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Possible values of lattice constant of silicene growth on substrate: Density functional calculation

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Abstract

We conducted calculations using First-Principles based on Density Functional Theory to determine the stability of monolayer silicene. A quasi-freestanding of monolayer silicene was applied as a model during calculations. We investigated the total energy and the atomic configuration using various lattice constant. We analyzed that a monolayer of silicene in a freestanding state will never be synthesized. Silicene merely can be synthesized only on the top of the substrate. We found some possible values of the lattice constants of monolayer silicene on the substrate, especially in recent experiment which was silicene on the top of Au[111]. We also investigated the electronic structure of silicene using various lattice constant. We assumed that the strain engineering can be truly applied in silicene, and in all group IV monolayer. This opportunity opening the possibility of silicene for application of topological quantum computing.

Keywords: Monolayer, Silicon, Stability, Strain, Synthesized.

1. Introduction

The existence of silicene was theoretically predicted by Kyozaburo Takeda and Kenji Shiraishi in 1994 [1]. Silicene exhibits two-dimensional (2D) crystal of silicon atom with a honeycomb structure. Research about silicene had not become an interest until the successful encapsulation of Graphene in 2004 [2]. Graphene is a 2D crystal with a honeycomb structure which is consist of carbon atom. Graphene exhibits some incredible electronic properties such as Dirac Cone shape in its electronic structure, Ballistic Transport, Quantum Hall Effect and Quantum Spin Hall Effect [2]. All unique properties of graphene exist due to the honeycomb crystal structure. All achievements in graphene triggers scientists to discover the possibility same structure in silicon case. The main reason because carbon atom and silicon atom are in the same group of periodic tables. Silicene also has a benefit compare to graphene because it is easily integrated with current silicon technology. Silicon atom also has a value of spin orbit coupling bigger than the value of graphene. Therefore, later some papers explain theoretically the existence of silicene and the electronic properties, which have the same tendency like reported by Takeda and Shiraishi [3-5]. Theoretically, silicene has a similar hexagonal geometry like graphene. However, silicene has a buckled structure which is different from graphene as planar sheet. This buckling structure and the existence of spin orbit coupling induce controllable opening band gap using Electric Field. Therefore, silicene is promising for application for topological quantum computing [6, 7].

First evidence of silicene which was synthesized on the top of substrate was reported in 2006 [8]. It was recognized as a silicon quantum wires on Ag[110]. Later in 2010, silicene could be synthesized on Ag[110] [9] and also as a sheet on Ag[111] [10] which is exhibit as a nanoribbon. The Ag has a closed package crystal system (CPCS), which is correspond to metal material. Later CPCS is commonly used as a substrate for silicene [8-18]. In particular Ag[111] is commonly used to growth a sheet of silicene [8-13]. The geometry of silicene sheet on Ag[111] has a hexagonal crystal structure with a buckling, which is the same as theoretical predictions [8-13]. Recently Au[111] emerge as another promising candidate as a substrate for silicene [14-18]. The Au also has CPCS, which also correspond to a metal substrate. The silicene sheet on Au[111] has elongated bond length compare to quasi-freestanding model and on Ag[111] [14, 15]. This elongation is correspond to tensile strain which is affected by mismatch the length of lattice constant between silicene and Au[111] surface. This elongation of bond length reduces the value of buckling and changed the electronic properties of silicene. Silicene on Au[111] with lattice constant 4.1 angstrom is reported has a planar shape similar to graphene [14-18]. The existence of planar silicene on Au[111] is also emphasized by spectroscopic method that present the sp^2 type hybridization, which is commonly exist in graphene [17].

In this paper we attempt to perform reliable first-principles calculation based on Density Functional Theory (DFT) of silicene sheet. We investigate the reliable values of lattice constant of silicene growth on the top of substrate. We investigated it using quasi-freestanding model like previous theoretical paper [1, 3-5]. However, we conducted more accurate and reliable calculations. The atomic forces were set less than 10^{-4} eV/angstrom, which is commonly set between 10^{-2} eV/angstrom and 10^{-3} eV/angstrom [3-5]. Therefore, our result exhibits the minimum energy of the structure, instead of the local minimum ones. We analyzed that a freestanding silicene will never be synthesized due to unstable buckling structure of silicene. We assume that silicene can be exist only on the top of substrate. We found that silicene with lattice constant 4.1 angstrom has a unique geometry property. Lattice constant with the value less than 4.1 angstrom, the buckling tends to decrease due to bond length increase. However, the lattice constant bigger than 4.1 angstrom, causes the buckling tends to increase. This evidence exhibits that silicene with lattice constant of 4.1 angstrom was possibly a critical point before the break of the covalent bond. We assume that the silicene with the lowest buckling can be synthesized in 4.1 angstrom lattice constant. If the strong interaction exist within substrate and silicene with lattice constant of 4.1 angstrom, we can obtain a planar ones like on Au[111] [14-18].

