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Original paper

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AB-INITIO SIMULATION OF HYDROGENATED GRAPHENE PROPERTIES

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Abstract. Ab-initio simulation of hydrogenated graphene properties was performed. At present, graphene is considered one of the most promising materials for the formation of new semiconductor devices with good characteristics. Graphene has been the subject of many recent investigations due to its peculiar transport, mechanical and others properties [1]. The chemical modification of graphene named as graphane has recently entered the investigation as a possible candidate to solve problems connected with the lack of a graphene bandgap. Graphane is a compound material consisting of two-dimensional graphene bonded by some atoms of hydrogen. The investigation shows that graphane has the three valley Γ-M-K band structure with the Γ valley, which has the smallest energy gap between the conductivity zone and the valence zone. The calculation of relative electron masses and non-parabolic coefficients in Γ, M and K valleys was performed. Based on the obtained characteristics, it is possible to implement a statistical multi-particle Monte Carlo method to determine the characteristics of electron transfer in heterostructure semiconductor devices. A research on modified graphene structures is important for fundamental science and technological applications in high-speed transistor structures operating in the microwave and very high frequency ranges.

Keywords: graphene, hydrogen, Quantum Espresso, ab-initio method, graphane.

Conflict of interests. The authors declare no conflict of interests.

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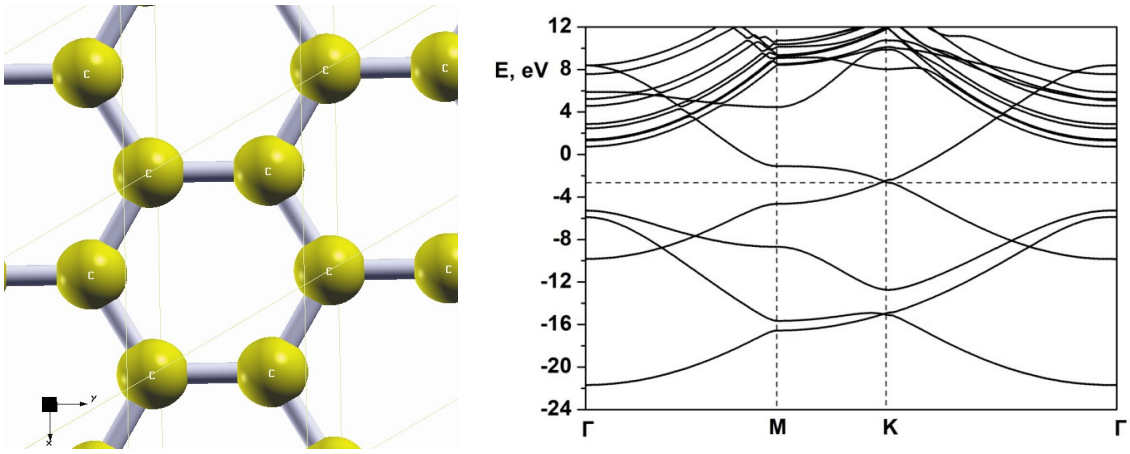
Introduction

A new promising material, graphene, which is a two-dimensional allotropic modification of carbon atoms, has attracted a lot of attention from scientists and researchers. Graphene can be thought of as a single thin layer of graphite, technologically separated from the bulk area of the structure (Fig. 1). Carbon atoms, usually one atomic layer thick, form a hexagonal crystal lattice and are connected via σ- and π-bonds. A number of researchers estimate that this material has high mechanical rigidity and record high thermal conductivity. The high mobility of charge carriers (maximum electron mobility among all known materials) makes it a promising material for use in a wide variety of applications, in particular, as a future basis for nanoelectronics and a possible replacement for silicon in integrated circuits [1]. The lack of a gap in the zone diagram can be solved by developing modified graphene structures by adding a number of atoms, such as hydrogen, fluorine and so on. Developments of modified graphene using hydrogen atoms are already known, one of which is called graphane [2–3]. Graphane is already a three-dimensional structure, in which a two-dimensional layer of carbon atoms is connected with hydrogen atoms, which can be positioned either above or below the layer of carbon atoms. Graphane is a semiconductor, which has a novel

structure and new properties. It is possible to create similar structures using other atoms, such as fluorine or lithium. A research on modified graphene structures will provide practical results for the development of high-speed transistor structures. To this purpose, the main objective of this work is to investigate parameters and characteristics of the hydrogenated graphene by the ab-initio method.

