Binary Doping of N-B and N-P into Graphene: Structural and Electronic properties

Hyo seok Kim[1] and Seong Sik Kim[1]

[1]Graduate School of EEWS, KAIST, 291 Daehak-ro, Yuseong-gu, Daejeon 305-701, Korea

E-mail: softmax1986@kaist.ac.kr

We investigate co-doping effects of conjugated P-N B-N with increasing of N concentration in the graphene sheets using a first principles based on the density functional theory. N doping sites of the graphene consider two possible sites (pyridinic and porphyrin-like). Energy calculation shows that additional doping of B atom in the porphyrin-like N doped graphene ($V+B-N_x$) is hard to form. At the low chemical potential of N, one N atom with additional doping in the graphene ($V+P-N_1$, $P/B-N_1$) has low formation energy on the other hand at high chemical potential of N, high concentration of N ($V+P-N_4$, $P/B-N_3$) in the graphene is governing conformation. From the results of electronic band structure calculation, it is found that $V+P-N_4$ and $P/B-N_3$ cases change the Fermi energy therefore type change is occurred. On the other hand, the cases of $V+P-N_1$ and N+B recover the electronic structure of pristine graphene.

INTRODUCTION

Graphene, a monolayer of carbon atoms forming a two-dimensional honeycomb lattice considered as one of the most promising crystalline forms of carbon has recently attracted significant attention. Because of its unique transport property, electronic and structural features, graphene is regarded as one of the best candidate materials to apply next generation electronic and energy device such as gas sensor device [1], bilayer graphene pseudo-spin field effect transistor [2], and metal-free catalyst electrode in the fuel cell [3] etc.

To adopt these applications, graphene needs to change its electronic structure for suitable purposes. One of common and effective ways to reconstruct the electronic structure of materials is the doping of foreign atoms in the target materials. So there are fluent theoretical and experimental researches to observe the properties of doped graphene [4],[5]. Experimental and theoretical research shows that there are many N dopoed conformation in the graphene and their electronic features are different such as p-type and n-type according to the N doping configuration of the graphene.[6],[7] Single doping effect of P and B doping on the graphene is also covered diversely.[8],[9] However co-doping effects of the graphene are still not understood completely. In order to control the electronic properties of graphene by doping, it is important to understand the stabilities and electronic states near the Fermi level when additional doping of second foreign atom is done on the N doping graphene.

In this paper, we reports the co-doping effects of P-N and B-N doping on the graphene sheets on the prospective of energetic stabilities and how changes electronic structure when
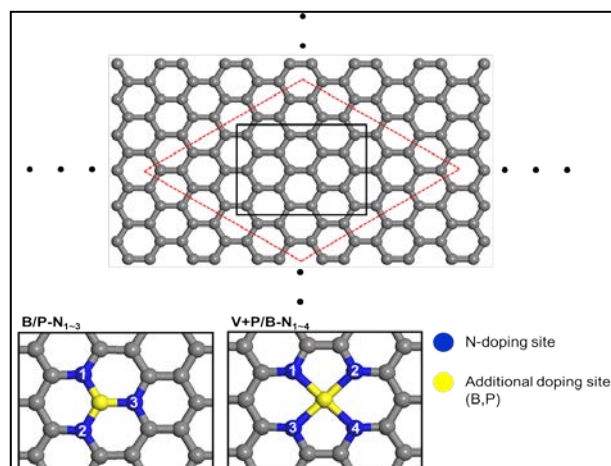
additional atoms (B/P) is conjugated with N doping graphene.

Fig. 1. Schematic atomic structure of various models about B/P-N doped graphene ($B/P-N_x$, x=1~3) and B/P-N doped graphene with a vacancy ($V+P/B-N_y$, y=1~4) x and y means the number of N atoms in the graphene sheets and red dotted line means the supercell.

METHODS

All the geometry optimization and energy calculation were performed on the basis of the spin-polarized DFT within the Perdew-Burke-

Ernzerhof (PBE) generalized gradient approximation (GGA)[10], as implement in the SIESTA code. [11] The wave function was expended with double - ζ plus polarization basis of localized

Table 1. Calculated formation energy of N doped graphene in the presence of vacancy and divacancy with increasing N atoms at the pyridinic sties and PN, BN doped graphene with increasing N atoms around the P/B atom