2. Materials and methods

First-principles calculations based on DFT were carried out by using PHASE/0 code [19-22]. The norm-conserving pseudo-potential developed by Troullier and Martins was used for silicon atom [23]. We set the cut off energies 40 Rydberg and 160 Rydberg respectively, for the wave function and charge density. We used the Local Density Approximation (LDA) for the exchange correlation energy. The LDA calculation is based on method developed by Perdew and Wang [24]. We set the *k*-point as $25 \times 25 \times 1$ using Monkhorst-Pack mesh grid [25]. We calculated the total energy of quasi-freestanding silicene sheet with some values of lattice constant. We optimized the atomic geometry for every value of lattice constant. In the optimized geometries, the atomic forces are less than 10^{-4} eV/angstrom and the total energy was converged within 10^{-10} eV/unit cell. We also conducted some band structure calculation, Density of States (DOS) and Projected Density of States (PDOS) of some values of lattice constant. For the band structure calculations, we used the same set of k-point like calculations to optimized atomic geometry above. For the DOS and PDOS calculation, we set the *k*-point as $96 \times 96 \times 1$ and used a Mesh method [26]. Finally, we conducted calculation of the charge density of electrons for several values of lattice constant. For the charge density calculation, we used the same parameter with the calculations to optimize atomic geometry.

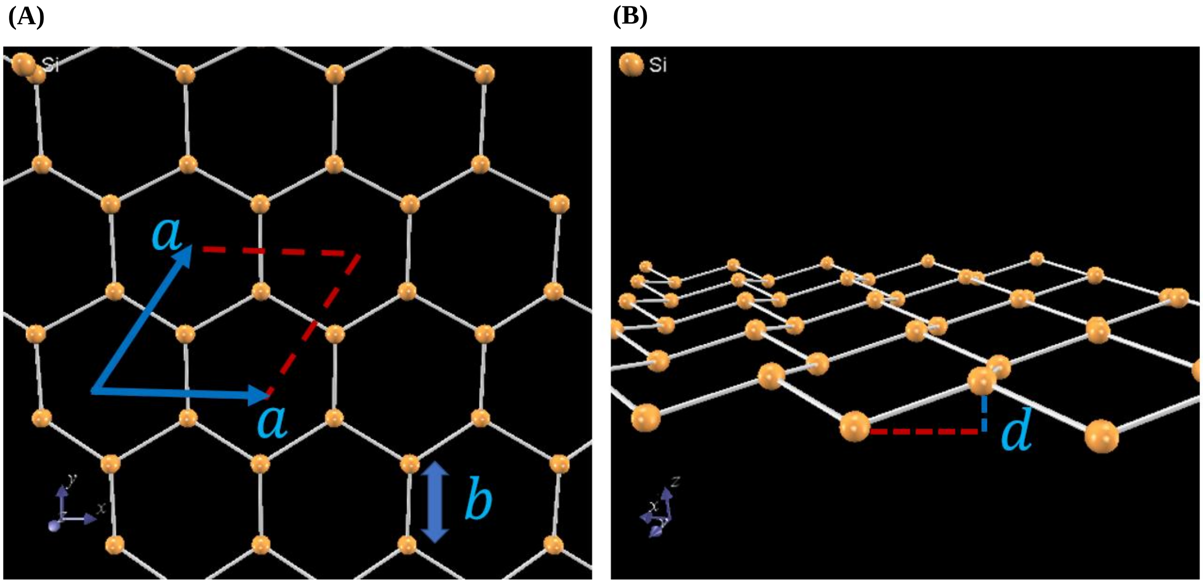

Figure 1 Atomic configuration of silicene: (A) top view, (B) side view.

