Unravelling the electrical properties of epitaxial Graphene nanoribbons

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The size-dependent electrical resistivity of single-layer graphene ribbons has been studied experimentally for ribbon widths from 16 nm – 320 nm. The experimental findings are that the resistivity follows a more dramatic trend than that seen for metallic nanowires of similar dimensions, due to a combination of surface scattering from the edges, band-gap related effects and shifts in the Fermi level that show a strong width dependence. We show that the Charge Neutrality point switches polarity below a ribbon width of around 50 nm, and that at this point, the thermal coefficient of resistance is a maximum. The majority doping type therefore can be controlled by altering ribbon width. We also demonstrate that an alumina passivation layer has a significant effect on the mean free path of the charge carriers within the graphene, which can be probed directly via measurements of the width-dependent resistivity. We propose a model for conduction that takes edge and confinement effects into account.

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There has been much interest in the properties of graphene since its isolation in 2004 [1, 2]. This is due in part to the strength of the C-C bond which leads to an in-plane Young’s modulus of order 1 TPa [3], and also to the unique electrical properties resulting from the specific band structure of this 2D material. Graphene devices suffer from a host of issues in that although the charge carriers have zero effective mass and can travel ballistically over large distances exceeding tens of microns, this is rarely seen in practice due to the influence of defects. Unlike similarly-sized metal structures, electrical transport in graphene is entirely dominated by surface effects for obvious reasons.

Given that the surface of graphene is invariably covered with contaminants from the atmosphere and chemical residues from device fabrication, this has a profound effect on its electrical properties with the result that graphene is usually unintentionally doped $p$-type. As a result of this the electrical resistivity is often orders of magnitude lower than expected and the contact resistance is often rather high [4-5], and the appropriate choice of metal electrode material is critical in order to avoid a Schottky-type contact. On the one hand, this propensity for doping potentially makes graphene useful as a gas sensor [6, 7] but on the other hand, it is difficult to control, and means that we often cannot realise its true potential of having ultra-high mobility charge carriers. Even in the absence of any ambient contaminants, the underlying substrate can have the effect of doping graphene, for example graphene on pristine SiO$_2$ has been shown to be $n$-type [8]. Of course, one can carry out investigations on atomically-clean, suspended devices under UHV and low-temperature conditions, but this is neither scalable nor commercially practical. Recent efforts have focused on ways of passivating the surface of graphene to mitigate against such unintentional doping, with varying degrees of success [5, 9-11]. This typically involves coating the graphene with a thin layer of oxide, commonly Al$_2$O$_3$ or TiO$_2$. The mode of deposition of this oxide also plays a role in determining the electrical characteristics of any devices thus made as this
determines the nature and prominence of defects. It has been shown [12] that ALD-deposited Al₂O₃ has fewer defects than thermally-evaporated Al₂O₃ and therefore graphene devices coated with it exhibit higher resistivity. Ultimately, the presence of the defects on the top and bottom surface leads to scattering of the electrons and holes within a graphene layer, and this gives rise to an effective mean free path, λ, which is significantly lower than the intrinsic one. This is similar to what happens in a doped semiconductor where the effect of doping is to increase the number of charge carriers which ultimately increases the conductivity, but the carriers end up with a reduced mobility and mean-free path.

Coupled with the fact that single-layer graphene (SLG) has no bandgap and a relatively low on/off ratio [13], it is clear that there are only very limited potential applications for this material. However, given that electrons in graphene can have relatively long coherence lengths of up to several hundred nm [14], one can make use of quantum size effects to artificially induce a bandgap. It has been shown in a number of reports in recent years that such quantum-confined structures, known as graphene nanoribbons (GNR) do indeed have a bandgap (ΔE) that scales as ΔE ∝ \frac{1}{w} where w is the width of the ribbon. The bandgap is of order 100-200 meV for 10 nm wide GNRs, reducing as the width decreases. Studies have also shown that the effective electron mobility appears to depend on GNR width [15], decreasing as ribbons get narrower. This is the same as saying that scattering and resistivity increase as ribbon width decreases. It should be pointed out that the same behaviour has been observed in metal nanowires for decades, but has not been described in terms of mobility, and is due to a combination of surface and grain-boundary scattering.

