Edge disorder induced Anderson localization and conduction gap in graphene nanoribbons

M. Evaldsson and I. V. Zozoulenko

Solid State Electronics, Department of Science and Technology,
Linköping University, 60174 Norrköping, Sweden

Hengyi Xu and T. Heinzel

Condensed Matter Physics Laboratory, Heinrich-Heine-Universität, Universitätsstr.1, 40225 Düsseldorf, Germany
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We study the effect of the edge disorder on the conductance of the graphene nanoribbons (GNRs). We find that only very modest edge disorder is sufficient to induce the conduction energy gap in the otherwise metallic GNRs and to lift any difference in the conductance between nanoribbons of different edge geometry. We relate the formation of the conduction gap to the pronounced edge disorder induced Anderson-type localization which leads to the strongly enhanced density of states at the edges, formation of surface-like states and to blocking of conductive paths through the ribbons.

Introduction. The discovery of single layer graphene sheets[1] has generated both surprise and interest over the past few years. Surprise because pure two-dimensional sheets were for a long time thought to be thermodynamically unstable[2]. Interest because graphene shows some extraordinary properties. Its charge carriers mimic relativistic particles and can be described by the Dirac equation[1, 3, 4]. Furthermore it has shown a high mobility both at room temperature and at a high degree of doping[5]. The latter makes graphene nano ribbons (GNRs) a strong candidate for building blocks in future electronic devices[6, 7]. However, one problem GNR-electronics faces is the absence of the energy gap which makes it difficult to control electronic and transport properties of the graphene-based devices. This problem can be addressed by making sufficiently narrow GNR:s and thereby augment the energy gap. The tight-binding calculations (or solutions of the Dirac's equation based on them) indicate that the width of the gap depends sensitively on the geometry of edges and the width of the nanoribbons[8, 9].

The fundamental question of band gap engineering in graphene nanoribbons has been recently addressed in several experimental studies[7, 10, 11] whose results have been strikingly different from the expectations based on the models for ideal GNRs. In particular, the conductance of the GNR did not exhibit the metallic behavior expected for the ideal zigzag ribbons. Moreover, the experiment did not show any difference between the armchair and zigzag GNRs. It is clear that the edges and the confinement are responsible for these observations, but no consensus has been reached yet on the origin of this remarkable behavior. The factors that might lead to this behavior include scattering on rough boundaries[7, 10, 12, 13, 14, 15], imperfections on the atomic scale[7], impurity scattering[16], electron interaction and/or modification of the electronic structure due to the edge effects[17, 18], and even the Coulomb blockade effects[20]. It should be stressed however that because of computation limitations most of the reported theoretical studies such as the calculations of the mobility edge[15], conductance calculations addressing the effect of the edge disorder[12, 13, 14], as well as the DFT-based electronic structure calculations[17, 18] (predicting the gap opening in otherwise semiconducting ribbons) are performed for narrow GNRs where the widths are far from the range of widths of nanoribbons studied experimentally (such as those of Ref.10). Because any edge effect is far stronger for a narrow ribbon it is not always clear how modeling in narrow ribbons and experiments in wide ribbons relate to each other.

In this paper we present a systematic study of the conductance of realistic edge-disordered GNRs whose dimensions are similar to those studied experimentally[7, 10, 11]. Our calculations are in excellent qualitative agreement with all the finding reported by Han *et al.*[10]. We find that only very modest edge disorder is needed to induce the energy gap in the otherwise metallic GNRs and to lift any difference in the conductance between nanoribbons of different edge geometry. We relate the formation of the conduction gap to the pronounced Anderson-type localization which is induced by edge disorder and leads to the strongly enhanced density of states at the edges and to blocking of the conductive channels through the ribbons.

Model. We describe graphene nanoribbons by the standard tight-binding Hamiltonian on a honeycomb lattice,

$$H = \sum_r V_r a_r^+ a_r - \sum_{r,r'} t_{r,r'} a_r^+ a_{r'}, \qquad (1)$$

where V_r is the external potential at the site r and $t_{r,r'} = 2.7$ eV is the overlap integral between neighboring sites r and r'. The summation of r runs over the entire GNR lattice while r' is restricted to the sites next to r. We

