Germanene-GaAs as super media for gas sensor

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Abstract. Current work deals with the effect of doping on the electrical properties of Germanene sheet as a gas sensor. present study involves a new two-dimension system based on Germanene doped with Gallium Arsenide (GaAs) to determine of it is electronic applications as gas sensing. The results showed an influence for the doping on the electrical and thermal conductivity. The I-V characteristics for the doping sheet gave clearly sensing for gas. Where the results showed the doped Germanene-GaAs gave good sensing for all gasses at different concentrations, and it showed the doped Germanene even at the lowest concentration has good sensing for the three studied gasses (NO2, CO2 and H2S). Likewise, this study was focused on the behavior of the thermal conductivity and conductance of each gas. The Germanene-GaAs structure can be used as gas sensor. The relax structures were done by employing the GGA/DZP density functional theory at the Siesta trunk – 426.

Keywords: Germanene, Doping, Sensor, GaAs.

1.Introduction
Synthesis of Graphene spurred the seek to get two-dimensional (2D) forms of other materials in group IV of the periodic table as predicted by Takeda and Shiraishi in 1994 [1]. The worthwhile synthesis of Silicene in 2012 [2] boost up the surge to obtain Germanene, a 2D form of germanium analogous to graphene, bolstered by another prediction in which Cahangirov et al. found that Germanene appears to be in low-buckled form [3]. Applying electric field [4], chemisorption of adatom species [5,6], giving periodic nano holes [7], doping [8], defects [9], and edge functionalization are possible means to achieve a band gap in Silicene and Germanene. Previously, edge functionalization has also been used as a tool for tuning the band gap in nanoribbons. Several theoretical and experimental studies have studied graphene allied materials for gas sensing [10-15]. Similar to Silicene, Germanene atoms are bonded in low buckled form which is generally instigated by the mixing of sp 2 and sp 3 hybridization of Ge atoms. It is predicted that Germanene may have stronger adsorption of atoms and molecules than graphene due to its buckled structure [5,16]. Xia et al. theoretically investigated common gas molecules adsorption behavior on Germanene. They have found that CO, CO2, H2O and N2 are physisorbed on Germanenene through van der Waals interactions whereas NO, O2, NO2 and NH3 are chemisorbed through tough covalent bonds [17,18]. Recently, Gupta et al predicted the possibility of Germanene in building new material as gas sensing with great sensitivity and stability [19]. Padiha and Pontes investigated the impact of Stone–Wales and vacancies induced electronic and transport properties. They discovered that Stone–Wales and divacancies destroy the dispersion relation near the Fermi level to create scattering centers to reduce the current in Germanene [20]. Still, Germanene gas sensing capability has not been studied much compared to graphene and Silicene. It is proven that defects, doping, and functionalization can certainly increase the surface – adsorbate interaction to improve the sensing activity of the materials [9]. In this study, we investigate doping induced gas
sensing capability of Germanene using density functional theory (DFT) calculations. The sensing properties of Germanene nanosheet are evaluated by considering I-V characterized, Electrical conductivity, thermal conductivity and charge transfer. Present study involves a new two-dimension molecular system based on Germanene doped with Gallium Arsenide (GaAs) to determine of it is electronic applications for gas sensing.

2. Methodology
First-principles DFT calculations combined with nonequilibrium Green’s function (NEGF) are used to analyze band gap of the structures. The exchange-correlation functional uses Generalized Gradient Approximation of Perdew–Burke–Ernzerhof (PBE) to solve Kohn-Sham equations and to expand electronic density. A double-$$\zeta$$ polarized basis set is adopted.

The Germanene nanosheet is modeled by $$1 \times 4 \times 14$$ supercell containing 224 Ge atoms. A vacuum space of 10 Å along the x direction in which the structures are not periodic to avoid the possible interactions between the periodically repeated unit cells. The Brillouin zone integration is sampled using Monkhorst–Pack grid of 1 $$\times$$ 1 $$\times$$ 1 k - points for structural relaxations, electronic properties, and charge transfer calculations. The density mesh cut-off is set to be 200 Hartree, and the structures are allowed to fully relax until the force on each atom becomes less than 0.04 eV/Å.

First, I-V characterized, electrical conductivity and thermal conductivity of the incident gases on the pristine Germanene nanosheet have been evaluated. Secondly, I-V characterized, electrical conductivity and thermal conductivity when gases adsorbed on Germanene with dopants have been gauged.

