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Migration of Impurities in the Structure of Graphene

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The laws of single-particle migration of atoms in the one-layer hexagonal structure are considered. It is accepted that impurity atom contacts with one of structure cell and can execute the single-order jumps. The exact solution of the infinite collection of microscopic equations of migration is written in the technique of the generating function and appropriate macroscopic characteristics are found. It is determined that the general pattern of transfer qualitatively coincides with the laws of particle diffuse propagation and rate of the propagation process in the graphene structure exceeds the same value for the comparable two-dimensional square array. The method for finding the exact solution of migration problem in the limited medium is formulated on the basis of the results for infinite medium. The migration pattern in the frontier area of the graphene sheet and in the structure modeling a carbon nanotube is defined. The probable variations of the observed characteristics connected with the presence of impurities as the result of migration processes are discussed.

Keywords: Graphene, Impurities, Migration, Generating function, Distribution of atoms.

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1. INTRODUCTION

Propagation of atoms in solids is one of the features of different physical processes and technologies [1-3]. In particular, particle transfer attracts attention of the researchers of nanostructures [4, 5] from the point of view of both the systematization of the accumulated empirical material and in order to form theoretical conceptions. Nanostructure is one of the most interest such objects. It represents an isolated layer of carbon atoms – graphene, which is the object of intent interest during last years [6]. There are many publications where transfer processes in graphene are the object of paramount or concomitant attention. The electron transfer, which defines serious prospects of applied usage, is discussed most often. Transfer of atoms, defects, and some types of excitations, for example, Frenkel excitons was found to be out of the attention of the majority of researches studying the common questions.

However, interest to impurity nanostructures still increases. This is determined by both the logics of basic concepts – consideration of more complex objects – and by the fact that presence of impurities involves considerable changes in the properties of "pure" structures and appearance of quite new features. In particular, it is established that presence of impurities of different types significantly changes the conductance of graphene that allows to use this effect as high-sensitive indicator of the corresponding pollutions [7, 8]. Essential influence of the presence of impurities on the transport characteristics of graphene is also shown [9, 10]. It is revealed that rather small impurity concentrations considerably influence the observed object properties. No doubt that this observation also extends to separate regions of the whole structure, thereby the question about the space distribution of impurities gains a special interest.

In the present work, we investigate the microkinetics of motion of different-type particles (hereinafter atoms) without prior approximations about macroscopic properties of the transfer process. A single-particle migration scheme is used here that, apparently, is adequate to the conditions of the real processes in nanostructures. It is clear that model of single-particle migration cannot cover all sides of the migration process: for example, interaction effect between migrating particles remains out of the analysis. However, due to the fact that impurity component plays an important role at a sufficiently low doping level, when interactions (collisions) of impurity atoms are wittingly low-probable, a single-particle model is some stage of coverage of the whole complex of such effects. The given consideration is virtually present in the work [11].

2. MODEL REPRESENTATION

Migration in a honeycomb structure (the structure of graphene) supposes jumps of atoms from the allowed positions to the neighbor ones. In the discussion of such processes, an overwhelming prevalence of the jumps by one step only is usually meant [1] ("closest neighbors") that is virtually evident and will be also used within the present work. In this case, however, some variants of the kinematics of atomic movement are possible, and the arrangement of the equilibrium positions of atoms in the structure is one of the possible attributes of the quantitative and, probably, qualitative difference in the migration mechanisms. A number of variants of possible positions is limited and completely determined by the structure symmetry.

Within the present work, we assume the variant of migration when migrating atoms are located inside (for convenience, in the center) of regular hexagons which the whole structure consists of. This suggests equality of the interaction with six closest carbon atoms and also the presence of six similar positions in the immediate neighborhood. In this case, a foreign atom looks as an interstitial impurity.

We note that the model represented here does not

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require an arrangement of foreign atoms in the plane of graphene surely. A point in the hexagon center can be interpreted as a projection of the nominal position on the plane of graphene (epicenter).