Method and peculiarities of a simulation of hydrogenated graphene properties

Ab-initio calculations have been performed by means of the Quantum Espresso [4] code, using the Perdew-Burke-Ernzerhof (PBE) parametrization of the generalized gradient approximation (GGA). A 40 Ry (1 Ry ≈ 13,605 eV) wave function cutoff and 160 Ry charge density cutoff have been considered. Brillouin zone has been sampled using a 24×24×1 Monkhorst–Pack grid. A 20 bohr (1 bohr ≈ $5{,}29 \cdot 10^{-11}$ cm) layer of vacuum is considered to separate the sheet from its periodical images.



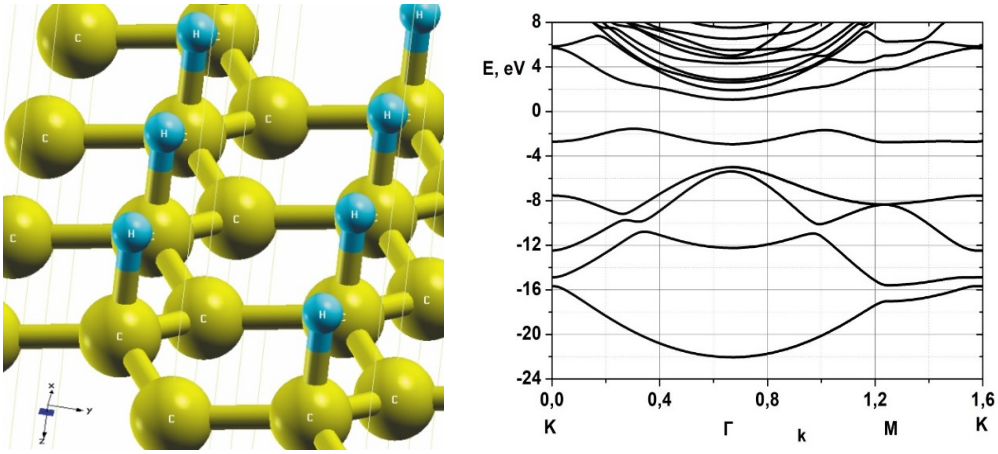
a *b*

Fig. 1. Graphene: *a* – features of arrangement of carbon (C) atoms; *b* – zone diagram

Results of modeling of parameters and characteristics of the hydrogenated graphene by the ab-initio method

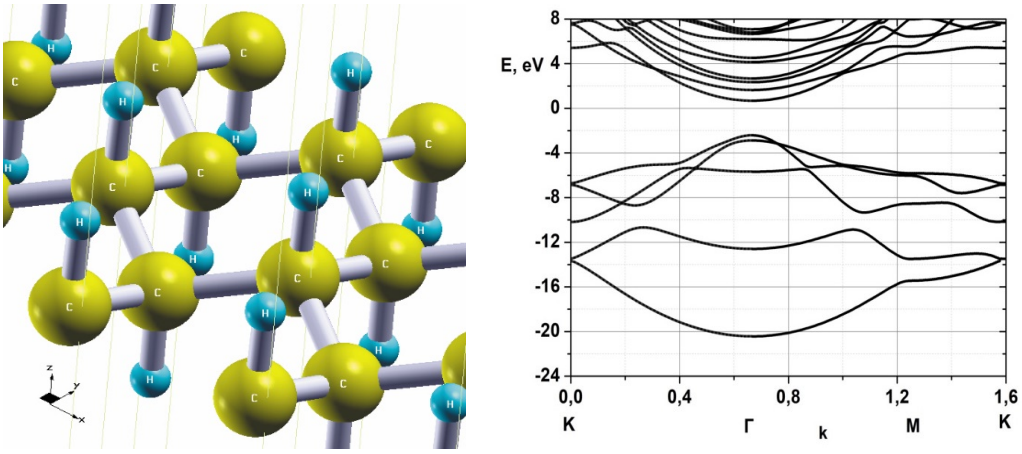
Relaxed structures for 100 % and 50 % hydrogenated and fluorinated graphene (from here on H100%, H50%, F100%, and F50%, respectively) are in agreement with the results already shown in the literature [2–3]. We show the results of modeling for the considered H50% and H100% structures in the Fig. 2 and 3.

