field increases can even render silicane NRs self-doped. Our results are helpful for understanding the electronic properties of silicane NRs and open up the possibility of using them in nanodevices.

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