Electronic transport through graphene nanoribbons with Stone-Wales reconstruction at edges and interfaces

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In this paper, we study the conductance of the graphene nanoribbons (GNRs) in the presence of the Stone-Wales (S-W) reconstruction, using the transfer matrix method. The ribbon is connected with semi-infinite quantum wires as the leads. The S-W reconstruction occurs on the edges and the interfaces between the electrodes and ribbon. When the reconstruction occurs on the edges, the conductance is suppressed considerably if the gate voltage \( V_g \) takes intermediate values around \( |V_g| \sim t_0 (t_0 \text{ being the hopping amplitude of graphene) in both positive and negative energy regions. In contrast, if \( V_g \) is close to the Dirac point or the band edges, the conductance is relatively insensitive to the edge reconstruction. The effect of edge reconstruction become less important with increasing ribbon width as expected. The S-W reconstruction occurs also possibly at the interfaces. In this case, the reconstruction suppresses identically the conductance in the entire range of \( V_g \) for armchair GNRs. For the zigzag GNRs, the conductance is strongly suppressed in the negative energy region, however the change of the conductance is relatively small in the positive energy region. We also analyze the transmission coefficients as functions of the channel index (the transverse momentum \( k_y \) of the leads) for the neutral armchair GNRs with interface defects. Interestingly, there are two transmission peaks appearing at \( k_y = \pi/3 \) and \( k_y = 2\pi/3 \) due to the unit cell doubling.

1. INTRODUCTION

Graphene is one of the carbon allotropes with extraordinary electronic properties,⁵,⁶, that make it prominent for potential applications in nano-electronic devices. In practice, one need to take the edge effects into account, since they could change the band structure and have important implications for the transport properties of nano-size graphene. The conventional edges like armchair and zigzag have been well studied, however they may not be robust against edge reconstructions in some realistic circumstances⁷. Indeed, the reconstructed edges have already been observed in experiments.⁸,⁹

One of the reconstructions is caused by the Stone-Wales (S-W) mechanism, which is obtained by 90° rotation of the carbon-carbon bond without changing total atom number. In Fig. 1 (a) and (c), we show two typical continuous edge reconstructions by the S-W mechanism, ac-757 in armchair graphene nanoribbons (AGNR) and zz-57 in zigzag graphene nanoribbons (ZGNR), respectively. Without hydrogen passivation, a single ac-757 defect contains two adjacent heptagons and one pentagon, while the zz-57 reconstruction consists of alternating heptagon and pentagon on the edges.⁰,¹¹ In contrast to the graphene nanoribbons (GNRs) with the ideal edges, the more realistic S-W edge reconstruction breaks electron-hole (e-h) symmetry and changes the band structures substantially.¹²,¹³, of which the effects on the transport of GNRs have attracted attention recently.¹⁴–¹⁶. It was found in Ref. ¹⁶ that in the wide and short GNRs the conductance change due to the S-W edge reconstruction is inconspicuous when the gate voltage is close to the Dirac point. While, in another Ref. ¹⁰ it is shown that in the narrow and long GNRs, the S-W defects at the edges modify the band structure and result in strong backward scattering, that suppresses the conductance. These two seemingly different scenarios may be attributed to the ribbon size, and also the distribution of the S-W defects. In this paper we study the transport through GNRs with the S-W defects periodically distributed on the ribbon edges. We also study the different effects of the S-W reconstructions when they occur at different positions, i.e, the ribbon edges or the heterojunctions between the ribbon and the electrodes.

The paper is organized as following. Our model and method are briefly introduced in Sec. 2, and more details can be find in Refs. ¹³,¹⁴. The effect of S-W reconstruction is given in Sec. 3, where we only consider the ac-757 and zz-57 reconstructions. The conclusion and summary are given in Sec. 4.

2. MODEL AND METHOD

The GNR is put in connection with semi-infinite quantum wires as the electrodes which are simulated by the square lattices. Since the edge reconstruction is in-
FIG. 1: (Color online.) The schematic illustration of S-W reconstruction on the ribbon edges (a, c), and at the interfaces (b, d) between the ribbon and the electrodes. The square lattices with width $M$ are the leads, and the current flows in the $x$-direction. $L$ and $N_a$ denotes the length and width (in terms of carbon atom number) for the GNRs, respectively. The evitable in the fabrication and transfer of GNRs, it can occur finally on both the ribbon edge and the interfaces between the GNRs and electrodes. Figs. 1 shows the geometry of GNRs with ac-757 and zz-57 reconstruction on the edges or interfaces. The Hamiltonian defined on this network can be expressed in a tight binding form

