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Strain-induced suppression of weak localization in CVD-grown graphene

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Abstract
We investigate the magnetic-field- and temperature-dependent transport properties of CVD-grown graphene transferred to a flexible substrate (Kapton) and subjected to externally applied strain. In zero magnetic field, a logarithmic temperature-dependent conductivity correction, resulting from strong electron–electron interaction, becomes weaker with the application of strains as large as 0.6% because of an increased rate of chiral-symmetry-breaking scattering. With the application of a perpendicular magnetic field, we also observe positive magnetoconductance at low temperature ($T = 5$ K) due to weak localization. This magnetoconductance is suppressed with increasing strain, concomitant with a rapid decrease of the intervalley scattering rate ($\tau^{-1}_i$). Our results are in good agreement with theoretical expectations and are consistent with a strain-induced decoupling between graphene and its underlying Kapton substrate.

1. Introduction
Graphene, a one-atom thick carbon film, has received a significant amount of research attention due to its unique electronic properties since it became experimentally available [1–3]. In contrast to conventional two-dimensional (2D) materials, such as Fe [4], Mg and Au thin films [5], quantum interference in pure graphene is affected by carrier chirality. Chirality originates from pseudo-spin, an additional quantum number, and inhibits the backscattering as a result of the unusual Berry phase of $\pi$ [6, 7]. Thus, in contrast to weak localization observed in normal metals where the Berry phase is $2\pi$ and constructive interference enhances back scattering, weak anti-localization (WAL) accompanied by a negative magnetoconductance (MC) at low field is expected in graphene at low temperature. However, this theoretically suggested WAL is expected to be seen only in defect-free (or suspended) graphene samples and is suppressed by a trigonal warping scattering rate ($\tau^{-1}_w$) that breaks time-reversal symmetry within a single valley and becomes more significant when the density of carriers is high [8, 9]. In addition, WAL is also eliminated at a high chirality breaking rate ($\tau^{-1}_z$) due to surface ripples, grain boundaries and dislocations [10–12]. Accordingly, weak localization (WL) is readily observed in imperfect graphene samples already harboring defects and is sensitive not only to the inelastic phase breaking scattering rate $\tau^{-1}_\phi$ but also (in contrast to normal metals) to a variety of elastic scattering mechanisms that mix chirality.

Despite expectations of WAL in relatively clean graphene with high mobility, WL in graphene has been widely reported and experimentally observed [13–15]. This is especially true for large-area graphene grown by chemical-vapor deposition (CVD) where impurities, defects and grain boundaries are omnipresent. The presence of WL is attributed to the dominance of intervalley scattering occurring at a rate ($\tau^{-1}_i$) that reflects the presence of short range interactions related to atomically sharp defects and impurities. This intervalley scattering occurs between different Dirac cones with opposite pseudo-spins, thus allowing backscattering. Therefore, WL in
Graphene sheets were grown on 25 nm-thick Cu foils by a well-developed CVD method as described in previous studies [29, 30]. The graphene sheets were identified using micro-Raman spectroscopy with a 532 nm laser source and were characterized by a large 2D to G intensity ratio (I_2D/I_G ≥ 2) as well as peak locations (G ~ 1580 cm^{-1}, 2D ~ 2700 cm^{-1}) as shown in figure 1 [31–33]. After growth, a 1–2 μm thick poly(methyl methacrylate) (PMMA) was spin cast onto the graphene. The Cu was then removed by etching in Fe(III)NO_3. Next, the PMMA supported graphene sheets were transferred onto the flexible Kapton substrates pre-patterned with Cr(6 nm)/Au(60 nm) contact pads arranged in a Hall bar geometry.

Strain was applied by bending the Kapton substrates using a specially-designed copper piece as illustrated in the inset of figure 1. The amount of strain was evaluated by a deviation from the zero strain position of the G and 2D peaks as measured by Raman spectroscopy [21–23]. Besides, under high uniaxial strain (>20%), a band gap opening is theoretically suggested due to the merging of two inequivalent Dirac cones [24]. Additionally, a strain-induced pseudo-magnetic field has been detected up to hundreds of Tesla which is approximately uniform across the distorted regime created by intentionally fabricated triangular nanobubbles on a graphene sheet [25]. These results are in good agreement with theoretical proposals [26–28].

