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 surface 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

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**THE STRUCTURE OF MONOATOMIC LAYER ON GRAPHITE SURFACE**

V.G. Kirichenko, A.A. Yampolskiy

V.N. Karazin Kharkiv National University
4 Svobody Sq., Kharkiv, 61022, Ukraine
E-mail: val_kir48@mail.ru
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Interest in monatomic hexagonal layers of graphite has appeared in the mid 40’s, last century [1]. In this work we calculated the monatomic graphite layer in the strong-coupling approximation. In graphite, each C-atom is sp$^2$-hybridized [2 - 6], orbital symmetry $s$-, $p_{\sigma}$- and $p_{\pi}$ located on the plane of the monatomic layer ($\sigma$-orbital); such orbitals are fully occupied and do not participate in the conduction. The fourth electron has a wave function $p_{\pi}$-symmetry; these orbitals are perpendicular to the atomic layer ($\pi$-orbital). These $\pi$-electrons are responsible for conductivity, and it will be further shown that energy band has both electrons and holes. $\pi$-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 $\pi$-band, that follows from the symmetry of the monolayer. The bottom $\pi$-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 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].

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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 nm, b = 0.24 nm. The top surface of the monatomic layer of graphite was selected with Harvard Chart XL 2.0 program. Flat hexagonal grid was used to represent experimental data (Fig.3).

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).
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 \( 1s^22s^22p^2 \) configuration. The radius of the atom is 0.62 Å. Tetravalent state of carbon is formed at \( 2s \) electron switches to the \( 2p \) state, that corresponds to the configuration \( 1s^22s^22p_x2p_y2p_z \). The hexagonal graphite lattice belongs to the space group \( C_6 / mmm - D_{4h} 6h \) with four atoms per unit cell. The parameter \( b \) primitive cell is 0.246 nm, the parameter \( d = 0.671 \) 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 Å 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

<table>
<thead>
<tr>
<th>Structure</th>
<th>Parameter of Unit cell a, nm</th>
<th>Parameter of primitive cell b, nm</th>
<th>The distance between adjacent layers c, nm</th>
<th>The height of the primitive cell d, nm</th>
<th>Links</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>0.146</td>
<td>0.246</td>
<td>0.3343</td>
<td></td>
<td>[16]</td>
</tr>
<tr>
<td></td>
<td>0.142</td>
<td>0.246</td>
<td>0.337</td>
<td></td>
<td>[1]</td>
</tr>
<tr>
<td></td>
<td>0.141</td>
<td>0.246</td>
<td>0.335</td>
<td>0.6701</td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td>0.1418</td>
<td>0.246</td>
<td>0.335</td>
<td>0.6707</td>
<td>[5]</td>
</tr>
<tr>
<td></td>
<td>0.1418</td>
<td>0.24612</td>
<td>0.67079</td>
<td></td>
<td>[19]</td>
</tr>
<tr>
<td></td>
<td>0.14</td>
<td>0.24</td>
<td></td>
<td></td>
<td>[18]</td>
</tr>
<tr>
<td>Graphene</td>
<td>0.142</td>
<td>0.246</td>
<td></td>
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<td>[17]</td>
</tr>
<tr>
<td>Grafan</td>
<td>0.142</td>
<td>0.242</td>
<td></td>
<td></td>
<td>[17]</td>
</tr>
<tr>
<td>Grafan, theory</td>
<td>≈ 0.153 (disagreement with the theory)</td>
<td>≈ 0.242 Å with the theory of consent</td>
<td></td>
<td></td>
<td>[17]</td>
</tr>
</tbody>
</table>

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 \( \Delta r \) 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](image)

![Fig. 5. The dependence of the deviations from the median plane depending on the distance r along the length of the unit cell edges.](image)

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.

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, stable ordering of carbon atoms is formed as part of Graphene in their zig-zag stacking, as in the case of carbyne [26].

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 layer of the plane. By increasing the area under review the linear dimensions of the surface graphite structure 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 waveness 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 graphite.

REFERENCES