Atmospheric adsorption on pristine and nitrogen-doped graphene: doping-dependent, spatially selective

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Abstract

Using Raman and photoemission spectroscopy, we probe the atmospheric adsorption on pristine and nitrogen p-doped graphene supported by SiO₂/Si. Laser annealing in vacuum led to a pronounced change in Raman spectra parameters, corresponding to a decrease in hole density due to adsorbate removal from the sample surface. We found that the shift inversely correlates with a degree of initial nitrogen doping, and thus less p-type adsorption doping takes place on graphene with a higher density of charge carriers with the same sign. The amount of hole doping required for the absence of atmospheric adsorption doping was found to be $n_{\text{noad}} = (3.87 \pm 0.31) \times 10^{13}$ cm⁻² (~2.3% of pyridine-like nitrogen), while the electronic doping required to fully compensate adsorption hole doping was $n_{\text{equil}} = (0.46 \pm 0.12) \times 10^{13}$ cm⁻² (~0.2% of graphitic nitrogen). We showed that atmospheric adsorption on pristine graphene increases the spatial charge carrier inhomogeneity; in contrast, the adsorption on nitrogen-doped graphene shows a spatially selective nature and reduces the inhomogeneity of charge carriers. This study is useful for graphene applications which require specific adsorption properties, as well as for taking these properties into account when designing graphene-based nanoelectronic devices.

Keywords: graphene, adsorption, doping, Raman spectroscopy, x-ray photoelectron spectroscopy

Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)
1. Introduction

Graphene, a monolayer sp² carbon allotrope, has become popular due to its extremely promising physical properties [1]. Among them, one can highlight the strong sensitivity of this 2D material to adsorbates [2–9]. On one hand, this leads to graphene being widely studied and engineered towards sensor applications [2]; on the other, such sensitivity causes significant modification of graphene properties, even when the material is simply air-exposed [3–8]. In particular, atmospheric adsorption leads to integral p-type doping in graphene due to acceptor H₂O and O₂ adsorbates [3–8]. This effect can be undesirable for graphene-based nanoelectronic devices operating in air; at the same time, such atmospheric adsorption phenomena make graphene a perspective material for chemical and environmental sensors, selective catalysis and other applications [2].

Since the atmospheric adsorption leads to a charge carrier density change in graphene, the preliminarily doped material can demonstrate different adsorption behavior compared to the pristine one [8, 10]. Recently we showed [8] that n-type doping of graphene leads to stronger atmospheric adsorption; furthermore, the adsorption tends to counterbalance both the initial ‘excess’ electronic density and spatial charge carrier inhomogeneity induced by the dopants. Since fully or partially opposite can be logically expected for the p-type doping case, this effect is interesting in terms of a range of possible applications. Thus, investigating the relationship between initial and atmospheric doping, as well as comparing the behavior of pristine and doped graphene, can open up new prospects for controlling the adsorption properties of this material, as well as extend the understanding of the effect.

A natural way to probe atmospheric adsorption on a 2D material is to conduct experiments under an air environment and in vacuum [8]; additionally, annealing is widely used to remove the adsorbates from the sample surface.

Raman spectroscopy is a versatile and non-destructive classical tool for obtaining information about the properties of graphene [11]. Several different Raman features of this material are known to be non-linearly doping-dependent [12], and thus they make it possible to determine the charge carrier sign or charge carrier density variations, as well as distinguish these from the substrate-induced strain in terms of the effect on the Raman spectra [13, 14]. X-ray photoelectron spectroscopy (XPS) is another classical quantitative tool that allows one to determine both the elemental composition and atomic chemical bonding type [15]. Combining these complementary methods allows one to obtain information on how adsorption on graphene occurs, depending on the presence and amount of initial doping of the material.

The purpose of this study is to probe and compare atmospheric adsorption on pristine and p-doped graphene in terms of the effect on charge carrier density by Raman and photoemission spectroscopy at normal pressure and upon laser annealing in vacuum.

