First Principles Study on The Effect of Single Beryllium and Magnesium Adatom on Germanane Monolayer Surface

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Abstract

Theoretical calculations predict that unlike the planar structure of graphene, the germanene also has stable, two-dimensional (2D), low-buckled, honeycomb structure which make it more interested in the field of optoelectronic applications recently, but the major issue with germanene are larger germanium-germanium (Ge-Ge) interatomic distance and zero energy band gap which become a great research gap. In this study, the effect of alkaline earth metal (AEM) Magnesium (Mg) and Beryllium (Be) adsorption on germanane monolayer within the density functional theory as implemented in Quantum ESPRESSO code has been investigated, Our calculated equilibrium hexagonal lattice constant a and the buckling height δ are found to be 4.047 Å and 0.689 Å respectively, among the chosen adsorptions sites (H, B and T) B side is found to be the most favourable side for both Be and Mg absorptions, due to the less adsorption energy and AEM-Ge distances. For the electronic properties. The Be and Mg adsorptions lead to semiconducting behaviour with direct gap of about 0.206 eV 0.629 eV for Be and Mg adsorption respectively. The obtained results are in agreement with many reported theoretical results.

Keywords: Germanene Monolayer, Density Functional Theory, Adsorption, Electronic Properties.
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Introduction

Recently, the monolayer honeycomb structure of germanium (Ge), germanene, has been successful synthesized through Ge molecular beam epitaxy using Au (1 1 1) surface as a substrate [1]. As reported by early theoretical works, germanene is a zero-band gap semimetal, same as graphene [2-3]. Moreover, being an analogue of graphene, germanene also possesses a feature such as linear band dispersion behavior around the Fermi level at the K point, which leads to have high carrier mobility [3]. Additionally, some fantastic features of germanene such as quantum spin Hall Effect [4-5], valley Hall Effect a tunable band gap [6-7] and topological insulators nature at room temperature [8] have been well investigated. Besides, the possibility of easier incorporation of germanene in nanoelectronics devices compared to graphene, tailoring the electronic and magnetic properties of germanene is of both fundamental and applied interest.

Theoretical calculation predicts that unlike the planar structure of graphene, the germanene has stable, two-dimensional, and low-buckled, honeycomb structure similar to that of silicane, but has much higher spin-orbit electronic properties than that of silicane, which is certainly of crucial importance in future electronics. As studies on germanene are rapidly increasing, now the major challenge in this field is the preparation of high-quality germanene. Compared with silicane, the germanene has larger Ge-Ge interatomic distance which can weaken the orbital overlaps, resulting in the big difficulty in constructing germanene. Even with excellent electronic and magnetic properties, germanene

suffers from zero energy band gap. Applying electric field [8], Absorption of adatom species [9], introducing periodic nanoholes [10], doping [11], and edge functionalization are possible means to address the above-mentioned difficulties.

Recently, the adsorption characteristics of alkali metal (AM), alkali-earth metal (AEM), and even 3d transition-metal (TM) adatoms on 2D surfaces such as Silicane [12] graphene [13-14] and stanene [15] was carried out as the most appealing and conventional strategy to tailor the electronic and magnetic properties of these materials. Similarly in our other work [16] a TM doping on germanene surface was carried out. In each case, a remarkable electronic and magnetic property has been achieved but still with some future recommendations on how the properties germanene can be tailored to suite more optoelectronic applications

To the best of our knowledge, the AEM doping or adsorption on germanene monolayer are still remains an open research question. Therefore, this work aimed at study the effect of AEM Magnesium (Mg) and Beryllium (Be) adsorption on germanane monolayer within the density functional theory.

