Manipulation of inherent properties of graphene through co-doping of Si and Ge atoms; a DFT study

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Abstract
This work examines the effect of co-doping the Si and Ge on the structure of graphene in terms of the structural, electronic and optical properties based on First-principles (FPS) density functional theory calculations. The immersion of impurity atoms was increased from 8.33% to 12.5% and their causes on pure graphene characteristics were investigated. It is observed that, co-doping of Si and Ge atoms in graphene leads to broadening of band gap at the Dirac K-point. We also found that, co-doping of silicon and germanium atoms in graphene lattice significantly changes its optical parameters in the visible range of spectrum. These results suggest a unique method to tailor the opto-electronic properties of graphene layer which can be realized on experimental basis as well.

Key words:
Graphene; doping; Fermi energy level; VASP; Dirac Point;

1. Introduction

Graphene [1] is a single allotrope of carbon atoms arranged in two-dimensional hexagonal lattice, discovered by Geim and Nosovelov in 2004 at Manchester university [2],[3]. In 21st century graphene has emerged as an attractive candidate for science and technology, particularly electronics [4], [5], energy storage and conversion [6], [8], sensing, and biomedical research [9] due to its unique structure and properties [10], [13]. Moreover, the absence of band gap in graphene might limit its use for real engineering applications where appropriate band gap is a requisite. The major reason for this zero band gap in pristine graphene is the identical atmosphere of two C-atom in its unit cell [14], [15]. Therefore, it is necessary to break this atmosphere in order to open the band gap of pristine graphene. For instance, the symmetry could be broken if atoms of carbon in unit cell are substituted or absorbed by foreign atoms. Depending on their nature, these foreign atoms shifts the Fermi energy level (E_F) up or down [16], [17]. Many studies [18], [20] reveal that the, graphene can be made semiconducting material by doping with different foreign atoms. Since graphene is zero band gap semi-metal while, Silicon (Si) and Germanium (Ge) are the semiconductors having wide band gap. Hence doping the graphene by these atoms can produce considerable band gap in its electronic structure [21], [25].

Very recently, FPS calculations based study reports that, doping the graphene with individual Si and Ge atoms can alter its optoelectronic parameters [26], [27]. However, in this study Si and Ge atoms are co-doped with the variation of dopant concentration. Hence, we have manipulated the Si-Ge co-doping effects on the intrinsic graphene by varying dopant concentration in constant size of super cell structure.

2. Computational method

In the present study, we have used DFT and pseudo potential method based first-principle calculations implemented in Vienna Ab-initio simulation package (VASP) [28], [29]; in order to investigate optoelectronic properties of pure as well as Si-Ge atom co-doped graphene. For the purpose of exchange-correlation energy functional, general gradient approximation (GGA) were used as described by Perdew-Burke-Ernzerhof (PBE) [30]. For the expansion of the ground state electronic wave function, the plane waves with energies up to 400eV cut-off were used. The model used in this study consists of 4×3 supercell of graphene containing 24 number of carbon atoms. In order to eliminate the dealing between adjacent layers a vacuum of 12 Å has been induced in the Z-direction. However, to achieve self-consistent results, the Brillion zone was sampled using 11×11×1 Γ-centered k-points. All the structures were relaxed until the potential on each was lower than the 0.02 eV/ Å and equivalent

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energy was lower than 10^{-6} eV. All the computations were done in spin-polarized mode.

3. Results and discussions

Initially we investigated and fully optimized the geometry of pure graphene sheet. After optimization, it was found that the lattice constant of pure graphene is as 2.4589Å. This result is in close agreement with the experimental value of 2.46 Å. The bond length between the carbon atoms was found to be 1.418 Å, which is in close agreement with previous calculated values [32]. The Figure 1 (a) and (b) shows the optimized geometry of 4×3 pure graphene supercell and band structure diagram. Our simulated results were found to be in good agreement with previous literature [33].

