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Citation: Lee, Joo-Hyoung, and Jeffrey C. Grossman. "Magnetic properties in graphene-graphane superlattices." Applied Physics Letters 97, no. 13 (2010): 133102. © 2010 American Institute of Physics

As Published: http://dx.doi.org/10.1063/1.3495771

Publisher: American Institute of Physics (AIP)

Persistent URL: http://hdl.handle.net/1721.1/79651

Version: Final published version: final published article, as it appeared in a journal, conference proceedings, or other formally published context

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AIP Applied Physics Letters

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Citation: Appl. Phys. Lett. **97**, 133102 (2010); doi: 10.1063/1.3495771
View online: http://dx.doi.org/10.1063/1.3495771
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v97/i13
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Magnetic properties in graphene-graphane superlattices

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(Received 1 August 2010; accepted 9 September 2010; published online 28 September 2010)

The magnetic properties of graphene-graphane superlattices with zigzag interfaces and separately varying widths are investigated by first-principles density functional calculations. It is demonstrated that magnetic states are energetically more stable than nonmagnetic ones due to the Stoner-type instability, and that antiferromagnetic spin configuration across the graphene strip is found to be the ground state, whereas the ferromagnetic ordering becomes metastable. The magnetic moments in the ferromagnetic states show a monotonic increase and saturation with the width of the graphene strip, independent of the graphane width due to the π-character of the spin densities. These findings point toward an alternative route for graphene-based applications without requiring physical cutting as in graphene nanoribbons. © *2010 American Institute of Physics*. [doi:10.1063/1.3495771]

Since its separation from bulk graphite,[1] graphene, a one-atom thick allotrope of carbon, has received enormous attention both from the point of its fundamental physics[2] and due to its potential for future electronics applications.[3] In addition, there have been numerous attempts to control graphene's structural, chemical, and electrical properties, which is feasible due to the structural and electronic flexibility of graphene. Deposition of foreign atoms such as Ca,[4] 3*d* transition metals,[5] or molecules,[6] nanoengineering graphene by defect domains[7] and substrate-induced modification of the electronic structure[8] are a few examples along this direction. Parallel to these studies on two-dimensional (2D) systems, one-dimensional (1D) graphene-based structures such as graphene nanoribbons (GNRs) have generated excitement for applications in electronic circuits because the electronic structure of GNRs can be geometrically tuned as in carbon nanotubes.[9–11]

Recently, there has been an increasing interest in realizing graphene electronic circuits *without* physical cutting due to the nontrivial experimental challenge in controlling and manipulating the geometry of GNRs. This could be achieved by subjecting graphene to an external potential that possesses a superlattice periodicity.[12–15] In addition, Singh and Yakobson demonstrated from first-principles calculations[16] that GNRs can be realized in a 2D graphene layer through hydrogen adsorption. They showed that a narrow, isolated graphene strip in the hydrogenated layer (nanoroad) possesses essentially the same electronic properties as GNRs such as the variable band gap as a function of the strip width, or edge (interface in this case) magnetism. Also, Xiang *et al.* showed[17] that even narrower GNRs can be attained through hydrogen adsorption to nanoribbons. This is possible due to phase separation between graphene and graphane arising from hydrogenation. While these results present an alternative route toward realizing GNRs through chemical adsorption, they have thus far dealt with extreme cases such as infinitely separated nanorods[16] or narrowing the width of 1D GNRs.[17] In addition to such cases, it is desirable to explore the effect of the width of the hydrogenated strip on the electronic properties of a graphene layer, which will provide further understanding of the properties of graphene superlattices.

