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Ab initio calculations of layered compounds consisting of sp^3 or sp+sp^2 hybridized carbon atoms

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The density functional theory method was used to study new layered carbon nanostructures consisting of sp^3- and sp+sp^2-hybridized atoms. The nanostructures are theoretically built on the basis of graphene 5 – 7 layers. As a result of calculations, it is found that the structures of two diamond-like bilayers and twenty-one graphyne layers are stable. The diamond-like bilayers have a band gap of $\sim$ 1.8 eV, so their properties should be semiconducting. For fourteen graphyne layers, the band gap is zero and their properties are metallic. Seven graphyne layers have band gaps ranging from 0.05 to 0.2 eV.

Keywords: graphene, diamond-like bilayers, graphyne layers, computer simulation.

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1. Introduction

There are three crystalline allotropic forms of carbon, such as carbyne, graphite and diamond, which consist of carbon atoms in two-, three- and four-coordinated states in the corresponding crystal structure [1]. The orbitals of valence electrons of carbon atoms in these compounds are sp-, sp^2- or sp^3-hybridized [2]. There are also various carbon nanostructures such as fullerenes, nanotubes, graphene layers, and others [3–5]. In most of these nanostructures, carbon atoms are in the states of sp^2-hybridization. It is necessary to investigate the possibility of the existence of diamond-like and carbyne-like carbon nanostructures consisting of sp^3- and sp-hybridized atoms, respectively. The theoretical analysis performed earlier showed that the existence of diamond-like layers of sp^3-hybridized atoms, as well as graphyne layers of sp+sp^2 atoms, is possible [6–13]. The structure of such layered carbon nanostructures can theoretically be constructed on the basis of polymorphic varieties of graphene [6, 10]. Earlier, we studied diamond-like bilayers and graphyne monolayers formed on the basis of the main polymorphic graphene varieties L_6, L_{4-8}, L_{3-12}, and L_{4-6-12} [6, 8, 10, 13]. The stability of diamond-like and graphyne-like layers correlates well with the stability of graphene layer precursors. Therefore, nanostructures formed from the most stable graphene polymorphs must be stable. According to theoretical calculations, one of the most stable structural varieties of graphene is L_{5-7} graphene [14, 15]. Graphenes, whose layers consist of pentagons and heptagons, has several polymorphic varieties of which L_{5-7a} and L_{5-7b} are the most stable [15]. Therefore, the study of diamond-like and graphyne layers formed from L_{5-7a} and L_{5-7b} graphenes was carried out in this work.

2. Calculation methods

To obtain the initial structures of diamond-like layers, the theoretical technique described in [1, 6] was used. The structures of these layers were obtained as a result of the formation of covalent bonds between atoms of parallel two-dimensional graphene-like precursors (Fig. 1). Six polymorphic graphene varieties were considered as precursors of diamond-like layers (Fig. 2).

Graphyne sp+sp^2 layers were built on the basis of two polymorphs of 5 – 7 graphene by replacing carbon-carbon bonds with fragments of diatomic carbyne chains according to the method described in [10,13]. Fig. 3 shows a diagram illustrating the construction of a structure of one graphyne layer based on the graphene L_{5-7a} layer. Each carbon atom in the graphene layer is covalently bonded to three neighboring atoms, so one, two, or three bonds can be replaced with a carbine chain. If each three-coordinated atom has all bonds with neighboring two-coordinated atoms, then layers of α-graphyne were obtained. When two bonds or one bond were replaced, the structure of β- and γ-graphyne varieties was formed, respectively.

