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# Atomic structure and electronic properties of binary graphane: Ab initio calculations

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**Abstract.** In this work, *ab initio* studies of a novel two-dimensional diamond-like nanostructure consisting of two polymerized graphenes are carried out. This nanostructure called binary graphane has a two-dimensional hexagonal lattice with the parameter  $a = 0.2737$  nm. The surface density, cohesive energy and indirect band gap of binary graphane are  $0.123 \mu\text{g}/\text{cm}^2$ , 6.64 eV/atom and 2.83 eV, respectively. It is also established that this layer must be stable up to 200 K.

## 1. Introduction

Carbon is a unique chemical element, on the basis of which a huge variety of inorganic compounds with significantly different structures and properties can be formed [1-9]. Although graphite and diamond are the most stable inorganic compounds under normal conditions [10], various molecular, tubular and layered carbon nanostructures consisting of  $\text{sp}^2$  or  $\text{sp}^2$ - $\text{sp}$  hybridized atoms have also been synthesized over the past thirty five years [10–13]. However, nanostructures consisting only of  $\text{sp}^3$  hybridized carbon atoms have not yet been discovered.

New experimental studies on nanoindentation of thin graphene films have shown that two-layered diamond-like nanostructures can be formed at high uniaxial stresses and demonstrate high strength comparable to those for diamond [14]. The structure of these binary layers has not yet been determined. Therefore, this paper is devoted to theoretical calculations of the possible structure, thermal stability and properties of a new two-dimensional structural variety of diamond formed during the polymerization of two graphene layers.

