

Electronic and Optical Properties of Heterostructures of Graphene and 2D Semiconducting Boron carbides

Lu Niu, Oliver Conquest, Carla Verdi, Catherine Stampfl
School of Physics, The University of Sydney, Sydney, 2006 Australia

Abstract

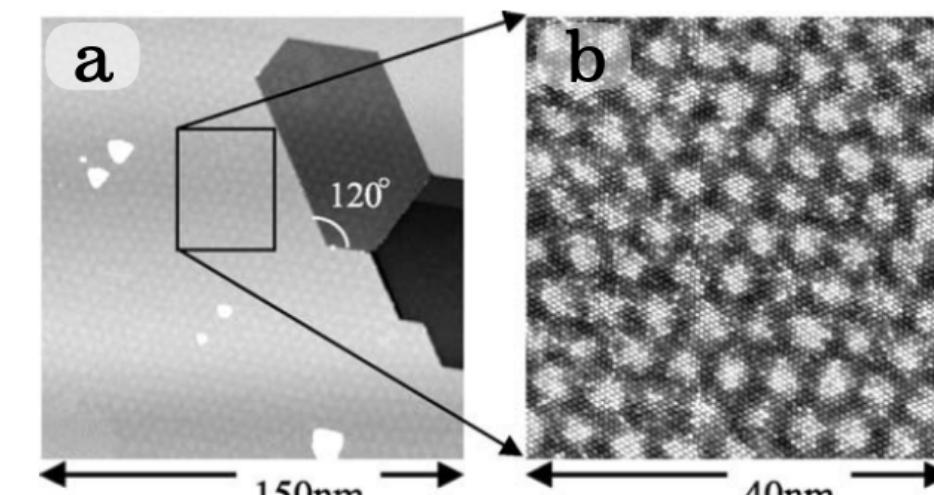
Integration of dissimilar two-dimensional (2D) materials is essential for nanoelectronics applications. For conventional 2D materials derived from bulk-layered crystals, vertical heterostructures can be realized by mechanical stacking [1]. Graphene has excellent electrical conductivity, mechanical and thermal properties, and high light transmittance in the visible light-infrared area. It has found applications in e.g. solar cells, lighting, and touch screens. However, graphene has been limited due to its zero band gap. One of the methods used to expand the application of graphene is to form heterostructures. Stacking different 2D materials together can form a double-layer or even multi-layer artificial materials that are maintained by van der Waals interactions [2]. Such materials are known as van der Waals heterojunctions. A wide range of physical properties can be obtained by such stacking, making van der Waals heterojunctions even more important than the 2D material itself.

A current research theme is investigating the prospect of developing plasmonic devices using 2D semiconductors [3]. Plasmonic modes in each class of van der Waals semiconductors have their own peculiarities, along with potential technological capabilities. Graphene (G) has an extremely high quantum efficiency for light-matter interactions, is strongly optically nonlinear and contains plasmons with unusual properties that are tunable and adjustable. Carbon and boron can mix to form numerous 2D compounds with strong covalent bonds, yet very few possess a bandgap for functional applications. Graphene-like BC₃ has been confirmed experimentally and is found to be semiconducting with an indirect bandgap of around 0.5 eV. Calculations have shown that nanostructures of graphene-like BC₃ possess preferable absorbance in the visible region and by changing the size of the nanostructure, the resonance peak position of the absorption spectrum can be effectively regulated [4].

In the present work we combine these two materials to study the electronic and optical properties of a series of graphene/boron-carbide heterostructures, starting with G/BC₃. We use density functional theory as implemented in the VASP (Vienna Ab initio Simulation Package) software and report the electronic band structure, density of states, complex dielectric function and the absorption spectra, and compare them with those of the respective isolated monolayers. Our results show potential metallic properties of G-BC₃ which needs to be confirmed by further calculations. The adsorption spectra also demonstrate characteristic peaks around 1200nm, 700nm, and between 350nm to 250nm.

