Electronic, structural and optical properties of Germanene- A DFT Study

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ABSTRACT

We use first-principles simulations to gain insight into the structural, electronic, and optical characteristics of two-dimensional honeycomb lattices. This study concentrates mainly on their features and the intricate connection between orbital hybridizations and electrical and optical properties. Germanene has been found to exhibit sp^2 hybridizations. The geometric structure, the electronic band structure, and the density of states are all significantly affected by these bonding arrangements. Moreover, it is anticipated that pure group IV monolayers will sustain the meta-stable & stable excited states. The zero band gap in Germanene alludes to its metallic nature. The theoretical ideas found in the present study are significant for both high-tech and fundamental applications.

Keywords: Germanene; Electronic properties; optical properties; honeycomb.

1. Introduction

There has been a lot of experimental and theoretical interest in two-dimensional (2D) materials. Along with graphene, other well-known group-IV mono layers consist of silicene, germanene, stanene, and plumbene. These layered structures are excellent for researching an extensive variety of physical, chemical, and material phenomena, mainly because of the complicated and peculiar fundamental atomic interactions and geometric aspects. Germanene is a two dimensional material composed of a single layer of Germanium atoms arranged in a honey comb lattice similar to grapheme, as a result, it exhibits unique optical and electronic properties that differ from its bulk counterpart Germanium, since its experimental realization in 2004[1-5]. Germanene, has emerged as a candidate for future electronics applications because of its extraordinary electronic and mechanical properties [6-8]. Inspired by the discovery of graphene, both experimental and theoretical researchers focus their research interests on the members of group-IV elemental 2D atomic-layer systems including silicene, germanene, and stanene. Compared with their bulk form, these 2D materials exhibit so many unusual properties such as high charge-carrier mobility, outstanding mechanical performance, and large surface-to volume ratio [9-11]. However, the intrinsic shortcoming of these group-IV 2D materials is gaplessness which gives rise to their poor performance in the FET applications. To our best knowledge, the key to develop 2D material-based electronics urgently lies in opening a tunable band gap in it. To achieve this, an alternative route is the realization of hetero structures.

Many strategies have been adopted for band gap engineering of graphene and silicene. However, there are still little efforts made to open the band gap of germanene by heterostructures[12-14].

In this paper, we explore electronic and optical properties of Germanene, by Ab-initio simulation package which is based on density functional theory (DFT). We will explain the significance of our findings for prospective applications and suggest future research and development directions. We may learn more about this interesting substance's inner workings and open the way for its incorporation into upcoming technologies, enabling improvements in areas like nanoelectronics, photonics, and quantum computing.

2. Computational Result:

All the Ab-initio calculations of Ge are performed by Quantum Espresso simulation package within the density functional theory (DFT) framework [15]. The generalized gradient approximation (GGA) is used to determine the exchange-correlation potential using the Perdew-Burke Ernzerh of (PBE) functional [16]. To estimate the interaction potential between the valence electrons and ionic core plane augmented wave (PAW) is used. To explore Ge, we constructed DFT-D3 van der Waals interaction [17]. The kinetic energy cut-off of 70 Ry and the charge density cut-off of 300 Ry are used throughout the computations for the plane wave. The Broyden Fletcher-Gold fard-Shanno (BFGS) algorithm was used to do the geometrical optimization of Ge. The structure was relaxed when the forces were less than 0.001 eV/A and the total energy criterion was set at 1 ×10−5 ev. In order to create the k-points for the irreducible Brillouin zone sampling for the geometrical optimization and electrical characteristics of the Ge, a set of 7 × 7 × 1 Monkhorst-pack grids were utilised, and a denser grid of 13 × 13 × 1 was used for the density of states (DOS). Additionally, we added a 10 vacuum to prevent the periodic interaction in the z-direction.

DFT in the GGA and linear response theory in the Random Phase Approximation (RPA) are used to calculate optical characteristics [18]. The optical characteristics of the Ge were estimated using the frequency-dependent complex dielectric function as follows:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \quad (1)$$

Which is defined as the linear response of the medium to electromagnetic radiation $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are real (dispersive) and imaginary (absorptive) parts of the dielectric function, respectively. The imaginary part of the dielectric function is obtained by

$$\varepsilon_2(\omega) = \frac{2\pi e^2}{\Omega\varepsilon_0}\sum_{c,v,k}|\langle\varphi_k^c|\hat{u}\times\vec{r}|\varphi_k^v\rangle|^2\,\delta[E_k^c-(E_k^v+E)] \quad (2)$$

Where the unit cell's volume is Ω, the electronic charge is e, the conduction and valence bands' wavefunctions are φ_k^c and φ_k^v, respectively, and the vector given by the polarisation of the electric field is u.

