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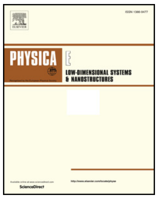

Energy bandgap engineering of graphene nanoribbon by doping phosphorous impurities to create nano-heterostructures: A DFT study

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ABSTRACT

Energy bandgap engineering is used to produce semiconductor heterostructure systems that perform processes such as the resonant tunneling in nanoelectronics and the solar energy conversion in solar cell applications. However, the performance of such systems degrades as their size is reduced. Graphene-based nanoelectronics has appeared as a candidate to enable high performance down to the single-molecule scale. Here, graphene nanoribbons (GNRs) can have bandgaps that are tunable by using chemical doping method. We have been predicted that bandgap engineering within a GNR may be achieved by varying the number and geometrical pattern of phosphorus (P) impurities in the GNS, so that we have carried out first-principles calculations of the energetic and electronic properties of P-doped GNR based on density functional theory (DFT) with Gaussian 09W packages. The geometric and electronic properties of the GNR with and without various dopants of phosphorus impurities were performed and discussed. Our results show that the electronic properties of GNR do not only depend on the phosphorus impurity concentrations, but also depend on the geometrical pattern of phosphorus impurities in the GNR. As a result, we can bandgap engineering of GNR by doping phosphorous impurities to create semiconductor heterostructure, which can be used in many important applications.

1. Introduction

The discovery of some nanostructures such as graphene which has unique electronic properties [1,2] has led to a number proposals for novel optoelectronic [3], photovoltaic [4], and nanoelectronics [5] applications. However, the lack of a bandgap has hindered more development of nanomaterial-based devices. Particularly applications of photovoltaic, there are a number of important ingredients which are key in designing materials for harvesting solar cell energy, based on the presence of a gap, which should preferably coincide with the visible spectrum range [6–8].

Recently, the graphene-based materials are used to great semiconductor heterostructure devices [9–11]. A semiconductor heterostructures are a sandwich of or junction between two dissimilar semiconductors with different bandgaps [12]. The requirement that each material is a semiconductor with unequal bandgaps is somewhat loose, especially on small length scales, where electronic properties depend on spatial properties. The heterostructure is useful to engineer the electronic energy bands in numerous solid state applications, including solar cells, semiconductor lasers and heater transistors [12,13]. There have been several attempts to induce such a bandgap in graphene-like materials, including doping, strain engineering, adsorbed atoms, and lateral confinement [14–16]. In particular, graphene nanoribbons (GNRs), which found by cutting the graphene sheet [17,18], exhibit semiconducting behavior in narrow samples less than ten nanometers wide. According to the regular edge shape along the extend direction, the GNR can be structured as zigzag GNR and armchair GNR [19].

The outstanding properties of GNRs are famous nowadays: their electronic properties powerfully depend on the shape, length, width and edge morphology [1,20,21]. It has been recently established that the electronic properties can be completely designed [22]. Actually, several methods have been developed to produce high-performance graphene devices via tuning their bandgaps to improve their semiconducting properties. Newly, many works have used First-principles calculations based on DFT to study the effect of chemical doping on the properties of graphene [14,23–27]. Chemical doping is a powerful method to tuning the electronic properties of carbon-based nanomaterials [23,28–32], and hence, it could be used to modify the electronic properties of GNRs. GNR has attracted more and more attention due to its unique electronic properties [19,33–37], thus using some features of GNRs, such as the semiconducting behavior and their quasi-1D character, that usually improves the exciton binding energies, one might

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envision using them as long-exciton lifetime donor materials for applications of photovoltaic.

In this work, we have made a try to present a systematic study of the effect of substitutional doping of phosphorus within the graphene nanoribbons with the aid of slowly increasing the concentration of phosphorus impurities and further examining the various isomers of the same doped configuration. We select phosphorus impurity for our study, using each individually as the dopant due to their nearly similar size to that of carbon, and deferring for the present time using a combination of phosphorus in host of C atoms. Substitutional impurities represent one of the methods to engineering the desired electronic properties. This phenomenon is assumed to be particularly important for applications in the future applications of heterostructure with tunable properties. In the following, we outline computational details for using density functional theory and describe the results for phosphorus doping in section 3. These results are discussed and finally concluded in section 4.

2. Computational details

We selected a GNR (2,2) as a model nanosensor, that consists consisted of 48 C atoms and in which the end atoms have been saturated with 12 hydrogen atoms to decrease the boundary effects, see Fig. 1. All calculations on the GNR were performed using DFT method as implemented in the Gaussian 09W package [38]. The hybrid functional B3LYP [39], which combines Becke's exchange [40] and Lee, Yang, and Parr's correlation [41] functionals with the 3-21G basis set [42], were used for the quantum-chemical calculations [42–45]. Before energy calculations on GNR with and without various concentrations of P atoms, all atoms could be relaxed. The electronic properties of GNR including the DOS analysis, total energies, dipole moments, highest occupied molecular orbital (HOMO) energies, Fermi level energies, lowest unoccupied molecular orbital (LUMO) energies, energy gaps, work functions, and change of energy gap are studied theoretically with numerous constructions of P impurities in different locations with the use of the above-stated stage of theory. Before dopants, all the atoms were relaxed when GNR included various concentrations of P impurities. By using the above-mentioned level of theory, the electronic properties of GNR are investigated theoretically with various constructions of P impurities in different locations. Before dopants, all geometrical structures were shown and all the atoms were relaxed when GNR included different concentrations of P impurities.