2. Experimental

Within the scope of this work, we define atmospheric adsorption as a self-sustained adsorption of ambient air components, among which H₂O and O₂ adsorbates act as dopants, on the experimental graphene [3–8].

Graphene was synthesized by chemical vapor deposition (CVD) at 1020 °C on Cu with CH₄ flow of 40 sccm and hydrogen flow of 10 sccm. The copper foil substrate, 99.999% pure Alfa Aesar, with a thickness of 25 µm and area of 10 × 30 cm², was pre-annealed for 1–2 h inside the synthesis chamber at 1060 °C under the flow of hydrogen (300 sccm) and argon (2000 sccm), with a base pressure less than 10⁻⁴ Torr. After the growth of graphene, the substrate was cooled down to room temperature at a rate described in detail elsewhere [16].

Graphene transfer to SiO₂/Si was performed using a ‘PMMA-mediated’ method [17]. PMMA (Poly(methyl methacrylate) with a molecular weight of 996 000 g/mol, dissolved in anisole, was spin-coated (3000 rpm, 1 min) on graphene supported by copper foil. Then, an aqueous solution of 0.1 M (NH₄)₂S₂O₈ was utilized for copper etching; the etching products were removed from graphene using a water/isopropyl alcohol mixture [18]. To remove the PMMA, the sample was kept in extra-pure glacial acetic acid [19] for 4 h.

Graphene was doped with atomic nitrogen generated by a magnetron discharge (ParaOne, PS-1200) with 5 sccm N₂ flow in a vacuum chamber, with the base pressure being less than 3 × 10⁻⁴ mbar. The plasma power was 10 W, while the processing time was 30 s (sample N1), 90 s (N2) or 60 s (N3). Such labeling is related to the resultant nitrogen concentration rather than the treatment time, and is explained in detail later in the results and discussion section. Changing the plasma power to 20 W did not noticeably affect the results.

To obtain Raman spectra, a Nanofinder HE (LOTIS TII) confocal Raman spectrometer was used. The spectral resolution was better than 3 cm⁻¹ (about 2.3 cm⁻¹ for the G peak and about 1.0 cm⁻¹ for the 2D peak). Raman radiation was excited with a 532 nm continuous solid-state laser. The spectra measurements were carried out in a pressure-controlled cell under an atmospheric environment or vacuum (less than 5 × 10⁻⁴ Pa) using laser power of 3 mW for 30 s exposition per spectrum; the laser spot diameter was ~1.5 µm.

Due to the potential to perform area mapping and change the laser power, a Raman source laser was used within the scope of this work, both to obtain spatial spectra scans and as a heat source for the same area point-by-point consistent annealing. The 10 mW power was empirically chosen for the annealing as a maximal value that does not affect graphene defectiveness in terms of D and D’ peak relative intensity [11]. The 3 mW power was proven not to affect the spectra through repeated measurements at the same point. Prior to the adsorption-related measurements, the samples were exposed to ambient air with a relative humidity ranging from 40% to 60% for at least two months. Then, Raman scans of 6 × 6 µm² (49 points per scan) were performed for the same areas of the experimental samples within the following sequence: measurement (3 mW, air-exposed)—annealing (10 mW, vacuum)—measurement (3 mW, vacuum). The measurements were performed under room temperature ambience.

Photoemission spectra were acquired using a PHI Quantera II spectrometer equipped with a monochromatized Al Kα
x-ray source (1486.6 eV energy) and a combined ion/electron charge neutralization gun. The spectra were fitted by Gaussian/Lorentzian convolution functions using a Unifit 2014 data processor. Asymmetry of the sp² component in C1s core level spectra was described with Doniach–Sunjić functions. The spectral background was optimized using a combination of Shirley and Tougaard functions simultaneously with the spectral fitting. Atomic fractions were calculated from peak areas using calibrated sensitivity factors.

