Distortion and electric-field control of the band structure of silicene

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received 26 October 2013; accepted in final form 24 January 2014
published online 25 February 2014

PACS 73.22.-f – Electronic structure of nanoscale materials and related systems
PACS 61.48.Gh – Structure of graphene
PACS 71.15.Mb – Density functional theory, local density approximation, gradient and other corrections

Abstract – Density functional theory with local density approximation for exchange and correlation functional is used to tune the electronic band structure of silicene monolayer. The cohesive energy of the free-standing monolayer increases (decreases) with the external electric field (distortion). Electrons in silicene behave like Dirac fermions, when the bond angle between the Si atoms is larger than \( \sim 102^\circ \). Large distortions destroy the electronic structure of silicene so that it is no longer a semi-metallic material, and the distorted silicene acts like an \( n \)-doped system. The electric field opens a band gap around the \( K \)-point in the Brillouin zone, which increases with electric field. The bond angle between the Si atoms is a key player to determine the presence or absence of Dirac cones in silicene.

Introduction. – In recent years, two-dimensional (2D) materials have gained intense interest not only from theory communities, but also from experimental scientists. 2D materials are interesting due to their unique physical properties. For example, 2D MoS\(_2\) is a direct band gap semiconductor, whereas 3D MoS\(_2\) is an indirect band semiconductor, while NbSe\(_2\) retains its metallic character both in 2D and 3D structures [1]. In contrast 2D Ge is a poor metal, whereas 3D Ge is a semiconductor [1]. Reduced dimensionality can sometimes help to reduce the defect formation energy of magnetic systems [2]. Light elements (e.g. C, Si, Ge)-based 2D structures have very unique properties. Graphene, which is a 2D crystal with carbon atoms arranged in the flat hexagonal lattice of graphite, has Dirac-like electronic structure with linear dispersion around the Fermi level (\( E_F \)) [3]. Therefore, graphene is considered to be a host for Dirac-type electrons, whose unusual properties have been studied extensively in graphene monolayers produced by mechanical exfoliation from graphite [4,5].

Silicene, which is a 2D buckled monolayer honeycomb structure of Si atoms, has also received much attention world-wide [4,5]. It is demonstrated by first-principles calculations that low-buckled silicene is dynamically stable and has a linear electronic dispersion relation near the \( K \)-points at the corner of the Brillouin zone (BZ) [6–10]. The stability of silicene can be understood from the nature of \( sp \) hybridization. Even if silicene is isoelectronic to graphene, Si has a larger ionic radius than C, which promotes \( sp^3 \)-type hybridization. On the other hand, \( sp^2 \)-type hybridization is energetically more favourable in C, whereas in a 2D layer of Si atoms, the bonding is formed by mixed \( sp^2 \) and \( sp^3 \) hybridization. Hence, silicene is slightly buckled and such buckling creates new possibilities for manipulating the dispersion of electrons in silicene and for opening an electrically controlled sublattice asymmetry band gap [11], which is not possible in graphene due to sublattice symmetry. The electronic \( \pi \) and \( \pi^* \)-bands derived from the Si \( 3p_z \) orbital disperse linearly to cross at \( E_F \), and the silicene electrons behave as massless Dirac fermions. This unusual property of silicene makes it a promising candidate for quantum spin Hall effects [7,12].

Recent experiments have analysed silicene on different substrates [13–15] with the hope to find out massless fermions. However, the results are somehow conflicting. Fleurence et al. [14] have shown that buckled silicene on ZrB\(_2\) has an energy gap at \( E_F \). The angle-resolved photoelectron spectroscopy (ARPES) experiment of 4×4 silicene showed a linear band structure, which is considered to be the fingerprint of Dirac fermions, and the Dirac point was

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measured to be 0.3 eV below $E_F$ [16]. In another experiment carried out by Chen and his co-workers [17], the Dirac point was $\sim 0.5$ eV below $E_F$. In both of these experimental works the Fermi velocity was close to the theoretical value of $\sim 10^6$ m/s [10]. On the other hand, density functional theory (DFT) calculations found linear dispersion only within an energy interval $\pm 0.40$ eV, which is smaller than the experimentally reported values [16,17]. In spite of these two pioneer experimental works, in a very recent experimental study [18] on the Landau level in silicene on Ag the absence of the characteristic signals was attributed to the Landau level, which does not agree with the previous experimental work of Vogt et al. [16] and Chen et al. [17].

