

Sensitivity Properties of Graphene with Metal Nanoparticles

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In this paper, we investigate the influence of metal nanoparticles on the sensitivity properties of graphene with respect to gas molecules adsorbed on its surface on the example of copper nanoparticles. The influence of the metal atom is taken into account by changing the hopping integral for the regions adjacent to it. Such features are due to the presence of a metal nanoparticle on the surface of a graphene nanoribbon which changes the hybridization of pi electrons in the immediate vicinity of the adsorption site of a metal atom. First of all we use the transition from a two-dimensional array corresponding to the sites of the graphene plane to a one-dimensional array for the determination of the density of states of the system under consideration. Secondly, we are based on the numerical diagonalization of the Hamiltonian for rectangular graphene nanoribbon in the tight-binding approximation. It allows us to estimate the response of the system based on the current-voltage characteristic for the tunneling contact of the graphene nanoribbon with different materials. In this paper we choose metal and quantum dots. The best results have been demonstrated in terms of sensitivity to adsorbed gas molecules for contacts with these materials. In this case, the tunnel current density is calculated from the density of states of the system. Decorating the graphene plane with copper nanoparticles significantly changes the resistance in the tunneling contact of the nanoribbon with the quantum dots or with the metal. Also we observe an increase in the sensitivity of graphene nanoribbons to impurities with an increase in the concentration of metal nanoparticles. Thus, we propose an approach based on the study of tunneling current, which has several advantages, since it allows optimizing the choice of the second sample to achieve the highest sensitivity. Equally important is the fact that various types of contacts may be more optimal for determining various types of impurities.

Keywords: Graphene nanoribbon, Conductivity, Metal particles.

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1. INTRODUCTION

One of the main features of graphene structures is the dependence of the electrophysical properties on the morphology of the material and the parameters of the external atmosphere. Molecules of various gases adsorbed on the surface of graphene structures, such as NO₂, NH₃, CO₂, etc., can change the resistance of materials several times, which makes it possible to create highly sensitive detectors of these gases based on graphene. The ease of processing, the possibility of alloying, miniaturization of the device, compatibility with various substrates, mechanical strength, high sensitivity and high temperature resistance make graphene promising for applications in various sensor devices. Due to its high electron mobility and low electrical noise at room temperature, graphene is an ideal matrix for a sensitive element.

Adsorption of gas molecules from the atmosphere can occur via a donor or acceptor mechanism and change the energy bands in graphene, due to which its conductivity changes significantly. However, the graphene plane is a chemical inert material and, to increase the sorption capacity, they are currently using either functionalization by various chemically active groups with respect to a certain atmospheric component, or the graphene plane is decorated with nanoparticles catalyzing the reaction with the required atmospheric component [1, 2].

Hybrid graphene structures with metal nanoparticles have great potential for various applications, such as chemical sensors, catalysts and photocatalysts,

fuel cells, bio-applications due to their individual as well as synergistic properties. Metal nanoparticles allow us to control catalytic activity by controlling the size, shape, coating and degree of dispersion, and graphene as a substrate can enhance sensitivity, providing excellent conductivity for electron capture and transport. Therefore, the catalytic activity of metal nanoparticles is one of the key factors in measuring the characteristics of hybrid structures with graphene.

In Ref. [3] it was shown that Pt/MWCNT cathode catalyst (multilayer carbon nanotube) in the corresponding mass percentage showed a higher productivity for the oxygen reduction reaction in a proton-exchange membrane fuel cell. Hybrids of silver nanoparticles with reduced graphene oxide exhibit better photocurrent generation. The catalytic activity of metal nanoparticles also affects the sensitivity of the gas sensor. Graphene with the deposition of platinum nanoparticles [4] showed a greater sensitivity to hydrogen than other thick films. In many cases, the sensitivity, selectivity can be enhanced by decorating graphene with metal nanoparticles using electrochemical methods or solution chemistry methods.

In this paper, we study the sensitivity properties of the hybrid structure of graphene with copper nanoparticles.

2. METHODS

Hamiltonian for graphene in the tight-binding approximation [5] from the point of view of the creation and annihilation operators of electrons can be written as:

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$$H_0 = -\sum_{\langle ij \rangle} t_{i,j} (C_i^+ C_j + C_i C_j^+), \quad (1)$$

where $t_{i,j}$ is the hopping integral between sites i and j , angle brackets indicate the summation over the nearest neighbors, C^+ is the creation operator and C is the annihilation operator for electrons. In our approach, a two-dimensional array of carbon atoms is renumbered in a one-dimensional array.

