

## Use of the Adsorbed Organic Molecules as Dopants for Creation of the Built-in Lateral $p$ - $n$ Junctions in a Sheet of Black Phosphorene

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This article discusses the attempt to create the built-in lateral  $p$ - $n$  junctions in a sheet of black phosphorene using the adsorbed organic molecules as dopants. Within the framework of the methods of the electron density functional and the ab initio pseudopotential, the valence electron density spatial distributions, the densities of electronic states, the band gaps and the core charges of a sheet of black phosphorene were obtained. On the sheet of black phosphorene, there was a homogeneous distribution of the valence electron density. The adsorption of carbamide molecules for diverse types of localization on the surface of a black phosphorene sheet led to the redistribution of electron density in it. It was evident that the charge regions of greater density in a black phosphorene sheet with adsorbed carbamide molecules were localized under the atoms of carbamide molecules, forming a common region of the electronic density elevated concentration. The removal of the molecules led to a decrease in their effect on the redistribution of the valence electron density in a black phosphorene sheet. The accumulation of the electric charge of a black phosphorene sheet in the region under the carbamide molecules in turn led to the emergence of regions on the black phosphorene sheet, in which the core charges changed the sign to the opposite. The homogeneity of the distribution of electron density in the black phosphorene sheet disappeared and areas of a spatial charge of different signs were formed. Such areas with charges of different signs create conditions, which are the main characteristic of  $p$ - $n$  junctions. Also it was established that the adsorption of the black phosphorene sheet with carbamide molecules led to a change in conductivity of a black phosphorene sheet.

**Keywords:** Built-in lateral  $p$ - $n$  junction, Black phosphorene, Organic molecules, Dopants, Adsorption, Ab initio calculation, Electrical charge.

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### 1. INTRODUCTION

Molecule doping is a flexible and effective method towards modulating the electronic properties of  $2D$  materials [1]. Molecules adsorbed onto the surface can influence transport in the  $2D$  material, for example, by introducing doping effects and a  $p$ - $n$  junction can thus be fabricated by locally doping the material [2]. A chemically doped  $p$ - $n$  junction was reported by researchers [3-5]. In work [1], the authors used benzyl viologen as an effective electron dopant to part of the area of a few-layer black phosphorus flake and achieve an ambient stable, in-plane  $p$ - $n$  junction. Such chemical doping with benzyl viologen molecules modulates the electron density and allows acquiring a large built-in potential in this in-plane black phosphorus  $p$ - $n$  junction.

Black phosphorus constitutes a new class of  $2D$  materials. It is intensively studied as a  $2D$  semiconductor [6-10]. Phosphorene, as a phosphorus analogue of graphene, refers to the monolayered black phosphorus crystal [11]. The presence of an appreciable direct band gap and high carrier mobility makes phosphorene a promising candidate for novel semiconductor applications [12]. The authors [13] reported that the band gap of phosphorene depends on the number of layers and the in-layer strain, and is significantly larger than the bulk value.

For extension of information about electronic properties of the black phosphorene sheet with the adsorbed organic molecules as dopants, the valence electron density spatial distribution, the densities of electronic states, the band gaps and the core charges have been calculated in the framework of the electronic density functional and ab initio pseudopotential.

### 2. METHODS OF RESEARCH

The calculations used the author's program code [14], which is based on the methods of the electron density functional and the ab initio pseudopotential. It implements the algorithm of self-consistent solution of Kohn-Sham equations in the local approximation, when only electronic variables are determined at fixed atomic cores. See [15] for more details.

