IOP Conf. Series: Materials Science and Engineering **367** (2018) 012051 doi:10.1088/1757-899X/367/1/012051

A First-principles Investigation of The Adsorption of CO and NO Molecules on Germanene

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Abstract. The adsorption of common pollutant gases on germanene is investigated using first-principles calculation by means of density functional theory. In this work, CO and NO molecules are used as pollutant gases. Our calculation results show that CO molecule is physisorbed on germanene, while NO molecule is chemisorbed since it opens band gap of germanene at the Dirac point. To investigate the mechanism of the adsorption process, we calculate the transfer of charges between germanene and gas molecules. In order to obtain understanding into the transformation of electron density upon the adsorption processes, Mulliken analysis is used to evaluate atomic charge of each atom. We found that electron charge of NO molecule obviously increased due to adsorption process, while CO molecule slightly increased.

Keywords. CO molecule, electron density, germanene, and NO molecule.

1. Introduction

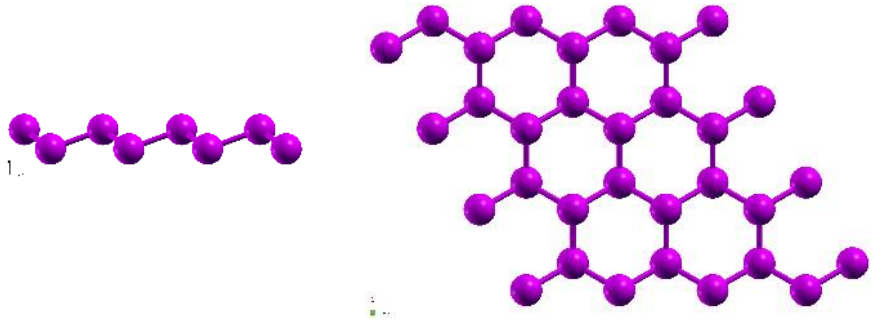
Carbon monoxide (CO) and nitric oxide (NO) are poisonous gases that are extremely dangerous for human health. They can cause a wide range of health effect form dizziness to brain damage or even death [1], [2]. Therefore, in order to reduce the amount of pollutant in the atmosphere, it is necessary to find material that has the ability to adsorb molecules especially pollutant gases. One of the most promising candidates is germanene (germanium analog to graphene). Graphene has a high sensitivity to the chemical environment [3]. Hence, germanene is expected to give a similar result. Experimentally, germanene has successfully grown on Pt (111) [4] and Au (111) [5] surface. In the previous studies, germanene has used as an adsorbent material for transition metal atoms[6], group IV elements [6], and organic molecules [7], [8]. Xia *et al* were also reported the ability of germanene to adsorb various gas molecules including CO and NO [9].In our study, we did further calculation in order to understand the mechanism of adsorption of CO and NO on germanene. We investigated the charge difference distribution and electron charge transfer in each system.

We carried out the first-principles electronic-structure calculations to investigate adsorption processes and its mechanism of CO and NO molecules on germanene. We use a 4 × 4 × 1 supercell of germanene which contains 32 germanium atoms with a concentration of CO and NO about 6.25 %.

2. Materials and methods

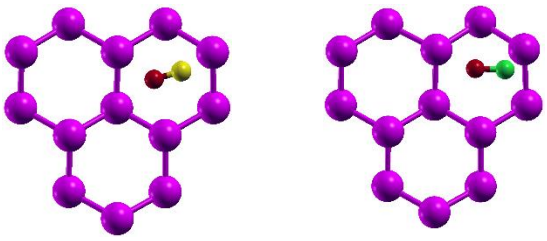
Unlike the fully planar honeycomb lattice of graphene, germanene is predicted to be buckled [10]. This buckled lattice is composed of two sub-lattice with different *z* coordinates (see Figure 1). Furthermore, we introduce CO and NO molecule on germanene as shown in Figure 2. To obtain the most stable geometry and electronic properties of the material we use density functional theory as implemented in Open Source Package for Material Explorer (OpenMX) code [6]. It has an efficient implementation of first-principles calculations by means of density functional theory that allow us to investigate electronic, magnetic, and geometrical structures of a wide variety of materials. The OpenMX code can be freely obtained through its official website.

OpenMX code is based on norm-conserving pseudopotentials [10] and the wave functions were expanded by a linear combination of multiple pseudo-atomic orbitals (LCPAO) [6], [10], [11]. All calculations were performed with Generalized-Gradient Approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) [12] as the exchange-correlation form. The vacuum space in the *z*-direction is set to 20 Å to avoid interactions between the neighboring layers. We use a 10 × 10 × 1 *k*-points in Brillouin zone for electronic structure calculation with energy convergence criteria is determined at 10^{-6} Hartree.