From the above comprehensive literature, it can be inferred that it is essential to investigate the nature of the Dirac point in silicene in different external perturbations, e.g., strain, pressure, electric field, etc. Silicene can be deposited on different substrates for practical applications and its electronic properties can be perturbed by strain or interfacial effect. So, from the applications point of view, we must investigate the desired properties against strain/distortion, which can be induced by the substrate. This effect cannot be ignored in real devices because there is always lattice mismatch whenever we grow a material on a substrate. In some cases, such distortion/strain is technologically beneficial and can be used to engineer the band structure of a material [19]. Therefore, in this paper, we inquire about the electronic structure and cohesion of silicene under distortions and electric fields.

Computational method. – The present calculations are performed in the framework of DFT [20] using linear combinations of atomic orbitals (LCAO) as implemented in the SIESTA code [21]. We used a double-$\zeta$ polarized (DZP) basis set for all atoms. We employed the local density approximation (LDA) as parametrized by Ceperly and Adler [22], for the exchange-correlation functional. We used standard norm-conserving pseudopotentials [23] in their fully nonlocal form [24]. We found that 200 Ry was enough to converge the lattice parameters and band structure of bulk Si and of silicene monolayer. The Brillouin zone integration was performed using Monkhorst-Pack grids of $45 \times 45 \times 1$.

The optimized lattice constant and the buckling parameter $\delta$ of silicene are 3.83 Å and 0.44, respectively, which are comparable with the previous work [7]. As mentioned in the introduction, when silicene is deposited on a substrate, then it is expected that it might distort slightly, therefore we considered different distortions. We mainly distort the bond angle between the Si atoms, that will also change the Si-Si bond length. In such distortions, the lattice parameters of silicene were kept at their optimized values. The distorted systems are denoted by $S_d (d=0-5)$. Here $S_0$ corresponds to pristine silicene. The bond angles (lengths) of all the studied systems are shown in table 1.

Table 1: Bond angle (in degrees) and length (in Å) between Si atoms in silicene. The first column shows different distortion systems $S_d (d=0-5)$.

| System | Bond angle | Bond length |
|--------|------------|-------------|
| $S_0$  | 116.28     | 2.500       |
| $S_1$  | 113.36     | 2.300       |
| $S_2$  | 107.85     | 2.367       |
| $S_3$  | 102.93     | 2.446       |
| $S_4$  | 98.00      | 2.530       |
| $S_5$  | 92.77      | 2.640       |

Results and discussion. – It is essential to discuss the cohesive energy of silicene under different strain and electric field. First, we calculated the cohesive energy of bulk Si. The calculated $E_c$ of bulk Si is $\sim 4.51$ eV, which is comparable with the experimental values 4.62–4.88 eV [7]. Once we confirmed that our bulk $E_c$ agrees with previous work, we calculate the $E_c$ of silicene which is $\sim 4.85$ eV. This value is also comparable with calculation using other functional and computational codes [7]. This shows that bulk Si is 0.34 eV per atom more stable than silicene. If we include the previously [7] LDA calculated zero point correction, then silicene is about 0.24 eV per atom higher than bulk Si.

Figure 1(a) shows the evaluation of the cohesive energy for different systems ($S_d (d=0-5)$) under external electric field. The horizontal solid line represents $E_c$ of bulk Si. Panel (b) shows the dipole moment (in atomic units (a.u.)) for different systems under external electric field.
Fig. 2: (Color online) Electronic band structure for silicene in zero electric field for different systems $S_d$. Labels (a)–(f) represent the different systems $S_0-5$ corresponding to different bond angles and lengths as mentioned in table 1. The horizontal line shows the Fermi level which is set to zero.

such a way that the bond angle between sublattice A and B changes, then $E_c$ becomes smaller, even smaller than bulk Si at higher strain. Though distortions decrease the $E_c$ of silicene, it may not be dynamically stable due to imaginary frequencies in the phonons mode along the $\Gamma$-$K$ direction of the BZ [10]. The increment (decrement) of $E_c$ in electric field (distortion) can be partially understood in terms of dipole-dipole interactions. Figure 1(b) shows the dipole moments under electric field for the different distortion systems $S_d$. We see that the electric field induces a dipole moment in silicene which grows with the strength of the electric field. Therefore, $E_c$ increases with the electric field. The marked difference between $E_c$ and dipole moment is the behaviour of silicene in the external field—the dipole moment increases linearly with the electric field, consistently with the previous work [25], but the cohesive energy does not follow a linear trend at higher fields. It is also noticeable that the distorted systems have larger induced dipole moment, and on the other hand, the distorted systems have lower $E_c$. So, the electronic polarization of valence electrons also contributes to the cohesive energy of silicene.