### 3. OBJECTS, RESULTS OF CALCULATION AND THEIR DISCUSSION

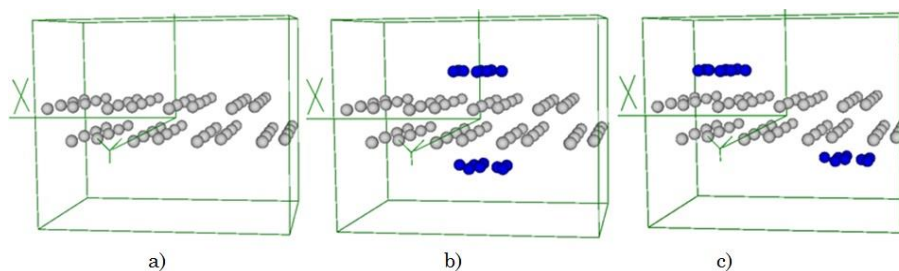
For the study of electronic properties of the sheet of black phosphorene with the adsorbed organic molecules as dopants, the model of the super-lattice was developed (Fig. 1a). The rhombic primitive cell of the super-lattice has the following parameters:  $a = 17.72 \text{ \AA}$ ,  $b = 13.08 \text{ \AA}$ ,  $c = 14.82 \text{ \AA}$ . The geometric properties of the primitive cell were such that it was convenient to use the Cartesian coordinate system. The dimensions of the primitive cell in the directions  $X$  and  $Y$  were chosen so that the translation of the cell organizes an infinite black phosphorene sheet. The size of the primitive cell in the direction  $Z$  was chosen to avoid the interaction of atomic planes transmitted in this direction. The atomic base contained 64 phosphorene atoms. The calculation was performed only for  $\Gamma$ -points of the Brillouin zone of super-lattice.

Carbamide (urea)  $(\text{NH}_2)_2\text{CO}$  was selected as adsorbed molecules.  $(\text{NH}_2)_2\text{CO}$  is the colorless crystalline substance having a melting point of  $132.7 \text{ }^\circ\text{C}$ . A primitive cell of a super-lattice with an atomic base for simulation of an infinite monolayer (which consisted of two atomic layers)

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sheet of black phosphorene with adsorbed carbamide molecules that were placed on both sides of the sheet of

black phosphorene or one against each other, or one offset each other were shown in Fig. 1b, c respectively.



**Fig. 1** – Primitive cells of a super-lattice with an atomic base for simulation of an infinite monolayer sheet of black phosphorene (a) and simulation of an infinite monolayer sheet of black phosphorene with adsorbed carbamide molecules for “one against each other” (b) and “one offset each other” type of localization (c)

The studies were to find changes in the electronic properties of an infinite monolayer sheet of black phosphorene with the adsorbed organic molecules of carbamide as dopants. For comparison, several distances between the carbamide molecules and the black phosphorene sheet were chosen. These distances were changed from 1.87 Å (the smallest distance between atoms that is equal to the sum of covalent radii of phosphorene atom and molecule’s atom) with subsequent increase up to 2.0 Å; 2.5 Å; 3.0 Å.

In Fig. 2, Fig. 3, the spatial distributions of valence electron density, their cross sections within the carbamide molecule and an infinite monolayer sheet of black phosphorene before adsorption were presented.

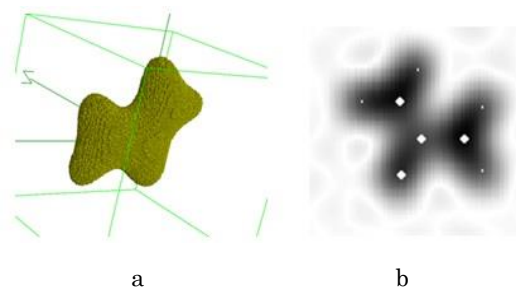
By concentration of valence electron density of the molecule plane, one can determine the intensity of the covalent bonds between the atoms within the molecule. On the sheet of black phosphorene, there was a homogeneous distribution of the valence electron density with charge on the phosphorene atoms cores  $-2.15e$ . The electric charge was evaluated in a spherical volume with the radius  $r = 1.32$  Å.

For localization of adsorbed carbamide molecules of “one against each other” and “one offset each other” types on black phosphorene sheet depending on the distance to the black phosphorene sheet, the maps of spatial distribution of valence electron density and their cross sections, the values of electric charge on the black phosphorene atoms were depicted in Fig. 4 and Fig. 5.