Arrangement of allowed positions in the structure is specified by two numbers. It is convenient to use double indexing and orient count direction of one integer index ("m") along the normal to the hexagon side, and of another one ("n") – parallel to the side. Migration equations in the dimensionless form are written as

$$\frac{d\varphi_{mn}}{d\tau} = \varphi_{m-2,n} + \varphi_{m+2,n} + \varphi_{m-1,n-1} + \\ +\varphi_{m-1,n+1} + \varphi_{m+1,n-1} + \varphi_{m+1,n+1} - 6\varphi_{mn}. \quad (1)$$

3. GENERAL PROPERTIES OF MIGRATION

Multiplying equations (1) by $\exp[i(ms_m + ns_n)]$, where s_m and s_n are the artificial parameters, and summing all equations, we reduce an infinite system of equations (1) to one equation for the Fourier sum (the generating function)

$$G = \sum_{m,n} \varphi_{mn} e^{i(ms_m + ns_n)} . \quad (2)$$

We have

$$\frac{dG}{d\tau} = \left[2\cos(2s_m) + 2\cos(s_m - s_n) + 2\cos(s_m + s_n)\right]G . \quad (3)$$

Assuming for certainty that particle is introduced into position (0, 0) in the initial moment, we write

$$G(s_m, s_n, \tau) = \exp\left[2(\cos 2s_m + 2\cos s_m \cos s_n - 3)\tau\right] . \quad (4)$$

Mean values $\overline{m}$ and $\overline{n}$ are determined by function (4) using the rules following from meaning of G(2)

$$\overline{m} = -i\frac{\partial G}{\partial s_m}(0,0,\tau) , \ \overline{n} = -i\frac{\partial G}{\partial s_n}(0,0,\tau) \quad (5)$$

that gives $\overline{m} = \overline{n} = 0$. This means that during random uncorrelated jumps position of the "mass center" of the distribution remains constant.

Subsequent distribution moments are found by the operations

$$\overline{m^2} = \frac{\partial^2 G}{\partial {s_m}^2}(0,0,\tau) , \ \overline{n^2} = \frac{\partial^2 G}{\partial {s_n}^2}(0,0,\tau) .$$

We obtain

$$\overline{m^2} = 12\tau , \ \overline{n^2} = 4\tau .$$

Discrepancy of the values $\overline{m^2}$ and $\overline{n^2}$ does not mean the distribution anisotropy, since change in the indexes m and n by unit corresponds to unequal shifts in the space. The root-mean-square distance from position of the initial localization is changed by the law

$$\left(\overline{r^2}\right)^{\frac{1}{2}} = 3\sqrt{2}a\tau^{\frac{1}{2}} , \quad (6)$$

where a is the distance between sites in the hexagon structure.

Result (6) quantitatively corresponds to the laws of the diffusion propagation in the simplest models of diffusion. However, propagation velocity differs from that obtained for other structures. It is not difficult to show that diffusion coefficient defined by (6) is considerably higher than the same value for square grating with the same distance between atoms that is connected with the increase in the number of channels of particle jumps.

Pattern of the site-by-site change in the probabilities of occupation positions is given by a set of functions $\varphi_{mn}(\tau)$. The obtained expression for function G in accordance with definition (2) gives the possibility to find any function φ_{mn} by the operation

$$\varphi_{mn}(\tau) = \frac{1}{(2\pi)^2}\int\int_{-\pi}^{\pi} G(s_m, s_n, \tau) e^{-i(ms_m + ns_n)} ds_m ds_n . \quad (7)$$

Thus,

$$\varphi_{mn}(\tau) = \frac{1}{(2\pi)^2}\int\int_{-\pi}^{\pi} \cos(ms_m) \times \\ \times \cos(ns_n) e^{2[\cos 2s_m + 2\cos s_m \cos s_n - 3]\tau} ds_m ds_n . \quad (8)$$

Expression (8) gains a special transparency within the asymptotic zone ($\tau >> 1$). Structure of the integrand is such that at large values of τ the contribution to the integration result gives quite narrow range of the values s_m and s_n in the vicinity of zero. Introducing quadratic approximation of the exponent (8) and integrating in infinity limits, we obtain

$$\varphi_{mn} \approx \frac{A}{\tau} e^{-\frac{m^2 + 3n^2}{24\tau}} , \ A = \frac{1}{4\sqrt{3}\pi} . \quad (9)$$

According to the way of cell indexation, formula (9) should be applied when difference $m - n$ is an even number. As seen, there is a general decreasing tendency of the values φ in the vicinity of position of the initial introduction by the law τ^{-1}. Here, with the increase in τ dependence of the result (9) on m, n decreases that corresponds to a gradual smoothing of the distribution in the stated zone.

