

Boron doped graphene nanostructures

Alexander Quandt^{1,2}, Cem Özdoğan³, Jens Kunstmann⁴, and Holger Fehske¹

¹ Institut für Physik der Universität Greifswald, Felix-Hausdorff-Str. 6, 17489 Greifswald, Germany

² CNR-IFN Trento, CSMFO group, Via Alla Cascata 56/c, 38050 Povo-Trento, Italy

³ Department of Computer Engineering, Çankaya University, Balgat, 06530 Ankara, Turkey

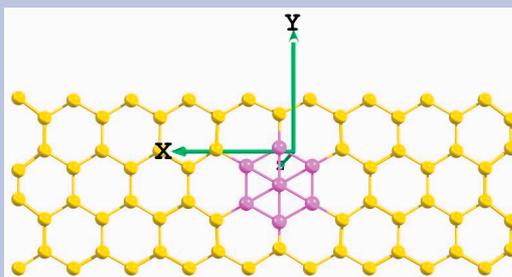
⁴ Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, 70569 Stuttgart, Germany

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Unit cell of B₇-doped armchair graphene nanoribbon.

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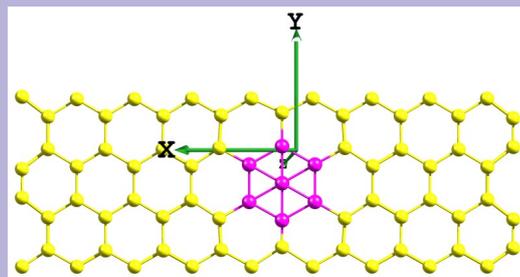
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* Corresponding author: e-mail holger.fehske@physik.uni-greifswald.de, Phone: +49-3834-864760, Fax: +49-3834-864701

We present results from an ab initio study of metallized semiconducting graphene nanostructures. Our model system consists of an alternating chain of quasi-planar B₇ clusters embedded into a semiconducting armchair nanoribbon. We observe the appearance of overlapping bands around the Fermi-level, with crystal momenta pointing into the direction of these boron chains. This observation could be a vantage point for the development of graphene nanodevices and integrated nanocircuits, based on existing technologies.



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1 Introduction The step from micro-sized electronics towards nanosized electronics would allow for a dramatic increase in the number of functional devices within a given chunk of matter, among other serious technological advantages like much higher clock rates, or lower voltages. But starting from existing technologies, such a step looks rather improbable, as VLSI [1] and even more advanced silicon based technologies require a complicated processing of raw silicon wafers to create functional devices. This includes a tedious layer-by-layer sequence of imaging, deposition and etching process steps. And the size of the resulting circuits is limited by the wavelengths of light used to project the masks for the various layers.

A basic material that could substitute raw silicon wafers within the nanodomain are broad sheets of single-layered graphite called graphene [2]. Although an infinite two-dimensional sheet of graphene shows a basic metallic behaviour [3], there are various techniques to produce large numbers of broad semiconducting sheets of graphene [4]. In contrast to silicon, those semiconducting sheets of

graphene do not even require a doping by foreign atoms to achieve a basic functionality as solid state transistors. On the other hand, in order to imprint integrated electronic circuits on a semiconducting piece of graphene, the most important precondition would be a method to wire various semiconducting areas on such a sheet. As long as we have to rely on standard microelectronic wiring, not much will be gained as compared to silicon.

In the following, we will discuss results from an ab initio study of a model system for functionalized semiconducting graphene sheets, where a basic metallization could be achieved by embedding alternating chains of B₇-clusters. In Section 2 we will shortly describe the chemistry behind our model system, and make a few remarks about our numerical simulations. Then in Section 3 we will discuss the main results of our studies. Finally in Section 4 we will summarize our main results and argue, why these findings could be a starting point for the development of novel techniques to lay out integrated graphene-based nanocircuits, based on existing technologies.