The real part of the dielectric function can be calculated from $\varepsilon_2(\omega)$, using the Kramer-Kronig relation.

$$\varepsilon_1(\omega) = 1 + \left(\frac{2P}{\pi}\right)\int_0^\infty \frac{\omega'^2\varepsilon_2(\omega')}{\omega'^2-\omega^2}d\omega' \quad (3)$$

The other optical parameters, such as Absorption coefficient $\alpha(\omega)$, Refractive index $n(\omega)$, and Optical conductivity $\sigma(\omega)$, can be estimated by calculating the real and imaginary part of the dielectric function.

$$\alpha(\omega) = \frac{\omega}{c}\sqrt{2\left(\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega)\right)} \quad (4)$$

$$n(\omega) = \sqrt{\left(\frac{\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} + \varepsilon_1(\omega)}{2}\right)} \quad (5)$$

$$\sigma(\omega) = \frac{\omega\varepsilon_2(\omega)}{4\pi} \quad (6)$$

3. Structural and Electronic Properties:

The initial step in each system's optimization procedure is to reduce its energy consumption in order to identify its most stable condition. The optimum Ge-Ge bond length, Ge-Ge-Ge bond angle, lattice constant, and buckling height for pure germanene were calculated to be 2.26Å, 115.71°, 3.83Å, and 0.47Å, respectively [19].

Our calculation for pure germanene agrees well with earlier conclusions derived from DFT simulations. Fig. 1 depicts the structures in their optimal states, both undoped and doped [20]

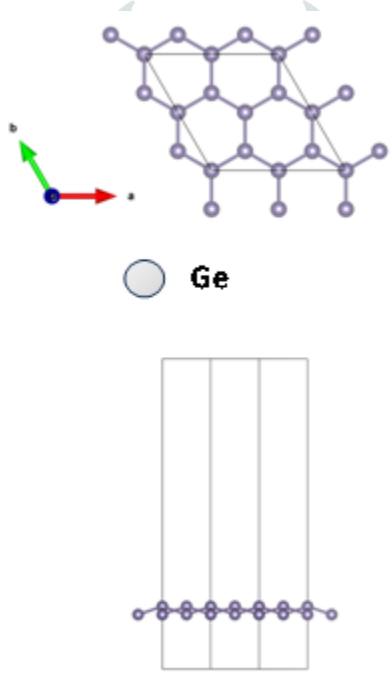

Fig.1. (a) Germanene

The structural and electronic properties of any material are very important factor to be considered for the electronic, optoelectronic and energy conversion devices such as photo detector, sensor, solar cell etc [20].

The electronic properties such as, density of states (DOS), partial density of states (PDOS) and energy band gap of germanene are shown in fig.2. The band gap of germanene is estimated along the high symmetry point $\Gamma \rightarrow M \rightarrow K \rightarrow \Gamma$ in the first Brillouin zone, as shown in Fig. 2(c). At the K- point, the germanene exhibits a zero band gap. It is consistent with previously reported theoretical estimates [21,22].

