

First Principles Study of Toxic Gas Molecules Adsorption on Group IVA (C, Si, Ge) 2-Dimensional Materials

(Kajian Prinsip Pertama Penjerapan Molekul Gas Toksik pada Kumpulan IVA (C, Si, Ge) Bahan 2 Dimensi)

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ABSTRACT

Two-dimensional materials from group IVA namely graphene, silicene, and germanene have gained research interest in various fields of applications recently due to their extraordinary properties. These substrates have been successfully synthesized and are found to have interesting gas sensing capabilities. In this work, first-principles study using density functional theory is carried out to investigate the adsorption of toxic gases such as CO, Cl₂, NO₂, and COCl₂ on these monolayers. We analyze the best adsorption site and orientation for these molecules on the monolayers by calculating the adsorption energy. Charge transfer, the density of state (DOS) and band diagram calculations are performed to explore the changes in their electronic and structural properties due to the adsorbed gas molecules. As for the sensing performance, crude estimations of the sensitivity and recovery time are performed. The results show that silicene and germanene monolayers are better at detecting CO and NO₂ as compared to graphene. They have a short recovery time for CO but a long recovery time for NO₂ implying that they are better for scavenging NO₂. Besides, silicene is also a better gas sensor for chlorine gas with a 44 min recovery time. As for graphene, it is the best gas sensor for phosgene among the substrates. This study gives a clear prediction of substrates for the detection of these toxic gases.

Keywords: Density functional theory; germanene; graphene; silicene; toxic gases

ABSTRAK

Bahan dua dimensi daripada kumpulan IVA iaitu grafin, silisen dan germanen telah menarik minat penyelidikan dalam pelbagai bidang aplikasi baru-baru ini kerana sifatnya yang luar biasa. Substrat ini telah berjaya disintesis dan didapati mempunyai keupayaan penderiaan gas yang menarik. Dalam penyelidikan ini, kajian prinsip pertama menggunakan teori fungsi ketumpatan digunakan untuk mengkaji penjerapan gas toksik seperti CO, Cl₂, NO₂ dan COCl₂ pada ekalapis ini. Kami menganalisis tapak penjerapan dan orientasi terbaik untuk molekul ini pada ekalapis dengan menghitung tenaga penjerapan. Pemindahan caj, ketumpatan keadaan (DOS) dan pengiraan rajah jalur dilakukan untuk meneroka perubahan dalam sifat elektronik dan struktur disebabkan oleh molekul gas terjerap. Bagi prestasi penderiaan, anggaran kasar sensitiviti dan masa pemulihan digunakan. Keputusan menunjukkan bahawa ekalapis silisen dan germanen lebih baik dalam mengesan CO dan NO₂ berbanding grafin. Mereka mempunyai masa pemulihan yang singkat untuk CO tetapi masa pemulihan yang panjang untuk NO₂ mengimplicasikan bahawa mereka lebih sesuai untuk menggarut NO₂. Selain itu, silisen juga merupakan sensor gas yang lebih sesuai untuk gas klorin dengan masa pemulihan 44 minit. Bagi grafin, ia adalah penderia gas terbaik untuk fosgen. Kajian ini memberi ramalan yang jelas tentang substrat untuk pengesanan gas toksik ini.

Kata kunci: Gas toksik; germanen; grafin; silisen; teori fungsian ketumpatan

INTRODUCTION

Since the isolation of graphene by Andre Geim and Konstantin Novoselov in 2004 (Novoselov et al. 2004), two-dimensional (2D) materials have become an active area of research in nanomaterials and nanotechnology due to their extraordinary properties (Patel et al. 2018; Pham et al. 2020; Thi Thu Hanh, Minh Phi & Van Hoa 2020). 2D or single-layer materials are materials resembling a large but very thin sheet consisting of single-layer atoms. These materials are very attractive and promising because of their unique electronic structures, extraordinary physical and chemical properties for use in electronics, sensor technology, catalysts, energy generation and storage, optoelectronics and spintronic (Pham et al. 2020; Yang, Jiang & Wei 2017).

Graphene, a single layer graphitic carbon in a honeycomb lattice structure is the most studied 2D material (Patel et al. 2018). The in-plane carbon-carbon bond in graphene is composed of sp^2 hybridization. This produces one σ bond and two π -bond, where the single p_z electron act as the free electron in graphene. This leads to graphene having semi-metallic properties; in other words, having zero bandgap and linear electronic dispersion at Dirac point (Novoselov et al. 2005). The formation of Dirac cone in its electronic band structure has given graphene many unique electronic properties such as high electron mobility and electrical conductivity at room temperature (Novoselov et al. 2005, 2004).

Graphene has very few crystal defects and this ensures a low level of electrical (Johnson) noise which then improved the sensitivity of the material (Schedin et al. 2007). As such, whenever there is an adsorption of molecules on the graphene sheet, either acting as a donor or acceptor, they can change the local charge carrier concentration which leads to step-like changes in resistance. Besides, since graphene is an atomic-thin layered carbon nanomaterial with a large surface-to-volume ratio, it also works as an excellent sensor because they provide a large adsorbing capacity for gas molecules and strong surface activities (Dai, Yuan & Giannozzi 2009; Leenaerts, Partoens & Peeters 2008; Yang et al. 2019). The application of graphene as a solid-state sensor to detect different gases has been widely investigated both experimentally (Schedin et al. 2007; Yang, Jiang & Wei 2017) and theoretically (Dai, Yuan & Giannozzi 2009; Leenaerts, Partoens & Peeters 2008; Wang et al. 2016).

Recently, silicene and germanene, 2D materials from the same group as graphene (group IVA) have come to the attention of researchers. Silicene has been successfully synthesized on Ag (111) substrate (Feng et al. 2012; Lalmi

et al. 2010) as well as other substrates such as zirconium diboride (Fleurence et al. 2012) and iridium (Meng et al. 2013). Similarly, germanene was also successfully grown on Pt(111) (Li et al. 2014) and Au(111) substrates (Dávila et al. 2014). Since they are having similar unique properties as graphene, basically, they are suitable in gas sensing applications as well. Interestingly, due to their buckled honeycomb structure, it is reported that they have much stronger molecules adsorption capabilities (Xia et al. 2014) as compared to their cousin graphene. This is mainly due to the sp^2 - sp^3 hybridization of Si and Ge atoms. Since then, various studies related to adsorbing gas molecules on silicene (Feng et al. 2014) and germanene (Xia et al. 2014) as well as their derivatives have been investigated to benchmark with its cousin graphene.

The release of toxic pollutants into the atmosphere which usually comes from combustion, chemical reaction or leakage from industry has become a major concern for the environment and health of the people in this world. Hazardous gases such CO, NO₂, Cl₂ and COCl₂ are among them from a long list of toxic gases. Carbon monoxide (CO) is mainly produced from improper combustion and this gas is difficult to detect because it is odourless, colourless, and tasteless. This gas is dangerous as it can displace oxygen in the blood which eventually leads to brain damage and death (Yang et al. 2019). Nitrogen dioxide (NO₂) is another pollutant that is produced mainly from combustion. This gas is usually reddish-brown with a pungent, acrid odor. Exposure to this gas can cause many respiratory issues such as lung damage and asthma. Chlorine gas (Cl₂) is a very reactive yellow-green gas at room temperature. Chlorine is commercially produced and used in many chemical industries. Accidental exposure to Cl₂ can pose a serious health issue to the eyes, skin as well as respiratory system. Besides, chlorine gas can also cause an explosion if it reacts with flammable materials. Another commonly used gas in the chemical industry is phosgene (COCl₂) which is a colourless gas with a soothing odour resembling freshly cut grass. Exposure to COCl₂ can cause suffocation which is not an immediate effect but rather a slow process (Patel et al. 2018). However, once the symptoms appear, usually it is too late for medical treatment. As such, sensitive toxic gas sensors are highly needed as a first-level detection system for the prevention of this kind of damages or even catastrophe.