3. Results and discussion

Firstly, we show the atomic configuration of a quasi-freestanding silicene sheet (Figure 1). In Figure 1A, it is completely clear that silicene has a hexagonal monolayer crystal system like graphene. The silicene lattice constant and the bond length in Figure 1A are symbolized by "a" and "b" respectively. For corrugation shape of silicene sheet in which correspond to the buckling, it is symbolized as "d" in Figure 1B. The lattice constant, the bond length and the buckling have an angstrom as a unit. Figure 1(A) shows that the silicene with lattice constant $a = 3.81$ angstrom due to one of the lowest energy configurations from the result of calculation in this report.

Then we perform calculations of total energy with some values of lattice constant (Figure 2(A)). We used the range of lattice constant between 2.25 angstrom to 4.80 angstrom. We found two values lattice constant which is correspond to the lowest of total energy. The first lowest total energy belongs to the lattice constant of 2.65 angstrom. The second lowest of total energy belongs to 3.81 angstrom. These results are consistent with the previous theoretical report [4, 5]. The lowest total energy means that the freestanding silicene is possibly synthesized in these values of lattice constant. Unfortunately, the freestanding silicene is never obtained experimentally. Even though some methods had been proposed theoretically and experimentally to realize it, but it has not been synthesized yet [27, 28]. In our argument, the lowest total energy does not mean the freestanding silicene can be easily synthesized in these values of lattice constant. The lowest total energy is indicated that the silicene can be synthesized on the top of substrate. We can see in Figure 2(B) which corresponds to the relation with the bond length of silicene and lattice constant. In the range of value from 2.50 angstrom to 3.10 angstrom in which the first lowest energy lattice constant is located, we can see that the bond length has the same values. In these range, the bond length of silicene was approximately 2.60 angstrom. On the other hand, the values of buckling also show the constant values, in which correspond to 2.00 angstrom (Figure 2(C)). These behaviours are contrary to common ones. When the lattice constant increases, the bond length will increase. On the other hand, the buckling will reduce. The total energy also decreases due to increasing the lattice constant. These common behaviours are due to increasing the lattice constant, which will reduce the strength of the covalent bond. Therefore, it will reduce the stability of the silicene sheet. Our calculation for the total energy shows the common behaviour (Figure 2A). On the other hand, the constant buckling and bond length are counterintuitive ones. These behaviours will be explained more detail in the charge density explanation in the second paragraph of page 7. We identify that the silicene in these ranges values of lattice constant is unstable. We assume that the silicene cannot be synthesized in these ranges, even on the top of substrate like commonly carry out.

The second lowest of total energy belonged to silicene with 3.81 angstrom of lattice constant (Figure 2(A)). We assume the range of lattice constants values in which correspond to the second lowest of total energy was from 3.10 angstrom to 4.15 angstrom. We assume these ranges of values due to the behaviour of the buckling. From Figure 2(C) we can see the buckling tends to decrease almost linearly due to increasing value of lattice constant. This behaviour exhibit possibilities of metastable states of silicene. These metastable states are indicated that the silicene still cannot be synthesized as a quasi-freestanding, but it is possible to be synthesized on the top of substrate. We divided this ranges into two parts, the first range is from 3.10 angstrom to 3.50 angstrom and the second range is from 3.50 angstrom to 4.15 angstrom. This assumption belonged to the behaviour of the bond length (Figure 2(B)). In Figure 2(B), the bond length in the first range tended to decrease due to increasing the value lattice constant. On the other hand, the second range tended to increase. Commonly, the increasing value of lattice constant will affect the bond length, which has tendency to increase the bond length. Therefore, in the first range is less stable compared to the second range, we assume that the silicene can be synthesized on the top of substrate in the second range values. Our assumption is completely relevant and well agree with experimental reports [8-18]. Even though, the first range was less stable than the second range, but it was also possible to obtain silicene on substrate with this range of values of lattice constant. One experimental report explains that the silicene with 3.16 angstrom lattice constant has been successfully synthesized on the top of MoS_2 [29].

