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# Unraveling the electronic properties of graphene with substitutional oxygen

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#### Abstract

We show abrupt changes in the electronic properties of graphene with different types of binding to oxygen. Whereas oxygen bonded to the basal plane in the form of functional groups *p*-type dopes graphene, we prove that substitutional (i.e. in-plane) oxygen *n*-type dopes it. Moreover, we determine that impurity scattering potentials introduced by these substitutional atoms are notably larger than those of conventional donors, e.g. nitrogen. Both facts ultimately result in a conduction asymmetry in the system with holes being scattered more strongly than electrons. These findings provide essential insights into the impact of oxygen in carbon nanomaterials such as graphene oxide, oxidized carbon nanotubes or novel two-dimensional  $\pi$ -conjugated organic frameworks, promising compounds for a wide range of applications including flexible electronics, catalysis, energy storage or biomedicine.

### 1. Introduction

Oxygen-containing carbon nanomaterials such as graphene oxide (GO); oxidized carbon nanotubes or two-dimensional (2D) organic frameworks, have recently attracted a significant research effort for their potential use in next generation nanoelectronic devices as well as other cutting-edge applications [1–5]. However, both structure and fundamental properties of C and O bonds in all these systems are not yet well known [6, 7]. For instance, despite the initial belief of oxygen being exclusively bound to graphene in the form of (out-of-plane) functional groups [1, 8], new scanning transmission electron microscopy (STEM) investigations in GO have additionally visualized the presence of different configurations of substitutional oxygen in the hexagonal lattice [9]. The possibility to implant O atoms within an extended  $sp^2$ -bonded carbon matrix is further intriguing: some of these heteroatoms (dopants or impurities) consist of triple-coordinated oxygen with three carbon neighbors, bonding configurations which are counterintuitive to the conventional wisdom [9, 10].

In the present study, we examine the electronic properties of graphene with substitutional oxygen configurations and reveal substantial differences with respect to the properties of graphene with oxygencontaining functional groups bound to the basal plane. This is done by developing a controlled plasma-based process able to implant oxygen in graphene, in combination with transport, scanning tunneling microscopy (STM) and spectroscopy measurements, and state-of-the-art atomistic calculations.

The manuscript is organized as follows. Section 2 describes the used theoretical and experimental methods, including electronic structure and transport calculations, the implantation of oxygen in graphene via a plasma immersion ion implantation process, device fabrication and electrical and scanning tunneling microscopy measurements. In section 3, we show and discuss our simulation and experimental results. Finally, our conclusions are summarized in section 4.

# 2. Methods

#### 2.1. Electronic structure calculations

Ab initio calculations were performed using DFT as implemented in the SIESTA code [11], widely used software for the simulation of doped graphene [12]. In order to mimic the experimental conditions, isolated oxygen-based impurities in graphene were simulated using  $9 \times 9$  graphene supercells containing 162 atoms, i.e. the atomic concentration of dopants is  $\approx 0.5\%$ . Specifically, it is  $n_0 \times 0.5\%$  where  $n_0$  is the number of oxygen atoms in the supercells. A vacuum region of 20 Å was included in the direction perpendicular to the graphene layer in order to avoid spurious effects between nonphysical periodic images. Calculations were done using norm-conserving Troullier-Martins pseudopotentials [13] to represent core electrons and a double- $\zeta$  polarized (DZP) basis set with 0.01 Ry energy shift to describe valence electrons. Exchange-correlation energies were addresed using the Perdew-Burke-Ernzerhof (PBE) functional [14] within the generalized gradient approximation (GGA). A  $15 \times 15 \times 1$  Monkhorst-Pack k-sampling [15] was used to sample the Brillouin zone, and the grid for real space integrations was determined by a 400 Ry cutoff. For all the configurations, both the lattice and the atomic coordinates were fully optimized until the maximal force was below 0.01 eV Å<sup>-1</sup> and the stress below 0.25 GPa. STM simulations for selected bias intervals, including the resonant states, were carried out using the STM utility in SIESTA, which is based on the Tersoff-Hamman approximation [16]. Due to the short-range character of the basis set used by SIESTA, the utility extrapolates the value of the wavefunction out to realistic tip-sample distances. We remark that we use a  $9 \times 9$  super-cell to avoid the insertion of an artificial gap in the system [17].

