

ELECTRONIC PROPERTIES OF PHOSPHORENE WITH VACANCIES: AB INITIO STUDY

Veranika Skachkova

Belarusian State University of Informatics and Radioelectronics, Minsk, Belarus

e-mail: skachkova@bsuir.by

Abstract. Vacancy influences on phosphorene electronic properties were investigated using Density Functional Theory for structures with one, two and three vacancies. It's shown that divacancy has the minimal formation energy. One and three vacancies lead to magnetic moment emergence on dangling bonds.

Keywords: density functional theory, electronic property, phosphorene, vacancy

1. Introduction

In the field of material investigation, 2D-materials, such as graphene, transition-metal dichalcogenides (TMD), silicene, germanene, hexagonal boron nitride (hBN), are of great importance, because of their unique properties. On the other side, progress in the field of micro- and nanoelectrical devices has lead to searching new 2D materials that can provide wider range of properties such as band gap and carrier mobility. One of such perspective materials is black phosphorus, the most stable phosphorus allotrope [1]. It has graphite-like structure with layers bonded to each other by weak van der Waals forces [2]. Monolayer of black phosphorus, named phosphorene, attracted great interest after two simultaneous reports by two different scientific groups about phosphorene-based FET (field effect transistor) manufacturing [3, 4]. Submitted devices had outstanding performance. Then numerous theoretical and experimental works showed that via its properties phosphorene has a great potential to electronic [5], optoelectronic [6-8], photovoltaic [9], spintronic [10] and sensor [11, 12] applications.

The reason of black phosphorus outstanding properties is its unique crystal structure, i.e. strong covalent bonds between atoms in one layer and weak van der Waals bonds between layers. It allows obtaining phosphorene by mechanical exfoliation method [3]. The outer electron shell of phosphorus atoms contains 5 electrons and each atom is saturated by covalent bonds of sp^3 hybridization. Puckered phosphorene structure lead to strong anisotropy of its properties: electron band structure [13-15], electron transport [16], optical [17-19], thermoelectric [20, 21] and mechanical [22, 23] properties.

Unlike graphene, phosphorene has sizable band gap that varies from 2 to 0.3 (bulk) eV depending on layer number [24]. This range of band gaps suggests that phosphorene films will find their place among other 2D materials [25]. Also phosphorene has high charge carrier mobility ($\sim 10^3$ $\text{cm}^2/\text{V}\cdot\text{s}$ at room temperature) [3] that is quite high to consider phosphorene as FET-channel material. The first phosphorene-based transistor was p-type with ambipolar behavior and current modulation of $\sim 10^5$ at room temperature [3]. Other work [26] presents transistor with hole mobility equal to 286 $\text{cm}^2/\text{V}\cdot\text{s}$ and on/off ratio more than 10^4 . Also the possibility of integral phosphorene-based devices was shown and 2D CMOS inverter consisted of p-type phosphorene-based and n-type MoS_2 -based transistors was manufactured.

Investigations of phosphorene-based transistor series [27] show field-effect mobility of $205 \text{ cm}^2/\text{V}\cdot\text{s}$ and on/off ratio of 10^5 . Authors note that field-effect mobility can be greatly influenced by traps in device and internal zone mobility can be much higher than field-effect mobility value.

The main two problems of phosphorene using on an industrial scale are impossibility of its obtaining by gas-phase deposition methods and quite high activity of black phosphorus thin films to air [28]. The second problem is because of lone pairs on phosphorene surface. Therefore, understanding the mechanism of vacancy formation is important because it leads to electronic and optical property changes during the fabrication process.

In this paper first principle calculations were carried out to investigate the influence of point defects, namely mono-, two and three vacancies, on structure and electronic properties of a phosphorene monolayer. The most stable kinds of vacancies were found by calculation of their formation energy.

2. Method description

Calculations of phosphorene electronic properties were carried out using spin-polarized density functional theory implemented in program VASP (Vienna Ab initio Simulation Package) [29]. Supercell, consisting of 4×4 phosphorene unit cells, was used for vacancy structure investigations. Vacuum layer of $\sim 17 \text{ \AA}$ was used to avoid interlayer interactions under periodic boundary condition. The calculations were performed with generalized gradient approximation (GGA), using Perdew-Burke-Ernzerhof functional (PBE). To take into account the dispersion interactions (van der Waals forces), DFT-D2 method of Grimme was used during geometry relaxation. The atomic core and valence electron interactions were described by augmented plane wave method (PAW). Optimization stopped when full energy difference between the last two steps was equal to $1 \cdot 10^{-6} \text{ eV}$. The cutoff energy was chosen to be 450 eV . A $3 \times 3 \times 1$ k-point mesh based on Gamma-centered Monkhorst-Pack scheme was used for all structures during structure relaxation.

