PHYSICS OF MOLECULES

A THEORETICAL STUDY OF MACROMOLECULE INTERACTION WITH THE QUASI-FREE-STANDING AND EPITAXIAL GRAPHENE FORMED ON THE SILICON CARBIDE POLITYPES

A. A. Lebedev✉, *S. Yu. Davydov*

Ioffe Institute, St. Petersburg, Russia

✉ shura.lebe@mail.ioffe.ru

Abstract. A two-level model of an organic macromolecule has been put forward in order to analyze theoretically the interaction of dangling molecular orbitals of the organic macromolecule with quasi-free-standing and epitaxial graphene. The model initially contains a completely filled (HOMO) and empty (LOMO) levels. Within the framework of the standard adsorption approach, the interaction of these levels with quasi-free and epitaxial graphene iswas considered. Silicon carbide polytypes were considered as substrates. Our estimates showed that the maximum transition of electrons from dangling bonds to epitaxial graphene took place for the $3C$-SiC substrate.

Keywords: two-level macromolecule model, single-layer graphene, semiconductor substrate

ТЕОРЕТИЧЕСКОЕ ИССЛЕДОВАНИЕ ВЗИМОДЕЙСТВИЙ МАКРОМОЛЕКУЛЫ С КВАЗИСВОБОДНЫМ И ЭПИТАКСИАЛЬНЫМ ГРАФЕНОМ, СФОРМИРОВАННОМ НА ПОЛИТИПАХ КАРБИДА КРЕМНИЯ

А. А. Лебедев✉, С. Ю. Давыдов

Физико-технический институт им. А.Ф. Иоффе РАН, Санкт-Петербург, Россия

✉ shura.lebe@mail.ioffe.ru

Аннотация. С целью теоретического анализа взаимодействия оборванных молекулярных орбиталей органической макромолекулы с однослойным квазисвободным и эпитаксиальным графенаом предложена двухуровневая модель органической макромолекулы, изначально содержащая полностью заполненный (HOMO) и вакантный (LOMO) уровни. В рамках стандартного адсорбционного подхода рассмотрено взаимодействие этих уровней с электронными состояниями квазисвободного и эпитаксиального графена. В качестве подложки рассмотрены политипы карбида кремния. Оценки показали, что максимальный переход электронов с оборванных связей на эпитаксиальный графен имеет место для подложки $3C$-SiC.

Ключевые слова: двухуровневая модель макромолекулы, однослойный графен, полупроводниковая подложка

Introduction

Graphene has the unique ability to detect adsorption of a single molecule (established in [1]), making it one of the most attractive candidates for resistive gas sensors [2−5], and recently for bio-sensors [6−10]. The objects typically considered in the latter case are macromolecules (MM), which are systems (plaques) with a large number of atoms and linear dimensions of the order of hundreds of angstroms. Neither the geometry of such a plaque nor the area of its contact with the substrate are known, and are furthermore not strictly fixed. It is clear that direct application of DFT (Density Functional Theory) methods is difficult in this case. For this reason, the bond (adhesion) of MM with single-layer graphene (SLG) is described in [11] by the model of dangling bonds (DBM), assumed to be responsible for stitching MM with SLG. The DBM offers a simplified algorithm for considering the problem, making it possible to obtain analytical expressions for charge transition from a macromolecule to graphene and the adhesion energy of a macromolecule in graphene.

Let us introduce the terminology for molecules. Electrons fill all the orbitals with the lowest energies in the ground state of the molecule. The orbital that has the highest energy among those filled in the ground state is referred to as HOMO (Highest Occupied Molecular Orbital). The orbital with the lowest energy is called LUMO (Lowest Unoccupied Molecular Orbital).

In this paper, the bond between a macromolecule and single-layer graphene is described by a two-layer model of a macromolecule with a lower HOMO level, and a vacant upper LUMO level [12−15]. This model is referred to as HLM (HOMO-LUMO Model).

