Role of grain boundaries in tailoring electronic properties of polycrystalline graphene by chemical functionalization

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\textbf{Abstract}

Grain boundaries, inevitably present in chemical vapor deposited graphene, are expected to have considerable impact on the development of graphene-based hybrid materials with tailored material properties. We demonstrate here the critical role of polycrystallinity on the chemical functionalization of graphene comparing ozone-induced oxidation with remote plasma hydrogenation. We show that graphene oxidation and hydrogenation occur in two consecutive stages upon increasing defect density: an initial step in which surface-bound functional groups are generated, followed by the creation of vacancies. Remarkably, we find that hydrogenation yields homogeneously distributed defects while ozone-induced defects are preferentially accumulated at the grain boundaries eventually provoking local cracking of the structure. Supported by quantum simulations, our experimental findings reveal distinct electronic transport regimes depending on the density and distribution of induced defects on the polycrystalline graphene films. Our findings highlight the key role played by grain boundaries during graphene functionalization, and at the same time provide a novel perspective to tailor the properties of polycrystalline graphene.

The growing activity in controlling the electronic properties of graphene via chemical functionalization is paving the way for novel solid-state electronic systems based on graphene composite materials \[1, 2\]. The hydrogenation to graphene \[3\], the fluorination to fluorographene \[4\], and the production of graphene oxide \[5, 6\] have been extensively studied and hold great potential for hybrid graphene-organic electronics \[7–10\], sensing \[11, 12\], and transparent flexible electrodes \[13, 14\]. To date, chemical vapor deposition (CVD) of graphene provides the best tradeoff between high quality material and large area production \[15, 16\]. The polycrystalline nature of these CVD graphene films \[17\], containing defective grain boundaries interconnecting individual single crystaline grains, is known to deteriorate the outstanding properties of graphene \[18, 19\] but, on the other hand, has also been shown to exhibit great potential for sensing applications \[20\]. Since covalent modification of the graphene basal plane goes hand in hand with the partial conversion from sp\(^2\) to sp\(^3\) bonding configuration, the introduction of such type of defects to the graphene lattice renders inevitable a marked degradation of its electronic and transport properties. Therefore, the exploitation of the full potential of graphene and graphene-based composites requires a precise control of the chemical nature of the formed defects together with their spatial distribution, as well as a comprehensive analysis of the influence of grain boundaries with enhanced chemical reactivity on the global chemical patterning and resulting material properties \[21, 22\]. At the same time, this knowledge should be complemented by a quantitative understanding of the corresponding electronic transport properties. In this work we demonstrate that ozone-induced oxidation and remote-plasma hydrogenation of CVD-grown graphene can be utilized to produce graphene materials with a precise control of the generated defect characteristics. By means of Raman spectroscopy and x-ray photoelectron spectroscopy
(XPS) we gain insight into the crystallographic and chemical nature of the generated defect states. We find that the produced structural imperfections can be derived from two different processes dominated either by the creation of surface-bound functional groups or the generation of vacancies. An analysis of the defect density, assessed by Raman spectroscopy and XPS, reveals that surface-bound epoxide and ether groups are the dominant functional species for graphene oxidation but show weak Raman activity. Raman mapping measurements show defect clustering around graphene grain boundaries for graphene oxidation with progressive etching of such grain boundaries at higher oxidation stages, whereas hydrogenation results in homogeneously distributed defect sites. Finally, we show that the corresponding decrease of the field effect mobility of ozone-treated and hydrogenated graphene devices are clearly correlated to the type and distribution of the induced defects, and can be very well reproduced by quantum transport simulations including epoxide and vacancy accumulation at graphene grain boundaries and homogeneous hydrogen distribution, respectively.