calculate the conductance of the GNRs on the basis of the standard Landauer formalism. The GNR is divided into a central region with the edge disorder of the length L the width W and connected to two semi-infinite leads (represented by ideal ribbons of the same width W) from which electrons are injected. On the edge of the GNR we model atoms missing from the lattice by setting the appropriate hopping elements $t_{r,r'}$ to zero. For the case of the armchair GNRs sites are removed in the outermost (edge) row with the probability p (see inset in Fig. 1 for illustration). For the case of the zigzag GNRs (which are less sensitive to edge disorder), one more site (next to the already missing one on the edge) is removed in the next row with the probability p'. Note that a particular choice of disorder on the edge is not very important, see Fig. 3 below and the related discussion. As graphene is known to have few crystal defects in general[5] we do not remove sites inside the GNRs. We also disregard the effect of capturing of H-atoms by the dangling bonds at the edge which is shown to be of a minor importance for the ribbons wider than a few nanometers.[17, 18].

The conductance is calculated on the basis of the Landauer formula, $G = -2e^2/h \int dE T(E) \frac{\partial f_{FD}(E-E_F)}{\partial E}$, where f_{FD} is the Fermi-Dirac function. To compute the transmission coefficient $T(E)$ we rely on our recent implementation of the recursive Green's function technique for GNRs [19]. In contrast to other existing implementations, this method does not require self-consistent calculations of the surface Greens function, which makes it far more efficient in comparison to other methods and allows studying GNRs of realistic dimensions.

Results and Discussion. Figure 1 shows the conductance of the armchair GNRs of varying lengths ($L = 24, 500, 1000$nm) and widths ($W = 24, 50, 74$nm) for two representative edge disorders $p = 5\%$ and 30%. The ribbon widths are nominally identical to those studied by Han *et al.*[10] (where the length was $L \sim 1\mu$m). Figure 1 (a) shows the conductance of the shortest and the most narrow ribbon, 24×24nm. Although no clear energy gap is present, the conductance is strongly affected at all degrees of disorder in comparison to the case of ideal GNRs. In wider ribbons of the same length, Fig. 1(b),(c), the conductance increases more steeply which is a direct consequence of increase of the number of propagating modes in the GNR of larger width. For longer ribbons, $L \gtrsim 0.2\mu$m, the energy gap comparable to the energy interval for the lowest propagating mode opens up in the conductance. Outside the energy gap the conductance is significantly damped compared to the ribbons without disorder. Notably, the energy gap in the vicinity of the Dirac point, and the conductance outside the Dirac point are practically saturated for the edge disorder as low as $p = 2-5\%$ and they change linearly as L increases. Qualitatively the same conductance (not shown here) is obtained for the zigzag GNRs with the disorder
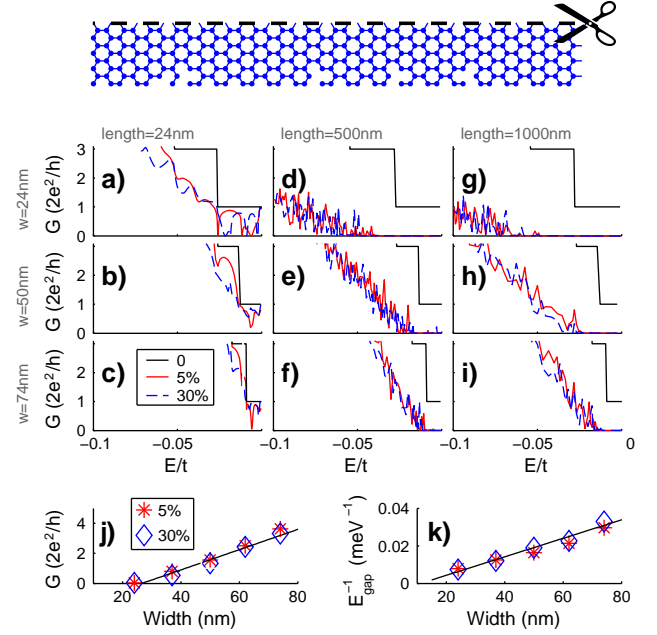

FIG. 1: (color online) (a)-(i) Conductance through armchair-GNR with edge disorder and length/width as indicated in the figure. The top inset illustrates the disordered edge with $p = 5\%$. (j) Average conductance in the energy interval $-0.061t < E < -0.049t$ versus ribbon width for $L = 1\mu$m armchair GNRs with p=5% and 30%. (k) E_{gap}^{-1} versus ribbon width for the same armchair GNRs as in (j). The solid lines in (j), (k) represent a fit as described in the text. We define the energy gap E_{gap} as the interval where $G \lesssim 10^{-3} \times 2e^2/h$ (which is consistent with the corresponding definition in [10]). Temperature $T = 0$.

strength $p = 30\%, p' = 50\%$.

