Original Article

DFT Study on Adsorption of Acetone and Toluene on Silicene

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Abstract: In this work, we investigated the adsorption mechanism of acetone and toluene on the surface of silicene by the quantum simulation method. The images of the potential energy surfaces for different positions of the adsorbate on the silicene surface were explored by Computational DFT-based Nanoscope tool for determination of the most stable configurations and diffusion possibilities. The charge transfer in order of $0.2 - 0.3$ electrons and the tunneling gap opening of $18 - 23$ meV due to acetone and toluene, respectively, suggest that silicene is considerably sensitive with these VOCs and can be used as the material in the fabrication of reusable VOC sensors.

Keywords: Volatile Organic Compound, Adsorption, Silicene, DFT, Cancer Detection.

1. Introduction

Cancer can be regarded as a rising threat towards modern societies. Detection of cancer at an early stage significantly improves the curability of disease; unfortunately, currently available methods for early diagnosis of cancer are scarce and inefficient. It is known that some Volatile Organic Compounds (VOCs) exist in the breath of cancer patients at different concentrations than in healthy people. In addition, their concentration gradients depend on the type of cancer [1, 2]. In fact, the concentration of Volatile Organic Compounds (VOCs) in cancer patients in the breath is different from that in normal

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people. As a result, measuring VOCs' concentration is expected to be a promising non-invasive cancer diagnosis. Unfortunately, their super-low concentration (about several ppm) is challenging us in designing a highly sensitive device for detecting VOCs. Therefore, development of new kinds of sensors that can detect VOCs with low concentrations at the early stage of cancer is desirable. Recently, the search for appropriate materials to fabricate VOC sensors became glowing. Among the potential candidates, 2D materials are attracting great attention from scientists since the discovery of graphene due to their large surface area to volume ratio.

Among the recently discovered 2D materials, silicene draws a great deal of attention from both theorists [3–8] and experimentalists [9-11]. Although the existence of free-standing silicene is yet to be reported experimentally, theoretical considerations already predict silicene to possess superior properties, such as an extremely high electronic conductivity comparable to graphene [12, 13] and the tunable band gap [14], all of which suggest the high performance of silicene in the electronic industry.

Many studies propose silicene as an extremely promising material for gas sensing applications [15–22]. However, most of these studies addressed only simple gases such as CO, NO, NO_2, O_2, NH_3, SO_2 [15, 18, 21], and CO_2, CH_4 [22]. To answer whether silicene can be used as a material for VOC sensors, one needs to systematically investigate the interaction of organic compounds with silicene.

In this study, we employ Density Functional Theory calculations to investigate the adsorption mechanism of acetone and toluene on the free-standing silicene to explore the possibility of making use of silicene to fabricate VOC sensors. These gases represent as the typical molecules of the ketones and aromatics chemical groups, respectively, of the different VOCs present in the breath of cancer patients.

2. Computational methods

All calculations were done using the software package Vienna Ab initio Simulation Package (VASP). The van der Waals interaction is taken into account by employing optPBE-vdW functional [23][24]. In this work, silicene is selected to be an adsorbent while acetone and toluene were chosen as adsorbates. The most favorable adsorption configurations of the adsorbate on the silicene substrate and the adsorption energy profile were determined by performing automatic scanning with *Computational DFT-based Nanoscope* [25]. A cutoff energy of 450 eV for the plane-wave basis set and a 3x3x1 Gamma-centered k-point mesh corresponding to the 4x4 super-cell were utilized. In order to eliminate the interaction between two adjacent monolayers of Si, a vacuum layer of 20 Å was added. All the structures were fully relaxed until the maximum residual Hellmann-Feynman force acting on each atom is smaller than 0.03 eV/Å. The charge transfer between components of the adsorption system was calculated by Bader charge analysis [26].
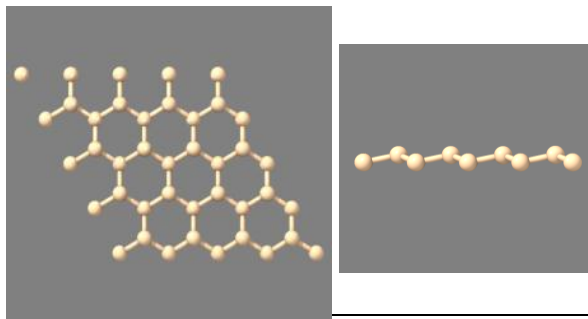

Figure 1. The 4x4 supercell model of pristine silicene. Top view (left) and side view (right).

