Bandgap engineering of zigzag graphene nanoribbons by manipulating edge states via defective boundaries

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Abstract
One of the most severe limits of graphene nanoribbons (GNRs) in future applications is that zigzag GNRs (ZGNRs) are gapless, so cannot be used in field effect transistors (FETs), and armchair GNR (AGNR) based FETs require atomically precise control of edges and width. Using the tight-binding approach and first principles method, we derived and proved a general boundary condition for the opening of a significant bandgap in ZGNRs with defective edge structures. The proposed semiconducting ZGNRs have some interesting properties one of which is that they can be embedded and integrated in a large piece of graphene without the need to completely cut them out. We also demonstrated a new type of high-performance all-ZGNR FET. Previous proposals of graphene FETs are all based on AGNRs.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
Graphene has attracted intensive research efforts due to its unique electronic and mechanical properties [1–3]. A recent experiment demonstrated a beautiful technique in fabricating graphene nanoribbons (GNRs) with atomically precise edges, suggesting the great potential of GNRs in future applications of graphene-based high-performance electronics [4]. Theoretical calculations showed that only two thirds of armchair graphene nanoribbons (AGNRs) with different widths are semiconducting, while zigzag graphene nanoribbons (ZGNRs) are gapless due to localized edge states at the Fermi level [5, 6]. It was also theoretically demonstrated that these bandgap-closing edge states survive in zigzag GNRs with a mixture of zigzag and armchair sites at boundaries [5, 7]. Recent theoretical works proved that the confinement by minimal boundaries generally does not produce an insulating GNR except for the armchair case [8, 9]. This theoretically predicted edge or orientation and width dependence of bandgap opening in GNRs provides serious limits in real applications of GNR-based electronic devices: first, gapless ZGNRs cannot be used in FETs, and second, the precise control of the width of AGNRs is required.

In this paper, using the tight-binding approach and the first principles method based on density functional theory (DFT), we derived and proved that when the number of A-site defects equals that of B-site defects at each boundary (A, B denotes two sublattices of graphene) at non-minimal boundaries, localized edge states in GNRs will be eliminated, and then a bandgap that is inversely proportional to the ribbon width will generally be open. We then showed that ZGNRs with defective boundaries that satisfy the bandgap opening conditions can be embedded and integrated in a large piece of graphene, which may have implications for the future design
of graphene-based integrated circuits. Finally, we demonstrate a new type of field effect transistor (FET) completely made of ZGNRS. Note that in all previously theoretically proposed GNR-based transistors [10], the AGNR is indispensable. It is worth mentioning here that since the long-range magnetic order is not stable in one-dimensional systems under finite temperature, we therefore stick to the non-magnetic case in this study.

2. Methods

The electronic structures have been calculated using the tight-binding approximation (TBA) or the DFT. Only the nearest-neighbor hopping energy (−2.7 eV) was taken into account in TBA calculations. DFT calculations have been performed using the Vienna ab initio simulation package (VASP) [11, 12] with the local density approximation for the exchange–correlation functional and the cut-off energy of 400 eV for the plane-wave basis set. Both approaches give essentially the same results as for the physics discussed in this work. The transport calculations have been done using a first principles approach combining the non-equilibrium Green’s function’s techniques (NEGF) and DFT via the ATK code [13–15]. In the transport calculations, the single-ζ polarization basis set is used.

