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# Electron Transport of Two Dimension Germanene Structures

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**Abstract:** In this study, the electron transport was calculated as a function of the width of the two dimension Germanene structures using Gollum program. We showed good relax of Germanene structures was obtained using GGA/DZP-DFT at SIESTA-trunk-462 of program. Electrical and thermal conductivity of the studied Germanene structures have been studies. The shape of the Germanene structure play a significant role in electrical and thermal conductivity calculations. I-V curve showed the Germanene structures have characters similar to the sensing type. These results of nanostructures offer that a suitable contact with the two electrodes have quite limited effect on the sensing behavior of the structures and this from the lowering of the energy gap between the HOMO of the structure and the Fermi level of the electrode in the forward and reverse bias.

**Key words:** Germanene, electrical conductivity, thermal conductivity, I-V curve, contact, HOMO

## INTRODUCTION

Graphene is the first two dimension material, it is discovery lead to a large amount of new and exciting physics (Novoselov *et al*., 2004). The $SP^2$ hybridized carbon atoms that the graphene consists are arranged in a planar configuration. Mermin-Wagner theorem (Mermin, 1968) states that a two dimension crystal cannot exhibit long-range order at any finite temperature but the remark that a single sheet of atoms is stable was at present fairly a surprise.

Nelson and Peliti (1987) implemented a theoretical study on the complicated interaction between crystalline order and thermal variations in crystalline membranes. Nelson and Peliti showed that the an-harmonic coupling between in-plane and out-of-plane lattice vibrations is significance for the stability of a membrane without this an-harmonic coupling the membrane would be fully wrinkled. As a result of this an-harmonic coupling, the membrane becomes overall more or less plane but the membrane displays strong intrinsic waves that are characterized by a power-law behavior of the atomic-displacement correlations functions. The system remains approximately two dimensional and approximately crystalline (Fasolino *et al*., 2007; Katsnelson and Fasolino, 2012; Katsnelson, 2012). At least for rigid systems such as graphene, this means that one can safely use the term “two dimensional crystal” for any practical resolution (Katsnelson and Fasolino, 2012).

Experimental studies have shown that freely graphene is indeed undulated (Mozorov *et al*., 2006). The notable rise of graphene has incited many scientists to search for alternative two dimension materials. The examination of this new two dimension materials has hardly begun, its potentials have not yet, completely materialized and the degree of its potential for new physics and devices remains largely unemployed. Silicon and germanium are the most obvious alternatives group 4 elements for graphene (Lay *et al*., 2014). All three elements germanium, silicon and carbon have four electrons in their outermost s and p orbitals. The diamond structure of silicon and germanium is the energetically most favorable crystal structure (Bundy, 1964). In diamond lattice the covalent bonds between the atoms are all the same and have a $SP^3$ hybridized S, $p_x$-$p_z$ character.

For carbon, another allotrope is found in nature that consists of a heap of sheets with a honeycomb structure. This carbon allotrope is named graphite and is under normal conditions more stable than the carbon allotrope that has the diamond structure (Bundy, 1989). The three in-plane covalent bonds of graphene make angles of 120° with each other and have a hybridized 2s, $2p_x$ and $2p_y$ character ($SP^2$). The $2p_z$ electrons are traveling and distributed throughout the whole carbon sheet, making the system metallic. These $2p_z$ orbitals give rise to the construction of the $\pi$ bonding and $\pi^*$ anti-bonding orbitals which are generally accountable for the van der Waals interaction between the graphene sheets in graphite. For silicon and germanium such graphite-like allotropes have not been found in nature and therefore, the silicon and germanium allotropes, from now denoted as Silicene and Germanene, respectively are interesting for synthesis.

