Use of the adsorption properties of graphene to create metamaterials

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Abstract. This paper considers the possibility of nanostructuring metamaterials using the adsorption properties of graphene. Using the effect of defects in the structure of graphene on its adsorption properties, the possibility of creating systems with controlled optical properties on its basis is shown.

1. Introduction
The general concept of metamaterials creating is obtaining structures with specified parameters. Graphene with it’s unique properties[1] opens up great prospects for this. But pure graphene is not always convenient an applied point of view. Considering graphene with defects in structure and impurity atoms adsorbed on it’s surface, we can obtain completely new properties. Then, leaning to control these properties we get the basis for creating low-dimensional metamaterials.

It is an important circumstance that adsorption and desorption make it possible to obtain desired characteristics using adsorbed atoms and molecules. In this connection, the study of adsorption properties [2–5] becomes an interesting direction in the physics of graphene.

2. Methods
In this paper, within the framework of the Anderson model, we consider the effect of graphene lattice defects on its adsorption properties. Disordered graphene (DG), as well as other disordered systems, is of great interest, because defects (impurity atoms, vacancies, etc.) are inevitable in real samples[3].

The Hamiltonian of the problem under consideration (with spin neglected) can be written as

\[ H = \sum_k \epsilon_k c_k^\dagger c_k + \sum_{q,\lambda} U_q \left( A^\dagger_{-q} A_k + B^\dagger_{+q} B_k \right) + E_a a^\dagger a + \beta a^\dagger_0 a_0^\dagger a_0 + \frac{1}{\sqrt{N}} \sum_k \left( V_{a0} c_k^\dagger a + V_{0a} a^\dagger c_k \right), \]  

Here \( \epsilon_k \) - is the spectrum of graphene electrons, \( N \) - is the number of atoms in the graphene lattice, \( c^\dagger \) (\( c \)) – is the creation (annihilation) operator of a graphene electron in the state \( |k\rangle \), \( k \) - is the two dimensional wave vector of graphene electrons,
\[ a^+ (a) \] is the creation (annihilation) operator of electron of adsorbate atom, \( V_{\text{ads}} \) is the hybridization matrix element, \( E_{\text{ad}} \) is the adatom electron energy, \( \mathcal{G} \) is the energy of Coulomb intra atomic electron repulsion, \( U_i = \sum U_i e^{-h \varepsilon_i} \), \( U_i \) is a random potential at the \( i \)-th site (for vacancies \( U \to \infty \)) graphene lattice, \( A_i^+ , A_i (B_i^+, B_i) \) are the creation (annihilation) operators of a graphene electron related to the A and B sublattices, respectively. First, retaining only the first two terms in Hamiltonian (1), we obtain the corresponding Green’s functions (GFs) (the case of isolated DG) and investigate the density of states (DOS). Then, using the obtained GFs as seed functions and complete Hamiltonian (1), we obtain the final GFs for the DG-adatom system. Taking into account the results of [16], we can write the following expression for DG GFs: \( G(k, \omega) = \left[ G_0^+(k, \omega) - T(\omega) \right]^{-1} \), where the energy part \( T(\omega) \) is a matrix is defined as [16]: \( T(\omega) = n U (1 - \mathcal{G}_0 (\omega))^{-1} \), \( n = N_{\mu} / N \) – is the concentration of defects, \( \mathcal{G}_0 (\omega) = N^{-1} \sum_i G_i (k, \omega) \), and \( G_i (k, \omega) \) is the GFs, corresponding to the Hamiltonian \( H_0 = \sum_i \varepsilon_i c_i^+ c_i \). For vacancies \( U \to \infty \), as a result, \( T(\omega) = -n \left( \mathcal{G}_0 (\omega) \right)^{-1} \). Below we will consider only vacancy-type defects. Finally, taking into account that \( G_0^+(k, \omega) = \omega - \varepsilon_i \), we obtain \( G(k, \omega) = \left[ \omega - \varepsilon_i - T(\omega) \right]^{-1} \). DOS (hereinafter, DOS is the density of states per graphene atom) is determined conventionally: \( \rho(\omega) = \pi^{-1} \ln \mathcal{G}(\omega-i0) \), where \( \mathcal{G}(\omega) = N^{-1} \sum_i G(k, \omega) \). Thus,

\[
\rho(\omega) = \frac{SB(\omega)}{2\pi^2 v_F^2 \hbar^2} \ln \left( \frac{\omega - \xi - A(\omega)}{\omega - A(\omega)} \right) + B^2(\omega) - \frac{S(\omega-A(\omega))}{B(\omega)} \left( \frac{\omega - \xi - A(\omega)}{\omega - A(\omega)} \right) \left( \frac{\omega - \xi - A(\omega)}{\omega - A(\omega)} \right),
\]

