First principle study of Germanium and Selenium doped monolayer black phosphorus

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ABSTRACT

Within the framework of density functional theory, we investigate the effects of dopants germanium and selenium on the electronic properties of monolayer black phosphorus. Dopants are introduced in two possible chemisorption and substitution configuration. Findings of this work suggest that germanium is optimal dopant in both the configurations since inpurity states need only low ionization energies to excite bound electrons to band edges. Band gap is tunable depending on dopant introduced. Selenium act as deep dopant in substitution configuration with increased band gap and in chemisorption configuration there is no effect on band gap where there is prominent increase in electron concentration .

Keywords: monolayer-black phosphorus, density functional theory, band structure

1 INTRODUCTION

Black phosphorus (BP) has attracted the attention of researchers due to its 2D nature and tunable bandgap and anisotropic effective mass [1-2]. Theoretical calculations show that band gap is thickness dependent from 0.35 - 2 eV. Its novel electronic properties and tunable band gap highly enhance its promising applications in electronic devices like high responsivity photodetectors, thin film solar cells and channel material for field effect transistors (FETs) [3-5]. FET have been fabricated with few layer BP as channel material [6-9].

Monolayer black phosphorus (m-BP) termed as phospherene has been fabricated by some groups by exfoliation [10]. Many studies have been carried out to find changes in electrornic properties due to applied stress in m-BP since it is potential material for thin film transistors. It is shown that electronic properties of m-BP can be enhanced by introducing foreign atom (dopant) [11-13]. Many dopant and defect related studies have also been done in order to find optimal dopants for m-BP. However, to the best of our knowledge first principle study on germanium (Ge) and selenium (Se) as dopants in m-BP has not been reported. In this paper, we carry out first principle calculations to explore the impact of Ge and Se dopants on electronic properties of phosphorene.

The rest of the paper is organized as follows, section 2 presents simulation methodology whereas section 3 presents electronic properties of m-BP and compares the electronic properties of Ge doped m-BP and Se doped m-BP. Finally the conclusion is given in Section 4.

2 SIMULATION SETUP

The first principle calculations have been carried within the framework of density functional theory (DFT) with the help of Quantum espresso. Projected Augmented Wave (PAW) pseudopotentials are used to describe core electrons where exchange correlation is described with general gradient approximation (GGA) schemes of Perdew-Burke-Ernzehof (PBE). The van der Waals (vdW) corrections are implemented using Grimme corrections. A 2 x 2 supercell is formed from unit cell to carry out dopant study calculations. A vaccum space of 15 Å is added along the direction of thickness to avoid interlayer vdW interactions.

A 8 x 8 x 1 Gamma centered Monkhorst-Pack scheme is used for structural relaxation of unit cell and dopant induced supercell with an energy cut-off of 100 Ry. Structural optimization is done till forces on each atom are less than 10^{-3}Ry/Å and the total energy change is less than 10^{-5}Ry.

To explore the relative stability in dopant configurations (Chemisorption and substitution) formation energy E_{form} has been calculated. μ_X and μ_Y are the energies of single atom in their particular state and a is the number of atoms being removed and b is number of foreign atoms added. $E_{tot (Undoped)}$ and $E_{tot (doped)}$ are the energies of structure before and after doping.

$$E_{form} = E_{tot (doped)} - E_{tot (Undoped)} + a(\mu_X) - b(\mu_Y)$$
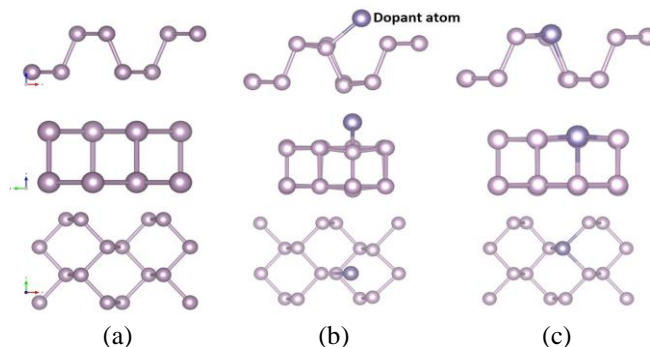

Fig. 1: (a) 2 x 2 super cell of m-BP, (b) Dopant atom doped in chemisorption configuration in supercell and (c) Dopant atom doped in substitution configuration in supercell.