Germanene, Silicene and graphene share a number of atypical and stimulating electronic properties. The electrons near the Dirac points (K and K’) behave as

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relativistic massless particles, near Dirac points the electronic states of graphene are described by a linear dispersion relation with a Fermi velocity of about 106 m/sec. Previously, the experimental studies have been obtained the charge carrier mobilities as high as 15000 $cm^2$/V sec (Mermin, 1968). Another mark of these two dimension Dirac materials is that they show an irregular quantum hall effect. However, a few differences between Germanene and Silicene on the one hand and graphene on the other hand. Firstly, the honeycomb lattice of graphene is fully planar while the honeycomb lattices of Germanene and Silicene are predicted to be buckled (Takeda and Shiraishi, 1994; Guzman-Verri and Voon, 2007; Cahangirov *et al*., 2009). Secondly, Germanene and Silicene have a much stronger spin-orbit coupling due to the larger atomic number of germanium and silicon in comparison to carbon. A small buckling will increase the spin-orbit coupling by orders of magnitude (Katsnelson and Fasolino, 2012). The spin-orbit coupling results in the opening of a small band gap at the Dirac points in the interior of the material, topological protected gapless helical modes at the edges of the two dimensional material and a quantum spin hall effect which is characterized by spin current transport via the edges modes (Kane and Mele, 2005a, b). The spin-orbit gap in graphene, Silicene and Germanene are <0.05, 1.55 and 23.9 meV, respectively (Boettger and Trickey, 2007; Gmitra *et al*., 2009; Abdelouahed *et al*., 2010; Liu *et al*., 2011; Ye *et al*., 2014). This worth that the quantum spin Hall state is only experimentally easy to get for Silicene and Germanene (Han *et al*., 2014; Konschu *et al*., 2010). The synthesis of Silicene is in 2010 (Aufray *et al*., 2010; Padova *et al*., 2010, 2011; Lay *et al*., 2012; Fleurence *et al*., 2012; Vogt *et al*., 2012) and Germanene in 2014 (Li *et al*., 2014; Davila *et al*., 2014; Bampoulis *et al*., 2014; Derivaz *et al*., 2015). Silicene has been grown on several substrates [Ag (1 1 0), Ag (1 1 1), $ZrB_2$ (0 0 0 1) and Ir (1 1 1)] and considered by a variety of surface science techniques (Aufray *et al*., 2010; Padova *et al*., 2010, 2011; Lay *et al*., 2012; Fleurence *et al*., 2012; Vogt *et al*., 2012).

Since, there are already several reviews on Silicene (Kara *et al*., 2012; Yamada-Takamura and Friedlein, 2014; Voon and Guzman-Verri, 2014), we will constrain ourselves here to Germanene. In the last few years, we have seen a flood of articles on other types of two dimension materials such as phosphorene, arsenene, transition metal di-chalcogenides organic crystals and artificial two dimension lattices (Wang *et al*., 2015). Our study in present paper focuses on the effect of the width of Germanene structures to investigate their structural, electronic and electrical properties.

## MATERIALS AND METHODS

The calculated electronic and electrical properties of the two dimension Germanene structures have been calculated using the GGA/DZP density functional theory. All calculations were carried out using the Siesta trunk-462 program (Artacho *et al*., 2014) and Gollum program "Version 1.0" (Ferrer *et al*., 2014). The Germanene nanosheet is modeled by 1×n×14 supercell where n = 2, 3 and 5 (labeled Ge1-Ge3, respectively). 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 1×1×1 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 <0.04 eV/Å.

## RESULTS AND DISCUSSION

Figure 1 shows the relax structures of the studied zigzag Germanene ZGe molecular systems of the same length 3.714 nm, they are labeled Ge1-Ge3 with different widths 0.913, 1.62 and 2.321 nm, respectively. From the result of the relaxation, the geometrical optimize parameters are the bonds Ge-Ge equal to 0.234-0.247 nm, the intra bond angles Ge-Ge-Ge are in the range (112.51-112-96°) and the Ge-Ge-Ge bonds zigzag ends equal to 113.44°. These values are in good agreement with the data