**Results and discussion**

Polycrystalline graphene films grown by CVD on Cu foils and transferred as described in the Methods section were exposed to either an ozone flux with a controlled temperature \( T \) or to remote hydrogen plasma at a defined acceleration voltage \( V_{acc} \) between the graphene sheet and the plasma electrodes. The effect of the ozone treatment and the hydrogenation on the crystal structure of the graphene films was investigated by Raman spectroscopy. Figures 1(a) and (b) show waterfall plots of Raman spectra for graphene ozonized at different \( T \) and hydrogenated at different \( V_{acc} \). The spectrum of the pristine films exhibits negligible defect-related features (\( D \) around 1340 cm\(^{-1}\)) and an integrated area Raman intensity ratio of \( A_{2D}/A_G \geq 4 \), confirming that the starting material is high quality, predominantly monolayer CVD graphene. A clear change in the spectra is observed upon ozone and hydrogen exposure, similar to previous work \([14, 23, 24] \).

For increasing \( T \) or \( V_{acc} \), a strong increase of the defect-related Raman mode (\( D \)) around 1340 cm\(^{-1}\) is accompanied by the evolution of the second defect-related mode (\( D' \)) around 1620 cm\(^{-1}\) and a vanishing of the second-order mode (\( 2D \)) around 2680 cm\(^{-1}\). These observations are consistent with literature and are attributed to the generation of lattice defects resulting in the gradual degradation and destruction of the graphene film \([25] \).

A more detailed evaluation of such data is presented in figures 1(c) and (d), where the Raman intensity ratio \( I_D/I_G \) as well as the integrated area Raman intensity ratio \( A_{2D}/A_G \) are plotted as a function of \( T \) and \( V_{acc} \). Starting from a pristine sample, \( I_D/I_G \) increases for increasing oxidation and hydrogenation until a maximum is reached at \( T = 70 \) °C and \( V_{acc} = −275 \) V. For further increasing \( T \) and \( V_{acc} \), \( I_D/I_G \) decreases again. \( A_{2D}/A_G \) starts at a value of 4 in both graphs and undergoes a strong breakdown for increasing \( T \) and \( V_{acc} \). The behavior of the \( D/G \) and \( 2D/G \) intensity ratios with varying lattice defects has been theoretically studied and can be used to extract the density of defects within the graphene sheet \([25–27] \).

Such calculations, adopted from Giro et al \([26] \) and Ferreira et al \([27] \), are drawn in figures 1(c) and (d) as red solid lines representing \( I_D/I_G \) and \( A_{2D}/A_G \) versus the relative defect density \( n_D/n_C \). The \( n_D/n_C \) scale, representing the ratio of the defect density \( n_D \) and the density of carbon atoms \( n_C \) in the graphene film, was adjusted to show agreement between the theoretical predictions and our experimental data. The experimentally observed peak for the \( I_D/I_G \) ratio and the breakdown of the \( A_{2D}/A_G \) ratio occur for a rather high relative defect density, close to 0.1%. Since for many applications a high number of defects is not beneficial, and due to the steep increase of \( I_D/I_G \) with temperature, a better way of accessing the low defect regime for the process of ozonization is essential. This can be achieved by an ozone treatment at low temperatures (in our case 50 °C) and varying the exposure time (see supplementary figure S1 for further information on defect generation). In comparison to the effect of the processing parameter temperature, the increase of \( I_D/I_G \) with the exposure time is less abrupt, allowing for better control in the low defect density range, which is particularly relevant for most applications of CVD graphene. The Raman analysis confirms that we have established processes for graphene oxidation as well as hydrogenation that allow for a precise control of the induced number of defects in the range \( 10^{-5} < n_D/n_C < 0.02 \).