3. Results and discussion

3.1. Structure of pristine silicene

The adsorbent system consists of a 4x4 silicene supercell as shown in Fig. 1. The geometrical parameters obtained in this work are compared to other literature values in Table 1. The buckling constant and nearest neighbor distance in the silicene obtained in the present work are 0.48 Å and 2.29 Å, respectively, which are in good agreement with literature values [14][27][28]. It can be seen our optimized pristine structure is close to that of the previous studies and the experiment [29].

Table 1. Structural parameters of pristine silicene

Method	a (Å)	Δz (Å)
PBE (CASTEP) [28]	3.86	0.45
PBE (VASP) [28]	3.87	0.45
PBE [14]	3.87	0.46
LDA [27]	3.83	0.44
LDA (VASP) [28]	3.83	0.44
LDA (CASTEP) [28]	3.82	0.44
LDA [29]	3.86	0.44
HSE06 (VASP) [28]	3.85	0.36
Exp. [on Ag(110)] [29]	3.88	
Exp. [on Ag(111)] [30]	3.30	0.20
This work	3.83	0.48

3.2. Structure of VOCs

Acetone C_3H_6O and toluene C_7H_8 are two organic compounds of the ketones and aromatics groups with the molecular structures displayed in Fig. 2. These two gases were chosen as the simple models for the ketones and aromatics playing the role of the important markers for lung, liver, and breast cancer [31]. Acetone contains two methyl groups attached to the C=O double bond while toluene consists of a methyl group attached to the hexagonal, planar benzene ring.

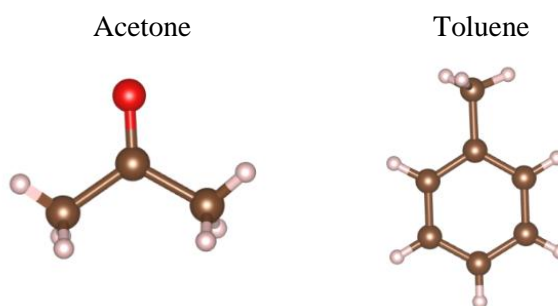

Figure 2. The molecular structure of acetone (left) and toluene (right).

3.3. Adsorption configuration

Acetone (Fig. 3) stays at a distance of 3.5 Å from the silicene surface with the oxygen being closest to silicene at a distance of 2.7 Å. The C=O double bond is not parallel but forms an angle of ca. 25° to

the silicene surface. This bond also points toward one lower layer silicon atom, which might be attributed to the favorable interaction between oxygen and silicon in their attempt to approach each other to lower the overall energy.

Toluene stays parallel with silicene at a distance of 3.4 Å (Fig. 3), with hydrogen being the closest atom to surface, at the height of 2.6 Å. The parallelism can be thought of as a result of the spatial extent in the xy plane of toluene molecule and the partially sp^2 hybridization state of silicon atoms. The flatter and larger the VOC, the more we can treat the adsorption as the approach of two flat objects (a floor tile on the floor). Obviously, the most stable configuration for lowest potential energy is parallelism. In addition, silicene, while buckled, is still considered to be closer to sp^2 rather than sp^3 [32], which might allow small interaction with the $p\pi$-conjugation ring in toluene.

3.4. Binding potential

It can be seen that the 2D projected Potential Energy Surface (PES) possesses the 4x4 periodicity due to the periodicity of the silicene supercell. Blue and black areas correspond to the favorable adsorption areas. For acetone, the minima stay on top of the line connecting two lower silicon atoms, while the maxima are on top of the line connecting two upper layer ones. For toluene, minima are on top of the line connecting one lower and one upper silicon atoms while maxima are on top of the line connecting two upper ones.
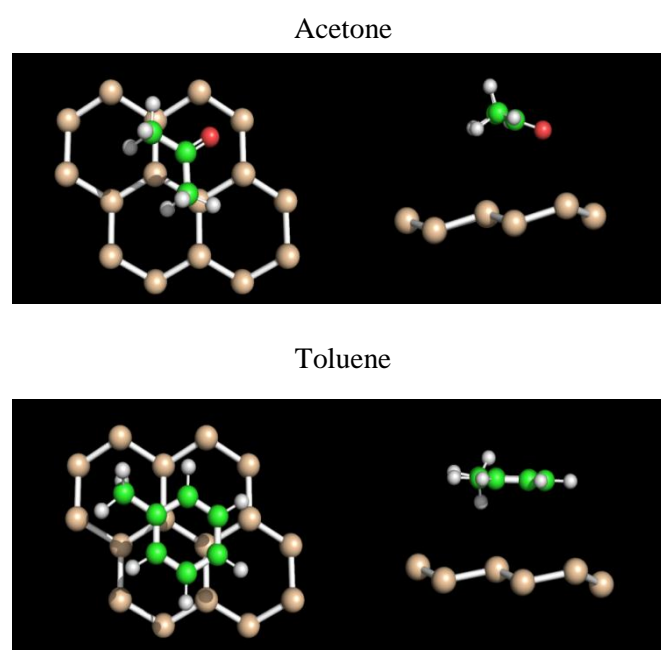
Acetone