As well as the top and bottom surfaces, the edges of graphene are also responsible for scattering. It has been shown both theoretically and experimentally [16-18] that the edge termination has an effect on the resistivity, with armchair edges leading to greater scattering than
zig-zag edges. It was subsequently shown [19] that this is due to the fact for the specific case of zig-zag edges with no disorder or chemical functionalisation, the electron wavefunctions are zero at the edge, so sliding electrons (i.e. those travelling along the edge) experience no scattering. However, for the case of some edge disorder, induced by either chemical functionalisation or edge roughness, both of which result from the processing steps required to fabricate the GNRs (particularly the Oxygen plasma etching step), there can be significant edge scattering. The fact that we observe no difference in resistivity of GNRs fabricated at different orientations within the same graphene grain indicates that the level of edge disorder is significant, and the edges are not exclusively either zigzag or armchair. Given that the Fermi wavelength of electrons in graphene is of order 1 nm, it is therefore no surprise that overall, scattering at the edges of patterned graphene is almost fully diffuse [14]. There is also the effect of [13] reduced effective GNR width due to doping-induced charge depletion at the edges that can extend more than 5 nm into the GNR from either edge. There is continued interest in fabricating all-graphene devices, where the active (doped) regions as well as the interconnects are all fabricated using graphene. In order for this to lead to devices that can compete with conventional CMOS devices, and in order to have tuneable bandgaps and useful on/off ratios, the scale of these devices must therefore be in the sub. 100-nanometer range.

In this article, we explore the combined effect of surface termination and ribbon width on the resistivity of graphene ribbons with widths in the range 16 nm – 320 nm, and with or without passivation layers of Al₂O₃ deposited by electron beam evaporation. Similar studies on metal interconnects [20, 21, 22] have shown that microstructure plays just as important a role in determining resistivity as the wire cross-section, particularly for widths/thicknesses around and below the electronic mean-free path. We anticipate that for graphene, as it has very little microstructure apart from folds and occasional grain boundaries, we will instead be sensitive to the
properties of the materials in contact with the top and bottom surfaces as well as the intriguing effects due to doping/disorder at the edges, coupled with the bandgap introduced by the lateral confinement.

The problem of size and surface-related conductivity effects in electrical materials has been around for over 80 years. It is known that the resistivity of metallic thin films increases as soon as the film thickness decreases below the effective electronic mean free path. In the mesoscopic regime where structures are large enough that discrete quantum effects are not noticeable, this effect was attributed to diffuse scattering at the film boundaries by Fuchs and Sondheimer [23, 24], and is commonly referred to as the FS model. This scattering leads to the notion of an effective mean free path which then depends on thickness. As resistivity is inversely proportional to mean free path, the resistivity consequently increases as dimensions reduce. The FS model has its roots in the semi-classical Boltzmann transport equation and essentially describes how the effective mean free path is modified in the presence of surface scattering, and is based on geometric arguments. As a result, it should be possible to apply it to metals, semiconductors and even graphene, as long as appropriate band structure effects and quantum size effects are taken into account. One must be careful when investigating electronic transport at these small length scales as they are comparable to the mean-free path, $\lambda$, so the transport is part ballistic, requiring analysis within the quantum regime, i.e. the Landauer-Büttiker formalism [25, 26], while also being partly diffusive. Previous work on metallic interconnects has shown that down to cross-sectional dimensions of the order 15-20 nm, or around $\lambda/2$, the FS model combined with grain-boundary scattering models offer an excellent fit to the experimental data.

In order to gain an understanding of the size-dependence of the electrical resistivity of graphene, we fabricated a series of single-layer graphene ribbons with widths ranging from 16 to 320 nm at three different lengths: 300, 450 and 600 nm. The wires were prepared by a multistep
process involving electron beam lithography, oxygen plasma etching and metallization, as shown in Figure 1.

**Figure 1.** Process flow. (a) Graphene is transferred onto 300nm thick SiO$_2$/Si; (b) e-beam resist is spin-coated, exposed and then developed leaving a template for (c) evaporation of a 7.5 nm thick layer of Al, which is oxidised to form insulating Al$_2$O$_3$; Sample is then exposed to an Oxygen plasma which removes the graphene everywhere apart from underneath the Al$_2$O$_3$ which is then (e) removed using HCl; (f) in the final step, Au/Cr electrodes are lithographically patterned on top of the graphene device.