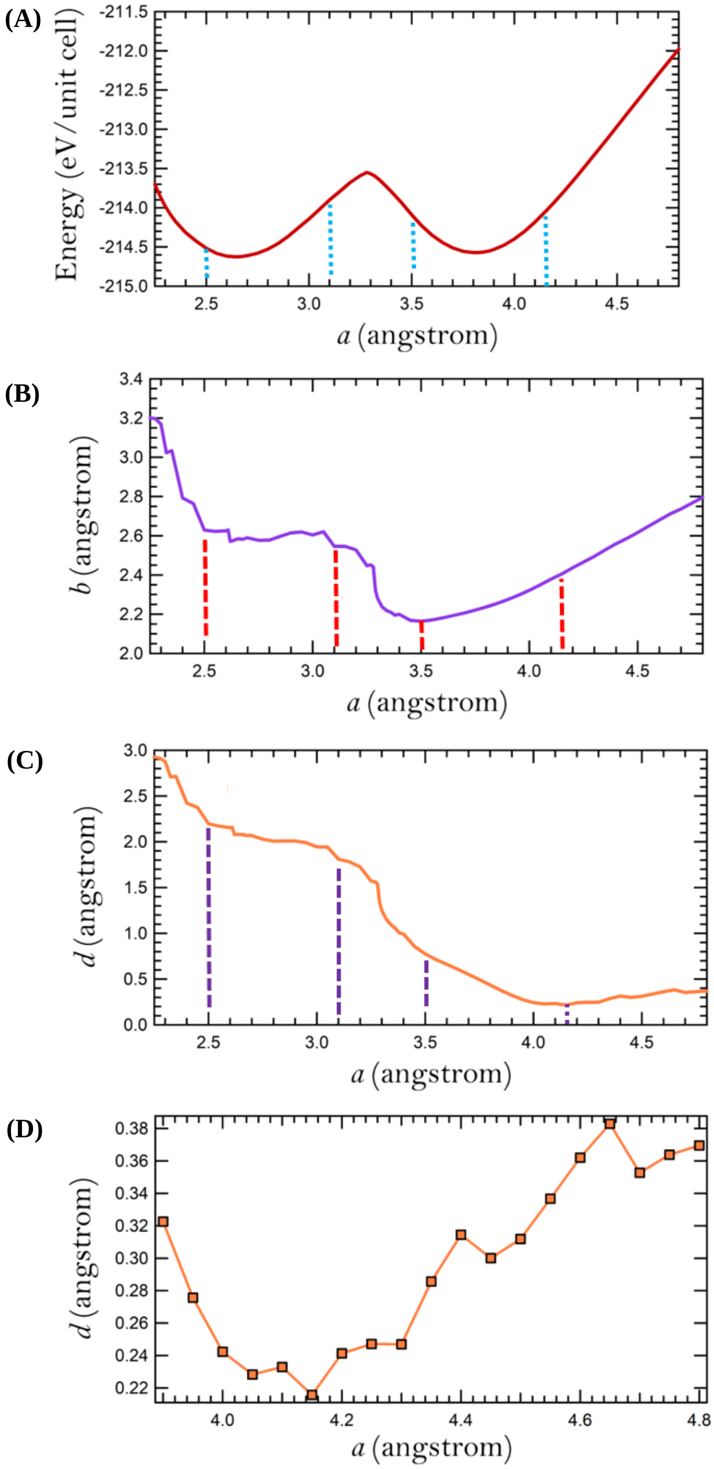

Figure 2 (A) The lattice constant vs the total energy, (B) the lattice constant vs the bond length, (C) the lattice constant vs the buckling, (D) the zoom of (C) around 3.90-4.80 angstrom of lattice constant.

The interesting behaviour of buckling exist around the value 4.15 angstrom of lattice constant (Figure 2(D)). In Figure 2(D), we exhibit the buckling from 3.90 angstrom to 4.80 angstrom. The buckling has a common behaviour from 3.90 to 4.15 angstrom. The buckling tends to decrease due to increasing lattice constant. On the other hand, the tendency has changed since the values of 4.15 angstrom. The buckling tends to increase due to the increase of lattice constant value. We assume that the 4.15 angstrom is the critical values of lattice constant. In approximation we set the range of critical values were between 4.10 and 4.20 angstrom. The critical point is related with the maximum of the length of the covalent bond. In our calculation we obtain the maximum bond length approximately 2.41 angstrom. The covalent bond has possibility to be broken by the bond length longer than this [30-31]. Therefore, in the range of critical values, we can synthesize the silicene with this maximum value of lattice constant. Our result is well agreed with the values of lattice constants on Au[111] which has a value 4.10 angstrom [14-18]. From Figure 2D, we can also obtain silicene with the lowest buckling around the critical point. The lowest values of buckling correspond to our calculation is 0.22 angstrom. If the strong interaction exists between silicene and substrate, a planar silicene can be synthesized in this range of critical value. The silicene on the Au[111] is the recent example. The Au[111] induces silicene to be synthesized on 4.10 lattice constant. The strong interaction between silicene and Au[111] reducing the buckling and produces a planar silicene.

