Electronic properties of hexagonal-shaped phosphorene nanorings

Vladimir V. Arsoski, Nemanja A. Čukarić, Dušan B. Topalović and Milan Ž. Tadić

Abstract—**We theoretically investigate properties of hexagonal phosphorene nanorings with normal and skewed zig-zag and armchair boundaries. The electronic structure, density of states and density distributions of electronic states are calculated numerically by the tight-binding method. We found that edge states, with energy in the band gap close to the Fermi level, appear in both ring types. These boundary states are found only along normal zig-zag and skewed armchair boundaries. Furthermore, there is a higher dispersion of the edge states around Fermi level in the case of ring with zig-zag boundaries, than in the case of ring with armchair edges.**

Index Terms—**phosphorene, nanoring, the tight binding, edge states.**

I. INTRODUCTION

Since its discovery, graphene [1] become a major topic in condense matter physics and launched intensive investigation in two-dimensional (2D) systems. The absence of an intrinsic band-gap, that was the main limitation of graphene, was overcomed by invention of other 2D materials such as transition metal dichalcogenides (TMDCs) [2, 3], silicene [4] and germanene [5].

Recently, a novel 2D material with large room temperature bandgap and mobility, named phosphorene, was successfully fabricated [6]. Phosphorene is a building layer of the most stable bulk phosphorous allotrope, the black-phosphorous (BP). Due to weak interlayer coupling of adjacent phosphorene sheets by Van der Waals interactions, it is possible to obtain a slab as thin as a single layer by simple method of mechanical exfoliation [6]. Bulk BP has modest band-gap at Z point of about 0.3 eV. However, a bandgap increases with decreasing thickness, and reaches value of approximately 1.94 eV at Γ point for a single-layer phosphorus sheet [7]. In a monolayer, each phosphorous atom is connected with three nearest neighbors by covalent bonds,

Vladimir V. Arsoski is with the School of Electrical Engineering, University of Belgrade, 73 Bulevar kralja Aleksandra, 11020 Belgrade, Serbia (e-mail: vladimir.arsoski@etf.bg.ac.rs).

Nemanja A. Čukarić is with the School of Electrical Engineering, University of Belgrade, 73 Bulevar kralja Aleksandra, 11020 Belgrade, Serbia (e-mail: cukaric@etf.bg.ac.rs).

Dušan B. Topalović is with the School of Electrical Engineering, University of Belgrade, 73 Bulevar kralja Aleksandra, 11020 Belgrade, Serbia and Vinča Institute of Nuclear Sciences, University of Belgrade, 12-14 Mike Petrovića Alasa, 11001 Belgrade, Serbia (e-mail: dusan.topalovic@vin.bg.ac.rs).

Milan Ž. Tadić is with the School of Electrical Engineering, University of Belgrade, 73 Bulevar kralja Aleksandra, 11020 Belgrade, Serbia (e-mail: tadic@etf.bg.ac.rs).

forming puckered structure [6] that is responsible for highly anisotropic electronic, conductive, thermal and optical properties of thin BP sheets [7-9]. Although this anisotropy imposes significantly complicated model than in case of graphene and TDMCs, it may lead to new functionalities of phosphorene based nanoelectronic [10] and photonic [11] devices.

In recent papers an important aspects for the application of phosphorene nanoribbons in state-of-art devices are proposed [12-14]. However, investigation of more complex morphologies such as quantum dots [15, 16] are relatively scarce. The aim of this paper is to examine in more details electronic properties of phosphorene nanorings. Hexagonal-shaped nanorings that are bounded by combination of normal and skewed zig-zag and normal and skewed armchair edges are analyzed. States that are "detached" from the bulk dispersion and "forced" into the bandgap are localized along appropriate edges in both types of ring. These, so called quasi-flat bands should appear in all kinds of nanorings, regardless of their shape, as a result of intrinsic high in-plane anisotropy of phosphorene.

