CHIN. PHYS. LETT. Vol. 35, No. 6 (2018) 067101

Effect of Chemical Doping on the Electronic Transport Properties of Tailoring Graphene Nanoribbons *

Yang Liu(刘洋), Cai-Juan Xia(夏蔡娟)**, Bo-Qun Zhang(张博群), Ting-Ting Zhang(张婷婷), Yan Cui(崔焱), Zhen-Yang Hu(胡振洋)

School of Science, Xi'an Polytechnic University, Xi'an 710048

(Received 22 January 2018)

The electronic transport properties of a molecular junction based on doping tailoring armchair-type graphene nanoribbons (AGNRs) with different widths are investigated by applying the non-equilibrium Green's function formalism combined with first-principles density functional theory. The calculated results show that the width and doping play significant roles in the electronic transport properties of the molecular junction. A higher current can be obtained for the molecular junctions with the tailoring AGNRs with $W = 11$. Furthermore, the current of boron-doped tailoring AGNRs with widths $W = 7$ is nearly four times larger than that of the undoped one, which can be potentially useful for the design of high performance electronic devices.

PACS: 71.15.Mb, 73.23.−b, 85.65.+h DOI: 10.1088/0256-307X/35/6/067101

Following the miniaturization of electronic devices, silicon-based devices have gradually reached the limits of their performance.[1] Atomic and molecular systems are of interest because of their unique behaviors that are different from those of macroscopic systems.[2] Recently, one-dimensional graphene nanoribbons (GNRs), which are cut off from the novel two-dimensional material-graphene, have been exhibiting great potential for next-generation nanoelectronics due to their unique electronic structures and transport characteristics, such as high carrier mobility,[3−7] quantum Hall effect,[8,9] bipolar electric field effect,[10] and tunable bandwidth.[11] There are two kinds of GNRs, which can be divided into armchair-type GNRs (AGNRs) and zigzag-type GNRs (ZGNRs) according to the shapes of edges cut from different directions.[12−15] The band gap of an AGNR as a function of the ribbon width W, ΔW, exhibits three distinct families with $\Delta(3p+1) > \Delta(3p) > \Delta(3p+2)$, where p is a positive integer, and for each family, the band gap is inversely proportional to the ribbon width.[16−18] Based on its unique electrical properties, AGNRs have been employed as the electrodes for several molecular devices.[19−30]

Furthermore, with the development of experimental technologies, it has become possible to tailor GNRs or even to introduce foreign atoms.[31−35] Jin *et al.* proved that the chain of carbon atoms can be prepared from the removal of carbon atoms of the graphene row by high energy electron irradiation a sputtering process.[36] Li *et al.* prepared GNRs with widths below 10 nm as electrodes and found that GNRs with widths below 10 nm are all semiconductors.[37] Zhang *et al.* fabricated a new doped graphene material showing good chemical properties in fuel cells by a thermal annealing method.[38] Zheng *et al.* introduced nitrogen (N) and boron (B) sequentially into selected locations on the graphene domain. The results show that B,N-graphene greatly improves the electrochemical performance of graphene compared with single-doped graphene and one-step hybrid electrodes.[39] In this work, we design a molecular junction based on doping tailoring AGNRs. The effects of doping on the electronic transport properties of AGNRs with different widths are investigated using the non-equilibrium Green's function (NEGF) based on density functional theory (DFT). We discover significantly width-tuned current-voltage (I–V) characteristic. Moreover, the I–V characteristic can be improved by doping.

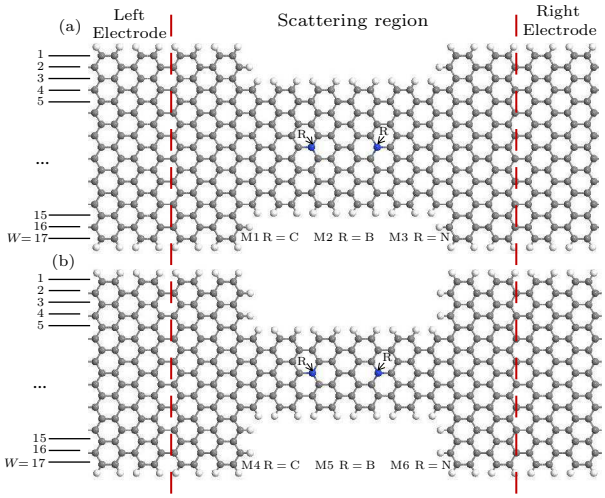

Fig. 1. Schematic of molecular junctions with different width tailoring AGNRs between two 17-AGNR electrodes: (a) $W = 11$, and (b) $W = 7$.