The nature of such generated crystallographic defects is rich, as illustrated in figure 2(a) where different types of defects are presented and classified into two general groups: (i) surface bound functional groups, e.g. epoxide (C–O–C), carbonyl (C=O), carboxyl (O–C=OH) (not depicted), hydroxyl groups (C–OH) and hydrogenated carbon atoms (C–H), and (ii) vacancies resulting from carbon etching. According to Eckmann et al \([28] \), Raman spectroscopy can also be used to probe the nature of lattice defects in graphene by evaluating the intensity ratio of the defect-related Raman modes \( I_D/I_G \). Figure 2(b) shows \( I_D/I_G \) for ozone treatments at different \( T \) and hydrogenation with varying \( V_{acc} \) as a function of \( n_D/n_C \), which was extracted from the \( I_D/I_G \) Raman intensity ratio. Starting at high values of \( I_D/I_G \) ~14.5 in the low defect density range, we find a transition to significantly lower \( I_D/I_G \) values with increasing defect density for both processes. Eckmann et al found an \( I_D/I_G \) ratio of ~13 to be the characteristic footprint of sp\(^3\)-hybridized defects in graphene and an \( I_D/I_G \) ratio of
∼7 to represent vacancy-type defects [28], indicated by horizontal dashed lines in figure 2(b).

Based on this analysis, as highlighted in the graph, we can conclude that the formation of surface-bound functional groups containing sp³-hybridized defects is dominant for ozone treatments at T < 70 °C, whereas process temperatures above 70 °C lead to the predominant generation of vacancies. The same interpretation applies for hydrogenation with $V_{acc} = -275 \text{ V}$ as a borderline between sp³-hybrid formation and the generation of vacancy-type defects. Interestingly these transitions show a clear coincidence with the maxima in the $I_{2D}/I_G$ versus $n_D/n_C$ curves of figures 1(c) and 1(d). Error bars reflect the corresponding standard deviations. Red solid lines represent theoretical calculations of $I_{2D}/I_G$ [26] and $A_{2D}/A_G$ [27] as a function of the relative defect density $n_D/n_C$, which were adjusted to fit the experimental data.
A detailed understanding of the chemical nature of the generated defects has been obtained from XPS. Figure 3 shows the normalized XPS spectra of the C1s signal, the O1s signal and the Cu2p signal comparing the cases of evolving oxidation (a) and hydrogenation (b). For ozone treatments at temperatures above 70 °C we find a drastic decrease of the total C1s signal and the total Cu2p signal. At the same time we observe a sharp increase of the O1s signal, which is accompanied by the evolution of a Cu2+ shakeup signal. The coincidence of the decreasing total carbon signal with the increasing total oxygen and the copper oxide related Cu2+ mode [30] indicates etching of the graphene sheet and the oxidation of the partially unprotected underlying copper substrate for T > 70 °C. This is further supported by the observation of strongly increasing CuO related contributions in the Cu2p 3/2 (supplementary figure S3) and the O1s (strong mode at 529.6 eV in figure 3(a)) (see also supplementary figure S4) signals. While oxidation of the Cu substrate upon ozone treatment yields an energetic upshift of the Cu2p signal compared to the pristine case, a clear shift towards lower energies, representative of a partial reduction of the Cu substrate [31], is present for highly hydrogenated samples. Further, in comparison to graphene oxidation, the less pronounced decrease of the total carbon signal observed for the case of hydrogenation confirms the assumption of a less severe carbon etching process. Figures 3(c)–(e) help to shed light on the actual binding configuration of carbon atoms in the graphene sheet upon oxidation ((c) and (d)) and hydrogenation (e) (see supplementary figures S5–S7 for detailed XPS evaluation of C1s). The relative contributions of oxidized graphene GO (figures 3(c) and (d)) and sp3 C–C bonds within the C1s signal are plotted versus T, t and Vacc. The graphs also include the corresponding relative defect density as derived from the Raman data. Besides the expected increase of GO with increasing T and t we find a clear correlation between the content of sp3 C–C species and nD/nC for oxidation as well as hydrogenation, which strongly suggests that the D-mode intensity in the Raman spectra of graphene is dominated by defects containing sp3-hybridized carbon atoms without any extrinsic...
adatom. Since such conformation is most likely to occur at vacancies in the graphene network, figures 3(c) and (e) indicate an enhanced vacancy generation for $T > 70 \, ^\circ \text{C}$ and $|V_{acc}| > 275 \, \text{V}$, in perfect agreement with the Raman data from figure 2 and XPS data from figures 3(a) and (b).