Method

In this work, calculations relating the adsorption of Be and Mg adatoms on germanene monolayer are performed using first-principles calculation based on DFT as implemented in QUANTUM ESPRESSO (QE) code [17]. The Perdew-Wang 91 generalized gradient approximation scheme (PW-GGA91) [18] has been used to approximate the electron exchange-correlation energy. The plane wave basis sets (Kresse, 1996), with the maximum kinetic energy cutoff up to ~ 460 eV was adopted for the valence electron wave functions. The norm-conserving Vanderbilt ultrasoft pseudopotentials [19] used includes four electrons for germanium ($2s^2 2p^2$), three electrons for Be ($4s^2 4p^1$), five electrons for Mg ($4s^2 4p^3$). The effect of Fermi-surface is treated with Marzari Vanderbilt smearing method with small Gaussian broadening of 0.002 Ry. The model of our system corresponds to a coverage of one Be or Mg adatom on a 4×4×1 germanene Monolayer supercell, plus a ~15A° vacuum layer, perpendicular to germanene along the *z*-axis to avoid inter-layer interactions. We have used the germanene lattice constant of 4.26 Å [20]. A small Be or Mg adatom on germanene is simulated along *z*-direction, perpendicular to germanene, while the *x* and *y* directions are parallel with the germanene surface. The Brillouin zone integration is performed using Monkhorst-Pack scheme [21] with 6× 6×1 Γ-centered *K*-point grids.

The calculated charge transfer and the electronic density of states are found using denser *k*-point mesh. First, after the convergence test of the system, the stable height at high symmetry has been obtained. The adsorption of Be and Mg on three adsorption sites: namely, the hollow site (H), which is directly to the center of the hexagonal rings of the germanene, the bridge site (B), which is in between the germanium-germanium bond; and finally, the top site (T), which is directly on top of one of the germanium atoms in the germanene monolayer are also considered in this work. This was followed by the relaxation of the entire system. A single isolated Be and Mg adatoms in a separated with a vacuum of length ~16 Å along *z*-direction.

Discussion

Germanene Monolayer

The germanene monolayer atomic geometries are optimized using BGFS within DFT-GGA as implemented in QE as the initial step. This type of calculation is done with variable-cell optimization so that other analysis uses these optimized both the cell and atomic coordinates, which is beneficial for less or defect-free structure and structural optimization. The bond length between Ge-Ge is 2.3312 Å which is in excellent agreement with the theoretical values reported by [22-23] and the bond angle of Ge-Ge-Ge is 120°. The unit cell and hexagonal lattice structure in 2-D viewed in Burai for monolayer germanene is illustrated in Figure 1.

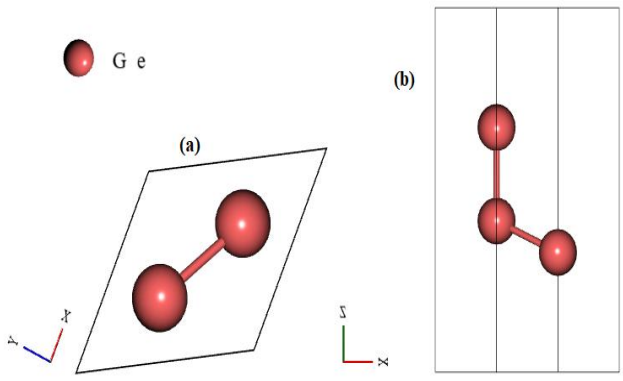

Figure 1:(a) Monolayer graphene unit cell (b) three-dimensional (3D) lattice structure.

From the figure one can see that the unit cell of monolayer germanene contains two germanium atoms. In addition, the shape of the unit cell of monolayer is said to be in a lozenge shape. The lattice structure of the monolayer can be seen to be as a monolayer of atoms with the axis of direction given in both Figure 1(a) & (b). Therefore, these structures are proven accordingly as Germanene monolayer, which is in excellent agreement with the reported results in [16, 22-23].

In order to obtain the most desirable site for alkaline earth metal (AEM) atoms adsorption on germanene monolayer, we firstly choose a (4 × 4×1) germanene supercell as our model, in which the distance between neighboring AEM adatoms is about 15.976Å. The optimized atomic structure

of the germanene supercell is shown in Figure 2. For more simplicity, we symbolize the sublattice along Z coordinate as sublattice A, and the other one as sublattice B. Our calculated equilibrium hexagonal lattice constant a and the buckling height δ are found to be 4.147 Å and 0.689Å respectively. The values are in good agreement with those reported by [16, 22-23].

