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THE STRUCTURE OF MONOATOMIC LAYER ON GRAPHITE SURFACE

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Monatomic surface layers of graphite were simulated on the basis of experimental data, which was obtained by scanning tunneling electron microscopy of atomically smooth surface of graphite. Values of relative deviation of the electron density were defined in the direction perpendicular to the plane of the layer. Increase in the degree of waviness layer to 2 nm are observed by increasing of linear dimensions under review graphite surface area of up to 25 nm. These results are confirmed by the data available for the graphene layers, which is caused by waviness defect. Indeed, defects such as vacancies and interstitial carbon atom are formed by increasing the number of cells to the surface layer up to 20.

KEY WORDS: graphite, surface, structure, graphene, electron density, defects

СТРУКТУРА МОНОАТОМНОГО ШАРУ НА ПОВЕРХНІ ГРАФІТУ

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На основі експериментальних даних, отриманих за допомогою скануючої тунельної мікроскопії атомарно гладкої поверхні графіту, промодельовано моноатомні поверхневі шари графіту. Визначені значення відносних відхилень електронної густини в напрямі перпендикулярному площині шару. При збільшенні лінійних розмірів ділянки поверхні графіту до 25 нм спостерігається збільшення ступеня хвилястості шару до 2 нм. Ці результати підтверджуються даними для вільних графенових шарів, хвилястість яких обумовлена дефектами. Дійсно, при збільшенні числа осередків поверхневого шару до 20 формуються дефекти типу вакансія і впроваджений атом вуглецю.

КЛЮЧЕВІ СЛОВА: графіт, поверхня, структура, графен, електронна густина, дефекти

СТРУКТУРА МОНОАТОМНОГО СЛОЯ НА ПОВЕРХНОСТІ ГРАФИТА

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На основе экспериментальных данных, полученных с помощью сканирующей туннельной микроскопии атомарно гладкой поверхности графита, промоделированы моноатомные поверхностные слои графита. Определены значения относительных отклонений электронной плотности в направлении перпендикулярном плоскости слоя. При увеличении линейных размеров обозреваемого участка поверхности графита до 25 нм наблюдается увеличение степени волнистости слоя до 2 нм. Эти результаты подтверждаются данными для свободных графеновых слоев, волнистость которых обусловлена дефектами. Действительно, при увеличении числа ячеек поверхностного слоя до 20 формируются дефекты типа вакансия и внедренный атом углерода.

КЛЮЧЕВЫЕ СЛОВА: графит, поверхность, структура, графен, электронная плотность, дефекты

Interest in monatomic hexagonal layers of graphite has appeared in the mid 40's, last century [1]. In this work we calculated the monoatomic graphite layer in the strong-coupling approximation. In graphite, each C-atom is sp^3 -hybridized [2 - 6], orbital symmetry s -, p_x - и p_y located on the plane of the monatomic layer (σ -orbital); such orbitals are fully occupied and do not participate in the conduction. The fourth electron has a wave function p_z -symmetry; these orbitals are perpendicular to the atomic layer (π -orbital). These π -electrons are responsible for conductivity, and it will be further shown that energy band has both electrons and holes. π -electron interaction is considered and representation of the energy bands of the graphite is obtained in [1] and it predicts the most important properties. The main conclusion is the presence of degeneracy between filled and empty π -band, that follows from the symmetry of the monolayer. The bottom π -band must be filled and the top - must be empty at absolute zero. Also the energy gap between the bands must be absent. Progress in the preparation of thin film methods allowed synthesizing a monolayer of graphite monolayer on the surface of nickel [7], the lanthanum hexaboride crystals [8], platinum [9], iridium and rhenium [10,11], titanium carbide [12].

The first monolayer of graphite in a free state is graphene. It was obtained by Geim and Novoselov [13, 14]. Graphene is allotropic form of carbon, that consisting of a monolayer of graphite, which has a number of non-conventional properties - good electrical conductivity, transparency, good mechanical properties, high mobility of charge carriers at room temperature, the possibility of quantum conductivity and the epitaxial layer deposition. It is interesting to note that the basic approximation of Solid State Physics - Born-Oppenheimer approximation (adiabatic approximation) is broken down in graphene. So, fluctuations in the ion cores of the lattice must be included as a disturbance in the form of phonons in the lattice in the construction zone theory of graphene [15].