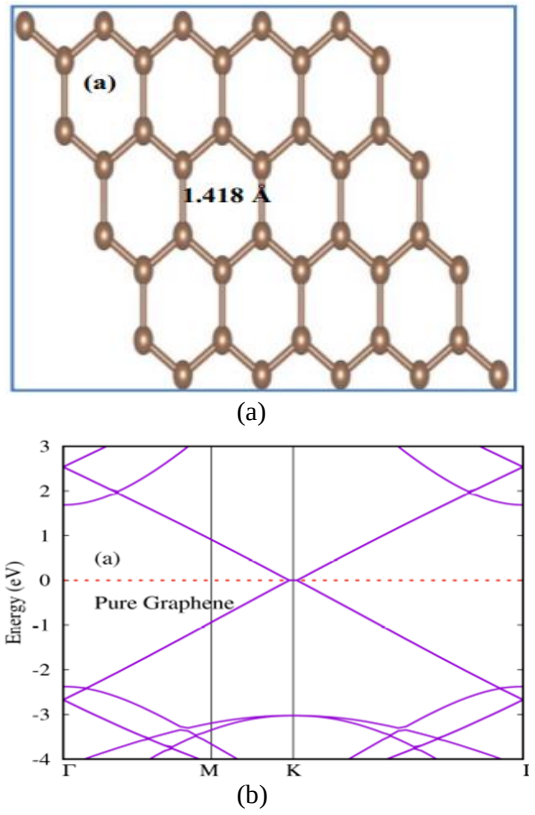


Fig. 1 (a) Pristine monolayer graphene sheet (b) Simulated electronic band structure of pristine graphene. After the geometry optimization, pure graphene doped with foreign atoms and their concentration is changed during our course work.

3.1 The structural and electronic parameters of Si-Ge co-doped grapheme

Figure 2 shows the simulated results for Si-C, Ge-C and C-C bond lengths. After Si-Ge co-doping, it is found that, via sp^2hybridization process the Si and Ge atoms forms the strong covalent bonds with neighboring C atoms. This overall change in lattice structure of pure graphene is due to doping of Si and Ge atoms. Our calculated results regarding structural parameters show consistency with the previous literature [34], [35].

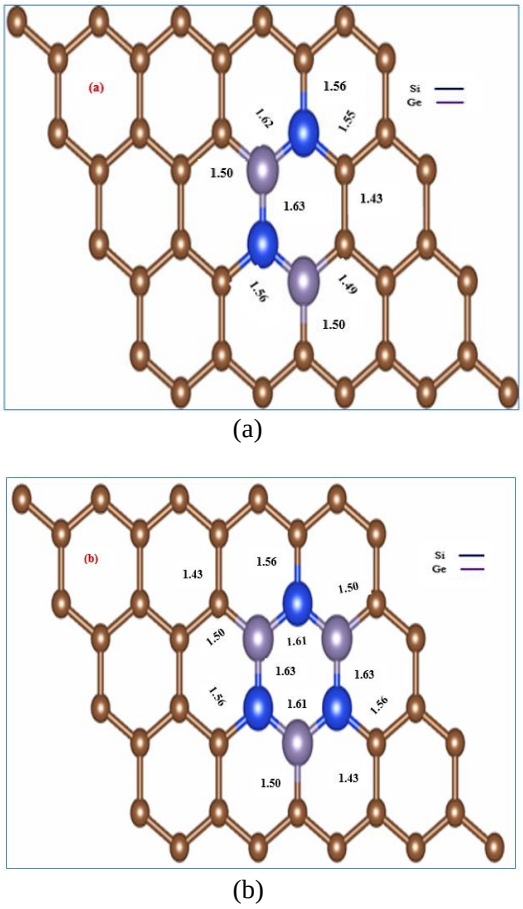


Fig. 2 Optimized structure of Si-Ge co-doped graphene with (a) 8.33 % and (b) 12.5 % dopant concentration

Later, we investigated the effects on electronic properties of graphene, co-doped with silicon and germanium atoms by varying dopant concentration. In Figure 3 it is clear that, band gap value induced in graphene structure changes with variation in dopant concentration. The substitution of 2SiGe atoms in graphene structure induced the band gap of approximately 0.9 eV at the Dirac point, which is consistent with previous studies [36], [39]. However, as the dopant concentration is increased (i.e., 3SiGe atoms) in graphene super cell, the induced band gap vanishes, which indicates the maximum crystal limit of material. Obtained results suggest that, doping the graphene with silicon and germanium atoms causes induction of fine band gap at Dirac point. These predictions are in complete agreement with previous reports [39], [40].