We also conducted the calculation of the electronic structure of silicene for several values of lattice constants. The Brillouin Zone (BZ) of silicene is shown in Figure 3. We calculated the band structure, Total Density of States (DOS) and Projected DOS in Figure 4,5 and 6 respectively. The calculation of charge density of electrons also has been conducted for several values of lattice constant and it is showed in Figure 7. We obtained the electronic structure of silicene with lattice constant 2.65 angstrom exhibit metallic behaviour (Figure 4(A), Figure 5(A) and Figure 6(A)). The metallic character is unnatural for silicon atoms, in which commonly covalent bond is preferable. As shown in Figure 7(A) and 7(B) it is obvious that charge density of electron has a close package surface behaviour like common metal. This result also represents the behaviour of silicene with the range of lattice constant 2.50 - 3.10 angstrom. The counterintuitive behaviour of the bond length and buckling is also due to the existence of the metallic bond. Commonly the buckling decreases and the bond length increases due to the increasing lattice constant. On the other hand, the bond length and the buckling remain constant. The strength of the covalent bond reduces. However, the metallic bond has a dominant instead of the covalent bond. Therefore, the metallic bond maintains the buckling and the bond length remains constant. Therefore, as mentioned earlier the silicene with these range values of lattice constant is unstable.

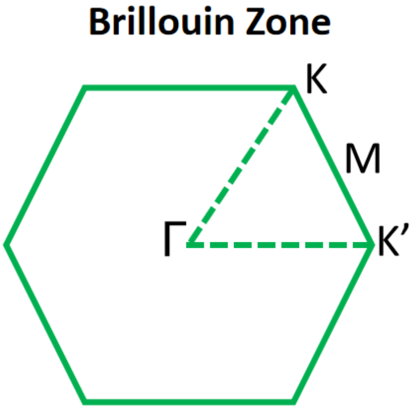

Figure 3 The Brillouin Zone (BZ) of silicene.

The next step, we obtained the calculation results for the value of lattice constant 3.20 angstrom. This result also represents the silicene with the range of lattice constant between 3.10 - 3.50 angstrom. The result of the electronic structure calculation is shown in Figure 4B, 5B and 6B. It is almost like the lattice constant 2.65 angstrom, in which the metallic behaviour still dominant than the covalent state. However, the electron density exhibits a tendency that the metallic behaviour has reduced (Figure 7(C) and 7(D)). The metallic bond has competed with the sp^3-sp^2 covalent bond, which naturally covalent bond exist in silicene as explained in previous theoretical papers [1, 3-5].

The second lowest total energy of silicene with lattice constant value of 3.81 angstrom, exhibit similar electronic structure with the previous theoretical reports [1,3-5]. The band structure of silicene exhibit semimetal behaviour. This evidence due to the existence of the Dirac Cone (DC) in the K-point of the BZ (Figure 4(C)). The DC represents free sp^3 orbitals, which was perpendicular to the silicene sheet (Figure 5(C) and 6(C)). The free sp^3 orbital interaction between nearest neighbor silicon atoms exhibit the π (pi) bond between silicon atoms. The sp^3-sp^2

covalent bond between silicon atom exist and it is represented by states between -1 eV and -5 eV or in the valence band (Figure 5(C) and 6(C)). The sp^3-sp^2 covalent bond between silicon atom exhibit a σ (sigma) bond in which maintain the stability of silicene layer. Figure 7 shows the electron densities, in which Figure 7(E) and 7(F) correspond to pi bond and sigma bond respectively. The existence of van-Hove Singularities (VHS) is also recognized in our electronic structure's calculation. The VHS exist around the Fermi level and deeply inside the valence band. In around Fermi level, the two VHS are located at -1 eV and 1 eV. These two VHS are represented by free sp^3 orbitals. On the other hand, for the deep inside the valence band, the two VHS are located at -7 eV and -9 eV. These VHS are represented by the s-orbital of silicon atoms.