The model devices are illustrated in Fig. 1. Here tailoring AGNRs with widths $W = 11$ or $W = 7$ are sandwiched between two AGNR electrodes with

*Supported by the National Natural Science Foundation of China under Grant Nos 11004156 and 11547172, and the Science and Technology Star Project of Shaanxi Province under Grant No 2016KJXX-45.

**Corresponding author. Email: caijuanxia@xpu.edu.cn

© 2018 Chinese Physical Society and IOP Publishing Ltd

$W = 17$. The widths of tailoring AGNRs with $W = 11$ (see Fig. 1(a)) and $W = 7$ (see Fig. 1(b)) are selected. The device is divided into three parts: left electrode, right electrode, and the scattering region. The length of the tailoring AGNRs and the scattering region are 22.7 Å and 36.9 Å, respectively. Some previous works have shown that center-doping is more stable than edge-doping.[29,40] Therefore, in this work, two elements in groups Ⅲ and V, namely B and N, are used as dopants, and they located on the center positions of the tailoring AGNRs. For simplicity, the undoped, B-doped and N-doped AGNRs with width $W = 11$ in Fig. 1(a) are named as M1, M2 and M3, respectively. The undoped, B-doped and N-doped AGNRs with width $W = 7$ in Fig. 1(b) are named as M4, M5 and M6, respectively.

The structural relaxation and the electronic transport properties of the molecular junctions are calculated by a fully self-consistent NEGF formalism combined with first-principles DFT, which are implemented in the Atomistix Toolkit (ATK) software package.[41–43] The cutoff energy is set to be 150 Ry. The Brillouin zone is sampled by $1 \times 1 \times 100$ k-point. The current of the system can be calculated using the Landauer–Büttiker formula[44] as follows:

$$I = \frac{2e}{h} \int T(E, V_b)[f_L(E - \mu_L) - f_R(E - \mu_R)]dE, \quad (1)$$

where $T(E, V_b)$ is the transmission coefficient of the system when the energy is E and the applied bias is V_b, $\mu_{L(R)}$ is the electrochemical potential of the left (right) electrode, f_L and f_R are the electron Fermi distribution functions of the left and right electrodes, respectively.

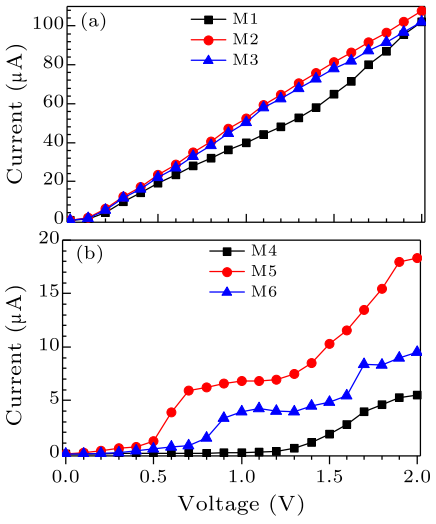

Fig. 2. Current–voltage curves for molecular junctions M1, M2, M3, M4, M5 and M6.

The I–V characteristics for different models in the bias range from 0 to 2.0 V are shown in Fig. 2. Most strikingly, the currents of the tailoring AGNRs with $W = 11$ are larger than those of the tailoring AGNRs with $W = 7$. The electronic transport properties of the tailoring AGNR junctions can be improved by doping. From Fig. 2(a), it can be seen that the currents of M2 and M3 are slightly higher than that of M1. However, in Fig. 2(b), when the width of tailoring AGNRs is $W = 7$, the currents of M5 and M6 are remarkably larger than that of M4. For example, the calculated current at 2.0 V is about 18.31 μA for M5, which is nearly four times larger than the current of M4, 5.50 μA. Furthermore, in view of the I–V characteristics, the B doping in the tailoring AGNRs with $W = 7$ is more useful than the N doping.

