Negative differential conductance in two-dimensional C-functionalized boronitrene

J T Obodo¹, K O Obodo² and U Schwingenschlögl¹
¹ PSE Division, KAUST, Thuwal 23955-6900, Saudi Arabia
² Department of Physics, University of Pretoria, South Africa
E-mail: udo.schwingenschlogl@kaust.edu.sa

Keywords: molecular electronics, boronitrene, differential conductance

Abstract

It recently has been demonstrated that the large band gap of boronitrene can be significantly reduced by C functionalization. We show that specific defect configurations even can result in metallicity, raising interest in the material for electronic applications. We thus study the transport properties of C-functionalized boronitrene using the non-equilibrium Green’s function formalism. We investigate various zigzag and armchair defect configurations, spanning wide band gap semiconducting to metallic states. Unusual I–V characteristics are found and explained in terms of the energy and bias-dependent transmission coefficient and wavefunction. In particular, we demonstrate negative differential conductance with high peak-to-valley ratios, depending on the details of the substitutional doping, and identify the finite bias effects that are responsible for this behavior.

1. Introduction

Two-dimensional materials today are attracting continuous interest for both basic scientific and technological reasons [1–3]. While graphene and its derivatives have been studied in detail, the interest in two-dimensional boron nitride, henceforth referred to as boronitrene, is growing rapidly. The material shares with graphene both the structure (lattice mismatch of 1.5%) and the total number of valence electrons of neighboring atoms. However, it is insulating with a very large band gap of 6.0 ± 0.5 eV [4]. Band gap tuning by functionalization with C has been realized by several groups and shows great potential for materials design, because the defects can be well controlled [5–8]. In particular, it recently has been demonstrated that the band gap can be reduced to the range required for typical semiconductor devices [9]. Indeed, materials based on B/C/N networks are interesting for numerous applications in nano-scale devices, energy harvesting, and catalysis, for example [10].

Heterostructures of boronitrene and graphene nowadays are subject of extensive experimental studies [11–13]. Interesting features, including negative differential conductance (increasing voltage leads to decreasing current and vice versa; NDC), have been reported, which can be exploited in low-noise amplification, high-frequency oscillators, analog-to-digital conversion, and digital logics [14]. NDC also has been found in N-doped graphene [15] and oligophenylene molecules sandwiched between graphene electrodes [16]. Its origin can be related, for example, to the bias dependence of interface states [17, 18], the orientation of molecular ligands [19], the tunneling through localized states [20, 21], and the change of molecular charge states [22, 23]. In the present work we study C-functionalized boronitrene (C-BN) and demonstrate that defect design not only can reduce the band gap but even can result in metallicity. We analyze the two-dimensional transport behavior, focusing on the metallic cases, and find extraordinary I–V characteristics, including NDC.

2. Computational methods

We use density functional theory as implemented in the SíESTA code [24] with an atomic orbital double-zeta polarized basis set. The core electrons are described by norm-conserving Troullier–Martin pseudopotentials.
including scalar relativistic corrections. The cutoff energy is set to 600 Ry and the local density approximation (Ceperley–Alder flavor) is employed for the exchange-correlation functional. All technical parameters are converged carefully and all the structures under investigation are optimized with a force threshold of 0.04 eV Å\(^{-1}\) (first the geometry of the unit cell and afterwards the atomic positions). C atoms are substituted in boronitrene (xz-plane) along either the armchair or the zigzag direction (z-axis) of the honeycomb structure.

Transport calculations are performed using the optimized geometries in the non-equilibrium Green’s function approach as implemented in the SMEAGOL code [25]. Periodic boundary conditions are imposed along the x-axis, while the transport direction is parallel to the z-axis. For sampling the Brillouin zone, we use

**Figure 1.** Band structures for (a) N substitution, (b) B substitution, and (c) BN pair substitution with C. Green, blue, and black color represents spin minority, spin majority, and spin degenerate bands, respectively.

**Figure 2.** C-BN configurations under study: (a) armchair line, (b) armchair single, (c) armchair staggered, (d) zigzag line, (e) zigzag single, and (f) zigzag staggered.
and $4 \times 1 \times 100$ and $4 \times 1 \times 1$ $k$-meshes for the leads and scattering region, respectively. The same convergence criteria are used as in the electronic structure calculations. The current $I(V)$ is calculated using the transmission coefficient $T(E, V)$ and the Landauer formula, where the bias $V$ is applied symmetrically to the electrodes. The complex integration to obtain the charge density is computed using 16 points on the semi-circle, 16 points parallel to the real axis, and 16 poles. At finite bias the integration over the real energies is evaluated using at least 500 points. An electronic temperature of 300 K is employed.

3. Equilibrium state properties

Substitutional C doping in boronitrene breaks the symmetry of the honeycomb structure (initial space group $P63mmc$, final space group $Pnmn$). We present in the following band structures along the $K$-{$\Gamma$}-$K'$ path, where $K = (0, 0, \frac{1}{2})$ and $K' = (\frac{1}{2}, 0, 0)$. Substitution of a single N and B atom, respectively, by C results in electron and hole doping, see figures 1(a), (b). On the other hand, replacing a BN pair by two C atoms gives no qualitative change of the band structure, in particular no spin polarization, but reduces only the band gap, see figure 1(c). We therefore have to turn to more complex substitution patterns in order to achieve specific properties. In the following we will study armchair line, single, and staggered configurations, see figures 2(a)–(c), and the respective zigzag configurations, see figures 2(d)–(f). In the transport calculations the leads and scattering region comprise 3 and 8 of the unit cells shown in figure 2, respectively.