Further calculations of the structure and electronic properties of layered carbon nanostructures were performed using the density functional theory (DFT) method in the Quantum ESPRESSO software package [16]. The calculations were performed using the generalized gradient approximation [17] only for valence electrons. The influence of ionic cores was taken into account by the method of the norm-conserving pseudopotential. For integration in the Brillouin

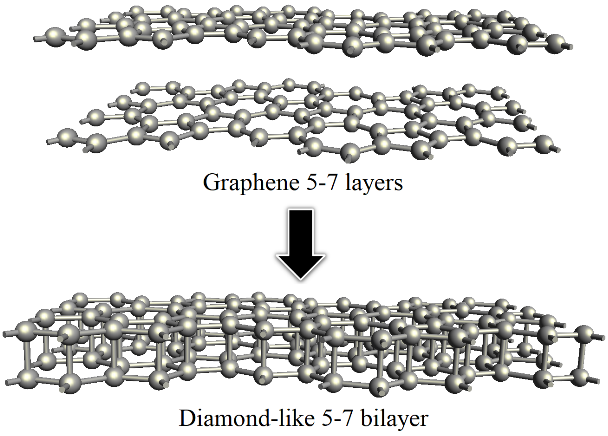

FIG. 1. Scheme of model obtaining of diamond-like bilayer from two graphene layers

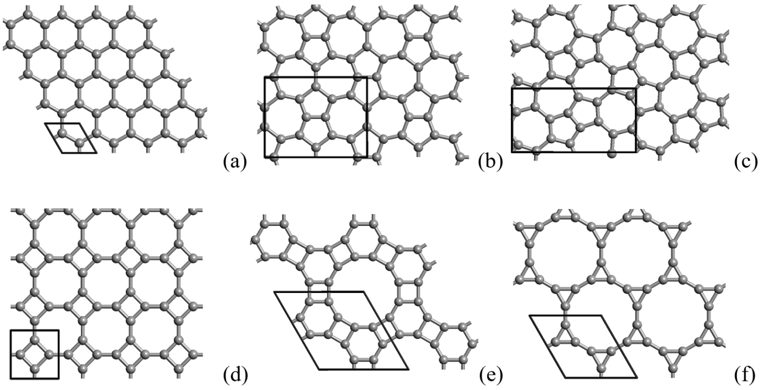

FIG. 2. Structures of graphene layers: (a) L_6; (b) L_{5-7a}; (c) L_{5-7b}; (d) L_{4-8}; (e) L_{4-6-12}; (f) L_{3-12}

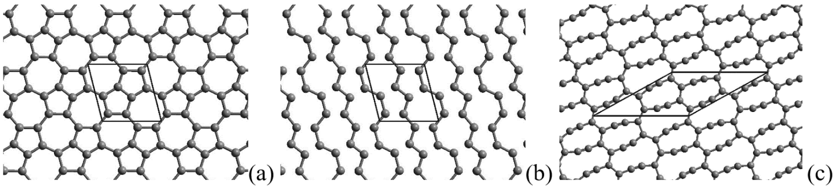

FIG. 3. Diagram of the structure formation of a graphyne γ1-L_{5-7a} layer: (a) the initial graphene L_{5-7a} layer; (b) cutting some of the interatomic bonds in the initial graphene and replacing them with fragments of diatomic carbine chains; (c) the optimized graphyne γ1-L_{5-7a} layer structure

zones, $20 \times 20 \times 1$ k-point grids were used. The kinetic energy cutoff value was taken equal to 800 eV. To reduce the mutual influence of neighboring carbon layers, unit cells with the parameter $c = 15$ Å were chosen. Modeling of phase transitions was carried out on the basis of the technique described in [6].

