First Principle Study of Phosphorus Nanotube: Structural, Mechanical and Electronic Properties

Attiqullah Abid Sherzad[1], Mohammad Jawad Niazi[1], Zardar Khan[2], Mansoor Zahirzai[1]

[1]Department of Physics, Faculty of Science, Nangarhar University, Afghanistan.

[2]Department of Chemistry, Faculty of Science, Nangarhar University, Afghanistan
Email: abidattiqullah@yahoo.ocm

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Abstract: Discovery of fullerene and other Nano-dimensional allotropes of carbon revolutionized the technology. Their properties were very different and interesting from their bulk counter parts. This made scientists to search for other materials, which are similar to graphite. In this quest, they searched many-layered structure like silicon, germanium, black phosphorus etc. In this research, first principle simulation based on density functional theory has been used with siesta performance to investigate structural, mechanical and electronic properties of the different geometrical phosphorus nanotubes. To perform calculation double zeta polarized basis set and generalized gradient approximation as exchange correlation energy functional have been used. After the calculation, we found three phosphorus nanotubes with different geometrical shapes armchair, zigzag and helical with different bods' length. Mechanical property of the each tube shows that mechanical strength of the armchair nanotube is comparatively high than other two zigzag and armchair nanotubes. Electronic properties of the nanotubes clearly indicate that they are semiconducting in nature and their properties depends on their chirality.

Keywords: bandgap, chirality, nanotube, strength, strain.

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1. Introduction

Miniaturization of objects has made our life easy. It has not only reduced the size of appliances that we use regularly but also increased their efficiency. After the discovery of SEM (Scanning Electron Microscope) in 1981 and Fullerene in 1985, a new era of science began. The word Nano came from a Greek word which means dwarf [1], [2].

Nano is used as prefix, which means one billionth of a unit. Nanomaterials are mater whose at least one dimension lies in nanometer range. There are plenty of nanomaterials in nature. These materials are also called low dimensional material. We may classify these low dimensional materials in four different forms. Zero dimensional, one dimensional two dimensional and three dimensional nanomaterials[3].

Nanomaterials are not new in nature. Lotus leaves are one of the examples of Nanostructures. In lotus leaves, papillae's are coated with hydrophobic wax crystals whose diameter lies in nanometer range. Chinese have been using gold nanoparticles as dye for more than 1000 years [4]. Clays are also example of nanoparticles [5].

Phosphorus covers approximately 0.1% of earth's crust. It has two most common allotropes i.e. white phosphorus and red phosphorus. White phosphorus is soft and waxy solid with P4 tetrahedral structure. Each P atom in white phosphorus is attached to other 3 P atoms by single bond. White phosphorus is most unstable and toxic allotrope of phosphorus. It changes to red phosphorus when heated or exposed to sunlight. Red phosphorus is another most common allotrope of phosphorus. It is polymeric in structure, in which P4 molecules form a long chain. It is more stable than white phosphorus. Red phosphorus is amorphous in nature and crystallizes into violet phosphorus when further heated. Another important allotrope of phosphorus is black phosphorus. White phosphorus turns into black phosphorus when heated under high pressure [6].

Black phosphorus (BP) is most stable allotrope of phosphorus [7]. It has layered structure similar to graphite. It was first synthesized in 1914. It is a good electrical and thermal conductor but less diamagnetic than white and red phosphorus. Unit cell of black phosphorus contains 8 atoms and its calculated density is 2.69 g/cc. Lattice constant of black phosphorus was first calculated by using x-ray. Unit cell of BP contains two layers. Each P atom is bonded to three neighboring. P atoms with bond length 2.18°A. Two of these lie in the plane of layer at 990 from each other and third lies between the layers at 1030 [6]. Crystal structure of black phosphorus is orthorhombic under normal conditions. It shows two reversible structural transitions at high pressures. First transition takes place around 5.5 GPa from orthorhombic to tetrahedral phase at room temperature, in which displacement of puckered layers and volume change occurs. Tetrahedral phase further changes to simple cubic structure at higher pres- sure of about 10 GPa. Simple cubic phase is stable even at 60 GPa. Orthorhombic and tetrahedral phase are semiconducting but simple cubic phase shows metallic nature. Near 4.7 K simple cubic phase of black phosphorus shows superconducting property[8].