4. 3. Equilibrium state properties

Figure 3. Band structures for the (a)–(c) armchair and (d)–(f) zigzag C-BN configurations defined in figure 2.
Figure 4. Transmission coefficients at zero bias for the (a)–(c) armchair and (d)–(f) zigzag C-BN configurations defined in figure 2.

Figure 5. Isosurface of the modulus of the transmission wavefunction, showing the contributions to the transmission at the Fermi energy for the metallic configurations. The isovalue is 0.015 electrons/\(a_B^3\).
According to figures 3(a), (b) the armchair line and single configurations have reduced direct band gaps of 1.1 and 2.5 eV, respectively, as compared to the theoretical (4.6 eV) [26] and experimental (6.0 ± 0.5 eV) [4] values of boronitrene. As to be expected, when more C atoms are introduced the reduction is more pronounced. The band gaps in figures 3(a), (b) appear at the K point, which represents the transport direction in real space. Since in the armchair line and single configurations the same amount of B and N atoms is substituted by C atoms, the conduction band minimum and valence band maximum in these cases are formed by π and π* bands, respectively. On the other hand, for the armchair staggered configuration we obtain a metallic nature, see figure 3(c), due to the extra electron introduced by replacing two B atoms and only one N atom per supercell by C atoms.

For the zigzag line and staggered configurations (being charge neutral substitutions) we observe band gaps of 2.3 and 1.6 eV, respectively, see figures 3(d), (f). Since the latter has both an indirect (2.3 eV) and a direct (2.5 eV) band gap, it is interesting from the optical perspective, even though the energy difference between the two band gaps...
gaps is relatively small. The zigzag single configuration, see figure 3(e), is found to be semiconducting, because the two extra electrons per supercell introduced by replacing two B atoms by C atoms fill an additional band. Interestingly, the band gap is exactly zero, which gives rise to a Dirac-like spectrum at the K’ point. The consequences are discussed below.

The zero bias transmission coefficient $T_{E, V = 0}$ is presented in figure 4 for the six configurations under investigation. Absence of a transmission channel at the Fermi energy in figures 4(a), (b), (d), (f) reflects the semiconducting characters as mentioned before. On the other hand, we find a single transmission channel at the Fermi energy in figures 4(c), (e), reflecting conductance quantization in the characteristic form of a one-dimensional wire. Figure 5 shows for the metallic configurations isosurface plots of the transmission wavefunction, representing the probability to find a charge carrier at a specific point in space. The results suggest transport through the $\pi$ conjugated states ($p_z$-like eigenchannels). The amplitude of the wavefunction decays fast away from the defects.

4. Finite bias calculations

High bias voltages are needed for tunneling electrons through the semiconducting configurations because of the rather large band gaps. For the metallic armchair staggered and zigzag single configurations the dependence of the current on the bias voltage, $I(V)$, is presented in figure 6. Both systems behave ohmic for small bias, as reflected by flat regions in the $dI/dV$ curves. At higher bias we obtain a strongly nonlinear behavior of $I(V)$ with regions of n-type NDC. The first such region appears for the armchair staggered configuration between 0.8 and 1.5 V and for the zigzag single configuration between 0.6 and 1.5 V. The corresponding peak-to-valley ratios are 1.8 and 6.5, respectively. These values are comparable to literature data for crystalline silicon for different doping levels [27, 28]. For graphene nanoribbons of various widths values between 1.3 and 10 have been reported [29]. Importantly, the order of magnitude is appropriate for application in switches and memory devices [30, 31].

Figure 7 shows the bias-dependent transmission coefficient, $T(E, V)$, which gives insight into the origin of the observed NDC. Reference biases of 0, 0.4, 1, and 1.2 V are investigated. We find a drastic reduction in the
tunneling for increasing bias voltage both for the armchair staggered and zigzag single configurations in the non-
ohmic region ($V > 0.2$ V). We observe also a change in the energy dependence of $T(E, V)$ around the Fermi
energy for the higher biases within the entire bias interval (orange color). This modification of the mobility of the
charge carriers combined with the changes of the available states in the leads under bias gives rise to the
observed NDC.

In conclusion, we have investigated the potential of C-BN in amplifier or switching devices. The material can
be tuned from insulating to semiconducting and further to metallic behavior by means of the orientation (zigzag
or armchair) and shape of the C defects. We have determined the electronic transport through C-BN employing
the non-equilibrium Green’s function formalism within a first-principles framework. In general, the material
develops a versatile nature with promising electronic properties due to the functionalization. In particular, we
observe bias regions of NDC for specific defect configurations with high peak-to-valley ratios. Our approach
allows us to systematically understand the transport characteristics in terms of the energy and bias-dependent
transmission coefficient and wavefunction.

Acknowledgments

Research reported in this publication was supported by the King Abdullah University of Science and Technology
(KAUST). The authors thank N Chetty for fruitful discussions.

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