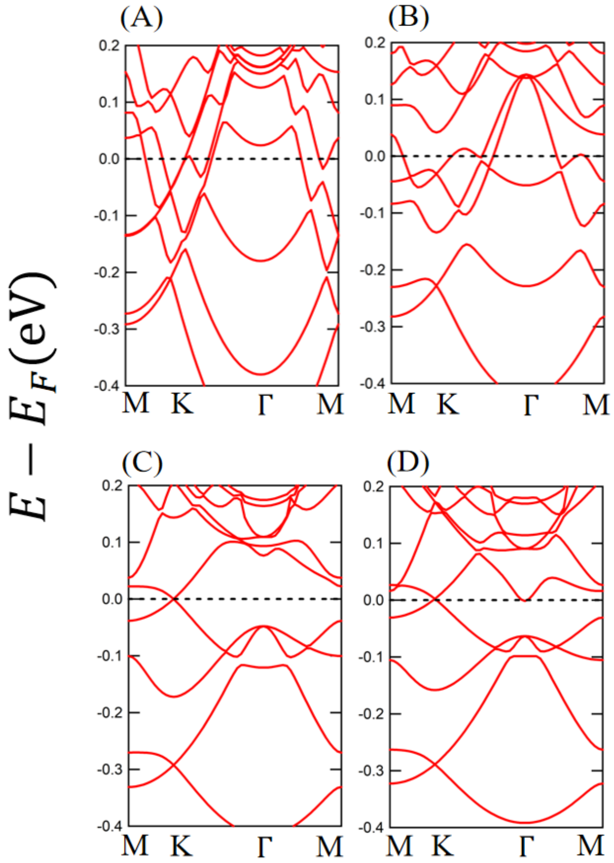

Figure 4 The band structure of quasi-freestanding silicene with lattice constant (A) 2.65 angstrom, (B) 3.20 angstrom, (C) 3.81 angstrom, (D) 4.10 angstrom. The Fermi energy is set as 0 eV.

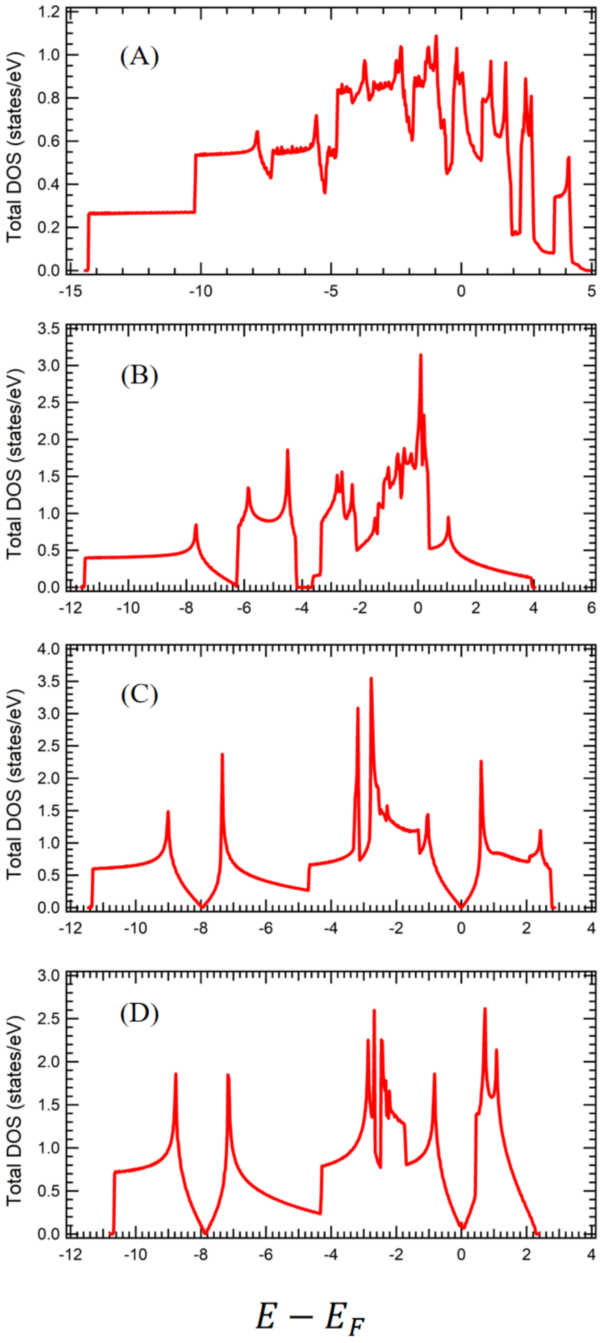

Figure 5 The Density of States (DOS) of quasi-freestanding silicene with lattice constant (A) 2.65 angstrom, (B) 3.20 angstrom, (C) 3.81 angstrom, (D) 4.10 angstrom. The Fermi energy is set as 0 eV.