3. Results and discussions

3.1. Geometric properties

Herein, the study starts with a pure GNR, which consists 48 carbon atom. Due to the periodic boundary conditions are absentee in quantum calculations for molecular structures, it is required to saturate the carbon dangling bonds with hydrogen atoms so that we added 12 atoms for the GNR ends. The structure of (2,2) GNR have 13.554 Å in length and 7.104 Å in width, as shown in Fig. 1(b). Based on the gotten results, the bond lengths of the C—C bond is 1.42 Å, see Fig. 1(b), which is in good agreement with previously reported values in other articles [46–48]. This system was optimized by using the DFT with the B3LYP hybrid functional and the absence of imaginary frequency at the same level verified the optimized structures correspond to the energy minima. Then, a pure GNR was doped with a number of P impurities.

We have optimized the configurations of nP-GNR for n = 1–6 through calculating the total energy by means of DFT calculations, where 36 different initial configurations as starting geometries for each combination of P impurity were studies. The geometric forms of all configurations described in Figs. 2–7. The relative total energies of all the considered structures of nP-GNR with respect to the ground-state structure are display in Table 1. In the GNR pure, we replaced one P impurity (n = 1) in place of a C atom in several locations as presented in Fig. 2. The distortion with respect to the GNR structure is expressed as the change in bond lengths of the structure, where the relaxed bond length of doped GNR increases with an increase in the number of impurities because the bond length of P impurity is bigger than C atom. It is found, the most stable structure is presented in Fig. 2(d), which has the largest total energy −57886.2 eV, see Table 1.

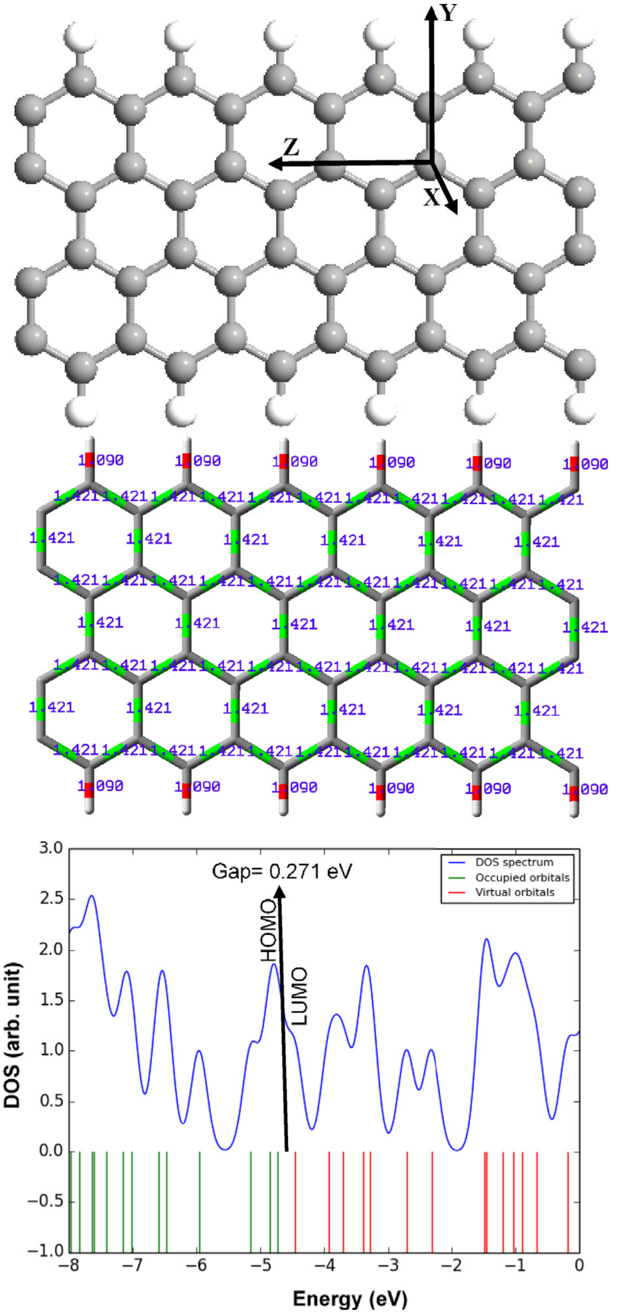

Fig. 1. The optimized geometry with bond lengths (in Å unit) and the density of state of a pure (2,2) GNR.

For case n = 2, we study two P impurity replacement at different locations, alternate locations in hexagon ring and gradually increasing to larger distances till the substitutions are at the diagonally opposite location, as shown in Fig. 3. The P impurity is likely to change to surrounding C atoms of the host. Therefore, when GNR is doped with P impurities, the P impurity also undergo sp2 hybridization and due to the nearly same size of C and P atom, no significant distortion in the 2-D structure of GNR is noted, exclude a change in adjoining bond length.