In the range of values $|m|, |n| >> \tau$ (peripheral zone), the contrary tendency takes place, namely, the increase in φ_{mn} with time. Maximum of the values φ for the corresponding position is achieved in the time moment

$$\tau_0 = \frac{m^2 + 3n^2}{24} ,$$

after that filling level φ starts to decrease.

4. MIGRATION IN THE LIMITED STRUCTURE

Presence of the structure boundaries makes significant changes in the pattern of the migration process, in any event, for the region adjacent to the edge. The above written results are directly applicable to such situations only on the limited time interval. However, at the realization of some techniques they can be used also for the determination of the general pattern of the process

development.

Let point of the initial localization of a particle is remote from the boundary on the distance $2d$, where d is the integer value corresponding to the accepted way of indexation in the "m" direction. We also will consider that graphene cleavage is "right", i.e. corresponds to the fixed number in the "m" direction, i.e. $2d$.

We mentally expand the limited hexagon structure to the adjacent space and simultaneously designate one more subject of migration at the initial moment in neophysical zone. Equations (1) and their solutions in a newly formed space are valid without restrictions, and all functions φ_{mn} due to linearity of equations have the form of a sum of two terms connected with two independent positions of the initial localization: the first term can be written in the form of (9), the second one – by the same way, but with the corresponding shift of index count.

If additional object is initially fixed in the point $4d + 2,0$, then the desired function φ_{mn} is written as

$$\varphi_{mn} = \frac{A}{\tau}\left\{ e^{-\frac{m^2+3n^2}{24\tau}} + e^{-\frac{(m-4d-2)^2+3n^2}{24\tau}} \right\}. \qquad (10)$$

Formula (10) gives $\varphi_{2d,n} = \varphi_{2d+2,n}$, $\varphi_{2d-1,n} = \varphi_{2d+3,n}$ etc. for all values of n and at any time moments. Cells of the numbers $2d$, $2d - 1$ belong to the real structure, and numbers $2d + 2$, $2d + 3$ correspond to the fictitious zone. Due to the equality of $\varphi_{2d,n}$ and $\varphi_{2d+2,n}$, transfer between corresponding cells is absent. Similarly, cells $2d - 1,n$, $2d,n$ and $2d + 3,n$, $2d + 2,n$ form equal, but oppositely directed fluxes into cells $2d + 1,n$ that again corresponds to the absence of the transfer through the conditional structure boundary cleaving cells $2d + 1,n$ in half. Thus, formula (10) represents a general pattern of migration in the limited medium. The second term of (10) represents reflection from the surface, or else drift compensation to the region of fictitious indexes.

The laws of migration as well as a number of other processes in closed (partially closed) structures, for example, carbon nanotubes are also of a special interest [12]. The absence of a boundary in one direction and considerable extent in another one (axial) provide adequacy of relations written for infinite medium (8), (9).

Physical identity of positions m and $m + ks$, where s is the integer tube circumference (s is even); k is the integer number, and m and $s - m$ are the double-valued distances of any position from the conditionally zero one, defines expression for φ_{mn} as a result of summing of the contributions from various ways of achievement of the desired point. The general expression is the following:

$$\varphi_{mn} = \frac{A}{\tau} e^{-\frac{3n^2}{24\tau}} \left(e^{-\frac{m^2}{24\tau}} + e^{-\frac{(s-m)^2}{24\tau}} + e^{-\frac{(s+m)^2}{24\tau}} + \right.$$
$$\left. + e^{-\frac{(2s-m)^2}{24\tau}} + e^{-\frac{(m+2s)^2}{24\tau}} + e^{-\frac{(m+3s)^2}{24\tau}} + \ldots \right). \qquad (11)$$

One can ascertain that formula (11) provides the necessary conditions of radial closure, namely, $\varphi_{mn} = \varphi_{m+s,n} = \varphi_{m+2s,n} = \ldots$.

If limit the numbering of positions by the value of s ($m < s$), then in a wide range of the τ change the main contribution belongs to the first two terms of (11).

Expression (11) suggests a right joining of graphene sheets without distortion of the regular structure that corresponds to "straight" nanotubes with chirality (m, 0).