(a) (b)

Figure 1. Buckled honeycomb lattice of germanene viewed from (a) *y*-*z* plane and (b) *x*-*y* plane. Purple balls represent germanium atoms.



(a) (b)

Figure 2. The most stable positions of (a) CO and (b) NO molecules on germanene. The purple, red, yellow, and green balls are germanium, oxygen, carbon, and nitrogen atoms respectively.

To evaluate the adsorption of gas molecules on germanene, the adsorption energy (Eads) is defined as:

$$E_{ads} = E_{molecule/germanene} - \left(E_{germanene} + E_{molecule}\right) \quad (1)$$

Where $E_{molecule}$, $E_{germanene}$, and $E_{molecule/germanene}$ are the total energy of the gas molecule, pristine germanene, and gas molecule adsorbed on germanene, respectively.

3. Results and discussion

Our structural calculations begin by finding lattice constant of germanene. We have a varied lattice constant value in a certain range to get the lowest energy system. Our calculation indicated that 4.053 Å provided the lowest ground state energy of germanene structure (see Figure 3). This result is in a good agreement with other work reported by Acun *et al* [13]. We also found that buckling height of honeycomb germanene about 0.692 Å, it also seems in a good agreement with other result reported by Scalise *et al* [14].

The most stable adsorption configurations of gas molecules on germanene are shown in Figure 2. By employing Equation 1, we can evaluate adsorption energy of each gas molecule. The corresponding results are listed in Table 1. Both CO and NO adsorption are spontaneous reactions. It means no external energy needed to perform the adsorption processes.Charges of the total density of states (DOS) were analyzed, as plotted in Figure 4, to investigate the adsorption type of each model. Our results showed that the electronic properties of germanene are semi-metal with zero-gap at the Dirac point. This is consistent with other calculation result reported by Ni *et al* [15]. Adsorption of CO molecule does not change the electronic properties of germanene. Therefore, CO molecule is physisorbed on germanene. However, we found that NO molecule is chemisorbed since it changes the electronic properties of germanene. These results are in a good agreement with previous calculation conducted by Xia *et al* [9]. The existence of NO molecule on germanene opened band gap at Dirac point about 0.18 eV.

The mechanism of adsorption process can be evaluated by investigating the interaction between gas molecules and atoms of germanene. We explore this interaction by considering charge transfer which can be verified through calculation of charge difference distribution ($\Delta\rho$) as defined in Equation 2.

$$\Delta\rho = \rho_{molecule/germanene} - \left(\rho_{germanene} + \rho_{molecule}\right) \quad (2)$$

Where $\rho_{molecule}$, $\rho_{germanene}$, $\rho_{molecule/germanene}$ are the charge density of the gas molecule, pristine germanene, and gas molecule adsorbed on germanene, respectively. The results are illustrated in Figure 5. The electron accumulation is depicted by the red region, while the blue region shows the electron loss. Electron flowed from blue region to red region. This result proves the presence of charge transfer between germanene and gas molecules.

To gain a better understanding of the mechanism of adsorption of gas molecules, we investigate the effective charge around each atom using Mulliken charge analysis. Its results are presented in Table 2.

Table 1. Energy and type of adsorption of CO/germanene and NO/germanene models.

Model	E_{ads} (eV)	Type of Adsorption
CO/germanene	-0.558	Physisorption
NO/germanene	-1.141	Chemisorption

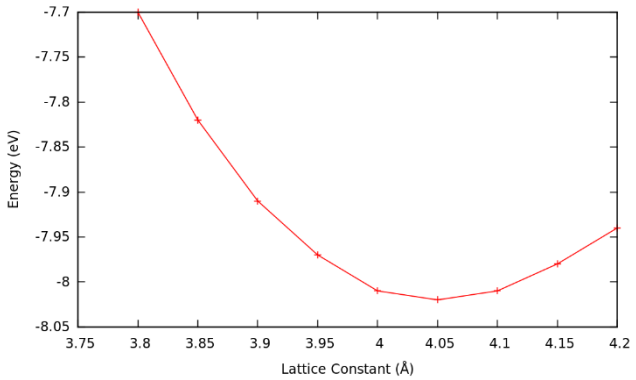


Figure 3. Lattice constant optimization of germanene structure.