#### 2.2. Transport calculations

Numerical calculations of the DC conductivity for different, randomly distributed oxygen configurations and concentrations in graphene lattice are carried out implementing the Kubo-Greenwood formalism. Such formalism is able to capture the qualitative behaviour of all (ballistic, diffusive, and localization) transport regimes and is applicable for systems consisting of millions of atoms [18, 19], as it is the case of our experimental devices. Doping and charge carrier scattering introduced by oxygen impurities in graphene are modelled by the following on-site ( $r_i$ ) potential:

$$V_i = \sum_{j=1}^{N} U_j e^{-|r_i - r_j|^2 / (2d^2)},$$
(1)

where *N* is the number of oxygen dopants occupying *j* sites with radius-vectors  $r_j$ , d = 0.63a (a = 0.142 nm is the lattice parameter) is an effective potential radius and the potential strenght  $U_j = -3\gamma$ , with hopping (integral)  $\gamma \approx 2.8$  eV. Vacancies are modelled as a site with zero hopping parameters to other sites. We note that the selected *d* and  $U_j$  values produce a good fitting to the DFT calculated results (figure 1(b)).

#### 2.3. Implantation of oxygen atoms in graphene

The influence of the kinetic energy on the implantation of oxygen in graphene has been theoretically calculated via molecular dynamics [20]. For a perpendicular angle of incidence, oxygen ions at energies between  $\sim$ 25–30 eV and  $\sim$ 100–105 eV have probabilities larger than 10% of being implanted in graphene's basal plane. Moreover, such calculations estimate that the probability to introduce vacancies or in-plane disorder in graphene is low (<1%) with processes undertaken at energies lower than  $\sim$ 35–40 eV.

In this work, oxygen is implanted in graphene at  $\sim$ 25 eV by developing a plasma immersion ion implantation, PIII, process. These are versatile and ultra-low energy processes commonly utilized to realize shallow doping in narrow channel devices made from conventional semiconductors [21]. The reactor used for our process has a parallel plate geometry and a high frequency generator operating at 13.56 MHz is capacitively coupled to the bottom electrode. We use O2 inlet gas at a constant flow 40 sccm mixed with 5 sccm Ar. We add the 5 sccm Ar to the mixture in order to decrease the breakdown voltage needed to ignite the plasma [21, 22] and hereby achieve the desired ultra-low energy irradiation. The pressure in the reactor during the 10 s process is  $\sim$ 30 mTorr, which ensures a low angular dispersion of the ions. In particular, the irradiation is carried out in the collisionless regime (or close to it) since the mean-free path of oxygen ions in plasma is  $\sim 1$  cm [22], which is similar to the plate separation in our reactor but larger than the sheath thickness for oxygen ions at our working pressure [23, 24]. This collisionless regime ensures a narrow energy distribution as well as a small angular dispersion, thus making our process well controlled. Ions in the plasma acquire a kinetic energy  $\epsilon_{\rm kin}$  given by  $\epsilon_{\rm kin} = qV_{\rm DC}$ , where q is the ion charge and  $V_{\rm DC}$  the DC bias voltage (the latter being the sum of the self-bias and the plasma potential). Due to the composition of our plasma (see optical emission spectroscopy measurements OES in supplementary



(a) Stable and representative [9] atomic configurations, electronic and transport properties of graphene with in-phase oxygen dopants. (a) Stable and representative [9] atomic configurations of oxygen impurities in graphene, here named C1 (top) and C2 (bottom). Charge balance in configuration C1 is calculated via Hirshfeld atomic populations. (b) Density of states (DOS) of pristine graphene (grey) and graphene with in-plane oxygen (blue) for configurations C1 and C2 (red line is DOS projected on oxygen atoms). Vertical dashed and dotted lines correspond to the Dirac point  $E_D$  and the Fermi level of graphene with the dopants, respectively. All contributions to the DOS were scaled for visualization purposes. (c) Calculated conductivity  $\sigma$  as a function of the carrier density *n* for different concentrations (shades of blue) of oxygen impurities (configurations C1, C2) in graphene.

information available online at stacks.iop.org/2DM/ 8/045035/mmedia), we assume q = 1. The required  $V_{\rm DC} \sim 25$  V is obtained in our PIII process for a platten power P  $\sim 4.5$  W. We measure  $V_{\rm DC}$  fluctuations  $\sim \pm 5$  V during the process.

