Computational Materials Science 154 (2018) 276–283

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Trivacancy and Stone-Wales defected silicene for adsorption of small gas molecules

Yanjun Xiao, Xiaoqing Lu, Siu Pang Ng*, Chi-Man Lawrence Wu*

Department of Materials Science and Engineering, City University of Hong Kong, Hong Kong Special Administrative Region
College of Science, China University of Petroleum, Qingdao 266580, Shandong, PR China

ARTICLE INFO

Keywords:
DFT
Silicene
Trivacancy
Stone-Wales
Bandgap

ABSTRACT

The adsorption characteristics of small gas molecules (CO_2, CO, H_2O, N_2, NO, NH_3, NO_2 and O_2) on trivacancy and Stone-Wales defected silicene were investigated by density functional theory calculations. The results reveal that CO, H_2O and N_2 are absorbed on trivacancy silicene in a physical way via van der Waals forces, whereas CO_2, NO, NH_3, NO_2 and O_2 are chemisorbed on trivancancy silicene via strong covalent (SisbndN or SisbndO) bonds. For Stone-Wales defected silicene, N_2, H_2O and CO_2 are physisorbed whereas CO, O_2, NO, NH_3, and NO_2 are chemisorbed. The chemisorption of gas molecules on trivacancy and Stone-Wales defected silicene widens the band gap. In particular, the NO_2 chemisorption on trivacancy or Stone-Wales defective silicene shows significant hole doping. Additionally, O_2 is found to be readily decomposed into two O atoms on trivacancy silicene due to the small energy barrier and large exothermic reaction heat. Our work offers a possible method to regulate the electronic properties of silicene for applications at the nanoscale.

1. Introduction

Two-dimensional materials such as graphene were found to have some special properties. For instance, with sp^2 hybridization of carbon atoms, graphene has huge specific surface area (2630 m^2/g) [1,2]. Past investigators found that modifying the surface of the nanosheet with doping or defects is an important way to tune its electronic properties [3]. Since the discovery of graphene, some other two-dimensional materials such as silicene, phosphorene, transition metal carbide and nitride-based MXenes have been investigated [4]. As carbon and silicon are both in group-IV of the periodic table, silicene is expected to behave like graphene [5]. It is a highly ordered silicon structure, arranged within a honeycomb lattice, known to have sp^2-sp^3 mixed hybridizations, and can be prepared on Ag, Ir and ZrB_2 substrates [6–8]. Theoretical studies showed that the defects can improve the electronic behavior of silicene [9,10], tailor thermal conductivity at room temperature [11], as well as improving magnetic response [12–14]. On the other hand, the adsorption behaviors of atoms or molecules on silicene have been theoretically explored to realize charge carrier doping [15], bandgap engineering [16,17], silicene-based catalysis [18], hydrogen separation [16], and use in field effect transistors [19,20] and gas sensing [21–24].

However, as far as we know, there are few systematic theoretical studies on the adsorption of small gas molecules on the surface of defective silicene. In this study, density functional theory (DFT) calculations were carried out to compare the electronic properties of trivacancy and Stone-Wales defected silicene upon the adsorption of small gas molecules (CO_2, CO, H_2O, N_2, NO, NH_3, NO_2 and O_2). One of the benefits of the vacancy defects is that it can enrich the adsorption configuration of the small gas molecules on the surface of silicene monolayer [23]. In addition, Stone-Wales defect, which exists generally in carbon nanotubes, graphene and similar materials, involves the change of connectivity of two π-bonded atoms with their rotation by 90° relative to the midpoint of their bond. In these materials, the repositioning is anticipated to have an imperative influence on the chemical, electrical, and mechanical properties [25]. These factors motivated us to choose trivacancy and Stone-Wales defected silicene sheets as the subject of our study. For convenience, we refer trivacancy silicene as T-silicene and Stone-wales defected silicene as S-silicene hereafter. Our theoretical investigation on adsorption structures, energies and band structures would provide prior knowledge on the adsorptions of different gases on defected silicene before carrying out experiments.

2. Methodology

DFT calculations were performed using the $Dmol^3$ program package in Material Studio of Accelrys Inc. The geometries and total energies were based on Perdew-Burke-Ernzerhof (PBE) functional calculated

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* Corresponding authors.
E-mail addresses: rollyng@cityu.edu.hk (S.P. Ng), lawrence.wu@cityu.edu.hk (C.-M.L. Wu).

https://doi.org/10.1016/j.commatsci.2018.08.001
Received 14 June 2018; Received in revised form 30 July 2018; Accepted 1 August 2018

with generalized-gradient approximation (GGA) [26–28]. The k-point of the Brillion zone is set as 6 × 6 × 1 for geometry optimization. The self-consistent field (SCF), which is used to control the electronic minimization, is set with a tolerance of 10^{-6} a.u. Here, long-range dispersion correction of Grimme [26] is integrated to treat the adsorption systems. The van der Waals correction is introduced based on the DFT-D method of Grimme. In addition, climbing-image nudged elastic band (NEB) method in Quantum Espresso package [26] was implemented to investigate the dissociation of O_2 on T-silicene. In Quantum Espresso, GGA with PBE functional was also chose to describe the exchange-correlation interaction. Van der Waals (vdW) correction was using the DFT-D method. The kinetic energy cutoff for wave functions and charge density were 30 Ry and 120 Ry given by standard solid state pseudopotentials [29]. The convergence threshold of 10^{-5} Ry/Borr for total energy and 10^{-4} Ry for total force were applied.