In order to shed a light on the origin of the conduction gap we study the local density of states (LDOS) in the GNRs. Figure 2 (a) shows the LDOS in an infinite ribbon (with leads) of the width of $W = 24$ nm and the length of the disordered region $L = 150$ nm (defect concentration $p = 1\%$) for the energy $E = -0.02t$. [For the shown disorder configuration and concentration, the transmission of the GNR is $T \approx 0.1$, which means that there is a conductive path that allows electron to pass through the ribbon from the left to the right lead]. The LDOS shows the Anderson-type localization with a strongly enhanced intensity near the defects at the ribbon edges (note the logarithmic scale of the plots!). A closer zoom demonstrates that in the direct vicinity of the defects the magnitude of the LDOS exceeds its value in the leads by $\sim 5-6$ orders of magnitude (see inset on the top). The overall pattern of the LDOS shows hills (large LDOS) and canyons (low LDOS) whose locations are clearly correlated with the position of the disorders at the edges. With further increase of the edge disorder concentration, a surface-like state with the enhanced density forms over the entire edge of the ribbon. When the edge
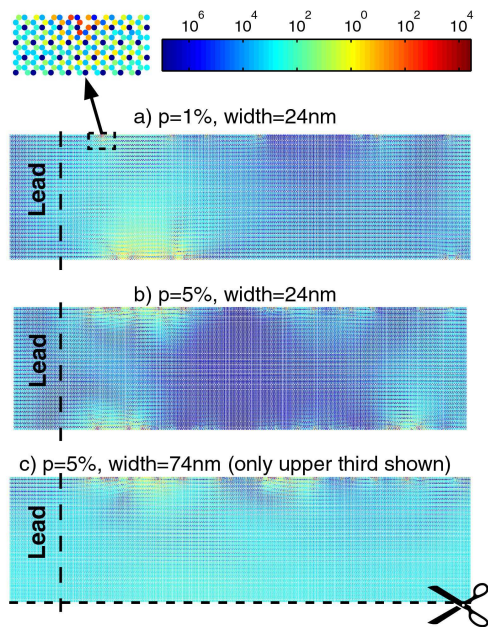
FIG. 2: (color online) The local density of states in a representative part of the edge-disordered region of infinite armchair nanoribbon (with leads) [note the logarithmic scale!]. The total width of the disordered region $L = 150$nm, $E = -0.02t$. The defect concentration (a) $p = 1\%$ (b) and (c) $p = 5\%$. (a),(b) $W = 24$nm; (c) $W = 74$nm.

disorder concentration increases the canyons deepen and widen and get extended over the whole width of the ribbon blocking the conductive pathes. This is illustrated in Fig. 2 (b) for a ribbon with the defect concentration $p = 5\%$ (transmission $T \sim 10^{-5} \times 2e^2/h$) where such a canyon (dark blue area) is clearly seen.

When the width of the ribbon increases the strong enhancement of the LDOS near the edges remains practically unaffected. This is illustrated in Fig. 2 (c), showing a wider ribbon of $W = 74$ nm with $p = 5\%$. However the disorder induced LDOS variations do not any longer extend over the entire width of the ribbon leaving a wide transmission path for electrons open. This explains the absence of the conduction gap in the wider ribbons. Note that calculated transmission in this case is $T \approx 2.5$ (with 5 propagating states in the leads).

Let us now compare quantitatively the results of our modelling to the corresponding experimental data of Han *et al.*[10]. The measured conductance has been shown to scale linearly with the GNR width, $G = \sigma \frac{W - W^0}{L}$,with $\sigma \approx 1.7$ mS and $W^0 = 15$ nm. Our fit gives the same linear dependence with close values of $\sigma \approx 5.2$ mS and $W^0 \approx 27$ nm, see Fig. 3(j). The experimental energy gap is shown to scale as $E_{gap}(W) = \frac{\alpha}{W - W^*}$ with $\alpha = 0.2$ eVnm and $W^* = 16$ nm. Our fit gives the linear scaling with $\alpha = 2.1$ eVnm and $W^* = 11$ nm (Fig. 3(k)). The experimentally extracted width $W^* \approx W^0$ was interpreted as an inactive edge width of GNR. The width of

the disorder region in our calculation is just one atomic row such that nominally inactive edge width is just a fraction of a nanometer. However, as shown above, the disorder-induced localization leads to the strong enhancement of the electron density in the surface-like states not participating in the transport. Their width on each side of the ribbon is $l_{loc} \sim 5 - 10$ nm which is consistent with calculated values of $W^*, W^0 \sim 2l_{loc}$. We therefore speculate that both W^* and W^0 can indeed be interpreted as inactive edges, whose width is however determined by the extent of the disorder induced localized surface-type states.