In the NEGF theory, the current of the system is calculated by the Landauer–Bütiker formula $I = \frac{2e}{h} \int T(E, V_b)[f_L(E - \mu_L) - f_R(E - \mu_R)]dE$, which is dependent on transmission spectra. Thus to further explore the electronic transport properties, we calculated the transmission spectra of undoped or doped tailoring AGNRs with different widths between two 17-AGNRs electrodes under zero voltage to understand the dramatic difference in conductance appearing in current-voltage curves as shown in Fig. 3. The average Fermi level is set as zero.

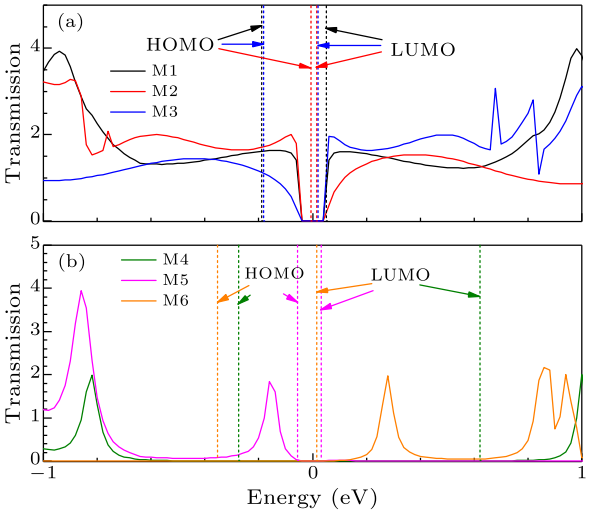

Fig. 3. Transmission spectra of models M1–M6 at zero bias. The Fermi level is set to be zero.

From Fig. 3(a), the position and the peaks of transmission for M1, M2 and M3 are almost the same. However, one can see that both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of M2 are obviously closer to the Fermi energy level leading to a smaller HOMO–LUMO gap (HLG) in contrast with M1 and M3, which induce an almost similar current in Fig. 2(a). When the width of the tailoring AGNRs changes to $W = 7$, the transmission coefficient peaks of M5 and M6 are larger than that of M4. Meanwhile, the coefficients of the HOMO and LUMO for M4 are zero, which reveal that the electronics transports are blocked. Furthermore, the HOMO and LUMO of M5 are more approaching the Fermi energy level compared with M6 and M4. As a result, the large transmission coefficient accounts for the high conductivity in M5.

The transmission coefficient can be related to the molecular orbitals, which have been modified by the electrodes. These modified molecular orbitals can be obtained from the molecular projected self-consistent Hamiltonian (MPSH) eigenstates. The HOMO and the LUMO are the main transmission channel because it is close to the Fermi energy. To explain the origin of the difference in conductance in Fig. 2, we calculate the LUMO-MPSH and HOMO-MPSH as shown in Figs. 4 and 5.

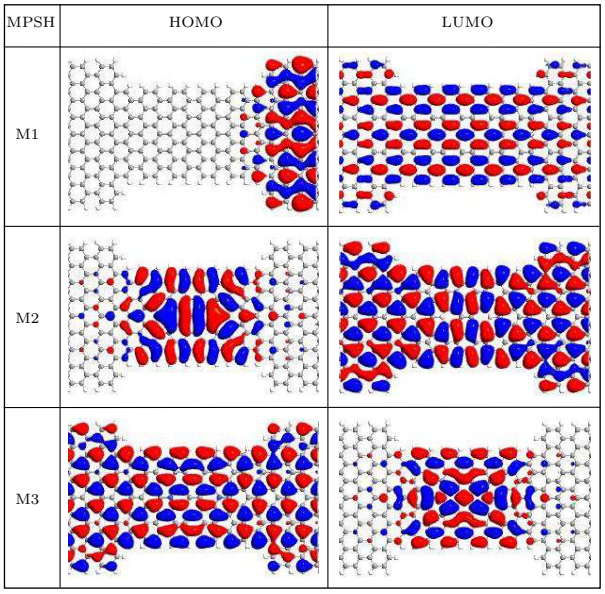

Fig. 4. MPSH distributions of HOMO and LUMO orbits of models M1, M2 and M3 at zero bias.

