

Semiconducting graphene

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In this paper we propose a simple way for structural modification of graphene yielding a non-zero band gap which is mandatory for prospective electronics applications. This can be achieved by creating a buffer layer graphene (BuLG) upon deposition on different crystalline silicon surfaces. Previous calculations have shown that the formation of such buffer layer on 4H-SiC results in lattice deformation of BuLG, due to the 8% mismatch between the (0001)Si crystal surface of SiC and the graphene lattices. Here, for elimination of the lattice deformation, we propose a replacement of the (0001)Si surface of SiC by hydrogen atoms. Using density functional simulations we show that the band gap of the corrugated graphene sheet is $\Delta E = 1.94$ eV (hydrogenated system) or $\Delta E = 1.21$ eV SiC/graphene system. Height of corrugation is equal to $h = 35.0 \pm 5.0$ pm. Two effects are responsible for the band gap opening: corrugation of the sheet, caused by the covalently bonded carbon atoms, and removal of electrons from the bonding π orbitals of graphene.

Keywords: silicon carbide, graphene, band gap, FET

INTRODUCTION

The electronic applications of graphene are hindered because of the vanishing band gap of its electronic band structure [1, 2]. Graphene's semi-metallic character prevents the construction of a field effect transistor (FET) with distinct ON and OFF states. Therefore, regardless of the ballistic transport and the amazing carrier mobility of $200\,000\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ [3], graphene is no match for silicon as a result of its lack of a proper band gap. Additional problems such as the absence of an established technology for its industrial scale production with acceptable quality [4], and the difficulties to be transferred to an insulating layer, make graphene application in electronics even more questionable. Chemical vapor deposition (CVD) technology is also a bad choice for creating graphene – insulator layers [5]. Graphitization of SiC at high temperatures [6, 7] is the other possible wafer-scale technology. The silicon carbide support to the graphene layers is either semiconducting with a band gap of 2.36 eV for 3C(β), or insulating with a band gap of 3.23 eV for 4H and 3.05 eV for 6H(α). This crystal, unfortunately, is too thick for field effect induction needed to switch ON/OFF a graphene FET channel.

Recently, a breakthrough in graphene electronics research has been reported [8]. A buffer layer synthesized on SiC(0001) surface has the properties of a semiconductor, with energy gap larger than 0.5 eV. The energy gap opens as the higher growth temperature improves the order of

covalent bonds between the graphene layer and SiC. The graphene top layer, commensurately bonded to the silicon carbide (0001) surface, is an example of a system, where the alignment of periodic covalent bonds to A or B sites breaks the chiral symmetry [9]. Finite size effect [10], on the other hand, cannot quantitatively explain the energy gap opening. Our interest in the topic is focused on performing *ab initio* simulations, which show that a prescribed bandgap could be opened and modified by a controllable corrugation of BuLG (buffer layer graphene) at the interface of the system of graphene/SiC.

Computational methods

Ab initio geometry optimizations were performed using the CP2K/Quickstep package [11, 12]. The DFT was applied within the generalized gradient approximation (GGA), using Perdew-Burke-Ernzerhof (PBE) functional [13]. Basis set DZVP-MOLOPT-SR-GTH [14], which is optimized for calculating molecular properties in gas and condensed phase, was applied to all atoms in the studied systems. For reducing the computational cost, the Gaussian and Plane-Wave (GPW) method [15, 16], as well as pseudopotentials of Goedecker-Teter-Hutter (GTH) [17, 18] were used. Dispersion interaction was taken into account *via* the DFT + D approach with D3 set [19].

It is usually difficult to achieve convergence of the SCF procedure in systems with small band gap or isoenergetic states, such as metals and semimetals. In order to improve convergence, the

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electronic temperature was introduced, using the Fermi-Dirac distribution method [20]:

$$f(E) = \frac{1}{e^{(E-E_f)/k_B T} + 1}$$

where: $f(E)$ is the probability for an electron to have energy E , E_f is the Fermi energy at temperature $T = 0$ K, k_B is the Boltzmann constant. All calculations were performed at $T = 300$ K. This method allowed for achieving convergence in all cases.