2 Chemical and numerical details In order to functionalize a large semiconducting piece of graphene, we have to search for nanomaterials with a compatible chemistry, and which provide the desired functionality. It turns out that an ideal binding partner for carbon is boron, its immediate neighbor in the periodic table [5]. Isolated substitutions of carbon atoms by boron atoms have quite recently been suggested for graphene [6], but those studies also reported a strong tendency of single boron atoms to migrate towards the open borders of graphene nanoribbons. This finding is in good agreement with similar findings from previous experimental and theoretical findings in the field of boron doped carbon nanotubes [7]. Therefore doping with single boron atoms could mainly be ruled out as a suitable pathway to functionalize bulk graphene, although it might remain quite important for manipulating the edge states of graphene nanoribbons [6].

Beyond the difficulties related to boron migration, a doping with single boron atoms does not make any use of the basic chemical compatibility between larger aggregates of boron and carbon. Small clusters of boron are of quasi-planar shape built from hexagonal B₇ pyramids [8], and they fit quite nicely into the basic honeycomb structure of graphene. And the electron-deficient nature of boron provides the necessary chemical flexibility to form stable bonding of such clusters with a surrounding carbon matrix [5]. Those effects and their corresponding energetics have been studied in some detail for nanotubular boron-carbon heterojunctions [9]. Furthermore, in their extended quasi-planar and tubular configurations, boron nanomaterials derived from these quasi-planar clusters turn out to be metallic [10]. Therefore, from a purely conceptual point of view, with small boron clusters we should have an optimum building block to metallize graphene.

All of our *ab initio* calculations and optimizations were carried out using the VASP package (version 4.6.28) [11, 12], which is a density functional theory [13] based *ab initio* code using plane wave basis sets and a supercell approach to model solid materials, surfaces, or clusters [14]. Electronic correlations were treated within the local-density approximation using the Perdew–Zunger [15] form of the Ceperley–Alder exchange–correlation functional [16], and the ionic cores of the system were represented by ultrasoft pseudopotentials [17] as supplied by Kresse and Hafner [18].

As model semiconducting graphene substrate we chose a semiconducting armchair graphene nanoribbon, whose unit cell is shown in Fig. 1a. Both, this unit cells and the unit cell for the doped armchair nanoribbon shown in Fig. 1b are characterized by a huge distance at right angles to the graphene layer (i.e. the *z*-direction in Figs. 1a and 1b), and another huge distance in the direction of the width of those nanoribbons (i.e. the *x*-direction in Figs. 1a and 1b). During structure optimizations, those huge distances were occasionally reset, in order to prevent the optimization algorithms from contracting the systems along those direc-

tions. In the *y*-direction shown in Figs. 1a and 1b, both unit cells repeat themselves periodically.

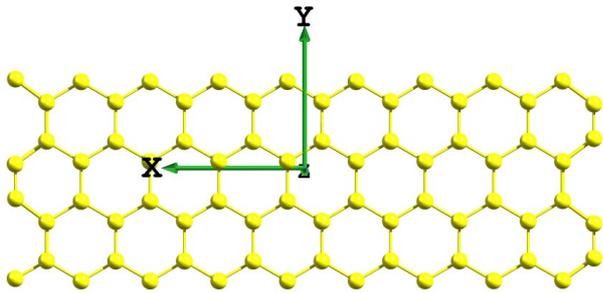
These structures were fully relaxed including lattice parameters and ions, using an optimal *k*-point mesh of (2x2x3) for *k*-space integrations. The optimized systems would finally undergo a series of static calculations, where we applied the tetrahedron method [19] for *k*-point sampling to determine accurate band structures as shown in Figs. 1e and 1f. Furthermore we determined the density of states of the systems shown in Figs. 1c and 1d during another static run, using four times the optimal size of the *k*-point mesh, in order to guarantee the proper resolution of small details.

3 Results and discussion Tight-binding theory [3,20] predicts all graphene nanoribbons with armchair border to be semiconducting, unless the number of dimers from one border of the nanoribbon to the other is $3n - 1$, with *n* being a natural number. We see that the number of dimers in Fig. 1a is 18, and therefore this nanoribbon should be semiconducting, which is confirmed by the results displayed in Figs. 1c and 1e.

