Is silicene stable in air?-First principles study of oxygen adsorption and dissociation on silicene

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Abstract

The oxygen adsorption and dissociation on pristine silicene surface are studied by use of first-principles in this letter. The oxygen adsorption and dissociation on pristine silicene surface are studied by use of first-principles in this letter. It is found that the pristine silicene is not stable in air because the oxygen molecule can be easily adsorbed and dissociated into two O atoms without overcoming any energy barrier on pristine silicene surface. In addition, dissociated oxygen atoms are relatively difficult to migrate on or desorbed from pristine silicene surface, leading to poor mobility of oxygen atom. As a result, silicene would be changed into Si-O compounds in air. The work will be helpful to reveal the detail of the interaction between oxygen molecules and pristine silicene surface, especially helpful to understand the stability of silicene in air.

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INTRODUCTION

Slicene, the silicon-based counterpart of graphene, has promoted from theoretical predictions to experimental observations in last few years \cite{1-5}. Theoretically, density functional theory (DFT) calculations on slicene show that $\pi$ and $\pi^*$ bonds linearly cross at the Fermi level, reflecting the semi-metallic or zero-gap semiconducting character of slicene \cite{6}. In addition, most of the other known features of slicene resemble those of graphene. Therefore, due to its unique structure and electronic properties of graphene-like two-dimension (2D) sheet, slicene has the potential to provide a new future for the electronics industry. Especially, it could be expected to offer an easily implemented alternative for the enhancement of the performance and scalability of the present silicon-based electronics. Interestingly, even before the synthesis of graphene, first-principles local-density approximation calculations predicted that a buckled honeycomb structure of Si could exist \cite{7, 8}, in contrast with the planar honeycomb structure of graphene. Furthermore, on the basis of the first-principles calculations of structure optimization, phonon modes, and finite temperature molecular dynamics, it is reported that although the planar and high-buckled structure of Si is unstable, the low-buckled (LB) honeycomb structure can be stable with an equilibrium buckling of $\Delta = 0.46 \text{ Å} \cite{9}$.

Experimentally, Nakano \textit{et al.} has reported the synthesis of slicene via the chemical exfoliation of CaSi$_2$ \cite{10}. Recently, the possible growth of the slicene sheet on Ag (111) has been reported \cite{11}. For example, Patrick Vogt \textit{et al.} report that they have provided compelling evidence for the synthesis of epitaxial slicene sheets on Ag (111) substrates though the combination of scanning tunneling microscopy and angular-resolved photoemission spectroscopy in conjunction with calculations based on density functional theory \cite{12}. But, it is worthy to be mentioned that, from all of the experiments of slicene synthesis, the Ag substrates may play a catalyst role in the formation and stabilization of the slicene sheet. More importantly, slicene sheet, particularly, only can be successfully synthesized in ultrahigh vacuum conditions and the experimental conditions for producing this silicon structure are quite strict. Thus, there is an urgent question to slicene sheet for its future applications: If the substrate and ultrahigh vacuum conditions are got rid of, is the pristine slicene stable in air? Further, if it is not truer, the previous theoretical studies on slicene may be no longer comprehensive.
To investigate the stability of silicene in air and reveal the details of its possible changes, oxygen adsorption and dissociation on silicene is studied by use of first-principles calculations in this letter. It is found that pristine silicene is not stable in air because the oxygen molecule can be adsorbed easily on the silicene sheet surface without overcoming any energy barrier, resulting in dissociation of oxygen molecule on silicene surface. Furthermore, dissociated oxygen atoms are correspondingly difficult to migrate on the silicene surface or desorbed from the silicene, leading to poor mobility of oxygen atom, especially, the Si-O compounds.

