Influence of strain and electric field on the properties of silicane*

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We investigate the influence of strain and electric field on the properties of a silicane sheet. Some elastic parameters of silicane, such as an in-plane stiffness of 52.55 N/m and a Poisson's ratio of 0.24, are obtained by calculating the strain energy. Compared with silicene, silicane is softer because of its relatively weaker Si–Si bonds. The band structure of silicane is tunable by a uniform tensile strain, with the increase of which the band gap decreases monotonously. Moreover, silicane undergoes an indirect–direct gap transition under a small strain, and a semiconductor–metal transition under a large strain. The electric field can change the Si–H bond length of silicane significantly. When a strong field is applied, the H atom at the high potential side becomes desorbed, while the H atom at the low potential side keeps bonded. So an external electric field can help to produce single-side hydrogenated silicene from silicane. We believe this study will be helpful for the application of silicane in the future.

Keywords: silicane, strain, electric field, first-principles calculation

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1. Introduction

Recently, the counterpart of graphene for silicon, namely silicene,[1–3] has attracted considerable attention. Silicene is a honeycomb monolayer which consists of Si atoms. Different from graphene, silicene is not flat but has a buckled structure.[2] However, theoretical studies have shown that silicene has similar electronic properties to graphene, possessing Dirac points at the corners of the hexagonal Brillouin zone.[2,4] Therefore it can be expected that the novel properties of graphene may also appear in silicene. Indeed, many interesting properties of silicene-based structures have been proposed in theory, such as quantum spin Hall effect,[5] electric field tunable gap,[6,7] symmetry-dependent transport properties,[8] and magnetoresistance.[8,9] Experimentally, the fabrication of silicene sheets and silicene nanoribbon on Ag surface have been reported by several groups,[10–13] and the graphene-like electronic signature is also confirmed.[11,12] One of the advantages of silicene is that it is compatible with the silicon-based modern electronics industry. Thus silicene is competitive in the future nanoelectronics.

Chemical functionalization such as hydrogenation is an important method to modulate the properties of nanostructures.[14–17] It is found that hydrogenated silicene, called silicane, transfers from semi-metal to insulator.[18–20] Since hydrogenated graphene, namely graphene, has been successfully synthesized,[21] the preparation of silicane is also hopeful. However, to date there are only a few studies focused on silicane and more are still needed to understand its properties.

In this work, we study the influence of strain and electric field on the properties of a silicane sheet. By calculating the strain energy, we obtain some elastic parameters such as in-plane stiffness and Poisson's ratio of silicane. The effect of a uniform strain on the band structure of silicane is also investigated and both the indirect–direct gap transition and the semiconductor–metal transition are observed. Finally we show that the electric field influences the Si–H bond length of silicane significantly, and it is possible to produce single-side hydrogenated silicene from silicane by applying a strong external electric field.

2. Calculation methods

All calculations are performed using the SIESTA code,[22] in which localized numerical atomic orbitals are employed. The generalized Perdew–Burke–Ernzerhof gradient approximation[23] is chosen as an exchange–correlation functional. Troullier–Martins norm-conserving pseudopotential[24] is adopted to describe the core-valence interaction. Energy cutoff for real space grid is set to 4081.71 eV (300 Ry, 1 Ry = 13.605 eV). The wavefunction is expanded by the double-zeta-polarized basis set. A $21\times21\times1$ k-mesh is used for the silicane primitive unit cell, and a $5\times5\times1$ mesh is used for the rectangle supercell. The convergence criterion for self-consistent calculations is 10^{-4} eV, and the maximum force acting on each atom is less than 0.01 eV/Å (1 Å = 0.1 nm). To avoid the interactions between the periodic images, a vacuum layer larger than 10 Å is added.

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3. Results and discussion

3.1. Elastic properties

Previous studies have shown that the chair-like silicane is the most stable one.[19,20] It has a buckled structure as shown in Fig. 1. According to our calculation, the optimized lattice constant is 3.93 Å, the height difference between two adjacent Si atoms is 0.72 Å, the Si–Si bond length is 2.38 Å, and the Si–H bond length is 1.53 Å. These results are consistent with previous studies,[19] indicating the parameters chosen in our calculation are reasonable.