Fig. 2, *a* shows the peculiarities of the arrangement of carbon (C) and hydrogen (H) atoms and Fig. 2, *b* – the zone diagram in the structure of 50 % hydrogenated graphene (or graphane of C2H1 type). The results are in good agreement with simulation data obtained by the GW (G is the Green function, W is the screened Coulomb potential) method (within 5 % accuracy, according to [3]). All the materials considered, with the exception of a number of modifications using fluorine atoms, are semiconductors and have non-degenerate conduction band minimum at the Γ point. We have extracted the effective mass and other parameters from the results of the density functional theory DFT-GGA simulations. Fig. 3, *a* shows the peculiarities of the arrangement of carbon (C) and hydrogen (H) atoms and Fig. 3, *b* – the zone diagram in the structure of 100 % hydrogenated graphene (or graphane of C2H2 type). From the analysis of these figures, which shows the dependences of the energy values E (eV) on the normalized value of the wave vector k, it is clear that the hydrogenated graphene is characterized by a three-valley Γ-M-K band diagram. Valley Γ is characterized by the smallest energy gap between the conduction and valence bands. When you are modeling the electronic characteristics and parameters of hydrogenated graphene it is necessary to analyze the parameters of all three valleys Γ, M, and K. The analysis of the data presented in Fig. 2 and 3 shows that the C2H2 graphene provides a larger energy gap between the conduction and valence valleys than the C2H1 graphene does.



a *b*

Fig. 2. 50 % hydrogenated graphene (graphane of C2H1 type): *a* – features of carbon (C) and hydrogen (H) atoms arrangement of; *b* – zone diagram



a *b*

Fig. 3. 100% hydrogenated graphene (graphane of C2H2 type): *a* – features of carbon (C) and hydrogen (H) atoms arrangement; *b* – zone diagram

The peculiarities of the total electrostatic potential distribution of $V_{bare} + V_H + V_{xc}$, where V_{bare}, V_H, and V_{xc} are the representation of bare potential, Hartree potential, and exchange-correlation potential, respectively, in the structure of 50 % hydrogenated graphene (C2-H1 graphane) are presented in Fig. 4.

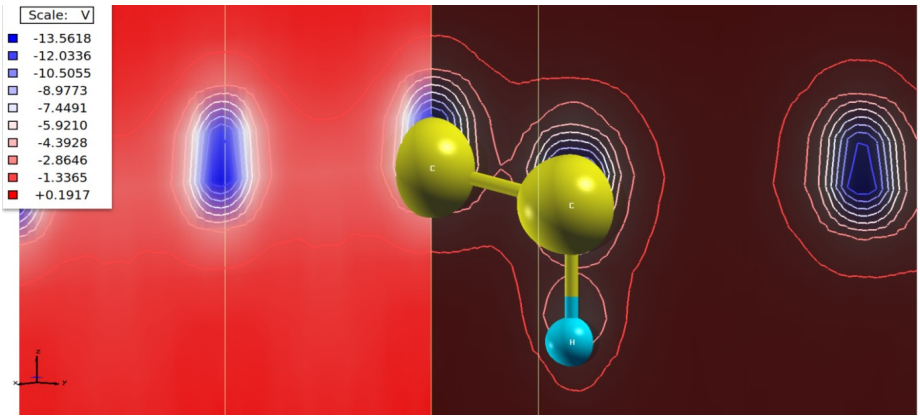


Fig. 4. Peculiarities of $V_{bare} + V_H + V_{xc}$ total electrostatic potential distribution in the structure of 50 % hydrogenated graphene (C2-H1 graphane)