#### 2.4. Device fabrication

Graphene was mechanically exfoliated onto highly doped silicon wafers with 300 nm of silicon dioxide on top. We use these well-known substrates since they avoid back-sputtering during the oxygenbased plasma treatment [25]. Single layer graphene was identified via optical contrast (figure 2(b)) and Raman spectroscopy (supporting information).

Stencil devices (so-called device type D1 in our study) are simple two-terminal devices where graphene flakes are directly contacted by using shadow masks. This avoids channel exposure to chemicals or heat treatments from lithographic processes [26]. In our study, flakes are contacted by depositing 50 nm Au on the graphene. The distance between contacts in all these devices is 30 micrometers.

Instead, devices of type D2 are four-terminal devices each with the same dimensions and fabricated on the same graphene flake. Each of these devices has a different area exposed to the oxygen. Metal electrodes in devices D2 were defined by electron beam lithography, EBL, using a double layer PMMA mask and depositing 5 nm/45 nm of Cr/Au in an electron-beam evaporator. Here, the 5 nm thick Cr is an adhesion film which avoids the removal of metal electrodes during lift-off processes. Lift-off of metal from undesired areas was performed in warm acetone, with wafers being rinsed in deionized water, DIW, and isopropyl alcohol, IPA. Nano patterning circular holes arranged in a triangular lattice with a variable spacing *s* was then also defined by EBL. To do so, a 40 nm thick layer PMMA was used this time. The EBL pattern was developed in IPA:DIW 7:3 at 5 °C for 30 s, with IPA used as a stopper. Then, sample was processed with the PIII process, as described above. Finally, the PMMA mask was then removed in acetone.

#### 2.5. Electrical measurements

Electrical measurements were undertaken in a Linkam LN600P stage in dry nitrogen. Prior to the measurements, a thermal treatment of 125 °C was performed to remove possible water from the surface. A constant bias DC voltage  $V_{DS}$  was applied between the source and drain contacts and the current *I* passing through the graphene field-effect transistors was measured for different gate voltages  $V_{\rm g}$  or carrier densities  $n = C_{\rm ox} V_{\rm g}/e$ . In the former expression  $C_{\rm ox}$ is the oxide capacitance per unit area and e is the elementary charge. We also note that, in our devices, the doping levels n for a given shift of the charge neutrality point  $\Delta V_{\rm CNP}$  are approximately equal to  $n \sim 0.072 \cdot 10^{12} \cdot \Delta V_{\text{CNP}}$  (cm<sup>-2</sup>). Moreover, longitudinal voltages  $V_{xx}$  were measured with the current traversing the sample in devices of type D2 in order to accurately obtain the conductivity  $\sigma$  and mobility  $\mu$  of these devices via 4-terminal measurements.



**Figure 2.** (a) Not-to-scale schematic of device type D1. Left panel represents the initial device with as fabricated graphene (grey) and right panel represents the device after graphene was exposed to the here developed ~25 eV oxygen plasma implantation process (red). (b) Conductance measurement of a stencil device subjected to the aforementioned ~25 eV oxygen plasma implantation process, showing a downshift of  $V_{\rm CNP}$  (dashed grey arrow). Upper-right inset: conductance measurement of a stencil device subjected to a plasma ashing process, showing an upshift of  $V_{\rm CNP}$  instead (dashed grey arrow), similar to other reports in literature [33, 34]. Lower-left inset: optical image of one of our stencil devices. Scale bar is 20  $\mu$ m.

Carrier mobility  $\mu$  in our devices was calculated at carrier concetrations  $\pm 5 \times 10^{11} \text{ cm}^{-2}$  (or equivalently, voltages  $\sim \pm 7 \text{ V}$ ) away from the charge neutrality point using:

$$\mu = \frac{d\sigma}{dV_g} \frac{L}{C_{ox} \cdot W} \tag{2}$$

where *L* and *W* are the length and width of the measured device area (i.e. region between voltage probes).

