Adsorption of Acetone and Toluene on Single-Vacancy Silicene by Density Functional Theory Calculations

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In this work, we investigated the adsorption mechanism of acetone and toluene on the surface of single-vacancy silicene by Density Functional Theory method with taking into account the van der Waals interaction via the optPBE-vdW functional. The potential energy surface and adsorption energy profile are obtained by using the Computational DFT-based Nanoscope tool. It is found that acetone prefers an inclined configuration while toluene favors the parallel one towards the substrate. The single-vacancy silicene maintains its metallic electronic structure after adsorption. The adsorption energies for acetone and toluene adsorptions are −0.36 eV and −0.57 eV, respectively. The Bader charge analysis shows a charge transfer of 0.17e and 0.30e for adsorption of acetone and toluene on silicene, respectively.

[doi:10.2320/mtatertrans.MT-MN2019022]

(Received January 7, 2020; Accepted April 17, 2020; Published July 25, 2020)

Keywords: adsorption, silicene, density functional theory, defect, acetone, toluene, volatile organic compound

1. Introduction

Detection of cancer in the early stage is crucial to the successful treatment of the disease. Tumor cells in the human body have been reported to generate volatile organic compounds (VOC) which can reflect the disease status.¹ The detection and analysis of VOC biomarkers from exhaled breath with the VOC sensor has been recognized as a new way to diagnose cancer and health checks owing to its quickness, non-invasive, cheapness, easy to use, and can capture data in real-time with high sensitivity. The two-dimensional (2D) materials such as graphene and MoS2 are expected to be the high performance materials for the gas sensors in detecting VOCs in the human’s exhaled breath.²,³ Similar to graphene and MoS2, silicene is expected to exhibit a promising performance in detecting the VOC molecules. In comparison with graphene, the band gap tuning - one of factors causing the change in electronic conductivity of - by an external electric field⁴ or by the binding adsorbates⁵ can be seen more profoundly in silicene.⁶

Silicene is a novel 2D material with many promising properties for electronic applications. Slightly buckled silicene exhibits the behavior of gapless semiconductors with a Dirac cone at the K points of Brillouin zone.⁷ When a perpendicular electric field is applied, the tunneling gap might open at Dirac K points.⁸-¹¹ The gap opening in the electronic structure of silicene (causing by an applied electric field, dopant, etc.) is in interest in applications of the logic devices. Density functional theory (DFT) calculations with taking the spin-orbit coupling effect into account show that silicene exhibits a topological phase transition from the quantum spin Hall state to the mediocre insulator as the out-of-plane electric field increases.¹² Silicene is recently suggested as a promising sensitive material for gas sensor applications.¹³-²⁴ A DFT study by Feng et al.¹³ on the adsorption of several common gas molecules on the perfect silicene reported that silicene exhibits significantly high reactivity towards NO2, O2, and SO2 with the adsorption energies being larger than 1.00 eV. Moreover, NO and NH3 can be adsorbed on silicene with a moderate adsorption energy (0.35 and 0.60 eV), indicating that silicene could be a good sensor towards detecting NO or NH3. The first-principles calculation by Aghaei et al.¹⁹ showed that silicene nanoribbons (SiNRs) are capable of detecting CO, NH3, and H2S with high sensitivity, but not appropriate to serve as a sensor for NO, NO2, and SO2. This is due to the fact that the later gases are strongly chemisorbed with covalent bonds to SiNRs causing a large number of electrons transferred to the SiNR. It is also found that doping a SiNR with a B atom can enhance the detection capability of N2 gas molecules. Another DFT calculation by Meshginalam et al.¹⁵ indicated that the pristine silicene possesses a strong sensitivity with NO and NO2 molecules, whereas it seems incapable of sensing to the other toxic gases due to the low absorption energy. The study also revealed that the defect silicene provides an absorption energy of 3, 3.5, 4 and 10 times greater than that of pristine silicene for adsorption of CO, NO2, NO and HCN molecules, respectively.

The above-mentioned works suggested a promising possibility for use of silicene as a sensitive material for gas sensor applications. However, the influence of defects in silicene which we often face under real experimental conditions, on the performance of silicene in the sensor applications for detecting the organic gases has not yet been considered. In order to understand the role of defects playing in the silicene-based gas sensors, we investigated the adsorption mechanism of some Volatile Organic Compounds (VOCs) on the single-vacancy silicene by using the DFT method. The geometric and electronic structures of the defect silicene with a single Si-vacancy was calculated. The properties of the defect silicene adsorbing acetone and toluene; such as the adsorption configuration, electronic

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structures before and after adsorption, adsorption energy, and charge transfer between silicene and VOC molecules were investigated.