Adsorption of single Beryllium and Magnesium adatoms on germanene monolayer

This section investigates the adsorption of two different metals, namely Be and Mg adatoms on germanene, thereby to provide comprehensive details of their effects on the electronic structure and density of states properties of single germanene monolayer. In view of these, feasible adsorption consequences, such as charge transfer between Be and Mg adatoms to germanene, *s*,*p*,*d*-hybridizations, electronic and structural changes have been carefully analyzed and reported.

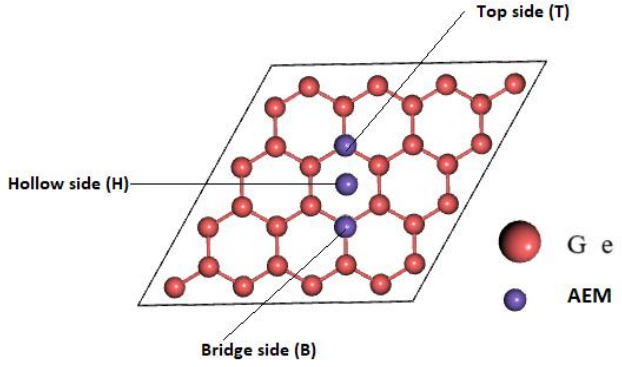

Figure 2: Typical illustration of the three adsorption sites HBT of a relaxed 4 × 4×1 germanene monolayer supercell.

However, these are the starting points towards the discussion of the next section, in which explanations on possible adsorption of AEM on germanene monolayer is given. This is the part of our contributions towards the realization of different types of AEM built on germanene monolayer surfaces. Because, direct integration of germanene with any system that can produces a semiconductor material can be the basis towards achieving high performance germanene/ AEM hybrid-based devices based on their higher carrier mobilities.

Normally, before getting the relaxed structures, the adatoms (Be and Mg) are first placed at the high-symmetry positions (H, B and T) sites in order to find the stable height for the adatoms. Initially, in that position and direction, the symmetry of the system breaks and subsequently the locally stable configurations will be found after relaxation. In Figure 2, the model configurations of the stable height for both AEM adatoms are shown, with adatoms along the *z*-axis and the germanene monolayer. However, the stable distance between the AEM adatoms with Ge atom can be measured. In this case, the measured stable distance between Be and Mg adatoms along the most stable adsorption side (B-side) was found to be around 2.13 Å and 3.60Å respectively. This indicated that the Be adatom has less distance which indicates that it probably be the most stable adatom on germanene monolayer. In order to affirm about the most stable adsorption sites, the adsorption energy was calculated at each chosen site for the each adatom.

Table 1: Calculated optimized structure of the adsorption energies and structural geometry for Be adatom on germanene, H, B and T sites:

	Adsorption sites	E_{ab} (eV)	$d_{Ge\text{-}AEM}$ (Å)	$\Theta^{o}_{AEM\text{-}Ge}$	$d_{Ge\text{-}Ge}$ (Å)
Be/Germanene	H	0.764	2.26	65.2	2.335
	B	0.671	2.13	34.5	2.335
	T	0.660	2.34	89.2	2.335
Mg/Germanene	H	1.172	3.91	39.9	2.345
	B	1.170	3.60	21.2	2.345
	T	1.174	4.05	89.9	2.345

The calculated adsorption energy was done by using the expression below [24].

$$E_{adsorp.} = (E_{Germanene} + E_{AEM}) - E_{AEM/Germanene} \quad (1)$$

where $E_{Germanene}$ is the total energy of the isolated pristine 4×4×1 germanene monolayer supercell, E_{AEM} is the total energy of the adatom, $E_{AEM/Germanene}$ is the total energy of an AEM on top of the germanene monolayer. Our calculated adsorption energies are summarized Table 1 below.

