Electron Transport in Disordered Graphene Nanoribbons

Melinda Y. Han,1 Juliana C. Brant,2,3 and Philip Kim1,2

1Department of Applied Physics and Applied Mathematics, Columbia University New York, NY 10027
2Department of Physics, Columbia University New York, NY 10027
3Department of Physics, Federal University of Minas Gerais, Belo Horizonte, MG, Brazil

(Dated: October 26, 2009)

We report an electron transport study of lithographically fabricated graphene nanoribbons of various widths and lengths at different temperatures. At the charge neutrality point, a length-independent transport gap forms whose size is inversely proportional to the width. In this gap, electron transport is localized, and charge transport exhibits a transition between simple thermally activated behavior at higher temperatures and a variable range hopping at lower temperatures. By varying the geometric capacitance through the addition of top gates, we find that charging effects constitute a significant portion of the activation energy.

PACS numbers: 73.22.-b, 85.35.-p

In recent years graphene has been celebrated for its potential as a new electronic material [1, 2]. However, the absence of an energy band gap in graphene poses a challenge for conventional semiconductor device operation. Previous work [3, 4, 5, 6] has shown that this hurdle can be overcome by patterning graphene into nanometer-size ribbons or constrictions. The resulting transport gap formation can be most simply attributed to quasi 1-dimensional (1D) confinement of the carriers, which induces an energy gap in the single particle spectrum [6]. Detailed experimental studies of disordered GNRs [7, 8, 9, 10, 11, 12], however, suggest that this observed transport gap may not be a band gap. In an effort to explain these experimental results, various theoretical explanations for the transport gap formation in disordered graphene nanostructures have been proposed, including models based on Coulomb blockade in a series of quantum dots [13], Anderson localization due to edge disorder [14, 15, 16, 17, 18], and a percolation driven metal-insulator transition [20]. Further systematic experiments are necessary to distinguish between these different scenarios.

In this letter, we study the scaling of the transport gap in graphene nanoribbons (GNRs) with various widths and lengths at different temperatures. We find that four different energy scales can be extracted from transport measurement. From the scaling of these characteristic energies with GNR width and length, we find evidence of a transport mechanism in disordered GNRs based on hopping through localized states whose size is close to the width of the GNRs.

GNRs with different lengths (L) and widths (W) were fabricated following the procedures described in [3]. Most experiments in this report were performed on back-gated GNRs on a substrate of highly doped silicon with a 285 nm thick SiO2 gate dielectric. An example of such a device is shown in the inset to Fig. 1(a). We measured electron transport in a total of 41 GNRs with 20 < W < 120 nm and 0.5 < L < 2µm at different temperatures 1.5 < T < 300 K. Additionally, we fabricated top-gated GNRs with 15 nm of hydrogen silsesquioxane (HSQ) and 10 nm of HfO2 as the gate dielectric material. The increased capacitive coupling allowed a comparative study of charging effects in back-gated GNRs.

GNR conductance is strongly suppressed for a region of back gate voltages Vg near the graphene charge neutrality point [3, 4, 8, 9, 10, 11, 12], suggesting the formation of a transport gap. Fig. 1(a) shows low bias differential conductance G = dI/dV as a function of Vg for a typical GNR. The transport gap region in back gate voltage, ΔVg, can be identified in this curve by extrapolating the smoothed dG/dVg to zero [8, 12]. We note that reproducible conductance peaks appear in the gap region [8, 12] (left inset Fig. 1(a)), which are indicative of resonant conduction paths through localized states inside the transport gap. In general, resonance peaks in the gap are less than 10% of the G values outside of the gap region.

The observed transport gap, ΔVg corresponds to an energy in the single particle energy spectrum: ∆m = ħνF/2πCgΔVg/|e|, where νF = 106 m/sec is the Fermi velocity of graphene [23] and Cg is the capacitive coupling of the GNR to the back gate. This geometric capacitance is strongly dependent on ribbon dimensions and we calculate it using a finite element model, obtaining, for example, Cg = 690 aF/µm2 and Δm = 200 meV for the particular device in Fig 1.

Away from the small resonant conductance peaks, the conductance is strongly suppressed in the transport gap, and the dominant charge transport can be described by thermally excited hopping between localized states [21]. We study the thermal activation of the off-resonant conduction in this regime by measuring Gmin, the minimum conductance for a given sweep of gate voltage Vg, at different temperatures (inset to Fig. 1(b)). Fig. 1(b) shows an Arrhenius plot for Gmin(T). Evidently, thermally excited transport exhibits two distinct behaviors at low and high temperature regimes, respectively, sepa-
rated by a characteristic temperature $T^*$. At high temperatures ($T > T^*$), the transport is simply activated: $G_{\text{min}} \sim \exp(-E_a/2k_B T)$, where $E_a = 285$ K is obtained from a linear fit of the Arrehenius plot (dashed line). At lower temperatures ($T < T^*$), however, $G_{\text{min}}$ deviates from the simple activation behavior and decreases more slowly with decreasing temperature than the activated transport would imply. In this low temperature regime, the overall behavior is consistent with variable range hopping (VRH), where $G \sim \exp(-(T_0/T)^\gamma)$, with $1/3 \leq \gamma \leq 1/2$ and a constant $T_0$, determined by the characteristics of the localized states [22].