2. Computational Method

All calculations based on the density functional theory were performed using the Vienna ab initio simulation package (VASP) with PAW potential.25,26) Because the van der Waals functionals are expected to be better than van der Waals correction schemes,27–30) we take the van der Waals interaction into account in all calculations by employing the optPBE-vdW functional30) for the aim to produce the results in better agreement with experiment.31) The adsorption configuration, the potential energy surface (PES) and adsorption energy profile were calculated by employing the Computational DFT–based Nanoscope tool.32)

To eliminate the interaction between two adjacent periodic images, a vacuum layer of 20 Å was added into the 4 × 4 supercell of the pristine silicene. A cutoff energy of 450 eV for the plane-wave basis set and a 3 × 3 × 1 Gamma-centered K-point mesh were utilized to yield the energy convergence. All structures were fully relaxed until the maximum Hellmann-Feynman force acting on each atom is less than 0.03 eV/Å.

Our model consists of sheet of a single-vacancy silicene (Fig. 1) built from a 4 × 4 supercell of the pristine silicene, and a VOC molecule which exists in the breath of cancer patients33) as an adsorbate. In this study, we choose acetone to represent the ketone organic group and toluene to represent the aromatic compounds.

3. Results and Discussions

3.1 Geometrical structure of single-vacancy silicene

The structure of the single-vacancy silicene is constructed by removing one Si atom from the 4 × 4 supercell of the pristine silicene. Two single-vacancy structures of the defect silicene were considered. The first one, named Structure A, in which the Si atoms around the vacancy position are collapsed and form a non-flat 12 edges polygon inside the red circle, is illustrated in Fig. 1(a). The second one, named Structure B, is demonstrated in Fig. 1(b). In the later structure, Si atoms nearby the vacancy form two distorted hexagons and two pentagons. The calculated total energy of the later (−145.307 eV) is significantly lower than the first (−122.252 eV) an amount of 23 eV, hence Structure B is the most energetically stable structure. The defect in structure B has horizontal and vertical symmetry axes. It includes an sp3–hybridized central carbon atom. The angles and edges of each distorted hexagon and pentagon are given in Table 1–Table 4. We hereafter consider this structure in the calculation of electronic structure, binding energy and adsorption characteristics of the system of silicene and VOC molecules.

3.2 Binding energy and potential energy surface

Figure 2 illustrates the binding energy difference calculated by the Computational DFT–based Nanoscope tool of an acetone molecule at various positions on the 4 × 4 supercell single-vacancy silicene. X and Y are the fractional coordinates along the two lattice vectors of the 4 × 4 supercell. The vertical axis corresponds to the binding energy difference in units of meV. The lowest binding energy is set at the z-axis’s origin. The upper image shows the 3D picture of the binding energy between two components of the gas molecule and silicene. The lower image is the projected of
the binding energy difference onto the plane (x,y) of silicene. The lighter color illustrates the higher energy area in which the molecule adsorption is less preferred, whereas the darker color reflects the area on the surface where the adsorption is more favorable. To see more clearly, we draw the PES of acetone on the 4 × 4 supercell single-vacancy silicene at the Cartesian coordinates of the center of mass of VOC molecule in Fig. 3 by extracted data from Fig. 2. As seen from Fig. 3, PES is slightly asymmetric, which is more negative on the right edge of the defect silicene structure, and the diffusion barrier between the most preferable adsorption areas (darkest areas) is estimated to be considerably low and approximates to 20 meV.

The geometric structure of the acetone adsorbed silicene is illustrated in Fig. 4, in which the acetone molecule orients nearly parallel to the substrate and its oxygen atom lies closest towards the substrate.

For the absorption of toluene on the single-vacancy silicene, as seen from Fig. 5 and Fig. 6, it is found that the PES is slightly asymmetric. PES is lower at the right edge of the defect silicene structure. In addition, the diffusion of the toluene molecule between the adjacent preferable adsorption areas costs a considerably small energy of approximately 30 meV.

Figure 7 illustrates the adsorption structure of the toluene molecule on the single-vacancy silicene. Toluene molecule locates on either side of the defect site. The molecule lies on a plane which is almost parallel to the substrate, and sits nearby the horizontal symmetry line of this defect structure.

### 3.3 Adsorption energy profile

The adsorption energy profile is calculated by using the Computational DFT-based Nanoscope tool, by which the adsorption energy is determined by:

#### Table 3 Edges of hexagon.

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<th>(1, 2)</th>
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<th>(3, 4)</th>
<th>(4, 5)</th>
<th>(5, 6)</th>
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#### Table 4 Edges of pentagon.