3. Results and Discussion
The optimized structure of a pristine Germanene sheet is shown in Fig. 1 (a). The calculated lattice constant (1 Å), Ge-Ge bond length (2.376 Å), and buckling distance (0.71 Å) found in optimized geometry are in good agreement with the previous findings [4,21,22]. We have investigated three toxic gases (H2S, NO2 and CO2) to bind with monolayer Germanene once exposed. To start the relaxation, the gas molecules can be placed at 3.2 Å sites as shown in Fig. 1. We started with H2S adsorption on Germanene monolayer, which is one of the toxic gases produced from industrial waste and extremely lethal at concentrations > 250 ppm [23]. The most stable configuration of H2S molecule adsorbed on Germanene is shown in Fig. 2 (a), where H2S is aligned parallel to the surface of Germanene, and the S atom is pointing towards the Germanene monolayer at a distance of (H2S=3.2 Å). Full structural relaxation shows a slight elongation in the H-S bond from 1.35 to 1.41 Å and H-S-H angle from (91.29 to 92.1) degree. The Ge-Ge bond length varies from (2.45 to 2.48) Å around the H2S molecule (Fig. 1 (a)). Another hazardous toxic gas, Nitrogen dioxide NO2, is one of the most common air pollutants and causes poisoning when inhaled. Traffic emissions are the primary source of nitrogen oxides, while some small concentrations of power plants and other industrial sources. The minima energy configuration of NO2 adsorbed Germanene and the molecule is positioned horizontally at a distance of 3.2 Å from the Germanene monolayer, as shown in Fig. 2 (b). N-O bond length is 1.245 Å and the angle is 134.3 degree. Finally, CO2 adsorption on a Germanene nanosheet was also studied. It is the most abundantly available greenhouse gas in the environment. By investigating all of the configurations, it has been found that horizontally adsorbed CO2 is the most stable configuration. This structure provides with a relatively large Germanene-CO2 distance of 3.79 Å as can be seen in Fig. 2 (c).
**Figure 1.** The Germanene a) pristine, (b–d) top and side view of pristine Germanene with H2S, NO2, and CO2 gasses respectively, and e) doped with GaAs, (f–h) top and side view of doped Germanene with H2S, NO2, and CO2 gasses, respectively.

Fig. 2 illustrates the effect of the concentration of the three gasses on the I-V characteristics of the pure Germanene. As seen, the pure Germanene has high sensitive for the used gasses, but approximately there is no an influence for the concentration of the gasses on the I-V curve except for H2S in which the approach of one H2S molecule from the surface of the Germanene sheet gave the sheet sensing appeared at 0.8 V. The sensing of the pure Germanene for NO2 and CO2 was appeared at 0.65 V and 0.6 V, respectively.
Fig. 2. The effect of the concentration of the gasses on the I-V curve of pristine Germanene a) H2S b) NO2 and c) CO2

Fig. 3 illustrates the behavior of the calculated conductance for pure Germanene as a function of the concentration gasses in the range of energy (-1 to 1) eV at room temperature. We showed the pure Germanene has a suitable electric conductance around the Fermi level in the absence and presence the effect of the gasses. High stability was observed of electrical conductance around Fermi energy for pure Germanene due to the effect of different concentrations of CO2 and H2S. While slightly variance in the value of electric conductance of pure Germanene was observed due to change the concentrations of NO2, all the concentrations of NO2 reduced the electrical conductance of the Germanene.

Fig. 3. The electrical conductance of Germanene as a function of the concentration of a) H2S b) NO2 and c) CO2

The behavior of thermal conductivity of the pure Germanene in the absence and presence of mentioned gasses in Fig. 4 has the same as for electrical conductance. Pure Germanene in the absence and presence of the CO2 and H2S has a stable value of thermal conductivity 1.14*10^-9 W/m.K. This value was reduced to 1.08*10^-9 W/m.K due to effect one molecule of NO2 and then reduced to 9.44*10^-10 at Fermi energy due to approach two molecules of NO2 from the Germanene surface. these results indicate to that the concentration of NO2 on pure Germanene play role in the measurements of electrical and thermal conductivity.
Fig. 5 illustrates the effect of the lowest and highest concentration of the three gasses on the electrical properties of Germanene. As seen from the I-V curves, the Germanene was appeared high sensing for one molecule of H2S gas at (0.8 and -0.8) V bias and reverse voltage. This behavior does not observe for the same concentration of NO2 and CO2 gasses. Therefore, at this concentration of gas the H2S play key factor for sensing the Germanene in comparison with the other gasses. At the high concentration of gas (six molecules of each gas), the pure Germanene was observed as gas sensor at (-0.15 and 0.15) V reverse and bias voltage. The electrical conductance for the studied structure at low concentration in Fig. 5 showed the presence of the molecule of these gasses reduced the conductance from 1.99 μS for pure Germanene to 1.689 μS in presence NO2 and 1.848 μS in presence H2S and CO2. The few reducing of the conductance means the mentioned gasses have not effect on the conductance of the pure Germanene. In the other hand, the calculated value of thermal conductivity for pure Germanene is 1.14*10^-9 W/m.K, this value was reduced to 1.11*10^-9 in presence low concentration of H2S and CO2, and to 1.06*10^-9 in presence the same low concentration of NO2. Generally, the electric conductance and thermal conductivity in absence and presence the gasses are stable around the Fermi energy.
Based these findings, while NO2 is chemisorbed on pristine Germanene, H2S is physically adsorbed and CO2 offers fairly weak physic-sorption that limits the use of pristine monolayer Germanene as a gas sensor for CO2 and H2S detection. A possible remedy to this obstacle is to improve the adsorption by the creation of defects and introducing foreign atoms. In this research, we focused on doping defects in order to enhance the sensitivity of Germanene nanosheet to the toxic gases. The doping defects which are made in the synthesis of nanomaterials could be enhancing the adsorption mechanism of the adsorb gas molecules with the host monolayers. Now, the effect of different concentrations for different gasses (H2S, CO2 and NO2) on the electronic properties of doped Germanene was studied and analyzed. Figure 6 showed the doped Germanene has more sensing than the pure, so, the doped Germanene gave good sensing for all gasses at different concentrations appeared at 0.65 V for bias voltage and -0.65 V for reverse voltage. This means the Germanene-GaAs structure can be used as gas sensor.