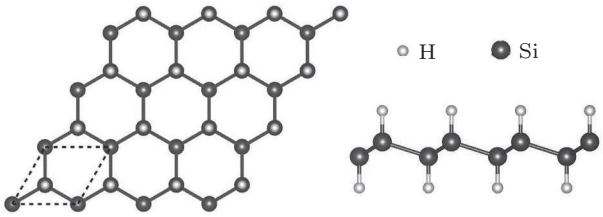


Fig. 1. Geometry structure of silicane sheet from top view and cross-section view. The dashed line indicates the primitive unit cell.

Silicane has a hexagonal lattice and is isotropic. Therefore, similar to other honeycomb monolayers, its elastic properties can be represented by two independent constants, the in-plane stiffness C and Poisson's ratio ν. The in-plane stiffness C is defined as $C = (1/S_0)(\partial^2 E/\partial\varepsilon^2)$, where S_0 is the equilibrium area, E is the total energy, and ε is the uniaxial strain. The Poisson's ratio is given by $\nu = -\varepsilon_{\text{trans}}/\varepsilon_{\text{axial}}$, where $\varepsilon_{\text{trans}}$ and $\varepsilon_{\text{axial}}$ represent the transverse and the axial strain, respectively. These elastic parameters can be obtained by calculating the strain energy.[25,26] First we construct a 4×3 rectangle supercell of silicane, as shown in Fig. 2(a). a_{Z} and a_{A} are the length of lattice vectors along the zigzag and armchair directions, respectively. Then small strains ε_{Z} and ε_{A} are applied to the supercell along these two directions. The range of the strain is from −0.02 to 0.02, in a step of 0.01. Thus a grid data containing 25 points is obtained, as shown in Fig. 2(b). At each point, the atomic position is relaxed, and the total energy is calculated. The strain-energy relationship can be fitted by the formula $E = a_1\varepsilon_{\text{Z}} + a_1\varepsilon_{\text{A}} + a_2\varepsilon_{\text{Z}}\varepsilon_{\text{A}} + E_0$, where E_0 is the total energy at the equilibrium lattice constant. The in-plane stiffness can be calculated by $(2a_1 - a_2^2/2a_1)/S_0$, and the Poisson's ratio is equal to $a_2/2a_1$. The fitted a_1 and a_2 are 557.85 eV and 270.05 eV, respectively, and the corresponding contour plot is given in Fig. 2(b). The calculated C and ν of silicane are 52.55 N/m and 0.24, respectively. The in-plane stiffness of silicane is smaller than that of silicene (62 N/m according to Ref. [21]), so the structure of silicane is more sensitive to the external strain compared with silicene. The difference of in-plane stiffness between silicane and silicene can be understood by their different Si–Si bond strength. The Si–Si bond length of silicane (2.38 Å) is larger than that of silicene (2.28 Å according to Ref. [19]), thus the Si–Si bond strength of silicane is weaker, leading to a smaller in-plane stiffness C.

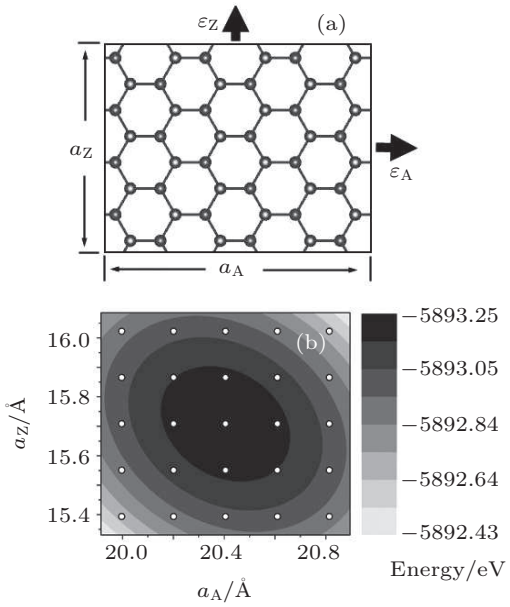


Fig. 2. (a) The 4×3 rectangle supercell of silicane used to calculate the elastic parameters. a_{Z} and a_{A} are the length of lattice vectors along the zigzag and armchair directions, respectively. Strain is applied to these two directions. (b) The data grid used to calculate the total energy, and the fitted counter plot of the strain-energy relation.