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<th>(3, 7)</th>
<th>(7, 8)</th>
<th>(8, 9)</th>
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<tr>
<td>Values</td>
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<td>2.264</td>
<td>2.274</td>
<td>2.492</td>
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</table>

Fig. 2 Binding energy difference of the acetone adsorbed single-vacancy silicene. X and Y are fractional coordinates in unit of supercell sizes along the two lattice vectors on the plane (x,y). The upper image illustrates the 3D binding potential, and the lower is the binding potential projected on the plane (x,y).
where $E_a$ and $E_{gas/silicene}$ are the total energy of the isolated gas molecule and pristine silicene. Formula (1), however, has an advantage in reducing the computational cost by eliminating the calculations of total energies for separated entities.

The adsorption energy profile for the acetone adsorbed single-vacancy silicene and toluene adsorbed single-vacancy silicene systems are depicted in Fig. 8. In this figure, the minimum corresponds to the adsorption energy $E_a$ of the most stable position of the molecule on silicene. $E_a$ is calculated to be $-0.36$ and $-0.59$ eV for acetone and toluene, respectively. It can be seen from the adsorption energy profile that $E_a$ of the acetone adsorption is smaller than that of toluene one while the distance from its center of mass to the substrate is closer (about 3.1 Å compared to 3.4 Å). $E_a$ decreases by about 10% due to the vacancy in the case of acetone adsorption in compared with that of the perfect silicene ($E_a = -0.40$ eV$^{35}$), whereas $E_a$ slightly decreases by 1% in the case of toluene adsorption ($E_a = -0.60$ eV for the perfect silicene$^{35}$). These findings suggest that the single-vacancy silicene might be more sensitive with toluene than with acetone and the vacancy might reduce the sensitivity of silicene against acetone.

3.4 Electronic properties

The band structure and density of states (DOS) for the acetone adsorbed single-vacancy silicene and toluene adsorbed single-vacancy silicene systems are shown in Fig. 9(a) and 9(b), respectively. In the DOS panels, the black line stands the total DOS of the systems, the colored lines demonstrate the partial DOS of each element. Acetone and toluene distributes into states close to the Fermi level, which possibly affects to the transport properties of single-vacancy silicene. The contributions of oxygen and carbon to DOS are significantly greater than that of the remaining elements. The metallic characteristics of the single-vacancy silicene is maintained after adsorption. The metallic characteristics of the single-vacancy silicene in this work might be caused by the high defect concentration. With the much larger supercell of pristine silicene, the single-vacancy silicene is expected to be a tunnel gap semiconductor. This question is opened for the further investigation of the VOC adsorption on the single-vacancy silicene with using a larger supercell size.

The Bader charge analysis shows that the charge transfer from the single-vacancy silicene to acetone is 0.17 electrons, and to toluene is 0.30 electrons, respectively. The adsorption of acetone and toluene on the surface of silicene exhibits the
physical adsorption’s behavior. Since the electronegativity of Si, C and O is 1.9, 2.55 and 3.44, respectively, the charge of Si has a tendency to transfer to the nearest C and O of the VOC molecules. In comparison with the perfect case in which the charge transfer gains 0.26 e and 0.31 e for acetone and toluene adsorption, respectively, the charge transfer considerably decreases the acetone adsorption of the single-vacancy silicene. The significantly smaller values of charge transfer and adsorption energy in the case of acetone adsorption would indicate the less sensitivity of the single-vacancy silicene toward acetone compared to the perfect silicene. These charge density differences visually demonstrated by Fig. 10 in which the charge accumulation and depletion are illustrated by the yellow and cyan clouds, respectively.

4. Conclusion

In this paper, we investigated the adsorption of acetone and toluene on the surface of the single-vacancy silicene by using the DFT calculations. Obtained results show that the adsorptions of acetone and toluene on the substrate exhibit the physical adsorption behavior. The single-vacancy silicene maintains its metallic electronic structure after the adsorption. The adsorption energies for acetone and toluene were found to be −0.36 eV and −0.57 eV, respectively. The charge transfers between the substrate and adsorbate molecules are 0.17 e (acetone) and 0.30 e (toluene). While the Si vacancy significantly affects the adsorption of acetone molecules, its effect on the toluene adsorption is considerably weak. These findings suggest a way to improve the selectivity of silicene against VOCs.

Acknowledgments

This research was supported by the Vietnam National
Foundation for Science and Technology Development (NAFOSTED) under Grant Number 103.01-2018.315. The authors are also thankful to the project on the establishment of Master’s Nanotechnology program under the contract between Japan Cooperation International Agency (JICA) and Osaka University.

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