From the two Tables 1, it has been observed that all the calculated adsorption energies are positive which indicated that there is a strong attraction between the Adatom at each chosen sites and process is exothermic. That is the releases energy is favorable meanwhile for the most favourable side we have chosen B side in both Be and Mg absorptions, this is because in each case the absorption energies are lesser and also the bond lengths a smaller when compare with the other sites. These results are in good agreement with many results such as [16, 22-23].

Electronic properties

For the electronic properties, we obtained the electronic band structure and densities of states (DOS) of germanene monolayer are shown in Figure 3 The Band structure was plotted along the high symmetry point Γ →M → K→Γ→A→L in the first Brillouin zone, as shown in Fig. 2(a). At the K- point, the germanene monolayer exhibits a zero-band gap with the Dirac cone similar to that of graphene and silicane. This result is good agreement with previously reported theoretical estimates [25-27].

The total density of states (TDOS) of germanene monolayer shown in Figure 2(b) indicated that the lowest valance bands (about 1.0 state/eV) occur between -6 and -3 eV while the highest valance band (about 4.6 state/eV) is between -1.1 and 2.2eV. This corresponds to the dominated by p orbital of germanium atom as reported by [26]. The lowest and highest conduction band of about 0.56 state/eV and 4.2 state/eV occurs at 6.6eV and 4.9eV respectively indicates the possible domination of both s and p orbitals of Ge atom confirming a possible strong covalent bonding in the germanene monolayer [25-27].

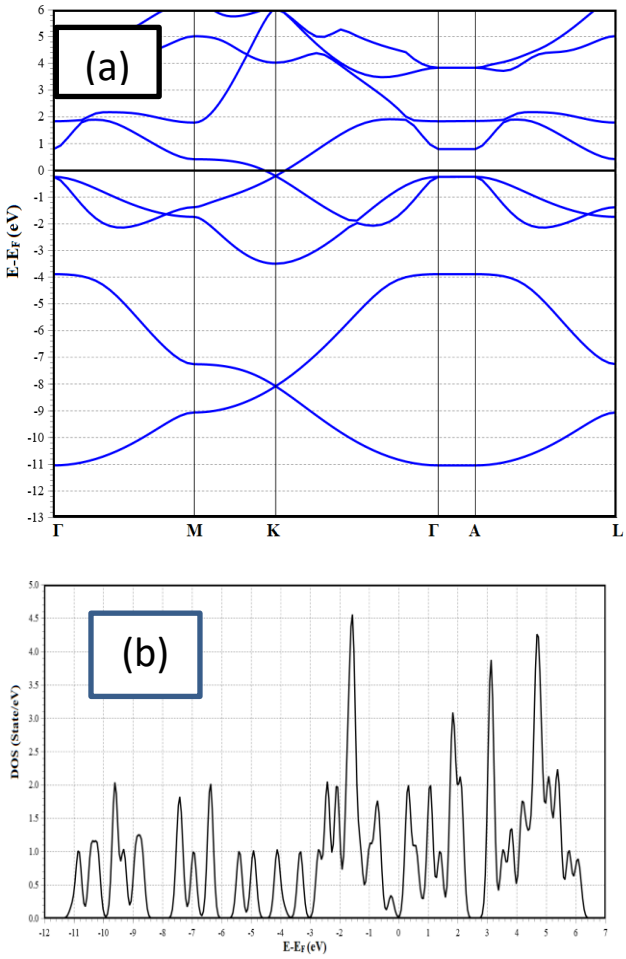

Figure 3: Band structure and Total Density of state (DOS) of pure germanene monolayer.

In other to investigate the electronic properties of AEM adatoms adsorbed germanene monolayer, we consider the calculated band structure and atomic projected density of state of the AEM/germanene at the most stable adsorption side as shown in Figure 2 and 3 for Be/Germanene and Mg/Germanene at B-side respectively.