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It has direct band gap of magnitude 0.3 eV. BP is a p-type semiconductor[9]. Single layer of black phosphorus is called Phosphorene. Phosphorene was first synthesized by using mechanical exfoliation technique. Phosphorene is finite band gap 2-D material in contrast to graphene which has zero band-gap. Phosphorene has direct band gap of magnitude between 0.75- 2 eV and carrier mobility 1000 cm2V −1s−1. Crystal structure of Phosphorene is different from other 2-D layered materials. Phosphorene has puckered structure along armchair direction and bilayer configuration along zigzag direction. Armchair and zigzag direction corresponds to crystallographic x and y axis respectively[10].

Its local bonding configuration clearly reflects anisotropic structure of Phosphorene. In zigzag direction bond angle (hinge angle) is 94.30 and neighboring P-P bond length is 2.253 ˚A, whereas in armchair direction equivalent dihedral angle is1030 and neighboring P-P bond length is 2.287 ˚A [11].

Lattice constants along zigzag direction and armchair direction are 3.3 ˚A and 4.53 ˚A respectively. Puckered structure of phosphorene is because of presence of sp3 character of chemical bond at the surface[7]. Because of unique puckered honeycomb structure, phosphorene shows anisotropic mechanical, electrical and optical properties [10].

There is another type of phosphorene known as blue phosphorene. The structure of blue phosphorene is buckled similar to the structure of silicene. In blue phosphorene P-P bond length is 2.29 ˚A [12]. Experimentally calculated electronic band gap of blue phosphorene is 1.10 eV. Band gap of blue phosphorene decreases with increasing layers[13].

Phosphorene nanoribbon (PNR) can be obtained from phosphorene sheet. A phosphorene nanoribbon is one-dimensional structure of phosphorene with width less than 100 nm. Depending on their edge structures their electronic and mechanical properties varies [9]. PNR obtained by cutting Phosphorene along armchair direction is called Arm-Chair PNR (APNR) whereas PNR cut along zigzag direction is called zigzag PNR (ZPNR). However, ZPNRs are energetically more favorable than APNRs. Total energy of both kind of nanoribbons decreases with increase in width of ribbon. ZPNRs are metallic in nature whereas APNRs are semiconducting with indirect band gap. The band gap of APNRs decreases with increase in width of nanoribbons. [14]. Another one dimensional Nano structure of phosphorous is phosphorous nanotubes (PNT) which can be obtained by rolling the sheet of phosphorene. If single sheet of phosphorene is folded then it is called Single Walled Nanotube. In Multi-walled Nanotube many concentric cylinders forms a nanotube. These nanotubes can also be classified in three types based on their chirality i.e. Zigzag PNT, Armchair PNT and Helical PNT [15].

If a sheet is folded along R (a , b) to form tube, then it is called Chiral tube (a , b) and R is chiral vector. Chirality for Zigzag PNT is (a , 0) i.e. it is formed by folding the sheet parallel to x axis. These tubes are achiral. Chirality for armchair PNT is (a , a). These tubes are also achiral in nature. Helical PNT are obtained for chirality (a , b). These tubes are chiral in nature i.e. their mirror image differ from their original image[15].Mechanical properties of the Phosphorus were investigated with using of the first principle DFT calculations. Investigation shows that mechanically Phosphorene is very flexible and it can sustain stress up to 18 GP and 8 GP in zigzag and arm chair direction respectively and can hold critical strain up to 30 GP [16]. Mechanical properties of the Phosphorene under uniaxial deformation were studied with using of the first principle calculation method. it shows that both the young's modulus and ultimate strain are highly anisotropic and non-linear and also found that the in plane young's modulus in perpendicular direction to pucker is half of that in parallel direction whereas ultimate strain is much higher in perpendicular direction to pucker [17]. Electronic and mechanical properties of the Phosphorene were studied and found that under a large enough isotropic tensile strain monolayer Phosphorene loses its puckered structure and become at structure like graphene. It also illustrate that electronic properties of Phosphorene highly depend upon magnitude and direction of applied strain. It also showed that under both isotropic compressive strain and isotropic tensile strain Phosphorene initially has direct indirect transition and then transition to metal take place[18].