$$
\hat{H} = -\sum_{ij,i'j'} t_{ij,i'j'} \hat{C}^\dagger_{ij} \hat{C}_{i'j'} - V_g \sum_{ij} \hat{C}^\dagger_{ij} \hat{C}_{ij},
$$

where $V_g$ is the gate voltage applied on the GNRs and $C_{ij}$ is the creation (annihilation) operator at lattice site $i,j$. $t_{ij,i'j'}$ is the hopping amplitude between two nearest neighbors $ij$ and $i'j'$. The hopping coefficients on the carbon hexagon edges is $t_0$ which is usually equal to $2.7eV$, while those on the deformed bonds belonging to heptagons or pentagons are taken from Refs. [12] as shown in Fig. 1 and Tab. I. For simplicity, the hopping parameters in the leads and the GNR-electrode interfaces are assumed to be $t_0$. The Fermi surface is set at zero energy, and the spin indices of electrons are omitted simply for convenience.

In the leads with width $M$, the quantum states can be labeled by the quantized transverse momenta $k_{y,n} = n\pi/(M + 1)$ which correspond to different conducting channels. According to the Landauer-Büttiker formula, the conductance is the summation over all the transmission coefficients $T_{n,n'}$ from channel $n$ to $n'$

$$
G = \frac{2e^2}{h} \sum_{n,n'}^{M} T_{n,n'}.
$$

$T_{n,n'}$ can be calculated using the transfer matrix method [13].

We assume all the S-W defects align in a periodic pattern on the boundaries of the GNRs with width $N_a$ and length $L$ (see Fig. 1(a, c)), which breaks the translational symmetry and the unit cell is doubled. The randomly distributed defects are not discussed in this article. The spectra of GNRs with periodic ac-757 and zz-57 edge defects are shown in Fig. 2 which are consistent with those in Refs. [9, 10]. It turns out the e-h symmetry is completely lost due to the existence of 5 and 7 atom rings on the edges. As a consequence, for the AGNRs with ac-757 defects, the conduction and valence bands touch at a positive energy $E > 0$ for $\text{mod}(N_a,3) = 1$ (see Fig. 2(a)). There appear four new subbands corresponding to edge...
FIG. 2: (Color online.) (a) is the band structure of AGNRs with ac-757 edge reconstruction, and (b) is that of ZGNRs with zz-57 edge reconstruction. Note that the unit cell is doubled by the reconstruction, and we take the length of the original unit cell in the pristine GNRs as unit, then the momentum $k_x$ belongs to the interval $[0, \pi]$.

states $^{10}$, indicated by colored lines in Fig. 2(a). For ZGNRs in the presence of the zz-57 reconstruction, the midgap band is no longer flat, but bends towards the valence band (see Fig. 2(b)). Furthermore, there occur additional midgap subbands with higher energy. These new features of the energy spectra due to the edge reconstruction might affect the transport properties finally.

3. TRANSPORT THROUGH AGNRS AND ZGNRS WITH S-W DEFECTS

FIG. 3: (Color online.) The normalized conductance $G/M$ as functions of the gate voltage $V_g$ for AGNRs with S-W reconstruction on the ribbon edges (a) and (b) and at the interfaces (c) and (d). The black curves are the conductance $G_0$ of the pristine AGNRs for comparison. Inset of (b) shows the ratio $G_D/G_0$ as a function of the width at $V_g = 0$ and $\pm t_0$.

We explore in details the transport properties of GNRs with ac-757 and zz-57 reconstructions in this section. Figures (a) and (b) show the normalized conductances $G_D/M$ of AGNRs with periodic S-W defects on the ribbon edges as functions of the gate voltage $V_g$. The overall e-h asymmetry of the conductance data is mainly due to the odd-number-atom rings at the interfaces between the leads and the AGNRs which makes the lattice non-bipartite. The conductance is suppressed considerably in the intermediate energy region $0.7t_0 < V_g < 2t_0$ and $-2.7t_0 < V_g < -0.7t_0$ by the ac-757 edge reconstruction, where the trigonal warping effect is important which is incompatible with the symmetry of heptagon and pentagon. For $V_g$ close to zero energy or the band edges, $G_D$ is almost the same as that of pristine AGNRs denoted by $G_0$, as shown in Fig. 3(a), except that the position of the minimal conductance shifts slightly from zero towards a negative value. This is due to the breaking e-h symmetry by the ac-757 edge reconstruction, which results in the shift of the touch point of the valence and conduction bands where the D.O.S. as well as the conductance is minimal.

In Figs. (a) and (b), we also show the size effect on the conductance. When the ribbon length increases, the electrons experience more scattering from the S-W edge defects leading to the further suppression of the conductance as shown in Fig. 3(a). While, the increase of the ribbon width has two effects, one is yielding more conducting channels leading to the linear dependence of the conductance on the width, the other is weakening the edge effect so that the conductance converges to that of pristine AGNRs when the ribbon width is increased, as shown in Fig. 3(b) and its inset.

