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ELECTRONIC PROPERTIES OF PHOSPHORENE WITH VACANCIES: AB INITIO STUDY

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I. INTRODUCTION

In the field of material investigation 2D-materials, such as graphene, transition-metal dichalcogenides, silicene, germanene, hexagonal boron nitride, are of great importance, because of their unique properties. One of such perspective 2D-material is phosphorene that is elemental material. Unlike graphene, it has sizable band gap from 2 (monolayer) to 0.3 eV (bulk material) [1]. Also phosphorene has high charge carrier mobility ($\sim 10^3$ cm²/V·s at room temperature) [2]. Because of puckered structure, its electronic and optical properties have strong anisotropy [3]. Because of phosphorene sensitivity to environmental conditions (oxidized in air), understanding of 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 was carried out to investigate influence of point defects, namely mono-, two and three vacancies, on structure and electronic properties of phosphorene monolayer. The most stable kinds of vacancies were found by calculation of formation energy.

II. METHOD DESCRIPTION

Supercell, consisting of 4×4 phosphorene unit cells, with and without vacancies was constructed. Phosphorene electronic property investigations were carried out using Density Functional Theory implemented in program VASP (Vienna Ab initio Simulation Package)[4]. 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. 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 $1 \cdot 10^{-6}$ eV. Cutoff energy was chosen to be 450 eV and vacuum layer thickness was equal to 17 Å to avoid layer interaction on each other. A 3×3×1 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 – supercell with vacancy full energy; N – quantity of atoms in the perfect supercell; E_b – full energy of perfect supercell.

III. RESULTS AND DISCUSSION

Results of the preliminary structure, band and DOS simulations of the initial phosphorene supercell are presented in the Table1 and on Figure 1 (a, b, c). Band gap is equal to 0.8 eV.

For monovacancy calculations atom 10 was removed (Figure 1a). One atom removing leads to three dangling bond appearance 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.

Positive-monovacancy emergence leads to changing of bond length between nearby atoms (Table 1). Besides, there is a magnetic momentum appears in the system, concentrated on 2 and 4 atoms and equal to

0.327 μ_B . Atom 9 almost has no magnetic momentum because of absence of electron on it. Formation energy calculated via equation (1) is 4.65 eV. It means that positive vacancy formation require significant energy cost.

Neutral vacancy in phosphorene structure leads to structure modification (Figure 2c). In this case however charge redistribution occurs in such way that there is no magnetic momentum emerge in the system. Vacancy formation energy is equal to 1.96 eV.

Maximal magnetic momentum is observed in the structure with negative charged vacancy (Figure 1e), distributed mainly on p-orbitals of 2, 4 and 9 atoms (0.216, 0.217 and 0.178 μ_B , respectively) (Figure 1h). Negative-vacancy formation energy is equal to 0.6 eV.

Band structure investigation of phosphorene with monovacancies showed that vacancy presence lead to transition from direct band semiconductor to indirect one.

Table 1 – Structure parameters of phosphorene structures with vacancies

	L1-2, Å	L3-4, Å	L2-5, Å	L4-6, Å	L9-7, Å	L9-8, Å	D2-9, Å	D4-9, Å	D2-4, 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
V0	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
V9-10	2.198	2.198	2.237	2.237	-	-	-	-	3.079
V2-10	-	2.255	-	2.268	2.230	2.214	-	2.395	-
V7-8	2.254	2.254	2.224	2.224	-	-	3.472	3.472	3.399

Three cases of phosphorene with two vacancies were observed: with deleted atoms from one sub-layer (atoms 2 and 10 (Figure 1d), atoms 7 and 8), and from different sub-layers (atoms 9 and 10). Structure relaxation results are presented in Table 1.

In the case of two vacancies on one sub-layer (V2-10) (Figure 1d), 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 band gap is not direct in this case anymore. Because of structure rebuilding, there is no magnetic momentum observed in the system (Figure 1i). Formation energies of described vacancies are 1.86 eV/vacancy (V9-10), 0.67 eV/vacancy (V2-10) and 1.59 eV/vacancy (V7-8). This result reveals that formation of vacancy cluster is more likely than monovacancy.

Two different structures of three vacancies were investigated. In the first case (2, 9 and 10 atoms are deleted) formation energy is equal to 1.08 eV/vacancy. VBM (valence band maximum) namely consist of px and pz orbitals. Also magnetic momentum is appeared, equal to 0.437 μ_B concentrated on atom 4 which has dangling bond.

In the case, when 7, 8 and 9 atoms are deleted (Figure 1f), atoms 11 (12) and 13 (14) moved toward each other and create a new bond, equal to 2.373 Å, to preserve sp³ hybridization. Bond length between 13 (14) and 15 atoms become equal to 2.239 Å. Atom 10 remains with dangling bond. New levels appear in the phosphorene band gap (Figure 1j): 0.31 eV above VBM and 0.12 eV below CBM (conduction band minimum). Magnetic moment is emerged in this structure, equal to 0.457 μ_B , because of dangling bond on atom 10. Formation energy is equal to 0.67 eV/vacancy.