	3D bulk structure	Monolayer
a	4.38 Å	4.626 Å
b	3.31 Å	3.351 Å
b1	2.17 Å	2.243 Å
b2	2.204 Å	2.261 Å
θ	49.74°	48.41°
φ	20.96°	21.41°

Table I. Planar lattice constants (a,b) and structural lattice constants (b1,b2, θ, φ) of Bulk and monolayer black phosphorus are shown.

3 RESULTS AND DISCUSSION

3.1 Properties of monolayer black phosphorus

BP is a layered material belongs to D_{2h}^{18} space group having a orthorhombic unit cell. Lattice parameters of bulk BP are shown in Table I. The layers in BP are weakly connected by van der Waals forces, thus exfoliation of monolayer from bulk is easier and done by several groups [10]. Monolayer BP has a buckled honeycomb structure as shown in Fig 1. The lattice parameters of monolayer BP are shown in Table I and corresponding structural constants are shown in Fig 2.

Monolayer BP has direct bandgap of 1.01 eV as shown in Fig 3 which is smaller than experimental bandgap 1.55eV. It is well known that DFT underestimates bandgap of semiconductors and insulators due to localized and semi-localized of DFT functionals. Obtained bandgap matches with the previous work [12] performed with semilocal PBE describing exchange correlation energy.

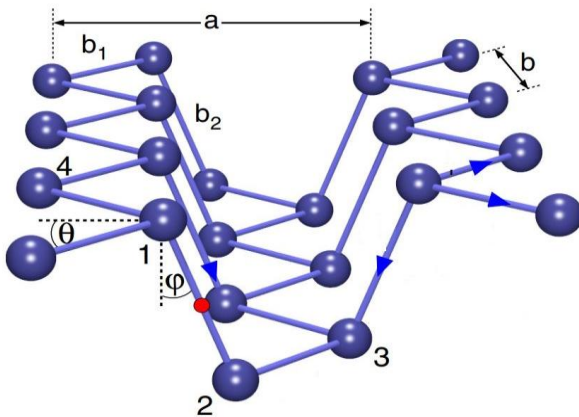### 3.2 Germanium doped m-BP

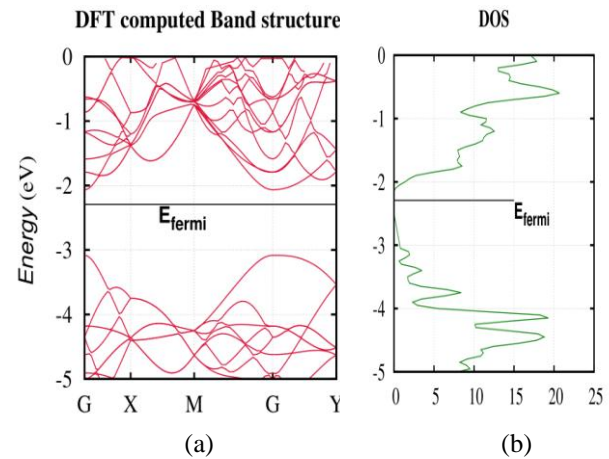Fig. 2 : Structural and Lattice constants of BP

Fig. 3: (a) Electronic band structure and (b) DOS of undoped 2 x 2 m-BP supercell.

Monolayer black phosphorus has been doped with Germanium with two possible configurations chemisorption and substitution. Formation energy calculations reveal that Chemisorption configuration is relatively more stable than substitution.
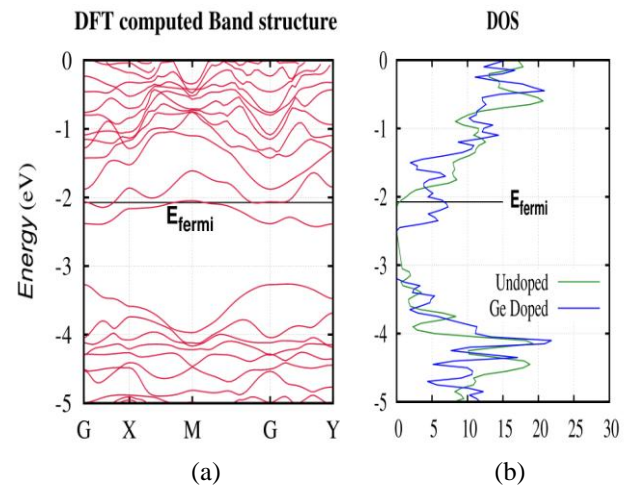

Fig. 4 : (a) Electronic band structure and (b) DOS of Ge doped 2 x 2 m-BP supercell with Chemisorption configuration