The peculiarities of electrostatic potential distribution of only potential distribution $V_{bare} + V_H$ in the structure of 50 % hydrogenated graphene (graphane) C2-H1 are presented in Fig. 5. A comparison of the modelling results shown in Fig. 4 and 5 allows to estimate the exchange-correlation potential V_{xc}.

Effective electron masses for graphane of C2H1 and C2H2 have been calculated taking into account the value of the energy gap between the conduction and valence bands for the Γ-M-K valleys [5]. Effective electron mass for C2H1 and C2H2 graphane of the Γ-valley equals 0,787 and 0,838, respectively. The calculation of the non-parabolic coefficients for C2H1 and C2H2 materials for the Γ-valley gave the values of 0,0958 eV^{-1} and 0,0521 eV^{-1}, respectively.

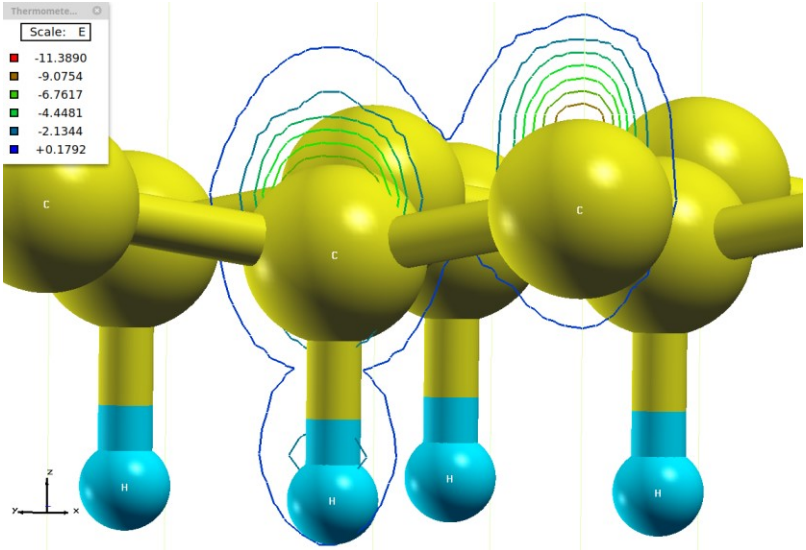


Fig. 5. Peculiarities of $V_{bare} + V_H$ electrostatic potential distribution in the structure of 50 % hydrogenated graphene (C2-H1 graphane)

Conclusion

Ab-initio simulation of hydrogenated graphene properties was performed. Ab-initio calculations have been performed by means of the Quantum Espresso code, using the Perdew-Burke-Ernzerhof parametrization of the generalized gradient approximation GGA.

Basic electrophysical parameters and characteristics of hydrogenated graphene material characterized by Γ-M-K band structure are considered. It is noted that Γ-valley is characterized by the smallest energy gap between conduction and valence zones. The calculated values of the effective electron mass and the non-parabolic coefficients for the Γ-M-K band structure valleys are obtained. Based on the obtained characteristics, it is possible to implement the parameters of hydrogenated graphene in a statistical multi-particle Monte Carlo program to determine the characteristics of electron and hole transfer in heterostructure semiconductor devices.

The investigation of modified graphene with hydrogen and other substances is important for fundamental science and technical applications in high-speed transistor structures operating in the microwave and very high frequency ranges.

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Authors' contribution

Murav'ev V.V. proposed the idea of investigation of hydrogenated graphene.
Mishchenka V.N. carried out the simulation of hydrogenated graphene properties.

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