III. CONCLUSIONS

In this work structure, stability and electronic properties of vacancies in phosphorene monolayer were explored using density functional theory. The most stable vacancies were found. Results reveals that configurations with two and three vacancies more stable than monovacancy. All investigated vacancies influence on phosphorene electronic properties. In the case of three vacancies new levels appear in the band gap. Thus band structure could be modulated by introducing vacancies.

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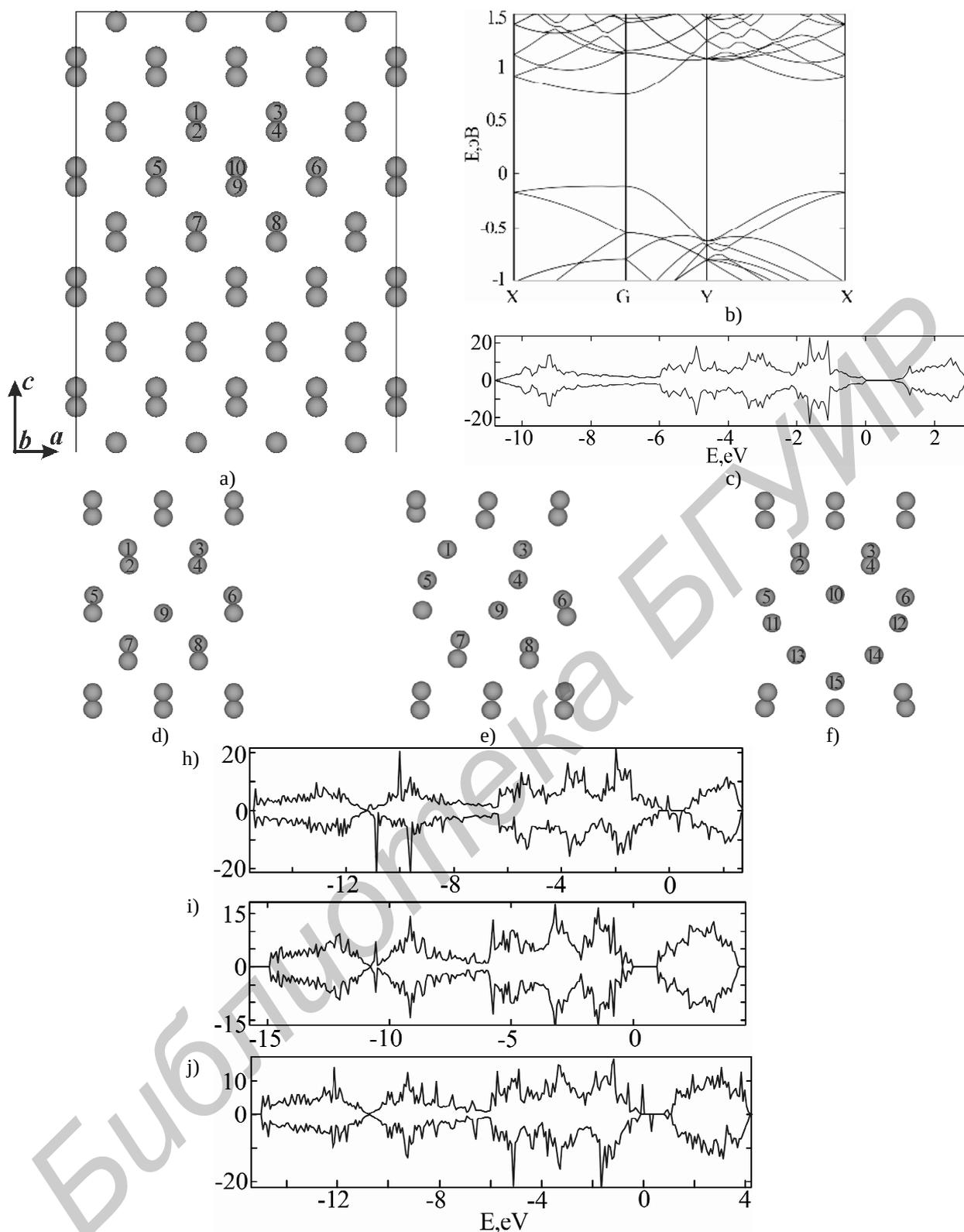


Figure 1 - (a) Phosphorene supercell and its (b) band structure and (c) DOS. Geometries of the most stable vacancies after relaxation: negative monovacancy (d), two vacancies (e) and three vacancies (f) and their DOS (h, i and j, respectively)

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