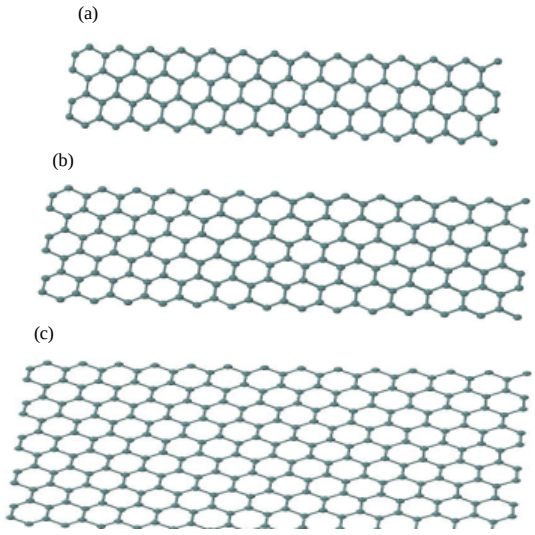


Fig. 1: The relax structures of zigzag Germanene: a) Ge1; b) Ge2 and c) Ge3

Table 1: $E_{Tot}$, HOMO, LUMO and $E_{gap}$ for ZGe molecular systems

| Germanene system | HOMO (eV) | LUMO (eV) | $E_{gap}$ (eV) | $E_F$ (eV) |
|---|---|---|---|---|
| Ge1 | -4.00440 | -3.72823 | 0.27617 | -3.8664 |
| Ge2 | -4.00644 | -3.73301 | 0.27343 | -3.8698 |
| Ge3 | -4.00685 | -3.73473 | 0.27212 | -3.8709 |

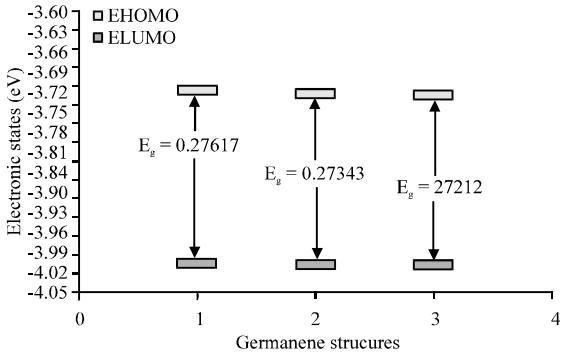


Fig. 2: LUMO-HOMO separation of zigzag Germanene molecular systems

by Acun *et al.* (2015) and John and Merlin (2016) and refer to a suitable GGA/DZP method used for relaxation of the ZGe molecular systems.

Table 1 shows the calculated values of the minima total energy $E_{Tot}$ , HOMO, LUMO energies, $E_{gap}$ and Fermi energy $E_F$ of the ZGe molecular systems. As in Table 1 increasing the width of the ZGe structure decrease the total energy of the system. Figure 2 illustrated the total energy of the ZGe molecular systems. The HOMO energy levels were increased linearly with increasing the width of the structure. On the other side in all ZGe structures there are few differences between the obtained values of HOMO and LUMO energies, this character gave these structures to have semiconducting behavior. The calculated values of $E_{gap}$ in Table 1 are reflection of the low separation between the LUMO and HOMO energies, the lower value of $E_{gap}$ is 0.139 eV for Ge3 of larger width (higher number of electrons) and the higher value of $E_{gap}$ is 0.676 eV for GR1 of the smaller width. In general, the energy gap was decreased with increasing the width of the ZGe structure. Figure 3 illustrates the LUMO-HOMO energy gap of the ZGe molecular structures. Fermi energy level $E_F$ for ZGe molecular systems was calculated as the mid-level between the valence and conduction bands. $E_F$ is independent on the number of germanium atoms in each molecular system but depends on the frontier orbitals. Ge3 has the large value of $E_F$, this indicates to that the electrons in this structure has a large escaping tendency and refers to the weakening in the HOMO and LUMO energy values (Lipkowitz *et al.*, 2009; Zhang and Sarkar, 2011). Figure 4 illustrates the $E_F$ of ZGe molecular systems.

