# Geometric and Electronic Structures as well as Thermodynamic Stability of Hexyl-Modified Silicon Nanosheet

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S Supporting Information

ABSTRACT: The successful synthesis and outstanding properties of graphene have promoted strong interest in studying hypothetical graphene-like silicon sheet (silicene). Very recently, 2D silicon nanosheet (Si-NS) stabilized by hexyl groups was reported in experiment. We here present an atomiclevel investigation of the geometric stability and electronic properties of Si-NS by density functional calculations and molecular dynamics simulations. The most stable structure of the hexyl-modified Si-NS corresponds to the one in which the hexyl groups are regularly attached to both sides of the sheet, with the periodicity of the hexyl groups on the sheet being 7.17 Å, in good agreement with the experimental value of 7.1 Å. The electrostatic repulsion effect of the hexyl groups could be an



important reason for the favorable structure. The electronic structure of the hexyl-modified Si-NS shows a direct band gap that is not sensitive to the length of the alkyl group but sensitive to the strain effect, which can be used to tune the gap continuously within the whole strain range we considered. Finally, both the first-principles and the force-field-based molecular dynamics simulations show that the most stable structure of the hexyl-modified Si-NS could maintain its geometric configuration up to 1000 K.

#### INTRODUCTION

Low-dimensional materials, such as graphene and silicene, are the current focus of substantial research activity in nanotechnology<sup>1-8</sup> because graphene was successfully synthesized and endowed great potentials in the applications of electronics and spintronics.<sup>9–14</sup> Semiconducting property is highly desired to implant graphene into any real integrated circuit. However, experiments have shown that supernarrow graphene nanoribbon could become semiconducting only when its width is reduced to sub-10-nm.<sup>15-19</sup> Another challenge for the development of graphene is the difficulty to integrate it into current Sibased nanotechnology. Thus, the fabrication of other similar 2D honeycomb monolayer structures becomes important.

The question has been raised whether other group IV elements have a stable 2D structure. As a counterpart of graphene, the honeycomb structure of silicon (silicene) was proposed.<sup>20-24</sup> Lalmi et al. reported the successful synthesis of 2D silicene on Ag(111) surface based on STM,<sup>25</sup> and Vogt et al. presented more details of experimental evidence of monolayer silicene sheet grown on a close-packed Ag(111) surface.<sup>26</sup> Unlike the individual graphene sheet freely suspended on a microfabricated scaffold in vacuum or air,<sup>5</sup> it remains an arguments whether 2D silicon sheet with large size and oxygen-free surfaces can exist without substrates due to the sp<sup>3</sup> bonding nature of silicon.<sup>27</sup>

Recently, Nakano et al. reported the synthesis of ndecylamine-modified<sup>28</sup> and phenyl-modified<sup>29</sup> silicon nanosheet (Si-NS) with nanoscale thickness and microscale area. Very recently, the same experimental group showed the first evidence, by means of FT-IR and XPS, that the layered structure of hexyl-modified Si-NSs could collapse and transform to individual sheets,<sup>1</sup> in which 50% of the dangling silicon bonds are bound to the hexyl groups, whereas the other 50% of the Si-H groups do not react. Regardless of the structural difference, this observation is similar to the alkyl-terminated silicon surface.<sup>30</sup> There are two advantages for this hexylmodified Si-NS: it is a semiconductor, in contrast with the gapless graphene, and it can be easily implanted into the traditional Si-based semiconductor industry. Naturally, it is highly desired to explore the geometric and electronic properties as well as the thermodynamic stability of the alkylmodified Si-NS at an atomic level.

Density functional theory (DFT) calculations and molecular dynamics (MD) simulations were applied to investigate the structure and electronic properties of the hexyl-modified Si-NS. Our results show that due to the electrostatic repulsion effect of

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Figure 1. Band structures of (a) 2D silicon (silicone), (b) hydrosilylation of layered polysilane  $(Si_6H_6)$ , (c) the most stable  $Si_8H_4(C_6H_{13})_4$ , and (d) the most stable  $Si_8H_4(CH_3)_4$ .

the hexyl groups the most stable geometric structure corresponds to the one in which the hexyl groups are regularly attached to both sides of the sheet. By attaching different lengths of alkyl groups, we found that the computed energy gap of the alkyl-modified Si-NS is close to 1.6 eV at the DFT level, which is not sensitive to the length of the alkyl groups. However, the band gap of the hexyl-modified Si-NS can be tuned by applied strain. Furthermore, both the first-principles and the force-field-based molecular dynamics simulations show that the most stable structure of the hexyl-modified Si-NS could maintain its geometric configuration up to 1000 K in the time period we considered.

