Graphene polymorphs

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Abstract. Ab initio calculations of twelve structural varieties of graphene were carried out using the density functional theory method. The structure of non-hexagonal graphene species contains topological defects 4, 5, 7, 8, 10, or 12, which deform the layers. The sublimation energy of graphene polymorphs decreases with increasing degree of layer structure deformation compared to hexagonal graphene. In the electronic structure of graphene layers L4-12 and L4-6-12 at the Fermi level, there are band gaps 0.59 and 0.37 eV wide, so these layers must be semiconductors.

1. Introduction

Allotropic carbon forms: carbyne, graphite, and diamond, are distinguished by hybridization of atomic electron orbitals – sp, sp2 and sp3, respectively [1, 2]. This is a consequence of different atom coordination in the structure [3]. In the structure of carbyne, each atom in the first coordination sphere has two atoms, in graphite (graphene) - three and in diamond - four. In the structure of polymorphs, the coordination and, as a consequence, the hybridization of atoms is the same, however, the distribution of valence electrons is different, because the relative arrangement of neighboring atoms in the structure of polymorphs is not the same [4, 5]. Therefore, the properties of polymorphic forms of carbon compounds should differ, but significantly less than the properties of carbon allotropes. For example, graphene polymorphs may exist [6–17]. Hexagonal graphene is a conductor, and graphene with semiconductor properties is required for use in electronics. Some polymorphs of graphene can probably be semiconductors. Therefore, it is necessary to search for new stable graphene polymorphs with such properties.

There are only four main polymorphic graphene varieties – these are ordinary hexagonal graphene L6, as well as L4-8, L3-12 and L4-6-12 graphene polymorphs [3, 11]. Atoms in the structure of these polymorphs are in equivalent structural positions. Interest in the study of these graphene layers is due to the fact that compounds with atoms in equivalent positions should be the most stable. Indeed, in the most stable structures of graphite and diamond, all atoms are in equivalent positions, out of the various fullerenes the most stable is C60 fullerene, the positions of atoms in the structure of which are equivalent. However, the equivalence of the structural positions of graphene layers is not the only factor that can affect their stability. Various topological defects are found in graphene polymorphs, due to which the structure becomes deformed and properties change [18, 19]. The smallest deformations of the structure are caused by defects 5 and 7, while the main polymorphs of graphene L4-8, L3-12 and L4-6-12 consist of topological defects that cause significantly larger distortions of the structure. It is necessary to search for new graphene polymorphs that would be the most stable and at the same time possess semiconductor
properties. As possible structures of this type, layers of 5–7 topological defects and other structural types in which atoms are in non-equivalent structural positions should be considered.

2. Graphene polymorphs and calculation methods

Twelve polymorphic graphene forms were selected as objects of the study (table 1). The first four of these layers L_6, L_4-8, L_3-12 and L_4-6-12 are the main types of graphene with equivalent atomic positions (n=1). In the next four layers L_4-6-8a, L_4-10, L_4-12 and L_4-6-8b, there are two different atomic positions (n=2). Four more layers L_5-7a, L_5-7b, L_4-6-8a, L_5-7c, in three of which n=3 and in the last layer n=4 were also studied. Atomic positions in graphene are characterized by the Wales ring parameters given in table 1. In addition, the layers differ in the type and number of topological defects encountered in their structure.

The optimization of the layer structure and the calculations of their energy and electronic properties were performed using the QUANTUM ESPRESSO package [20] within the density functional theory (DFT) [21] method in the generalized gradient approximation (GGA) [22]. The calculations were performed for stacks of graphene layers, the distance between the layers in which was 10 Å. The interlayer distance was chosen large enough so that the neighboring layers did not affect each other. For DFT calculations, a set of 12 × 12 × 12 k-points was used.

| Layer | Figure | n | Rng_1 | Rng_2 | Rng_3 | Rng_4 | M | Topological defects per unit cell |
|-------|--------|---|-------|-------|-------|-------|---|-----------------------------|
| L_6   | (a)    | 6^3 | -     | -     | -     | 1     | - | 0                           |
| L_4-8 | (b)    | 4^18^2 | -    | -     | -     | 1     | - | 1                           |
| L_3-12 | (c) | 3^112^2 | -   | -     | -     | 1     | 2 | 1                           |
| L_4-6-12 | (d) | 4^16^12^1 | -   | -     | -     | 1     | 3 | 1                           |
| L_4-6-8a | (e) | 4^16^18^1 | 6^18^2 | -   | -     | 2:1   | - | 2                           |
| L_4-10 | (f)   | 4^10^2 | 4^10^1 | -   | -     | 2:1   | - | 1                           |
| L_4-12 | (g)   | 4^12^2 | 4^12^1 | -   | 1:1   | 3    | - | 1                           |
| L_4-6-8b | (h) | 4^16^18^1 | 6^8^1 | -   | -     | 1:1   | - | 1                           |
| L_5-7a | (i)   | 5^17^2 | 5^17^2 | 5^7^2 | -     | 1:2:1 | - | 2                           |
| L_5-7b | (j)   | 5^17^2 | 5^17^2 | 5^7^2 | -     | 1:2:1 | - | 4                           |
| L_4-6-8c | (k) | 6^3 | 4^16^8^1 | 6^8^1 | -   | 1:1:1 | - | 2                           |
| L_5-7c | (l)   | 5^1 | 5^7^2 | 5^7^2 | 7^1   | 1:3:6:2 | - | 6                           |

