Carbon 127 (2018) 57–63

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Room-temperature ferromagnetism from an array of asymmetric zigzag-edge nanoribbons in a graphene junction

Hosik Lee [a], Hyun-Jung Lee [b], Sung Youb Kim [a, *]

[a] School of Mechanical, Aerospace and Nuclear Engineering, Ulsan National Institute of Science and Technology (UNIST), Ulsan, 44919, South Korea
[b] Department of Physics, Pohang University of Science and Technology(POSTECH), 77 Cheongam-Ro, Namgu, Pohang, 37673, South Korea

ARTICLE INFO

Article history:
Received 12 July 2017
Received in revised form
18 October 2017
Accepted 25 October 2017
Available online 27 October 2017

ABSTRACT

Room-temperature ferromagnetism in graphene layers with defects has been experimentally measured. Despite disagreement around the intrinsic origin of carbon magnetism, experimental evidence has supported the existence of paramagnetism or ferromagnetism in carbon materials. Convincing theoretical explanations, however, have not yet been proposed. In this work, density functional theory calculations were used to suggest a plausible explanation for this phenomenon as it is observed at the zigzag grain boundaries of a mismatched single-double-single-layer graphene junction. We identified asymmetric zigzag-edge graphene nanoribbons that display ferromagnetic properties in a graphene junction structure. Two ferromagnetic asymmetric zigzag graphene nanoribbons displayed antiferromagnetic coupling in a defect-free structure at the grain boundary. The introduction of a vacancy or N-substitutional defect was found to destroy the magnetism on one side only; the nanoribbon on the other side continued to display a large ferromagnetic exchange coupling. The ferromagnetic nanoribbon in the junction was ferromagnetically correlated with other nanoribbons in the two-dimensional junction array, yielding a Curie temperature well-above room temperature. Moreover, the ferromagnetic correlation was observed regardless of the arrangement of the magnetic layers, enabling ferromagnetic ordering within the graphene junction array.

1. Introduction

Carbon-based magnetism in materials such as graphene and graphite has been intensively investigated over recent decades [1–19]. Ferromagnetism and a large background diamagnetic signal has been observed in graphite nodules [3], highly oriented pyrolytic graphite [4], proton-irradiated graphite [5], graphite grain boundaries [6], reduced graphene oxide [7], and hydrogenated epitaxial graphene [19]. Skeptics who question the existence of carbon ferromagnetism have suggested that the measurements originate from magnetic impurities; however, intrinsic carbon ferromagnetism has been supported by numerous experimental studies [1,3–7,17–19]. Nevertheless, controversy surrounding this issue has persisted.

Theoretical models of ferromagnetism have been proposed based on vacancy or vacancy–hydrogen complexes [8], a negatively curved graphitic surface containing seven- or eight-membered rings [9], localized edge states at zigzag edges [10–13], or graphene nanoribbons with asymmetric zigzag edges such that the edge carbon atoms on one side are passivated by one hydrogen atom and those on the other side are terminated by two hydrogen atoms along the edges [13,14]. An effective explanation of carbon ferromagnetism would require identification of a two- or three-dimensional carbon network structure with electron spin-polarization as well as strong ferromagnetic coupling among the magnetic moments. In view of these two requirements, vacancy or vacancy–hydrogen complexes in graphene or negatively curved graphitic surfaces would not be expected to display long-range ferromagnetic coupling among the magnetic moments. According to the Lieb theorem [15], the Hubbard model Hamiltonian, and density functional theory (DFT) calculations [10,13], the localized edge states at a zigzag graphene nanoribbon should display long-range ferromagnetic ordering along the edge and antiferromagnetic coupling between the two edges. A graphene nanoribbon with asymmetric zigzag edge passivation, on the other hand, would be expected to exhibit ferromagnetic coupling both along and between the edges, as predicted previously using the

* Corresponding author.
E-mail address: sykim@unist.ac.kr (S.Y. Kim).

https://doi.org/10.1016/j.carbon.2017.10.082
0008-6223/

Hubbard model Hamiltonian and DFT calculations [13,14]. Graphene nanoribbons with asymmetric zigzag edge passivation form the only carbon network structure with ferromagnetic coupling, to the best of our knowledge; however, experimental magnetism measurements have remained elusive because the realization of an asymmetric zigzag-edge termination configuration poses a considerable challenge in practice. The ferromagnetic ordering in a graphene nanoribbon with asymmetric termination could potentially be disturbed by edge modifications, such as z_{211}, in which one out of three edge atoms is passivated by two hydrogen atoms and the other two by one hydrogen atom [16]. Aside from the practical issues around preparation, a graphene nanoribbon with asymmetric zigzag edge passivation is a quasi-one-dimensional structure in which the spins are localized only along the zigzag edges. This type of quasi-one dimensional structure is not thought to display ferromagnetism at finite temperatures, and at least a two-dimensional structure is needed for ferromagnetism at finite temperatures. Despite the difficulties associated with a quasi-one-dimensional structure, graphene nanoribbons with asymmetric zigzag edge termination represent one of the strongest candidate configurations that may be useful for studying the origin of carbon ferromagnetism. Ferromagnetic coupling in this structure has only been shown to be theoretically predicted.

