Electronic Structure Properties of Graphene/Boron-Nitride Layered Systems

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Abstract

We explore the properties of systems composed of two or three layers of graphene and hexagonal boron nitride (h-BN) using the Vienna *Ab-Initio* Simulation Package (VASP), a software package for performing first principles simulations based on density functional theory (DFT). Particular attention is given to the contribution of inter-layer dispersion interactions, which are modeled within VASP by the “DFT-D2” method of Grimme. We obtain the binding and van der Waals energies, and inter-layer separations for the most stable stacking configurations of each of the following systems: h-BN/graphene, graphene/h-BN/graphene, h-BN/graphene/h-BN, h-BN/h-BN/graphene, and graphene/graphene/h-BN. We observe that the addition of h-BN layers to graphene structures induces a band gap, ranging from 0.024 eV, for the graphene/h-BN/graphene arrangement, to 0.16 eV, for the h-BN/graphene/h-BN arrangement. These results, specifically band gaps on the same order as those of silicon and germanium, indicate that graphene/h-BN layered structures may have applications in electronics.

Introduction

Graphene is a two-dimensional, honeycomb lattice populated entirely by carbon atoms. Since its isolation and characterization in 2004\(^1\), there has been much interest in integrating graphene into electronics, due to its remarkable electronic and structural properties. Graphene’s high thermal and electrical conductivities, in addition to its compact size and low noise, make it ideal as a current carrier in integrated circuits. If graphene is to carry current through a transistor, it must be made to exhibit, or included as a part of a structure that exhibits, a band gap on the order of 100 meV to 1 eV. Graphene transistors have been demonstrated prior to this writing\(^2\), however, due to the difficulty of inducing an appreciable band gap in graphene, all have suffered low gain, among other limitations, and none have been suitable to replace existing transistors.

We explored the effects of adding layers of hexagonal boron nitride (h-BN) to graphene structures, intending to evaluate the plausibility of using graphene/h-BN layers in transistor construction. Hexagonal boron nitride is a honeycomb lattice with a parameter of 2.52 Å, which is only slightly larger than graphene’s 2.46 Å. It has already been demonstrated that it is possible to grow graphene directly on h-BN and vice-versa by means of chemical vapor deposition\(^3\). Consequently, h-BN is a suitable companion for graphene. Because h-BN, alone, is an insulator with a band gap of 5.2 eV, we hoped to observe that a system composed of layers of graphene and h-BN would have a moderate band gap within our target range of 100 meV to 1 eV.
Instruments and Methods

The computational investigation was conducted using the Vienna *Ab-Initio* Simulation Package (VASP) version 5.1.8. Stated most concisely, VASP’s function is to relax the overall structure of any given infinitely repeating lattice toward its lowest energy configuration. VASP relaxes both the electronic structure and the ionic positions using an iterative process. Initially, the ionic positions are held constant, in line with the Born-Oppenheimer approximation, and the minimum energy electron configuration is found by means of density functional theory (DFT). DFT is based on the idea that the minimum energy configuration for any system of electrons in a given static, external potential is uniquely determined by its three-dimensional electron density function. Thus, DFT avoids the computationally difficult problem of solving the many-electron Schrödinger equation by instead solving for the equilibrium electron density. All properties of the system can then be determined by functions of its density (called “density functionals”). Once the electronic structure has been relaxed, VASP finds the potential around each ion and moves them toward their local minima. This process is repeated until the change in energy between successive steps is below a given threshold, indicating that the system has converged.

Most implementations of DFT, including earlier versions of VASP (through version 4), do not accurately handle van der Waals interactions between atoms. The most recent release of VASP, however, includes a semi-empirical approximation of dispersion interactions which was originally described by Grimme\(^4\), and which is referred to as “DFT-D2.” The DFT-D2 method adds a dispersion term \(E_{\text{disp}}\) to the system’s total energy. As described by Bučko *et al.*\(^5\), the dispersion energy is of the following form:

\[
E_{\text{disp}} = -s_6 \sum_{i=1}^{N_a} \sum_{j=1}^{N_a} \sum_{L} \sum' \frac{C_{6}^{ij}}{|r_{i,0} - r_{j,L}|^6} f\left(\frac{|r_{i,0} - r_{j,L}|}{R_{ij}}\right)
\]

In effect, the \(E_{\text{disp}}\) is a sum over all pairs of atoms in the lattice. For each pair, the dispersion energy goes as \(r^{-6}\); for “small” values of \(r\), the dispersion energy is driven to zero by the “damping function” \(f\), which is defined as follows:

\[
f(r) = \frac{1}{1 + \exp \left(-d \left(\frac{r}{R_{ij}} - 1\right)\right)}
\]

All of the constants in the above equations \((s_6, C_{6}^{ij}, d, \text{ and } R_{ij})\) were determined for every pair of elements so as to maximize agreement with experimental data. Existing computational work\(^5\) has
demonstrated that the DFT-D2 method significantly increases the accuracy of DFT simulations in systems where dispersion interactions are significant.

