Electronic properties of graphene nanoribbons doped with zinc, cadmium, mercury atoms

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ABSTRACT

The effect of substitutional impurities as Zinc (Zn), Cadmium (Cd) and Mercury (Hg) on electronic properties of graphene nanoribbons (GNRs) was investigated by using Density Functional Theory (DFT). A substantial change in the electronic properties of GNR structures was observed while changing the position of dopant atom from the edge to the center of armchair graphene nanoribbons (AGNRs) and zigzag graphene nanoribbons (ZGNRs). The calculations are shown that the electronic band gap of GNRs can be controlled depending on the position of dopant atoms. The calculated electronic band structures for both AGNRs and ZGNRs show spin-dependent metallic or semiconductor behavior according to the position of dopant atoms. From the Density of States (DOS) information, quasi-zero-dimensional (Q0D) and quasi-one-dimensional (Q1D) type behaviors are observed. It is shown that because the doped ZGNRs had the lowest total energies, ZGNRs are energetically more stable than AGNRs.

1. Introduction

Graphene is two-dimensional material established by a sheet of carbon (C) atoms arranged in order a hexagonal lattice. It is an allotrope of carbon in the structure of a plane of sp^2 bonded atoms with a molecule bond length of 0.142 nm, has emerged as an interesting material of the 21st century [1]. Graphene and its different types have the potential to be used in various applications impact on electronic and optoelectronic devices, chemical sensors, nanocomposites and energy storage [2,3]. Graphene can be seen as the fundamental essential principle of a kind of materials with different dimensionalities, such as one-dimensional nanoribbons or nanotubes, zero-dimensional fullerenes or three-dimensional graphite [4–6]. The first of these, graphene nanoribbons are one-dimensional structures. ZGNR and AGNR are classified as zigzag and armchair according to shape of the edges in GNRs. It is known that in general ZGNRs are metallic, while AGNRs are known as the metallic or semiconductor properties depending on its widths and edge states [7–10]. AGNR is expressed as non-magnetic semiconductors while the magnetic ground states of ZGNR make them convenient a suitable for spintronic applications [11–15]. Theoretical and experimental investigations are still going on GNRs. In order to

investigate these structures better, DFT has been applied to explore the electronic behavior. The determination of the electronic band structures of GNRs and the effects of the dopant atoms on the electronic band structures have been examined in various studies [16].

In the some theoretical studies that can be examined, transition metals (TMs) are used as a metal dopant or adatoms to achieve the spin-dependent structures [17,18]. It is already known that the electronic properties of GNRs are strongly dependent on the dopant atoms. With doping with some TMs, it has been reported significant changes in electronic band structures of the GNRs [19,20]. Correspondingly, using TMs it has provided the opportunity to investigate the changes in the spin dependencies and to control the electronic band gap.

Previous results obtained that the doping location along the nanoribbons are important in terms of manipulating the electronic properties of GNRs [21]. In this study, the effect of group IIB metals as Zn, Cd and Hg substitutional doping at four successive positions of the ZGNRs and the AGNRs are studied using DFT method with spin-polarized generalized gradient approximation (SGGA) as exchange-correlation. The electronic behavior of the doped GNRs has been explained in detail by calculating the band structures, the density of states (DOS), the total energies of the investigated structures.

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Fig. 1. The supercell of graphene nanoribbons with substitutional doping for (a) AGNR, (b) ZGNR.

2. Computational details

The calculations were based on spin-polarized DFT using SGGA, implemented in the Atomistix ToolKit-Virtual NanoLab (ATK-VNL) software for the investigated structures [22]. For the integration of the Brillouin zone, $1 \times 1 \times 100$ k-points were used within the Monkhorst-Pack scheme [23]. In the calculations, the AGNRs and ZGNRs passivated with hydrogen (H) atoms for the different atom widths (N_a for AGNR and N_z for ZGNR) have been investigated. Because nanoribbons with different widths are exhibited similar behavior to each other in the calculations, only nanoribbons had 8 atoms width have been investigated in detail in this study. The density mesh cut-off energy was used as 500 eV and the maximum applied force to the nanoribbons was selected less than $0.05 \text{ eV/\AA}$. The investigated nanoribbons are constrained two directions along x and y-axis, while they are infinite in the z-direction.

Supercells of AGNR and ZGNR had 8 atoms widths are shown in Fig. 1. Gray, white and red atoms are represented C, H and substitutional dopant atoms (Zn, Cd, Hg), respectively. The electronic band structure and the DOS have been carried out for the A1, A2, A3, A4 doping sites of the AGNRs and Z1, Z2, Z3, Z4 doping sites of the ZGNRs. To determine the energetically stable structure, the total energy (E_T) of each structure has been calculated.