In this work, in order to have a better understanding between the families of group IV 2D materials, on their gas sensing capabilities, a comparative study of their interaction with toxic gases such as CO, Cl₂, NO₂ and

COCl_2 was investigated using the first-principles method. The optimal adsorption positions and orientations of the molecules on the monolayers are determined by calculating the adsorption energy. Charge transfer, the density of state (DOS) and band diagram calculations are performed to explore the changes in their electronic and structural properties due to the influence of different adsorbed gas molecules. Meanwhile, we also evaluate the sensitivity and recovery time for the substrate in order to further look at the sensing performance of graphene, silicene, and germanene on toxic gases.

COMPUTATIONAL DETAILS

Quantum ESPRESSO software package is used to perform first-principles calculations based on density functional theory. Plane-wave pseudopotential approach, employing Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA), is used to treat the exchange and correlation potentials (Giannozzi et al. 2009). GGA is used because it will not lead to a strong bonding of the molecules and if molecules bind in GGA, they will bind in a real system (Leenaerts, Partoens & Peeters 2008). Kinetic and charge density cut off are set as 70 Ry and 560 Ry respectively, while the Monkhorst-Pack k -point mesh is set as $5 \times 5 \times 1$ to sample the Brillouin zone. These values were determined after performing convergence tests. To minimize systematic errors, the same supercells and k -point grids are used for all calculations (Dai, Yuan & Giannozzi 2009). Gaussian smearing with a width of 0.01 Ry is used to assist the convergence.

Structural optimization of the adsorption system is performed until it reached cut-off maximum force of 10^{-3} Ry/Bohr using Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm while the convergence threshold on total energy (which is the difference of the total energy between the two consecutive self-consistency cycles) is set as 10^{-4} Ry. The interaction between 2D materials and gas molecules, will involve van der Waals (vdW) interaction. This interaction is necessary to be compensated in order to provide more accurate results. Therefore, Grimme's DFT-D2 dispersion correction is employed (Grimme 2006). It should be noted that the DFT-D2 van der Waals correction might slightly overestimate the adsorption energy, possibly in the order of a few kJ/mol (Raya, Ansari & Shong 2021). In DOS calculation, the tetrahedron method is employed where the k -point is set to a denser mesh of $20 \times 20 \times 1$.

In each adsorption system, pristine graphene (Gra), silicene (Si) and germanene (Ge) are modeled in a

3×3 supercell with hexagonal structure as shown in Figure 1. Each of the supercells consists of 18 atoms and the in-plane lattice constant, a is 7.403 Å for Gra, 11.551 Å for Si and 12.15 Å for Ge. The in-plane constant is also the distance between the neighbouring gas molecules. A vacuum space of 15 Å is set in the c -axis to avoid the interaction between the adjacent units. For gas molecules namely CO, NO_2 , Cl_2 and COCl_2 adsorption on the Gra sheet, interactions are tested at three highly symmetric positions as shown in Figure 1(a) namely hollow (H), bridge (B) and top (T). For silicene and germanene, since they have buckled structure, the top position has two possible sites namely $T1$ and $T2$ which represent atom that is in-plane and buckled position, respectively, as shown in Figure 1(b) and 1(c).

We investigate the interaction of gas molecules with the monolayer sheets at all possible adsorption sites. Different orientations of gas molecules, as shown in Figure 1(d), are considered for the adsorption process. Based on the position and orientation, adsorption of gas molecules in each monolayer that produces minimum total energy for the system are then chosen. These adsorption systems are then relaxed to produce the optimized structure for the adsorbent-adsorbate system. Adsorption energy (E_{ad}), which reflects the interaction between the material and the adsorbate, was calculated using

$$E_{ad} = E_{\text{monolayer/adsorbate}} - E_{\text{monolayer}} - E_{\text{adsorbate}} \quad (1)$$

where $E_{\text{monolayer}}$ represents the energy of the monolayer without adsorbate; $E_{\text{monolayer/adsorbate}}$ is the energy of the optimized structure of gas adsorbed on monolayer and $E_{\text{adsorbate}}$ is the energy of the isolated gas molecule. The adsorption energy of foreign species on the monolayer is an important criterion to evaluate its chemical reactivity (Yang et al. 2019). To find the total energy of the isolated gas molecule, a cubic supercell of $10 \times 10 \times 10$ Å is used to model them. Kinetic cut-off is set as 50 Ry while the k -point mesh is $2 \times 2 \times 2$. A negative E_{ad} value will indicate that the adsorption of the gas molecule on the surface of the monolayer is energetically favourable while a positive value means unstable. The greater the absolute value of the adsorption energy the more stable the system (Wang et al. 2016) while a smaller value means less stability of the adsorption system.

Once the preferred sites and orientation of the adsorbates are determined from the adsorption process,

band structures and density of state are calculated and analyzed. To study the charge transfer Q , we utilize Lowdin population analysis (Lowdin 1970) which focuses on the valence charge density only. Studying the charge transfer is important as it is closely related to the interaction between the gas molecule and monolayers. Charges from the molecules as well as the adsorbed system are computed and compared. The difference between the charges generally corresponds to the trends of charge transfer.

RESULTS AND DISCUSSION

To ensure the accuracy of our computation, the optimized

structure of 1×1 monolayer for pristine graphene (Gra), silicene (Si) and germanene (Ge) are computed and compared with other values from various literature. From Table 1, it is found that all the computed structural parameters of the monolayers are within less than 5% uncertainty, suggesting that the adopted methods are good enough to describe the behaviour and properties of this research. Hence, based on these optimized structural parameters, the 3×3 supercells are modelled for the gas adsorption system with coverage of one molecule per 18 atoms of the monolayer or 0.056 ML. Figure 3 shows the density of state (DOS) and the band structure for the pristine 3×3 monolayers for comparison with the adsorption systems later.

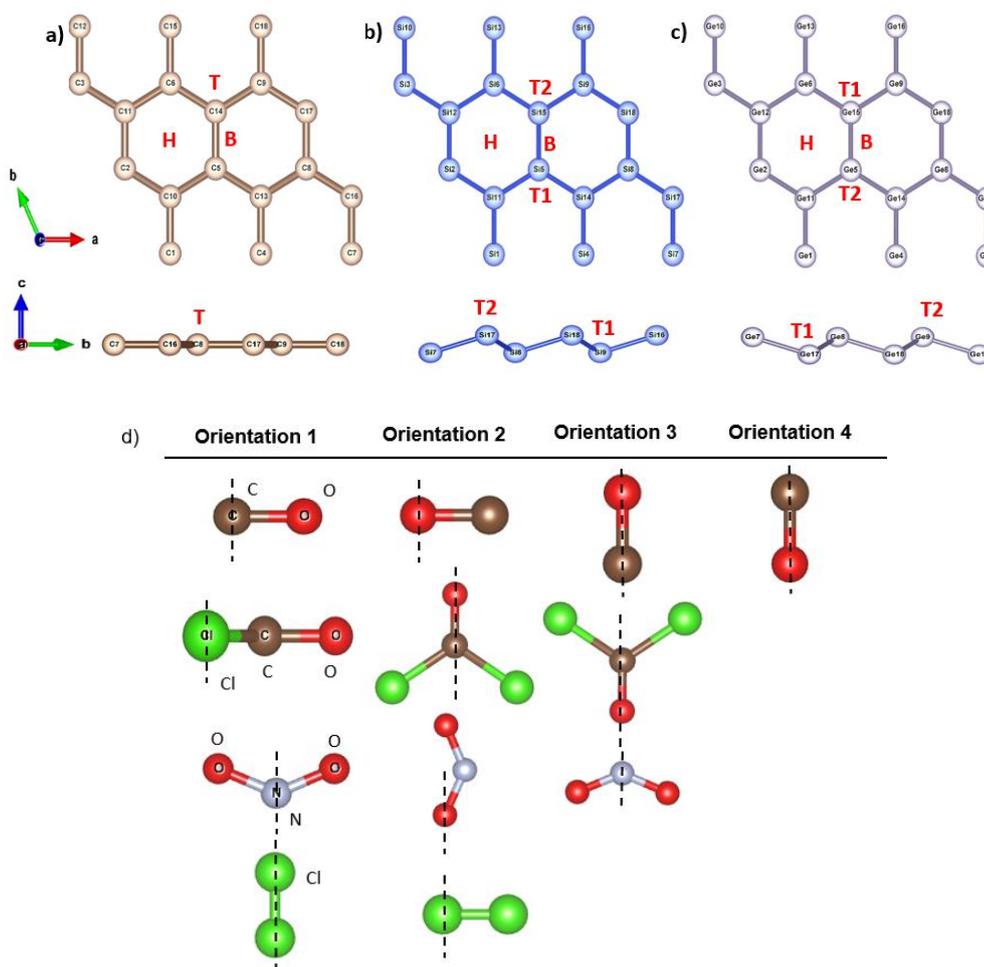


FIGURE 1. Top and side view for 3×3 supercells of a) graphene (Gra) b) silicene (Si) and c) germanene (Ge) with the preferential site for adsorption. d) Different orientations of gas molecules (side view) used in the adsorption process. Colour brown, red, grey and green represents C, O, N, and Cl, respectively. The dashed line represents the atom that adsorbs at the particular symmetry site

