

International Journal of Modern Physics B
Vol. 32 (2018) 1840030 (5 pages)
© World Scientific Publishing Company
DOI: 10.1142/S0217979218400301



Energy spectrum of graphene with adsorbed potassium atoms

S. P. Repetsky* and I. G. Vyshyvana

*Taras Shevchenko National University of Kyiv
Institute of High Technologies,
4g, Akad. Glushkova Ave., Kyiv 02033, Ukraine
srepetsky0208@gmail.com

E. Ya. Kuznetsova

*National Aviation University,
1, Kosmonavta Komarova Ave., Kyiv 03058, Ukraine*

S. P. Kruchinin*

*Bogolyubov Institute for Theoretical Physics,
National Academy of Sciences of Ukraine,
14b, Metrolohichna Str., Kyiv 03680, Ukraine
sergeikruchinin@yahoo.com*

Accepted 6 February 2018

Published DD March 2018

In the present work, we study the influence of adsorbed impurities, namely potassium atoms, on the energy spectrum of electrons in graphene. The electron states of the system are described in the frame of the self-consistent multiband strong-coupling model. It is shown that, at the ordered arrangement of potassium atoms corresponding to a minimum of the free energy, the gap arises in the energy spectrum of graphene. It is established that, at the potassium concentration such that the unit cell includes two carbon atoms and one potassium atom, the latter being placed on the graphene surface above a carbon atom at a distance of 0.286 nm, the energy gap is equal to ~ 0.25 eV. Such situation is realized if graphene is placed on a potassium support.

Keywords: Graphene; adsorbed potassium atoms; strong-coupling model.

PACS number: 68.43.Bc

1. Introduction

One of the ways of the targeted change in the properties of graphene with the purpose to apply it in nanoelectronics is the introduction of impurities of different

*Corresponding author.

S. P. Repetsky et al.

elements. The presence of impurities can cause a change in the symmetry of a crystal lattice and the appearance of additional energy gaps, whose widths depend on the types of impurities and their concentrations. The studies showed that substitutional impurities and adsorbed atoms affect differently the energy spectrum of electrons in graphene.¹⁻³ In Ref. 1, in the frame of density functional theory with the use of the method of pseudopotential, the electron structures of an isolated graphene monolayer, a double layer of graphene, three-layer graphene and graphene grown on ultrathin layers of hexagonal boron nitride (h-BN) were investigated. It was shown that the energy gap 57 meV in width appears in graphene grown on an h-BN monolayer.

Graphene with impurities of aluminum, silicon, phosphorus and sulfur was studied in Ref. 2 within the method analogous to the above-mentioned one. It was shown that graphene with a 3% phosphorus impurity has a gap 0.67 eV in width.

The electron structure of graphene was studied in the frame of density functional theory in Ref. 3. There, the possibility for a gap in the energy spectrum of graphene to be opened at the introduction of the impurities of boron and nitrogen atoms (gap width is 0.49 eV) and the impurity of boron atoms and lithium atoms adsorbed on the surface (gap width is 0.166 eV) was shown.

In Ref. 4, in the Lifshitz one-band one-electron model, it was established that the gap 0.45 eV in width in the electron energy spectrum arises in graphene deposited on the potassium support. It was assumed⁴ that its appearance is related to a change in the crystal symmetry. This assumption is corroborated by the results of the earlier work,⁵ where the influence of the atomic order on the energy spectrum and the electrical conductivity of the alloy were analytically considered in the Lifshitz one-band model. It was established⁵ that, at the long-range order of the alloy, the gap in the electron energy spectrum appears. Its width is equal to the difference of the scattering potentials of the alloy components. It was found that, in the case where the Fermi level enters the gap, the metal-dielectric transition happens at a long-range order in the alloy. However, no clear comprehension of the nature of the influence of impurities and a support on the energy gap appearance is available.

In the present work, we study the influence of adsorbed impurities, namely potassium atoms, on the electron energy spectrum of graphene. The electron states of the system are described in the frame of the self-consistent multiband strong-coupling model.