Special attention was paid to the effects of van der Waals interactions in the systems studied. This was done for two reasons. First, van der Waals forces are primarily responsible for binding layers of graphene and/or h-BN together, meaning that their contribution is important in determining the structural properties of the lattice. Second, as of this writing, most computational investigations into systems composed of graphene and/or h-BN have been conducted without consideration for van der Waals interactions (see, for example, Zhong et al.\textsuperscript{6}, Tang et al.\textsuperscript{7}, and Xu et al.\textsuperscript{8}), using only the relatively simplistic LDA method. Despite the fact that LDA produces good agreement with experimental results in systems of carbon and boron nitride, we were curious how our results using DFT-D2 would compare to previous LDA estimates.

In total, seven different systems composed of one to three layers of graphene and h-BN were investigated. Single layers of graphene and h-BN were studied so that the results could be used as a baseline and compared to experimental data. A two layer system with one layer of each graphene and h-BN was studied. Lastly, the following four three-layer systems were studied: graphene/h-BN/graphene, h-BN/graphene/h-BN, graphene/graphene/h-BN, and h-BN/h-BN/graphene. In cases where multiple stacking arrangements were possible, all plausible arrangements were tested to identify which was most stable (lowest in energy). For example, the three possible stacking arrangements for the two-layer system are shown in Figure 1 below.

![Figure 1](image)

**Figure 1:** The three possible stacking arrangements for the two-layer system. The arrangements are named according to the scheme used by Zhong\textsuperscript{6}, as follows: (a) AA, (b) AB (nitrogen), (c) AB (boron)

Based on the results of the two-layer system, it was concluded that AB stacking arrangements would always be preferred over AA arrangements. Thus, for the three-layer systems, only variants of AB arrangements were tested. These arrangements are not illustrated for sake of space.
Results

The results of the structural minimizations are summarized in Table 1 below.

<table>
<thead>
<tr>
<th>System</th>
<th>Lattice Parameter (Å)</th>
<th>Inter-layer Separation (Å)</th>
<th>Free Energy (eV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>2.470</td>
<td>N/A</td>
<td>-9.298</td>
</tr>
<tr>
<td>h-BN</td>
<td>2.512</td>
<td>N/A</td>
<td>-8.852</td>
</tr>
<tr>
<td>G/h-BN: AA</td>
<td>2.492</td>
<td>3.327</td>
<td>-9.083</td>
</tr>
<tr>
<td>G/h-BN: AB (boron)</td>
<td>2.497</td>
<td>3.130</td>
<td>-9.091</td>
</tr>
<tr>
<td>G/h-BN: AB (nitrogen)</td>
<td>2.488</td>
<td>3.321</td>
<td>-9.085</td>
</tr>
<tr>
<td>G/h-BN/G</td>
<td>2.477</td>
<td>3.123</td>
<td>-9.177</td>
</tr>
<tr>
<td>h-BN/G/h-BN</td>
<td>2.498</td>
<td>G/G: 3.314</td>
<td>-9.172</td>
</tr>
<tr>
<td>h-BN/G/h-BN</td>
<td>2.483</td>
<td>h-BN/h-BN: 3.149</td>
<td>-9.033</td>
</tr>
<tr>
<td>h-BN/h-BN/G</td>
<td>2.500</td>
<td>h-BN/h-BN: 3.049</td>
<td>-9.036</td>
</tr>
</tbody>
</table>

Table 1: Quantitative results of the structural minimizations of all seven systems. For sake of space, the three-layer results are only shown for the most stable stacking arrangements.

In general, it was observed that arrangements with boron overtop of carbon were preferred whenever possible. This is evident in Table 1, where the AB (boron) arrangement had the least free energy and lowest inter-layer separation of any of the two-layer stacking arrangements. The relative stability of boron over carbon also applied to the three-layer systems, as shown below.