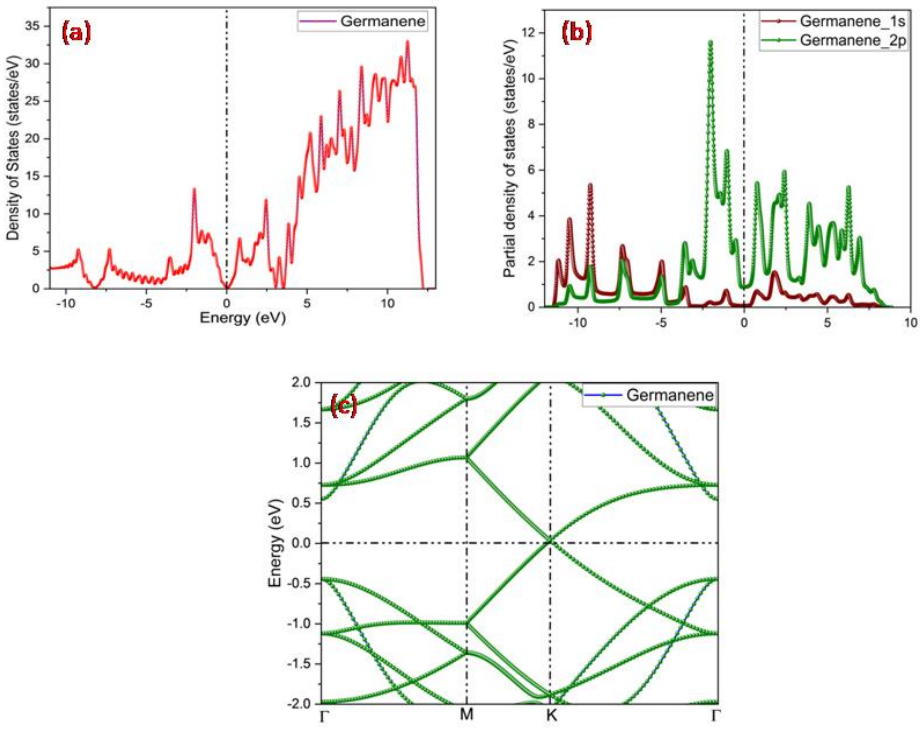

Fig.2. (a) density of states (b) partial density of states (c) energy band gap of Germanene

The total density of states (TDOS) and partial density of states (PDOS) of germanene are shown in Fig. 2. (a) and 2(b). In Fig.2. (a) and (b), the lowest conduction bands for germanene occur between -11.46 and -3.23 eV and are dominated by the s orbitals of germanene. The top of the valence band occurs within the range -3.23 to 0 eV and dominated by p orbital of germanene. The conduction band of germanene is dominated by p orbital of germanene and occurs within range from 0 to 8.4 eV. The top of conduction band occurs within the range 0 to 10 eV and dominated by p orbital of Ge.

3.1. Optical Properties:

Material's optical properties must be investigated in order to understand their properties for usage in optoelectronic systems and devices [23]. When exposed to electromagnetic radiation, the optical characteristics characterize the behavior of the material [23]. As a result, understanding the material's optical characteristics is crucial for establishing their usefulness and usability for optoelectronic applications [24].

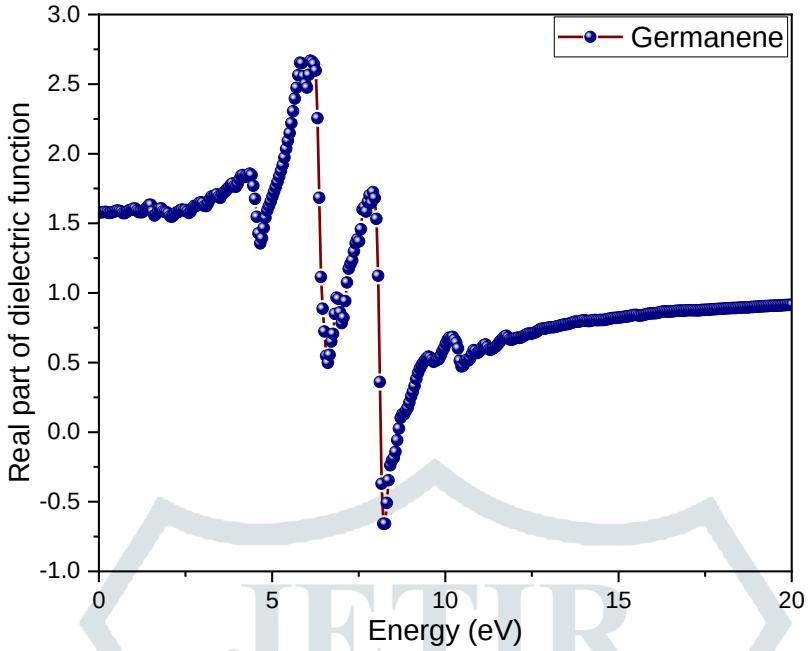

Fig.3. real part of die electric function of Germanene

Many experimental and Theoretical studies reveal that the optical characteristics of materials are affected by the thickness of the film. Germanene's optical characteristics were computed using thin films. To the best of our knowledge, the optical properties have been described in the theoretical analysis of germanene. To compute the optical properties of germanene, the real and imaginary parts of the dielectric function, as well as other optical parameters such as the absorption coefficient, optical conductivity, reflection coefficient, loss function, and so on, are required [25]. The real component of the dielectric function describes how much material has been polarised as a result of an external electric field driven dipole, while the imaginary part of the dielectric function describes how much photon energy is absorbed by the materials. The real part of the dielectric function of germanene, is depicted in Fig 3.The real component of the wave function at zero frequency can be used to derive the static dielectric function $\varepsilon(0)$ [26].