Toluene

Figure 3. The adsorption configuration of acetone (top) and toluene (bottom) on the surface of silicene. Green, red, white, grey balls represent carbon, oxygen, hydrogen, and silicon, respectively.

3.5. Band structure and charge transfer

Upon adsorption of VOCs, the electronic band structure of silicene displays a gap opening in the order of tens of meV (see Table 2 and Fig. 5**Error! Reference source not found.**), through which

silicene turns from a zero-gap conductor to a semiconductor. Opening a band gap might lead to the decreasing of electrical conductivity, which implies the possibility of detecting VOCs by monitoring the conductance of silicene upon exposure to a breath containing VOCs. The larger the band gap, the larger the change in electrical conductance.

Acetone adsorption opens a band gap of 18 meV at Dirac K point while adsorption of toluene opens a slightly larger band gap of 23 meV. These small band gaps are in accordance with the physical adsorption mechanism of these two gases on silicene.
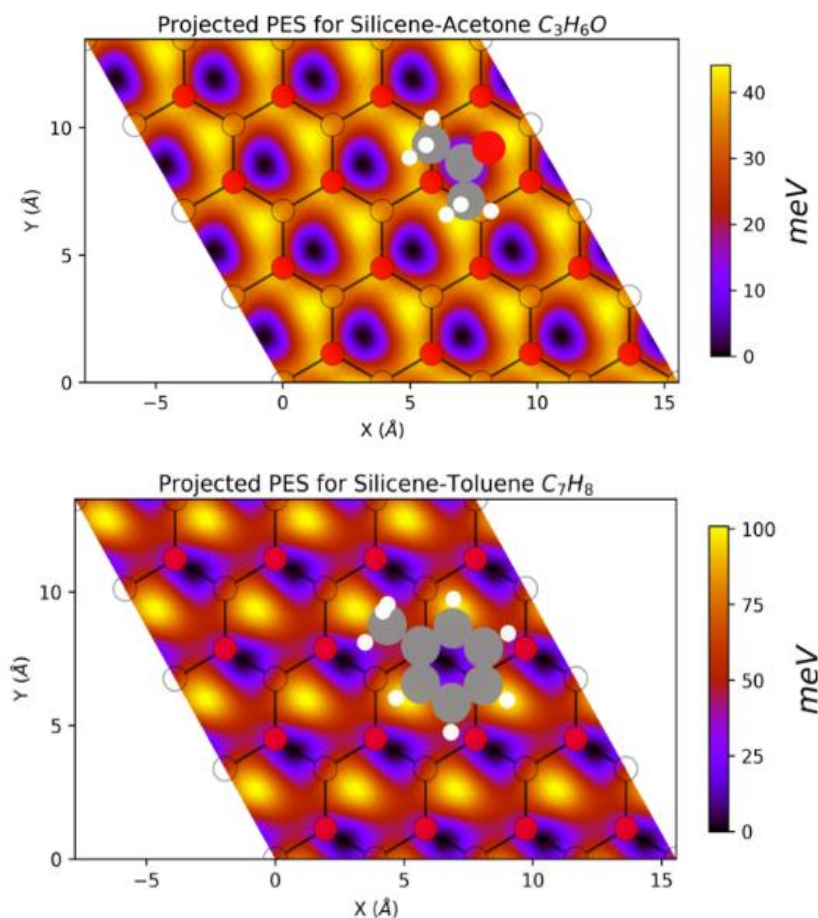

Figure 4. The extended 2D projected Potential Energy Surface for the adsorption of acetone (upper) and toluene (lower) on the surface of silicene. The 2D projected PES is superimposed onto the silicene supercell. Red circles represent upper layer silicon atoms, while transparent ones represent lower layer silicon atoms, and black segments are the bonds connecting them. The energies are shifted so that the most stable position corresponds to zero. X and Y axes on 2D projected PES are the coordinates of the COM of the VOC. The representative favorable adsorption position of the VOC is also shown.