Elastic, vibrational and electronic properties of Phosphorene were studied with the using of first principle simulation method and investigated very anisotropic mechanical response while calculating in plane and out of plane elastic constants. Observation showed that it possess smaller in plane stiffness along both the directions and concluded that in plane deformation highly affects the size and nature of band gap [19].

2.Materials and Methods

We used SIESTA to perform first principle simulation based on DFT. We used GDIS molecule modeler to model phosphorus nanotubes. To perform calculation we used double zeta polarized basis set with generalized gradient approximation as XC Functional. PBE form of exchange correlation functional is used. To optimize the structure of nanotube we sampled the reciprocal space by a Monkhorst pack grid of $100 \times 1 \times 1$ k points. Conjugate gradient method is used to optimize the structure with forces on each atom less than 0.01 eV/˚A. A

cutoff energy equal to 250 Ry is used. After optimization of structure and minimization of energy, relaxed coordinate are used to calculate the electronic and mechanical properties of the each structure.

3.Result and discussion

3.1 Structure of nanotubes

To start our calculation, we modeled the phosphorus nanotube and used Conjugate Gradient Method to optimize structures the each phosphorus nanotube. To optimize the structure 300 maxi- mum SCF iterations were used. After optimization, we obtained three different geometric structures of the phosphorus nanotube with different bond lengths as illustrated in figure 1. We found that there were two types of bond lengths in armchair and zigzag nanotubes, while in helical nanotube three types of bond lengths were present. These nanotubes with different bond lengths are shown in following figures 1. 2. 3. Bond lengths for armchair nanotubes are 2.3118 ˚A and 2.222 ˚A and for zigzag nanotubes are 2.257 ˚A and 2.248 ˚A. For helical nanotube, bond lengths are 2.234 ˚A, 2.221 ˚A and 2.309˚A.

3.2 Mechanical properties of the nanotubes

To study the mechanical property of nanotubes, we applied tensile strain along the axis of the tube. With the variation of strain from 2% to 26% by the variation amount of 2%, we studied its effect on all the three nanotubes. We found that on increasing the strain in nanotubes, stress increases up to a maximum value and then it starts decreasing as shown in figure 2. It shows tube breaks after that particular strain. This particular value of stress after which tube breaks is called mechanical strength of that tube. It is found that mechanical strength of armchair nanotube is 2.0446 GP while mechanical strength of zigzag nanotube is found to be 1.2031 GP and mechanical strength of helical nanotube is found to be 1.7252 GP.

3.3 Effect of strain on band-gap of nanotube

We also found that application of tensile strain on nanotube affects its band structure. Under normal condition (without application of any electric field or strain etc.), armchair nanotube is semiconducting in nature with band gap 0.221 eV. We applied strain from 2% to 26% with a variation of 2% and found that band gap increases up to 10% of applied strain and then band gap starts decreasing up to 20% of strain as shown in figure no.3. After 20% of applied strain, it becomes metallic in nature. Band gap of helical nanotube is 0.05 eV at normal condition and it increases up to 14% of applied strain. After that, it starts decreasing and become metallic after 20% of applied strain as illustrated in figure no. 6. Helical nanotube is also semiconducting in nature. Zigzag nanotube is semiconducting in nature with band gap of 0.0053 eV. On application of strain, first, it becomes metallic at 6% of applied strain and then band opening appears at 8% of applied strain. This band gap decreases up to 16% of applied strain and then increases as shown in figure no. 7.

3.4 Variation of bandgap with applied electric field

To study the variation of applied electric field on band gap, we applied electric field along the axis of each tube and normal to the axis of each tube. We applied electric field from 0.2 eV/˚A to 1.0 eV/˚A with variation of 0.2 eV/˚A as illustrated in figure no.4. When we applied electric field along the axis of tube, we noticed that there is no variation in band gap of any of the three tubes but when we applied electric field perpendicular to the each axis of the tube, band gap varies in all the three nanotubes. In armchair nanotube when we applied electric field band gap decreases, while band gap of the zigzag nanotube increases. Helical nanotube become metallic in nature on application of the applied field.