The monolayer graphene was grown on Cu foil (predominantly (110)) substrates by CVD (Chemical Vapor Deposition) and then transferred onto 300nm thick SiO$_2$ on p-doped Si substrates by a wet transfer method. These were then spin-coated with electron beam resist PMMA 950A2 (70nm thick) and baked at 200°C for 2mins. Graphene ribbons of different width and length, $w$ & $L$, respectively were created using a Crestec CABL-9000 High Resolution Electron Beam
Lithography System using 100pA beam current and 50kV acceleration voltage. Development was performed in 3:7 water: isopropanol solution for 10s at 25°C. A 7.5nm thick layer of aluminum was deposited by electron beam evaporation at the rate of 0.1Å/s, followed by liftoff in acetone. The sample was then treated with an oxygen plasma in a low power Diener Plasma Asher for 15s to remove the graphene that was not protected by the aluminum etching mask. After the plasma etching, the samples were soaked in 0.1 molar HCl solution for 2 days to allow complete removal of the aluminum mask, leaving the graphene ribbons. Then 5nm/50nm Cr/Au contacts were patterned and deposited on the ribbons by electron beam lithography and evaporation. Finally, for some samples, an 8nm alumina passivation layer was deposited by e-beam evaporation at the rate of 0.1Å/s. Electrical characterization of each device was performed using a Keithley 4200 Semiconductor Characterization System. Experiments were carried out at room temperature (293K) and liquid nitrogen temperature (77K) as well as at an intermediate temperature of 200K.

Figure 2. (a) One of the devices without alumina passivation layer on top. The graphene nanoribbon in the middle is 20nm wide and 600nm long. The Au electrodes are visible on either side; (b) zoom-in on the GNR region; (c) Optical image showing an array of devices arranged on a single chip.

Figure 2 shows a Scanning Electron Microscope (SEM) image of a 20 nm wide ribbon to illustrate the geometry used. To minimise contact resistance, band-bending and current-crowding
effects, the GNR is connected to wedge structures (all one piece) which are in turn connected to metal electrodes that are several microns away. In order to minimise Joule heating, the current was kept below 10 $\mu$A during testing. Subtracting the average resistance of devices that have no GNRs between wedge structures from the resistance of a normal device gives the resistance of each GNR. A plot of the measured resistivity, i.e. sheet resistance, $R_s = R \frac{w}{L}$ as a function of the wire width is shown in Figure 3(a), from which we can see that the resistivity starts to significantly increase once the wire width decreases below about 50 nm, in agreement with what others have seen experimentally and predicted [27, 28]. In Figure 3(b), we show results for a similar batch of devices, but under vacuum conditions and at three different temperatures between 77K and 293K. This shows the same overall trend, and that the resistivity decreases with increasing temperature, as expected for graphene.
Figure 3. (a) Resistivity Vs width for unpassivated GNRs (600 nm length); (b) Resistivity Vs width for a different batch of unpassivated GNRs as a function of temperature, showing the expected decrease in resistivity with increasing temperature; (c) resistivity Vs width for unpassivated and Al₂O₃-passivated devices showing that passivated devices have higher resistivity; (d) Variation of CNP on GNR width shows a transition in polarity around a width of 50 nm.

In line with what others have observed, we see that the resistivity varies from one batch to another due to varying levels of contamination arising from the specific fabrication procedures and the age of the graphene sample. It is well known that graphene is particularly susceptible to unintentional doping from the environment, and so various strategies have been employed to reduce this including a variety of chemical, thermal and physical treatments. Nonetheless, passivation is a commonly used technique to mitigate against unwanted ageing effects. We have fabricated
further devices, but with a top alumina layer, deposited as described above. One would expect that passivated devices will experience less unwanted doping, and will therefore have a higher resistivity but will otherwise display the same characteristics as the in-passivised ones, as shown by the results in Figure 3(c). In order to understand the dramatic increase in resistivity for ribbon widths below around 50 nm, we ultimately need to explore the nature of conduction in such systems. One route towards this, which is particular to 2D systems, is measurements of the charge neutrality point (CNP), or Dirac point, i.e. the gate voltage at which the conductance of a graphene device reaches its minimum value, as the unintentional dopants are compensated for at this voltage. In this work, the CNP was measured by sweeping the back-gate voltage from -5 V to 5 V. As shown in Figure 3(d), the CNP also varies with GNR width. We have observed on all devices (multiple batches comprising >100 GNRs) that the CNP switches polarity from predominantly p-type to n-type once the ribbon width is below around 50 nm. Different batches exhibit different ranges of CNP, with the most contaminated samples having a CNP of order 50V, and the cleanest samples having a CNP close to 0V. In all cases, we find the dependence of CNP on GNR width to be approximately linear.