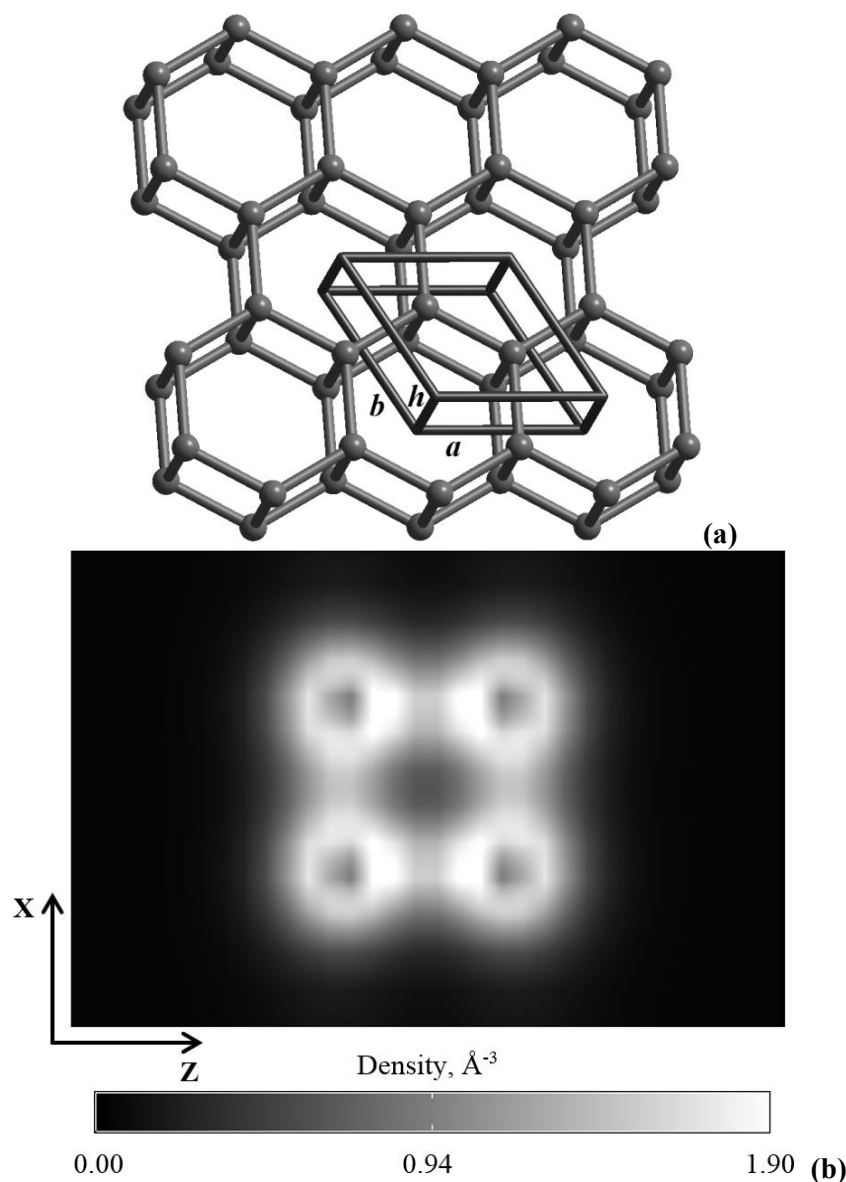
## 2. Methods

Calculations of structural parameters and properties of the layered carbon phase are performed by the density functional theory (DFT) method using the Quantum ESPRESSO software package [15]. The DFT method used the generalized gradient approximation (GGA) with the exchange-correlation energy functional in the Perdew-Burke-Ernzerhof formulation [16]. The influence of the ion cores was taken into account through the Troullier-Martins norm-conserving pseudopotentials [17]. The calculations are carried out for the following  $k$ -point grid:  $12 \times 12 \times 6$ . Wave functions were decomposed by a truncated basis set of plane waves. The cutoff energy are 60 Rydberg. The geometrical optimization of the binary graphane unit cell was carried out until the values of atomic forces and stresses were less than 10 meV/nm and 0.1 GPa, respectively. Simulation of graphane annealing is performed by the molecular dynamics method using the  $6 \times 6 \times 3$   $k$ -point grid with the time step of 0.5 fs.



### 3. Results

The structure of the desired two-dimensional polymorphic variety of diamond can be obtained as a result of the operation of linking two parallel graphene layers according to the method proposed in [1,18]. According to carbon terminology, this layer was named binary graphane. The crystal structure of binary graphane obtained after geometric optimization is shown in figure 1a.



**Figure 1.** (a) Structural fragment of binary graphane. (b) Electron density distribution of binary graphane on the (110) plane of the hexagonal unit cell.