3. Results and discussion

We first focus on a ZGNR with an edge structure with defects as shown in figure 1(a). The edge structure can be specified by a quadruple of segment lengths in units of the graphene lattice constant (a = 2.46 Å), (N_{B,1}, N_{A,1}, N_{B,2}, N_{A,2}). So the number of two-coordinated carbon atoms at the edge belong to the A (B) sublattice, N_A (N_B), equals N_{A,1} + N_{A,2} (N_{B,1} + N_{B,2}). It is well known that there exist edge states with E = 0 for a semi-infinite graphene with a zigzag edge if 2π/3 < k_y a ≤ π. The edge state entirely localizes at the edge for k_y a = π, and otherwise decays exponentially away from the edge [5]. When two zigzag edges form a ZGNR and the edge states from both edges interact with each other, the edge states still degenerate at k_y a = π, while a small gap that decreases exponentially with the nanoribbon width opens elsewhere. The band structure of a perfect ZGNR in a supercell corresponding to (9, 0, 0, 0) is reproduced in figure 1(b). Due to band folding, there are six bands (marked as red) corresponding to 2π/3 < k_y a ≤ π. We find that these bands originating from edge states are removed and thus an energy gap opens if N_A = N_B. An example of the band structure corresponding to a (3, 3, 3, 3) edge structure is shown in figure 1(c), and the squared wavefunctions in the inset clearly indicate they are extended states with the form, sin(k_y x), which has more nodes for larger energies. Therefore, the energy of the valence band maximum (VBM), hence the energy gap, is inversely proportional to the nanoribbon width. For the case of either N_A < N_B or N_A > N_B, some of the edge states will remain as shown in figures 1(d) and (e), though the perfectly localized edge state is destroyed. The squared wavefunctions in the insets of figures 1(d) and (e) show the edge states are exponentially decaying away from the edge, so the energy gap due to the interaction between the states at opposite edges also decreases exponentially with respect to the nanoribbon width.

![Figure 1.](image-url)
the bulk belonging to A (B) sublattice, we have the following graphene sheet with from the following arguments. Considering a semi-infinite edge states that lead to bandgap opening can be understood the same nanoribbon might provide useful implications in the possibility to tune bandgaps with different edge structures on length of the edge structure is shown in figure2(b). The variation of bandgaps with respect to the characteristic function of the nanoribbon width can be seen in figure 2(a). These two distinct behaviors of the bandgap variation as a function of bandgaps as a function of the segment length (\(N_a\)) for different widths. All bandgaps are calculated with TBA.

These two distinct behaviors of the bandgap variation as a function of the nanoribbon width can be seen in figure 2(a). The variation of bandgaps with respect to the characteristic length of the edge structure is shown in figure 2(b). The possibility to tune bandgaps with different edge structures on the same nanoribbon might provide useful implications in the design of nanoribbon-based electronic devices.

The above-mentioned condition for the elimination of edge states that lead to bandgap opening can be understood from the following arguments. Considering a semi-infinite graphene sheet with \(N_A^a (N_B^a)\) two-coordinated carbon atoms at the edge and \(N_A^b (N_B^b)\) three-coordinated carbon atoms in the bulk belonging to A (B) sublattice, we have the following equation by the conservation of coordinate numbers,

\[
2N_A^a + 3N_A^b = 2N_B^a + 3N_B^b.
\]

Since the total number of carbon atoms in each sublattice is \(N_{A(B)} = N_{A(B)}^a + N_{A(B)}^b\), the above equation can be rewritten as

\[
3(N_A^a - N_B^a) = N_A^a - N_B^a,
\]

which means the relation between \(N_A^a\) and \(N_B^a\) is the same as that between \(N_A^b\) and \(N_B^b\). The band structure of graphene in the tight-binding approximation is calculated by

\[
E(\psi_A(r)) = t[\psi_A(r) + \psi_B(r - R_1) + \psi_B(r - R_2)]
\]

\[
E(\psi_B(r)) = t[\psi_A(r) + \psi_B(r + R_1) + \psi_A(r + R_2)],
\]

where \(t\) is the hopping energy, \(\psi_A(r)\) and \(\psi_B(r)\) are the wavefunctions on A and B atoms belonging to the same unit cell at a discrete coordinate \(r\), and \(R_1\) and \(R_2\) are graphene lattice vectors as shown in figure 1(a). For \(E = 0\), equations (1) and (2) are decoupled. There are \(N_A^a\) equations with \(N_B^a\) unknowns for (1) and \(N_A^b\) equations with \(N_B^b\) unknowns for (2). So if \(N_A^a > N_B^a\), (1) will have no solution while (2) will have solutions on sublattice A. A similar conclusion will be arrived at for \(N_A^a < N_B^b\). The fact that the wavefunction will reside on the sublattice with more atoms can be observed by comparison of the insets in figures 1(d) and (e).