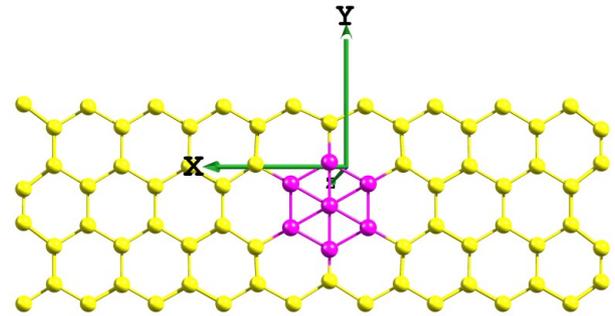
We found this to be an ideal model system for studying a possible metallization of semiconducting graphene sheets by small boron clusters. It is still small enough to keep the runtime of *ab initio* simulations reasonably low, but nevertheless large enough to allow for a comfortable embedding of a whole B₇-unit, as depicted in Fig. 1b. Note that Fig. 1b already shows the results of a structure optimizations carried for our boron doped model system, and thus what we observe here is an intact boron cluster being stabilized by the surrounding carbon matrix. This surely confirms our earlier conjecture about the basic compatibility of both chemical elements.

As the unit cell shown in Fig. 1b will repeat itself in the periodic *y*-direction, the boron doped graphene nanoribbon will contain an alternating chain of boron clusters, separated by a single carbon honeycomb. To a certain extent, that simple model system will already cover an important technological aspect of any practical attempt to functionalize semiconducting graphene sheets by embedded cluster units. Suppose that some clever experimentalist will develop a method to implant boron cluster units into graphene (see Section 4). This in itself would already be a great achievement, and one should not necessarily assume that the layout of these clusters might be perfect. Therefore we should rather assume that a basic functionalization made of small boron clusters will not consist of homogeneous and straight lines of boron being a few atoms thick. Most likely, those structures will consist of disordered and rather inhomogeneous alternating chains of boron clusters running across a suitable graphene substrate.

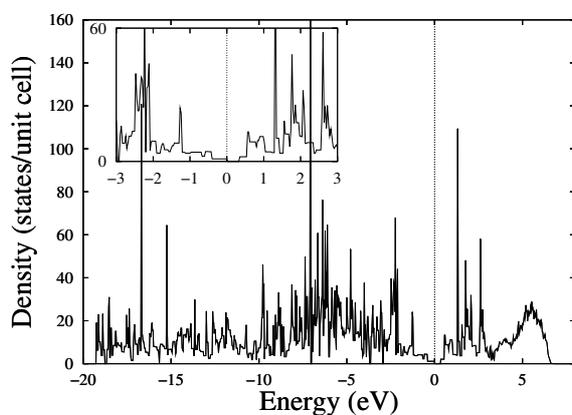
For that reason we think that our model system shown in Fig. 1b should be an reasonable starting point to develop a first intuition for the basic behaviour of a semiconducting substrate functionalized by a whole network of alternating



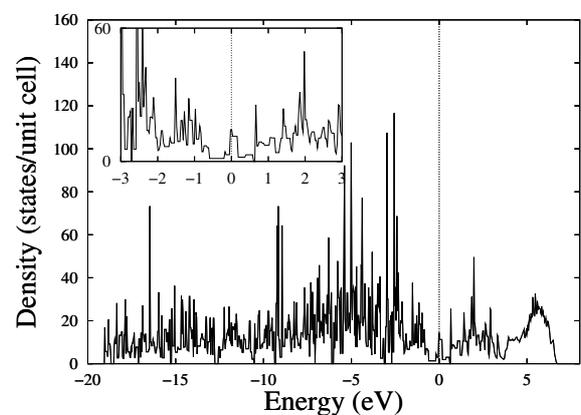
a) Optimized unit cell of armchair graphene nanoribbon. The system extends periodically along the y -direction.