The aforementioned GNR transport gap and temperature dependent characteristics are typical of all GNRs with $W \lesssim 80$ nm, so that $\Delta_m$, $E_a$, and $k_BT^*$ can be determined for each of these narrow GNRs. These three representative energy scales are plotted as a function of $W$ in Fig 2. In this graph, we note that (i) there is a clear separation between these energy scales, setting a

FIG. 1: (a) Differential conductance of a GNR with $W$ = 36 nm and $L$ = 500 nm, plotted as a function of back gate voltage. Dashed lines highlight measurement of $\Delta V_g$. Right inset shows an atomic force microscope image of the device. Scale bar is 500 nm Left inset shows a close-up of conductance within the gap regime plotted as a function of $V_g - V_D$, where $V_D = 21$ V is the gate voltage for the charge neutrality point. (b) $T$ dependence of the minimum conductance of the same GNR in (a). The dashed line is a fit to simple activated behavior: the dotted line is a fit to variable range hopping with $\gamma = 1/2$ and $T_0 = 460$ K. An arrow highlights the position of $T^*$. Inset shows conductance versus $V_g$ at several temperatures.

FIG. 2: GNR transport energy scales: $\Delta_m$ (solid), $E_a$ (shaded), and $k_BT^*$ (open) plotted as a function of GNR width. Circles correspond to ribbons of $L = 500$ nm. Triangles, squares, and stars correspond to ribbons of length 1, 1.5, and 2 $\mu$m, respectively. The dashed lines are the fits described in the text.

general relation: $\Delta_m > E_a > k_BT^*$ for given $W$; (ii) $\Delta_m$, $E_a$, and $T^*$ depend sensitively on $W$ but not $L$; and (iii) the energy scales are reasonably well described by inverse proportion to the lateral confinement of the GNR. The length independence can be noticed by comparing characteristic energies of the GNRs with similar $W$ but different $L$ (represented by different symbols in Fig. 2), and suggests that these three energy scales are 1D intensive properties of GNRs. To show this, we define the normalized width $w = (W - W_0)/a_0$, where $a_0 = 0.142$ nm is the carbon-carbon bond length and $W_0$ is an offset introduced phenomenologically. Then, we find that all energy scales can be reasonably fit (dotted lines): $\Delta_m^0 = \Delta_m^0/w$; $E_a = E_a^0/w$; $T^* = T_0^*/w$ with the proportionality parameters $\Delta_m^0 = 36.3$ eV, $E_a^0 = 3.39$ eV, and $k_BT_0^* = 347$ meV, respectively, with $W_0 = 12$ nm held fixed for all three fits [22].

Edge disorder in the GNRs tends to induce wavefunction localization, with a localization length that decreases rapidly with decreasing energy, resulting in a transport gap with strongly localized states at energies between the mobility edges [14]. The size of this mobility gap is larger than the clean band gap of an ideal ribbon; Querlioz et al. calculate the scaling prefactor $\Delta_m^0 \approx 32.2$ eV, averaged over many configurations of edge disorder [17]. The close match of our data to theoretical prediction supports the view that atomic defects at the graphene edges create localized states. We point out, however, that the observed energy scales lie within the range of disorder potential fluctuation created by the charged impurities in the SiO$_2$ substrate [20], making it difficult to exclude the contribution of a substrate disorder induced transport gap, as discussed in a recent experiment on transport in thermally annealed GNRs [12].
On the other hand, \( E_0^a/\Delta_m^b \approx 0.1 \); i.e., the activation energy at higher temperatures is an order of magnitude smaller than \( \Delta_m \). This observation excludes the scenario that extended states carry current via thermal activation across the transport gap. Instead, we interpret the simply activated behavior as a signature of 1D nearest neighbor hopping (NNH) through localized states within the transport gap \( \Delta_B^\text{cr} \). In this picture, disorder at the edges tends to produce a rapid variation in the local density of states over the whole width of the ribbon, blocking the conductive paths and leading to a quasi-1D arrangement of localized states \cite{11}. Martin and Blanter predict \cite{19} that the energy spacing between nearest neighbor states is determined by \( \sim t'/w \), where \( t' \approx 0.2t \) is the hopping matrix element between second nearest neighbor carbon atoms in graphene, so that \( E_0^a \sim 2t' = 1.2 \text{ eV} \). Our measured value for this scaling prefactor, 3.39 eV, is somewhat larger than this prediction, which may be explained by the contribution of a charging energy to the hopping energy \( E_a \), discussed in more detail below.

