Activation of magnetic moments in CVD-grown graphene by annealing

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Effects of annealing on chemical vapor deposited graphene are investigated via a weak localization magnetoresistance measurement. Annealing at 300 °C in inert gases, a common cleaning procedure for graphene devices [1, 2], is found to raise the dephasing rate significantly above the rate from electron-electron interactions, which would otherwise be expected to dominate dephasing at 4 K and below [3–7]. This extra dephasing is apparently induced by local magnetic moments activated by the annealing process, and depends strongly on the backgate voltage applied.

I. INTRODUCTION

The first graphene samples made into electronic devices came from flakes exfoliated from bulk graphite, and were only a few microns in size [8, 9]. The discovery that graphene could also be grown over large areas, using a chemical vapour deposition (CVD) process on metal films, opened up many technological possibilities that were unimaginable with exfoliated flakes. One application proposed in the early days of graphene research was spintronics, making use of potentially long spin lifetimes in carbon-based materials. Although the hope of graphene spintronics persists, experimental realizations remain less impressive than theoretical proposals [10, 11].

Despite the promise of CVD-grown graphene for technology, this growth technique tends to yield samples with more defects, such as carbon vacancies and domain boundaries, compared to exfoliated graphene [12]. In fact, defects like those found in CVD graphene are believed to be a potential source of magnetic moments that would spoil spintronic applications[13]. At the same time, the interaction of magnetic moments with conduction electrons in graphene is predicted to be different than what is observed in conventional metals, offering new avenues to realize correlated electronic states [14].

Here, we present an unexpected characteristic of defects in CVD graphene: we show that the relatively gentle annealing process typically used to remove residues from graphene devices [1, 2, 15–20] significantly enhances the quantum mechanical phase-breaking (dephasing) rate measured via weak localization (WL) [5], and that this dephasing is due to the activation of magnetic moments. Although data from phase coherent measurements at cryogenic temperatures might seem unrelated to applications at room temperature, our results imply that these activated defects create a fast mechanism for spin relaxation that would limit the use of CVD graphene in spintronics. At the same time, this finding sheds light on the microscopic origin of local moments in this form of graphene, and demonstrates that samples grown by CVD will be a fruitful platform to study interactions between magnetic moments and electrons in graphene.

II. EXPERIMENTAL METHODS

Multiple samples were prepared by transferring commercial CVD graphene (ACS Materials Co., MA) onto n-doped Si wafers with a 295 nm SiOx dielectric. In some samples, a 30 nm HfO2 film was grown by atomic layer deposition (ALD) at 100 °C on the SiOx before transferring graphene [Fig. S1 inset]. Hall bars with a width and a length of 30 µm by 30 µm were defined by electron beam lithography. Cr/Au (5/80nm) ohmic contacts were used to apply a bias current, I, and measure longitudinal and transverse voltages, Vxx and Vxy [Fig. 1(a)], then Vxx was converted into resistivity ρ or conductivity σ ≡ ρ−1 using the geometric aspect ratio of the Hall bar. The carrier density, n, was tuned using the backgate voltage, VG, and measured via low-field Hall effect.

FIG. 1. (a) Schematic of the sample geometry and measurement setup. Pink indicates CVD graphene, yellow indicates Au/Cr electrodes. The dielectric stack shown here includes the SiOx. (b) Schematic of the thermal annealing setup. (c) Change in conductivity as a function of charge carrier density, before and after Ar annealing. Inset: same data as a function of gate voltage. (d) Magnetoresistivity before and after Ar annealing, with fits to WL theory. Fit parameters before annealing: \(\tau_i^{-1}=160±45 \text{ ns}^{-1}, \tau_e^{-1}=33±2 \text{ ns}^{-1}\); after annealing: \(\tau_i^{-1}=215±90 \text{ ns}^{-1}, \tau_e^{-1}=60±5 \text{ ns}^{-1}\). Fits included data over a larger field range [21].

Annealing was performed in Ar, N2, forming gas (5%
H₂/95% N₂, hereafter H₂/N₂), or under vacuum, using a simple thermal annealer [Fig. 1(b)]. Samples wire-bonded into ceramic chip carriers were loaded into the annealer, then pumped to a base pressure of 3 × 10⁻³ mbar (gas anneal) or < 10⁻⁵ mbar (vacuum anneal). For gas annealing, the chamber was pumped-and-flushed, then the flow rate adjusted using a needle valve until a pressure of 200 mbar was attained. Samples were annealed for 1 hour at 300 °C, then cooled to room temperature in the same atmosphere as the annealing step, and immediately transferred to the cryostat. After evacuating the cryostat and adding He exchange gas, samples were cooled to 4.2 K for measurement. The total air exposure time after annealing was less than one minute.