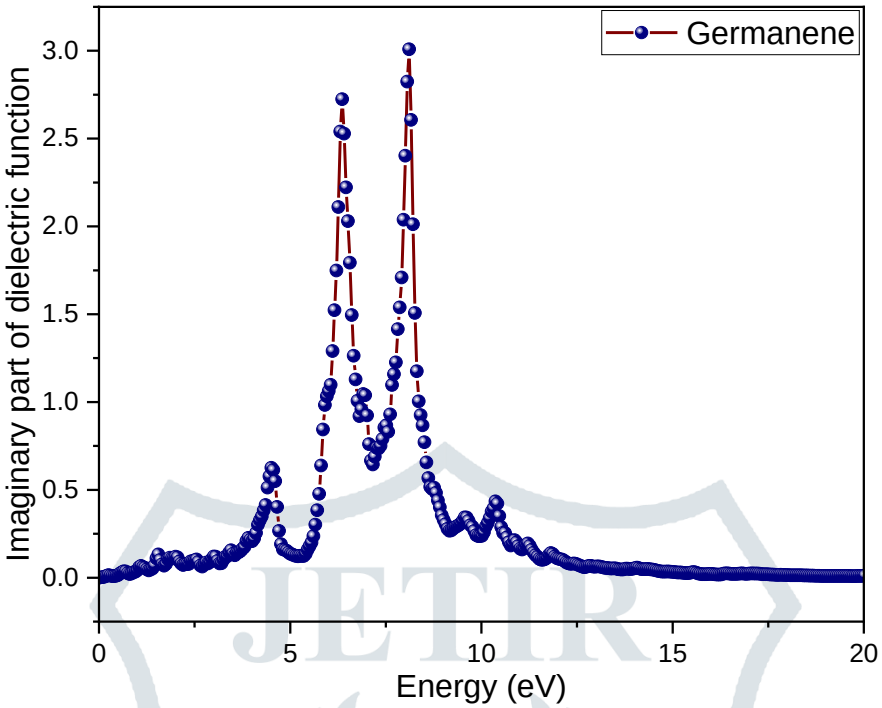

Fig.4. Imaginary part of dielectric function of Germanene

The static dielectric function $\varepsilon(0)$ value of germanene, is 0 ev, as shown in Fig. 4.By using the value of the static dielectric function $\varepsilon(0)$, the band structure of these materials can be calculated by the Penn model defined by $\varepsilon(0) = 1 + \left(\hbar\omega_p / E_g\right)^2$.

The imaginary part of the dielectric function is directly related to the electronic band structure. In Fig. 4, the edge (first critical points) of optical absorption of germanene occurs at 0 eV [27]. This is related to the transition from the valance band maximum to conduction band.

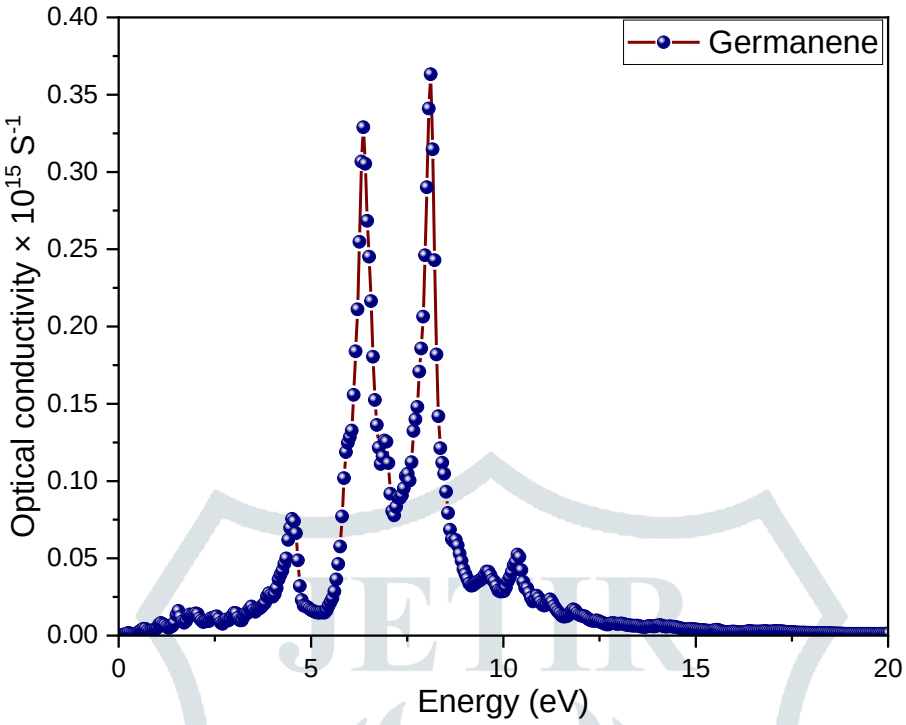

Fig.5. Optical conductivity of Germanene

The conduction of free charge carriers over a range of photon energy is described by optical conductivity. Figure 5 depicts the frequency-dependent optical conductivities of germanene.