Recent experiments [5,6,17–19] suggested an important hypothesis: ferromagnetism may only be observable in multi-layer graphene layers with defects, and paramagnetism is observed in single-layer graphene. Room temperature ferromagnetism has been measured at the grain boundaries of multi-layer graphene [6] and proton-irradiated graphite [5], but only low-temperature paramagnetism has been observed in single-layer graphene [17,18]. These results suggest that ferromagnetism originates from defect structures only in multi-layer graphene, for example, with a mismatched grain boundary. In this study, we performed DFT calculations of the zigzag grain boundary in a mismatched single-double-single-layer graphene junction (hereafter referred to as a graphene junction) to explain room-temperature carbon ferromagnetism. Surprisingly, curved ferromagnetic graphene nanoribbons with asymmetric zigzag edge termination were identified in the graphene junction. The double graphene layers in the middle region consisted of an upper and lower graphene nanoribbon with an asymmetric zigzag grain junction. The magnetic correlation between the upper and lower graphene nanoribbons was antiferromagnetic, but a single vacancy defect at the grain boundary destroyed the magnetic moments of the upper (lower) graphene nanoribbon without altering the ferromagnetism of the lower (upper) graphene nanoribbon in the junction structure. We also found that the magnetic coupling between the two junctions became ferromagnetic, and the two-dimensional array of graphene junctions exhibited long-range ferromagnetic order. B or N defects present in the vacancy exhibited similar effects. It should be noted that an asymmetric graphene nanoribbon formed in the junction structure, thereby resolving the challenges around practical realization. The spatial fluctuations that worked against the long-range magnetic order in the quasi-one-dimensional system were overcome due to the inter-junction coupling in the two-dimensional array of the graphene junction structure. The inter-junction coupling was found to be ferromagnetic, regardless of whether the upper (lower) layer magnetic moments in the graphene junction were coupled with the upper (upper) layer magnetic moments in the nearby graphene junction or with the lower (upper) layer, thereby enhancing the possibility of magnetic array formation.

2. Computational details

We performed *ab initio* density functional theory calculations of mismatched single-double-single-layer graphene junctions. The structural optimization and calculation of the electronic and magnetic properties were carried out using the plane-wave package, Quantum-Espresso [20]. The local density approximation exchange correlation functional theory was employed together with non-relativistic ultrasoft pseudopotentials [21]. The wave functions were expanded using plane waves with a kinetic energy cutoff of 30 Ry. Twelve k-points were uniformly selected in the edge direction for Brillouin zone integration. A supercell geometry was used, in which each plane was separated from its replica by 10 Å in both the edge-to-edge and layer-to-layer directions. The double structure was designed with a capacity for vacancies by considering 140 atoms in the calculations.

3. Results and discussion

To investigate the mismatched magnetic geometry in the multi-layer graphene layers, we construct mismatched single-double-single graphene layers, as shown in Fig. 1 (a). The grain boundaries between the layers were designed to have a zigzag configuration and were expected to contain magnetic moments. Each graphene layer consisted of six zigzag chains of carbon atoms. Initially, the solid lines in Fig. 1 (a) indicated unit cell boundaries. The single graphene layers on the right and left sides were positioned at the vertical middle of the central double graphene layer. The unpassivated edge atoms of the single layers were shifted vertically to form bonds with the central double graphene layer. The opposing zigzag edge carbon atoms in the single graphene layers were passivated using single hydrogen atoms, represented by small (blue) circles. After geometric optimization, the central flat double graphene layer took on the shape of a carbon nanotube with sp^3 bonding at the grain boundaries. We found magnetic moments both in the central carbon nanotube regions and at the zigzag edges of the single layer graphene. Finite size effect were reduced by increasing the size of the single-layer graphene structures from six to ten zigzag chains measuring ~2 nm long, as shown in Fig. 1 (b), which plots the spin densities of the ferromagnetic and antiferromagnetic states of the central region. The mismatched single-double-single graphene junction assumed an antiferromagnetic ground state with an exchange energy gain of 39 meV per unit cell. The calculated results suggested that room-temperature ferromagnetism in the carbon material was not attributed to the mismatched structure itself.

In an effort to explain the room-temperature ferromagnetism, we introduced vacancy defects in the graphene junction, as indicated by green dashed circles in Fig. 2 (a). A vacancy was created in the upper layer of the central region of each unit cell, and all atoms were relaxed. Surprisingly, the spin polarizations in the upper layer in which the vacancies were located nearly disappeared, as shown in Fig. 2 (b). This effect was accompanied by the disappearance of anti-ferromagnetic coupling between the spins in the upper and lower layers, leaving only ferromagnetic correlations observed in the lower layer. The magnitude of the spin polarization was maximized at the left and right ends of the lower layer, as indicated by the green dashed circles in Fig. 2. The ferromagnetic and antiferromagnetic coupling between the largest spin moments of 0.25 μ_B were considered, and the ferromagnetic state was found to be energetically favored by 5.4 meV per unit cell. Because the unit cell was doubled to include vacancy defects, the magnetic exchange energy of each of the largest spin moments was 2.7 meV. The atomic sites with the largest spin moments, which were marked by green circles in Fig. 2 (c), could be mapped to a pseudo-one-dimensional Ising chain model, as shown in Fig. 2 (d). The magnetic coupling constants between the spin moments along the left and right boundaries were denoted J_2 and J_3, respectively. The weak