Here we show, for CVD-grown graphene, that externally applied strain suppresses WL in a systematic way. Quantitative analysis of strain-induced changes in MC reveals a suppression of WL that arises because of a significantly decreased intervalley scattering rate. However, the phase coherence length remains relatively invariant in the considered strain range, because of an unexpected decrease in dephasing rate that compensates a decreased diffusivity. We speculate that our observed puzzling decrease in dephasing rate may be attributed to a strain-induced decoupling between the graphene and the underlying Kapton substrate.

2. Sample preparation and measurements

Graphene sheets were grown on 25 μm-thick Cu foils by a well-developed CVD method as described in previous studies [29, 30]. The graphene sheets were characterized by large 2D to G intensity ratio (I_2D/I_G ≥ 2) as well as peak locations (G ~ 1580 cm^{-1}, 2D ~ 2700 cm^{-1}) as shown in figure 1 [31–33]. After growth, a 1–2 μm thick poly(methyl methacrylate) (PMMA) was spin cast onto the graphene. The Cu was then removed by etching in Fe(III)NO_3. Next, the PMMA supported graphene sheets were transferred onto the flexible Kapton substrates pre-patterned with Cr(6 nm)/Au(60 nm) contact pads arranged in a Hall bar geometry.

Strain was applied by bending the Kapton substrates using a specially-designed copper piece as illustrated in the inset of figure 1. The amount of strain was evaluated by the classical derived formula [34] given by ε = 4ht/d^2, where h is the peak height of the curvature, t is the total thickness of PMMA/graphene/Kapton, and d is the span of the Kapton arc measured at the copper base. Prior to electrical measurement, gold wires were attached to Cr/Au contact pads by indium dots. Measurements were taken consecutively on the same sample under different strains without breaking the gold wire contacts. Care was also taken to avoid excess heating of the sample from the soldering gun given that PMMA polymer is not high-temperature resilient. However, attempts to characterize samples with curvature opposite to that shown in the inset of figure 1 gave rise to electrical shorting of the contacts with the base of the copper holder and also introduced difficulties in repairing broken contacts.

Transport measurements were carried out using a LR700 17 Hz AC resistance bridge on samples loaded into a Quantum Design physical property measurement system. The temperature can be controllably varied from 5 to 300 K and magnetic fields up to 7 T applied perpendicular to the graphene sheets.

3. Results

Figure 2 shows a logarithmic temperature dependence of normalized conductivity from 5 to 150 K at zero strain. This dependence extends to higher temperature (~250 K) at the highest strain of 0.6%. The conductivity is normalized with respect to the value measured at T_0 = 5 K [4], i.e.

\[
\Delta \sigma^N(T) = \frac{\sigma(T) - \sigma(T_0)}{\sigma(T_0)} = A_R \ln \frac{T}{T_0} \tag{1}
\]

where A_R is the normalized prefactor of the ln(T) dependence. However, at temperatures on the order of 150 K and above, optical phonons are frozen out [3] and the acoustic electron–phonon interaction dominates. The temperature boundary for the onset of electron–phonon scattering for graphene is marked by the Bloch–Grüneisen temperature given by T_BG ≈ 54/kB n cm/K where n is the density of carriers, measured in units of 10^{12} cm^{-2} [35, 36]. For our sample, n spans from 1.45 to 1.70 × 10^{13} cm^{-2} at 300 K based on the Hall effect measurements performed under each of those strains (indicating n is essentially constant under various strains). Such n values correspond to a T_BG ranging
from 206 K to 223 K, which is in good agreement with our experimental observation (figure 2) that the logarithmic corrections to the conductivity are unaffected by phonons at \( T < T_{BG} \). In addition as shown in the inset to figure 2, \( A_R \) drops from 1.2 and 0.6 to the same value of 0.3 for two different samples with strain \( \varepsilon \) applied over the range 0–0.6%. As will be discussed in section 4.2, we attribute this strain-induced reduction in \( A_R \) to a decrease in the Fermi-liquid constant \( F_0 \).

