Peierls Transition Of Graphene Nanoribbons: Crossover From Polyacetylenes To Graphene

Tatsuo Suzuki

Tokyo Metropolitan College of Industrial Technology, 8-17-1, Minami-Senju, Arakawa-ku, Tokyo 116-8523, Japan

Abstract. Graphene nanoribbons (GNRs) are stripes of single layered graphenes with a finite width. The electronic states of GNRs are different by the edge conditions (armchair edges or zigzag edges). The results of tight-binding approximations are that the hydrogen terminated zigzag GNRs are metallic, and the hydrogen terminated armchair GNRs are metallic or semiconducting. But the narrowest hydrogen terminated GNRs are polyacethlenes, that are semiconducting. The reason of this contradiction is that the structures of polyacethlenes are changed by the Peierls transition. Therefore the effects of the Peierls transition of GNRs from polyacetylenes to graphene were examined systematically using density functional theory with structural optimizations.

Keywords: gaphene, nanoribbon, edge, armchair, zigzag, polyacetylene, Peierls transition, bond length
PACS: 73.22.-f, 72.80.Vp, 71.30.+h, 72.80.Le, 71.20.Rv, 36.20.Kd

INTRODUCTION

Graphene nanoribbons (GNRs) are stripes of single layered graphenes with a finite width. The electronic states of GNRs are different by the edge conditions, those are armchair edges or zigzag edges (Fig. 1). The results of tight-binding approximations [1] are that the hydrogen terminated zigzag GNRs are metallic, and the hydrogen terminated armchair GNRs are metallic or semiconducting. But the narrowest hydrogen terminated GNRs are polyacethlenes, those are semiconducting. The reason of this contradiction is that the structures of polyacethlenes are changed by the Peierls transition. First-principles calculations [2-5] show that the hydrogen terminated armchair GNRs are semiconducting, but the energy gaps of these calculations do not agree one another. Therefore in this paper, more accurate first-principles calculations were done, and the effects of the Peierls transition of GNRs from polyacetylenes to graphene were examined systematically.

COMPUTATIONAL METHOD

The electronic states of GNRs were calculated using density functional theory with structural optimizations. All calculations were performed using *Gaussian 03* package [6] with periodic boundary conditions. These calculations did not include spin-polarized effects. I wanted to calculate the electronic states using the hybrid B3LYP exchange and correlation functions combined with 6-311+G(d,p) basis set, but unfortunately these calculations did not converge. Therefore armchair GNRs (N=2, 3) and zigzag GNRs (N=1, 2) were calculated using B3LYP/6-311G(d,p); armchair GNRs (N=4, 5, 6, 7, 8, 9, 10) and zigzag GNRs (N=3, 4, 6) were B3LYP/6-31G(d); a zigzag GNR (N=5) was B3LYP/6-31G; and zigzag GNRs (N=7, 8, 9) were B3LYP/3-21G.

RESULTS AND DISCUSSION

Calculated band structures are shown in Fig. 2. And the energy gaps are shown in Fig. 3, which include the results of other first-principles calculations [2-5] and the experiment values of polyacetylenes [7]. The calculated values of this work agree well with the experiment values. The reason of this agreement is that the hybrid B3LYP exchange and correlation functions are used in this work. The results of tight-binding approximations [1] are that armchair GNRs are metallic when N=3M-1 (M is an integer), but the calculations of this work show that all armchair GNRs are semiconducting. This result is coincident with other first-principles calculations [2-5] qualitatively.

The calculated bond lengths between carbon atoms of armchair GNRs are shown in the top of Fig. 4, which include the experiment value of cis-polyacetylenes [8] and the bond length of bulk graphene calculated using B3LYP/3-21G. The

identification number of bond of the horizontal axis is explained in Fig. 1. The bond lengths of b series agree completely with the bond lengths of c series. The bond lengths between carbon atoms connected with a hydrogen atom (a1 and aN) are much shorter than other bond lengths. The bond lengths of dimer lines of cis-polyacetylene (a1 and a2 of N=2) are the same, so the effect of the Peierls transition does not appear as the difference among bond lengths in armchair GNRs. The inner bond lengths of armchair GNRs agree with the bond length of bulk graphene.