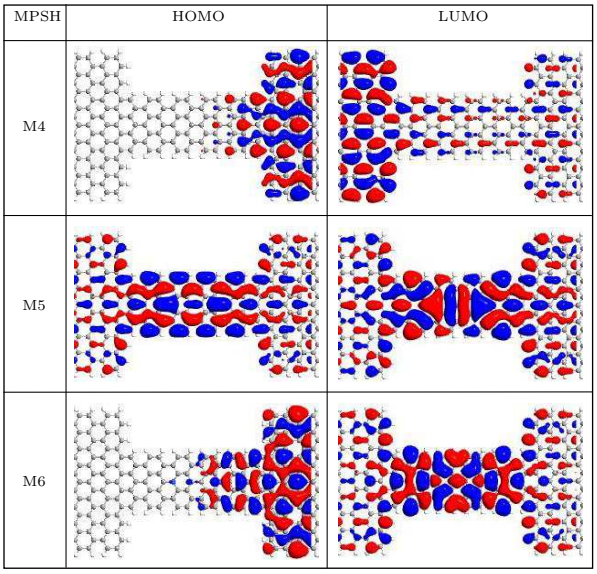

Fig. 5. MPSH distributions of HOMO and LUMO orbits of models M4, M5 and M6 at zero bias.

It can be seen from Fig. 4 that there is just one delocalized MPSH orbital for all three models: the HOMO-MPSH orbital of M1 localized on the right, the HOMO-MPSH orbital of M2 and the LUMO-MPSH orbital of M3 localized on the central regions, which results in a similar I–V characteristic curve shown in Fig. 2(a). However, in Fig. 5, one can see that there is one delocalized MPSH orbital for M4 and M6, and two delocalized MPSH orbital for M5. The localized MPSH-HOMOs for M4 and M6 induce the low transmission coefficients in Fig. 3(b).

In summary, we have explored the electronic transport properties of undoped or doped tailoring AGNRs with different widths between two 17-AGNR electrodes using the non-equilibrium Green function based on density functional theory. The results indicate that the width and doping of tailoring AGNRs play significant roles in the transport properties of the molecular junctions. The currents of the tailoring AGNRs with $W = 11$ are larger than those of the tailoring AGNRs with $W = 7$. The B doping in the tailoring AGNRs with $W = 11$ can evidently enhance the current more than the N doping. The current of B-doped tailoring AGNRs with widths $W = 7$ is nearly four times larger than that of the undoped one, which can be potentially useful for the design of high performance electronic devices.

References

[1] Husain M M and Kumar M 2015 *Org. Electron.* **27** 92
[2] Ji G M, Li D M, Fang C F, Xu Y Q, Zhai Y X, Cui B and Liu D S 2012 *Phys. Lett.* A **376** 773
[3] Berger C, Song Z M, Li X B, Wu X S, Brown N, Naud C, Mayou D, Li T B, Hass J, Marchenkov A N, Conrad E H, First P N and Heer W A D 2006 *Science* **312** 1191
[4] Du X, Skachko I, Barker A and Andrei E Y 2008 *Nat. Nanotechnol.* **3** 491
[5] Orlita M, Faugeras C, Plochocka P, Neugebauer P, Martinez G, Maude D K, Barra A L, Sprinkle M, Berger C, Heer W A D and Potemski M 2008 *Phys. Rev. Lett.* **101** 267601
[6] Neugebauer P, Orlita M, Faugeras C, Barra A L and Potemski M 2009 *Phys. Rev. Lett.* **103** 159902
[7] Ahmed S and Yi J B 2017 *Nano-Micro Lett.* **9** 699
[8] Zhang Y B, Tan Y W, Stormer H L and Kim P 2005 *Nature* **438** 201
[9] Novoselov K S, Jiang Z, Zhang Y, Morozov S V, Stromer H L, Zeitler U, Maan J C, Boebinger G S, Kim P and Geim A K 2007 *Science* **315** 1379
[10] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubbnos S V, Grigorieva I V and Firsov A A 2004 *Science* **306** 666
[11] Han M Y, Özyilmaz B, Zhang Y B and Kim P 2007 *Phys. Rev. Lett.* **98** 206805
[12] Niimi Y, Matsui T, Kambara H, Tagami K, Tsukada M and Fukuyama H 2006 *Phys. Rev.* B **73** 085421
[13] Nakada K, Fujita M, Dresselhaus G and Dresselhaus M S 1996 *Phys. Rev.* B **54** 17954
[14] Chen Y P, Xie Y E and Yan X H 2008 *J. Appl. Phys.* **103** 063711
[15] Zheng H X, Wang Z F, Luo T, Shi Q W and Chen J 2007 *Phys. Rev.* B **75** 165414
[16] Son Y W, Cohen M L and Louie S G 2006 *Phys. Rev. Lett.* **97** 216803
[17] Cai Y Q, Zhang A H, Feng A P and Feng Y P 2011 *J. Chem. Phys.* **135** 184703
[18] Long M Q, Tang L, Wang D, Wang L J and Shuai Z G 2009 *J. Am. Chem. Soc.* **131** 17728
[19] Xie L, Chen S Z, Zhou W X and Chen K Q 2017 *Org. Electron.* **46** 150
[20] Xie F, Fan Z Q, Liu K, Wang H Y, Yu J H and Chen K Q