(2)

where \( \xi \) – is the width of graphene Brillouin zone (\( |\xi| \leq 3 \text{eV} \)), and \( A(\omega) \) and \( B(\omega) \) can be written as

\[
A(\omega) = \frac{n N(\omega)}{\left( N(\omega) \right)^2 + \pi^2 \left( \rho_0 (\omega) \right)^2}, \quad B(\omega) = \frac{\pi \omega}{\left( N(\omega) \right)^2 + \pi^2 \left( \rho_0 (\omega) \right)^2},
\]

\[
\rho_0 (\omega) = \frac{1}{N} \sum_i \delta (\omega - \varepsilon_i) = \frac{S N \phi}{\pi v_F^2 \hbar^2}, \quad N(\omega) = \frac{S N \phi}{2 \pi v_F^2 \hbar^2} \ln \left( \frac{\omega^2 - \xi^2}{\omega^2} \right),
\]

(3)

It can easily be seen that, at \( n \to 0 \), \( \rho \to \rho_0 \). The \( S \) value can be determined from the natural condition of one atom of undoped graphene containing one electron in the 2p- state, i.e. \( k \rho_0 (\omega) d\omega = 1 \), where \( \varepsilon_i \) – the Fermi energy, which is zero for undoped graphene. This condition yields: \( S = 2 \pi v_F^2 \hbar^2 / |\xi^2| \). Fig.1 shows DG DOS (2). Hereinafter, we assumed that \( |\xi| = 3 \text{eV} \). According above-considered sequence of operations, we rewrite Hamiltonian (1) so as to make the GFs of isolated DG seed ones. Then
Using Hamiltonian (4), for adatom GFs we obtain

\[ H = \sum_{k,\sigma} \epsilon_k(\omega) c_{k,\sigma}^\dagger c_{k,\sigma} + E_n \sum \sigma a_{\sigma}^\dagger a_{\sigma} + \beta a_{\sigma}^\dagger a_{\sigma} a_{\sigma}^\dagger a_{\sigma} + \frac{1}{\sqrt{N}} \sum_{k,\sigma} \left( V_{\alpha,\sigma} c_{k,\sigma}^\dagger a_{\sigma} + V_{\beta,\sigma} a_{\sigma}^\dagger c_{k,\sigma} \right) \]

where \( \epsilon_k(\omega) = \epsilon_k + T(\omega) \). Using Hamiltonian (4), for adatom GFs we obtain \( G_\omega^{-1}(\omega) = \omega - \epsilon_k - \Sigma(\omega) - i\Gamma(\omega) \), where \( \epsilon_k = E_n + \Delta n_k \), \( \Gamma(\omega) = \pi V_{\sigma}^2 \rho(\omega) \), \( \Sigma(\omega) = \pi^{-1} P \int \Gamma(\omega') d\omega' / (\omega - \omega') \), and \( n_k \) is the adatom occupation number. For the adatom DOS \( \rho_s(\omega) = \pi^{-1} \text{Im} G_\omega \) we obtain

\[ \rho_s(\omega) = \pi^{-1} \Gamma(\omega) \left[ \left( \omega - \epsilon_k - \Sigma(\omega) \right)^2 + \Gamma^2(\omega) \right] \]

The shift function can be written as

\[ \Sigma(\omega) = \frac{B V^2}{\omega^2} \left[ \frac{\ln \left( \frac{x^2 + B^2 - (\omega + A)^2}{2B(\omega + A)} \right)}{2B(\omega + A)} - \frac{\ln \left( \frac{x^2 + B^2 - (\omega + A)^2}{2B(\omega + A)} \right)}{2B(\omega + A)} \right] \]

\[ - \frac{(\omega + A)V^2}{2\xi^2} \ln \left( \frac{x^2 + B^2 - (\omega + A)^2}{2B(\omega + A)} \right) + 4B^2(\omega + A)^2 \]

\[ \left( B^2 + (\omega + A)^2 \right) \]

3. Results and discussion

At \( n \to 0 \) natural transition occurs: \( \Sigma(\omega) \to V^2 \Lambda(\omega) \). The shift function is shown in the fig.2. From fig.2 we can see, that the strongest dependence of the shift function on the vacancies concentration is observed near zero \( \pm 1 \text{eV} \). For high energies, the shift function is independent on the vacancies concentration. It means, that the hybridization shift of adatom quasi-level is determined, in the main, by substrate atom, with which adatom interacts directly.

![Fig. 1. Density of states of DG at different vacancy concentrations.](image1)

![Fig. 2. Shift function.](image2)

4. Conclusions

Thus, in this paper we see that the disorder in the structure caused by various defects or impurity atoms affects the adsorption properties of graphene. In particular, the disorder may contribute to the appearance of an energy gap in the graphene spectrum. Moreover, the energy gap is determined by degree of structure disorder, as well as the adsorption(energy) characteristics of the atoms and molecules, that are adsorbed on graphene. Controlling disorder degree, and selecting energy parameters of adsorbable material, we can control the energy bandgap of graphene spectrum. Ability of controlled action on the width of band gap mean
control the optical properties of the resulting material. And low-dimensional systems with controlled optical parameters is a base for nanostructuring of metamaterials[7]. The difficulties associated with experimental possibilities of implementing the results obtained in this paper are determined by the ability to work with a real samples on nano-scales, and, in a sense, put barrier on this way. But this limitation is already particular and doesn’t exclude this opportunity theoretically. And the discussion problems of practice realization considered concepts out of scope of this paper and can be particular interest.

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