Stability and Tunable Electronic Structure of Planar Phosphorus Nanotubes

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Abstract. The stability and electronic properties of planar phosphorous nanotubes with different chirality are investigated within the formulation of density functional theory. Armchair phosphorous nanotube (APNT) is found to be energetically most favorable with very small formation energy (0.08 eV). APNT also possess highest tensile strength (~ 2 GPa), among the considered nanotubes. Armchair and helical PNTs are semiconducting while zigzag PNT is metallic in nature. We found that the application of strain and external electric field greatly modifies the electronic band structure of given PNTs. We believe that planar APNT can be realized and its tunable electronic properties may be useful for nanoelectronics.

INTRODUCTION

The discovery of carbon nanotubes (CNTs) [1] and successful exfoliation of graphene has revolutionized the nanotechnology. The properties of CNT and graphene are very different from their bulk counterpart due to dimensionality effect. After successful exfoliation of graphene [2] in 2004, enormous amount of attention has been received from the researchers to explore other similar layered structures. Graphene can be regarded of the mother of all two-dimensional (2D) crystals, since various nanostructures can be constructed from it by folding in a desired form. One of the layered structures beyond graphene is black phosphorus. After successful exfoliation of few layers phosphorene [3], it has drawn particular attention in recent times. Note that phosphorous in bulk structure exhibit various allotropic forms such as black, blue, white and red phosphorous.

Phosphorene (2D honeycomb structure of P atoms) possesses stable structures in puckered (black) and buckled (blue) allotropic form. One can obtain one dimensional (1D) phosphorus nanotubes (PNTs) by folding 2D phosphorene in a tubular form. The first theoretical prediction of PNT was given by G. Seifert and E. Hernandez in 2000 [4]. They have studied the properties of black phosphorus based nanotubes. Till now, black and blue phosphorus based nanotubes have been investigated which have puckered and buckled structure, respectively. We are interested in the investigation of the properties of planar phosphorus nanotube. Our main objective of this paper is to study the structural, electronic and mechanical properties of planar PNTs with different chirality. We will see that these planar PNTs are energetically favorable with small formation energy.

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COMPUTATIONAL DETAILS

SIESTA (*Spanish Initiative for Electronic Simulations with Thousands of Atoms)* is used to study the properties of PNTs. Numerical atomic orbital type of basis set is used with a cutoff energy equal to 250 Ry for double zeta polarized basis set. Perdew-Burke-Emzerhof (PBE) semi-local exchange-correlational functional is used to describe exchange and correlation effects. Conjugate gradient method is used to optimize the structure with forces on each atom less than 0.01 eV. For optimization of structure, reciprocal space sampling was done by Monkhorst pack grid of 100×1×1 k points. After fully minimization of energy, relaxed coordinate were used to study the structural and electronic properties. To study the effect of electric field and mechanical properties of PNT, Monkhorst pack grid of 50×1×1 k points were used.

RESULTS AND DISCUSSION

We have modeled 3 different types of nanotubes i.e. armchair phosphorus nanotube (APNT), zigzag phosphorus nanotube (ZPNT) and helical phosphorus nanotube (HPNT). In order to check the relative stability of these nanotubes, we calculated their formation energy, which is defined as the energy required to form these nanotubes from their 2D counterpart i.e.,phosphorene. The following formula is used to calculate relative formation energy [5]:

$$E_f = \frac{E_{PNT} - nE_P}{n}$$

where E_{PNT} is total energy of PNT, E_P is energy per atom of planar phosphorene and n is the no. of atoms in PNT. Formation energy, diameter and band-gap of different PNTs are given in table 1 and the relaxed structures of these nanotubes with different bond lengths are shown in FIGURE 1. Small negative formation energy of 1D planar PNTs reveals the possibility of their existence in planar tubular form. It is notable that APNTs are energetically most favorable among the considered tubular structures with formation energy close to zero.