**2.6. Scanning tunneling microscopy measurements** STM measurements were performed with etched-W tips at a base pressure  $< 2 \times 10^{-10}$  mbar and a temperature of 9–10 K using an Infinity system (Scienta Omicron). The measurements were taken in constant current mode by applying a bias voltage to the sample. Prior to the STM measurements, the sample was annealed in vacuum at a temperature of 500 °C to remove possible atmospheric adsorbates on the sample.

# 3. Results and discussion

## 3.1. Atomistic calculations

Figure 1(a) shows the relaxed atomic structure of two stable and observed [9] configurations of oxygen implanted in graphene, calculated via Density Functional Theory (DFT). These configurations are: (i) graphitic substitution (here called configuration C1), where oxygen binds to the three neighbour carbon atoms (i.e. graphitic oxygen); and (ii) pair of oxygen atoms substituting two nearest neighbour carbon atoms (configuration C2). The top panel of figure 1(a) also shows the charge redistribution induced by the O substitution in configuration C1. Briefly, a localized electron depletion is shown at carbon atoms bonded to oxygen (blue color), while an extended (and overall larger) electron accumulation appears at remaining neighbouring carbon atoms (green color). Such behaviour is generic and also occurs in configuration C2 and more complex (and also possible [9]) configurations with vacancies involved (see additional details and figures S1-S3 in supporting information). These evidences indicate that substitutional oxygen is an electron donor, which can be intuitively related to the fact that oxygen has more valence electrons than carbon.

Figure 1(b) shows the DFT calculated total density of states (DOS, blue line) and the DOS projected onto oxygen atoms (red line) for the two highlighted configurations C1 and C2, all plotted against the DOS of pristine graphene (grey area). The overall effect of oxygen dopants in graphene is to separate the Dirac point, E<sub>D</sub>, (dashed line) away from the Fermi level,  $E_F$ , shifting it towards negative values ( $E_F$  is set to 0 eV in our calculations). This behaviour is directly related to the fact that in-plane oxygen *n*-type dopes graphene, evidence that is also clearly observed in the bandstructures of these systems shown in figure S4, supporting information. Furthermore, substitutional oxygen introduces sharp resonant states with peaks at energies  $E_{res}$  close to  $E_D$  (i.e. at low energies), fact that can be ascribed to a strong perturbing potential introduced by substitutional oxygen in graphene [27] (see further details below and in supporting information). In particular, these resonances appear at energies  $|E_{\rm res} - E_{\rm D}| = 0.05$  eV and 0.1 eV for cases C1 and C2, respectively.

Figure 1(c) contains tight-binding, TB, calculations of the conductivity as a function of carrier density n for graphene devices with configurations C1 and C2 randomly positioned (figure S6 in supporting information) at different concentrations. These simulations allow us to understand the qualitative behaviour of graphene transistors containing these distinct impurities. Impurity scattering in the TB calculations (obtained as best fit to the DFT calculated local DOS, see figure S5 in supporting information) is an attractive, strong and primarily short-range perturbing potential with a depth of 8.4 eV (further details about the impurity potential are described in the supporting information). First, figure 1(c)shows a net *n*-type doping in devices containing both configurations as demonstrated by the left-shift of the conductivity minimum (or charge neutrality point,  $V_{\rm CNP}$ ) when increasing the concentration of oxygen dopants (grey arrows). Moreover, an overall lower conductivity of both electrons and holes is observed for larger concentration of oxygen impurities, as a result of increased scattering in the device. In more detail, the conductivity suppression is particularly marked at low energies (or carrier densities), which is a direct consequence of the sharp resonant states occurring close to  $E_D$  in these systems. In addition, we also observe a higher conductivity of electrons with respect to holes at large energies (carrier densities). Such transport asymmetry is not induced by resonant-scattering but can be ascribed to doping fluctuations occurring in the device due to the randomly distributed *n*-type (oxygen) dopants in graphene [28, 29].