In this work, we employ first-principles calculations based on density functional theory (DFT) to explore the magnetic properties of graphene superlattices (GSLs), which are modeled with a repeated structure of pure and hydrogenated graphene (graphane) strips. By considering GSLs with zigzag-type interfaces between graphene and graphane regions (ZGSLs) and varying the widths of each strip separately, it is demonstrated that the magnetic states in ZGSLs are energetically more stable than nonmagnetic (NM) ones, and that the magnetic moments exist only in the graphene region due to the lack of π electrons in the graphane strip. Our calculations further show that magnetic properties of GSLs remain the same regardless of the graphane width, implying that even a singly hydrogenated carbon chain makes the graphene strip completely isolated. Taken together, these results point toward a different synthesis route in graphene electronics that could allow flexible patterning without physical cutting.

All first-principles calculations are performed within DFT as implemented in the Vienna *ab initio* simulation package (VASP),[18] using a 550 eV plane-wave cutoff, Vanderbilt-type ultrasoft pseudopotentials,[19] and the generalized gradient approximation of Perdew and Wang[20] for the exchange-correlation energy. GSLs are simulated with an artificial periodicity perpendicular to the graphene layer with 18 Å separation. To perform the Brillouin zone integration, Gaussian smearing is employed with a smearing parameter of 0.05 eV and 319 irreducible **k**-points are used to ensure convergence in the magnetic moments.

The ZGSLs investigated in the present work are composed of periodically alternating graphene-graphane strips as shown in Fig. 1. The size of system is represented by the number of pure (N_C) and hydrogenated (N_H) carbon chains in a unit cell. Here, we consider the case of dual hydrogenation, in which H atoms are attached on both sides of graphene. This geometry was shown to have the lowest energy of hydrogenated graphene structures[16] because (i) the second H-atom removes radicals that are generated after the adsorption of the first H-atom, and (ii) the strain, induced by the buckling when a C atom is passivated with an H-atom, is

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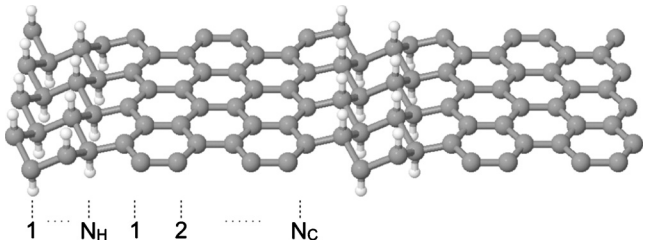

FIG. 1. Interface geometries of ZGSLs with $(N_H,N_C)=(2,4)$. C and H atoms are represented by gray and white spheres, respectively.

compensated if two carbon atoms are hydrogenated from the opposite side, which further lowers the energy.

For ZGSLs of the type shown in Fig. 1, we find two possible magnetic configurations by plotting the net spin density, $\zeta=\rho_\uparrow-\rho_\downarrow$ (Fig. 2), where $\rho_\uparrow$ ($\rho_\downarrow$) represents the density of spin-up (down) electrons. In Fig. 2(a), spin densities are ferromagnetically (FM) aligned at the two interfaces, whereas antiferromagnetic (AFM) ordering is realized in (b). As is clear from Fig. 2, ζ is well localized near the interfaces. Since nonzero ζ arises from partially-paired p_z orbitals at the interface, the hydrogenated region possesses essentially no net spin density. It should be noted that although ζ is plotted for $(N_H,N_C)=(3,5)$ in Fig. 2, ZGSLs with other (N_H,N_C) values show the same behavior in ζ.

