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\textsubscript{B}, Si\textsubscript{N}, P\textsubscript{B} and P\textsubscript{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\textsubscript{B}, Si\textsubscript{N} and P\textsubscript{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 \(\text{Si}_B\) and \(\text{P}_B\). Afterwards, one N atom is also removed and replaced by Si or P atom denoted as \(\text{Si}_N\) and \(\text{P}_N\). 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 \(\text{Si}_B\), \(\text{Si}_N\) and \(\text{P}_B\) 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 \textit{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 eV\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 \(\text{Si}_B\), \(\text{Si}_N\), \(\text{P}_B\) and \(\text{P}_N\) defect structures. Fig. 1 presents the relaxed geometries for (a) \(\text{Si}_B\) and (b) \(\text{Si}_N\) in a \(6 \times 6\) supercell. The relaxed geometries for \(\text{P}_B\) and \(\text{P}_N\) defects exhibit the same buckling as for the \(\text{Si}_B\) and \(\text{Si}_N\) 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:

\[
E_f^{\text{tot}}[X] = E_{\text{tot}}^[X] - E_{\text{tot}}^[h\text{-BN}] + \sum n_i \mu_i. \tag{1}
\]

\(E_{\text{tot}}^[X]\) 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 \(\mu_i\) 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 \(\alpha\)-rhombohedral boron. The chemical potentials for \(\mu_{\text{Si}}\) and \(\mu_{\text{P}}\) 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 \(\text{Si}_B\), \(\text{Si}_N\), \(\text{P}_B\) and \(\text{P}_N\) are constrained to vary within the \(\Delta\mu\) values \([32]\) as
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,

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

The variables $\mu_e$ 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 $\mu_e$ (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 |

Table 2. The dependence of the defect-induced structural properties on the various charge states. The $\Delta_h$ (Å) 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 |
|        | $\Delta_h$ | 1.29 | 1.29 | 0.90 | 0.30 | 0.30 |
| Si$_N$ | d    | 1.96 | 1.96 | 1.94 | 1.96 | 1.99 |
|        | $\Delta_h$ | 1.61 | 1.61 | 1.50 | 1.65 | 1.67 |
| P$_B$  | d    | 1.71 | 1.71 | 1.70 | 1.64 | 1.67 |
|        | $\Delta_h$ | 0.96 | 0.96 | 0.90 | 0.31 | 0.35 |
| P$_N$  | d    | 1.90 | 1.91 | 1.88 | 1.86 | 1.86 |
|        | $\Delta_h$ | 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 $\Delta_h$. 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 $\Delta_h$. 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]:

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

(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 $\mu_e$) showing the possible transition levels within the band gap of pristine 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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