Original Article

Absorption of Isopropanol on Surface of Defect Silicene

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Abstract: In this work, we investigate the defect structure of silicene with a vancacy and the adsorption mechanism of isopropanol on the surface of defected silicene by employing the Density Functional Theory method. The adsorption profile was determined based on the van der Waals functional optPBE-vdW, and the charge transfer between isopropanol and silicence was calculated by Bader charge analysis method. In the defected silicene, Si vacancy preferably forms on the lower layer of the bulking structure. As a Si vacancy is introduced, silicene exhibits a metallic behaviour with zero bandgap. Due to the losing electron of the defected silicene, isopropanol is adsorbed on the surface with the most favourable adsorption configuration in which oxygen atom towards the surface of silicene. Isopropanol adsorption on the defected silicene opens a tunnelling gap, resulting in the milli-gap characteristics of the adsorbed silicene system. The adsorption profile of this volatile organic compound on the defected silicene implies the physics adsorption characteristics. The adsorption energy for isopropanol was found to be -0.40 eV. In addition, the charge transfer of 0.24 electron was obtained.

Keywords: Adsorption, Silicene, DFT theory, Defect, isopropanol, Volatile Organic Compound.

1. Introduction

Silicene is a novel 2D material with many promising properties for application in electronics [1–9]. Silicence is also strongly expected to be a high sensitive material for the use in gas sensing application [10–17]. Pristine silicene with defects has been investigated by several authors [18–21]. However, the adsorption of gases on such a structure has yet been concerned. Furthermore, the previous works on the

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adsorption of gases mostly performed on the perfect silience without considering the defects which often appear in the real samples under the experimental conditions. Especially, the adsorption mechanism of Volatile organic compounds (VOCs) – the gases whose appearance is considered as an important signal in detecting the lung cancer in patient breath – has not been understood well. Silicene with and without defects can be expected to be a promising material in the sensing applications used for detection of VOC in human breath. The understanding of mechanism of VOC adsorption is needed before applying this material to applications [22-25].

In this work, in order to explore the adsorption mechanism of Volatile Organic Compounds on the defected 2D materials as well as to further enhance the gas sensing ability of silicene, we investigate the adsorption of Isopropanol on the surface of silicene with a vacancy defect by employing the Density Functional Theory (DFT) method with taking the van der Waals interaction into account.

2. Computational Method

All calculations based on density functional theory were performed using the Vieanna ab initio simulation package (VASP) [26–29], with PAW potential [30, 31]. We includes van der Waals interaction into our calculations by utilizing optPBE-vdW functional [32], because inclusion of van der Waals interaction is proved to produce results in better agreement with experiment [33,34] and van der Waals functionals are expected to be better than van der Waals correction schemes [35,36]. The adsorption profile was explored by using the Computational DFT-based Nanoscope [37].

In order to avoid the interaction between silicene layers, a vacuum of 20 Å was set between two adjacent silicene layers. A cutoff energy of 450 eV for the plane-wave basis set and a 3x3x1 Gamma-centered kpoint mesh were utilized to yield sufficient energy convergence. All the structures were fully relaxed until the residual Hellmann-Feynman force acting on each atom is less than 0.03 eV/Å. Our model consists of a single-vacancy silicene (Figure 2) built from a 4x4 supercell of pristine silicene, and a VOC based on the chemical functional groups present in the breath of cancer patients [38]. In this study we choose isopropanol to represent the ketone group to represent the aromatic compounds.

3. Results and Discussion

3.1 Stable Structures of Defected Silicene

Silicene, a graphene analogue of silicon, has three the structures: planar, low buckling and high buckling. The detail structure parameters of different optimized pristine silicene structure obtained from the DFT calculations are listed in Table 1. In Table 1, the lattice constant a, nearest neighbor distance d and height of buckled h of the three structures are given [39-41]. The last column shows the calculated total energy of the present work. The total energy of the pristine silicene with low buckling structure is the lowest and thus low buckling is the most stable structure. The silicene with low buckling structure is used in this investigation (Figure 1).

Table 1. Structure parameters of different pristine silicene structures.