3. Results

As the result of DFT-GGA calculations, geometrically optimized structure of twelve graphene polymorphs was found (figure 1). The crystal lattices of layers L_6, L_3-12, L_4-6-12 and L_5-7c are hexagonal, crystal lattices of L_4-10, L_4-12, L_4-6-8a, L_5-7a, L_5-7b, L_4-6-8b are oblique, in the L_4-8 layer the lattice is cubic, and in the L_4-6-8a layer it is rectangular. The unit cells of graphene layers contain from 2 to 16 atoms (table 1, figure 1). The degree of deformation of the layer structure was characterized by the Def parameter calculated as the sum of the absolute values of the difference of the angles between bonds in graphene polymorphs and an angle of 120° between bonds in hexagonal graphene. This parameter varies from 0 to 120°. The calculated values of the sublimation energies for graphene polymorphs vary from 6.45 to 7.78 eV atom. The maximum sublimation energies after hexagonal graphene are observed for layers L_5-7a and L_5-7b. For most layers, the band gap at the Fermi level is absent, however, two layers L_4.
and L_{4.6.8e} have band gaps with the corresponding widths of 0.59 and 0.37 eV and their properties must be semiconductor.

The analysis of the results made it possible to detect the sublimation energy ($E_{\text{sub}}$) dependence of graphene polymorphs on the degree of distortion of their structure, characterized by the deformation parameter (Def) (figure 2). In addition, it was established that the sublimation energy ($E_{\text{sub}}$) and, therefore, the layer stability correlate with the relative number of topological defects per atom ($\Sigma / N$) (table 2).
Table 2. Structural characteristics and properties of graphene polymorphs (a, b are the lengths of the elementary translation vectors, γ is the angle between the translation vectors, N is the number of atoms in the unit cell, Def is the deformation parameter, $E_{\text{total}}$ is the total specific energy, $\Delta E_{\text{total}}$ is the total specific difference energy, $E_{\text{sub}}$ is the sublimation energy, $E_g$ is the band gap).

| Graphene | The lattice parameters a (Å) | b (Å) | γ (°) | N (atom) | Def (°) | $\Sigma / N$ | $E_{\text{total}}$ (eV atom$^{-1}$) | $\Delta E_{\text{total}}$ (eV atom$^{-1}$) | $E_{\text{sub}}$ (eV atom$^{-1}$) | $E_g$ (eV) |
|----------|-------------------------------|-------|-------|----------|--------|-------------|-------------------------------|----------------------------------|------------------------|--------|
| L$_6$    | 2.471                         | 120   | 2     | 0        | 0      | 0           | -157.34                      | 7.78                             | 0                      | 0      |
| L$_4$-8  | 3.429                         | 90    | 4     | 60       | 0.5    | -156.78     | 0.56                         | 7.22                             | 0                      | 0      |
| L$_3$-12 | 5.130                         | 120   | 6     | 120      | 0.5    | -156.22     | 1.14                         | 6.64                             | 0                      | 0      |
| L$_4$-6-12 | 6.713                       | 120   | 12    | 60       | 0.33   | -156.65     | 0.70                         | 7.08                             | 0                      | 0      |
| L$_4$-6-8a | 3.801                      | 4.554 | 90    | 6        | 46.53  | 0.33        | -156.80                      | 0.54                             | 7.24                   | 0      |
| L$_4$-10 | 4.642                         | 115.0 | 6     | 79.53   | 0.5    | -156.27     | 1.07                         | 6.71                             | 0                      | 0      |
| L$_4$-12 | 5.914                         | 129.6 | 8     | 88.95   | 0.5    | -156.01     | 1.33                         | 6.45                             | 0.59                  | 0      |
| L$_4$-6-8b | 5.517                      | 4.476 | 113.6 | 8        | 34.25  | 0.25        | -156.91                      | 0.43                             | 7.35                   | 0      |
| L$_5$-7a | 4.776                         | 104.0 | 8     | 31.3    | 0.5    | -157.05     | 0.29                         | 7.49                             | 0                      | 0      |
| L$_5$-7b | 10.413                        | 4.779 | 117.5 | 16      | 28.9   | 0.5         | -157.07                      | 0.27                             | 7.51                   | 0      |
| L$_4$-6-8e | 7.879                      | 147.6 | 12    | 24.06   | 0.17   | -157.04     | 0.3                          | 7.48                             | 0.37                  | 0      |
| L$_5$-7c | 6.193                         | 120   | 12    | 66.4    | 0.5    | -156.83     | 0.51                         | 7.27                             | 0                      | 0      |

Figure 2. The dependency graph of the sublimation energy ($E_{\text{sub}}$) of graphene polymorphs on the deformation parameter (Def).

4. Conclusion
Thus, in the course of research by the DFT-GGA method, the structure, electronic properties, and energy characteristics of twelve polymorphic graphene forms were calculated. The dependence of the sublimation energy of graphene layers on the degree of distortion of their structure is established in comparison with the structure of hexagonal graphene. Two graphene polymorphs were found, both of which should have semiconductor properties and sufficient stability to exist stably under normal conditions.

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