METHOD

All calculations are performed by using the VASP (Vienna \textit{ab initio} simulation package) within the projector augmented-wave (PAW) approach\cite{13}. The ground state of the electronic structure is described within density functional theory (DFT) using the generalized gradient approximation (GGA) with PW91 exchange correlation functional\cite{14}. The energy cutoff for expansion of wave functions and potentials is 550 eV. The single layer silicene sheet is modeled with a 6×6×1 unit cell containing 72 Si atoms, which is separated with a 15 Å vacuum layer in the z-axis direction. Monkhorst-Pack special k-point method\cite{15} is used with a grid of 1×1×1. The entire systems are relaxed by conjugate gradient method until the force on each atom is less than 0.05 eV/Å. To optimize the O\textsubscript{2} molecule dissociation path, the climbing image nudged elastic band (CINEB) method\cite{16} is used in the present study.

RESULTS AND DISCUSSIONS

adsorption of single O atom on silicene

To study the adsorption and dissociation of O\textsubscript{2} molecule on pristine silicene surface, a Low-buckled silicene sheet with the super cell 6×6×1 has been firstly optimized and a lattice constant of \(a = 23.15\) Å and \(c = 0.46\) Å are obtained (corresponding \(a = 3.86\) Å in unit cell.), in well agreement with the previous report\cite{17}. After that, single O atom is put on the pristine silicene surface with four typical adsorption sites. They are the center site of the Si\textsubscript{6} ring, the bridge site of two nearest Si atoms, the top site of a Si atom, the top site of a neighboring Si atom at same layer, marked with No. 1, No. 2, No. 3, and No. 4,
respectively, as shown in Fig. 1(a). Sites No. 3 and No. 4 are different due to the buckling of the silicene sheet. We calculated the adsorption energy ($E_{ad}$), which is defined as:

$$E_{ad} = -[E(Si_{64}O) - E(Si_{64}) - 1/2 \times E(O_2)]$$

where the $E(Si_{64}O)$ and $E(Si_{64})$ are the total energy of the silicene supercell model with and without adsorption of one O atom, respectively. $E(O_2)$ is the total energy of O$_2$ molecular in vacuum. The calculated adsorption energy $E_{ad}$ and adsorption distance $D$ (defined as the distance from the adsorbate to the substrate plane, namely, the difference between the z-axis coordinate of the adsorbate and the average of z-axis coordinate of all surface atoms) for the adsorption of an O atom on different sites of silicene sheet are listed in Table 1.

It is found that the strongest adsorption energy of the adsorbed O atom on silicene is observed on the bridge sites (Site No. 2) of Si$_6$ ring with the adsorption energy of 2.395 eV and the adsorption distance 1.544 Å, reflecting the most stable adsorption site is the bridge site. The corresponding Si-O bond length of neighboring Si atoms is 1.714 Å as well as another is 1.734 Å. The minor difference of two Si-O bond lengths originates from covalent interaction between O atom and neighboring Si atoms, resulting in one Si atom moving up after adsorption, as shown in Fig. 1(b).

**migration of single O atom on silicene**

It is well known that O atoms are ready to react with other foreign atoms when O$_2$ molecule is dissociated into O atoms and O atom is adsorbed at the bridge sites of two nearest Si atoms. Before the reaction happens, O atoms need to diffuse on the silicene surface to meet other foreign atoms. Therefore, the migration of O atom on the silicene surface is also necessary to be considered. In order to find the optimized migration pathways, the climbing nudged elastic band (CNEB) method is used. After calculations, it is found that there are two migration pathways for O atom to move. One is 2-3-2, another is 2-4-2, respectively, as shown in Fig. 2 (a), where No. 2 and No. 4 represent different top site along two pathways. Next, the energy profile along the optimized migration pathway for single O atom migrated on the silicene surface is obtained, as shown in Fig. 2 (b). Moreover, it is found that the energy barrier is 1.183 eV as well as another is 1.048 eV, which are almost equal. Compared
with the energy barrier (0.72 eV) of O atom migration on graphene that has been reported by H. J. Yan et al. [18], it shows that the O atom migration will be more difficult on silicene surface, resulting in the poor mobility of O atom under room temperature. Therefore, it implies that O atom is not easy to move from one bridge site to another bridge site on silicene surface.