TABLE 1: Chirality, no. of atoms, diameter, formation energy and band gap of all the considered nanotubes

PNT	Chirality	No. of Atoms	Diameter(Å)	Formation Energy (eV/Atom)	Band-gap (eV)
Armchair	(3,3)	72	7.54	-0.08	0.22
Zigzag	(5,0)	120	7.20	-1.07	0.00
Helical	(4,2)	112	7.50	-0.29	0.05

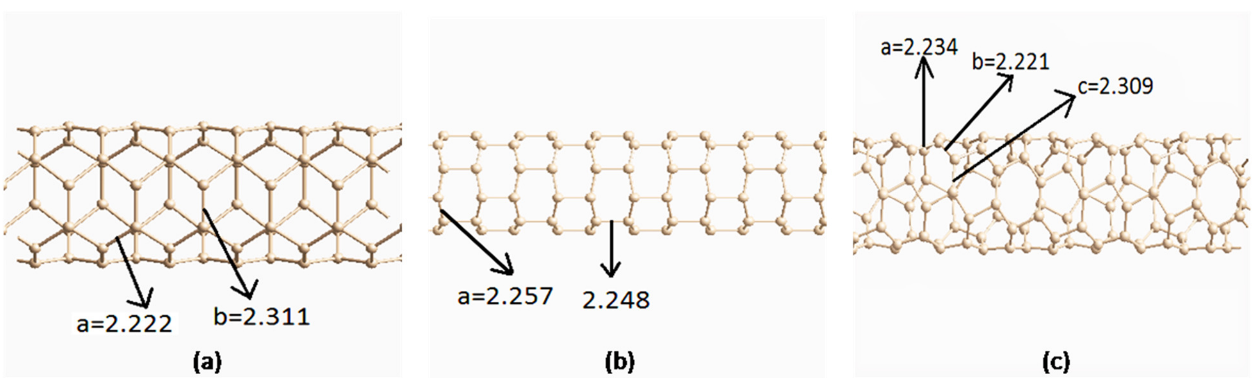

FIGURE 1: Relaxed structures of different nanotubes with their chirality and bond lengths in Å (a) APNT (3,3) (b) ZPNT (5,0) (c) HPNT (4,2)

Next, we study the mechanical properties of considered nanotubes by applying the tensile strain ranging from 2% to 26% in intervals of 2%, along the axis of the tube. The point where the applied strain gives the maximum value of the stress in the stress-strain curve gives us the mechanical strength of the nanotube. From FIGURE 2(a) we can conclude that, among the three nanotubes, APNT (ZPNT) has the highest (lowest) mechanical strength i.e, it can withstand a mechanical strain of 22% (20%) with corresponding stress value of 2.04 GPa (1.20 GPa). On the other hand, for HPNT the ultimate strain and stress values are 22% and 1.72 GPa, respectively. Stress-strain curve of APNT and ZPNT shows ductile nature while HPNT shows brittle nature.