Description of the proposed model

Let us consider the adsorption of a macromolecule by SLG within the framework of HLM. The HOMO and LUMO energies of a free macromolecule are denoted as ε^0_- and ε^0_+, respectively. The occupation numbers for HOMO and LUMO at zero temperature (0 K) are by definition equal to $n^0_- = 2$ and $n^0_+ = 0$. The HOMO and LUMO energies for a macromolecule adsorbed by SLG with the output work φ_{SLG} are taken to be equal to

$$\varepsilon_{\mp} = \varepsilon^0_{\mp} + \varphi_{SLG}.$$

The energy gap between LUMO and HOMO is $\Delta_{LH} = \varepsilon_+ - \varepsilon_-$. According to the description in [11], the densities of states (DOSs) per spin projection on the HOMO and LUMO orbitals interacting with graphene are expressed as

$$\rho_{\mp}(\omega) = \frac{1}{\pi} \frac{\Gamma_{\mp}(\omega)}{(\omega - \varepsilon_{\mp} - \Lambda_{\mp}(\omega))^2 + \Gamma^2_{\mp}(\omega)}, \tag{1}$$

where ω is the energy variable; $\Gamma_m(\omega)$, $\Lambda_m(\omega)$ are the broadening and shift functions, respectively;

$$\Gamma_{\mp}(\omega) = \pi V^2_{\mp} \rho_{SLG}(\omega),$$

and the shift function $\Lambda_{\mp}(\omega)$ is a Hilbert transform of $\Gamma_{\mp}(\omega)$ ($V_{\mp}$ is the matrix element of HOMO-LUMO coupling with the electronic spectrum of SLG, $\rho_{SLG}(\omega)$ is the DOS of free-standing single-layer graphene).

The DOS of free-standing graphene in the low-energy approximation is equal to

$$\rho_{SLG}(\omega) = \begin{cases} |\omega|/\zeta, & |\omega| < \zeta, \\ 0, & |\omega| \geq \zeta, \end{cases}$$

where ζ is the cutoff energy, $\zeta = \sqrt{\pi\sqrt{3}/4}t$; t is the energy of the electron transition between the nearest neighbors in graphene, $t \approx 3$ eV.

Then the broadening and shift functions of an arbitrary level interacting with graphene have the form

$$\Gamma(\omega) = \pi V^2 \rho_{SLG}(\omega), \quad \Lambda(\omega) = (V^2 \omega / \zeta^2) \ln[\omega^2 / (\zeta^2 - \omega^2)].$$

We represent DOSs (1) in the form introduced in [11]:

$$\rho_{\pm}(\omega) \approx \frac{1}{\pi} \frac{\Gamma_{\mp}}{(\omega - \overline{\varepsilon}_{\mp})^2 + \Gamma^2_{\mp}}, \tag{2}$$

where $\overline{\varepsilon}_{\mp} = \varepsilon_{\mp} + \Lambda_{\mp}$, $\Lambda_{\mp} = \overline{\varepsilon}_{\mp}(V_{\mp}/\zeta)^2 \ln[\overline{\varepsilon}^2_{\mp}/(\zeta^2 - \overline{\varepsilon}^2_{\mp})]$, $\Gamma_{\mp} = \pi V^2_{\mp} \rho_{SLG}(\overline{\varepsilon}_{\mp})$.

The equation $\omega - \varepsilon_{\mp} - \Lambda(\omega) = 0$ defines the values of $\overline{\varepsilon}_{\mp}$. If we assume that $V_- = V_+ = V$, we can prove that a sufficient condition for replacing expression (1) with expression (2) is that the inequality $|\varepsilon_{\pm}| < \zeta/e$ be fulfilled.

