Structure of graphane polymorphs

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Abstract. Calculations of the structure and electronic properties for five structural variations of graphane were performed within the framework of density functional theory (DFT) with generalized gradient approximations (GGA). The electron densities of states and band structure of graphene crystals have been calculated. It has been established that the band gap for graphane polymorphs varies from 5.50 eV to 5.65 eV. Sublimation energy of graphane layers with different structure was varying from 11.33 to 11.48 eV per C-H molecular group.

1. Introduction
Graphane layers obtain by joining one hydrogen atom to each of the carbon atoms of the graphene layer [1]. Hydrogenographane layers were experimentally synthesized in 2009 [2]. Graphane (unlike graphene) is a dielectric. Hydrogenographane layers consist of carbon atoms in the sp³ hybridization [3]. Perhaps, structural types of hydrogenographane layers with different properties can exist that may be of interest in terms of using them as a basis for electronic devices. In this study, we investigated the structure and electronic properties of the five main polymorphic types of hydrogenographane layers.

2. Methods
For practical use of graphane layers it is desirable obtaining layers of graphane with non-carbon atoms attached to only one side of the layer. However, studies carried out earlier in [5] are showed, that these layers are strongly deformed and tend to form structure like a scroll, which makes them unsuitable for use as a basis for nanoelectronic devices. Therefore, in this study we analyzed only hydrogenographane layers with hydrogen atoms attached to both sides of graphane layer.

As shown by theoretical analysis, there are only five different ways in connection with non-carbon atoms of graphane layer on both sides, so that the positions of all the carbon atoms were crystallographically equivalent. Various structural types of graphane layers with non-equivalent positions of carbon atoms may be more, but layers with equivalent positions of the atoms should be the most thermodynamically stable.

Figure 1 shows the initial graphene layers to which the non-carbon atoms can join with the upper side of layer (atoms highlighted in gray), or with the lower side of layer (atoms marked black color). The first of these types of connection, T1, corresponds hydrogenographane layer described in [2,3]. Three ways to join T2, T3, and T4 were considered earlier in [6,7]. The possibility of existence the fifth main structural type, T5, of hydrogenographane layers studied for the first time in this paper.

Theoretically built hydrogenographane layers of the five main types were subjected to geometrical optimization by the methods of density functional theory (DFT) [8] within the generalized gradient approximations (GGA) [9]. Calculations were carried out for the layers arranged in a three-dimensional structure, but the distance between the layers (at the same time it was a unit cell period along the crystallographic c-axis) was chosen sufficiently large (10 Å), so that layers do not affect the
structure of the adjacent layers and their properties. Densities of electron states calculated using k-point set of $12 \times 12 \times 12$. The wave functions are displayed on a truncated basis set of plane waves. The dimension of the set of basis functions has been limited by the value $E_{\text{cutoff}} = 1$ keV.

Figure 1. Possible ways of attachment of hydrogen atoms on two sides of the graphene layer: (a) T1; (b) T2; (c) T3; (d) T4; (e) T5.

3. Results and Discussion

Images of five structural types of graphane layers, geometrically optimized by the DFT-GGA, are shown in Figure 2. The structural characteristics of the layers are shown in Table 1. Hydrogenographane layers of various types have very different structures. The layers also have various unit cells which differ by parameters and number of contained atoms (Figure 2 and Table 1). The unit cells of graphane layers contain from four to sixteen atoms and characterized by hexagonal (Hex), triclinic (Tr), and orthorhombic (Ort) crystal systems. The density of hydrogenographane layers ranges from 0.77 to 0.88 mg per m$^2$ that exceeds the density of graphene layers of 0.74 mg per m$^2$.

Table 1. The structural parameters and properties the main types of graphane layers (T1–T5), as well as hexagonal graphene ($L_6$).

| Type of layer | T1    | T2    | T3    | T4    | T5    | $L_6$ |
|--------------|-------|-------|-------|-------|-------|-------|
| Crystal system | Hex   | Tr    | Tr    | Ort   | Ort   | Hex   |
| a, Å         | 2.5532| 2.542 | 4.616 | 4.571 | 5.006 | 2.491 |
| b, Å         | 5.021 | 5.021 | 5.626 | 4.350 | 4.440 |       |
| $\gamma$, ° | 120   | 59.56 | 56.26 | 90    | 90    | 120   |
| $E_{\text{total}}$, eV/u.c. | -346.74 | -693.08 | -693.29 | -1385.99 | -1385.29 | -314.64 |
| $E_{\text{total}}$, eV/(CH) | -173.37 | -173.27 | -173.32 | -173.25 | -173.22 |       |
| $E_{\text{sub}}$, eV | 11.48  | 11.38 | 11.43 | 11.36 | 11.33 | 7.76  |
| $\Delta E_{\text{sub}}$, eV | 3.72   | 3.63  | 3.67  | 3.60  | 3.57  | 0     |
| $\Delta$, eV | 5.55   | 5.50  | 5.54  | 5.51  | 5.65  | 0.00  |
| $\rho$, mg/m$^2$ | 0.77   | 0.79  | 0.88  | 0.87  | 0.78  | 0.74  |
| $N$, at.     | 4     | 8     | 8     | 16    | 16    | 2     |