As shown by the data in figure 3, the experimentally determined correction to the magnetoconductance (MC), defined as \( \Delta \sigma (B) = \sigma (B) - \sigma (B = 0) \), is positive as would be expected for weak localization (WL). The data taken at 5 K (symbols) clearly show that WL as measured by \( \Delta \sigma (B) \) is uniformly suppressed at all magnetic fields with increasing strain (\( \varepsilon \)). Insight into the underlying mechanisms responsible for this strain-induced suppression of WL is gained by using theory [8] which for graphene explicitly provides an expression for the correction to MC in the diffusive regime as,

\[
\Delta \sigma (B) = \frac{e^2}{2\pi^2 \hbar} \left[ F \left( \frac{1}{\tau_{\phi}^{-1}} \right) - F \left( \frac{1}{\tau_{\phi}^{-1} + 2\tau_i^{-1}} \right) \right] - F \left( \frac{\tau_B^{-1}}{\tau_{\phi}^{-1} + \tau_i^{-1} + \tau_e^{-1}} \right)
\]

where

\[
F (z) = \ln z + \Psi \left( \frac{1}{2} + \frac{1}{z} \right), \quad \tau_B^{-1} = \frac{4eDB_\perp}{\hbar}
\]

and \( \Psi (x) \) is the digamma function. Here, we average the magnetic field over the parabolically curved graphene plane as

\[
B_\perp = \frac{d}{l} B
\]

where \( l \) is the length of the curved portion of the strained sample. Since the spin–orbital coupling in graphene is negligible [37, 38], here only the perpendicular component of applied magnetic field contributes to the phase breaking events. As previously noted \( \tau_{\phi}^{-1} \) is the phase breaking rate due to inelastic scattering whereas the intervalley scattering rate \( \tau_i^{-1} \) and intravalley scattering rate \( \tau_e^{-1} = \tau_{\phi}^{-1} + \tau_i^{-1} \) (comprising the sum of trigonal warping and other chirality breaking terms) are elastic scattering rates.

The diffusivity, \( D = \hbar v_F / 4e^2 R_s \sqrt{\pi \hbar} \), can be directly calculated using the measured values of sheet resistance \( R_s \), carrier density \( n \) (determined from the Hall effect) and the known value \( v_F = 10^6 \text{ m s}^{-1} \) for the Fermi velocity of graphene. The dependence of \( D \) on \( \varepsilon \) shown in figure 4(a) reveals a dramatic decrease from 43 to 6 cm² s⁻¹ when strain increases from 0% to 0.6%. This decrease is primarily due to the significant rise in \( R_s \) from 2.1 to 18 kΩ/□. These strain-induced trends are consistent with the physical notions that lattice distortion decreases the nearest-neighbor hopping energy [9, 39] and at the same time introduces in the graphene sheet more ripples and defects which act as scattering centers.

Implementation of a least-squares regression algorithm using the data (symbols) in figure 3 in equation (2) allows us to extract out the strain dependence of the three unknown scattering parameters: the phase breaking scattering rate (\( \tau_{\phi}^{-1} \)), the intervalley scattering rate (\( \tau_i^{-1} \)) and the intravalley scattering rate (\( \tau_e^{-1} \)). The quality of the fits is shown by the solid lines in figure 3 and the dependence of the best-fit scattering rates, \( \tau_{\phi}^{-1} \) and \( \tau_i^{-1} \), on strain plotted in figure 4(b). From the fits we find that \( \tau_{\phi}^{-1} \) exceeds by three orders of magnitude the values of \( \tau_{\phi}^{-1} \) and \( \tau_i^{-1} \), thereby rendering the last term in equation (2) negligible and the determination of \( \tau_e^{-1} \) imprecise. For these reasons we only plot \( \tau_{\phi}^{-1} \) and \( \tau_i^{-1} \) in the figures.
The decrease of $\tau_i^{-1}$ with increased strain, which looks counterintuitive at first glance, may be explained in terms of weakened Coulomb interactions as a result of strain-induced decoupling between the graphene sheet and the Kapton. The graphene is more tightly attached to the Kapton than it is to the PMMA substrate. The graphene is strongly attached to the PMMA substrate, according to E McCann et al [8], it is reasonable to expect that the intervalley scattering rate is less than the phase breaking rate ($\tau_i^{-1} < \tau_\phi^{-1}$). In our case, the ratio of $\tau_i^{-1}/\tau_\phi^{-1}$ drops from 0.814 to 0.095 as strain increases from 0 up to 0.6%.