Thus, $70 \, ^\circ \text{C}$ and $V_{acc} = -275 \, \text{V}$ correspond to threshold values of the ozone and hydrogen treatment below which the generated defects have an sp$^3$ character due to oxygen or hydrogen adsorption and above which vacancy-type defects are induced. We would like to note that due to the small difference in binding energy of C–C–sp$^3$ and C–H, their separate contributions could not be resolved with our XPS setup. However, considering figure 2(b) where $-275 \, \text{V}$ marks the threshold voltage above which vacancy generation is dominant, we can conclude that also in the case of hydrogenation, C–C–sp$^3$ containing groups related to vacancies and not C–H groups are the major contribution to the XPS signal and dominate the corresponding Raman D-mode intensity. In contrast to the temperature dependent oxidation and graphene hydrogenation in figures 3(c) and (e), the time dependent ozone treatment at low substrate temperature of $50 \, ^\circ \text{C}$ in figure 3(d) yields high GO contents without significant formation of vacancies, which could be used to produce high quality functional graphene films. Furthermore, a detailed analysis of the C1s XPS core level spectra (supplementary figures S5–S7) shows that oxidation at elevated temperature favors the generation of vacancies in combination with carbonyl and carboxyl groups while longer ozone exposure at low temperature leads to predominant incorporation of hydroxyl, epoxide or ether groups, in good agreement with the predictions of theory [32–34]. Interestingly, while the oxidized graphene (GO) content measured by XPS reaches values as high as 40%, the relative defect density derived from Raman is orders of magnitude lower. We argue (see supplementary information) that this can be the case if the induced defects do not cause strong Raman D-peak features, as has been predicted for certain arrangements of epoxy groups, ether groups as well as epoxide-hydroxyl combinations [35, 36].

While the chemical composition of induced defect states in graphene has been partially studied for graphene oxidation [14, 23, 37] and hydrogenation [38, 39], only little is known about their spatial distribution. In contrast to the possible homogeneous distribution of chemisorbed oxygen on graphene [40], defect clustering was observed for graphene hydrogenation [41] and graphene oxide [42] and is theoretically also predicted for graphene oxidation and hydrogenation [33, 43]. We performed high resolution Raman mapping at the very same position on transferred graphene samples for six different oxidation and hydrogenation stages in order to gather further information about the spatial defect distribution (see supplementary figures S8–S10 for a full discussion on Raman maps of $I_G/I_D$, $I_{2D}/I_G$, $I_{2D}/I_G$ and the G-peak position, $p–G$). The evaluated Raman maps of $I_D/I_G$ and $p–G$ of ozone-treated and hydrogenated graphene are depicted in figures 4(a) and (b), respectively. As indicated by the solid lines on top of the $I_D/I_G$ maps, on average, the Raman maps reproduce the Raman data from figure 1. $I_D/I_G$ increases with increasing oxidation and hydrogenation, reaches a maximum between stages 4 and 5 for graphene oxidation and at stage 4 for hydrogenated graphene, before it decreases again for highly defective stages.

