

## The Interaction of Air Pollutant Molecules with Germanene and Silicene: a Density Functional Theory Study

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### ABSTRACT

We investigate the adsorption of atmospheric pollutants on germanene and silicene using density functional theory (DFT) calculations. In this study, we use carbon monoxide (CO) and nitric oxide (NO) as the pollutant molecules. Electronic properties of germanene and silicene are explored to obtain a good understanding in the adsorption process. Our calculation results show both germanene and silicene provide an identical mechanism of adsorption. Germanene and silicene adsorb CO and NO spontaneously with physisorption and chemisorption types for CO and NO molecules, respectively. We also conduct the Mulliken charges calculations to evaluate the transformation of atomic charges due to the adsorption process. From Mulliken charge calculation results we can confirm the existence of charge transfer between the adsorbent materials and the pollutant molecules. This phenomenon lies behind the occurrence of the adsorption process.

**Keywords:** DFT, germanene, interaction, pollutant molecules, silicene

### INTRODUCTION

An atmospheric pollutant is a hazardous substance in the air that has harmful effects on humans and the ecosystems. Carbon monoxide (CO) and nitric oxide (NO) are two of the most dangerous gases in our atmosphere, it can cause various health effect from dizziness to death (Ischiropoulos et al., 1996; Raub et al., 2000). Both CO and NO gases are available abundantly in the atmosphere since they are produced by vehicles and industrial exhaust gases. By this fact, it is clear that we need to find material that has the ability to adsorb pollutant gases such as CO and NO. In this study, we compare the adsorption ability of germanene and silicene with CO and NO molecules as adsorbed materials. Germanene and silicene are analog to graphene but they use germanium and silicon atoms instead. Since graphene exhibit excellence sensitivity to its chemical environment (Schedin et al., 2007), germanene and silicene are expected to show similar result or even better. Some previous theoretical studies have reported the ability of germanene and silicene to adsorb various gas molecules by using density functional theory. Hu et al. (2014) reported that NH<sub>3</sub>, NO, and NO<sub>2</sub> chemically adsorbed on silicene. Another calculation conducted by Xia et al showed that N<sub>2</sub>, CO, CO<sub>2</sub> are

physically adsorbed while NH<sub>3</sub>, NO, NO<sub>2</sub>, O<sub>2</sub> are chemically adsorbed on germanene (Xia et al., 2014). In our study, we did calculations in order to understand the mechanism of adsorption of CO and NO on both silicene and germanene. We investigated the charge difference distribution and then calculated the charge per atom before and after adsorption process.

On the experimental studies, germanene was successfully grown on Pt(111) and Au(111) (Li et al., 2014; Dávila et al., 2014), as well as silicene on Ag(111), ZrB<sub>2</sub>(0001), and Ir(111) surfaces (Jamgotchian et al., 2012; Fleurence et al., 2012; Meng et al., 2013).

### EXPERIMENTAL SECTION

#### Material and Methods

We carried out the first-principles electronics-structure calculations by means of density functional theory (DFT) to find out the possibility of using germanene and silicene as adsorbent material for CO and NO molecules through the adsorption mechanism. In this study, we use a 4 × 4 × 1 supercell of each germanene and silicene which contains 32 atoms with the concentration of CO and NO about 6.25%. All calculations in this research were performed using Open Source Package for Material Explorer (OpenMX) code (Ozaki,

2003) with Generalized-Gradient Approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) (Perdew et al, 1996) as the exchange-correlation form. OpenMX is based on the norm-conserving pseudopotentials (Troullier and Martins, 1991), the wave functions were expanded by a linear combination of multiple pseudo-atomic orbitals (LCPAO) (Ozaki, 2003; Ozaki and Kino, 2004). A  $10 \times 10 \times 1$  k-points in Brillouin zone is used for electronic structure calculation to gain the desired result, energy convergence criteria are adjusted at  $10^{-5}$  Hartree. Large enough vacuum space in the z-direction is used to prevent interactions between adjacent slabs for both germanene and silicene.