Moreover, the dramatically reduced intervalley scattering is the key factor to the suppression of WL. In graphene, restricted by the chiral nature of the carriers, backscattering is inhibited within a single valley. However, it can be restored by intervalley scattering through mixing two valleys with opposite helicities (−1 and +1). Therefore, when strain decreases the intervalley scattering rate ($\tau_i^{-1}$) and increases the intervalley scattering length ($L_i^{-1}$), WL becomes suppressed due to the reduction of backscattering in the more strained samples.

The decrease of $\tau_\phi^{-1}$ with increased strain, which looks counterintuitive at first glance, may be explained in terms of weakened Coulomb interactions as a result of strain-induced decoupling between the graphene sheet and the Kapton substrate. The graphene is strongly attached to the Kapton before transfer onto the Kapton. When under externally applied strain, the graphene is slightly separated from the underlying Kapton. Ripples are an important source of lattice deformation leading to the destruction of WL as shown in previous studies [10]. For graphene loosely attached to its substrate, according to E McCann et al [8], it is reasonable to expect that the intervalley scattering rate is less than the phase breaking rate ($\tau_i^{-1} < \tau_\phi^{-1}$). In our case, the ratio of $\tau_i^{-1}/\tau_\phi^{-1}$ drops from 0.814 to 0.095 as strain increases from 0 up to 0.6%.

4. Discussion

4.1. Weak localization under strains

Weak localization (WL) in graphene is theoretically predicted to be suppressed under strain [9, 11, 12], since by altering the hopping energy, lattice distortion is equivalent to a local effective gauge field that breaks time-reversal symmetry within each Dirac cone. In our case, we did not wash the PMMA off the graphene after transferring the PMMA/graphene bilayer onto the Kapton. Accordingly, the graphene is more tightly attached to the PMMA than it is to the Kapton. As a result, strain applied to our PMMA/graphene samples by bending the Kapton substrates into the convex shape shown in the inset of figure 1 introduces compressive strains and hence more ripples on the PMMA/graphene and thus weakens the coupling between PMMA/graphene and the underlying Kapton. Ripples are an important source of lattice deformation leading to the destruction of WL as shown in previous studies [10]. For graphene loosely attached to its substrate, according to E McCann et al [8], it is reasonable to expect that the intervalley scattering rate is less than the phase breaking rate ($\tau_i^{-1} < \tau_\phi^{-1}$). In our case, the ratio of $\tau_i^{-1}/\tau_\phi^{-1}$ drops from 0.814 to 0.095 as strain increases from 0 up to 0.6%.

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observed previously in micro-sized graphene samples \[10, 14, 41\]. Given the relatively large size of our graphene samples \((L \gg L_\phi)\), mesoscopic fluctuations are averaged over large-area inhomogeneities \[15\] and such observed CF may arise from impurities associated with the scattering centers on the substrates \[42\]. Therefore, a decreased coupling between the graphene sheet and the Kapton leads to a reduced interaction with those impurities, thereby less CF under higher strains. Likewise, such a decoupling may also reduce the short range interactions \(V_o\) with point defect scattering centers on the Kapton substrates, which results in the remarkable decrease of \(\tau^{-1}_i \approx V_o^2 \) \[3, 43\].

4.2. Electron–electron interaction under strains

The weakened coupling between graphene and underlying Kapton substrates caused by strain also affects the electron–electron (EE) interaction and hence the value of \(A_R\), the prefactor for the \(\ln(T)\) dependence of conductivity (see figure 2 inset). For a 2D system at low temperature, the correction to conductivity \((B = 0\) T\) usually comes from the additive contributions of an EE interaction term and a WL term, which can be written as \[36, 44\]

\[
\delta \sigma_{2D} = \delta \sigma_{ee} + \delta \sigma_{WL}.
\]

with \[35, 36\]

\[
\delta \sigma_{ee} = -A(F_0^0) \frac{\pi^2}{2} \ln \frac{h \tau_i^{-1}}{k_B T}
\]

and \[8, 35\]

