

## Band dispersion of monolayer insulating Boron Nitride: A minimal tight-binding model study

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**Abstract.** We report here a tight-binding minimal model for single layer boron nitride (s-BN) taking into account of the site energy of boron and nitrogen atoms along with electron hopping parameters into third nearest neighbors. The electronic Green's functions are calculated by using Zubarev's Green's function technique. Finally the band dispersions for s-BN are computed numerically and plotted for different tight-binding parameters to give a wide band gap of  $E_g = 5.01\text{eV}$

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### 1. Introduction

Graphene is a two dimensional single layer carbon atom system which has attracted enormous research interests due to its remarkable electronic properties [1-3]. Its honeycomb lattice is ascribed to  $sp^2$  hybridized network of carbon atoms. The  $p_z$  bands cross at the Fermi level in the reciprocal space of graphene. The absence of the gap is related to the equivalence of the two carbon sub-lattices of graphene [1]. A significant modification in the electronic properties of the semi metallic graphene can be expected, where the two sub-lattices are made inequivalent. Hexagonal boron nitride (h-BN), with a similar lattice constant but different boron and nitrogen sub-lattices, is suggested to be a suitable choice as a sub-lattice to introduce the in-equivalence in the graphene lattice [4]. For example, a gap of  $\sim 0.053$  eV is predicted for graphene deposited on h-BN substrate [4]. The  $SiO_2$  substrate is reported to introduce a gap of 0.0350 eV in graphene due to strong covalent interaction [5]. The angle resolved photoemission spectroscopy (ARPES) shows a gap of  $\sim 0.0260$  eV at Fermi level in epitaxial graphene on a SiC substrate [6]. The h-BN is emerging as a

system which is finding applications for graphene electronic devices. The h-BN is an insulator having large energy gap ( $E_g = 5 - 7\text{eV}$ ), and high degree of purity. Since graphene and boron nitride interact weakly, the h-BN can be used as a buffer layer between a substrate and graphene leaving its intrinsic electronic properties unaffected by disorder. Graphene devices on h-BN have shown to exhibit enhanced mobility, reduced carrier inhomogeneity and reduced intrinsic doping [7]. The h-BN can be applied as space and atomic –thin tunneling barrier. Since these first applications of boron nitride (s-BN) is fundamental research, the interaction in single layer boron nitride (s-BN) has been increasing steadily. The theoretical studies on s-BN and bilayer boron nitride (b-BN) have been reported. Topsakal et.al. [8] have made density functional theory (DFT) study of electronic, magnetic and elastic properties of s-BN and boron nitride nanoribbons. The DFT studies of graphene on h-BN have confirmed the opening of gap in graphene [9, 10, 11]. Despite the above theoretical studies, no energy gap has been measured in graphene on BN [12]. Rubeiro et.al. [11] have reported the tight-binding fit to the graphene obtained by DFT taking only nearest-neighbor electron hopping. The crucial issue of band gap opening and at the same time preserving the exceptional linear dispersion of graphene near Dirac point can be achieved by using suitable substrates. In contrast to graphene, the isoelectric h-BN crystal with strong partially ionic  $sp^2$  hybridized in plane bonding between boron and nitrogen atoms has a wide energy gap resulting from a significant difference of electronegativities between onsite atoms. The band structure similarities between these two materials can lead to amazing physical properties of the combined system. Here we address a tight-binding model calculation for s-BN taking up to third-nearest-neighbor electron hoppings and obtain the fitting parameters like onsite energies of boron and nitrogen atoms as well as the hopping parameters.

## **2. A Minimal Tight-Binding Model for s-BN**

In the periodic table of elements, carbon is placed between boron and nitrogen with nitrogen having more electronegativity than boron and the difference only in the number of 2p electrons. Since the honey comb structure of graphene originates from  $sp^2$  hybridized in-plane bonding, the proximity of electron energies of 2s and 2p states in carbon, boron and nitrogen results in the formation of similar structure in the case of boron nitride. Graphene and s-BN have identical lattices, but in contrast to zero energy gap in graphene, the gap in s-BN is 5.9 eV (5.4 eV for bulk BN). The difference between two materials can be explained within tight-binding (TB) approach. The unit cell of the two dimensional hexagonal structure of singlelayer boron nitride (s-BN) contains two

inequivalent A and B sub-lattices. It is equivalent to assume that boron (nitrogen) is on the A (B) sub lattices.