3. Results and discussion

We first investigate the structure and composition of pristine and doped graphene samples under atmospheric conditions. Secondly, we focus on the nature and type of doping in the nitrogen-treated graphene samples. Finally, we discuss the change in carrier density and structural features of pristine and doped graphene samples upon laser annealing in vacuum.

Raman spectra of pristine and nitrogen-doped graphene are shown in figure 1. For all samples, the G and 2D peaks characteristic of graphene are present [11]. The spectra of N1–N3 samples treated with nitrogen plasma are typical of doped graphene: they show pronounced D and D' peaks which arise in the presence of defects [11]. Furthermore, a smaller relative intensity is observed for the 2D peak, which is known to be suppressed by disorder and additional charge carriers [11, 12]. Alongside both G and 2D peak upshifts of 3–6 cm⁻¹, generally observed in the spectra of nitrogen-treated experimental samples, these features are indicative of a p-type doping [12]. The upshift increases from sample N1 to N3, the D and D' peaks become more pronounced, while the 2D peak relative intensity decreases, all indicating a doping increase [12].

The surface composition measured by XPS clearly indicates the incorporation of nitrogen in the graphene structure. In figure 2, we present the C1s and N1s photoemission spectra for N1–N3 samples, taken after N₂ plasma treatment (the survey spectra are given in the supplementary material file 1, figure S1 (stacks.iop.org/JPhysD/53/045302/mmedia)). A summary of the atomic concentrations is presented in table 1.

![Figure 1](https://example.com/fig1.png)
**Figure 1.** Typical Raman spectra of pristine and nitrogen-doped graphene N1–N3 under an atmospheric environment.

![Figure 2](https://example.com/fig2.png)
**Figure 2.** N1s (a) and C1s (b) photoemission spectra acquired after the N₂ plasma treatment for 30 s (N1), 90 s (N2) and 60 s (N3). The labels Nₚ and N₉ correspond to pyridinic and graphitic nitrogen, respectively.

| Sample | C, % | Csp², % | C/Si ratio | Nₚ, % | N₉, % | Csp²/N ratio |
|--------|------|---------|------------|-------|-------|--------------|
| N1     | 97.8 | 72.7    | 2.61       | 1.7   | 0.5   | 27.5         |
| N2     | 97.5 | 88.4    | 1.40       | 2.2   | 0.3   | 25.4         |
| N3     | 97.3 | 71.0    | 2.56       | 2.3   | 0.4   | 21.2         |

We describe the C1s spectrum by the intense component at 284.5 eV binding energy corresponding to sp² C–C bonding in the graphene lattice [20, 21]. Other spectral components are related to different carbon species in PMMA residuals according to [22]: C–C sp³ at 285.2 eV, C–O at 286.2 eV and O–C=O at 288.5 eV. The N1s spectra can be described by two components labeled Nₚ and N₉ at 400.0 and 402.2 eV, respectively, associated with pyridinic and graphitic nitrogen [23, 24]. The peak at 400.0 eV can also relate to amine and pyrrolic impurities; however, these incorporated nitrogen configurations are more likely to form under NH₃ treatment [25] rather than N₂, used in the present work, which is known to mainly introduce pyridinic and graphitic sites [26]. Nevertheless, we do not exclude the possibility of the presence of small quantities of pyrrolic and amine nitrogen, undistinguishable in N1s spectra.

