

A hybrid density functional study of silicon and phosphorus doped hexagonal boron nitride monolayer

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Abstract. We present a hybrid density functional study of silicon (Si) and phosphorus (P) doped hexagonal boron nitride (*h*-BN). The local geometry, electronic structure and thermodynamic stability of Si_B, Si_N, P_B and P_N are examined using hybrid Heyd-Scuseria-Ernzerhof (HSE) functional. The defect induced buckling and the local bond distances around the defect are sensitive to charge state modulation $q = -2, -1, 0, +1$ and $+2$. The $+1$ charge state is found to be the most energetically stable state and significantly reduces the buckling. Based on the charge state thermodynamic transition levels, we noted that the Si_B, Si_N and P_B defects are too deep to be ionized, and can alter the optical properties of *h*-BN material.

1. Introduction

A recently synthesized single layer of hexagonal boron nitride (*h*-BN) has received great research attention due to its excellent mechanical properties, large exciton binding energies and high thermal conductivity [1, 2, 3, 4, 5]. The *h*-BN monolayer has a similar structural arrangement to graphene [6, 7] but differ in electronic properties. The *h*-BN monolayer has a wide band gap of around 6 eV [1, 5, 8], while graphene is a zero band gap material [6, 7]. These properties make the *h*-BN monolayer a suitable candidate for various advanced technological applications, including the optoelectronic applications in the ultraviolet energy range [1, 5, 8]. Furthermore, the *h*-BN monolayer is thermodynamically stable at room temperature [9].

During the synthesis of *h*-BN films, various defects are usually observed [5, 10, 11, 12]. For instance, an electron beam irradiation mostly leads to the formation of point defects [5, 10]. The presence of defects in *h*-BN alters the various known properties and also imposes new valuable properties. Defects such as vacancies, antisites and carbon (C) impurities in *h*-BN are in a high spin state [13, 14, 15, 16]. Since the defect spin states can be easily affected by the modulation of electronic chemical potential, the studies of charged defects received great research attention [17, 18]. The charged defect structures, defect formation energies and defect transition energy levels within the band gap are usually interesting properties to be investigated [17, 18].

The Si atom, an element that is below C on the periodic table, is well known for its technological importance. Therefore, it is expected that the creation of Si defects could make the properties of the *h*-BN more fascinating. Previous experimental and theoretical studies reported that the incorporation of Si impurity in the boron site is exothermic whereas in the nitrogen site is endothermic [13, 19, 20, 21, 22, 23, 24]. Previous studies using the generalized gradient approximations with the Perdew, Burke and Ernzerhof functional (GGA-PBE) [25]



within the framework of density functional theory (DFT) also reported that Si introduces the impurity mid gap states [13, 19]. Considering the deficiency of GGA-PBE exchange correlation functional on the prediction of the band gap, hybrid functionals are required [26]. Phosphorus (P) which is the nearest neighbour of Si and an element below nitrogen on the periodic table can be an important defect in the *h*-BN monolayer. Although, there is already study of P doped *h*-BN [27], an understanding of the charged defect structures, defect formation energies and the defect transition energy levels is still scarce, more especially when using the hybrid functionals.

In this paper, the relative stability, structural and electronic properties of Si and P doped *h*-BN structures are studied using the hybrid density functional theory. The impurity defects are created in the following manner; one B atom from *h*-BN monolayer is removed and replaced by Si or P atom, and denoted as Si_B and P_B . Afterwards, one N atom is also removed and replaced by Si or P atom denoted as Si_N and P_N . These defects have shown to have an influence on the structural properties of the *h*-BN monolayer by creating a large buckling. The induced buckling and the local bond distances around the defect are sensitive to charge state modulation. Based on the thermodynamic transition levels, we noted that the Si_B , Si_N and P_B defects are deep and therefore can have a great influence on the luminescence of the *h*-BN monolayer.

2. Computational details

Our first principles calculations were performed on the framework of density functional theory (DFT) within the Vienna *ab initio* simulation packages (VASP) code. [28] For the exchange-correlation interactions, the hybrid Heyd-Scuseria-Ernzerhof (HSE) functional [26] was used. This functional predicts an excellent band gap and correct position of the charge state transition level [29]. The projector augmented wave (PAW) method [30] was used for pseudopotential construction. The plane wave energy cutoff was set to 500 eV. For the Brillouin zone integration, the Monkhorst-Pack scheme [31] was used to generate the k-points. In this study, a $4 \times 4 \times 1$ k-point mesh was employed. The atomic coordinates were allowed to relax until the residual atomic forces reduce to smaller than $0.01 \text{ eV}\text{\AA}^{-1}$ and the total energy was allowed to converge within the 10^{-7} eV . To avoid spurious interlayer interactions, a 15 Å vacuum spacing was set along the z-axis.

