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The stability and electronic structure of Fe atoms embedded in zigzag graphene nanoribbons

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ARTICLE INFO

Article history:

Received 19 December 2013

Accepted 29 January 2014

Available online 5 February 2014

Keywords:

Stability

Energy

Electronic structure

Embed in

Zigzag graphene nanoribbons

ABSTRACT

The stability and electronic properties of the Fe atoms embedded in divacancy defects in graphene nanoribbons (GNR) with zigzag-shaped edges have been studied by first-principles calculations. When Fe is positioned in the middle of the ribbon, it has little effect on the edge C atoms, which reserves the flat edges of graphene nanoribbons. On the other hand, when Fe atom is near the edge, structural distortion takes place resulting in tilted-edge structure with low energies. This indicates that the Fe atoms prefer to occupy divacancy sites near the edges. This is also in consistent with the analyses of electronic structures. Meanwhile, our results reveal that embedding Fe atom in the graphene nanoribbons is an effective method to make the GNR possessing metallic properties.

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1. Introduction

Graphene, a member of the class of two-dimensional (2D) materials discovered by Professor Andre Geim's research group at the University of Manchester [1]. It possesses a high aspect ratio, excellent thermal stability, mechanical and physical properties [2–7], and is expected to be widely used in future nanoelectronics. It consists of a hexagonal array of sp^2 -bonded carbon atoms, just like those found in bulk graphite. 2D materials display very interesting properties, and are fundamentally different from the 3D materials we encounter everyday. The discovery of 2D materials means that scientists now have access to materials of all dimensionalities, including 0D (quantum dots, atoms) and 1D (nanowires, carbon nanotubes).

Graphene nanoribbons (GNRs), formed by cutting graphene along the specific direction, especially with zigzag-shaped edges, have attracted much attention because of the spin polarization localized at the edges [8,9]. The electrons at the edges are spin-polarized and aligned ferromagnetically along each edge but antiferromagnetically across the other edge. Scientists have put forward a lot of proposals for spintronics applications, on account of the spin control of the edge states by using a transverse electric field [8,10], a magnetic field [11,12], and roughness at the edges

[13]. Many methods have been taken steps to altering the transport properties of GNRs by introducing vacancies [13,14], non-magnetic impurities [15,16], or by chemical functionalization of the edges [14,17].

As we all know, doping nonmagnetic materials with transition metal (TM) atoms is an efficient way to induce magnetism [18]. According to this theory, TM atoms can be either adsorbed as interstitial impurities [19–24] or substitutionally embedded in vacancies of graphene and GNRs [25–28]. At room temperature, TM atoms adsorbed on graphene should be inclined to form metal clusters [29–31]. In fact, TM atoms embedded in vacancies are very stable, with large binding energies [25,28], and incorporation of TM atoms in vacancies has been realized experimentally [31,32]. When TM atoms are in divacancies, the binding energies are slightly reduced.

The edges play an important role for the stability and electronic properties in GNRs which are doped with TM atoms [33]. On the basis of theoretical and experimental studies, adsorbed TM atoms tend to migrate toward the edges [20–24,34]. However, for TM atoms embedded in divacancy defects, the effects of edges on the stability and the electronic properties have not been reported yet.

In this paper, the stability and electronic properties of the Fe atoms embedded in divacancy defects in graphene nanoribbons with zigzag-shaped edges have been proposed and studied by first-principles calculations. We examine the effects of edges on the stability. It indicate that the Fe atoms prefer to occupy divacancy sites near the edges. The analyses of electronic properties can lead to

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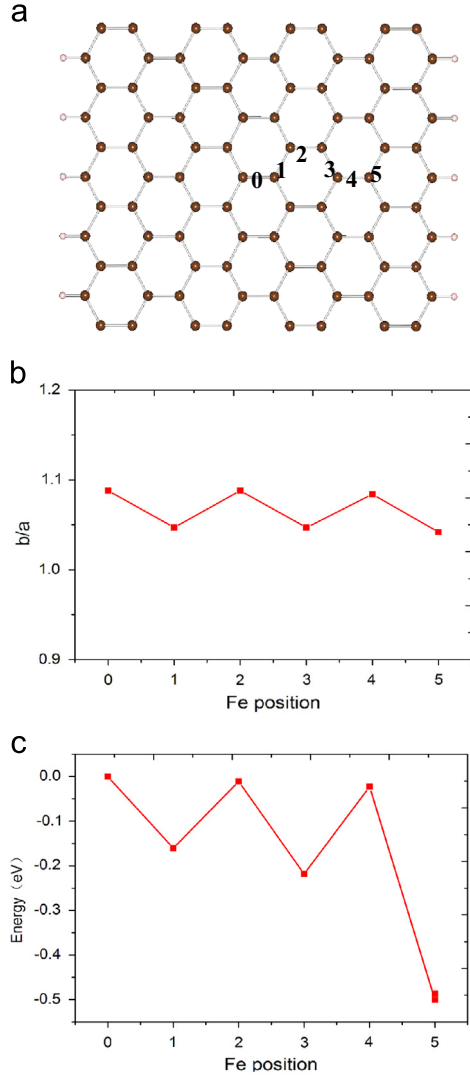


Fig. 1. (a) The structures of a pristine GNR with zigzag-shaped edges, 0, 1, 2, 3, 4 and 5 is the position of Fe atom. (b) The b/a values of the C_4 pore for different positions of Fe, where a and b are perpendicular and parallel to the missing C dimer, respectively. (c) The relative energies of ground state for different position of Fe atom.

identical result. Furthermore, Fe atom embedded in graphene nanoribbons can change GNRs from a semiconductor to a metal.