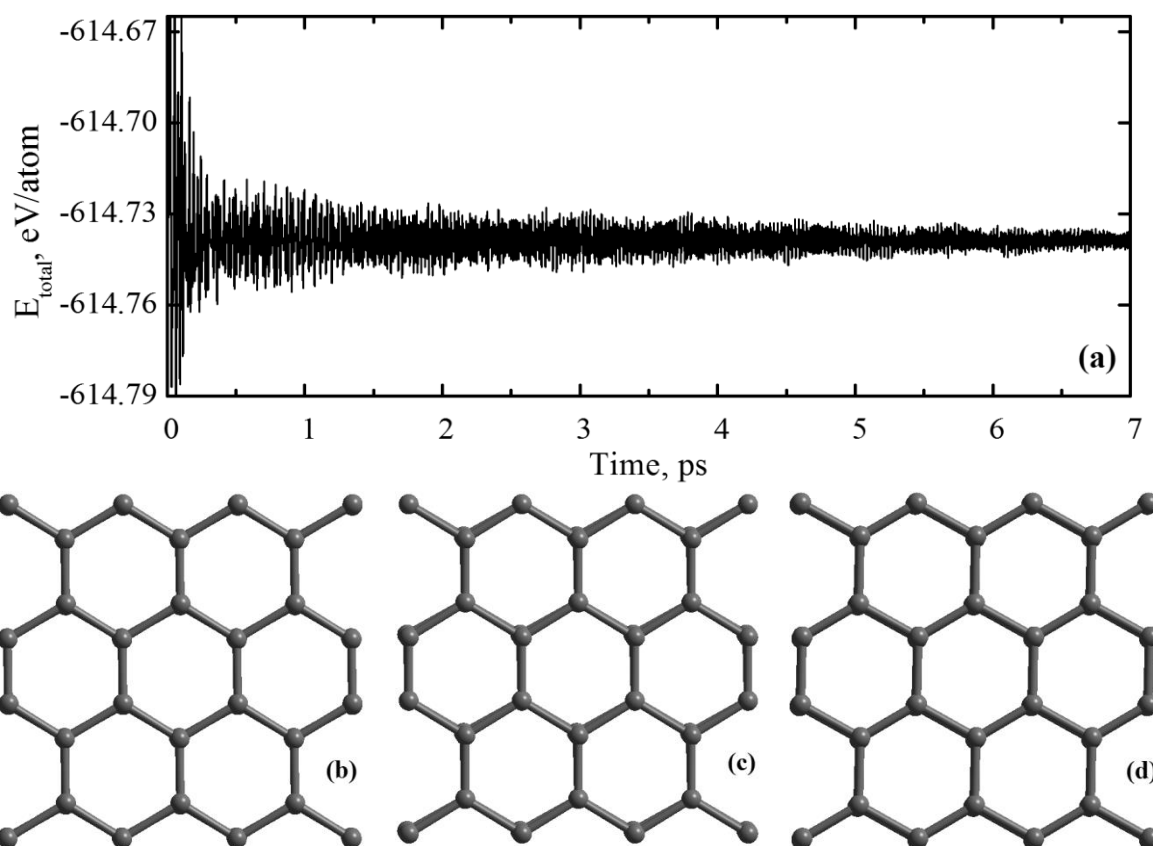
The two-dimensional hexagonal unit cell of binary graphane with the parameter  $a = 0.2737$  nm contains four carbon atoms (figure 1a). The layer thickness ( $h$ ) is 0.1597 nm. The atomic coordinates in fractions of the  $a$ ,  $b$ , and  $h$  parameters are listed in Table 1. All atoms in the structure of binary graphane are located in two parallel planes and are in  $sp^3$  hybridization states as indicated by the localization of electron density along interatomic bonds (figure 1b). The lengths of three carbon-carbon bonds at each atom are equivalent and equal to 0.1580 nm, and the length of the fourth bond perpendicular to the plane of diamond-like layer is 0.1597 nm. The bond lengths in binary graphane are 1.4–2.5 % larger than the

calculated bond length in cubic diamond. The bond angles are 90 or 120° only. The deformation *Str* and *Def* parameters of the diamond-like structure introduced in [2,19] are 0.11 nm and 90.0°, respectively. The surface density of binary graphane is 0.123  $\mu\text{g}/\text{cm}^2$ , which is 60 % higher than those for graphene [10].

The cohesive energy value of the binary layer calculated as the difference between the total energies of the bonded and isolated atoms is 6.63 eV/atom, which is 15 and 7% less than the corresponding calculated energy values of cubic diamond and high density LA4 diamond polymorph [19]. To assess the thermal stability of the new diamond-like layer, the annealing of its structure is carried out at 200 K using the molecular dynamics method. Figure 2a shows the dependence of the total energy change on the annealing time. After annealing for 7 ps, neither destruction nor significant deformation of the structure is observed (figures 2b-d), which indicates the stability of binary graphane at temperatures up to 200 K.