## **COMPUTATIONAL DETAILS**

A supercell model of  $Si_8H_4(C_6H_{13})_4$  was used for the hexylmodified Si-NS. All DFT calculations and MD simulations were performed with the Vienna ab initio simulation package.<sup>31</sup> In the DFT calculations, we have adopted the generalized gradient approximation with the Perdew, Burke, and Enzerhoff functional.<sup>32</sup> Self-consistent procedures were done with a convergence criterion of  $10^{-5}$  eV in energy. A vacuum thickness of 18 Å, a cutoff energy of 500 eV, and  $7 \times 7 \times 1$ Monkhorst-Pack *k*-mesh grid points were found to be good enough for numerical convergence.

In both the first-principles-based MD (FP-MD) and the force-field-based MD (FF-MD) simulations, we have only included the  $\Gamma$  point for integration in the *k* space and chosen the time step of 1 fs and the simulation temperature of 1000 K for MD simulations. For the FP-MD simulations, we have taken the Nosé algorithm for temperature control, with the first 0.5 ps for equilibration and the subsequent 5 ps for production. For the FF-MD simulations, the Dreiding force field was chosen to describe the interatomic interaction, and the atom motion was simulated by solving Newton's classical equations of motion, with the first 1 ps for equilibration and the subsequent 100 ps for production.<sup>33</sup>

## RESULTS AND DISCUSSION

To test the reliability of our method as well as to get the results of pure and hydrogenated silicenes for comparison, we first calculated their geometric and electronic structures. For simplicity, the hydrogenated silicene sheet is called H-silicane. The optimized Si–Si bond length in the pure silicene is 2.26 Å, which agrees well with other theoretical result of 2.25 Å.14 Because the H atoms pull the bonding Si atoms out of plane in H-silicane, the lengths of Si-Si bonds increase by about 4.8% to 2.36 Å, in good agreement with available experimental results of 2.35 Å.34 The angles between adjacent Si-Si bonds in Hsilicane are 111.4°, and the buckling height of Si atoms is 0.72 Å, both of which agree well with the reported values of 111° and 0.72 Å, respectively.<sup>35</sup> The calculated electronic properties of silicene show striking similarity to graphene: in particular, the gap is closed at the K point of the Brillouin zone, and the dispersion around this point is linear (Figure 1a). This can be explained as the silicon atoms in silicene are sp<sup>2</sup> hybridized.<sup>14</sup> Because the silicon atoms are sp<sup>3</sup> hybridized in H-silicane, a direct energy gap of 2.30 eV is clearly observed in Figure 1b, which is consistent with the previous theoretical result of 2.17 eV.<sup>34</sup> In addition to hydrogenation, silicene can also be stabilized by the hexyl  $(-C_6H_{13})$  or methyl groups  $(-CH_3)$ . As shown in Figure 1c,d, the direct energy gaps for the most stable structures of  $Si_8H_4(C_6H_{13})_4$  and  $Si_8H_4(CH_3)_4$  are nearly the same, namely, 1.66 and 1.67 eV, respectively. The details of the geometric and electronic structures will be discussed in the following.

To determine the most stable structure of the hexyl-modified Si-NS  $[Si_8H_4(C_6H_{13})_4]$ , we constructed 12 possible structures. Six nonequivalent configurations are identified according to their symmetry, as presented in Figure 2a–f (for details, see the Supporting Information (SI)). DFT calculations indicate that  $Si_8H_4(C_6H_{13})_4$ -a (Figure 2a) is the most stable structure, in which the hexyl groups distribute on both sides of the sheet, and the periodicity of the hexyl groups on the sheet is 7.17 Å, close to reported experimental result (sharp peak at  $2\theta = 12.4^{\circ}$ 



**Figure 2.** Schematic diagrams for six types of  $Si_8H_4(C_6H_{13})_4$  isomers. Circles represent the connecting positions of the hexyl groups on the Si-NS: red circle is on top and blue circle is below. (a) Most stable structure  $Si_8H_4(C_6H_{13})_{4}$ -a (the hexyl groups distribute most uniformly on both sides of the sheets). (b)  $Si_8H_4(C_6H_{13})_4$ -b (the attached hexyl groups stand in a zigzag line on the sheet). (c)  $Si_8H_4(C_6H_{13})_4$ -c and (d)  $Si_8H_4(C_6H_{13})_4$ -d with unequal number of attached hexyl groups on two sides of the sheet. (e)  $Si_8H_4(C_6H_{13})_4$ -e (four hexyl groups gather on the same side of the silicon six-member ring). (f)  $Si_8H_4(C_6H_{13})_4$ -f (the highest-energy structure of  $Si_8H_4(C_6H_{13})_4$ , in which the hexyl groups are concentrated on one side of Si-NS).