The aim of this work is the research of the structure of monoatomic layer on the real atomic surface of highly oriented graphite, obtained using scanning tunneling microscopy and computer modeling monoatomic layer on the graphite surface.

METHODS OF EXPERIMENTAL RESEARCH

Highly oriented graphite crystal served as the object of research. The purification of the graphite surface and the formation of a real atomic surface of a layered type of crystal was produced by cleaving the top layer of crystal before measurement. The research of the graphite surface was produced by scanning tunneling electron microscopy in normal conditions by the scanning tunneling microscope STM – 1. The experimental data were used to construct three-dimensional charts monoatomic graphite layer with a program Harvard Chart XL 2.0, that shows the structure of the first surface layer of graphite and its connection with the second surface layer.

RESULTS AND DISCUSSION

Topographical image of the nanostructure surface of graphite unit cells is shown in Fig.1: ordered rows of hexagonal graphite structure are observed in the area of highly oriented graphite, that obtained by scanning tunneling current mode of stabilization with maximizing. The unit cell has the shape of a hexagon and consists of atoms with different levels of the local electronic density of states. Partitioning according to the scheme of the experimental data (Fig. 2) was carried out in all possible directions $a = 0.14 \text{ nm}$, $b = 0.24 \text{ nm}$. The top surface of the monoatomic layer of graphite was selected with Harvard Chart XL 2,0 program. Flat hexagonal grid was used to represent experimental data (Fig.3).

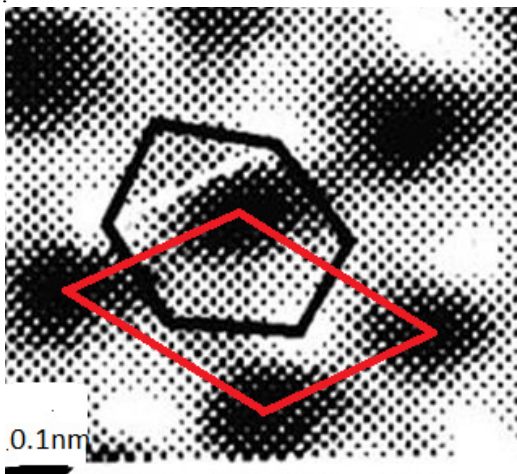


Fig. 1. The topographical image of the surface of graphite. Unit cell (hexagon) and a primitive (60° - rhombus) are show

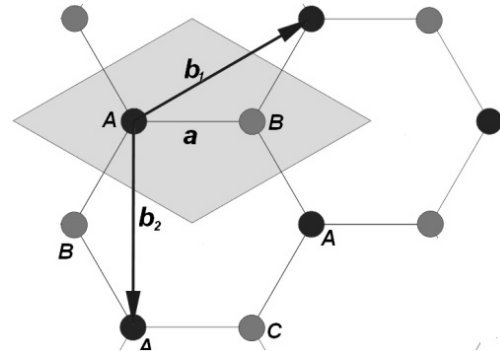


Fig. 2. Partitioning scheme of the experimental data concerning the node (A). The first neighbors B, the second - marked (A), the third as C.

The fact of the modulation of the vertical component, the ribs (a) of the unit cell and the ribs (b) of the primitive structure of the cell, is important in the experimental data obtained by the electron density on the graphite surface (Fig.3). That displays the modulation of electron density of atoms on a graphite surface. Significant periodic deviations is noted at the height of the image of two neighboring atoms (to be exact - the provisions of the local electron density maxima).