A close look at the $I_D/I_G$ maps, however, reveals a clear difference in the spatial distribution of the induced defect sites. For the ozone-treated sample a pronounced line-shaped structure of enhanced defect density is observed in stage 3, separating defective regions from less affected regions (see supplementary figure S9 for more Raman maps of oxidized samples). This structure is maintained for the subsequent oxidation stages. The presence of such highly defective lines strongly suggests an accumulation of defects at the graphene grain boundaries. The above mentioned structure is even better resolved in the $p–G$ maps in which defect-decorated grain boundaries appear as red shifted lines. The corresponding $I_{2D}/I_{2G}$ maps (see supplementary figure S8) further indicate that not only surface-bound groups accumulate at the grain boundaries, but also that vacancy accumulation is observed at high oxidation stages, which leads to a preferential etching of the grain boundaries. In the case of hydrogenation, however, such a structuring is not observed; instead, $I_{2D}/I_G$ exhibits a homogeneous distribution across the sample. All structures that can be observed in the $I_D/I_G$ Raman maps of hydrogenated graphene can be traced back to bilayer graphene or wrinkles by a comparison with the corresponding optical micrograph (supplementary figure S10). Solely in stage 6, a line-like structure can be recognized that could indicate the position of grain boundaries in the hydrogenated sample. In addition, also the $p–G$ maps of the hydrogenated sample show no fine structuring and thus no indication for a preferential defect allocation at the grain boundaries. Together with the homogeneous distribution of vacancies in the corresponding $I_{2D}/I_{2G}$ maps (see supplementary figure S10) we conclude that the hydrogenation of graphene, in contrast to the ozone treatment, yields a random distribution of defects. This drastic difference between graphene oxidation and hydrogenation is highlighted in the schematics in figures 4(a) and (b) and can be explained by the different nature of the functionalization mechanisms involved during oxidation and hydrogenation. In the oxidation process, the sample is exposed to an ozone atmosphere at elevated temperature. In contrast, hydrogen ions are accelerated towards the graphene sheet in our hydrogenation process. Therefore, we propose that the enhanced reactivity of grain boundaries [21], which determines the inhomogeneous defect distribution in the ‘chemical’
process of oxidation, is overruled in the much more ‘physical’ process of hydrogenation, thus leading to the observed homogeneous defect distribution.

Using the controlled graphene modification and based on the analysis of the structural and chemical composition as well as the spatial distribution of the created defects, we now consider the resulting effect on the electronic properties of the CVD graphene sheets. For this study, back-gated field-effect transistors were fabricated using Si/SiO₂ as the device substrate (see methods section) and the field-effect mobility of positive charge carriers was extracted after several consecutive steps of oxidation and hydrogenation (see supplementary figure S11 for detailed information on transistor evaluation). The resulting data for graphene oxidation and hydrogenation are depicted in figures 5(a) and (b), respectively, where the calculated field-effect mobility μ of several devices are normalized to the pristine value μ₀ and plotted versus the relative defect density nD/nC. Our measurements reveal a generally decreasing trend of the mobility for increasing oxidation rate with two distinct regimes: an initial slow decrease of the mobility with increasing defect density, down to μ/μ₀ ≈ 0.3, followed by a strong breakdown of the device mobility for 10⁻⁴ < nD/nC < 10⁻³. This defect concentration approximately corresponds to full saturation of the grain boundaries in the sample, assuming an average grain size of ~1–3 μm. The data corresponding to ozone treatments at T > 70 °C are represented by open symbols, and show a clear coincidence with the mobility breakdown. Our discussion of the XPS and the Raman data confirmed that above this temperature, the ozone treatment results in a predominant generation of vacancies. The observed decay of the carrier mobility at the same ozonization temperature suggests
a strong correlation between the induced vacancies and the electronic transport. On the other hand, the initial slow decrease of the mobility observed at low \( n_D/n_C \) can be correlated with a transport regime dominated by oxygen-containing defects with sp²-hybridized carbon species. For the case of hydrogenation, we do not observe such a strong transition, but rather a continuous evolution at \( n_D/n_C \approx 5 \times 10^{-4} \) from the high-mobility regime to the low-mobility regime. Here, none of the data points corresponds to a process for which significant vacancy formation is expected.

To understand the effect of ozone and hydrogen treatment on the electronic properties of CVD graphene, and in particular the preferential generation of defects at the grain boundaries, we have performed simulations of electronic and charge transport in realistic polycrystalline graphene samples [44].