3. Results and discussion

3.1. Diamond-like bilayers

As a result of the DFT calculations of the cross-linked graphene L_{5-7} layer structures, the possibility of stable existence of two new structural varieties of diamond-like bilayers was established. The new DL_{5-7a} and DL_{5-7b} bilayers have orthorhombic unit cells, in contrast to the hexagonal or tetragonal DL_6, DL_{4-8}, DL_{4-6-12} and DL_{3-12} bilayers (Table 1). The unit cell parameters of the initial graphene layers and diamond-like bilayers are given in Table 1. The lengths of the elementary translation vectors of diamond-like DL_{5-7a} and DL_{5-7b} bilayers are 10 – 13 % longer than the corresponding values for the initial graphene layers. The bilayer thickness is ~ 1.608 Å. The interatomic bond lengths are in the range from 1.5376 to 1.6268 Å in the bilayer structures. The angles between covalent bonds in the diamond-like DL_{5-7a} and DL_{5-7b} bilayers vary from 89.56 to 140.83 °, while the smallest (60 °) and largest (150 °) angles are observed in the DL_{3-12} and DL_{4-6-12} bilayers. The pores of the maximum diameter are approximately 2.08 Å. The structures of the DL_{5-7a}, DL_{5-7b}, and DL_6 bilayers are the least stressed in comparison with the structure of cubic diamond, since the total deviations of the bond angles from the diamond angle (109.47 °) take the smallest values. The most stressed layered nanostructures are the DL_{4-6-12} and DL_{3-12} bilayers.

TABLE 1. Calculated structural parameters and properties of the initial graphene layers, cubic diamond, and diamond-like bilayers (a, b, and N are the unit cell parameters; Δ_{Ed} is the difference total energy relative to the diamond total energy)

Structure	Symmetry group	a, Å	b, Å	N, atoms	Density, mg/m^2	Δ_{Ed}, eV/atom	Band gap, eV
L_6	*p6/mmm*	2.4872	2.4872	2	0.745	−0.04	—
L_{5-7a}	*cmmm*	7.5183	5.8942	16	0.720	0.22	—
L_{5-7b}	*pbam*	8.9919	4.6430	16	0.764	0.20	—
L_{4-8}	*p4/mmm*	3.4687	3.4687	4	0.663	0.52	—
L_{4-6-12}	*p6/mmm*	6.8116	6.8116	12	0.596	0.66	—
L_{3-12}	*p6/mmm*	5.2563	5.2563	6	0.500	1.09	—
Diamond	$Fd\bar{3}m$	3.5969	3.5969	8	—	0.00	5.61
DL_6	*p6/mmm*	2.7369	2.7369	4	1.230	1.22	1.86
DL_{5-7a}	*cmmm*	8.2607	6.4825	32	1.192	1.32	1.88
DL_{5-7b}	*pbam*	10.1451	5.2704	32	1.194	1.31	1.68
DL_{4-8}	*p4/mmm*	3.8218	3.8218	8	1.092	1.55	2.38
DL_{4-6-12}	*p6/mmm*	7.5116	7.5116	24	0.980	1.65	1.41
DL_{3-12}	*p6/mmm*	5.8204	5.8204	12	0.816	2.00	1.36

The surface densities of the diamond-like DL_{5-7a} and DL_{5-7b} bilayers are 1.192 and 1.194 mg/m^2, respectively, and exceed that for hexagonal L_6 graphene by 65 % (Table 1). The total energy calculations of the bilayers showed that the most stable layers should be the diamond-like DL_6, DL_{5-7a}, and DL_{5-7b} bilayers, since their total energies are higher than those for cubic diamond by 1.22 – 1.32 eV/atom. The least stable bilayer is DL_{3-12}, for which the difference total energy (Δ_{Ed}) is 2.00 eV/atom. Diamond-like bilayers with minimum total energies are formed from the most stable graphene layers (Table 1). The calculated data analysis showed that the value of Δ_{Ed} decreases linearly with an increase in the surface density of the bilayer. It should be noted that the DL_{5-7a} and DL_{5-7b} bilayers should be less stable than thirty-three three-dimensional diamond polymorphs studied in [18], since the different energies of these bilayers are higher than the corresponding energies of these diamond polymorphs by at least 0.19 eV. However, the two new bilayers are more stable than diamond-like CA1 (T-carbon) and CA12 phases, which consist of polymerized tetrahedranes [18, 19].