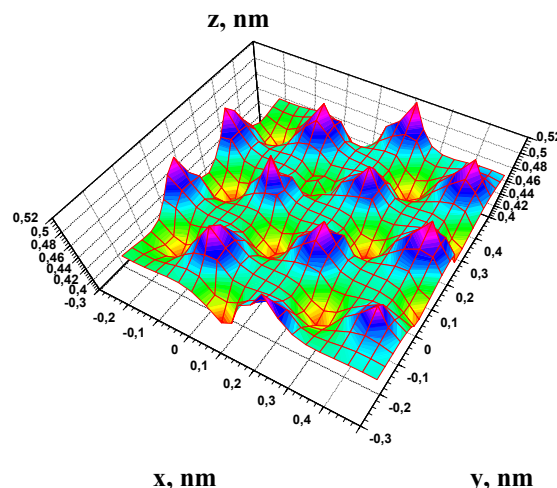


Fig 3. The electron density distribution of 7 unit cells

STM allows us to observe the spatial distribution of the atoms around the electron density, expressed in the values of the coordinates z . Neutral carbon atom in the ground state is divalent and has $1s^2 2s^2 2p^2$ configuration. The radius of the atom is 0.62 \AA . Tetravalent state of carbon is formed at $2s$ electron switches to the $2p$ – state, that corresponds to the configuration $1s^2 2s 2p_x 2p_y 2p_z$. The hexagonal graphite lattice belongs to the space group $C6 / m m c - D 4 6 h$ with four atoms per unit cell. The parameter b primitive cell is 0.246 nm , the parameter $d = 0.671 \text{ nm}$, the theoretical density of this crystal is equal to 2.267 g / cm^3 . Carbon atoms form a regular grid of hexagons with the distance between atoms 1.42 \AA in each plane. Connections inside the layers, which are covalent, are trigonal hybrids ($2s, 2p_x, 2p_y$) [5, 6]. The unit cell parameters are consistent with the data presented by other authors (see table).

Table

Graphite structure parameters

Structure	Parameter of Unit cell a, nm	Parameter of primitive cell b, nm	The distance between adjacent layers c, nm	The height of the primitive cell d, nm	Links
Graphite	0.146		0.3343		[16]
	0.142	0.246	0.337		[1]
	0.142	0.2464	0.335	0.6701	[6]
	0.141	0.246		0.67	[5]
	0.1418	0.246	0.335		[4]
	0.1418	0.24612		0.67079	[19]
	0.14	0.24			[18]
Graphene	0.142	0.246			[17]
Grafan	0.142	0.242			[17]
Grafan, theory	≈ 0.153 (disagreement with the theory)	$\approx 0.242 \text{ \AA}$ with the theory of consent			[17]

Real monoatomic layer of graphite crystal atoms are observed deviations from the equilibrium electron density, which is represented relative to a weighted average plane and the three nearest neighbors of the central carbon atoms are deflected in the opposite direction. This is confirmed by the data on the values of the electron density variations within the unit and primitive cells.

These absolute values Δr deviation from the median plane depend on the distance r along the length of the ribs and primitive elementary cells (Fig. 4, 5). It should be noted that the size of the ribs in the graphene hexagon grid somewhat larger (0.246 nm), than on the graphite surface (0.24 nm), which is possible due to the interaction interlayer carbon atoms in graphite.

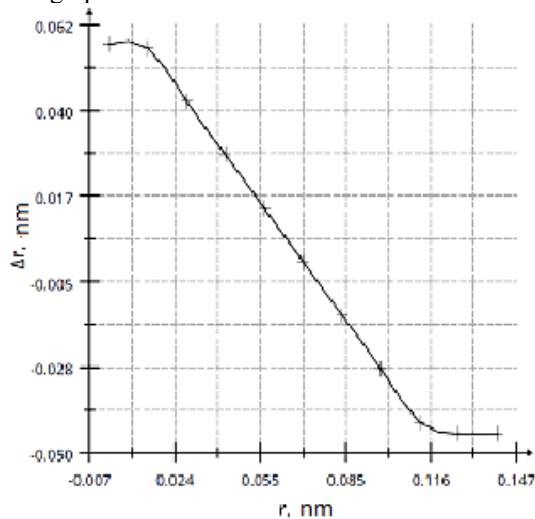


Fig. 4. The dependence of the deviations from the median plane depending on the distance r along the length of the unit cell edges

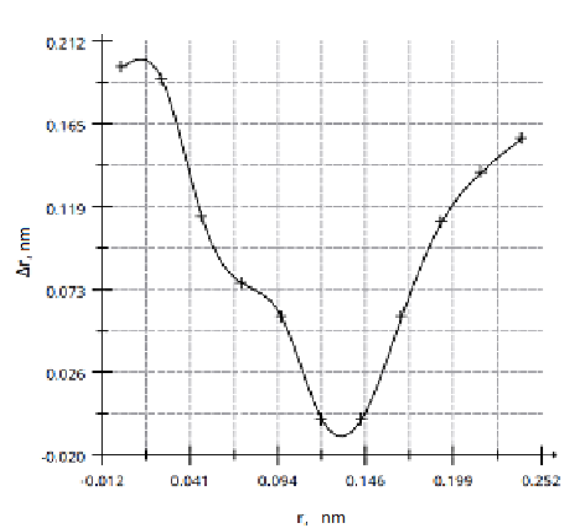


Fig. 5. The dependence of the deviations from the median plane depending on the distance r along the length of the unit cell edges.