N doped Graphene				PN doped Graphene				BN doped Graphene			
V_1	[eV]	V_2	[eV]	$V_1 \rightarrow P$	[eV]	$V_2 \rightarrow V+P$	[eV]	$V_1 \rightarrow B$	[eV]	$V_2 \rightarrow V+P$	[eV]
V_1	8.15	V_2	8.03	P	2.58	V+P	3.88	B	4.06	V+B	9.21
V_1-N_1	5.27	V_2-N_1	7.48	P-N_1	1.95	V+P-N_1	2.49	B-N_1	2.21	V+B-N_1	7.94
V_1-N_2	4.25	V_2-N_2	6.37	P-N_2	1.77	V+P-N_2	2.12	B-N_2	1.51	V+B-N_2	5.42
V_1-N_3	2.39	V_2-N_3	4.35	P-N_3	1.73	V+P-N_3	1.97	B-N_3	1.26	V+B-N_3	4.49
		V_2-N_4	2.38			V+P-N_4	1.82			V+B-N_4	4.38

orbitals for all atomic orbitals. An energy mesh cut -off of 200 Ry and k-point mesh to 8x8x1 in the Monkhost-Park scheme. [12] Optimization of the force and total energy was performed with an accuracy of 0.02 eVA^{-1} and 1 meV, respectively.

As you can see the fig. 1, we first consider the two conformations of graphene, one vacancy and divacancy of N doped graphene and then put additional atoms (P/B) in these structures, P/B-N and V+P/B-N respectively. The other variables of our calculation is that the number of N atoms around the P/B atoms (P/B-N_x, V+P/B-N_y, x = 1~3 y = 1~4). So we consider 14 models in order to discuss the energetic and electronic properties resulting from co-doping PN and BN into the graphene sheets. We chose a 5x5 supercell oriented along directions parallel to graphene sheets. The vacuum region of the supercell along the direction perpendicular to the graphene is set to be 25Å.

To discuss the energetics of BN and PN co-doped graphene, we defined the formation energy:

$$E_{formation} = E_{doped} + x\mu_C - (E_{pristine} + y\mu_N + \mu_{B/P}) \qquad (1)$$

where E_{doped} and $E_{pristine}$ are energies of the optimized graphene with co-doped and pristine graphene sheets respectively. μ_C, μ_N and $\mu_{B/P}$ are the chemical potential of carbon and nitrogen and additional atoms (B/P) respectively. *x* is the number of carbon atoms removed from the graphene sheet during defect formation and *y is* the number of nitrogen atoms added.

The binding energies that are reported below refer to the most stable binding sites. The binding/adsorption energy (BE) of additional atoms on defect motifs is calculated as:

$$E_{B/P\text{-binding}} = E_{P/B\text{-doped}} - (E_{N\text{-doped}} + \mu_{B/P}) \qquad (2)$$

where $E_{B/P\text{-doped}}$ is the energy of the B or P atoms adsorbed defective N-doped graphene configuration, $E_{N\text{-doped}}$ is the energy of defective N-doped graphene configuration and $\mu_{B/P}$ is the chemical potential of an isolated P and B atom.

RESULTS & DISCUSSION

1. Energetics

To discuss the energetic of PN and BN double doped graphene we calculate the formation energy, $E_{formation}$. Table 1 shows the calculation of formation energies. For PN/BN doped cases, all N rich structures (P/B-N_3, V+P/B-N_4) have the lowest formation energy. BN-double doped graphene with the vacancy is the higher energy than any other co-doped cases, even higher than single N doped case with presence of divacancy. This results show it is hard to form the V+B-N_α (α = 1~4) when B atom is doped on the N doped graphene sheets with the divacancy. Another result shows since two N atoms around B/P atom, B-N_β (β=1~3) doped graphene have lower formation
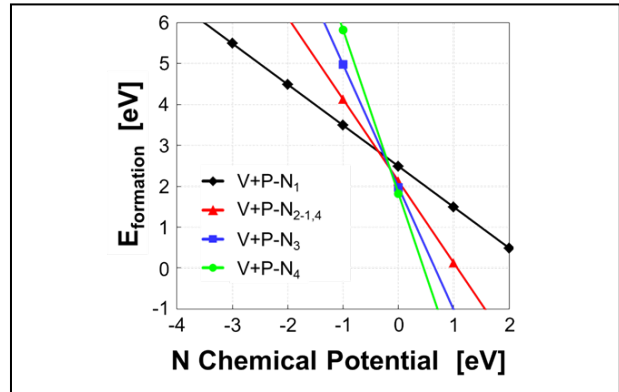
energy than P-N_β doped graphene.

Fig. 2. Calculated formation energies of V+P-N_α (α = 1~4) as a function of the N chemical potential μ_N.