To study the electronic properties of the diamond-like bilayers, the band structures and the density of electronic states were calculated. For all bilayers, the calculations of the electron energies in the Brillouin zones were carried out in the planes specified by the vectors k_1 and k_2. Fig. 4 shows the calculated band structure for the most stable DL_{5-7b} bilayer. It was found that the widths of the direct band gap in the DL_{5-7a} and DL_{5-7b} bilayers are 1.88 and 1.68 eV, respectively, which are 66 – 70 % less than that for cubic diamond (Table 1). The spectrum of electronic states in the Brillouin zone of the diamond-like DL_{5-7b} bilayer is also shown in Fig. 4. The minimum band gap, determined as the difference between the electron energies of the bottom of the conduction band and the top of the valence band, for the diamond-like DL_{5-7a} bilayer is 1.40 eV, which is 10 % less than the corresponding value for the DL_{5-7b} bilayer. Only for the diamond-like DL_{4-6-12} bilayer, the band gap values determined from the band structure and the spectrum of electronic states coincide. Therefore, the new DL_{5-7a} and DL_{5-7b} bilayers must be semiconductors with an indirect band gap.

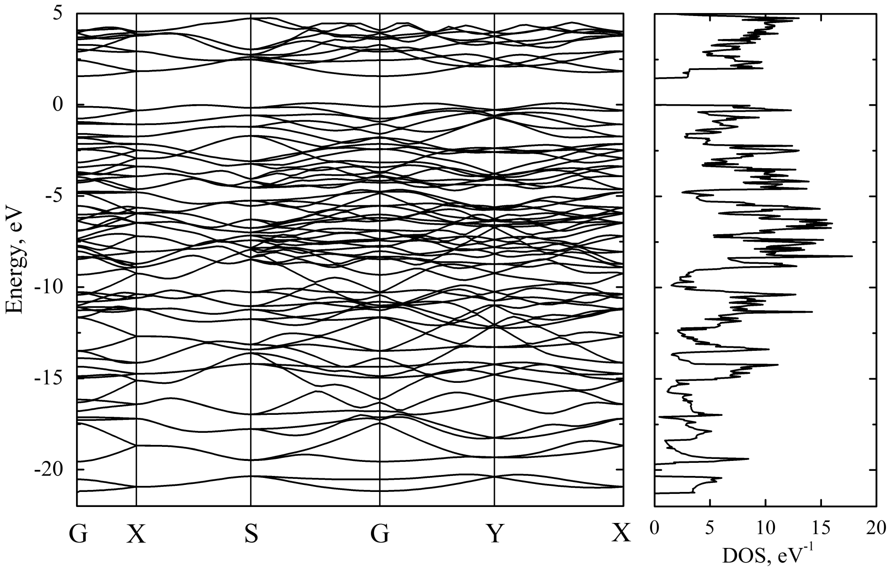

FIG. 4. Electronic band structure and density of states (DOS) of the diamond-like DL$_{5-7b}$ bilayer

One of the ways to experimentally obtain diamond-like materials is strong compression of precursors consisting of sp^2-hybridized atoms [2, 20, 21], therefore, the phase transitions of bilayer graphenes into diamond-like bilayers under uniaxial compression were simulated. As a result of the compression of the initial graphene L$_{5-7}$ layers along the 001 crystallographic axis, the formation of covalent bonds between adjacent graphene layers occurs. Fig. 5 shows the graphs of the dependences of the difference in total energy on the distance between adjacent layers, illustrating the first order phase transitions. The diamond-like DL$_{5-7a}$ and DL$_{5-7b}$ bilayer structures are formed when the initial graphene layers approach each other at a distance of 1.758 Å (Fig. 5). The pressure at which the "bilayer graphene L$_{5-7a}$ $\rightarrow$ DL$_{5-7a}$ bilayer" structural transformation occurs is 12.9 GPa, while the pressure for the "L$_{5-7b}$ $\rightarrow$ DL$_{5-7b}$" phase transition is 10.0 GPa. These values are much less than the calculated values of the formation pressures of cubic and hexagonal diamonds [22].