The vacancy formation energy E_v was calculated using equation:

$$E_v = E_t - \frac{N-1}{N} E_b, \quad (1)$$

where E_t is the total energy of supercell with a vacancy; N is the number of atoms in a perfect supercell; E_b is the total energy of perfect supercell.

3. Results and discussions

Geometric structure, electron band structure and electron density of states (DOS) obtained by simulations for the initial phosphorene supercell are presented in Table 1 and in Fig. 1. Band gap is $\sim 0.9 \text{ eV}$ that is less than the results of experimental measurements [4] or hybrid functional calculations [30] because of the well-known drawback of exchange-correlation functional. As can be seen from the band structure, phosphorene is a direct-band semiconductor with notable dispersion difference: zigzag direction has more flat zones comparing to armchair direction. It means that carrier mobility in the armchair direction is more than in the zigzag direction. The valence band maximum (VBM) mainly consist of p_z - atomic orbitals located on different levels of the layer, while charge distribution of conduction band minimum (CBM) is located on s and p atomic orbitals in one plane [31].

For monovacancy calculations atom 10 was deleted (Figure 1, a). One atom removing leads to three dangling bonds on adjacent P atoms in phosphorene. Because of phosphorene flexibility, two of the dangling bonds bind to each other. And the third bond may have positive, neutral or negative charge, depending on whether it has 0, 1 or 2 electrons. Emergence of positive monovacancy leads to changing the bond length between nearby atoms (Table. 1). Besides, there appears a magnetic momentum in the system, concentrated on atoms 2 and 4, equal to $0.327 \mu_B$. Atom 9 almost has no magnetic momentum because of

absence of electron on it. The energy of vacancy formation, calculated by equation (1), is equal to 4.65 eV. It means that positive vacancy formation require significant energy cost. DOS investigation reveals that there is one additional band gap state mainly at the expense of p-orbitals appears; slight spin splitting of p_y and p_x orbitals near to Fermi level being observed.

Neutral vacancy in phosphorene structure leads to structure modification. However, in this case the charge redistribution occurs in such way that no magnetic momentum emerges in the system; the vacancy formation energy being equal to 1.96 eV. The new state forms near to Fermi level mainly on account of p_z -orbital.