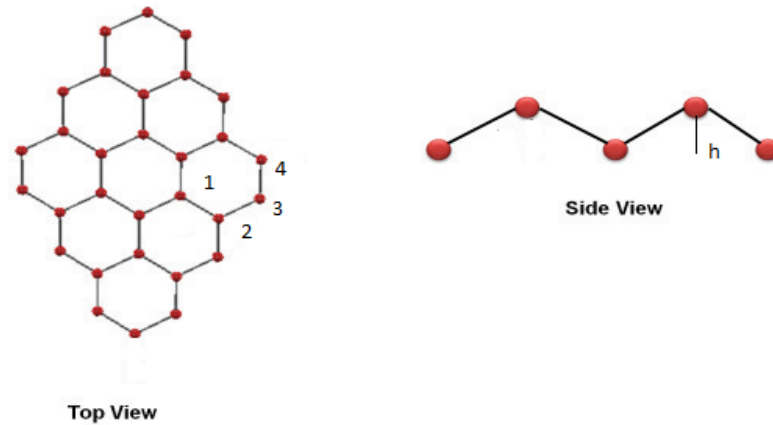| Structure	a (Å)	d (Å)	h (Å)	E (eV)
Planar	3.99 [39]	2.00	0.00	-106.4645
Low Buckling	3.88 [41]	2.28 [41]	0.43 [41]	-106.5326
High Buckling	2.78 [40]	2.37 [40]	2.08 [40]	-106.4319

Figure 1. The top and side view of the low buckling pristine silicene. The distances between each atomic pair are $d_{12} = d_{23} = d_{34} = 2.29$ Å, $d_{13} = 3.38$ Å, and the buckling height $h = 0.43$ Å.

To construct the defected silicene with a Si vacancy, one Si atom is removed from the supercell as illustrated by Figure 2. As one Si atom of the silicene is removed, there is a broken structure at the defect position. The Si bond lengths slightly change from 2.3257 Å to 2.3265 Å, while the bond angles keep almost unchanged and equal to 60 degree (Figure 3). The distance between Si atoms in pairs (1,2), (2,3) and (3,1) is 3.69833(0) Å. This value is longer than the Si-Si bond length in the pristine silicene.

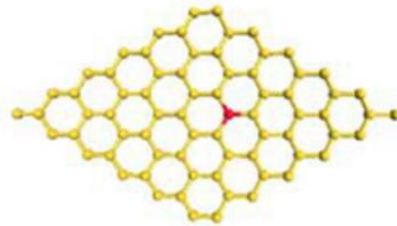Figure 2. One Si atom is removed from the super cell to construct the defected silicone.
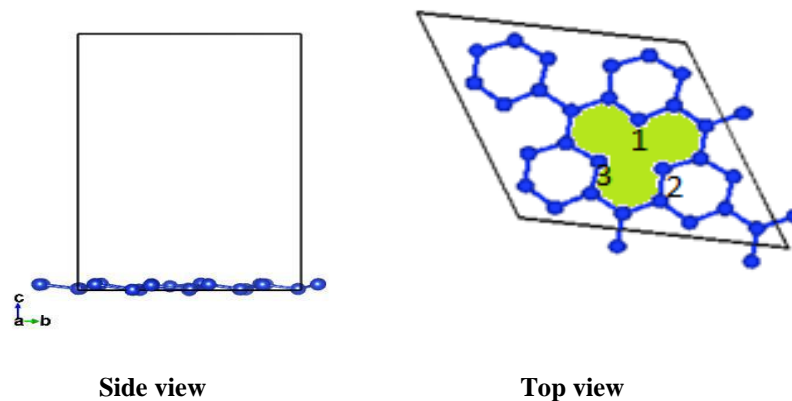

Side view   Top view

Figure 3. The side view and top view of the stable vacancy structure.

3.2. Adsorption Configuration

Isopropanol as one of the typical volatile organic compounds whose appearance and concentration change in the human breath are considered as an important signal for detecting the lung cancer at early stage. Isopropanol has the chemical formula C_3H_8O in which two groups CH3 share the group H-C-HO. The structure formulas are shown in Figure 4.
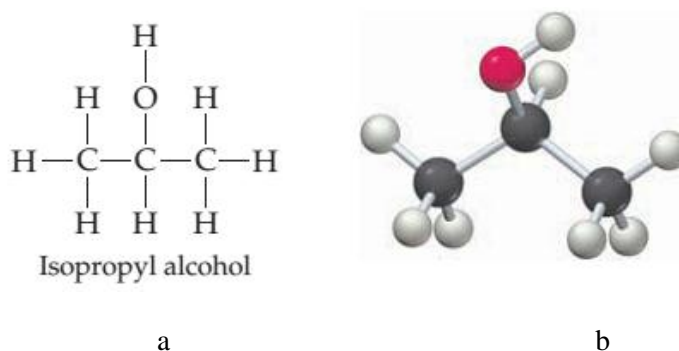

a　　　　　　　　　　　　　　　　　　b

Figure 4. The planar structure formula(a) and the space structure formula (b) of isopropanol.

