ELECTRONIC PROPERTIES OF HYDROGENATED HEXAGONAL BORON NITRIDE (h-BN): DFT STUDY

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ABSTRACT

In this work, we have constructed the hydrogenated hexagonal boron nitride (h-BN) by placing hydrogen atom at different surface sites. The possibility of hydrogen adsorption on the BN surface has been estimated by calculating the adsorption energy. The electronic properties were calculated for different hydrogenated BNs. The theoretical calculation was based on the Density Functional Theory (DFT). The electron-exchange energy was treated within the most conventional functional called generalized gradient approximation. The calculated band gap of pure BN is 3.80 eV. The adsorption of two H-atoms at two symmetrical sites of B and N sites reduces the band gap value to 3.5 eV. However, in all other combination the systems show dispersed band at the Fermi level exhibiting conducting behavior. Moreover, from the analysis of band structure and Density Of States we can conclude that, the hydrogenation tunes the band gap of hexagonal boron nitride.

Keywords: BN monolayer, hydrogenated, band gap, metallic, adsorption energy.

Introduction

The exfoliation of ultrathin 2D carbon sheet called graphene from the bulk graphite has given the new direction in the field of digital technology (Novoselov \textit{et al.}, 2004). However, the implementation of graphene as the novel electronic material in the advancement of new technology has plenty of draw backs due to the absence of band gap. The nanoscale materials
exhibiting graphene like properties with finite band gap can be a perfect replacement. The exfoliation of 2D graphene like materials from the same group element can be crucial. In this regard, 2D Boron Nitride (BN) with hexagonal lattice looks promising as the presence of sp² hybridized B-N bonds is same as the C-C bond in graphene (Wang et al., 2017; Fujimoto, 2017). The other reason being the finite value of band gap, low density, great thermal conductivity, chemically stable, high tensile strength etc. The most common methods like Chemical Vapor Deposition (CVD) and segregation method (Ortiz et al., 2018; Shi et al., 2010) are used to exfoliate 2D graphene like hexagonal materials namely, BN, ZnS, ZnO, CdO, Silicene, Germanene, transition metal chalcogenides (TMDs), etc., (Lalrinkima et al., 2019; Mak et al., 2010; Rai et al., 2018; Kaur et al., 2016) from wurtzite structures. They are used as anti-oxidation layer (due to its thermal conductivity), lubricants, in the field of nanoelectronics, cosmetics etc., (Wang et al., 2017; Fujimoto, 2017). Its large band gap is studied to be utilized as non-conducting substrate in electrical applications (McCulloch et al., 2000). BN has also been extensively used for performance FETs (Meric et al., 2010), substrate of graphene based FETs (Meric et al., 2010) as well as metal decorated BN for hydrogen storage (Zhang et al., 2017). Rigorous research is in progress on h-BN as a gas sensor. DFT study shows a promising gas sensing ability of the h-BN in the presence of external electric field (Zhang et al., 2017). Chen et al., (2010) performed DFT study using Vienna ab initio simulation package (VASP) of the hydrogenation on boron nitride nanoribbons and it was observed that depending upon the percentage of hydrogenation, there was transition from semiconductor-half-metal-metal (Chen et al., 2010). Rad & Ayub (2016) using Gaussian 09 suite studied the ability of nickel decorated BN nano-cluster for hydrogen molecule storage. Li et al., (2008) also performed ab initio calculations on the hydrogenated boron nitride nanotubes using the SIESTA package where they showed the possibility of tuning the magnetic properties of the boron nitride nanotubes upon hydrogenation and also by creating defects (Li et al., 2008). Increase in population have increased the demand for fossil fuels. Fossil fuels being limited in nature, also contributes in the environmental pollution. Hydrogen has many advantages over the fossil fuel due to its light weight, high energy density and produces water upon combustion meaning it doesn’t contribute in the environmental pollution (Bromley, 2002). The major problem for hydrogen to be utilized as an energy carrier, lies in its storage. The present techniques are risky and not cost effective.