Intriguingly, some of the trends observed for substitutional oxygen are distinctly different from conventional n-type dopants in graphene such as nitrogen. Nitrogen heteroatoms are weaker impurities (potential depth  $[17] \sim 3$  eV) and therefore introduce broader resonances peaking at energies  $E_{res}$  further away from  $E_D$  [27] ( $|E_{res} - E_D| > 0.2$  eV in most of the configurations containing substitutional nitrogen [17, 30]). In turn, electron-hole asymmetry for energies up to 1 eV in graphene with substitutional nitrogen is principally inherited from the resonantscattering-induced asymmetry in the underlying scattering rate [31]; and therefore a larger hole conductivity/mobility occurs in graphene devices with nitrogen dopants [18, 31]. The latter has been already demonstrated in experiments [32]. We further highlight that *n*-type doping and lower conductivity/mobility of hole carriers are also distinctive characteristics with respect to other cases such as the presence of out-ofplane oxygen-containing functional groups, vacancies or molecular oxygen. Oxygen functional groups bonded to the basal plane are well-known to *p*-type dope graphene [33, 34] due to the larger electronegativity of O atoms (which tend to pull electrons from C atoms and leave holes in the 2D hexagonal lattice [35]). Vacancies or adsorbed molecular oxygen cannot explain these distinct trends either: whereas vacancies do not dope the monolayer and their presence reduces equally the conductivity/mobility of electrons and holes [36, 37], adsorbed molecular oxygen reduces electron mobility and *p*-type dopes the monolayer [38].

#### 3.2. Experimental results and analysis

In the following, we realize and characterize graphene devices with in-plane oxygen dopants, ultimately confirming the aforementioned theoretical predictions. The insertion of oxygen in the graphene lattice is achieved here via irradiation engineering [39], by developing a novel plasma immersion ion implantation [21], PIII, process at a controlled kinetic energy  $\sim 25$  eV (Methods). Such ultra-low energy process predominantly introduces in-plane and point-like oxygen impurities in graphene, as

confirmed by Raman spectroscopy (figures S7, S8 in supporting information), transport and STM measurements shown below. This is in clear contrast to other oxygen plasma techniques (e.g. plasma ashing at arbitrary energies [33, 34]) or common, much less well-controlled wet-chemistry methods used to fabricate GO [1, 9], all creating different types of bonding between oxygen and graphene including both, in-plane configurations and out-of-plane functional groups [1, 9, 33, 34]. A more detailed evaluation of our implantation process in terms of density of oxygen and other defects introduced in the hexagonal lattice, as well as optical emission spectroscopy (OES) data assessing the elemental composition of the plasma, can be found in the supporting information.

In order to probe the electronic and transport properties of graphene with in-plane oxygen impurities, we fabricate (Methods) two different types of devices (D1 and D2) from exfoliated graphene flakes. All these devices are non-encapsulated [26, 40, 41], which enable us to measure their electrical properties with and without the oxygen implantation process described above, thus allowing for a direct comparison of results from the same device. D1 (figure 2(a)) are simple two-terminal devices where graphene flakes are contacted by using shadow masks to avoid channel exposure to chemicals or heat treatments from lithographic processes [26]. These devices are nevertheless sufficient to accurately examine the type and levels of doping in graphene by examining any shift occurring in the charge neutrality point,  $V_{\rm CNP}$ , between measurements undertaken before and after an irradiation process [32-34]. In particular, graphene is *n*-type doped after the controlled  $\sim 25 \text{ eV}$ oxygen irradiation, as demonstrated by the significant left-shift (grey dashed arrow) of  $V_{CNP}$  (vertical lines) in their conductance, G, vs gate voltage,  $V_{g}$ , graph (figure 2(b)). As mentioned above, this trend is a strong evidence pointing towards the implantation of oxygen in the graphene lattice. This behaviour is opposed to the common *p*-type doping (i.e. rightshift of  $V_{\rm CNP}$ ) observed for instance when exposing these devices to traditional plasma ashing (see upperright inset figure 2(b), grey dashed arrow), a process which is known to functionalize graphene with out-of-plane oxygen containing groups [33, 34, 42]. Moreover, we also highlight that the left-shift of  $V_{\rm CNP}$  observed in D1 devices after the  $\sim$ 25 eV oxygen irradiation process is  $\Delta V_{\rm CNP} \sim 11-14$  V. In our devices, these values correspond to variation of doping levels  $\sim 10^{12}$  cm<sup>-2</sup>. Similar doping levels are also estimated from our DFT calculations via n = $\frac{|E_{\rm D}|^2}{\pi\hbar^2 v_{\rm f}^2}$ , with  $|E_{\rm D}|$  being of the order of ~0.1 eV (figure 1(b)).