Main hypothesis

The interactions of graphene with the SiC interface have been studied employing theoretical and experimental methods [21-24]. Those investigations describe the top layer on the silicon carbide as a graphene buffer with unique properties. A theoretical DFT study performed by Varchon *et al.* [21] explores the electronic structure of 4H-SiC (3×3 R30 surface cell in Wood's notation) with a graphene buffer layer, demonstrating the opening of a band gap. The connection between graphene (BuLG) corrugation and energy gap opening is explored for the first time in our previous publication, using *ab initio* methods [25].

Here, we continued the research on the nature of the band gap opening by constructing a model, where hydrogen atoms are responsible for sheet corrugation and electron withdraw effect. Another model, featuring a more realistic SiC substrate, was also studied. With every silicon atom from the SiC (0001) substrate, covalently bonded to graphene, an electron from the delocalized π system is removed. This is because the hybridization of the bonded C atom changes from sp^2 to sp^3 and a p electron is withdrawn from the graphene. As both hydrogen and silicon atoms can form covalent bonds with the C atoms from the graphene sheet, similar degree of corrugation and band gap values are expected for both models.

The suggested models are realistic enough to be supported by analytical results (within the continuum model), namely, the energy spectrum for the carriers of periodically corrugated graphene sheet is given by the Mathieu equation which yields an energy gap with the correct order of magnitude for the experimentally relevant values of the height and period of corrugation [25].

Structural model and electronic properties of graphene on (0001)Si plane of 6H- SiC

Our structural model includes a graphene sheet and its silicon carbide substrate. The substrate consists of the Si atoms, covalently bonded to graphene and their neighboring carbon atoms. The initial mutual orientation of graphene and SiC, shown in Figs. 1a and 2a, is taken from experimental data [22, 26]. It was concluded that the lattices of graphene and SiC are 30° rotated with respect to one another [26]. This rotation is taken into account. Silicon carbide geometry is built taking into account the SiC unit cell [27]. The final model is based on a 2×2 graphene cell, situated on top of a 3×3 R30 SiC surface cell, Fig. 1a (the unit cells are marked by blue and purple lines). Silicon atoms that are not in direct contact with carbon atoms from graphene (small green spheres in Fig. 1a) are removed, as they are not expected to form covalent bonds and alter the electronic structure of the graphene layer.

In the first numerical experiment, we replaced the SiC layer with hydrogen atoms covalently bonded to the respective sp^3 -hybridized carbon atoms of BuLG, Fig. 1b. After geometry optimization, this leads to a corrugation in the system with $h_1 = 35.0 \pm 5.0$ pm and a period of 250 – 260 pm, Fig. 1c. As a result, a band gap opens in the system BuLG/ hydrogen atoms with $\Delta E = 1.94$ eV, Fig. 1d. It should be noted that calculations with the same DFT method/basis give a zero band gap for pristine graphene [28].

Having shown that periodic corrugation, caused by covalently bonded hydrogen atoms, opens a bandgap, we built a more realistic model of the system SiC/BuLG, than those used in Ref. [25]. This model takes into account all carbon neighbors of the silicon atoms, Fig. 2a. In the previous model, Ref. [25], some bonds of the silicon atoms were hydrogen terminated. The system consists of 72 graphene carbon atoms, bonded to a SiC layer.

The system has a total spin of zero and is in a singlet ground state. Geometry optimization was performed altering the positions of all atoms, with the exception of silicon. Silicon atoms are fixed, as expected in the rigid silicon carbide crystal. Periodic cell dimensions are as follows: $a = 1529$ pm, $b = 1529$ pm and $c = 1716$ pm, with $\alpha = 90^\circ$, $\beta = 90^\circ$ and $\gamma = 60^\circ$ angles, α - between a and c, β - between b and c, and γ - between a and b.