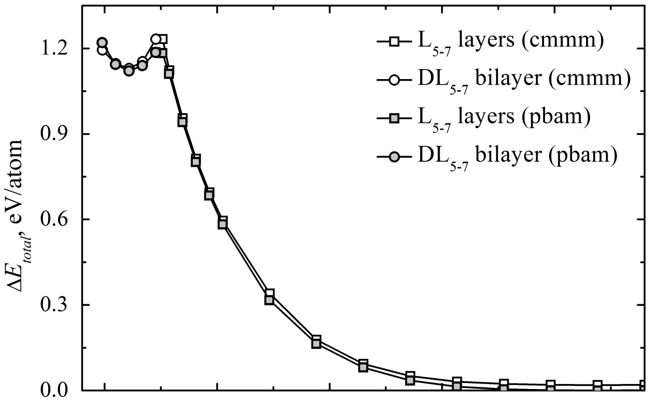

FIG. 5. Dependences of the difference total energy (ΔE_{total}) on the interlayer distance for the phase transitions of graphene layers into diamond-like bilayers

3.2. Graphyne-like layers

Based on the graphene L$_{5-7a}$ layer, the initial structures of one α-, four β- and four γ-graphyne layers were theoretically constructed. Twenty-eight original graphyne layers of γ- and β-structured varieties, as well as one α-structure were built on the basis of the graphene L_{5-7b} layer. Calculations by the DFT-GGA method of the geometrically optimized structure of graphyne layers showed that only two α-layers, one γ-layer, and eighteen structural varieties of β-layers retained the original graphyne structure (Table 2). Images of the structures of these stable layers are shown in Figs. 6 and 7. In the course of optimization, the structures of unstable γ-type layers were transformed into structures of different graphene layers or into structures of graphyne layers with a smaller relative number of sp-hybridized atoms (Fig. 8).

TABLE 2. The structural, energy and electronic characteristics of graphyne L_{5-7} layers (P is the number of non-equivalent structural positions of atoms; N is the number of atoms in the unit cell; ρ is the layer density; ΔE_{total} calculated as E_{total} minus total energy of the hexagonal graphene layer; E_{sub} is the sublimation energy; Δ is the band gap width at the Fermi energy level E_F)

Graphyne layer	P	N, atoms	ρ, mg/m^2	ΔE_{total}, eV/atom	E_{sub}, eV/atom	Δ, eV	E_F, eV
α-L_{5-7a}	10	32	0.37	1.10	6.66	0.00	−4.69
β1-L_{5-7a}	12	24	0.46	1.10	6.66	0.00	−4.71
β2-L_{5-7a}	12	24	0.46	1.05	6.71	0.00	−4.64
β3-L_{5-7a}	12	24	0.48	0.98	6.78	0.00	−4.84
β4-L_{5-7a}	7	24	0.48	0.98	6.78	0.00	−4.83
α-L_{5-7b}	16	64	0.36	1.10	6.66	0.00	−4.64
β1-L_{5-7b}	12	48	0.47	1.03	6.73	0.00	−4.58
β2-L_{5-7b}	24	48	0.46	1.10	6.66	0.00	−4.60
β3-L_{5-7b}	24	48	0.46	1.22	6.54	0.00	−4.55
β4-L_{5-7b}	24	48	0.47	1.01	6.75	0.17	−4.78
β5-L_{5-7b}	24	48	0.47	1.01	6.75	0.08	−4.59
β6-L_{5-7b}	24	48	0.46	1.08	6.68	0.00	−4.57
β7-L_{5-7b}	12	48	0.46	1.05	6.71	0.11	−4.57
β8-L_{5-7b}	48	48	0.47	1.04	6.72	0.18	−4.66
β9-L_{5-7b}	24	48	0.47	1.04	6.72	0.20	−4.70
β10-L_{5-7b}	10	48	0.48	0.98	6.78	0.00	−4.91
β11-L_{5-7b}	10	48	0.48	0.98	6.78	0.11	−4.99
β12-L_{5-7b}	12	48	0.46	1.10	6.66	0.00	−4.59
β13-L_{5-7b}	24	48	0.47	1.03	6.73	0.05	−4.68
β14-L_{5-7b}	10	48	0.48	0.98	6.78	0.00	−4.91
γ1-L_{5-7b}	8	32	0.62	1.03	6.73	0.00	−4.24