III. RESULT AND DISCUSSION

Figure 1(c) compares σ(nₛ) of a sample before and after annealing in Ar. The conductivity itself rose slightly, while the gate voltage required to reach the charge neutrality point, Vₘₙₖ, decreased from 88 V to 18 V. The quantum correction to the perpendicular magnetoconductivity, σ(B⊥), also changed after annealing [Fig. 1(d)]. To interpret this change, phase (τ⁻¹) and intervalley (τ⁻¹) scattering rates were extracted from Δσ(B⊥) = σ(B⊥) − σ(0) using fits to the standard WL expression for graphene [5, 22],

\[
\Delta \sigma(B⊥) = \frac{e^2}{\pi \hbar} \left[ F\left(\frac{\tau_{g}^{-1}}{\tau_{\psi}^{-1}}\right) - F\left(\frac{\tau_{g}^{-1}}{\tau_{\psi}^{-1} + 2\tau_{i}^{-1}}\right)\right],
\]

where \(\tau_{g}^{-1} = 4eDB⊥/h\), \(F(z) = \ln(z) + \psi(0,5 + z⁻¹)\), diffusion constant \(D = \frac{\sigma_{nh}e^2}{2\pi\epsilon\epsilon_{r}m_{e}}\) and \(v_f = 10^{6}\) m/s for graphene. A third term reflecting intravalley scattering is omitted here for clarity as it did not affect the extracted \(\tau_{\psi}^{-1}\) or \(\tau_{i}^{-1}\), but was included in the fitting [21].

Both \(\tau_{g}^{-1}\) and \(\tau_{i}^{-1}\) rose due to annealing. The rise in \(\tau_{g}^{-1}\) reflects increased short-range scattering due to changes in the interaction between graphene and SiO₂ dielectric, caused by the annealing itself [2]. The significant rise in \(\tau_{\psi}^{-1}\) is more surprising, and is the central focus of this work.

Electron-electron (e-e) and electron-phonon (e-p) interactions are well known dephasing mechanisms in metallic systems. Below 50 K in graphene the e-e rate dominates, and at 4 K the e-p rate is negligible in comparison [5–7]. The e-e dephasing rate in graphene is [5, 7, 22–24]:

\[
\tau_{ee}^{-1} = \frac{k_{B}T}{\hbar} \left(\frac{\ln\left(\frac{\pi}{2}g\right)}{g}\right), \quad g = \frac{\sigma_{n}e^2}{\epsilon^2}.
\]

For the data in Fig. 1(d), Eq. 2 predicts \(\tau_{ee}^{-1} = 33\) ns⁻¹ before annealing, matching the measured value \(\tau_{ee}^{-1} = 33±2\) ns⁻¹. After annealing, the calculated value from Eq. 2 is barely changed, \(\tau_{ee}^{-1} = 32\) ns⁻¹, but the measured value rises to \(\tau_{ee}^{-1} = 60±5\) ns⁻¹. Fig. 2 extends this analysis to a range of \(n_s\). Before annealing, measured \(\tau_{ee}^{-1}\) coincide almost exactly with calculated \(\tau_{ee}^{-1}\) [Fig. 2(c)]. After annealing, on the other hand, \(\tau_{ee}^{-1}\) exceeds \(\tau_{ee}^{-1}\) everywhere, with the difference, \(\tau_{ee}^{-1} ≡ \tau_{ee}^{-1} - \tau_{ee}^{-1}\), growing larger with \(n_s\) [Fig. 2(d)]. Taken together, Figs. 2(c) and 2(d) indicate that e-e interaction dominates dephasing in samples as deposited, but new interactions emerge in Ar-annealed samples that add 10’s of ns⁻¹ of excess dephasing.

As an inert gas, Ar is not expected to create chemical modifications to graphene at temperatures of only a few hundred °C. Indeed, transmission electron microscope investigations have confirmed that anneals such as those performed here do not affect perfect graphene, but that polymer resist and other residues begin to break down in the 150 to 250 °C temperature range, and radicals formed during that process may interact with dangling bonds at graphene defect sites [20]. Our observations are consistent with the reports of Ref. 20, that the influence of annealing on defect activation is via the thermal decomposition of residues rather than the gas itself.