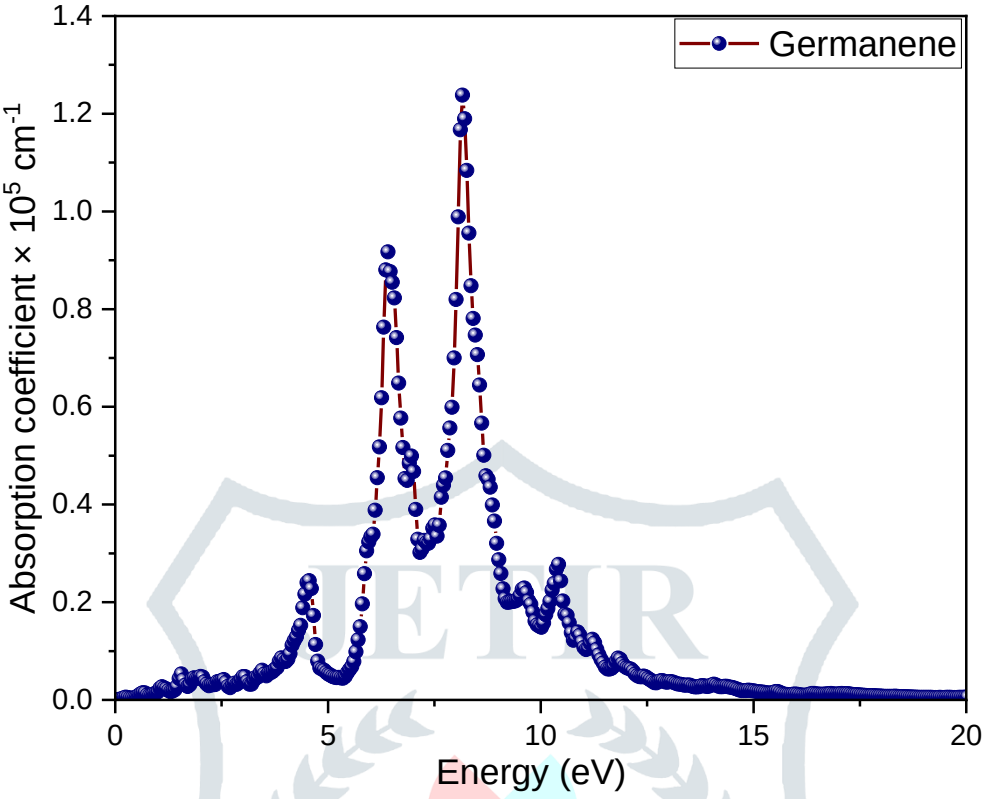

Fig.6. Absorption coefficient of Germanene

Fig.6.shows that absorption coefficient of germanene is minimum, which corresponds to the fundamental band gap. The absorption coefficient describes how much photon energy the substance absorbs. It is an important parameter in optoelectronic applications such as photodiodes, solar cells, and so on. Figure 6 exhibits the absorption coefficient of germanene, as well as an absorption spectrum in the 0 to 1.20 eV regions. The absorption coefficient of Germanene is found to have maximum value of 1.23. It is also noted that when energy increases, the absorption coefficient drops.