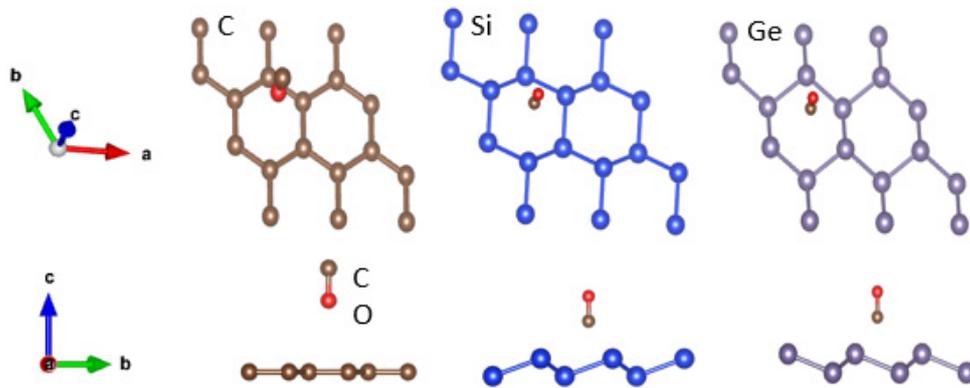


FIGURE 2. Adsorption at hollow site for Gra/CO, Si/CO and Ge/CO with different orientation from top and side view

TABLE 1. Comparison of lattice constant a , bond length d and buckled height Δx computed using GGA with other results value from different literature

Details	a (Å)		d (Å)		Δx (Å)	
	Current work	Literature	Current work	Literature	Current work	Literature
Graphene	2.47	2.463 (Yu et al. 2014) 2.47 (Chan, Neaton & Cohen 2008; Feng et al. 2014)	1.425	1.43 (Hamid et al. 2021; Wang et al. 2016)	-	-
Silicene	3.85	3.8 (Yu et al. 2014) 3.88 (Feng et al. 2014)	2.272	2.278 (Yu et al. 2014) 2.29 (Feng et al. 2014)	0.469	0.451 (Yu et al. 2014) 0.46 (Feng et al. 2014)
Germanene	4.05	4.058 (Xia et al. 2014)	2.439	2.41 (Thi Thu Hanh, Minh Phi & Van Hoa 2020)	0.692	0.66 (Thi Thu Hanh, Minh Phi & Van Hoa 2020)

TABLE 2. Most stable position and orientation P/O, adsorption energy E_{ad} , height from the $H_{adsorbent-gas}$, charge transfer to the molecule Q_{tran} and band gap E_g for the most stable configuration for adsorbate on the monolayers

Adsorption system	P/O	(eV)	(Å)	(e)	(meV)
Gra/CO	H/O4	-0.077	3.082	0.0018	1.0
Si/CO	H/O3	-0.113	3.065	0.0538	41.5
Ge/CO	H/O3	-0.155	3.054	0.0612	54.1
Gra/NO ₂	T/O1	-0.310	2.942	0.1873	7.6
Si/NO ₂	T2/O1	-1.344	1.954	0.4298	64.2
Ge/NO ₂	T2/O1	-1.136	2.142	0.3976	67.0
Gra/Cl ₂	T/O1	-0.197	3.005	0.0404	10.6
Si/Cl ₂	T2/O1	-0.918	2.135	0.5658	26.7
Ge/Cl ₂	T2/O1	-0.697	2.333	0.525	4.1
Gra/COCl ₂	H/O1	-0.283	3.347	0.0073	13.7
Si/COCl ₂	T2/O1	-0.186	3.523	0.0014	1.3
Ge/COCl ₂	T2/O1	-0.187	3.543	-0.0023	8.8

From the adsorption process, four gas molecules are adsorbed on three different monolayers or substrates. Table 2 shows the adsorption energy for the most stable adsorption site and orientation for the adsorption systems. In the CO adsorption process, we found that the hollow site is the preferred binding site for all the monolayers even though the orientations are different (as shown in Figure 2). Both Si and Ge prefer orientation 3 while Gra is orientation 4. The height of the molecules from the surfaces is quite similar ≈ 3.0 Å which shows a 24% increase from the initial height of 2.5 Å. Clearly, this shows that there is a repulsion force due to the mutual repulsion between electron clouds of atoms. This prompts that CO is physically adsorbed rather than chemisorbed in this process. Due to the weak adsorption energy, there are no changes to the structures of the monolayers but a small elongation of 0.01 Å from the initial bond length of 1.13 Å is recorded for all the monolayers. There is a very weak charge transfer of 0.0018 e, 0.0538 e and 0.0612 e from the monolayers namely Gra, Si and Ge to the molecules. With the weak charge transfer and low, this can further show that CO undergoes physisorption on the monolayers.

For molecule NO_2 , it is found that it binds with orientation 1 at top site of Gra and $T2$ site for both Si and Ge monolayer. Due to stronger binding energy, as compared to CO, N atom is pulled towards the monolayers where we can see a decrease in angle between O-N-O. Initially, the angle is at 134° , but after adsorption and relaxation, the angle is reduced to 130° in Gra/ NO_2 and 125° in both Si/ NO_2 and Ge/ NO_2 . The bond length O-N elongated from 1.19 Å to 1.22 Å (Gra/ NO_2), 1.24 Å (Si/ NO_2) and 1.23 Å (Ge/ NO_2). The adsorption of NO_2 on Gra is at moderate adsorption energy of -0.31 eV while at strong adsorption energy of -1.344 eV at silicene and -1.136 eV at Ge. From $H_{\text{adsorbent-gas}}$, we found that NO_2 molecule is repelled from the Gra monolayer changing from an initial 2.5 Å to an optimized position of 2.94 Å. This suggests that they are bound physically by van der Waals force. As for Si and Ge layers, we find that they are bounded closer to the layer with a 22% and 14.4% decrease in height. The Si and Ge monolayer structures experienced small changes to the sites in which the molecule is adsorbed where their corresponding bonds experience increase in bond length by 2.2% and 1.6%, respectively. There is a large charge transferred from the monolayer to the molecule. From Table 2, we found that 0.1873 e, 0.4298 e, and 0.3976 e charges are transferred from the Gra, Si and Ge monolayers to the molecule, respectively. Due to high adsorption energy as well as

high charge transfer, NO_2 are chemisorbed to silicene and germanene layers. We can say that both of the monolayers are strongly reactive to the gas molecule.