The three  $\sigma$  bands resulting due to  $sp^2$  hybridization are located in s-BN plane, while the two overlapping  $2p^z$  orbitals form  $\pi$  bands perpendicular to the plane. Therefore  $\sigma$  and  $\pi$  orbitals can be analyzed independently. We restrict our TB model calculations to  $\pi$  energy bands, because they are responsible for unique electronic properties of s-BN. In reference to our TB model for graphene [13, 14], the model for s-BN is written as

$$\begin{aligned}
 H = & \left( \sum_{i,\sigma} E_B a_{i,\sigma}^\dagger a_{i,\sigma} + \sum_{j,\sigma} E_N b_{j,\sigma}^\dagger b_{j,\sigma} \right) + \left( \sum_{i,\sigma} V_i a_{i,\sigma}^\dagger a_{i,\sigma} + \sum_{j,\sigma} V_j b_{j,\sigma}^\dagger b_{j,\sigma} \right) \\
 & - \sum_{\alpha,i,j,\sigma} t_\alpha (\gamma_\alpha(i,j) a_{i,\sigma}^\dagger b_{j,\sigma} + \gamma_\alpha^*(i,j) b_{i,\sigma}^\dagger a_{j,\sigma}) \\
 & - \sum_{i,j,\sigma} t_2 \gamma_2(i,j) (a_{i,\sigma}^\dagger a_{j,\sigma} + a_{j,\sigma}^\dagger a_{i,\sigma}) \quad (1)
 \end{aligned}$$

The first term in Hamiltonian (H) given in equation (1) represents the energy  $E_B(E_N)$  for boron (nitrogen) with their corresponding electron creation operator  $a_{i,\sigma}^\dagger(b_{i,\sigma}^\dagger)$  at site  $i$  with spin  $\sigma$ . The second term in  $H$  describes impurity interaction at boron (nitrogen) atomic sites with potential  $V$ . The third term in  $H$  describes the inter site hopping interaction of electrons with hopping parameters  $t_\alpha$  and dispersion  $\gamma_\alpha(i,j)$  between sites  $i$  and  $j$  and  $\alpha = 1,3$  represents the first and third nearest- neighbor electron hoppings. The last term describes the second neighbor hopping interaction. The Fourier transformation of the Hamiltonian gives the dispersion energies as  $\epsilon_{\alpha,k} = -t_\alpha \gamma_\alpha(k)$  and dispersion  $\gamma_\alpha(k)$  is defined as  $\gamma_\alpha(k) = \sum e^{i\vec{k} \cdot \vec{\delta}_\alpha}$  where  $\vec{k}$  and  $\vec{\delta}_\alpha$  represent the electron momentum and relative position of the atomic sites. The dispersion is shifted to  $K$  point to investigate band gap of s-BN at Dirac point. The final expression of  $\epsilon_{\alpha,k}$  is not given here.

### 3. Calculation of Green's functions and quasiparticle bands

The two Green's functions associated with boron site electron are defined as

$$A_1(k, \omega) = \ll a_{k,\sigma} ; a_{k,\sigma}^\dagger \gg_\omega ; A_2(k, \omega) = \ll b_{k,\sigma} ; a_{k,\sigma}^\dagger \gg_\omega \quad (2)$$

The Green's functions are calculated by Zubarev's techniques [15]. The coupled equations are

$$(\omega - \epsilon_B(k))A_1(k, \omega) = \frac{1}{2\pi} + \epsilon_{13k}A_2(k, \omega) \quad (3)$$

$$(\omega - \epsilon_N(k))A_2(k, \omega) = \epsilon_{13k}^*A_1(k, \omega) \quad (4)$$

where  $\epsilon_B(k) = E_B + Vx_B + \epsilon_{2k}$ ,  $\epsilon_N(k) = E_N + Vx_N + \epsilon_{2k}$  and  $\epsilon_{13k} = \epsilon_{1k} + \epsilon_{3k}$ , where  $x_B$  and  $x_N$  are impurity concentrations. The solution of equation (2) and (3) leads to

$$A_1(k, \omega) = \frac{1}{2\pi} \left( \frac{\omega - \epsilon_N(k)}{|D(\omega)|} \right) \quad (5)$$

where  $|D(\omega)| = (\omega - \epsilon_B(k))(\omega - \epsilon_N(k)) - |\epsilon_{13k}|^2$ . With  $|D(\omega)| = 0$ , we get the two quasiparticle bands as

$$w_{s,k} = E_0 + \epsilon_{2k} - (-1)^s \frac{1}{2} \sqrt{E_g^2 + 4|\epsilon_{13k}|^2} \quad (6)$$