3.2. Band gap under a uniform strain

It is well demonstrated that the properties of nanostructures can be tuned by strain.[25–28] In this section we discuss the influence of the uniform strain on the properties of silicane using the hexagonal unit cell. At each point of tensile strain ranging from 0 to 0.2 with a step of 0.01, we calculated the strain energy, which is the energy difference between strained and equilibrium states, as well as the band gaps. The results are plotted in Fig. 3(a). It can be seen that the strain energy E_{s} monotonously increases with the increase of the strain. The harmonic region lies between $0.00 < \varepsilon < 0.03$, beyond which higher order terms are not negligible and the E_{s}–ε curve becomes inharmonic.

Silicane has an indirect band gap, with the valence band maximum (VBM) located at Γ point, and the conduction band minimum (CBM) at M point in the equilibrium state, as shown on the left side of Fig. 3(b). The band gap is 2.26 eV. The influence of strain on the band structure is significantly important, and shows the following features.

(i) When tensile strain is applied, an indirect–direct gap transition is observed. The middle panel of Fig. 3(b) is the band structure of silicane with a strain of 0.1. The VBM remains at Γ point, but the CBM changes from M to Γ. Therefore, the band gap becomes direct. The estimated threshold strain of the indirect–direct gap transition is about 0.0025. The observed results are in agreement with other studies.[19]

(ii) The band gap of silicane decreases almost linearly with the increase of the strain, which can be understood as follows: when the tensile strain is applied, the bond length increases and the bond strength decreases for Si–Si bond; thus the gap between the bonding and antibonding states becomes smaller, leading to the decrease of the band gap. Moreover, when ε reaches 0.2, the CBM and VBM of silicane coincide at Γ point as shown on the right side of Fig. 3(b). So silicane undergoes a semiconductor–metal transition with the increase of the strain.

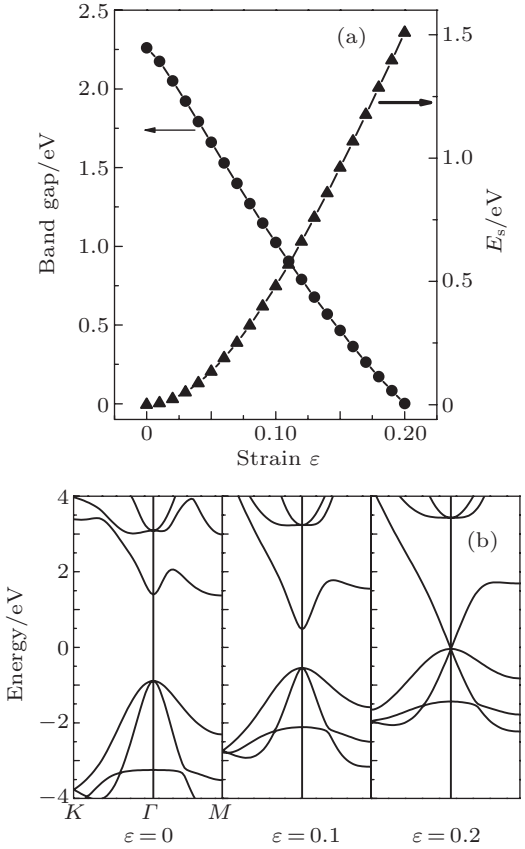


Fig. 3. (color online) (a) The band gap and strain energy E_s of silicane as a function of uniform tensile strain. (b) Band structure of silicane under strain values of 0.0, 0.1, and 0.2.