The paper is organized as follows. In Section II we present the tight binding model that is theoretical framework for our calculations. Next, we calculate the electronic structure, the density of states and integrated probability distribution of the edge states in Sec. III. Finally, we summarize our results and give certain conclusions in Sec. IV.
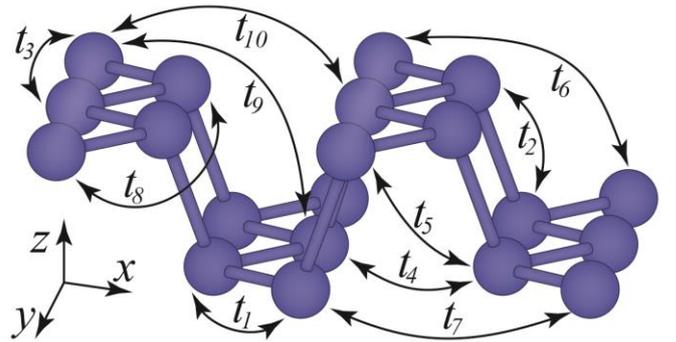

Fig. 1. Schematic representation of the in-plane hopping parameters for the TB model, given by Hamiltonian (1).

II. THEORETICAL MODEL

A. The electronic structure

We model quantum ring by the tight-binding model where Hamiltonian is given by

$$H = \sum_{i \neq j} t_{ij} c_i^+ c_j. \qquad (1)$$

Here the summation runs over all lattice sites of nanoring, t_{ij} is the transfer energy between i-th and j-th sites, and c_i^+ (c_j) is the creation (annihilation) operator of electron on site $i(j)$. It has been shown that a simple model, described by five in-plane parameters [17], gives correct results for devices based on the single layer phosphorene [12, 13, 15]. For a thin sheet, a simple quantum confinement picture in vertical direction is satisfactory, but the bandgap is underestimated due to oversimplified picture of inter- and intra-layer hopping links. Here we use more complex description which employs ten in-plane hopping parameters in the TB model that results in more precise description of the band-gap for single-layer phosphorene, as well as for multilayer phosphorene when additional five inter-layer parameters are included in the model [7]. We used Bravais lattice parameters [18] to calculate distances for corresponding hopping links between sites. The in-plane hopping links are schematically depicted in Fig. 1. The transfer energies [7] and calculated hopping lengths are explicitly given in Table I.

B. The density of states

In the above model we disregarded the finite temperature effect. Therefore, the electronic density of states (DOS) is obtained as a sum of the Dirac δ functions. In order to account finite line width the discrete energy levels E_i are broadened to a Gaussian-shape function. The resultant energy DOS is

$$D(E) = \frac{1}{\sqrt{2\pi}\sigma_E} \sum_i \exp\left(-\frac{(E - E_i)^2}{2\sigma_E^2}\right), \qquad (2)$$

where the Gaussian real mean square (RMS) width is denoted by σ_E.

TABLE I
SUMMARY OVERVIEW OF THE TRANSFER ENERGIES (IN eV) AND CALCULATED DISTANCES (IN Å) FOR CORRESPONDING HOPPING BETWEEN LATTICE SITES IN TERMS OF THE TB HAMILTONIAN. THE HOPPING LINKS ARE SCHEMATICALLY DEPICTED IN FIG. 1.

h	t_h [eV]	d_h [Å]
1	−1.486	2.2236
2	+3.729	2.2444
3	−0.252	3.3136
4	−0.071	3.3341
5	+0.019	3.4747
6	+0.186	4.2448
7	−0.063	4.3763
8	+0.101	5.1869
9	−0.042	5.3850
10	+0.073	5.4893

C. The electronic density distribution

The eigenvectors, that are output from the TB model, are weights of the on-site localization. To obtain more realistic real space distribution we use the square of the weight coefficients u_i which is smoothed by Gaussian blur which has standard deviation σ_r. This way, we obtain the electronic density distribution

$$|\Psi(x, y)|^2 = \frac{|u_i|^2}{\sqrt{2\pi}\sigma_r} \sum_i \exp\left(-\frac{(\mathbf{r} - \mathbf{r}_i)^2}{2\sigma_r^2}\right). \qquad (3)$$