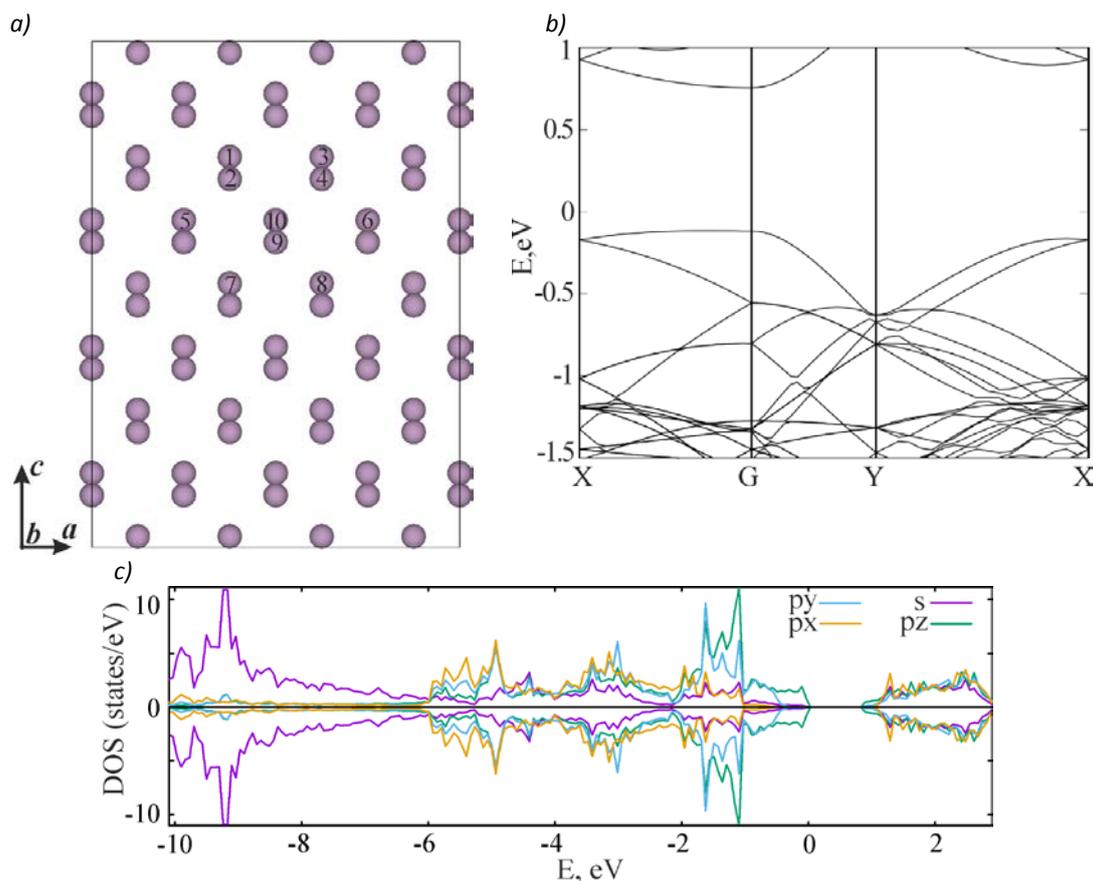


Fig. 1. Phosphorene supercell (a), its band structure (b) and DOS (c)

Table 1. Structure parameters of phosphorene structures with vacancies

	L_{1-2} , Å	L_{3-4} , Å	L_{2-5} , Å	L_{4-6} , Å	L_{9-7} , Å	L_{9-8} , Å	D_{2-9} , Å	D_{4-9} , Å	D_{2-4} , Å
V0	2.255	2.255	2.221	2.221	2.221	2.221	3.521	3.521	3.306
V ⁺	2.213	2.213	2.211	2.211	2.177	2.177	3.288	3.288	3.030
V ⁰	2.248	2.248	2.197	2.197	2.330	2.330	2.493	2.493	2.963
V ⁻	2.198	2.198	2.192	2.192	2.192	2.192	3.473	3.473	3.200
V ₉₋₁₀	2.198	2.198	2.237	2.237	-	-	-	-	3.079
V ₂₋₁₀	-	2.255	-	2.268	2.230	2.214	-	2.395	-
V ₇₋₈	2.254	2.254	2.224	2.224	-	-	3.472	3.472	3.399

Maximal magnetic momentum of $0.91 \mu_B$ is observed in the structure with negative charged vacancy (Fig. 2, a), distributed mainly on p-orbitals of atoms 2, 4 and 9 (0.216 , 0.217 and $0.178 \mu_B$, respectively). The negative-vacancy formation energy is equal to 0.6 eV. The

calculated DOS (Fig. 2, c) reveals that spin splitting of band gap states is located near to Fermi level: spin-up state – 0,03 eV below and spin-down state – 0,18 eV above Fermi level. The band structure investigation of phosphorene with monovacancies showed that vacancy presence leads to transition from a direct band semiconductor to indirect one (Fig. 2, b).