3. Results and discussion

3.1. Effect of group IIB atoms on electronic properties of AGNRs

The electronic band structures of the AGNRs doped with Zn atom are shown for different dopant atom sites in Fig. 2. From now on, in the electronic band structure representations of the investigated structures, spin up and spin down bands are shown black and red lines, respectively. In Fig. 2(a), when the Zn doped structure at the A3 site has a band gap of 0.08 eV for the spin down band and metallic behavior for the spin up band. Considering the electronic band structure for all dopant atom sites in Fig. 2(a), the calculated band gap results show that AGNRs doped with the Zn atom have metallic behavior. In the investigated AGNR structures, spin-dependent electronic band structure is

observed. Fig. 2(b) shows the DOS of the structures doped with Zn atom from A1 to A4 sites. Non-equilibrium spin density in which one spin band shows conducting behavior while the other one state reveals semiconducting behavior. Generally, while the spin up bands are getting rarer, spin down bands are getting denser around the Fermi level. Also, QOD behaviors have been observed at A2, A3, A4 sites in the DOS near the Fermi level [23].

The band structures of Cd doped AGNRs are shown in Fig. 3(a). Spin-dependent semiconductor behavior in the electronic band structures is shown in the investigated AGNRs with Cd dopant atom. These structures have direct band gaps with changing between 0.36 eV and 0.46 eV. In Fig. 3(b), the DOS of Cd doped AGNR are shown. In doping at A3 site case, dense spin up band are found to be formed near the Fermi level.

The band structures of Hg doped AGNRs are shown in Fig. 4(a). For Hg doping at A1 and A2 sites, the electronic band gaps of the structures are calculated as 0.59 eV and 0.23 eV for the spin up bands, respectively. As Hg atom settled into the center of AGNR, the spin dependent properties of the band structure are disappeared as is seen from A3 and A4 sites. When the position of the dopant atom is changed, the energy levels of both spin up and spin down bands are started to overlap. The calculated results show that Zn doped AGNRs have a metallic behavior whereas Cd and Hg doped AGNRs are exhibited the semiconductor properties.

In Fig. 4(b), it is shown that Hg doped AGNR structures exhibit semiconductor behavior. As the position of the dopant atom shifts to the center of AGNR, the electronic states are getting further away from the Fermi level. For doped structures at A1, A2 and A3 sites, with settle like states near to the Fermi level, show typical QOD behavior [24].

3.2. Effect of group IIB atoms on electronic properties of ZGNR

The electronic band structures of Zn doped ZGNRs are shown in Fig. 5(a). The calculations show that ZGNRs with doped Zn atom at Z1 and Z4 sites have metallic behavior. Also, the spin dependency in the electronic structure for the Z2 site with 0.50 eV and Z3 site with 0.70 eV band gap values of ZGNRs is observed as the semiconductor behavior for the spin down bands. As doped atom approaches the center of the

Fig. 2. a) Band structures and b) DOS of AGNRs doped with Zn atom for different doping sites, i) A1, ii) A2, iii) A3, iv) A4. Fermi level is shown with the blue dashed line in this study. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

structure, the band gap closes. In Fig. 5(b), the Z1 structure shows broad, settle like, spin up and down bands with Q0D behavior just at Fermi level.

The electronic band structure of Cd doped ZGNRs are investigated in Fig. 6(a). The band gaps of ZGNRs with doped Cd at Z1, Z2, and Z3 sites are calculated as 0.48 eV, 0.13 eV and 0.11 eV, respectively and exhibit semiconductor behavior with decreasing band gap values. For doping at center of the structure, namely the Z4 site, the electronic band structure shows metallic behavior. DOS results are shown in

Fig. 3. a) Band structures and b) DOS of AGNRs doped with Cd atom for different doping sites, i) A1, ii) A2, iii) A3, iv) A4.

Fig. 6(b). It is shown that the electronic band gap is narrower as the dopant atom is moved to the center of ZGNR. Also, the Q0D and the Q1D behaviors have been observed in the DOS results [25,26].

The electronic band structure of Hg doped ZGNRs are shown in Fig. 7(a). As it is seen in Hg doped ZGNRs, the investigated structures for different doping sites exhibit semiconductor behavior except for Z4 site which shows the metallic behavior. In Fig. 7(b), DOS results clearly show that similar to the ZGNR with Cd, as dopant atom placed near to the center of the structure, the band gap of the structures is getting smaller.

Fig. 4. a) Band structures and b) DOS of AGNRs doped with Hg for different doping sites, i) A1, ii) A2, iii) A3, iv) A4 are given.