For the bombardment time of 90s (N2), we observe a following decrease in N functionalities compared to the 60s treatment (N3). This change in the N1s spectra is in consensus with the C/Si intensity ratio, confirming the partial carbon atom removal from graphene on SiO₂/Si substrate under 90 s plasma treatment. It indicates that at this bombardment time, the doping procedure becomes less productive, and the defects introduced by nitrogen plasma treatment are no longer associated with dopants; instead, nitrogen atoms already incorporated in the graphene lattice are subsequently removed. While the Raman spectra are consistent with these
results from the incorporated nitrogen concentration point of view, they do not have a linear relationship with the treatment time in terms of the carbon vacancy introduction and, therefore, D peak intensity, as in [25]. This can be explained by the fact that Raman and XPS spectra are typically measured in different areas: while the former is local (6 × 6 µm² in the present work), the latter is more integral, applied in this case to 200 × 200 µm². At the same time, the effects of plasma etching depend on the defect type [27], and are most pronounced in the areas where more initial defects are already present.

Figure 3. Diagrams of 2D and G Raman peak positions for pristine and nitrogen-doped graphene (a) under atmospheric environment, and (b) after laser annealing in vacuum (the point scatter is seen to reduce after the annealing due to adsorbate removal); the number of points corresponding to each peak position value (c) and (e) under atmospheric environment, and (d) and (f) after laser annealing in vacuum.

Table 2. Carrier density due to nitrogen doping calculated after XPS measurements \( p_{\text{calc}} \), as well as the average carrier density change due to desorption in vacuum after laser annealing \( \Delta p_{\text{exp}} \), for the experimental graphene.

| Sample  | \( p_{\text{calc}} \times 10^{13} \text{ cm}^{-2} \) | \( \Delta p_{\text{exp}} \times 10^{13} \text{ cm}^{-2} \) |
|---------|---------------------------------|-----------------|
| Pristine | 0                               | 0.46            |
| N1      | 1.89                            | 0.33            |
| N2      | 3.03                            | 0.13            |
| N3      | 3.14                            | 0.12            |
present, such as grain boundaries. After the nitrogen incorporation reaches saturation with respect to time, the subsequent plasma treatment primarily leads to disordering of the already strongly defective regions, which is thermodynamically favorable. Simultaneously, at this stage, it has a smaller effect (related mostly to nitrogen removal) on more structured areas, which can be studied by Raman spectroscopy. Due to the scope of this work, the sample labelling thus follows the resultant nitrogen concentration and Raman data, rather than the treatment time.

Three common bonding configurations are normally obtained when incorporating nitrogen into the graphene lattice: pyridinic N (sp²-hybridized), pyrrolic N (sp³-hybridized) and graphitic N (sp²-hybridized) [28]. According to the photoemission data presented in figure 2, N₂ plasma treatment of graphene mainly leads to pyridinic and graphitic nitrogen incorporation. Pyridinic nitrogen is known to introduce about 0.45 holes per nitrogen atom, while graphitic nitrogen leads to electronic doping of -0.54 electrons/atom [29]. The nature of p-type doping by pyridinic nitrogen is not due to the presence of the N atom itself, but is due to a carbon vacancy, which results in a lack of electrons in the π-system [24]. The amount of pyridinic nitrogen in the plasma-treated samples is substantially higher than that of graphitic nitrogen as measured by XPS (table 1), which obviously implies an overall p-type doping effect, in agreement with the Raman data presented in figure 1. It should be noted that graphene transfer to a SiO₂/Si substrate can lead to an additional doping effect due to the interfacial charge redistribution [30], charge transfer from H₂O/O₂ molecules [31] or an increase in external scattering sites due to the polymer residue [22].

Considering that the adsorbates present on the sample surface under atmospheric conditions introduce additional p-type doping of graphene [3–8], laser annealing with 10 mW power was performed for all samples in vacuum (~10⁻⁸ mbar) for the adsorbate removal (see the experimental section for full details of the measurement/annealing/measurement sequence). It should be noted that for a sensitive material such as graphene, the vacuum condition itself is sufficient to notice-able changes in the Raman spectra [8]; laser annealing can be expected to enhance its effectiveness in relation to adsorbate removal through additional energy transfer. Moreover, the calculations given in [8] showed that the effects of graphene and substrate lattice compressibility on Raman spectra are negligible at pressures below atmospheric pressure.