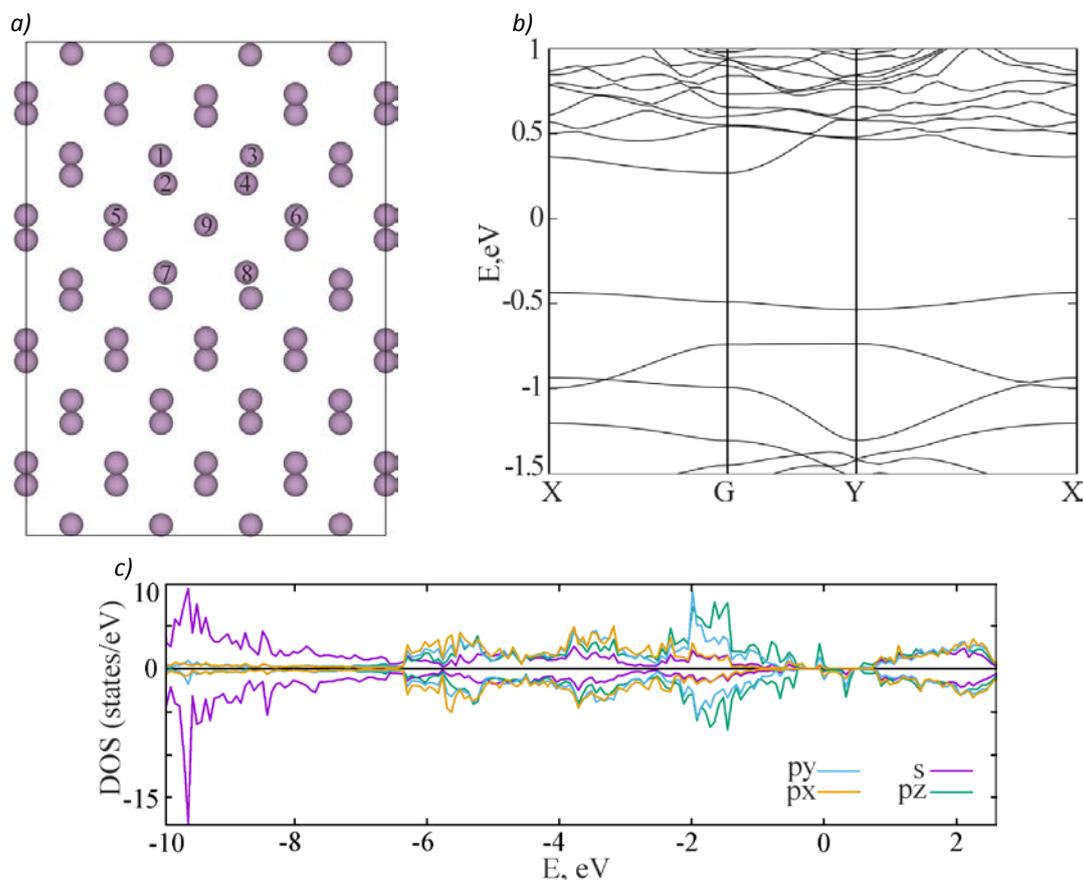


Fig. 2. Geometry of the negative monovacancy after relaxation (a), its band structure (b) and DOS (c)

Three cases of phosphorene with two vacancies were observed: with deleted atoms from different sub-layers: atoms 9 and 10 (Fig. 3, a) and from one sub-layer: atoms 2 and 10 (Fig. 3, b), atoms 7 and 8 (Fig. 3, c). The structure relaxation results are presented in Table 1. In the case of two vacancies in one sub-layer (V_{2-10}) (Fig. 3, b), the strong lattice deformation occurs which, however, leads to the best stability of this defect structure. New bonds are formed: 4-9 and 1-5, equal to 2.39 Å. Band structure investigation showed that in this case the band gap is not direct anymore (Fig. 3, d). Because of structure rebuilding, there is no magnetic momentum observed in the system (Fig. 3, e). Formation energies of described vacancies are 1.86 eV/vacancy (V_{9-10}), 0.67 eV/vacancy (V_{2-10}) and 1.59 eV/vacancy (V_{7-8}). This result reveals that the existence of vacancy cluster in phosphorene structure is more likely than that of one vacancy.

Two different structures of three vacancies were investigated. In the first case, when atoms 2, 9 and 10 were deleted (Fig. 4, a), the formation energy is equal to 1.08 eV/vacancy. VBM (valence band maximum) namely consist of p_x and p_y orbitals. Also the magnetic momentum is appeared, equal to 0.44 μ_B concentrated on atom 4 which has dangling bond. In the case, when atoms 7, 8 and 9 are deleted (Figure 4, b), atoms 11 (12) and 13 (14) are moving toward each other and create a new bond, equal to 2.373 Å, to preserve sp^3 hybridization. Bond length between atoms 13 (14) and 15 become equal to 2.239 Å; atom 10

remaining with a dangling bond. New levels appear in the phosphorene band gap (Fig. 4, c): 0.31 eV above VBM and 0.12 eV below CBM (conduction band minimum). In this structure the magnetic moment is emerged, equal to $0.457 \mu_B$, because of a dangling bond on atom 10. Projected DOS calculation (Fig. 4, d) reveals spin splitting states in the band gap. Formation energy is equal to 0.67 eV/vacancy.