Our value for the energy gap is about of factor of ~ 10 larger than the experimentally extracted one. One of the reasons for this difference can be attributed to the phase breaking effects that would suppress localization of electrons. Recent experiments indicate that the phase coherence length in graphene $l_\phi \sim 3 - 5\mu$m@0.25K and $\sim 1\mu$m@1K. It is therefore reasonably to expect that in the measurements of Han *et al.* (performed at $T > 1.7K$) l_ϕ is smaller than the device length ($L \sim 1$ μm), such that the inelastic processes may play an important role in formation/suppression of the gap. In real ribbons the energy gap in the conductance might be due both to modification of the electronic structure caused by edges (as the DFT calculations show[17, 18]) as well as due to Anderson-type localization as discussed above. The later is expected to depend on the coherent length (and thus to be temperature sensitive when $l_\phi < L$), whereas the former is practically not affected by the temperature. Thus, experimental study of the conduction gap in the mK range (i.e. exploring the transitions between the regimes $l_\phi > L$ and $l_\phi < L$) might shed more light on the origin of the gap. Another factor that might strongly affect the gap formation is the electron interaction. Indeed, because the LDOS is enhanced by many orders of magnitude near the edge imperfections, it is reasonable to expect that the Hartree potential would contribute significantly to the total confining potential and thus affect the conduction gap. We therefore hope that our results will motivate further studies of electron interaction and phase breaking effects in realistic GNRs.

All the results presented above correspond to zero temperature. We also performed calculations in the temperature range 0-200K which, as expected, show gradual suppression of the gap as temperature raises. The energy broadening at 200K is roughly the same as the energy gap for the 24nm-wide ribbon and hence at this temperature the gap disappears due to the temperature averaging.

In real samples fabricated by etching techniques a variation of the ribbon width near the edges is expected to be much larger in comparison to the model used above, of the order of at least several nanometers[7, 10]. Figure 3 shows the conductance of the armchair GNR with the boundary modelled as a superposition of Lorentzians (see inset for illustration of a typical edge). We focus on the
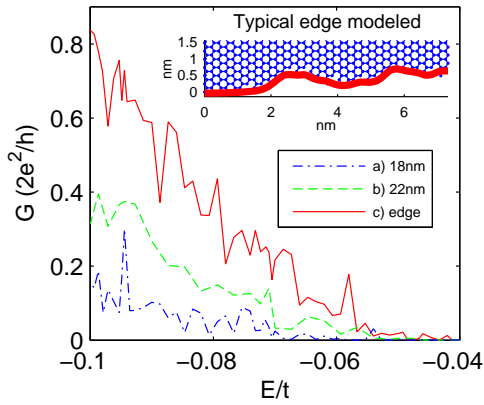
FIG. 3: (color online) Conductance for a $W = 24$nm wide armchair GNR with extended edge disorder as shown in the inset; $L = 1\mu$m. The legend indicates the minimum width of the ribbon. Each transmission curve is averaged over a set of edge contour configuration with the same minimum width. Red solid curve is averaged transmission for a ribbon with impurities in the outermost row only. Temperature $T = 0$.

1μm long and 24nm wide armchair GNR with the edge of the narrowest constriction of 18nm and 22nm. For the ribbons with the largest width variation the overall conductance is somehow suppressed and the energy gap increases. However, even though the conductance is apparently more strongly affected for the ribbons with larger width variation, the conductance of the GNRs for different models of a disordered edge is qualitatively very similar. We therefore expect that the utilized model of the imperfect edge (with missing atoms in the outermost row) already captures all the essential physics of realistic GNRs.

It is important to stress that in the striking contrast to the GNRs, the Anderson-type localization near the edges is absent in conventional heterostructure semiconductor wires because their edges are smooth on an atomic scale. It should be also noted that the strong enhancement of the LDOS near defects at the edges and formation of the surface-like state for sufficiently high disorder concentration can be detected with the help of STM [26].

Recently an alternative explanation of the energy gap in GNR:s based on the assumption of the Coulomb blockaded (CB) transport regime in GNR has been suggested by Sols *et al.* [20]. While we do not challenge their theory as such, our findings indicate that bare presence of a slightly disordered edge (much weaker that it would be required for the CB regime) is already sufficient to explain the gap formation.

