Band engineering and elastic properties of strained armchair graphene nanoribbons: semiconductor vs metallic characteristics

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An odd number of zigzag edges in armchair graphene nanoribbons and their mechanical properties (e.g., Young’s modulus, Poisson ratio and shear modulus) have potential interest for bandgap engineering in graphene based optoelectronic devices. In this paper, we consider armchair graphene nanoribbons passivated with hydrogen at the armchair edges and then apply the strain for tuning the bandgaps. Using density functional theory calculations, our study finds that the precise control of strain can allow tuning the bandgap from semiconductor to metallic and then again switching back to semiconductor. In addition, we also show that the strained graphene nanoribbon passivated with hydrogen molecules can have large out-of-plane deformations demonstrating the properties of relaxed shape graphene. We express the strain induced by hydrogen in terms of binding energy. Finally, we characterise the effect of strain on the mechanical properties that can be used for making straintronic devices based on graphene nanoribbons.

I. INTRODUCTION

The thinnest two dimensional (2D) materials, e.g., graphene, MoSe2 and other TMDs materials have potential interest for making next generation optoelectric, spintronic, straintronic devices that might have performance better than conventional silicon devices. For example, the measurement of charge mobility in the graphene CMOS devices is far better than the best silicon devices. Evidence from experimental measurements confirmed that 2D materials possess unique physical properties, e.g. half integer quantum Hall effect, non-zero Berry curvature and Zak’s phase, high mobility charge carriers. Although graphene as a material is exciting at the level of making optoelectronic devices, its bandgap opening is still one of the biggest challenge, e.g. graphene does not have any bandgaps at the Dirac point. However, by using several state-of-the-art techniques and possibility of considering different 2D materials, e.g. MoSe2, one can easily control the bandgaps. Also, a small bandgap opening in graphene is achieved by considering the effect of spin-orbit coupling, strain and magnetic field. One can also make optoelectronic devices from armchair graphene nanoribbons, which possess a large bandgap opening at the Γ-point. In these armchair graphene nanoribbon devices, bandgaps can be created in a desired fashion by precise control of the width of the nanoribbon.

Strain engineering in graphene is promising for straintronic and spintronic applications. Possible ways of creating strain in graphene is to modify the in-plane and out-of-plane deformations among the carbon atoms. For examples, in plane and out-of-plane deformations in graphene can lead to the formation of relaxed shape graphene. When graphene is relaxed due to precise edge engineering, the localized eigenstates, created due to strain engineering, can lead to several observed interesting phenomena such as conduction and valence band crossings, spin hot spots as well as measurements of decoherence time. Large in-plane and out-of-plane deformations can also be made by growing graphene on a flexible substrate, where not only the lattice mismatch between graphene and the substrate induces strain but also the flexible substrate can be bended for the purpose of inducing strain. Edge fictionalization of graphene nanoribbons by -H, -H2, -O, -Br can also lead to in-plane and out-of-plane deformations and can be used for engineering of graphene bandgaps.

The mechanical properties, e.g. the Poisson ratio, Young’s and shear moduli, of graphene have been characterized by using both experimental and theoretical techniques. The experimental value of Young’s modulus of bulk graphite is 0.02 TPa, but its value for stack of graphene sheets is 0.5 TPa, for a monolayer of graphene oxide is 0.15 TPa and for a freestanding monolayer graphene membrane is 0.1 TPa. In Ref. authors also reported that the intrinsic breaking strength of graphene is 10 GPa. Ab initio calculations of graphene find the value of Young’s modulus to be 1.11 TPa in Ref. and to be 1.24 TPa in Ref., where thickness of graphene is 0.34nm. By using the semiempirical nonorthogonal tight-binding (TB) method, the Young’s modulus of graphene is reported as 1.206 TPa. In summary, the values of Young’s modulus reported recently are in close agreement between experimental and theoretical studies within numerical errors. Hence, it is confirmed that the values of Young’s modulus are extremely large in comparison to other conventional semiconductor materials. Therefore, finding the value of graphene Young’s modulus in several different conditions is important for the applications in designing the devices for straintronic, spintronic and optoelectronic applications.

In this paper, we consider armchair graphene nanoribbons functioning their armchair edges by -H and -H2.
FIG. 1. (color online) Schematics of 7 zigzag edges of armchair graphene nanoribbon. We apply compressive stress at the armchair edge while tensile stress at the zigzag edge. Such type of strain engineering allow us to investigate the influence of strain on the bandengineering of graphene nanoribbon.

