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Rare-earth atoms adsorption on epitaxial graphene: Analytical estimates

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Epitaxial single-layer graphene (SLG) is considered as a „tool" for extracting rare earth metal (REM) atoms from the environment. Estimates of the charge transition Z_a between adatoms and graphene and the values of the adsorption energy E_{ads} for a single REM adatom and, taking into account dipole-dipole repulsion, at their final concentration up to monolayer are given. The influ-ence of the SiC substrate on Z_a and E_{ads} is discussed.

Keywords: nonzero adatoms concentration, dipole-dipole repulsion, SiC substrate.

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The main methods of „mining" of rare earth metals (REMs), which are becoming increasingly sought after, are the extraction of REM atoms from aqueous solutions [1], weathered rock [2], and FeNdB and SmCo permanent magnets [3]. A method for extracting REM atoms by adsorbing them on mesoporous carbon with DNA molecules attached to it was detailed in [4], and the use of pyrolytic carbon materials for the same purpose was discussed in [5]. Thus, the problem of interaction of REMs with carbon structures is a relevant one. The simplest structure of this kind is single-layer graphene (SLG), which cannot exist in a completely free state and, consequently, cannot serve as a tool for REM „mining." Therefore, the present study is focused on the adsorption of REM atoms on epitaxial graphene (epigraphene) formed on silicon carbide polytypes. The substrate material was chosen for the following reasons: first, SiC polytypes are used to obtain SLG and BLG (bilayer graphene) by thermal desorption of silicon atoms from the surface of silicon carbide; second, graphene/SiC structures are used often in nanoelectronic devices [6].

As far as we know, the issue of adsorption of a single rare earth atom on free single-layer graphene has been discussed for the first time in [7,8]. If fairly rough (semi-quantitative at best) estimates of the adsorption energy are sufficient, it may be assumed that one s- orbital of a REM with energy ε_s interacts with p_z- orbitals of graphene carbon atoms. The Green's function of a REM adatom then takes the form

$$G_s^{-1}(\omega) = \omega - \varepsilon_s - \Lambda_G(\omega) + i\Gamma_G(\omega), \qquad (1)$$

where ω is the energy variable and $\Lambda_G(\omega)$ and $\Gamma_G(\omega)$ are the shift and broadening functions, respectively, of the s state of the adatom caused by its interaction with SLG, which are defined unambiguously by the model of density of states of graphene $\rho_G(\omega)$. The M-model [9] was used as $\rho_G(\omega)$ in [7]. It was demonstrated in [10] that the M-model and the low-energy approximation to the electron spectrum of graphene (linearization of the density of states in energy near Dirac point ε_D) yield close occupation numbers of adatoms. It follows from (1) that density of states $\rho_s(\omega) = -\pi^{-1}\mathrm{Im}G_s(\omega)$ at the s level of an adatom is a pseudo-Lorentzian contour with the distribution center and half-width depending on ω. The following simplification is often used in the theory of adsorption and epitaxial layers: energy ω^*, which is the root of equation

$$\omega - \varepsilon_s - \Lambda_G(\omega) = 0, \qquad (2)$$

is taken as the center of a Lorentz distribution, and $\Gamma_s(\omega^*)$ is assumed to be the half-width at half maximum.

Let us consider the regime of weak binding of an adatom with a substrate first: $V_s^2 \ll t^2$, where V_s is the matrix element of interaction of the s orbital of a REM atom and the p_z orbital of a carbon atom and t is the energy of electron hopping between the nearest neighbors in graphene (hopping energy). In this case, the ε_s level of a free atom shifts to position $\omega^* \equiv \bar{\varepsilon}_s \approx \varepsilon_s + \Lambda_G(\varepsilon_s) \sim \varepsilon_s$; here and elsewhere, the bar above indicates that the symbol characterizes an adsorbed atom. Density of states (per spin projection) $\bar{\rho}_a(\omega)$ and adatom charge Z_a (at zero temperature) may then be defined approximately as

$$\bar{\rho}_a(\omega) \approx \frac{1}{\pi}\frac{\Gamma_s}{(\omega - \bar{\varepsilon}_s)^2 + \Gamma_s^2}, \overline{Z}_a \approx \frac{2}{\pi}\arctan\frac{\bar{\varepsilon}_s - \varepsilon_F}{\Gamma_s}, \qquad (3)$$

where $\Gamma_s = \Gamma_G(\bar{\varepsilon}_s)$ and ε_F is the Fermi level (zero for undoped graphene). The results of calculation of charge transfer between REMs and SLG, which is numerically equal to Z_a, are presented in Fig. 6 [7]; Table 4 in the same study lists the values of adsorption energy E_{ads}. Note that the M-model of the density of states of free graphene [9] was used in [7], and its work function was taken to be equal to $\varphi_{\text{SLG-1}} = 5.11$ eV [11], while its current generally accepted value is $\varphi_{\text{SLG-2}} = 4.5$ eV [10]. Since ratio $(\varphi_{\text{SLG-1}} - \varphi_{\text{SLG-2}})/\varphi_{\text{SLG-1}} \sim 0.1$ and REM atom ionization energies $I \sim 5{-}6$ eV [12], the trends of variation of Z_a and E_{ads} in the lanthanide series, which were revealed in [7], evidently remain valid at $\varphi_{\text{SLG-2}} = 4.5$ eV.