Here $\mathbf{r}_i$ is the vector containing coordinates of the i-th atomic site and $\mathbf{r}$ is the real space position vector.
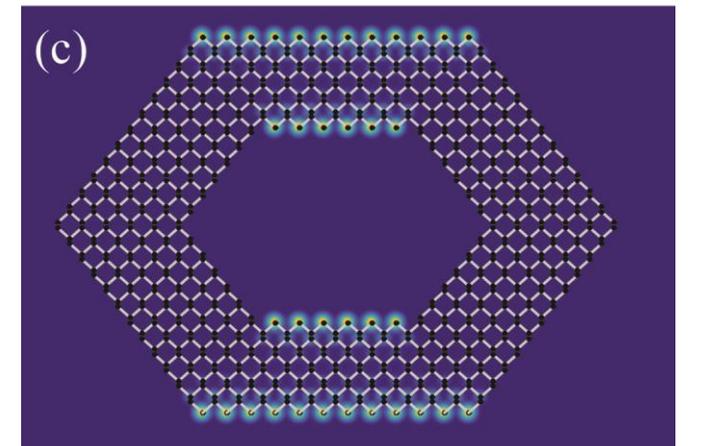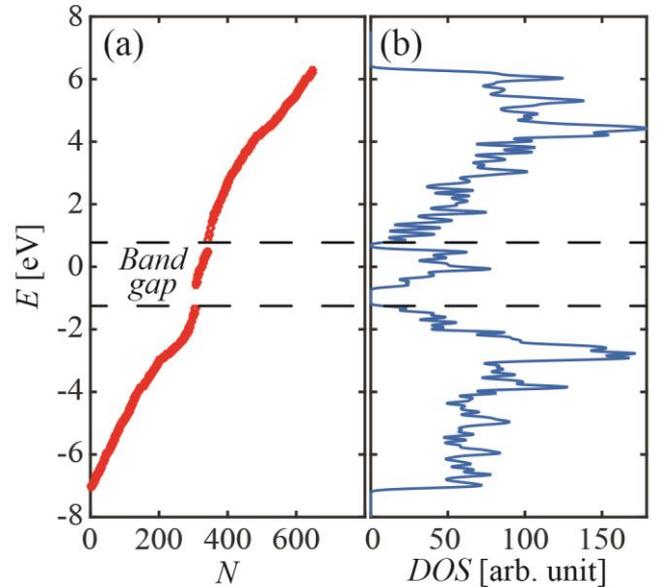

Fig. 2. (a) The eigen-energies of HEX-ZZ ring with N_{out}=12 and N_{in}=6 and (b) corresponding energy density of states. (c) The overall electronic density distribution of the edge states.

III. NUMERICAL RESULTS AND DISCUSSION

We analyze hexagonal-shaped nanorings with both, zig-zag and armchair boundaries. Our aim is to compare results for rings with different type of boundaries but of the same size.