The numerical values of some structural parameters characterizing the layers of L_{5-7} graphyne are shown in Table 2. The unit cells of the layers are orthorhombic and monoclinic, containing from 24 to 64 atoms. The values of the vectors of elementary translations a and b vary in the range from 8.0 to 25.9 Å. The number of different structural positions (P) of atoms in the unit cells is minimal for the β4-L_{5-7a} layer ($P = 7$), the maximum value of this parameter is observed for the β8-L_{5-7b} layer ($P = 48$). The ratio of the number of atoms in the sp- and sp^2-hybridization states varies from 1:1 in the graphyne γ1-L_{5-7b} layer to 2:1 in the β-type layers and 3:1 in the α-graphyne layers. The layer density is minimal for the α-type layers (0.36 – 0.37 mg/m^2), the maximum density (0.62 mg/m^2) is observed for the γ1-L_{5-7b} graphyne layer. For the β-type graphyne layers, the density is $\sim$ 0.47 mg/m^2. The layer density of the graphyne layers is lower than the layer density of 0.74 mg/m^2 for hexagonal graphene (Table 2).

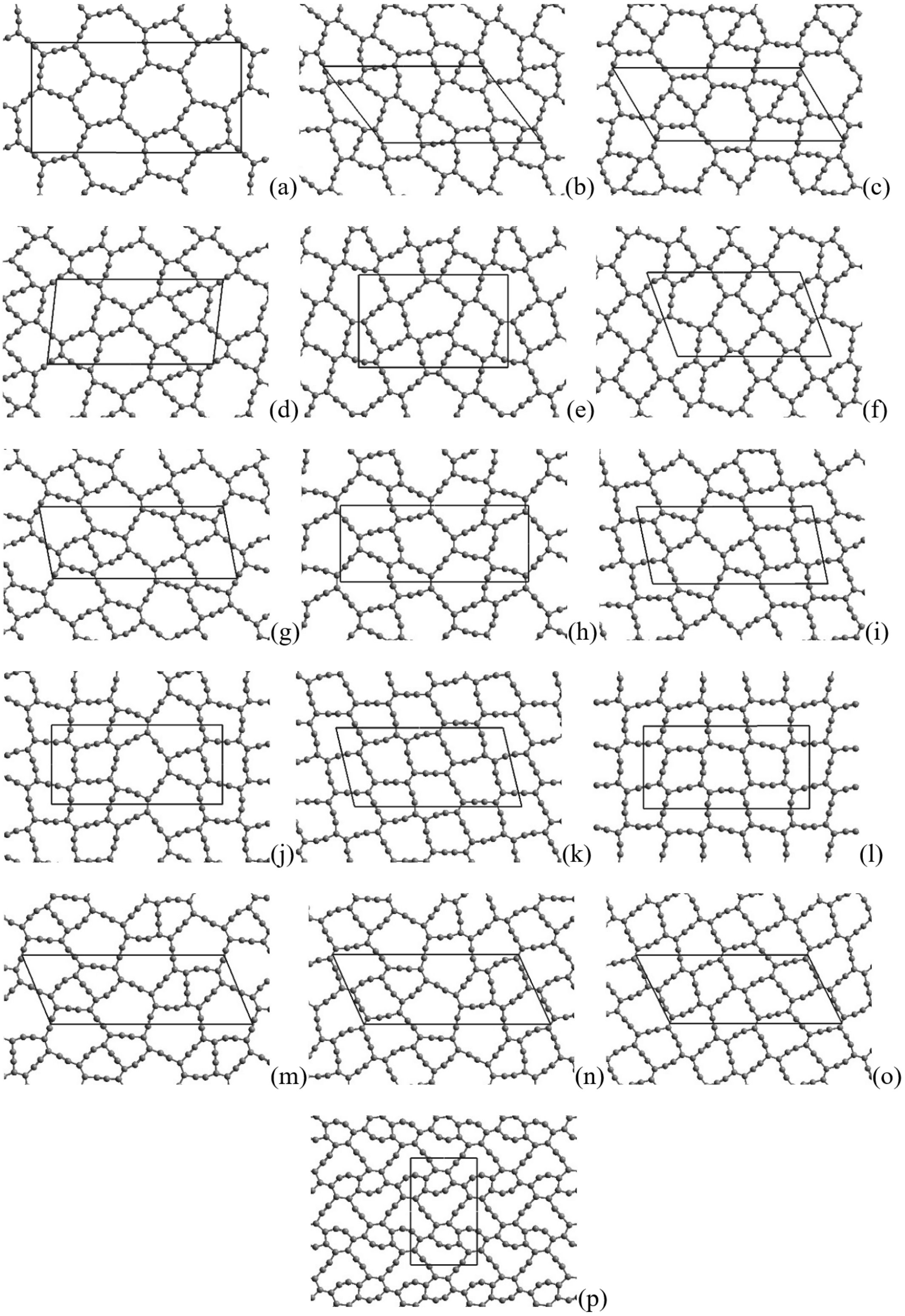

FIG. 6. Geometrically optimized structures of stable graphyne layers: (a) α-L$_{5-7b}$; (b) β1-L$_{5-7b}$; (c) β2-L$_{5-7b}$; (d) β3-L$_{5-7b}$; (e) β4-L$_{5-7b}$; (f) β5-L$_{5-7b}$; (g) β6-L$_{5-7b}$; (h) β7-L$_{5-7b}$; (i) β8-L$_{5-7b}$; (j) β9-L$_{5-7b}$; (k) β10-L$_{5-7b}$; (l) β11-L$_{5-7b}$; (m) β12-L$_{5-7b}$; (n) β13-L$_{5-7b}$; (o) β14-L$_{5-7b}$; (p) γ1-L$_{5-7b}$

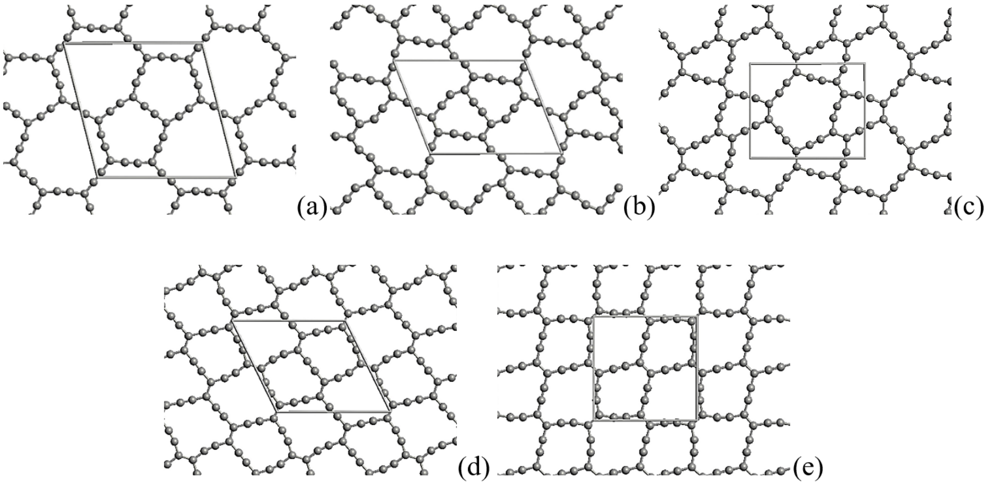

FIG. 7. Geometrically optimized structures of stable graphyne layers: (a) α-L$_{5-7a}$; (b) β1- L$_{5-7a}$; (c) β2- L$_{5-7a}$; (d) β3- L$_{5-7a}$; (e) β4-L$_{5-7a}$