On the other hand, we found that Cl_2 has a very strong binding energy in Si (0.918 eV) followed by Ge (0.697 eV) and is weakly attached to Gra (0.197 eV). The molecule binds to $T2$ site for both Si and Ge while at the top site for Gra in orientation 1. Due to the strong adsorption energy, the height of the molecule from the surface is reduced by 0.365 Å for Si monolayer followed by 0.167 Å for Ge. However, for Gra, it is increased by 0.505 Å. Bond length of Cl-Cl increased from 1.99 Å (Liu et al. 2014) (bond length of gas Cl_2 before adsorption) to 2.602 Å (Si), 2.449 Å (Ge) and 2.024 Å (Gra). The increase in bond length makes it easier to dissociate into Cl atom. According to Li et al. (2016), chlorination of monolayer silicene can happen when exposed to low coverage of gas chlorine where they tend to adsorb on the top of the buckled atom. In this case, chlorination happens in Si and Ge but not Gra. On the other hand, the binding energy is weak in Gra, there are no changes to its structure. However, for Si and Ge, both monolayers expanded 2.4% and 1.1%, respectively, at the preferential sites. There is a large charge transfer from monolayer to molecules 0.5658 e (Si) and 0.525 e (Ge). Since Gra/ Cl_2 is not strongly bound, only a small quantity of charge 0.0404 e is transferred between the substrate and the adsorbate. Based on the charge transfer, the height of gas molecules as well as the binding energy, we can tell that Cl_2 is chemically adsorbed on Si and Ge while physically adsorbed for Gra (Liu et al. 2014).

In phosgene adsorption, it is found that it binds at the hollow site of Gra while at $T2$ for Si and Ge with orientation 1. E_{ad} for Si and Ge are similar which is around -0.18 eV, while it is -0.283 eV for Gra. The height of the molecule is more than 3.3 Å from the monolayer suggesting that the adsorbate is physically adsorbed on the surface. This can be further strengthened by the low charge transfer recorded as they are less than 0.008 e for all the cases (Table 2). As for the geometrical structures, we found that there are basically no changes to the monolayer upon adsorption of the adsorbates and the adsorbate itself has less than 1% changes at the Cl-C bond.

To further study their reactivity and electronic properties, the total density of states (DOS), partial density of states (PDOS) and their band diagram are computed. For CO adsorption, DOS and band diagram are shown in Figure 4. For DOS of CO on Gra, we can see that the Dirac point of Gra (where DOS is zero) is visible. A

comparison can be made with DOS from Figure 3 for pristine graphene. Orbital hybridization happens at the -4.8 eV and 2.2 eV by p -orbital of CO and p -orbital of Gra, but since they are far away from the Fermi level, the Gra state is nearly unaltered by the adsorption of CO. Similar observations are found for CO adsorption on Si and Ge where there is no evidence of orbital hybridization happens near the Fermi level. From the band diagram, we found that there are tiny band gaps opening at all the substrates namely 1.3, 41.5 and 54.1 meV for Gra, Si and Ge, respectively. Based on the bandgap values, Gra/CO is considered as a semimetal while for Si/CO and Ge/CO, they are considered as very weak semiconductors. It should be noted that PBE method usually underestimates the band gaps of semiconductor materials which means that the value could be higher than the actual values. Although underestimation exists, this does not influence the relative comparison (Ma et al. 2015).

NO₂ is paramagnetic in its gaseous form meaning it has one unpaired electron. From the DOS in Figure 5, there is hybridization between O $2p$ -orbital from NO₂ with $2p$ -orbital of the substrates namely Gra, Si, and Ge near the Fermi level. This process has altered the substrate initial state causing the Fermi level to shift towards the valence bands inferring NO₂ acts as an acceptor which induces hole charge carriers. In this process, NO₂ can be considered as a p -type dopant. Based on the band diagram, an impurity band can be seen in between the conduction and valence bands (compare with the band diagram in Figure 3). This band is actually due to the O $2p$ -orbital of NO₂ as can be seen from the DOS. There are small bandgaps recorded in the band diagram with 7.6, 64.2 and 67 meV opening for Gra, Si and Ge, respectively. We found that Gra, Si and Ge are very sensitive to NO₂ molecules.

Figure 6 shows the DOS and band diagram of chlorine gas adsorption on the monolayers. From the figure, we see that for Ge/Cl₂ adsorption, orbitals are mixing between Cl $3p$ -orbital and Ge $4p$ -orbital at -2.946, -0.746 and -0.746 eV at the valence band. For Gra/Cl₂, hybridization occurs at -2.801, -2.501 and 0.765 eV between Cl $3p$ -orbital and Gra $2p$ -orbital. Although some of these hybridizations happen near Fermi level, it turns out that the Dirac point is unaffected. However, for Si/Cl₂, Fermi level is shifted towards the valence band due to hybridization at 0 eV between Si and Cl₂ orbitals. This indicates that Cl₂ can be a p -dopant which is similar to NO₂. This might be also due to chlorination process as mentioned in Li et al. (2016). Large charge transfer can be seen from the adsorption process and this prompts

that they are binding together via covalent bonding. The impurity band line from Cl₂ stems from Cl $3p$ -orbital can be seen crossing between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the substrates.

From the DOS analysis as can be seen from Figure 7 on COCl₂ adsorption, we see that Gra is more reactive than its counterpart Si and Ge. This is because hybridizations between Cl $3p$ -orbital, O $2p$ -orbital and C $2p$ -orbital at -3.515 eV at the valence band and 0.499 eV at the conduction band are stronger than those recorded in Si/COCl₂ and Ge/COCl₂. Due to all orbital mixing, charge transfer between monolayer and molecule increases (Table 2) although in a very small amount. Since charge transfer and are particularly weak, from the band diagram, basically the Dirac point is unaltered for all the substrate. A tiny bandgap of 13.7, 1.3 and 8.8 meV for Gra, Si and Ge, respectively, are measured in the adsorption process.

There are a few evaluations that can be used to check on the capabilities of the monolayer as a gas sensor (Tian, Liu & Yu 2018). However, in this work, we only look at the electrical conductivity and recovery time. In their initial state (without any toxic gas adsorption), Gra, Si and Ge monolayers exhibit a very high conductivity at the Dirac point because of linear energy dispersion and having relativistic massless Dirac fermions. When gas molecules are adsorbed on the monolayer, they affect the local charge carrier concentration and as such, change the conductivity of the monolayer. The electrical conductivity of materials is proportional to a factor related to the bandgap expresses as (Li 2012; Zhang et al. 2021).

$$\sigma \propto e^{-E_g/2k_B T} \quad (2)$$

where E_g is the bandgap; k_B is the Boltzmann constant; and T is the temperature in Kelvin. Since resistivity is just the inverse of conductivity, the sensor response or sensitivity, S (Zhang et al. 2015) is universally defined as

$$S = \left(\frac{\Delta R}{R_{initial}} \right) \times 100\% \quad (3)$$

where ΔR is the difference of resistance before and after adsorption and $R_{initial}$ is the resistance before adsorption. Based on Equations (2) and (3) as well as bandgaps as shown in Table 2, we can make a crude estimation for the sensitivity of the substrate on the toxic gases. We found

that Si and Ge monolayers are more sensitive to CO and NO₂ gas molecules than to other toxic gases. Silicene also shows a tendency to gas Cl₂. As for Gra, it is most sensitive to COCl₂.

The recovery time of a gas sensor is also a very important parameter that can be considered. Generally, the recovery time of a sensor reflects the desorb speed of the gas sensor to the detected gas (Tian, Liu & Yu 2018). If the time is shorter, this means that the performance is better but sometimes in practical engineering applications, if the recovery time is too short, it will be difficult for data collection during gas detection (Patel et al. 2018; Zhang et al. 2021). Theoretically, the recovery time of the sensor follows the well-known Arrhenius

expression given as

$$\tau = V^{-1} e^{\left(\frac{E_a}{k_B T}\right)} \quad (4)$$

where V^{-1} corresponds to the attempt frequency which is related to the atomic vibration around 10¹²-10¹³ per second (Sholl & Steckel 2009). As for E_a (eV), this is the energy barrier that needs to be overcome for desorption which can be set as the opposite of E_{ad} (Patel et al. 2018; Zhang et al. 2021). When the adsorption energy is high, it will take more time for the molecule to be desorbed from the layer. Table 3 shows the computed recovery time for the adsorption of toxic gases on the monolayers with increasing temperature.