The geometry of the problem and one of the ways of such numbering are presented in Fig. 1A: t_0 , t_1 , t_2 are the hopping integrals in the presence of metal atoms on graphene. In the figure under the graphene plane, the point O denotes the location of the metal nanoparticle: r_1 is the radius of the first circle, which contains bonds with the hopping integral t_1 . The ring between r_1 and r_2 contains bonds with the hopping integral t_2 (Fig. 1B).

It should be noted that the presence of a metal atom on the surface of graphene changes the hybridization of pi-electrons in the immediate vicinity of the metal atom. Here we consider the metal nanoparticle in the center of the honeycomb. This leads to a change in the hopping integral for the nearest sections. The C=C bonds in which both C atoms interact with the Cu (t_1) atom, and the C=C bonds in which only one C atom interacts with the Cu (t_2) atom decrease more and the hopping integral increases. Here we use the following values for the hopping integrals: $t_0 = 2.7$ eV [6, 7], $t_1 = t_0$ and $t_2 = 1.5 t_1$.

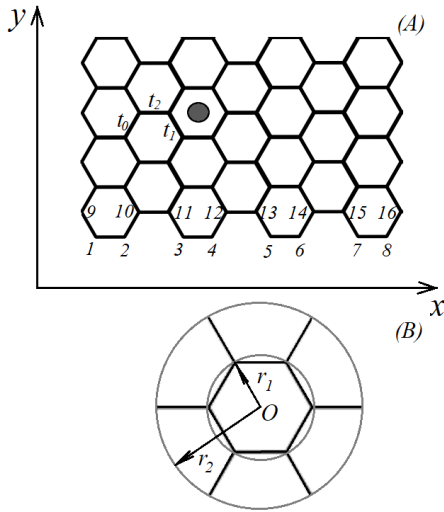


Fig. 1 – The geometry of the problem. (A) Numbering method. Here gray circle on the graphene lattice denotes a metal atom. (B) Areas with different hopping integral

In order to take into account the impurities adsorbed on the graphene surface, it is necessary to change the Hamiltonian (1):

$$H = H_0 + H_{imp}, \quad (2)$$

$$H_{imp} = \sum_l (V_l C_k^+ C_l + e_l C_l^+ C_l)$$

where e_l describes the energy levels of the impurity, V_l is the overlap between energy levels of the impurity and graphene.

Then Hamiltonian (2) is numerically diagonalized and we find the density of states for graphene with impurities [8, 9].

As well-known, the expression for the contact current density is given by the formula:

$$j = \sum_{p,q} \int_{-\infty}^{+\infty} d\varepsilon \cdot \text{Im} G^A(p, \varepsilon + eU) \cdot \text{Im} G^B(q, \varepsilon) \times \left(\frac{4\pi e |T|^2}{1 + \exp(\varepsilon/k_B T)} - \frac{4\pi e |T|^2}{1 + \exp((\varepsilon + eU)/k_B T)} \right), \quad (3)$$

where U is the voltage between contacts, $G^{A,B}$ is the Green function for A and B materials, k_B is the Boltzmann constant, T is the temperature. Here we use the “rough” contact approximation (matrix element of the tunneling operator between states p and q is equal to constant T), when graphene plane is perpendicular to the surface of the contact material.

Using the Sokhotski-Plemelj formula $\text{Im}(x + i0) = -\pi\delta(x)$, we can rewrite equation (3) in the form:

$$j = 4\pi e |T|^2 \int_{-\infty}^{+\infty} d\varepsilon \cdot v_A(\varepsilon + eU) v_B(\varepsilon) \times \left(\frac{1}{1 + \exp(\varepsilon/k_B T)} - \frac{1}{1 + \exp((\varepsilon + eU)/k_B T)} \right), \quad (4)$$

where $v_A(\varepsilon) = \sum_p \delta(\varepsilon - \varepsilon_p^A)$, $v_B(\varepsilon) = \sum_q \delta(\varepsilon - \varepsilon_q^B)$ are the tunneling densities of states of the contacts A and B , respectively, $\delta(x)$ is the Dirac delta function, which has very useful properties for us in the case when

$$\delta(f(x)) = \sum_k \frac{\delta(x - x_k)}{|f'(x_k)|} \quad \text{and} \quad \int_{-\infty}^{+\infty} \delta(x - a) f(x) dx = f(a),$$

where x_k are the roots of $f(x) = 0$.