Let us move on to the case of a finite concentration of adatoms and assume that REM atoms form a 2D hexagonal lattice. We then introduce degree of coverage $\Theta = N/N_{\mathrm{ML}}$, where $N(N_{\mathrm{ML}})$ is the concentration of adatoms in a submonolayer (monolayer). If the surface of graphene is assumed to be covered with closely packed disks with radii R centered at the vertices and centers of hexagons (see Fig. 1.27 *a* in [12]), $\Theta = r_{af}^2/R^2$, where r_{af} is the radius of a rare earth atom. Note that the distance between nearest neighbors in bulk REM samples is $a_f \approx 2r_{af}$; therefore, $a_{\mathrm{Gr}}/a_f \sim 0.4$ (see [12] and Table 1.4 in [13]). The results of DFT (density functional theory) calculations [14] do indeed confirm that REM atoms on graphene form two-dimensional islands with hexagonal close packing.

Let us consider the dependence of adsorption characteristics on degree of coverage Θ of graphene with REM adatoms by modeling the layer of REM adatoms by a hexagonal lattice of parallel dipoles formed by the charges of adatoms and their images in the substrate [15,16]. The magnitude of charge transfer, which is numerically equal to adatom charge itself $Z_a(\Theta)$, is specified by the self-consistent equation

$$\overline{Z}_a(\Theta) = \frac{2}{\pi}\arctan\frac{\varepsilon_s - \varepsilon_F - \Theta^{3/2}\xi\bar{Z}_a(\Theta)}{\Gamma_s}. \qquad (4)$$

Here, $\xi = 2e^2 l_{ads}^2 N_{\mathrm{ML}}^{3/2} A$ is the dipole-dipole repulsion constant, e is the elementary charge, l_{ads} is the adsorption bond length, $A \approx 10$ is a coefficient [15,16], and $\varepsilon_F = 0$ for undoped graphene. Assuming that $N_{\mathrm{ML}} = a_f^{-2}$ and $l_{ads} = a_f$, we obtain $\xi \approx 150\,\mathrm{eV}$. Setting $\varepsilon_s = 1.5\,\mathrm{eV}$ and $\Gamma_s = 0.5\,\mathrm{eV}$ for numerical estimates, we find that the adatom change in a monolayer is $Z_a(1) \approx \varepsilon_s/\xi \sim 0.01$ at $\Theta = 1$, which is almost two orders of magnitude lower than the charge of a single REM adatom. This is depolarization that results from any interaction of atoms in the adsorbed layer [15,16]. It is assumed in this case that the lattice of adatoms is compressed uniformly with an increase in Θ, maintaining its hexagonal structure. Dependence $\Delta\varphi_{\mathrm{EG}}(\Theta)$ of the work function of epitaxial graphene (EG, epigraphene), which is equal to $\Delta\varphi_{\mathrm{EG}}(\Theta) = -\Theta\Phi Z_a(\Theta)$, where $\Phi = 4\pi e^2 l_{ads}^2 N_{\mathrm{ML}}$, is similar to the dependence shown in Fig. 9.1 in [16]. This figure makes it clear how charge $Z_a(\Theta)$ of adatoms decreases with an increase in their concentration. As before, we set $l_{ads}^2 N_{\mathrm{ML}} = 1$ and find $\Phi \approx 180\,\mathrm{eV}$. Thus, an SLG monolayer reduces the work function of epigraphene by almost 2 eV.