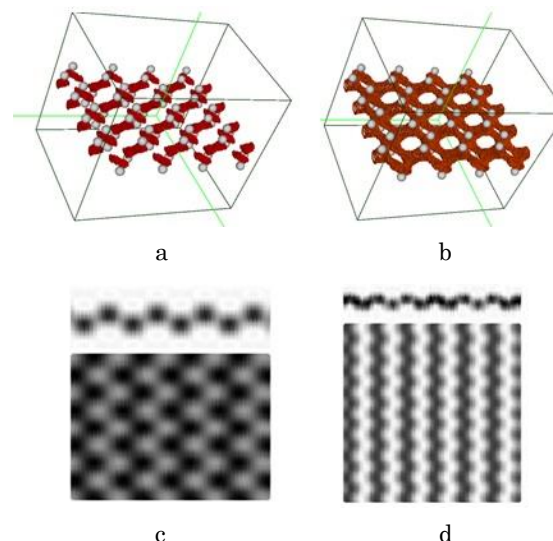
It was evident that the charge regions of greater density in a black phosphorene sheet with adsorbed carbamide molecules were localized under the atoms of carbamide molecules, forming a common region of the electronic density elevated concentration, covering the atoms of black phosphorene and atoms of carbamide molecules. The removal of the molecules led to a decrease in their effect on the redistribution of the valence electron density in a black phosphorene sheet that was confirmed by the calculated electric charges on the black phosphorene atoms located directly under the molecules (see Fig. 4c, Fig. 5c). It was believed that the location of molecules at computed distances from the black phosphorene sheet is a chemical adsorption.

The accumulation of the electric charge of a black phosphorene sheet in the region under the carbamide molecules in turn led to the emergence of regions on the black phosphorene sheet, in which the core charges changed the sign to the opposite. That is, the homogenei-

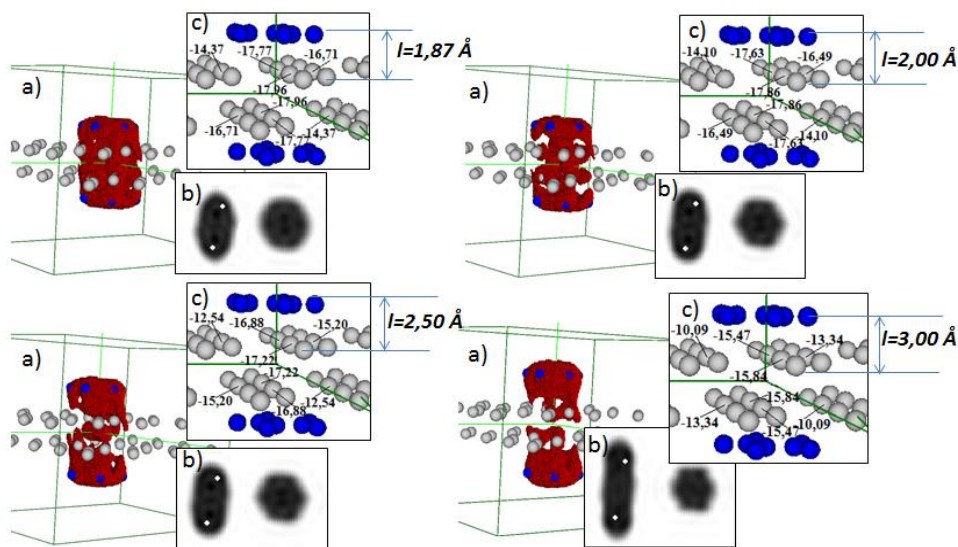
ty of the distribution of electron density in the black phosphorene sheet disappeared, and areas of a spatial charge of different signs, which are a prerequisite for creating of the built-in lateral  $p$ - $n$  junctions, were formed (Fig. 6). The values of the electric charge on the black phosphorene atoms, which are located directly under the carbamide molecules, at various adsorption distances for “one against each other” and “one offset each other” types of localization were given in Table 1, Table 2.