We then apply compressive strain to the system along y-direction and tensile strain along x-direction. This leads with possible application connected with opening and closing the bandgaps. In other words, the armchair graphene nanoribbons can be used for dual purposes of semiconductor and metallic. Within density functional theory calculations, our study show that the graphene and graphene with -H functional group can not induce significant values of out-of-plane deformations while graphene with -H2 functional group does induce large out-of-plane deformations exhibiting the properties of relaxed shape graphene. Such strain engineering can lead to tuning the bandgaps from semiconductor to metal and then again switching back to semiconductor. The binding energy calculations of hydrogen on graphene allow to quantify the effect of strain on the bandengineering of graphene nanoribbons. Finally, we discuss the effect of strain on the Poisson ratio, Young’s and shear modulii of graphene nanoribbons.

The paper is organized as follows. In Sec. II we provide computational details of density functional theory calculations for generating strain on graphene nanoribbon. In Sec. III we present the results for bandengineering, poisson ratio, Young’s and shear modulii of graphene, graphene edge functioning with H and H2. Finally, in Sec. IV we summarize our results.

II. COMPUTATIONAL METHODS

Density Functional Theory (DFT) calculations for 7 zigzag edges of armchair graphene nanoribbons are performed in the Quantum Espresso software package, where periodic boundary conditions are implemented in the simulations. Ultrasoft pseudopotentials and plane wave basis set with a kinetic energy and charge density cut-off at 100Ry and 800Ry are used. We include exchange and correlation effects within the Perdew-Burke-Ernzerhof (PBE) Functional. Van der Waals interactions are also included with the Semiempirical Grimme’s DFT-D2 corrections terms. We use orthorhombic 4.34Å × 24.78Å × 15.01Å size of supercell that contains 7 zigzag edges of an armchair graphene nanoribbon. In the supercell, we have 14 atoms for the graphene nanoribbon, 18 atoms for the graphene nanoribbon with armchair edge functioning with H and 22 atoms for the graphene nanoribbon with armchair edge functioning with H2. During geometry optimization, all atoms in all the three directions and x-axis of the supercell are fully relaxed until the forces on atoms are smaller than 0.01 eV/Å. We have tested several k-point samplings and calculations are performed at (6,1,3) k-points sampling fulfilling the above convergence criteria. The optimized lattice parameters along the x-direction are 4.34Å for graphene, 4.29Å for graphene with armchair edge functioning with H, 4.30Å for graphene with armchair edge functioning with H2. The optimized widths (distance between C-C atoms) of 7 zigzag edges of armchair graphene nanoribbons are 7.1353 Å (bare graphene), 7.33Å (graphene edge functioning with H), 7.56 Å (graphene edge functioning with H2). The XCrySDen program was used to draw the molecular structure. For strain engineering of graphene nanoribbons, we have applied the compressive stress through the armchair edge and then frozen the y-coordinates of the armchair edge atoms while allowing the other coordinates to be fully relaxed. We also fully relaxed the x-axis of the supercell.

III. RESULTS AND DISCUSSIONS

Bandgaps of the armchair graphene nanoribbon depend on the width of the ribbon. If the armchair nanoribbon contains an odd number of zigzag edges then the armchair graphene nanoribbon possesses a finite bandgap opening at the Γ point and interesting for making semiconductor devices. For an even number of zigzag edges, the armchair graphene nanoribbon has a zero band gap opening and thus possesses metallic properties. When strain is implemented in the armchair graphene nanoribbon with odd number of zigzag edges, then such a nanoribbon possesses the properties of both semiconductor and metal. In this paper, we are interested in tuning the bandgap from a semiconducting to metallic and then bringing it back to the semiconductor with the application of strain engineering. Hence, we consider the 7
FIG. 3. (color online) Band structures and Density of States (DOS) of graphene nanoribbon, graphene nanoribbon armchair edge functioning with H, and graphene nanoribbon armchair edge functioning with $H_2$.

FIG. 4. (color online) Band engineering in the armchair graphene nanoribbon with the application of strain in three cases: (a) graphene nanoribbon, (b) graphene nanoribbon functioning with hydrogen at the armchair edge and (c) graphene nanoribbon functioning with $H_2$ molecule at the armchair edge. We see that the bandgap completely closes at the particular value of strain for the case of graphene nanoribbons functioning with H and $H_2$.