in XRD pattern, indicating molecular-scale periodicity of 7.1 Å, which is a strong support for the fact that the fabricated  $Si_8H_4(C_6H_{13})_4$  has collapsed to individual sheets).<sup>1</sup> Furthermore, we found the sharp peak in the XRD pattern could also be explained by the vertical distance from the hexyl group to the silicon surface, as the hexyl chains are not perpendicular to the silicon surface but have an angle of 57.7°, resulting in a vertical distance of 7.15 Å from the hexyl group to the silicon surface (Figure 3). The specific bond lengths and bond angles



Figure 3. Top and side views of the most stable structure  $Si_8H_4(C_6H_{13})_4$ -a of the hexyl-modified Si-NS.

of the most stable  $Si_8H_4(C_6H_{13})_4$  structure are given in Table S1 in the SI. Mulliken population analysis for the hexylmodified Si-NS indicates that 0.69 electrons are transferred from the Si-sheet to each attached hexyl group, which leads to an electrostatic repulsion effect of the hexyl-groups. Because of the repulsion effect, when we go from H-silicane to the hexylmodified Si-NS, the optimized Si–Si bond length is enlarged from 2.35 Å to 2.45 Å, and the sublattice constant is expanded from 3.83 to 4.05 Å, which agrees well with the experimental value of 4.09 Å.

Other structures in Figure 2b–f are energetically less stable than that in Figure 2a by 0.76, 0.87, 0.94, 2.23, and 2.66 eV, respectively (see Table S2 in the SI). In Si<sub>8</sub>H<sub>4</sub>(C<sub>6</sub>H<sub>13</sub>)<sub>4</sub>-b, the attached hexyl groups stand in a zigzag line on both sides of the sheet, with a separation of 3.85 Å between adjacent hexyl groups along the same zigzag, while the nearest distance between hexyl groups of the neighboring zigzags is 6.61 Å. In both Si<sub>8</sub>H<sub>4</sub>(C<sub>6</sub>H<sub>13</sub>)<sub>4</sub>-c and Si<sub>8</sub>H<sub>4</sub>(C<sub>6</sub>H<sub>13</sub>)<sub>4</sub>-d, the hexyl groups on two sides of the sheets are not equally distributed. In the unit cell, one hexyl group is on one side while three hexyl groups are on the other side, with a distance of 3.93 Å between the closest hexyl groups. The asymmetric arrangement of the hexyl groups on two sides could result in bending of the Si-NS, which would be harmful for fabricating monolayer nanosheet in experiment. For Si<sub>8</sub>H<sub>4</sub>(C<sub>6</sub>H<sub>13</sub>)<sub>4</sub>-e, the four hexyl groups gather on the same silicon six-member ring of the Si-NS, which might lead to an enhanced local stress in this adsorptive configuration and hence a structural instability. Among the six isomers,  $Si_8H_4(C_6H_{13})_4$ -f has the highest energy, in which the hexyl groups are concentrated on one side of the Si-NS. The hexyl groups in this structure are evenly spaced with a separation of 3.86 Å, which seems to be too crowded for the hexyl groups, resulting in an electrostatic repulsion among them and the highest energy of the structure.

To understand the size dependence of the alkyl groups on their arrangement when attached to the Si-NS, we replaced hexyl  $(-C_6H_{13})$  with a shorter length of alkyl group, methyl  $(-CH_3)$ . In correspondence to the hexyl-modified Si-NS, six possible configurations of the methyl-modified Si-NSs are considered, and their relative energies are listed in Table S2 (see the SI). Similar to Si<sub>8</sub>H<sub>4</sub>(C<sub>6</sub>H<sub>13</sub>)<sub>4</sub>-a, the most stable structure turns out to be Si<sub>8</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>4</sub>-a, in which equal number of methyl groups are regularly attached to both sides of the sheet. Other isomers, from Si<sub>8</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>4</sub>-a by 0.07, 0.13, 0.09, 0.12, and 0.32 eV, respectively. In the highest-energy structure, Si<sub>8</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>4</sub>-f, all of the methyl groups are linked to one side of the sheet.