3.5 Electronic properties of nanotubes with different chirality

In our DFT based calculations, we found that electronic properties of PNT depends upon the chirality of nanotubes as shown in figure 5. We have modeled 3 different types of tubes i.e. arm chair nanotubes with chirality (a,a), zigzag nanotubes with chirality (a,0) and helical nanotubes with chirality (a,b). We found that armchair tube with cirality (3,3) have bandgap of the order of 0.221 eV, for zigzag tube with chirality (5,0) band gap is found to be on the order of 0.0053 eV and for helical tube with chirality (2,4) band gap is found to be 0.05 eV. It shows that all the three nanotubes i.e. armchair, helical and zigzag nanotubes are semiconducting in nature.

(a): Armchair nanotube with chirality(3,3)

(b): Zigzag nanotube with chirality(5,0)

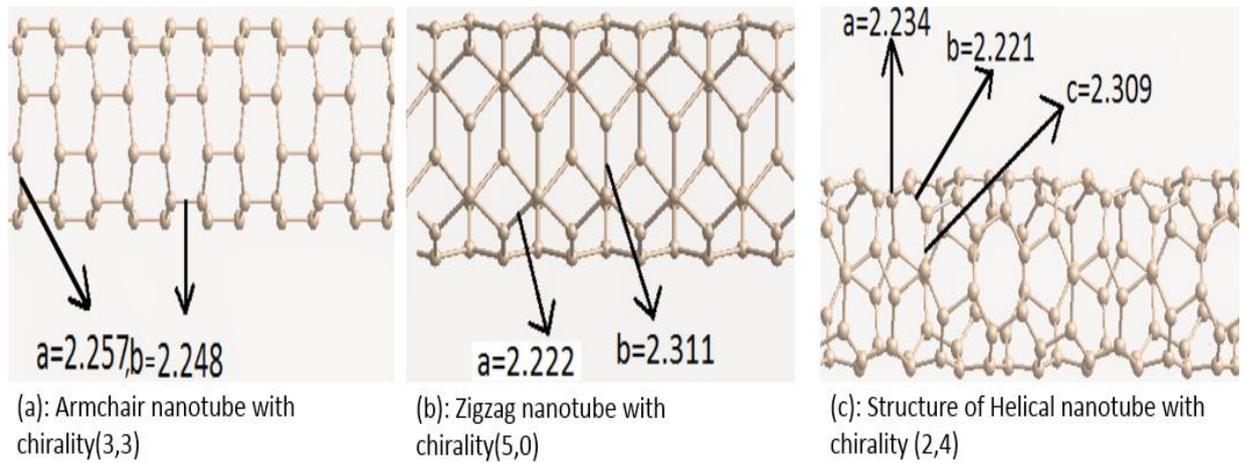(c): Structure of Helical nanotube with chirality (2,4)

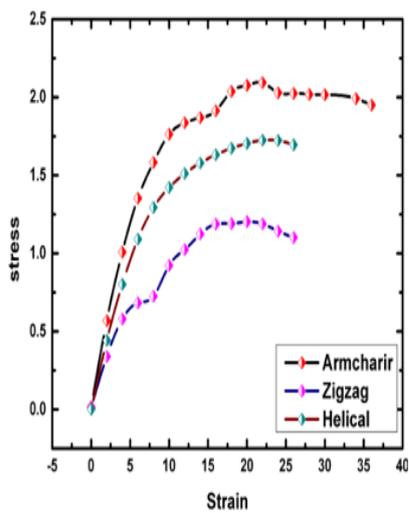Figure 1: Structures of the different Nanotubes

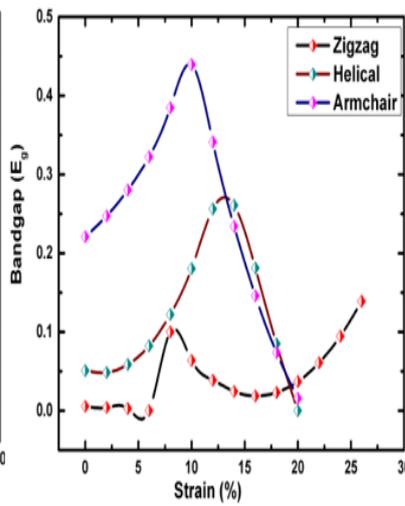Figure 2: Graph between stress and tensile strain for three nanotubes