Figures 3(a) and (b) present 2D-G diagrams for the experimental samples before and after laser annealing in vacuum. As was shown in [13, 14], such diagrams are useful for visual doping descriptions in graphene due to non-linear dependence of Raman peak positions on charge carrier density [12]. The latter allows us to highlight separate directions for n- and p-type doping increases, as well as to distinguish doping and strain effects. As the vacuum condition and laser annealing lead to adsorbate removal from the sample surface, the point clouds experience a pronounced shift along the hole doping line seen in figures 3(a) and (b). Along with the change in the 2D/G intensity ratio observed during the Raman experiments, this allows us to exclude the strain factor from the considerations. However, while visualizing the hole density decrease, the 2D-G diagrams show the strong overall point scatter, especially for the atmospheric environment, where the points are strongly affected by a probabilistic adsorption process. Therefore, we also give the number of points corresponding to each peak position in figures 3(c)–(f), presenting individual peak shifts statistically and more clearly (note that the 2D peak experiences a weaker shift as the carrier density changes [12]). Apart from the shift, the effect of desorption is also evident in position distribution narrowing after the annealing, most noticeably for the G peak. As the adsorbates get removed, the effect of incorporated nitrogen can be distinguished: the initial doping of graphene is manifested in ascending arrangement of the point clouds along the hole doping line observed in figures 3(b), (d) and (f), corresponding to an increasing percentage of pyridinic nitrogen.

Since the electrons introduced in graphene by graphitic nitrogen partially compensate the p-doping effect of the pyridine nitrogen [29], it would be reasonable to calculate the resultant hole density in doped graphene based on XPS data p calc: its values for the experimental graphene are presented in the second column of table 2. At the same time, it is possible to obtain a charge carrier density decrease in graphene during the desorption due to laser annealing in vacuum Δp exp from a combination of characteristic Raman spectra parameters (primarily the G and 2D peak positions) [12], which is presented in the third column of table 2, averaged over the scanned areas. The 2D/G intensity ratios have generally increased by 0.03–0.09 after laser annealing, indicating the charge carrier density decrease as well [12]; however, they were not informative for charge carrier density estimation since their values were also strongly affected by the destruction of the graphene sp² lattice during nitrogen incorporation [11], as can be seen in figure 1.
It can be seen from table 2 that the $\Delta p_{\text{exp}}$ values gradually decrease, which suggests that the adsorption softens with increasing initial $p$-type doping as the Fermi level of graphene is already below the Dirac point, and the pyridic nitrogen sites, which dominate over the graphitic ones in the studied samples, introduce charge carriers with the same signs as basic atmospheric acceptor $\text{H}_2\text{O}$ and $\text{O}_2$ groups. The fact that doping with the same charge carrier sign as the adsorbate makes adsorption doping less energetically favorable is in conceptual agreement with other works on the subject, such as [32, 33]. Comparing this observation with the results presented in [8, 32] allows us to extend this assessment of the $n$-type doping, which contrariwise increases the adsorptivity, introducing impurity energy levels suitable for the electron exchange [32].

Figure 4 shows the dependence of the charge carrier density change after laser annealing on $p_{\text{calc}}$ obtained from XPS data, with the scatter of values on the scans (semi-transparent points were calculated for the peak positions at each scan point).

It is seen from figure 4 that the intersection of the dependency with a vertical axis allows us to determine the required amount of doping $p_{\text{noad}}$, which will expectedly lead to the absence of adsorption doping by introducing charge carriers with the same sign. The estimation gives $p_{\text{noad}} = (3.87 \pm 0.31) \times 10^{13} \text{cm}^{-2}$, which corresponds to ~2.3% of pyridine-like nitrogen $N_p$.

