Biaxial strain effects on the electronic properties of silicene: the density-functional-theory-based calculations

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Abstract. The effects of biaxial strain on the electronic properties of silicene are studied by carrying out the density-functional-theory (DFT) calculations. We simulate planar and buckled structures and find that the buckled structure is more stable than the planar one. We next apply biaxial strain up to 12% and find that the applied tensile and compressive strains below 8% do not change the electronic structure. At tensile strains of 8% or more, the Dirac point at K-point shifts up from the Fermi level, indicating that such tensile strain behaves as $p$-type doping. Meanwhile at the compressive strains of 8% or more, the Dirac point at K-point shifts down from the Fermi level, indicating that such compressive strain behaves as $n$-type doping. We find that silicene remains stable for the applied strain up to 12%. We also calculate the Fermi velocity around K-point, which is found to be $9.1 \times 10^5$ m/s.

Keywords: Silicene, buckled structure, biaxial strain

1. Introduction

Since graphene was successfully fabricated [1], theoretical and experimental studies of two dimensional materials (2D-materials) having graphene-like structure such as 2D-silicone (silicene) and 2D-germanium (germanene) have attracted much attention [2–7]. It was reported that $\pi$-band contributes to the electron conduction band [8, 9]. An experimental observation of the electronic properties of graphene shows that the Dirac cone appears on the edge of the Brillouin zone [10]. Graphene was grown on various substrates such as sapphire [11], h-BN [12], and Pt (111) [13]. As for the 2D-silicone, silicon sheets was synthesized [5]; however, the formed silicon sheet was immediately capped by foreign atoms. The difficulty of fabrication of silicene is that, in nature, there is no silicon whose structure resembles like graphite so that silicene cannot be fabricated by using mechanical stripping [10]. Silicene could be synthesized by using chemical reduction method; however, the produced material behaves as insulator [7].

One of efforts to have understanding of silicene is by performing quantum-based DFT simulations [14–18] since the DFT calculational results [19–22] frequently agree with those of the experimental measurements. The DFT studies predicted that silicene has stable buckled structure instead of planar structure [14, 15, 17], and a linear dispersion characteristic appears at the K-point with the Fermi velocity of $5.3 \times 10^5$ m/s [23]. Several studies were conducted
to study the effect of strain on the electronic properties of silicene [24–26]. It was shown as the strain increases, the band gap at K-point decrease. The structure of silicene breaks at strain 14% and 18% for zigzag and armchair geometry, respectively [18]. As for the influence to the Dirac cone, at strain more than 5%, the Dirac cone is 0.06 eV shifted above the Fermi level [27]. The Dirac cone is also shifted above the Fermi level when the tensile strain of +10% is applied, and it is shifted below the Fermi level when the compressive strain of 8% is applied [28]. The stability of silicene was also studied by using a molecular dynamics simulation that silicene is stable at 0 K but it breaks at room temperature [29]. Therefore, the study of the electronic structure of silicene is essential to explore the behavior of such materials to be plausible candidates for the electronic devices such as a tunneling-field-effect transistor. In this paper, we study the electronic properties of silicene by performing the DFT calculations. We first check the stability of silicene by carrying out calculation on planar and buckled structures. We apply tensile and compressive strain up to 12% and analyze its influence to the electronic structures.

2. Computational Methods
We carry out the DFT calculations on the strain application on silicene. We use code PHASE [30], which is based on the plane wave basis set. We use the norm-conserving pseudopotential and the local density approximation (LDA) [31] as the exchange-correlation functional. A cutoff energy of 40 Ry and a 6×6×1 Monkhorst-Pack mesh grid [32] are used in the calculation. We relax atoms so that the atomic force is less than 5.0 × 10⁻³ eV/Å. To neglect the interlayer interaction, we apply a 15 Å vacuum parameter perpendicular to the silicene sheet. The unit cell consists of two atoms whose lattice vectors are \( \vec{a}[1/2, \sqrt{3}/2, 0] \) and \( \vec{b}[-1/2, \sqrt{3}/2, 0] \).

We first calculate the total energy with respect to the cell volume to find the optimized lattice constant. The calculated data is then fitted by using the Birch-Murnaghan equation of sates (BM-EOS) in Eq. 1 [33,34],

\[
E(V) = E_0 + \frac{9}{16} V_0 B_0 \left[ \left( \frac{V_0}{V} \right)^{\frac{3}{2}} - 1 \right]^3 B'_0 + \left( \left( \frac{V_0}{V} \right)^{\frac{3}{2}} - 1 \right)^2 \left( 6 - 4 \left( \frac{V_0}{V} \right)^{\frac{3}{2}} \right)
\]

where \( E_0, V_0, B_0, \) and \( B'_0 \) are parameters obtained from the fitting, which are the minimum energy, optimized cell volume, bulk modulus, and first derivative of the bulk modulus at \( V = V_0 \), respectively. To investigate the stable configuration of silicene, we simulate planar and buckled structures by introducing a buckling parameter and calculating cohesive energy by using \( E_{\text{coh}} = E_{\text{silicene}} - 2E_{\text{Si}} \), where \( E_{\text{coh}}, E_{\text{silicene}}, \) and \( E_{\text{Si}} \) are the cohesive energy, total energy of silicene in two-atoms unit cell, and energy of an individual silicon atom calculated from the bulk structure, respectively.