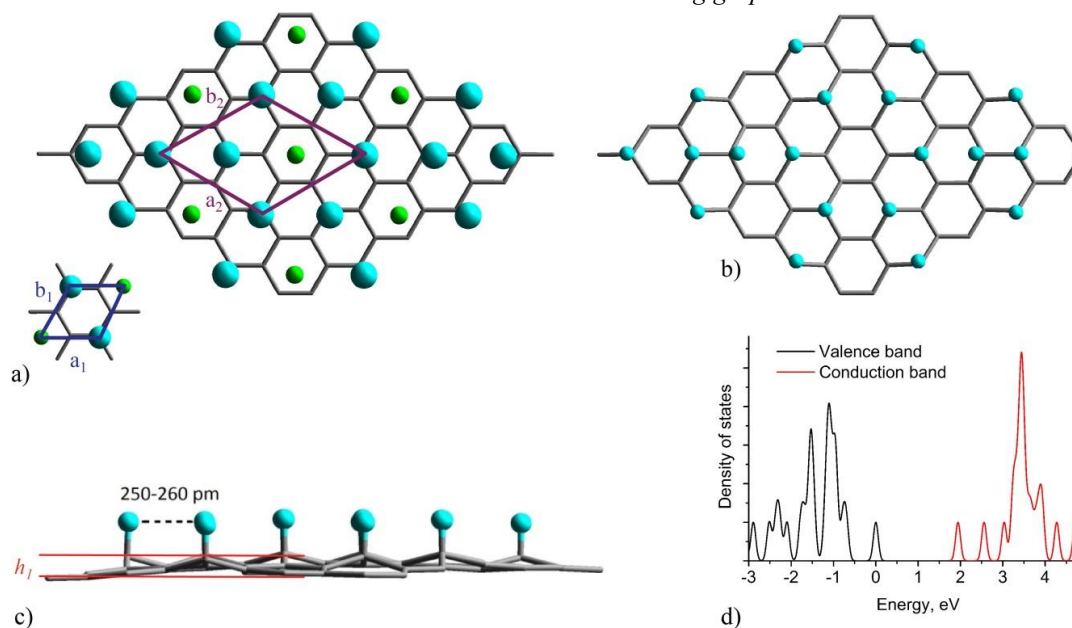


Figure 1. a) The orientation of graphene (dark grey sticks) and nearest atoms from the substrate: the cyan and green spheres represent the Si atoms of the 3×3 R30 surface cell of SiC. The inset shows the basis vectors $a_1 = b_1$ marked by blue lines. The cyan spheres represent Si atoms, closest to the C atoms of graphene. The cyan spheres form a new 2×2 surface cell with $a_2 = b_2$ basis vectors (purple lines) in graphene. b) The cyan spheres represent Si atoms, which are replaced by H atoms. c) The optimized structure with H atoms, where h_1 is the height of the corrugation of BuLG ($h_1 = 35.0 \pm 5.0$ pm). d) Density of states, simulated as molecular orbitals. The valence band (black line) and the conduction band (red) are separated by a gap $\Delta E = 1.94$ eV.