Figure 5(c) shows the results of the simulations for the ozone process, in which the carrier mobility is calculated for increasing concentration of epoxide groups. In order to investigate the importance of defect distribution and vacancy formation, we compare a random distribution of groups (blue) with the case of an accumulation of epoxide groups only at the grain boundaries (red). After reaching the saturation threshold of the grain boundaries by epoxide defects (vertical dashed line), vacancies are gradually added (open symbol data points).
Graphene grain boundaries start to crack upon full oxygen coverage \cite{34} leading to a large number of vacancies, which results in drastically reduced mobility values, in good agreement with the experimental data. Such breakdown of the mobility is not present when epoxide defects are homogeneously distributed throughout the sample, highlighting the significant role that defect distribution plays in the electrical properties of ozone-treated polycrystalline graphene. The simulations for hydrogen termination are depicted in the inset of figure 5(b) for a random distribution (green) and an accumulation of oxygen at only the grain boundaries (yellow). Since the corresponding experimental data show a smooth transition from a high-mobility to a low-mobility regime, in agreement with the Raman mapping experiments (figure 4), our simulations thus suggest a random distribution of hydrogen defects. Such interpretation is further corroborated by the large variation of device characteristics for oxidized graphene compared to the uniform behavior of the hydrogenated graphene devices. For a preferential generation of defects at the grain boundaries, as is the case for the ozone treatment, the dependence of $\mu/\mu_0$ markedly depends on the orientation and average size of grains within the individual devices, which is expected to vary from device to device; such variability is observed in figure 5(a). On the other hand, for a random distribution of defects (as expected for the hydrogenation process) no device to device variation is expected, as manifested in the data in figure 5(b).

In conclusion, we report on a fundamental study of the effect of ozone treatment and hydrogen plasma on the chemical, structural, and electronic properties of polycrystalline graphene, providing a route to carefully control not only the density but also the type of defects introduced to pristine CVD graphene sheets. We found that the nature of the induced defects exhibits a transition from dominant carbon-hybrid formation to vacancy generation at threshold values $70^\circ$C and $-275$ V for the oxidation temperature and acceleration voltage during hydrogenation, respectively. Additionally, we observed that the $D$-peak Raman spectrum of defective graphene is dominated by sp$^3$-hybridized C–C bonds while defects related to surface-bound functional groups do not seem to exhibit significant Raman footprints. Raman mapping revealed strong accumulation of sp$^3$-defects and vacancies at grain boundaries for low and high oxidation stages, respectively, while hydrogenation leads to homogeneous defect distribution regardless of the type of defect. Finally, we have found that the preferential accumulation of epoxide groups and vacancies at grain boundaries is responsible for charge transport in ozone-treated polycrystalline graphene films, whereas random hydrogen distribution can reproduce the behavior observed upon graphene hydrogenation. Our results significantly improve the current understanding of the influence of functionalization on polycrystalline graphene, providing a solid foundation for the utilization of graphene in real applications.

**Methods**

**Graphene growth and transfer**

Graphene was grown via CVD on copper foils in a hot wall growth reactor \cite{46}. A copper foil substrate was heated to 1000 $^\circ$C under a hydrogen flow of 28 sccm and pre-annealed for 45 min. Thereafter, graphene was grown in a two-step process for 30 min/5 min applying a mixture of methane (0.5 sccm/7.5 sccm) and hydrogen (16 sccm/16 sccm) at a total pressure of 30 mbar/40 mbar. For transfer, the graphene-copper foil was resist-coated and floated on an aqueous etching solution (FeCl$_3$ + HCl) overnight to selectively remove the copper foil substrate. After careful rinsing with deionized water, the resist-supported graphene sheets were transferred onto a 285 nm thick layer of SiO$_2$ on Si. The supportive resist was removed by thorough solvent cleaning. Cleanliness of the transferred graphene films was verified by optical microscopy and Raman spectroscopy (see supplementary information).

**Ozone treatment of graphene**

Graphene sheets were oxidized utilizing an ozone generator and a hot plate. An oxygen flow was applied through the ozone generator. Variation of the oxygen flow rate as well as ozonization power enabled control of the ozone concentration in the gas stream. Samples were placed on a hot plate and covered with a glass beaker. The beaker was then continuously flushed with the ozone-containing gas stream. The hot plate was utilized to investigate the effect of substrate temperature on the oxidation process.

