Dynamical stability and electronic structure of *β*-phosphorus carbide nano-wires

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Abstract In this work, β-phosphorus carbide 1D nano-wires (PCNWs) are investigated in the framework of density functional theory. The dynamical stability of the considered β-PCNWs at 300 K is verified using *ab initio* molecular dynamics calculations. According to the results on the band structure calculations, β-PCNWs can be semiconductors, semimetals or metals depending on their size and form. Thus, owning to their unique shape and high tunability of electronic properties β-PCNWs may be used in optical and photovoltaic nanodevices.

Keywords: nanowires, structural stability, phosphorus carbide, 2D materials

1. Introduction

In the last decade, the number of new two-dimensional (2D) materials has been constantly growing. Advanced theoretical and novel experimental approaches make it possible to obtain hybrid 2D materials [1-4]. Recent theoretical predictions [5,6] and experimental investigations [7] have proven the existence of several allotropes of a new 2D material, phosphorus carbide (PC). Depending on its structure PC can be metallic, semi-metallic or semiconductor [5].

The predicted allotropes exhibit thermal stability and possess well tunable electronic structure [8]. In addition, the possibility of rolling of α-PC monolayer to a PC nanotube at room temperature under compressive strain has been found has been shown [9]. Another predicted *γ*-allotrope of PC with an InSe-like structure has been shown to have promoted adsorption of lithium atoms, which render its application in rechargeable batteries [6]. Furthermore, *γ*-PC has been found as a good material for gas sensing and storage devices [10]. Very recently, β-PC has been fabricated via a novel carbon doping technique [11]. Theoretical and experimental studies have shown the existence of different β-PC phases which may have a potential for application in nanodevices [11, 12].

In this work using first-principles calculations we studied the structural stability and electronic band structure of β_0- and β_1-PC 1D nano-wires.

2. Simulation Details

The computational simulations were performed by using the Vienna ab initio simulation package (VASP) [13] within the framework of the density functional theory.

one need to evince that it cannot undergo any structural changes that lower its energy. In practice, at the first-principles level, the verification can be done using AIMD simulations

To evince the dynamical stability of the considered structures, the ab initio molecular dynamics calculations [14] which is the most common method for low dimensional materials [15] were implemented. The structure optimization and band structure calculations the Perdew–Burke–Ernzerhof (PBE) functional with generalized gradient approximation (GGA) [16] was selected with an energy cutoff of 400 eV. All the structures were fully optimized until the forces become smaller than 0.01 eV/Å.

The optimized unicells of the considered β_0- and β_1 allotropes of PC are shown in Figure 1. The calculated lattice constants of β_0- and β_1-PC are a = 5.050 Å and b = 2.915 Å and a =

4.725 and b = 2.915, respectively. The results are in good agreement with the available references [4].

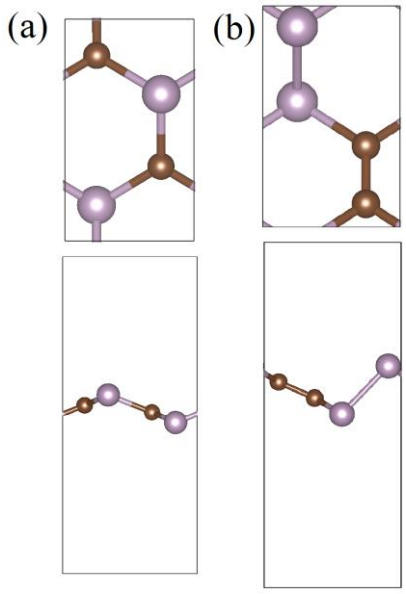

Figure 1. The optimized unicells of the considered (a) β_0- and (b) β_1 allotropes of PC.