3.3. Response of geometry structure to electric field

Zhou *et al.* have demonstrated that the structure of graphene can be changed significantly by an electric field.[29] Thus how the geometry structure of silicane changes under an electric field is also an interesting topic. To address this issue, we applied an electric field perpendicular to the silicane sheet, as illustrated in Fig. 4. The H1 and S1 atoms are in the high potential side, and the H2 and Si2 atoms are in the low potential side. Experimentally, a possible way to apply the electric field is to emanate it from a tip utilized in scanning tunneling microscopy (STM). The Si–H bond lengths of silicane in different electric fields are also shown in Fig. 4. With the increase of electric field, the Si1–H1 bond length increases rapidly, whereas the influence of electric field on the Si2–H2 bond length is much smaller. When the electric field increases to 5.43 eV/Å, the Si1–H1 bond length, and the Si2–H2 bond length increase to 2.06 Å, 1.65 Å respectively. As the field further increases to 5.44 eV/Å, the H1 atom becomes desorbed, the distance between H1 atom and the sheet is larger than 3 Å, and the Si2–H2 bond length is approximately 1.6 Å. Then we turned off the field and re-optimized the structure. It is found that the H1 atom would not re-bond to the sheet, and a silicene sheet with one side hydrogenated was obtained. The single-side hydrogenated silicene is ferromagnetic with 1.0-μ_B magnetic moment per unit cell,[30] therefore it is promising for applications in future spintronics. Our results indicate that it is possible to produce the single-side hydrogenated silicene from silicane by applying a strong external electric field. The different behaviors of the two bond lengths can be understood by the charge transfer in silicane in an electric field. Once the electric field is applied, the potential of H1 becomes the highest, thus electrons accumulate around H1, making H1 negatively charged. As a result, the electrostatic force acting on H1 moves it away from the sheet, increasing the Si1–H1 bond length. Meanwhile, the electric field is largely screened by the charged H1 atom, hence its influence on other atoms is weaken, and the change of the Si2–H2 bond length is much smaller.

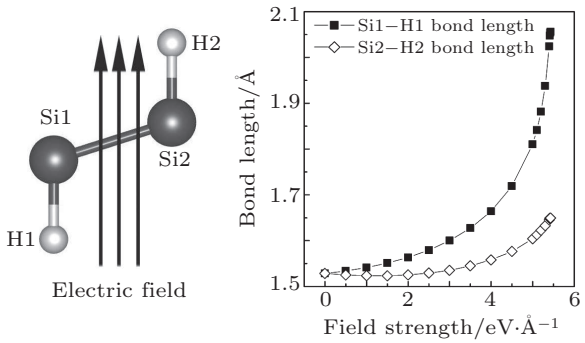


Fig. 4. (color online) Variation of the Si1–H1 and Si2–H2 bond length of silicane under an electric field perpendicular to the sheet.

4. Conclusion

We investigated the influence of strain and electric field on the properties of silicane sheet. Some elastic parameters of silicane, such as an in-plane stiffness of 52.55 N/m and a Poisson's ratio of 0.24, are obtained by calculating the strain energy. Compared with silicene, silicane is softer because of its relatively weaker Si–Si bonds. The band structure of silicane is tunable by a uniform tensile strain, with the increase of which the band gap decreases monotonously. Moreover, silicane undergoes an indirect–direct gap transition under a small strain, and a semiconductor–metal transition under a large strain. The electric field can change the Si–H bond length of silicane significantly. When a strong field is applied, the H atom at the high potential side becomes desorbed, while the H