Assembling all of this information, we can summarise the findings thus far:

- GNR resistivity increases as ribbon width decreases below 50 nm
- Passivation causes the resistivity to increase as it reduces the doping levels
- GNR resistivity increases with decreasing temperature
- CNP switches polarity for ribbon widths of around 50 nm

In order to understand this behaviour, we must recognise that there are several independent effects influencing the resistivity, including edge scattering, overall dopant concentration and carrier mobility, all of which depend on width. Single-layer graphene is a 2D material, so in
principle the charge carriers do not scatter from the top or bottom surface, and instead only see the edges. The effect of the unintentional doping from adsorbed/deposited material on the graphene surface is to create local charge puddles within the graphene, which act as local scatterers [29]. Therefore, we can describe the resistivity as comprising two terms, a bulk, width-independent value which is dominated by this doping and the width-dependent term which starts to become relevant for ribbon widths comparable to the carrier mean free path.

Although, as we have stressed, the electronic structure of graphene is fundamentally different to that of a metal or semiconductor, the FS model should still be applicable as it is agnostic with respect to any particular conduction mechanism. In this article, we will compare what it predicts against a fully quantum model. To calculate the resistivity of a nanostructure, there are a number of experimental parameters — the mean-free path $\lambda$, the proportion of electrons specularly reflected from the ribbon edges $p$, the ribbon width, $w$ and the bulk resistivity $\rho_0$. The quantity $p$ varies in the range $0 \leq p \leq 1$, where $p = 0$ and $p = 1$ correspond to fully diffuse and fully specular reflection, respectively. The very fact that we experimentally observe an increasing resistivity with decreasing ribbon width indicates that within the framework of this model $p \neq 1$, and the overwhelming experimental evidence in the literature is that $p \sim 0$, i.e. scattering from graphene edges is fully diffuse. From this model, we obtain for the width-dependent component of resistivity, $\rho_{w(w)}$:

$$\rho_w(w) = \frac{\rho_0}{1 - \frac{3(1)}{2w(1-p)} \int_1^\infty \left(\frac{1}{x^3} - \frac{1}{x^5}\right)^{1-c\frac{w}{x}} - c\frac{w}{x} \frac{dx}{x}}$$  \hspace{1cm} \text{Equation (1)}$$

This expression can be approximated to simple algebraic relationships in the limiting cases
$w << \lambda$ and $w >> \lambda$. We are in the regime where $w \sim \lambda$ in which case it is normally necessary to numerically evaluate Equation (1). However, to within a few percent, which is within the experimental error associated with resistivity measurement and uncertainty in $w$, Fuchs and Sondheimer also calculated a simple analytical approximation to Equation (1), which is given in Equation (2):

$$\rho_w(w) = \rho_0 \left[ 1 + \frac{3}{8} (1 - p) \frac{\lambda}{w} \right]. \quad \text{Equation (2)}$$