3. Simulation Results

First, we created β_0- and β_1-PCNWs consisting of 12 atoms and more by the rippling of β_0-PC and β_1-PC monolayers along their armchair (APCNW) and zigzag (ZPCNW) directions. Further, the dynamical stability of the created PCNWs is systematically checked using AIMD calculations conducted at 300 K during the period time 10 ps. It is found that the stable β_0- and β_1-APCNWs of the smallest/biggest size consist of 12/40 atoms. Stable β_0-ZPCNWs may consist of 32 to 44 atoms, while β_1-ZPCNWs consists of 24 to 44 atoms. For PCNWs found to be stable, we next calculated the band structure. Figure 2 presents the bandgap size of the considered PCNWs as a function of their size.

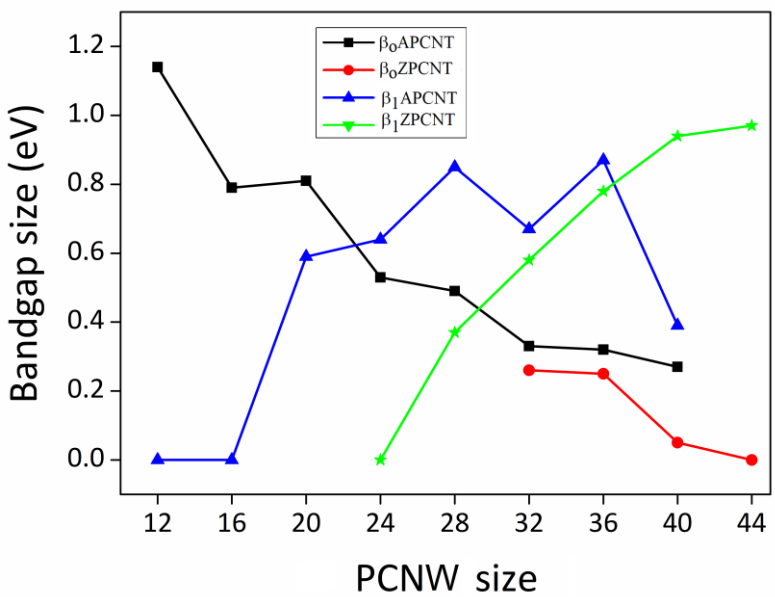

Figure 2. The bandgap size as a function of size of β_0- and β_1-APCNW and β_0- and β_1-ZPCNW.

Figure 3 shows the optimized atomic (upper panels) and band (lower panels) structures of β_0-APCNWs. As it is seen from Figure 3, β_0-APCNWs may have different forms such as triangle and star-like structure. Depending on the size, the β_0-APCNWs vary from a direct (wire consisting of 12 atoms) to an indirect bandgap semiconductor. According to Figure 2 with increasing the size of β_0-APCNWs from 12 atoms to 40 atoms its bandgap size decreases drastically from 1.14 eV to 0.27 eV.

The atomic and band structures of stable β_1-APCNWs are presented in Figure 4. Based on the geometry optimization results, the APCNWs are characterized by a star-like structure. The band structure calculations (Figure 2) suggest β_1-APCNWs may have a zero bandgap (wires consisting of 12 and 16 atoms), or to be a direct (wires consisting of 20 atoms) and an indirect (wires consisting of 24 to 40 atoms) bandgap semiconductors. Based on the results presented in Figure 2, the bandgap size of β_1-APCNWs is increasing by leaps from 0 eV up to 0.87 eV with increasing their size.