The change of the transport behavior across the temperature \( T^\ast \) allows a further comparison of our data to theory. In a very recent theoretical work, the NNH and VRH crossover is calculated to occur at \( T^\ast = E_a/k_B\alpha \), where \( \alpha \approx 8 \) was estimated numerically \cite{25}. In our experiment, we obtain \( E_0^a/k_B T^\ast = 9.8 \), reasonably consistent with this theoretical prediction, lending further support to a model of charge transport via thermally activated hopping between localized states.

An alternative approach to probing the GNR transport gap is measurement of the non-linear transport characteristics \cite{2}. Fig. 3(a) shows differential conductance, \( dI/dV_b \), as a function of \( V_b \) and source-drain bias voltage \( V_g \). Transport through the GNR at finite \( V_b \) shows a strong non-linear \( I-V \) characteristic when \( E_F \) is in the transport gap regime, which is most extreme when \( V_g \) is near the charge neutrality point of the GNR (Fig. 3(b), black curve). The non-linear gap \( \Delta V_b \) can be defined where a steep increase of current appears in logarithmic scale (Fig. 3(b), green curve).

In our previous study \cite{2}, the energy corresponding to \( e\Delta V_b \) was interpreted to be the band gap of the GNR. However, this naive interpretation should be carefully reconsidered for edge disordered GNRs, where the charge transport is dominated by hopping through localized states. Indeed, from the plot of \( \Delta V_b \) vs \( W \) (Fig 3(c)), we notice that \( \Delta V_b \) depends strongly on \( L \), and is not well determined by \( W \) alone, unlike the previous three characteristic energy scales \( \Delta_m, E_a, \) and \( k_B T^\ast \). Since the charge transport in the disordered GNRs is diffusive, it is likely that electric field is driving transport in the transport gap. Indeed, if we convert \( \Delta V_b \) into the corresponding critical electric field \( E_{cr} = \Delta V_b /L \), we restore a reasonable scaling behavior, where \( E_{cr} \) depends only on \( W \) and not on \( L \) (Fig. 3(d)).

In disordered systems in which transport is dominated by hopping through localized states, applied electric field \( E \) plays a similar role to temperature. Thus we can treat the electric field as an effective temperature: \( k_B T^\text{eff} = eE L_c \), where \( L_c \) is the averaging hopping length between localized states \cite{27}. Noting that the transition from NNH dominated transport to VRH transport occurs at \( T^\ast \), we can estimate \( L_c \approx k_B T^\ast /eE_{cr} \). For most GNRs in this experiment we find that \( W < L_c < 2W \) (Fig. 3(d) inset). The fact that \( L_c \approx W \) supports our claim that hopping transport through the ribbons is effectively 1D.

Finally, we discuss the effect of Coulomb charging in GNRs. Several previous works have discussed the role of Coulomb blockade and charging effects on the transport gap in GNRs and graphene constrictions \cite{8,12,13}. In principle, in a GNR with hopping between localized states, we expect Coulomb interactions to open a soft Coulomb gap near the Fermi surface, which can be incorporated into the total hopping energy \( E_0 \) in addition to the single particle energy level spacing \( t'/w \), so that \( E_0 \approx t'/w + E_c \), where \( E_c \) is the Coulomb charging energy. \cite{19,26,28}. In order to quantify the contribution of charging energy \( E_c \) to the hopping energy \( E_0 \), we perform a comparative transport measurement on GNRs with different gate coupling. Fig. 4 shows the temperature dependent minimum conductance \( G_{\text{min}}(T) \) for a back gate
only GNR (device I) and a GNR with both top and back gates (device II) with the similar W and L. While device I has usual capacitive coupling to the back gate, (i.e., \( C_I \approx C_g \)), \( C_{II} \) for device II is much closer to the top gate, leading to a larger capacitance: \( C_{II}/C_I \approx 4 \). From the thermally activated Arrhenius behaviors in the high temperature regime (dashed lines), we obtain the activation energies of the two devices, \( E_{aI}^{\prime} = 15 \text{ meV} \) and \( E_{aII}^{\prime} = 8.4 \text{ meV} \) averaged over two devices of type I and four of type II. Considering the smaller charging energy contribution for a top gated device, smaller values of the activation energy are indeed expected, if Coulomb effects are appreciable in the GNR.