At zero temperature and Fermi level ε_F, the HOMO-LUMO occupation numbers are determined by the expression

$$n_{\mp} = \frac{2}{\pi} \text{arccot} \frac{\text{sgn}(\overline{\varepsilon}_{\mp}) - \varepsilon_F / |\overline{\varepsilon}_{\mp}|}{\pi \{V_{\mp}/\zeta\}^2}. \tag{3}$$

For $\varepsilon \equiv \overline{\varepsilon}_+ = -\overline{\varepsilon}_-$, we have

$$Z_{\mp} = \pm[1 - (2/\pi)\arctan(\zeta^2/\pi V^2).$$

The total charge transferred from a macromolecule to SLG is equal to $Z_{SLG} = -(Z_- + Z_+)$, i.e., there is no charge transfer between them. At $\varphi_{SLG} > 0$, the quantity Z_- increases, and $|Z_+|$ decreases, so consequently SLG gains electrons and acquires n-type conductivity. At $\varphi_{SLG} < 0$, the situation is reversed and SLG has p-type conductivity. The band gap at $e\varepsilon/\zeta < 1$ is expressed as

$$\overline{\Delta}_{LH} = \Delta_{LH}[1 + (V/\zeta)^2 \ln(\varepsilon/\zeta)] < \Delta_{LH} = 2\varepsilon.$$

Molecular fragments of O_2, NO, NH, CH_2, NH_2 and CH_3 were considered in [11] as sources of dangling bonds. If the values of ε^0_- and ε^0_+ are estimated assuming

$$\varepsilon^0_- = \min\{I_{mol}\}, \quad \varepsilon^0_+ = \max\{A_{mol}\},$$

where I_{mol}, A_{mol} is the ionization energy and electron affinity (the values of these energies for the above molecules are given in [16]), and since for free-standing single-layer graphene [11],

$$\phi_{SLG} = 4.5 \text{ eV and } V/\zeta \sim 1,$$

then we obtain for NO and NH molecules

$$\varepsilon_+ / |\varepsilon_-| \sim \overline{\varepsilon}_+ / |\overline{\varepsilon}_-| \sim 1,$$

so the estimates obtained by equality $\varepsilon \equiv \varepsilon_+ = \varepsilon_-$ are accurate in order of magnitude. For the remaining molecules considered in [11], $\varepsilon_+/|\varepsilon_-| \approx 0.6$.

Adsorption of macromolecules on epitaxial graphene

The adsorption of a macromolecule on epigraphene is described by the same approach as in the previous section, assuming weak coupling between graphene and the substrate, with $\Gamma'_{\mp}(\omega)/t << 1$, i.e., considering quasi-free-standing graphene. This mode is implemented technologically, guaranteeing that the unique properties of free-standing graphene are largely preserved.

Table 1

Values of key parameters for macromolecule/SLG/SiC polytype structure

Polytype	D	E_g	X	$\omega_{sc} - \varepsilon_D$
		eV		
3C	0	2.40	4.00	–0.70
8H	0.25	2.86	3.58	–0.51
21R	0.29	2.96	3.52	–0.50
6H	0.33	3.00	3.45	–0.45
15R	0.40	3.06	3.33	–0.37
27R	0.44	3.13	3.27	–0.34
4H	0.50	3.23	3.17	–0.29

Notations: E_g is the band gap, χ is the electron affinity, ω_{sc} is the energy of the center of the forbidden zone, ε_D is the mid-band gap energy; D is the degree of hexagonality of polytypes, indicated by letters corresponding to the Bravais lattice (C for cubic, H for hexagonal, R for rhombohedral).

Then, resorting to the same simplifications as in the previous section, we obtain the LUMO and HOMO occupation numbers of the form

$$\tilde{n}_{\mp} \approx \frac{2}{\pi} \text{arccot} \frac{\tilde{\varepsilon}_{\mp} - \varepsilon_F}{\tilde{\Gamma}_{\mp}}, \tag{4}$$

where $\tilde{\varepsilon}_{\mp} = \overline{\varepsilon}_{\mp} + \Lambda'_{\mp}(\tilde{\varepsilon}_{\mp})$, $\tilde{\Gamma}_{\mp} = \pi V_{\mp}^2 \rho_{SLG}(\tilde{\varepsilon}_{\mp})$.