Figure 4 (a) show the calculated structure of Be adsorbed on the B-side (Be@B-side) of the germanene monolayer, this shows a complete semiconducting nature with opened direct gap of about 0.206 eV along the Γ-A high symmetry points. This result is in agreement with many results reported in [16, 25-27].

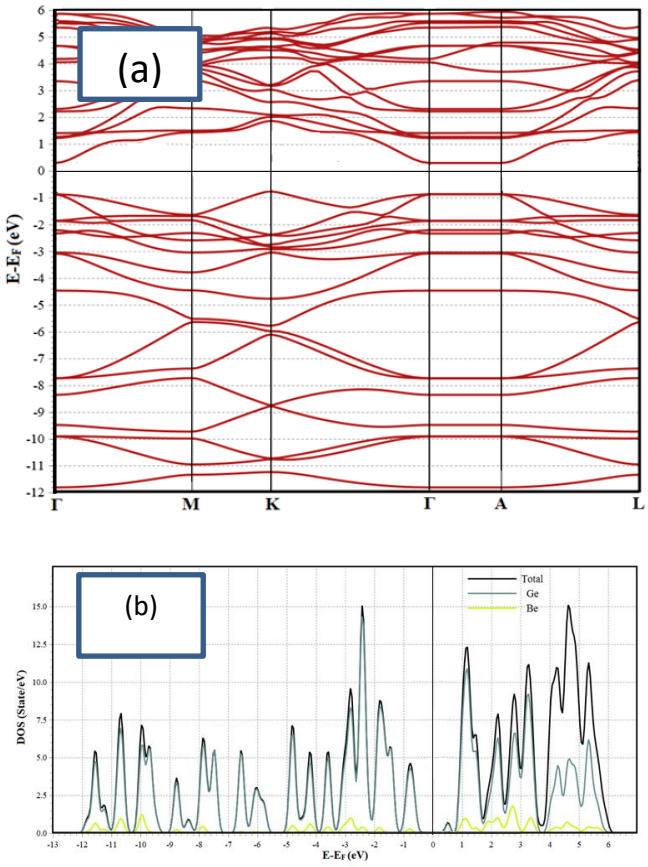

Figure 4: Band structure and Atomic projected Density of state (ADOS)of Be atom on germanene monolayer Be@B-side.

For the obtained atomic density of state (ADOS) of Be@B-side monolayer between -13 to 6eV as shown Figure 4(b). It was observed that that the Ge atom presence is quite similar to the case of pure germanene monolayer, where the p(s) orbitals are the main contributor to form the electronic structure in the considered energy range from − 13 to 6 eV. As expected, the electronic state belonging to the Be adatom throughout the energy range, confirming a possible mixture of ionic and covalent bonding. These finding are in good agreements with the previous results by [16].

Figure 5(a) show the calculated structure of Mg adsorbed on the B-side (Mg@B-side) of the germanene monolayer, this shows a character with that of Be@B-side, only with opened direct gap of about 0.629eV along the Γ-A high symmetry points. Similarly, this result is in agreement with many results reported in [25-27]. For the obtained atomic density of state (ADOS) of Be@B-side monolayer between -13 to 6eV as shown Figure 5(b). It was observed that that the Ge atom presence is quite similar to the case of pure germanene monolayer, where the p(s) orbitals are the main contributor to form the electronic structure in the considered energy range from − 13 to 6 eV. As expected, the electronic state belonging to the Be adatom throughout the energy range, confirming a possible mixture of ionic and covalent bonding. These finding are in good agreements with the previous results by (Pang, et al, 2015).

