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Short-Range Order and Electronic Properties of Epitaxial Graphene

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Abstract: One of the most rapidly developing areas of modern materials science is the study of graphene and materials on its basis. The experimental investigations have revealed different types of defects on the surface of graphene that form the ordered structures of atomic configurations. In the present work, the value of short-range order parameter for different configurations of foreign atoms in a graphene layer was calculated. The effect of various factors on the density of electronic states and electrical resistance in graphene was also investigated. The type of the ordering of foreign atoms in graphene rather than the concentration of impurities, was shown to be responsible for the change in the conductivity of graphene.

INTRODUCTION

Graphene and its derivatives are investigated very actively, because they are considered as the most promising components for new-type electronic devices. Graphene is characterized by high carrier mobility, thermal conductivity, and electrical conductivity and also by the dependence of these properties on modification of the material structure and the nature of external impacts. Experimental investigations have shown that the surface of graphene contains many defects forming the ordered structures of various configurations, including the replacement of a certain number of carbon atoms on gas atoms. The modern equipment can detect up to two thousand defects per square micrometer of a carbon material surface.

THEORY

The most common configurations of the gas in two-dimensional graphene are pyrrole, pyridine, and replacing ones (all of them corresponding to the defects of replacement type). Theoretical investigations have shown that these structural defects should have influence on electronic transport properties of graphene up to the type of conductivity change [1]. We have attempted to describe the influence of temperature, structural defects, and other factors on the electronic properties of graphene.

In our approach, we suppose the presence in the graphene layer of the structures with short-range order arising in graphene in the process of its synthesis, and consider the subsequent adsorption of gases on the surface. In the proposed model, the quantitative and qualitative characteristics of defects in graphene structure are described by a short-range order parameter [2].

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(a) (b)

FIGURE 1. Illustration of (a) the case of ordering of atoms in graphene and (b) the case of stratification in graphene

We have created a computer program to calculate this characteristic for all sorts of possible configurations of gas and carbon atoms, as well as for the case of ordering (Fig. 1a) and stratification (Fig. 1b) in a two-dimensional graphene layer. The results of our calculation are represented in Table 1.

Low-temperature characteristics of the graphene density of states (DOS) was calculated by the method of temperature Green's functions [3]. The calculation of contributions to DOS was conducted taking into account the multiple elastic electron scattering on impurities and structural inhomogeneities of the short-range order type. The following expression for the relaxation time was obtained:

$$\frac{1}{2\tau} = \frac{1}{2\tau_{\text{imp}}}\left[1 + \frac{1-c}{N}\sum_{i=0}^{N}\alpha_i BT\right]. \tag{1}$$

Here $B = \pi\hbar^{-2}kR^2m \approx 0.1\ \text{K}^{-1}$, R is the radius of the first coordination sphere, m is electron mass, c is the impurity concentration, N is the number of atoms in the range of structural inhomogeneities, $\Sigma\alpha_i$ is the sum of the short-range order parameters. Finally, $\tau_{\text{imp}}^{-1} = 2\times10^{15}\text{s}^{-1}$ is the inverse electron relaxation time calculated taking into account multiple elastic scattering on impurities.

The obtained expression for the contribution to the disordered graphene DOS is the following:

$$\Delta\nu = \frac{1}{\hbar^2 v_{\text{F}}^2}\left[\frac{\hbar}{2\tau}\ln\left(1 + \frac{p_0 v_{\text{F}}(p_0 v_{\text{F}} - 2\varepsilon)}{\varepsilon^2 + (\hbar/(2\tau))^2}\right) + 2\varepsilon\,\text{arctg}\left(\frac{p_0 v_{\text{F}}(\hbar/(2\tau))}{(\hbar/(2\tau))^2 + (\varepsilon - p_0 v_{\text{F}})\varepsilon}\right)\right], \tag{2}$$

where p_0 is electron momentum, $\varepsilon = \hbar k v_{\text{F}}$ is electronic spectrum in ideal graphene near the Fermi energy, and $v_{\text{F}} \approx 10^6$ m/s is the Fermi velocity.