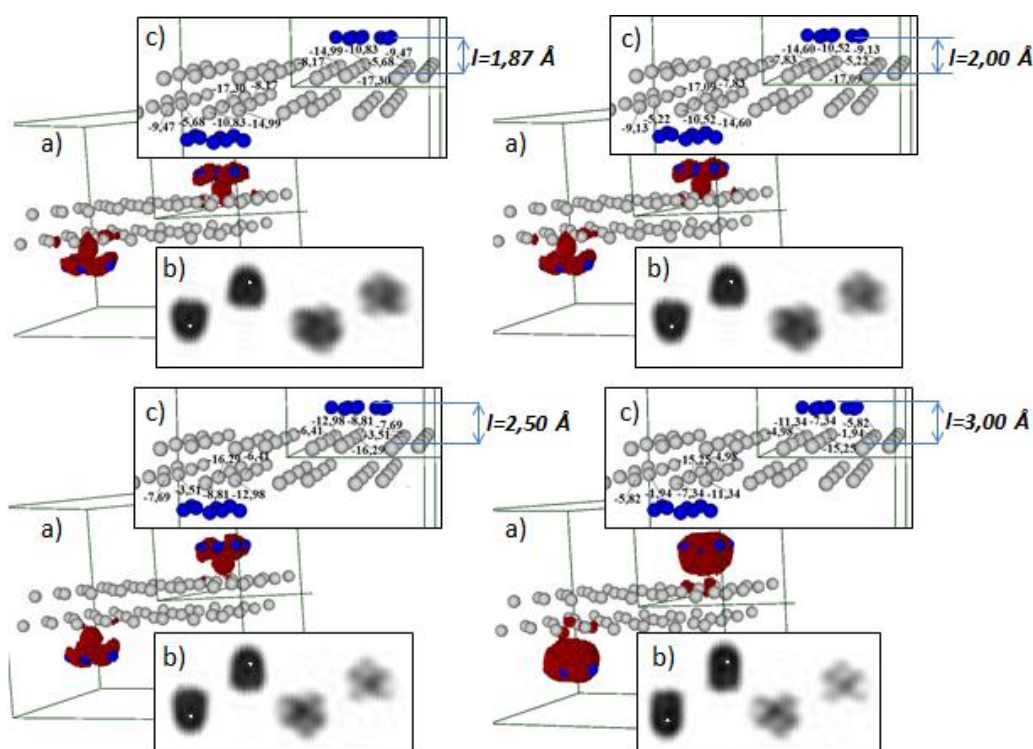
**Fig. 2** – Spatial distribution of valence electron density within the interval of 0.5-0.6 of the maximum value (a) and their cross section (b) within the carbamide molecule



**Fig. 3** – Spatial distribution of valence electron density of an infinite monolayer sheet of black phosphorene within the interval of 0.1-0.2 (a) and 0.2-0.3 (b) of the maximum value and their cross sections in planes [110] and [100] in one primitive cell (c) and in the image of the black phosphorene sheet covering several primitive cells (d)



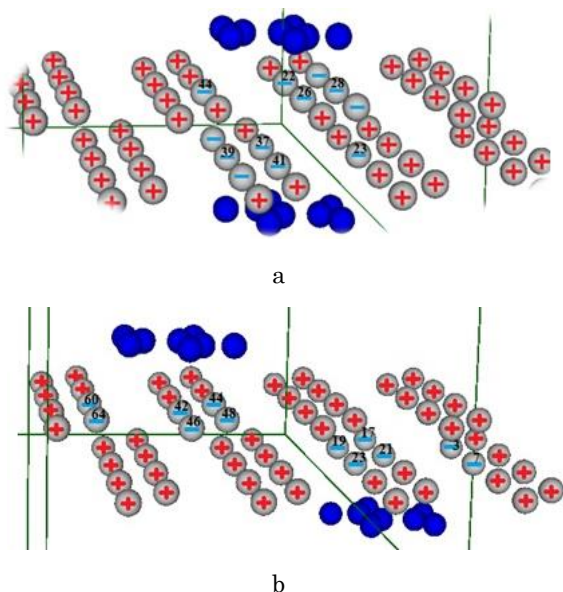
**Fig. 4** – Spatial distribution of valence electron density of an infinite monolayer sheet of black phosphorene with adsorbed carbamide molecules for “one against each other” type of localization within the interval of 0.1-0.2 of the maximum value (a), their cross sections in planes [110] and [100] (b), values of electric charge of black phosphorene atoms, which are located directly under the molecules (c) at different adsorption distances