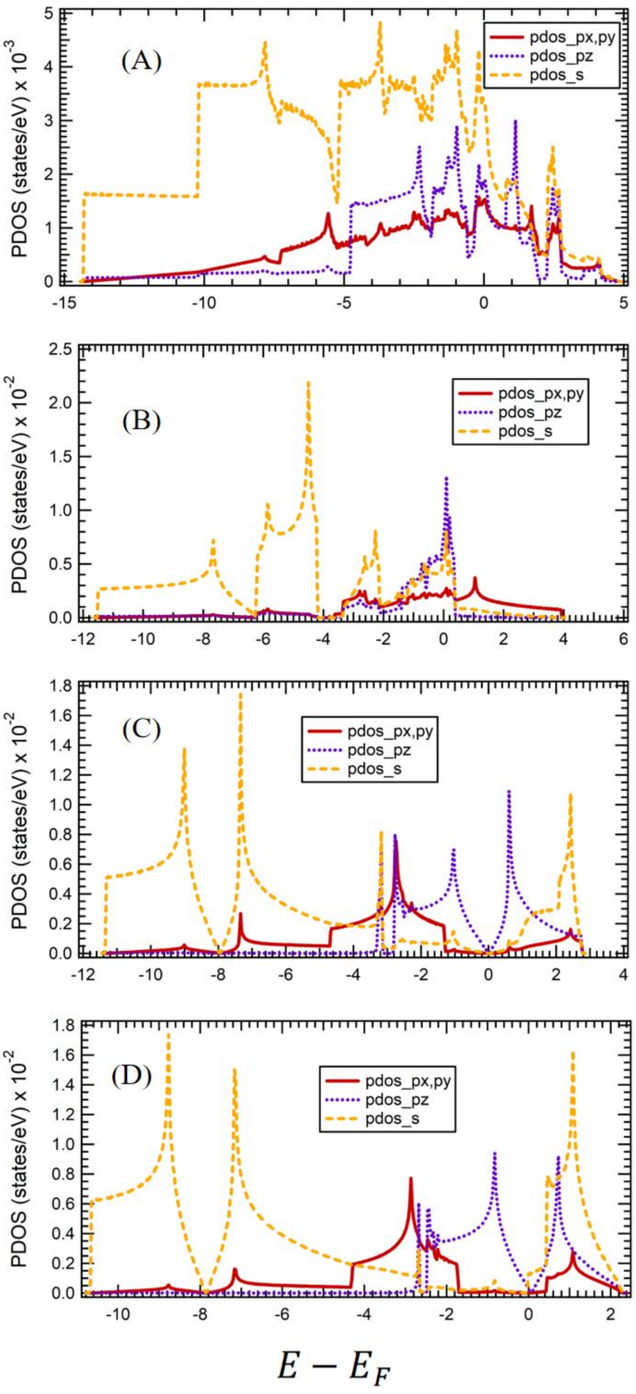

Figure 6 The Projected Density of States (PDOS) of quasi-freestanding silicene with lattice constant (A) 2.65 angstrom, (B) 3.20 angstrom, (C) 3.81 angstrom, (D) 4.10 angstrom. The Fermi energy is set as 0 eV.

