Magnetic Properties of Mn Doped Armchair Graphene Nanoribbon

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Magnetic Properties of Mn Doped Armchair Graphene Nanoribbon

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We investigate the electronic structure and magnetism of an armchair graphene ribbon doped with Mn by first-principles density functional calculations. Mn atoms are doped at the edge of the ribbon, with different densities. The local magnetic moment due to Mn atom is 5 $\mu_B$/Mn for dilute doping and 4.5 $\mu_B$/Mn for heavy doping. The structures of Mn doped at both edge of graphene ribbon were optimized in ferromagnetic and antiferromagnetic states to find the stable magnetic states of the two opposite ferromagnetic edges. Our calculations show that the ground state is ferromagnetic for heavy doping and does not have a preferable configuration for dilute doping because of the small energy difference. These structures have application in nanoelectronics and spintronics. [doi:10.2320/matertrans.MB200815]

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Keywords: graphene nanoribbon, doping, magnetization

1. Introduction

As another 1D structure of carbon, besides carbon nanotube,1,2 graphene nanoribbon3,4 is of great interest, both theoretically and experimentally.5–9 Nanoribbon is a stripe of a graphene sheet, like an unrolled nanotube. The electronic structure of the ribbon is therefore similar to nanotube and depends on its geometry, but it is also affected by the open boundaries at the edge.10–12 The edges of the ribbons are usually saturated with hydrogen atoms at the experimental fabricated samples. These structures are outstanding subjects for theoretical studies from magnetic point of view as well as the nanosize effect due to their narrow width which provides a 1D structure.13 These objects can be interesting from experimental point of view as well, as candidates for several applications such as nanoelectronics, and spintronics. The unsaturated edges can be functionalized and are suitable for chemical reaction. Therefore, doping of graphene ribbon is a suitable way to provide new material designs with interesting properties applicable in nanoelectronics and spintronics. Properties of doped armchair ribbons with various atoms from s-type elements to 3d transition metals (TM) have been calculated computationally.13 Theoretical calculations on doped graphene and bilayer graphene with TM and Mn have been also reported.14,15 In this work we investigate the magnetization and electronic structure of Mn doped armchair ribbon $N = 8$ with various doping densities by first-principles density functional calculations. The effect of doping on the edge of the nanoribbon and the stability of the doped structures will be discussed.

2. Computational Method

An armchair graphene ribbon $N = 8$ is considered with 2 unit cells in a periodic box, so that it is infinite in the one dimension. The dimensions of the cell are taken to be such that there is 10 Å vacuum space between the neighboring cells. Figure 1 depicts the structure inside the simulation box. The edge of the structure shown in this figure is doped with Mn by the following densities: (1) 1 Mn atom at 1 edge, (2) 2 Mn atoms, 1 at each edge, (3) 4 Mn atoms, 2 at each edge of the ribbon. The structures are optimized using a spin-polarized first-principles pseudopotential plane-wave approach, based on the density functional method and ultrasoft pseudopotentials using VASP software16,17 and generalized gradient approximation for the exchange-correlation energy.18 The cutoff energy for the plane wave expansion is taken 400 eV in all the cases. The Brillouin zone was sampled with $1 \times 1 \times 8$ k-points for optimization of the structures and $1 \times 1 \times 260$ k-points for calculation of density of states (DOS). The relaxation of the structures is continued until the force on each atom is less than 0.001 eV/Å.

3. Results and Discussions

Doped structures of ribbon with different doping densities were optimized. The optimized structures are depicted in Fig. 2. The C-C bond length at the edge of the pure ribbon in its optimized structure is 1.26 Å. After doping of the ribbon with 1 Mn atom at the edge (Fig. 2(b)), the C-C bond length near the doped site increases to 1.32 Å. This bond length increases to 1.37 Å by increasing the doping density to 2 atom at edge (Fig. 2(c)). In the undoped pure ribbon, the dangling bonds at the edge overlap and make a triplet bond, while in the Mn doped structure, these dangling bonds are saturated by $d$ orbitals of Mn atom and the C-C bonds of edge change to double bond. The binding energy of the Mn atom with the ribbon is shown in Table 1. In this table the binning energy is obtained from eq. (1),

$$ E_B = \frac{(E_{\text{Ribbon}}) + nE_{(\text{Mn})} - E_{(\text{Ribbon}+\text{Mn})}}{n} $$

(1)

where $E_{(\text{Ribbon})}$ is the total energy of the optimized pure
ribbon, \( n \) is the number of Mn atoms in the supercell, \( E_{\text{Mn}} \) is the total energy of the a free Mn atom, and \( E_{\text{Ribbon+Mn}} \) is the total energy of the optimized structure of the doped ribbon. The binding energies are more than 3 eV, indicating that there is chemical bonding between Mn atoms and the ribbon. Therefore, once the Mn atom reaches the edge of the ribbon it attaches to the edge and makes a chemical bonding with it. The binding energy is bigger for the structure with heavy doping (structure of Fig. 2(c)) because of the interaction of the adjacent Mn atoms at the edge, which lowers the total energy.