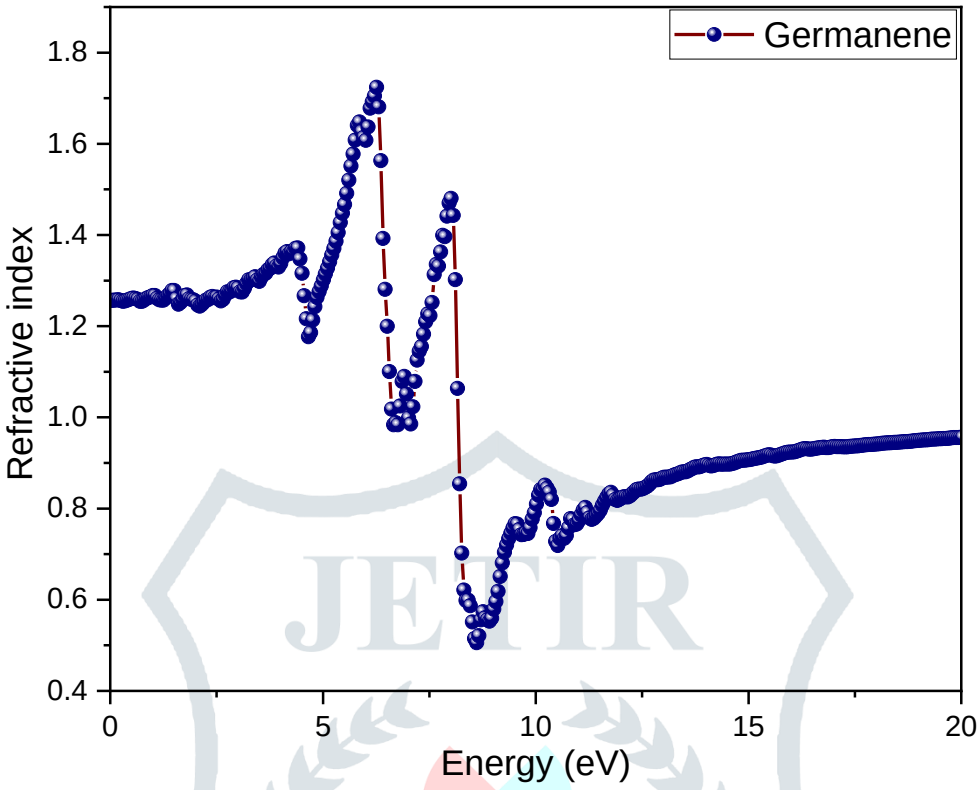

Fig.7. Refractive index of Germanene

. Fig.7 depicts the refractive index of germanene. The static refractive index $n(\omega)$ of germanene, is 1.27 which agrees well with experimental data [28]. The refractive index $n(\omega)$ describes how much electromagnetic radiation refracts after entering the substance. It's also worth noting that the refractive indices of these materials are larger at low energy levels and decrease with increasing energy [29]

The electron energy loss function [30-32] describes the energy loss of a fast-moving electron between the top of the valence band and the bottom of the conduction band.

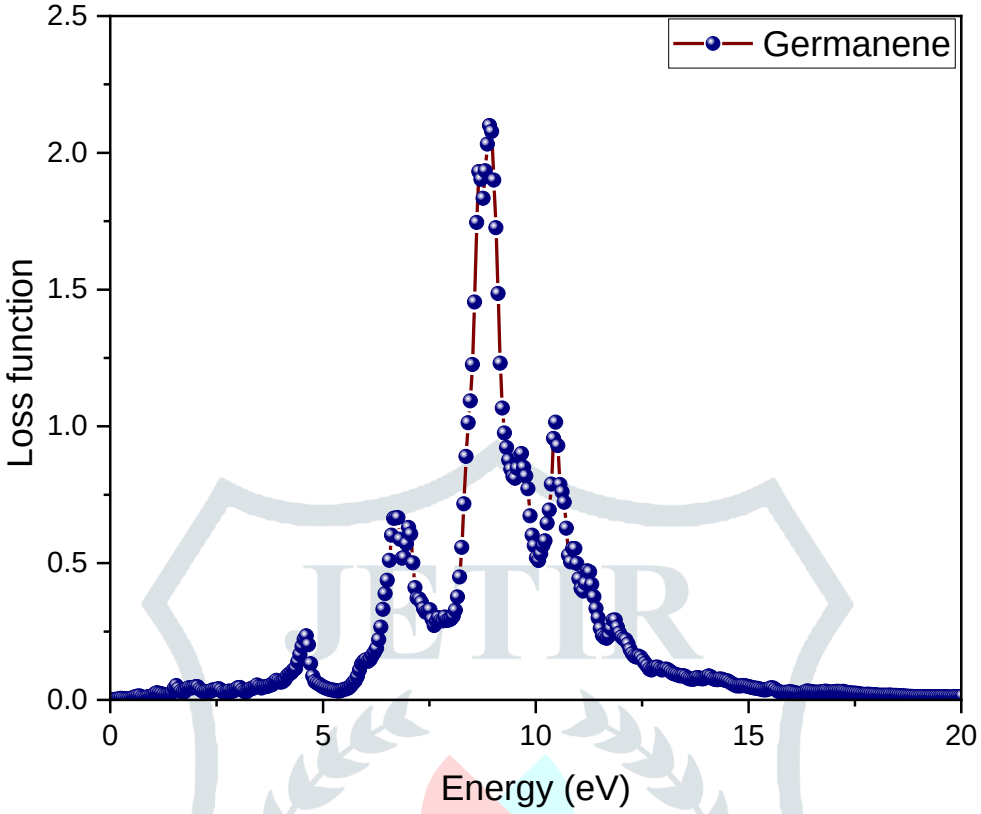

Fig.8. Loss function of Germanene

Figure 8 depicts the electron energy loss functions of germanene. The EELS spectrum of these materials and heterostructures is scattered over a range of energies, with the greatest values being 2.4eV for germanene. Plasma energy $\hbar\omega_D$ is the highest peak of EELS in these materials. [33-35].