When the zz-57 defects locate at the interfaces between the leads and the AGNR, the heptagons and pentagons at the interfaces strongly scatter electrons and suppress the conductance in the entire region of the gate voltages as shown Figs. (c) and (d). In this case, we take a relatively large ribbon width $N_a \geq 200$, so that we can focus on the reconstruction at the interfaces and ignore those on the ribbon edges, i.e., we are liberated to choose the conventional armchair edges. In this setup, the conductance data are obviously insensitive to the size as shown in Figs. (c) and (d).

Next, we consider the transport properties of ZGNRs with the S-W reconstruction. Without edge reconstruction, the lattice of the ZGNR connected with the leads is still bipartite unlike the case of AGNRs, therefore the conductance data remains e-h symmetric as shown with the black curves in Fig. 3. When the zz-57 reconstruction is presented on the edges, the e-h symmetry is broken due to the occurrence of heptagons and pentagons, and the midgap band is not flat anymore (see Fig. 2(b)). This is reflected in the conductance data near $V_g = 0$ in the inset of Fig. (a), where the peak position shifts from zero (black curve) toward a positive value (red curve) and is enhanced due to the dispersion of the midgap band induced by the edge reconstruction. Except for the shift of the midgap peak, the zz-57 edge reconstruction barely changes the conductance data for small gate voltage. This situation holds roughly in the energy interval $|V_g| < 0.5t_0$ and $|V_g| > 2.3t_0$. For the intermediate en-
ribbon length (see Fig. 5(a)) since increasing the ribbon size, however the intensity is strongly dependent on the length. This leads to the trans-construction on the ribbon edges (a) and (b) and at the interfaces (c) and (d). The black curves are the conductance $G_0$ of the pristine ZGNRs for comparison. Inset of (a) shows the data of $G_0$ (black line) and $G_D$ (red line) with $L = 40$ and $N_a = 80$ in the energy region $[-0.2t_0, 0.2t_0]$.

energy region $0.5t_0 < |V_g| < 2.3t_0$, the influence of the edge reconstruction is obvious. Figure 4(b) shows the width dependence of the conductance data, which also implies the edge effect is not important in wide ribbons.

Figures 4(c) and (d) show the conductance data with the ac-757 reconstruction at the interfaces between the leads and the ZGNR. A relatively large width $N_a = 200$ is taken so that the ribbon edges do not have essential effect on the bulk transport, and can be chosen as zigzag pattern for the simplicity of computation. The e-h symmetry is obviously broken. The conductance in the negative energy region is strongly suppressed by the scattering from the heptagons and pentagons at the interfaces. In the positive energy region, the influence of the ac-757 deformation is not strong, and besides the reduction of the conductance as expected, there is a small region $0 < V_g < 0.2t_0$ where the conductance is actually enhanced. Similar to the case of AGNRs, the conductance is insensitive to the ribbon sizes when the S-W reconstruction occurs at the interfaces.

Finally, we show the transmission coefficients at $V_g = 0$ through different channels $k_y$, which is related to the states localized at the interfaces of the electrodes and the GNRs[14][15]. For pristine AGNRs connected with the leads, it is the zigzag pattern that occurs at the interfaces. As well known there are energy states localized at the zigzag boundaries with momenta ranging from $2\pi/3$ to $4\pi/3$ [14][20], which are also involved in electron transmission as long as their localization length is comparable with the ribbon length. This leads to the transmission peak around $k_y = 2\pi/3$ as shown in Figs. 5(a) and (b). The peak position is not sensitive to the ribbon size, however the intensity is strongly dependent on the ribbon length (see Fig. 5(a)) since increasing the ribbon length reduces the number of the midgap states extending from one interface to the other [16].

When the ac-757 reconstruction occurs at the edges of AGNRs, the e-h symmetry is broken and the touch point of the conduction and valence bands shifts upward as shown in Fig. 2(a). As a consequence, the maximal transmission peak moves slightly from $k_y = 2\pi/3$ toward a smaller value, accompanied by additional satellite peaks as shown in Fig. 5(c). These satellite peaks arise because of the boundary condition of the zigzag interface is modified by the 2z-57 edge reconstruction.