In our calculation, the periodic boundary condition is arranged with the supercell setting. A model of 5 × 5 pristine silicene (P-silicene) containing 50 silicon atoms is built. A vacuum height of 20 Å is added above the silicene sheet, for avoiding the interaction between two adjacent silicene sheets in z-axis (perpendicular to the silicene sheet). The adsorption energies (E_a) of the adsorption systems are calculated by

$$E_a = E_{gas\text{-}silicene} - (E_{gas} + E_{silicene}) \tag{1}$$

where $E_{gas\text{-}silicene}$ donates the total energy of the gas molecular adsorbing on intrinsic or defective silicene sheet; E_{gas} and $E_{silicene}$ donate the energies of gas molecule and pristine or silicene sheet with trivacancy and Stone-Wales defect, respectively. An adsorption system with large negative value of E_a is regarded as stable.

3. Results and discussion

3.1. Band structures of T-silicene and S-silicene

The P-silicene in a 5 × 5 supercell after optimization is shown in Fig. 1a. It was found to have lattice constant of 3.860 Å and layer thickness of 0.470 Å, and agreed well with previous theoretical results [6]. The T-silicene, created by removing three Si atoms in P-silicene, has the optimized structure shown in Fig. 1b. The stability of such vacancy defect with up to six missing atoms had already been studied in a previous work based on first-principle calculations [23]. The formation energy of our T-silicene is 5.88 eV, which agrees well with a previous study [23]. For S-silicene, the four adjacent six-membered Si rings of a pyrene-like region are changed into two five-membered and two seven-membered rings, as shown in Fig. 1c. The formation energy of S-silicene was found to be 2.21 eV, which is similar with former study [21].

Fig. 1d shows that there is a distinct Dirac point at the high symmetry point of P-silicene, reflecting its semi-metal performance. As shown in Fig. 1e, the Dirac point disappeared in T-silicene and exhibited an indirect bandgap. The valence band was moved to above the Fermi level due to the reduced electrons of the valence band after removing the three Si atoms. This phenomenon is consistent with previous study such that the Dirac points were easily changed position with importing defects or dopants in graphene and silicene [24]. The bandgap of T-silicene has a very small value of 0.002 eV. The band structure of S-silicene is quite different from that of P-silicene. As shown in Fig. 1f, although the bandgap is direct, the energy bands of S-silicene appear to be condensed, with bandgap of 0.026 eV.

3.2. Energetics of the adsorption systems

Before investigating the adsorption effect of CO, CO_2, N_2, H_2O, NO, NH_3, NO_2 and O_2 on T- and S-silicene, we calculated the adsorption energy, charge transfer, shortest distance between the gas molecule and P-silicene, and the change of band gaps after adsorption of small gas molecules. Similar to previous studies [30,31], P-silicene was found to exhibit remarkably high activity toward O_2 and NO_2 with the adsorption energies being greater than 1.00 eV. Besides, NO and NH_3 can be adsorbed on silicene with a mild adsorption energy (0.34 and 0.59 eV), whereas N_2, H_2O and CO_2 are physisorbed on P-silicene with weak van

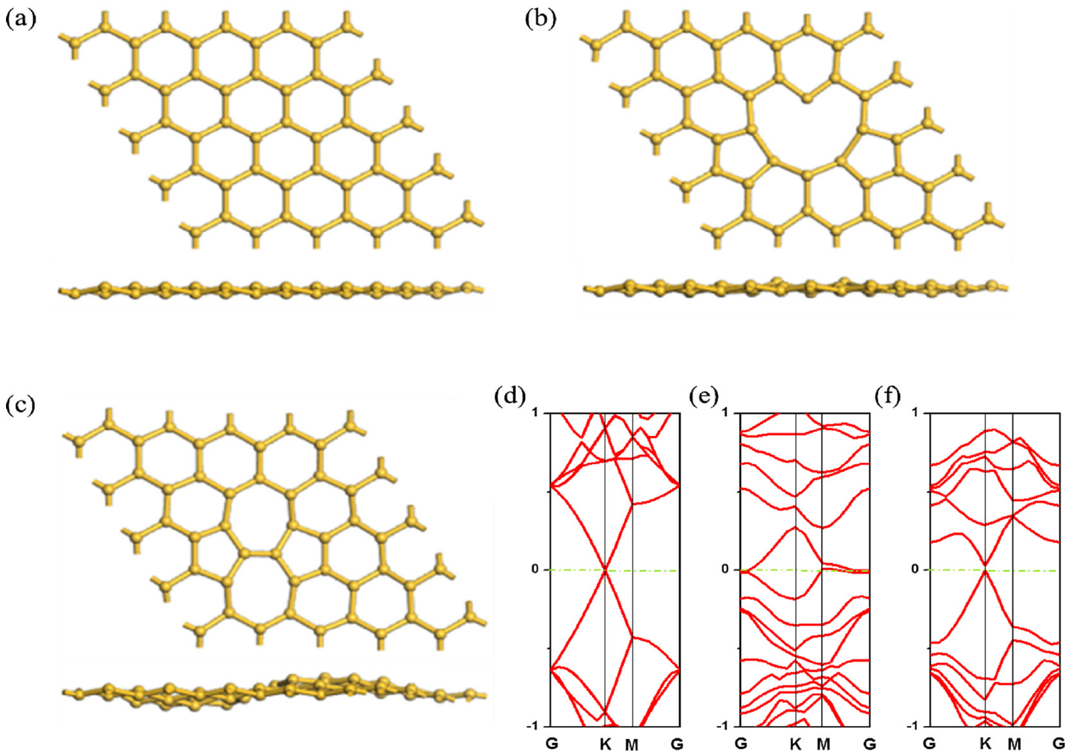

Fig. 1. The structure of (a) pristine silicene (the side and top view, respectively); (b) trivacancy silicene; (c) Stone-Wales defective silicene; the band structure (with Fermi level set to zero) of (d) pristine silicene; (e) trivacancy silicene; (f) Stone-Wales defective silicene.