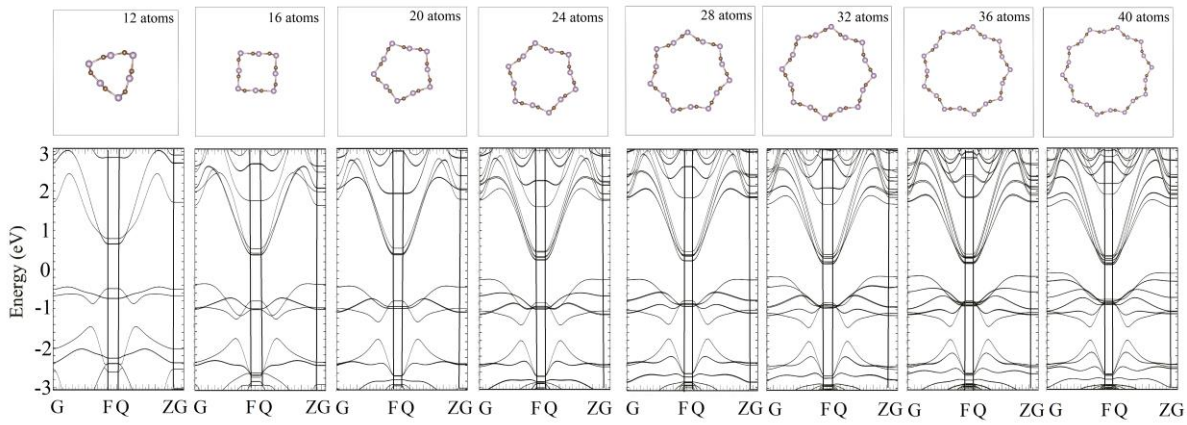

Figure 3. The atomic (the upper panel) and band (the lower panel) structures of β_0-APCNWs.

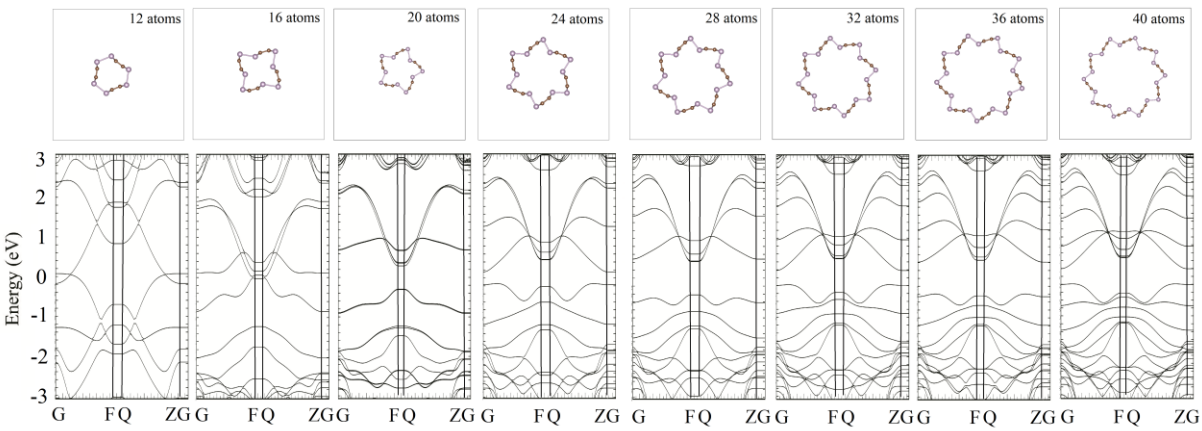

Figure 4. The atomic (the upper panel) and band (the lower panel) structures of β_1-APCNWs.

ZPCNWs have been found less stable then APCNWs. In case of β_0-ZPCNWs, there are only four stable configurations, which are shown in Figure 5. The β_0-ZPCNWs consisting of 32 to 40 atoms are direct bandgap semiconductors while β_0-ZPCNW consisting of 44 atoms has a zero bandgap (see Figure 5, lower panels). With increasing the size, the bandgap size of β_0-ZPCNWs decreases as it is shown in Figure 2. β_0-ZPCNWs have six stable configurations whish are presented in Figure 6. The most interesting results are found for band structure of β_1-ZPCNWs. It is predicted that β_1-ZPCNW consisting of 24 atoms is metallic. β_1-ZPCNWs consisting of 28 to 40 atoms are indirect bandgap semiconductors, and β_1-ZPCNW consisting of 44 atoms is a direct bandgap semiconductor (see Figure 6, lower panels). Differently from

other PCNWs here the bandgap size of β_1-ZPCNWs significantly increases with size from 0 eV to 0.97 eV (see Figure 2).