Therefore, the only unknown quantities are $\lambda$ and $p$. It is not uniquely possible to determine both from any set of resistance vs width measurements alone. What we can do however, is consider the extreme case of fully diffuse scattering as reported in Reference [13] and long mean free path. Typical values of $\lambda$ in the literature are of the order tens to hundreds of nm at room temperature [12, 14], depending on the specific type of encapsulation used. The longest mean free path reported at room temperature is of the order 500 nm for graphene encapsulated in hexagonal BN [30]. Given that we are instead using an oxide layer which is defect-rich, we expect that 500 nm will be the absolute upper limit on $\lambda$. We can use Equation (2) to predict the expected variation of resistivity on ribbon width for this extreme case, as shown in Figure 4(a), which appears to be in rather good agreement with what is seen experimentally. We have taken the uncertainty in ribbon size due to edge roughness and effective width into account by plotting two curves – the upper and lower ones correspond to ribbons 10 nm narrower and 10 nm wider than the nominal width, respectively.
Figure 4. (a) Plot of equation (2) for ribbons 10 nm narrower (upper curve) and 10 nm wider (lower curve) than the nominal ribbon width, superimposed on the data from Figure 3(a). Although the fit of the upper curve appears qualitatively good, it is based on physically unreasonable concepts. Plots are for the extreme case \( \lambda = 500 \text{ nm} \), \( p = 0 \) (fully diffuse scattering); (b) Solid line: Plot of Equation (6) for the overall resistivity of a GNR with best fit parameters \( \lambda = 150 \text{ nm}, p = 0.05 \), dashed line: plot of Equation 10 for \( \lambda = 150 \text{ nm} \). (c) Solid line: Plot of Equation (6) for another device, with best fit parameters \( \lambda = 200 \text{ nm}, p = 0.25 \); dashed line: plot of Equation (10) for \( \lambda = 220 \text{ nm} \) (d) another batch of devices with (upper curve, \( \lambda = 70 \text{ nm}, p = 0.1 \)) and without (lower curve, \( \lambda = 100 \text{ nm}, p = 0.1 \)) an Al passivation layer.

In contrast, typical values obtained for metallic nanowires are \( p = 0.25 \) and \( \lambda = 40 \text{ nm} \) [20]. Nonetheless, although the fit to the experimental data is quite good, it is not physically reasonable to assume that the mean free path is so long at room temperature or that the wires are 10 nm
narrower than their actual physical size. Imaging using SEM and AFM reveals that the GNR width fluctuates by ± 2 nm at most. Ultimately, there will of course be edge scattering, but we cannot ignore the fact that the CNP depends dramatically on ribbon width, and this must somehow be taken into account. The CNP data presented in Figure 3(d) shows that ribbons narrower than around 50 nm are predominantly $n$-type whereas wider ones are $p$-type. This is simply a consequence of the fact that the edges will tend to be oxidised and have an increased electron density and a higher Fermi level than the bulk (top and bottom) surfaces. We would expect anomalous transport characteristics at the point where the majority charge carriers switch polarity, which is also where the resistivity starts to change most noticeably. This is further revealed in the temperature dependence of resistance (Figure 3(b)), from which we extract the TCR (Temperature Coefficient of Resistance), which we find to be in the expected range of -0.001 to -0.004 Ohm/degree K [31]. However, a careful analysis of the data reveals that this has a strong dependence on GNR width, as shown in Figure 5, where we see a peak in the TCR at a GNR width of around 40-50 nm, similar to the width at which the CNP switches polarity.
Figure 5. (a) Variation of the TCR (Temperature Coefficient of Resistance) vs GNR width showing a peak at around 40 nm, close to the width at which the CNP switches sign; (b) illustration of the concept of $n$-type edges and $p$-type bulk as revealed by the width dependence of the CNP.

The peak in TCR indicates that at this width, electron-phonon scattering is enhanced. The exact mechanism behind this is as yet unclear and warrants further investigation. This is the width at which the overall GNR has equal amounts of $n$-type and $p$-type doping, and during a transport measurement, equal numbers of electrons and holes will be flowing in opposite directions, increasing the opportunities for carrier scattering. This is also around the width at which the bandgap starts to become noticeable. Multiple studies have shown that the concentration of charge carriers is increased at the edges of a GNR [17, 18, 29, 32, 33], so it is no surprise that for narrow wires, the edge states can start to dominate.

For graphene, as the dispersion relationship is linear rather than parabolic, the resistivity is determined by the quantum of conductance ($\frac{e^2}{h}$), and is of the form:

$$\rho = \frac{h}{e^2 \sqrt{\pi n}}$$  \hspace{1cm} \textit{Equation (3)}
where \( n \) is the density of charge carriers.