In quest for promising hydrogen storage materials, we have carried forward our work with h-BN monolayer. In this paper, we have investigated the hydrogen adsorption ability at different sites by calculating the adsorption energy at different sites. Also, we have calculated the energy band structures, DOS to highlight the effect of the hydrogenation on the electronic and structural properties of h-BN monolayer.

**Materials and Methodology**

A 2D graphene like hexagonal monolayer structure has been constructed
from Boron and Nitrogen atoms by taking the experimental lattice constant \(a=b=2.502 \text{Å} \) (Caldwell et al., 2019). The hydrogen atoms are adsorbed at different surficial sites, as shown in Fig. 1. The B and N atom has taken the hexagonal lattice and are allowed to extend in x-y plane. However, the transverse repetition of BN layers along the z-axis has been terminated by taking the vacuum of 10 Å. The vacuum along z-axis has been introduced to break the transverse symmetry which prevent the inter layer interaction. The hexagonal structure was optimized by conjugate gradient (CG) method till HF-force reaches 0.01 eV/Å. The calculated optimized lattice constant is found to be \(a=b=2.486 \text{Å} \) which is consistent with the experimental one (Caldwell et al., 2019). The electronic structure calculations was carried out by a DFT-based computational code “SIESTA” which works with pseudo-potential and numerical nano-orbitals (NAOS) (Soler et al., 2002). The most common functional like generalized gradient approximation (PBE-GGA) is used for exchange correlation of valence electrons. To calculate the band structure, hybrid functional are considered as more accurate. As, the hybrid functional are expensive, so we performed our calculations using PBE-GGA which provides the result in close range. The first Brillouin zone was sampled with optimized k-mesh 8x8x1 in Monkhorst-pack scheme. The adsorption energy has been calculated from Eq. (1):

\[
E_{ad} = \frac{-1}{2} \left[ E_{sys} - (E_{slab} + nE_{atom}) \right] \quad (1)
\]

Where \(E_{sys} \) is the energy of total system, \(E_{slab} \) is the energy of monolayer BN, \(n \) is the number of adsorbed atoms and \(E_{atom} \) is the energy of single hydrogen atom.

**Results & Discussion**

The optimized lattice constant was used for the calculation of electronic properties. We have considered number of h-BN monolayer with hydrogen atom at different atomic sites. We have studied ten hydrogenated BN monolayers with H-atoms at different sites on the surface. The adsorption energy were also calculated for different hydrogenated BN monolayers. Since PBE-GGA underestimates the band gap, we have found a band gap of 3.8eV which is less than the reported value for pure BN monolayer which lies in the range of 3.6-6.2eV which are obtained theoretically using first principle study based on Density Functional Theory (DFT) using different approximations on Vienna ab initio simulation package, Spanish Initiative for Electronic Simulation with Thousands of Atoms, QUANTUM EXPRESSO as well as from different experimental techniques like laser-induced fluorescence measurements, Ultraviolet Lasing of Hexagonal Boron Nitride, luminescence excitation spectroscopy etc., (Solozhenkoa et al., 2001; Fan et al., 2011; Zupan & Kolar, 1972; Lopatin & Konusov, 1992; Watanabe et al., 2004; Kaloni & Mukherjee, 2011; Schuster et al., 2018; Gao, 2012; Zhou et al., 2010; Elias, 2019; Ba et al., 2017; Beiranvand & Valedbagi, 2015; Topsakal et al., 2009). The formation of band gap in monolayer BN is mainly due to the contribution of B-p and N-p orbitals similar to graphene. The \(sp^2\) hybridization gives strong covalent bond as a result the system BN monolayer does not interact with the host elements very easily.
Figure 1: Hexagonal Structure of (a) pure BN (b) H-atom at top of BN surface (c) H-atom at top and bottom sides of both BN (H-green, B-blue, N-red)

