Role of Grain Boundaries in Tailoring Electronic Properties of Polycrystalline Graphene by Chemical Functionalization

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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 here demonstrate 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 graphane[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 crystalline grains, is known to deteriorate the outstanding properties of graphene [18,19] but, on the other hand, has also been shown to exhibit great sensing capabilities[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-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, as 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 1a and 1b 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 $A_{2D}/A_G > 4$, 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[10,14,23]. 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[24].

A more detailed evaluation of such data is presented in Figures 1c and 1d, 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[24–26]. Such calculations, adopted from Giro *et al.*[25] and Ferreira *et al.*[26], are drawn in Figure 1c and 1d 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 2a 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.*,[27] 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 $I_D/I_{D'}$. Figure 2b shows $I_D/I_{D'}$ 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 $I_D/I_{D'}$~14.5 in the low defect density range, we find a transition to significantly lower $I_D/I_{D'}$ values with increasing defect density for both processes. Eckmann *et al.* found an $I_D/I_{D'}$ ratio of ~13 to be the characteristic footprint of sp^3-hybridized defects in graphene and an $I_D/I_{D'}$ ratio of ~7 to represent vacancy-type defects[27], indicated by horizontal dashed lines in Figure 2b. Based on this analysis, as highlighted in the graph, we can conclude that the formation of surface-bound functional groups containing sp^3-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 V as a borderline between sp^3-hybrid formation and the generation of vacancy-type defects. Interestingly these transitions show a clear coincidence with the maxima in the I_D/I_G versus n_D/n_C curves of Figures 1c and 1d. We note that the steep transition in $I_D/I_{D'}$ and the low saturation value of $I_D/I_{D'}$~2.5 for the ozone-treated samples suggest a more pronounced graphene etching for graphene oxidation compared with graphene hydrogenation.

A detailed understanding of the chemical nature of the generated defects has been obtained from XPS. Figure 3 shows exemplary XPS spectra of the C1s signal (a) and the Cu2p signal (b) comparing the cases of pristine graphene and advanced stages of hydrogenation and oxidation. With respect to the pristine film, a decrease of the main component of C1s signal is observed for both oxidation and hydrogenation, with more drastic changes in the case of ozone treatment. While upon hydrogenation the Cu2p signal is downshifted in energy compared to the pristine case, representative of a partial reduction of the Cu substrate[29], a clear shift towards higher energies and an additional feature denoted as Cu^{2+} shakeup for the oxidized sample indicates severe oxidation of the copper foil[30]. A quantitative analysis of the data for ozonized samples is shown in Figure 3c where the total concentrations of the C1s, the O1s and the Cu^{2+} shakeup peaks are plotted versus T. For temperatures above 70°C we observe a strong decrease of the C1s signal, accompanied by a sharp increase of the O1s and Cu^{2+} signals. The coincidence of the decreasing total carbon signal with the increasing total oxygen and the copper oxide related Cu^{2+} mode indicates etching of the graphene sheet and the oxidation of the partially unprotected underlying copper substrate for T>70°C, as illustrated in Figure 3b. This is further supported by the observation of strongly increasing CuO related contributions in the Cu2p 3/2 (Supplementary Figure S3) and the O1s (Supplementary Figure S4) signals.

Figures 3d and 3e help to shed light on the actual binding configuration of carbon atoms in the graphene sheet upon oxidation and hydrogenation, respectively (see Supplementary Figure S5-S7 for detailed XPS evaluation of C1s). The relative contributions of oxidized graphene GO (only Figure 3d) and sp^3 C-C bonds within the C1s signal are plotted versus T and V_{acc}. Both graphs also include the corresponding relative defect density as derived from the Raman data. Besides the expected increase of GO with increasing T we find a clear correlation between the content of sp^3 C-C species and n_D/n_C 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 sp^3-hybridized carbon atoms without any extrinsic adatom. Since such conformation is most likely to occur at vacancies in the graphene network, Figures 3d and 3e indicate an enhanced vacancy generation for T>70°C and $|V_{acc}|>275$ V, in perfect agreement with the Raman data from Figure 2 and XPS data from Figure 3c. Thus, 70°C and V_{acc}=-275 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 XPS. However, considering Figure 2b where -275 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. Noteworthy, we found that an oxidation process at low a substrate temperature of 50°C can yield GO contents of 40% without significant formation of vacancies (Supplementary Figure S8), which could be used to produce high quality functional graphene films. Furthermore, a detailed analysis of the C1s XPS core level spectra 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[31–33]. 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, Figure S8) 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 epoxy-hydroxyl combinations[34,35].