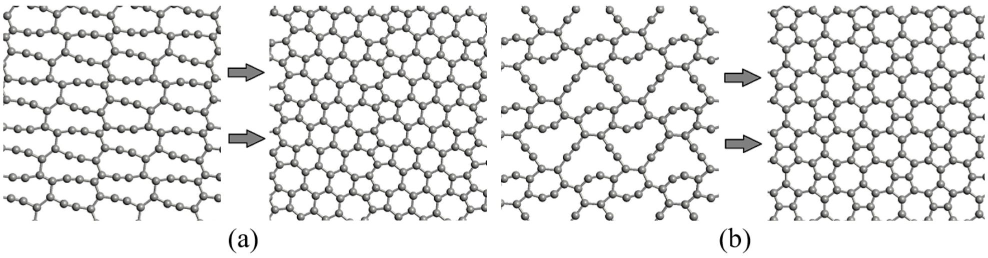

FIG. 8. Transformation of the structure of graphyne γ-L$_{5-7a}$ layers during geometric optimization: (a) a graphyne γ1-L$_{5-7a}$ layer is transformed to a graphene L$_{5-6-7a}$ layer; (b) a graphyne γ3-L$_{5-7a}$ layer is transformed to a graphene L$_{5-7a}$ layer

The difference energy ΔE_{total}, calculated as the difference between the total energies in the graphyne layers and the hexagonal graphene layer, varies from 0.98 to 1.22 eV/atom. This indicates a lower stability of graphyne layers compared to graphene layers. However, the sublimation energies of 6.66 – 6.78 eV/atom for the graphyne L$_{5-7b}$ layers fall within the range of values typical for carbon compounds that stably exist under normal conditions. The maximum sublimation energy is observed for the β3-L$_{5-7a}$, β4-L$_{5-7a}$, β10-L$_{5-7b}$, β11-L$_{5-7b}$, and β14-L$_{5-7b}$ layers (Table 2). Apparently, these graphyne layers should be the most stable.

The DFT-GGA calculations of the band structure and density of electronic states of the graphyne L$_{5-7}$ layers showed that the density of electronic states is zero at the Fermi energy for seven layers, and the band gap varies from 0.05 to 0.20 eV. The band gap for the remaining fourteen layers is zero. The Fermi energy (E_F) varies in the range from -4.99 to -4.24 eV (Table 2).

4. Conclusions

Thus, a number of new carbon nanostructures according to specially developed algorithms were theoretically built on the basis of graphene L$_{5-7a}$ and L$_{5-7b}$ layers. These new nanostructures were two diamond bilayers and thirty-eight graphyne layers. As a result of the DFT-GGA calculations, it was found that diamond-like bilayers and twenty-one graphyne layers have stable structures. After geometric optimization, the structure of seventeen graphyne layers turned out to be unstable. These layers, consisting of sp+sp^2-hybridized atoms, tend to transform their structure into the structure of graphene layers, consisting only of sp^2-hybridized atoms. The band gap for most of the stable graphyne layers is zero, while for the rest of the graphyne layers, it does not exceed 0.2 eV. Diamond-like layers have a direct band gap of 1.88 and 1.68 eV for the DL$_{5-7a}$ and DL$_{5-7b}$ bilayers, respectively. The new polymorphic varieties of graphyne, apparently, can be experimentally obtained by polymerization of molecules, the structure of the carbon framework of which is close to the structure of the corresponding graphyne layers [23]. The diamond-like bilayers based on L$_{5-7}$ graphene can be obtained by uniaxial compression of these graphene bilayers at pressures of $\sim$ 11 GPa.

The practical application of the new carbon nanostructures with a layered structure is possible in electronics and as molecular sieves [24, 25].

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