FIG. 5. (color online) Isosurface charge distribution in (a) and energy vs density of states in (b) of armchair graphene nanoribbon for armchair edge functioning with hydrogen molecule ($-H_2$) under 15% compressive strain. Notice that the out-of-plane deformations are significantly large that provided the relaxed shape graphene nanoribbon similar to Ref. 27,28.

zigzag edges of the armchair graphene nanoribbon and then apply the compressive stress at the armchair edge. The armchair ribbon is also allowed to elongate in the x-direction. The schematics of the strained armchair graphene nanoribbon is shown in Fig. 4

In Fig. 2 we have plotted the isosurface charge distributions on 7 zigzag edges of armchair GNRs for three different cases: (i) bare GNRs (Fig. 2 (a)), (ii) GNRs with H at the armchair edge (Fig. 2 (b)) and (iii) GNRs with $H_2$ at the armchair edge. As can be seen in Fig. 2 the distributions of isosurface charge in these GNRs are different because different functional groups in GNRs induce slightly different strains. Hence bandgap opening of these ribbons are expected to be different. The bandstructures and density of states of these GNRs are shown
can be achieved even at much smaller values of strain (approximately at 3% of strain) for the case of graphene nanoribbon passivated with H$_2$. The bandgap closing can be seen due to the effect of strain because applied strain decreases the width of the ribbon. When the ribbon width becomes closer to the width of the 6 (even number) zigzag edge armchair graphene nanoribbon then the metallic behavior in the band engineering of graphene nanoribbon can be seen.\cite{26,66,67}

Using finite element method simulations, authors in Ref.\cite{27,28} have shown that the relaxed shape graphene nanoribbon has potential interest for graphene-based strain engineering devices\cite{27,28,66,67} as well as for the observation of quantum phenomena e.g. discrete energy levels, pseudospin decoherence time and nontrivial topological phases.\cite{18,29,66,67} When the out-of-plane deformations are large as can be seen in Fig. 3 (a) for the case of graphene passivated with hydrogen, we observe a relaxed shape graphene nanoribbon. In Fig. 3 (b) we have plotted the density of states and find the bandgap reopening in the graphene nanoribbon.

Now we turn to the discussions of mechanical properties observed in the armchair graphene nanoribbon due to externally applied compressive strain from the y-direction and tensile strain in the x-direction.

In Fig. 6 (a), we plot the relative total energy density (i.e., energy density difference relative to graphene). This total energy is used to calculate the Young’s modulus, shear modulus and the binding energy of hydrogen. In this figure, we find that the total energy density increases significantly for the case of graphene passivated with $-H_2$ molecules (circles) at 12% of strain which provides an indication of relaxed shape graphene.\cite{28} In Fig. 6 (b), we plot the binding energy of hydrogen in the graphene which allows to estimate the strain generated by hydrogen on the graphene nanoribbon. The binding energy is found by using the expression:\cite{68}

$$BE = U[Gr(H, H_2)] - U[Gr] - U[H], \tag{1}$$

where $BE$ is the binding energy, $U[Gr(H, H_2)]$ is the total energy of graphene with passivation layer, $U[Gr]$ is the total energy of graphene and $U[H]$ is the total energy of hydrogen in vacuum. As can be seen in Fig. 6 (b), the binding energy of hydrogen in the graphene passivated with $-H_2$ enhances significantly after 12% of strain, which provides a clear indication of relaxed shape graphene (i.e., very large out-of-plane deformations).

Finally, we investigate the effect of strain on the Young’s modulus, Poisson ratio and shear modulus of graphene nanoribbon. The Young’s modulus is calculated by using the expression:\cite{68}

$$Y = \frac{1}{A_0} \frac{d^2U}{d\varepsilon_y^2}. \tag{2}$$

where $A_0$ is the optimized area without imposing any strain, $U$ is the total energy, and $\varepsilon_y$ is the externally applied compressive strain. In Fig. 7 (a), we find that the
Young’s modulus of graphene passivated with $H_2$ is larger than the Young’s modulus of graphene and graphene passivated with H. Young’s modulus also increases as we increase the strain and then sharply decreases providing an indication of saturation value of the Young’s modulus. The numerical values of Young’s modulus presented in Fig. 7(a) are consistent with the experimental and theoretical values reported in the literature.\cite{OliaeiMotlagh2018, Apalkov2018, Feng2018}

The Poisson ratio is another important physical quantity characterizing the mechanical properties of materials.\cite{OliaeiMotlagh2018, Apalkov2018, Feng2018} By applying compressive external strain, $\varepsilon_y$, in the graphene in the y-direction, and by using the supercell of DFT calculations to record the resulted strain in the x-direction, $\varepsilon_x$, we find the Poisson ratio from the expression, $\nu = \varepsilon_x/\varepsilon_y$ as $\nu = 0.25$ for graphene, $\nu = 0.25$ for graphene passivated with H and $\nu = 0.22$ for graphene passivated with $H_2$. Since the Poisson ratios for all three cases are almost the same ($\nu = 0.25$ (Gr), 0.25 (Gr-H), and 0.22 (Gr-$H_2$)), we can draw a conclusion that the Poisson ratio of graphene is unaffected by the passivation of -H and $H_2$ at the armchair edge.