## RESULTS AND DISCUSSION

### Geometrical Properties

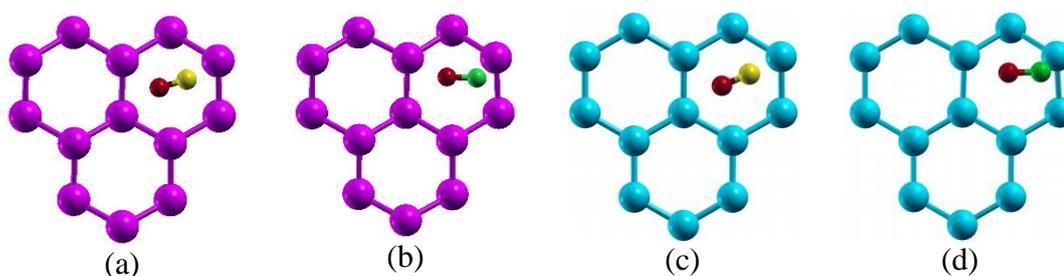
In the geometry optimization calculations, we found that lattice constant of germanene and silicene are about 4.053 Å and 3.890 Å, respectively. These results seem in a good agreement with other works reported by Acun *et al.* (2015) and Gimbert *et al.* (2014). After the most stable geometries of are obtained, then we introduce CO and NO molecules on both germanene and silicene surfaces to evaluate the formation energy of each system. The stable positions of CO and NO molecules on both adsorbent surfaces are

shown in **Figure 1**. Then, the formation energy ( $E_{form}$ ) is obtained by simple arithmetic formulation as defined in **Equation 1**:

$$E_{form} = E_{molecule/adsorbent} - (E_{molecule} + E_{adsorbent}) \quad (1)$$

Where  $E_{molecule}$ ,  $E_{adsorbent}$ , and  $E_{molecule/adsorbent}$  are the total energy of the molecule, pristine adsorbent, and gas molecule adsorbed on adsorbent material, respectively. We have four different systems, they are CO adsorbed on germanene, NO adsorbed on germanene, CO adsorbed on silicene, and NO adsorbed on silicene. For simplification, we call them with CO/germanene, NO/germanene, CO/silicene, and NO/silicene, serially. By using **Equation 1**, we get formation energy of each system. Our results are listed in **Table 1**.

The adsorption processes that occur on all of our systems are spontaneous reactions since they exhibit negative values on their formation energies. It means the adsorption processes can be done without any external energy needed. This becomes an essential requirement for every adsorbent material. Although both germanene and silicene yield same negative values of formation energies, there is a notable difference happen. Our calculation result as listed in **Table 1** shows that silicene provide higher formation energy compared to germanene. It means adsorption and also desorption processes on silicene is easier to happen than germanene.



**Figure 1.** The most stable positions of the pollutant molecules on various systems: (a) CO/germanene, (b) NO/germanene, (c) CO/silicene, and (d) NO/silicene. The purple, cyan, red, yellow, and green balls are germanium, silicon, oxygen, carbon, and nitrogen atoms, respectively.