While the chemical composition of induced defect states in graphene has been partially studied for graphene oxidation[14,23,36] and hydrogenation[37,38] , only little is known about their spatial distribution. In contrast to the possible homogeneous distribution of chemisorbed oxygen on graphene[39], defect clustering was observed for graphene hydrogenation[40] and graphene oxide[41] and is theoretically also predicted for graphene oxidation and hydrogenation[32,42]. 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 S9- S11 for a full discussion on Raman maps of I_G, I_D/I_G, $I_D/I_{D'}$ and the G-peak position). The evaluated Raman maps of I_D/I_G of ozone-treated and hydrogenated graphene are depicted in Figure 4a. As indicated by the solid lines on top of the 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 S10 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 corresponding $I_D/I_{D'}$ maps (see Supplementary Figure S9) further indicate that not only do 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 such a structuring is not observed; instead, I_D/I_G exhibits an even distribution across the sample. All structures that can be observed in the Raman maps of hydrogenated graphene can be traced back to bilayer graphene or wrinkles by a comparison with the according optical micrograph (Supplementary Figure S11). Solely in stage 6, a line-like structure can be recognized that could indicate the position of grain boundaries in the hydrogenated sample. Together with the homogeneous distribution of vacancies in the correlated $I_D/I_{D'}$ maps (see Supplementary Figure S11) 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 Figure 4b 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/SiO_2 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. The resulting data for graphene oxidation and hydrogenation are depicted in Figures 5a and 5b, respectively, where the calculated field-effect mobility μ of several devices are normalized to the pristine value μ_0 and plotted versus the relative defect density n_D/n_C. 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 $\mu/\mu_0 \approx 0.3$, followed by a strong breakdown of the device mobility for $10^{-4} < n_D/n_C < 10^{-3}$. 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 sp^3-hybridized carbon species. For the case of hydrogenation we do not observe such a strong transition, but rather a continuous evolution at $n_D/n_C \approx 5\text{x}10^{-4}$ 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[43]. Figure 5c 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). Epoxide groups were chosen since they represent the most probable conformation upon oxygen adsorption [31,32] and, compared to e.g. hydroxyl groups, exhibit the strongest perturbation of the electronic transport[44]. Based on the simulations, the strong breakdown of the mobility observed in Figure 5a can be explained by the accumulation of defects at the grain boundaries. This breakdown of the mobility occurs when the concentration of epoxide groups in the grain boundaries reaches saturation (vertical dashed line in Figure 5c). Graphene grain boundaries start to crack upon full oxygen coverage[33] 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 ozonized CVD graphene. The simulations for hydrogen termination are depicted in the inset of Figure 5b for a random distribution (green) and an accumulation of hydrogen 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 μ/μ_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 5a. 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 5b.

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°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 chemical vapor deposition (CVD) on copper foils in a hot wall growth reactor[45]. A copper foil substrate was heated to 1000°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.

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 µ-Raman setup. The system is equipped with a liquid N_2-cooled detector in combination with an 1800/mm and a 1200/mm grating allowing for a spectral resolution of 0.5 cm^{-1}/0.75 cm^{-1}. A 100x magnification objective lens was used to obtain a laser spot of approx. 0.5 µm. 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 x 10^{-9} mbar with non-monochromatic Al Kα 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.

Simulations: We considered large-area polycrystalline graphene models with a random distribution of grain boundary orientations and morphologies, generated using molecular dynamics simulations[46]. 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[43,44] $\sigma(E) = e^2 \rho(E) \lim_{t\to\infty} \frac{\partial}{\partial t} \Delta X^2(E,t)$, 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 $\mu(E) = \sigma(E)/en(E)$, where n(E) is the electron density, obtained by integrating the density of states. To produce Figures 5b(inset) and 5c, 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 saturate. 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[47,48].