- [1] K. S. Novoselov, A. Mishchenko, A. Carvalho, A. H. Castro Neto, 2D materials and van der Waals heterostructures, *Science* 353, 9439 (2016).
- [2] Bin Qiu, Xiuwen Zhao, Guichao Hu, Weiwei Yue, Junfeng Ren and Xiaobo Yuan, Optical Properties of Graphene/MoS₂ Heterostructure: First Principles Calculations, *Nanomaterials*, 8, 962 (2018).
- [3] A. Agarwal, M. S. Vitiello, L. Viti, A. Cupolillo and A. Politano, Plasmonics with two-dimensional semiconductors: from basic research to technological applications, *Nanoscale*, 10, 8938 (2018).
- [4] J. Chen, X.-L. Cheng, H. Zhang, Plasmon Excitation in BC₃ Nanostructures from First Principles, *Plasmonics*, 14, 109 (2019).

(a) Scanning Tunneling Microscopy images of a BC₃ sheet with a honeycomb structure.



[5] Solid State Communications 136 (2005) 22–25

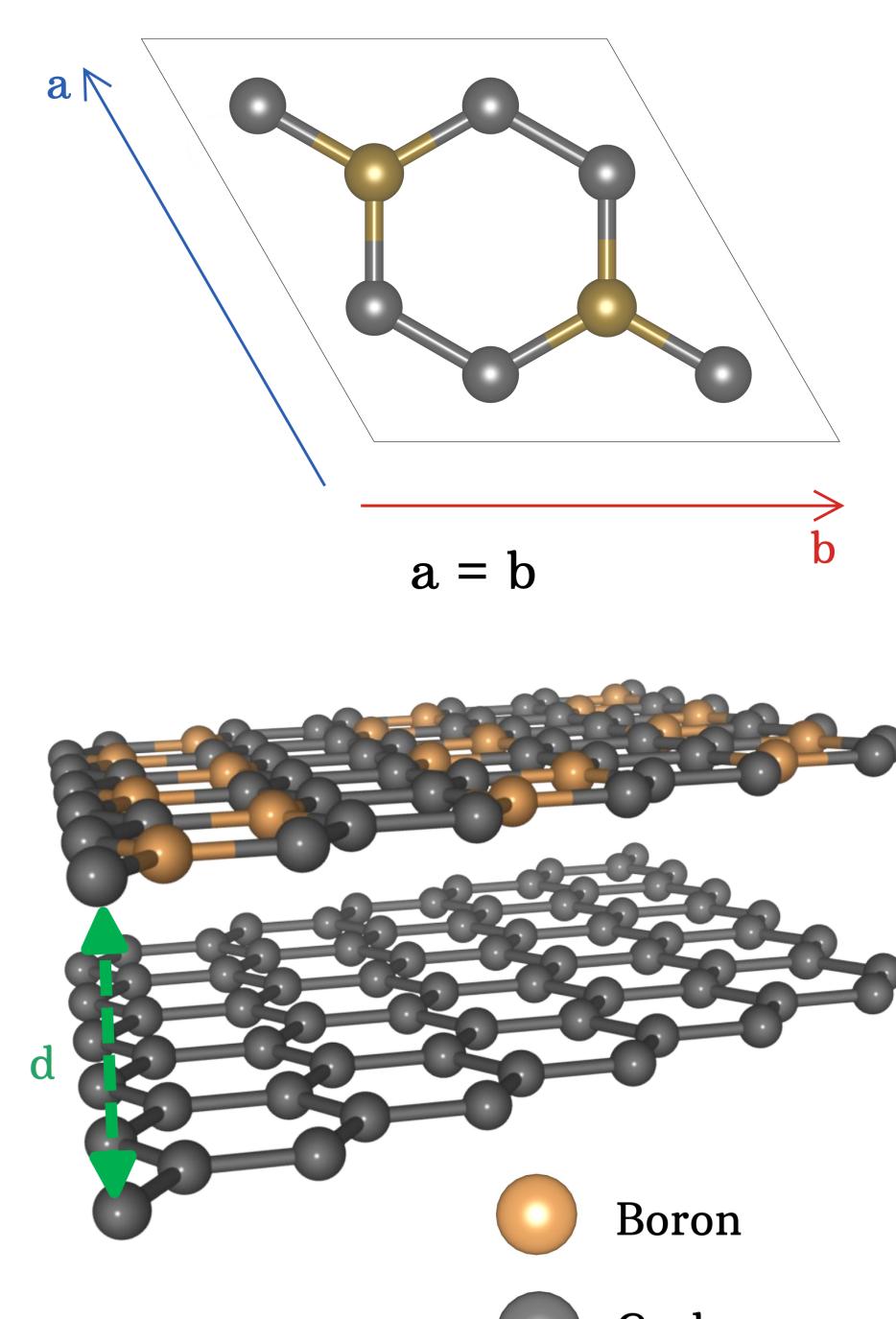
The Calculation Approach