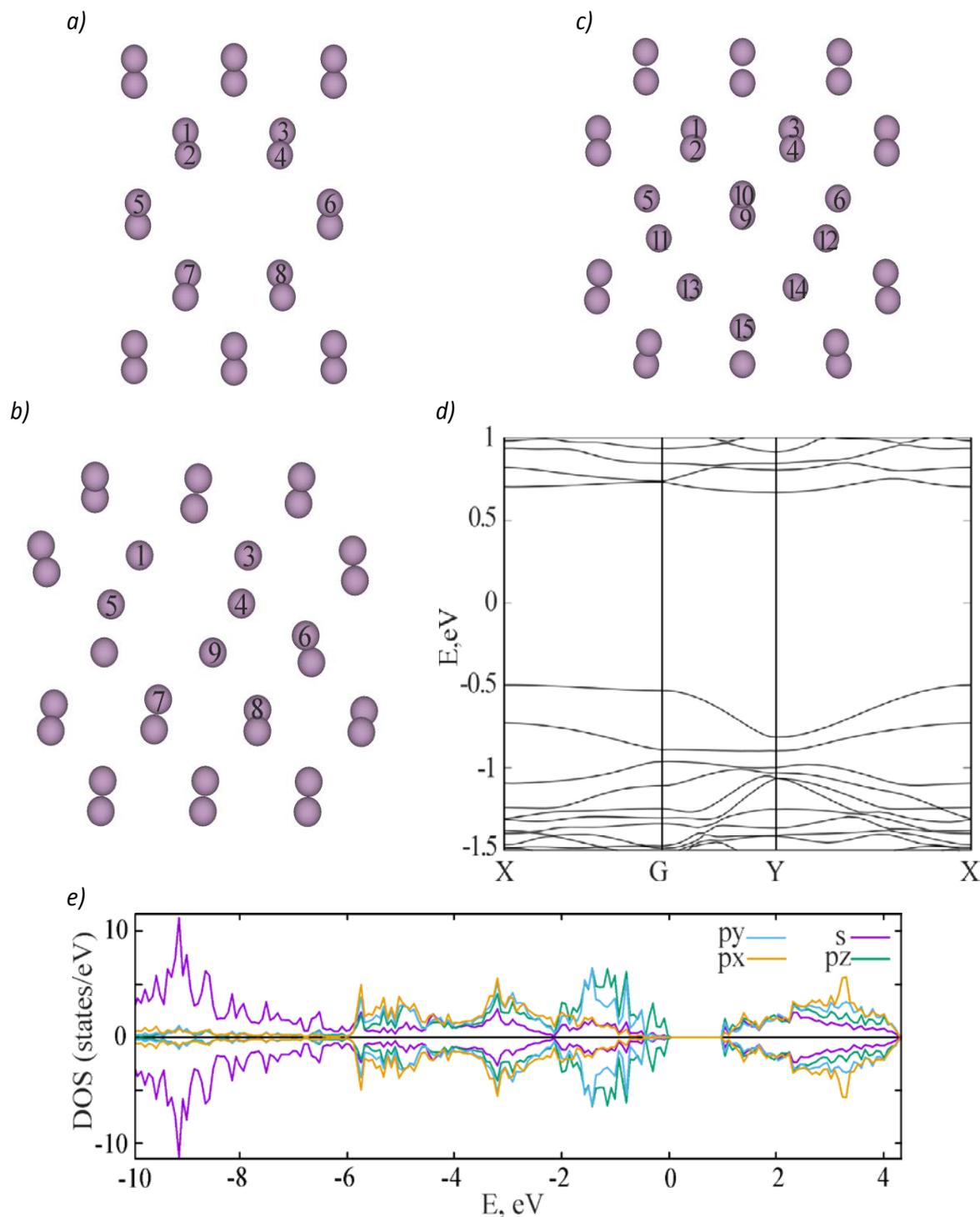


Fig. 3. Geometry of divacancies after relaxation: deleted atoms from one sublayer (a, c) and from different sub-layers (b); (d) band structure of (b)-divacancy and its DOS(e)

