

# 2D $B_xC_{1-x}$ Layers as Predicted by the Cluster-Expansion Approach

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In this work, the cluster-expansion method combined with extensive first-principles calculations is used for predicting the most stable 2D  $B_xC_{1-x}$  ( $x \leq 0.5$ ) layers. For concentrations of B up to  $\approx 38\%$ , the honeycomb structure of the boron-carbon compound is preserved, whereas for larger concentrations, the boron atoms tend to form 2D clusters and/or ribbons that are fragments of a triangular boron sheet. Our studies indicate that the incorporation of boron into graphene is energetically unfavorable even for low concentrations of B, however, the graphene-like structure of the  $B_xC_{1-x}$  layer may be stabilized by a metallic substrate.

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## 1. Introduction

Graphene studies provided the excitement and impact to explore properties of planar one-atom thick layers of the whole plethora of other materials. Investigation of two-dimensional single layer systems is important since they do not only exhibit intriguing properties but also are parent structures of one-dimensional nanotubes and zero-dimensional nanocages. Graphene doped with boron (and also other elements) is among extensively studied planar structures, since it should exhibit a variety of structural and electronic properties that depend on the composition [1–3] and can lead to new functionalities.

The 2D boron-carbon compounds were studied theoretically earlier, using several computational methods [1, 2]. The purpose of those studies was mainly to investigate the possibility of band-gap opening in graphene induced by doping with boron. However, it is also of interest to investigate atomistic structural details of the C-B systems and their stability for a wide range of boron concentrations.

In this work, we develop strategies for predicting the most stable 2D  $B_xC_{1-x}$  layers. The idea is to find 2D materials that preserve the honeycomb structure and can complement graphene in properties. The modeling of these structures is done using the cluster-expansion technique combined with extensive first-principles calculations.

## 2. Calculation details

In our studies of  $B_xC_{1-x}$  systems, we employ the cluster expansion method together with the *ab initio* density functional theory (DFT) calculations of total energies. The first principles DFT calculations are done using the Quantum-ESPRESSO package [4]; the projected augmented wave (PAW) method and the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional are used. The cluster-expansion computations are done using the Alloy-Theoretic Automated Toolkit (ATAT) [5].

The ATAT package uses the total energies obtained from the Quantum-ESPRESSO code and tries to find the best cluster expansion for the given set of structures

and energies available at any step of the calculation. Furthermore, it proposes new structures to be calculated in order to improve the cluster expansion. The search over 2D boron-carbon structures is limited in our calculations to unit cells with 12 atoms per cell.

The cluster-expansion technique is a method to calculate the distribution of the alloy constituents on the crystal lattice. Therefore by using this approach, we can mainly explore how the B and C atoms are arranged in the honeycomb structure at a given concentrations of the constituents. In principle, this would limit our studies to those  $B_xC_{1-x}$  layers that preserve the honeycomb structure. In practice, however, thanks to the structural optimization, we obtain also some of the structures that go beyond the graphene-like honeycomb structure.

## 3. Results and discussion

With the cluster-expansion technique, we are able to predict low energy 2D  $B_xC_{x-1}$  structures for boron concentrations  $x \leq 0.5$ . In Fig. 1, we show the structure of the most stable layers for various compositions resulting from mixing B and C atoms. Some of those structures have been previously reported in Ref. [1], where the authors have used a more advanced method for searching over the most stable structures. The agreement between our and the previous predictions validates our search methodology for concentrations at least up to 50%. From Fig. 1, we can learn that for all concentrations of B, the impurity atoms tend to be as close to each other as possible, either by forming chains of atoms that are up to third nearest neighbors (Figs. 1a–c, e, f) in the graphene-like structure or the B atoms are evenly distributed like in the case of the  $B_{0.25}C_{0.75}$  structure (Fig. 1d), or the B atoms form triangular motifs embedded in the graphene structure (Fig. 1g). It is important to note that the  $B_{0.25}C_{0.75}$  ( $BC_3$ ) honeycomb sheet has been experimentally synthesized epitaxially on  $NbB_2$  (0001) [6]. Finally, in Fig. 1h we show the distorted 2D structure of boron derived from the honeycomb structure upon structural optimization. This demonstrates a known fact [7] that the graphene-like boron sheet is unstable with respect to shearing perturbation.