Density Functional Theory; generalized-gradient approximation (PBE) with D3(BJ) dispersion correction; VASP Code: Plane-wave basis sets (energy cut-off 450 eV);

Special k-point sampling ($12 \times 12 \times 1$); Supercell (8 atoms for Graphene and BC₃ monolayers, 16 atoms for bilayer G-BC₃); Optimized lattice constant BC₃, $a = 5.165 \text{ \AA}$ (Exp: $a = 5.2 \text{ \AA}$) [6]

Optimized lattice constant graphene, $a = 4.936 \text{ \AA}$ (or 2.468 \AA for the unit cell) G-BC₃ heterostructure uses same lattice constant as BC₃ G under 5% strain;

[6] H. Tanaka solid state communications 136 22–25 (2005)



Binding Energy: G-BC₃ heterostructure

$$E_b = E_{\text{G-BC}_3} - E_{\text{Graphene}} - E_{\text{BC}_3}$$

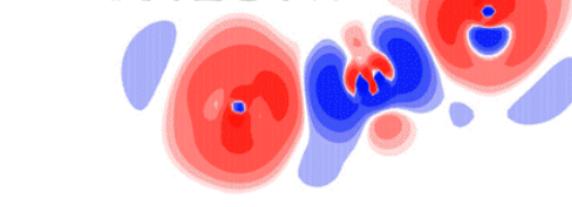
Where E_b is the binding energy;

$E_{\text{G-BC}_3}$ is the energy of the bilayer Graphene-BC₃ system;

E_{Graphene} is the energy of monolayer graphene;

E_{BC_3} is the energy of monolayer BC₃.