After calculating the Young’s modulus and Poisson ratio, we can finally find the shear modulus, $G$, by using the expression,

$$G = \frac{Y}{2(1+\nu)}, \quad (3)$$

The shear modulus with respect to applied compressive strain is plotted in Fig. 7(b). Similar to Young’s modulus, shear modulus also increases as we increase the strain until it reaches the saturation value.

IV. CONCLUSION

In summary, we have studied the effect of strain on the band engineering (e.g., semiconductor vs metallic) and the mechanical properties (e.g. Young’s modulus, shear modulus and Poisson ratio) of armchair graphene nanoribbons passivated with hydrogen and hydrogen molecules at the armchair edges. We have shown that the strain can be used for tuning the bandgap from semiconductor to metallic, and then strain can again be used to tune the bandgaps from metallic characteristics to semiconductor. We have also shown that at the large values of strain in graphene nanoribbons passivated with hydrogen molecules, large out-of-plane deformations in graphene nanoribbon can show the properties of relaxed shape graphene. We have quantified the strain induced by hydrogen molecules on graphene nanoribbons in terms of the binding energy. Finally, we have shown that the Young’s and shear modulii increase as we increase the strain until they reach to their maximum values while the Poisson ratio is independent to the passivation materials. Our findings of bandgap tuning and exploration of mechanical properties can be used in designing novel optoelectronic devices, as well as for straintronic applications.

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1. C. Androulidakis, E. Koukaras, M. Poss, K. Papagelis, C. Galiotis, and S. Tawfick, Physical Review B 97, 241414 (2018)
2. A. Mannix, Z. Zhang, N. Guisinger, B. Yakobson, and M. Hersam, Nature nanotechnology 13, 444 (2018)
3. R. Wu, I. K. Drozdov, S. Eltinge, P. Zahl, S. Ismail-Beigi, I. Božović, and A. Gozar, Nature nanotechnology, 1(2018)
4. L. Feng, K. Yabuoshi, Y. Sugimoto, J. Onoda, M. Fukuda, and T. Ozaki, Physical Review B 98, 195311 (2018)
5. H. Hapuarachchi, S. D. Gunapala, Q. Bao, M. I. Stockman, and M. Premaratne, Physical Review B 98, 115430 (2018)
6. S. A. Oliaei Motlagh, J.-S. Wu, V. Apalkov, and M. I. Stockman, Phys. Rev. B 98, 081406 (Aug 2018)
7. A. K. Geim and K. S. Novoselov, Nature materials 6, 183 (2007)
8. J. N. Coleman, M. Lotya, A. O’Neill, S. D. Bergin, P. J. King, U. Khan, K. Young, A. Gaucher, S. De, R. J. Smith, I. V. Shvets, S. K. Arora, G. Stanton, H.-Y. Kim, K. Lee, G. T. Kim, G. S. Duesberg, T. Hallam, J. J. Boland, J. J. Wang, J. F. Donegan, J. C. Grunlan, G. Moriarty, A. Shmeliov, R. J. Nicholls, J. M. Perkins, E. M. Grieveson, K. Theuwissen, D. W. McComb, P. D. Nellist, and V. Nicolosi, Science 331, 568 (2011)
9. N. Savage, Nature 483, S30 (2012)
10. S. Manzeli, D. Ovchinnikov, D. Pasquier, O. V. Yazyev, and A. Kis, Nature Reviews Materials 2, 17033 (2017)
11. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, Science 306, 666 (2004)
12. L. Liao, Y.-C. Lin, M. Bao, R. Cheng, J. Bai, Y. Liu, Y. Qu, K. L. Wang, Y. Huang, and X. Duan, Nature 467, 305 (2010)
13. T. Yang, B. Zheng, Z. Wang, T. Xu, C. Pan, J. Zou, X. Zhang, Z. Qi, H. Liu, Y. Feng, et al., Nature communications 8, 1906 (2017)
D. J. Rizzo, G. Veber, T. Cao, C. Bronner, T. Chen, F. Zhao, H. Rodriguez, S. G. Louie, M. F. Crommie, and F. R. Fischer, Nature **560**, 204 (2018)

O. Gröning, S. Wang, X. Yao, C. A. Pignedoli, G. Borin Barin, C. Daniels, A. Cupo, V. Meunier, X. Feng, A. Narita, K. Müllen, P. Ruffieux, and R. Fasel, Nature **560**, 209 (2018)

S. Prabhakar and R. Melnik, Scientific reports **7**, 17365 (2017)

I. Burmistrov, I. Gorny, V. Y. Kachorovskii, M. Katsnelson, J. Los, and A. Mirlin, Physical Review B **97**, 125402 (2018)