**Fig. 5** – Spatial distribution of valence electron density of an infinite monolayer sheet of black phosphorene with adsorbed carbamide molecules for “one offset each other” type of localization within the interval of 0.1-0.2 of the maximum value (a), their cross sections in planes [110] and [100] (b), values of electric charge of black phosphorene atoms, which are located directly under the molecules (c) at different adsorption distances

In the course of calculation, the values of band gap width of an infinite monolayer sheet of black phosphorene for “one against each other” and “one offset each other” localization types depending on the adsorption distance were obtained, which were shown in Fig. 7 and in Table 3. For “one against each other” type of localization, there was a significant increase in the band gap width of an infinite monolayer sheet of black phosphorene

to almost 11 eV at an adsorption distance of 2.0 Å. But for “one offset each other” type of localization at the same adsorption distance of 2.0 Å, there was recorded a decrease in the band gap width to 0.1 eV. Note that in these calculations the band gap width of the infinite monolayer sheet of black phosphorene before adsorption was 6.8 eV (round marker in Fig. 7).



**Fig. 6** – Distribution of electric charge of an infinite monolayer sheet of black phosphorene with adsorbed carbamide molecules for “one against each other” (a) and “one offset each other” (b) types of localization

**Table 1** – Charge values of black phosphorene atoms, which are located directly under the molecules, for “one against each other” type of localization

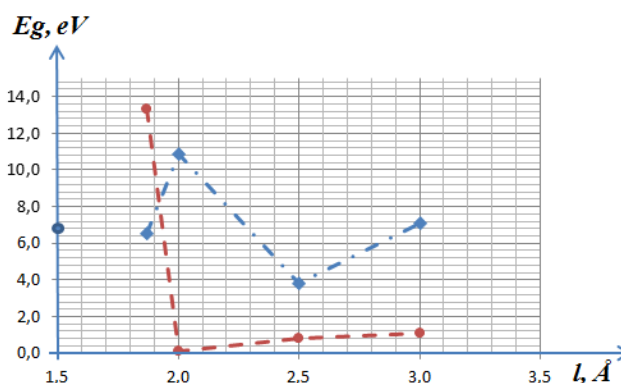
number of P atoms from Fig. 6a	1.87 Å	2.0 Å	2.5 Å	3.0 Å
22	-17.77	-17.63	-16.88	-15.47
23	-14.37	-14.10	-12.54	-10.09
26	-17.96	-17.86	-17.22	-15.84
28	-16.71	-16.49	-15.20	-13.34
37	-17.96	-17.86	-17.22	-15.84
39	-16.71	-16.49	-15.20	-13.34
41	-17.77	-17.63	-16.88	-15.47
44	-14.37	-14.10	-12.54	-10.09

**Table 2** – Charge values of black phosphorene atoms, which are located directly under the molecules, for “one offset each other” type of localization

number of P atoms from Fig. 6b	1.87 Å	2.0 Å	2.5 Å	3.0 Å
3	-9.47	-9.13	-7.69	-5.82
7	-5.68	-5.22	-3.51	-1.94
17	-10.83	-10.52	-8.81	-7.34
19	-14.99	-14.60	-12.98	-11.34
21	-17.30	-17.09	-16.29	-15.25
23	-8.17	-7.83	-6.41	-4.98
42	-17.30	-17.09	-16.29	-15.25
44	-8.17	-7.83	-6.41	-4.98
46	-10.83	-10.52	-8.81	-7.34
48	-14.99	-14.60	-12.98	-11.34
60	-5.68	-5.22	-3.51	-1.94
64	-9.47	-9.13	-7.69	-5.82

