Accurate computational studies of carbon doped two-dimensional boron-nitride

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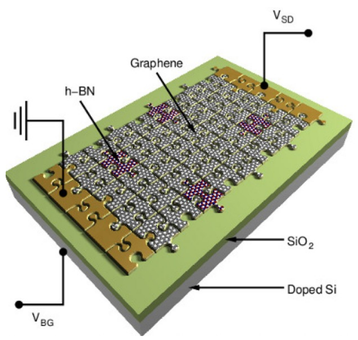
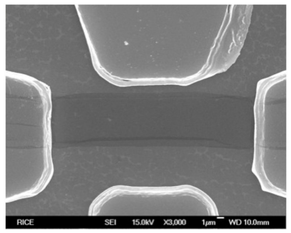
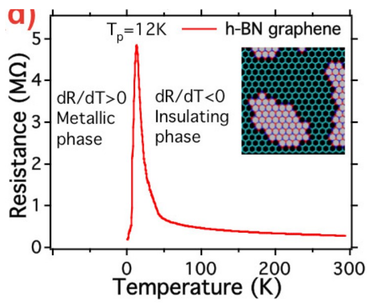
Single layer "h-BN+ graphene" (BCN)



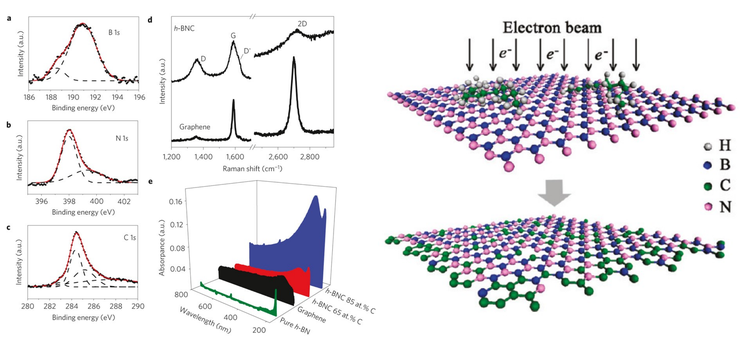




Anomalous insulator metal in boron nitride-graphene hybrid atomic layers : Li Song *et al.* arXiv:1105.1876v2transition

- Boron nitride is a **synthetic material** - discovered in the early 19th century.
- **Hexagonal boron nitride (h-BN)** is the equivalent in structure of **graphite**.
- **The partly ionic** structure of BN layers in h-BN reduces covalency and electrical conductivity, and induces a **large band gap**.

Synthesizing single-layer BCN systems



Growth of mono- and few-atomic-layer BN sheets

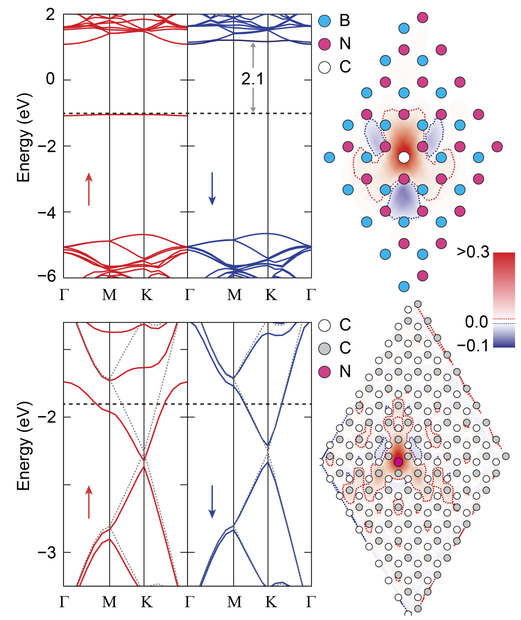
- Mechanical cleavage (*Appl. Phys. Lett.* **92** 133107, 2008).
- Chemically derived exfoliation (*Appl. Phys. Lett.* **93** 223103, 2008; *Adv. Mater.* **21** 2889, 2009).
- Electron beam sputtering (*Phys. Rev. Lett.* **102** 195505, 2009; *Nano Lett.* **9** 2683, 2009).
- Chemical vapor deposition (*Nano Lett.* **10** 3209, 2010; *Nano Lett.* **10** 4134, 2010; Nanotechnology **22** 215602, 2011).

Atomic layers with hybridized BN and C domains

- **Chemical vapor deposition** (Nat. Mater. **9** 430, 2011)
- **Electron-beam-induced substitutional carbon doping of BN** (ACS Nano **5** 2916, 2011).