2. Strong-Coupling Model Theory

The dependence of the energy of an electron on the wave vector for graphene is calculated from the equation for Green's function poles for the electron subsystem⁶⁻¹⁰:

$$\det \|\varepsilon \delta_{\gamma\gamma'} \delta_{ii'} - h_{i\gamma, i'\gamma'}(\mathbf{k}) - \Sigma_{i\gamma, i'\gamma'}(\mathbf{k}, \varepsilon)\| = 0. \quad (1)$$

In formula (1), $h_{i\gamma, i'\gamma'}(\mathbf{k})$ is the Fourier transform of the hopping integral, $\Sigma_{i\gamma, i'\gamma'}(\mathbf{k}, \varepsilon)$ is the mass operator of electron-electron interaction, and i is the

Energy spectrum of graphene with adsorbed potassium atoms

number of a node of the sublattice in the unit cell. Here, γ is a superindex which incorporates the quantum numbers for the principal energy eigenvalue $\tilde{\varepsilon}$, the standard quantum numbers of angular momentum l and m , and the z -component of spin σ .

The mass operator of electron–electron interaction $\Sigma_{i\gamma,i'\gamma'}()$ is determined from the system of equations

$$G(\mathbf{k}, \varepsilon) = \|\varepsilon\delta_{\gamma\gamma'}\delta_{ii'} - h_{i\gamma,i'\gamma'}(\mathbf{k}) - \Sigma_{i\gamma,i'\gamma'}(\mathbf{k}, \varepsilon)\|^{-1}, \quad (2)$$

$$\Sigma_{i\gamma,i'\gamma'}(\mathbf{k}, \varepsilon) = \Sigma_{i\gamma,i'\gamma'}^{(1)}(\mathbf{k}, \varepsilon) + \Sigma_{i\gamma,i'\gamma'}^{(2)}(\mathbf{k}, \varepsilon), \quad (3)$$

$$\begin{aligned} \Sigma_{i\gamma,i'\gamma'}^{(1)}(\mathbf{k}, \varepsilon) &= -\frac{1}{4\pi iN} \int_{-\infty}^{\infty} d\varepsilon_1 \sum_{\mathbf{k}_1} f(\varepsilon_1) \Gamma_{i\gamma,i'\gamma'}^{(0)i_2\gamma_2,i_1\gamma_1}(\mathbf{k}; \mathbf{k}_1; \mathbf{k}_1) \\ &\quad \times [G_{i_1\gamma_1,i_2\gamma_2}(\mathbf{k}_1, \varepsilon_1) - G_{i_1\gamma_1,i_2\gamma_2}^*(-\mathbf{k}_1, \varepsilon_1)], \end{aligned} \quad (4)$$

$$\begin{aligned} \Sigma_{i\gamma,i'\gamma'}^{(2)}(\mathbf{k}, \varepsilon) &= -\left(\frac{1}{2\pi iN}\right)^2 \iint_{-\infty}^{\infty} d\varepsilon_1 d\varepsilon_2 \\ &\quad \times \sum_{\mathbf{k}_1 \mathbf{k}_2} f(\varepsilon_1) f(\varepsilon_2) \Gamma_{i\gamma,i'\gamma'}^{(0)i_2\gamma_2,i_1\gamma_1}(\mathbf{k}; \mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}; \mathbf{k}_1) \\ &\quad \times \{ [G_{i_2\gamma_2,i_5\gamma_5}^*(-\mathbf{k} + \mathbf{k}_1 + \mathbf{k}_2, \varepsilon - \varepsilon_1 - \varepsilon_2) G_{i_1\gamma_1,i_4\gamma_4}(\mathbf{k}_1, \varepsilon_1) \\ &\quad - G_{i_2\gamma_2,i_5\gamma_5}(\mathbf{k} - \mathbf{k}_1 - \mathbf{k}_2, \varepsilon - \varepsilon_1 - \varepsilon_2) G_{i_1\gamma_1,i_4\gamma_4}^*(-\mathbf{k}_1, \varepsilon_1)] \\ &\quad \times [G_{i_6\gamma_6,i_3\gamma_3}(\mathbf{k}_2, \varepsilon_2) - G_{i_6\gamma_6,i_3\gamma_3}^*(-\mathbf{k}_2, \varepsilon_2)] \\ &\quad + [G_{i_2\gamma_2,i_5\gamma_5}(\mathbf{k} - \mathbf{k}_1 - \mathbf{k}_2, \varepsilon - \varepsilon_1 - \varepsilon_2) \\ &\quad - G_{i_2\gamma_2,i_5\gamma_5}^*(-\mathbf{k} + \mathbf{k}_1 + \mathbf{k}_2, \varepsilon - \varepsilon_1 - \varepsilon_2)] \\ &\quad \times [G_{i_1\gamma_1,i_4\gamma_4}(\mathbf{k}_1, \varepsilon_1) G_{i_6\gamma_6,i_3\gamma_3}(\mathbf{k}_2, \varepsilon_2) \\ &\quad - G_{i_1\gamma_1,i_4\gamma_4}^*(-\mathbf{k}_1, \varepsilon_1) G_{i_6\gamma_6,i_3\gamma_3}^*(-\mathbf{k}_2, \varepsilon_2)] \} \\ &\quad \times \Gamma_{i_4\gamma_4,i'\gamma'}^{i_5\gamma_5,i_6\gamma_6}(\mathbf{k} - \mathbf{k}_1 - \mathbf{k}_2, \varepsilon - \varepsilon_1 - \varepsilon_2; \mathbf{k}_2, \varepsilon_2; \mathbf{k}_1, \varepsilon_1). \end{aligned} \quad (5)$$