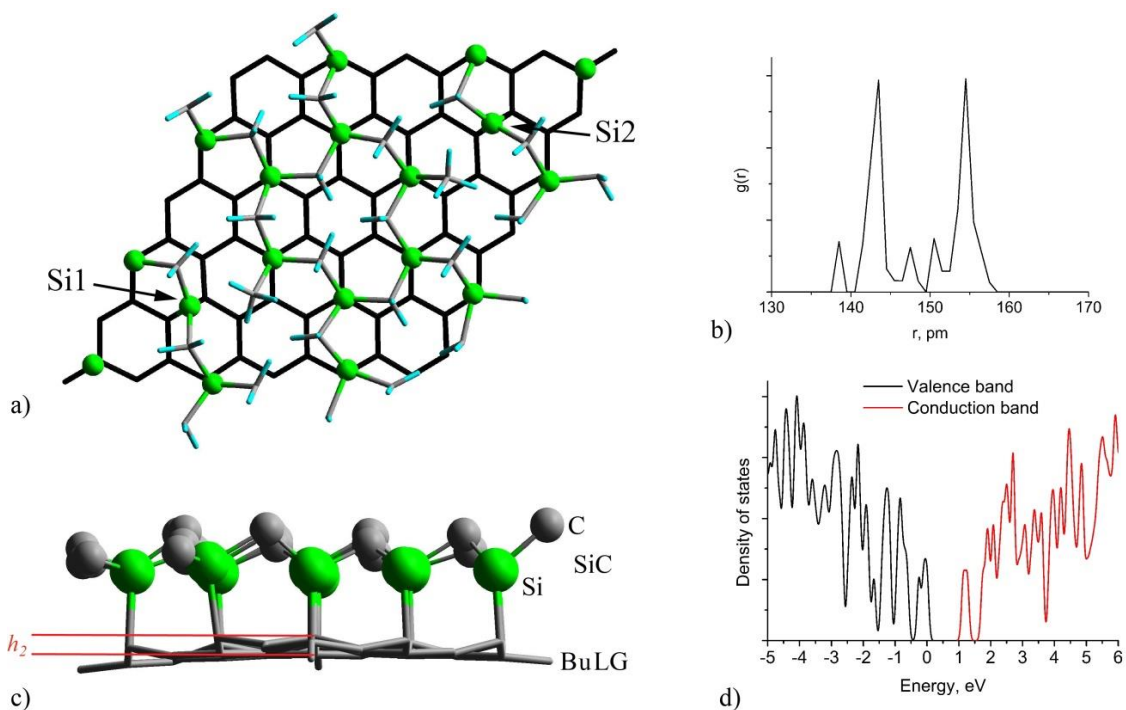


Figure 2. a) The structure of SiC/BuLG model – one unit cell (color coding: C – gray, Si – green, H – light blue). b) The carbon-carbon radial distribution function of graphene. Distances of 143 pm correspond to chemical bonds between sp^2 -hybridized C atoms, while 154 pm is the mean bond length between sp^3 -hybridized C atoms. c) SiC/BuLG structure, viewed along the direction perpendicular of the bisector of the angle between a and b axis, $h_2 = 35.0 \pm 5$ pm. d) Density of states. The valence band (black line) and the conduction band (red line) are separated by an energy gap $\Delta E = 1.21$ eV.

In the optimized structure, the carbon atoms of the graphene layer, bonded to silicon atoms, are sp^3 -hybridized. Most of the Si atoms participate in a covalent bond with one C atom from graphene. Exceptions are Si1 and Si2, shown on Fig. 2a, that form covalent bonds with two carbon atoms. This effect is caused by the proximity of two graphene C atoms to Si1 and Si2, instead of one.

RDF (radial distribution function) of carbon atoms from the graphene layer is presented in Fig 2b. The bonds between sp^2 -hybridized carbon atoms are represented as the first maximum, with mean C-C distances of 143 pm. This value is equivalent to the mean C-C bond lengths of pristine graphene, observed at 142 pm [28]. The second maximum, located at 154 pm, corresponds to single C-C bonds between sp^2 -hybridized and sp^3 -hybridized carbon atoms. The average distance between the pairs of covalently bonded silicon atoms and sp^3 -hybridized carbon atoms is 196 pm. Interaction with the SiC layer induces corrugation in the graphene (BuLG). The corrugation period is in the interval 250 – 260 pm, close to the 267 pm distance between the aligned Si atoms in the 6H-SiC (0001) surface. The corrugation of BuLG is caused by the repeating sp^3 -hybridized carbon atoms covalently bonded to Si. It should be noted that covalently bonded hydrogen atoms (Fig 1c) or silicon atoms (Fig 2c) induce the same degree of corrugation to the BuLG. Its height ($h_1=h_2$) is in the range of 35.0 ± 5.0 pm. Energy gap of the SiC/BuLG system is $\Delta E = 1.21$ eV, Fig 2d. This value is lower by 0.73 eV than the band gap of the previously described hydrogenated system.

CONCLUSIONS

Graphene should possess a band gap for the 2D material to be used in electronic applications, especially for field effect transistors (FETs) construction. A semiconducting material is necessary for the channel of the FETs, as they should possess ON/OFF states as logic elements. Using density functional simulations, we established that the band gap of the corrugated graphene sheet is equal to $\Delta E = 1.94$ eV (hydrogenated system) or $\Delta E = 1.21$ eV (SiC/BuLG system). Results are in agreement with the experimental value $\Delta E > 0.5$ eV for a similar system [8]. The height of corrugation $h = 35.0 \pm 5.0$ pm is equal in both cases. Two synergic effects are responsible for the band gap opening: corrugation of the sheet, caused by the covalently bonded atoms, and removal of electrons from the bonding π orbitals of graphene. In our cases, corrugation is caused by aligned covalently bonded H or Si atoms, with a period of 250 – 260 pm. Also, with every H

or Si atom, an electron from the delocalized π system is removed. This is because the hybridization of the bonded C atom changes from sp^2 to sp^3 and a p electron is withdrawn from the graphene. Both studied models, featuring hydrogen and silicon, show that the nature of the covalent bonded atom is not crucial for obtaining the band gap opening, but rather the synergy between the two effects.

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