In comparison with the gapless graphene or silicene, the alkyl-modified Si-NSs manifest different electronic properties. Both  $Si_8H_4(C_6H_{13})_4$ -a and  $Si_8H_4(CH_3)_4$ -a have a direct band gap at the  $\Gamma$  point in the Brillouin zone. This is mainly due to the sp<sup>3</sup> hybridized bonding nature of the Si atoms. As shown in Figure 1c,d, the values of the direct energy gap for Si<sub>8</sub>H<sub>4</sub>(C<sub>6</sub>H<sub>13</sub>)<sub>4</sub>-a and Si<sub>8</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>4</sub>-a are very close, being 1.66 and 1.67 eV, respectively. Figure 4a,b shows the total densities of states (DOS) for  $Si_8H_4(C_6H_{13})_4$ -a and  $Si_8H_4(CH_3)_4$ -a as well as the partial densities of states (PDOS) for the methyl-group, the hexyl group, and the Si atoms. For  $Si_8H_4(C_6H_{13})_4$ -a, strong overlaps appear in the PDOS for the Si atoms and the hexyl group around -3.5 and -3.0 eV. Similarly, for Si<sub>8</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>4</sub>-a, sharp overlaps exist in the PDOS for the Si atoms and the methyl group around -6.5 and -3.8 eV. These results indicate that there are strong hybridizations between the orbitals of the Si atom and the hexyl or methyl groups. The hybridization is stronger in  $Si_8H_4(C_6H_{13})_4$ -a than in  $Si_8H_4(CH_3)_4$ -a, which could be understood by the fact that longer alkyl groups are more advantageous to stabilize the Si-NS. Interestingly, we found that the band gaps of the Si-NSs attached by the methyl and hexyl groups are quite similar. To examine whether the length of the alkyl groups affects the band gap, different lengths of alkyl groups are considered, as shown in Figure 4c. It is clear that the energy gaps of the alkyl-modified Si-NSs vary very little, from 1.67 eV for n = 1 to 1.66 eV for n = 10. (*n* is the length index of the alkyl groups.) Therefore, the alkyl-modified Si-NSs are direct-gap semiconductors whose gaps are not sensitive to the length of the attached alkyl groups. Furthermore, we found that the distinct peaks at the highest occupied molecular orbital (HOMO) contribute mainly from the Si p orbitals, while the peaks at the lowest unoccupied molecular orbital (LUMO) originate predominantly from the Si s and p orbitals. This means that the Si atoms make the major contribution to both HOMO and LUMO, which could be the reason why the energy gaps of the alkyl-modified Si-NSs are



Figure 4. Density of states (DOS) plots of (a)  $Si_8H_4(C_6H_{13})_4$ -a and (b)  $Si_8H_4(CH_3)_4$ -a. (c) Energy gap of the most stable alkyl-modified Si-NSs with respect to alkyl length index *n*. (d) Energy gap of  $Si_8H_4(C_6H_{13})_4$ -a as a function of strain  $\eta$ .

insensitive to the length of the attached alkyl groups. It is further supported by the charge density isosurfaces of the Si-NSs. In Figure 5, the charge densities of the valence bands



Figure 5. Charge densities of the valence bands (VBs) and the conductive bands (CBs) for (a,c) Si<sub>8</sub>H<sub>4</sub> $(C_6H_{13})_4$  and (b,d) Si<sub>8</sub>H<sub>4</sub> $(CH_3)_4$ , respectively, at  $\Gamma$  point. The isosurface is 0.002 e/Å.

(VBs) and the conductive bands (CBs) at the  $\Gamma$  point are found to be only localized on the silicon atoms in both Si<sub>8</sub>H<sub>4</sub>(C<sub>6</sub>H<sub>13</sub>)<sub>4</sub> and Si<sub>8</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>4</sub>, indicating no relationship to the lengths of the attaching groups, which is consistent with the PDOS analyses.