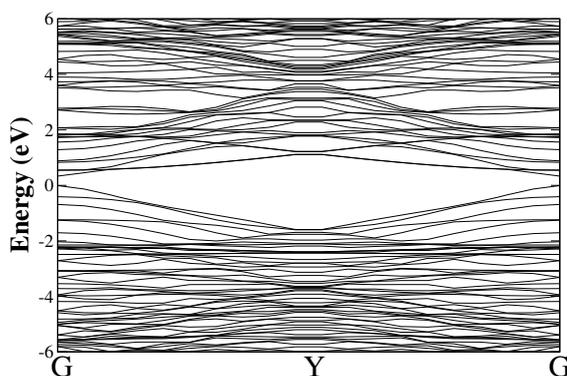
b) Optimized structure of B_7 doped armchair graphene nanoribbon. This system also extends periodically along the y -direction.



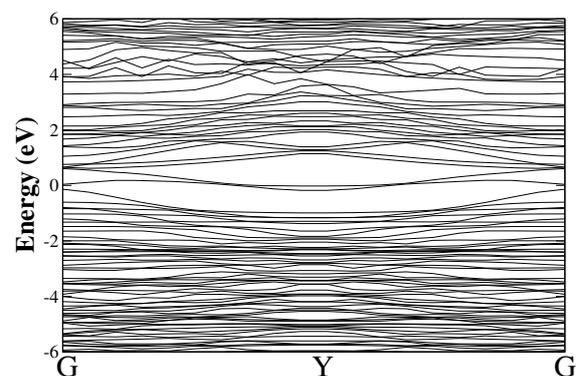
c) Density of states for the armchair graphene nanoribbon shows semiconducting behaviour.



d) Density of states for the doped armchair graphene nanoribbon shows metallic behaviour.



e) Band structure in the k_y -direction of the armchair nanoribbon shows a gap.



f) Band structure in the k_y -direction of the doped armchair nanoribbon reveals overlapping bands at the Fermi level.

Figure 1 Comparison between a semiconducting armchair nanoribbon (left) and its metallized counterpart (right), which has been doped with an alternating chain of B_7 -clusters.

chains of boron clusters. To increase the disorder of the boron chains, one mainly has to increase the size of the unit cell shown in Fig. 1b along the y -direction, such that

clusters at different y -distances from each other may be embedded within a single unit cell. Next step could be to move the various clusters within one unit cell to the right

or left along the x -direction. It might also be necessary to increase the unit cell along the x -direction, in order to allow for the embedding of larger boron clusters, or to place several clusters in order to analyze the interaction between neighboring boron chains.

The electronic effects on the surrounding carbon matrix by the simplest alternating chains of boron clusters depicted in Fig. 1b may be studied by comparing its density of states shown in Fig. 1d to the density of states for the underlying armchair nanoribbon shown in Fig. 1c. We immediately notice the absence of an electronic gap, that was so characteristic of the underlying graphene matrix. Instead, the density of states shown in Fig. 1d predicts a metallic behaviour.

A glimpse at Figs. 1e and 1f shows that this metallic behaviour is obviously caused by the appearance of overlapping bands in the range of the original gap. Furthermore, the k -vectors used to plot these band structures all point in the y -direction, whereas in the x - and y -directions, those bands remain flat. This points towards a basic conductivity, which is mainly based on Bloch states with a crystal momentum k pointing into the direction of the alternating boron chains.

But in order to quantify any partial localization or delocalization of the conducting states related to these boron chains, and in order to reveal the basic electron transport mechanisms along these chains, one would have to carry out calculations that are beyond the scope of this paper.

4 Summary and outlook We showed that a semi-conducting armchair graphene nanoribbon may be metallized by alternating chains of boron atoms embedded into this structure. Furthermore the Bloch states that lead to this behaviour are characterized by a crystal momentum k pointing into the direction of these chains. Therefore one is certainly tempted to further expand on these findings by drawing a naive picture of conducting "dotted" lines of boron clusters, which may serve as a basic wiring within a semiconducting graphene substrate. However, so far we have indications rather than a proof, that these alternating boron chains would really function the way they are supposed to do.