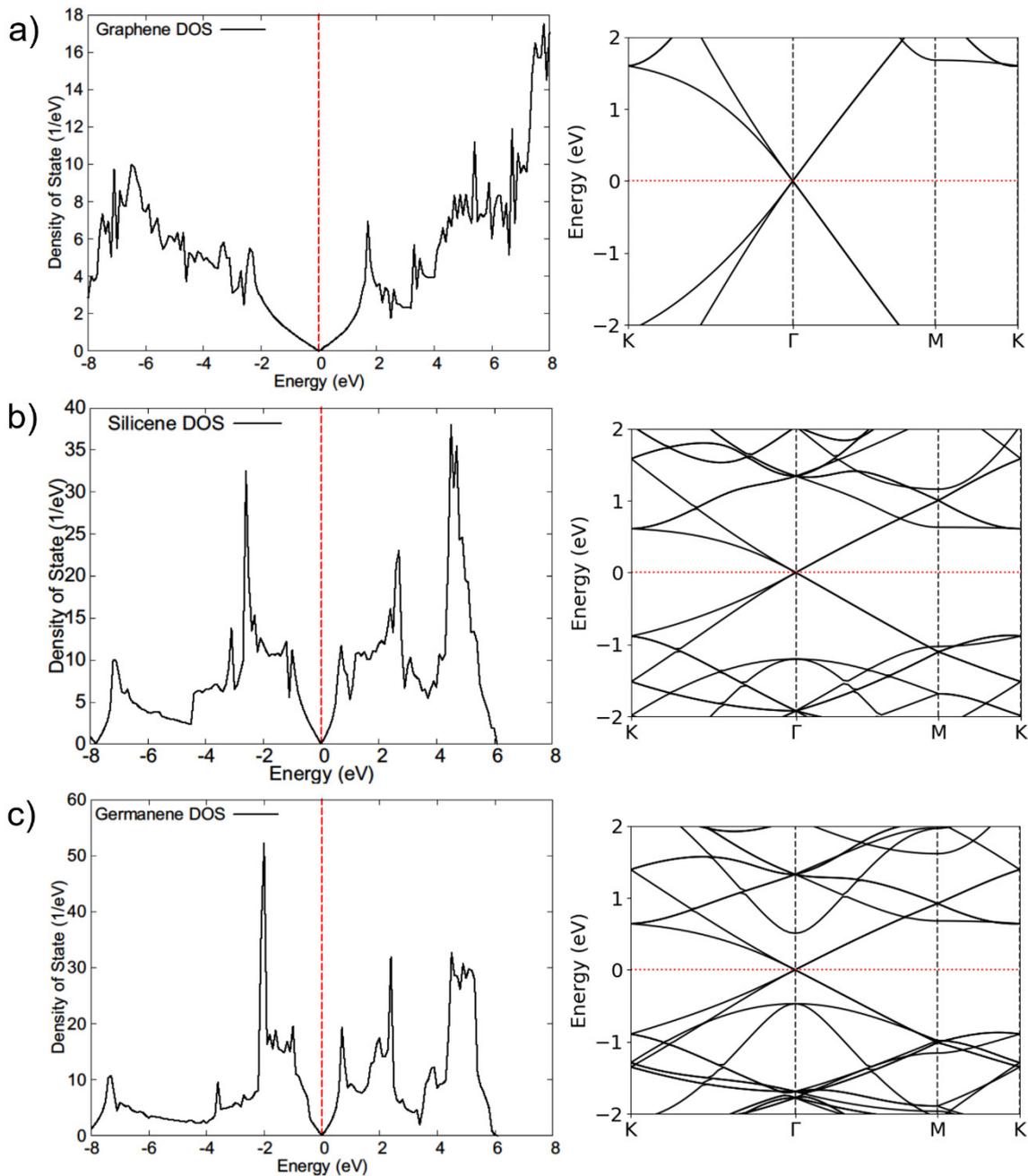


FIGURE 3. Density of state and band diagram for pristine a) graphene b) silicene and c) germanene 3×3 monolayers. The red dashed line shows the Fermi level

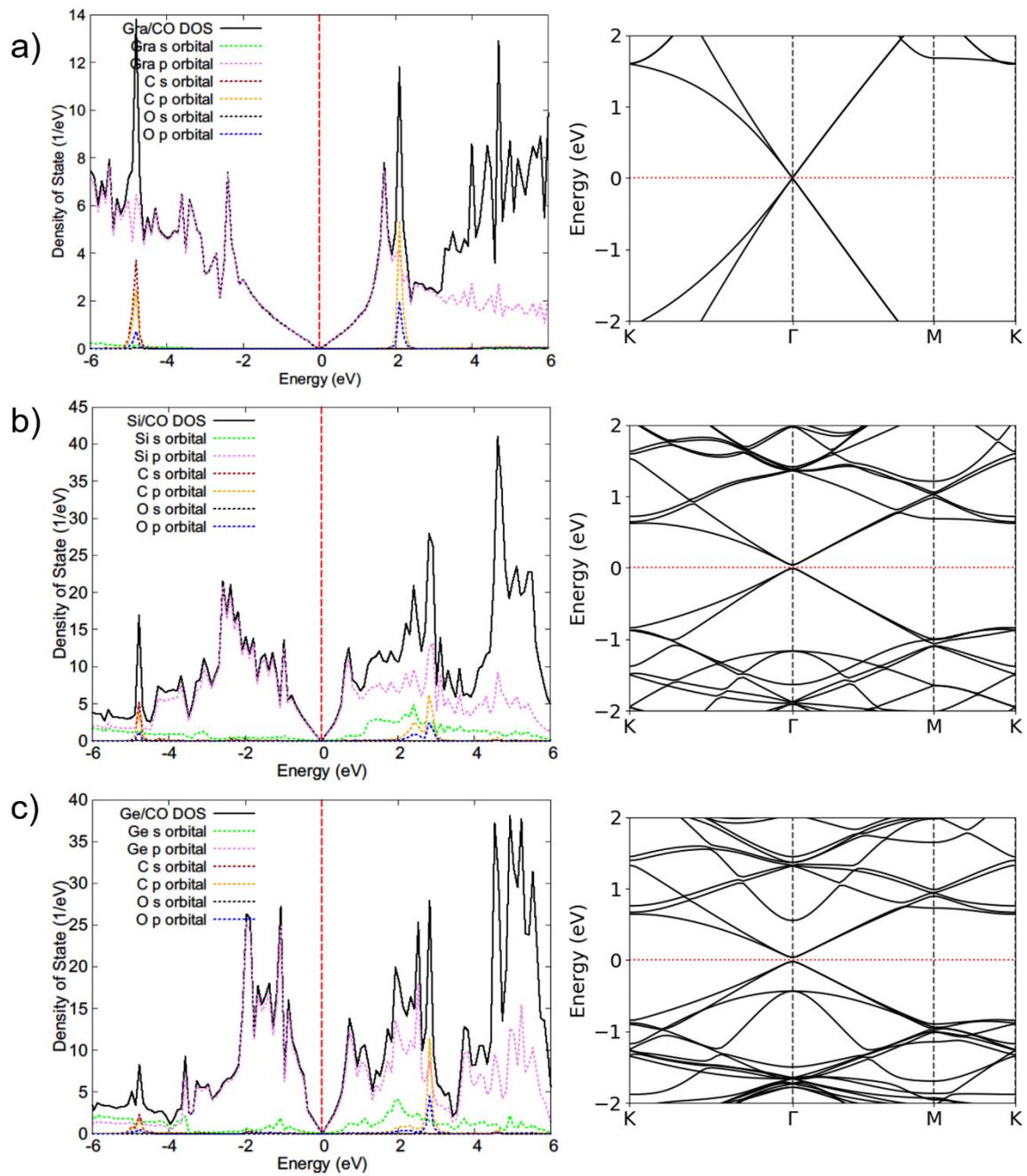


FIGURE 4. Density of state and band diagram for adsorption of CO gas molecule on a) graphene, b) silicene and c) germanene monolayer

