Synthetic Metals 223 (2017) 172–183

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet

Influence of bias on the electronic structure and electrical conductivity and heat capacity of graphene and boron nitride multilayers

Raad Chegel

Physics Department, Faculty of Science, Malayer University, Malayer, Iran

ARTICLE INFO

Article history:
Received 27 August 2016
Received in revised form 8 November 2016
Accepted 10 November 2016
Available online 25 November 2016

Keywords:
BN/graphene/BN trilayers
Tight binding
Electronic structure
Electrical conductivity
Heat capacity
Thermal conductivity

ABSTRACT

The electronic structure, electrical conductivity, heat capacity and thermal conductivity of BN and BN/graphene/BN with three and five layers are investigated using the tight binding approximation and Green's function method. The BN/graphene/BN trilayers show narrow band gap unlike to BN trilayers where which have wide band gap. The energy gap of BN trilayers decreases linearly with electric field unlike to the BN/graphene/BN trilayers. The magnitude of changes in the band gap for BN trilayers are much higher than the BN/graphene/BN trilayers. The electrical conductivity, heat capacity and thermal conductivity are zero for BN trilayers and it increases with temperature until reaches maximum value then decreases. The electrical conductivity of BN/graphene bilayers is larger than BN bilayers. For all cases, the heat capacity has a Schottky anomalies.

1. Introduction

Graphene single layer is a two-dimensional allotrope of carbon which has been most investigated in the previous decade due to its novel potential applications [1,2]. In the graphene single layer, the valence and conduction bands cross at Dirac points in the reciprocal space and the 2D-graphene is a zero-gap semiconductor [3–5]. The zero band gap in graphene is due to the equivalence of the two carbon sublattices and the band gap opening is occurs by removing the sublattice equivalence [6]. Recently the graphene-like materials such as GaN, BN, BN/graphene and BN/graphene/BN (BN/G/BN) have also been studied [7–16]. The BN sheet has a lattice constant similar to graphene and unlike to graphene which has zero band gap, the BN is an insulator with a large energy gap due to the consisting of boron and nitrogen atoms [17]. The multilayer systems containing a few layers layer of graphene like sheets can be stacked differently with different horizontal shifts between graphene planes, leading to different stacking categories AAA-, ABA (Bernal) and ABC (rhombohedral) [18,19]. In AAA- stacked, the layers are exactly aligned, in ABA- stacked the half of the atoms of top and bottom layers lie directly over the center of a hexagon in the center layer and in the ABC stacking the atoms of the top layer lies above the centers of the hexagons in the bottom layer [20,21]. The control of the band gap for Controlling the band gap of multilayer graphene sheet is an important method to develop their application in electronics devices and it can be achieved by different methods such as strain, doping and external fields [22–28]. Note that the band gap modification for other nano-structure such as nanotubes nanoribbons has been investigated by different method such as density functional theory and tight binding [29–38]. Sandwiching the layers of graphene with BN layers (or vice versa) can cause changes in the electronic structure of the system and their effects have been studied by several authors theoretically [6,28,39–42]. Ribeiro et al. have studied the stability of boron nitride bilayers and found the hopping parameters and the onsite energies by fitting a tight binding empirical model to the DFT results [17]. Using density functional theory, it has been show that band gap of graphene/BN and BN/BN bilayers increases and decreases in presence of electric field [28]. The stacking geometries and interlayer distances significantly affect the electronic structure of graphene/h-BN systems and the graphene/h-BN systems can be transited from metallicity to semiconductor by increasing h-BN layers [43]. In bilayer strained boronitrenes the degeneracy of π valence bands at K points lifted with the electric field increasing and the intralayer hopping parameter changes little with increasing the electric field [44]. The mechanical properties of BN bilayers is are approximately constant with and without the electric field and the equilibrium strain energy decreases linearly by increasing the magnitude of applied electric field [45]. By Zhang et al. it is found that graphene/BN/graphene trilayers with AAA, ABA and ABC stackings orders are metallic independent of stacking formats [46]. Kim et al. found that the BN layer sandwiched by graphene systems has the small

E-mail address: raad.chegel@gmail.com (R. Chegel).

http://dx.doi.org/10.1016/j.synthmet.2016.11.005
0379-6779/

energy gap and the trilayer BN/G/BN has large gap of 117 meV which decreases as the number of BN layer increases [47]. The optical properties of multilayers BN/G/BN are strongly subjective to the polarization of the light without significant dependence of to the thickness and stacking order [10]. In the multilayer BN/G/BN structures, the band gap is significantly dependent on the stacking order and it is about 150 and 31 meV for ABA and ABC stacking [48]. Using the tight binding model it is found that the electrical and thermal conductivities of single- and few- layers graphene reduce in terms of temperature compared to the pristine case [49–51]. In this study, we calculated the electronic structure, heat capacity, electrical and thermal conductivity for BN/G/BN multilayers using tight-binding Hamiltonian model by using of the Kubo-Greenwood formula. The effects of different stacking and electric field is included in our calculations. The remainder of this paper is organized as follows. In the next section, we explain the theoretical aspects of our work. In Section 3, the electronic structure, DOS, electrical conductivity, heat capacity and thermal conductivity of BN and BN/G/BN with three and five layers have been investigated.