Conclusion:

In summary, the structural, electronic and optical properties of germanene, were calculated by using DFT. These materials exhibit excellent photodetection in a wide range of wavelengths. The computed band gap of germanene was 0 ev. The optical properties such as the real and imaginary components of the dielectric function, absorption coefficient, and optical conductivity of germanene, were also calculated using DFT and RPA method. The absorption coefficients of germanene have maximum values of 1.23. If we make hetrostructure of germmene with other 2D material such as Tranastion metal dichalconides (TMDs) then it can be used in different optoelectronic devices like photo-detectors, solar cells, and in optical communication.

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References:

[1]. Hauser A W and Schwerdtfeger P 2012 Methane-selective nanoporous graphene membranes for gas purification Phys. Chem. Chem. Phys. 14 13292–8.

[2]. Ponomarenko L A, Schedin F, Katsnelson M I, Yang R, Hill E W, Novoselov K S and GeimA K 2008 Chaotic dirac billiard in graphene quantum dots Science 320 356–8

[3]. Zhou Q, Coh S, Cohen M L, Louie S G and Zettl A 2013 Imprint of transition metal d orbitals on a graphene Dirac cone Physical Review B 88 235431

[4].Nieszporek K and Drach M 2015 Alkane separation using nanoporous graphene membranes Phys. Chem. Chem. Phys. 17 1018–24

[5]. Houssa M, Dimoulas A and Molle A 2015 Silicene: a review of recent experimental and theoretical investigationsJ. Phys. Condens. Matter 27 253002

[6]. Pi X, Ni Z, Liu Y, Ruan Z, Xu M and Yang D 2015 Density functional theory study on boron-and phosphorus-doped hydrogenpassivatedsilicene Phys. Chem. Chem. Phys. 17 4146–51

[7]. Zhao T, Zhang S, Wang Q, Kawazoe Y and Jena P 2014 Tuning electronic and magnetic properties of silicene with magnetic superhalogens Phys. Chem. Chem. Phys. 16 22979–86

[8]. Osborn T H, Farajian A A, Pupysheva O V, Aga R S and Voon L C L Y 2011 Ab initio simulations of silicene hydrogenation Chem. Phys. Lett. 511 101–5

[9]. Le Lay G 2015 2D materials: silicene transistors Nat. Nanotechnol. 10 202

[10]. Pamungkas M A, Setyowati D A and Abdurrouf 2018 AIP Conference Proceedings 2021 Optical Properties of Ga-doped Silicene and as-doped Silicene: First Principle Calculations pp 050014

[11]. M. Zeng, Y. Xiao, J. Liu, K. Yang, L. Fu, Exploring Two-Dimensional Materials toward the Next-Generation Circuits: From Monomer Design to Assembly Control, Chem Rev. 118 (2018) 6236–6296. https://doi.org/10.1021/acs.chemrev.7b00633.

[12]. R. Mas-Ballesté, C. Gómez-Navarro, J. Gómez-Herrero, F. Zamora, 2D materials: To graphene and beyond, Nanoscale. 3 (2011) 20–30. https://doi.org/10.1039/c0nr00323a.

[13]. B. Rahman Rano, I.M. Syed, S.H. Naqib, Elastic, electronic, bonding, and optical properties of WTe_2 Weyl semimetal: A comparative investigation with $MoTe_2$ from first principles, Results Phys. 19 (2020). https://doi.org/10.1016/j.rinp.2020.103639.

[14]. C. Liu, H. Zhang, Z. Sun, K. Ding, J. Mao, Z. Shao, J. Jie, Topological insulator Bi_2Se_3 nanowire/Si heterostructure photodetectors with ultrahigh responsivity and broadband response, J Mater Chem C Mater. 4 (2016) 5648–5655. https://doi.org/10.1039/c6tc01083k.

[15]. X. Li, J. Yang, First principles design of spintronics materia National Sciences Review, 2016, 3 (3), DOI:10.1093/nsr/nww026.

[16]. J. P. Perdew, K. Burke and M. Ernzerhof, *ERRATA Generalized Gradient Approximation Made Simple [Phys. Rev. Lett. 77, 3865 (1996)]*, 1997.

[17]. A. Lawal, A. Shaari, R. Ahmed, N. Jarkoni, First-principles investigations of electron-hole inclusion effects on optoelectronic properties of Bi_2Te_3, a topological insulator for broadband photodetector, Physica B Condens Matter. 520 (2017) 69–75. https://doi.org/10.1016/j.physb.2017.05.048.

[18]. M. I. Naher, M. Mahamudujjaman, A. Tasnim, R.S. Islam, S.H. Naqib, Ab-initio insights into the elastic, bonding, phonon, optoelectronic and thermophysical properties of $SnTaS_2$.