Figure 3 compiles the excess dephasing rate, \(\tau_{ee}^{-1}\), for a variety of annealing recipes, and leads to several observations. When annealing is performed in vacuum, \(\tau_{ee}^{-1}\) is very small, rising only to ~10 ns⁻¹ (constant in \(n_s\)) even after 5 hours of annealing. For anneals in a gas environment, \(\tau_{ee}^{-1}\) is significantly larger, growing with \(n_s\) by an amount that does not depend on the choice of gas. \(\tau_{ee}^{-1}\) also increases at low \(n_s\), most noticeably for samples annealed in H₂/N₂.

Upon closer examination, the rise in \(\tau_{ee}^{-1}\) at low \(n_s\) in the
H$_2$/N$_2$-annealed data from Fig. 3a appears to be related to the gate voltage applied, rather than specifically to the reduction in carrier density, with the minimum in $\tau_{ee}^{-1}(V_G)$ consistently occurring at $V_G = 0$. The charge neutrality point, $V_{n=0}$, was much larger for H$_2$/N$_2$ ($V_{n=0}=60$ V) compared to Ar ($V_{n=0}=18$ V) or N$_2$ ($V_{n=0}=31$ V), so larger negative $V_G$ was applied to H$_2$/N$_2$-annealed samples to reach the low density regime. Further insight into the importance of $V_G$, independent of $n_s$, is gained by measuring the $n_s$-dependent dephasing rate for a particular annealed sample, repeatedly shifting the Dirac point through exposure to ambient atmosphere [Fig. 4] [25]. ① represents $\tau_{ee}^{-1}$ for the sample immediately after an hour of annealing in H$_2$/N$_2$ ($V_{n=0}=60$ V), ②-④ represent subsequent one hour exposures to ambient atmosphere ($V_{n=0}=92,109,140$ V), then ⑤ represents an additional one hour anneal in H$_2$/N$_2$ ($V_{n=0}=70$ V). Calculated $\tau_{ee}^{-1}$ for the different exposures fall along a single curve [Fig. 4(a)], reflecting the fact that $\sigma(n_s)$ does not change through these different steps. Measured $\tau_{ee}^{-1}$ also fall along a single curve for the low-$n_s$ part of each scan, for ①-④. However, the onset of the upturn in $\tau_{ee}^{-1}$ at high $n_s$ shifts to higher and higher densities with exposure to air, while the minimum in $\tau_{ee}^{-1}$ remains pinned to $V_G = 0$ [arrows in Fig. 4(b)]. This seems to indicate that the upturns in $\tau_{ee}^{-1}$ and $\tau_{xx}^{-1}$ at high density are connected to the electric field between the graphene and the backgate rather than to the carrier density itself.

The persistent upturn in $\tau_{xx}^{-1}$ at large $n_s$ (strongly negative $V_G$), even after extended exposure to air, indicates that the activation of a dephasing mechanism by annealing is robust. A second annealing step (⑤) following the multiple exposures to air results in $V_{n=0}$ shifting back to 70 V, while $\tau_{xx}^{-1}$ increases above even the values observed after the first anneal (③). As was the case for ①-④, the minimum in $\tau_{xx}^{-1}$remains at $V_G = 0$.

Just as the activated dephasing mechanism does not seem to depend on the choice of annealing gas, it also does not depend on the substrate. In order to test for a possible influence from the substrate [26–29], Fig. 3 includes data from a sample, annealed in Ar gas, on a wafer where ALD-grown HfO$_2$ covers the SiO$_x$ [Fig. S1 inset]. HfO$_2$ layers are amorphous when grown at the low temperatures used here, presumably with a defect density and type different from those found in thermal silicon oxide [30]. The mobility of the HfO$_2$ sample was similar to the samples on SiO$_x$, in contrast to previous reports of mobility enhancement by screening due to high-$\kappa$ dielectrics[31, 32]: this may indicate that the mobility in our samples is limited by defects in the graphene rather than charged-impurity scattering. More importantly, the measured $\tau_{xx}^{-1}$ for the HfO$_2$ sample is nearly identical to that of the SiO$_x$ sample [21]. From this, we tentatively conclude that the defects relevant to the dephasing enhancement lie in or on the graphene itself, rather than in the substrate.