The resistance of the epitaxial graphene was calculated in the same way as the electrical conductivity in the disordered carbon nanotubes with short-range order:

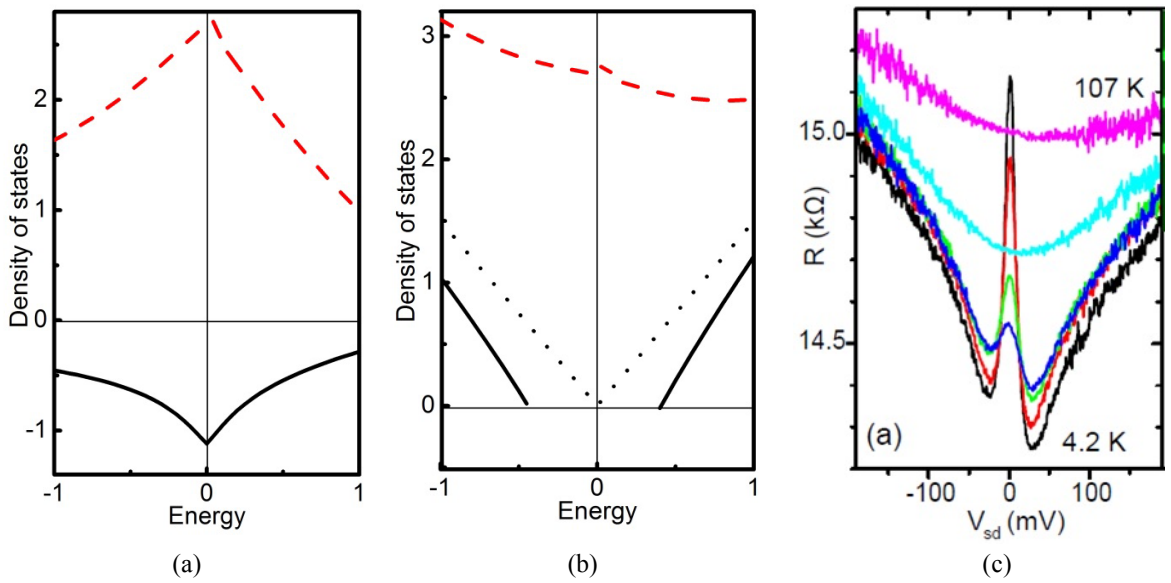
$$\sigma = \frac{e^2\tau n}{m}, \tag{3}$$

where e and m are the electron charge and mass, respectively, n is the number of current carriers. Then, according to (3), the contribution to resistance of graphene from electron scattering on impurities and defects in the structure has the following form:

$$\rho(T) = \frac{m}{e^2 n\tau} = \frac{m}{e^2 n}\left(\frac{1}{\tau_{np}} + 2\pi U_0^2 \nu_0 \frac{c(1-c)}{N}\sum_i \alpha_i BT\right). \tag{4}$$

TABLE 1. The value of the short-range order parameters for various configurations of structural defects in graphene for the first and second coordination spheres

The type of defects	The order parameter for specific spheres	
	α_1	α_2
Replacing	0.463	0.778
Pyrrole	0.429	0.753
Pyridine	0.22	0.716



(a) (b) (c)

FIGURE 2. The calculated DOS contribution (a) for the case of ordering (the solid line) and stratification (the dashed line). DOS for pure graphene (dotted line), (b) the resultant DOS for the case of stratification (the dotted line) and ordering (the solid line); (c) the experimental differential conductance for different temperature values [5]