The calculated bond lengths between carbon atoms of zigzag GNRs are shown in the bottom of Fig. 4, which include the experiment values of trans-polyacetylenes [8] and the bond length of bulk graphene. The bond lengths of carbon atoms connected with a hydrogen atom (d1, e1, dN, and eN) are shorter, but the bond lengths of outer vertical bonds (f1 and FN-1) are longer than other bond lengths. The bond lenghs of trans-polyacetylene (d1 and e1 of N=1) are not the same, which is the appearance of the Peierls transition. The bond lengths of the width N=2 (d1, e1, d2, and e2 of N=2) are almost the same, so the effect of the Peierls transition is not clear. But the bond lengths of the width N=3 (d2 and e2 of N=3) does not agree with each other, so this is the appearance of the Peierls transition also. In the wider zigzag GNRs, the bond lengths of d series agree with the bond lengths of e series. Therefore the effects of the Peierls transition vanish rapidly increasing the ribbon width. The inner bond lengths of zigzag GNRs does not agree with the bond length of bulk graphene. The bond lengths of zigzag chains (d series and e series) are shorter than the bond length of bulk graphene, and the bond lengths of vertical bonds (f series) are longer than the bond length of bulk graphene.

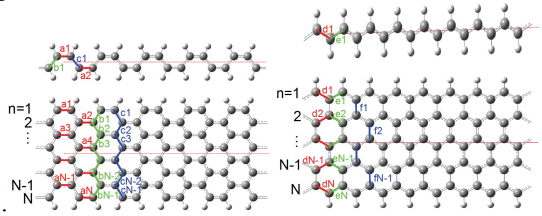

FIGURE 1. (Left top) cis-polyacetylene. (Left bottom) armchair GNR with N dimer lines. (Right top) trans-polyacetylene. (Right bottom) zigzag GNR with N zigzag chains.

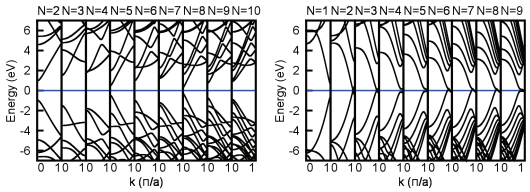

FIGURE 2. The calculated band structures. (Left) armchair GNRs. (Right) zigzag GNRs.

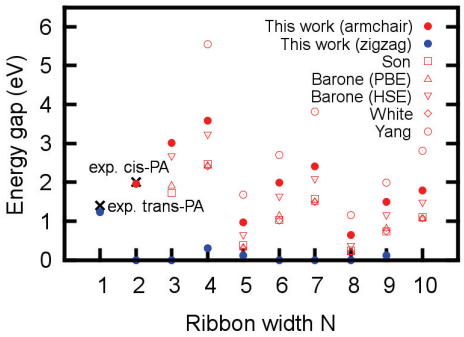

FIGURE 3. The energy gaps of GNRs. Round solid marks are calculated values of this work. Red is armchair, and blue is zigzag. Red open marks are other first-principles calculations of armchair GNRs [2-5]. Black cross marks are the experiment values of polyacetylenes [7].

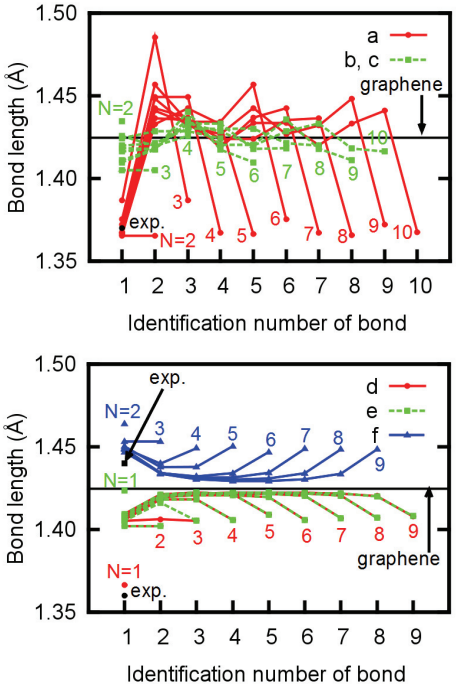

FIGURE 4. The calculated bond lengths between carbon atoms. of armchair GNRs. Black line is the bond length of bulk graphene calculated using B3LYP/3-21G. (Top) Armchair GNRs. Black mark is the experiment value of cis-polyacetylenes [8]. (Bottom) Zigzag GNRs. Black marks are the experiment values of trans-polyacetylenes [8].

REFERENCES

1. K. Nakada, et al., *Phys. Rev. B* **54**, 17954 (1996).
2. Y.-W. Son, et al., *Phys. Rev. Lett.* **97**, 216803 (2006).
3. V. Barone, et al., *Nano Lett.* **6**, 2748 (2006).
4. C. T. White, et al., *Nano Lett.* **7**, 825 (2007).
5. L. Yang, et al., *Phys. Rev. Lett.* **99**, 186801 (2007).
6. M. Frisch, et al., *Gaussian 03, Revision D.01*, Gaussian, Inc., Wallingford CT (2004).
7. C. R. Fincher, et al., *Phys. Rev. B* **20**, 1589 (1979).
8. C. S. Yannoni, et al., *Phys. Rev. Lett.* **51**, 1191 (1983).