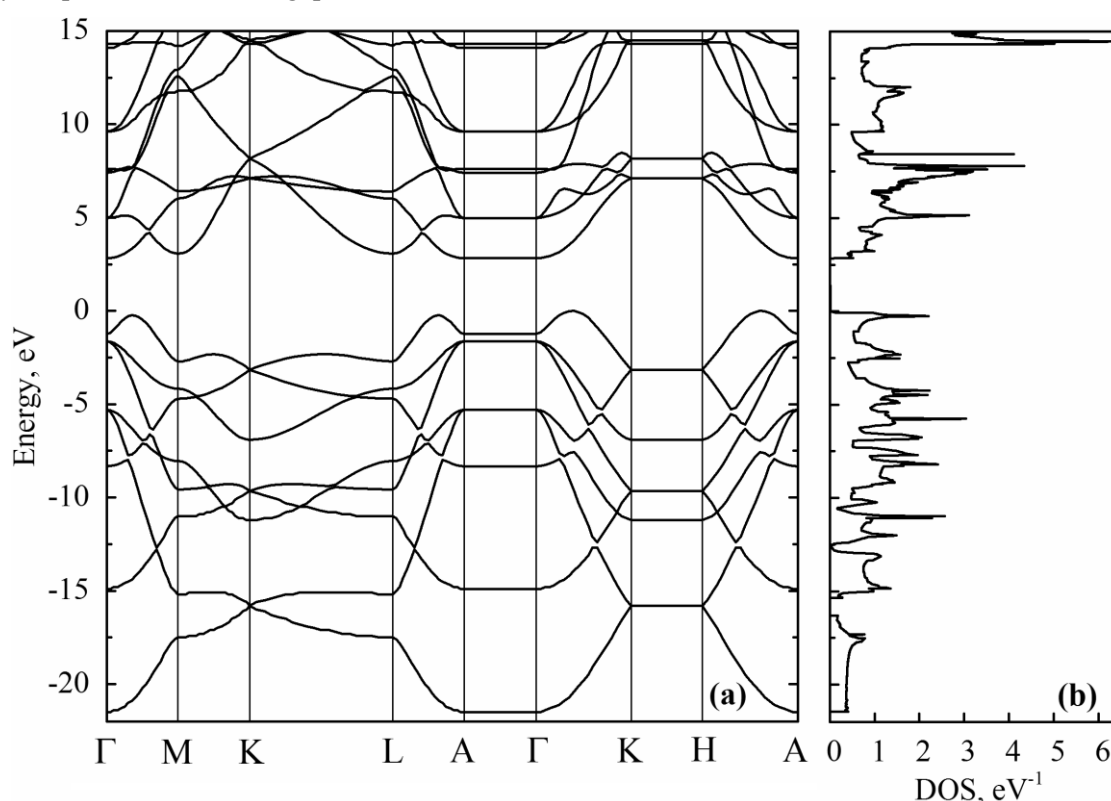
**Table 1.** Relative atomic coordinates in the hexagonal unit cell of binary graphane.

Number	$x_a$ , arb. un.	$y_b$ , arb. un.	$z_h$ , arb. un.
1	0.33333	0.66667	0.00000
2	0.66667	0.33333	0.00000
3	0.33333	0.66667	1.00000
4	0.66667	0.33333	1.00000



**Figure 2.** (a) Dependence of the total energy on the heat treatment time of binary graphane at 200 K. The structure of binary graphane during annealing: (b) 145, (c) 3386, and (d) 7000 fs.

The electronic properties of binary graphane are investigated as a result of calculations of the band structure and the electron density of states (DOS). The electron energies were calculated between five high symmetry points on eight routes ( $\Gamma$ M, MK, KL, LA, A $\Gamma$ ,  $\Gamma$ K, KH, and HA) in the Brillouin zone for the hexagonal lattice. The electronic band structure of this layer is shown in figure 3a. The minimum difference in the electron energy values of the conduction band bottom and valence band top is 3.49 eV, which is 50 % less than the corresponding calculated value for cubic diamond. Figure 3b shows the electron density of states. As a result of analyzing the DOS spectrum, the indirect bandgap value of binary graphane is calculated (2.83 eV). Consequently, the studied two-dimensional diamond polymorph must be a wide-gap semiconductor.



**Figure 3.** (a) Electron band structure of binary graphane. (b) Electron density of states of binary graphane.

#### 4. Conclusions

In this work, *ab initio* calculations of the geometrical optimized structure, cohesive energy, thermal stability and electronic properties of binary graphane layer consisting of two polymerized graphene layers are carried out. It is established that the structure of binary graphane has a two-dimensional hexagonal lattice with the surface density of 0.123  $\mu\text{g}/\text{cm}^2$ . Since the cohesive energy of this layer is 15 % less than the corresponding energy of cubic diamond then it can stably exist up to 200 K. In addition, binary graphane should be a wide-gap semiconductor with an indirect band gap of 2.83 eV.

#### Acknowledgments

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