**Figure 2:** Ball-and-stick visualizations of the most stable stacking arrangements for the three-layer systems: graphene/h-BN/graphene (a), h-BN/graphene/h-BN (b), graphene/graphene/h-BN (c), and h-BN/h-BN/graphene (d).

Overall, the results of the structural minimizations are solid; the minimum energy lattice parameters for graphene and h-BN (see Table 1) are within tolerable range of the accepted values, at 2.470 Å versus 2.462 Å for graphene, and 2.512 Å versus 2.52 Å for h-BN. All of the layered systems had equilibrium lattice parameters between these two values, as expected. The relative stability of arrangements with boron over carbon is in agreement with previous computational work.

Once the minimum energy stacking arrangements were found, more quantitative data about the energy and electronic properties were calculated for each arrangement. This data is contained in Table 2.
<table>
<thead>
<tr>
<th>System</th>
<th>Band Gap (meV)</th>
<th>Cohesive Energy (meV/atom)</th>
<th>vdW Energy (meV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>&lt;1</td>
<td>N/A</td>
<td>54.12</td>
</tr>
<tr>
<td>h-BN</td>
<td>4680</td>
<td>N/A</td>
<td>65.19</td>
</tr>
<tr>
<td>G/h-BN</td>
<td>73.4</td>
<td>17.02</td>
<td>103.2</td>
</tr>
<tr>
<td>G/h-BN/G</td>
<td>24.5</td>
<td>27.05</td>
<td>118.8</td>
</tr>
<tr>
<td>h-BN/G/h-BN</td>
<td>159</td>
<td>33.58</td>
<td>124.0</td>
</tr>
<tr>
<td>G/G/h-BN</td>
<td>49.3</td>
<td>22.53</td>
<td>110.0</td>
</tr>
<tr>
<td>h-BN/h-BN/G</td>
<td>78.2</td>
<td>35.41</td>
<td>127.7</td>
</tr>
</tbody>
</table>

Table 2: Additional data for each system’s minimum energy arrangement. The cohesive energies were produced using the free energies contained in Table 1, by subtracting out the single layer energies. Van der Waals energies were estimated within VASP.

Lastly, full band structures were calculated for each system’s minimum energy arrangement, and are shown below.

Figure 3: Band structures around the K point for all systems. Insets are included for the three-layer systems to detail the structures’ characteristics near the K points.

Overall, the band structure data match with expectations. Graphene is known, from experiment, to have little, if any, band gap. The gap in h-BN was estimated at 4.68 eV, which is somewhat below the accepted value of 5.2 eV. The discrepancy is understandable, however, given that DFT simulations are known to underestimate band gaps in many materials.
Conclusions and Future Work

Considering this project’s original motivation, we are most interested in the data obtained for the band gaps in each system (see Table 2). The largest estimated band gap was 159 meV in the h-BN/G/h-BN system. This is an appreciable gap, on the same order as that of silicon, and indicates that fully functional transistors composed of graphene and h-BN layers are at least within the realm of possibility. In order to further explore this possibility, we would need to conduct additional research on ways that this gap could be increased and/or modulated. There are numerous possibilities. First, graphene/h-BN nanoribbons, which would presumably be employed in actual integrated circuit applications, would likely have differing band gaps depending on their shape and/or chirality. Second, electric fields could be used to modulate the band gap in graphene/h-BN systems, as is currently done in field-effect transistors, and as was demonstrated by Tang\(^7\) in graphene layered systems. Third, stress is an effective modulator of band gaps in graphene/h-BN systems, as shown by Zhong\(^6\). Lastly, the presence of a substrate (e.g. SiO\(_2\)) for the layered systems could alter their band structures. Research in some or all of these areas would be the next step in the quest to produce a workable design of a functional graphene/h-BN transistor.

Our research thus far does seem to exclude one method, that of adding additional h-BN layers one atop the other, of further increasing the band gap in G/h-BN systems. The addition of a single h-BN layer to graphene produces a system with an overall band gap of 73.4 meV (see Table 2). The addition of a second layer adjacent to the original, to make h-BN/h-BN/G, increases that gap only slightly, to 78.2 meV. Presumably, the addition of a third layer would produce an even smaller increase, then the fourth a yet smaller increase, and so on. Ultimately, we predict that the h-BN/G/h-BN system has a band gap which is very nearly the largest attainable by any G/h-BN layered system. Admittedly, these predictions are somewhat speculative at this point; this is another area that could use further research.
References