2. Model and method

Our calculations are performed within first-principles DFT under the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) [35], including spin polarization. The Vienna Ab-initio Simulation Package (VASP) is used to perform all calculations [36–38]. Ion cores are modeled with projector augmented wave (PAW) potentials [39,40]. A plane-wave basis set with a maximum plane-wave energy of 500 eV is used for the valence electron wave functions. All parameters in the calculation are chosen to converge the total energy to 0.01 eV. In zigzag GNRs, the ribbon width is determined by the number of zigzag chains (m) across the ribbon. To examine the stability of a single Fe atom, we employed a $m \times n$ planar supercell ($m=8$ and $n=6$), where n is the number of the primitive cells along the ribbon axis of pristine GNR. Here pristine GNRs are defined as those which have edge dangling bonds passivated with a single hydrogen per edge C

Table 1

The energies of the Fe-DV complex are compared for various spin configurations of the Fe atom at different positions (n) in Fig. 1(a). Here δE denotes the energies of different spin configurations with respect to the lowest energy of each Fe position, and ΔE represents the energies relative to the $\uparrow\uparrow\uparrow$ configuration for the Fe atom at site 0. The tilted-edge structure is only formed when Fe is positioned at site 5.

Fe position	Configuration	Energy(eV)	δE (meV)	ΔE (meV)
0	$\downarrow\downarrow$	-444.497656	24	24
0	$\uparrow\uparrow\uparrow$	-444.521784	0	0
0	$\downarrow\uparrow$	-444.500357	21	21
1	$\downarrow\downarrow$	-444.682044	0	-160
1	$\uparrow\uparrow\uparrow$	-444.681335	1	-159
1	$\downarrow\uparrow$	-444.677376	5	-155
1	$\uparrow\downarrow$	-444.681611	1	-159
2	$\downarrow\downarrow$	-444.367998	164	153
2	$\uparrow\uparrow\uparrow$	-444.532717	0	-11
2	$\downarrow\uparrow$	-444.512208	21	9
2	$\uparrow\downarrow$	-444.440677	92	81
3	$\downarrow\downarrow$	-444.739871	1	-217
3	$\uparrow\uparrow\uparrow$	-444.739884	1	-217
3	$\downarrow\uparrow$	-444.733387	8	-210
3	$\uparrow\downarrow$	-444.740169	0	-218
4	$\downarrow\downarrow$	-444.535302	9	-14
4	$\uparrow\uparrow\uparrow$	-444.540424	4	-19
4	$\downarrow\uparrow$	-444.528784	16	-7
4	$\uparrow\downarrow$	-444.544689	0	-23
5	$\downarrow\downarrow$	-445.008691	0	-486.9
5	$\uparrow\uparrow\uparrow$	-445.008475	0.2	-486.7
5	$\downarrow\uparrow$	-445.008041	0.7	-486.2
5	$\uparrow\downarrow$	-445.008475	0.2	-486.7
5 (Tilted edge)	$\downarrow\downarrow$	-445.022410	0	-500.6
5 (Tilted edge)	$\uparrow\uparrow\uparrow$	-445.020186	2	-498.6
5 (Tilted edge)	$\downarrow\uparrow$	-445.020208	2	-498.6
5 (Tilted edge)	$\uparrow\downarrow$	-445.022391	0.1	-498.5

atom, as shown in Fig. 1(a). We tested a larger 8×10 supercell and confirmed that the 8×6 supercell is sufficiently large to achieve the numerical convergence of relative energies. A vacuum region of 15 Å was applied along the z direction to avoid interaction between images.

3. Results and discussion

3.1. Stability

In graphene and GNRs, TM atoms can be either adsorbed as interstitial impurities on the sheet [19–24] or substitutionally embedded in vacancies [25–28]. Likewise in GNRs, the large binding energy is 7.03 eV for the Fe atom in the 8×6 supercell, when it is embedded in the divacancy (DV) labeled as 0 in Fig. 1(a). Because of the more effective reconstruction of the dangling bonds around the divacancy, the binding energy of the Fe-DV complex decreases to 5.51 eV in the large 8×10 supercell. The binding energy far outweighs the adsorption energy 0.66 eV ($E_{\text{adsorption}} = E_{\text{GNRS}} + E_{\text{single Fe}} - E_{\text{tot}}$) [41] and the cohesive energy (4.29 eV) of bulk Fe, so the structure that we design is fairly stable. The height between Fe and the ribbon sheet is 0.58 Å.

3.2. Energy

In this paper, we define the spin configuration of the Fe atom and the edges as xYz , where x and z ($=\uparrow$ for spin-up and \downarrow for spin-down) denote the spin states of the left and right edges, respectively, and Y ($=\uparrow$ for spin-up and \downarrow for spin-down) is the spin state of the Fe atom between the edges. For the spin-up state of the Fe atom, there are four possible spin configurations, $\uparrow\uparrow\uparrow$, $\downarrow\uparrow\downarrow$, $\downarrow\uparrow\uparrow$, $\uparrow\downarrow\downarrow$. The energies of these spin configurations are compared in Table 1.

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