Mismatch scale grating period in planes tangential to the surface of each of the crystal layers, leads to a normal to the surface of the crystal near the boundary stresses. These forces acting in both the vertical and horizontal directions can realize a state of equilibrium at a relatively low level fluctuations [22 – 24]. Such equilibrium state must have a certain vertical depth of modulation of the crystal surface to align the scale on the surface and in the bulk. Formation of the spatial modulation of the surface layer takes place under the action of the physical mechanism of formation of defects, therefore the role of defects, that accompany this process, may be significant

Increasing the degree of undulation of the layer to 2 nm is observed with an increase in the area under review graphite surface of the linear dimensions of 25 nm (Fig.6). These results are confirmed by the data available for the graphene layers, which undulation due to defects.

Ideal two-dimensional film in the free state can not be obtained due to its thermodynamic instability. But if the film has the defects or it will be deformed in the space (a third dimension), such a "non-ideal" film can exist without contact with the substrate [20]. In [21] it was shown that there are free graphene film surface and form a complex undulating shape, with lateral dimensions spatial inhomogeneities about 5-10 nm and a height of 1 nm. The results obtained in this paper waviness parameters are in good agreement with data reported for graphene.

Indeed, in this case, defects such as vacancies and interstitial carbon atom are formed by increasing the number of cells of the surface layer to 20. Fig. 7 shows a topographic image of the electron density distribution in the surface layer of monoatomic 20 unit cells. Defect (vacancy) occurs in tandem with embedded carbon in bottom right of the image.

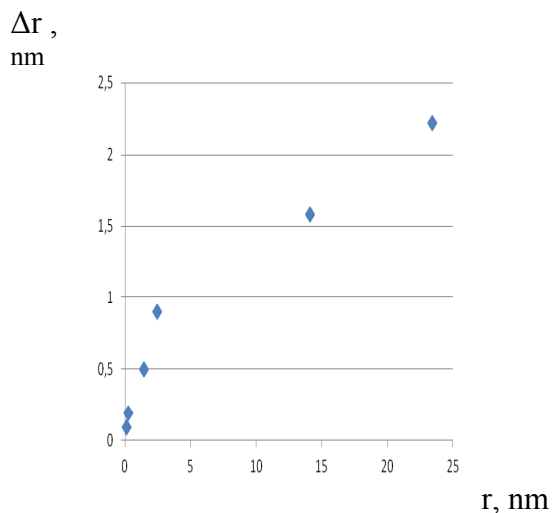


Fig. 6. Dependence waviness monatomic layer by scaling the length of the graphite surface

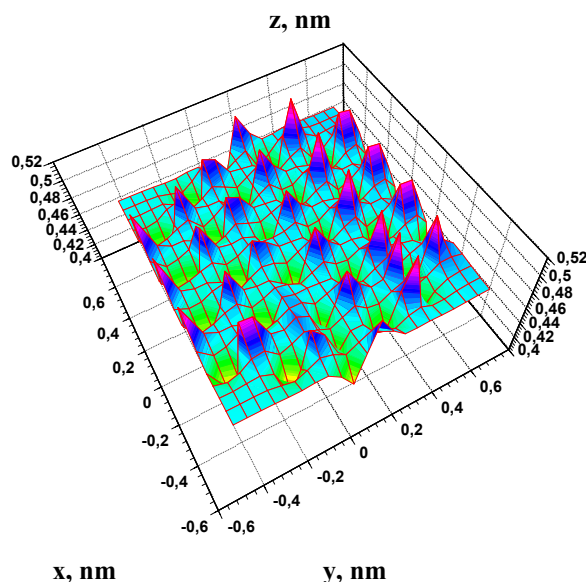


Рис. 7. The distribution of electron density in the unit cells 20. Defects (vacancies) with the embedded-atom is located at bottom right

The simplest defects that break down the translational symmetry of graphene are isolated 5- and 7-gons. But the formation of such defects is energetically unfavorable because it requires quite a strong distortion of the hexagonal structure. Much more likely a combination thereof. [25] On the other hand, stable ordering of carbon atoms is formed as part of Graphene in their zig-zag stacking, as in the case of carbyne [26].