What Equation (2) shows us is that as the dimension of a conductor drops below the bulk mean free path, in the presence of strong surface scattering, the effective mean free path becomes defined by the width of the conductor (or whichever dimension is constrained). However, for the case of graphene, the carrier density is variable, depending on the gate voltage, and depends on the CNP. Specifically, at the Dirac point \( n = CNP \times 0.72 \times 10^{15} \, m^{-2} + n_i \) where \( n_i \) is the intrinsic carrier density [34]. Given that our measurements show \( CNP \propto (w - w_i) \), where \( w_i \) is the width at which the CNP inverts (typically 50 nm), and with a constant of proportionality, \( A \), that is unique to each sample, i.e. \( CNP = A(w - w_i) \), we can incorporate this in equation (3) to obtain an effective resistivity due to the variation in carrier density:

\[
\rho_n = \frac{h}{e^2} \frac{1}{\lambda \sqrt{\pi (n_i + 0.72A \times 10^{15}(w - w_i))}}.
\]  

*Equation (4)*

The subscript denotes that this refers to the variation in resistivity caused by variation in carrier density. This shows an even weaker dependence on width than the surface scattering term in Equation (3) and on its own is also insufficient to obtain a good fit to the data.

Although we have ascertained that there are two factors (edge scattering variation of carrier density) contributing to the width dependence of resistivity of GNRs, they are not due to different scattering mechanisms, so we cannot resort to Matthiessen’s rule to determine their combined effect. Instead, we must directly combine our findings to derive a relationship between resistivity and wire width that takes both effects into account. The approach we are taking is to define an effective mean free path, \( \lambda_w \) and by induction, \( \rho \propto \frac{1}{\lambda} \), so we can infer that \( \frac{\rho_w}{\rho} = \frac{\lambda}{\lambda_w} \). Using this relationship to re-arrange Equation (2), we find that
Replacing the mean free path with the effective mean free path in Equation (4), we find the final empirical expression for the resistivity of a GNR using the FS framework as:

\[
\rho_n = \frac{n}{e^2} \frac{1 + \frac{3}{2}(1-p)\frac{\lambda}{w}}{\lambda \sqrt{\pi(n + 0.72A \times 10^{15} (w - w_d))}}.
\]  

Equation (6)

In other words, the resistivity roughly scales as \( w^{-\frac{3}{2}} \) as opposed to \( w^{-1} \) which is the case for surface scattering alone.

In Figure 4(b), we show a best fit to the data presented in Figure 4(a), and in Figure 4(c) we show the best fit for a different device (data from Figure 3(c)). For the devices we have assessed, the best fit results are tabulated in Table 1.

| Device Number | Al Passivation layer | FS Mean free path, \( \lambda \) (nm) | Quantum model Mean free path, \( \lambda \) (nm) | Specularity parameter, \( p \) |
|---------------|----------------------|--------------------------------------|---------------------------------|-------------------|
| 1             | No                   | 150                                  | 150                            | 0.05              |
| 2             | No                   | 200                                  | 220                            | 0.25              |
| 3             | No                   | 100                                  | 105                            | 0.1               |
| 4             | Yes                  | 70                                   | 72                             | 0.1               |
These results show us that within the FS framework, the mean free path in a graphene nanoribbon device on SiO₂ can be as long as 200 nm at room temperature, and that edge scattering can cover the whole range from almost fully diffuse to 25% specular unlike earlier reports that indicate scattering is always fully diffuse [14]. In the devices investigated here, the effect of the alumina passivation layer was to increase the resistivity by reducing the mean free path, i.e. increasing the scattering within the GNR. This indicates that e-beam evaporated Al which is subsequently oxidized is in fact not particularly desirable in some respects, although it leads to increased device reliability. Measurements taken under ambient conditions show much less time variation in current-voltage characteristics of devices passivated in this way.