CONDENSED
MATTER
THEORY



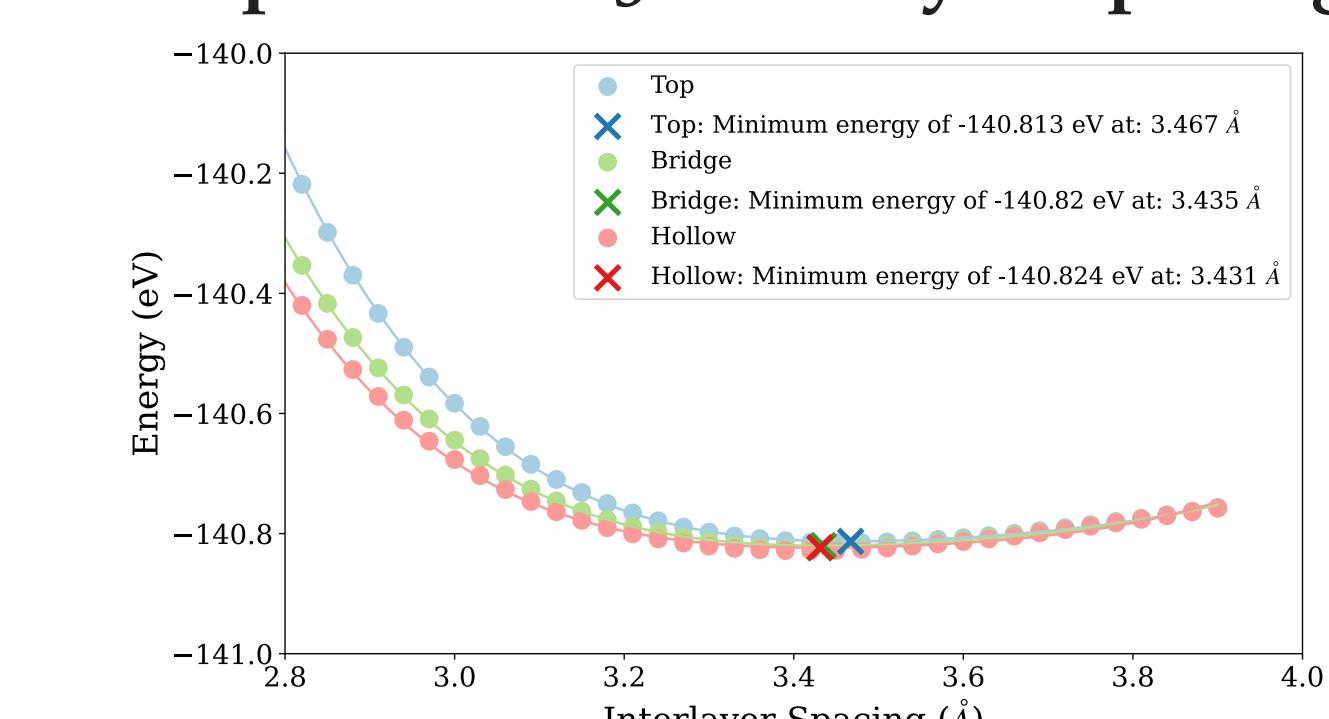
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Favourable Bilayer Geometry