The adsorption profile of isopropanol on silicene helps us to evaluate the sensitivity and selectivity of silicene towards the volatile organic compounds. When isopropanol comes close the surface of silicene, the silicene will adsorb it. The defect of silicene can enhance or reduce the adsorption ability of silicene with respect to volatile compounds. In our calculation, isopropanol molecule is put at the various positions on the surface of silicene. After optimization, the favorable adsorption configuration of isopropanol on the surface of defected silicene was found with oxygen atom towards the surface of silicene as illustrated in Figure 5. The distance from isopropanol to the substrate is about 3.466 Å, the center of the isopropanol is almost directly above the broken position of the substrate.
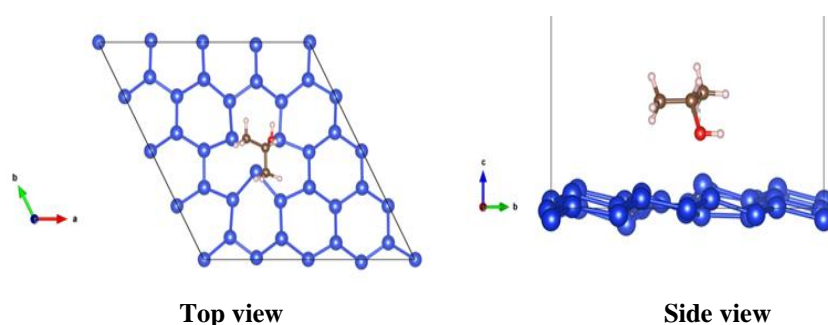

Top view　　　　　　　　　　　　　　**Side view**

Figure 5. The side view and top view of the stable structures of the isopropanol adsorption.

3.3. Adsorption Profile

By using Computational DFT-based Nanoscope tool, the adsorption energy can be calculated based on the following equation

$$E_a = E_{gas/silicene} - E_{saturation.} \quad (1)$$

By physical consideration, this is equivalent to the traditional formula [42]:

$$E_a = E_{gas/silicene} - E_{gas} - E_{silicene}, \quad (2)$$

where E_a and $E_{gas/silicene}$ are the adsorption energy and the total energy of the VOC/silicene complex, $E_{saturation}$ is the total energy of the VOC/silicene at the status where the VOC molecule and silicene are far enough to each other so that there is no interaction between the two this components. Frankly, the saturation state reaches when VOC molecule and silicene can be considered as the two isolated systems. Here, the total energy of these three systems can be calculated in the same framework. With varying the distance of molecule and adsorbent substrate, the adsorption energy profile can be calculated without considering the separated contents. With this calculation technics, the advantage of reducing the computational cost by the eliminating the calculation of the energy of separated entities can be obtained. To take the van der Waals interaction into account, we employed the van der Waals functional optPBE-vdW in the total energy calculation.

Figure 6 demonstrates the adsorption profile of isopropanol adsorbed silicene. The adsorption profile of this volatile organic compound on the defected silicene implies the physical adsorption characteristics. As similar to the results of the structure optimization, the lowest energy is of the status in which the distance between Oxygen atom and silicene surface is at 3.466 Å. At this status, the adsorption energy is determined to be -0.40 eV.
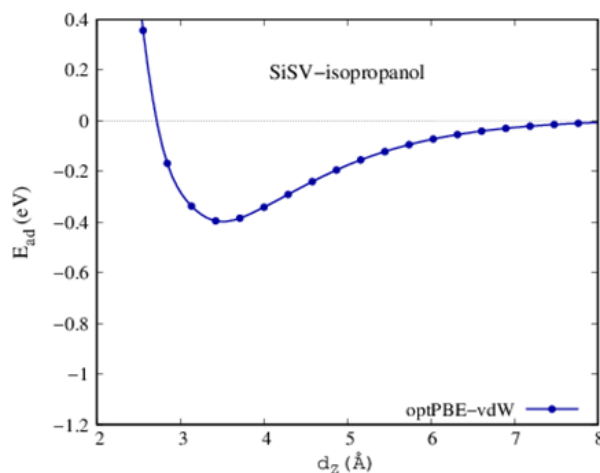

Figure 6. Adsorption profile for the isopropanol adsorbed silicene. d_z is distance from Oxygen atom to surface.