To have some physical arguments for the behaviour of $E_c$ under electric field, and to know why $E_c$ changes with $E$ and distortion, we calculated the electronic band structures of silicene under different distortions $S_d$ and electric fields. Our calculated electronic structures are shown in fig. 2. The electronic structure of pristine silicene (fig. 2(a)) shows that it is a zero-band-gap semiconductor similar to graphene. The Dirac point is located at the $K$-point and coincides with the Fermi level $E_F$, consistently with the previous calculations [7,10].

Figure 2(b)–(f) also shows the band structure of silicene under different distortions. It is interesting to note that strain does not induce any band gap opening. This behaviour is consistent with the well-studied system graphene [26,27]. When the structure of silicene is distorted, the linear dispersion relation at $K$ near the
Fermi energy is preserved, and the Dirac point \( E_D \) is shifted below the Fermi energy at higher distortions. Note that silicene retains the semi-metallic band structure up to the bond length (angle) \( \leq 2.37 \text{ Å} (107.85^\circ) \), which is close to the bulk Si values. Major changes in the electronic structure around the \( \Gamma \)-point are also visible. The \( \Gamma \) degenerate band around \( -2 \text{ eV} \) also retains its degenerate behaviour under the studied distortions. However, when silicene is distorted this degenerate band moves towards the Fermi energy and finally reaches it before transforming into metallic silicene. Similarly the high-energy bands around \( 2 \text{ eV} \) also move towards the Fermi energy at higher strains. So, as we increase the bond angle, the lowest conduction band of silicene near the \( \Gamma \)-point drops and is filled. At higher strains, all bands cross the Fermi energy and silicene is no longer semi-metallic. This suggests that silicene can absorb such small deformations before changing its electronic structure. Such behaviour of silicene advises that it can be used in nanodevices provided that one does not cross this distortable limit. From these calculations, we can infer that the bond angle (length) between the Si atoms in silicene plays a vital role to control the Dirac cones. We believe that the experimentally determined scattered results [14,16–18] may not only be to the interface effect [28], but also to different distortions, which change the bond angle of silicene, when deposited on a substrate.

Even distortion changes the electronic structure, and at higher strain (bond angles smaller than \( \sim 107^\circ \)) the Dirac point moves below the Fermi energy and retains its linear dispersion. The location of the Dirac point is very important and it can be used to engineer the carrier (holes or electrons) concentration \( \rho \). For a 2D Dirac system, \( \rho \) can be estimated from the distance between \( E_D \) and \( E_F \), using the expression \( \rho = sgn(E_D - E_F)((E_D - E_F)^2)/\pi \beta^2 [29] \), where \( \beta \) can be calculated from the linear dispersion around \( K \) as \( E_K + k = \pm \beta k \). The interpretation of fig. 2 in terms of \( \rho \) shows that silicene behaves as a \( n \)-type doped system beyond system \( S_2 \), \( E_D \) is shifted below the Fermi energy and \( \rho \) is negative for distorted silicene. This suggests that such distortion can behave as a self-doping in silicene. The physical mechanism of this behaviour can be understood from the band structure (see fig. 2), where the highest occupied states at the \( \Gamma \)-point move towards the Fermi energy under different strains. At bond angle \( \sim 102^\circ \) (\( S_3 \)) (compressed about 11%), the occupied states (strain-free case) become unoccupied and cross the Fermi energy and silicene behaves as a \( n \)-type doped system. We see from these band structures that the band structure of silicene under small strain follows the linear dispersion relation at the \( K \)-point. Such strains can only lower the Dirac point, \( i.e. \), changing the carriers type. Strain is a good tool to engineer the band structure of silicene. Chemical doping, \( e.g. \), Li, C, H, Co, dramatically changes the band structure and silicene does not have a linear dispersion relation around the \( K \)-point in the BZ. Such chemical doping may either transform silicene to a metallic or insulating compound. It seems that the electronic structure can be tuned either by strain or by electric field. Indeed, large strain or \( E \)-field can destroy the linear dispersion relation.