Table 2: Electrical conductivity (G), width (d) and total Energy ($E_T$) for ZGe molecular systems

| Germanene system | Ge1 | Ge2 | Ge3 |
|---|---|---|---|
| d (nm) | 0.913 | 1.62 | 2.321 |
| Electrical conductivity (μsec) | 0.2323E-3 | 0.5423E-3 | 0.3312E-3 |

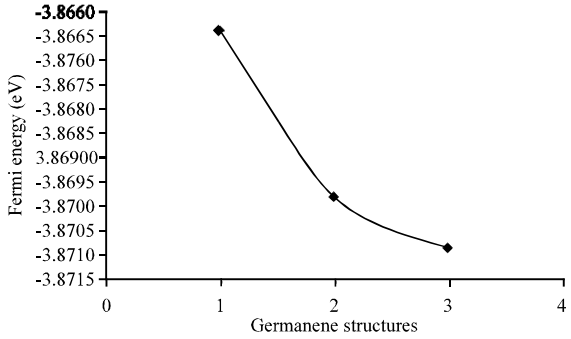


Fig. 3: Fermi energy of zigzag Germanene molecular systems

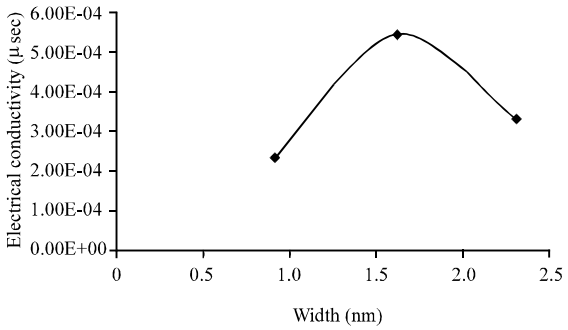


Fig. 4: G as a function of width of zigzag Germanene molecular systems

After the relaxation, each ZGe molecular structure was placed between two electrodes and then each molecule structure plus limited layers of electrodes were for a second time allowed to produce the relax structures. The structures are relaxed at Siesta-trunk-462 code by employing the GGA/DZP density functional theory. And the electrical properties were calculated by employing the Gollum program.

Table 2 illustrates the calculated values of the electric room temperature electrical conductivity G corresponding to the width d ( nm ) for each ZGe molecular structure.

Table 2 showed the room temperature electrical conductivity G varied independently on the increasing of the width of the ZGe structures. The behavior of G of the studied structures is as:

Ge2>Ge1>Ge3

This behavior may return to the shape of the ZGe molecular system in other words, to the two dimensions