To confirm these observations, we fabricated and measured devices of type D2. These are multiple transistors made from the same graphene flake, where each device has the same dimensions but a



Figure 3. (a) Not-to-scale schematic of device type D2. It has non-patterned (left) and patterned (middle, right) devices with different number of nano-dots. (b)  $\sigma$  vs V<sub>g</sub> for different devices of the study. Regions with a larger area exposed to the ~25 eV oxygen implantation have a higher number of circular dots. To do so, all patterned devices have five lines of dots with different separation distances s (legend). Four devices are shown here with separation distances s = 14, 22, 34 and 42 nm, corresponding to the different shades of blue. Lower inset shows an optical image of the multi-terminal device, with graphene area marked with dashed line (scale bar is 10  $\mu$ m). Upper inset shows the normalized mobility difference  $\Delta \mu$  between holes *h* and electrons *e*,  $(\mu_{\rm h} - \mu_{\rm e})/(\mu_{\rm h} + \mu_{\rm e})$ with respect to the non-patterned device (in %) in all devices as a function of s.

different area exposed to the oxygen treatment. The latter is done by using a lithographic nano-patterned mask with a different number of dots (of equal size) in each transistor. Ultimately, all devices have dots arranged in five lines, and the number of dots in each device is controlled by the dot-to-dot distance s (figure 3(a), upper-right inset). Here, we leave one transistor not exposed to oxygen (control device) in order to assess the residual doping of the graphene flake after the lithographic process (figure 3(a), device on the left). D2 also allows us to accurately estimate conductivity/mobility values of all transistors via 4terminal electrical measurements. Figure 3(b) shows the conductivity  $\sigma$  values of the different channel regions vs Vg in devices of type D2 exposed to the ~25 eV oxygen plasma implantation process, confirming the *n*-type doping already observed in devices D1. In particular, the device not exposed to oxygen irradiation (i.e. control device, black line) shows a residual *p*-type doping and a larger conductivity/mobility of hole carriers, trends widely attributed to atmospheric contaminants and/or lithography residues [26, 33, 34]. On the other hand, graphene devices exposed to the  $\sim 25$  eV process exhibit lower conductivities of both electron and holes and a down-shift of  $V_{\rm CNP}$  (i.e. *n*-type doping, see dashed arrow) which correlate to their total area exposed to oxygen (i.e. smaller s). Quantitatively, the observed left-shifts of  $V_{\rm CNP}$  ( $\Delta V_{\rm CNP}$ ) are up to  $\sim$ 14 V. This value corresponds to doping levels  $\sim 10^{12}$  cm<sup>-2</sup>, which is consistent with the values observed in devices D1 and those calculated via DFT (figure 1(b)). Additionally, we also observe an asymmetric carrier transport with smaller  $\sigma$  and mobility  $\mu$  of holes with respect to electrons in the devices with smaller s. All these experimental features are in agreement with the inclusion of different configurations of substitutional oxygen in graphene (figures 1(b) and (c) and figure S1 in supporting information). We also emphasize that all these observations are in line with the fact that in-plane oxygen dopants primarily act as neutral [28] rather than charged impurities: unscreened attractive Coulomb impurities would induce the opposite electron–hole asymmetry [43].

Finally, we have used scanning tunnelling microscopy to examine the implanted oxygen heteroatoms within the hexagonal carbon lattice. For this purpose, we have performed the oxygen irradiation process at  $\sim$ 25 eV on a  $\sim$ 1 cm<sup>2</sup> highly oriented pyrolytic graphite (HOPG) sample. Due to the weak interlayer coupling present in graphite, the perturbation induced by point defects in graphene and graphite systems can be considered equivalent [37]. In fact, graphite is routinely used as model system to reproduce and image the creation of controlled point defects in graphene via STM [44]. Figure 4(a) reveals areas with pristine honeycomb lattice along with defective regions. Defects have lateral dimensions up to  $\sim 2$  nm, compatible with point-like defects and their associated electronic perturbations [37, 44, 45]. Besides occasional areas with clustered defects (marked by ""), impurities have apparent out-of-plane heights below  $1 \pm 0.2$  Å, consistent with other previously observed in-plane heteroatoms in the honeycomb lattice [30, 46]. The shape of these defects depends on the hexagonal lattice symmetry and the nature of the impurity [30, 46, 47]. Also, the fact that figure 4(a) shows several defects in the hexagonal lattice of HOPG agrees with the large variety of configurations of oxygen in graphene recently visualized in GO via STEM [9] and possible vacancy defects [48] which may occur during our irradiation process. By performing STM-imaging simulations of oxygen atoms in graphene (figures 4(b)-(d)) we are able to identify some of the defects in figure 4(a). For instance, we note the characteristic three- [37, 47] and two- [47] fold symmetry features (panels b and c) corresponding to configurations C1 and C2 in figure 1, respectively. Also, we distinguish a pair of oxygen atoms substituting two sixth-nearest neighbour carbon atoms (panel d). Moreover, we highlight