2. Theoretical method

We employed the tight binding model to investigate the electronic properties of tri- and penta- layers (3L- and 5L-) of BN and BN/G/BN in the presence of electric field. The 3L- and 5L- unit cells contain three and five layers with 6 and 10 inequivalent atoms A_i and B_i where A_i and B_i refer to atoms on two sub-lattices in the same layer I [i = 1–3 or 5]. In AA- stacking, the A(B) atoms in one layer are located directly above the A(B) atoms in the neighboring layer and for AB- stacking, the A atoms of one plane sit over the center of hexagons in the other plane and only half of the atoms are located directly above each other. In order to calculate the band structure and density of state (DOS) of these structures, we derive their respective Hamiltonians. In the second quantization notation, for all stacked multilayers, the Hamiltonian is divided into three parts:

$$H = H_0 + H_{inter-layer} + H_{bias}$$

Where the H_0, $H_{inter\text{-}layer}$ and H_{bias} are:

$$H_0 = -t\sum_m \sum_{\alpha,\beta=A,B} \sum_n c_{n,\sigma}^{\alpha_m\dagger} c_{n+\delta_m}^{\beta_m}$$

$$H_{inter-layer} = \gamma \sum_{m,m'} \sum_{\alpha,\beta=A,B} \sum_n c_{n,\sigma}^{\alpha_m\dagger} c_n^{\beta_{m'}}$$

$$H_{bias} = \sum_m \sum_{\alpha=A,B} \sum_n [\varepsilon_0^{\alpha_m} + \varepsilon_1^{\alpha_m}(\boldsymbol{F})] c_n^{\alpha_m\dagger} c_n^{\beta_m}$$

where α and β indicate the A and B sites inside the Bravais lattice unit cell. $c_{n,\sigma}^{\alpha\dagger}\left(c_{n,\sigma}^{\alpha}\right)$ represents the creation (annihilates) of an electron with spin σ on site n at sub-lattice α. $\varepsilon_0^{\alpha}(\boldsymbol{F})$ is an on-site energy for α type atom in the presence of electric field. For graphene (BN) sheet, in the absence of an electric field, the difference between on-site energies of the two inequivalent A and B sub-lattices is zero (non-zero). The t is the hopping to the nearest neighbors and δ is positions of the nearest neighbors of each sub-lattice, respectively. The indexes m, m' = 1-3 (1–5) refers to layer number in 3L- (5L-), respectively. The $\varepsilon_0^{\alpha_m}[\varepsilon_1^{\alpha_m}(\boldsymbol{F})]$ is the on-site energy for α atom at the m-th layer in the absence (presence) of the electric field. In 3L- sheet, for positive and negative biases, the electrostatic potentials $\pm U, 0, \mp U$ are applied to top, center and bottom layers, respectively, where the electrostatic potential U is proportional to the electric field **F**. In the 5L- sheet, the positive and negative biases $\pm U, \pm\frac{U}{2}, 0, \mp\frac{U}{2}, \mp U$ are applied on the highest to the lowest layers, respectively. Because of the existence the of two atoms in the unit cell each layer, the Hamiltonian of 3L- and 5L-sheet with different stacking are 6×6 and 10×10 matrixes. For example for 3L-BN with AAA- stacking in presence of positive bias, the total Hamiltonian in the matrix form in the momentum space is given by:

$$H_{AAA}^{BN} = \begin{pmatrix} \varepsilon_B - U & \phi_{BN}(k) & 0 & \gamma_{BN} & 0 & 0 \\ \phi_{BN}^*(k) & \varepsilon_N - U & \gamma_{BN} & 0 & 0 & 0 \\ 0 & \gamma_{BN} & \varepsilon_B & \phi_{BN}^*(k) & 0 & \gamma_{BN} \\ \gamma_{BN} & 0 & \phi_{BN}(k) & \varepsilon_N & \gamma_{BN} & 0 \\ 0 & 0 & 0 & \gamma_{BN} & \varepsilon_B + U & \phi_{BN}(k) \\ 0 & 0 & \gamma_{BN} & 0 & \phi_{BN}^*(k) & \varepsilon_N + U \end{pmatrix}$$