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References

[1] Guzmán-Verri G G and Lew Yan Voon L C 2007 *Phys. Rev. B* **76** 075131
[2] Cahangirov S, Topsakal M, Akturk E, Sahin H and Ciraci S 2009 *Phys. Rev. Lett.* **102** 236804
[3] Kara A, Enriquez H, Seitsonen A P, Lew Yan Voon L C, Vizzini S, Aufray B and Oughaddou H 2012 *Surf. Sci. Rep.* **67** 1
[4] Ding Y and Ni J 2009 *Appl. Phys. Lett.* **95** 083115
[5] Liu C C, Feng W and Yao Y 2011 *Phys. Rev. Lett.* **107** 076802
[6] Drummond N D, Zolyomi V and Fal'ko V I 2012 *Phys. Rev. B* **85** 075423
[7] Ni Z, Liu Q, Tang K, Zheng J, Zhou J, Qin R, Gao Z, Yu D and Lu J 2012 *Nano Lett.* **12** 113
[8] Kang J, Wu F and Li J 2012 *Appl. Phys. Lett.* **100** 233122
[9] Xu C, Luo G, Liu Q, Zheng J, Zhang Z, Nagase S, Gao Z and Lu J 2012 *Nanoscale* **4** 3111
[10] Lalmi B, Oughaddou H, Enriquez H, Kara A, Vizzini S, Ealet B and Aufray B 2010 *Appl. Phys. Lett.* **97** 223109
[11] Vogt P, De Padova P, Quaresima C, Avila J, Frantzeskakis E, Asensio M C, Resta B, Ealet A and Le Lay G 2012 *Phys. Rev. Lett.* **108** 155501
[12] De Padova P, Quaresima C, Ottaviani C, Sheverdyaeva P M, Moras P, Carbone C, Topwal D, Olivieri B, Kara A, Oughaddou H, Aufray B and Le Lay G 2010 *Appl. Phys. Lett.* **96** 261905
[13] Aufray B, Kara A, Vizzini S, Oughaddou H, Leandri C, Ealet B and Le Lay G 2010 *Appl. Phys. Lett.* **96** 183102
[14] Zhu F, Dong S and Cheng G 2011 *Chin. Phys. B* **20** 077103
[15] Lu D, Yang Y, Xiao Y and Zhang X Y 2011 *Chin. Phys. B* **20** 118101
[16] Kang J, Wu F and Li J 2011 *Appl. Phys. Lett.* **98** 083109
[17] Kang J, Wu F, Li S S, Xia J B and Li J 2012 *Appl. Phys. Lett.* **100** 153102
[18] Houssa M, Scalise E, Sankaran K, Pourtois G, Afanas'ev V V and Stesmans A 2011 *Appl. Phys. Lett.* **98** 223107
[19] Ding Y and Wang Y 2012 *Appl. Phys. Lett.* **100** 083102
[20] Zhang P, Li X D, Hu C H, Wu S Q and Zhu Z Z 2012 *Phys. Lett. A* **376** 1230
[21] Elias D C, Nair R R, Mohiuddin T M G, Morozov S V, Blake P, Halsall M P, Ferrari A C, Boukhvalov D W, Katsnelson M I, Geim A K and Novoselov K S 2009 *Science* **323** 610
[22] Soler J M, Artacho E, Gale J D, Garca A, Junquera J, Ordejon P and Sanchez-Portal D 2002 *J. Phys: Condens. Matter* **14** 2745
[23] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
[24] Troullier N and Martins J 1990 *Solid State Commun.* **74** 613
[25] Topsakal M, Cahangirov S and Ciraci S 2010 *Appl. Phys. Lett.* **96** 091912
[26] Kang J, Li J, Wu F, Li S S and Xia J B 2011 *J. Phys. Chem. C* **115** 20466
[27] Zhang Y, Hu C H, Wen Y H, Wu S Q and Zhu Z Z 2011 *New. J. Phys.* **13** 063047
[28] Zhang Y, Wen Y H, Zheng J C and Zhu Z Z 2009 *Appl. Phys. Lett.* **94** 113114
[29] Zhou J, Wu M M, Zhou X and Sun Q 2009 *Appl. Phys. Lett.* **95** 103108
[30] Zhang C and Yan S 2012 *J. Phys. Chem. C* **116** 4163