3. Results and discussion

The structural relaxation of the following defects in a *h*-BN monolayer was carried out; a B or N atom get replaced by Si or P impurity to have Si_B , Si_N , P_B and P_N defect structures. Fig. 1 presents the relaxed geometries for (a) Si_B and (b) Si_N in a 6×6 supercell. The relaxed geometries for P_B and P_N defects exhibit the same buckling as for the Si_B and Si_N defects respectively, therefore are not shown.

To examine the relative stability of these defects in the neutral charge state, their formation energies are calculated using the following equation;

$$E_f[X]^0 = E_{\text{tot}}[X]^0 - E_{\text{tot}}[h\text{-BN}] + \sum_i n_i \mu_i. \quad (1)$$

$E_{\text{tot}}[X]^0$ is the total energy of the relaxed *h*-BN supercell with Si or P defect and $E_{\text{tot}}[h\text{-BN}]$ is the total energy of pristine *h*-BN supercell. The integer n_i in Eqn.1 indicates the total number of B or N replaced (provided n_i is negative) or impurity atoms added into the system creating the defects (provided n_i is positive). The symbol μ_i represents the atomic chemical potentials for B, N, Si and P atoms. The N chemical potential is obtained from the converged energy of nitrogen gas (N_2) and for B, the energy is taken from the α -rhombohedral boron. The chemical potentials for μ_{Si} and μ_{P} are taken from the converged energies of Si in diamond-like structure and P in the body centered cube (BCC) structure respectively. The formation energies of the identified impurity defects Si_B , Si_N , P_B and P_N are constrained to vary within the $\Delta\mu$ values [32] as

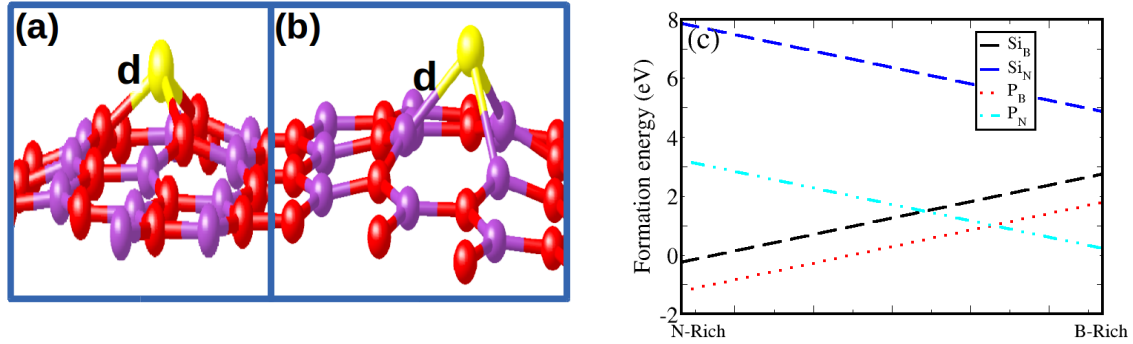


Figure 1. The optimized structures for (a) Si_B and (b) Si_N defects. The optimized geometries for P_B and P_N defects show the same buckling as for Si_B and Si_N defects. The purple, red and pink atoms represent the B, N and Si respectively. The letter d is the distance between impurity and nearest neighbor host atom. (c) The dependence of the formation energies of Si_B , Si_N , P_B and P_N impurity defects on the change in chemical potential $\Delta\mu$.

shown on Fig. 1(c). The minimum and maximum $\Delta\mu$ values of -2.64 eV and 2.64 eV (in good agreement with the previous studies [33, 34]) correspond to N-rich and B-rich extreme conditions respectively. This is to determine the growth condition in which these defects will prefer to form at a very reasonable energies.

Fig. 1(c) shows that the Si_B defect is stable under the N-rich conditions having the formation energy of -0.24 eV. This is evidence that the formation of Si-N bond is likely to occur exothermically during the synthesis of this system, in agreement with the previous studies [22, 23]. Although Si_N defect prefers the B-rich environment, it possesses the highest formation energy of about 6.00 eV. Fig. 1(c) also shows that the P_B defect is more stable in the N-rich condition. This suggests that P_B defect can easily bond with N atom. The P_N defect shows an opposing trend. These results imply that the stability of these defects greatly depends on the environment condition that corresponds to the highest amount of atomic hosts that surround the defect. Previous studies [17, 18, 33] reported that, in most cases, it cost less energy to create vacancies, antisites and impurities on the B site than on the N site in a h -BN monolayer.