**Table 1.** Formation energies of various systems are presented in eV units, types of adsorption are also shown.

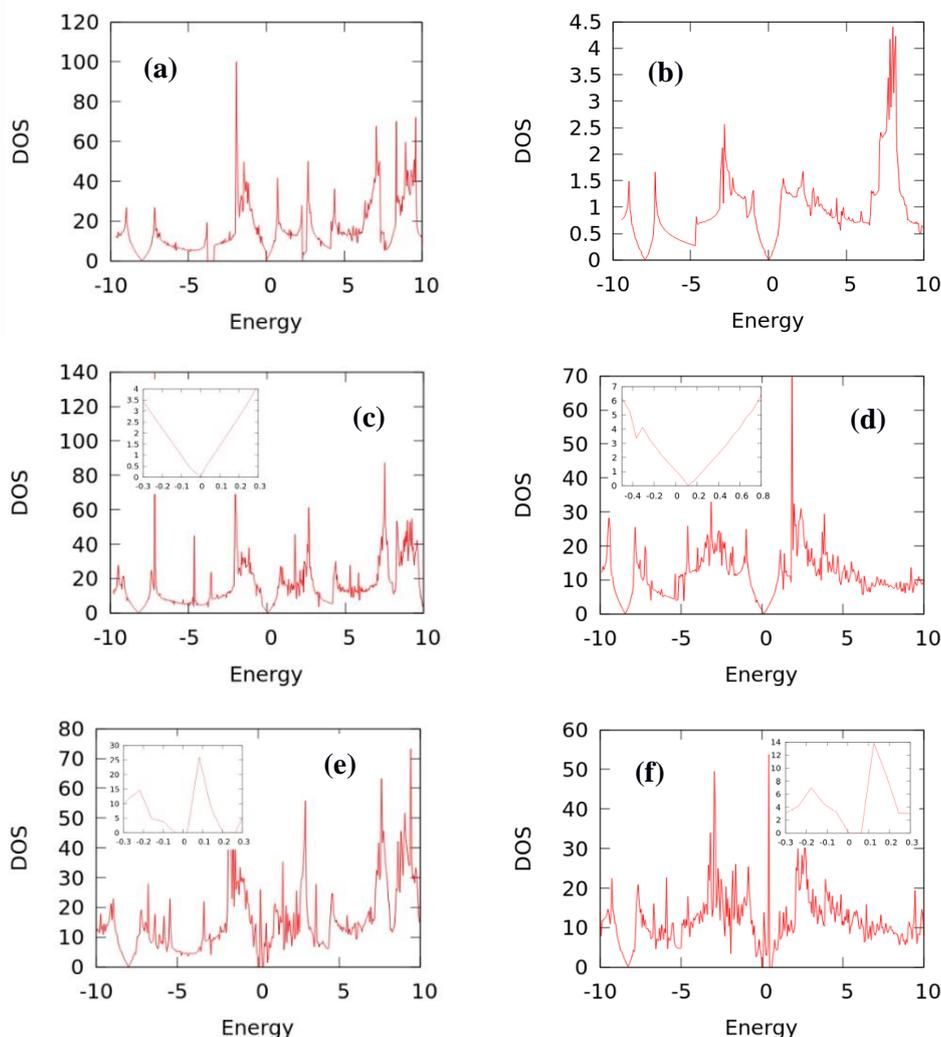
System	Formation energy (eV)	Type of adsorption
CO/germanene	-0.558	Physisorption
NO/germanene	-1.141	Chemisorption
CO/silicene	-0.005	Physisorption
NO/silicene	-0.022	Chemisorption

Therefore from the formation energy point of view, we can sum up that both germanene and silicene have the ability to adsorb CO and NO molecules with spontaneous reactions, but it is more likely to happen in silicene than in germanene.

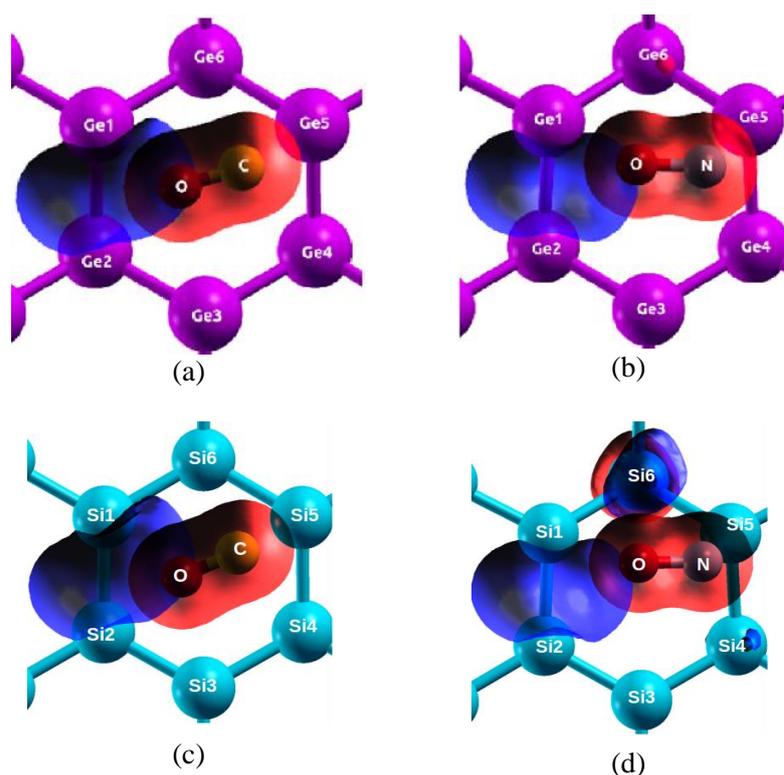
### Electronic Properties

The charges of the total density of states (DOS) were analyzed to determine the type of adsorption in each system, as plotted in **Figure 2**. The electronic properties of germanene are semi-metal with zero-gap at the Dirac point as well as silicene. Both germanene and silicene as adsorbent materials exhibit identical result in reacting to the presence of CO and NO molecules. Adsorption of CO molecule does not change the electronic properties of