Charge transfer was determined by Bader charge analysis. By comparison of the charge before and after adsorption of VOC molecules, the magnitude and direction of charge transfer can be inferred. The results for charge transfer analysis are displayed in **Error! Reference source not found.**. In both gases, the electron clouds shift from the free-standing silicene to the VOC molecule, which is consistent with

the fact that the electronegativity of silicon (1.8) is lower than that of carbon (2.5), hydrogen (2.1), and oxygen (3.5), respectively. The charge transfer magnitude is in the range of 0.2 – 0.3 electrons (Table 2) corresponding to the opened gap of 18 – 23 meV.
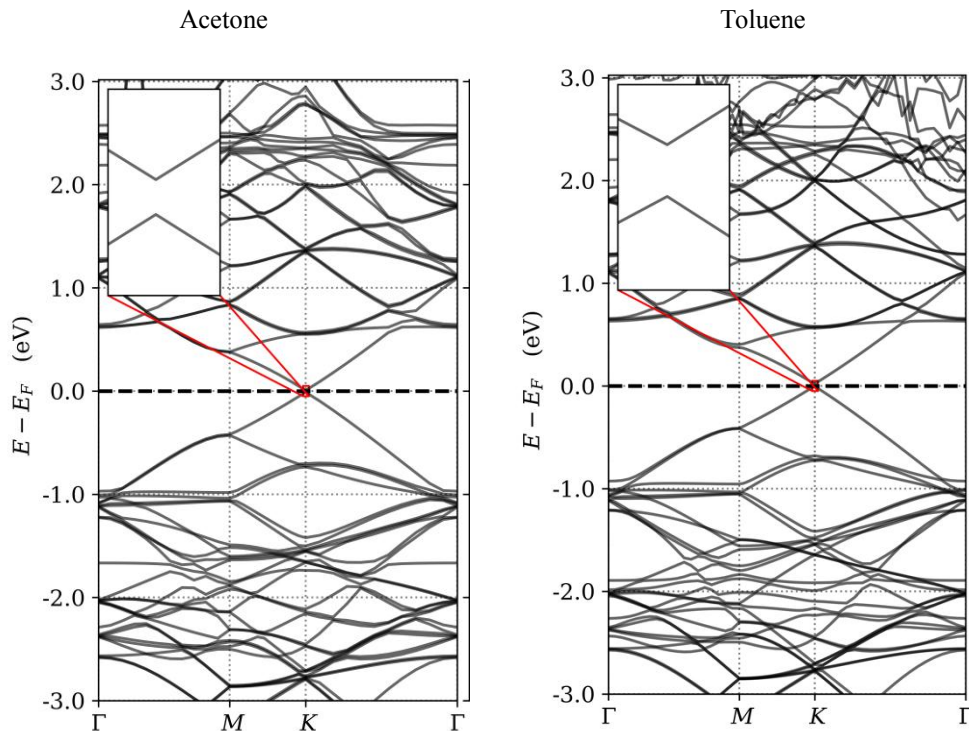
Acetone   Toluene

Figure 5. The electronic band structures of the adsorption systems silicene-acetone (left) and silicene-toluene (right). The inset shows the enlarged band gap.

Table 2. Electronic band gap opening and charge transfer upon VOC adsorption.

VOCs	Charge transfer (electrons)	Band gap (meV)
Acetone	0.26	18
Toluene	0.31	23

4. Conclusions

We have investigated the adsorption mechanism of acetone and toluene on the surface of free-standing silicene by using the quantum simulation based on the Density Functional Theory implementing the van der Waals functional optPBE-vdW. The pictures of PES, favorable adsorption configurations, electronic structure, and charge transfer were obtained. Due to the VOC adsorption, a tunneling gap in order of several ten meV is opened in the electronic structure of silicene, resulting in its semiconductor characteristics. It is also found the charge transfer of 0.26 – 0.31 electrons between VOCs and silicene. These values are considerably larger than that in graphene, suggesting a possibility of the use of this 2D material in the sensing devices, especially in VOC sensors.

Acknowledgments

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