**Table 3** – Band gap width of an infinite monolayer sheet of black phosphorene with adsorbed carbamide molecules for “one against each other” and “one offset each other” types of localization

Distance ( $l$ ), Å	“one against each other”		“one offset each other”	
	Eg, a.u.	Eg, eV	Eg, a.u.	Eg, eV
1.87	0.24	6.53	0.49	13.33
2.0	0.40	10.88	0.004	0.10
2.5	0.14	3.81	0.03	0.82
3.0	0.26	7.07	0.04	1.09



**Fig. 7** – Change of the band gap width of an infinite monolayer sheet of black phosphorene with adsorbed carbamide molecules for “one against each other” (blue line) and “one offset each other” (red line) types of localization

#### 4. CONCLUSIONS

Within the framework of the methods of the electron density functional and the ab initio pseudopotential, based on own program code, the valence electron density spatial distribution, the densities of electronic states, the band gaps, the charges of core regions of a black phosphorene sheet with the adsorbed organic molecules as dopants were obtained.

The adsorption of carbamide molecules for diverse types of localization on the surface of a black phosphorene sheet led to the redistribution of electron density in it and the formation of electric charge areas with different signs, which is a prerequisite for creating the built-in lateral  $p$ - $n$  junctions. “One offset each other” type of localization had the greatest impact on the electric charge of black phosphorene atom cores.

The adsorption of carbamide molecules for diverse types of localization on the surface of a black phosphorene sheet led to a change in conductivity of a black phosphorene sheet. There was a significant increase in the band gap width for “one against each other” type of localization. “One offset each other” type of localization caused a considerable decrease in the band gap width.

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### Використання адсорбованих органічних молекул як легуючих домішок для створення вбудованих латеральних $p$ - $n$ переходів у листі чорного фосфору

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У цій статті розглядається спроба створення вбудованих латеральних  $p$ - $n$  переходів у листі чорного фосфору з використанням адсорбованих органічних молекул як легуючих домішок. У рамках методів функціоналу електронної густини та псевдопотенціалу із перших принципів отримано просторові розподіли густини валентних електронів, густини електронних станів, заборонені зони та заряди на атомних остовах у листі чорного фосфору. Спостерігався однорідний розподіл густини валентних електронів у листі чорного фосфору. Адсорбція молекул карбаміду для різноманітних типів локалізації на поверхні листа чорного фосфору призвела до перерозподілу електронної густини в ньому. Області заряду більшої густини в листі чорного фосфору з адсорбованими молекулами карбаміду локалізувалися під атомами молекул карбаміду, утворюючи загальну область підвищеної концентрації електронної густини. Віддалення молекул призвело до зменшення їх впливу на перерозподіл густини валентних електронів у листі чорного фосфору. Накопичення електричного заряду в листі чорного фосфору на ділянках під молекулами карбаміду в свою чергу спричинило виникнення областей у листі чорного фосфору, в яких заряди на атомних остовах змінювали знак на протилежний. Однорідність розподілу електронної густини в листі чорного фосфору зникла і утворилися ділянки просторового заряду різного знаку. Такі області з зарядами різних знаків створюють умови, які є основою характеристикою  $p$ - $n$ -переходів. Також було встановлено, що адсорбція в листі чорного фосфору молекулами карбаміду призвела до зміни провідності листа чорного фосфору.

**Ключові слова:** Вбудований латеральний  $p$ - $n$  перехід, Чорний фосфорен, Органічні молекули, Легуючі домішки, Адсорбція, Розрахунки із перших принципів, Електричний заряд.