In the case of a semiconductor substrate, DOS with the band gap E_g can be represented as

$$\rho_{sc}(\omega) = \begin{cases} \overline{\rho}_{sc}, & |\Omega_{sc}| \geq E_g / 2, \\ 0, & |\Omega_{sc}| < E_g / 2, \end{cases}$$

where $\overline{\rho}_{sc} = \text{const}$, $\Omega_{sc} = \omega - \omega_{sc}$ (ω_{sc} is the bandgap center [17]).
Then,

$$\overline{\Gamma}_{sc} = \pi V_{sc}^2 \overline{\rho}_{sc}, \quad \Lambda_{sc}(\omega) = (\overline{\Gamma}_{sc} / \pi) \ln[(\Omega_{sc} - E_g / 2) / (\Omega_{sc} + E_g / 2)].$$

where V_{sc} is the matrix element of the interaction between the semiconductor and SLG.
The LUMO and HOMO occupation numbers are determined by Eq. (4). The case when $\varepsilon_F = \varepsilon_D = 0$ corresponds to doped SiC polytype and pristine SLG, the case when $\varepsilon_F = \omega_{sc}$ corresponds to pristine polytype and doped SLG.

As an example, consider adsorption of a macromolecule on SLG formed by SiC polytypes. The energy parameters of these polytypes and the degree of their hexagonality D are taken from [18] (Table 1).

In the case of pristine polytypes ($\varepsilon_F = \omega_{sc}$), the values of $\tilde{n}_{\mp}$ in the series $3S \rightarrow 4N$ increase, and the total charge $\tilde{Z} = 2 - \tilde{n}_- - \tilde{n}_+$ on the macromolecule decreases. In this case, the electrons are transferred into SLG, which acquires a charge $-\tilde{Z}$. Thus, the SLG formed on $3S$-SiC acquires the greatest charge. Furthermore, the charge transition between the macromolecule and the SLG/polytype SiC structure is influenced by polytype face selected.

For example, the electron work functions for Si- and C-faces of the SLG/$6H$-SiC structure differ by about 1.5 eV [19]. A more rigorous approach to describing adsorption of atoms and molecules on epitaxial graphene is outlined in [17]. However, the simplifications made seem acceptable for estimating charge transfer in situations with scarce experimental data. For example, the calculations from the first principles [20] indicate that HOMO energies lie in the range from -12 to -4 eV (relative to vacuum). Comparing the data in Tables 1 and 2, we can see that the ionization energies I used for estimates in this work and in [11] are close to the lowest values of HOMO energies. Unfortunately, LUMO energies are not given in [20].

T a b l e   2

Ionization energies of molecules [16]

Molecule	O_2	NO	CH_2	NH_2	CH_3
I, eV	12.1	9.3	10.4	10.2	11.4

Conclusion

Compared with the DBM model used in [11], the HLM model proposed in this study allows to considerably reduce the number of theoretical parameters. We should emphasize, however, that experimental data are required to more accurately determine the values of the theoretical parameters even in the case of HLM. The common expectations held by the authors of model theories for numerical calculations from the first principles, allowing to assess the applicability of the models, are likely unrealistic, since detailed data on the geometry of the adsorbed macromolecule are generally unavailable.

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THE AUTHORS

LEBEDEV Alexander A.
Ioffe Institute of RAS
26 Polytekhnicheskaya St., St. Petersburg, 194021, Russia
shura.lebe@mail.ioffe.ru

DAVYDOV Sergey Yu.
Ioffe Institute of RAS
26 Polytekhnicheskaya St., St. Petersburg, 194021, Russia
Sergei_Davydov@mail.ru

СВЕДЕНИЯ ОБ АВТОРАХ

ЛЕБЕДЕВ Александр Александрович − *руководитель отделения твердотельной электроники Физико-технического института имени А. Ф. Иоффе РАН.*
194021, Россия, г. Санкт-Петербург, Политехническая ул., 26
shura.lebe@mail.ioffe.ru

ДАВЫДОВ Сергей Юрьевич − *доктор физико-математических наук, ведущий научный сотрудник лаборатории физики полупроводниковых приборов Физико-технического института имени А. Ф. Иоффе РАН.*
194021, Россия, г. Санкт-Петербург, Политехническая ул., 26
Sergei_Davydov@mail.ru