3. Results and Discussion
We calculate the total energies with respect to the cell volumes for planar and buckled structures and fit the calculated results to the BM-EOS. As shown in Fig. (Fig. 1), the buckled structure has lower energies than the planar one, indicating that the buckled structure is more stable than the planar one. We also calculate the cohesive energies and find that the buckled structure has 0.02 eV lower cohesive energy than the planar one. Comparing with graphene, the calculated cohesive energy of graphene is 0.19 eV, which is 1.37 eV lower than that of silicene (1.56 eV).

We apply the biaxial strain and calculate the buckling parameters and Si-Si bondlengths (Fig. 2). As the strain increases the buckling parameter decreases while the Si-Si bondlength increases. The increase of strain enlarges the lattice parameter; then the distance between silicon atoms increases, and vice versa, to maintain the stability of the silicene structure. The optimized buckling parameter and Si-Si bondlength of the zero-strain are 0.40 Å and 2.24 Å, respectively. The largest buckling parameter calculated at strain -10% is found to be 112.9% higher while...
Figure 1. The calculated data (circle and square) and the BM-EOS fitting result (solid line) of total energies versus cell volumes for planar (black) and buckled (blue) structures.

Figure 2. Strain effect to the buckling parameter (left axis, circle points) and Si-Si bondlength in silicene (right axis, square points).

Figure 3. Charge density distribution near the (a) $\pi$-bond valence, (b) $\pi$-bond conduction, (c) $\sigma$-bond valence and (d) $\sigma$-bond conduction band in unit $e/(a.u)^3$, calculated at $\pm 0.05$ eV from the Fermi level.

Figure 4. Full charge density distribution near $\sigma$-bond for (a) silicene and (b) graphene. The $\pi$-bonds are shown in (c) and (d) for silicene and graphene, respectively. The unit is in $e/(a.u)^3$.

the smallest one calculated at strain 12% is 49.9% lower than that of the zero-strain calculation. As for the bondlength, the largest and the smallest ones are 16.9% higher and 3.7% lower than that of the zero-strain calculation. We next calculate the partial charge density distribution of $\pi$-bonds and $\sigma$-bonds in the valence and conduction bands calculated at $\pm 0.05$ eV from the Fermi level, as shown in Fig. 3. The $\pi$-bond charge in the valence band (Fig. 3(a)) is lower than that in the conduction band (Fig. 3(b)). This lower charge originates from the asymmetric wave function, which does not obey the inversion symmetry while the higher $\pi$-bond charge in the conduction band originates from the symmetric wave function. Conversely, the higher $\sigma$-bonds
occur in the valence band (Fig. 3(c)) instead of the conduction band (Fig. 3(d)). We also calculate the total charge density for silicene (Fig. 4(a)) and graphene (Fig. 4(b)) and we show that silicene has lower bond charge density than graphene, indicating that the bond in silicene is weaker than that in graphene. The larger bondlength of Si-Si bond in silicene, which is found to be 2.24 Å comparing to that in graphene of 1.44 Å, contributes to the lower bond in silicene. Meanwhile, the lower $\pi$-bond causes silicene has a buckled structure, as we mentioned above that the most stable structure of silicene is the buckled structure.

Figure 5. Band structures of the strained silicene (a) ±4%, (b) ±6%, (c) ±8% and (d) ±10%. The band structures of the tensile, compressive, and zero-strain are shown in blue, red and black lines, respectively.

To know the effects of strain to the electronic structures, we calculate band structures (Fig. 5). The calculated band structure of the zero-strain is shown by the black line in Fig. 5. The presence of cross linear at the K-points shows the characteristic of silicene, the Dirac cone, as in graphene. The center point of the Dirac cone lays at the Fermi level, which is in agreement with results of the previous studies [14,35]. The Dirac cone is due to electrons following the relativistic Dirac fermion [10]. Our calculated Fermi velocity is $9.1 \times 10^5$ m/s, which is in agreement with that of the previous studies ($\approx 10^5$ m/s) [23,36,37].

We apply compressive and tensile strains up to 10%. Our calculational results show that the applied strains equal or less than 6% do not change the electronic structure, for instance, the Dirac point remains at the Fermi level. The applied strain of 8% slightly shifts the position of the Dirac cone at the K-point, the tensile strain shifts up while the compressive strain shifts down. The applied strains of ±10% result larger shift than those of ±8% but have similar behavior that the tensile strain shifts the Dirac cone up and the compressive strain shifts it down from the Fermi level. This shift indicates that the applied tensile strain behaves as the p-type doping and the compressive strain behaves as the n-type doping. We also calculate the tensile strain of 12% and clarify the similar behavior with the results of the strain 8% and 10%. From our calculation, silicene remains stable by the application of strain 12%.

4. Conclusion
We have carried out calculations on the electronic structures of silicene. As for the silicene structure, we found that the buckled structure is stable while the planar one is metastable. We applied biaxial strain and found that the applied strain of 8% – 12% shifts the Dirac point up from the Fermi level while the compressive strain shifts it down. Thus, the tensile strain behaves as p-type doping while the compressive strain behaves as n-type doping.
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