Nevertheless the basic concept behind a functionalization through the imprinting of dotted lines of boron clusters on graphene sheets is rather similar to the basic concepts underlying VLSI [1]: Take a suitable substrate material, and create a functional network of devices mainly by imprinting the right architecture on this substrate. Unfortunately, in our case we cannot make use of the familiar VLSI type of processing sequence, which implies imaging, deposition and etching. Simply because the basic elements will only be three boron atoms wide, which is way below the wavelength of light used by current imaging systems. And the bulk material is too thin to be etched away.

What about deposition? Here we might find a somewhat better situation. In fact, the deposition of larger boron clusters into silicon wafers is an industrial standard for the

design of transistors within the 45 nm range of gate sizes [21]. Of course one should not expect a resolution of a standard (focused) cluster source to be within the size range of the alternating chains boron clusters described above, which is only a few Å. But as theorists we would naively assume that boron cluster implantation might also be tried for graphite, thus generating an extended speckle pattern, or chains of larger boron islands within different layers of graphene.

These larger boron islands should deliver the same basic functionality as the small boron clusters described above [5,10,22], and depending on the intensity of the cluster source, several neighboring graphene layers might actually contain copies of roughly the same pattern. Those could finally be peeled off by the standard method described in [2], in order to study the imprinted nanopatterns in more detail. As long as the boron islands remain reasonably small and not too distant from each other, such a processing could be an interesting basis for the systematic development of a graphene-based sub-lithographic layout of functional nanostructures, using existing technologies.

In the end, to content oneself with a clumsy lithographic device layout for an extremely promising nanosubstrate like graphene would simply be a waste. But with boron, there seems to be at least one element at hand, which could provide key materials properties for future graphene-based nanoarchitectures.

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References

- [1] C. Mead and L. Conway, Introduction to VLSI Systems (Addison-Wesley, Reading, 1980).
- [2] K. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, *Science* **306**, 666 (2004).
- [3] R. Saito, G. Dresselhaus, and M. S. Dresselhaus, *Physical Properties of Carbon Nanotubes* (Imperial College Press, London, 1998).
- [4] X. Li, X. Wang, L. Zhang, S. Lee, and H. Dai, *Science* **319**, 1229 (2008).
- [5] A. Quandt and I. Boustani, *ChemPhysChem* **6**, 2001 (2005).
- [6] T. B. Martins, R. H. Miwa, A. J. R. da Silva, and A. Fazzio, *Phys. Rev. Lett.* **98**, 196803 (2007).
- [7] E. Hernandez, P. Ordejon, I. Boustani, A. Rubio, and J. A. Alonso, *J. Chem. Phys.* **113**, 3814 (2000).
- [8] I. Boustani, *Phys. Rev. B* **55**, 16426 (1997).
- [9] J. Kunstmann and A. Quandt, *J. Chem. Phys.* **121**, 10680 (2004).
- [10] J. Kunstmann and A. Quandt, *Phys. Rev. B* **47**, 035413 (2006).
- [11] G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996).
- [12] G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).

- [13] W. Kohn and L. Sham, Phys. Rev. B **140**, 1133 (1965).
- [14] M. P. Teter, M. C. Payne, and D. C. Allan, Phys. Rev. B **40**, 12255 (1989).
- [15] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
- [16] D. Ceperley and B. Alder, Phys. Rev. Lett. **45**, 566 (1980).
- [17] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
- [18] G. Kresse and J. Hafner, J. Phys.: Condens. Matter **6**, 8245 (1994).
- [19] P. E. Blöchl, O. Jepsen, and O. K. Andersen, Phys. Rev. B **49**, 16223 (1994).
- [20] K. Nakada, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, Phys. Rev. B **54**, 17954 (1996).
- [21] K. Kirkby, R. Gwillan, A. Smith, and D. Chivers, Ion Implantation Technology (Proceedings of the 16th International Conference on Ion Implantation Technology), AIP Conference Proceedings, Vol. 866 (AIP Press, New York, 2006).
- [22] H. Tang and S. Ismail-Beigi, Phys. Rev. Lett. **99**, 115501 (2007).