The total energy per one molecular C-H group ($E_{\text{total}}$) ranges from -173.37 to -173.22 eV (Table 1). Sublimation energy ($E_{\text{sub}}$) was made as a result of the calculation of the difference between the total energy of a single C-H molecular group in hydrogenographane layer and the energy of isolated carbon and hydrogen atoms (the estimated value of these energies equal to $-149.56$ and $-12.33$ eV/atom, correspondently).
In result of calculations (In the calculation process,) the specific sublimation energy per one carbon atom of graphane layer was found. The numerical values of sublimation energy hydrogenographane layers are in the range of 11.33 to 11.48 eV/atom which are 3.57–3.7 eV greater than the value of the specific sublimation energy of hexagonal graphene layer (Table 1). Apparently this is due to higher strength carbon-hydrogen bond as compared with the carbon-carbon bond between the π electrons of graphene layer. The maximum sublimation energy is observed for the T1-type layer and the minimum is observed for T5, but the relative energy difference is only 1.3 %, which indicates the possibility of stable existence of all main polymorphic types of graphane.

The results of measuring the lengths of interatomic bonds and the angles between them are shown in Table 2. The carbon-carbon bond lengths vary in the range of 1.5459 to 1.5830 Å, whereas the carbon-hydrogen bond lengths are in the interval of 1.1094 to 1.1183 Å. The bond angles in graphane layers differ from the angle of 109.47 ° which is characteristic of the atomic positions in the diamond structure. The total deviation of bond angles from the diamond angle is characterized by a deformation parameter Def, which quantifies the degree of tension of the structure in comparison with the diamond structure. The minimum value of Def (10.87 °) was observed for T1-type graphane layer, the maximum value (22.33 °) was observed for T5-layer. This is a good explanation of the sublimation energy difference of structural types, because the sublimation energy minimum is observed for strained layers, while the maximum of E_{sub} is typical for the layer with the smallest deformation parameter (Tables 1 and 2).

The calculated electron densities of states for five graphane layers are shown in Figure 3. The numerical values of band gaps are shown in Table 1. The band gap (Δ) of graphene layers were in the range of 5.50 to 5.65 eV. This indicates that all hydrogenographane layers, regardless of the type, should exhibit structural dielectric properties.
Figure 3. The density of electron states hydrogenographane layers of different types: (a) T1; (b) T2; (c) T3; (d) T4; (e) T5 (zero energy was taken by the Fermi energy).

Table 2. The bond lengths and bond angles in graphane layers.

| Type of layer | T1   | T2   | T3   | T4   | T5   |
|---------------|------|------|------|------|------|
| L_1(C-C) Å    | 1.5467 | 1.5796 | 1.5530 | 1.5506 | 1.5701 |
| L_2(C-C) Å    | 1.5467 | 1.5459 | 1.5530 | 1.5830 | 1.5476 |
| L_3(C-C) Å    | 1.5467 | 1.5459 | 1.5530 | 1.5830 | 1.5559 |
| L_4(C-H) Å    | 1.1183 | 1.1124 | 1.1128 | 1.1094 | 1.1139 |
| ϕ_{12}, °     | 111.25 | 112.27 | 112.28 | 112.44 | 112.00 |
| ϕ_{13}, °     | 111.25 | 112.27 | 112.28 | 112.44 | 117.77 |
| ϕ_{14}, °     | 107.63 | 106.61 | 107.85 | 107.42 | 105.94 |
| ϕ_{23}, °     | 111.25 | 110.60 | 111.04 | 112.39 | 107.44 |
| ϕ_{24}, °     | 107.63 | 107.41 | 106.50 | 106.47 | 106.55 |
| ϕ_{34}, °     | 107.63 | 107.41 | 106.50 | 106.47 | 106.45 |
| Def, °        | 10.87  | 13.71  | 14.74  | 16.91  | 22.33  |

4. Conclusions

Thus, the crystal structure and electronic properties of five main structural types of hydrogenographane layers were calculated by the DFT-GGA method. The layers were obtained by attachment of hydrogen atoms to the graphene layer L_6. Calculations of the band structure and density of electronic states graphene compounds indicate that their electronic properties to be different from each other slightly and all hydrogenographane layers should bad conduct electricity. Local carbonization and making of graphene ribbons on dielectric layer of graphene are possible for hydrogenographane layers of any of the five main structural types. Different nanoelectronic devices
can be obtained as a result of this process. Perhaps some of the polymorphic types of graphane may be preferable to deal with these problems; therefore this question remains open and should be studied in future research.

**Acknowledgments**

The authors thank Foundation of Perspective Research of Chelyabinsk State University for the financial support.

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