2015 *Org. Electron.* **27** 41
[21] He J and Chen K Q 2012 *J. Appl. Phys.* **112** 114319
[22] Zeng J and Chen K Q 2015 *J. Mater. Chem.* C **3** 5697
[23] Song Y, Xie Z, Zhang G P, Ma Y and Wang C K 2013 *J. Phys. Chem.* C **117** 20951
[24] Ye M, Xia C J, Yang A Y, Zhang B Q, Su Y H, Tu Z Y and Ma Y 2017 *Chin. Phys. Lett.* **34** 117101
[25] Huang J, Xu K, Lei S L, Su H B, Yang S F, Li Q X and Yang J L 2012 *J. Chem. Phys.* **136** 064707
[26] Song Y, Xie Z, Ma Y, Li Z L and Wang C K 2014 *J. Phys. Chem.* C **118** 18713
[27] Zhang D H, Yao K L and Gao G Y 2011 *J. Appl. Phys.* **110** 013718
[28] Ren H, Li Q X, Luo Y and Yang J L 2009 *Appl. Phys. Lett.* **94** 173110
[29] Zhao P, Liu D S, Li S J and Chen G 2013 *Phys. Lett.* A **377** 1134
[30] Zhu S C, Yao K L, Gao G Y and Ni Y 2013 *Solid State Commun.* **155** 40
[31] Solís-Fernández P, Okada S, Sato T, Tsuji M and Ago H 2016 *ACS Nano* **10** 2930
[32] Xu J, Jang S K, Lee J, Song Y J and Lee S 2014 *J. Phys. Chem.* C **118** 22268
[33] Guo X S, Lu B A and Xie E Q 2011 *Chin. Phys. Lett.* **28** 076803
[34] Błoński P, Tuček J, Sofer Z, Mazaínek V, Petr M, Pumera M, Otyepka M and Zbořil R 2017 *J. Am. Chem. Soc.* **139** 3171
[35] Yang R, Zhang L C, Wang Y, Shi Z W, Shi D X, Gao H J, Wang E G and Zhang G Y 2010 *Adv. Mater.* **22** 4014
[36] Jin C H, Lan H P, Peng L M, Suenaga K and Iijima S 2009 *Phys. Rev. Lett.* **102** 205501
[37] Li X L, Wang X R, Zhang L, Lee S and Dai G J 2008 *Science* **319** 1229
[38] Zhang C Z, Mahmood N, Yin H, Liu F and Hou Y L 2013 *Adv. Mater.* **25** 4932
[39] Zheng Y, Jiao Y, Ge L, Jaroniec M and Qiao S Z 2013 *Angew. Chem.* **125** 3192
[40] Zeng J, Chen K Q, He J, Fan Z Q and Zhang X J 2011 *J. Appl. Phys.* **109** 124502
[41] Atomistix Toolkit version 2008 02. Quantum Wise A/S (www.quantumwise.com)
[42] Brandbyge M, Mozos J L, Ordejón P, Taylor J and Stokbro K 2002 *Phys. Rev.* B **65** 165401
[43] Taylor J, Guo H and Wang J 2001 *Phys. Rev.* B **63** 245407
[44] Buttiker M, Imry Y, Landauer R and Pinhas S 1985 *Phys. Rev.* B **31** 6207