Now we investigate the electronic structure of silicene in the presence of an external electric field \( E \). The calculated band structure of silicene around the Dirac point for various electric fields and distortions \( S_2 \) are shown in fig. 3. The band gap in silicene is opened due to breaking of inversion symmetry by the electric field since the potentials seen by the atoms at the sites \( i \) and \( j \) are different. In this situation, the finite value of the on-site energy difference \( \Delta \) arises due to the potential difference and hence we can write \( \Delta = \alpha(V_i - V_j) \), where \( \alpha \) and \( V_i \) (\( V_j \)) are the proportionality constant and the potential seen by the atom at the site \( i \) (\( j \)), respectively. For constant electric field between the sheets, the potential difference \( \Delta V = V_i - V_j = eE\delta = F\delta \), where \( F \) is the electric field intensity and \( \delta \) is the buckling parameter of silicene, which is nonzero (zero) for silicene (graphene). This finite value of \( \delta \) in silicene breaks the symmetry of silicene in the presence of electric field and helps in opening up a band gap in silicene.

We also found that the band gap \( E_g \) increases linearly with electric field \( E \) (not shown here), similar to fig. 1(b). It will be essential to estimate this proportionality constant \( \gamma (E_g = \gamma F) \), which can be estimated from the slope of \( E_g \) vs. \( E \). For this purpose, we varied \( E \) from 0.0 to 1.0 \( \text{V/Å} \) and calculated \( E_g \) at the \( K \)-point for each value of \( E \). Our estimated \( \gamma \) for pristine silicene was 0.098 \( \text{eV/Å} \), which is comparable with the previous values [7,11]. Figure 3(f) shows \( \gamma \) of all systems. It also shows that \( \gamma \) increases linearly with distortion irrespective of the location of the Dirac point. It is interesting to note that the curvature of bands decreases almost inversely with \( E \), and at higher \( E \), the dispersion around \( K \) becomes parabolic, consistently with the tight-binding approximation [11]. This indicates the global linearity of the effective masses with the electric field. Hence, the band gap and the effective masses are proven to be proportional to \( E \).

Before summarizing our work, we must note that the band gaps and the band widths are usually underestimated by DFT-LDA, which can be corrected by GW-type calculations [30–32]. Previous GW calculations show a \( \sim 50 \) to 140\% enhancement of the band gap as compared with DFT-LDA calculations [31,32]. Therefore, it is speculated that our calculated \( E \)-field–induced band gaps and band widths may be larger than those shown in figs. 2 and 3. In the light of previous GW calculations [30,31], the \( \pm 0.4 \text{ eV} \) width of the linear regime [16,17], the corrected DFT picture, may not be so far from the measurements. Nevertheless, both GW and LDA predict a linear dispersion relation around the \( K \)-point and semi-metallic behaviour in low buckled silicene [30].

In summary, we used DFT to elucidate the origins of the experimentally determined different Dirac points in...
Fig. 3: (Color online) Band structure (Dirac points) of silicene under different strain and $E$-field. Labels (a)–(e) represent the different systems $S_0$–$S_4$ corresponding to different bond angles and lengths as mentioned in table 1. The horizontal line shows the Fermi level which is set to zero. Whereas panel (f) shows the slope $\gamma$ of the different systems $S_2$.

silicene. We showed that the cohesive energy of silicene decreases with distortions and increases with external electric fields. The band structure calculated at different distortions and electric fields showed that as silicene was distorted, the cohesive energy decreased due to unoccupied states at $\Gamma$, and at larger distortions, the Dirac cones also shifted below $E_F$ and silicene behaved as an $n$-doped silicene. This $n$-type behaviour of silicene also
participated in lowering its cohesive energy. From our DFT-LDA calculations, we came to the conclusion that silicene can retain the semi-metallic band structure when the bond angle between its Si atoms is closer to the bond angle between the Si atoms in bulk Si. Therefore, the scattered experimental reports about the position of the Dirac point may be attributed to different distortions of silicene on different substrates. We believe that it is not only the interfacial effect, but also the bond angle between the Si atoms that destroys the Dirac cones in silicene. These two factors can determine the existence or nonexistence of the semi-metallic nature of silicene, when deposited on a substrate.

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GR acknowledges the cluster facilities of NCP, Pakistan. The author is grateful for insightful discussions with Victor M. Garcia-Suarez and J. M. Morbec.