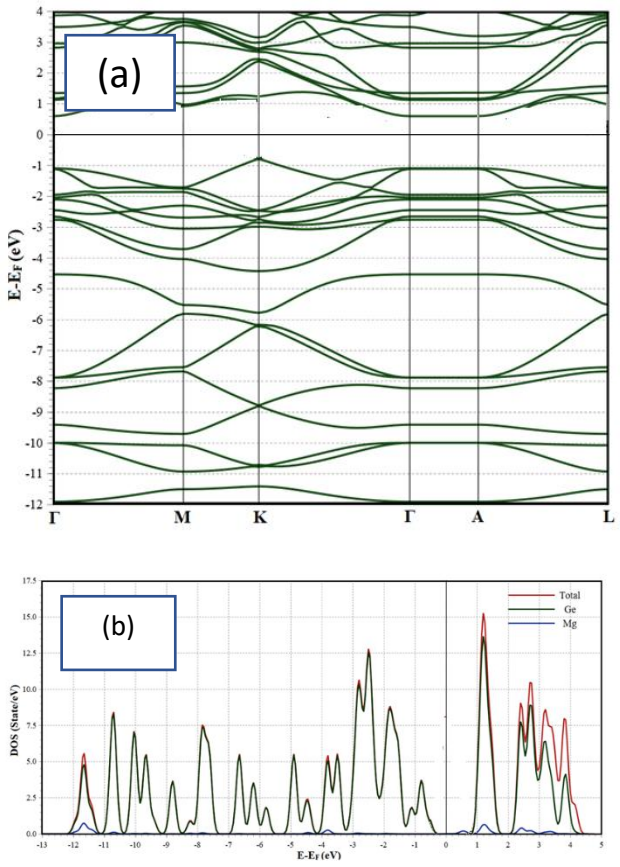

Figure 5: Band structure and Atomic projected Density of state (ADOS) of Mg atom on germanene monolayer Mg@B-side

Conclusion and Future Prospective

Conclusively, first principal plane waves pseudopotential calculations within the frame-work of density functional theory (DFT), are employed to investigate the structural and electronic properties of Be and Mg-adsorption on germanene monolayer. The findings reveal that equilibrium hexagonal lattice constant a and the buckling height δ are found to be 4.047 Å and 0.689 Å respectively, among the chosen adsorption's sites (H, B and T) B side is found to be the most favourable side for both Be and Mg absorptions, due to the less adsorption energy and AEM-Ge distances. For the electronic properties. The Be and Mg adsorptions lead to semiconducting behaviour with direct gap of about 0.206 eV 0.629 eV for Be and Mg adsorption respectively. The obtained results are in agreement with many reported theoretical results.

The results from this study demonstrated that improving the electronic features of germanene, enhances its mobile character and these can be achieved through functionalization or doping techniques with a new model. Therefore, further research is required to speed up the practical applicability of these materials at small scale. Our results obtained from this work confirm the findings of a recent study which show that the electronic properties of germanene could be transformed from semi-metallic to metallic even with the low adsorption of Alkaline earth Thus, further research in the following areas is recommended:

1. Further investigation into quantum transport in germanene with more AEM is required.

2. It will be interesting to investigate the effect of other Metallic materials on electronic properties of germanene; example, Ca, Mn, Fe etc. which are often used for epitaxial growth in micro-electronics production for potential applications.

3. Although, this study has not considered the combine influence of the adsorbed atoms (Be and Mg), it is suggested that subsequent study should at least try to capture those properties, such as exchange interactions between the AEM with germanene.