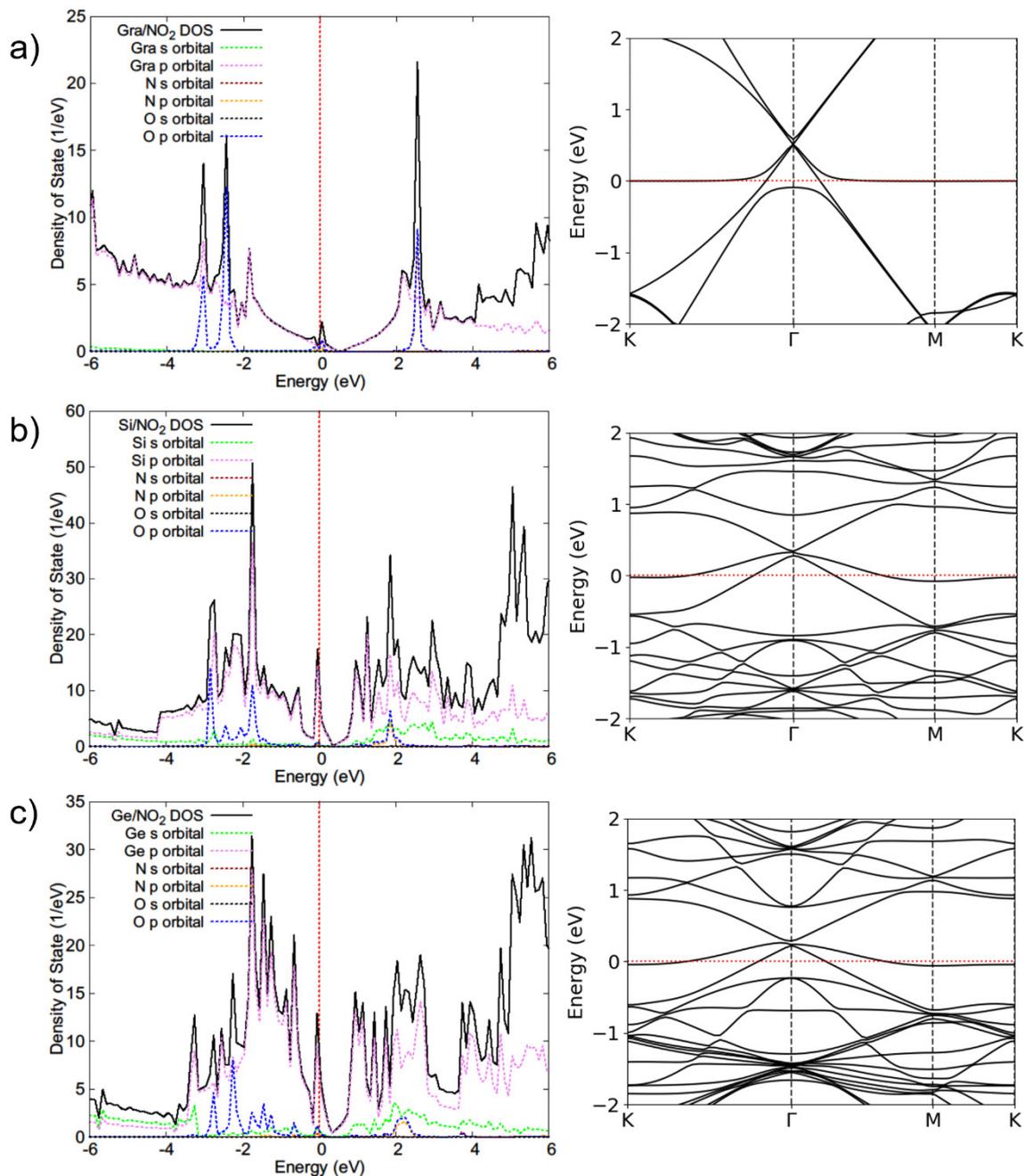


FIGURE 5. Density of state and band diagram for adsorption of NO_2 gas molecule on a) graphene, b) silicene and c) germanene monolayer

The results show that at room temperature, all the systems had recovery time in nanosecond except for Si/NO_2 , Ge/NO_2 , Si/Cl_2 , and Ge/Cl_2 . Si/NO_2 and Ge/NO_2 system has a very long recovery time at room

temperature making it impractical as a gas sensor. However, as the operating temperature increase, e.g., at 500 K, NO_2 molecule only takes around 35.3 s and 0.282 s, respectively, to dispatch itself from the monolayer. A more practical recovery time is shown by the Si and Ge for adsorbed gas chlorine by which requires only 44 min and half a second to recover.

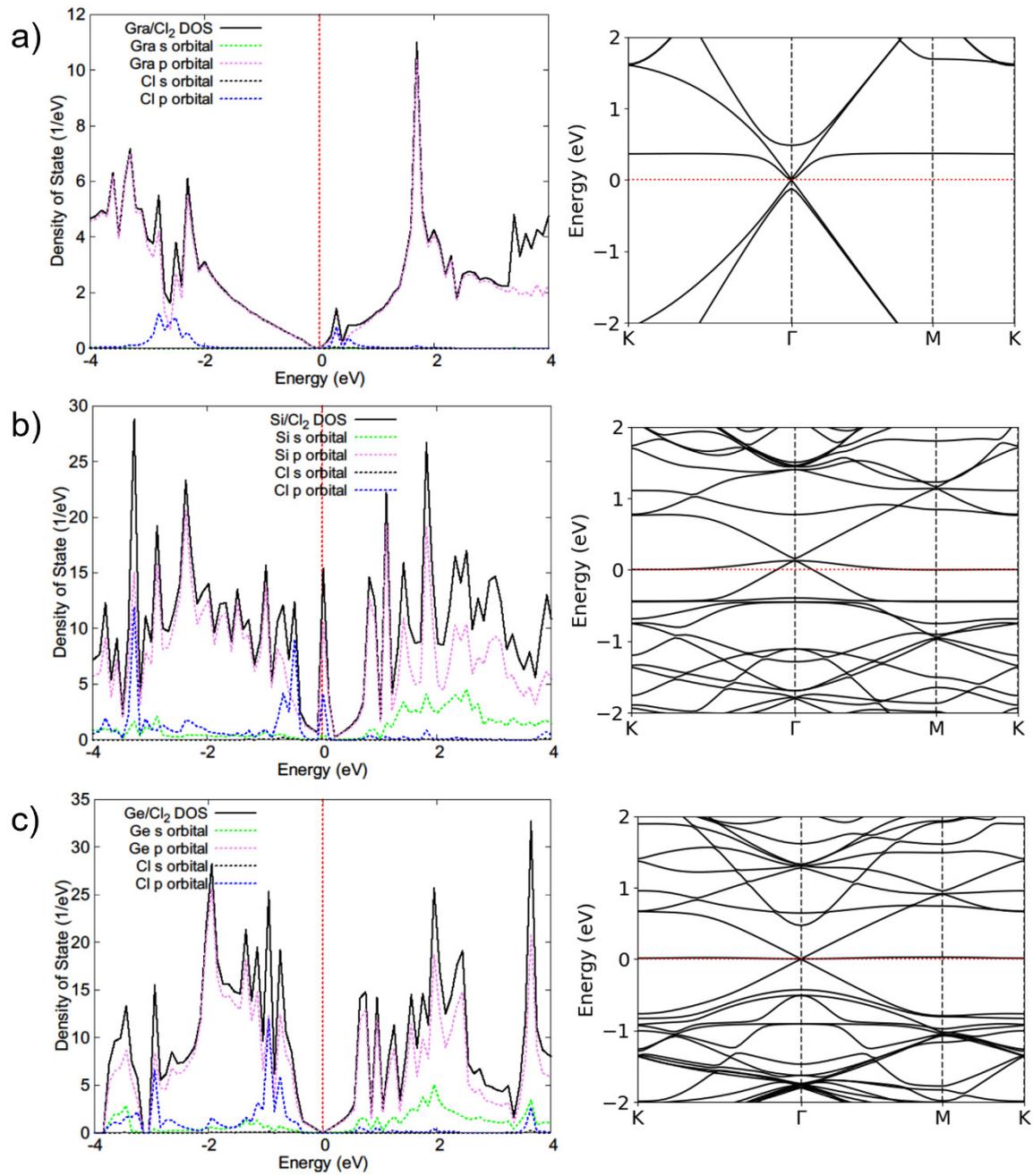


FIGURE 6. Density of state and band diagram for adsorption of Cl_2 gas molecule on a) graphene, b) silicene and c) germanene monolayer