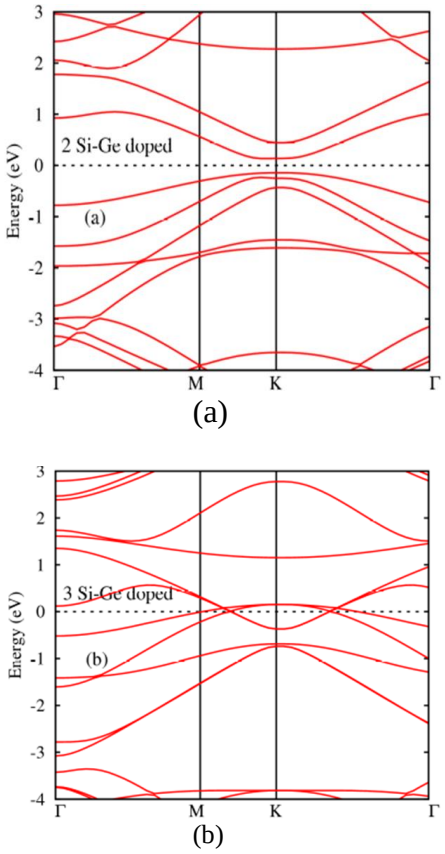


Fig. 3 Band structures of Si-Ge co-doped graphene with (a) 8.33 % and (b) 12.5 % dopant concentration

3.2 Optical parameters of Si-Ge co-doped graphene

After optimization of electronic parameters, we used Random Phase Approximation (RPA) [41] approach within density function theory calculation method in order to investigate the optical characteristics of intrinsic and Si-Ge co-doped graphene. First we calculated the value of dielectric constant i.e **(ε=ε′ +iε″)**. After calculating the value of dielectric constant, we can easily get the values of the refractive index '***n***', extinction coefficient '***k***', absorpion coeffiient '***α***' and reflectivity '***R***'. The detail of technique used for calculating mentioned parameters is elucidated in Ref. [42], [43]. The optical parameters which we have calculate are in close agreement with previous work [18], [23], [44].

Figure 4(a-c (c) show the variation of the refractive index plots of pristine as well as Si-Ge co-doped graphene with varying dopant concentration.The static refractive index value is 2.7 in case of pure graphene. It is also clear that, its least crest value appears at approximately 5eV. However, the static refractive index value is increases after Si-Ge co-doping. Its value is 3.75 in case of 2SiGe co-doping as shown in Figure 4(b).

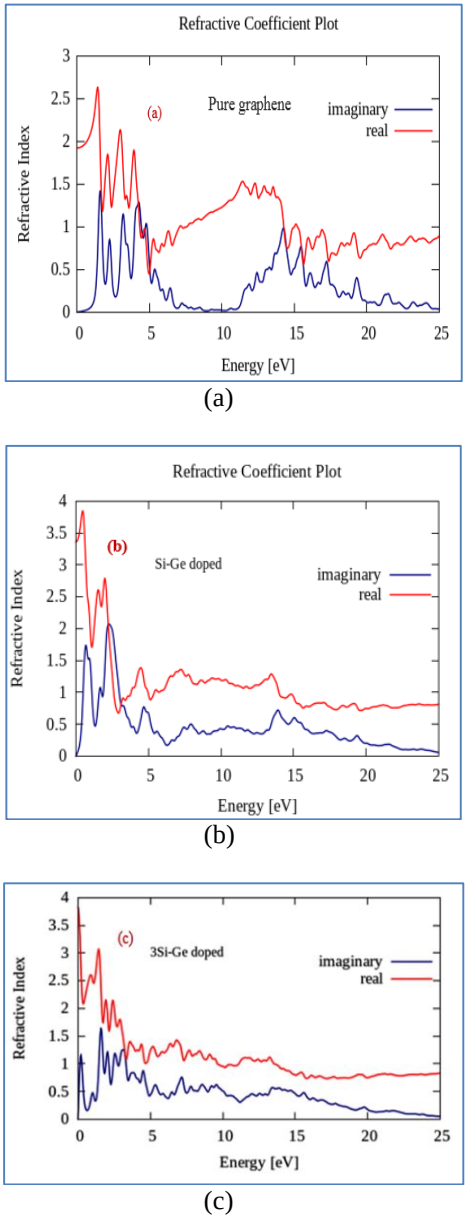
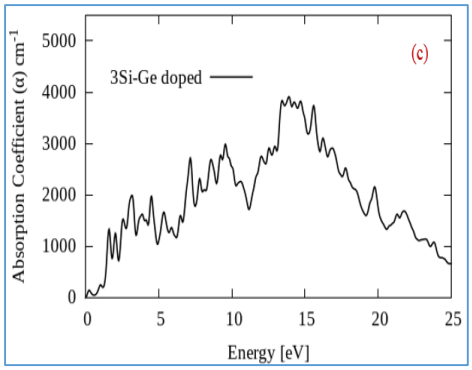