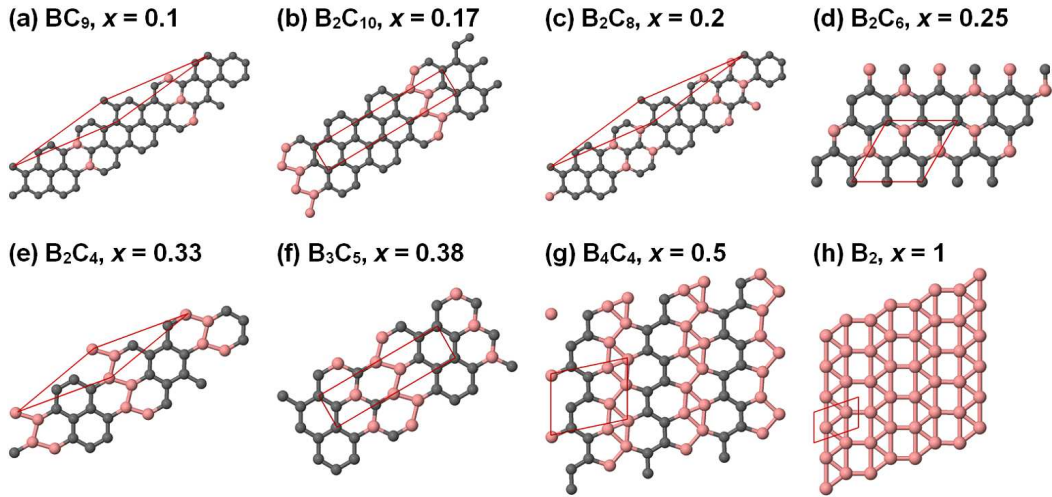


Fig. 1. The most stable 2D structure of  $B_xC_{1-x}$  ( $x \leq 0.5$ ) for the boron-carbon system. The structures (a)–(f) preserve the honeycomb structure, whereas (g) possesses boron triangular motifs embedded in the graphene structure. In (h) it is shown the distorted 2D structure of boron derived from the honeycomb structure upon structural optimization. For each structure, we show the unit cell used for calculations and the number of atoms ( $B_nC_m$ ) in the cell.

The formation energies for the  $B_xC_{1-x}$  layers obtained from the cluster-expansion approach are shown in Fig. 2a. In this figure, two sets of data are provided. The blue squares correspond to formation energies calculated with respect to graphene ( $x = 0$ ) and the ideal graphene-like structure of boron ( $x = 1$ ). However, as mentioned above, the graphitic hexagonal boron sheet is not stable because boron has only three valence electrons (instead of four like carbon) and not all bonding states are filled. Let us note that the graphene-like structure of boron can be stabilized by charge transfer from a metallic substrate [8]. If it is the case, then the calculated by us negative formation energies may suggest that on metallic substrates, the doping of graphene with boron is energetically favorable. The second set of data shown in Fig. 2b by red circles corresponds to formation energies calculated for the same  $B_xC_{1-x}$  layers as before, but with respect to the distorted honeycomb structure of boron shown in Fig. 1h. Since the distorted structure is lower in energy by 670 meV/atom than the ideal one, this makes the incorporation of boron atoms into graphene energetically unfavorable.

Except for one structure,  $B_{0.25}C_{0.75}$  all other  $B_xC_{1-x}$  layers are metallic. This is in agreement with recent theoretical predictions where it was shown that among other  $B_nC_m$  layers only the  $BC_3$  structure has an indirect gap of 0.52 eV [1]. In Fig. 2b, we show the density of states for the  $B_{0.1}C_{0.9}$  structure. It is clear from the figure that the layer is metallic with a finite density of states at the Fermi level.

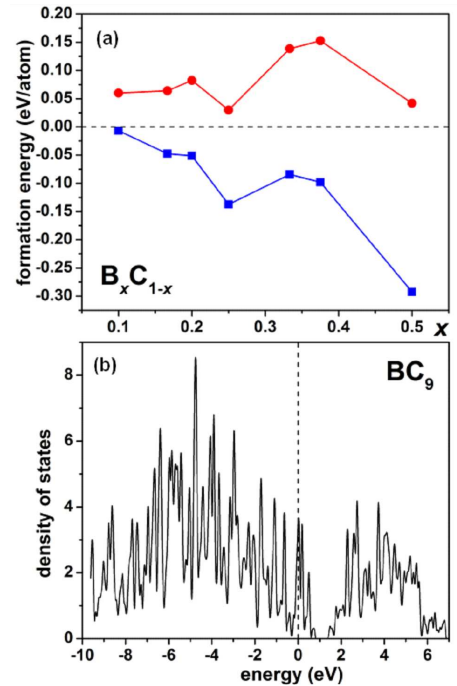


Fig. 2. (a) Formation energies of  $B_xC_{1-x}$  ( $x \leq 0.5$ ) calculated with respect to graphene and the perfect (blue squares) and distorted (red circles) two-dimensional honeycomb structure of boron. The solid lines are guide to the eye. (b) Density of states for  $BC_9$  ( $x = 0.1$ ). The dashed line denotes the Fermi level.

#### 4. Conclusions

We predict that high concentrations (up to  $\approx 38\%$ ) of B atoms can be incorporated into the graphene network without destroying it. Most of the 2D  $B_xC_{1-x}$  structures are metallic. A free-standing honeycomb boron layer is not stable due to electron deficiency. However, boron hexagonal layer on a metallic substrate can be stabilized by charge transfer from the substrate. This makes the incorporation of boron atoms into the graphene structure energetically feasible.

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