REFERENCES

[1] Lebegue S. and Eriksson O., Phys. Rev. B, 79 (2009) 115409.
[2] Rahman G., Victor M. Garcia-Suarez and Morbec J. M., J. Magn. & Magn. Mater., 328 (2012) 104.
[3] Neto A., Guinea F., Peres N., Novoselov K. and Geim A., Rev. Mod. Phys., 81 (2009) 109.
[4] Novoselov K. S., Geim A. K., Morozov S. V., Jiang D., Zhang Y., Dubonos S. V., Grigorieva I. V. and Firsov A. A., Science, 306 (2004) 666.
[5] Geim A. K. and Novoselov K. S., Nat. Mater., 6 (2007) 183.
[6] Takeda K. and Shiraishi K., Phys. Rev. B, 50 (1994) 14916.
[7] Drummond N. D., Zolyomi V. and Falk V. I., Phys. Rev. B, 85 (2012) 075423.
[8] Durgun E., Tongay S. and Ciraci S., Phys. Rev. B, 72 (2005) 075420.
[9] Zhang M. et al., Chem. Phys. Lett., 379 (2003) 81.
[10] Cahangirov S., Topkasal M., Akturk E., Sahin H. and Ciraci S., Phys. Rev. Lett., 102 (2009) 236804.
[11] Ni Z., Liu Q., Tang K., Zheng J., Zhou J., Qin R., Gao Z., Yu D. and Lu J., Nano Lett., 12 (2012) 113.
[12] Liu C.-C., Feng W. and Yao Y., Phys. Rev. Lett., 107 (2011) 076802.
[13] Padova P. E., Quaresima C., Ottaviani C., Shverdyvaeva P. M., Moras P., Carbone C., Topkasal D., Olivieri B., Kara A., Oughaddou H., Aufray B. and Lay G. L., Appl. Phys. Lett., 96 (2010) 261905.
[14] Fleurancq A., Friedlein R., Ozaki T., Kawai H., Wang Y. and Yamada-Takamura Y., Phys. Rev. Lett., 108 (2012) 245501.
[15] Meng L., Wang Y., Zhang L., Du S., Wu R., Li L., Zhang Y., Li G., Zhou H., Hofer W. A. and Gao H. J., Nano Lett., 13 (2013) 685.
[16] Vogt P., De Padova P., Quaresima C., Avila J., Frantzeskakis E., Asensio M. C., Resta A., Eal et B. and Le Lay G., Phys. Rev. Lett., 108 (2012) 155501.
[17] Chen L., Liu C., Feng B., He X., Cheng P., Ding Z., Meng S., Yao Y. and Wu K., Phys. Rev. B, 109 (2012) 056804.
[18] Lin C.-L., Arafune R., Kawahara K., Kanno M., Tsukahara N., Minamitani E., Kim Y., Kawai M. and Takagi N., Phys. Rev. Lett., 110 (2013) 076801.
[19] Rahman G., Phys. Rev. B, 18 (2010) 134410.
[20] Hohenberg P. and Kohl W., Phys. Rev., 136 (1964) B846.
[21] Soler J. M. et al., J. Phys.: Condens. Matter, 14 (2002) 2745.
[22] Perdew J. P. and Zunger A., Phys. Rev. B, 23 (1981) 5048.
[23] Hamann D. R., Schlüter M. and Chiang C., Phys. Rev. Lett., 43 (1979) 1494.
[24] Kleinman L. and Bylander D. M., Phys. Rev. Lett., 48 (1982) 1425.
[25] Amorim R. G., Zhong X., Mukhopadhyay S., Pandey R., Rocha A. R. and Karn S. P., J. Phys.: Condens. Matter, 25 (2013) 195801.
[26] Choi S.-M., Jhi S.-H. and Son Y.-W., Phys. Rev. B, 81 (2010) 081407.
[27] Rakhit B. and Mahadevan P., Phys. Rev. B, 82 (2010) 153407.
[28] Wang Y.-P. and Cheng H.-P., Phys. Rev. B, 87 (2013) 245430.
[29] Lazzeri M. and Mauri F., Phys. Rev. Lett., 97 (2006) 266407.
[30] Huang S., Kang W. and Yang L., Appl. Phys. Lett., 102 (2013) 133106.
[31] Wei W. and Jacob T., Phys. Rev. B, 88 (2013) 045203.
[32] Qiue R., Zheng J., Luo G., Liu Q., Qin R., Zhou J., Yu D., Nagase S., Mei W.-N., Gao Z. and Lu J., NPG Asia Mater., 4 (2012) e6.