Fig. 2 shows formation energy of V+P-N_α as a function of the N chemical potential (μ_N). When chemical potential is low, the dominant structure becomes V+P-N_1. On the other hand when μ_N increases to an N-rich condition, under high N precursor, the V+P-N_4 should be stabilized. This is possible because the formation energy difference between V+P-N_1 and V+P-N_4 is just

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0.67 eV. In this manner, $P-N_1/P-N_3$ and $B-N_1/B-N_3$ doped graphene also changes their favorable structures according to N chemical potential because the energy differences of $P-N_1/P-N_3$ and $B-N_1/B-N_3$ are 0.22 eV and 0.95 eV respectively.
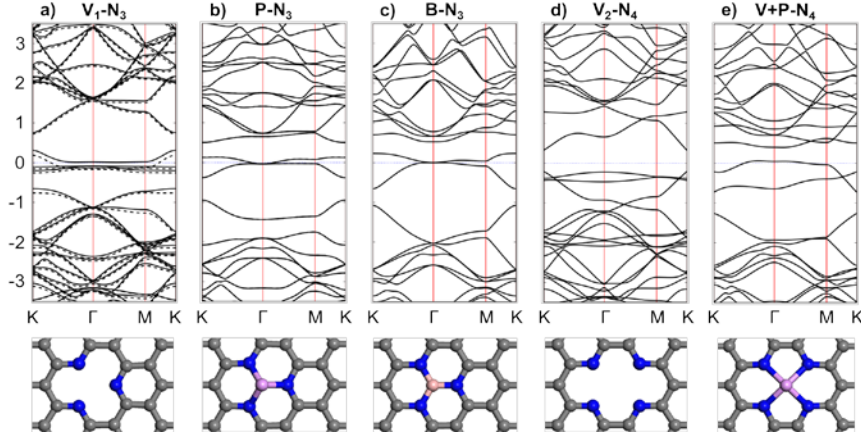
PN/BN doped graphene which is the highest possible six structures, $P/B-N_3$, $P/B-N_1$, $V+P-N_1$ and $V+P-N_4$.

Fig. 3 shows the band structure and optimized atomic structures of PN and BN doped

Fig. 3. The band and optimized structure of V_1-N_3 (a) ,$P-N_3$(b), $B-N_3$ (c), V_2-N_4 (d) and $V+P-N_4$(e). The black dashed line represents the spin polarization of down spin. And blue dotted line represents the Fermi level. The optimized structure in the blue, pink and yellow atom represents the N atom, P atom and B atom respectively.

Table 2 shows that the binding energies of additional atoms (B/P) on the N doped graphene which is one of the factors to determine the stabilities of double doped graphene. $V+B-N_\beta$ have the lowest binding energy which means that B atom and graphene sheet are weekly bonded each other. So it is high possible to dissociate from the graphene sheet. These results are same in terms of formation energy. Except for $V+B-N_\beta$ case, with increasing N atoms around the P/B atoms the binding energy of additional doping becomes lower. These results show that even though the formation energy is relatively higher, once $P/B-N_1$ and $V+P-N_1$ are formed, the stability of these structures are higher than $P/B-N_3$ and $V+P-N_4$

graphene with presence of maximum number of N atoms around B and P atom. Recent theoretical research shows the electronic properties of V_1-N_3 and V_2-N_4.[4] P atom in the structure of $P-N_3$ (Fig. 3.b) is above the graphene sheet, 0.93 Å. P atoms preserve its sp^3 character, and the bond with tetrahedral-like configuration, with bond angle close to 99°. The P-N bond length is 1.78 Å which is quite large compared to 1.42 Å for C-C sp^2 bonds. The B atom of the $B-N_3$ is in the graphene sheet (Fig. 3 c), preserving the sp^2 bonding nature of pristine graphene. The bond length of B-N is 1.46 Å which is similar to the C-C bond length of the pristine graphene. At the V+P-N4 cases, on the other hand, P atoms is just slightly above the graphene sheets, 0.54 Å with bond angle close to 87.4° and bond length of P-N is 1.99 Å.

The electronic structure of V_1-N_3 has its Fermi level below the valance band. However when B/P atom is attached on the graphene sheets, (Fig. 3 b, c, e) the type changes occur from p-type to n-type. This change occurs because of the passivation of the vacancy. So the many N atoms activate as the dopant materials. And the electronic states of near the Fermi level is disappeared and new states generate from V_1-N_3 and V_2-N_4 to $P/B-N_3$ and $V+P-N_4$.