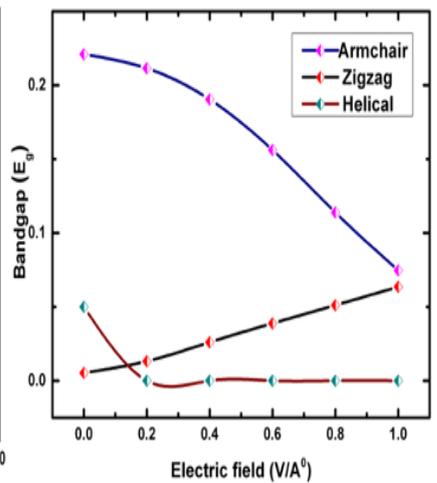Figure 3: Graph between band-gap and tensile strain for three nanotubes

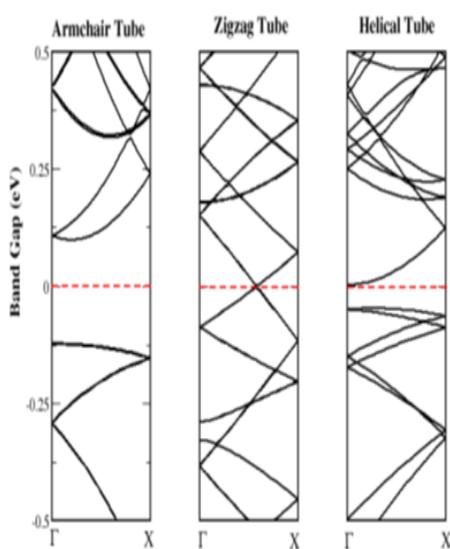Figure 4: Graph between band-gap and applied electric field for three nanotubes.

Figure 5: Energy band diagram for three tubes with different chirality.
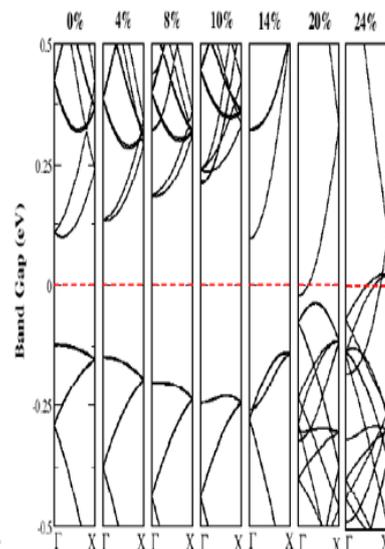

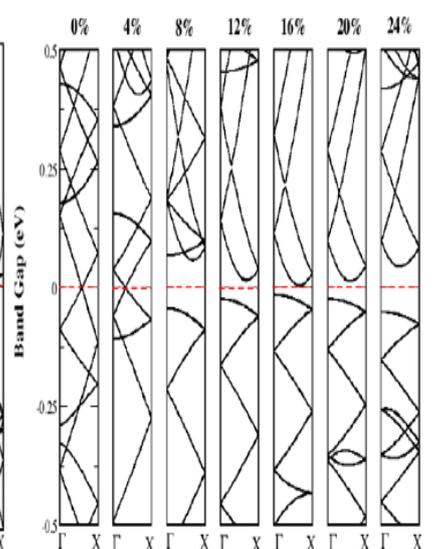Figure 6: Change in band gap with applied tensile strain for armchair nanotube

Figure 7: Change in band gap with applied tensile strain for zigzag nanotube

4.Conclusion

In summary, we studied structural, electronic and mechanical properties of the armchair, zigzag and helical phosphorus nanotubes. We found that electronic properties of the each nanotube depends upon its chirality. For different chirality, band structure of each tube is changed. All the three nanotubes are semiconducting in nature. Armchair nanotube has band gap of 0.221 eV, Helical nanotube has band gap of 0.05 eV and Zigzag nanotube has band gap of 0.005 eV. Mechanical properties of each nanotube is also chirality dependent. Mechanical strength of Armchair nanotube is 2.0446 GP, Zigzag nanotube is 1.0231 GP and Helical nanotube is 1.7252 GP. Calculation shows that maximum mechanical strength for Armchair nanotube is at 22% of applied strain, for Zigzag nanotube is at 20% of applied strain and for Helical nanotube is at 22% of applied strain. Band gap of nanotube is sensitive to applied strain. Variation in band gap appears with variation in applied strain.

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