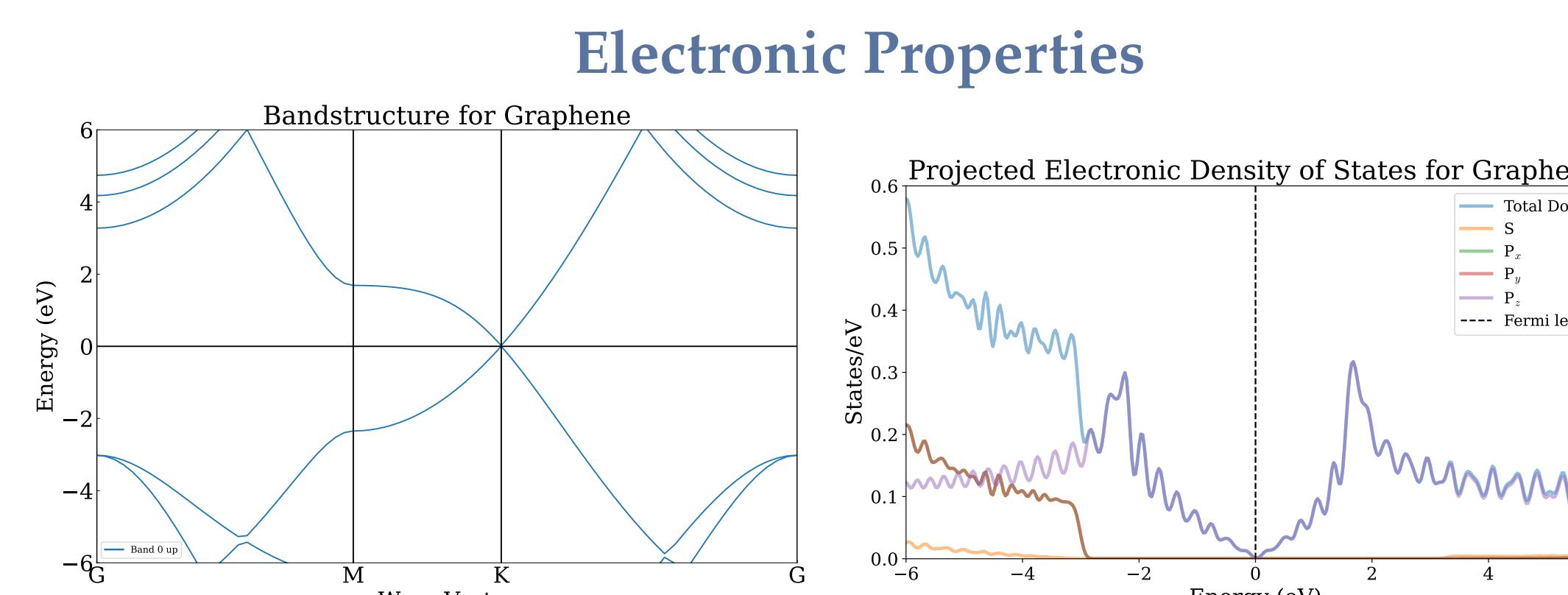
	Top	Hollow	Bridge
Relative binding energy (eV)	0.011	0	0.004
Interlayer distance (Å)	3.467	3.431	3.435