Fig. 4 represents the band and optimized structures of PN and BN doped graphene consists of the one N atom conjugated with P/B atom

PN doped Graphene				BN doped Graphene			
	$V_1 \rightarrow P$ [eV]	$V_2 \rightarrow V+P$ [eV]			$V_1 \rightarrow B$ [eV]	$V_2 \rightarrow V+P$ [eV]	
P	-5.57	V+P	-4.17	B	-4.08	V+B	1.18
$P-N_1$	-3.32	$V+P-N_1$	-4.99	$B-N_1$	-3.06	$V+B-N_1$	0.46
$P-N_2$	-2.49	$V+P-N_2$	-2.38	$B-N_2$	-2.74	$V+B-N_2$	-0.95
$P-N_3$	-0.67	$V+P-N_3$	-2.38	$B-N_3$	-1.13	$V+B-N_3$	0.13
		$V+P-N_4$	-0.57			$V+B-N_4$	1.99

cases.

Table 2. Calculated binding energy of the B/P atoms on the graphene sheet with increasing N atoms around the P/B atom

2. Structural & Electronic properties

Based on above energetic calculations, we further investigate the electronic structures of the
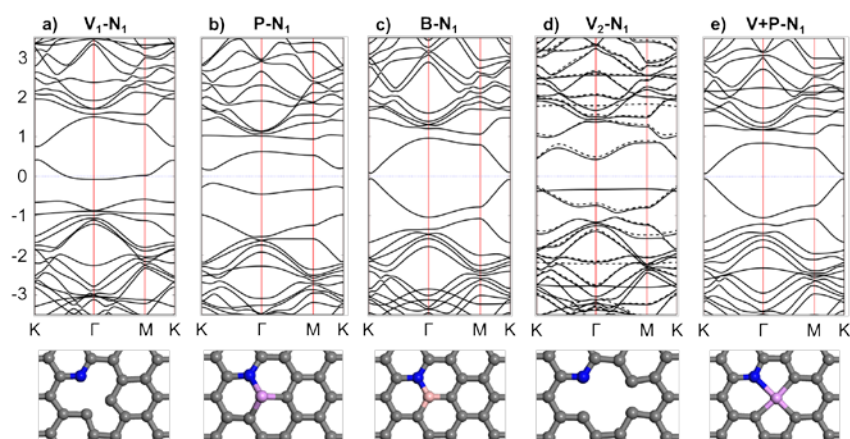
which forms when the low chemical potential of nitrogen is produced. Except for the P-N$_1$, B-N$_1$ and V+P-N$_1$(Fig. 4 c, e) preserve the sp^2 like bonding which have the planarity of the graphene sheet. And the bonding length of P-N and B-N is 1.46 Å and 2.03 Å respectively and P-C and B-C

DFT calculation implemented as SIESTA code. Our results showed that with the chemical potential of N atom, stable structure was different. The electronic properties of PN/BN double doped graphene categorized two different changes. One was the type changing from p-type to n-type. The

Fig. 4. The band and optimized structure of V$_1$-N$_1$ (a) ,P-N$_1$(b), B-N$_1$ (c), V$_2$-N$_1$ (d) and V+P-N$_1$(e). The black dashed line represents the spin polarization of down spin. And blue dotted line represents the Fermi level. The optimized structure in the blue, pink and yellow atom represents the N atom, P atom and B atom respectively.

bonding is 1.86 Å and 1.5 Å respectively. On the other hand, P-N$_1$ case (Fig. 4 b) preserves its P atom properties, sp^3 nature. Bond lengths of P-C bond and P-N bond are 1.8 Å. Bond angles of C-P-N and C-P-C are 97.22° and 96.56 Å respectively.

The electronic structure of V$_1$-N$_1$ case is investigated experimentally and theoretically.[13] which refers that the graphene composed of pyridinic boning of N atoms is p-type. The B-N$_1$ and V+P-N$_1$ of the electronic band structure dramatically changes from the V$_1$-N$_1$ and V$_2$-N$_1$. These two conformations of the electronic property recover Dirac dispersion of the pristine graphene and the localized states (V$_2$-N$_1$) near the Fermi level disappear. On the other hand P-N$_1$ of the band structure has bipolar property which is no electronic states at the Fermi level and many electronic states near the Fermi level. The difference electronic property nature of the P-N$_1$ comes from the P atom nature which has sp^3 bonding.

CONCLUSION

We studied the structural properties of the PN and BN co-doped graphene with different defect conformation and increasing the N atom concentration around the P/B atom and also calculated electronic properties. We performed

other was the recovery of the pristine graphene. We expected to explain the basic understanding of the co-doping effects of the graphene.

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