We further investigate the effect of charge state q on the formation energies and structural properties of the defects mentioned above. The formation energy in the charge state q is written by extending Eq. (1) to include the information of q as follows,

$$E_f[X]^q = E_{\text{tot}}[X]^q - E_{\text{tot}}[h\text{-BN}] + \sum_i n_i \mu_i + q(\mu_e - E_v). \quad (2)$$

The variables μ_e and E_v are the electronic chemical potential and the position of the valence band maximum (VBM) [29]. Our formation energies are allowed to vary with respect to the electronic potential μ_e (Fermi level position) that ranges within the h -BN band gap of 5.73 eV obtained from our HSE calculations as shown on Fig. 2. The correction term calculated by adopting the method developed by Komsa *et al.*[35] was also added into Eq. (2) to significantly reduce the effects of spurious electrostatic interactions of the charge with its periodic images.

Table 1 presents the formation energies of the charged defects calculated at zero electronic

Table 1. The calculated formation energies in eV (at Fermi level equal to zero) of the defects Si_B , Si_N , P_B and P_N in different charge states calculated in their favourable rich conditions.

Defects	-2	-1	0	+1	+2
Si_B	9.25	3.85	-0.24	-2.73	-1.73
Si_N	11.13	6.28	4.26	3.29	3.65
P_B	9.99	4.54	-1.27	-2.63	-2.60
P_N	11.83	5.83	0.22	0.11	1.28

chemical potential. Considering charged Si_B and P_B , it is noted that the creation of holes (+1 and +2 charge states) is exothermic and the addition of electrons (-1 and -2 charge states) is endothermic. The addition of electrons can require a high amount of formation energy penalty of around 9.00 eV in the -2 charge state. In the case of charged Si_N and P_N defects, both positive and negative charge states injections give positive formation energies. Fig. 1 shows that the defected structures have a significant buckling around the impurity defect. We also find that the uncharged Si impurity on the N site (Si_N) has more buckling ($h = 1.50 \text{ \AA}$) than Si impurity on the B site (Si_B) which has $h = 0.90 \text{ \AA}$. The same trend is also seen in the case of P_B and P_N defects, where P_N has a higher buckling height than P_B . We also observe the relatively large bond length distances d around the Si defect in Si_N , than in Si_B . The large bond is the consequences of Si or P atom trying to preserve its sp^3 bonding when interacting with either B or N atom and imposing a tetrahedral-like geometry in the h -BN sheet.

Table 2. The dependence of the defect-induced structural properties on the various charge states. The Δ_h ($\text{\AA}$) is the buckling height of defect impurity X from the h -BN monolayer.

		-2	-1	0	+1	+2
Si_B	d	1.81	1.80	1.71	1.62	1.62
	Δ_h	1.29	1.29	0.90	0.30	0.30
Si_N	d	1.96	1.96	1.94	1.96	1.99
	Δ_h	1.61	1.61	1.50	1.65	1.67
P_B	d	1.71	1.71	1.70	1.64	1.67
	Δ_h	0.96	0.96	0.90	0.31	0.35
P_N	d	1.90	1.91	1.88	1.86	1.86
	Δ_h	1.55	1.54	1.48	1.51	1.51

We further investigate the effect of charge doping on the structural properties shown on Table 2. We note that an addition of a -1 charge into Si_B and P_B defects further increases the distance d and buckling height Δ_h . This might be the result of the Coulomb repulsion between the induced electron around the defect and valence electrons in the nitrogen orbitals. It is also noted that the creation of holes in Si_B and P_B defects significantly reduces the distances d and the buckling height Δ_h . This reveals that the removal of an electron from the defect orbital reduces the possible Coulomb repulsion between the impurity atom and its nearest neighbor atoms. Interestingly, this reduction is energetically favourable. The addition of both -1 and +1 charge into Si_N and P_N defects increases the buckling slightly. This structural strain is noted to be energetically unfavourable.

Lastly, the transition energy levels $\varepsilon(q/q')$ are deduced from the formation energies for Si_B , Si_N , P_B and P_N impurity defects using the expression [32];

$$\varepsilon(q/q') = \frac{E_f[X]^q - E_f[X]^{q'}}{q' - q}, \quad (3)$$

where $E_f[Si]^q$ and $E_f[Si]^{q'}$ denote the formation energies at the VBM for the charge states q and q' respectively.