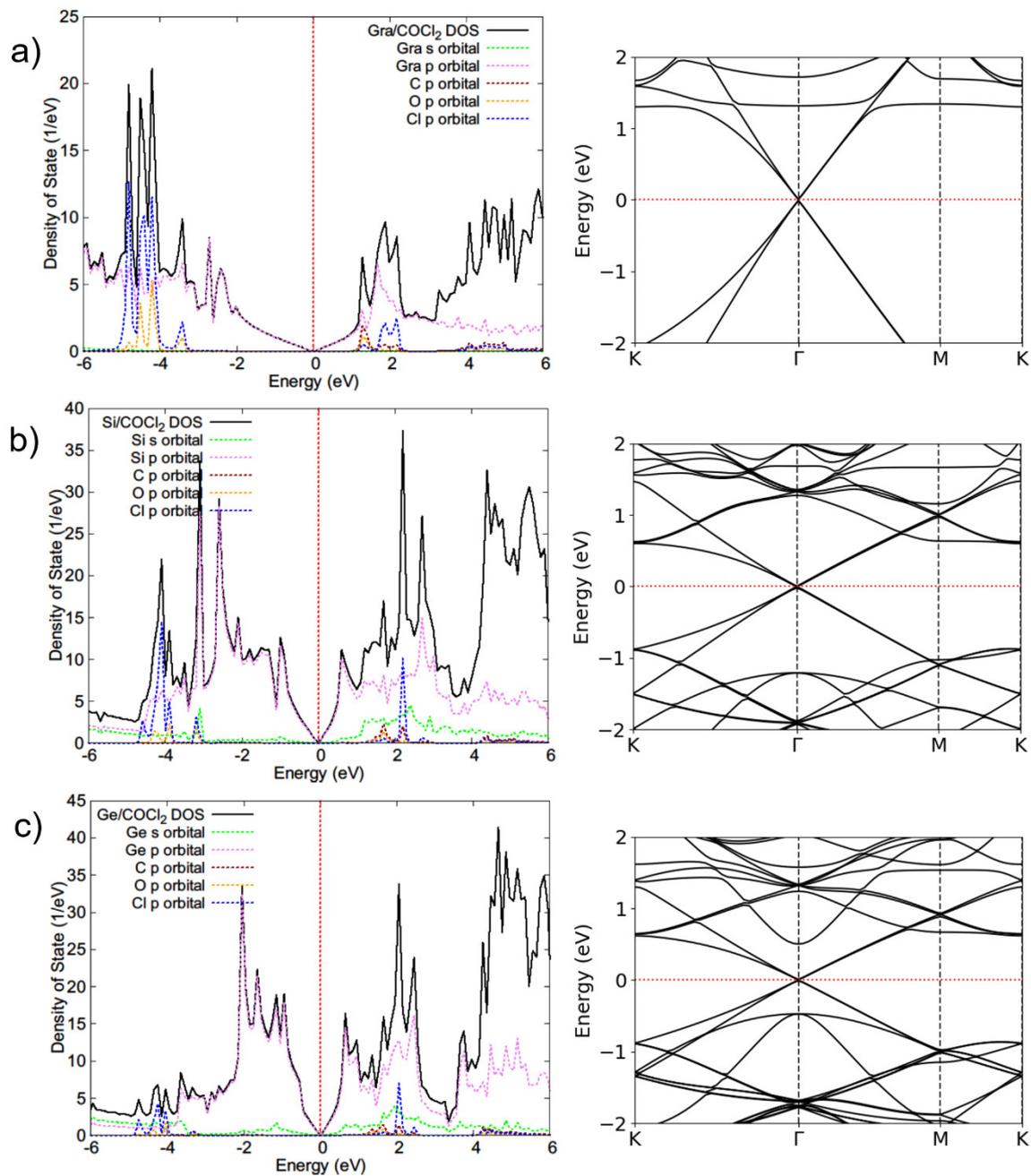


FIGURE 7. Density of state and band diagram for adsorption of COCl₂ gas molecule on a) graphene, b) silicene and c) germanene monolayer

TABLE 3. Recovery time for adsorption system

Adsorption System	τ (s)			
	300 K	400 K	500 K	600 K
Gra/CO	1.97×10^{-11}	9.34×10^{-12}	5.97×10^{-12}	4.43×10^{-12}
Si/CO	7.91×10^{-11}	2.65×10^{-11}	1.37×10^{-11}	8.90×10^{-12}
Ge/CO	4.02×10^{-10}	8.97×10^{-11}	3.65×10^{-11}	2.00×10^{-11}
Gra/NO ₂	1.61×10^{-7}	8.05×10^{-9}	1.33×10^{-9}	4.02×10^{-10}
Si/NO ₂	3.79×10^{10}	8.59×10^4	35.3	0.195
Ge/NO ₂	1.22×10^7	2.06×10^2	0.282	3.49×10^{-3}
Gra/Cl ₂	2.04×10^{-9}	3.04×10^{-10}	9.67×10^{-11}	4.52×10^{-11}
Si/Cl ₂	2.64×10^3	0.369	1.79×10^{-3}	5.14×10^{-5}
Ge/Cl ₂	0.512	6.05×10^{-4}	1.06×10^{-5}	7.16×10^{-7}
Gra/COCl ₂	5.68×10^{-8}	3.68×10^{-9}	7.12×10^{-10}	2.38×10^{-10}
Si/COCl ₂	1.33×10^{-10}	2.21×10^{-10}	7.50×10^{-10}	3.65×10^{-10}
Ge/COCl ₂	1.39×10^{-9}	2.27×10^{-10}	7.67×10^{-11}	3.72×10^{-11}

CONCLUSIONS

A comparative study of interaction with toxic gases such as CO, Cl₂, NO₂, and COCl₂ and the family of group IVA 2D materials namely Gra, Si, and Ge has been carried out. First-principle calculation based on DFT computed using Quantum ESPRESSO has been used to calculate the energy, geometrical structures and electronic properties of the adsorption system. Upon adsorption of CO, it is found that Si and Ge are more sensitive than Gra in detecting the toxic gas mainly because of their bigger bandgap. They undergo a weak physical interaction with low adsorption energy between 0.07- 0.16 eV. Recovery times are within 0.02 - 0.4 ns. As for NO₂, Gra has moderate adsorption energy while Si and Ge recorded strong adsorption energy. NO₂ molecule adsorbed chemically onto Si and Ge, prompting a strong orbital hybridization near the Fermi level and causing it to shift towards the valence band. Si and Ge are more sensitive to NO₂ as compared to Gra. However, they have a long recovery time while Gra is

within microsecond. This shows that Gra is better as a gas sensor while Si and Ge are good for scavenging. In chlorine gas case, Si is the most sensitive followed by Ge. Cl₂ is chemisorbed onto Si and Ge while physically adsorbed in Gra. Orbital hybridization happens near the Fermi level causing a Fermi level shift toward the valence band for Si but unaffected for Gra and Ge. Gra has the best recovery time which is around 2 ns followed by Ge (0.5 s) and Si (44 min). The physical adsorption of gas phosgene on monolayers has shown that Gra is better in sensing its presence than Si and Ge. This is mainly due to stronger hybridization near Fermi level which causes a bigger bandgap than others. The recovery time for them ranges from 0.1 - 56 ns.