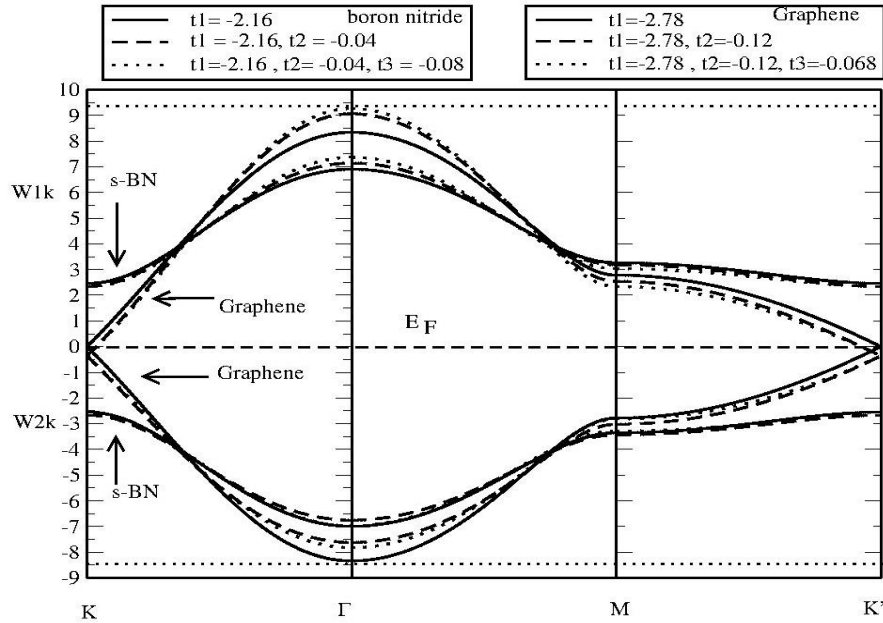
We get the upper conduction band for  $s = 1$  and the lower valence band for  $s = 2$  with a band gap  $E_g = E_B - E_N$ . The effective mid-point of the band gap is  $E_0 + \epsilon_{2k}$  with  $E_0 = \frac{(E_B + E_N)}{2}$ . This indicates that  $E_0$  is affected by second nearest-neighbor hopping parameters ( $t_2$ ) and the band gap  $E_g$  is affected by the first hopping ( $t_1$ ) and third hopping parameters ( $t_3$ ). In absence of second and third-nearest-neighbor-hoppings, the quasiparticle bands depend on  $E_B$ ,  $E_N$  and  $t_1$  as shown by Robeiro et.al. [11] i.e.

$$w_{s,k} = E_0 - (-1)^s \frac{1}{2} \sqrt{E_g^2 + 4|\epsilon_{13k}|^2} \quad (7)$$

At the corners of the Brillouin zone, we have  $w_{1k}, w_{2k} = \frac{1}{2} (E_B + E_N) \pm \frac{1}{2} E_g$ , with  $E_g = E_B - E_N$  defining the band gap at K point. Since the onsite energies  $E_B$  for boron atom and  $E_N$  for nitrogen atom are not the same, the symmetry between A and B sub-lattices is broken. Hence a band gap of magnitude  $E_g$  opens at the  $K(K')$  point. In the first approximation, the energies  $E_B$  and  $E_N$  could be close to energies of B  $2p_z$  and N  $2p_z$  states in corresponding atoms. For such choice,  $E_g \approx 0.2$  eV, while a wider energies gap between the conduction and valence band is observed in s-BN. This can be explained by the difference in electro negativities of boron and nitrogen atoms leading to  $E_B \gg E_N$ . The valence band is mainly constituted by nitrogen sublattice, while conduction band originates from boron  $2p_z$  states.

#### 4. Results and Discussion

Here we try to obtain the tight-binding fitting parameters for graphene and s-BN systems for zero band gap for graphene and wide band gap  $E_g = 5.01 eV$  for s-BN. We have computed numerically the conduction band  $w_{1k}$  and the valence band  $w_{2k}$  given in equation (6) and dispersions are shown in fig.1 in  $K - \Gamma - M - K'$  directions in momentum space. The conduction band  $w_{1k}$  and valence band  $w_{2k}$  of graphene touch each other at Dirac point (K-point) for graphene. The on-site energies  $E_a = E_b = 0$  for graphene and hopping parameter  $t_1 = -2.78 eV$ ,



**Fig. 1.** The plot of band energy dispersion of graphene and s-BN at  $K - \Gamma - M - K'$  point for different hopping integrals  $t_1, t_2$  and  $t_3$  respectively.

$t_2 = -0.12 eV$  and  $t_3 = -0.08 eV$ . However two bands are displaced below Dirac point due to hopping parameters  $t_2$  and  $t_3$ . Further the band width is maximum i.e.  $W_G \cong 18 eV$  which is comparable to  $16.5 eV$  [16] at the center of the Brillouin zone ( $\Gamma$ -point). On the other hand the band dispersion for s-BN is shown in fig.1 for site energies  $E_B = 2.46 eV$  for boron,  $E_N = -2.55 eV$  for nitrogen and hopping parameters  $t_1 = -2.16 eV$ ,  $t_2 = -0.04 eV$  and  $t_3 = -0.08 eV$ . Under this condition, band gap for s-BN becomes  $E_g = E_{B-} - E_N = 5.01 eV$  at the Dirac point or  $K/K'$  point which is comparable to  $5.9 eV$  measured

experimentally [8] and the mid-point of the bands is fixed nearly at the Dirac point i.e.  $E_0 = \frac{E_B + E_N}{2} \cong -0.045 \text{ eV}$ . This shows that the s-BN system is a wide gap insulator. Further the band width is the highest  $W_{BN} \cong 13 \text{ eV}$  for s-BN.

## 5. Conclusions

We present here a tight-binding model for s-BN system taking the electron hopping upto third nearest-neighbor and site energies of boron and nitrogen. The band dispersion is computed numerically for s-BN with fitting energy parameters. In conclusion, we state that the tight-binding fitting energy parameters of monolayer graphene and single layer boron nitride systems could be used for further studies.

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