Dopant atom is introduced at the centre of the 2 x 2 supercell and has been relaxed structurally till forces acting on each atom are less than the threshold. To evaluate the effect of dopant on electronic properties of monolayer BP, electronic bandstructure and density of states (DOS) have been calculated. As shown in Fig 4 for chemisorption configuration of dopant, the band gap reduced to 0.88 eV from 1.01 eV. DOS reveal extra states available at conduction band compared to undoped m-BP. Projected density of states (PDOS) in Fig 8 reveal that the energy states introduced are due to Ge dopant. Since the electron in

electron in P_X orbital is free and contribute to energy level at conduction band. Fermi surface calculations show that the Fermi level lies close to the conduction band where the dopant induced states lie. This suggests that Ge chemisorption doped m-BP is rich in free electrons and good for conduction.

The band gap of Ge doped m-BP in substitution configuration is 0.8 eV as shown in Fig. 5 DOS show that extra states are available at valence band compared to undoped m-BP. PDOS reveal that energy states introduced are resulting of bonds Ge has formed with 3 of neighbour Phosphorus atoms. Both the electrons in P orbital are involved in bonds along with a hole. Femi surface calculations show that Fermi level lies close to valence band. This indicates that Ge substitution configuration results in p-type semiconductor.

3.3 Selelnium doped m-BP

Monolayer black phosphorus is also doped with Selenium in two possible configurations Chemisorption and Substitution.

The electronic band structure in Fig 6 shows that the band gap of Selenium doped m-BP with chemisorption configuration is same as the undoped m-BP with value of 1.01 eV. Furthur DOS reveal that the dopant atom states contribute to the energy states for valence band and intermediate dopant level has not been introduced in forbidden energy range. This indicates increased electron concentration which can be excited to conduction band by applying voltage for better conduction.
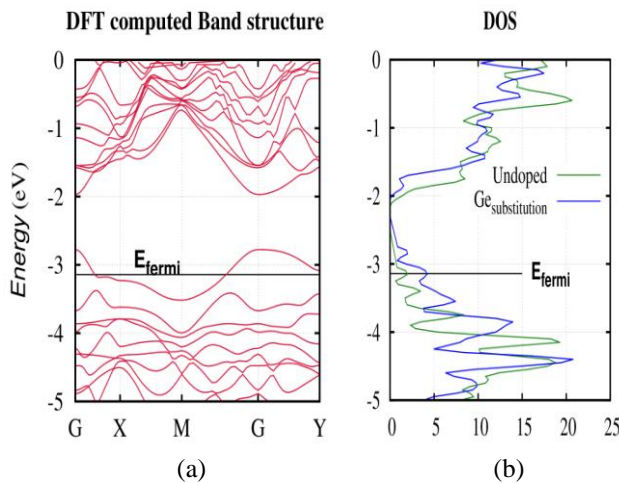
Fig. 5 : (a) Electronic band structure and (b) DOS of Ge doped 2 x 2 m-BP supercell with substitution configuration

Fig 7 shows the band structure for Selenium doped m-BP with subsitution as configuration. From band structure we can observe that band gap has increased to 1.31 eV. Selenium doping with substitution configuration results in
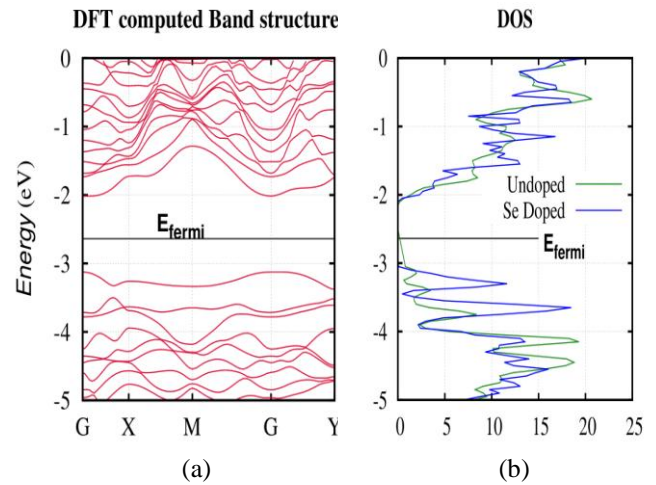
Fig. 6 : (a) Electronic band structure and (b) DOS of Se doped 2 x 2 m-BP supercell with Chemisorption configuration .