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REFERENCES

- Chan, K.T., Neaton, J.B. & Cohen, M.L. 2008. First-principles study of metal adatom adsorption on graphene. *Physical Review B* 77(23): 235430.
- Dai, J., Yuan, J. & Giannozzi, P. 2009. Gas adsorption on graphene doped with B, N, Al, and S: A theoretical study. *Applied Physics Letters* 95(23): 232105.
- Dávila, M.E., Xian, L., Cahangirov, S., Rubio, A. & Le Lay, G. 2014. Germanene: A novel two-dimensional germanium allotrope akin to graphene and silicene. *New Journal of Physics* 16(9): 095002.
- Feng, B., Ding, Z., Meng, S., Yao, Y., He, X., Cheng, P., Chen, L. & Wu, K. 2012. Evidence of silicene in honeycomb structures of silicon on Ag(111). *Nano Letters* 12(7): 3507-3511.
- Feng, J.W., Liu, Y.J., Wang, H.X., Zhao, J.X., Cai, Q.H. & Wang, X.Z. 2014. Gas adsorption on silicene: A theoretical study. *Computational Materials Science* 87: 218-226.
- Fleurence, A., Friedlein, R., Ozaki, T., Kawai, H., Wang, Y. & Yamada-Takamura, Y. 2012. Experimental evidence for epitaxial silicene on diboride thin films. *Physical Review Letters* 108(24): 245501.
- Giannozzi, P., Baroni, S., Bonini, N., Calandra, M., Car, R., Cavazzoni, C., Ceresoli, D., Chiarotti, G.L., Cococcioni, M., Dabo, I., Dal Corso, A., de Gironcoli, S., Fabris, S., Fratesi, G., Gebauer, R., Gerstmann, U., Gougoussis, C., Kokalj, A., Lazzeri, M., Martin-Samos, L., Marzari, N., Mauri, F., Mazzarello, R., Paolini, S., Pasquarello, A., Paulatto, L., Sbraccia, C., Scandolo, S., Sclauzero, G., Seitsonen, A.P., Smogunov, A., Umari, P. & Wentzcovitch, R.M. 2009. QUANTUM ESPRESSO: A modular and open-source software project for quantum simulations of materials. *Journal of Physics: Condensed Matter* 21(39): 395502.
- Grimme, S. 2006. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *Journal of Computational Chemistry* 27(15): 1787-1799.
- Hamid, M.A.B., Chan, K.T., Raymond Ooi, C.H., Zainuddin, H., Mohd Shah, N. & Shahrol Nizam, N.N. 2021. Structural stability and electronic properties of graphene/germanene heterobilayer. *Results in Physics* 28: 104545.
- Lalmi, B., Oughaddou, H., Enriquez, H., Kara, A., Vizzini, S., Ealet, B. & Aufray, B. 2010. Epitaxial growth of a silicene sheet. *Applied Physics Letters* 97(22): 223109.
- Leenaerts, O., Partoens, B. & Peeters, F.M. 2008. Adsorption of H₂O, NH₃, CO, NO₂, and NO on graphene: A first-principles study. *Physical Review B* 77(12): 125416.
- Li, L., Lu, S.Z., Pan, J., Qin, Z., Wang, Y.Q., Wang, Y., Cao, G.Y., Du, S. & Gao, H.J. 2014. Buckled germanene formation on Pt(111). *Advanced Materials* 26(28): 4820-4824.
- Li, S.S. 2012. *Semiconductor Physical Electronics*. 2nd ed. Springer Science & Business Media.
- Li, W., Sheng, S., Chen, J., Cheng, P., Chen, L. & Wu, K. 2016. Ordered chlorinated monolayer silicene structures. *Physical Review B* 93(15): 155410.
- Liu, X.Y., Zhang, J.M. & Xu, K.W. 2014. Chlorine molecule adsorbed on graphene and doped graphene: A first-principle study. *Physica B: Condensed Matter* 436: 54-58.
- Lowdin, P.O. 1970. *Advances in Quantum Chemistry*. Vol. 5. Elsevier.
- Ma, L., Zhang, J.M., Xu, K.W. & Ji, V. 2015. A first-principles study on gas sensing properties of graphene and Pd-doped graphene. *Applied Surface Science* 343: 121-127.
- Meng, L., Wang, Y., Zhang, L., Du, S., Wu, R., Li, L., Zhang, Y., Li, G., Zhou, H., Hofer, W.A. & Gao, H.J. 2013. Buckled silicene formation on Ir(111). *Nano Letters* 13(2): 685-690.
- Novoselov, K.S., Geim, A.K., Morozov, S.V., Jiang, D., Katsnelson, M.I., Grigorieva, I.V., Dubonos, S.V. & Firsov, A.A. 2005. Two-dimensional gas of massless Dirac fermions in graphene. *Nature* 438(7065): 197-200.
- Novoselov, K.S., Geim, A.K., Morozov, S.V., Jiang, D., Zhang, Y., Dubonos, S.V., Grigorieva, I.V. & Firsov, A.A. 2004. Electric field effect in atomically thin carbon films. *Science* 306(5696): 666-669.
- Patel, K., Roondhe, B., Dabhi, S.D. & Jha, P.K. 2018. A new flatland buddy as toxic gas scavenger: A first principles study. *Journal of Hazardous Materials* 351: 337-345.
- Pham, K.D., Ly, T.H., Vu, T.V., Hai, L.L., Nguyen, H.T.T., Le, P.T.T. & Khyzhun, O.Y. 2020. Gas adsorption properties (N₂, H₂, O₂, NO, NO₂, CO, CO₂, and SO₂) on a Sc₂CO₂ monolayer: A first-principles study. *New Journal of Chemistry* 44(43): 18763-18769.
- Raya, S.S., Ansari, A.S. & Shong, B. 2021. Adsorption of gas molecules on graphene, silicene, and germanene: A comparative first-principles study. *Surfaces and Interfaces* 24: 101054.
- Schedin, F., Geim, A.K., Morozov, S.V., Hill, E.W., Blake, P., Katsnelson, M.I. & Novoselov, K.S. 2007. Detection of individual gas molecules adsorbed on graphene. *Nature Materials* 6(9): 652-655.
- Sholl, D.S. & Steckel, J.A. 2009. *Density Functional Theory: A Practical Introduction*. John Wiley & Sons.
- Thi Thu Hanh, T., Minh Phi, N. & Van Hoa, N. 2020. Hydrogen adsorption on two-dimensional germanene and its structural defects: An *ab initio* investigation. *Physical Chemistry Chemical Physics* 22(14): 7210-7217.
- Tian, W., Liu, X. & Yu, W. 2018. Research progress of gas sensor based on graphene and its derivatives: A review. *Applied Sciences* 8(7): 1118.
- Wang, W., Zhang, Y., Shen, C. & Chai, Y. 2016. Adsorption of CO molecules on doped graphene: A first-principles study. *AIP Advances* 6(2): 025317.
- Xia, W., Hu, W., Li, Z. & Yang, J. 2014. A first-principles study of gas adsorption on germanene. *Physical Chemistry Chemical Physics* 16(41): 22495-22498.

- Yang, S., Jiang, C. & Wei, S.H. 2017. Gas sensing in 2D materials. *Applied Physics Reviews* 4(2): 021304.
- Yang, S., Lei, G., Xu, H., Xu, B., Li, H., Lan, Z., Wang, Z. & Gu, H. 2019. A DFT study of CO adsorption on the pristine, defective, In-doped and Sb-doped graphene and the effect of applied electric field. *Applied Surface Science* 480: 205-211.
- Yu, S., Li, X.D., Wu, S.Q., Wen, Y.H., Zhou, S. & Zhu, Z.Z. 2014. Novel electronic structures of superlattice composed of graphene and silicene. *Materials Research Bulletin* 50: 268-272.
- Zhang, X., Wang, J., Chen, D. & Liu, L. 2021. The adsorption performance of harmful gas on Cu doped WS₂: A first-principle study. *Materials Today Communications* 28: 102488.
- Zhang, X., Yu, L., Wu, X. & Hu, W. 2015. Experimental sensing and density functional theory study of H₂S and SOF₂ adsorption on Au-Modified Graphene. *Advanced Science* 2(11): 1500101.

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