Substitutional doping with Zn, Cd and Hg dopant atoms have generated additional bands in the electronic band structure of the AGNRs and ZGNRs. Depending on the doping sites and type of the dopant atom, differences in the total energy values have been obtained. The total energies per C atom and the energy band gap values of each investigated structure doped with group IIB atoms have been given in Table 1, Table 2 and Table 3. The bare AGNR and bare ZGNR for total energy per C atom were calculated as -125.26 eV and -125.08 eV, respectively.

The ZGNRs doped with Zn atom reach the lowest total energies and

Fig. 5. a) Band structures and b) DOS of ZGNRs doped with Zn atom for different doping sites, i) Z1, ii) Z2, iii) Z3, iv) Z4.

more stable than other structures doped with Cd and Hg atoms. Generally, the total energies of doped ZGNRs are energetically more favorable than AGNRs. For GNRs doped with Zn, the structures with dopant near to the center of the ribbon are energetically more favorable than the structures with dopant near to the edge of the ribbon. However, for Cd and Hg doped structures an opposite behavior is calculated. For Cd and Hg doped structures with dopant near to the edge of the ribbon are energetically more favorable than structures with dopant near to the center of the ribbon.

Fig. 6. a) Band structures and b) DOS of ZGNRs doped with Cd atom for different doping sites, i) Z1, ii) Z2, iii) Z3, iv) Z4.

4. Conclusion

The effect of dopant atoms on the electronic properties of GNRs has been studied by first-principles calculations using DFT. The AGNRs and ZGNRs with the substitutional dopant atoms provide a large scale of electronic properties based on different doping positions for the same ribbon width. Most of the investigated structures show magnetic properties with different doping sites except Hg atom. For Hg doped structures, the doping sites near the center of the ribbon do not produce spin dependent behavior. The electronic band structure for all of ZGNR

Fig. 7. a) Band structures and b) DOS of ZGNRs doped with Hg atom for different doping sites, i) Z1, ii) Z2, iii) Z3, iv) Z4.

reveals spin-dependent metallic behavior. Among the structures with different dopant atoms, the Zn doped GNRs is more stable than other structures. In the DOS calculations of many investigated cases, Q0D and Q1D type density behaviors have been found. Some of these behaviors of states which are near or at the Fermi level which directly affect the electronic behavior of the investigated structure. These results present the significance of changing the electronic properties of GNRs by controlling the placement of doping.

Table 1

Total energies per C atom and energy band gap of AGNR and ZGNR structures doped with Zn atom for $N_{a,z} = 8$. Structures without any band gap value shows metallic behavior.

Site	Total energy per C atom (eV)	Spin up		Spin down	
		Eg (eV)	Direct	Eg (eV)	Direct
A1	−213.49	–	–	–	–
A2	−213.48	–	–	–	–
A3	−213.50	–	–	0.08	No
A4	−213.51	–	–	–	–
Z1	−229.69	–	–	–	–
Z2	−229.50	0.21	No	0.50	No
Z3	−229.76	0.96	No	0.70	Yes
Z4	−229.53	–	–	–	–

Table 2

Total energies per C atom and energy band gap of AGNR and ZGNR structures doped with Cd atom for $N_{a,z} = 8$. Structures without any band gap value shows metallic behavior.

Site	Total energy per C atom (eV)	Spin up		Spin down	
		Eg (eV)	Direct	Eg (eV)	Direct
A1	−193.65	0.36	Yes	0.26	Yes
A2	−193.63	0.14	Yes	0.30	Yes
A3	−193.53	0.06	Yes	0.19	Yes
A4	−193.52	0.46	Yes	0.25	Yes
Z1	−205.83	0.48	Yes	0.43	No
Z2	−205.80	0.13	No	0.30	Yes
Z3	−205.72	0.11	No	0.37	Yes
Z4	−205.71	–	–	–	–

Table 3

Total energies per C atom and energy band gap of AGNR and ZGNR structures doped with Hg atom for $N_{a,z} = 8$. Structures without any band gap value shows metallic behavior.

Site	Total energy per C atom (eV)	Spin up		Spin down	
		Eg (eV)	Direct	Eg (eV)	Direct
A1	−193.48	0.59	Yes	0.69	Yes
A2	−193.37	0.24	No	0.38	Yes
A3	−193.39	0.23	No	0.23	No
A4	−193.17	0.43	Yes	0.43	Yes
Z1	−205.75	0.50	Yes	0.41	No
Z2	−205.72	0.18	No	0.21	Yes
Z3	−205.52	0.46	No	0.23	Yes
Z4	−205.35	–	–	–	–

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