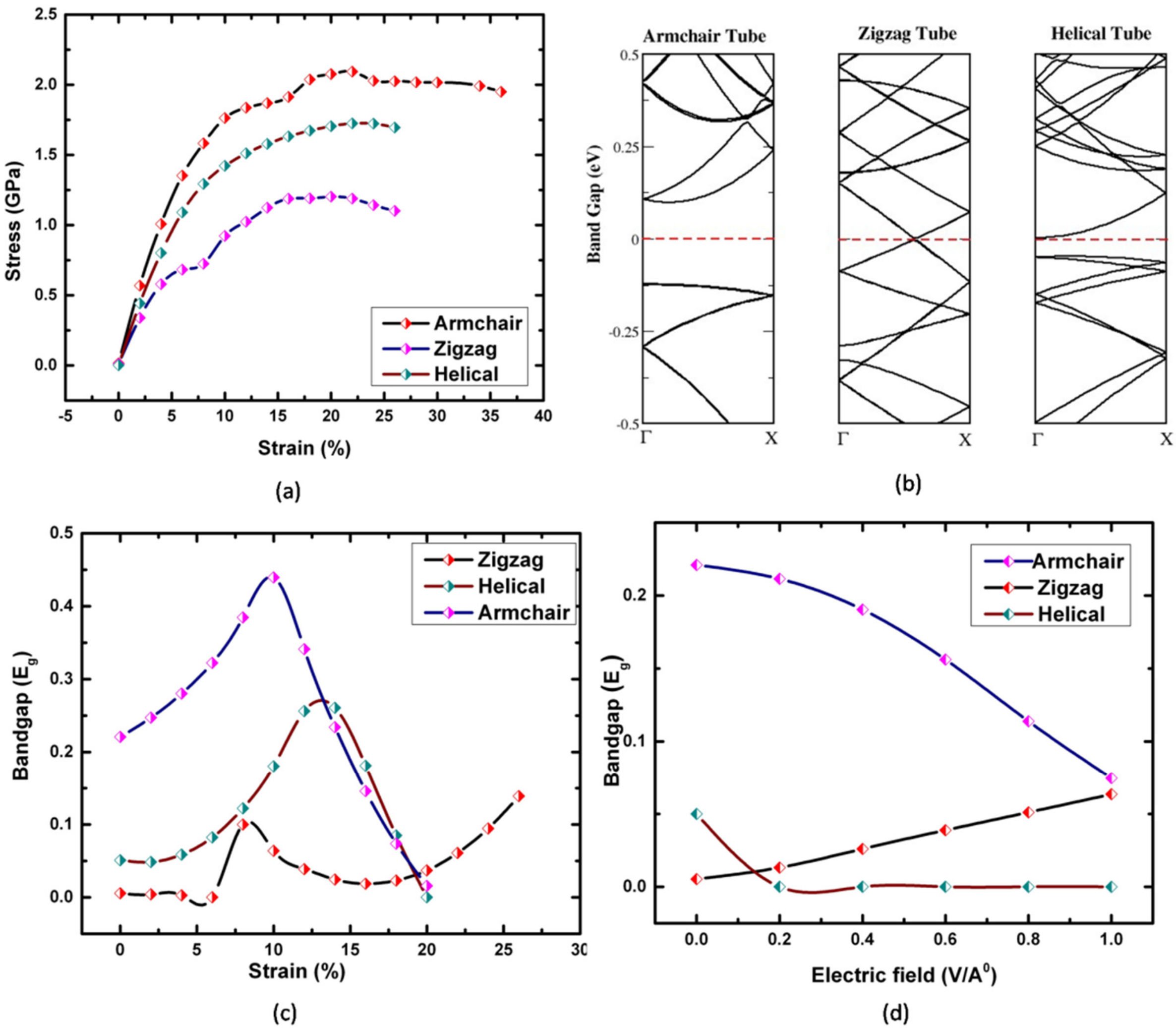

FIGURE 2: (a) strain vs. stress curve, (b) energy band diagram (c) band gap vs. strain curve and (d) band gap vs. electric field curves for three different edge nanotubes.

Tuning the Electronic Structure of PNTs

We found that the electronic properties of PNTs depend on their Chirality. APNT and HPNT are semiconducting while ZPNT is comes out to be semi-metallic (FIGURE 2(b) and Table 1). There are various means by which one can modify the electronic structure of low-dimensional materials, the most common are mechanical strain and external electrical field. Under normal condition APNT (HPNT) is semiconducting in nature. Application of tensile strain up to 10% (14%) continuously increases the bandgap of these tubes but further increase in strain decreases the bandgap till it becomes zero at 20% (20%) this is due to the simultaneous shift of conduction band minima and valence band maxima towards the fermi level. Hence semiconductor to metal transition occurs in APNT and HPNT. ZPNT is semimetallic in nature, however, on the application of strain, band opening appears at 8% which decreases to minimum at 16% of applied strain and shows increase on further increasing the magnitude of strain.

In order to study the variation of applied electric field on electronic structure of PNTs, perpendicular electric field normal to axis of tube is applied. The band gap varies with the applied field normal to axis of tube. In APNT, band gap decreases with applied electric field while in ZPNT band gap increases from zero to ~0.07 eV. HPNT become metallic in nature on application of applied field (FIGURE 2(d)). The variation of bandgap with applied electric field arises due to redistribution of charge along the diameter of the tube.

CONCLUSIONS

In summary, energetic and electronic structure tuning with external strains and electric fields are performed on planar phosphorous nanotubes with different chirality. Small value of formation energy of considered nanotubes particularly APNT, suggests its possible ease of realization. The electronic and mechanical properties of PNTs depend upon its chirality. APNT and HPNT are semiconducting in nature while ZPNT is semi metallic. APNT and HPNT can bear up to 22% of tensile strain while ZPNT can bear up to 20% of tensile strain. Electronic band structure of PNTs is sensitive to applied strain and electric field e.g. band gap gets open up in ZPNT and the magnitude of band gap can be tuned for APNT and HPNT by both strain and electric field. The possibility of the formation of planar nanotubes particularly APNT and its tunable electronic structure may ignite the experimentalist for its fabrication.

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