Finally, we also performed conductance calculations studying the effect of charged impurities which is believed to be the main mechanism of scattering in the bulk graphene[23, 24]. We model them by adding randomly the onsite potential $V_i = \frac{e}{4\pi\epsilon_0\epsilon_r a_{cc}}$ [25], where $\epsilon_r = 5$ and $a_{cc} = 1.42$Å is the carbon-carbon atom distance. For realistic impurity densities $n \sim 1 \times 10^{16}$m^{-2} and strength $V_i \sim$

0.3eV [23, 24] we find that the conductance remains practically unaffected, which rules out the charged impurities as the origin of the energy gap formation in the GNR.

Conclusion. We study the effect of the edge disorder on the conductance on the GNRs and find that even a very modest defect concentration causes a strong Anderson type localization at the edges giving rise to the conduction gap in accordance to recent experiments.

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[1] K. S. Novoselov, *et al.*, Science, **306**, 666 (2004).
[2] L. D. Landau and E. M. Lifshitz, *Statistical Physics, Part I* (Pergamon, Oxford, 1980).
[3] K. S. Novoselov, *et al.*, Nature, **438**, 197 (2005).
[4] Y. Zhang, Y.-W. Tan, H. L. Stormer, P. Kim, Nature **438**, 201 (2005).
[5] F. Schedin, *et al.*, Nature materials **6**, 652 (2008).
[6] K. S. Novoselov, A. K. Geim, Nature Materials **6**, 183 (2007).
[7] Z. Chen, Y.-M. Lin, M. J. Rooks and P. Avouris, Physica E **40**, 228 (2007).
[8] M. Fujita, K. Wakabayashi, K. Nakada and K. Kusakabe, J. of the Phys. Soc. of Japan **65**, 1920 (1996).
[9] K. Nakada, M. Fujita, G. Dresselhaus and M. S. Dresselhaus, Phys. Rev. B **54**, 17954 (1996).
[10] M. Y. Han, B. Özyilmaz, Y. Zhang, and P. Kim, Phys. Rev. Lett. **98**, 206805 (2007).
[11] X. Li, X. Wang, L. Zhang, S. Lee and H. Dai, Science **319**, 1229 (2008).
[12] E. Louis, J. A. Vergés, F. Guinea, and G. Chiappe, Phys. Rev. B **75**, 085440 (2007).
[13] D. Gunlycke, D. A. Areshkin, and C. T. White, Appl. Phys. Lett. **90**, 142104 (2007).
[14] T. C. Li and S.-P. Lu, Phys. Rev. B **77**, 085408 (2008).
[15] D. Querlioz, Y. Apertet, A. Valentin, K. Huet, A. Bournel, S. Galdin-Retailleau, and P. Dollfus, Appl. Phys. Lett. **92**, 042108 (2008).
[16] A. Lherbier, B. Biel, Y.-M. Niquet, and S. Roche, Phys. Rev. Lett. **100**, 036803 (2008).
[17] Y.-W. Son, M. L. Cohen, and S. G. Louie, Phys. Rev. Lett. **97**, 216803 (2006); L. Yang, C.-H. Park, Y.-W. Son, M. L. Cohen, and S. G. Louie, Phys. Rev. Lett. **99**, 186801 (2007).
[18] V. Barone, O. Hod and G. E. Scuseria, Nano Lett. **6**, 2748 (2006).
[19] H. Xu, T. Heinzel, M. Evaldsson and I. V. Zozoulenko, Phys. Rev. B, 2008, in press (arXiv:0804.0375v1 [cond-mat.mes-hall]).
[20] F. Sols, F. Guinea, and A. H. Castro Neto, Phys. Rev. Lett. **99**, 166803 (2007).
[21] F. Miao *et al.*, Science **317**, 1530 (2007).
[22] S. Russo *et al.*, Phys. Rev. B **77**, 085413 (2008).
[23] T. Ando, J. Phys. Soc. Japan **75**, 074716 (2006).
[24] E. H. Hwang, S. Adam, and S. Das Sarma, Phys. Rev. Lett. **98**, 186806 (2007).
[25] J. Alicea and M. P. A. Fisher, Phys. Rev. B **74**, 075422 (2006).
[26] Y. Kobayashi, K. I. Fukui, T. Enoki, K. Kusakabe, Y. Kaburagi, Phys. Rev. B 71, 193406 (2005).