This can't be exactly achieved, since phosphorene has high in-plane structural anisotropy. Therefore, we analyze rings with similar widths and sizes. The size of the outer ring boundary is defined by the number of hexagonal plaquets N_{out} along each side of hexangular contour which encircles the ring. The inner size N_{in} is determined by the size of the hexagon that is removed from the interior in order to make ring. We account finite line width by spreading each eigenstate to Gaussian form with the standard deviation $\sigma_E = 50/\sqrt{2}$ meV. To better visualize the real space distribution of the edge states we plot the sum of electronic densities of all in-gap states. We use the standard Gaussian blur $\sigma_r = d_{sr}/3.42$, where $d_{sr}=(d_1+d_2)/2$ is the average length of the covalent bonds.
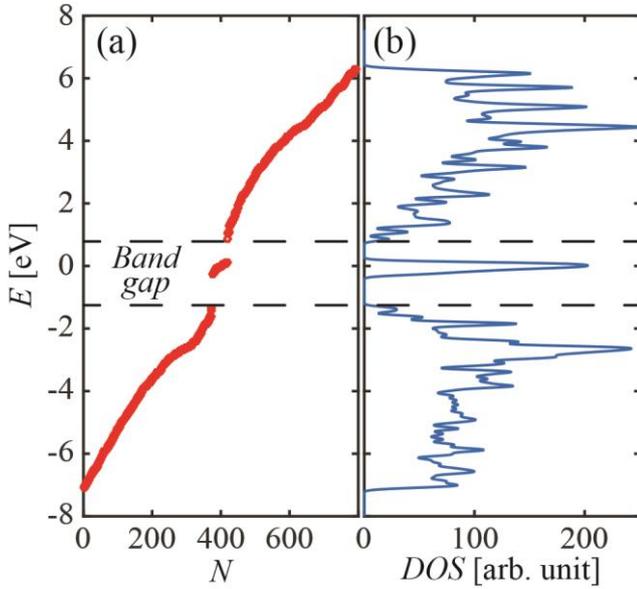

Fig. 3. (a) The eigen-energies of HEX-AC ring with N_{out}=8 and N_{in}=4, and (b) corresponding energy density of states. (c) The overall electronic density distribution of the edge states.

In Fig 2.(a) we show the electronic structure in hexagonal-shaped ring enclosed with normal and skewed zig-zag boundaries denoted by HEX-ZZ. Due to structural symmetry of the ring all electronic states are double degenerated. This symmetry may be broken by external magnetic or in-plane electric field. Along the eigenvalues, we display the corresponding energy DOS. Note that there is a wide dispersion of the in-gap states and some of them almost reach the bottom of the conduction band. Calculated value for the band gap is 2.172eV. This is somewhat higher than the value for the infinite phosphorene sheet, which is an effect of lateral confinement in such a small nanostructure. Next, we show the overall electronic density distribution of the in-gap states in Fig. 2(c). We note that normal and skewed zig-zag edges alternate along the ring boundary. The localization of edge states is along normal zig-zag boundaries, while there are no edge states along skewed zig-zag boundaries. Similar localization of states is found in phosphorene nanoribbons with the same type of edges [14]. Bearing in mind that the hexagonal ring consists of "connected ribbons", localization follows the expected behavior.

Next, we show the energies and DOS in hexagonal-shaped ring with normal and skewed armchair boundaries (HEX-AC) in Fig. 3(a) and (b), respectively. All states are double degenerated due to symmetry. Unlike the HEX-ZZ rings, the edge states are piled around the Fermi level away from the conduction and the valence band. The value of the band gap is 2.2 eV, which is close to the value for the HEX-ZZ ring. As found for phosphorene nanoribbons [14], the in-gap states exist only along skewed armchair boundaries. We note that states on the upper and the lower boundary are separated with relatively long ribbons. However, these vertically positioned ribbons don't support in-gap states. Therefore, it will be difficult to connect these boundaries in terms of the electronic transport.

IV. CONCLUSION

The electronic structure of hexangular phosphorene nanorings has been theoretically investigated by means of the tight-binding model. All states are double degenerated because of rings symmetry. We found that edge states appear in both types of rings. These states are found along normal zig-zag and skewed armchair boundaries. Due to large anisotropy, edge states may appear on various types of boundaries. Apart from hexagonal-shaped phosphorene nanorings, these states should appear in all other structures regardless on a shape. There is a relatively small energy difference between the in-gap states. However, the states that reside on the upper boundaries are physically separated from the states with similar localization on the lower boundary. Namely, the upper and the lower part of both type of ring are connected with either normal armchair or skewed zig-zag ribbons. Therefore, topological effects related to the application of perpendicular magnetic field will be very hard to attain. Investigation of electronic structure in the presence of a magnetic field will be the subject of our future research.

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