As a material in graphene contact, we choose a metal (5a) or quantum dots (5b). The electronic spectrum for them can be written in the following form:

$$\varepsilon_p^A = \frac{p^2}{2m}, \quad (5)$$

$$\varepsilon_p^A = \varepsilon_0 - \Delta \cdot \cos(p),$$

where p is the momentum, m is the effective electron mass in a metal; ε_0 is the energy of quantum well electrons, Δ is the overlap integral, which is determined by the overlapping of the electron wave functions in the neighboring “wells” of the quantum dots.

3. RESULTS AND DISCUSSION

The dependence of the density of the tunneling current for a rectangular nanoribbon of 30×9 atoms on voltage for two contacts is presented in Fig. 2.

Note that for both contacts with the metal and with the quantum dots, a decrease in resistance is observed in the case of the presence of metal nanoparticles on graphene.

Further, we study the effect of the number of metal particles adsorbed on a graphene nanoribbon on the current-voltage characteristics for the tunneling contact with the metal (Fig. 3A) or with the quantum dots (Fig. 3B).

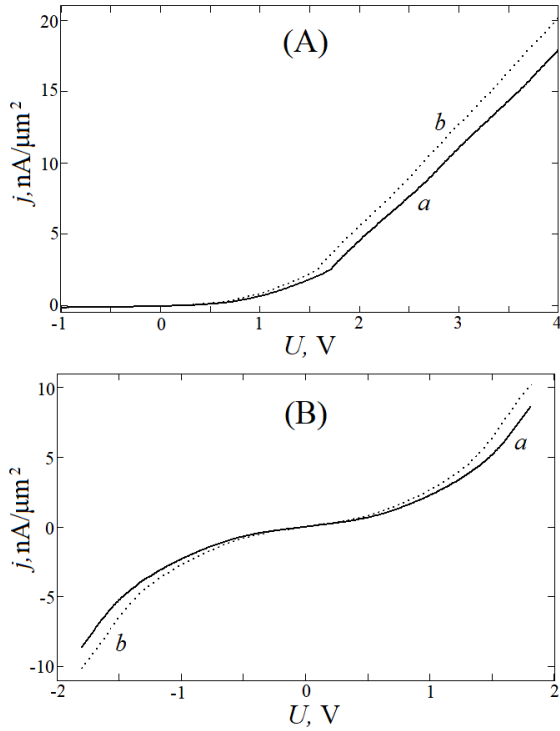


Fig. 2 – The dependence of the tunneling current density for graphene nanoribbon on voltage; contact with the metal (A), contact with the quantum dots (B): a) without metal nanoparticle, b) with one copper nanoparticle

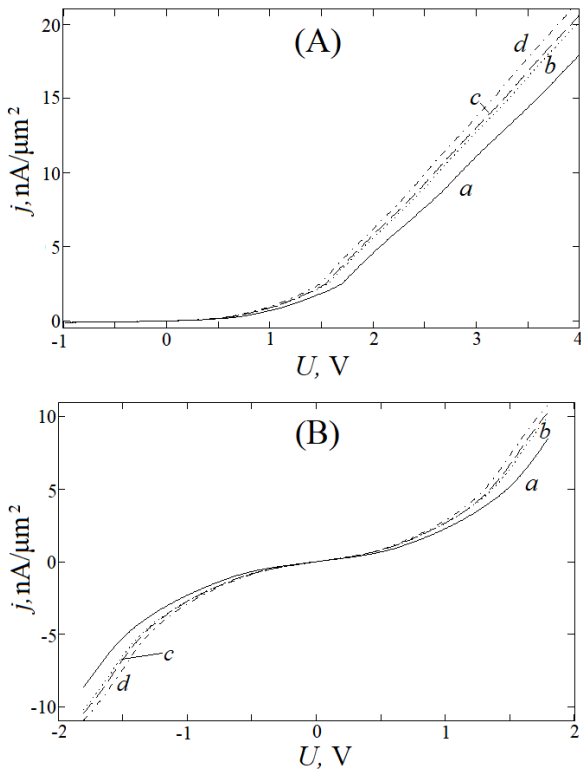


Fig. 3 – The dependence of the tunneling current density for a 30×9 atoms nanoribbon on voltage; contact with the metal (A), contact with the quantum dots (B): a) without Cu nanoparticle, b) 1 Cu nanoparticle, c) 2 Cu nanoparticles and d) 3 Cu nanoparticles