3.3. Electronic Structure and Charge Transfer of Isopropanol Adsorbed Silicene

The band structure and Density of State (DOS) of the isopropanol adsorbed silicene are shown in Figure 7. As can be seen from Figure 7, the metal characteristics of the defected silicene changes after adsorption. Isopropanol adsorption opens a tunneling gap of 3 meV in electronic structure of the defect silicene, resulting in the mili-gap characteristics of the adsorption system. The indirect band gap is opened between K and A high symmetrical k-point of the first Brillouin zone. The electron orbitals of isopropanol distribute in the range of energy lower than 1.0 eV and hybridize with the p-orbitals of Si.

Bader charge analysis shows that the charge transfer from the defected silicene to isopropanol molecule is 0.24 electrons. This value is much large than the charge transfer of toxic gases adsorbed on graphene. It suggests that the electronic conductivity of the defected silicene will considerably decrease when the isopropanol molecules are adsorbed on its surfaces (Figure 8).
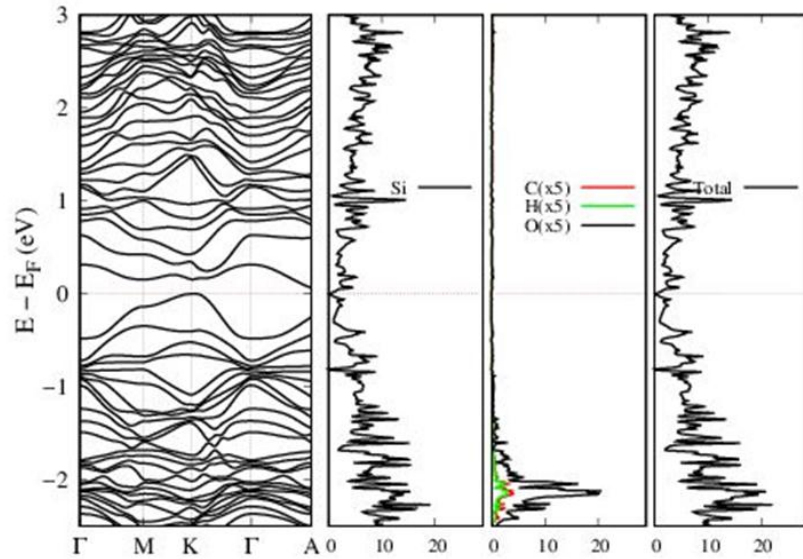
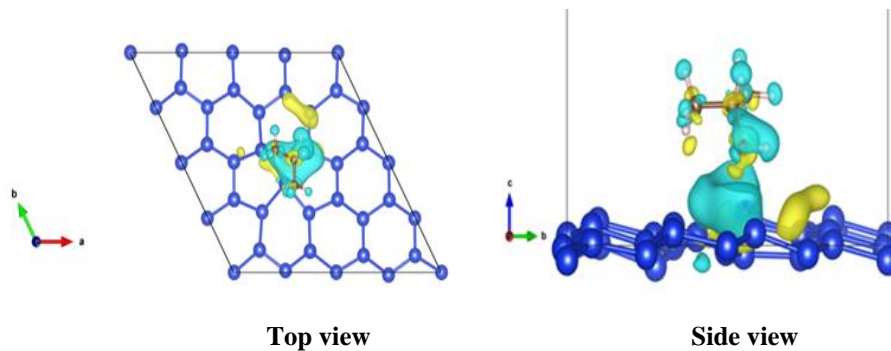Figure 7. Band structure and DOS of the isopropanol adsorbed silicene.

Top view   **Side view**

Figure 8. Charge density difference: the top and side views. Yellow represents the charge accumulation and green represents the charge depletion.

4. Conclusion

In this paper**,** we investigate the defected structure of silicene with a vacancy and the adsorption mechanism of isopropanol on surface of defected silicene by employing Density Functional Theory method. The results suggest that vacancy defect prefers to form a 12-edges shape. The center of this shape preferably caches the isopropanol molecules during adsorption. Isopropanol adsorption opens a tunneling gap of defected silicene, resulting in the indirect milli-gap characteristics of the adsorption system. The adsorption profile of this volatile organic compound on defected silicene implies the physical adsorption characteristics and the adsorption energy was found to be -0.40 eV. In addition, the charge transfer of 0.24 electron was obtained, suggesting a considerably change in electronic conductivity of silicene during the adsorption.

Acknowledgements

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