The role of annealing temperature was also explored (data not shown). Below 200 °C, annealing had minimal effect on $\tau_{xx}^{-1}$ for any of the inert gases. At 250 °C the effect was similar to, though less strong than, the 300 °C data shown here. For
Magnetic moments are believed to emerge at graphene defects, including vacancies [13, 36], impurities [11, 37], and strain fluctuations [38, 39]. In most cases, the interactions of defect-bound moments with conduction electrons are predicted to strengthen at low carrier density due to weaker screening [13, 36, 40, 41]. We find, in contrast, that \( \tau_\text{\textit{e}} \) increases at higher \( n_\text{s} \) and, more importantly, depends more on the electric field due to \( V_G \) than on the carrier density itself since gas annealed samples show the minimum near \( V_G = 0 \). It may be, therefore, that the magnetic moments being activated by gas annealing are of a different type than has been previously reported in experiment or studied theoretically.

**IV. DEPHASING MECHANISM**

The effect of an in-plane magnetic field on WL can reveal spin-related mechanisms for dephasing. Magnetic fields, \( B_\parallel \), applied in the plane of a graphene sheet influence \( \sigma(B_\parallel) \) in two ways. First, ripples in the graphene create an out-of-plane local magnetic field, fluctuating randomly across the graphene even when \( B_\parallel \) is applied exactly along the average plane of the sample. These out-of-plane components break time reversal symmetry locally, yielding an additional dephasing mechanism that grows quadratically with \( B_\parallel \) [33]. Second, \( B_\parallel \) aligns local magnetic moments with Lande g-factor \( g \) once \( g_\mu_B B_\parallel \gg k_B T \). When free to rotate, these moments contribute to dephasing through spin flip scattering of conduction electrons, but that mechanism is suppressed when the moments are aligned by \( B_\parallel \) [33–35].

Cooling the graphene samples in a dilution refrigerator equipped with a two-axis magnet enabled \( \sigma(B_\parallel) \) measurements with finite \( B_\parallel \), at temperatures low enough that spins could be aligned by \( B_\parallel \) before dephasing due to ripples was significant. Fig. 5 shows WL data for an \( \text{H}_2/\text{N}_2 \)-annealed sample at 100 mK. (This sample was annealed at 350 °C to maximize \( \tau_\text{\textit{e}} \).) The line shape of \( \sigma(B_\parallel) \) changes when in-plane field is applied, and fits to Eq. 1 confirm that \( \tau_\text{\textit{e}} \) drops from 95 ns\(^{-1} \) (\( B_\parallel = 0 \)) to 24 ns\(^{-1} \) at \( B_\parallel = 0.7 \) T, where \( g_\mu_B B_\parallel/k_B T \sim 10 \) with \( g = 2 \). Ripples would have induced the opposite effect (increased \( \tau_\text{\textit{e}} \) for higher \( B_\parallel \)). This data shows that spin flips induced by magnetic moments are the predominant mechanism for excess dephasing after annealing, contributing at least 70 ns\(^{-1} \).

![FIG. 5. Perpendicular field magnetoconductivity lineshape, \( \Delta \sigma(B_\perp) \), for an \( \text{H}_2/\text{N}_2 \)-annealed sample changes dramatically with in-plane magnetic field, \( B_\perp \). Solid lines are fits to Eq. 1. Extracted \( \tau_\text{\textit{e}} \) decreases from 95±10 ns\(^{-1} \) at \( B_\perp = 0 \), to 24±3 ns\(^{-1} \) at \( B_\perp = 700 \) mT (\( T = 100 \) mK).](image-url)
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SUPPLEMENTARY INFORMATION

Section 1. Thermal annealer

The sample rests on a copper sheath covering a halogen projector bulb. The temperature of the copper sheath is monitored with a thermocouple, and the power of the bulb is adjusted with a variable transformer to keep the copper at the desired temperature. Sample temperatures were confirmed to match those of the copper using a mock sample with a fine-wire thermocouple glued on the wafer surface. Temperatures of the thermocouple and copper were found to match under both in gas and in vacuum annealing conditions.