When the S-W reconstruction occur at the interfaces, there is an additional zero energy transmission peak at $k_y = \pi/3$ with smaller intensity, besides the original one at $k_y = 2\pi/3$, as shown in Fig. 4(d). The positions of these two peaks deviate from $\pi/3$ and $2\pi/3$ for small ribbon length $L$, though they converge to $\pi/3$ and

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**FIG. 4:** (Color online.) The normalized conductance $G/M$ as functions of the gate voltage $V_g$ for ZGNRs with S-W reconstruction on the ribbon edges (a) and (b) and at the interfaces (c) and (d). The black curves are the conductance $G_0$ of the pristine ZGNRs for comparison. Inset of (a) shows the data of $G_0$ (black line) and $G_D$ (red line) with $L = 40$ and $N_a = 80$ in the energy region $[-0.2t_0, 0.2t_0]$.

**FIG. 5:** (Color online.) The transmission coefficients in different $k_y$-channels for AGNRs without any reconstructions (a, b), with the S-W reconstruction on the edges (c) and at the interfaces (d). The vertical dashed lines mark the position of $2\pi/3$.

**FIG. 6:** (Color online.) (a) is the transmission coefficients in different $k_y$-channels for AGNRs with S-W reconstruction at the interfaces with various lengths $L$. (b) is the subband structures relevant for the transport at zero gate voltage in ZGNRs with the S-W edge reconstruction (see also Fig. 2(b)). The black dashed lines mark the momenta $\pi/3$ and $2\pi/3$. 

When the S-W reconstruction occur at the interfaces, there is an additional zero energy transmission peak at $k_y = \pi/3$ with smaller intensity, besides the original one at $k_y = 2\pi/3$, as shown in Fig. 4(d). The positions of these two peaks deviate from $\pi/3$ and $2\pi/3$ for small ribbon length $L$, though they converge to $\pi/3$ and...
2\pi/3 eventually as L increases as shown in Fig. 6(a). As expected, this variation coincides with that of the zero energy momenta with the width \( N_g \) of the corresponding ZGNRs with zz-57 edge reconstruction shown in Fig. 6(b). However, these momenta given in Fig. 6(a) do not have a naive one-to-one correspondence, because the momentum \( k_x \) in Fig. 6(b) belongs to the folded Brillouin zone (BZ), while \( k_y \) in Fig. 6(a) corresponds to the unfolded BZ. In fact, for ZGNRs with zz-57 edge reconstruction, the translational symmetry is broken with unit cell doubled, then the two states with momenta \( k \) and \( \pi + k \) in the unfolded BZ are mixed leading to new states with momentum \( k \) in the folded BZ. Therefore in Fig. 6(b), the zero energy state at \( k_x = 2\pi/3 \) in the folded BZ corresponds to the mixing of two momenta \( 2\pi/3 \) and \( 5\pi/3 \) in the unfolded BZ, which match the two conducting channels with \( k_y \sim 2\pi/3 \) and \( \pi/3 \) in the leads, respectively. The same holds for the zero energy state at \( k_x = \pi/3 \) in the folded BZ, which corresponds to the mixing of the two momenta \( \pi/3 \) and \( 4\pi/3 \) in the unfolded BZ also corresponding to the two conducting channels in the leads also with \( k_y \sim \pi/3 \) and \( 2\pi/3 \). Thus, we obtain two transmission peaks at \( \pi/3 \) and \( 2\pi/3 \) in Fig. 6(a).

4. CONCLUSION AND SUMMARY

In the presence of edge reconstructions, the band structure of GNRs change substantially. For example, the e-h asymmetry may be lost completely and the midgap bands may appear in both AGNRs of ZGNRs with their edges reconstructed by the S-W mechanism. This could eventually affect the transport through GNRs, in particular those with small size, which is crucial for designing the GNR-based nano-devices.

When the S-W reconstruction occurs on the ribbon edges, the conductance \( G_D \) in the intermediate energy region around \( V_g \sim t_0 \) is suppressed considerably, in contrast, \( G_D \) changes little for \( V_g \) close to zero energy or band edges. When the S-W reconstruction occurs at the interfaces between the GNRs and the electrodes, the conductance is suppressed in the entire region of \( V_g \) for AGNRs, while the conductance of the ZGNRs shows strong e-h asymmetry, i.e., it is strongly suppressed in the negative energy region, but change only a little in the positive energy region. Therefore, to pursue high conductance of GNRs, the defects should be avoided in heterojunctions between the electrodes and the GNRs.

We also study the transmission coefficients in different channels of AGNRs with possible S-W reconstructions when \( V_g = 0 \). If the zigzag pattern occurs at the interfaces, there is only one transmission peak at \( k_y \sim 2\pi/3 \), with possible satellite peaks in the presence of ac-757 defects on the ribbon edges. However, in the presence of zz-57 reconstruction at the interfaces, two transmission peaks appears at \( \pi/3 \) and \( 2\pi/3 \) attributed to the unit cell doubled by the alternating heptagon and pentagon. Our study may be useful in designing the GNR-based nano-devices.

5. ACKNOWLEDGEMENTS

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