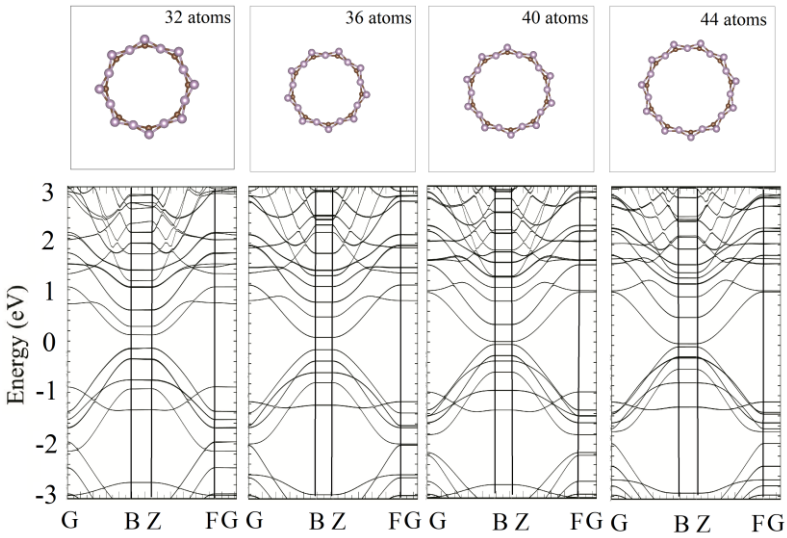

Figure 5. The atomic (the upper panel) and band (the lower panel) structures of β_0-ZPCNWs.

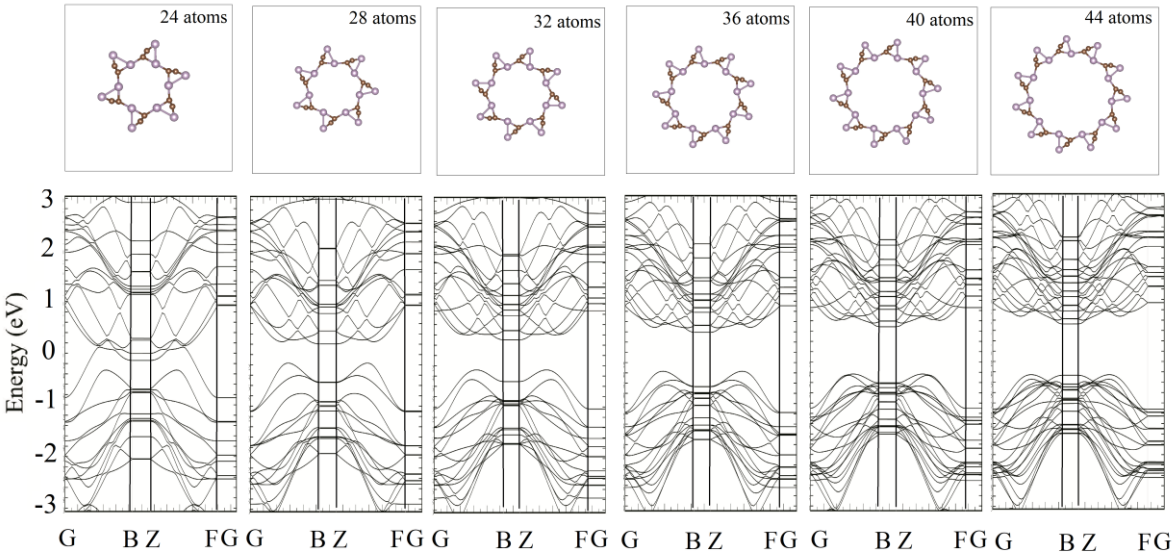

Figure 6. The atomic (the upper panel) and band (the lower panel) structures of β_1-ZPCNWs.

4. Conclusions

In conclusion, our theoretical predictions show the existence of β-PCNWs of different sizes and unique shapes. These β-PCNWs also possess existing electronic properties. Particularly, the bandgap size of β-PCNWs is directly depends on their size. Such tunability of the band structure suggests β-PCNWs as a perfect material for application in optoelectronic nanodevices.

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