- The relative bilayer top, hollow and bridge sites are tested by fixing the graphene layer and translating the BC₃ layer.
- The hollow site shows the most favorable binding energy and is the preferred Graphene-BC₃ configuration.

Graphene-BC₃ Interlayer Spacing

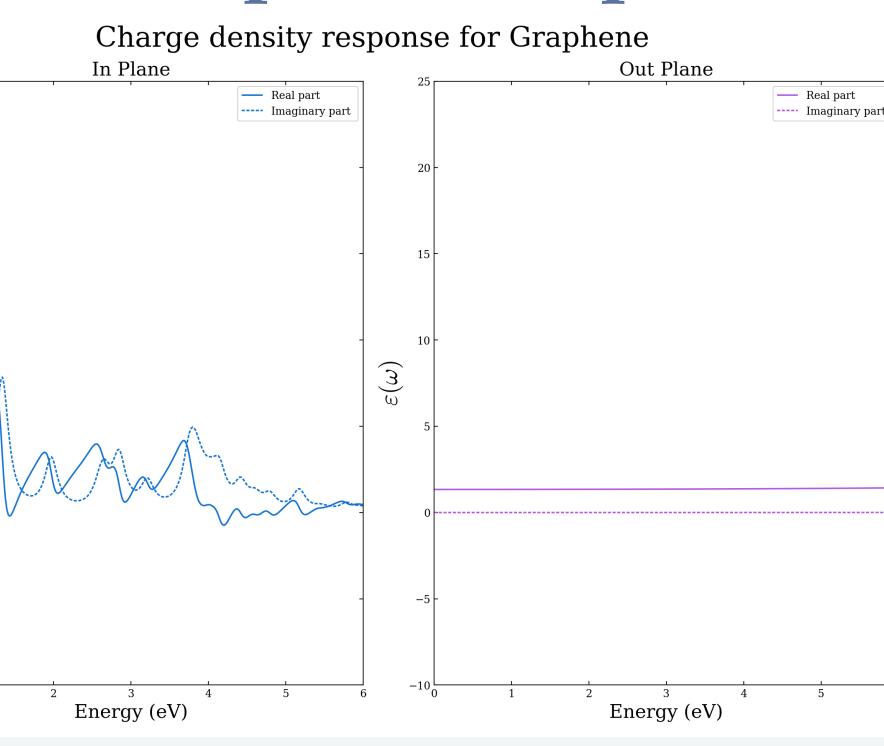


Graphene

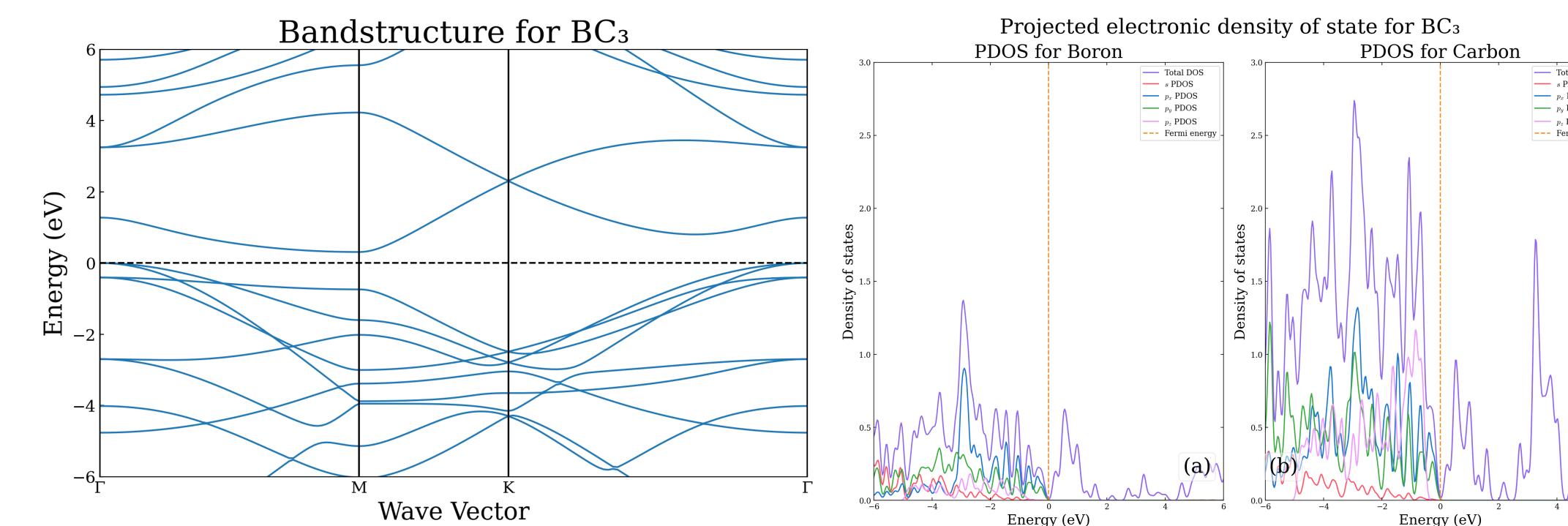


- Graphene's well-known semimetallic behavior is shown by the Dirac cone at the Fermi level (0 eV).
- Broad in-plane dielectric response from the NIR and across the visible spectrum.