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Author Contributions:

M.Se. and M.B. performed all experimental work. M.Sa. supervised the XPS experiments. A.W.C. and J.E.V.G. performed the quantum transport simulations. M.Se., A.W.C, J.E.V.G, S.R. and J.A.G. analyzed, discussed and interpreted the data. All authors co-wrote, reviewed and approved the manuscript.

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Figure 1 Raman analysis of ozone- and hydrogen-treated CVD graphene. Waterfall plot of exemplary Raman spectra of CVD graphene after oxidation at different temperatures (**a**) and hydrogenation at different acceleration voltages (**b**). Spectra were normalized to the G-peak intensity. **c** and **d,** Raman peak intensity ratio I_D/I_G (black) and integrated intensity ratio A_{2D}/A_G (blue) as a function of substrate temperature (ozonization) and acceleration voltage (hydrogenation), respectively. Several measurement spots in the film were averaged for each data point plotted in panels **c** and **d**. Error bars reflect the corresponding standard deviations. Red solid lines represent theoretical calculations of I_D/I_G[25] and A_{2D}/A_G[26] as a function of the relative defect density n_D/n_C, which were adjusted to fit the experimental data.

Figure 2 Nature of induced crystallographic defects. a, Schematic of different types of defects induced upon ozone treatment and hydrogenation, illustrating various functional groups such as epoxide (C-O-C), carbonyl (C=O), hydroxyl groups (C-OH), and hydrogenated carbons (C-H) as well as vacancies due to carbon etching[28]. **b**, Raman peak intensity ratio $I_D/I_{D'}$ versus the relative defect density n_D/n_C for graphene oxidation (black squares) and graphene hydrogenation (blue circles). Error bars reflect the corresponding standard deviations. Horizontal dashed lines mark values of $I_D/I_{D'}=13$ and $I_D/I_{D'}=7$.

Figure 3 XPS analysis of ozone- and hydrogen-treated CVD graphene films. XPS spectra of the C1s (**a**) and the Cu2p (**b**) signals comparing pristine graphene (black) with graphene at advanced hydrogenation (blue) and oxidation stages (red). **c,** Total concentration of the C1s, O1s and Cu^{2+} signal as a function of substrate temperature during ozonization. **d** Relative content of oxidized graphene GO and sp^3 C-C bonds within the C 1s signal after ozone treatment plotted versus substrate temperature. **e**, Relative content of sp^3 C-C bonds within the C 1s signal for graphene hydrogenation. The relative defect density n_D/n_C as assessed by Raman spectroscopy is also included in panels **d** and **e**. Background in panels **c-e** represents the evolution of graphene etching.

Figure 4 High resolution Raman maps. a, Raman maps of I_D/I_G of CVD graphene for consecutive stages of oxidation (top) and hydrogenation (bottom). The white and black solid lines over the I_D/I_G maps correspond to the theoretical I_D/I_G vs n_D/n_C curve[25] and roughly mark the positions of the six recorded oxidation and hydrogenation stages. Map size is 40 x 20 μm^2. **b**, Schematic of polycrystalline graphene with grain boundaries (blue); defects (red) accumulate at grain boundaries in the case of ozone treatment and show homogeneous distribution in the case of hydrogenation.

Figure 5 Electronic transport in functionalized CVD graphene. a and **b**, Field-effect mobility as a function of the relative defect density for six different transistors (each symbol representing a device) for graphene oxidation and hydrogenation, respectively. The mobility data are normalized to the mobility of clean devices. Open symbols represent ozone treatments at substrate temperatures above 70°C. The relative defect density n_D/n_C was calculated from the integrated area D/G Raman intensity ratio; nine measurement spots within the 10x10 μm^2 transistor channels were averaged to create one data point. **b** (inset)**,** Simulation of μ/μ_0 for increasing amount of hydrogen defects with a random distribution (green) and accumulated at grain boundaries (yellow). The vertical dashed line represents the saturation of the grain boundaries with hydrogen. **c**, Simulation of μ/μ_0 for an increasing amount of epoxide defects with random distribution (blue) and accumulated at 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).