Section 2. Weak localization fitting process and analysis

Weak localization fits were made to resistivity data, instead of conductivity as expressed in Eq. 1 (main text), using

\[ \rho(B) = \alpha(B - B_0) + \rho_0 - \rho_0^2 \frac{e^2}{\pi \hbar} \left[ F \left( \frac{\tau_{\alpha}^{-1}}{\tau_{\phi}^x} \right) - F \left( \frac{\tau_{\beta}^{-1}}{\tau_{\phi}^x + 2 \tau_i^{-1}} \right) - 2F \left( \frac{\tau_{\beta}^{-1}}{\tau_{\phi}^x + \tau_i^{-1}} \right) \right] \]

The third term in the equation above, missing from Eq. 1, was found to be strongly suppressed by the enormous \( \tau_i^{-1} \) in CVD graphene and therefore irrelevant to the extraction of \( \tau_i^{-1} \) and \( \tau_\varphi^{-1} \). This equation adds several parameters to those two rates, which appear in Eq. 1:

- An offset field \( B_0 \) was included to take into account the residual field in our superconducting magnet.
- The zero-field resistivity \( \rho_0 \equiv \rho(B = B_0) \).
- A linear-in-\( B \) term, \( \alpha(B - B_0) \), was added to the resistivity, accounting for any offset of voltage probes that would mix Hall and longitudinal voltages.

Data were fit to this equation using a multi-step process involving two magnetic field ranges: \( \pm 10 \) mT [c.f. Fig. 1d] and \( \pm 100 \) mT [Fig. S1]. In general, fine scans over the smaller field range enabled a more accurate determination of the smaller rate, \( \tau_\varphi^{-1} \), whereas coarser data over the larger field range was important for determining \( \tau_i^{-1} \), and the value of \( \tau_i^{-1} \) itself affected the determination of \( \tau_\varphi^{-1} \). The fitting process was:

1. Determine \( \rho_0 \) and \( B_0 \) from Lorenzian fits to the peak of \( \rho(B) \)
2. Fit \( \pm 100 \) mT range to determine \( \alpha, \tau_\varphi^{-1}, \tau_i^{-1} \)
3. Fixing \( \alpha, \rho_0, B_0 \) and using \( \tau_\varphi^{-1} \) and \( \tau_i^{-1} \) from above as initial parameters, fit \( \pm 10 \) mT range.
4. Fixing \( \alpha, \rho_0, B_0, \tau_\varphi^{-1} \) and using \( \tau_i^{-1} \) from above as initial parameter, fit \( \pm 100 \) mT range. If there is a significant change in \( \tau_i^{-1} \), repeat from step 2.
5. Error bars for \( \tau_\varphi^{-1} \) were determined by trying different combinations of \( \tau_i^{-1} \) and \( \tau_\varphi^{-1} \) to check how far \( \tau_\varphi^{-1} \) could be off before the fit was visually bad.

Section 3. Graphene on HfO

Figure 3 in the main text shows \( \tau_i^{-1} \) from a sample on HfO-covered SiO, annealed in Ar. In addition to this data, a full set of measurements was taken on this sample. Fig. S2 shows the measured \( \tau_\varphi^{-1} \) and expected \( \tau_\varphi^{-1} \) before any annealing occurred, confirming \( \tau_\varphi^{-1} \) is consistent with \( \tau_\varphi^{-1} \). After annealing in vacuum for 1 hour, \( \tau_\varphi^{-1} \) and \( \tau_\varphi^{-1} \) are nearly unchanged, again consistent with each other. Only after annealing in Ar does \( \tau_\varphi^{-1} \) rise significantly above \( \tau_\varphi^{-1} \), as it does for samples directly sitting on SiO. One difference between graphene on HfO2 and graphene on SiO2 was that \( V_{n=0} \) did not shift significantly due to the annealing on HfO2, whereas on SiO2 the shift was often several 10’s of volts. Instead, \( V_{n=0} \) for the HfO2 remained within 10 V of zero.
FIG. 1. Magnetoconductivity before and after Ar annealing, with fits to WL theory (black solid lines), over the larger ±100 mT range. Inset: Schematic of the sample including a HfO$_2$ ALD layer (grey) on top of the SiO$_x$.

FIG. 2. Measured ($\tau_{\text{meas}}^{-1}$) and expected ($\tau_{\text{ee}}^{-1}$) dephasing rates for graphene on a HfO$_2$-covered substrate (a) before annealing, (b) after vacuum annealing, and (c) after Ar annealing.