deep level dopant ie. Energy levels introduced by dopant are not close to band edges and lie at centre of bandgap.
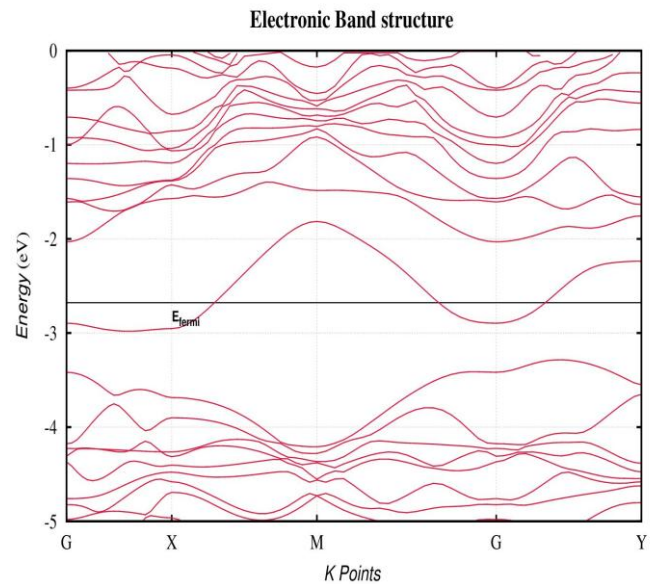
Fig. 7 : (a) Electronic band structure of Se doped 2 x 2 m-BP supercell with substitution configuration

Selenium doped m-BP with chemisorption configuration increases the electron density in valence band ie bound electrons. Since for conduction free electrons are needed Selenium fails to provide them, and the fermi level is not close to any of band edge which means neither of electron and hole concentration are dominat making it semiconductor which is not different from undopoed m-BP. Since electron concentration increased, applying voltage will make the bound electrons free and free carrier concentration will be large compared to undoped m-BP.
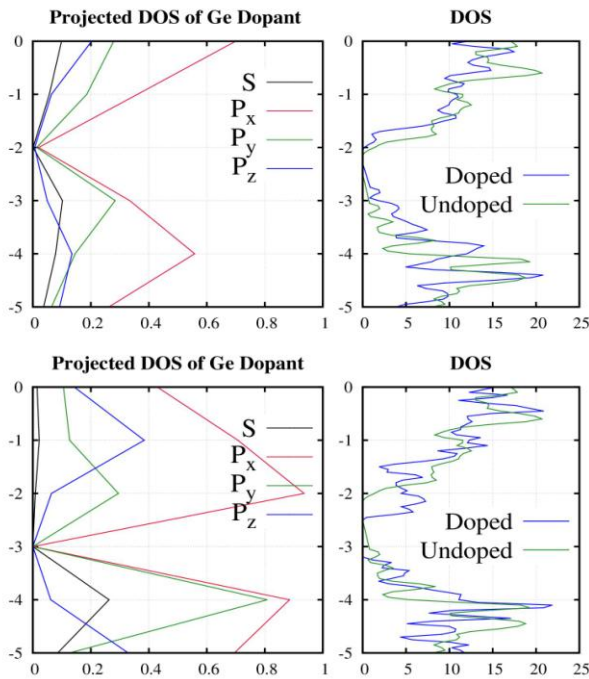
Fig. 8 : (a) PDOS and (b) DOS of Ge doped 2 x 2 m-BP supercell with substitution configuration, (c) PDOS and (d) DOS of Ge doped 2 x 2 m-BP supercell with Chemisorption configuration.

Selenium dopant when doped with substitution configuration in m-BP acts as deep level dopant which introduces the energy levels in centre of bandgap. Applying voltage will excite the bound electrons to conduction band. Moreover Selenium dopant in substitution configuration can be used as trap centre since it acts as deep dopant.

4 CONCLUSION

The effects of dopants Germanium and Selenium on electronic properties monolayer BP has been studied using first principles method in this work. For both the dopants Ge and Se chemisorption configuration is relatively stable than substitution configuration. Selenium in chemisorption configuration does not act as shallow level dopant but it increases the electron concentration in valence band. In substitution configuration Selenium presents itself as deep level dopant with increased band gap of overall structure. Germanium presents as the optimal dopant for m-BP with introduction of shallow energy levels at conduction band in case of chemisorption and at valence band in case of substitution configuration. Since ionization energies are low Germanium is optimal dopant for n-type (Chemisorption) and p-type (Substitution) in different configurations.

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