The 3L-BN/G/BN with AAA- stacking has two forms as:

$$H_{AAA}^{BN/G/BN}(xy) = \begin{pmatrix} \varepsilon_B - U & \phi_{BN}(k) & 0 & \gamma_{BC} & 0 & 0 \\ \phi_{BN}^*(k) & \varepsilon_N - U & \gamma_{NC} & 0 & 0 & 0 \\ 0 & \gamma_{NC} & \varepsilon_C & \phi_{CC}^*(k) & 0 & \gamma_{BC} \\ \gamma_{BC} & 0 & \phi_{CC}(k) & \varepsilon_C & \gamma_{NC} & 0 \\ 0 & 0 & 0 & \gamma_{NC} & \varepsilon_N + U & \phi_{BN}(k) \\ 0 & 0 & \gamma_{BC} & 0 & \phi_{BN}^*(k) & \varepsilon_B + U \end{pmatrix}$$

$$H_{AAA}^{BN/G/BN}(xx) = \begin{pmatrix} \varepsilon_B - U & \phi_{BN}(k) & 0 & \gamma_{BC} & 0 & 0 \\ \phi_{BN}^*(k) & \varepsilon_N - U & \gamma_{NC} & 0 & 0 & 0 \\ 0 & \gamma_{NC} & \varepsilon_C & \phi_{CC}^*(k) & 0 & \gamma_{NC} \\ \gamma_{BC} & 0 & \phi_{CC}(k) & \varepsilon_C & \gamma_{BC} & 0 \\ 0 & 0 & 0 & \gamma_{BC} & \varepsilon_B + U & \phi_{BN}(k) \\ 0 & 0 & \gamma_{NC} & 0 & \phi_{BN}^*(k) & \varepsilon_N + U \end{pmatrix}$$

where $\varphi_{BN}(k)$ and $\varphi_{CC}(k)$ are the energy dispersion for a BN and graphene mono layer single sheet, γ_{BN}, γ_{BC} and γ_{NC} are the interlayer hopping between BN, BC and NC atoms in the different layers, respectively. As shown in Eq. (1), the tight binding Hamiltonian requests hopping interactions, interlayer hopping and on site energies for calculations.

In H(xx) [H(xy)] case the B-C-B and N-C-N (B-C-N) atoms are placed in one direction. In the absence of electric field, the on-site energies for B and N atoms are assumed to be +2.33 and −2.50 eV, respectively with respect to the carbon on-site energy [52]. The nearest neighbors hopping integrals in the same layer are $t_{CC} = 3$, $t_{BC} = 2.7$, $t_{NC} = 3.14$ and $t_{BN} = 2.81$ eV [52,53]. We assume that the interlayer parameter between sub-lattices α and β in the BN bilayers is $\gamma_{BN} = t_{BN}/6$ and it is $\gamma_{XC} = t_{XC}/10$ for different stacked BN/G/BN multilayers, respectively [X = B/N].

Here we study the Hamiltonian by the Green function approach. For trilayer sheet, using the Hamiltonian Eq. (1), the Green function is written as:

$$\boldsymbol{G}_{ij}(\tau) = \begin{pmatrix} G^{A_1A_1} & G^{A_1B_1} & G^{A_1A_2} & G^{A_1B_2} & G^{A_1A_3} & G^{A_1B_3} \\ G^{B_1A_1} & G^{B_1B_1} & G^{B_1A_2} & G^{B_1B_2} & G^{B_1A_3} & G^{B_1B_3} \\ G^{A_2A_1} & G^{A_2B_1} & G^{A_2A_2} & G^{A_2B_2} & G^{A_2A_3} & G^{A_2B_3} \\ G^{B_2A_1} & G^{B_2B_1} & G^{B_2A_2} & G^{B_2B_2} & G^{B_2A_3} & G^{B_2B_3} \\ G^{A_3A_1} & G^{A_3B_1} & G^{A_3A_2} & G^{A_3B_2} & G^{A_3A_3} & G^{A_3B_3} \\ G^{B_3A_1} & G^{B_3B_1} & G^{B_3A_2} & G^{B_3B_2} & G^{B_3A_3} & G^{B_3B_3} \end{pmatrix}$$

with the Green function elements $G_{ij}^{\alpha\beta}(\tau) = -\left\langle \tau c_i^{\alpha}(\tau) c_j^{\beta+}(0) \right\rangle$ is obtained by ensemble averaging on the ground state of the system and $\tau = it$ is the imaginary time and τ is the time ordering operator.