**adsorption and dissociation of O\(_2\) molecule on silicene**

Owing to the similar structure and electronic properties between silicene and graphene, it is worthwhile to mention that O\(_2\) molecule can be stable at the graphene sheet. It has been reported that when one O\(_2\) molecule put on the graphene sheet with different orientations, it prefers to stay parallel to the graphene basin plane and locate in the middle of a C\(_6\) ring with an adsorption height of 2.82 Å. It implies that O\(_2\) molecule can be adsorbed physically on the graphene surface [18]. Moreover, dissociation of O\(_2\) molecule on graphene is an endothermal process, and the energy barrier of the dissociation reaction is very high (2.39 eV). Those data shows that dissociation of O\(_2\) at the graphene sheet is physically not favorable. Combined with other previous reports [19, 20], we can conclude that the pristine graphene is stable in air. However, we demonstrate that the O\(_2\) at the silicene sheet is in a completely different manner.

To investigate the stability of silicene in air, the oxygen adsorption and dissociation on silicene must be studied. In addition, to imitate the actual condition, the influence of the concentration of O\(_2\) molecule for adsorption and dissociation can not be ignored. Considering the probable influence of the concentration of O\(_2\) molecule for adsorption and dissociation on silicene surface, we test the pristine silicene under different concentration of O\(_2\) molecule by use of unit cell 1×1×1, super cell 2×2×1, and super cell 3×3×1, respectively. Firstly, the unit cell (1×1×1) is used to adsorb two O atoms. The concentration of O\(_2\) molecule is 100% in terms of unit cell (composed of two Si atoms). It is found that, locating on the top of the Si atoms, one O atom is up as well as another is down. The corresponding Si-O bond length is all 1.554 Å. Subsequently, super cell 2×2×1, and 3×3×1 are used to test the adsorption and dissociation of O\(_2\) molecule with the initial distance 2.7 Å both vertical and parallel to the silicene basin plane. After calculations, the optimized results show that whatever the concentration of O\(_2\) is, O\(_2\) molecule can be easily adsorbed and dissociated
into two O atoms. It implies that the concentration of O$_2$ molecule has no influence to its adsorption on silicene surface. Thus, we still adopt super cell $6 \times 6 \times 1$ mentioned above to accomplish the next work.

To study the adsorption and dissociation of O$_2$ molecule on pristine silicene, O$_2$ molecule is put above the silicene surface with different orientations (both parallel and vertical to the silicene basin plane) and distance. There are two different types and every type includes three different cases. One is O$_2$ molecule put above the silicene surface vertically with three different initial distances, 1.48 Å, 2.70 Å and 4.23 Å, respectively. Another is O$_2$ molecule put above the silicene surface parallel with three different initial distances, 1.50 Å, 2.70 Å and 4.15 Å, respectively. It is found that the O$_2$ molecule can be easily adsorbed and dissociated into two O atoms on bridge site and top site on silicene surface except for the case with initial distance 4.23 Å vertical to substrate plane, which corresponding adsorption energy is about 0 eV, reflecting hardly any interaction between oxygen and silicene surface. Instead, although the O-O bond is not broken in the case with initial distance 4.15 Å parallel to substrate plane, but the O-O bond length of 1.52 Å in contrast with the free O-O bond length 1.23 Å shows that the interaction of two O atoms is very weak. On the other hand, from all of the calculated adsorption energy, the 4.916 eV with initial distance 1.50 Å vertical to silicene surface is highest, indicating the corresponding structure is the most stable structure where the O$_2$ molecule is dissociated into two O atoms on bridge site and top site in same Si$_6$ ring. Therefore, the case with initial distance 2.70 Å parallel to the silicene plane is used to illustrate the detail of the oxygen adsorption and dissociation on silicene.