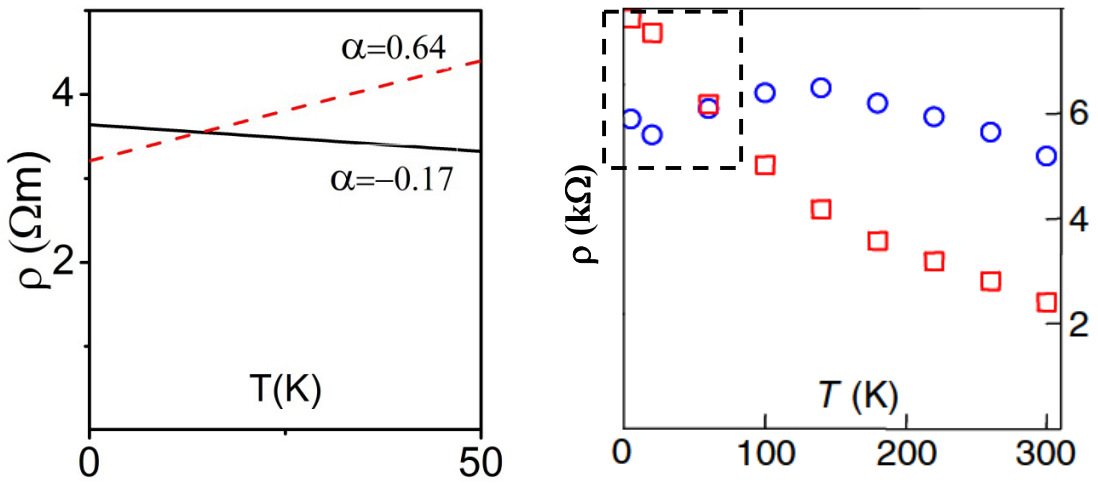
RESULTS AND DISCUSSION

We analyzed the influence of the sign of short-range order parameters sum on the contribution to DOS and resistivity at a fixed temperature near the Fermi level. The sign of the sum of short-range order parameters is changed from negative to positive value in doped and degassed graphene, as well as in the case of the ordering-stratification restructuring, which takes place under the influence of various external factors (such as annealing, for example). We used the calculated values of short-range order parameters for the construction of plots for DOS and electrical resistance using expressions (2) and (4), respectively. Figure 2a represents the calculated DOS near the Fermi level in the case of ordering (the solid line) and stratification (the dashed line). The contribution to DOS in the first case is negative, and positive in the second case. The linear contribution to DOS of pure graphene (the dashed line) [4] and the resulting sum of contributions in the case of stratification (the solid line) and ordering (the dotted line), are represented in Fig. 2b. Evidently from Fig. 2b, the opening gap at the Fermi level is due to the negative contribution to DOS connected with electron scattering on impurities and structural inhomogeneities in the case of ordering. Metallization of graphene is associated with the positive contribution to DOS in the case of stratification. The curve for the case of stratification agrees qualitatively with experimental data [5] given in Fig. 2c. In [5], DOS of graphene was investigated at various temperatures. Based on these data, we can assume that defects in the graphene samples investigated in [5] are located mainly in the second coordination sphere, as in the case of stratification.

To analyze the influence of different types of short-range ordering in graphene structure on the temperature dependence of resistivity, we also considered the cases of ordering and stratification. In Fig. 3a one can see that the graphene resistance decreases when temperature rises in the first case, which is characteristic for semiconductors (the solid line). Increasing resistance with temperature increase is typical for the case of stratification (the dashed line). Such temperature dependence of resistance is characteristic for metals. Two possible variants of temperature dependence of resistance have been found in graphene in the experimental work [6] (Fig. 3b).

CONCLUSION

The present theoretical investigation of epitaxial graphene based on the concept of short-range order parameters suggests the following conclusions:



(a) (b)

FIGURE 3. (a) The contribution to resistance calculated for the cases of ordering (the solid line) and stratification (the dashed line); (b) experimental data on resistance of graphene [6]

1. The value of short-range order parameters is different for various types of short-range ordering of local structure. Wherein, the short-range order parameter decreases when a number of atoms of other sort increases in the short-range ordered structure, but the concentration of these atoms in the graphene sample is constant.

2. The change of the type of structure defects in graphene from substituting to pyridine results in the metallization of graphene, as a consequence of the increase in the contribution of DOS at the Fermi level, which is confirmed by the data obtained in [5].

3. The change in the sign of the sum of short-range order parameters in the process of restructuring from ordering to stratification, leads to a change in the temperature dependence of conductivity type, i.e. the contribution to resistance from electron scattering on the short-range ordering areas may go up (for the case of stratification) or fall (for ordering case) when temperature rises. Similar temperature dependencies have been found in [6].

4. The change in the sign of the sum of short-range order parameters in the case of ordering or stratification results in the opening or closing of the gap at the Fermi level.

Thus, we have shown that the very type of local ordering of the foreign atoms in graphene is responsible for the change in the type of conductivity of graphene, not concentration of impurity atoms.

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