At this point, we should address the fact that the modified FS model we have proposed is somewhat phenomenological in nature in the manner in which we have combined it with the quantum description of graphene’s resistivity (Equation (3)), and it does provide us with an excellent fit to the experimental data. Specifically, it does not expressly explain why the charge density varies with width, which we would like to address. We should explore what is to be expected on the basis of the actual band structure of graphene and within the fully quantum Landauer-Büttiker formalism. As has been shown in Reference [27], we can also describe a GNR in terms of two distinct mean free paths, $\lambda_m$ and $\lambda_D$, due to surface and bulk defect scattering, respectively, where $\lambda_m$ is defined as $\lambda_m = w(v_\parallel/v_\perp)$ and where $v_\parallel$ and $v_\perp$ are the longitudinal and transverse electron velocities of each conduction mode (channel), respectively. This has the form

$$\lambda_m = w \sqrt{\left(\frac{2wE_f}{m\hbar v_f}\right)^2 - 1}.$$  

Equation (7)

where $E_f$ and $v_f$ are the Fermi energy and velocity, respectively, typically 0.2 eV and $1\times10^6$ m/s, and $m$ refers to the $m$th mode.
The total conductance is

$$G = \frac{2e^2}{h} \sum m \frac{1}{1+L\left(\frac{1}{\lambda_D} + \frac{1}{m}\right)}. \quad \textit{Equation (8)}$$

Where the summation is over all conduction channels (of energy $E_m$), i.e. for $E_m \leq E_f$. The number of channels is given by the number of electron modes that can fit across the GNR width, which is $2w/\lambda_F$ where $\lambda_F$ is the Fermi wavelength of the electrons. From this expression, we can calculate the effective resistivity to be

$$\rho = \frac{h}{2e^2} \left( \frac{1}{\lambda_D + 1.5w^{1.5} \sqrt{\frac{2E_f}{h\nu_f}}} \right). \quad \textit{Equation (9)}$$

This approach assumes that the transmission probability of all modes are the same and equal to 1, which is not physically reasonable as there will be scattering at the interfaces, so the calculated resistivity will need to be scaled accordingly. This expression predicts that resistivity varies mostly as $w^{-\frac{3}{2}}$, as we found phenomenologically in Equation (6). The one issue we must still address however, is that of the variation we observe in CNP Vs width. The CNP is a measure of the charge density, which is related to the Fermi level, $E_f$, so to first order we can take the assumption that $E_f$ is of the form $E_f = B(50-w)$, where $B$ is a constant and $w$ is in nm. This form takes into account the fact that wires become increasingly $n$-type (corresponding to a higher $E_f$) as width decreases. In reality, the sign of $E_f$ is not relevant for our evaluation of the mean free path, so we will only consider its absolute value. This is similar to what we found earlier when we explored conductivity
in terms of doping levels. Combining this empirical finding with the quantum calculation above, we obtain for the final expression of resistivity in a GNR assuming fully diffuse scattering at the edges:

\[
\rho = \frac{h}{2e^2} \left( \frac{1}{\lambda_{D} + 1.5W^{1.5}} \sqrt{\frac{2E|S|\lambda_{D} - w}{h\nu_f}} \right)^{\frac{3}{2}}.
\]

Equation (10)

In Figure 4, we show the fits of this formula to the resistivity Vs width data, which are very similar to the fits obtained using our modified FS model, and with two fitting parameters: bulk mean free path (\(\lambda_{D}\)) and scaling factor, which we assume to be the same for all conduction modes. The values for \(\lambda_{D}\) that we obtain are in Table 1, and are very close to those found from the modified FS model, with the greatest deviation occurring for the device with the least diffuse edge scattering. The key fact here is that one can describe the transport in terms of the semi-classical Boltzmann equation with a quantum correction and obtain values for the mean free path and edge scattering parameter which is what one would use to describe a metallic system. Our results show that edge scattering is not always fully diffuse, and on average tends to be around 10% specular. Similar fits can be obtained using a fully quantum approach but where we assume fully diffuse edge scattering, with similar or slightly longer mean free paths. Using this model, we find that the mean free path is up to 220 nm for unpassivated devices and down to 72 nm for Alumina-passivated ones.

To summarise, we have shown that graphene nanoribbons with dimensions below 100 nm display some unusual characteristics not seen in larger structures, namely significant edge scattering, a CNP that switches sign at a GNR width of around 50 nm, and evidence for a peak in
the electron-phonon scattering rate at or around the same width. The addition of an alumina passivation layer may reduce sensitivity to atmospheric conditions but it also significantly reduces the mean free path for conduction. We have demonstrated that the width-dependence can be explained equally by a quantum model which assumes fully diffuse edge scattering and a model based on the Fuchs-Sondheimer model for partly diffuse surface scattering but with slightly shorter mean free paths.

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