In practice, disorders are inevitable in the fabrication of GNRs that are involved in lithographic patterning and etching. We therefore considered a disordered edge structure as shown in figure 3: a ZGNR with one \((3, 3, 2, 3)\) unit (as shaded in the figure) plus 10 \((3, 3, 3, 3)\) units in one supercell. Here, the \((3, 3, 2, 3)\) unit can be treated as a disorder in the \((3, 3, 3, 3)\) edge structure. Our tight-binding calculations show that the disorder will induce localized states inside the bandgap (as shown in the figure) that may not contribute to transport, and compared to the edge structure without the disorder, the energy gap between extended states in the disordered structure is bigger than the bandgap of the perfect one. In real experiments, statistically speaking, the gap-opening boundary condition is always satisfied, so our findings presented here may have implications for recent experiments showing that the transport gap of GNRs is inversely proportional to the width, and independent on the orientations or edges of GNRs [16].

An interesting property of nanoribbons with a bandgap opening edge structure is that if a wide nanoribbon is joined with a narrow nanoribbon, the electronic structure of the wide nanoribbon near the Fermi energy is not altered with electrons still confined in the wide nanoribbon. An example of a nanoribbon with a width of \(L = 12\sqrt{3}a\) and a \((3, 3, 3, 3)\) edge structure joined with a nanoribbon with the same edge structure and a width of \(L = 5\sqrt{3}a\) is shown in figure 4(a). The band structure of the compound system near the Fermi energy (the conduction and valence band) in figure 4(b) is almost the same as that of the stand-alone nanoribbon shown in figure 1(c). The charge distribution of the state at VBM in figure 4(a) and the local density of states in figure 4(c) clearly indicate that the wavefunction is only localized in the wide nanoribbon. The confinement can be understood from the bandgap difference of two nanoribbons with different widths. Note that the integrated

![Figure 2](image-url)
GNRs discussed here can be also regarded as a special type of graphene antidot lattice structure proposed earlier [17]. This property makes it possible to fabricate individual nanoribbon-based electronic devices by patterning rows of holes in a large piece of graphene avoiding complete cutout and gluing them together, which might be beneficial for the integration of future graphene-based electric circuits. On the experimental side, the patterned graphene nanostructures discussed here can be obtained experimentally by using techniques such as bottom-up chemical synthesis [18], templated self-assembly of block copolymers [19] or direct writing using a helium ion beam [20]. The periodically patterned structure may be formed by first forming resist patterns on the graphene sheet followed by templated self-assembly of block copolymers in the region where the resist has been removed and etching of graphene by using the copolymer patterns as the mask. On the other hand, the random patterns can be formed by direct writing using a helium ion beam. Prior to the lithography processes, an alignment mark may be formed on the wafer by using an appropriate graphene edge as a reference so as to align the patterns in specific directions with respect to the underlying graphene lattice structure.

Finally, we show a FET completely made of ZGNRs as shown in figure 5. In all previous theoretically proposed GNR-based FETs, the AGNR is an indispensable component due to the fact that pure ZGNR is metallic. Here, the proposed FET consists of two pure ZGNR electrodes (left and right), and a ZGNR with a defective (2, 2, 2, 2) edge structure. In the inset of the figure, the current–voltage (I–V) curve is shown for the zero gate voltage. The bias range of the zero current comes from the bandgap of the defective ZGNR in the center, confirming the bandgap opening condition we derived from the tight-binding approach. The currents as a function of gate voltage for different bias voltages suggest that the on–off ratio of this proposed FET is bigger than 1000. Compared to the previously proposed all-GNR based FET that used two ZGNRs and one AGNR [10], the FET suggested here has two obvious advantages. First, the complicated contacts between differently orientated AGNR and ZGNRs are avoided. Second, the precise control of ribbon width is not required.

4. Conclusion

In conclusion, using the tight-binding approach, we derived a general boundary condition for the band gap opening in the ZGNRs with defective edges: when the number of A-site defects equals that of B-site defects, the ZGNRs are semiconducting. We further showed that the semiconducting ZGNRs generated this way can be integrated in a large piece of graphene by correctly patterning holes, which may be useful for the future large-scale integration of GNR-based devices. Finally, we demonstrated using first principles calculations for a high-performance FET completely made of ZGNRs. Results presented in this paper may be used to explain the recent experimental measurements showing
that the transport gap always exists independently of the crystallographic orientations of GNRs. We expect these findings to provide impetus for new experiments as well as motivations for new ideas in designing ZGNR-based electronic devices.

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