Compared with dissociation reaction energy 2.39 eV of graphene in air, when we put oxygen molecule above the silicene surface basin plane with initial distance 2.70 Å, it is surprisingly found that the oxygen molecule can be easily adsorbed and dissociated into two O atoms on silicene surface without overcoming any energy barrier. That is to say, the silicene is not stable in air. To visually illustrate the detail of O$_2$ molecule adsorption and dissociation on silicene surface, the evolution from free O$_2$ molecule to dissociated O atom is shown in Fig. 3. When the free oxygen molecule is put above the silicene surface with initial distance 2.7 Å, the corresponding O-O bond length is 1.235 Å, as shown in Fig. 3(a). As the optimized process continues, the distance between the oxygen molecule and silicene surface basin decreases, leading to one O atom adsorbed on top site on silicene surface with
the total energy of -353.919 eV, as shown in Fig. 3(b). It is worthwhile to note that the orientation of oxygen has changed from vertical to almost parallel to silicene surface, while the corresponding O-O bond length and the Si-O bond length are 1.563 Å and 1.720 Å, respectively. It indicates that the interaction between oxygen and silicene surface becomes stronger and the O-O bond strength becomes weakened. Subsequently, the dissociation of oxygen molecule happens, resulting in one O atom adsorbed on bridge site of neighboring Si atom with Si-O bond length of 1.740 Å and 1.711 Å but another still adsorbed on top site with Si-O bond length of 1.565 Å, as shown in Fig. 3 (c). The corresponding total energy decreases to -357.798 eV. Finally, the optimized structure shows that the oxygen molecule dissociates into two O atoms. One O atom locates on top site where the Si-O bond length is 1.570 Å, while another O atom adsorbs on bridge site where the Si-O bond lengths are 1.711 Å and 1.732 Å, respectively, as shown in Fig. 3(d). The corresponding total energy evolution can be seen in Fig. 3(e), in which the majorization structures are marked with (a), (b), (c), and (d). The abrupt turn of total energy changes from -353.919 eV (marked with (b)) to -357.798 eV (marked with (c)) exactly reflects the oxygen dissociation on silicene.

**SUMMARY**

In summary, the oxygen adsorption and dissociation on pristine silicene surface are studied by use of first-principles in this letter. It is found that the pristine silicene is not stable in air because the oxygen molecule can be easily adsorbed and dissociated into two O atoms without overcoming any energy barrier on pristine silicene. In addition, dissociated oxygen atoms are relatively difficult to migrate on the silicene surface or desorbed from pristine silicene surface, leading to poor mobility of oxygen atom and the Si-O compounds. The work will be helpful to understand the stability of silicene in air and will widen the application of silicene. Moreover, it implies that some previous works on pristine silicene are not comprehensive.

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TABLE I: Calculated adsorption energy $E_{ad}$ and adsorption distance $D$ for the adsorption of an O atom on different sites of silicene sheet.

| Sites  | 1(center) | 2(bridge) | 3(top1)  | 4(top2) |
|--------|-----------|-----------|----------|---------|
| $D$(Å) | 0         | 1.544     | 2.406    | 2.237   |
| $E_{ad}$(eV) | -0.694   | 2.395     | 1.379    | 1.241   |
A list of figures

1. (Color online) (a) Schematic views of four adsorption site for single O atom on pristine silicene surface and (b) top and side views of the bridge sites.

2. (Color online) (a) Top view of the optimized migration pathway of an O atom migration along the pathway from site No. 2 to site No. 3 then to site No. 2 and its energy profile along the pathway on the silicene surface. (b) Top view of the optimized migration pathway of an O atom migration along the pathway from site No. 2 to site No. 4 then to site No. 2 and its energy profile along the pathway on the silicene surface. (Red color and yellow color represent O atoms and Si atoms, respectively)

3. (Color online) The diagrammatic sketch of oxygen adsorption and dissociation on silicene.
FIG. 1: (Color online) (a) Schematic views of four adsorption site for single O atom on pristine silicene surface and (b) top and side views of the bridge sites.

FIG. 2: (Color online) (a) Top view of the optimized migration pathway of an O atom migration along the pathway from site No. 2 to site No. 3 then to site No. 2 and its energy profile along the pathway on the silicene surface. (b) Top view of the optimized migration pathway of an O atom migration along the pathway from site No. 2 to site No. 4 then to site No. 2 and its energy profile along the pathway on the silicene surface. (Red color and yellow color represent O atoms and Si atoms, respectively)

FIG. 3: (Color online) The diagrammatic sketch of oxygen adsorption and dissociation on silicene.