References

1. M. E. Dávila, Xian, L., Cahangirov, S., Rubio, A., & Le Lay, G. New Journal of Physics, 16(9), 095002. 2014.
2. S., Cahangirov, Topsakal, M., Aktürk, E., Şahin, H., & Ciraci, S. Physical review letters, 102(23), 236804. 2009.
3. N. J. Roome, & Carey, J. D. ACS applied materials & interfaces, 6(10), 7743-7750. (2014).
4. C. C. Liu, Feng, W., & Yao, Y., Physical review letters, 107(7), 076802. (2011).
5. A. Acun, Zhang, L., Bampoulis, P., Farmanbar, M. V., van Houselt, A., Rudenko, A. N., & Zandvliet, H. J. Journal of physics: Condensed matter, 27(44), 443002. (2015).
6. Z. Ni, Liu, Q., Tang, K., Zheng, J., Zhou, J., Qin, R., ... & Lu, J. Nano letters, 12(1), 113-118. (2012).
7. C. Si, Liu, J., Xu, Y., Wu, J., Gu, B. L., & Duan, W. Physical Review B, 89(11), 115429. 2014.
8. S. S. Li, Zhang, C. W., Ji, W. X., Li, F., Wang, P. J., Hu, S. J., ... & Liu, Y. S. Physical Chemistry Chemical Physics, 16(30), 15968-15978. (2014).
9. Y. C. Cheng, Zhu, Z. Y., Mi, W. B., Guo, Z. B., & Schwingenschlögl, U. Physical Review B, 87(10), 100401. (2013).
10. M. W. Chuan, Wong, K. L., Hamzah, A., Rusli, S., Alias, N. E., Lim, C. S., & Tan, M. L.. Current Nanoscience, 16(4), 595-607. (2020).
11. Q. Pang, Zhang, Y., Zhang, J. M., Ji, V., & Xu, K. W. Nanoscale, 3(10), 4330-4338. (2011).
12. H. Sahin, & Peeters, F. M. Physical Review B - Condensed Matter and Materials Physics, 87(8), 085423. (2013).

13. S. Abubakar, Rahman, M. M., Abdullahi, Y. Z., Zainuddin, H., Muhida, R., & Setiyanto, H. Graphene, 1(2), 78-85. (2013).
14. M. M. Rahman, Abdullahi, Y. Z., Shuaibu, A., Abubakar, S., Zainuddin, H., Muhida, R., & Setiyanto, H. Journal of Computational and Theoretical Nanoscience, 12(9), 1995-2002. (2015).
15. J. Chen, Wang, Z., Dai, X., Xiao, J., Long, M., & Chen, T. Physica E: Low-dimensional Systems and Nanostructures, 124, 114365. (2020).
16. S. L. Usman, Shuaibu, A., & Maharaz, M. N. Computational And Experimental Research In Materials And Renewable Energy, 7(1), 9-26. (2024).
17. P. Giannozzi, Baroni, S., Bonini, N., Calandra, M., Car, R., Cavazzoni, C., ... & Wentzcovitch, R. M. Journal of physics: Condensed matter, 21(39), 395502. (2009).
18. J. P. Perdew, Burke, K., & Ernzerhof, M. J. P. R. L. Perdew, burke, and ernzerhof reply. Physical Review Letters, 80(4), 891. (1998).
19. J. Furthmüller, Käckell, P., Bechstedt, F., & Kresse, G. Physical Review B, 61(7), 4576. (2000).
20. L. Zhang, Bampoulis, P., van Houselt, A., & Zandvliet, H. J. Applied physics letters, 107(11). (2015).
21. H. J. Monkhorst, & Pack, J. D. Physical review B, 13(12), 5188. (1976).
22. D. Coello-Fiallos, Tene, T., Guayllas, J. L., Haro, D., Haro, A., & Gomez, C. V. Materials Today: Proceedings, 4(7), 6835-6841. (2017).
23. D. M. Hoat, Nguyen, D. K., Ponce-Perez, R., Guerrero-Sanchez, J., Van On, V., Rivas-Silva, J. F., & Cocoletzi, G. H. Applied Surface Science, 551, 149318. (2021).
24. R. Hussain, Saeed, M., Mehboob, M. Y., Khan, S. U., Khan, M. U., Adnan, M., ... & Ayub, K. RSC advances, 10(35), 20595-20607. (2020).
25. M. R. H. Mojumder, arXiv preprint arXiv:2201.02676. (2022).
26. J. E. Padilha, & Pontes, R. B. Solid State Communications, 225, 38-43. (2016).
27. W. Q. Meysam Bagheri Tagani, Qiwei Tian, Sahar Izadi Vishkayi, Li Zhang, Long-Jing Yin, Yuan Tian, Lijie Zhang, and Zhihui Qin." Applied Physics Letters 121, no. 5 (2022).