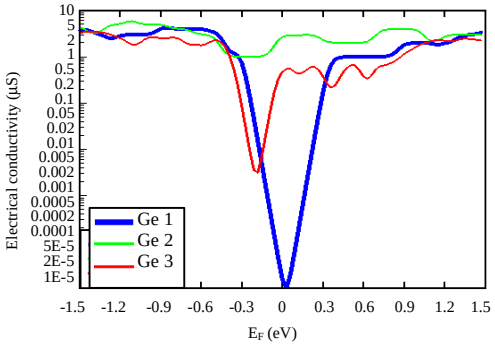


Fig. 5: The electrical conductivity in μsec of the ZGe molecular systems

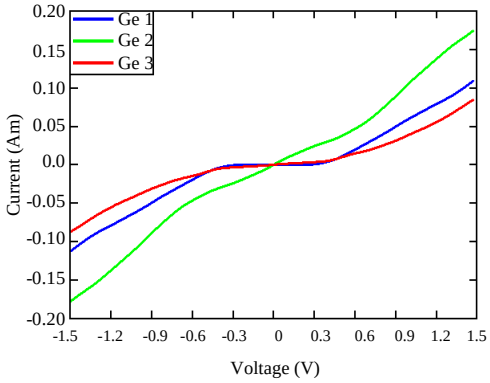


Fig. 7: The I-V curve of the ZGe molecular systems

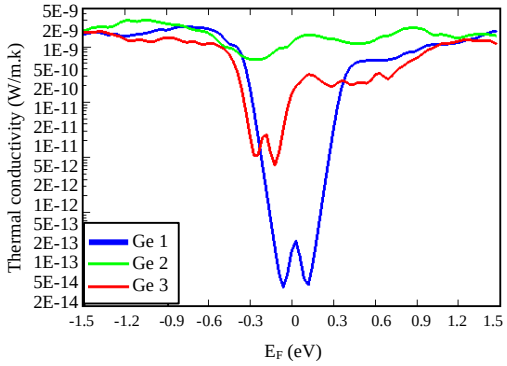


Fig. 6: The thermal conductivity of the ZGe molecular systems

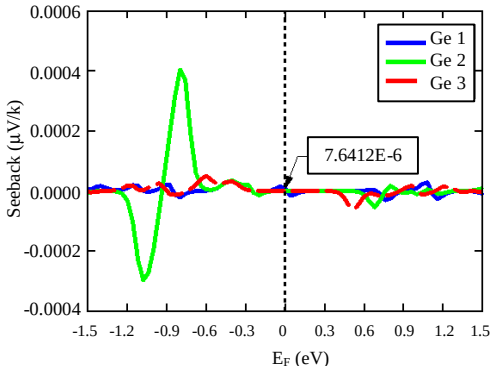


Fig. 8: Seebeck coefficient of the ZGe molecular systems

length and width of each molecular system. Figure 5 shows the relation of the width with the G of ZGe molecular systems.

Figure 6 declares the electrical conductivity of the three structures of ZGe is in the order of Ge2>Ge1>Ge3. The electrical conductivities of Ge2-Ge3 are 4.337, 3.596 and 3.203 μsec, respectively. This result return to the open channel of charge transfer can each structure has.

Figure 7 declares the thermal conductivity of the ZGe molecular systems. The results showed the thermal conductivity of ZGe structures has the same behavior of electrical conductivity. The thermal conductivity of ZGe1 is $1.638*10^{-9}$ W/m. k, it is increased to $1.806*10^{-9}$ W/m. k for ZGe3 and to $1.968*10^{-9}$ W/m. k for ZGe2. The shape of the structure play a significant role in thermal conductivity calculations.

Each ZGe molecular structure was placed in between two contacts electrodes. The 1.5 V bias voltage was applied in direction of the molecular structure. Fermi level of the contacts electrodes was fixed in the middle of the gap between the LUMO and HOMO. Figure 8 declares the ZGe structures have characters similar to the sensing type. For ZGe3, ( 0.7 and -0.7 ) V are the required bias and reverse voltages for sensing for ZGe2. The required bias voltage and reverse voltage for sensing are 0.45 and -0.45 V for ZGe1 and ZGe3 with an insulating area lies in that range of voltage. These results are very valued ever, since, the behavior of the studied ZGe nanostructures decreases totally the high effects of appeared temperature in the from the past macro devices. The calculations of I-V curve of these kinds of nanostructures offer that a suitable contact with the two electrodes have quite limited effect on the sensing behavior of such structures. Above results are from the lowering of the energy gap between the HOMO of the structure and the Fermi level of the electrode in the forward and reverse bias (Zhang and Sarkar, 2011; Mazhir *et al*., 2016; Acun *et al*., 2015).

The behavior of Seebeck coefficient for the studied ZGe sheets was illustrated in Fig. 9 where the Seebeck coefficient of the three structures of ZGe is in the order of Ge1>Ge2>Ge3. The Seebeck coefficient of Ge1-Ge3 are $7.641*10^{-6}$, $-3.950*10^{-8}$ and $1.265*10^{-10}$ μV/k, respectively. The maximum contribution in Ge1 and Ge3 is due to holes while the maximum contribution in Ge2 is due to electrons in which the Seebeck voltage is correlated with an anti-symmetry distribution of electrons around the Fermi level.