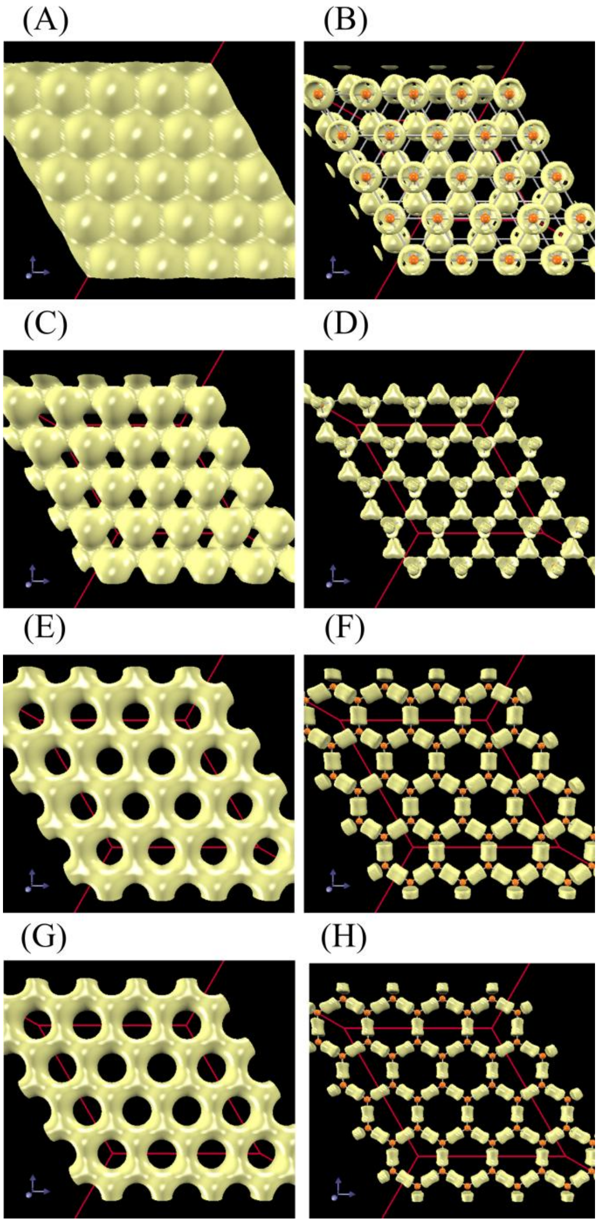

Figure 7 The charge density of quasi-freestanding silicene with lattice constant of 2.65 angstrom (A) isosurface 0.026 bohr^{-3}and (B) 0.058 bohr^{-3}; 3.20 angstrom (C) isosurface 0.025 bohr^{-3} and (D) 0.057 bohr^{-3}; 3.81 angstrom (E) isosurface 0.029 bohr^{-3} and (F) 0.057 bohr^{-3}, 4.10 angstrom (G) isosurface 0.028 bohr^{-3} and (H) 0.057 bohr^{-3}.

The electronic structure of silicene with lattice constant 4.10 angstrom exhibits almost similar properties with the 3.81 angstrom. The evidence of the DC also exists in the band structure, which is in the K-point of BZ (Figure 4(D)). The VHS also exists around the Fermi level and deeply inside the valence band (Figure 5(D)). Around the Fermi energy, only one VHS is recognized, which is located at -0.6 eV. On the other hand, in the deep inside of the valence band, we recognized two VHS. The VHSs are located at -7 eV and -8.6 eV respectively. The reducing number of VHS around the Fermi energy is due to the moving of state at Γ point, which correspond to s-orbital of silicon atom (Figure 4(D) and 6(D)). In our argument, the semi-metallic character still exists, which is indicated that the structure is the stable one. The silicene with 4.10 angstrom can be synthesized on the top of substrate. The electron charge density in Figure 7(G) and 7(H) emphasize this argument. The existence of pi bond and sigma bond which is correspond to Figure 7(G) and 7(H) respectively is indicated this stability. However, the electron density around the bond is indicated to reduce compared to the 3.81 angstrom ones (compare Figure 7(F) and 7(H)). This evidence represents the strength of the covalent bond has reduced due to increasing the length of the bond. On the other hand, the pi bond exhibits the same density with the 3.81 angstrom structure (compare Figure 7E and 7G). This evidence is point out the strength of the pi bond just slightly reduce. The pi bond has a dominant rule compared to the sigma bond in silicene with lattice constant of 4.10 angstrom.

The possibilities of silicene can be synthesized with several values of lattice constant represents the strain engineering can be adapted in this material. The buckling control due to the values of lattice constant emphasizes that the silicene has an extraordinary property. The buckling control and a control by applied electric field has opened the silicene become the best candidate for topological quantum computer.

4. Conclusion

In summary, we conducted a reliable calculation due to the existence and the stability of silicene. We conclude that the freestanding silicene is difficult to realize it. However, silicene only can be synthesized on the top of substrate. The most possible ranges of lattice constant in which silicene can be synthesized is between 3.50 and 4.15 angstrom. Around the values of 4.10 - 4.20 angstrom of lattice constant is a critical point of the covalent bond. The critical point indicates that the maximum of the length of the covalent bond. The silicene with the lowest buckling can be synthesized between 4.10 and 4.20 angstrom of the lattice constant. The buckling has a value approximately 0.22 angstrom. The buckling may become zero, if the interaction between silicene and substrate are strong enough. Therefore, the planar silicene can be synthesized in these range of lattice constant. This theoretical evidence has emphasized the existence of planar silicene on Au[111].

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