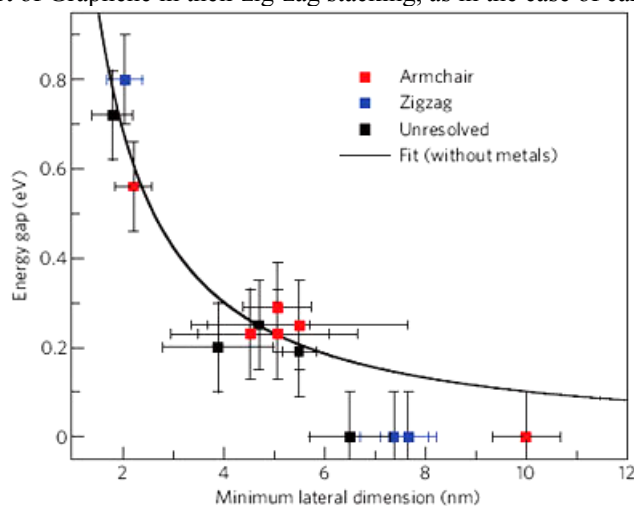


Fig. 8. The dependence of the band gap of the lateral size of graphene quantum dot structure with different edges [27]

As it turns out, most of the particles whose size is less than 10 nm, has a "zigzag" metal edges and exhibits electrical properties rather than semiconductor [27]. On the other hand, in the semiconductor quantum dot in the band gap E_g graphene zone depends on the size of the minimum cross-by law $L E_g = (1.57 \pm 0.21)/L^{1.19 \pm 0.15}$ (where E_g is measured in eV, and L – nm) - in full compliance with the theoretical dependence $E_g = 1.68/L$ (Fig. 8). The nanoribbons width of 2-3 nm and a length of 20-30 nm, in which the edges of a specific proportion of the zigzag sections more than the "chair", the value of E_g less than nanoribbons is the same width, but with a "chairlifts" edges [27]. In connection with the results is an important analysis and control of lateral heterogeneities on the surface of monatomic layers of graphite.

CONCLUSIONS

Modeling monoatomic layers of graphite based on the data scanning tunneling electron microscopy of graphite surface shows a periodic modulation of the electron density at the surface of the monatomic layer at modeling 7×7 – type cells. Computer modeling of the structure of mononuclear cells of the surface layers was carried out on the basis of technology developed by the partitioning of the experimental values of the surface electron density.

The monoatomic surface layers of graphite, the values of the absolute deviations of the electron density in the

direction perpendicular to the plane of the layer. By increasing the area under review the linear dimensions of the graphite surface to 25 nm, an increase in the degree of undulation of the layer to 2 nm. These results are confirmed by the data available for the graphene layers, which is caused by waviness defect. Indeed, when increasing the number of cells of the surface layer 20 to form defects such as vacancies and interstitial carbon atom. These scaling properties of monatomic layer on atomically clean surfaces of graphite must be considered in the analysis of the formation of graphene and graphane.