**Graphene hydrogenation**

Hydrogenation of the as-grown graphene films was achieved in a remote DC hydrogen plasma system at 0.9 mbar of H$_2$ flow. Samples were placed 15 cm from the plasma discharge region. A variable acceleration voltage, $V_{acc}$, was applied between the sample and the plasma electrodes. All samples were hydrogenated for 20 min.

**Raman spectroscopy**

Raman spectra were recorded using an Ar-ion laser at 514.5 nm in a $\mu$-Raman setup. The system is equipped with a liquid N$_2$-cooled detector in combination with an 1800 mm$^{-1}$ and a 1200 mm$^{-1}$ grating allowing for a spectral resolution of 0.5 cm$^{-1}/0.75$ cm$^{-1}$. A 100× magnification objective lens was used to obtain a laser spot of approx. 0.5 $\mu$m. Automatic acquisition of several spots and Raman maps was possible with the use of a piezo stage in combination with an autofocus unit. Typical spectra were integrated for 2 s. A background signal was subtracted from the presented data when necessary. Single Lorentzian peaks were fitted to
the data at positions of the $D, G, D'$ and 2D modes to extract all necessary information.

**X-ray photoelectron spectroscopy**

The measurements were performed with graphene films on Cu foils to avoid any artefacts related to possible contaminants of the transfer procedure. Measurements were performed in an XPS system at a base pressure of $5 \times 10^{-9}$ mbar with non-monochromatic Al $K\alpha$ radiation at an operating power of 20 mA at 12.5 kV. Spectra were acquired using a SPECS Phoibos 100 hemispherical analyzer with an MCD-5 detector at a pass-energy of 25 eV with a 0.025 eV step size. The intensity of the signals was normalized by the total number of counts for the specific measurement taking into account the differences in the sensitivity factor for each measured chemical element.

**Electronic transport**

In order to characterize the electronic properties of the oxidized graphene sheets, field-effect devices were produced, where $p$-doped Si wafers covered with 285 nm of thermal SiO$_2$ and with thermally evaporated Ti/Au (10 nm/50 nm) electrodes were used as device substrates. After transfer and resist removal, the graphene channel region was defined with optical lithography by etching in an oxygen plasma (300 s at 200 W). A second thermal evaporation step of Au together with optical lithography was used to contact the graphene channel. The graphene transistor devices were ozonized at 50 °C in steps of 5 min until the defect density reached saturation at this temperature. In order to reach higher defect densities, the substrate temperature was then gradually increased. The resulting defect density after each oxidation step was extracted from the measured Raman spectra.

**Simulations**

We considered large-area polycrystalline graphene models with a random distribution of grain boundary orientations and morphologies, generated using molecular dynamics simulations [47]. The electrical properties of the samples were analyzed by following the time evolution of electronic wave packets and computing the conductivity with the Kubo formula [44, 45] $\sigma(E) = \epsilon^2 p(E) \lim_{t \to \infty} \frac{\partial}{\partial t} \Delta X^2(E, t)$, where $\rho(E)$ is the density of states and $\Delta X^2(E,t)$ is the mean-square spreading of the wave packet. We deduced the charge mobility using $\mu(E) = \sigma(E)/\epsilon n(E)$, where $n(E)$ is the electron density, obtained by integrating the density of states. To produce figures 5(b) (inset) and (c), we chose $n(E)$ to match the mobility of the experimental samples prior to functionalization. We then added epoxide or hydrogen defects to the graphene sample until reaching a density where the grain boundaries were saturated. At this point, we introduced vacancy defects at the sites of clustered epoxide defects. In accordance with the experimental transport measurements, no vacancies were introduced for the case of hydrogen defects. Tight binding parameters for epoxide and hydrogen defects on graphene were taken from the literature [48, 49].

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