Our calculated energy differences (ΔE) between NM and FM states show that FM states becomes more stable than NM ones for all (N_H,N_C) pairs. ΔE between FM and NM states ranges from 40 to 60 meV in general, and becomes as high as 127 meV. On the other hand, FM states are generally energetically less stable than AFM ones, and the relative stability between FM and AFM states can be understood by considering the spin densities on different sublattices. As is seen from Fig. 2(a), $\rho_\uparrow(\rho_\downarrow)$ is distributed on different sublattices near opposite interfaces within the graphene region for FM states. This requires the spin direction of a sublattice to be flipped in going from one interface to the other,[21] which leads to a finite energy cost. In contrast, AFM states possess $\rho_\uparrow$ and $\rho_\downarrow$ on different sublattices as shown in Fig. 2(b), and the spin direction in a sublattice is preserved throughout the graphene strip. Since, however, the spin density shows an exponential decay proportional to $[2\cos(k_y a_y/2)]^{2n}$, where k_y is the y-th component of a 2D wave vector $\mathbf{k}$ and a_y the lattice constant in the y-direction, respectively, at the n-th zigzag chain from the interface,[22] the required energy for the spin flip is expected to be small. Indeed, the ΔE between FM and AFM states is found to be less than 10 meV in general (the largest ΔE in our calculations is only 26 meV).

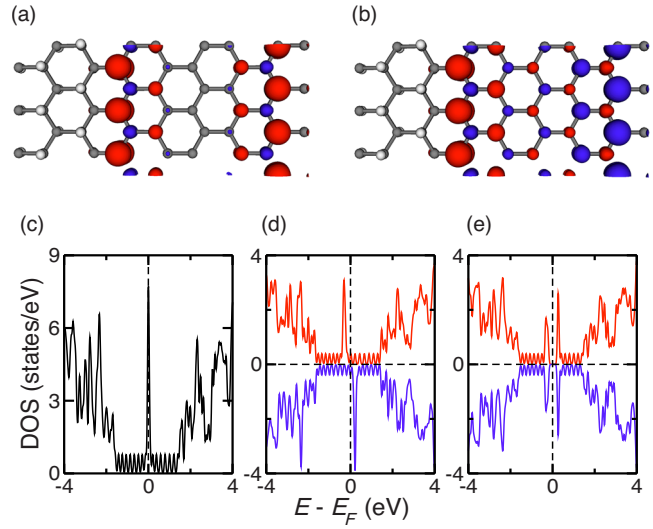

FIG. 2. (Color online) (a) Contour plot of the spin density of a ZGSL with $(N_H,N_C)=(3,5)$ for a FM state. Spins are in the same direction at the interfaces. (b) Same as in (a) but for an AFM state. Shown are the spin densities at $\pm 0.3\mu_B/\text{Å}^3$. Density of states with $(N_H,N_C)=(3,5)$ for (c) NM, (d) FM and (e) AFM states, respectively. In (d) and (e), positive and negative values correspond to spin-up and -down electrons, respectively.

In order to understand the origin of the appearance of magnetic states, we plot the density of states (DOS) of ZGSLs for the $(N_H,N_C)=(3,5)$ case in Figs. 2(c)–2(e). As is clear in Fig. 2(c), a sharp peak appears at the Fermi level in NM states, leading to a Stoner-type instability in the system. The instability is removed by either splitting the peak depending on the spin component as in FM states [Fig. 2(d)] or developing a nonzero gap which is manifested by AFM states [Fig. 2(e)]. As is seen from the figure, the DOS changes only around the Fermi level when the instability is removed, and other energy levels essentially remain the same.

In order to further examine the nature of FM states, in Fig. 3(a) we plot the unit cell magnetic moment (μ) of FM ZGSLs as a function of N_C values for different numbers of hydrogenated carbon chains. Note that due to the periodicity of the graphene superlattices, only $N_C=2p$, where p is an integer, is possible for even N_H values, whereas $N_C=2p+1$ when N_H assumes odd integers. For all N_H values, μ becomes zero when $N_C=1$ and 2 because the graphene strip is too narrow to support separate states that are localized at the interface. For odd numbers of hydrogenated carbon chains, μ becomes nonzero at $N_C=3$, where $\mu=0.35\mu_B$, whereas $\mu=0.42\mu_B$ is obtained with $N_C=4$ for $N_H=2p$. Moreover, μ tends to become saturated toward $2\mu_B/3$ for