Employing the ratio \( E_{aI}^{\prime}/E_{aII}^{\prime} \approx 0.5 \), we now can estimate the charging energy contribution quantitatively. Assuming that the single particle energy level spacing \( t'/w \) is similar for both GNRs due to their similar dimensions, we obtain \( E_{aI}^{\prime} - E_{cI}^{\prime} = E_{aII}^{\prime} - E_{cII}^{\prime} = t'/w \), where the charging energy ratio of device I and II are given by \( E_{aI}^{\prime}/E_{aII}^{\prime} = C_{II}/C_I \approx 4 \). The resulting estimate for the charging energy contribution, \( E_{aI}^{\prime}/E_{aII}^{\prime} \approx 0.6 \), indicates that the Coulomb charging effect provides a substantial portion of the activation energy.

In conclusion, we investigate length and width dependent resistance scaling in GNRs. Temperature dependent and electric field dependent transport characteristics indicate that charge transport in the transport gap of the disordered GNR is dominated by localized states, where the Coulomb charging effects play an important role.

The authors thank M. Fogler, I. Martin, K. Ensslin, D. Goldhaber-Gordon, A. Young, P. Cadden-Zimansky, I. Aleiner, and B. Altshuler for helpful discussion. This work is supported by the ONR MURI, FENA, NRI, DARPA CERA. Sample preparation was supported by the DOE (DE-FG02-05ER46215). JCB was supported by CNPq, Brazil.

---

[1] A. K. Geim and K. S. Novoselov, Nat Mater 6, 183 (2007).
[2] A. K. Geim and P. Kim, Scientific American 298, 68 (2008).
[3] M. Y. Han et al., Phys. Rev. Lett. 98, 206805 (2007).
[4] Z. Chen et al., Physica E 40, 228 (2007).
[5] X. Li et al., Science 319, 1229 (2008).
[6] K. Nakada et al., Phys. Rev. B 54, 17954 (1996); K. Wakabayashi et al., Phys. Rev. B 59, 8271 (1999); M. Ezawa, Phys. Rev. B 73, 045432 (2006); Y. W. Son, M. L. Cohen, and S. G. Louie, Phys. Rev. Lett. 97, 216803 (2006); L. Brey and H. A. Fertig, Phys. Rev. B 73, 235411 (2006); V. Barone, O. Hod, and G. E. Scuseria,Nano Letters 6, 2748 (2006).
[7] L. A. Ponomarenko et al., Science 320, 356 (2008).
[8] C. Stampfer et al., Phys. Rev. Lett. 102, 056403 (2009).
[9] F. Molitor et al., Phys. Rev. B 79, 075426 (2009).
[10] K. Todd et al., Nano Letters 9, 416 (2009).
[11] X. Liu et al., [arXiv:0812.4028]
[12] P. Gallagher, K. Todd and D. Goldhaber-Gordon, [arXiv:0909.3886]
[13] F. Sols, F. Guinea, and A. H. CastroNeto, Phys. Rev. Lett. 99, 166803 (2007).
[14] D. Gunlycke, D. A. Areshkin, and C. T. White, Appl. Phys. Lett. 90, 142104 (2007).
[15] A. Lherbier, et al., Phys. Rev. Lett. 100, 036803 (2008).
[16] M. Evaldsson et al., Phys. Rev. B 78, 161407(R) (2008).
[17] D. Querlioz et al., Appl. Phys. Lett. 92, 042108 (2008).
[18] E. R. Mucciolo, A. H. Castro Neto, and C. H. Lewenkopf, Phys. Rev. B, 79, 075407 (2009).
[19] I. Martin and Y. M. Blanter, Phys. Rev. B 79, 235132 (2009).
[20] S. Adam et al., Phys. Rev. Lett. 101, 046404 (2008).
[21] Since the typical size of the transport gap in the GNRs in this work is much larger than the thermal energy, we ignore thermally excited transport via delocalized states outside of the gap.
[22] N. F. Mott, Phil. Mag., 85, 385 (1969).
[23] A. H. CastroNeto et al., Rev. Mod. Phys. 81, 109 (2009).
[24] This offset can either be ascribed to the critical length scale of the edge localized states [3, 16], to the critical percolation length scale [20], or to simply experimental inaccuracy of the width determination due to over-etching underneath the etch mask [3].
[25] A. S. Rodin and M. M. Fogler, [arXiv:0909.3820]
[26] M. M. Fogler, S. Teber, and B. I. Shklovskii, Phys. Rev. B 69, 035413 (2004).
[27] B. I. Shklovskii, Sov. Phys. Semicond. 6, 1964 (1973).
[28] A. L. Efros and B. I. Shklovskii, in Electron-Electron Interactions in Disordered Systems, edited by A. L. Efros and M. Pollak (North-Holland, Amsterdam, 1985), p. 409.