Let us proceed to estimating the adsorption energy of REM atoms on SLG, which may be presented as a sum of ionic and metallic components [7,16]: $E_{ads}(\Theta) = E_{ion}(\Theta) + E_{met}(\Theta)$, where the contribution of potential energy E_{pot}, which is independent of Θ, was omitted. The ionic component may be estimated using a simple electrostatic formula: $E_{ion}(\Theta) \approx -Z_a^2(\Theta)e^2/4l_{ads}$. According to [7], the metallic component of adsorption energy for a single atom may be presented as $E_{met}(0) \approx -3\hbar^2/8m_e r_{af}^2$, where m_e is the electron mass and it is taken into account that the kinetic energy of an electron is on the order of $\hbar^2/2m_e r_{af}^2$ in a free atom and on the order of $\hbar^2/2m_e l_{ads}^2$ in an adatom [7]. In a monolayer, when the atomic s-electron is almost completely delocalized due to transition to the conduction band of epigraphene, we have $E_{met}(1) \approx -\hbar^2/2m_e r_{af}^2$. Thus, $E_{ion} \approx -1.4\,\mathrm{eV}$, $E_{met} \approx -1.3\,\mathrm{eV}$, and $E_{ads} \approx -2.7\,\mathrm{eV}$ correspond to the adsorption of a single REM atom; in a monolayer, the adsorption energy per single adatom is $E_{ads} \approx E_{met} \approx -1.7\,\mathrm{eV}$. It should be noted here that the latter estimate is valid for adsorption of atoms that do not interact with each other. However, since a REM monolayer is 2D, one needs to take into account the delocalization of three electrons (two s and one d) and the additional contribution of the interaction of f and d orbitals [17]. The $|E_{ads}| \approx 1.7\,\mathrm{eV}$ estimate obtained here agrees closely with the results of numerical calculations of the adsorption energy for Nd and Gd (1.88 and 1.61 eV, respectively), but exceeds significantly the results for Eu (0.90 eV) and Yb (0.32 eV) (see Table 1 in [14]).

Just as in [7], we have so far considered the regime of weak binding of adatoms with graphene. This is the regime suitable for nanoelectronics, since it ensures that graphene retains its unique properties. However, the opposite case is of interest for REM „mining." In the strong binding regime with $V_s^2 \gg t^2$, epigraphene is superseded by a hexagonal lattice of weakly bound dimers consisting of REM and carbon atoms. It is easy to demonstrate that the binding energy of such carbon dimers is $E_b = 2V_2(1 - 2\alpha_c^2/3)/\alpha_c$ [18,19], where the covalent energy of a σ-bond of the p_z orbital of carbon with the s REM orbital is $V_2 = 1.42(\hbar^2/m_e l_{ads}^2)$, polar energy $V_3 = (\varepsilon_p + I_{\mathrm{REM}})/2$, bond covalence $\alpha_c = V_2/\sqrt{V_2^2 + V_3^2}$, $\varepsilon_p = -11.07\,\mathrm{eV}$ is the energy of the p state of a carbon atom [20], and $I = 5{-}6\,\mathrm{eV}$ is the REM ionization energy [12]. Inserting the calculated values of $V_2 \approx 1.14\,\mathrm{eV}$, $V_3 \approx 2.1{-}2.5\,\mathrm{eV}$, and $\alpha_c \approx 0.48{-}0.55$ into the above formula, we obtain $E_b \approx 3.3{-}4.0\,\mathrm{eV}$. Note that the V_2 matrix elements were estimated for so-called a-type (atop) adsorption, when an adatom is bound to a single carbon atom. However, it was demonstrated in [14] that c-type (center) adsorption with an adatom located above the center of a carbon hexagon is more energetically favorable. These cases (together with b-type (bridge) adsorption) were discussed in detail in [21], where a simple model was used to demonstrate that the maximum value of adsorption energy of a single atom depends only weakly on the type of adsorption (see Fig. 5 in [21]).

To conclude, let us examine briefly how the presence of a SiC- substrate affects the above results. According to [22], energies $\bar{\omega}_c$ of the centers of band gaps of SiC polytypes are (in eV): $-0.70\,(2C)$, $-0.51\,(8H)$, $-0.50\,(21R)$, $-0.45\,(6H)$, $-0.36\,(15R)$, $-0.34\,(27R)$, and $-0.29\,(4H)$, where Dirac point ε_D of undoped SLG is assumed to correspond to zero energy. Using the Haldane–Anderson model to characterize the density of states of the SiC

substrate [14,15] ($\rho_{\mathrm{SiC}}(\omega) = \rho = \mathrm{const}$ at $|\Omega_c| \leqslant E_g/2$ and 0 at $|\Omega_c| > E_g/2$, where $\Omega_c = \omega - \omega_c$ and E_g is the band gap of a SiC polytype), we obtain the function of broadening of epigraphene states: $\Gamma_{\mathrm{EG}}(\omega) = \tilde{\Gamma} = \mathrm{const}$ at $|\Omega_c| \leqslant E_g/2$ and 0 at $|\Omega_c| > E_g/2$. The shift function is $\Lambda_{\mathrm{EG}}(\omega) = (\tilde{\Gamma}/\pi) \ln |(\Omega_c - E_g/2)/(\Omega_c + E_g)|$. In the regime of weak graphene-substrate binding, $\tilde{\Gamma} = \pi \tilde{V}^2 \rho \ll E_g$ ($\tilde{V}$ is the matrix element of graphene-substrate interaction; the tilde above the symbol indicates that is corresponds to epigraphene), epigraphene Dirac point shift $\delta\varepsilon_D \approx -4\omega_c \tilde{\Gamma}/E_g$, and $|\Delta\varphi_{\mathrm{SLG}}| = |\delta\varepsilon_D| \ll |\omega_c|$. Therefore, the results reported in [7] are perfectly suitable for rough estimation in the presence of a substrate. The model approach to characterizing the influence of a substrate on the adsorption properties of epigraphene was discussed in sufficient detail in [23].