Table 1: Experimentally and theoretically reported band gap value of pristine h-BN monolayer. Other reported band gap values are provided in references.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Experimental and DFT Method</th>
<th>Band Gap (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fluorescence excitation spectra (Exp.)</td>
<td>4.02</td>
<td>(Solozhenko et al., 2001)</td>
</tr>
<tr>
<td>2</td>
<td>DFT using Projector Augmented Wave (PAW) Potential and PW91 as functional.</td>
<td>4.64</td>
<td>(Topsakal et al., 2009)</td>
</tr>
</tbody>
</table>

However, we intend to study the adsorption ability of BN monolayer by adding H-atoms on the surface. Among ten hydrogenated BN monolayers only two of them exhibit semiconducting behavior in which H-atoms are symmetrically placed at the top and bottom. The calculated band gap of hydrogenated BN monolayers are 3.5 eV and 3.9 eV for B1N1 and B2N2 respectively. The result of Density Of States and band structure shows that B1N1 and B2N2 hydrogenated system shows the nature of an insulator with finite band gap 3.5-3.9 eV [Fig. 2a & Fig. 3(a,b)]. The rest of hydrogenated BN monolayer shows metallic behavior due to the presence of dispersed band around the fermi energy [Fig. 2(b,c)]. The dispersed band around the Fermi energy may be accounted by the H-atoms having single electron which behave like a free charge carriers on the surface of the BN monolayer.

In order to examine the ground state stability of the hydrogenated system we have calculated the adsorption energy from Eq. (1) by adding the H-atoms on the surface at different atomic sites. The adsorption energies for different hydrogenated systems has been displayed in Fig. 3d. The adsorption energy measures the ability of BN monolayer as a host for incoming H-atom. Moreover, the negative value of adsorption energy gives the ground state stability and predicts the suitable location for H-atom to reside in the host BN monolayer. Among all hydrogenated BN monolayer that we have considered in our study only two systems like B-t-b-c-N (Hydrogen at top bottom and centre site) and B-2N (Hydrogen at top, bottom of Boron) has given the negative value of adsorption energy resembling an exothermic process.
Figure 2: Total Density Of States - (a) pure BN (BN-black), 1H-atom each at the top of BN (B1N1-red), 1H-atom each at the top & bottom of BN (B2N2-green) (b) 1H-atom at B & 2H-atoms at N (B1N-green), 2H-atoms at B (B2N-red), 2H-atoms at B & 1H-atom at N (B2N1-blue), 1H-atom at B & 2H-atoms at N (BN2-black) and (c) 2H-atoms at BN & 1H-atom at centre (2B-c-N2-black), 2H-atoms at BN & 2H-atoms at top-bottom of centre site (2B-tb-N2-green) , 2H-atoms at BN & 3H-atoms at top-bottom-centre (2B-tcb-N2-blue).

Figure 3: Band structure (a) 1H-atom each at the top of both BN (b) 1H-atom each at the top & bottom of both BN (c) pure BN and (d) Adsorption energy of different hydrogenated h-BN

Conclusion

We have calculated the electronic properties of pristine BN monolayer and hydrogenated BN monolayers from the first principles calculation with generalized gradient approximation as electron exchange-correlation functional. The calculated band gap for the BN was found to be 3.8 eV. Also upon hydrogenation no structural deformation was observed. Most of the hydrogenated BN monolayers exhibit
metallic properties except for B1N1 and B2N2 with paired symmetric hydrogen on top and bottom. Our random sampling of adsorption of H-atoms on the surface of BN monolayer gives positive values. But still there are few hydrogenated system with negative value of adsorption energy which predicts that BN monolayer is a suitable host for adsorbing hydrogen atoms and the work can be further expanded for its hydrogen storage suitability by checking other parameters like gravimetric density(weight percentage) etc. Also, selective hydrogenation can be considered as one of the mechanism to tune the band gap of the h-BN.

References