In addition, the dependency intersection with a horizontal axis gives a required electronic doping $n_{\text{equil}}$. Which under an atmospheric environment results in an equilibrium state with a zero carrier density due to full compensation of adsorption doping. It can be estimated as $n_{\text{equil}} = (0.46 \pm 0.12) \times 10^{13} \text{cm}^{-2}$, corresponding to ~0.2% of graphitic nitrogen $N_C$. Graphene $n$-doped to smaller electronic density values is expected to change the charge carrier sign when exposed to the atmospheric environment. It should be noted that both $p_{\text{noad}}$ and $n_{\text{equil}}$ will be, in principle, substrate-dependent [8, 34, 35] due to charge transfer at the interface [30], electron–phonon coupling screening [36, 37] and other substrate-related effects.

Both doped graphene and graphene with adsorbates present on its surface tend towards an increase in the spatial charge carrier inhomogeneity, which is known to distort the G peak profile [8, 38]. Figure 5 presents such profiles plotted for each sample, before and after laser annealing in vacuum; the peaks are shifted to overlap for better clarity, the lower scale relates to the atmospheric environment and the upper one to the annealed samples in vacuum, as indicated by the colors and arrows.
It is seen from figure 5 that for pristine graphene, the G peak is distorted under atmospheric conditions, while annealing in vacuum leads to its symmetrization. At the same time, the opposite is observed for doped graphene: a more symmetric G peak is observed here in the case of air-exposed samples. This leads to a very interesting conclusion. The presence of adsorption p-type doping leads to spatially inhomogeneous hole introduction, which distorts the G peak of pristine graphene as the adsorbates get attached to its surface. In the initially p-doped graphene, the adsorption process turns out to be spatially selective to balance the local charge carrier deficiencies arising from unevenly distributed nitrogen sites, thus reducing the inhomogeneity and at the same time introducing additional holes, increasing the overall charge carrier density. This logical but not obvious observation correlates with the results for n-doped graphene, in which selective adsorption p-type doping compensates both charge carrier inhomogeneity and density through the electron–hole recombinations [8].

In general, 2D materials are extremely sensitive, even to small external influences. This study additionally focuses attention on the fact that such a trivial and commonly neglected factor as an atmospheric environment notably affects the properties of graphene, changing its carrier density by values to the order of $10^{12}$ cm$^{-2}$. Thus, precise engineering of nanoelectronic devices requires taking the described effects into account if their functional elements can be air-exposed.

**Conclusion**

In this work, we present Raman and photoemission spectroscopy studies of the adsorption properties of pristine graphene and graphene, p-doped with nitrogen. We found that laser annealing with 10 mW of power in vacuum ($\sim 10^{-5}$ mbar) led to a pronounced decrease in hole density due to acceptor adsorbate removal from the sample surface by 0.46, 0.33, 0.13 and 0.12 $\times 10^{13}$ cm$^{-2}$ for pristine graphene and graphene with increasing doping, respectively. The shift inversely correlated with a degree of initial nitrogen doping, indicating that less p-type adsorption doping takes place for graphene with a higher density of charge carriers of the same sign. The amount of initial p-type doping required for the absence of atmospheric adsorption doping was estimated as $p_{\text{noad}} = (3.87 \pm 0.31) \times 10^{13}$ cm$^{-2}$, corresponding to $\sim 2.3\%$ of pyridine-like nitrogen. Furthermore, the electronic doping required to fully compensate adsorption hole doping under the atmospheric environment was $n_{\text{equl}} = (0.46 \pm 0.12) \times 10^{13}$ cm$^{-2}$, corresponding to $\sim 0.2\%$ of graphitic nitrogen. Finally, we found that adsorption leads to a distortion of the Raman G peak profile corresponding to an increase in spatial charge carrier inhomogeneity in pristine graphene, while for nitrogen-doped graphene, the opposite occurs: the adsorption turns out to be spatially selective to reduce the inhomogeneity. This study is useful for graphene applications which require certain adsorption properties, as well as for taking these properties into account when designing graphene-based nanoelectronic devices.

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