As can be seen from Fig. 3, the introduction of additional metal nanoparticles significantly affects the shape of the current-voltage characteristic for both contacts with the metal and the quantum dots, which manifests itself in an increase in current. Note that without a copper nanoparticle it is not possible to detect the presence of one impurity molecule (the current-voltage characteristics for the case with and without impurities coincide).

We now study the response of the system depending on the concentration of copper nanoparticles (Fig. 4), which is given by the formula:

$$\Delta R = \frac{|R_{Me} - R_0|}{R_0} \quad (6)$$

where R_0 is the resistance in contact without a metal nanoparticle, R_{Me} is the resistance in contact with copper nanoparticles.

According to Fig. 4, we can conclude that response (6) increases with increasing concentration of copper nanoparticles, which is consistent with many experimental results for ohmic resistance [10, 11].

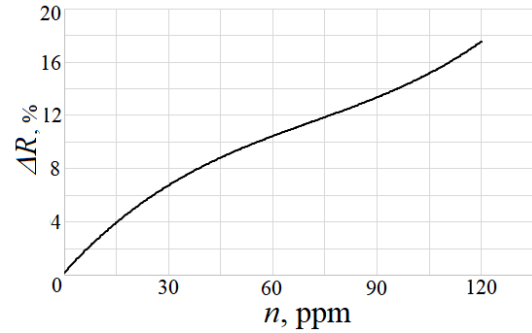


Fig. 4 – Dependence of ΔR on the concentration of copper nanoparticles for the contact with metal

4. CONCLUSIONS

In conclusions we formulate the following main results.

1. A method for calculating the tunneling current of the contact of graphene nanoribbon with metal taking into account metal nanoparticles is proposed.

2. The introduction of copper nanoparticles leads to significant changes in the resistance in the tunneling contact of the nanoribbon with the metal and the quantum dots.

3. An increase in the response of the system with an increase in the concentration of metal nanoparticles that decorate the graphene plane is demonstrated, which leads to an increase in the sensitivity of graphene to impurities.

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Властивості чутливості графена до металевих наночастинок

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У роботі досліджено вплив наночастинок металу на властивості чутливості графена відносно молекул газу, адсорбованих на його поверхні на прикладі наночастинок міді. Вплив атома металу враховується шляхом зміни стрибкового інтегралу для прилеглих до нього областей. Такі особливості зумовлені наявністю металевих наночастинок на поверхні графенової нанострічки, яка змінює гібридизацію пі-електронів у безпосередній близькості до місця адсорбції атома металу. Перш за все, ми використовуємо перехід від двовимірного масиву, що відповідає ділянкам площини графена, до одновимірного масиву для визначення щільності станів системи що розглядається. По-друге, ми ґрунтуємося на чисельній діагоналізації гамільтоніана для прямокутної нанострічки графена у наближенні жорсткого зв'язку. Це дозволяє оцінити реакцію системи на основі вольт-амперної характеристики для тунельного контакту нанострічки графена з різними матеріалами. У роботі ми вибираємо метал та квантові точки. Найкращі результати були продемонстровані щодо чутливості до адсорбованих молекул газу для контактів з цими матеріалами. У цьому випадку тунельна щільність струму обчислюється із щільності станів системи. Оздоблення площини графена мідними наночастинками суттєво змінює опір у тунельному контакті нанострічки з квантовими точками або з металом. Також ми спостерігаємо підвищення чутливості графенових нанострічок до домішок із збільшенням концентрації металевих наночастинок. Таким чином, ми пропонуємо підхід, заснований на вивченні тунельного струму, який має ряд переваг, оскільки дозволяє оптимізувати вибір другого зразка для досягнення найбільшої чутливості. Не менш важливим є той факт, що різні типи контактів можуть бути більш оптимальними для визначення різних типів домішок.

Ключові слова: Графенова нанострічка, Провідність, Металеві частинки.