REFERENCES

- Wallace P.R. The Band Theory of Graphite // *Phys. Rev.* – 1947. - Vol.71. – No.1. – P.622 – 634.
- Joseph Callaway. Teoriya energeticheskoy zonnnoy struktury [Energy band theory]. – M.: Mir, 1969. – 360p.
- Dyadin Yu.A. Grafit i ego soyedineniya vklyucheniya [Graphite and its inclusion compounds] // *Sorosovskiy zhurnal [Soros journal]*. – 2000. – Vol. 6. – No.10. – P.43 – 49.
- Podgornyy D.A. Uglerod vo vsem svoym mnogoobrazii [Carbon in all its diversity] // Chelyabinsk, 2014. – 31p. (in Russian)
- Zhmurikov E.I., Bubnenkov I.A., Dryomov V.V. i dr. Grafit v nauke i yadernoy tekhnike [Graphite in science and nuclear engineering] // Novosibirsk, 2013. – 193 p.
- Knunyants I. L. (gl. red.) *Khimicheskaya entsiklopediya: v 5 tomakh [Chemical Encyclopedia: in 5 volumes]*. Vol. 1. – *Abyatsionnyye materialy [Ablative materials]*. – M.: Sov. Enc. [Soviet encyclopedia]. – 1988. – 623 p. (in Russian)
- Shelton J.C., Patil H.R., Blakely J.M. Equilibrium segregation of carbon to a nickel (111) surface: A surface phase transition // *Surf. Sci.* – 1974. - Vol.43. – No.1. – P.493-520.
- Oshima C., Bannai E., Tanaka T., Kawai S. Carbon layer on lanthanum hexaboride (100) surface // *Jpn. J. Appl. Phys.* – 1977. – Vol. 16. - P.965.
- Zi-Pu H., Ogletree D., Hove M. V., Somorjai G. Leed theory for incommensurate overlayers: Application to graphite on Pt(111) // *Surf. Sci.* – 1987. – Vol. 180. – P. 433.
- Kholin N., Rut'kov E., Tontegode A. The nature of the adsorption bond between graphite islands and iridium surface // *Surf. Sci.* – 1984. – Vol. 139. – P.155.
- Gall N.R., Mihailov C.N., Rutkov E.V., Tontegode A.Ya. Harakter adsorbtsionnoi svyazi mejdu monosloem grafitu i poverhnostyu reniya [Character adsorption connection between the graphite and the rhenium surface monolayer] // *FTT.* – 1985. – Vol. 27. – P. 2351. (in Russian)
- Nagashima A., Nuka K., Itoh H., Ichinokawa T., Oshima C. et al. Electronic states of monolayer graphite formed on TiC(111) surface // *Surf. Sci.* – 1993. – P. 291.
- Novoselov K.S., Geim A.K., Morozov S.V., Jiang D., Zhang Y. et al. Electric field effect in atomically thin carbon films // *Science.* – 2004. – Vol.306. – P. 666.
- Novoselov K. S., Jiang D., Schedin F., Booth T. J., Khotkevich V. V. et al. Two-dimensional atomic crystals // *Proc. Nat. Acad. Sci. USA.* – 2005. – Vol. 102. – P. 10451.
- Pisana S. et al. Breakdown of the adiabatic Born-Oppenheimer approximation in graphene // *Nature Materials.* – 2007. – Vol. 6. – P. 198. DOI:10.1038/nmat1846.
- Goncharov V.V. Grafit v reaktorostroyenii [The graphite in reactor]. // *AE.* – 1957. – Vol.2. – P. 398-409.
- D.C. Elias, R. R. Nair, T. M. G. Mohiuddin, S. V. Morozov, P. Blake, M. P. Halsall, A. C. Ferrari, D. W. Boukhvalov, M.I. Katsnelson, A.K. Geim, K. S. Novoselov. Control of Graphene's Properties by Reversible Hydrogenation: Evidence for Graphane // *Science.* – 2009. – Vol.323. – P.610–613.
- Kirichenko V.G., Melnikova E.S. The features of structure of nanometric surface layers of graphite // *The Journal of Kharkiv National University, physical series: "Nuclei, Particles, Fields"*. – 2009. – No.880. – Iss.4(44). - P.103-108.
- iznedr.ru/books/item/f00/s00/z0000019/st035.shtm
- Bunch J. S. et al. Coulomb Oscillations and Hall Effect in Quasi-2D Graphite Quantum Dots *Nano Lett.* 5, 287 (2005) DOI:10.1021/nl048111+
- Boehm's 1961 isolation of graphene. Graphene
- Kirichenko Valeriy G., Kuklin Vladimir M. The Formation of the Multiscale Structures on the Crystal Surfaces and Conversion of Crystals Under Phase Transformations // *Electron Microscopy and Multiscale Materials Modelling.* – 2007. – P.177.
- Ramstad A., Brocks G., Kelly P.J. Theoretical study of Si (100) surface reconstruction // *Phys. Rev.* – 1995. – Vol.51. – No.20. – P.1450-1457.
- Alekperov S.D., Vasilyev S.I., Leonov V.B., Panov V.I., Semenov A.E. Issledovaniye asimmetrii atomnogo izobrazheniya poverkhnostnoy reshetki grafitu metodom STM [The study of the atomic image of the surface of the graphite lattice asymmetry by STM] // *Doklady AN SSSR. Fizika.* . – 1989. – Vol.307. – No.5. – P.1104-1109. (in Russian)
- Kirichenko V.G. The formation of topological defects on graphite's surface // *East Eur. J. Phys.* – 2015. – Vol.2. – P.80-84.
- Kirichenko V.G., Yampolskiy A.A. The formation of one dimensional structure in monoatomic layer on graphite surface// *East Eur. J. Phys.* – 2015. – Vol. 2. – No.3. – P.70-73.
- Ritter K.A., Lyding J.W. // *Nature Mater.* – 2009. – Vol.8. – P. 235.