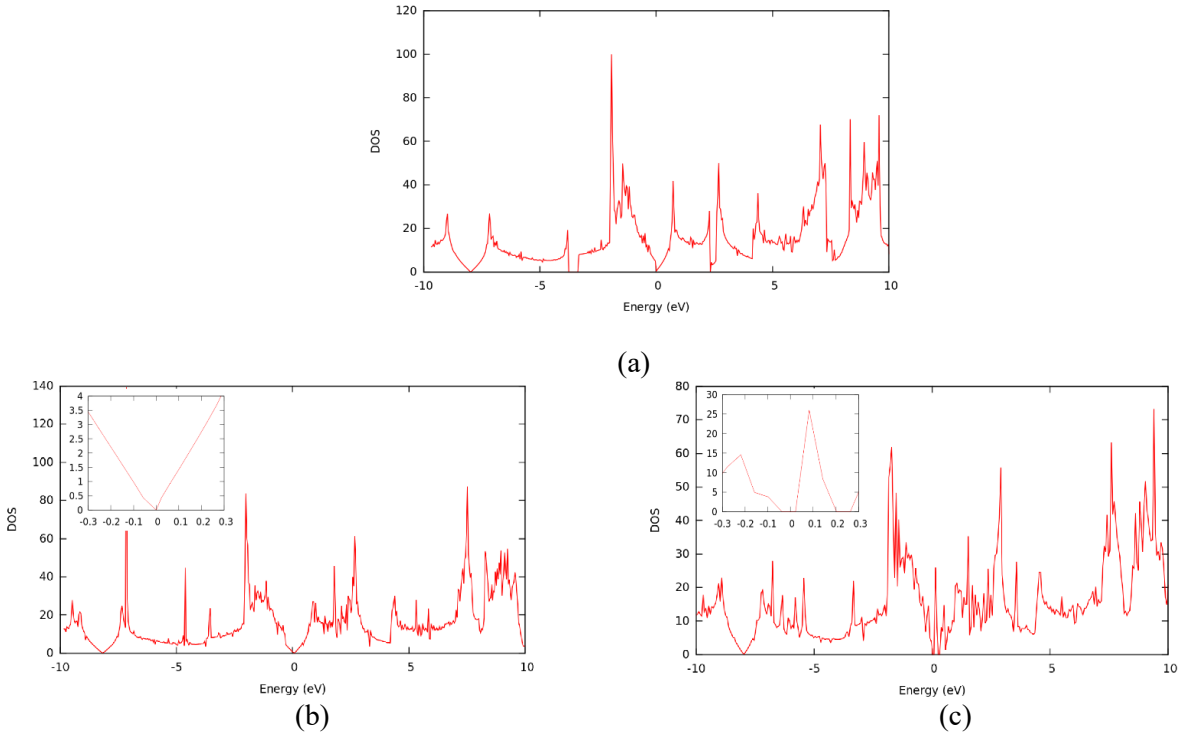


Figure 4. Total density of states of (a) germanene (b) CO/Germanene (c) NO/Germanene.

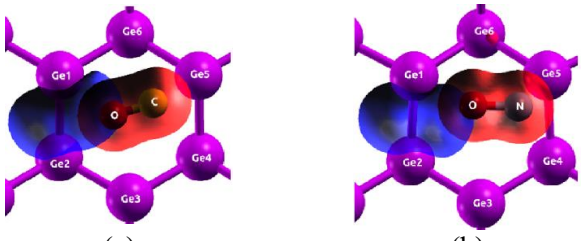


Figure 5. Charge difference distribution of (a) CO/germanene and (b) NO/germanene models. The red and blue regions indicate the positive and negative values. Only gas molecules and its neighboring germanium atoms are shown.

Table 2. Atomic charges (*e*) of gas molecules and neighboring atoms of germanene based on Mulliken charge analysis

Atom	Before adsorption	After adsorption	
		CO/germanene	NO/germanene
Ge1	4.000	3.961	3.922
Ge2	4.000	4.004	4.011
Ge3	4.000	3.981	3.952
Ge4	4.000	4.026	3.987
Ge5	4.000	3.981	3.848
Ge6	4.000	4.030	4.043
O_{CO}	6.341	6.370	-
C	3.659	3.640	-
O_{NO}	6.211	-	6.268
N	4.790	-	5.004

Since each gas molecule is adsorbed to germanene, the accumulated charge can be observed around gas molecules. It causes an increase in the electron charge of CO and NO molecules about 0.010 *e* and 0.271 *e*, respectively.

4. Conclusions

In summary, with first-principles calculations, the adsorption of CO and NO molecules on the germanene sheet was successfully investigated. Our results showed the adsorption processes of both CO and NO molecules are a spontaneous reaction but with different type of adsorption. CO molecule is physisorbed on the germanene, while NO molecule is chemisorbed. Mulliken charges analysis result indicated that significant charge transformation ensued between germanene and NO molecule but much smaller in CO molecule.

Acknowledgments

This work was funded by*Bantuan Pendanaan Perguruan Tinggi Badan Hukum Direktorat Penelitian Universitas Gadjah Mada* under contract No. 376/DIT.LIT/2017. The calculations in this research were performed using the high-performance computing facilities (DSSDI) at Universitas Gadjah Mada.

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