Optical Properties

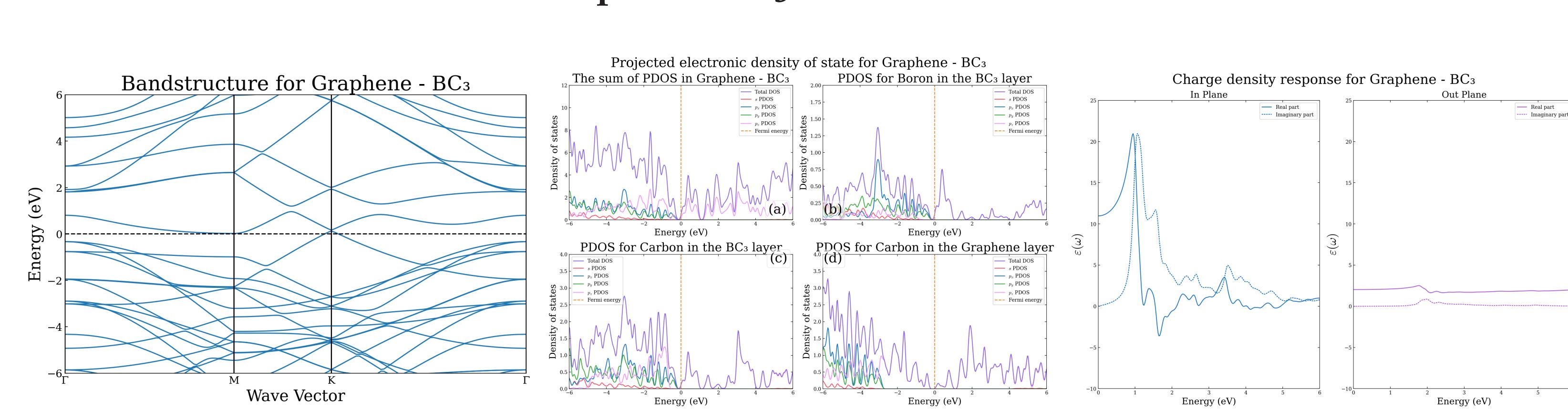


BC₃



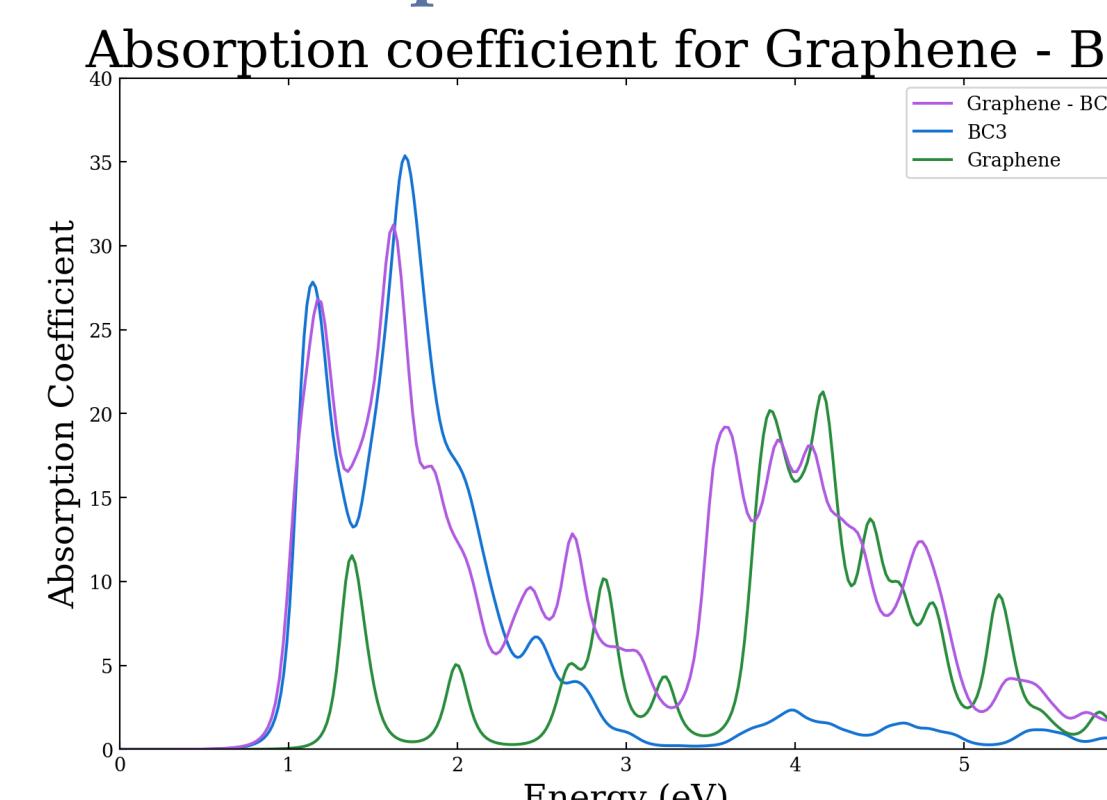
- Unlike graphene, BC₃ shows semiconducting behavior with a band-gap of 0.327 eV.
- Relatively stronger in-plane dielectric response in the NIR and long wavelength visible range compared to Graphene.