In formula (5), $\Gamma_{i_1\gamma_1,i_4\gamma_4}^{i_2\gamma_2,i_3\gamma_3}(\mathbf{k}_1, \varepsilon_1; \mathbf{k}_2, \varepsilon_2; \mathbf{k}_3, \varepsilon_3)$ is the vertex part of the mass operator of electron–electron interaction given by the expression

$$\begin{aligned} \Gamma_{i_1\gamma_1,i_4\gamma_4}^{i_2\gamma_2,i_3\gamma_3}(\mathbf{k}_1, \varepsilon_1; \mathbf{k}_2, \varepsilon_2; \mathbf{k}_3, \varepsilon_3) &= \sum_{n_1, n_2, n_3} \Gamma_{n_1 i_1 \gamma_1, n_4 \gamma_4}^{n_2 i_2 \gamma_2, n_3 i_3 \gamma_3}(\varepsilon_1; \varepsilon_2; \varepsilon_3) \\ &\quad \times \exp[-i\mathbf{k}_1(\mathbf{r}_{n_1, i_1} - \mathbf{r}_{n_4}) - i\mathbf{k}_2(\mathbf{r}_{n_2, i_2} - \mathbf{r}_{n_3}) \\ &\quad + i\mathbf{k}_3(\mathbf{r}_{n_3, i_3} - \mathbf{r}_{n_4})], \end{aligned} \quad (6)$$

$$\mathbf{r}_{ni} = \mathbf{r}_n + \boldsymbol{\rho}_i, \quad (7)$$

$$\Gamma_{n_1 i_1 \gamma_1, n_4 \gamma_4}^{(0) n_2 i_2 \gamma_2, n_3 i_3 \gamma_3}(\varepsilon_1; \varepsilon_2; \varepsilon_3) = \tilde{v}_{n_3 i_3 \gamma_3, n_4 \gamma_4}^{(2) n_1 i_1 \gamma_1, n_2 i_2 \gamma_2}, \quad (8)$$

$$\tilde{v}_{n_3 i_3 \gamma_3, n_4 \gamma_4}^{(2) n_1 i_1 \gamma_1, n_2 i_2 \gamma_2} = v_{n_3 i_3 \gamma_3, n_4 \gamma_4}^{(2) n_1 i_1 \gamma_1, n_2 i_2 \gamma_2} - v_{n_1 i_1 \gamma_1, n_3 i_3 \gamma_3}^{(2) n_2 i_2 \gamma_2, n_4 \gamma_4}. \quad (9)$$

S. P. Repetsky et al.

In relation (7), \mathbf{r}_n is the radius–vector of a node of the crystal lattice, $\boldsymbol{\rho}_i$ is the radius–vector of a node of the sublattice i . In formula (9), $v_{n_3 i_3 \gamma_3, n_1 i_1 \gamma_1, n_2 i_2 \gamma_2}^{(2)}$ is a matrix element of the Hamiltonian of binary electron–electron interaction.⁷ In formulas (4) and (5), $f(\varepsilon)$ is the Fermi function. Over the index $i\gamma$, which is present twice in formulas (4) and (5), the summation should be made.

To calculate the electron spectrum of graphene with adsorbed potassium atoms, we chose the wave functions of the $2s$ and $2p$ states of neutral noninteracting carbon atoms as the basis. In the calculation of matrix elements of the Hamiltonian, we took three first coordination spheres. The energy spectrum of graphene was calculated for the temperature $T = 0$ K. In the calculations, we neglect the renormalization of vertices of the mass operator of electron–electron interaction. In other words, we set

$$\Gamma_{n_1 i_1 \gamma_1, n i \gamma}^{n_2 i_2 \gamma_2, n_3 i_3 \gamma_3}(\varepsilon_1; \varepsilon_2; \varepsilon_3) = \tilde{v}_{n_3 i_3 \gamma_3, n i \gamma}^{(2) n_1 i_1 \gamma_1, n_2 i_2 \gamma_2} \quad (10)$$

in relation (5).