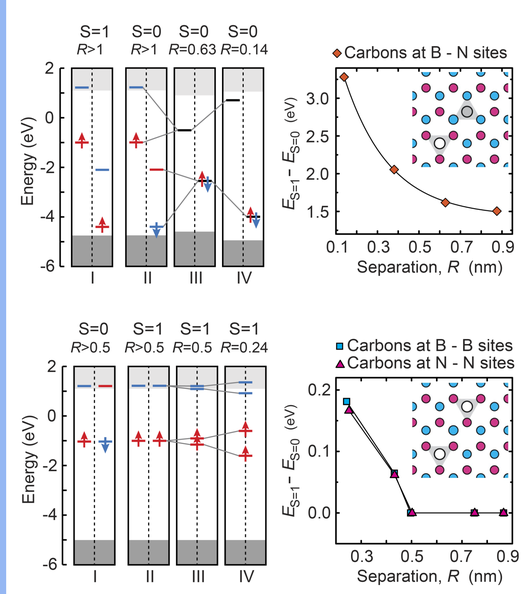
Local magnetic moments induced by an isolated substitutional C atom in BN

Spin-resolved band structure and spin density for an isolated **C** atom substituting a B atom in **h-BN**



Spin-resolved band structure and spin density for an **N** atom in **graphene**

Interaction of two local moments Induced by two C atoms



Two **C** are at **B-N** sites

S=0 :
- **"Ionic bond"** for R < 1 nm.
- Spin-splitting collapses.
- Overlapping of impurity-state wavefunctions shifts the two spin-degenerate impurity states away from each other.

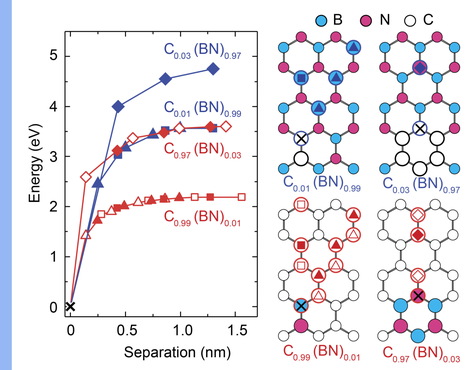
S=1 :
- **"Anti-bonding"** character, independent of R.
- Due to the node, wavefunction overlapping is negligible.

Two **C** are at **B-B** sites or **N-N** sites

S=0 :
- No charge transfer because both sites have same "electronegativity" .
- **"Anti-bonding"** character.

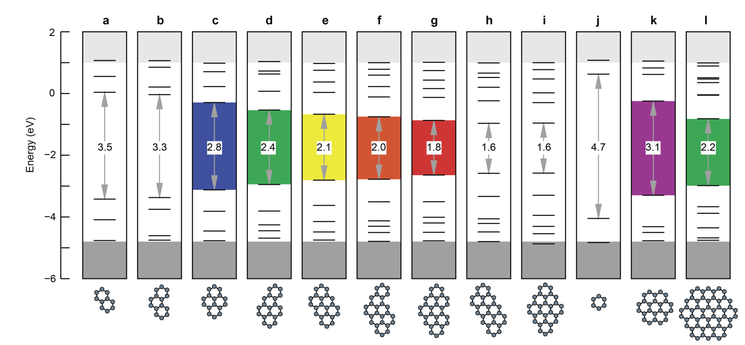
S=1 :
- Two spin-up wavefunctions overlap and split into two hybridized states.
- **"Bonding"** character, two C atoms equally share electrons at the hybridized states.
- The size of the splitting due to the hybridization depends on the separation.

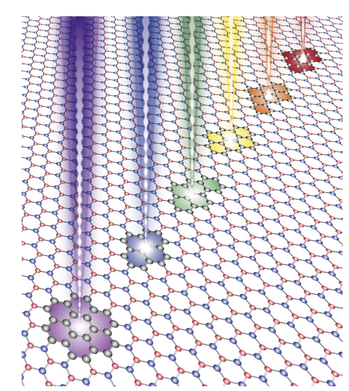
Clustering of C atoms embedded in BN



- Recent **experimental investigations** on 2D-BCN materials reveal that **graphene and h-BN form domains** but do not fully phase-segregate.
- Our study shows, in terms of formation energy, that both C and BN have a very **strong tendency to form pairs and clusters** .
- The **"zigzag"** and the **"armchair"** types of separations **show no distinction** in their energy trends for the C-C pair in h-BN or B-N pair in graphene.
- Likewise, **equivalent and inequivalent sub-lattice site** separations **follow the same trend** for B-N in graphene.

Graphene quantum dots embedded in h-BN





- Our HSE calculations predict that electronic **gaps can be gradually spanned, matching the entire visible electromagnetic spectrum**, depending on the size and symmetry of the C clusters.
- **Increasing number of C rings** stacks more states in the gap of h-BN, and **reduces the electronic gap**.
- The six-fold symmetry allows multiple degenerate states, and **gaps for symmetric C clusters vary relatively slowly with increasing number of C rings**.

- **HSE06** hybrid functional in the **VASP** code.
- Plane-wave projector augmented-wave (**PAW**) method
- Energy cutoff of **700 eV** for all our calculations.
- The BCN nanostructures are modeled in **200 atom** computational cells, **10 x 10** of the two atom unit-cell.
- The Brillouin zone is sampled by a Γ-centered **10 x 10 x 1 k-point** meshes for the unit-cell, and equivalent meshes for larger simulation cells.

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