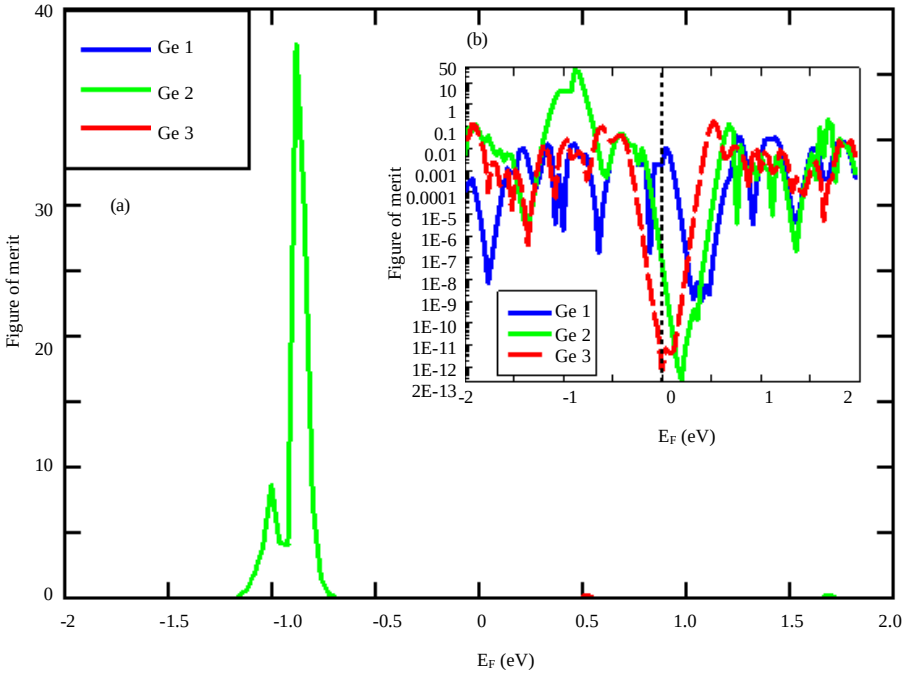


Fig. 9: Figure of merit of the ZGe molecular systems

Figure 9 shows the figure of merit (the measure of effectiveness, efficiency, performance of a device, system or method) behavior of ZGe molecular systems as a function of $E_f$(eV). It is noticed the structure Ge2 has maximum value at (E-$E_f$ = -0.88 eV) while Ge1 has maximum value at fermi level as shown in Fig. 9.

## CONCLUSION

From the above results, one can conclude that the geometrical optimize parameters are in good agreement with the data in previous studies and refer to a suitable GGA/DZP method used for relaxation of the two dimension Germanene structures. The increasing the width of the Germanene structure decrease the total energy of the structure. Also, the energy gap was decreased with increasing the width of the Germanene structure. On the other hand, Fermi energy level $E_F$ for Germanene molecular systems was calculated as the mid-level between the valence and conduction bands. Fermi energy is independent on the number of germanium atoms in each molecular system but depends on the frontier orbitals. The asymmetrical distribution of electrons moving in the material and around the Fermi level gives a greater value of Seebeck coefficients depends on the number and position of it.

The shape of the Germanene structure play a significant role in electrical and thermal conductivity calculations, the electrical and thermal conductivity of the studied Germanene structures are in the order of Ge2>Ge1>Ge3. I-V curve showed the Germanene structures have characters similar to the sensing type. These results of nanostructures offer that a suitable contact with the two electrodes have quite limited effect on the sensing behavior of the structures and this from the lowering of the energy gap between the HOMO of the structure and the Fermi level of the electrode in the forward and reverse bias.

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