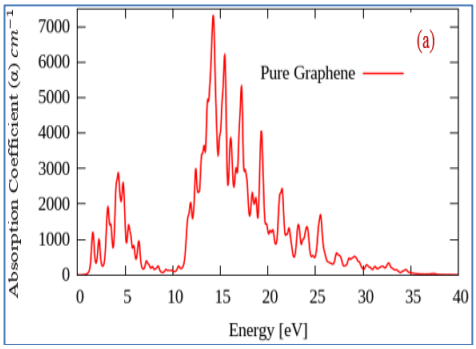
Fig. 4 (a) Refractive index plot of pure (b) 2Si-Ge atom co-doped and (c) 3Si-Ge atom co-doped grapheme

Similarly, the maximum peaks of extinction coeffficient (k) appears at 1 eV and 5 eV with intensities at 1.45 and 1.3 respectively. Though, after 2Si-Ge co-doping, the value of first highest peak converges towards smaller value at 0.7 eV with an intensity of 1.75 as shown in Figure 4(b). Similarly, same changes were observed as the doping concentration is increased as described clearly in Figure 4(c). This behaviour suggests that co-doping of silicon and gemanium atoms in graphene can change its optical parameters.The absorption coefficient (α) plots of intrinsic and silicon and germanium co-doped graphene systems are

represented in Figure 5. In case of pure graphen, two major peaks appears at approximately 4.5 eV and 14 eV with intensities of $\sim 3000 cm^{-1}$ and $7300 cm^{-1}$respectively as reprented in Figure 5(a). These results are relaible as compared to the past literature [45]. Moreover, in a pure graphene zero absorption peak appears at 0-0.5 eV and 7-11 eV energy range. However , after co-doping of graphene with Si and Ge atoms, the absorption coefficient peak starts from the energy level of ~ 0 eV, indicating red shif as shown in Figure 5 (b)-(c).



(a)



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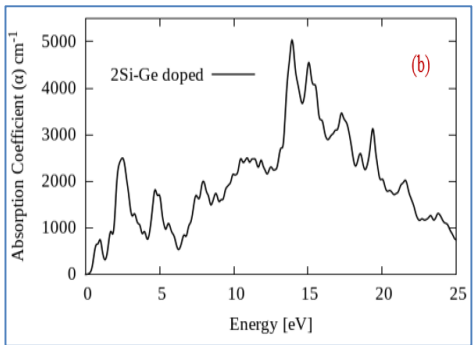
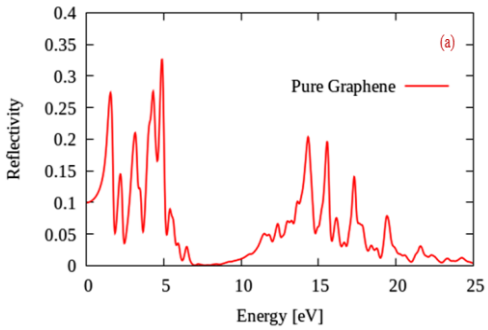


(c)

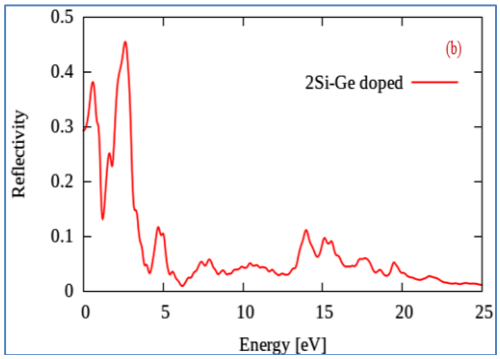
Fig. 5 Absorption coefficient of (a) pure (b) 2Si-Ge atom co- doped and (c) 3Si-Ge atom co-doped grapheme