Figure 5. I-V curves at low and high concentration of H2S, CO2 and NO2, conductance and thermal conductivity for pristine Germanene at low concentration

The effect of different concentrations of the three gasses on the electrical conductance of the doped germane was shown in Fig. 7. Firstly, we showed the conductance of the doped Germanene 0.20 µS is less than for the pure. Also, the conductance of the new doped Germanene-GaAs was reduced to...
below 1 µS due to presence the gasses at different concentrations, the value of conductance at room temperature was varied depending on the concentration for each gas. Fig. 8 showed the thermal conductivity of the Germanene was reduced to $1.25 \times 10^{-10}$ due to doping by the GaAs. In all cases of doped Germanene with different concentrations of H2S, NO2 and CO2 gasses the thermal conductivities were slightly reduced in comparison with the pure Germanene in presence the same gasses at the same concentrations. This result may be return to the effect of the Ga and As atoms in the structure of the Germanene, and therefore, effect on the transmittance and the number of open channels in pure Germanene.

![Figure 7](image1.png)

**Figure 7.** Conductance of doped Germanene- GaAs at different concentrations of a)NO2  b)H2S and c) CO2

![Figure 8](image2.png)

**Figure 8.** Thermal conductivity of doped Germanene- GaAs at different concentrations of a) NO2, b)H2S and c) CO2

Fig. 9 illustrates the I-V curves, electric conductance and thermal conductivity for the doped Germanene-GaAs at the lowest and highest concentrations of NO2, H2S and CO2 gasses. At low concentration (one molecule for each gas), the doped Germanene has good sensing for the three gasses...
appeared at -0.55 V and 0.55 V reverse and bias voltages. Means the doped Germanene-GaAs sheet is a gas sensing at the low concentration. At high concentration of gasses (six molecules for each gas), the doped sheet appeared sensing for the gas at 0.64 and -0.64 bias and reverse voltage with few differences in the corresponding current depends on the type of the gas. The conductance at room temperature and thermal conductivity of the doped Germanene due to the effect the lower and the higher concentrations of the three gasses in Fig. 9 showed the conductance of the doped Germanene at high concentration is larger than that at low concentration of all gasses, but the electric conductance at low concentration is more stable around Fermi energy than that at high concentration. The same behavior was observed for the thermal conductivity, with low values of thermal conductivity for doped Germanene in comparison with those in presence high concentration of gasses.

![Figure 9. I-V curves, conductance and thermal conductivity for doped Germanene-GaAs at low and high concentration of H2S, CO2 and NO2.](image-url)
4. Conclusions
From the results of electric properties of the pristine or pure Germanene and doped Germanene-GaAs in absence and presence different concentrations of H2S, NO2 and CO2 gasses, one can conclude the following: The pristine Germanene has high sensitive for the H2S, NO2 and CO2 gasses. Also, lightly variance in the value of electric conductance at room temperature of pure Germanene was observed due to change the concentrations of NO2. The electric conductance and thermal conductivity in absence and presence the gasses are stable around the Fermi energy. It was found that doping in Germanene change the respective electrical properties significantly. The electrical properties portrayed by the I-V characterization of the Germanene nanosheet system with doping defect (replacements) are changed as a consequence of the charge-transfer mechanism between Germanene-gas molecules. The results showed the doped Germanene-GaAs gave good sensing for all gasses at different concentrations. The Germanene-GaAs structure can be used as gas sensor. The thermal conductivities for doped Germanene with different concentrations of H2S, NO2 and CO2 gasses are slightly reduced compared with the pure Germanene in presence the same gasses at the same concentrations. The conductance of the doped Germanene at high concentration is larger than at low concentration of all gasses, but the electric conductance at low concentration is more stable around Fermi energy than that at high concentration. We showed the doped Germanene at the lowest concentration has good sensing for the three gasses.

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