**Figure 4.** STM image and simulations. (a) 8 nm  $\times$  8 nm measured STM image (I = 0.5 nA, V = 0.5 V) of highly oriented pyrolytic graphite after the ~25 eV oxygen irradiation process. Scale-bar indicates the apparent out-of-plane height of the image. From this bar, one can observe that the apparent out-of-plane heights of the identified defects are ~ 1 Å. (b) DFT-based STM image calculated for single oxygen substitutions, configuration C1 in figure 1(a). (c) DFT-based STM image calculated for double pair oxygen substituting two first nearest neighbour carbon atoms, configuration C2 in figure 1(a). (d) DFT-based STM image calculated for double pair oxygen substituting two sixth-nearest neighbour carbon atoms. We identify all these defects in the experimental image, panel (a) (see squares). Occasional areas with clustered defects are marked by '\*'.





the importance of configuration C2 to strongly support the effective implantation of oxygen in the lattice by our irradiation process: contrary to the three-fold symmetry of C1, this two-fold symmetry in configuration C2 cannot be created by two neighbour outof-plane impurities [46], nor by two close vacancies in the hexagonal lattice (figure S9 in supporting information). Moreover, this pattern cannot be created by a chemisorbed epoxy group bonded to two first neighbor carbon atoms in the hexagonal lattice either (configuration which shows a circular pattern [49]). Instead, C2 exhibits a unique pattern resulting only from two first-neighbor heteroatoms implanted in the hexagonal lattice. We note that a comparable pattern is also observed in graphene with two first neighbor substitutional nitrogen atoms [30]. Additional analysis of the STM data shown in figure 4 can be found in supporting information. For completeness, figure 5(a) shows scanning tunnelling spectroscopy, STS, measurements of an insolated defect similar to the one shown in figure 4(d). The differential conductance (dI/dV) data shows resonances at a negative bias. Such resonances are in good agreement with the theoretical DOS calculated in figure 5(b). In particular, by plotting the DOS as a function of the energy (in eV), the peaks of both dI/dV and the DOS appear at the same positions, once more, in clear agreement with the presence of substitutional oxygen in the hexagonal lattice.

### 4. Conclusions

In conclusion, we have studied the electronic structure and transport properties of substitutional oxygen atoms in graphene by developing a novel and controlled plasma implantation process at ultralow energy ( $\sim 25$  eV). Our combined theoretical and experimental study involving complementary techniques such as transport measurements, Raman spectroscopy, STM microscopy and atomistic calculations demonstrates that substitutional oxygen *n*-type dopes graphene and creates an asymmetric conduction in the material with holes being scattered more strongly than electrons. The behaviour of these impurities is thus different to (out-of-plane) oxygencontaining functional groups [33-35] bonded to graphene, which demonstrates how different types of C and O bonds can influence the electronic properties of sp<sup>2</sup> carbon allotropes. From a practical point of view, this understanding is important to assess the impact of oxygen in carbon nanomaterials including graphene oxide and oxidized carbon nanotubes [1, 3-5, 50], and may be relevant for other related systems such as novel two-dimensional  $\pi$ -conjugated organic frameworks [2]. Moreover, oxygen is ubiquitously present and used to handle and process sp<sup>2</sup> carbon allotropes [1–3, 33, 34, 41, 42, 51, 52]. Therefore, these findings are relevant to move all these nanomaterials from laboratory to industry.

#### Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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