Similarly, notable changes are also observed in the range of 7-11 eV energy intervals. It is observed that after Si-Ge co-doping in highest absorption peak at 14 eV in the regard of pure graphene gets smaller values where as the leasts absorption crest appearing at approximately 4.5 eV and shifts towards lower potential limits. From calculated absorption parameters we can perdict that, co-dopng of graphene with Si and Ge atoms causes overall decline in absorption coefficient but provides a red-shift in absorption spectrum at visible energy region.

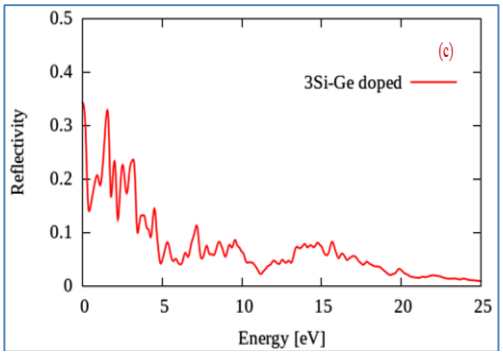
The reflectivity diagrams for intrinsic and and Si-Ge atom co-doped grphene are presented in Figure 6(a) to 6(c). For investigating the considerations of Si-Ge atom co-doping on the reflectivity of graphene, the energy intervals are considered from 0 to 25 eV. There are three main peaks in reflectivity plots of pure graphene having intensity of ~ 0.28, 0.33 and 0.21 at energy levels of ~ 1.5 eV, ~ 4.5 eV and ~ 14 eV as presented in Figure 6(a), respectively [23], [43].



(a)



(b)



(c)

Fig. 6 Reflectivity plot of (a) pure (b) 2Si-Ge atom co-doped and (c) 3Si-Ge atomco-doped graphene.

However,the intensity of two main peaks appearing at energy level of approximately 4.5 eV and 14 eV has been reduced when atoms of Si and Ge are co-doped into graphene rings, as depicted in Fig.6(b) and 6(c). Also, the first peak appearing in the reflectivity plot of pure graphe at intensity of 0.28 at energy level of 1.5 eV in inreased upto intensity of approximately 0.39 and 0.35 for 2Si-Ge and 3Si-Ge co-doped graphene as shown in Fig. 6(b) and 6(c) respetively. It can be concluded that, co-doping of pure graphene by Si and Ge atoms increases the static reflectivity and also reduces the reflectivity in the range of lower energy values as depicted in Fig. 6(b) and 6(c) respectivily[23,43].

4. Conclusions

This study invesigated the effect of Si and Ge co-doping on the structural and optoelectronic properties of graphene based on FPS-DFT calculations. The concentration of dopant atoms were increased from 8.33% to 12.5% and their effects on pure graphene characteristics were investigated. It was found that, the substitution of 2Si-Ge atoms in graphene structure induced the band gap of ~0.9 eV at the Dirac point where as, by increasing the dopant concentration (3Si-Ge atoms) in graphene supercell, the induced band gap again vanished, which indicates the maximum crystal limit of material. For optical parameter calculatons, it is observed that, the co-doping of silicon and germanium atoms in graphene causes the variations in n and k peak values. It is also found that, the peak appearing at 4.5 eV energy in the spectrum of pure graphene shows a red-shift in absorption spectrum at visible energy region when Si and Ge atoms are co-doped into graphene. Moreover, co-doping of silicon and gemanium atoms causes absorption spectrum to start at 0 eV energy. Similarly, in case of reflectivity parameters, co-doping of Si and Ge atoms causes reduction in crest intensities in greater potential levels while increase in crest intensities is found in smaller potential limits. At the last, we can suggest that, co-dopig of silicon and germanium atoms in graphene can induce direct band gap in semiconducting graphene and also produce new trends in optical parameters which can provide an opportunity for graphene to be fuctional in the engineering world, specially in the fiels of photonics and nanoelectronics.

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