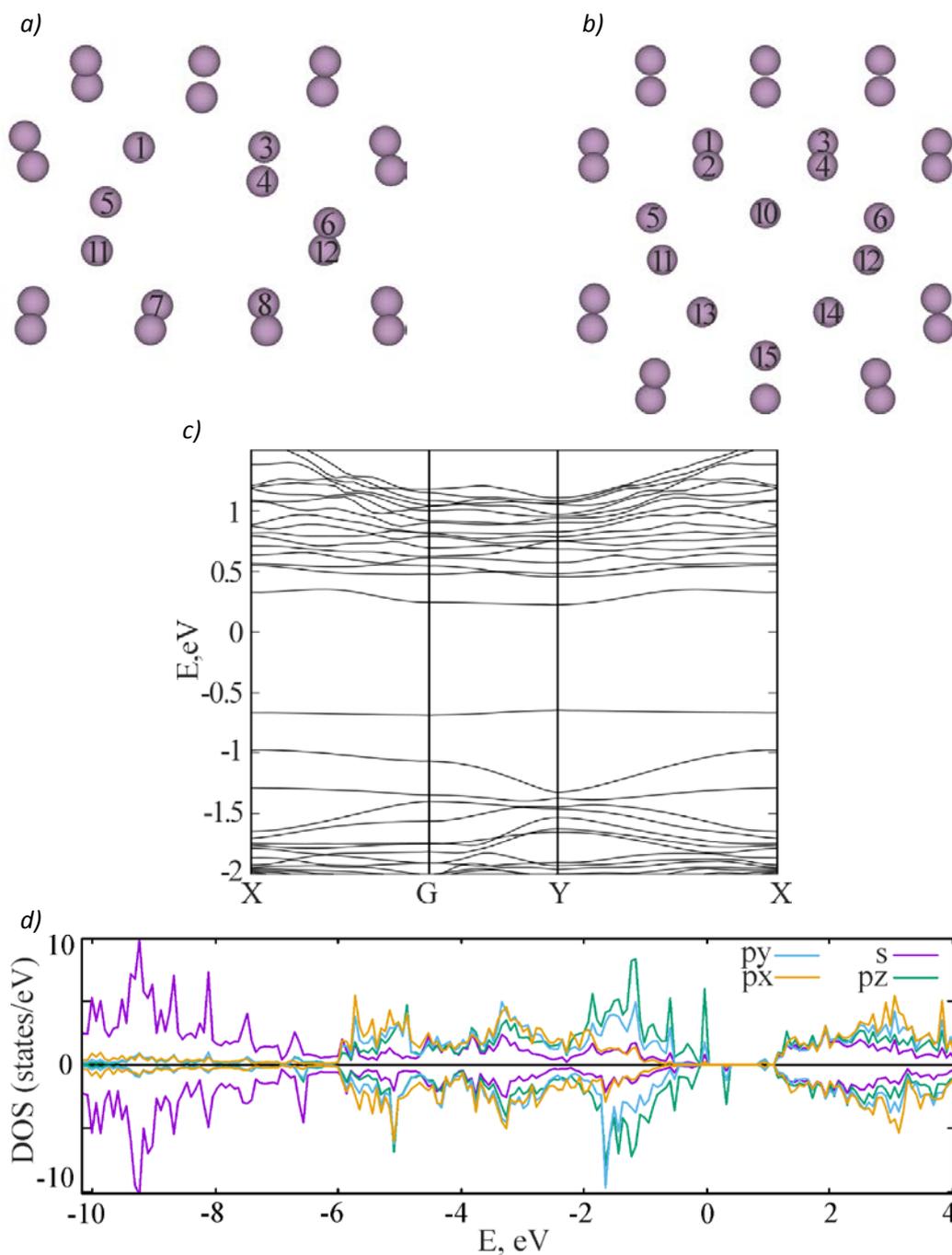


Fig. 4. Geometry structure of vacancy V_{2-9-10} (a) and V_{7-8-9} (b); band structure (c) and DOS (d) of vacancy V_{7-8-9}

4. Conclusions

In this work structure, stability and electronic properties of vacancies in phosphorene monolayer were explored using density functional theory calculations. The most stable vacancy structures were found. The results reveal that configurations with two and three vacancies need less energy for formation. All investigated vacancies have strong influence on phosphorene electronic properties. In the cases of mono- and three-vacancies magnetic moment appears via the uncompensated charge on dangling bonds. Thus band structure could be modulated by introducing vacancies.

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