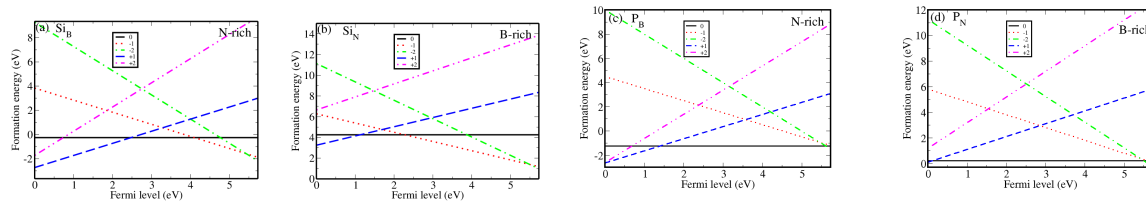


Figure 2. Calculated defect formation energies for (a) Si_B , (b) Si_N , (c) P_B and (d) P_N impurity defects in different charge states as a function of the Fermi level (electronic potential μ_e) showing the possible transition levels within the band gap of pristine h -BN monolayer.

Fig. 2 presents the variations in the formation energies for Si_B , Si_N , P_B and P_N impurity defects in different charge states as a function of the Fermi level (electronic potential μ_e) and also shows the possible transition levels within the band gap of pristine h -BN monolayer. In the case of Si_B defect, Fig. 2 (a) shows that the +1 charge state is stable from the top of VBM to the mid gap. The transition level of +1/0 is 2.52 eV above the VBM. The -1 charge state is stable from $\mu_e = 4.09$ eV to 5.39 eV with reference to the VBM. Showing the transition level of 0/-1 at 1.64 eV below the conduction band minimum (CBM). This indicates that the defect levels +1/0 and 0/-1 in Si_B are possibly too deep to be ionized. Fig 2 (a) also shows the transition level of -1/-2 at 0.43 eV. In the case of Si_N defect, Fig. 2 (b) shows that the +1 charge state is stable from the top VBM to the $\mu_e = 1.26$ eV (which is equal to +1/0 transition level). The 0 charge state is preferred in a relatively narrow range of $\mu_e = 1.10$ eV. The -1 charge state is stable at a large range of $\mu_e = 3.29$ eV, exhibiting the transition level of 0/-1 at 2.25 eV above the VBM. This indicates that this defect level is relatively deep. The results reveal that the Si impurity defect might have impact on the luminescence of h -BN monolayer.

Fig. 2 (c) shows that an addition of +1 into P_B is energetically favourable from the top of the VBM to $\mu_e = 1.50$ eV. The neutral charge state ranges from $\mu_e = 1.50$ eV to 5.62 eV. The defect transition level of +1/0 appears to be deep at 1.50 eV, whereas the transition level of 0/-2 is noted at 0.13 eV below the CBM. In the case of P_N , Fig. 2 (d) shows that the neutral charge state is the most energetically favourable for a wide range of band gap (about 5.35 eV), but when the μ_e is close to the VBM or CBM the +1 or -2 charge state is the most energetically favourable, respectively. The corresponding transition levels of +1/0 and 0/-2 are 0.16+VBM and 0.22-CBM respectively. This indicates that the P_N defect can relatively be easily ionized and could not have significant influence on the luminescence of h -BN monolayer.

4. Conclusions

Using hybrid density functional theory, we investigated the effect of Si and P impurity defects (Si_B , Si_N , P_B and P_N) in the h -BN monolayer. The local geometry, electronic structure and thermodynamic stability are examined using hybrid Heyd-Scuseria-Ernzerhof (HSE) functional. The response of these properties on the charge state modulation $q = -2, -1, 0, +1$ and $+2$ was also examined. These impurity defects cause a significant buckling in the h -BN monolayer. This structural distortion is mainly due to the effect of Si and P impurity trying to impose their sp^3 nature of bonding in the sp^2 bonded system (h -BN monolayer). The addition of electrons further increases the bond distances and the buckling heights around these Si_B , Si_N , P_B and P_N defects and is also endothermic. However, the creation of holes in Si_B and P_B defects significantly decreases the buckling height and is exothermic. Based on the charge state

thermodynamic transition levels, we noted that the Si_B , Si_N and P_B are too deep to be ionized and therefore can affect the luminescence of h -BN material.

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6. References

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