Graphene-BC₃ heterostructure



- Interaction between Graphene and BC₃ layers results in possible metallic behaviour.
- Low energy response dominated by characteristic BC₃ peaks around 1 eV and 1.5 eV, graphene character is more prominent higher energies.

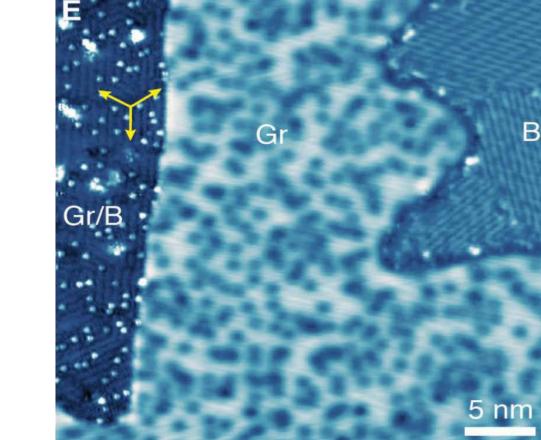
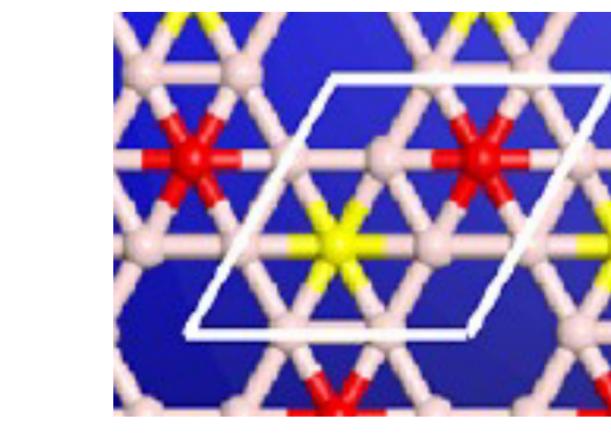
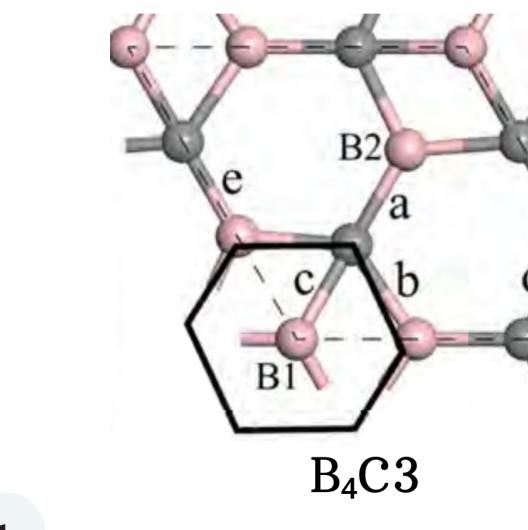
Absorption Coefficient



Characteristic adsorption peaks are found for G-BC₃ around 1200nm, 700nm, and 450nm with a broader set of peaks in the UV between 350nm to 250nm. Peaks for G-BC₃ are generally shifted to lower energies compared to Graphene.

Future Work

- Future work comparative studies with HSE06 functional;
- Further investigation will look at G-B₄C₃, G-B bilayers.



Recently, Borophene and Graphene bilayer integration has been demonstrated experimentally; STM topography image of lateral and vertical heterostructures between borophene and graphene. Liu and Hersam, *Sci. Adv.* 2019; 5

Conclusion

- Hollow site coordination is the favored configuration of the graphene-BC₃ heterostructure.
- G-BC₃ shows potentially metallic behavior, more work is needed to confirm these results, further optimization and more accurate functionals.
- Characteristic peaks adsorption peaks for G-BC₃ have been identified.

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