3. Energy Spectrum of Graphene with Potassium Atoms

In Fig. 1, we show the dependence of the electron energy ε in graphene with adsorbed potassium atoms on the wave vector \mathbf{k} . The vector \mathbf{k} is directed from the Brillouin zone center (point Γ) to the Dirac point (point K).

In Fig. 1, the structural periodic distance from a potassium atom to a carbon atom is 0.28 nm.

It is seen from Fig. 1 that, at the ordered arrangement of potassium atoms, a gap in the energy spectrum of graphene arises. Its value depends on the concentration of adsorbed potassium atoms, their location in the unit cell, and the distance to carbon atoms. We established that, at the potassium concentration such that the unit cell includes two carbon atoms and one potassium atom, the latter being placed on the

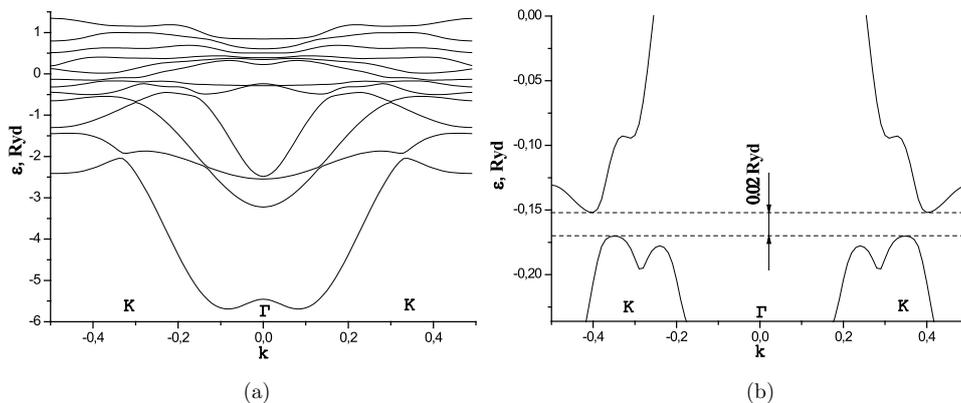


Fig. 1. Dependence of the electron energy on the wave vector \mathbf{k} in graphene with potassium impurity.

Energy spectrum of graphene with adsorbed potassium atoms

graphene surface above a carbon atom at a distance of 0.286 nm, the energy gap is ~ 0.25 eV. The location of the Fermi level in the energy spectrum depends on the potassium concentration and is in the energy interval $-0.36 \text{ Ryd} \leq \varepsilon_F \leq -0.23 \text{ Ryd}$. Such situation is realized, if graphene is placed on a potassium support.

4. Conclusion

We have established that at the potassium concentration such that the unit cell includes two carbon atoms and one potassium atom, the latter being placed on the graphene surface above a carbon atom at a distance of 0.286 nm, the energy gap is ~ 0.25 eV. Such situation is realized if graphene is placed on a potassium support.

Acknowledgments

The present work was partially supported by The National Academy of Sciences of Ukraine (project No. 0116U002067).

References

1. C. Yelgel and G. P. Srivastava, *Appl. Surf. Sci.* **258**, 8338 (2012).
2. P. A. Denis, *Chem. Phys. Lett.* **492**, 251 (2010).
3. D. Xiaohui *et al.*, *Phys. Lett. A* **365**, 3890 (2011).
4. T. M. Radchenko, A. A. Shylau and I. V. Zozoulenko, *Phys. Rev. B* **86**, 035418 (2012).
5. V. F. Los' and S. P. Repetsky, *J. Phys. Condens. Matter.* **6**, 1707 (1994).
6. S. P. Repetsky *et al.*, *J. Mod. Phys.* **5**, 1896 (2014).
7. S. P. Kruchinin, S. P. Repetsky and I. G. Vyshyvana, *Spin-Dependent Transport of Carbon Nanotubes with Chromium Atoms*, eds. J. Bonca and S. Kruchinin (Springer Science + Business Media, Dordrecht, 2016), pp. 67–95.
8. S. Kruchinin and H. Nagao, *Int. J. Mod. Phys. B* **26**, 1230013 (2012).
9. S. Kruchinin, H. Nagao and S. Aono, *Modern Aspect of Superconductivity: Theory of Superconductivity* (World Scientific, 2010), p. 232.
10. S. P. Repetsky *et al.*, *Metallofiz. Noveishie Tekhnol.* **39**, 1017 (2017).