\[
\delta \sigma_{WL} = -\frac{\pi^2}{2} \ln \left[ 1 + 2 \frac{\tau_i^{-1} - 1}{\tau_i^{-1} - 1 + 1} \frac{\tau_i^{-1} - 1}{\tau_i^{-1} - 1 + 1} \right]
\]

where the coefficient \(A(F_0^0)\) is determined by the strength of the interaction and \(F_0^0\) is the Fermi-liquid constant. Given that in our case \(\tau_i^{-1} \ll \tau_i^{-1} \ll \tau_i^{-1} \sim \tau_i^{-1}\) (these rates are all independent of temperature except \(\tau_i^{-1}\)), the second term in equation (7) is negligible when considering temperature dependence, and the first term is always much smaller compared to the value of equation (6) at all strains, implying a low temperature \((B = 0\) T\) correction to conductivity mainly from EE interaction. However, for the sample with \(R_s < 1\) k\(\Omega\), a higher \(\tau_i^{-1}\) is observed, suggesting that \(\delta \sigma_{WL}\) may become comparable to \(\delta \sigma_{ee}\), hence explaining a higher \(A_R\) for this particular sample. Therefore, when conductivity is normalized with respect to its value at 5 K, the temperature dependence is specifically derived as

\[
\Delta \sigma^N(T) \approx \Delta \sigma_{ee} = A_R \ln \frac{T}{T_0}
\]

where

\[
A_R \approx A(F_0^0) = 1 + c \left[ 1 - \ln \left( 1 + \frac{1 + F_0^0}{F_0^0} \right) \right]
\]

with the parameter \(c\) denoting the number of triplet channels involved in EE interactions. In our case, we have \(h \tau_i < k_B T < h / \tau_i\), which means two electrons from different valleys do not contribute to the number of triplet channels, thus constraining \(c\) to the value \(c = 7\) \[35\]. Moreover, unlike the conventional 2D system, large angle scattering (e.g. backscattering) is strongly suppressed by the constraint of chirality, which suggests a relatively small absolute value of \(F_0^0\) when compared to that of GaAs and Si \[35, 45\]. In our system, \(\tau_\phi^{-1}\) is very high, and based on Hall measurements taken at \(T = 5\) K under various strains, the carrier density \(n\) is essentially constant. This means strain does not cause further trigonal warping \(\tau_\phi^{-1} \propto n^2\). Thus the huge intravalley scattering rate \(\tau_\phi^{-1}\) is mainly due to a large chirality breaking rate under strain. Hence, \(F_0^0\) becomes more negative and gives rise to a drop in \(A_R\).

On the other hand, strain also decouples graphene from its substrate by introducing more ripples. According to the nature of the Coulomb interaction in graphene on a substrate, despite a slightly decreased dielectric constant (less screening), the inelastic scattering by charged impurities can be suppressed as a result of an increased distance \(\langle r_{\phi} \rangle\) between external charged impurity and the graphene sheet, which behaves as an exponential factor \(e^{-\langle r_{\phi} \rangle}\) in Coulomb potential \(\varphi(q)\) \[46, 47\]. So even a small separation is able to give a noticeable decrease in \(\varphi(q)\). This argument clarifies the puzzling reduction in \(\tau_\phi^{-1}\). However, since \(\tau_\phi^{-1}\) does not show a dramatic strain-induced decrease, the coulomb potential should not change considerably by strain. Otherwise, it would have overwhelmed the increase in the magnitude of \(F_0^0\) by chirality breaking and lead to an increase in \(A_R\).

5. Conclusion

In summary, we find that WL in CVD-grown graphene can be suppressed by applying external strains, which can be explained in terms of reduced intervalley scattering as a result of the strain-induced decoupling between PMMA/graphene and Kapton substrates. Also, we attribute the logarithmic temperature dependence of conductance at zero magnetic field mainly to the EE interaction below the Bloch–Gruneisen temperature in highly resistive samples \((R_s > 2\) k\(\Omega\)). The small value of the prefactor, \(A_R\), at high strain is attributed to the huge chirality breaking rate where large angle scattering is possible and leads to a relatively high amplitude of angle-averaged Coulomb potential. Our results not only provide a coherent understanding of strain-affected transport properties in graphene, but also give a penetrating insight into the different scattering processes in graphene when subjected to external strains.

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