We believe that the above analysis proves that epitaxial SLG is a convenient „tool" for extracting rare earth atoms from the environment. The same is true for epitaxial BLG (bilayer graphene) and FLG (few-layer graphene).

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] I. Anastopoulos, A. Bhatnagar, E.C. Lima, J. Mol. Liq., **221**, 954 (2016). DOI: 10.1016/j.molliq.2016.06.076

[2] A.M. Borst, M.P. Smith, A.A. Finch, G. Estrade, C. Villanova-de-Benavent, P. Nason, E. Marquis, N.J. Horsburgh, K.M. Goodenough, C. Xu, J. Kynický, K. Gerak, Nat. Commun., **11**, 4386 (2020). DOI: 10.1038/s41467-020-17801-5

[3] A. Vardanyan, A. Guillon, T. Budnyak, G.A. Seisenbaeva, Nanomaterials, **12**, 974 (2022). DOI: 10.1021/acsami.0c09393

[4] C.E. Unsworth, C.C. Kuo, A. Kuzmin, S. Khalid, D. Saha, ACS Appl. Mater. Interfaces, **12**, 43180 (2020). DOI: 10.1021/acsami.0c10184

[5] M. Nogueira, M. Bernardo, M. Ventura, I. Matos, F. Pinto, N. Lapa, Processes, **12**, 2257 (2024). DOI: 10.3390/pr12102257

[6] A.A. Lebedev, P.A. Ivanov, M.E. Levinshtein, M.E. Mokhov, S.S. Nagalyuk, A.N. Anisimov, P.G. Baranov, Phys. Usp., **189** (8), 754 (2019). DOI: 10.3367/UFNr.2018.10.038437.

[7] S.Yu. Davydov, Phys. Solid State, **55** (7), 1536 (2013). DOI: 10.1134/S1063783413070093.

[8] Z.Z. Alisultanov, Low Temp. Phys., **39**, 172 (2013). DOI: 10.1063/1.4791767

[9] S.Yu. Davydov, G.I. Sabirova, Phys. Solid State, **53** (3), 654 (2011). DOI: 10.1134/S1063783411030061.

[10] S.Yu. Davydov, O.V. Posrednik, Phys. Solid State, **57** (8), 1686 (2015). DOI: 10.1134/S1063783415080053.

[11] D. Niesner, T. Fauster, J. Phys.: Condens. Matter, **26**, 393001 (2014). DOI: 10.1088/0953-8984/26/39/393001

[12] *Physical quantities. Handbook*, edited by I.S. Grigoriev, E.Z. Meilikhov (Energoatomizdat, M., 1991).

[13] C. Kittel, *Introduction to solid state physics* (Wiley, N.Y., 1971).

[14] X. Liu, C.Z. Wang, M. Hupalo, Y.X. Yao, M.C. Tringides, W.C. Lu, K.M. Ho, Phys. Rev. B, **82**, 245408 (2010). DOI: 10.1103/PhysRevB.82.245408

[15] S.Yu. Davydov, S.V. Troshin, Phys. Solid State, **40** (8), 1583 (2007). DOI: 10.1134/S1063783407080318.

[16] S.Yu. Davydov, A.A. Lebedev, O.V. Posrednik, *Elementary introduction to the theory of nanosystems* (Lan, St. Petersburg, 2014).

[17] W.A. Harrison, G.K. Straub, Phys. Rev. B, **36**, 2695 (1987). DOI: 10.1103/physrevb.36.2695

[18] W.A. Harrison, Phys. Rev. B, **27**, 3592 (1983). DOI: 10.1103/PhysRevB.27.3592

[19] S.Yu. Davydov, O.V. Posrednik, Phys. Solid State, **57** (4), 837 (2015). DOI: 10.1134/S1063783415040095.

[20] W.A. Harrison, Phys. Rev. B, **31**, 2121 (1985). DOI: 10.1103/PhysRevB.31.2121

[21] T.L. Einstein, J.R. Schrieffer, Phys. Rev. B, **7**, 3629 (1973). DOI: 10.1103/PhysRevB.7.3629

[22] S.Yu. Davydov, A.A. Lebedev, Phys. Solid State, **65** (12), 1966 (2023). DOI: 10.61011/PSS.2023.12.57638.4910k.

[23] S.Yu. Davydov, Phys. Solid State, **56** (7), 1483 (2014). DOI: 10.1134/S1063783414070087.

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