[19]. Naher, M.I., Naqib, S.H. An ab-initio study on structural, elastic, electronic, bonding, thermal, and optical properties of topological Weyl semimetal TaX (X = P, As). *Sci Rep* **11**, 5592 (2021). https://doi.org/10.1038/s41598-021-85074-z.

[20]. M.M. Furchi, A. Pospischil, F. Libisch, J. Burgdörfer, T. Mueller, Photovoltaic effect in an electrically tunable Van der Waals heterojunction, Nano Lett. 14 (2014) 4785–4791. https://doi.org/10.1021/nl501962c.

[21]. L. Kou, Y. Ma, Z. Sun, T. Heine, C. Chen, Two-Dimensional Topological Insulators: Progress and Prospects, Journal of Physical Chemistry Letters. 8 (2017) 1905–1919. https://doi.org/10.1021/acs.jpclett.7b00222.

[22]. Y. Deng, Z. Luo, N.J. Conrad, H. Liu, Y. Gong, S. Najmaei, P.M. Ajayan, J. Lou, X. Xu, P.D. Ye, Black phosphorus-monolayer MoS_2 van der Waals heterojunction p-n diode, ACS Nano. 8 (2014) 8292–8299. https://doi.org/10.1021/nn5027388.

[23]. M. Y. Li, C.H. Chen, Y. Shi, L.J. Li, Heterostructures based on two-dimensional layered materials and their potential applications, Materials Today. 19 (2016) 322–335. https://doi.org/10.1016/j.mattod.2015.11.003.

[24]. X. Wei, F.G. Yan, C. Shen, Q.S. Lv, K.Y. Wang, Photodetectors based on junctions of two-dimensional transition metal dichalcogenides, Chinese Physics B. 26 (2017). https://doi.org/10.1088/1674-1056/26/3/038504.

[25]. S. Jiang, K. Krymowski, T. Asel, M.Q. Arguilla, N.D. Cultrara, E. Yanchenko, X. Yang, L.J. Brillson, W. Windl, J.E. Goldberger, Tailoring the Electronic Structure of Covalently Functionalized Germanane via the Interplay of Ligand Strain and Electronegativity, Chemistry of Materials. 28, (2016), 8071–8077. https://doi.org/10.1021/acs.chemmater.6b04309.

[26]. Y. Wang, Y. Ding, Strain-induced self-doping in silicene and germanene from first-principles, Solid State Commun. 155 (2013) 6–11. https://doi.org/10.1016/j.ssc.2012.10.044.

[27]. Chiappe D, Scalise E, Cinquanta E, Grazianetti C, van den Broek B, Fanciulli M, Houssa M and Molle A 2014 Two-dimensional Si nanosheets with local hexagonal structure on a MoS2 surface Adv. Mater. 26 2096–101

[28]. Liu H, Gao J and Zhao J 2013 Silicene on substrates: a way to preserve or tune its electronic properties The Journal of Physical Chemistry C 117 10353–9

[29]. Houssa M, Pourtois G, Afanas' ev V V and Stesmans A 2010 Can silicon behave like graphene A first-principles study Appl. Phys. Lett. 97, 112106.

[30]. P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari and R. M. Wentzcovitch, QUANTUM ESPRESSO: A modular and open-source software project for quantum simulations of materials, *Journal of Physics Condensed Matter*, , DOI:10.1088/0953-8984/21/39/395502.

[32]. A. Dal Corso, Pseudopotentials periodic table: From H to Pu, *Comput Mater Sci*, 2014, **95**, 337–350. 31] H. Li, Y. Yu, X. Xue, J. Xie, H. Si, J.Y. Lee, A. Fu, Electroic and optical properties of germanene/MoS_2 heterobilayers: first principles study, J Mol Model. 24 (2018). https://doi.org/10.1007/s00894-018-3855-9.

[33]. X. Chen, Q. Yang, R. Meng, J. Jiang, Q. Liang, C. Tan, X. Sun, The electronic and optical properties of novel germanene and antimonene heterostructure, 23, (2016),DOI: https://doi.org/10.1039/C6TC01141A.

[34]. C. Tan, Q. Yang, R. Meng, Q. Liang, J. Jiang, X. Sun, H. Ye, X. P. Chen, An AlAs/germanene heterostructure with tunable electronic and optical properties: Via external electric field and strain, J Mater Chem C Mater. 4 (2016) 8171–8178. https://doi.org/10.1039/c6tc02951e.

[35]. V. Khuong Dien, W.B. Li, K.I. Lin, N. Thi Han, M.F. Lin, Electronic and optical properties of graphene, silicene, germanene, and their semi-hydrogenated systems, RSC Adv. 12 (2022) 34851–34865. https://doi.org/10.1039/d2ra06722f.