5. CONCLUSIONS

Non-linearity of the connection between the observed effects and impurity concentration is the premise to a wide variation of the corresponding characteristics due to the transfer of impurity particles. Since in the absence of interaction between migrating atoms (this is the suggestion of the present work) non-stationary migration corresponds to a gradual equalizing of concentrations, then macromanifestations of any effect depending on the concentration in the power which exceeds unit will decrease if the total number of particles remains. Thereby, the temperature increase defining the intensification of migration can be considered as nanomaterial "annealing" which provides the decrease or, otherwise, the increase in a certain parameter according to its dependence on the local concentration. Here, a further cooling of the sample – distribution freezing – within the analysis premises does not lead to the restoration of the initial properties, i.e. it is irreversible.

Of course, real conditions of application of nanomaterials and the corresponding technological processes can be connected with significant number of additional circumstances, such as, the presence of drains, or, inversely, sources on the structure edges, coming on the surface and evaporation from it, etc. that can considerably change the laws of redistribution of particles and parameters connected with migrating component. The role of some circumstances (for example, the structure finiteness) was discussed above. As a general observation, one should state that the mentioned additional circumstances complicate the migration processes and their analysis, but, on the other hand, they determine additional resources in relation to the variation of the desired characteristics and formation of the controllable modes of operation of the corresponding elements. Tracking of the change in the corresponding parameters in time or at the temperature change can be the agent of diagnostic of nanosample states and character of its defectiveness.

Since at sufficiently general assumptions conduction of the medium is proportional to the relaxation time, which, in turn, is inversely proportional to the scatterer concentration, non-uniformity of the impurity distribution and evolution of this distribution because of the migration lead to the variation of the local conduction and change in the integral conduction of the sample. In this case, the presence of rather dense limited bunches of impurities decreases the general conduction to a lesser degree than the same general quantity of the impurity material after migration equalizing of the concentration. Because of this fact, results of the macroscopic experiment, which do not take into account the spatial distributions of impurities, do not lead to unique conclusions about the character and general level of defectiveness.

Comparison of the transfer characteristics of graphene and some collections of such formations (microscopically thin layer of graphite) would allow to specify

the notions about the features of impurity localization on the hexagon carbon lattice and transfer mechanism. The same comparison of the characteristics for a simple single-layer carbon nanotube and comparable with multilayer one could give the additional information due to the fact that difference in diameters of adjacent layers would create the discrepancy of the transfer conditions in layers [11].

The main premises and methodical techniques of the given work concede significant development and extension to other, more complex or modified, objects of the analysis.

REFERENCES

1. B.S. Bokstain, *Diffuziya v metallah* (M.: Metallurgiya: 1978).
2. V.B. Brik, *Diffuziya i fazovye prevrashcheniya v metallah i splavah* (K.: Nauk. dumka: 1985).
3. S.I. Sydorenko, Yu.M. Makogon, S.M. Voloshko, *Materialoznavstvo tonkoplivkovyh nanostruktur. Dyfuziya i reaktsii* (K.: Nauk. dumka: 2000).
4. D.K. Ferry, S.M. Goodnick, J. Bird, *Transport in Nanostructures* (Cambridge University Press: Hardbound: 2009).
5. D.I. Ryzhonkov, V.V. Levina, E.L. Dzidziguri, *Nanomaterialy* (M.: Binom. Laboratoriya znaniy: 2008).
6. A.K. Geim, K.S. Novoselov, *Nat. Mater.* **6**, 183 (2007).
7. T.O. Wehling, K.S. Novoselov, S.V. Morozov, E.E. Vdovin, M.I. Katsnelson, A.K. Geim, A.I. Lichtenstein, *Nano Lett.* **8**, 173 (2008).
8. B. Huang, Z.Y. Li, Z.R. Liu, G. Zhou, S.G. Hao, J. Wu, B.L. Gu, W.H. Duan, *J. Phys. Chem. C* **112**, 13442 (2008).
9. J.H. Chen, C. Jang, E.D. Williams, M.S. Fuhrer, M. Ishigami, *Nat. Phys.* **4**, 377 (2008).
10. Ch. Jian-Hao, L. Liang, W.G. Cullen, E.D. Williams, M.S. Fuhrer, *Nat. Phys.* **7**, 535 (2011).
11. Yu.E. Ananieva, N.S. Eliseeva, P.O. Krasnov, A.A. Kuzubov, A.S. Fedorov, *Zhurnal Sibirskogo federalnogo universiteta*, Seriya "Khimiya" **3** No3, 305 (2010).
12. A.V. Eletskii, *Phys. Usp.* **52**, 209 (2009).