Atomistic Interrogation Of B-N Co-Dopant Structures And Their Electronic Effects In Graphene

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Figure S1. Example of a rough graphene film created during doped graphene growth. The height variation across the substrate is several tens of nanometers, which makes atomic-resolution imaging impossible. Co-doped samples suffer most severely from this problem, and flat, clean areas are impossible to identify on these samples.
Figure S2. Large area topograph of sample BG2 showing the presence of graphitic boron, dopant configurations STM1 and STM2, and other more complex dopant features.

Figure S3. Additional B/N co-dopant configurations in graphene (carbon atoms: yellow; nitrogen atoms: purple; and boron atoms: light blue) for which DFT calculations were performed and for which results appear in Table 1. Symmetry distinct bond lengths near the B/N cluster, from the relaxed structures based on DFT, are listed below in the order in which they appear moving from upper left to lower right.
**Figure S4.** Visualization of the structures discussed in the text as (a) STM1 and (b) STM2. A top view and a side view are shown with a space filling representation created using VESTA\(^1\). (C atoms brown, N atoms blue, B atoms green). The 7x7 supercell is indicated by the dashed lines. Selected local bond lengths are superposed in units of angstrom.
Figure S5. Correlation between computed work function shifts and Dirac point energy shifts for the structures reported in Table 1 of the main text. The linear regression has slope 0.77 and intercept -0.04 eV.

Figure S6. N 1s and C 1s XPS data for Nitrogen-doped (NH$_3$-grown CVD) graphene used to obtain atomic nitrogen concentrations of 1.15% (NG5) and 0.81% (NG4). N 1s data was measured at a photon energy of 520 eV and C 1s data was measured using photon energy of 420 eV, so that the 1s electrons in both cases are emitted with kinetic energy values in the same range (~120 eV), to obtain an accurate atomic concentration ratio.
Figure S7. Peak fitting of the experimental N 1s XPS data to identify relative concentrations of different nitrogen species in the N-doped graphene films shown in Fig. S3. The higher concentration of nitrilic (N bound to one carbon atom (N1) and pyridinic (N bound to two carbon atoms (N2) as compared to graphitic nitrogen (3 carbon bonds (N3)) results in p-type graphene, as discussed in detail in ref. 22 of main text. Details of the peak fitting, summarized in Table S1 are used to correlate doping level with work function shifts based on measurements of p-type graphene shown in Fig. 5 of the main text.

Table S1. Atomic concentration of N-dopants in different forms (N1, N2, N3 and NO) based on XPS data (Figs. S6-S7). N1 (nitrilic) and N2 (pyridinic) dopants have a p-doping effect in graphene while N3 (graphitic) dopants n-dope graphene. The doping effect of surface nitrogen oxide (NO) is unknown. Concentrations are used to correlate doping effect (number of p-type N-dopants minus number of n-type N-dopants, \( N_p - N_n \), obtained as \((N1+N2)-N3\)) with work function change (\( \Delta W.F. \)) in graphene. N1 and N2 type dopants have binding energy ranges in close proximity; both types are included in peak 0 in the fit of N 1s XPS for NG4 (Fig. S7).

<table>
<thead>
<tr>
<th></th>
<th>Total N</th>
<th>N1</th>
<th>N2</th>
<th>N3</th>
<th>NO</th>
<th>( N_p - N_n )</th>
<th>( \Delta W.F. )</th>
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<tr>
<td>NG4</td>
<td>0.81%</td>
<td>0.57%</td>
<td>0.21%</td>
<td>0.03%</td>
<td>0.36</td>
<td>0.4 eV</td>
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<tr>
<td>NG5</td>
<td>1.15%</td>
<td>0.49%</td>
<td>0.13%</td>
<td>0.39%</td>
<td>0.14%</td>
<td>0.23</td>
<td>0.2 eV</td>
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References