Hybrid density functional study of 2D graphene-boron nitride nanostructures

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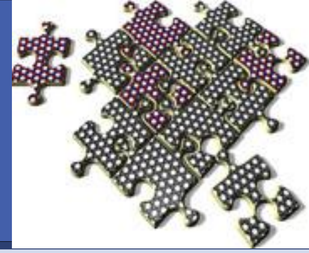


Motivation

- Graphene: unique electronic structure and transport properties, zero band gap
- Hexagonal BN (h-BN): wide band gap (5.7 eV), lattice constant ~graphene
- Hybrid BNC materials for band gap tunability and to achieve desired properties
- Uniform and continuous synthesis of 2D h-BNC films on large area: L. Ci et al, Nature Materials **8**, 430 (2010)
- Strong tendency of h-BN and graphene to form domains and not fully phase segregate
- Structural features and band gap distinct from parent materials
- Numerous possible technological applications in nano-electronics, optical devices, field emission, catalysis

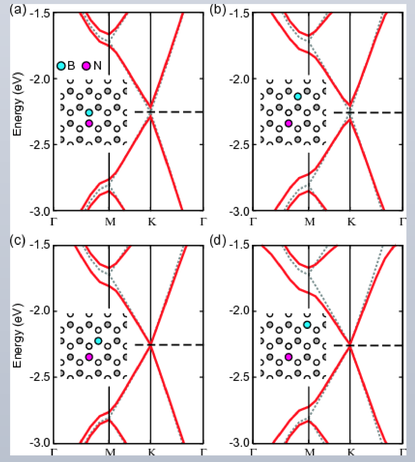
Calculation details

- DFT-HSE06 calculations using VASP, Projector Augmented Wave method (PAW)
- 700 eV plane-wave energy cutoff, 5x5x1 supercell (50 atoms)
- 10x10x1 supercell (200 atoms) for spin-polarized calculations

Low concentration of BN substitutions in graphene

- Substituent atoms occupying adjacent and different sublattice sites open 0.25 eV gap
- Band gap increases with increasing B and N separation
- 1-3 meV gap observed for B, N occupying same sublattice
- Electronic structures near fermi level result from hybridization of B, N and graphene bands
- B and N separation determines degree of hybridization near the Γ point, larger separations yield more localized flat bands

AB-type substitution



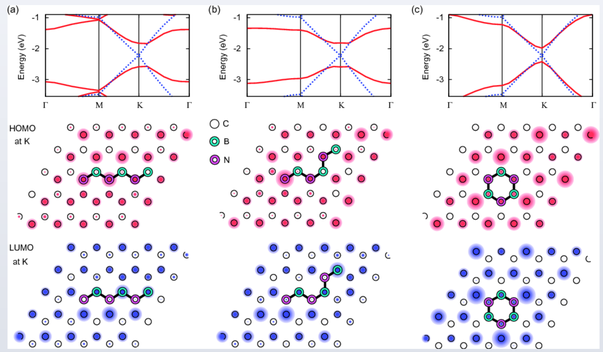
AA-type substitution

BN chains and hexagonal rings in graphene

Bandstructures

Site-projected wavefunction at K point for topmost VB

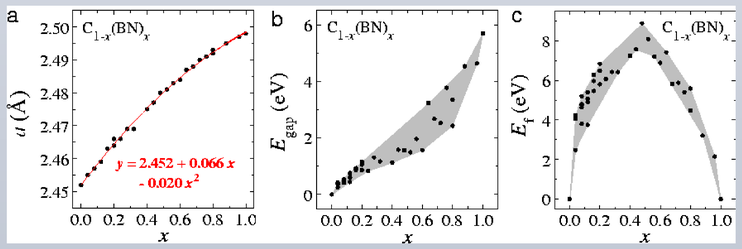
Lowermost CB



- Zigzag, armchair configurations disturb graphene symmetries and open ~0.75 eV gaps
- Hexagonal configuration, the most stable of the three, opens 0.44 eV gap but maintains graphene symmetry throughout
- Electric transport mainly through C network for BN hexagonal rings, whereas B and N atoms also contribute for zigzag and armchair configurations

Selected properties of 2D BNC nanostructures

Lattice constant (Å) **Band gap (eV)** **Formation energy (eV)**



- Multiple dots for a given concentration indicate more than one configuration
- Relaxed lattice constants follow a quadratic trend
- Band gap and formation energy are sensitive to configuration type and show large variation
- Formation energies for a pair or cluster of substituting atoms are always lower than random distribution or open chains

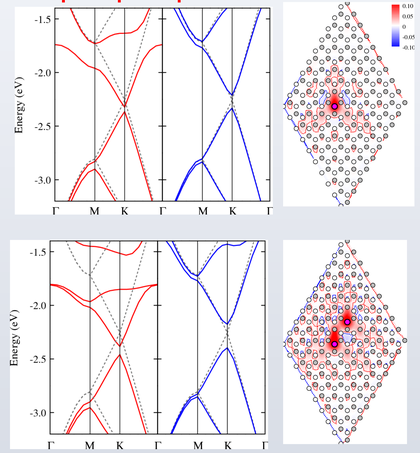
Magnetic studies of N substitutions in graphene

Bandstructure **Spin density**

Spin-up **Spin-down**

Single N substitution

- Partial occupation of both spin-up and down components leads to a net magnetic moment for single N substitution
- Spin density diffuses over long range and encompasses almost 4 nearest neighbor atoms



Di-nitrogen substitution

- Ferromagnetic spin-ordering for N atoms on same type of sublattice
- Antiferromagnetic ordering for N atoms on different sublattice sites

Summary

- Properties of 2D-BNC systems gradually tuned by varying BN concentration
- Electronic structures of BNC systems with low concentration of BN are influenced by sublattice symmetries of graphene
- Different configurations display distinct electronic structures
- In sync with experiments, a strong tendency to form domains exists both for low concentration of BN in graphene and low concentration of C impurities in BN
- Spin studies reveal that spin-ordering depends on sublattice type: ferromagnetic alignment observed for substituent atoms on same type of sublattice

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