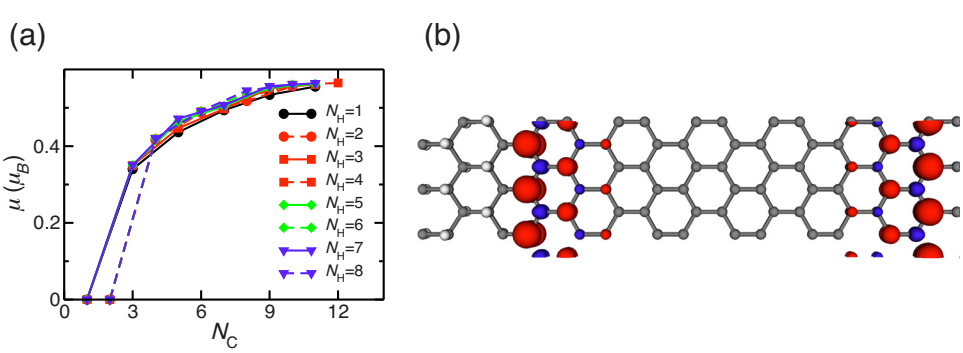

FIG. 3. (Color online) (a) Magnetic moments per unit cell (in units of μ_B) of ZGSLs as a function of N_C for different N_H values and (b) contour plot of ζ for $(N_H,N_C)=(3,11)$. Plotted is the contour at $\zeta=\pm 0.3\mu_B/\text{Å}$.

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sufficiently large N_C values due to partial pairing of the π electrons at the interfaces.[23] The increase in μ is found to be a combined effect of additional carbon chains as is clear by comparing Fig. 2(a) with Fig. 3(b), and enhanced magnetic moment within a chain. Surprisingly, the monotonic increase in μ as a function of N_C is independent of the width of the graphane strip, which implies that the interaction between the interface states across the graphane region is negligible. This is due to the large distance between C atoms at different interfaces, which prevents the interaction between the electrons on the C atoms, and lack of the π-bonding between graphene and graphane regions.

Noting a close resemblance in the magnetic properties to those of zigzag graphene nanoribbons,[9] our results show that GSLs hold the potential for graphene-based spintronics applications. However, GSLs could be more advantageous than GNRs from the standpoint of developing applications: while several processes such as lithographic,[24] chemical methods[25] and unzipping nanotubes[26] are proposed to synthesize GNRs, it is nontrivial to achieve atomic-scale control on the edge shape, and finely controlled wafer size patterns using GNRs are difficult to fabricate.

Recently, a monolayer of a 30-inch graphene sheet was successfully fabricated through chemical vapor deposition[27] and high-quality graphene of >300 nm in diameter was grown on commercially available cubic β-SiC/Si substrates,[28] which would be particularly useful for mass production of graphene-based devices. Moreover, as demonstrated with H-passivated Si surfaces[29] zigzag interfaces in GSLs can be realized in a precise manner by removing H atoms from graphane, which is now available.[30] With these advances, patterning "nanoribbons" into a large scale for practical applications would be more feasible using GSLs than GNRs, through chemical functionalization of selected graphene regions without degrading electronic properties.

In conclusion, in the present work we examined the magnetic properties of graphene-graphane superlattices with zigzag-interfaces from first-principles by separately varying the widths of graphene and graphane strips. It was shown that the magnetic properties of the superlattices are entirely determined by the graphene region due to the π-character of the spin density. These results help to generalize the results on the graphene nanoroads[16] and hydrogenated nanoribbons[17] by demonstrating that GNRs are completely separated by narrow graphane nanoribbons, even as narrow as a single chain, in 2D GSLs. Our findings thus suggest that a novel graphene nanostructure such as "dense GNR bundles" could become achievable more easily with GSLs than nanoribbons, with a potential for future spintronics applications with a variable spin-current density.

This work was supported by the National Science Foundation through the Network for Computational Nanotechnology under Grant No. EEC-0634750, and computations were performed at the National Energy Research Scientific Computing Center.

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