For the application into real systems, Si-NSs have to be grown on a flexible substrate, and the lattice constant mismatch would inevitably lead to a strain effect in the Si-NSs.<sup>25,26</sup> Plenty of experimental and theoretical studies have indicated that the band gaps of graphene sheets are strain-tunable.<sup>36–39</sup> In this scenario, it is feasible and desirable to explore the effect of the strain on the band gap of the Si-NSs. In particular, for Si<sub>8</sub>H<sub>4</sub>(C<sub>6</sub>H<sub>13</sub>)<sub>4</sub>-a, the equilibrium lattice constant with zero strain,  $c_0$ , is obtained by minimizing the total energy. The strain acting on the Si-NS can be represented by  $\eta = (c - c_0)/c_0$ , where c is the Si-NS lattice length along the strain direction. Positive and negative values of  $\eta$  imply elongation and compression, respectively. Electronic structure calculations show that the  $Si_8H_4(C_6H_{13})_4$ -a has direct band gap under different strain, which is presented as a function of  $\eta$  in Figure 4d. The gap decreases, from 1.95 to 1.13 eV, almost linearly with the increase in  $\eta$  within the whole strain range we considered. Thus, the energy gap of the alkyl-modified Si-NSs can be continuously tuned with applied strain. It should be noted here that the band gap of semiconducting materials is usually underestimated by DFT at the GGA level. For a better prediction of the band gap, one should resort to hybrid functionals such as  $\rm HSE06^{40}$  or even more accurate GW calculations<sup>41,42</sup> containing the self-interaction correction; however, the computational demands of such methods are prohibitively high. Without very expensive computations, we believe that the decreasing trend of the band gap obtained in the present work should be qualitatively reasonable for the potential applications of the functionalized Si-NSs in nanoelectronics and photocatalysis.

Besides the energetic stability of the hexyl-modified Si-NSs, the thermodynamic stability is another important property that should be taken into account because temperature is always a key factor in the experimental production of materials. Nakano et al. showed that the hexyl-modified Si-NSs were fabricated at the temperature of 383 K.<sup>1</sup> Considering the practical application of nanosheets, a higher temperature of 1000 K was used to characterize the thermodynamic stability in our FP-MD simulations. In Figure 6a,b, we find that  $Si_8H_4(C_6H_{13})_{4}$ -a can keep its configuration in 5 ps simulation time, showing its high thermal stability. Figure 6b displays a periodically slight fluctuation with a length of ~30 Å and a height of 5 Å for the hexyl-modified Si-NS structure. Similar to the observed ripples in suspended layers of graphene,<sup>5</sup> the ripples in the hexylmodified Si-NS were proposed to be caused by thermal



**Figure 6.** Geometric configurations of (a)  $Si_8H_4(C_6H_{13})_{4}$ -a and (b)  $Si_8H_4(CH_3)_{4}$ -a after 5 ps FP-MD simulations at 1000 K, (c)  $Si_8H_4(C_6H_{13})_4$ -f after 100 ps FF-MD simulations at 1000 K, and (d)  $Si_8H_4(C_6H_{13})_4$ -a and (e)  $Si_8H_4(CH_3)_4$ -a after 100 ps FF-MD simulations at 1000 K.

fluctuations in the materials. To explore the thermodynamic stability of  $Si_8H_4(C_6H_{13})_{4}$ -a in a longer simulation time, we carried out FF-MD simulations beyond the limitation of the FP-MD due to its very expensive cost in CPU time, which shows that a bigger supercell,  $Si_{200}(C_6H_{13})_{100}H_{140}$ , of  $Si_8H_4(C_6H_{13})_{4}$ -a can also keep its configuration in 100 ps. Therefore, both first-principles and force-field based MD simulations show that the most stable structure of the hexylmodified Si-NS could maintain its geometric conformation up to 1000 K. In contrast, the highest-energy structure  $Si_8H_4(C_6H_{13})_4$ -f is crimped like a tube in FF-MD simulations. (See Figure 6c.)

### CONCLUSIONS

In summary, we have performed a comprehensive theoretical study on the geometric and electronic properties as well as the thermodynamic stability of the hexyl-modified Si nanosheets. By means of DFT calculations, the 2D honeycomb Si-NS can be stabilized by attaching hexyl groups, and the hexyl groups in the most stable structures distribute on both sides of the Si-NS with a distance of 7.17 Å between neighboring hexyl groups. Electronic structure calculations indicate that the energy gaps of the alkyl-modified Si-NS, being about 1.65 eV, are not sensitive to the length of the attached alkyl groups. Moreover, the gaps of the hexyl-modified Si-NS can be continuously tuned by the strain, showing a linearly decreasing relationship with increasing strain. Furthermore, both first-principles and force-field-based MD simulations elucidate that the most stable geometric structure of the hexyl-modified Si-NS can keep its configuration up to 1000 K, which implies that it is experimentally feasible and promising for future applications in nanoelectronics.

### ASSOCIATED CONTENT

### **S** Supporting Information

Optimized geometric structures and Cartesian coordinates of the  $Si_8H_4(C_6H_{13})_4$  isomers and the relative energies of the  $Si_8H_4(C_6H_{13})_4$  and  $Si_8H_4(CH_3)_4$  isomers. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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