The magnetic moment of the doped ribbons is reported in Table 1. The magnetic moment is \( \frac{5}{2} \mu_B \) for structures of Fig. 2(a) and (b), and \( \frac{7}{2} \mu_B \) for Fig. 2(c). The magnetic moments are local at Mn atoms, as can be noticed from the spin density sketched in Fig. 3 for the heavy doped ribbon (structure of Fig. 2(c)). According to the figure, the high spin densities are localized at Mn atoms, and the C atoms of the ribbon carry no spin. In this case the Mn atoms at each edge interact with each other and the magnetic moment decreases to \( \frac{4.5}{2} \mu_B \) compared to that of light doping with \( \frac{5}{2} \mu_B \), while the total energy increases according to Table 1, because of the overlap of \( d \) orbitals of the Mn atoms.

The interaction of Mn with C atoms of the ribbon happens through hybridization of \( d \) orbitals of Mn with \( p \) orbitals of C. In Fig. 4 we show the local density of states (LDOS) of the Mn atom and ribbon separately for the dilute doped structure of Fig. 2(a). Figure 4(a) shows the LDOS of the ribbon, and the contribution of \( s \) and \( p \) orbitals of C in the LDOS of the ribbon, while in Fig. 4(b) we show the LDOS of Mn and the contribution of \( s, p \) and \( d \) orbitals of Mn in the LDOS. The positive DOS is sketched for spin up and the negative values are for spin down electrons. According to Fig. 4(a) the \( s \) orbitals of C do not have contribution in the DOS at the binding area, the contribution in DOS is from the \( p \) orbitals. Figure 4(b) in the same way shows the big contribution of the \( d \) orbitals of Mn atom in the binding area of DOS.

The Mn atoms at the edges of the heavy doped structure are in ferromagnetic state. The coupling of the Mn atoms at the two opposite edges (Fig. 2(b) and (c)) can be ferromagnetic (FM) or antiferromagnetic (AF). These structures are optimized in FM and AF cases to find the stable magnetic state. The difference in the total energies in FM and AF cases are shown in Table 1. The state of magnetization of the Mn atoms of the edge when there is 1 Mn atom at each edge is not preferable for none of FM and AF states. Although the AF state is energetically favorable, but the

![Fig. 2](image1.png)

Fig. 2 Structures of doped armchair ribbon with different doping densities: (a) 1 Mn atom at 1 edge, (b) 2 Mn atoms, 1 at each edge, (c) 4 Mn atoms, 2 at each edge.

<table>
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<th>Structure</th>
<th>( E_B ) (eV/Mn)</th>
<th>( \Delta E = E_{\text{FM}} - E_{\text{AF}} ) (meV)</th>
<th>( \mu_{\text{Mn}} ) at FM state (( \mu_B ))</th>
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<tr>
<td>1 Mn at 1 edge</td>
<td>3.21</td>
<td>—</td>
<td>5</td>
</tr>
<tr>
<td>1 Mn at each edge</td>
<td>3.17</td>
<td>-7</td>
<td>5</td>
</tr>
<tr>
<td>2 Mn at each edge</td>
<td>3.67</td>
<td>36</td>
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![Fig. 3](image2.png)

Fig. 3 Spin density of Mn doped ribbon (structure of Fig. 2(c)). “Low” means zero spin density and “High” means highest spin density.

![Fig. 4](image3.png)

Fig. 4 Local density of states (LDOS) of Mn doped ribbon with 1 Mn atom at 1 edge (Fig. 2(a)). (a) LDOS of the ribbon, (b) LDOS of Mn atom. The positive DOS is for spin up and the negative values are for spin down electrons.
difference in the energies is so small (7 meV). In case of heavy doping with 2 Mn atoms at each edge, the favorable state is FM. The energy difference between FM and AF states is large enough (36 meV) to consider the FM state stable at room temperature.

Effect on Mn doping on the electronic structure of ribbon is also interesting to consider. The pure ribbon $N = 8$ is a semiconductor with energy gap 0.45 eV. When doped with 1 Mn atom (Fig. 2(a)), the gap decreases to 0.36 eV. Doping with 2 Mn atoms, with 1 Mn at each edge, reduces the gap to 0.33 eV in its AF state. The energy gap in the FM state is different for spin up and spin down channels. It is 0.57 eV for spin up channel and 0.26 eV for spin down channel. Figure 5 shows the DOS for this case. According to the figure, there are energies below Fermi energy that the spin up channels have (i.e. have nonzero DOS) but spin down channels do not (i.e. have zero DOS). On the other hand, in energies between 0.2–0.5 eV spin up channels do not have state while spin down channels have. This property can lead to spin selective conduction by choosing a suitable bias voltage. When the ribbon is doped with 2 Mn atoms at each edge, the structure becomes metallic, and it has conducting channels for both spin up and spin down carriers. This structure is stable in FM state, with reasonable energy difference from AF state, so that it can stay in FM state at room temperature.

4. Conclusion

Using the results obtained from first-principles calculations, we have discussed the effect of doping an armchair nanoribbon with Mn atom with different densities. Our calculations reveal that the semiconductor ribbon becomes metallic by heavy doping of its edge with Mn. The magnetic moment in this structure is pretty high, equal to 4.5 $\mu_B$/Mn, and the structure is ferromagnetic. Doping with lower densities of Mn reduces the energy gap of the ribbon, and still provides a large magnetization. By doping with 1 atom at each edge of the ribbon, the structure can have spin selective conduction depending on the external bias. This system does not have any preference between ferromagnetic and antiferromagnetic states. These structures are suitable for spintronic and nanomagnetism applications.

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REFERENCES