adsorbent materials (see **Figure 2 (c)** and **(d)**). Therefore adsorption of CO is categorized as physisorption process through van der Waals interaction between adsorbent materials and gas molecules. On the contrary, the NO adsorption is classified as chemisorption process since it is able to open band gap of adsorbent materials about 0.18 eV. So the electronic properties of the material are no longer semi-metal but turned into the semiconductor with narrow 0.18 eV band gap. The covalent bonds occur in  $\text{Ge}_5\text{-N}$  and  $\text{Si}_5\text{-N}$  (see **Figure 3 (b)** and **(d)**) with bond length about 2,2 Å and 1,9 Å, respectively. In addition, this result also tells us about the possibility of using germanene and silicene as sensor materials application for NO molecule.



**Figure 2.** Density of states (DOS) of (a) pristine germanene (b) pristine silicene (c) CO/germanene (d) CO/silicene (e) NO/germanene (f) NO/silicene systems. These figures represent the electronic properties of each system.



**Figure 3.** Charge difference distribution of (a) CO/germanene (b) NO/germanene (c) CO/silicene and (d) NO/silicene systems. The red and blue regions indicate the positive and negative values. Electron charges flowed from blue region to red region. Only pollutant molecules and its neighboring atoms of adsorbent materials are shown.

**Table 2.** Atomic charges of pollutant molecules and neighboring atoms of adsorbent materials 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 <sub>CO/germanene</sub>	6.341	6.370	-
C <sub>CO/germanene</sub>	3.659	3.640	-
O <sub>NO/germanene</sub>	6.211	-	6.268
N <sub>NO/germanene</sub>	4.790	-	5.004
Si1	4.000	3.991	3.996
Si2	4.000	3.972	4.011
Si3	4.000	3.979	3.942
Si4	4.000	3.990	3.988
Si5	4.000	3.988	3.770
Si6	4.000	3.988	3.969
O <sub>CO/silicene</sub>	6.341	6.369	-
C <sub>CO/silicene</sub>	3.659	3.660	-
O <sub>NO/silicene</sub>	6.211	-	6.261
N <sub>NO/silicene</sub>	4.790	-	5.042

The mechanism of adsorption process can be explained by investigating the interaction between pollutant molecules and adsorbent materials. We explore this by considering the existence of charge transfer between pollutant molecules and adjacent atoms of adsorbent materials. The present of charge transfer can be verified through calculation of charge difference distribution ( $\Delta\rho$ ) as defined in **Equation 2**.

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

Where  $\rho_{molecule}$ ,  $\rho_{adsorbent}$ ,  $\rho_{molecule/adsorbent}$  are the charge density of the pollutant molecule, adsorbent material, and pollutant molecule adsorbed on adsorbent material, respectively. The results are illustrated in Figure 3. The accumulation and the loss of charge are depicted by positive and negative values of the charge difference distribution, respectively. This result confirms the presence of charge transfer between adsorbent materials and pollutant molecules.

In order to acquire a better understanding of the adsorption processes, we did Mulliken charge analysis. The charge around each atom is calculated by adding population over *sp* orbital. Its results are presented in **Table 2**.

**Figure 3** shows the presence of charge accumulation around each pollutant in all systems. These are consistent with the results provide by Mulliken charge analysis as shown in **Table 2**. The charge of CO and NO molecules are increased due to the adsorption processes, CO molecule receives additional charge from germanene by 0.010 *e* and from silicene by 0.029 *e*. While NO molecule receives 0.271 *e* and 0.303 *e* from germanene and silicene surfaces, respectively.

## CONCLUSIONS

We carried out first-principles calculations by means of density functional theory (DFT) to investigate the interactions between pollutant molecules and adsorbent materials. In this research, we use CO and NO as pollutant molecules, while for adsorbent material we use germanene and silicene. Our calculation results show that both germanene and silicene exhibit identical adsorption processes in response to the presence of CO and NO molecules. The mechanism of interactions between pollutant molecules and adsorbent materials can be

evaluated by investigating the charge difference distributions and charge transfer between them. By using Mulliken charge analysis we successfully confirm the existence of charge transfer from adsorbent materials to pollutant molecules. The total charge of CO molecule is increased by 0.010 *e* after adsorbed on germanene and by 0.029 *e* after adsorbed on silicene. While the charge of NO molecule increases about 0.271 *e* and 0.303 *e* after adsorbed on germanene and silicene, respectively.

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